

SYNTHESIS OF 9,12-*o*- AND 9,10-*m*-CARBORANYL-DITHIOLS AND -DISELENOLS FROM S_2Cl_2 OR Se_2Cl_2 AND *o*- AND *m*-CARBORANES *

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Summary

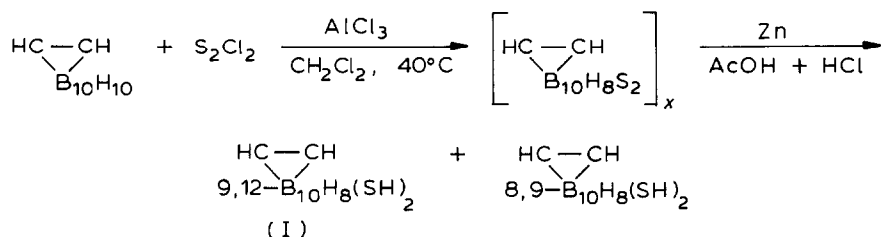
The synthesis of 9,12-*o*- and 9,10-*m*- $C_2H_{10}B_{10}(EH)_2$ ($E = S, Se$) from *o*- and *m*-carboranes and E_2Cl_2 in the presence of $AlCl_3$ is described. The reactions of these compounds have been investigated, a number of derivatives have been obtained (thio- and seleno-alkoxides, cyclic thio- and seleno-acetals and ketals), and their 1H and ^{11}B NMR spectra are reported.

Results and discussion

As shown earlier, *o*- and *m*-carboranes treated with S_2Cl_2 or Se_2Cl_2 in the presence of $AlCl_3$ with subsequent reduction of the reaction products with zinc and hydrochloric acid in AcOH yield 9-*o*- and *m*-carboranylthiols and 9-*o*- and *m*-carboranyl-selenols, respectively [1,2]. This is a convenient method for synthesizing derivatives of *o*- and *m*-carboranes with B–S and B–Se σ -bonds. Plesek et al. report [3] that treating *o*- and *m*-carboranes with an excess of sulfur in the presence of large amounts of $AlCl_3$ at 130°C, and the subsequent reduction of the yielded products with $NaBH_4$ in ethanol results in the formation of 9,12-*o*-carboranyldithiol and 9,10-*m*-carboranyldithiol, respectively.

We found that when excessive S_2Cl_2 or Se_2Cl_2 is treated with *o*- and *m*-carboranes in the presence of $AlCl_3$ in CH_2Cl_2 solution, two atoms of sulfur or selenium are introduced into the carborane cage. Heating S_2Cl_2 and *o*-carborane (molecular ratio 2/1) in CH_2Cl_2 in the presence of $AlCl_3$ evidently yields oligomers with B–S–S–B bridges. Reducing these products with zinc and hydrochloric acid in AcOH or $NaBH_4$ in ethanol yields mainly 9,12-*o*-carboranyldithiol (I), as well as a negligible amount ($\sim 3\%$) of a substance that is probably 8,9-*o*-carboranyldithiol:

* *o*-Carborane: 1,2-dicarbasclododecaborane(12),
m-Carborane: 1,7-dicarbasclododecaborane(12).



The reaction of *m*-carborane with S_2Cl_2 (molecular ratio 1/2) in CH_2Cl_2 solution in the presence of AlCl_3 proceeds in a manner similar to that of *o*-carborane. Reduction of intermediate oligomers yields 9,10-*m*-carboranyldithiol (II) with no trace of other isomers. Nevertheless, the reaction is more difficult to achieve than for *o*-carborane.

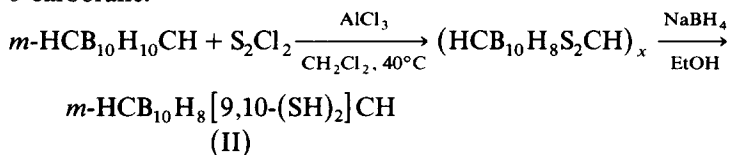


TABLE 1

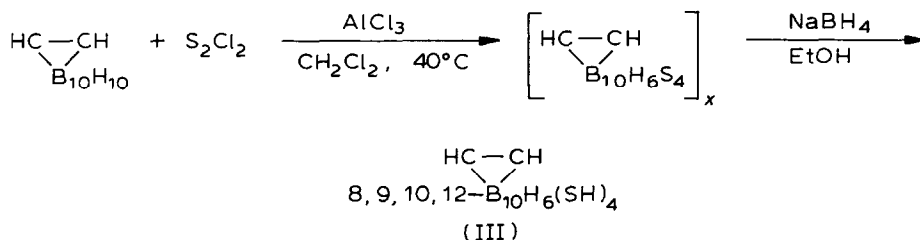
 ^{11}B NMR SPECTRAL DATA OF THE COMPOUNDS OBTAINED

Compound	Solvent	$\delta(^{11}\text{B})^a$ (ppm) ($J(\text{BH})$ (Hz))
I	CH_2Cl_2	B(9,12) 4.8 (0); B(8,10) 7.0 (155); B(4,5,7,11) -14.2 (161); B(3,6) -16.7 (170)
II	CH_2Cl_2	B(9,10) -1.5 (0); B(5,12) -5.1 (161); B(4,6,8,11) -13.5 (168); B(2,3) -21.5 (183)
III	CCl_4	B(9,12) 6.8 (0); B(8,10) -0.6 (0)
IV	CH_2Cl_2	B(9,12) 0.2 (0); B(8,10) -6.4 (149); B(4,5,7,11) -13.6 (168); B(3,6) -15.5 (181)
V	CH_2Cl_2	B(5,12) -5.0 (164); B(9,10) -5.9 (0); B(4,6,8,11) -12.8 (171); B(2,3) -19.9 (181)
VI	CH_2Cl_2	B(9,12) 7.5 (0); B(8,10) -9.4 (152); B(4,5,7,11) -14.9 (164); B(3,6) -17.1 (155)
VII	CCl_4	B(9,10) 0.97 (0); B(5,12) -7.8 (160.8); B(4,8,6,11) -14.00 (169.7); B(2,3) -21.4 (181.6)
VIII	CCl_4	B(9,12) 3.6 (0); B(8,10) -8.3 (156); B(4,5,7,11) -14.0 (164); B(3,6) -16.2 (151)
VIII	CCl_4	B(9,12) 3.6 (0); B(8,10) -8.3 (156); B(4,5,7,11) -14.0 (164); B(3,6) -16.2 (151)
IX	CCl_4	B(9,10) -3.95 (0); B(5,12) -7.0 (173); B(4,8,6,11) -13.4 (166); B(2,3) -20.0 (183)
X	CD_3COCD_3	B(9,12) 10.4 (0); B(8) -0.08 (156); B(10) -6.9 (156); B(3,6,4,5,7,11) -3.95 (156); -16.2 (154)
XI	CD_3COCD_3	B(9,10) 5.2 (0); B(5) 0.8 (178); B(12) -4.8 (166); B(4,6,8,11) -13.7 (156); -15.7 (149); B(2,3) -19.8 (185)
XII	CCl_4	B(9,12) 7.0 (0); B(8) -1.7 (149); B(10) -7.1 (154); B(4,5,7,11) -14.7 (120); B(3,6) -16.0 (144)
XIII	CCl_4	B(9,10) 2.4 (0); B(5) -0.1 (200); B(12) -4.5 (159); B(6,8,4,11) -12.8 (166); -14.4 (154); B(2,3) -18.3 (185)
XIV	CCl_4	B(9,10) 2.6 (0); B(5,12) -3.5 (178); B(4,11,6,8) -14.8 (166); B(2,3) -20.4 (183)

^a δ (ppm) related to $\text{BF}_3 \cdot \text{OEt}_2$.

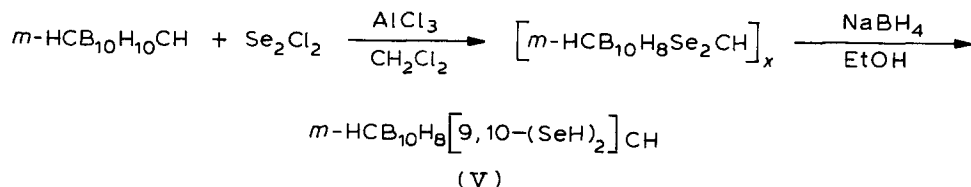
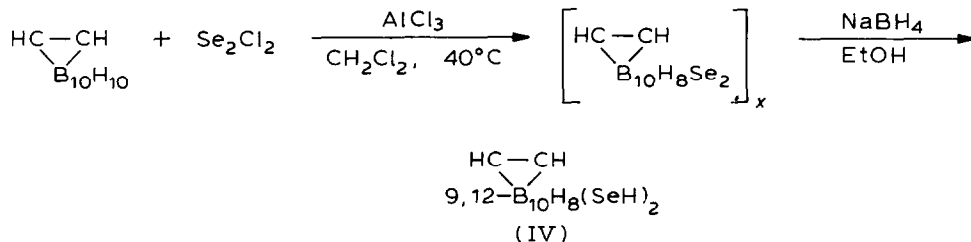
The structures of dithiols I and II were confirmed by ^1H and ^{11}B NMR spectra (Table 1).

By treating *o*-carborane with excessive S_2Cl_2 in CH_2Cl_2 solution in the presence of AlCl_3 , it became possible to introduce four sulfur atoms into the *o*-carborane cage, obtaining 8,9,10,12-*o*-carboranyltetrathiol (III) whose structure was confirmed by ^{11}B NMR and mass spectra.



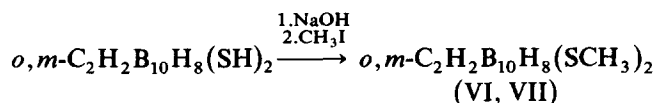
In the case of *m*-carborane, even a large excess of S_2Cl_2 does not allow more than two SH groups to be introduced into the *m*-carborane cage.

When Se_2Cl_2 and *o*- and *m*-carborane (molecular ratio 2/1) are heated in CH_2Cl_2 solution in the presence of AlCl_3 , oligomeric compounds with B-Se-Se-B bridges evidently form along with other products. Reduction of these compounds with NaBH_4 in ethanol yielded 9,12-*o*-carboranyldiselenol (IV) and 9,10-*m*-carboranyldiselenol (V), respectively:

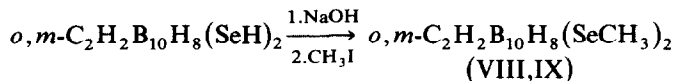


The diselenols obtained, IV and V, are very sensitive towards oxygen, and should therefore be synthesized in an inert atmosphere. The structures of these diselenols were confirmed by ^1H and ^{11}B NMR spectra.

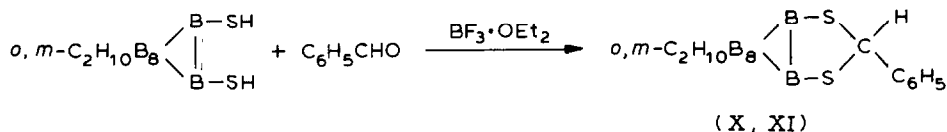
We have also studied some transformations of the carbonyldithiols and carbonyldiselenols obtained. It was proved that in an alkali solution *o*- and *m*-carboranyldithiols easily form the corresponding alkoxides, which yield, when treated with alkyl halides, bis(alkylthio)-*o*- and -*m*-carboranes.



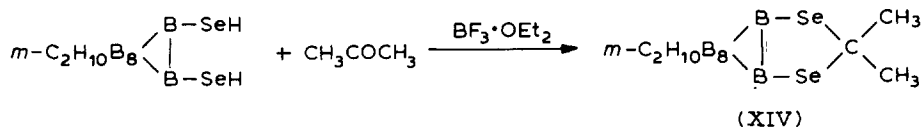
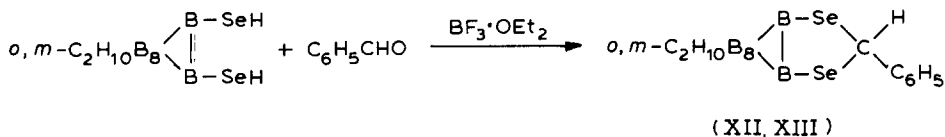
The action of CH_3I on an alcohol solution of IV or V and sodium hydroxide gave 9,12- $(\text{CH}_3\text{Se})_2$ -1,2- $\text{C}_2\text{H}_{10}\text{B}_{10}$ (VIII) and 9,10- $(\text{SeCH}_3)_2$ -1,7- $\text{C}_2\text{H}_{10}\text{B}_{10}$ (IX):



In the presence of Lewis acids, *o*- and *m*-carboranyldithiols easily react with aldehydes, yielding the corresponding cyclic *o*- and *m*-carboranylmercaptals:



In the case of *o*- and *m*-carbonyldiselenols, VI and VII, treatment with aldehydes or ketones in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ also easily yielded cyclic carboranyl-selenoacetals and carboranylselenketals:



The formation of mercapto- and seleno-acetals confirms the adjacent positioning of two SH or SeH groups in the *o*- or *m*-carborane cage.

A comparative analysis of the ^{11}B NMR spectra of the mercapto- and seleno-acetals obtained (X–XIII) with the ^{11}B NMR spectra of unsubstituted dithiols and diselenols shows that different substituents (Ph and H) at the carbon atom in the 5-membered ring make two parts of the carborane icosahedron magnetically non-equivalent to each other, as regards the symmetry plane passing through the carbon atom, and the centre of the bonds between boron atoms and Se or S atoms at an angle of 90° to this plane. Considerable magnetic non-equivalence of the boron atoms in positions 5 and 12 was observed in the *m*-carborane icosahedron for both *m*-mercapto- and *m*-seleno-acetals. It was somewhat weaker for atoms in positions 4, 6, 8 and 11. Boron atoms in positions 9 and 10 remained equivalent (as they have substituents), even though their signal was registered on the weak field part of the scale.

Similarly, in the ^{11}B NMR spectra of *o*-mercaptoacetal and *o*-selenoacetal, due to a varying magnetic environment, magnetic non-equivalence was most pronounced for the boron atoms in positions 8 and 10; it was somewhat weaker for the outlying 4, 5 and 7, 11 boron atoms. At the same time, the magnetic equivalence of boron atoms bonded to substituents (positions 9 and 12) remained unchanged, although, compared to unsubstituted dithiols and diselenols, their signal was registered on the weak field part of the scale.

If the carbon atom has identical substituents in the 5-membered ring of the ketal (XIV), the symmetry of the carborane cage and, therefore, the equivalence of boron atoms, is not disturbed. This was confirmed by the ^{11}B NMR spectrum of compound XIV.

Experimental

All solvents and reagents were dried and distilled before use. Experiments with Se_2Cl_2 were carried out in an inert atmosphere. Reactions were followed by TLC on Silufol plates. ^1H and ^{11}B NMR spectra were obtained on a Bruker WP-200SY spectrometer; mass spectra on a MS-30 AEI spectrometer. Silica gel (L 100/160) was used for column chromatography.

9,12-Bis(mercapto)-*o*-carborane (I). 7.8 g (58.6 mmol) of AlCl_3 was added to a solution of 2.8 g (19.4 mmol) of *o*-carborane in 25 ml of CH_2Cl_2 at -50°C . 5.3 g (38.9 mmol) of S_2Cl_2 was added dropwise to the obtained suspension in 5 ml of CH_2Cl_2 at -15°C , with subsequent heating while boiling for 6 h. After cooling, the mixture, in the form of a viscous liquid, was poured into water. The precipitate obtained was filtered, washed in water and dried in vacuo over P_2O_5 . 4.4 g of dry product (A) was obtained, with an additional 0.7 g of A obtained from the mother liquor.

(a) 4 g of NaBH_4 was added in portions to 5.1 g of product A suspended in 150 ml of 2% NaOH alcohol solution. The mixture was stirred for 7 h at 20°C (until TLC indicated that A had disappeared), and poured into water. The filtered solution was saturated with CO_2 , the precipitate was extracted with ether, and the organic layer was washed in water and dried over MgSO_4 . After removal of the solvent and crystallization, 3.0 g (74%) of I was obtained, m.p. $235\text{--}236^\circ\text{C}$ (cyclohexane). According to TLC, it contained $\sim 3\%$ of 8,9-bis(mercapto)-*o*-carborane. ^1H NMR (CDCl_3): $\delta(\text{S-H})$ 0.58 ppm. Found: C, 11.96; H, 5.81; B, 51.39; S, 30.88. $\text{C}_2\text{H}_{12}\text{B}_{10}\text{S}_2$ calcd.: C, 11.52; H, 5.80; B, 51.85; S, 30.77%.

(b) Excessive Zn (dust) was carefully added to 2.6 g of product A suspended in 100 ml of EtOH/HCl (10/1) mixture. After boiling for 6 h and pouring into water, the product was extracted with ether. The organic layer was separated and washed with water. The dithiol obtained was cleaned through K-salt in the usual way. After removal of the solvent and crystallization, 1.3 g of *B,B'*-dithiol was obtained, m.p. $235\text{--}236^\circ\text{C}$. According to TLC, it contained 3% of 8,9-bis(mercapto)-*o*-carborane.

9,10-Bis(mercapto)-*m*-carborane (II). 7.4 g (57.9 mmol) of AlCl_3 was added to a solution of 2.2 g (15.3 mmol) of *m*-carborane in 25 ml of CH_2Cl_2 at -50°C , and at -15°C 4.12 g (30.5 mmol) of S_2Cl_2 in 5 ml of CH_2Cl_2 was added dropwise. The temperature was then gradually raised and the reaction mixture boiled for 10 h (until TLC indicated that *m*-carborane had disappeared). The mixture was poured into water, the product was extracted with ether, and the organic layer was separated, washed in water, and dried over MgSO_4 . 2.5 g of NaBH_4 was added in portions while stirring to a suspension of the product obtained after removal of the solvent in 100 ml of a 2% NaOH alcohol solution. The mixture was stirred for 4 h at room temperature and poured into water. The water solution was saturated with CO_2 , and the resulting precipitate extracted with ether. 2.9 g of residue from the organic layer after evaporation was, according to GLC, a mixture of 78% 9,10-bis(mercapto)-*m*-carborane (II), and 22% 9-mercapto-*m*-carborane. After chromatography on silica

gel (with hexane/methylene chloride, 4/1, as eluant), the following was obtained: 1.8 g (56%) of 9,10-bis(mercapto)-*m*-carborane (II), m.p. 193–194°C (hexane). ^1H NMR (CDCl_3): $\delta(\text{S-H})$ 0.66 ppm. Found: S, 30.88; $\text{C}_2\text{H}_{12}\text{B}_{10}\text{S}_2$ calcd.: S, 30.77%.

8,9,10,12-Tetra(mercapto)-*o*-carborane (III). To a solution of 2.8 g (19.4 mmol) of *o*-carborane in 30 ml of CH_2Cl_2 at -50°C was added 7.8 g (58.6 mmol) of AlCl_3 , and at -15°C , 10.6 g (77.8 mmol) of S_2Cl_2 in 10 ml of CH_2Cl_2 . The reaction mixture was boiled for 6 h and poured into water; the precipitate obtained was filtered, washed in water and dried in vacuo over P_2O_5 . 7.7 g of residue was obtained. 4 g of this residue was reduced by 2 g of NaBH_4 in 100 ml of 2% NaOH alcohol solution. After standard treatment, the mercaptane obtained was cleaned by sublimation (220°C , 1 mmHg), and chromatography on silica gel (with benzene as eluant). 0.7 g of III was obtained, m.p. 349–350°C, m/z 272 (M^+). Found: S, 46.34. $\text{C}_2\text{H}_{12}\text{B}_{10}\text{S}_4$ calcd.: S, 47.05%.

9,12-Bis(selenol)-*o*-carborane (IV). To a solution of 4.63 g (32.1 mmol) of *o*-carborane in 50 ml of CH_2Cl_2 at -50°C , 12.7 g (95.5 mmol) of AlCl_3 was added; at -15°C , 14.7 g (64.2 mmol) of Se_2Cl_2 in 10 ml of CH_2Cl_2 was added dropwise. Mixing continued while boiling the solution for 10 h (until TLC indicated that *o*-carborane had disappeared). The mixture was poured into ice-cold water, and the precipitate obtained was filtered, washed with CH_2Cl_2 and dried in vacuo over P_2O_5 . 16.9 g of precipitate was obtained.

4.3 g of the precipitate obtained in 75 ml of 1% NaOH alcohol solution was reduced by 1.0 g of NaBH_4 and stirred at room temperature for 4 h. The reaction mixture was treated under an argon atmosphere with deaerated water, then poured into water. After adding dilute HCl, the precipitate obtained was extracted with ether. The diselenol obtained was cleaned through Na-salt in the usual way. After drying over MgSO_4 and removing the solvent, the product was crystallized from hexane. 1.5 g of IV was obtained, m.p. (decomp.) 150–152°C, m/z 302 (M^+). ^1H NMR (CH_2Cl_2): $\delta(\text{Se-H})$ 1.78 ppm. Found: B, 36.28. $\text{C}_2\text{H}_{12}\text{B}_{10}\text{Se}_2$ calcd.: B, 35.88%.

9,10-Bis(selenol)-*m*-carborane (V). From 4.4 g (30.55 mmol) of *m*-carborane, 12 g (90.2 mmol) of AlCl_3 and 13.8 g (60.3 mmol) of Se_2Cl_2 , similar to the above procedure for *o*-carborane, 15.9 g of dry product was obtained after boiling for 10 h.

2.5 g of this product in 50 ml of 1% NaOH alcohol solution was reduced by 0.5 g of NaBH_4 and stirred for 6 h at 20°C . After treatment similar to that above for IV, 0.96 g of V was obtained, m.p. 129–130°C (hexane), m/z 303 (M^+). ^1H NMR (CH_2Cl_2): $\delta(\text{Se-H})$ 1.67 ppm. Found: B, 35.56. $\text{C}_2\text{H}_{12}\text{B}_{10}\text{Se}_2$ calcd.: B, 35.80%.

9,12-Bis(methylthio)-*o*-carborane (VI). To 0.4 g of I in 10 ml of absolute alcohol, were added 0.088 g Na and 0.54 g CH_3I . After boiling for 4 h, the reaction mixture was evaporated to dryness. After adding benzene, the residual NaI was filtered. The benzene mother liquor was washed out with 10% KOH and water, and the product dried over MgSO_4 . 0.4 g (89%) of VI was obtained, m.p. 110–111°C (hexane/toluene). Found: C, 20.67; H, 6.74; S, 26.80. $\text{C}_4\text{H}_{16}\text{B}_{10}\text{S}_2$ calcd.: C, 20.31; H, 6.82; S, 27.11%.

9,10-Bis(methylthio)-*m*-carborane (VII). Preparation as described above for VI, from 0.3 g of II and 0.07 g of Na in 10 ml of absolute alcohol with 0.5 g CH_3I , after crystallization from hexane, 0.3 g (88%) of VII was obtained, m.p. 121–122°C. Found: C, 20.67; H, 6.73; S, 26.98. $\text{C}_4\text{H}_{16}\text{B}_{10}\text{S}_2$ calcd.: C, 20.31; H, 6.82; S, 27.11%.

9,12-Bis(methylseleno)-*o*-carborane (VIII). To 1.0 g of IV in 20 ml of absolute

alcohol were added 0.22 g of Na and 1.36 g of CH_3I . After stirring for 0.5 h at 20°C , the reaction mixture was evaporated to dryness and treated with benzene. The precipitate was separated and the benzene layer washed with 5% KOH and water, and dried over CaCl_2 . After the solvent was removed, the residue was subjected to chromatography on silica gel (with chloroform/hexane, 2/1, as eluant). 0.9 g (82%) of VIII was obtained, m.p. $93\text{--}94^\circ\text{C}$ (hexane). Found: C, 14.42; H, 5.25; B, 33.22. $\text{C}_4\text{H}_{16}\text{B}_{10}\text{Se}_2$ calcd.: C, 14.52; H, 4.88; B, 32.76%.

9,12-Bis(methylseleno)-m-carborane (IX). From 0.43 g of V in 10 ml of absolute alcohol, 0.095 g of Na and 0.59 g of CH_3I , in the way described above for VIII, after cleaning on a silica gel column (with benzene as eluant) and crystallizing from hexane, 0.3 g (64%) of IX was obtained, m.p. $120\text{--}121^\circ\text{C}$. Found: C, 14.20; H, 4.90; B, 34.47. $\text{C}_4\text{H}_{16}\text{B}_{10}\text{Se}_2$ calcd.: C, 14.54; H, 4.88; B, 32.76%.

4-Phenyl-1,2-(o-9',12'-carboranyl)-3,5-dithiopentane (X). To a solution of 0.3 g of I in 10 ml of dry ether, 0.2 ml of $\text{BF}_3 \cdot \text{OEt}_2$ and 0.15 ml of benzaldehyde were added while stirring at 5°C . Precipitation was immediate. After stirring for 4 h at 20°C , the precipitate was filtered, washed in water, and dried in vacuo over P_2O_5 . 0.3 g (75%) of X was obtained, m.p. (decomp.) $275\text{--}276^\circ\text{C}$ (benzene/THF). Found: C, 37.04; H, 5.40; S, 21.08. $\text{C}_9\text{H}_{16}\text{B}_{10}\text{S}_2$ calcd.: C, 36.64; H, 5.42; S, 21.55%.

4-Phenyl-1,2-(m-9',10'-carboranyl)-3,5-dithiopentane (XI). From 0.2 g of II in 10 ml of dry ether, 0.1 ml of $\text{BF}_3 \cdot \text{OEt}_2$ and 0.10 ml benzaldehyde, in the manner described above for X, 0.2 g (69%) of XI was obtained, m.p. $272\text{--}273^\circ\text{C}$ (benzene). Found: C, 36.32; H, 5.36; S, 21.70. $\text{C}_9\text{H}_{16}\text{B}_{10}\text{S}_2$ calcd.: C, 36.64; H, 5.42; S, 21.56%.

4-Phenyl-1,2-(o-9',12'-carboranyl)-3,5-diselenopentane (XII). To 0.34 g of IV in 10 ml of dry ether at 5°C , 0.1 ml of $\text{BF}_3 \cdot \text{OEt}_2$ and 0.12 ml of benzaldehyde were added. The reaction mixture was mixed for 4 h at 20°C . The precipitate was filtered, washed in water and hexane, and dried in vacuo over P_2O_5 . After crystallization from toluene, 0.36 g (82%) of XII was obtained, m.p. (decomp.) 280°C . Found: C, 27.36; H, 4.29; B, 28.36. $\text{C}_9\text{H}_{16}\text{B}_{10}\text{Se}_2$ calcd.: C, 27.69; H, 4.13; B, 27.72%.

4-Phenyl-1,2-(m-9',10'-carboranyl)-3,5-diselenopentane (XIII). From 0.4 g of V in 10 ml of dry ether, 0.2 ml of $\text{BF}_3 \cdot \text{OEt}_2$ and 0.14 ml of benzaldehyde, following the procedure described above for XII, 0.44 g (85%) of XIII was obtained, m.p. (decomp.) $258\text{--}260^\circ\text{C}$ (toluene). Found: C, 28.40; H, 4.55; B, 28.20. $\text{C}_9\text{H}_{16}\text{B}_{10}\text{Se}_2$ calcd.: C, 27.69; H, 4.13; B, 27.72%.

4,4'-Dimethyl-1,2-(m-9'',10''-carboranyl)-3,5-diselenopentane (XIV). To 0.43 g of II in 10 ml of dry acetone at 0°C was added 0.5 ml of $\text{BF}_3 \cdot \text{OEt}_2$. The mixture was left for 12 h at 20°C . The residue, after excessive acetone was evaporated off, was treated with water, and the precipitate was filtered, washed with hexane, and dried in vacuo over P_2O_5 . After chromatography on silica gel (with benzene as eluant) and crystallization from hexane, 0.35 g (73%) of XIV was obtained, m.p. $195\text{--}196^\circ\text{C}$. Found: C, 17.40; H, 4.51; B, 32.55. $\text{C}_5\text{H}_{16}\text{B}_{10}\text{Se}_2$ calcd.: C, 17.54; H, 4.71; B, 31.61%.

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