

“Synthesis, Reactivity and Structural Studies of Dicarboranyldiselenides”

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1. Introduction

The explosive growth of organochalcogen chemistry, over the last years, can be attributed to the specific properties of organic chalcogenide compounds, which fit the requirements of modern organic synthesis. Most of them are well adapted to chem-, regio- and stereo-selectivities. In addition, they can be used in mild experimental conditions, which are compatible with the stability of the substrates and products in the preparation of unsaturated and functional complex molecules, especially in the field of natural products.¹ Although the first organoselenium compound was prepared by Wöhler and Siemens in 1847,² only in the early 1970s did the chemistry of organoselenium compounds become a versatile tool in organic chemistry.³ After that, the organoselenium chemistry developed rapidly, mainly in the area of selenocarbohydrates, selenoaminoacids, and selenopeptides. The selenium group can be introduced in an organic substrate via both nucleophilic and electrophilic reagents.

Organoselenium anions are powerful nucleophiles and are usually prepared “in situ” because of their sensitivity to air oxidation.⁴ They can be prepared from diaryl diselenides by reaction with reducing agents, of which NaBH₄ is the most used,⁵ from insertion of elemental selenium into lithium and Grignard reagents,⁶ and from diorganoyl diselenides by reduction with alkali metals⁷ or alkali hydrides.⁸ Vinyl selenides are also important reagents and intermediates in organic synthesis⁹ and among a large list of described transformations, the ability of these compounds to participate in the formation of carbon-carbon bonds by the Ni-catalyzed cross-coupling reactions with magnesium or zinc reagents is remarkably interesting. After being introduced in an organic substrate, the organoselenium group can easily be removed by selenoxide syn elimination¹⁰ and [2,3] sigmatropic rearrangement.¹¹ In addition, the carbon-selenium bond can also be replaced by a carbon-hydrogen,¹² carbon-halogen,¹³ carbon-lithium,¹⁴ or carbon-carbon bond.¹⁵ Thus, in general, organoselenium species can be efficiently introduced, manipulated, and removed in a variety of ways under mild conditions.

There is no question that the discovery of selenoproteins and selenium-containing enzymes, especially of the mammalian enzyme, glutathione peroxidase, is largely responsible for the great interest in selenium biochemistry which has developed in recent years. However, the synthetic potential of this class of organoelemental compounds has only recently received the attention of organic chemists. The association between selenium and liver pathology dates from the initial observations of Schwarz and Foltz that selenium could prevent liver necrosis in rats fed with a selenium-deficient diet. This observation led rapidly to the recognition that a number of previously unexplained deficiency diseases in various species of animals were selenium-responsive.¹⁶

Organoselenium compounds have been described as promising pharmacological agents in view of their unique biological properties: antioxidant activity,¹⁷ antiinflammatory activity,¹⁸ gastric mucosal damage prevention,¹⁹ neuroprotection,²⁰ chemotherapeutic²¹ and chemopreventive activity²² are some of these properties.

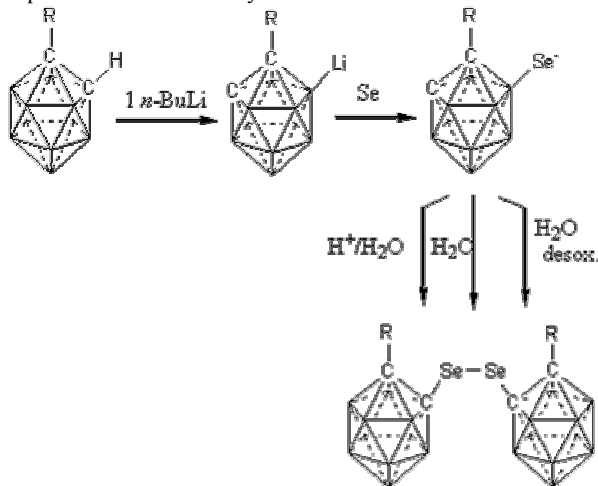
o-Carborane can be viewed similar to a benzene ring. Some researchers consider that boron clusters have a pseudo-aromatic character which parallel the benzene's aromaticity. Furthermore the size of a carborane is comparable to a rotating benzene. In the way that diaryldiselenides exist, dicarboranyldiselenides may also be produced. In this paper we report on the first dicarboranyldiselenides, their characterization either by spectroscopic or X-ray diffraction techniques and some of their reacting possibilities. Carboranyl selenium chemistry is in its infancy. Up to now research in which Se is bonded to the Carborane cluster has been restricted to the coordination chemistry of [Se₂C₂B₁₀H₁₀]²⁻,²³ and [SeC₂B₁₀H₁₁].²⁴

Results and Discussion

Synthesis and Spectroscopic studies

Although the use of organoselenols as reagents is a drawback in synthesis in view of the difficulties in preparing and handling these very volatile, bad-smelling, toxic and air-sensitive compounds, they can not be disregarded. This is why the synthesis of the synthetically important selenol 1-SeH-2-R-1,2-*closo*-C₂B₁₀H₁₀ (R= Me, Ph) was the first target in this research. We assumed that the synthetic procedure could be similar to that for the related thiol 1-SH-2-R-1,2-*closo*-C₂B₁₀H₁₀ (R= Me, Ph).²⁵ Thence Li[2-R-1,2-*closo*-C₂B₁₀H₁₀] (R= Me, Ph) salt was prepared by the direct metalation of 1-R-1,2-C₂B₁₀H₁₁ with *n*BuLi (1:1 ratio) in diethyl ether followed by the addition of finely ground selenium powder. It was expected that 1-SeH-2-R-1,2-*closo*-C₂B₁₀H₁₀ would be obtained after acidification of the medium but attempts to trap or detect these species were unsuccessful (Scheme 1). The addition of hydrochloric acid and the subsequent work-up gave yellow solids. ⁷⁷Se NMR solution analysis of the Me substituted solid in d-HCCl₃ has shown a resonance at 389 ppm. No resonance for Se-H was observed in the ¹H NMR spectra. Besides, the ¹¹B{¹H} NMR spectra were different from these of the starting compounds. Diselenides formation, (1-Se-2-R-1,2-*closo*-C₂B₁₀H₁₀)₂ (R= Me, Ph), was then postulated. The IR spectra display the typical ν(B-H) absorption at frequencies above 2600 cm⁻¹, characteristic of *closo* carboranes. The ¹H-, ¹¹B- and ¹³C{¹H}-NMR data of these compounds in d-HCCl₃ are in complete agreement with the diselenide proposed structures which were later confirmed by X-ray crystallography. The MALDI-TOF-MS spectra were recorded for (1-Se-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂ and (1-Se-2-Ph-1,2-*closo*-C₂B₁₀H₁₀)₂. Molecular ion peaks with the right isotopic distribution were observed for both compounds

although in low intensity. The peak observed at $m/z = 472$ (M , 14%) for (1-Se-2-Me-1,2-*closo*- $C_2B_{10}H_{10}$)₂ corresponds to the diselenide $^{12}C_6^{1}H_{26}^{11}B_{18}^{10}B_2^{78}Se_2$ whereas the highest peak found at $m/z = 237$ ($M/2$, 100%) corresponds to the symmetrical fragmentation $^{12}C_3^1H_{13}^{11}B_{10}^{78}Se^+$. For compound (1-Se-2-Ph-1,2-*closo*- $C_2B_{10}H_{10}$)₂ the molecular ion peak at 597 (M , 2%) is very weak but the one at $m/z = 299$ ($M/2$, 100%) corresponding to the symmetrical fragmentation is the highest. This could suggest a weaker Se-Se bond in the latter either due to an intramolecular Se...X interaction, or because of the higher electron density of the Ph ring that would deplete of electron density the Se-Se bond.

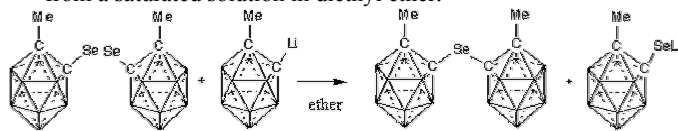


Scheme 1. Synthesis of diselenide species (1-Se-2-R-1,2-*closo*- $C_2B_{10}H_{10}$)₂ (R= Me, Ph).

Preparation of 1-SH-1,2-*closo*- $C_2B_{10}H_{11}$ is complicated by the existing equilibrium, in certain solvents, between the monolithiated *o*-carborane species and the dilithiated and unsubstituted ones.²⁶ In dimethoxyethane, however, 1-SH-1,2-*closo*- $C_2B_{10}H_{11}$ is obtained in 93% yield.²⁷ The attempted synthesis of (1-Se-2-H-1,2-*closo*- $C_2B_{10}H_{10}$)₂ was carried out in the same conditions as for 1-SH-1,2-*closo*- $C_2B_{10}H_{11}$. As the final stage in this preparation is the addition of HCl to produce the monothiol, which for these Se compounds would be the oxidation to the diselenide, upon the addition of hydrochloric acid almost one equivalent of selenium as a red amorphous species, which rapidly turns gray and shiny ($\approx 95\%$ recovery after centrifugation after 30 min) was obtained. The $^{11}B\{^1H\}$ NMR analysis of the reaction solution after selenium addition, clearly shows the presence of a different species than $Li[1,2\text{-}closo\text{-}C_2B_{10}H_{11}]$, probably $Li[1\text{-}Se\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{11}]$, that goes back to the starting 1,2-*closo*- $C_2B_{10}H_{12}$ after protonation. This result is in contradiction with a recent publication²⁴ that reports the synthesis and isolation of the moisture- and air-stable selenol 1-SeH-1,2-*closo*- $C_2B_{10}H_{11}$ by using the same method described for us for 1-SH-1,2-*closo*- $C_2B_{10}H_{11}$. However, our results agree with Zakharkin and al. that reported that selenide compounds oxidize easily with oxygen.²⁸

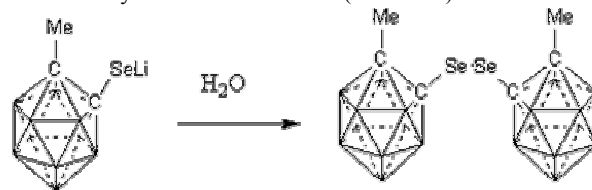
The synthesis of the diselenide (1-Se-2-R-1,2-*closo*- $C_2B_{10}H_{10}$)₂ (R=Me, Ph) compounds was achieved by oxidative work up. As it was thought that the proton from the hydrochloric acid solution was the oxidizing agent, protonation was tried using either H₂O or deoxygenated H₂O however, in all cases stable diselenide (1-Se-2-R-1,2-*closo*- $C_2B_{10}H_{10}$)₂ (R=Me, Ph) compounds were obtained. In order to prove that $Li[1\text{-}Se\text{-}2\text{-}R\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10}]$ was the first step of the reaction and confirm that selenium oxidation takes place irrespective of using either acid or H₂O, a complexation reaction was performed. To a solution of 1-methyl-

carborane in dry diethyl ether was added *n*-BuLi and selenium powder. Once the black selenium disappeared, $[AuClPPH_3]$ was added and a solid precipitated. The yellowish solid $[Au(1\text{-}Se\text{-}2\text{-}Me\text{-}1,2\text{-}C_2B_{10}H_{10})(PPH_3)]$ was characterized by elemental analysis, IR, 1H -, ^{11}B -, $^{31}P\{^1H\}$ - and $^{13}C\{^1H\}$ -NMR spectroscopy. The IR displayed $\nu(B-H)$ bands in the range 2590-2561 cm^{-1} which is consistent with the *closo* fragment. In agreement with this, the $^{11}B\{^1H\}$ -NMR spectrum appears in the range -5.96 and -9.12, typical for a *closo* cluster. The $^{31}P\{^1H\}$ -NMR spectrum displays one signal at 37.4 ppm. Full proof of complexation by $[1\text{-}Se\text{-}2\text{-}Me\text{-}1,2\text{-}C_2B_{10}H_{10}]$ was obtained after good crystals for X ray diffraction were grown from a saturated solution in diethyl ether.



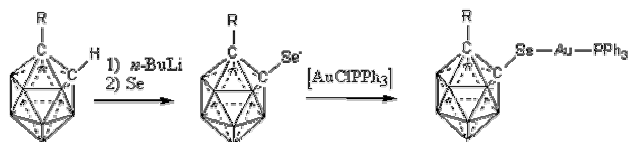
Scheme 2. Synthesis of selenide species (2-Me-1,2-*closo*- $C_2B_{10}H_{10}$)₂Se.

Treatment of the diselenide (1-Se-2-R-1,2- $C_2B_{10}H_{10}$)₂ compounds (R= Me, Ph) with a stoichiometric amount of $Li[2\text{-}R'\text{-}1,2\text{-}C_2B_{10}H_{10}]$ (R'= Me, Ph) gave the symmetrical selenide (2-Me-1,2- $C_2B_{10}H_{10}$)₂Se only for R=R'=Me see Scheme 2. The stable (2-Me-1,2- $C_2B_{10}H_{10}$)₂Se derivative was obtained as a yellow crystalline solid. The byproduct $Li[1\text{-}Se\text{-}2\text{-}R\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10}]$ can be recovered as the starting diselenide by oxidation with water (Scheme 3).



Scheme 3. Recovery of (1-Se-2-Me-1,2-*closo*- $C_2B_{10}H_{10}$)₂.

Recent studies show that the use of sterically encumbered groups and intramolecularly coordinating groups has been successful in synthesizing some stable organoselenium compounds. Intramolecular Se...X interactions have been found for X= H,²⁹ S,³⁰ O,³¹ F,³² N,³³ Cl,³⁴ and Br.³⁵ The ^{77}Se NMR chemical shift is informative about the Se...X non-bonding interactions because the resonance is downfield shifted. The ^{77}Se NMR chemical shift of (1-Se-2-Me-1,2-*closo*- $C_2B_{10}H_{10}$)₂ exhibits a single resonance at 389 ppm., which is downfield with respect to the diaryldiselenides, naphtyldiselenide and diphenyldiselenide that appear at 436 and 463 ppm respectively.³⁶ The 1H NMR spectrum of (1-Se-2-Me-1,2-*closo*- $C_2B_{10}H_{10}$)₂ show two doublets, of equal intensity one for each methyl group, at 2.08 and 1.86 ppm with a $^4J(Se,H) = 2.5$ Hz.



Scheme 4. Reaction of diselenide (1-Se-2-Me-1,2-*closo*- $C_2B_{10}H_{10}$)₂ with $[AuClPPH_3]$.

Molecular and crystal structures of (2-Me-1,2-*closo*- $C_2B_{10}H_{10}$)₂Se, (1-Se-2-Me-1,2-*closo*- $C_2B_{10}H_{10}$)₂, (1-Se-2-Me-1,2-*closo*- $C_2B_{10}H_{10}$)₂toluene, (1-Se-2-Ph-*closo*-1,2- $C_2B_{10}H_{10}$)₂ and $[Au(1\text{-}Se\text{-}2\text{-}Me\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10})(PPH_3)]$.

Good crystals for the title compounds were grown from mixtures of acetone and toluene. The structure of (2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂Se confirmed that two carborane moieties are bridged by one selenium atom (Figure 1) while the structures of (1-Se-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂, (1-Se-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂·toluene and (1-Se-2-Ph-*closo*-1,2-C₂B₁₀H₁₀)₂ clearly confirmed the Se-Se bond formation (Figures 2, 3 and 4). The structure of [Au(1-Se-2-Me-1,2-*closo*-C₂B₁₀H₁₀)(PPh₃)] confirmed complexation of [1-Se-2-Me-1,2-C₂B₁₀H₁₀] ligand (Figure 5).

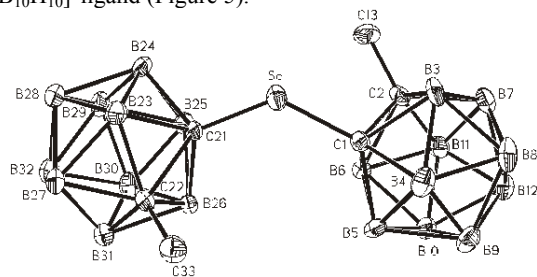
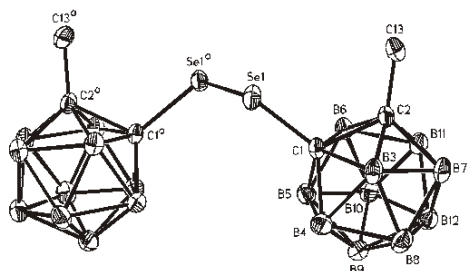


Figure 1. A view of (2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂Se showing 50% displacement ellipsoids. Hydrogen atoms are omitted for clarity.

Compound	1	2	2'	3	4	
Formula	C ₁₂ H ₁₂ B ₁₀ Se	C ₁₂ H ₁₂ B ₁₀ Se ₂	C ₁₂ H ₁₂ B ₁₀ Se ₂	C ₁₂ H ₁₂ B ₁₀ Se ₂	C ₁₂ H ₁₂ B ₁₀ Se ₂	C ₁₂ H ₁₂ B ₁₀ Se ₂
	393.43	472.39	564.52	596.52	695.43	
	13.9969(3)	7.1599(4)	23.4834(11)	8.0368(4)	7.93370(10)	
	11.7558(5)	7.8129(5)	9.5944(2)	12.3095(5)	18.8060(4)	
	14.2199(5)	21.7731(15)	13.8538(6)	14.0307(7)	17.7509(4)	
	90	95.738(2)	90	90	90	
	118.572(2)	90.839(2)	119.4851(14)	91.717(5)	91.4646(7)	
	90	115.038(3)	90	90	90	
	2054.86(12)	1095.80(12)	2717.12(18)	1387.42(11)	2647.59(9)	
	4	2	4	2	4	
<i>P</i>	<i>P</i> 2/ <i>m</i> (No. 14)	<i>P</i> -1 (No. 2)	<i>C</i> 2/ <i>c</i> (No. 15)	<i>P</i> c (No. 7)	<i>P</i> 2/ <i>m</i> (No. 14)	
	-100	-100	-100	-100	-100	
	0.71073	0.71073	0.71073	0.71073	0.71073	
<i>V</i>	1.272	1.432	1.380	1.428	1.745	
	18.16	33.65	27.27	29.75	70.02	
2 σ (<i>I</i>)	0.0553	0.0502	0.0346	0.0374	0.0	
> 2 σ (<i>I</i>)	0.0745	0.1199	0.0739	0.0690	0.0	

$\int |F_o|/|F_c| \sin \pi w R2 = \{ \sum [w(F_o^2 - F_c^2)]^2 / \sum w(F_o^2)^2 \}^{1/2}$

Table 1. Crystallographic Data for (2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂Se (**1**), (1-Se-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂ (**2**), (1-Se-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂·toluene (**2'**), and (1-Se-2-Ph-1,2-*closo*-C₂B₁₀H₁₀)₂ (**3**) and [Au(1-Se-2-Me-1,2-*closo*-C₂B₁₀H₁₀)(PPh₃)] (**4**)



(4).

Figure 2. A view of (1-Se-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂ showing 50% displacement ellipsoids. Hydrogen atoms are omitted for clarity.

Symmetry and conformations of the four non-complexed selenide and diselenide compounds vary considerably. (2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂Se (**1**) and (1-Se-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂ (**2**) have pseudo two-fold symmetry with the pseudo two-fold axis going through the selenium atom in former compound and through the midpoint of the Se-Se bond in latter compound (Figures 1 and 2). The bonding parameters

in both halves of the pseudo symmetric molecules are very similar (Tables 2 and 3).

The diselenide molecule of (1-Se-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂·toluene (**2'**) has crystallographic two-fold symmetry with the symmetry axis going through the midpoint of the Se-Se bond (Figure 3). Despite of the differences in the crystallographic symmetry, the conformations and bond parameters of (1-Se-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂ and the diselenide molecule of (1-Se-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂·toluene are very similar. Most of the bond parameters gathered in Table 3 are equal within experimental errors and only a few minor differences, like differences in the dihedral values of the C(33)-C(22)···C(2)-C(13) can be noticed.

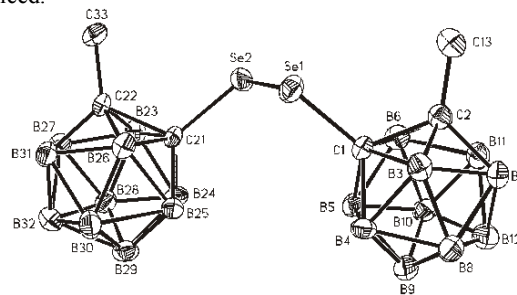


Figure 3. A view of the diselenide molecule of (1-Se-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂·toluene showing 50% displacement ellipsoids. Hydrogen atoms are omitted for clarity. Super script "a" refers equivalent position $-x, y, -z+1/2$.

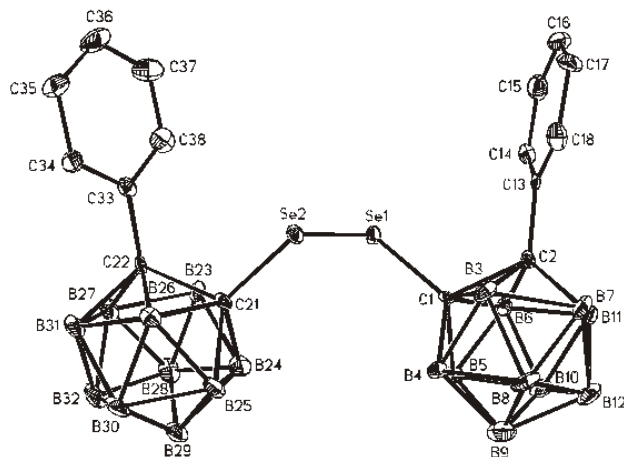


Figure 4. A view of (1-Se-2-Ph-1,2-*closo*-C₂B₁₀H₁₀)₂ showing 50% displacement ellipsoids. Hydrogen atoms are omitted for clarity.

(1-Se-2-Ph-1,2-*closo*-C₂B₁₀H₁₀)₂ (**3**) has only very approximate two-fold symmetry as mutual orientations of the phenyl groups are markedly different (Figure 4). However, expectedly the corresponding bond lengths and angles in both halves of the molecule are very similar (Table 3).

Conformations of the four selenide and diselenide molecules are quite similar as those of the corresponding carboranyl thioethers and disulfides.³⁷

In the diselenide compounds the absolute values of the C_c-Se-Se-C_c and C_c-C_c-Se-Se torsion angles (C_c refers cluster carbon) are very similar varying only within 3.0 and 6.5°, respectively. However, orientations of the C(2)-C(13) and C(22)-C(33) bonds, and thus the mutual molecular conformations of the whole molecules, are very different in the selenide and diselenide compounds. The C(13)-C(2)···C(22)-C(33) dihedral angle is -151.5(2)° for (2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂Se but the corresponding angles for the diselenide bridged compounds (1-Se-2-Me-1,2-*closo*-

$C_2B_{10}H_{10}_2$, (1-Se-2-Me-1,2-*closo*- $C_2B_{10}H_{10}_2$)-toluene and (1-Se-2-Ph-*closo*-1,2- $C_2B_{10}H_{10}_2$) are 3.1(4), 8.65(15) and $-12.7(4)^\circ$, respectively. The second selenium atom in the bridge is the reason for the differences. The observed dihedral values are comparable with those of the similar thioethers and disulfide compounds.³⁷

In (2-Me-1,2-*closo*- $C_2B_{10}H_{10}_2$)₂Se the C(1)-Se-C(21) angle is 110.11(11) $^\circ$. This value is near to the value 109.6(2) $^\circ$ found in $(C_5Me_5)_2Se$ (C_5Me_5 = pentamethylcyclopentafienyl)³⁸ and indicates that the C-Se-C angle is the normal in 1, but very slightly opened from the tetrahedral value of 109.5 $^\circ$.

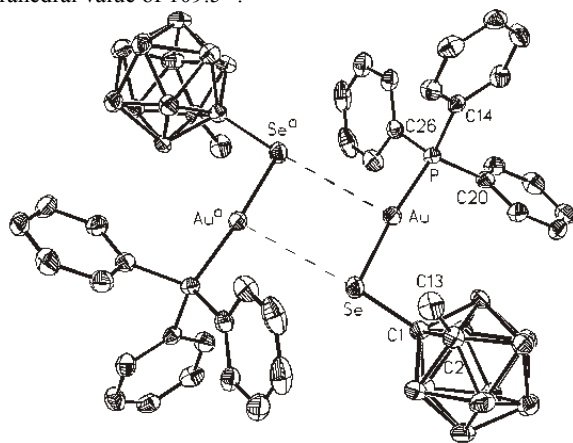


Figure 5. A view of [Au(1-Se-2-Me-1,2-*closo*- $C_2B_{10}H_{10}_2$)(PPh₃)] showing formation of centrosymmetric dinuclear [{Au(1-Se-2-Me-1,2-*closo*- $C_2B_{10}H_{10}_2$)(PPh₃)}₂] unit. Thermal displacement ellipsoids are drawn at 50% level. Super script “a” refers equivalent position $-x$, $-y$, $1-z$, and hydrogen atoms are omitted.

The reason for the small opening of the C_c -Se- C_c angle can be the mutual steric repulsion of the boron cages. There are several short intramolecular contacts of H atoms between the cages like H(5)⋯H(26) (2.54 Å), H(5)⋯H(33C) (2.54 Å), H(6)⋯H(25) (2.49 Å) H(6)⋯H(26) (2.41 Å). The steric repulsions may be one of the reasons of the nonexistence of the monothioethers with more bulky substituents in the clusters because now also the substituent and the cage may repel each other.

There are also minor bond length differences between the four carborane compounds. In the selenide (2-Me-1,2-*closo*- $C_2B_{10}H_{10}_2$)₂Se, the C_c - C_c bond lengths are 1.699(3) and 1.712(3) Å. In the two diselenide structures with methyl substituents at the cluster carbons C(2) and C(22), the C_c - C_c distances are very similar [1.701(7), 1.702(7) and two 1.6897(17) Å], while in (1-Se-2-Ph-1,2-*closo*- $C_2B_{10}H_{10}_2$) the distances are 1.726(6) and 1.741(7) Å. Even the differences are minor between the Me and Ph substituted compound, and not both significantly different, the trend observed agrees with the observation that contribution of an aryl substituent to the lengthening C_c - C_c bond is greater than that of non-aryl substituent. However, the differences for these selenium compounds are smaller than those observed for the corresponding sulphur substituted compounds.³⁷

Se-C(1)	1.937(3)
Se-C(21)	1.933(3)
C(1)-C(2)	1.699(3)
C(21)-C(22)	1.712(3)
C(2)-C(13)	1.511(4)
C(22)-C(33)	1.514(4)

C(1)-Se-C(21)	110.11(11)
Se-C(1)-C(2)	117.67(16)
Se-C(21)-C(22)	117.52(17)
C(1)-C(2)-C(13)	118.9(2)
C(21)-C(22)-C(33)	118.8(2)

C(2)-C(1)-Se-C(21)	96.71(19)
C(22)-C(21)-Se-C(1)	97.07(18)
Se-C(1)-C(2)-C(13)	-10.9(3)
Se-C(21)-C(22)-C(33)	-12.2(3)
C(13)-C(2)⋯C(22)-C(33)	-151.5(2)

Table 2. Selected bond lengths (Å), angles and torsion angles (deg) for (2-Me-1,2-*closo*- $C_2B_{10}H_{10}_2$)₂Se (1).

Compound	2	2'	3
Se(1)-Se(2)	2.3012(8)	2.3026(3)	2.3038(7)
Se(1)-C(1)	1.948(5)	1.9526(11)	1.945(5)
Se(2)-C(21)	1.953(5)		1.949(5)
C(1)-C(2)	1.701(7)	1.6897(17)	1.726(6)
C(21)-C(22)	1.702(7)		1.741(7)
C(2)-C(13)	1.518(7)	1.5157(18)	1.499(7)
C(22)-C(33)	1.516(7)		1.504(7)
Se(2)-Se(1)-C(1)	102.23(15)	101.94(4)	102.58(13)
Se(1)-Se(2)-C(21)	103.16(15)		103.54(14)
Se(1)-C(1)-C(2)	117.6(3)	115.58(8)	115.3(3)
Se(2)-C(21)-C(22)	115.9(3)		115.4(3)
C(1)-C(2)-C(13)	118.8(4)	118.91(10)	120.2(4)
C(21)-C(22)-C(33)	119.2(4)		120.2(4)
C(1)-Se(1)-Se(2)-C(21)	99.1(2)	101.94(7)	-98.9(2)
C(2)-C(1)-Se(1)-Se(2)	111.2(3)	111.53(9)	-113.7(3)
C(22)-C(21)-Se(2)-Se(1)	109.8(3)		-116.3(3)
Se(1)-C(1)-C(2)-C(13)	-5.8(6)	-4.61(16)	4.8(5)
Se(2)-C(21)-C(22)-C(33)	-4.4(6)		1.6(5)
C(13)-C(2)⋯C(22)-C(33)	3.1(4)	8.65(15)	-12.7(4)

Table 3. Selected bond lengths (Å), angles and torsion angles (deg) for (1-Se-2-Me-1,2-*closo*- $C_2B_{10}H_{10}_2$)₂ (2), (1-Se-2-Me-1,2-*closo*- $C_2B_{10}H_{10}_2$)-toluene (2') and (1-Se-2-Ph-1,2-*closo*- $C_2B_{10}H_{10}_2$) (3). For 2' Se(2), C(21), C(22) and C(33) refer Se(1), C(1), C(2) and C(13) at equivalent position $-x$, y , $-z+1/2$.

A further interesting difference between (2-Me-1,2-*closo*- $C_2B_{10}H_{10}_2$)₂Se, (1-Se-2-Me-1,2-*closo*- $C_2B_{10}H_{10}_2$)-toluene and (1-Se-2-Ph-1,2-*closo*- $C_2B_{10}H_{10}_2$) can be noticed in the Se- C_c - C_c - C_{Me} torsion angles. The angles in the selenium bridged compound are $-10.9(3)^\circ$ and $-12.2(3)^\circ$ while in the diselenide compounds the absolute values of the relevant torsion angles vary from 1.6(5) to 5.8(6) $^\circ$. These small differences are difficult to explain. However, there are short intramolecular H(Me)⋯Se contacts between selenium atom and one of the hydrogen atoms of each methyl group in (2-Me-1,2-*closo*- $C_2B_{10}H_{10}_2$)₂Se. The Se⋯H(13c) distance of 2.72 Å and the Se⋯H(13c)-C(13) angle of 124 $^\circ$ indicate hydrogen bond. Also the Se⋯H(33c) distance of 2.96 Å is shorter than the sum of van der Waals radii (3.10-3.35 Å) but the Se⋯H(33c)-C(33) angle is quite narrow (106 $^\circ$). Also there are no short intermolecular Se⋯H contacts (below 2.80 Å) in diselenide compounds.

Au-Se	2.4254(6)
Au⋯Se ^a	3.4782(6)
Au-P	2.2740(13)
Se-C(1)	1.955(5)
P-C(14)	1.814(5)
P-C(20)	1.821(5)
P-C(26)	1.806(5)
C(1)-C(2)	1.703(7)
C(2)-C(13)	1.508(7)
P-Au-Se	174.82(4)
Se-Au⋯Se ^a	94.86(2)
Au-Se-C(1)	97.40(15)
Se-C(1)-C(2)	119.1(3)
C(13)-C(2)-C(1)	118.1(4)
Se-C(1)-C(2)-C(13)	-1.9(6)
Au-Se-C(1)-C(2)	107.2(3)

^a refers to the equivalent position of $-x$, $-y$, $1-z$.

Table 4. Selected interatomic distances (Å), angles and torsion angles (deg) for [Au(1-Se-2-Me-1,2-*closo*- $C_2B_{10}H_{10}_2$)(PPh₃)] (4).

In [Au(1-Se-2-Me-1,2-*closo*- $C_2B_{10}H_{10}_2$)(PPh₃)] (4) the metal is almost linearly bonded to the phosphorous atom of the bulky PPh₃ group (Figure 5) and the selenate ion with the

P-Au-Se bond angle of 174.82(4)^o (Table 4). The C_c-C_c distance of 1.703(7) Å is comparable with those of the present methyl substituted Se carboranes (Tables 2-3).

Two [Au(1-Se-2-Me-1,2-*closo*-C₂B₁₀H₁₀)(PPh₃)] unit have formed a dinuclear complex in the solid state (Fig. 5), where two Se...Au bridging contacts of 3.4783(6) Å between two neighbouring molecules exist. These contact distances are *ca.* 0.12 Å shorter than the sum of corresponding van der Waals radii. The Au...Au distance in the dinuclear unit is 4.0684(4) Å. Thus in this compound there is no direct Au...Au interaction similar to the one found in [Au(1-Se-2-H-1,2-*closo*-C₂B₁₀H₁₀)(PPh₃)] compound²⁵ but the association happens through Au-Se-Au bridge.

The shortest intramolecular selenium hydrogen contact in the gold complex is 2.86 Å [Se...H(13b)], but the Se...H(13b)-C(13) angle is quite narrow (114^o).

Experimental section

Materials and Methods. Commercial *o*-carborane, 1-methyl-*o*-carborane and 1-phenyl-*o*-carborane were sublimed under high vacuum at 0.01 mm Hg prior to use. Solvents were placed under vacuum to eliminate dissolved oxygen. A 1.6 M solution of *n*-butyllithium in *n*-hexane was used as purchased. All reactions were carried out under a dinitrogen atmosphere employing Schlenk techniques. Microanalyses were performed by using a Perkin-Elmer 240 B microanalyser. IR spectra were obtained as KBr pellets on a Nicolet 710-FT spectrophotometer. The ¹H-NMR (300.13 MHz), ¹³C{¹H}-NMR (75.47 MHz), ¹¹B-NMR (96.29 MHz), ³¹P{¹H}-NMR (121.5 MHz) and ⁷⁷Se-NMR (57 MHz) spectra were recorded on a Bruker ARX 300WB spectrometer. Chemical shift values for ¹H-NMR spectra were referenced to an internal standard of SiMe₄ in deuterated solvents. Chemical shift values for ¹¹B-NMR spectra were referenced relative to external BF₃.OEt₂. Chemical shift values for ³¹P{¹H}-NMR spectra were referenced relative to external 85% H₃PO₄. Chemical shift values for ⁷⁷Se-NMR spectra were referenced relative to external SeMe₂. Chemical shifts are reported in units of parts per million downfield from the reference, and all coupling constants are reported in Hertz. The mass spectra for anionic species were recorded in the negative ion mode using a Bruker Biflex MALDI-TOF-MS [N₂ laser; λ_{exc} 337 nm (0.5 ns pulses); voltage ion source 20.00 kV (Uis1) and 17.50 kV (Uis2)].

Synthesis of (1-Se-2-Me-1,2-C₂B₁₀H₁₀)₂

To a solution of 1-methyl-*o*-carborane (100 mg, 0.63 mmol) in dry diethyl ether at 0°C was added *n*-BuLi (0.4 mL, 0.63 mmol). The mixture was stirred at this temperature for 30 min, then maintained at room temperature for the same period, and cooled again to 0°C, at which point selenium powder (50 mg, 0.63 mmol) was slowly added over a period of 30 min. The resulting solution was stirred at 25°C for 1 hour. Then 10 mL of water was added. The mixture was thoroughly shaken, and the two layers separated. The organic layer was dried over MgSO₄. The filtrate was evaporated to give a yellow solid. Yield: (131 mg, 88%). Crystals were obtained from slow evaporation of acetone solution. Anal. Calcd for C₆H₂₆B₂₀Se₂: C, 15.25; H, 5.55. Found: C, 15.26; H, 5.45. FTIR (KBr): ν (cm⁻¹) 2936 (C-H); 2610, 2546, 2564, 2584, 2572 (B-H). ¹H-NMR (CD₃COCD₃): δ 2.08 (d, ¹J(Se,H)= 2.5, Me), 1.86 (d, ¹J(Se,H)= 2.5, Me). ¹H{¹¹B}-NMR (CD₃COCD₃): δ 2.49 (s, B-H), 2.23 (s, B-H), 2.08 (d, ¹J(H,H)= 2.5, Me), 2.03 (s, B-H), 1.86 (d, ¹J(H,H)= 2.5, Me). ¹¹B-NMR (CD₃COCD₃): δ -1.9 (d, ¹J(B,H)= 145, 1B), -4.1 (d, ¹J(B,H)= 156, 1B), -8.3 (d, ¹J(B,H)= 137, 8B). ¹³C{¹H}-NMR (CD₃COCD₃): δ 79.7 (s, C_c), 66.6 (s, C_c), 24.7 (s, Me). MALDI-TOF-MS (m/z): 472 (M, 14%), 237 (M/2, 100%).

Synthesis of (1-Se-2-Ph-1,2-C₂B₁₀H₁₀)₂

This compound was prepared analogously to the method described for (1-Se-2-Me-1,2-C₂B₁₀H₁₀)₂, using 1-Ph-1,2-*closo*-C₂B₁₀H₁₁ (100 mg, 0.45 mmol), *n*-BuLi (0.28 mL, 0.45 mmol) and selenium (36 mg, 0.45 mmol) as starting materials to afford a yellow solid. Yield: 104 mg (77%). Good crystals for X-ray diffraction were grown from acetone solution by slow evaporation. Anal. Calcd for C₁₆H₃₀B₂₀Se₂: C, 32.21; H, 5.07. Found: C, 31.95; H, 5.32. FTIR (KBr): ν (cm⁻¹) 2932, 2931 (C-H) (cm⁻¹); 2603, 2569 (B-H). ¹H-NMR (CDCl₃): δ 7.49-7.28 (m, Ph, 10H), 3.00-0.9 (m, B-H, 20H). ¹H{¹¹B}-NMR (CDCl₃): δ 7.49-7.28 (m, Ph, 10H), 2.56 (s, B-H, 4H), 2.44 (s, B-H, 12H), 2.31 (s, B-H, 4H). ¹¹B-NMR (CDCl₃): δ -2.0 (d, ¹J(B,H)= 147, 2B), -8.9 (d, ¹J(B,H)= 141, 6B), -10.8 (d, ¹J(B,H)= 171, 2B). ¹³C{¹H}-NMR (CDCl₃): 130.50, 130.03, 127.80, 126.50 (s, C_{aryl}), 85.51 (s, C_c), 67.81 (s, C_c). MALDI-TOF-MS (m/z): 597 (M, 2%), 299 (M/2, 100%).

Synthesis of (2-Me-1,2-C₂B₁₀H₁₀)₂Se

To a solution of 1-methyl-*o*-carborane (17 mg, 0.11 mmol) in dry diethyl ether at 0°C was added *n*-BuLi (0.07 mL, 0.11 mmol). The mixture was stirred for 30 min at 0°C and at room temperature for 30 min more. Then a solution of (1-Se-2-Me-1,2-C₂B₁₀H₁₀)₂ (50 mg, 0.11 mmol) in dry diethyl ether (15 ml) was added. The slurry was refluxed for 2 h. The resulting mixture was then washed with water (10 ml) and 0.5 M Na₂CO₃ aqueous solution (2x15 ml). The organic layer was dried over MgSO₄. The diethyl ether filtrate was evaporated at the vacuum to give a yellow solid. Recrystallization from petroleum ether provided crystals. Yield: 35 mg (84.1%). Anal. Calcd for C₆H₂₆B₂₀Se: C, 18.32; H, 6.66. Found: C, 18.35; H, 6.98. FTIR (KBr): ν (cm⁻¹) 2955, 2923 (C-H); 2576 (B-H). ¹H-NMR (CDCl₃): δ 2.06 (s, Me), 2.02 (s, Me). ¹H{¹¹B}-NMR (CDCl₃): δ 2.43, 2.27, 2.19, 2.14 (m, B-H), 2.06 (s, Me), 2.02 (s, Me). ¹¹B-NMR (CDCl₃): δ -1.13 (d, ¹J(B,H)= 154, 1B), -4.22 (d, ¹J(B,H)= 156, 1B), -8.93 (d, ¹J(B,H)= 121, 8B). ¹³C{¹H}-NMR (CDCl₃): δ 69.24 (s, C_c), 50.99 (s, C_c), 25.42 (s, Me), 24.95 (s, Me). MALDI-TOF (m/z): 393 (M, 2%), 377.60 (M-Me, 22.5%), 237 (M-Me-carboranyl, 100%).

Synthesis of [Au(1-Se-2-Me-1,2-C₂B₁₀H₁₀)(PPh₃)]

To a solution of 1-methyl-*o*-carborane (78 mg, 0.49 mmol) in dry diethyl ether (10 mL) at 0°C was added *n*-BuLi (0.31 mL, 0.49 mmol). The mixture was stirred at this temperature for 30 min, then maintained at room temperature for the same period, and cooled again to 0°C, at which point selenium powder (39 mg, 0.49 mmol) was slowly added over a period of 30 min. The resulting solution was stirred at 25°C for 1 h. Then [AuClPPh₃] (242 mg, 0.49 mmol) was added and stirred at room temperature overnight. After filtered off a violet solid, the organic solution was dried over MgSO₄. The filtrate was evaporated to obtain a yellowish solid. Yield 146 mg (43%). Crystals were grown from a saturated solution in diethyl ether. Anal. Calcd for C₂₁H₂₈Au₁B₁₀PSe: C, 36.27; H, 4.06. Found: C, 36.51; H, 4.29. FTIR (KBr): ν (cm⁻¹) 2926, 2855 (C-H); 2590, 2575, 2573, 2561 (B-H); 1479, 1435, 1101, 743, 690, 535 (PPh₃). ¹H-NMR: δ 2.08 (d, ¹J(H,H)= 2.5, 3H), 1.92 (d, ¹J(H,H)= 2.5, 3H). ¹H{¹¹B}-RMN: δ 2.08 (d, ¹J(H,H)= 2.5, 3H), 1.92 (d, ¹J(H,H)= 2.5, 3H), 2.77 (s, B-H), 2.40 (s, B-H), 2.2 (s, B-H), 2.00 (s, B-H). ¹¹B-NMR: δ -5.96 (br s, 6B), -9.12 (d, ¹J(B,H)= 156, 4B). ³¹P{¹H}-NMR: δ 37.4 (s, PPh₃). ¹³C{¹H}-NMR: δ 134.3 (d, ¹J(C, H)= 14, Ph), 131.9 (s, Ph), 129.3 (d, ¹J(C, H)= 12, Ph), 128.7 (s, Ph), 64.5 (s, C_c), 25.83 (s, Me).

X-ray Structure Determinations of (2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂Se, (1-Se-2-Me-1,2-*closo*-C₂B₁₀H₁₁)₂, (1-Se-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂toluene, (1-Se-2-Ph-1,2-*closo*-C₂B₁₀H₁₀)₂ and [Au(1-Se-2-Me-1,2-*closo*-C₂B₁₀H₁₀)(PPh₃)]. Single-crystal data collections were performed at ambient

temperature on a Nonius KappaCCD diffractometer at -100°C using graphite monochromatized Mo K α radiation. Totals of 6748, 6010, 4917, 7433 and 16157 reflections were collected for (2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂Se, (1-Se-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂, (1-Se-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂·toluene, (1-Se-2-Ph-1,2-*closo*-C₂B₁₀H₁₀)₂ and [Au(1-Se-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂(PPh₃)] giving 3776 ($R_{\text{int}} = 0.0371$), 3700 ($R_{\text{int}} = 0.0455$), 2581 ($R_{\text{int}} = 0.0322$), 4390 ($R_{\text{int}} = 0.0509$) and 4651 ($R_{\text{int}} = 0.0358$) independent reflections, respectively. Crystallographic data are presented in Table 1.

The structures were solved by direct methods using the SHELXS-97 program and least-squares refinements were performed using the SHELXL-97 program.³⁹ For all compounds, non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were included in the calculations at fixed distances from their host atoms and treated as riding atoms using the SHELXL-97 default parameters. (1-Se-2-Ph-1,2-*closo*-C₂B₁₀H₁₀)₂ crystallizes in a noncentrosymmetric space group, and absolute configuration was determined by refinement of Flack's x parameter.

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Supporting Information Available: Tables of X-ray experimental details, hydrogen atom positional parameters and thermal parameters, anisotropic thermal parameters, interatomic distances and angles for (2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂Se, (1-Se-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂, (1-Se-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂·toluene, (1-Se-2-Ph-1,2-*closo*-C₂B₁₀H₁₀)₂ and [Au(1-Se-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂(PPh₃)]. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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