Dalton Transactions

Synthesis and Cluster Structure Distortions of Biscarborane Dithiol, Thioether, and Disulfide

Journal:	*Dalton Transactions*
Manuscript ID	DT-ART-12-2023-004289.R1
Article Type:	Paper
Date Submitted by the Author:	23-Jan-2024
Complete List of Authors:	Riffle, Jared; University of South Carolina, Department of Chemistry and Biochemistry Hemingway, Tyler; University of South Carolina, Department of Chemistry and Biochemistry Smith, Mark; University of South Carolina, Department of Chemistry and Biochemistry Peryshkov, Dmitry; University of South Carolina, Department of Chemistry and Biochemistry

ARTICLE

Synthesis and Cluster Structure Distortions of Biscarborane Dithiol, Thioether, and Disulfide

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

DOI: 10.1039/x0xx00000x

Jared R. Riffle[a], Tyler M. Hemingway[a], Mark D. Smith[a], and Dmitry V. Peryshkov[a]*

The synthesis and structural characterization of the first sulfur-containing derivatives of C,C-biscarborane {*ortho*-C_2B_{10}}$_2$ cluster – thiol, thioether, and disulfide- is reported. The biscarboranyl dithiol $(1\text{-HS-}C_2B_{10}H_{10})_2$ exhibits the exceedingly long intracluster carbon-carbon bond length of 1.858(3) Å, which is attributed to the extensive interaction between lone pairs of thiol groups and the unoccupied molecular orbital of carborane cluster. The structures of doubly deprotonated biscarboranyl dithiolate anion $(1\text{-S-}C_2B_{10}H_{10})_2^{2-}$ with various countercations feature even longer carbon-carbon bond of 2.062(10) Å within the cluster along with the short carbon-sulfur bond of 1.660(7) Å, both indicative of significant delocalization of electron density from sulfur atoms into the cluster.

Introduction

Chemistry of boron clusters, like $C_2B_{10}H_{12}$ has been actively investigated, with recent expansions into materials science, batteries, ligand design, medicinal chemistry, and catalysis.[1–13] Among numerous cluster compounds, $C_2B_{10}H_{12}$ or carboranes, containing two carbon atoms and ten boron atoms in the core, stand out as remarkably robust neutral molecular molecules with a unique electronic delocalization and steric profile. The electronic structure of 3-D aromatic carboranes bears an analogy to that of arenes and features a set of delocalized molecular orbitals within the cluster.[14–16]

Boron and carbon cluster vertices in carboranes exhibit orthogonal reactivity.[1] The B–H bonds of the cluster are largely non-polarized and exhibit reactivity similar to that of aromatic C–H bonds engaging in electrophilic substitution and oxidative addition to low-valent late transition metal centers.[17–19] In the derivatives of carboranes, boron atoms of the cluster behave as strong σ-donors for exohedral groups. In contrast, the C–H bonds in carboranes are relatively acidic (pK_a is ca. 23) and can be deprotonated with reagents such as n-butyllithium resulting in the formation of metalated carbanions, which can be derivatized with electrophiles.[20–22] The carbon atoms of *ortho*-$C_2B_{10}H_{12}$ form σ-bonds to exohedral substituents with the possibility of electronic communication through π-donation from those groups to the cluster. Thus, the cluster exhibits electron-withdrawing behavior with respect to a group connected to its carbon atoms.[23–26]

The donation from the substituents at carbon atoms increases electron density in the cluster LUMO orbital, which has a σ*(C–C) antibonding orbital as a significant component. The population of this σ* orbital leads to weakening of the intracluster C–C bond and an increase in the C–C interatomic distance. The C–C bond length in the parent unsubstituted cluster is cf. 1.624(8) Å,[27] which is longer than the “standard” single bond between *sp*^{3}-hybridized carbon atoms in ethane (1.54 Å) due to the delocalized bonding in the carborane cage. Extensive computational studies ascribed the trend in lengthening of the cluster carbon–carbon bond and the concomitant shortening of the exohedral bonds to the efficiency of negative hyperconjugation between the lone pairs at the substituent groups and the antibonding σ^*_{C-C} orbital of the *ortho*-carborane cluster.[28–30] According to calculations, *ortho*-carborane disubstituted with NH_2 or SH groups would have the longest intracluster C–C bonds for the first- and second-row element substituents.[31] Experimentally, the recently reported diamine derivative $(MesCH_2N(H))_2(C_2B_{10}H_{10})$ and $(MesN(H))_2(C_2B_{10}H_{10})$ exhibits some of the longest C–C bonds (1.931(3) Å and 1.990(4) Å, respectively).[32–34] Additionally, calculations suggest that negative hyperconjugation is expected to be even more pronounced in the corresponding deprotonated disubstituted clusters with intracluster carbon-carbon distance elongation, which exceeds

---

[a] *Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter St., Columbia, South Carolina 29208, United States. Email: peryshkov@sc.edu*

Electronic Supplementary Information (ESI) available: experimental procedures, crystallography details, and NMR spectra. See DOI: 10.1039/x0xx00000x. CCDC 2314227-2314232.

2.1 Å, leading to the partial opening of the cluster cage from the *closo*- to the *nido*- form.[28,31]

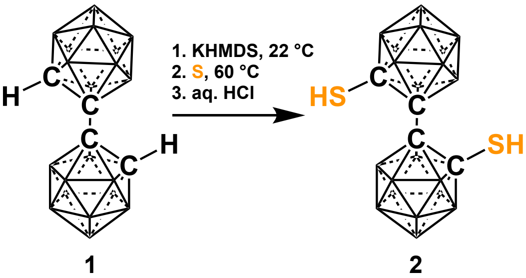
In contrast to the increasingly developing chemistry of icosahedral carboranes, its carbon-linked two-cluster derivative, 1,1′-bis(*o*-carborane) $(C_2B_{10}H_{11})(C_2B_{10}H_{11})$ (biscarborane) remains relatively unexplored despite being known for a comparably long time.[35–38] The structure of biscarborane can be compared to that of biphenyl where two aromatic rings may exhibit a significant degree of electronic communication. Indeed, the chemical reduction of biscarborane leads to structural changes in both clusters where the individual clusters open with intracluster C–C bonds elongating accompanied by the shortening of the intercluster C–C bond.[39–41] Presumably, the presence of two linked electron-accepting clusters in biscarborane will lead to even more pronounced interaction with exohedral substituents at its remaining carbon atoms with stronger π-donation of their lone pairs into biscarborane, which will be indicated by the further elongation of intracluster carbon-carbon bonds.

While numerous *C*-substituted derivatives of *closo*-$C_2B_{10}H_{12}$ clusters have been reported, the derivatization of biscarborane is largely limited to biscarborane acting as a chelating group, i.e. the formation of five-member cycles with both cluster carbon atoms bound to either a transition metal center or a heteroatom.[42–49] To the best of our knowledge, there have been only one literature report for the attachment of pairs of donor groups (dihydro-1,2-oxazines) to two carbon atoms of biscarborane.[50] In our previous work, we have reported the attempt to install two phosphine groups on both carbon atoms of biscarborane, which, instead of the target diphosphine, led to the intramolecular B–H bond activation driven by the reduction of one of the boron clusters.[51,52] Thiolates represent another large class of donor groups with lone pairs, and single-cage carboranyl thiolates have been utilized in ligand design for catalysis as well as for decoration of metal surfaces and nanoparticles.[53–64,25] With the double-cage biscarborane, we sought to functionalize its carbon atoms with thiol groups to obtain an insight into the substituent effects on the cluster structure.

In this work, we report the synthesis and structural characterization of biscarborane dithiol, which exhibits the strikingly long intracluster C–C bond length of 1.858(3) Å. The local distortion of the cluster bonding can be manipulated even further, as we demonstrate by the deprotonation of biscarborane dithiol, which led to partial cluster opening and remarkably long C–C bond distance of 2.062(10) Å in its anionic dithiolate form. We also report the synthesis and structure of biscarboranyl bis(methylthio)ether and biscarboranyl disulfide.

Results and Discussion

Biscarboranyl dithiol was prepared by a procedure similar to the synthesis of *ortho*-carboranyl dithiol, which involves deprotonation of cluster carbon vertices and the subsequent reaction with sulfur.[20,65] However, we found that the more sterically hindered biscarborane requires higher temperature and longer reaction time in comparison with the relatively facile formation of $(HS)_2C_2B_{10}H_{10}$ at room temperature. The C–H bonds of 1,1′-bis(*ortho*-carborane) **(1)** were deprotonated using potassium hexamethyldisilazane (KHMDS) in THF at room temperature.[21,22,66] The doubly *C*-metalated cluster was isolated and elemental sulfur was added to its THF solution, which then was heated at 60 ºC for 24 hours. The reaction mixture was quenched with aqueous HCl and the biscarboranyl dithiol $(HS\text{-}C_2B_{10}H_{10})_2$ (**2**) was isolated after extraction to dichloromethane in 40% yield as a white solid.



Scheme 1. The synthesis of biscarboranyl dithiol $(HS\text{-}C_2B_{10}H_{10})_2$ (**2**) from biscarborane **1**.

The ^1H NMR spectrum of biscarborane dithiol in $CDCl_3$ exhibits a characteristic resonance for the S-H proton at 4.19 ppm. Single crystal X-ray diffraction revealed the molecular structure of the dithiol. The thiol groups in **2** are arranged in the *trans*- orientation relative to each other. The main structural feature of **2** is the long intracluster C1–C2 bond distance of 1.858(3) Å (cf. C1–C2 = 1.690(3) Å for the parent biscarborane).[36] This significantly elongated cluster carbon-carbon bond can be compared to that in *ortho*-carborane thioethers (1.803(2) Å in 1,2-$(SMe)_2$-*ortho*-$C_2B_{10}H_{10}$, and 1.799(3)Å in 1,2-$(SPh)_2$-*ortho*-$C_2B_{10}H_{10}$)[67,68]. Summary of C–C and C–S bond lengths for relevant carboranyl sulfur-containing derivatives and biscarboranyl congeners reported in this work is given in Table 1. Note that the crystal structure of corresponding dithiol 1,2-$(HS)_2$-*ortho*-$C_2B_{10}H_{10}$ has not been yet reported. The significant elongation of the carbon-carbon bond in **2** is due to electronic factors, namely the interaction of sulfur atom lone pair and the LUMO of the cluster.

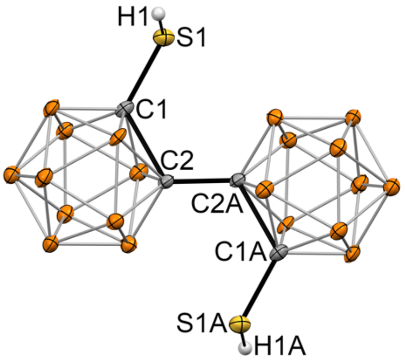


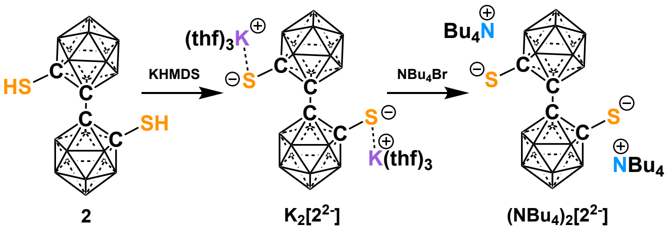
Figure 1. The displacement ellipsoid plot (50% probability) of biscarboranyl dithiol $(HS\text{-}C_2B_{10}H_{10})_2$ (**2**). Hydrogen atoms of biscarborane cluster are not shown. Selected distances (Å): C1–C2 = 1.858(3) Å, C2–C2A = 1.530(5), C1–S1 = 1.762(3).

The intercluster C2–C2A bond length is 1.530(5) Å, which is comparable to that in the parent unsubstituted biscarborane (1.534(1) Å).[69] The C1–S1 bond length in **2** is 1.762(3) Å, which is comparable to the single carbon-sulfur bonds in aromatic thiols.

Table 1. Intracluster carbon-carbon and exohedral carbon-sulfur bond lengths in representative literature examples of *ortho*-carboranyl and biscarboranyl (this work) thiols, thiolates, and thioethers.

thiocarborane	C–C distance, Å	C–S distance, Å
parent *ortho*-carborane $C_2B_{10}H_{12}$[27]	1.629(5)	–
1-C_5H_5N-2-SH-$C_2B_{10}H_{10}$[70]	1.730(3)	1.775(2)
[H-N,N,N,N-tetramethylnaphthalene diamine][1-S-2-Ph-$C_2B_{10}H_{10}$][71]	1.836(5)	1.729(4)
1,2-$(SMe)_2$-$C_2B_{10}H_{10}$[68]	1.803(1)	1.761(1)
1,2-$SCH_2(CH_2OCH_2)_2CH_2S$-$C_2B_{10}H_{10}$[72]	1.858(5) /1.826(5)	1.742(4) / 1.752(4)
parent biscarborane $(C_2B_{10}H_{11})_2$[36]	1.690(3)	–
(HS-$C_2B_{10}H_{10})_2$ (**2**)	1.858(3)	1.762(3)
([K(THF)$_3$]$_2$(S-$C_2B_{10}H_{10})_2$ (K$_2$[**2**$^{2-}$]).	2.022(2)	1.710(1)
[NBu$_4$]$_2$(S-$C_2B_{10}H_{10})_2$ ((NBu$_4$)$_2$[**2**$^{2-}$])	2.030(9) / 2.062(10)	1.636(8) Å / 1.660(7) Å
(MeS-$C_2B_{10}H_{10})_2$ (**3**)	1.898(1)	1.756(1)

Deprotonation of dithiol **2** can be expected to lead to an even larger increase in exohedral π-bonding of the cluster. We examined the structures of several thiolate salts derived from **2** that differ in the coordinating ability of the counter cation: K$_2$[**2**$^{2-}$], (HNEt$_3$)$_2$[**2**$^{2-}$], and (NBu$_4$)$_2$[**2**$^{2-}$]. Their synthesis and structures are described below.



Scheme 2. Deprotonation of biscarborane dithiol and formation of potassium salt [K(THF)$_3$]$_2$(S-$C_2B_{10}H_{10})_2$ (K$_2$[**2**$^{2-}$]) and tetrabutyl ammonium salt [NBu$_4$]$_2$(S-$C_2B_{10}H_{10})_2$ ((NBu$_4$)$_2$[**2**$^{2-}$]).

The potassium dithiolate K$_2$[**2**$^{2-}$] was prepared by the deprotonation of dithiol **2** with KHMDS in THF. The single crystals of (K(THF)$_3$)$_2$[**2**$^{2-}$] were grown from THF solution. The biscarboranyl dithiolate anion adopted the *trans*- orientation of thiol fragments with two potassium cations coordinated to each sulfur atom (K···S distances are 3.137(1) Å and 3.242(1) Å). The intracluster C1–C2 bond distance is exceptionally long at 2.022(2) Å. This distance is comparable with that of the related deprotonated hydroxycarborane anions 1-O$^-$-2-Ph-$C_2B_{10}H_{10}$ with either protonated "proton sponge" or triphenylmethylphosphonium counter cations (2.001(3) Å and 2.065(7) Å, respectively).[28] The substantial degree of delocalization of the negative charge from sulfur into the cluster is also manifested by the short exohedral C1–S1 bond of 1.710(1) Å. This bond length is shorter than that in the parent neutral **2** (1.762(3) Å). The electronic conjugation of two clusters in biscarborane core of K$_2$[**2**$^{2-}$] is demonstrated by the shortening of the intercluster C2–C2A bond to 1.507(2) Å.

The effect of a weak counter cation coordination can be demonstrated by the crystal structure of the tetralklyammonium salt (NBu$_4$)$_2$[**2**$^{2-}$], which was obtained by the ion exchange from K$_2$[**2**$^{2-}$]. The structure of (NBu$_4$)$_2$[**2**$^{2-}$] similarly features trans- orientation of sulfur atoms on the biscarborane scaffold. The C1–C2 / C3–C4 bond distances are also similarly long at 2.030(9) and 2.062(10) Å. The absence of coordination of sulfur atoms to the cation results in the drastic shortening of carbon-sulfur distances to 1.636(8) Å and 1.660(7) Å in (NBu$_4$)$_2$[**2**$^{2-}$]. These bond lengths are within the range of carbon-sulfur double bonds in thioketones. Furthermore, the intercluster C–C bond is shortened to 1.459(8) Å. These structural distortions of the *closo*-biscarborane cluster in (NBu$_4$)$_2$[**2**$^{2-}$] draw nearer to those of the biscarboranyl dianion (*nido*-$C_2B_{10}H_{11})_2^{2-}$ obtained by Hawthorne and co-workers in chemical reduction of biscarborane with sodium metal where the intracluster C–C distance is 2.414(4) Å and intercluster C=C double bond is 1.377(4) Å. The structure of (NBu$_4$)$_2$[**2**$^{2-}$] also features two close S···H–C contacts between the thiolate and alkylammonium cation (2.523(2) Å and 2.634(2) Å) that correspond to the S···C distances (3.384(9) Å and 3.420(9) Å),

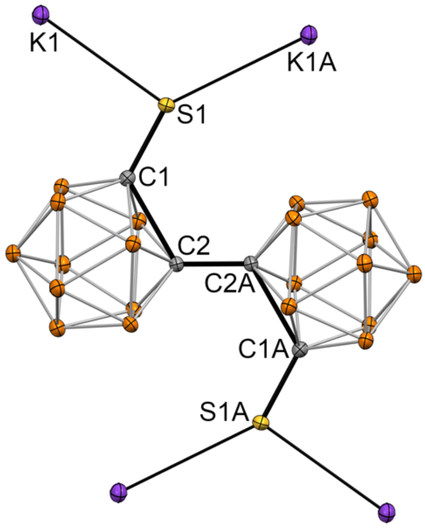


Figure 2. The displacement ellipsoid plot (50% probability) of [K(THF)$_3$]$_2$(S-$C_2B_{10}H_{10})_2$ (K$_2$[**2**$^{2-}$]). Hydrogen atoms of biscarborane cluster are not shown. THF molecules coordinated to potassium cations are not shown. Selected distances (Å): C1–C2 = 2.022(2), C1–S1 = 1.710(1), C2–C2A = 1.507(2) Å, S1–K1 = 3.137(1), S1–K1A = 3.242(1).

which are shorter than van der Waals radii sum for sulfur and carbon.

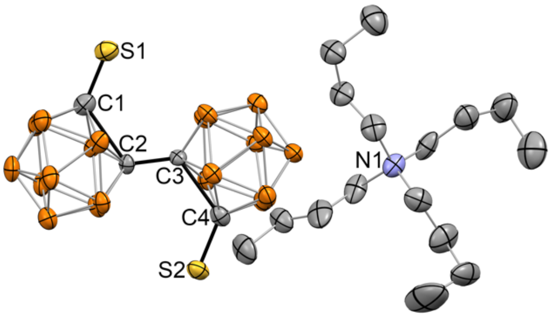
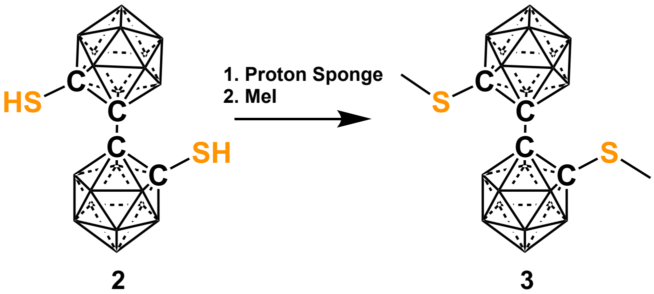


Figure 3. The displacement ellipsoid plot (50% probability) of $[NBu_4]_2(S\text{-}C_2B_{10}H_{10})_2$ ($(NBu_4)_2[\mathbf{2}^{2-}]$). Hydrogen atoms of biscarborane cluster are not shown. Only one cation-anion pair present in the asymmetric unit is shown. Selected distances (Å): C1–C2 = 2.030(9), C3–C4 = 2.062(10), C1–S1 = 1.660(7), C4–S2 = 1.636(8), C2–C3 = 1.459(8).

The crystal structure of triethylammonium salt $(HNEt_3)_2[\mathbf{2}^{2-}]$ provides another case of cluster bond distortions in the series of deprotonated $\mathbf{2}^{2-}$ anions (see Supporting Information for details). The intracluster C–C bond is similarly long at 2.046(2) Å, the intercluster C–C bond is relatively short at 1.502(1) Å, and exohedral C–S bond length is 1.713(1) Å. Each $HNEt_3$ cation is hydrogen-bonded to thiolate sulfur atoms with the S···N distance of 3.161(2) Å and nearly linear N–H···S angle of 176(2)º.

Deprotonation of the dithiol **2** in THF led to a color change from colorless to yellow/orange. The spectrum of **2** contains only the absorption band below 300 nm in the UV region of the spectrum. In contrast, the spectrum of $[\mathbf{2}^{2-}]$ contains an additional broad band spanning from 300 to 450 nm with the maximum at 340 nm that is consistent with its orange color. The density functional theory calculations of the electronic structure using ADF[73] with the hybrid PBE0 functional and the TZP basis set for **2** and ATZP basis set[74] for $[\mathbf{2}^{2-}]$ demonstrated the difference between the magnitude of the HOMO-LUMO energy gap for neutral **2** (5.45 eV) and its free deprotonated anion $[\mathbf{2}^{2-}]$ (3.48 eV). Notably, for both **2** and $[\mathbf{2}^{2-}]$ the HOMO represents lone pairs at sulfur atoms and LUMO is mostly localized within the biscarborane cluster with the lobes corresponding to the antibonding interactions for the intracluster carbon-carbon bonds and π-bonding interactions with respect to intercluster carbon-carbon bonds and exohedral carbon-sulfur bonds (see Supporting Information for details). In addition, HOMO-3 for $[\mathbf{2}^{2-}]$ dianion consists of lobes representing π-bonding interactions between cluster carbon and sulfur atoms as well as the intercluster carbon-carbon bond indicating a significant thioketone character of its carbon-sulfur bonds.

Carboranyl thiols are known to be readily converted to corresponding thioethers.[67,68] We found that deprotonation of **2** with "proton sponge" (1,8-bis(dimethylamino)naphthalene) and subsequent addition of iodomethane resulted in the formation of biscarboranyl bis(methylthio)ether **3**. The ^1H NMR spectrum exhibited the presence of the characteristic resonance at 1.56 ppm for the $S\text{-}CH_3$ group and the absence of the signal from the S–H group of the parent dithiol. Single crystal X-ray diffraction study revealed the elongation of the intracluster C1–C2 bond length at 1.898(1) Å, which is even more pronounced than that of the corresponding bond in the dithiol **2** at 1.858(3) (Figure 4). Notably, the C1–C2 in **3** is longer than the intracluster carbon-carbon bonds in the previously reported carboranyl thioethers $1,2\text{-}(SMe)_2\text{-}C_2B_{10}H_{10}$ (1.803(2) Å) and $1,2\text{-}(SPh)_2\text{-}C_2B_{10}H_{10}$ (1.799(3) Å)[67,68], which can be attributed to the stronger electron-accepting property of the biscarborane cluster in comparison with the parent single-cage carborane. The C1–S1 bond length in **3** is 1.756(1) Å, which is comparable with that in $1,2\text{-}(SMe)_2\text{-}C_2B_{10}H_{10}$ (1.761(1) Å).



Scheme 3. The synthesis of biscarboranyl bis(methylthio)ether $(MeS\text{-}C_2B_{10}H_{10})_2$ (**3**).

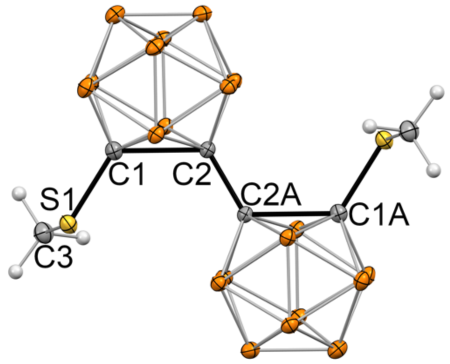
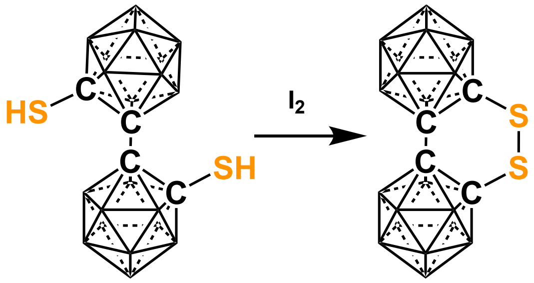


Figure 4. The displacement ellipsoid plot (50% probability) of $(MeS\text{-}C_2B_{10s}H_{10})_2$ (**3**). Hydrogen atoms of biscarborane cluster are not shown. Selected distances (Å): C1–C2 = 1.898(1), C1–S1 = 1.756(1), C2–C2A = 1.522(1).

During the synthesis of **2**, we also isolated biscarboranyl disulfide **4** as a minor side product. The disulfide **4** was also produced in quantitative yield by oxidation of dithiol **2** with iodine. The crystal structure of **4** features the intracluster bond length C1–C2 of 1.676(3) Å, which is significantly shorter than that in dithiol **2** 1.858(3) Å, and similar to that in the parent biscarborane (1.690(3) Å). The intercluster distance C2–C3 distance is 1.535(3) Å, which is comparable to that in the parent biscarborane and dithiol **2**. The C1–S1 distance in the disulfide



Scheme 4. The synthesis of biscarboranyl disulfide $(S\text{-}C_2B_{10}H_{10})_2$ (**4**).

(1.790(2) Å) is longer than that in the biscarboranyl dithiol (1.762(3) Å).

Given the similarities between aromatic carborane clusters and arenes, the structure of the biscarboranyl disulfide **4** can be compared with the reported structure of 2,2'-biphenyl disulfide (Figure 5).[75] The carbon-sulfur distances in these compounds are virtually identical. However, there is a slightly shorter S–S bond in the biscarboranyl disulfide at 2.034(1) Å than in biphenyl disulfide (2.066(1) Å). The longer C–S bonds and shorter intra-cluster C–C bonds in the biscarboranyl disulfide indicate that there is no longer as large of an impact from sulfur lone pairs on cluster bonding in this molecule. The torsion angle C1–C2–C3–C4 is smaller in the case of the biscarboranyl disulfide at 25.2(3)º than the same angle in biphenyl disulfide C1–C2–C3–C4 at 36.7(2)º. This decrease in the torsion angle is attributed to the larger biscarborane C-C bonds and shorter S-S bond.

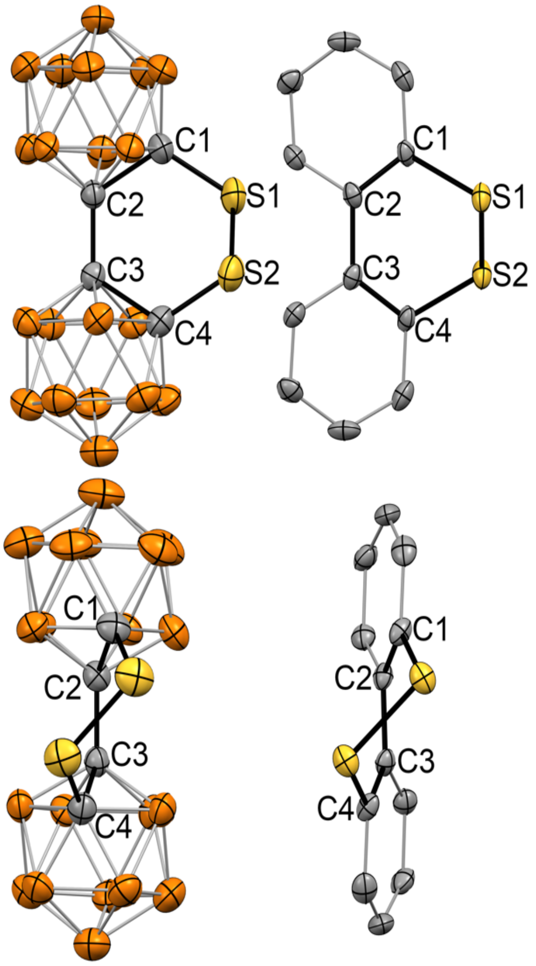


Figure 5. The displacement ellipsoid plots (50% probability) of biscarboranyl disulfide $(S\text{-}C_2B_{10}H_{10})_2$ (**4**, left) and biphenyl disulfide[75] (right). Hydrogen atoms are not shown. Selected distances (Å) and angles (°) in biscarboranyl disulfide: C1–C2 = 1.676(3), C1–S1 = 1.790(2), S1–S2 = 2.034(1), C1–C2–C3–C4 = 25.2(3); and in biphenyl disulfide: S1–S2 = 2.066(1), C1–C2–C3–C4 = 36.7(2).

Conclusions

In conclusion, we synthesized a series of sulfur-functionalized biscarborane clusters which serve as the first examples of biscarborane clusters bearing independent donor groups at both carbon atoms. Biscarborane dithiol, deprotonated dithiolate, and bis(methyl)thioether feature exceedingly long intracluster C–C bond lengths, consistent with the increased π-donation of sulfur atom lone pairs into the electron-accepting boron cluster. These distortions of the boron cage bonding are more significantly pronounced in these biscarborane-based derivatives than in the analogous single cluster carborane examples, likely due to the stronger electron-withdrawing nature of two linked clusters in comparison with only one. For example, the tetrabutylammonium salt of the deprotonated biscarborane thiol $[NBu_4]_2(S\text{-}C_2B_{10}H_{10})_2$ exhibits the longest cluster C–C bond length of 2.030(9) Å and the shortest C–S bond of 1.660(7) Å indicative of a double bond. The exploration of coordination chemistry of the potentially redox- and proton-responsive biscarboranyl dithiol ligand is underway.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This material is based upon work supported by the National Science Foundation under grant CHE-2154828. We are grateful to the Advanced Support for Innovative Research Excellence program of the Office of the Vice President for Research at the University of South Carolina.

Notes and References

1 R. N. Grimes, *Carboranes, Third Edition*, Academic Press, Amersterdam ; Boston, 3 edition., 2016.
2 M. F. Hawthorne, *Boranes and Beyond: History and the Man Who Created Them*, Springer, New York, NY, 2023.
3 S. P. Fisher, A. W. Tomich, S. O. Lovera, J. F. Kleinsasser, J. Guo, M. J. Asay, H. M. Nelson and V. Lavallo, *Chem. Rev.*, 2019, **119**, 8262–8290.
4 A. B. Buades, V. Sanchez Arderiu, D. Olid-Britos, C. Viñas, R. Sillanpää, M. Haukka, X. Fontrodona, M. Paradinas, C. Ocal and F. Teixidor, *J. Am. Chem. Soc.*, 2018, **140**, 2957–2970.
5 J. M. Stauber, E. A. Qian, Y. Han, A. L. Rheingold, P. Král, D. Fujita and A. M. Spokoyny, *J. Am. Chem. Soc.*, 2020, **142**, 327–334.
6 P. Stockmann, M. Gozzi, R. Kuhnert, M. B. Sárosi and E. Hey-Hawkins, *Chem. Soc. Rev.*, 2019, **48**, 3497–3512.
7 Z. J. Leśnikowski, *J. Med. Chem.*, 2016, **59**, 7738–7758.
8 A. Saha, E. Oleshkevich, C. Vinas and F. Teixidor, *Advanced Materials*, 2017, **29**, 1704238.
9 M. Scholz and E. Hey-Hawkins, *Chem. Rev.*, 2011, **111**, 7035–7062.
10 B. J. Eleazer and D. V. Peryshkov, *Comments on Inorganic Chemistry*, 2018, **38**, 79–109.
11 B. C. Nussbaum, A. L. Humphries, G. B. Gange and D. V. Peryshkov, *Chem. Commun.*, 2023, **59**, 9918–9928.
12 S. A. Shackelford, J. L. Belletire, J. A. Boatz, S. Schneider, A. K. Wheaton, B. A. Wight, H. L. Ammon, D. V. Peryshkov and S. H. Strauss, *Organic Letters*, 2011, **13**, 2795–2796.
13 A. Marfavi, P. Kavianpour and L. M. Rendina, *Nat Rev Chem*, 2022, **6**, 486–504.

14 Z. Chen and R. B. King, *Chem. Rev.*, 2005, **105**, 3613–3642.
15 J. Poater, M. Solà, C. Viñas and F. Teixidor, *Angew. Chem. Int. Ed.*, 2014, **53**, 12191–12195.
16 J. Poater, C. Viñas, M. Solà and F. Teixidor, *Nat Commun*, 2022, **13**, 3844.
17 Y. Quan, Z. Qiu and Z. Xie, *Chem. Eur. J.*, 2018, **24**, 2795–2805.
18 R. M. Dziedzic and A. M. Spokoyny, *Chem. Commun.*, 2019, **55**, 430–442.
19 Y. Quan and Z. Xie, *Chem. Soc. Rev.*, 2019, **48**, 3660–3673.
20 A.-R. Popescu, A. D. Musteti, A. Ferrer-Ugalde, C. Viñas, R. Núñez and F. Teixidor, *Chemistry – A European Journal*, 2012, **18**, 3174–3184.
21 K. P. Anderson, H. A. Mills, C. Mao, K. O. Kirlikovali, J. C. Axtell, A. L. Rheingold and A. M. Spokoyny, *Tetrahedron*, 2019, **75**, 187–191.
22 H. D. A. C. Jayaweera, M. M. Rahman, P. J. Pellechia, M. D. Smith and D. V. Peryshkov, *Chem. Sci.*, 2021, **12**, 10441–10447.
23 Y. Endo, T. Sawabe and Y. Taoda, *J. Am. Chem. Soc.*, 2000, **122**, 180–181.
24 Y. Taoda and Y. Endo, *Tetrahedron Letters*, 2003, **44**, 8177–8181.
25 A. M. Spokoyny, C. W. Machan, D. J. Clingerman, M. S. Rosen, M. J. Wiester, R. D. Kennedy, C. L. Stern, A. A. Sarjeant and C. A. Mirkin, *Nature Chem*, 2011, **3**, 590–596.
26 J. Schulz, R. Clauss, A. Kazimir, S. Holzknecht and E. Hey-Hawkins, *Angewandte Chemie International Edition*, 2023, **62**, e202218648.
27 A. R. Turner, H. E. Robertson, K. B. Borisenko, D. W. H. Rankin and M. A. Fox, *Dalton Trans.*, 2005, 1310–1318.
28 L. A. Boyd, W. Clegg, R. C. B. Copley, M. G. Davidson, M. A. Fox, T. G. Hibbert, J. A. K. Howard, A. Mackinnon, R. J. Peace and K. Wade, *Dalton Trans.*, 2004, 2786–2799.
29 M. A. Fox, R. J. Peace, W. Clegg, M. R. J. Elsegood and K. Wade, *Polyhedron*, 2009, **28**, 2359–2370.
30 G. B. Gange, A. L. Humphries, D. E. Royzman, M. D. Smith and D. V. Peryshkov, *J. Am. Chem. Soc.*, 2021, **143**, 10842–10846.
31 J. M. Oliva, N. L. Allan, P. v. R. Schleyer, C. Viñas and F. Teixidor, *J. Am. Chem. Soc.*, 2005, **127**, 13538–13547.
32 J. Li, R. Pang, Z. Li, G. Lai, X.-Q. Xiao and T. Müller, *Angewandte Chemie International Edition*, 2019, **58**, 1397–1401.
33 Y. Wu, J. Zhang and Z. Xie, *Chinese Chemical Letters*, 2019, **30**, 1530–1532.
34 N. Mandal and A. Datta, *Chem. Commun.*, 2020, **56**, 15377–15386.
35 J. A. Dupont and M. Frederick. Hawthorne, *J. Am. Chem. Soc.*, 1964, **86**, 1643–1643.
36 S. Ren and Z. Xie, *Organometallics*, 2008, **27**, 5167–5168.
37 A. J. Welch, in *50th Anniversary of Electron Counting Paradigms for Polyhedral Molecules : Historical and Recent Developments*, ed. D. M. P. Mingos, Springer International Publishing, Cham, 2021, pp. 163–195.
38 K. Cao and C.-Y. Zhang, *European Journal of Organic Chemistry*, 2022, **2022**, e202200737.
39 T. D. Getman, C. B. Knobler and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1990, **112**, 4593–4594.
40 T. D. Getman, C. B. Knobler and M. F. Hawthorne, *Inorg. Chem.*, 1992, **31**, 101–105.
41 D. Zhao, J. Zhang, Z. Lin and Z. Xie, *Chem. Commun.*, 2016, **52**, 9992–9995.
42 D. A. Owen and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1970, **92**, 3194–3196.
43 D. E. Harwell, M. D. Mortimer, C. B. Knobler, F. A. L. Anet and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1996, **118**, 2679–2685.
44 L. E. Riley, T. Krämer, C. L. McMullin, D. Ellis, G. M. Rosair, I. B. Sivaev and A. J. Welch, *Dalton Transactions*, 2017, **46**, 5218–5228.
45 R. J. Jeans, A. P. Y. Chan, L. E. Riley, J. Taylor, G. M. Rosair, A. J. Welch and I. B. Sivaev, *Inorg. Chem.*, 2019, **58**, 11751–11761.
46 A. C. Phung, J. C. Fettinger and P. P. Power, *Organometallics*, 2023, **42**, 1649–1657.
47 M. Diab, K. Jaiswal, D. Bawari and R. Dobrovetsky, *Israel Journal of Chemistry*, 2023, **63**, e202300010.
48 C. Zhang, J. Wang, Z. Lin and Q. Ye, *Inorg. Chem.*, 2022, **61**, 18275–18284.
49 M. J. Martin, W. Y. Man, G. M. Rosair and A. J. Welch, *Journal of Organometallic Chemistry*, 2015, **798**, 36–40.
50 S. L. Powley, L. Schaefer, W. Y. Man, D. Ellis, G. M. Rosair and A. J. Welch, *Dalton Trans.*, 2016, **45**, 3635–3647.
51 Y. O. Wong, M. D. Smith and D. V. Peryshkov, *Chem. Eur. J.*, 2016, **22**, 6764–6767.
52 Y. O. Wong, M. D. Smith and D. V. Peryshkov, *Chem. Commun.*, 2016, **52**, 12710–12713.
53 R. D. Adams, J. Kiprotich, D. V. Peryshkov and Y. O. Wong, *Chem. Eur. J.*, 2016, **22**, 6501–6504.
54 H. A. Mills, C. G. Jones, K. P. Anderson, A. D. Ready, P. I. Djurovich, S. I. Khan, J. N. Hohman, H. M. Nelson and A. M. Spokoyny, *Chem. Mater.*, 2022, **34**, 6933–6943.
55 R. D. Adams, J. Kiprotich, D. V. Peryshkov and Y. O. Wong, *Inorg. Chem.*, 2016, **55**, 8207–8213.
56 Y. Li, Q. Jiang, Y. Li, X. Shen, H. Yan and V. I. Bregadze, *Inorg. Chem.*, 2010, **49**, 5584–5590.
57 S. V. Timofeev, O. B. Zhidkova, E. M. Mosolova, I. B. Sivaev, I. A. Godovikov, K. Y. Suponitsky, Z. A. Starikova and V. I. Bregadze, *Dalton Trans.*, 2015, **44**, 6449–6456.
58 J. Wang, F. Xu, Z.-Y. Wang, S.-Q. Zang and T. C. W. Mak, *Angewandte Chemie International Edition*, 2022, **61**, e202207492.
59 L. Schwartz, L. Eriksson, R. Lomoth, F. Teixidor, C. Viñas and S. Ott, *Dalton Trans.*, 2008, 2379–2381.
60 S. Liu, J. Zhang, X. Wang and G.-X. Jin, *Dalton Trans.*, 2006, 5225–5230.
61 Z. Wang, H. Ye, Y. Li, Y. Li and H. Yan, *J. Am. Chem. Soc.*, 2013, **135**, 11289–11298.
62 F. Teixidor, M. A. Flores, C. Viñas, R. Sillanpää and R. Kivekäs, *J. Am. Chem. Soc.*, 2000, **122**, 1963–1973.
63 Z.-Y. Wang, M.-Q. Wang, Y.-L. Li, P. Luo, T.-T. Jia, R.-W. Huang, S.-Q. Zang and T. C. W. Mak, *J. Am. Chem. Soc.*, 2018, **140**, 1069–1076.
64 J. J. Schwartz, A. M. Mendoza, N. Wattanatorn, Y. Zhao, V. T. Nguyen, A. M. Spokoyny, C. A. Mirkin, T. Baše and P. S. Weiss, *J. Am. Chem. Soc.*, 2016, **138**, 5957–5967.
65 C. Vinas, R. Benakki, F. Teixidor and J. Casabo, *Inorg. Chem.*, 1995, **34**, 3844–3845.
66 J. C. Axtell, K. O. Kirlikovali, R. M. Dziedzic, M. Gembicky, A. L. Rheingold and A. M. Spokoyny, *European Journal of Inorganic Chemistry*, 2017, **2017**, 4411–4416.
67 J. Llop, C. Viñas, J. M. Oliva, F. Teixidor, M. A. Flores, R. Kivekas and R. Sillanpää, *Journal of Organometallic Chemistry*, 2002, **657**, 232–238.
68 A. Laromaine, C. Viñas, R. Sillanpää and R. Kivekäs, *Acta Cryst C*, 2004, **60**, o524–o526.
69 W. Y. Man, G. M. Rosair and A. J. Welch, *Acta Cryst E*, 2014, **70**, 462–465.
70 A. S. Batsanov, M. A. Fox, T. G. Hibbert, J. A. K. Howard, R. Kivekäs, A. Laromaine, R. Sillanpää, C. Viñas and K. Wade, *Dalton Trans.*, 2004, 3822–3828.
71 R. Coult, M. A. Fox, W. R. Gill, K. Wade and W. Clegg, *Polyhedron*, 1992, **11**, 2717–2721.
72 F. Teixidor, C. Vinas, J. Rius, C. Miravitlles and J. Casabo, *Inorg. Chem.*, 1990, **29**, 149–152.
73 G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders and T. Ziegler, *J. Comput. Chem.*, 2001, **22**, 931–967.

74 E. Van Lenthe and E. J. Baerends, *J. Comput. Chem.*, 2003, **24**, 1142–1156.
75 I. Bernal, F. Somoza and J. S. Ricci Jr., *Heteroatom Chemistry*, 1998, **9**, 65–74.