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PAPER

Synthesis, structural, spectroscopic and electrochemical studies of carborane substituted naphthyl selenides†

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New unsymmetrical selenides bearing an *o*-carborane and a naphthalene ring as the substituents were prepared by the cleavage of the corresponding diselenides. The compounds were characterized by means of spectroscopic and analytical methods. ^{77}Se NMR signals of the selenium atoms attached to the carbon atoms of the carborane cages are shifted downfield in comparison to those bonded only to the aromatic rings, indicating an electron withdrawing effect of the *o*-carboranyl substituent. Compounds 1-(2-R-1,2-dicarba-*closo*-carboranyl)naphthyl selenides (R = Me, **1**; Ph, **2**) were characterized by means of single crystal X-ray diffraction. The influence of the electronic nature of the substituents attached to the selenium atoms on the structural parameters and packing properties of naphthyl selenides are discussed. Theoretical calculations and cyclic voltammetry (CV) studies were carried out to compare the bonding nature of carboranyl and analogous aryl selenium compounds. Cyclic voltammetry studies of naphthyl carboranyl mono and diselenides have shown that the carboranyl fragment polarizes the Se lone pair making it less prone to generate a Se–Se bond.

Introduction

The rapid advancement in organoselenium chemistry during the past decades has been achieved through the discovery of new synthetic methods and the subsequent characterization of an increasing number of compounds.[1] Organoselenides have been shown to play an important role in a number of biochemical transformations,[2] and in materials science as the precursors for metal organic chemical vapour deposition (MOCVD) processes.[3] A major factor with an impact on the structure, reactivity, and pharmacological activity of organoselenium compounds, is believed to be the inter- and intra-molecular interactions involving the *p*-type lone pairs of the selenium atoms. Such interactions can affect the conformational rigidity of the molecules and play a key role, for instance, in chirality transfer[1b,4] and stabilization of the intermediates in biochemical reactions.[5]

The *p*-type lone pair orbitals of the selenium atoms (n_p(Se)), as well as *s*-type lone pair orbitals, will suffer steric compression if they are located at distances shorter than the sum of van der Waals radii. Such steric interactions are usually accompanied by severe exchange repulsions.[6] However, the steric compression also causes nonbonding interactions involving direct orbital overlap between the atoms placed within such distances, as S···S–O in 1,5-dithiacyclooctane 1-oxide, *etc.*[7] n_p(Se) may interact with σ^*(X–X) in RR′Se···X_2 (X = halogen). The resulting unsymmetrical σ-type n(Se)···σ^*(X–X) three center–four electron (3c–4e) interactions[8] can be attractive, if the exchange repulsions are suitably controlled. The naphthalene 1,8-positions provide a good system to investigate such nonbonding interactions since the distances between the selenium atoms at those positions are close to the sum of the van der Waals radii minus 1.0.[9] It has been demonstrated that such interactions are the factors determining the fine structures of 1-[10] and 1,8-disubstituted[11] naphthalene derivatives. These factors may also have an effect on the catalyst platforms,[12] proton sponges[13] and sensors for selective ion recognition[14] in the naphthalene derivatives.

o-Carborane, 1,2-dicarba-*closo*-dodecaborane, is an icosahedral cluster with ten boron atoms and two neighboring carbon atoms,[15] and can be formally regarded as a pseudo-sphere with a 0.81 nm outside diameter,[16] with a molecular volume similar to that of a hypothetically rotating benzene ring. Some researchers consider that boron clusters have a pseudo-aromatic character which parallels the aromaticity of benzene.[17] The unique properties of carborane molecules, such as thermal stability,[18] electron-withdrawing character,[19] and lipophilicity make them promising candidates as the precursors for liquid crystals,[20] NLO (nonlinear optical) materials,[21] or as boron rich carriers for cancer treatment and diagnosis in Boron Neutron Capture Therapy (BNCT),[22] among others.[23]

During the past decades the chemistry of carboranyl sulfides, disulfides,[24] selenides,[25] diselenides,[26] and their related metallic

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complexes has been developed.[27] Due to our broad interest in carboranyl chalcogenides, we decided to explore synthetic ways for the preparation of carborane substituted naphthyl selenides, and to compare the influence of *o*-carboranyl or aryl groups on the structure and spectroscopic features of the obtained compounds. The results of our investigation are presented in the current paper.

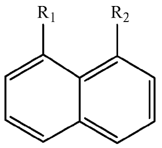
Results and discussion

1. Synthesis and characterization of the species

Organoselenides can be prepared from diaryl diselenides by reaction with alkali metals,[28] or alkali hydrides.[29] The asymmetric carboranylnaphthyl selenides 1-(2-R-1,2-dicarba-*closo*-carboranyl)naphthyl selenides (R = Me, **1**; Ph, **2**), and 1-(phenylselenyl)-8-(2-methyl-1,2-dicarba-*closo*-carboranylselenyl) naphthalene (**3**) have been prepared by cleavage of organic dinaphthyl diselenide with the corresponding lithiated *o*-carboranes (Scheme 1 and Chart 1). The optimized experimental synthetic conditions, as well as the spectroscopic and analytical data for the obtained compounds, are given in the experimental section.

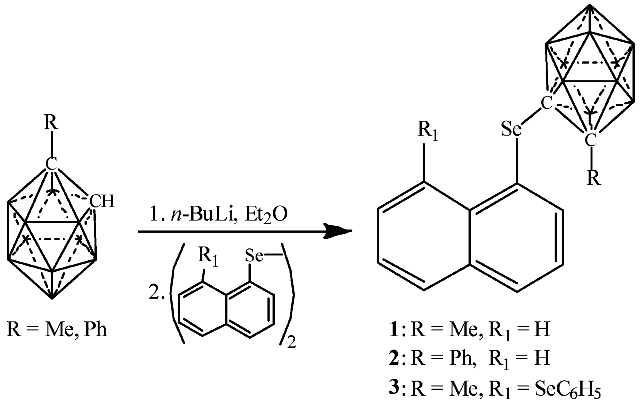
It has been established that *closo*-carboranyl groups exert a strong electron-withdrawing effect on the substituent.[30] The electron-withdrawing character of the *closo* cluster has been observed for *closo*-carboranylmonophosphines, and the effect of the *closo*-carboranyl fragment on the ^{31}P NMR chemical shifts were calculated,[31] as had been done for organic phosphines.[32] In order to know the cluster influence on the ^{77}Se NMR chemical shifts in *closo*-carboranyl selenides, ^{77}Se NMR spectra of compounds **1–3** have been recorded. The ^{77}Se NMR chemical shifts and coupling constants for compounds **1–3**, together with selected literature data for naphthyl selenides[10a,11f] are listed in Table 1. For compounds **1–3**, the ^{77}Se NMR resonances appear at δ 480.5, 495.9 and 552.3 ppm, clearly downfield with respect to those of the analogous arylnaphthyl selenide or 1-methylselenyl-8-arylselenylnaphtalene derivatives, which appear at δ 356.2, 361.0,[10a] 379.6, 434.3,[11f] 427.7[11f] and 453.9[11f] ppm (See Table 1). Due to the strong electron withdrawing character of the *o*-carboranyl group,[19] the chemical shift values for **1–3** are shifted downfield with regard to the data found for the selenium atoms bound to aromatic carbon atoms. Although ^{77}Se NMR chemical shifts are due to several factors, in this particular case the chemical shifts correlate well with the stronger electron-withdrawing character of the *o*-carboranyl group

Table 1 ^{77}Se NMR chemical shifts[a] and $^4J(^1Se,^8Se)$ coupling constants for 1-R^1-8-R^2-$C_{10}H_6$



R^1	R^2	$\delta(^1Se)$	$\delta(^8Se)$	$^4J(^1Se,^8Se)$
H	C_6H_5Se[10a]	—	361.0	—
H	*p*-$CH_3C_6H_4Se$[10a]	—	356.2	—
H	*p*-$NO_2C_6H_4Se$[10a]	—	379.6	—
H (**1**)	1-Se-2-CH_3-1,2-$C_2B_{10}H_{10}$	—	480.5	—
H (**2**)	1-Se-2-C_6H_5-1,2-$C_2B_{10}H_{10}$	—	495.9	—
CH_3Se	C_6H_5Se[11f]	235.4	434.3	322.4
CH_3Se	*p*-$CH_3C_6H_4Se$[11f]	234.5	427.7	330.9
CH_3Se	*p*-$NO_2C_6H_4Se$[11f]	240.1	453.9	272.5
C_6H_5Se (**3**)	1-Se-2-CH_3-1,2-$C_2B_{10}H_{10}$	431.5	552.3	329.7

[a] Relative to $(CH_3)_2Se$ in $CDCl_3$.



Scheme 1 General reaction of compounds synthesis.

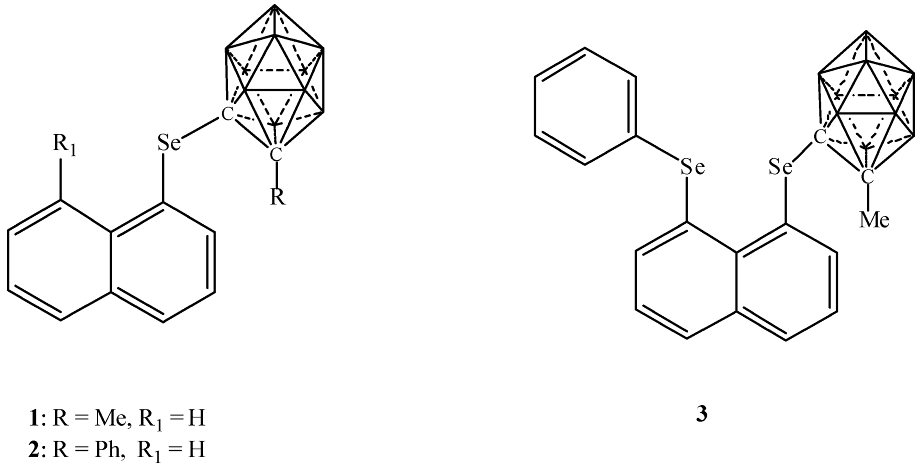


Chart 1 Graphical representation of the carboranylnaphthyl selenides (compounds **1–3**).

in comparison to the phenyl group. Furthermore, the nature of the substituent bonded to the other cluster carbon atom, or at the 8 position of the naphthyl group, tunes the ^{77}Se NMR chemical shift, 480.5 ppm for **1** ($R = CH_3$), 495.9 ppm for **2** ($R = C_6H_5$) and 552.3 ppm for **3** ($R = CH_3$, $R_1 = SeC_6H_5$).

The $^{13}C\{^1H\}$ chemical shifts of the cage carbon atoms bound to the selenium atoms, found at 68.12, 73.23 and 71.48 ppm for compounds **1**, **2** and **3** respectively, are shifted upfield in comparison to the values found for the carbon cluster atoms bearing methyl or phenyl substituents, which appear at 78.19, 78.38 and 87.02 ppm for compounds **1**, **3** and **2**, respectively. Upon prolonged acquisition times, two satellite lines due to the $^1J(^{13}C,^{77}Se)$ became visible at either side of the signals at chemical shifts 68.12, 73.23 and 71.48 ppm for compounds **1**, **2** and **3**, confirming the presence of the C–Se bond. One-bond couplings, $^1J(^{13}C,^{77}Se)$, are negative and strongly depend on the hybridization state, *i.e.*, the *s*-character of the coupled selenium and carbon atoms.[33] The coupling constants $^1J(^{13}C,^{77}Se)$ can reach high values ranging from 4 to 249 Hz.[34] Typical ranges for $^1J(^{13}C,^{77}Se)$ are 10–100 Hz for selenium attached to sp^3 carbon atoms (larger values if heteroatoms are attached to C),[35] 90–162 Hz for C═C–Se (sp^2 carbon atoms; aromatic or olefinic)[35b] and 184–193 Hz for C≡C–Se (*sp* carbon atoms).[34] A large $^1J(^{13}C,^{77}Se)$ value indicates a strong electron-withdrawing capacity of the substituents attached to the selenium atom,[36] and hence a more positively charged Se atom.[37] The $^1J(^{13}C,^{77}Se)$ values are 167.87 Hz for **1**, 170.65 Hz for **2**, and 178.97 Hz for **3**. The magnitude of $^1J(^{13}C,^{77}Se)$ in compounds **1–3** is markedly increased when compared with phenylselenium derivatives (*e.g.* in diphenylselenide: $^1J(^{13}C,^{77}Se) = 103.1$ Hz).[38] These high values also support a stronger electron-withdrawing character for the carboranyl, compared to aryl groups. In addition, these values are closer to those reported for selenium atoms bound to *sp*-hybridized carbon atoms (187.40 Hz for PhC≡CSeMe), than to the ones for sp^2-hybridized carbon atoms (115.5 Hz for PhCH═CHSeMe).[39]

^{77}Se and $^{13}C\{^1H\}$ NMR spectra values agree very well with the explanation that when one of the substituents at the selenium becomes more electron-withdrawing, such as the *o*-carborane cluster, a π-donation from the Se lone pair of electrons to the carbon atom of the cluster may occur. This, in turn, increases the C–Se electron overlap population, thus increasing $^1J(^{13}C,^{77}Se)$.

2. X-ray diffraction studies of 1 and 2

The structural studies of the compounds **1** and **2** are of particular interest in establishing the general structural peculiarities of selenocarboranyl substituted naphthalenes, comparing them to those of 1-(arylselenyl)naphthalenes,[10a] and for studying the influence of the *o*-carboranyl group on structural parameters and solid state packing of the molecules. Single crystals of **1** and **2** were obtained by slow evaporation of hexane and acetone solutions, respectively. Compound **1** crystallizes in the triclinic *P*-1 space group with two molecules per unit cell, whereas compound **2** crystallizes in the monoclinic $P2_1/c$ space group with four molecules per unit cell.† General views of their molecular structures are shown in Fig. 1 and 2. Crystallographic data for **1** and **2** are presented in Table 2. Selected interatomic distances, angles, and torsion angles for **1** and **2** are collected in Table 3.

Table 2 Crystallographic data for **1** and **2**

	1	2
Chemical formula	$C_{13}H_{20}B_{10}Se$	$C_{18}H_{22}B_{10}Se$
fw	363.36	425.43
Temp (K)	298(1)	298(1)
Cryst system	Triclinic	Monoclinic
Space group	*P*1_ (#2)	$P2_1/c$ (#14)
a (Å)	7.589(2)	10.759(4)
b (Å)	16.898(4)	14.445(3)
c (Å)	7.614(2)	13.734(4)
α (deg)	84.03(2)	
β (deg)	113.26(2)	99.32(2)
γ (deg)	85.61(2)	
V (Å^3)	884.8(5)	2106.2(9)
Z	2	4
D_{calcd} (g cm^{-3})	1.364	1.342
F(000)	364	856
No. of reflns collected	2678	2659
No. of parameters	218	262
R1 [$I > 1.5\sigma(I)$][a]	0.052	0.045
wR2 [$I > 1.5\sigma(I)$][b]	0.040	0.032
GOF	2.95	1.97

[a] $R = (\Sigma\|Fo| - |Fc\|)/\Sigma|Fo|)$. [b] $R_\omega = \{\Sigma\omega(|Fo| - |Fc|)^2/\Sigma\omega Fo^2\}^{1/2}$.

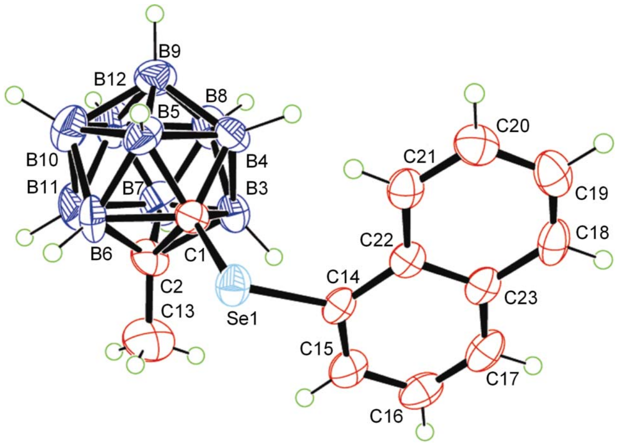


Fig. 1 Structure of **1** with displacement ellipsoids shown at the 50% probability level.

Earlier X-ray investigations carried out on monosubstituted naphthyl selenides 1-(p-$YC_6H_4Se)C_{10}H_6$ showed that two types of conformers may be adopted by these molecules depending on the Y group: i) the Se–C_{phenyl} bond being almost perpendicular to the naphthyl plane for Y = Cl, Br, CO_2Et and, ii) the Se–C_{phenyl} bond being parallel to the naphthyl plane for Y = OMe.

The corresponding dihedral angles between the $C_{cluster}$–Se bond and the naphthyl plane (C(1)–Se(1)–C(14)–C(22) in compound **1** and C(1)–Se(1)–C(19)–C(27) in compound **2**, see Fig. 1 and 2) were found to be 95.16° and 96.03°, respectively, indicating first structural type (i) for these molecules, being the carboranyl group oriented away from the naphthyl plane in order to reduce the repulsions between the naphthyl group and the carborane cage.

The Se–C_{naph} bond length for **1** (1.924(6) Å) is close to those previously observed for 1-(p-$YC_6H_4Se)C_{10}H_7$ derivatives[10a] (1.914(3) Å for Y = OMe, 1.919(4) Å for Y = Cl, 1.922(5) Å for Y = Br and 1.929(4) Å for Y = CO_2Et). The Se–$C_{cluster}$ (Se(1)–C(1)) bond length (1.971(5) Å) is 0.036 Å in average longer than found in (2-Me-1,2-*closo*-$C_2B_{10}H_{10})_2Se$ (1.937(3) and 1.933(3) Å).[24c] The

Table 3 Selected bond distances (Å), angles (°), and torsional angles (°) around the selenium atom in compounds **1** and **2**

Compound **1**		Compound **2**	
Bond distances (Å)			
Se(1)–C(1)	1.971(5)	Se(1)–C(1)	1.940(4)
Se(1)–C(14)	1.924(6)	Se(1)–C(19)	1.925(4)
C(1)–C(2)	1.697(8)	C(1)–C(2)	1.734(6)
Angles (°)			
C(1)–Se(1)–C(14)	102.7(2)	C(1)–Se(1)–C(19)	101.0(2)
Se(1)–C(1)–C(2)	118.3(3)	Se(1)–C(1)–C(2)	117.3(2)
Se(1)–C(14)–C(15)	118.0(4)	Se(1)–C(19)–C(20)	118.2(4)
Se(1)–C(14)–C(22)	121.0(4)	Se(1)–C(19)–C(27)	121.5(4)
Torsional angles (°)			
Se(1)–C(1)–C(2)–C(13)	−6.0(7)	Se(1)–C(1)–C(2)–C(13)	−4.6(5)
C(2)–C(1)–Se(1)–C(14)	90.0(4)	C(2)–C(1)–Se(1)–C(19)	103.8(3)
C(1)–Se(1)–C(14)–C(15)	−94.0(4)	C(1)–Se(1)–C(19)–C(20)	−88.2(4)
C(1)–Se(1)–C(14)–C(22)	95.1(4)	C(1)–Se(1)–C(19)–C(27)	96.0(3)
Se(1)–C(14)–C(15)–C(16)	−173.5(4)	Se(1)–C(19)–C(20)–C(21)	−177.8(4)
Se(1)–C(14)–C(22)–C(23)	171.7(3)	Se(1)–C(19)–C(27)–C(28)	176.5(3)

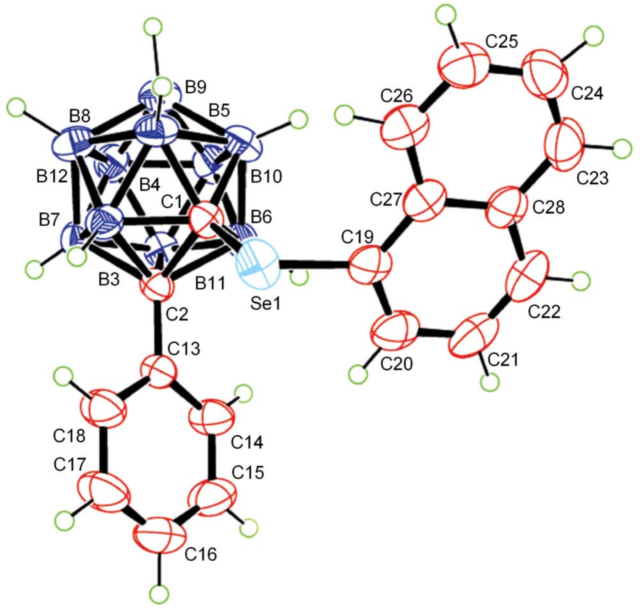


Fig. 2 Structure of **2** with displacement ellipsoids shown at the 50% probability level.

$C_{cluster}$–Se–C_{naph} (C(1)–Se(1)–C(14)) angle value (102.7(2)°) is in the range (100–106°) observed for aromatic selenides.[40] The $C_{cluster}$–$C_{cluster}$ (C(1)–C(2)) distance is 1.697(8) Å and the $C_{cluster}$–$C_{cluster}$–Se (C(2)–C(1)–Se(1)) angle is 110.11(11)°.

The Se–C_{naph} (Se(1)-C(19)) (1.925(4) Å), Se–$C_{cluster}$ (Se(1)-C(1)) (1.940(4) Å) bond lengths and $C_{cluster}$–Se–C_{naph} (C(19)-Se(1)-C(1)) angle values (101.02(2)°) for **2** are close to those found for compound **1**.

3. Solid state packing of naphthyl selenides

Both compounds, **1** and **2**, form dimers in the solid state *via* π-stacking of the naphthyl rings, aided by Se···π interactions. The motif is similar in both cases (Fig. 3), but not identical, since the stacked naphthyl rings in the crystal structure of compound **1** pack facing each other coincidentally and in an inter-digitized fashion, being the selenium atom located above the 5-position (C(18)) of the neighboring naphthyl group, whereas in the case of compound **2** the stacked rings are shifted, so that the selenium atoms interact with the 4-position (C(22)) of the neighboring naphthyl group.

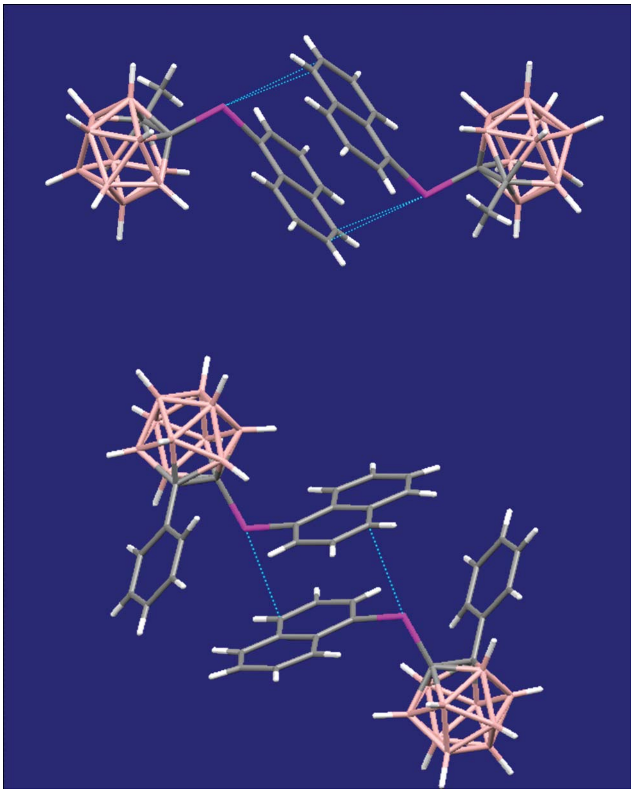


Fig. 3 Representation of the dimers formed in the crystal structures of compounds **1** (top) and **2** (bottom). Se···π interactions are depicted as dotted blue lines. White = H, pink = B, grey = C, purple = Se.

Further differences arise between both crystal lattices. In compound **1**, the dimers form ribbons through C_{naph}–H···H–B interactions (Fig. 4), while the methyl group does not seem to participate in any relevant interactions. In contrast, the phenyl group in compound **2** establishes significant contacts, such as C_{phenyl}–H···H–B interactions, yielding a much more complex 3D array of molecules. Nevertheless, in bulk, both crystal structures show layer-type organization of the molecules. Alternative aromatic and carborane 2D domains are observed in the crystal lattices. The

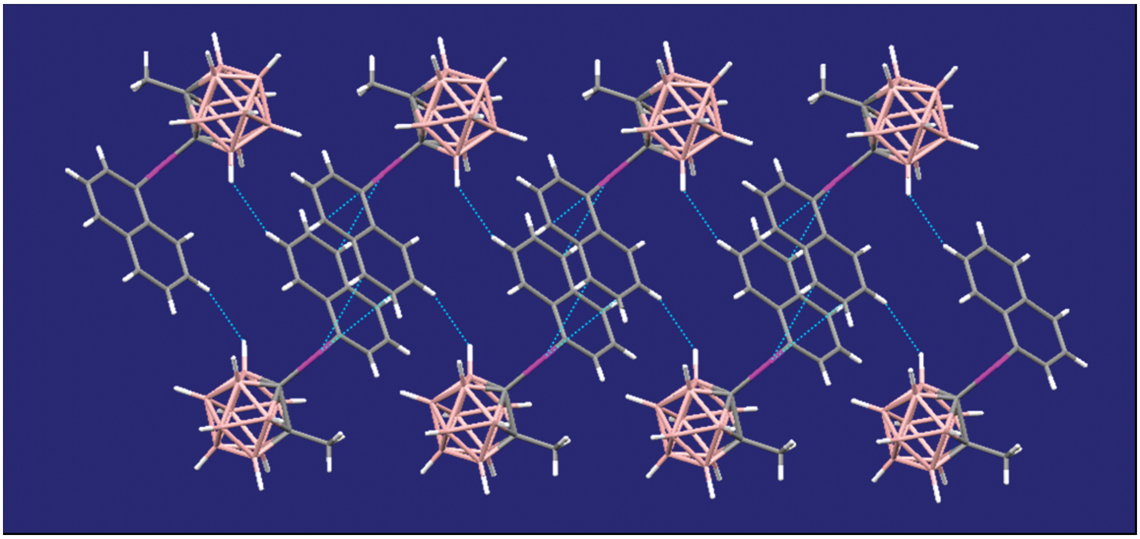


Fig. 4 A perspective of the ribbons established *via* C_{naph}–H $\cdots$ H–B contacts between dimers in the crystal structure of compound **1**. The interactions of importance are depicted as dotted blue lines. White = H, pink = B, grey = C, purple = Se.

layers lay parallel to the crystallographic *ac* and *bc* planes in the case of compounds **1** (Fig. 5), and **2** (Fig. 6), respectively.

4. Electrochemical study

Electrochemical oxidation studies carried out on dinaphtho[1,8-*b*,*c*]-1,5-diselenocin,[41] 3,4-dihydro-2*H*-naphtho[1,8-*b*,*c*]-1,5-diselenocine[42] and 1,8-bis(methylselenyl)naphthalene[41] showed reversible oxidation behaviour for these compounds, as an evidence for the stabilization of the cation-radicals by the lone pair of the neighbouring chalcogen atom. For the monosubstituted 1-methylselenylnaphthalene, irreversible oxidation at the potential of +0.82 V was reported.[41] Therefore, the electrochemical reversibility appears to be associated with the existence of two atoms, geometrically very close, having lone pairs. When only one selenium atom is present in the molecule, the anodic electrochemical response is irreversible.

In order to study the influence of the *o*-carboranyl group on the electrochemical properties of 1-monosubstituted naphthyl selenides, and to explore the possible stabilization of oxidized species by the participation of the lone pair of the neighbouring selenium atom at the 8-position, we have performed an electrochemical study of compounds **1** and **3**.

The cyclic voltammogram recorded for **1** is presented in Fig. 7. This voltammogram exhibits an irreversible oxidation process +1.75 V (peak A), and an irreversible oxidation (peak C) at +2.5 V, both *vs.* Ag/AgCl. Normally, organic selenides having alkyl and/or aryl groups show the irreversible electrochemical oxidation behaviour.

In comparison to compound **1**, **3** oxidises even at a higher potential (the oxidation wave starts at about +1.45 V

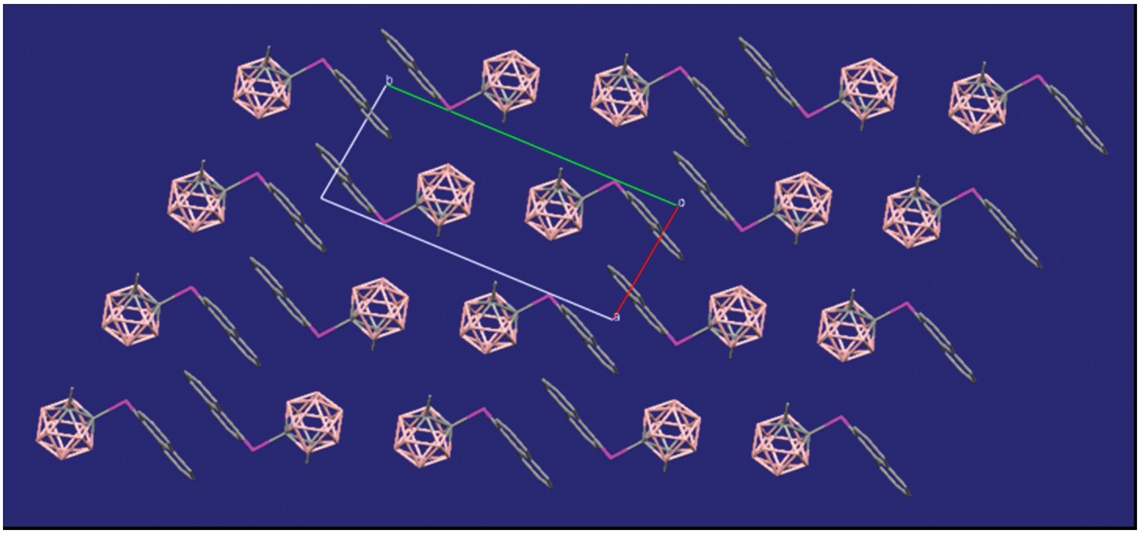


Fig. 5 A perspective of the packing in the crystal lattice of compound **1**, showing the alternate layers formed parallel to the crystallographic *ac* plane. Pink = B, grey = C, purple = Se; hydrogen atoms omitted for clarity.

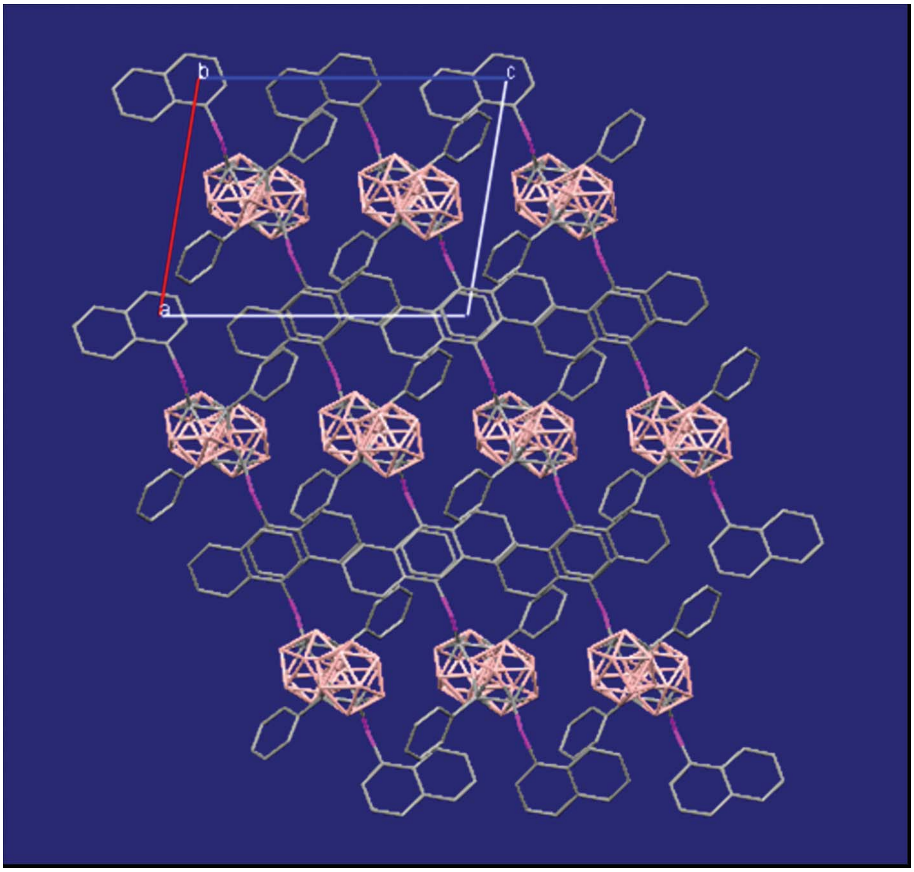


Fig. 6 A perspective of the packing in the crystal lattice of compound **2**, showing the alternate layers formed parallel to the crystallographic *bc* plane. Pink = B, grey = C, purple = Se; hydrogen atoms omitted for clarity.

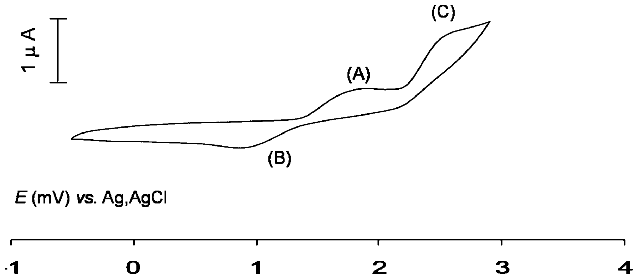


Fig. 7 Cyclic voltammograms acquired at 500 mV s^{-1} scan rates for: 10 mM 1-(2-Me-1,2-dicarba-*closo*-carboranyl)naphthyl selenide (**1**) dissolved in a 0.1 M $LiClO_4$ acetonitrile solution.

vs. Ag/AgCl). The corresponding reduction wave is also shifted towards more negative values (about 0.3–0.4 V *vs.* Ag/AgCl).

These data are consistent with the electron-polarizing ability of the carborane cluster, so that the electron pairs on the selenium, or sulfur, are less likely to be removed (oxidized) and therefore less able to generate new Se–Se bonds for example. This is true both for **1** with one Se, or for **3** with two Se. The difficulty of oxidation is even higher for 1-(2-Me-1,2-dicarba-*closo*-carboranyl)naphthyl sulfide. Most likely in these cases Se–O or S–O bonds are generated, causing the irreversibility of the system.

5. Theoretical approach

Why do the molecular structures of **1** and **2** appear as shown in Fig. 1 and 2, respectively? Which factor would operate to determine the structure of **3**, although it is not analyzed, yet? The structures of **1** and its 8-methylselenyl derivative (**4**) have been optimized employing the 6–311+G(d) basis sets for Se and the 6-31+G(d) basis sets for C, B, and H of the Gaussian 03 program.[43] Calculations are performed at the density functional theory (DFT) level of the Becke three parameter hybrid functionals with the Lee–Yang–Parr correlation functional (B3LYP). Two conformers are optimized to be stable, which are called **1** (**A$_1$**) and **1** (**A$_2$**). The structures are shown in Fig. 8.[44] **1** (**A$_1$**) is the global minimum and **1** (**A$_2$**) is a local one. The observed structure is consistent with the global minimum, **1** (**A$_1$**). However, we must be careful since the energy difference is very small. It is only 1.3 kJ mol^{-1}, which corresponds to [**1** (**A$_2$**)]/[**1** (**A$_1$**)] = 0.59 in a non-polar solvent at 298 K, although thermal and solvent effects are not considered in the calculations. Why is the **1** (**A$_1$**) conformer the one observed in the crystals? The **1** (**A$_1$**) structure of the extended form would be more suitable for the π-stacking of the naphthyl planes in crystals than **1** (**A$_2$**), in addition to the global minimum nature of **1** (**A$_1$**) by 1.3 kJ mol^{-1}, as compared to **1** (**A$_2$**).

The structure of **4** has also been optimized with the same method as used for **1**, where the partial structure of **1** (**A$_1$**) is assumed for the naphthyl selenylcarborane moiety. Two structures have been optimized. They are **4** (**A$_1$A**) and **4** (**A$_1$B**), where the Me–Se bond is

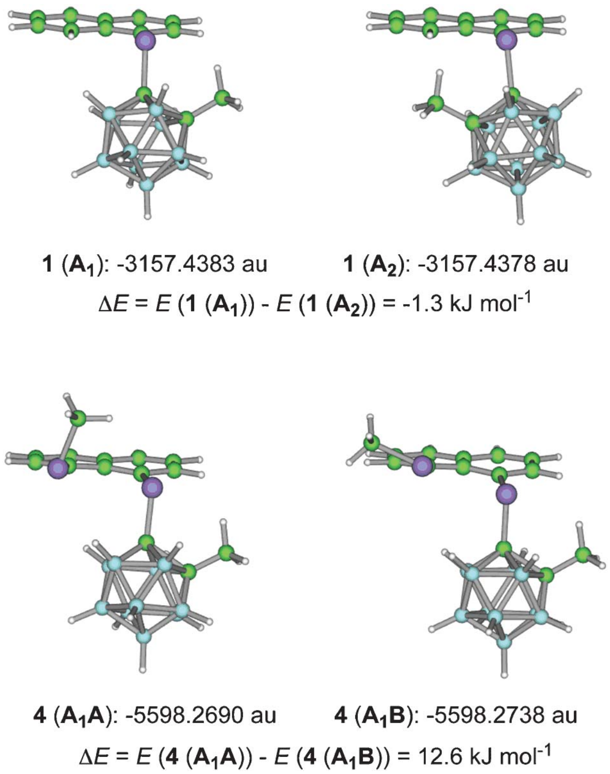


Fig. 8 Predicted structures of **1** and **4**, together with the energies.

perpendicular to the naphthyl plane in **4** (**A$_1$A**) and it is almost on the plane in **4** (**A$_1$B**), respectively. **4** (**A$_1$B**) is predicted to be more stable than **4** (**A$_1$A**) by 12.6 kJ mol^{-1}. The structure of **3** would be close to that optimized in **4** (**A$_1$B**), although the SeMe group in **4** should be replaced by the SePh group in **3**.

The n_p(Se) of the selanylcarborane group in **4** lies on the naphthyl plane, since the Se–C(carborane) bond is fixed perpendicular to the naphthyl plane due to the bulkiness of the carborane group. Therefore, the conformation of the SeMe group in **4** is limited to the cases where it is also perpendicular to the naphthyl plane (**4** (**A$_1$A**)) or on the plane (**4** (**A$_1$B**)). Whereas **4** (**A$_1$B**) is stabilized by the n_p(Se)$\cdots\sigma^*$(Se–C) 3c–4e interaction, **4** (**A$_1$A**) must be destabilized by the n_p(Se)$\cdots n_p$(Se) 2c–4e interaction. The energy difference between **4** (**A$_1$B**) and **4** (**A$_1$A**) (E (**4** (**A$_1$A**)) – E (**4** (**A$_1$B**)) = 12.6 kJ mol^{-1}) seems smaller than expected based on the above discussion. It must be due to the 0.243 Å longer Se$\cdots$Se nonbonding distance in **4** (**A$_1$A**) as compared to that in **4** (**A$_1$B**). The longer distance must avoid the disadvantageous exchange energy due to the n_p(Se)$\cdots n_p$(Se) 2c–4e interaction in **4** (**A$_1$A**). The torsional angles between the C$_{\text{cluster}}$–Se or C$_{\text{methyl}}$–Se bond and the naphthyl plane (ϕ) (see Fig. 8, bottom, for a clear illustration of such angles) in **4** (**A$_1$A**) are predicted to be 84.3° and 70.0°, respectively. The smaller ϕ (see Fig. 8, bottom) 70.0° directs n_p(Se) of the SeMe group away from the Se atom at the 1-position in **4** (**A$_1$A**), which also avoids the disadvantageous exchange energy.

Conclusions

The preparation, spectroscopic, structural and electrochemical properties of unsymmetrical selenides bearing naphthyl and *o*-carboranyl substituents have been described. It has been shown that the introduction of an *o*-carboranyl cage leads to a downfield shift of the selenium atom bonded to the naphthalene ring in ^{77}Se NMR spectra compared to analogous aryl derivatives, due to the electron withdrawing properties of the *o*-carborane cage. The X-ray structural analyses of molecules **1** and **2** have shown conformations with the carboranyl groups oriented away from the naphthyl plane. Both **1** and **2**, form dimers in the solid state *via* π-stacking of the naphthyl rings, aided by Se$\cdots\pi$ interactions. Cyclic voltammetry investigations of **1** and **3** reveal that the carboranyl fragment, in agreement with the ^{77}Se NMR chemical shifts, polarizes the Se lone pair, making it less prone to generate a Se–Se bond.

Experimental

Materials and methods

All reactions were performed in a nitrogen atmosphere using Schlenk techniques. Solvents were freshly distilled over sodium benzophenone prior to use. The purity of the starting materials was analysed by NMR spectroscopy and thin layer chromatography. 1-Methyl-*o*-carborane and 1-phenyl-*o*-carborane were purchased from Katchem Ltd. (Prague). The dinaphthyl 1,1′-diselenide and bis(8-phenylselenyl)-1,1′-diselenide were prepared according to the methods described in the literature.[45] *n*-Butyl lithium (1.6 M solution of in hexanes) was purchased from Fluka, diluted in dry hexane, and titrated using the double Gilman titration method.[46] $AgNO_3$, $LiClO_4$, Et_4NCl (all Aldrich), and acetonitrile (Merck, dried over molecular sieves) were used in the electrochemical studies.

^{1}H-NMR (300.13 MHz), ^{13}C{^{1}H} NMR (75.47 MHz), ^{77}Se (75.48 Hz), and ^{11}B-NMR (96.29 MHz) spectra were recorded using a Bruker ARX-300 instrument. Chemical shift values for ^{1}H and ^{13}C{^{1}H}, ^{11}B, and ^{77}Se were referenced relative to $Si(CH_3)_4$, $BF_3{\cdot}O(C_2H_5)_2$, and $Se(CH_3)_2$ respectively. Chemical shifts are reported in units of parts per million downfield from the reference, and all coupling constants are reported in Hertz. MALDI-TOF mass spectra were recorded using a Bruker Biflex instrument (N_2 laser, λ_{exc} 337 nm (0.5 ns pulses); voltage ion source 20.00 kV (Uis1) and 17.50 kV (Uis2)). Electrospray were recorded using a Bruker Esquire 3000 instrument by the direct insertion method. IR spectra were obtained from KBr pellets on a Nicolet 710-FT spectrophotometer. Melting points were measured using a Stuart Scientific SMP10 apparatus. Microanalyses were performed using a Perkin-Elmer 240B microanalyser.

Voltammograms were acquired using three electrode cells. A 0.5 mm Φ Pt wire embedded in PTFE, a home-made Ag/AgCl (0.1 M Et_4NCl in acetonitrile), and a Pt sheet (~1 cm^2 area) were the working, reference, and counter electrodes, respectively. The reference electrode (RE) was checked with ferrocene solutions in acetonitrile, as recommended by IUPAC.[47] In this way, we have found that the potential of the used reference electrode is 0.72 ± 0.01 V more cathodic than that of Ag/Ag$^+$ (0.1 M $AgNO_3$ in acetonitrile). The latter electrode represented the reference for any other electrochemical data cited in the present paper from literature.

Synthesis of compound 1. To a solution of $1\text{-}CH_3\text{-}1,2\text{-}C_2B_{10}H_{11}$ (0.0384 g, 0.2430 mmol) in diethyl ether (3 mL), 0.42 mL of a 0.57 M solution of *n*-BuLi in hexanes (0.2430 mmol) were added at 25 °C. The resulting solution was stirred for 0.5 h at ambient conditions, and dinaphthyl 1,1′-diselenide (0.1000 g, 0.2430 mmol) in diethyl ether (10 mL) was added dropwise at the same temperature. The reaction mixture was stirred for an additional 1 h at ambient conditions, neutralized by 0.1 M HCl, and washed with a saturated aqueous solution of NaCl (10 mL). The ether layer was separated and evaporated in vacuum. The pure product was isolated by silica gel chromatography using graduate elution from $\mathrm{CHCl_3}$/hexane (1% $\mathrm{CHCl_3}$) to $\mathrm{CHCl_3}$/hexane (50% $\mathrm{CHCl_3}$) mixture as an eluent. Yield: 0.0679 g (77%). Pale yellow solid. M.p. 162 °C. NMR ^{1}H ($\mathrm{CDCl_3}$): δ 1.00–3.20 (br, B*H*), 2.28 (s, 3H, $\mathrm{C}H_3$), 7.46 – 7.66 (m, 3H, $\mathrm{C_{aryl}}$-*H*), 7.89 (d, 1H, *J*(HH) = 8.16, $\mathrm{C_{aryl}}$-*H*), 7.96 (d, 1H, *J*(HH) = 7.32, $\mathrm{C_{aryl}}$-*H*), 8.02 (d, 1H, *J*(HH) = 8.13, $\mathrm{C_{aryl}}$-*H*), 8.46 (d, 1H, *J*(HH) = 8.13, $\mathrm{C_{aryl}}$-*H*). NMR ^{13}C{^{1}H} ($\mathrm{CDCl_3}$): δ 25.49 ($\mathrm{C}H_3$), 68.12 [C_c, $^1J(^{13}\mathrm{C},^{77}\mathrm{Se}) = 167.87$], 78.19 ($C_c$), 125.60, 126.85, 127.10, 127.75, 127.88, 128.78, 132.60, 134.16, 135.06, 139.29. NMR ^{1}H [$\mathrm{(CD_3)_2CO}$]: δ 0.80–3.40 (br, B*H*), 2.38 (s, 3H, $\mathrm{C}H_3$), 7.57–7.73 (m, 3H, $\mathrm{C_{aryl}}$-*H*), 8.02 (d, 1H, *J*(HH) = 7.77, $\mathrm{C_{aryl}}$-*H*), 8.10 (d, 1H, *J*(HH) = 6.84, $\mathrm{C_{aryl}}$-*H*), 8.17 (d, 1H, *J*(HH) = 8.07, $\mathrm{C_{aryl}}$-*H*), 8.50 (d, 1H, *J*(HH) = 8.10, $\mathrm{C_{aryl}}$-*H*). NMR ^{77}Se ($\mathrm{CDCl_3}$): δ 480.48. NMR ^{11}B{1H}($\mathrm{CDCl_3}$): −8.13, −3.64, −1.83. IR (KBr): ν(cm^{-1}) 2592 (B–H). MALDI-TOF-MS (negative ions), (m/z): 363 (M$^-$; 2%, 157 ([$\mathrm{C_3B_{10}H_{13}}$]$^-$; 19%). Anal. calcd. for $\mathrm{C_{13}H_{20}B_{10}Se}$: C, 42.97; H, 5.55. Found: C, 43.01; H, 5.56.

Synthesis of compound 2. To a solution of 1-$\mathrm{C_6H_5}$-1,2-$\mathrm{C_2B_{10}H_{11}}$ (0.0530 g, 0.2430 mmol) in diethyl ether (3 mL), 0.48 mL of a 0.51 M solution of *n*-BuLi in hexanes (0.2430 mmol) were added at 0 °C. The resulting solution was stirred for 0.5 h at 0 °C, 0.5 h at room temperature, and cooled down again to 0 °C, followed by the slow addition of dinaphthyl 1,1′-diselenide (0.1000 g, 0.2430 mmol) in diethyl ether (10 mL). The reaction mixture was stirred for 0.5 h at 0 °C, warmed up to room temperature, and stirred for an additional week at ambient conditions. The precipitate was filtered off, the filtrate diluted by diethyl ether (30 mL), and washed with a saturated water solution of $\mathrm{Na_2CO_3}$ (50 mL), and NaCl (50 mL). The ether layer was separated, dried over $\mathrm{MgSO_4}$ and evaporated in vacuum. The pure product was isolated by two chromatographic separations using $\mathrm{CHCl_3}$/hexane (10% $\mathrm{CHCl_3}$) and finally a THF/hexane (5% THF) mixture as an eluent. Yield: 0.0816 g (79%). Pale yellow solid. M.p. 146 °C. NMR ^{1}H ($\mathrm{CDCl_3}$): δ 0.80–4.00 (br, B*H*), 7.29–7.64 (m, 9H, $\mathrm{C_{aryl}}$-*H*), 7.82 (d, 1H, *J*(HH) = 8.13, $\mathrm{C_{aryl}}$-*H*), 7.86 (d, 1H, *J*(HH) = 8.52, $\mathrm{C_{aryl}}$-*H*), 7.93 (d, 1H, *J*(HH) = 7.74, $\mathrm{C_{aryl}}$-*H*). NMR ^{13}C{^{1}H} ($\mathrm{CDCl_3}$): δ 73.23 (C_c, $J(^{13}\mathrm{C},^{77}\mathrm{Se}) = 170.65$), 87.02 ($C_c$), 125.34, 126.59, 126.81, 127.47, 128.00, 128.43, 128.57, 130.72, 131.99, 132.31, 133.87, 134.84, 138.92. NMR ^{77}Se ($\mathrm{CDCl_3}$): δ 495.94. NMR ^{11}B{1H} ($\mathrm{CDCl_3}$): δ −10.54, −8.52, −1.79. IR (KBr): ν(cm^{-1}) 2602 (B–H). MALDI-TOF-MS (negative ions), (m/z): 425 (M$^-$; 2%, 220 ([$\mathrm{C_8B_{10}H_{15}}$]$^-$; 27%). Anal. calcd. for $\mathrm{C_{18}H_{22}B_{10}Se}$: C, 50.82; H, 5.21. Found: C, 50.89; H, 5.20.

Synthesis of compound 3. To a solution of 1-$\mathrm{CH_3}$-1,2-$\mathrm{C_2B_{10}H_{11}}$ (0.0103 g, 0.0652 mmol) in diethyl ether (1 mL), 0.11 mL of a 0.62 M solution of *n*-BuLi in hexanes (0.0652 mmol) were added at 25 °C. The reaction mixture was stirred for 0.5 h at ambient conditions, followed by the slow addition of a suspension of bis(8-phenylselenyl)-1,1′-diselenide (0.0471 g, 0.0652 mmol) in diethyl ether (20 mL). The slurry was stirred for 4 h at 25 °C, and refluxed for 2 h. The reaction mixture was neutralized by 0.1 M HCl, and washed with a saturated solution of NaCl (10 mL). The ether layer was separated and evaporated in vacuum. The pure product was isolated by silica gel chromatography using graduate eluation from $\mathrm{CHCl_3}$/hexane (10% $\mathrm{CHCl_3}$) to $\mathrm{CHCl_3}$/hexane (50% $\mathrm{CHCl_3}$) mixture as an eluent. Yield: 0.0140 g (41%). Pale yellow oil. NMR ^{1}H ($\mathrm{CDCl_3}$): δ 1.10–3.10 (br, B*H*), 2.03 (3H, $\mathrm{C}H_3$), 7.26–7.54 (m, 8H, $\mathrm{C_{aryl}}$-*H*), 7.73 (d, 1H, *J*(HH) = 7.74, $\mathrm{C_{aryl}}$-*H*), 7.99 (d, 1H, *J*(HH) = 8.13, $\mathrm{C_{aryl}}$-*H*), 8.14 (d, 1H, *J*(HH) = 7.35, $\mathrm{C_{aryl}}$-*H*). NMR ^{13}C{^{1}H} ($\mathrm{CDCl_3}$): δ 25.18 ($\mathrm{C}H_3$), 71.48 (C_c, $^1J(^{13}\mathrm{C},^{77}\mathrm{Se}) = 178.97$ Hz), 78.38 (C_c), 125.91, 126.17, 126.66, 128.17, 128.28, 129.55, 133.08, 133.23, 134.03, 134.49, 134.82, 135.34, 136.17, 141.26. NMR ^{77}Se ($\mathrm{CDCl_3}$): δ 431.50 (*Se*–$\mathrm{C_6H_5}$), 552.26 (*Se*–$\mathrm{C_2(CH_3)B_{10}H_{10}}$, $^8J(^1\mathrm{Se},^8\mathrm{Se}) = 329.69$ Hz). NMR^{11}B{^{1}H} ($\mathrm{CDCl_3}$): δ −8.25, −3.69, −1.77. ES-MS in $\mathrm{CHCl_3}$/MeOH (1 : 1), (m/z): 550 (M$^+$ + $\mathrm{CH_3OH}$, 17%).

X-ray structural determination of 1 and 2. Colorless crystals of **1** and colorless crystals of **2** were grown by slow evaporation of hexane and acetone solutions, respectively. The intensity data were collected on a Rigaku AFC5R four-circle diffractometer with graphite-monochromated MoKα radiation (λ = 0.71069 Å) for **1** and **2**. The structures of **1** and **2** were solved by the heavy-atom Patterson methods, PATTY,[48] and expanded using Fourier techniques, DIRDIF94.[49] All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on a total of 2678 reflections for **1** and on 2659 for **2**, with 218 observed reflections [$I > 1.50\sigma(I)$] for **1** and 262 [$I > 1.50\sigma(I)$] for **2**, respectively. Variable parameters and converged with unweighted and weighted agreement factors of $R = (\Sigma \| Fo| - |Fc\|)/\Sigma |Fo|)$ and $R_\omega = \{\Sigma\,\omega(|Fo| - |Fc|)^2/\Sigma\,\omega Fo^2\}^{1/2}$ were used. For least squares, the function minimized was $\Sigma\,\omega(|Fo| - |Fc|)^2$, where $w = (\sigma_c^{\,2}|Fo| + p^2|Fo|^2/4)^{-1}$.

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