ARTICLE

The „chemical tug-of-war" in carborane clusters: distinct tuning on different sides of the cluster†,‡

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Dániel Buzsáki,[a#] Dalma Gál,[b#] Balázs Szathmári,[b] Tamás Holczbauer,[c] Antal Udvardy,[d] Júlia Kertész Szilágyiné,[b] Denis Kargin,[e] Clemens Bruhn,[e] Rudolf Pietschnig,[e] Zsolt Kelemen*[b]

The special C-C bond in the icosahedral *closo*-dicarbadodecaboranes and its high *plasticity* have been highlighted several times, which is reflected in the ease of tuning the C-C bond distance with different substituents. Apart from this special case, the other bonds within the carborane clusters have not been investigated yet. DFT calculations demonstrated that the elongation of C-B and B-B bonds is ruled by the same effects as the well investigated C-C bond; however, stretching of B-B generally requires more energy. These results indicate that the bonds of the carborane clusters do not differ significantly; in fact they possess similar properties. The computational results encouraged us to synthetize the most promising derivatives. The distinct tuning was achieved by the variation of π-donor substituents. In the case of the 9,10-*m*-carboranyl-disulfanide derivatives, the B9-B10 bond distance is elongated up to 1.92(2) Å.

Introduction

The three-dimensional carborane clusters[1] exhibit exceptional thermal and chemical stability,[2] tailorability, ambiphilic character, organomimic properties, and unusually low toxicity, which make them more suitable for different applications than traditional materials.[3-5] Since their first synthesis in 1962,[6-9] carboranes have been the focus of many synthetic and theoretical works due to their unique bonding situations and 3D aromaticity.[10-12] The most widely studied systems are the icosahedral *closo*-dicarbadodecaboranes ($C_2B_{10}H_{12}$ or their widely used trivial name carboranes), which show outstanding stability.[13-15] According to the position of the carbon atoms, *ortho* (1,2-$C_2B_{10}H_{12}$), *meta* (1,7-$C_2B_{10}H_{12}$) and *para* (1,12-$C_2B_{10}H_{12}$) isomers exist (**Figure 1**). Since the electronegativity of boron is less than that of carbon, the latter acts as strong electron-withdrawing unit.[13] Meanwhile, BH vertices with different electronic environments can be distinguished within the cluster framework,[16,17] which rules the reactivity of each boron vertex as well. Accordingly, in the case of *ortho* and *meta* structures, four different boron atoms can be distinguished

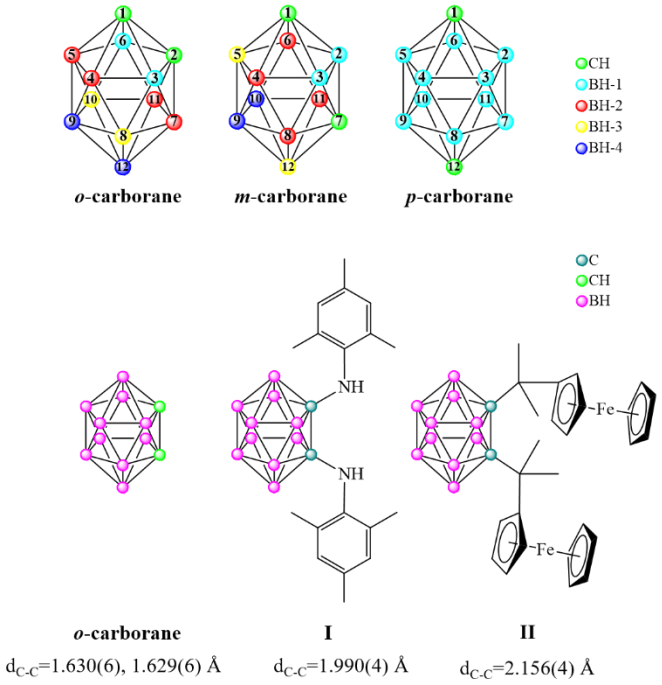


Figure 1 Top: The location of the carbon atoms and the chemically different boron atoms in the three different isomers of *closo*-dicarbadodecaboranes. The labelling of atoms in the clusters applied in this figure is used throughout the manuscript. Bottom: The C-C bond lengths in the case of the parent *o*-carborane (1.630(6) and 1.629(6) Å, in the crystal lattice two crystallographically independent but similar carborane units are present[19]) and the representative examples for C-C bond elongation induced by negative hyperconjugation and by steric bulks.

[a.] *Wigner Research Centre for Physics, P.O. Box 49, H-1525 Budapest, Hungary*
[b.] *Department of Inorganic and Analytical Chemistry Budapest University of Technology and Economics, Műegyetem Rkp 3., 1111 Budapest, Hungary*
[c.] *Chemical Crystallography Research Laboratory and Stereochemistry Research Group, Institute for Organic Chemistry, HUN-REN Research Centre for Natural Sciences, Magyar tudósok krt. 2, 1117 Budapest, Hungary*
[d.] *Department of Physical Chemistry, Institute of Chemistry, University of Debrecen, Faculty of Science and Technology, Egyetem tér 1., 4032 Debrecen, Hungary*
[e.] *Institute for Chemistry and CINSat University of Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany*
† Dedicated to Dr. Ilona Kovács on the occasion of her 65th birthday.
‡ Electronic supplementary information (ESI) available: Synthetic protocols, NMR spectra, crystal refinement data and details of DFT calculations.
# These authors contributed equally.

Please do not adjust margins

depending on the distance from the carbon atoms, while in the case of *para* structures, all boron atoms are chemically identical (**Figure 1**).[18] The C1-C2 bond in the parent *o*-carborane is longer (1.629-1.630 Å)[19] than a typical simple C-C bond (~1.52 Å), moreover, it can be easily modulated with different substituents (**Figure 1**). The term of plasticity was used to characterize this special bond, since its length varies between 1.38-2.16 Å in the case of 1,2-R_2-1,2-$C_2B_{10}H_{10}$.[19–22] As it was demonstrated, the variability of the C1-C2 bond could have steric as well as electronic origins. While in the first case the steric repulsion forces the separation of the two carbon atoms, the electronic effect is more complex and usually arises from the negative hyperconjugation between the π-system of substituents and the σ* orbitals of C1-C2 bond. Indeed, it is most effective in the case of good π-donor substituents as was demonstrated theoretically by Schleyer and Teixidor,[23] and was also supported experimentally.[21,22] According to this concept, Xiao and Müller have demonstrated that the length of the C1-C2 bond can increase up to 1.990(4) Å by applying amino groups to the system (**I**, **Figure 1**).[22]

Based on the DFT calculations of Teixidor and Schleyer, the distance between the carbon atoms could be elongated even more in the case of anionic systems. In the case of -CH_2- substitutions on the cluster carbon atoms (C1 and C2), the C1-CH_2 and C2-CH_2 distances shrink to the range of a double bond, while the C1-C2 distance in the *o*-carborane becomes so long (2.638 Å) that no bond critical points could be located between the two carbon atoms.[23] Interestingly, in the case of metallacarboranes, the significant elongation can lead to the formation of the so-called *pseudocloso* structures in which there is no chemical bond between the cluster carbon atoms.[24–27] The electronic modulation of the C1-C2 bond is indeed very efficient, however, it should highlighted the longest C1-C2 distances in neutral carborane systems (2.156 Å) can be achieved with bulky substituents (**II**, **Figure 1**).[28]

Finally, it is important to emphasize that *o*-carborane-based luminogens, where the π-system of the fluorophore is directly connected to the carborane cage via its carbon atoms, also exhibit elongated C–C bonds in the excited state (S1 or T1) due to charge transfer processes from the π-system of the fluorophore to the C-C antibonding orbital.[29]

Contrary to the deeply investigated carbon-carbon bond of *o*-carboranes, the possible modulation of the boron-boron and carbon-boron bonds has scarcely been investigated yet,[30] the slight B-B bond elongation in the case of 8,9,10,12-tetraphenyl-*o*-carboranes was attributed to negative hyperconjugation.[31] The question arises whether the same rules are in effect in the case of these bonds? Can the B-B bond be more elongated with strong π-donor substituents? To the best of our knowledge, there is no comprehensive study on the boron moiety of the carborane system despite its unique reactivity, while the carbon moiety is deeply investigated both theoretically and experimentally.

Computational details

For this study, B3LYP was chosen since related studies used this functional as well, therefore the results can be comparable with those pioneer works.[23,32] Since B3LYP have been criticized during the last years, other DFT functionals were tested and the results were validated by LNO-CCSD(T) method[33] as well, these data are presented in the ESI (**Table S1-S6**). All calculations have been carried out with Gaussian 09 program package[34], expect these local-CC calculations, which were performed with the MRCC program[33].

Full geometry optimization was performed for all molecules at the B3LYP/aug-cc-pVTZ level of theory (unless otherwise stated). Relaxed potential energy surface scans (hereinafter mentioned as "scan" throughout this study) were performed, in which one selected bond of the cluster was substantially increased by 0.1 Å, while the positions of the other atoms were not restricted. Since the number of the species does not change during this process, the effect of the entropy can be considered less significant, therefore electronic energies can be safely applied to estimate the flexibility of the chemically different bonds. Harmonic vibrational frequencies were calculated at that level which was used for the optimization, to establish the nature of the stationary points obtained, as characterized by zero negative eigenvalues of the Hessian for minima. Calculations on the electron density of the bond critical points and on the Wiberg bond indices[35,36] were performed with the Multiwfn program[37]. For the visualization of the molecular structures and the molecular orbitals, the MOLDEN[38] and IQmol[39] programs were used.

Results and discussion

Relaxed energy surface scans on the carborane systems

To investigate the flexibility of the bonds of the carborane cluster, "scans" were performed on all of the C-C, C-B and B-B bonds (in the main text, we focus on the elongation of the bonds, the effects of the bond shrinking can be found in **Figure S1** in the ESI). In *ortho* and *meta* systems, seven chemically different bonds can be distinguished (**Figure S2**), which is decreased to three in the case of *para*-carborane systems due to the higher D_{5h} symmetry compared to D_2 (**Figure 2** red lines). The effects in the case of all chemically different bonds are detailed in the ESI.

The carborane cluster can be considered as a rigid system, however, minor changes on the equilibrium bond lengths are easily compensated with small changes of other bonds, the energy is only 1.0-1.2 kcal/mol higher while increasing any bond length by 0.1 Å. (In the case of ethane, the increase of the energy is 2.4 kcal/mol at the same level of theory). The energy and the deviation of the energy increases gradually by further elongation of the bonds: the differences are between 12.7-22.0 kcal/mol, if the extension of the bond increases to 0.5 Å.

Figure 2 clearly shows that slightly less energy is required to stretch the C-C bond in *o*-carborane (green line) than C-B bonds (blue lines) in all isomers of the carboranes. The B-B bonds (red lines in **Figure 2**) need the most energy to elongate, and the

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

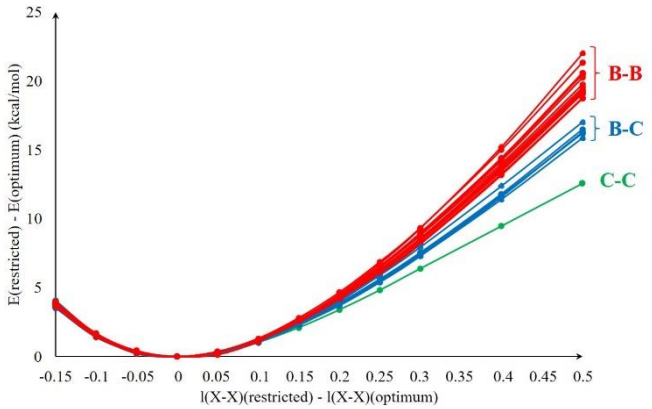


Figure 2 The difference in the energy compared to the optimized structure depending on the amount of elongation in different bonds of *o*-, *m*- and *p*-carboranes. Tabulated data are shown in **Table S8-S10** and the extension for bond shrinking can be found in **Figure S1** in the ESI.

various B-B bonds behave very similar, there is no significant difference between them. Furthermore, Bader analysis was performed on the restricted systems to check whether a bond critical point between the fixed two atoms still exists after the elongation of the bond (see **Table S7** in the ESI). It turned out that increasing the bond length results in the disappearance of the bond critical point, while a ring critical point appears between the two atoms as the density becomes lower than 0.1 a.u. It shows that the electronic interaction is still notable between the atoms of the stretched bonds, becoming more delocalized with the torsion of the system.

B2-B3 bond in the *m*-carborane system is the most difficult to elongate (it needs 22.0 kcal/mol to be extended by 0.5 Å at the B3LYP/cc-pVTZ level of theory). An explanation of this phenomenon can be that both of the two carbon neighbour atoms have an electron donating effect to the B2-B3 σ* orbital via 3c-2e interactions, thus more energy is required to increase the electron density of this orbital even further. As a verification of this theory, the farthest bonds from the carbon atoms (B9-B10 for *m*-carborane, and B9-B12 for *o*-carborane) requires the least energy to be stretched from all B-B bonds (it needs 19.2 kcal/mol to be extended by 0.5 Å), while also in the case of C-B bonds, the bond closest to the other carbon atom needs the most amount of energy to be elongated (17.0 kcal/mol to be extended by 0.5 Å).

In summary, it can be established that the B-B and B-C bonds do not behave significantly different to the C-C bonds, however they exhibit somewhat more rigid character, as more energy is required to elongate them. As was highlighted in the case of the C-C bond in the case of *o*-carboranes, the energy requires for the stretching can be counteracted by the π-donation of the substituents (via negative hyperconjugation).[23] In order to get more insight into the possible modulation of the B-B and B-C bonds, various substituents possessing different electronic properties were selected. Moreover, *t*Bu- and adamantyl groups were also used as a comparison to steric effects, which were shown to be a more beneficial factor to form longer C-C bonds.

In order to get comparable values, calculations of Teixidor and Schleyer on C-substituted *o*-carboranes[23] were repeated at higher level of theory. It is worth to mention that the formerly applied lower level of theory (B3LYP/6-31G*) gives very similar results to our B3LYP/aug-cc-pVTZ calculations, with the sole exception of anionic systems, where significant differences have observed in the optimized geometry. The reason of this discrepancy is probably the lack of diffuse functions in the 6-31G* basis set, which is usually required for the description of anionic systems.

As was demonstrated earlier and shown by our "scan" calculations, the C1-C2 bond in *o*-carborane requires the least energy to be elongated. Accordingly, in the case of C1-substitution with a highly donating group, the C1-C2 bond becomes much longer compared to the parent carborane (by 0.02-0.06 Å), while resulting in slightly shorter bonds around the other carbon atom.

The effect of the substitution on any of the boron atoms exhibits similar results regardless of carborane isomers (see in **Table S11-S19** for detailed information). If there is a carbon atom in the vicinity of the substituted boron atom, it attracts a stronger electron donation, resulting in a more significant stretch of the C-B bonds. In the case of the B-B bonds connected to the substituted atom, a smaller expansion can be observed compared to the C1-C2 bond elongation in the case of C-substitution, and the C1-C2 bond is also much less affected (less than 0.02 Å). In the case of anionic substituents on the carbon atom, the length of the C1-C2 bond in case of *o*-carborane becomes much longer (by up to 0.67 Å, see **Table S20-S22** in the ESI) than in neutral clusters due to the greatly increased π-donating effect. Bader analysis shows the delocalization of the bond, as a ring critical point – also observed in the case of "scan" calculations – which can be located between the carbon compared to neutral systems (see more data in **Table S7**).

Surprisingly, the boron substitution with an anionic group adjacent to a carbon atom results in exceptionally long C-B distance (even above 0.7 Å, the cage was opened). Moreover, B-B bonds can also be expanded by up to 0.28 Å resulting in great changes, even if the substitution does not happen in the proximity of the carbon atoms (more data in **Table S11-S19**). According to the level of the elongation the selected substituents can be distinguished into three classes. The greatest elongations occur in the case of strongly π-donating anionic substituents such as $-O^-$ and $-S^-$, medium elongation happens in the case of neutral strong π-donor substituents (-OH, $-NH_2$, -SH), and very minor elongation can be observed in the case of substituents with low or no π-donor character ($-PH_2$, -Cl, -Me, $-SiH_3$).

Since π-donor substituents could have synergetic effect on the elongation of the C-C bond,[23] similar effect can be expected in the case of B-B bonds. Therefore, calculations were performed where systems substituted with two groups on adjacent cluster

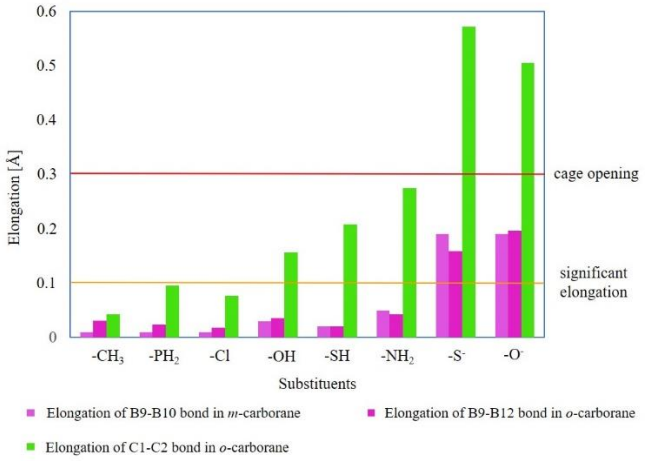
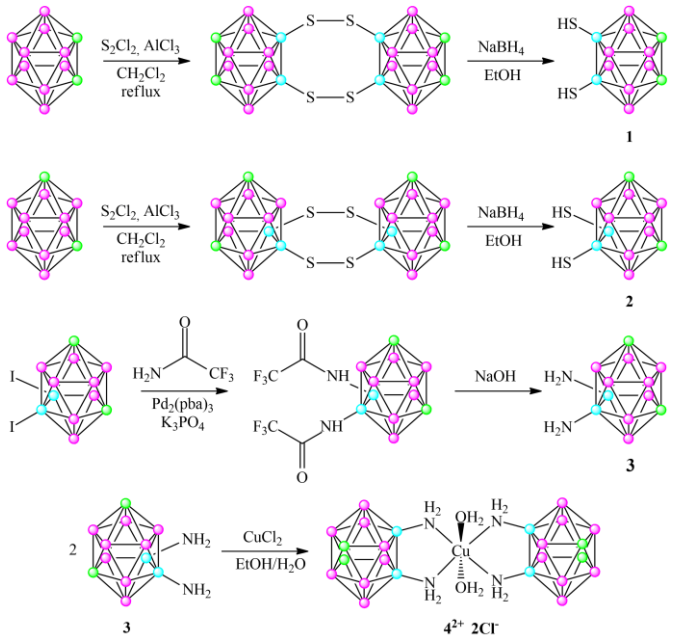


Figure 3 The effect of the different substituents on the B-B and C-C bonds of the carboranes

atoms. For this purpose, we compared the bond elongations in case of the substitution of the synthetically more available B9-B12 atoms in the *o*-carborane, and B9-B10 atoms in the *m*-carborane to the C1-C2 substituted compounds (**Figure 3**, tabulated data in **Table S23-S25**). In neutral clusters, the effect of double substitution on the bond lengths was more than additive (synergetic effect) in the case of carbon substitution (up to 0.27 Å of elongation could be observed), while the boron substitution led to a slight stretch in all adjacent bonds instead of focusing on a single one. In anionic systems, the elongation spreads around both the C-, and the B-substituted systems. However, the effect is so strong that it results a 0.19 Å increase in the B9-B10 bond of 9,10-O^- (0.20 Å for B9-B12 bond in the *ortho* analogue) and 0.19 Å increase in the B9-B10 bond of 9,10-S^- substituted compounds (0.16 Å for B9-B12 bond in the *ortho* analogue). Finally, it is worth to mention that sterically crowded systems were investigated as well, since the longest C-C carborane bond was achieved by steric repulsion. The effect of bulky groups (*t*Bu and adamantyl) has also been investigated by applying double substitution on both C1 and C2 atoms, and on the B9 and B12 atoms (at B3LYP/6-31G*). The elongation of the disubstituted bond is higher than in case of strong π-donating substituents in neutral systems (by up to 0.52 Å in C1-C2, and 0.10 Å in B9-B12 substitution, see **Table S26** in the ESI), however, it is definitely less impactful than applying anionic π-donor substituents. Therefore, substitution with anionic groups (or even good neutral π-donor groups) can be promising to push the upper limit of the B-B bond lengths.

Encouraged by the DFT calculations the most promising candidates were synthetized in order to prove the hypothesis concerning the possible B-B bond modulation. As our calculations established that the antipodal B-B bonds (B9-B12 bond in *o*-carborane B9-B10 in *m*-carboranes) are the most plastic B-B bonds we planned to introduce the proper substituents into these positions, which are known to be suitable for electrophilic substitutions as well. The corresponding SH substituted 9,12-dithiol-*o*-carborane (**1**) and



Scheme 1 Synthesis of **1**, **2**, **3** and **4**

9,10-dithiol-*m*-carborane (**2**) compounds were already known before,[40] but no crystal structures have been published yet. We have prepared both of them in slightly modified reaction procedures (with 82% yield for **1** and 76% yield for **2**) , and we were able to grow suitable crystals using vapour diffusion technique (acetone/hexane). The experimentally obtained B-B bond length is 1.790(4) Å in case of *o*-carborane and 1.815(4) Å in case of *m*-carborane derivative (**Figure 4**), longer than that in the parent *o*-carborane (1.776 Å). These values are in excellent agreement with our computationally predicted bond lengths, thus providing more support to our chosen DFT method. Amino groups were also shown to be effective in the elongation of B-B bonds, therefore the corresponding diamino-substituted derivatives were planned to be synthetized as well. The introduction of amino groups into the carborane cluster is a highly challenging approach. However, following the cross-coupling reaction method developed by Hawthorne,[41] we were able to synthetize the corresponding double substituted 9,10-diamino-*m*-carboranes (**3**, **Scheme 1**) from the corresponding amide derivative (isolated yield is 86%). Our attempt to get the corresponding *o*-carborane derivative failed, probably due to the more sensitive character of the *o*-carborane compounds towards the applied basic conditions.

Investigating ^{11}B NMR chemical shifts provides valuable information about the electronic environment of the different vertices of the cluster. The downfield resonance in the ^{11}B NMR spectra of compounds **2** and **3** at -1.8 and 2.9 ppm, respectively, does not split into a doublet in the ^{11}B NMR spectra, indicating that these resonances correspond to the boron atoms at the 9 and 10 vertices. The somewhat more downfield chemical shift observed in compound **3** is consistent with the enhanced donor ability of the amino groups, resulting in increased electron

This journal is © The Royal Society of Chemistry 20xx

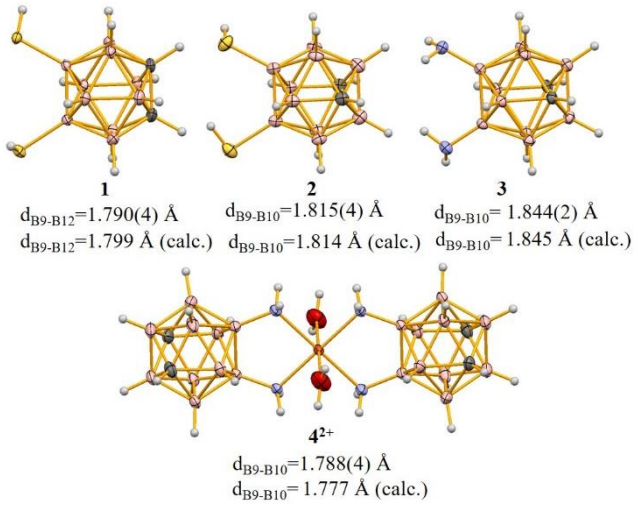


Figure 4 Solid state structure of **1, 2, 3** and $\mathbf{4^{2+}}$ and the corresponding B9-B12 (in the case of **1**) and B9-B10 (in the case of **2**, **3** and $\mathbf{4^{2+}}$) bond lengths (both experimental and calculated). Ellipsoids are shown at 30% probability. Disordered hydrogen atoms are omitted for clarity.

density at the 9 and 10 vertices. Suitable crystals for SC-XRD were grown from acetone and the B9-B10 bond length in the crystal of compound **3** is 1.844(2) Å, which is somewhat longer compared to the dithiol derivatives, supporting the better π-donor ability of the amino group. which was conducted in ethanol using a 1:2 stoichiometry $CuCl_2$ and **3** (isolated yield is 84%).

Structural characterization of **4** reveals a hexacoordinate copper center in a square bipyramidal coordination environment, in which two water molecule are in the axial positions. As a consequence of the coordination of the lone pair, negative hyperconjugation towards the cluster has been ceased to operate, indeed the antipodal B-B bond became significantly shorter (d_{B9-B10}=1.788(4) Å) than the same bond in the free ligand (**3**, d_{B9-B10}=1.844(2) Å). Despite the above discussed promising results, the elongation of the B-B bond remains minor (~0.05 Å), even in the computational results suggested, much stronger π-donor substituents are required. On the other hand, good π-donor groups usually become good nucleophiles as well, which may lead to the deboronation of the carborane cluster. The deprotonation of the dithiol derivatives seemed to be a reasonable compromise between nucleophilicity and good π-donor character. First, *n*-BuLi was applied as a base, but the corresponding Li-salt was insoluble in aprotic solvents (tetrahydrofuran, acetonitrile, dimethoxyethane), moreover the crystallization remained unsuccessful even using

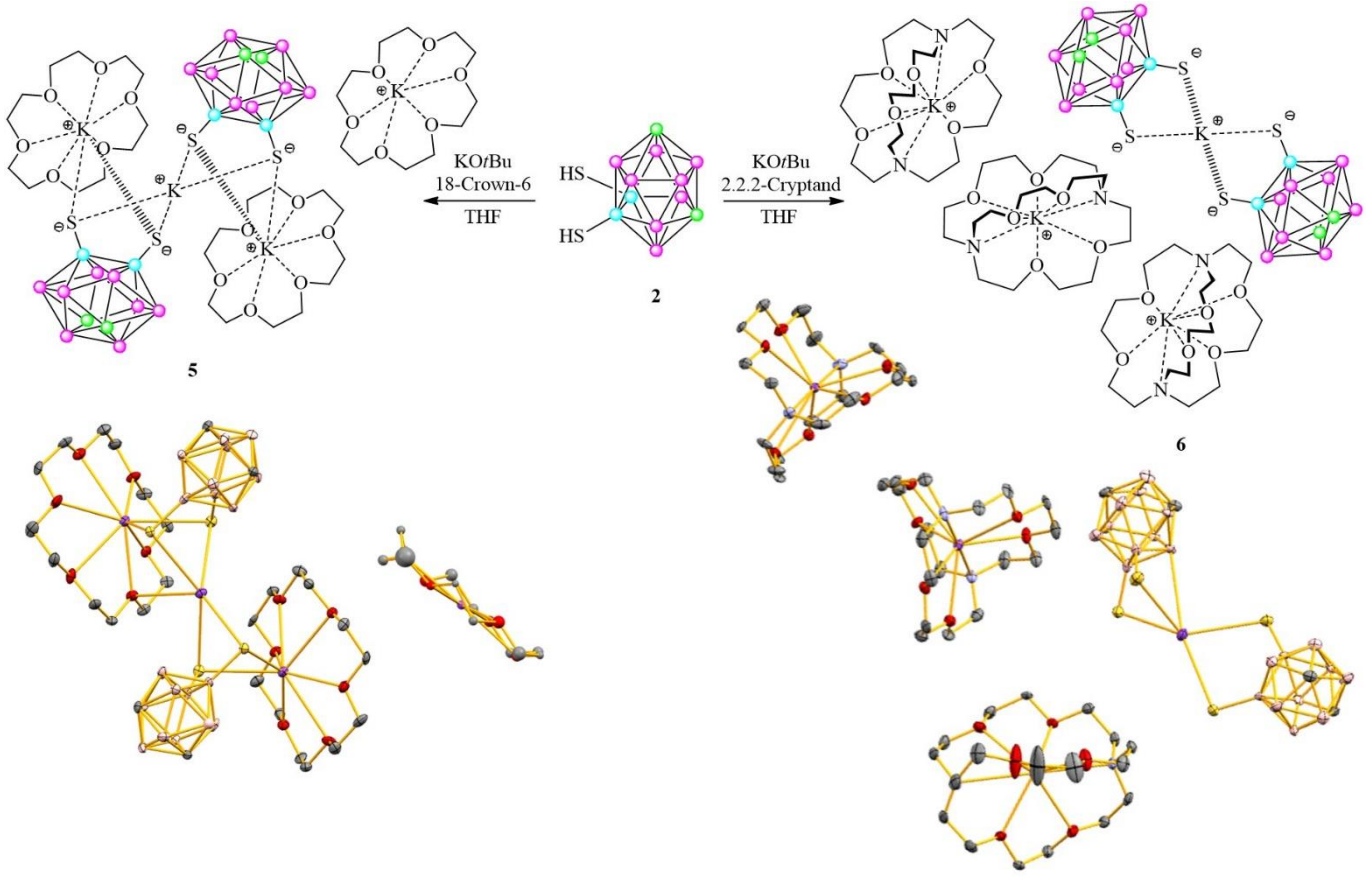


Figure 5 Synthesis of **5** and **6** and the obtained crystal structures. Ellipsoids are shown at 30% probability and all hydrogen atoms and solvent molecules are omitted for clarity. In case of **5** the individual crown ether is disordered, indeed some of the atomic positions cannot be refined anisotropically. The atomic positions which cannot be refined anisotropically are represented by a spherical model.

complexing agents (TMEDA or 12-crown-4). As a next attempt, we tried potassium-hydride for the. deprotonation and the resulting white powder proved to be insoluble in aprotic solvents, and any efforts at crystallization and proper characterization were again unsuccessful. However, repeating the reaction in the presence of 18-crown-6 the solubility of the product increased significantly (isolated yield is 58%). Investigating the $^{11}B\{^1H\}$ NMR chemical shifts of the obtained solution enables us to draw similar conclusions as those observed after replacing the SH group with a better π-donor NH_2 group. The resonance corresponding to the boron atoms at the 9 and 10 vertices appears more downfield (4.1 ppm in acetonitrile) compared to the same vertices in the starting compound (-1.6 ppm in the same solvent), which foreshadows the better donation towards the cluster. Small, but suitable crystals for SC-X-ray measurements can be grown from THF-hexane mixture. Investigating the obtained solid state structure of **5** (**Figure 5**), it can be established that the asymmetric unit contains two carborane moieties and four potassium cations: both carborane units showed similar alignment in the structure, as each $–S^-$ units coordinates to a potassium cation. Among the four potassium cations two have similar chemical environment, besides they were complexed by one crown ether, two $–S^-$ units of the carborane system coordinated to each of them, achieving the coordination number of 8, characteristic for potassium. In contrast, potassium cation complexed by both carborane units has a coordination number 6, which was complemented by the coordination of one of the oxygen atoms of the neighbouring crown ether. The fourth potassium is complexed by the crown-ether and two addition THF molecules and further three THF molecules are in the crystal cell. The number of the THF in the crystal lattice fits with the ^1H NMR spectra recorded after the dissolution of the obtained crystals in DMSO-*d6*.

Interestingly, the two carborane units have different B9-B10 bond lengths, they are 1.87(2) Å and 1.92(2) Å, thus more than 0.1 Å increment can be achieved after deprotonation. Although this bond length is remarkably long, it does not meet the expectations from the calculations (1.972 Å). This variance can be explained by the strong coordination of the electron acceptor potassium cations, which decreases the strength of the electron donation from the $–S^-$ moieties towards the clusters. Recrystallization of **5** from acetonitrile results in a slightly different solid state structure with similar structural motif (**Figure S3** in ESI), but in this case the fourth potassium was coordinated by one of the $–S^-$ moieties as well. The B9-B10 bond lengths are 1.870(5) Å and 1.877(7) Å, which are somewhat shorter than the previous case.

In order to achieve a longer B9-B10 bond, the full complexation of the counter ion is required to hinder its electron acceptor properties. Therefore, the deprotonation reaction was repeated in the presence of 2.2.2-cryptand, which has a much higher affinity for the potassium cation compared to the crown ether. After one hour, a white solid precipitated, which was washed with diethyl ether (yield 64%). The solid was recrystallized several times. Finally, we were able to grow suitable crystals from acetonitrile (see structure of **6** in **Figure 5**). The asymmetric unit of the obtained crystal contains two carborane moieties and four potassium cations. However, interestingly, only three cations were able to be complexed by 2.2.2-cryptand. The remaining one potassium was complexed by the two anionic carborane units. Surprisingly, one water molecule (probably as a trace from acetonitrile) coordinated to this potassium as well (see **Figure S4** in ESI). These results highlighted an astonishing observation that the carborane units exhibit comparable affinity to potassium than the 2.2.2-cryptand. Accordingly, the elongation of the B9-B10 bond is 1.890(19) Å and 1.89(2) Å, which is very similar to **5** (1.87(2) Å and 1.92(2) Å). Finally, it is worth mentioning that attempts were made to replace the alkali cations with non-coordinating tetraalkyl ammonium cations, but the low solubility of these materials in organic solvents do not allow the proper characterization of the products.

Conclusions

We have demonstrated by DFT calculations that substituting on any side of the carborane can highly impact the structure of the core of the icosahedral cluster. The negative hyperconjugation described in the case of C-substituted *o*-carboranes operates for the B-substituted systems as well, although with a diminished effect thus much stronger π-donor substituents are required to achieve significant bond elongation of B-B bonds. The effect of the substituents has a synergetic effect, therefore systems with two highly donating groups resulted in the longest B-B bonds among the investigated molecules. In order to underline our DFT proposed concept, we have synthetized new B-substituted carboranes with the strong donor sulfanide groups. Indeed, the solid state structure showed significant bond elongation, while supporting the concept that B-B bonds in the carborane behave similarly to their carbon containing counterparts, enabling the fine-tuning of the electronic properties on all sides of the cluster. As a matter of fact, electronic modification of the cluster B-B bonds can influence the photophysical properties of carborane-fluorophore conjugates, as previously shown with C-C bonds in carbon-substituted *o*-carborane systems, expanding

Please do not adjust margins

the possibility of their application as luminescent solid state materials. Additionally, as demonstrated in this study with a copper complex, the newly synthesized double-substituted carboranes can act as ligands for transition metal complexes,

Conflicts of interest

There are no conflicts to declare.

Data availability

Electronic supplementary information (ESI) available: Synthetic protocols, NMR spectra, crystal refinement data and details of DFT calculations. CCDC numbers: 2333790-2333793, 2371840, 2379108 and 2379109

Acknowledgements

ZK is grateful for the general support of János Bolyai Research Scholarship, Project UNKP-23-5-BME-419 and OTKA (FK-145841) provided by the Hungarian National Research Development and Innovation Office. DG is grateful for the general support of Project EKOP-24-3-BME-312 provided by the Hungarian National Research The project supported by the Doctoral Excellence Fellowship Programme (DCEP) is funded by the National Research Development and Innovation Fund of the Ministry of Culture and Innovation and the Budapest University of Technology and Economics, under a grant agreement with the National Research, Development and Innovation Office (DG, BS). Development and Innovation Office. We are grateful for the funding from the Hungarian National Research, Development and Innovation Fund under grant number TKP2021-NVA-04 and TKP2021-EGA-02 provided by the Ministry of Innovation and Technology of Hungary. AU is grateful the Project no. RRF-2.3.1-21-2022-00009 titled National Laboratory for Renewable Energy, have been implemented with the support provided by the Recovery and Resilience Facility of the European Union within the framework of Programme Széchenyi Plan Plus, and are gratefully acknowledged. Part of the crystallographic study was carried out using the infrastructure of Eötvös Loránd University Institute of Chemistry (ELTE-CrystalLab) and HUN-REN-ELTE Protein Modelling Research Group and it was supported by the European Union and the State of Hungary and co-financed by the European Regional Development Fund (VEKOP-2.3.3-15-2017-00018). We would like to thank the contribution of Máté Kovács, Péter Kucsera and Zsófia Harcsa-Pintér.

Notes and references

1 R. N. Grimes, Carboranes, *third ed., Academic Press*, 2016
2 A. M Spokoyny, New Ligand Platforms Featuring Boron-Rich Clusters as Organomimetic Substituents *Pure and Appl. Chem.* 2013, **85**, 903–919.
3 X. Zhang, L. M. Rendina, M. Müllner, Carborane-Containing Polymers: Synthesis, Properties, and Applications, *ACS Polymers Au* 2024*,* **4**, 7-33.
4 J. F. Valliant, K. J. Guenther, A. S. King, P. Morel, P. Schaffer, O. O. Sogbein, K. A. Stephenson, The Medicinal Chemistry of Carboranes *Coord. Chem. Rev.* 2002, **232**, 173–230.
5 M. Scholz, E. Hey-Hawkins, Carbaboranes as Pharmacophores: Properties, Synthesis, and Application Strategies *Chem. Rev.*, **2011**, *111*, 7035–7062.
6 T. P. Onak, R. H. Williams, H. G. Weiss, The Synthesis of $B_4C_nH_{2n+4}$ Compounds from Pentaborane-9 and Alkynes Catalyzed by 2, 6-Dimethylpyridine*, J. Am. Chem. Soc.*, 1962, **84**, 2830–2831.
7 M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, M. S. Cohen, Carboranes. I. The Preparation and Chemistry of 1-Isopropenylcarborane and Its Derivatives (a New Family of Stable Closoboranes), *Inorg. Chem.*, 1963, **2**, 1111–1115.
8 M. M. Fein, D. Grafstein, J. E. Paustian, J. Bobinski, B. M. Lichstein, N. Mayes, N. N. Schwartz, M. S. Cohen, Carboranes. II. The Preparation of 1- and 1,2-Substituted Carboranes *Inorg. Chem.*, 1963, **2**, 1115–1119.
9 D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. S. Cohen, M. M. Fein, Carboranes. III. Reactions of the Carboranes, *Inorg. Chem.,* 1963, **2**, 1120–1125.
10 R. B. King, Three-Dimensional Aromaticity in Polyhedral Boranes and Related Molecules, *Chem. Rev.* 2001, **101** (5), 1119–1152.
11 P. R. Von Schleyer, K. Najafian, Stability and Three-Dimensional Aromaticity of Closo-Monocarbaborane Anions, CBn-1Hn-, and Closo-Dicarboranes, C2Bn-2Hn, *Inorg. Chem.*, 1998, **37** (14), 3454–3470.
12 J. Poater, M. Solà, C. Viñas, F. Teixidor, π Aromaticity and Three-Dimensional Aromaticity: Two Sides of the Same Coin, *Angew. Chem. Int. Ed.*, 2014, **53**, 12191–12195.
13 V. I. Bregadze, Dicarba-Closo-Dodecaboranes C2B10H12 and Their Derivatives, *Chem. Rev.*, 1992, **92**, 209–223.
14 D. Olid, R. Núñez, C. Viñas, F. Teixidor, Methods to Produce B-C, B-P, B-N and B-S Bonds in Boron Clusters, *Chem. Soc. Rev.*, 2013, **42**, 3318–3336.
15 V. I. Bregadze, Fifty Years of Carborane Chemistry: The History of Discovery and the First Results, R*uss. Chem. Bull*, 2014, **63**, 1021–1026.
16 G. R. Kracke, M. R. VanGordon, Y. V. Sevryugina, P. J. Kueffer, K. Kabytaev, S. S. Jalisatgi, M. F. Hawthorne, Carborane-Derived Local Anesthetics Are Isomer Dependent, *Chem. Med. Chem*, 2015, **10** , 62–67.
17 I. Bennour, F. Teixidor, Z. Kelemen, C. Viñas, M-Carborane as a Novel Core for Periphery-Decorated Macromolecules. *Molecules*, 2020, **25**, 2814–2814.
18 L. Serrano-Andrés, D. J. Klein, P. Von Ragué Schleyer, J. M. Oliva, What Electronic Structures and Geometries of Carborane Mono- and Ortho-, Meta-, and Para-Diradicals Are Preferred? *J. Chem. Theory and Comp.*, 2008, **4**, 1338–1347.
19 M. G. Davidson, T. G. Hibbert, J. A. K. Howard, A. Mackinnon K. Wade, Definitive crystal structures of *ortho*-, *meta*- and *para*-carboranes: supramolecular structures directed solely by C–H···O hydrogen bonding to hmpa (hmpa = hexamethylphosphoramide), *Chem. Commun.*, 1996, 2285–2286.
20 J. Llop, C. Viñas, J. M. Oliva, F. Teixidor, M. Flores, Modulation of the C-C Distance in Disubstituted 1,2-R2-*o*-Carboranes. Crystal Structure of *Closo* 1,2-(SPh)2-1,2-C2B10H10. *J. Organomet. Chem.*, 2002, **657**, 232–238.
21 Y. Wu, J. Zhang, Z. Xie, An Example of Extraordinary Long C–C Single Bond in 1,2-Diarylamino-*o*-Carborane*, Chin. Chem. Lett.,* 2019, **30**, 1530–1532.
22 J. Li, R. Pang, Z. Li, G. Lai, X. Q. Xiao, T. Müller, Exceptionally Long C–C Single Bonds in Diamino-*o*-Carborane as Induced by

Please do not adjust margins

Please do not adjust margins

Negative Hyperconjugation, *Angew. Chem. Int. Ed.,* 2019, **58**, 1397–1401

23 J. M. Oliva, N. L. Allan, P. V. R. Schleyer, C. Viñas, F. Teixidor, Strikingly Long C···C Distances in 1,2-Disubstituted Ortho-Carboranes and Their Dianions, *J. Am. Chem. Soc.*, 2005, **127**, 13538–13547.

24 N. Carr, D. F. Mullica, E. L. Sappenfield, F. G. Stone, Closo to Hyper-Closo Transformations in a Tungstacarborane Cage System: Crystal Structure of [NEt4][W2(μ-CC6H4Me-4)(CO)2(H5-7,8-Me2-7,8-C2B9H9){η6-7,8-Me2-7,8-C2B9H8-10-(CH2C6H4Me-4)}]. *Organometallics*, 1992, **11**, 3697–3704.

25 P. T. Brain, M. Bühl, J. Cowie, Z. G. Lewis, A. Welch, Synthesis and characterisation of pseudocloso iridium and ruthenium diphenyl carbaboranes. Molecular structures of 1,2-Ph2-3-(η-C6H6)-3,1,2-pseudocloso-RuC2B9H9 and 1,2-Ph2-3-(cym)-3,1,2-pseudocloso-RuC2B9H9(cym =p-cymene) and individual gauge for localised orbitals calculations on carbametallaboranes *J. Chem. Soc., Dalton Trans***.** 1996, **2**, 231–237.

26 J. H. Kim, M. Lamrani, J. W. Hwang, First Tetrathiolate-Bridged Dinuclear Molybdacarbaboranes: Scission and Formation of the C-C Cluster Bond during Oxidation Processes *Chem. Commun.*, 1997, 1761–1762.

27 F. Teixidor, M. A. Flores, C. Vinas, R. Sillanpää, R. Kivekäs, Exo-Nido-Cyclooctadienerhodacarboranes: Synthesis, Reactivity, and Catalytic Properties in Alkene Hydrogenation, *J. Am. Chem. Soc.,* 2000, **122**, 1963–1973.

28 a) D. A. Brown, W. Clegg, H. M. Colquhoun, J. A. Daniels, I. R. Stephenson, K. Wade*,* A Pentuply-Bridging Carbonyl Group: Crystal and Molecular Structure of a Salt of the 1-Oxo-2-Phenyl-1,2-Dicarbadodecaborate(12) Anion, [LH]+[O(Ph)C2B10H10]- (L = 1,8-N,N,N′,N′-Tetramethylnaphthalenediamine) *Chem. Commun.*, 1987, **12**, 889–891. b) B. W. Hutton, F. MacIntosh, D. Ellis, F. Herisse, S. A. Macgregor, D. McKay, V. Petrie-Armstrong, G. M. Rosair, D. S. Perekalin, H. Tricas, A. J. Welch, Unprecedented Steric Deformation of Ortho-Carborane. *Chem.Comm.*, 2008, **42**, 5345–5347.

29 a) K. Tanaka, M. Gon, S. Ito, J. Ochi, Y. Chujo**,** *Coord. Chem. Rev.*, 2022, **472**, 214779..b) Y. Cai, S. Han, J. Xiao, Y. Lin, Q. Chen, Z. Zhao, A. Qin, B. Z. Tang**,** *Angew. Chem. Int. Ed.*, 2020, **59**, 9686–9692.c) Shi, C.; Sun, H.; Tang, X.; Lv, W.; Yan, H.; Zhao, Q.; Wang, J.; Huang, W. Variable photophysical properties of phosphorescent iridium(III) complexes triggered by closo- and nido-carborane substitution. *Angew. Chem. Int. Ed*. 2013, **52**, 13434-13438. d) Sun, H.; Liu, S.; Lin, W.; Zhang, K. Y.; Huang, X.; Huo, F.; Yang, H.; Jenkins, G.; Zhao, Q.; Huang, W. Smart responsive phosphorescent materials for data recording and security protection. Chem. Eur. J. 2014, **32**, 9940-9951. e) Zhu, L.; Tang, X.; Yu, Q.; Lv, W.; Yan, H.; Zhao, Q.; Huang, W. Tuning the optical properties of 2-thienylpyridyl iridium complexes through carboranes and anions. *Chem. Commun.* 2016, **52**, 12494-12497. f) S. Sinha, Z. Kelemen, E. Hümpfner, I. Ratera, J.-P. Malval, J. P. Jurado, C. Viñas, F. Teixidor, R. Núñez, *Chem. Commun.*, 2022, **58**, 10450.

30 M. M. Balakrishnarajan, R. Hoffmann, Polyhedral Boranes with Exo Multiple Bonds: Three-Dimensional Inorganic Analogues of Quinones *Angew. Chem. Int. Ed.*, 2003, **42**, 1805–1808

31 Z. Kelemen, A. Pepiol, M. Lupu, R. Sillanpää, M. M. Hänninen, F. Teixidor, C. Viñas, Icosahedral Carboranes as Scaffolds for Congested Regioselective Polyaryl Compounds: The Distinct Distance Tuning of C-C and Its Antipodal B-B, *Chem. Commun.*, 2019, **55**, 8927–8930.

32 a) J. Poater, M. Solà, C. Viñas, F. Teixidor, π Aromaticity and Three-Dimensional Aromaticity: Two sides of the Same Coin? *Angew. Chem. Int. Ed.* 2014, **53**, 12191–12195 b) J. Poater, C. Viñas, I. Bennour, S. Escayola, M. Solà, F.Teixidor, Too Persistent to Give Up: Aromaticity in Boron Clusters Survives Radical Structural Changes, *J. Am. Chem. Soc.*, 2020, **142**, 9396–9407 c) D. Buzsáki, M. B. Kovács, E. Hümpfner, Z. Harcsa-Pintér, Z. Kelemen, Conjugation between 3D and 2D Aromaticity: Does It Really Exist? The Case of Carborane-Fused Heterocycles. *Chem. Sci.,* 2022, **13**, 11388–11393. d) D. Buzsáki, D. Gál, Z. Harcsa-Pintér, L. Kalabay, Z. Kelemen, The possible aromatic conjugation via the different edges of (car)borane clusters − Can the relationship between 3D and 2D aromatic systems be reconciled? *Chem. Eur. J.* 2024, e202402970

33 a) P. R. Nagy, M. Kállay, Approaching the Basis Set Limit of CCSD(T) Energies for Large Molecules with Local Natural Orbital Coupled-Cluster Methods, *J. Chem. Theory Comp.* 2019, **15**, 5275–5298. b) M. Kállay, P. R. Nagy, D. Mester, Z. Rolik, G. Samu, J. Csontos, J. Csóka, P. B. Szabó, L. Gyevi-Nagy, B. Hégely, I. Ladjánszki, L. Szegedy, B. Ladóczki, K. Petrov, M. Farkas, P. D. Mezei, Á. Ganyecz, The MRCC Program System: Accurate Quantum Chemistry from Water to Proteins*, J. Chem. Phys* 2020, **152**, 074107. c) P. Nagy, State-of-the-art local correlation methods enable affordable gold standard quantum chemistry for up to hundreds of atoms, *Chem. Sci.*, 2024,**15**, 14556-14584

34 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Had, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. P. Jr., F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, O. Yazyev, A. J. A., R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz; Cioslowski, J.; Fox, D. J. Gaussian 09. 2009**.**

35 K. B. Wiberg, Application of the Pople-Santry-Segal CNDO Method to the Cyclopropylcarbinyl and Cyclobutyl Cation and to Bicyclobutane, *Tetrahedron* 1968, **24**, 1083–1096.

36 I. Mayer, Bond Order and Valence Indices: A Personal Account. *J. Comput. Chem.* 2006, **28**, 204–221.

37 T. Lu, F. Chen, Multiwfn: A Multifunctional Wavefunction Analyzer. *J. Comput. Chem.* 2012, **33**, 580–592.

38 G. Schaftenaar, J. H. Noordik, Molden: A Pre- and Post-Processing Program for Molecular and Electronic Structures. *J. Comput. Aided Mol. Des.,* 2000, **14**, 123–134.

39 A. T. B. Gilbert, IQmol Molecular Viewer. Available at: Http://Iqmol.Org (Accessed October, 2012)

40 L. I. Zakharkin, I. V. Pisareva, Synthesis of 9,12-o- and 9,10-m-Carboranyl-Dithiols and -Diselenols from S2Cl2 or Se2Cl2 and o- and m-Carboranes. *J. Organomet. Chem.* 1984, **267**, 73–79.

41 Y. Sevryugina, R. L. Julius M. F. Hawthorne, Novel Approach to Aminocarboranes by Mild Amidation of Selected Iodo-carboranes, *Inorg. Chem.* 2010, **49**, 10627–10634.

 This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins