

Supporting Information

Chlorinated Polyhedral Selenaboranes Revisited by Joint Experimental/Computational Efforts: The Formation of *closo*-1-SeB₉Cl₉ and the Crystal Structure of *closo*-SeB₁₁Cl₁₁

Willi Keller,^{*[a]} Matthias Hofmann,^[b] Hubert Wadepohl,^[b] Markus Enders,^[b] Jindřich Fanfrlik,^[c] and Drahomír Hnyk^{*[d]}

[a] Institut für Chemie, Universität Hohenheim, Garbenstrasse 30, 70599 Stuttgart, Germany

[b] Anorganisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany

[c] Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences, Flemingovo nám. 2, 166 10 Praha 6, Czech Republic

[d] Institute of Inorganic Chemistry of the Czech Academy of Sciences, 250 68 Husinec-Řež, Czech Republic

Experimental Section

Instrumentation

1- and 2-D ^{11}B NMR spectra were recorded on Varian Inova 300 (^{11}B 96.188 MHz) and, for more recent spectra, either on Bruker AVANCE III 500 (^{11}B 160.388 MHz) and AVANCE III HD 600 (^{11}B 192.552 MHz). Homo-decoupled ^{11}B and ^{77}Se NMR spectra were recorded on a Bruker AVANCE 400 (^{11}B NMR 128.30 MHz, ^{77}Se 76.27 MHz). ^{11}B and ^{77}Se chemical shifts are referenced either to external $\text{BF}_3\cdot\text{OEt}_2$ or Me_2Se . The NMR spectra were processed using SpinWorks 4 (v 4.2.3.0 Kirk Marat, University of Manitoba, Canada) software. High- and low-resolution mass spectra were obtained on a Finnigan MAT 8230 with electron ionization at 70 eV.

General Procedures and Materials

All manipulations were conducted using standard high vacuum or inert atmosphere techniques as described by *Shriver*.¹ Solvents were reagent grade, dried and purified according to standard procedures. Boron trichloride and diselenium dichloride (Sigma-Aldrich) were freshly vacuum-distilled before use. Diboron tetrachloride was prepared by co-condensation of BCl_3 with copper-vapor onto cooled walls ($-196\text{ }^\circ\text{C}$) of a reactor similar to that described by Timms.² After repeated fractionation, B_2Cl_4 exhibited a vapor pressure of 44 Torr at $0\text{ }^\circ\text{C}$.

Syntheses of *closo*- SeB_5Cl_5 (1a), *closo*-1- SeB_9Cl_9 (2) and *closo*- $\text{SeB}_{11}\text{Cl}_{11}$ (1b). In a typical reaction, 3.45 g (21.1 mmol) of B_2Cl_4 and 0.63 g (2.75 mmol) of Se_2Cl_2 were condensed *in vacuo* into a 1 l flask equipped with a seal-constriction and a break-seal joint and thereafter the flask was sealed. The mixture was heated in an oven at $350\text{ }^\circ\text{C}$ for 30 min and allowed to cool to room temperature over a period of 20 h resulting in a black shining mirror (Se) and an mustard-olive-green amorphous solid together with colorless and red (B_9Cl_9) crystals. All volatile compounds were vacuum-evaporated at $0\text{ }^\circ\text{C}$ into the vacuum-line and the remaining residue was thoroughly extracted 5 times with 15 mL of BCl_3 into a separate flask. The part

which was insoluble in BCl₃ was separated by a frit which was repeatedly extracted 5 times with each 15 ml BCl₃. After evaporation of the extractant BCl₃ at 0 °C, the residue was separated by *in vacuo* fractional sublimation to give approximately 50 mg of SeB₅Cl₅ (**1a**) (at a T_{subl} . 50 °C) and 30 mg of SeB₁₁Cl₁₁ (**1b**) (at a T_{subl} . 250 °C), and approximately 10 mg of SeB₉Cl₉ (**2**) (at a T_{subl} . 200 °C), each fraction as white solid. each as white solids and afforded for isolation final crystallization steps by slowly cooling of sealed, evacuated samples from 200 °C (for **1a**) or 350 °C (for **1b**) to room temperature. Selenaborane **2** could only be enriched by extraction of the non-volatile fraction with BCl₃. Further purification was achieved by repeated vacuum-sublimation/crystallization processes, but the samples of **2** always contained conglomerating selenaborane **1b** (see Figure S8).

Data for **1a**: MS³ m/z (rel. int.): 310 (35, M⁺); 275 (2, [M-Cl]⁺); 229 (1, [M-BCl₂]⁺); 194 (100, [M-BCl₃]⁺); exact mass calcd for ⁸⁰Se¹¹B₅³⁵Cl₅ 309.80731; found 309.80974; ¹¹B NMR (ppm, CDCl₃) 23.2 (B6), 4.6 (B2-5) with cross-peak in ¹¹B¹¹B COSY NMR. ⁷⁷Se NMR (ppm, CDCl₃) -146.2 ppm.

Data for **1b**: MS³ m/z (rel. int.): 588 (100, M⁺); 553 (2, [M-Cl]⁺); 506 (4, [M-BCl₂]⁺); 471 (31, [M-BCl₃]⁺); exact mass calcd for ⁸⁰Se¹¹B₁₁³⁵Cl₁₁ 585.67625; found 585.68137; ¹¹B NMR (ppm, CDCl₃) 17.3(B12), 3.9 (B2-6), -3.3 (B7-11) with cross-peaks to B2-6 and B12 in ¹¹B¹¹B COSY NMR. ⁷⁷Se NMR (ppm, CDCl₃) -31 ppm.

Data for **2**: MS m/z (rel. int.): 495 (100, M⁺); 377 (60, [M-BCl₃]⁺); exact mass calcd for ⁸⁰Se¹¹B₉³⁵Cl₉ 493.72316; found 493.72241; ¹¹B NMR (ppm, CDCl₃) 53.0 (B10), 16.8 (B2-5), 1.7 (B6-9) with cross-peaks to B2-5 and B10 in ¹¹B¹¹B COSY NMR.

Computational Details

Magnetic shielding was calculated using the GIAO-PBE1PBE method incorporated into Gaussian09⁴ utilizing the 6-311+G** basis with the B3LYP/6-311+G** geometries that were found to be minima on the respective potential energy surfaces, i.e NIMAGs =0. The GIAO-

PBE1PBE method was also applied to the computations of J - and K -coupling constants, the former referring to the total isotope-dependent spin-spin coupling term. The IAO/IBO method⁵ was used to connect quantitative SCF wave functions to a qualitative chemical picture, the nature of the orbitals naturally emerges. The IBOview program was used.⁵ The corresponding input files for the latter were generated at the B3LYP/def2-TZVP level using the Turbomole7.3⁶ program package. The molecular ESP surfaces were computed at the HF/def2-TZVP level using the Gaussian09 and Molekel4.3^{7,8} programs. Interaction energies were computed at the DFT-D3/TPSS/TZVPP level with the Turbomole (7.3) software and Cuby4.⁹ Two-body interaction energy (ΔE^2) was computed as the energy difference between the energy of the dimer and the sum of monomer energies. The many-body interaction energy (ΔE^{MB}) was computed as the difference between the sum of ΔE^2 values and the interaction energy between the central molecule and the whole first layer. Interaction energy was decomposed using symmetry-adapted perturbation-theory (SAPT) methodology. The simplest truncation of SAPT (SAPT0) decomposition¹⁰ was performed with the recommended jun-cc-pVDZ basis set¹¹ using PSI4¹² program.

Crystallographic Details

Crystal data and details of the structure determinations are compiled in Table 1. Full shells of intensity data were collected at low temperature with an Agilent Technologies Supernova-E CCD diffractometer (Mo- K_{α} radiation, microfocus X-ray tube, multilayer mirror optics). Detector frames (typically w -, occasionally j -scans, scan width 0.5°) were integrated by profile fitting.^{13,14} Data were corrected for air and detector absorption, Lorentz and polarization effects¹⁴ and scaled essentially by application of appropriate spherical harmonic functions.¹⁴⁻¹⁶ Absorption by the crystal was treated numerically (Gaussian grid).^{14,15,17} An illumination correction was performed as part of the numerical absorption correction.¹⁵ The structures were solved by the charge flip procedure²⁸ and refined by full-matrix least squares methods based on F^2 against all unique reflections.¹⁹ All atoms were given anisotropic displacement parameters. Further details of the crystal structure investigation may be obtained from FIZ Karlsruhe on quoting the deposition number CSD 2251721

CCDC 2251721 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre's and FIZ Karlsruhe's joint Access Service via <https://www.ccdc.cam.ac.uk/structures/>

Table S1. Crystal data and refinement details for **1b**

Revision date	15.05.2017 11:59:35 CEST UTC+02:00 encif	
1.71		
Identification code	ex_wk1	
Comment(s)	W. Keller SeB11	
Empirical formula	B11 Cl11 Se	
Formula weight	587.82	
Temperature	120(1) K	
Wavelength	Mo K α , 0.71073 Å	
Crystal system	monoclinic	
Space group	P 1 21 1 (<i>IT</i> Nr. 4)	
Space group (Hall symbol)	P 2yb	
Unit cell dimensions	$a = 8.85030(9)$ Å	$\alpha = 90^\circ$
	$b = 26.9786(2)$ Å	$\beta = 118.7986(14)^\circ$
	$c = 9.14388(9)$ Å	$\gamma = 90^\circ$
Volume	1913.24(4) Å ³	
<i>Z</i>	4	
Density (calculated)	2.041 Mg·m ⁻³	
Absorption coefficient	3.479 mm ⁻¹	
<i>F</i> ₀₀₀	1104	
Crystal size	0.398 · 0.391 · 0.240 mm ³ (irregular)	
θ range for data collection	2.542 to 32.365 °	
Reflections collected	121819	
Independent reflections [<i>R</i> _{int}]	13175 [0.0359]	
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	12843	
Index ranges ^s <i>h</i> , <i>k</i> , <i>l</i>	-13 ... 13, -40 ... 40, -13 ... 13	
Completeness to $\theta = 25.242^\circ$	100.0 %	
Absorption correction	Gaussian	
Transmission factors: max, min	1.000, 0.205	
Structure solution	iterative (SUPERFLIP (Palatinus, 2007-2009))	
Refinement method	Full-matrix least-squares on <i>F</i> ² (ShelXL (Sheldrick, 2015) Vers. 2016/6)	
Data / restraints / parameters	13175 / 1 / 415	
Goodness-of-fit on <i>F</i> ²	1.085	
Final <i>R</i> indices [<i>F</i> _o > 4 σ (<i>F</i> _o)] <i>R</i> (<i>F</i>), <i>wR</i> (<i>F</i> ²)	0.0190, 0.0384	
Final <i>R</i> indices (all data) <i>R</i> (<i>F</i>), <i>wR</i> (<i>F</i> ²)	0.0203, 0.0387	
Absolute structure parameter	0.0035(14)	
Difference density: rms, max, min	0.061, 0.448, -0.353 e·Å ⁻³	
Diffractionmeter	Agilent SuperNova, Dual, Cu at zero, Eos	
X-ray source	microfocus X-Ray tube	
Hydrogen atoms	undef	

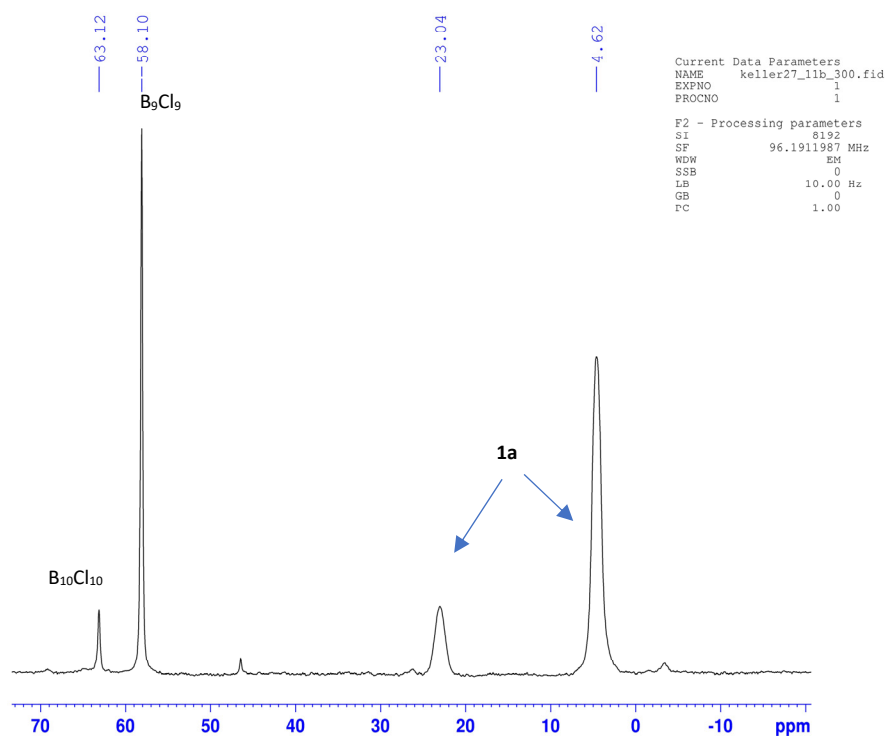


Figure S1: 96.19 MHz ^{11}B NMR spectrum of the first sublimable fraction (volatiles 0 °C – 180 °C HV) from the pyrolyzate with mainly *closo*- SeB_5Cl_5 (**1a**) and the boron subhalides B_9Cl_9 and $\text{B}_{10}\text{Cl}_{10}$ in CDCl_3 .

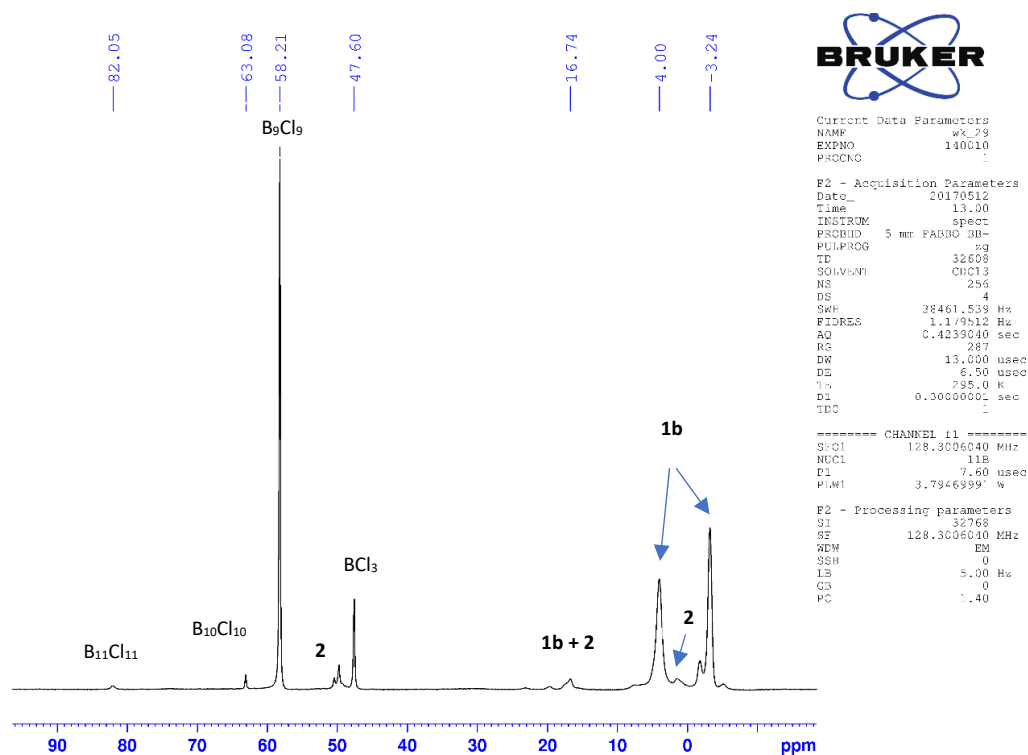


Figure S2: 128.3 MHz ^{11}B NMR spectrum of the second sublimable fraction (volatiles 180 °C – 350 °C HV) from the pyrolyzate with mainly *closo*- $\text{SeB}_{11}\text{Cl}_{11}$ (**1b**), *closo*- SeB_9Cl_9 (**2**) and the boron subhalides B_9Cl_9 , $\text{B}_{10}\text{Cl}_{10}$ and traces of $\text{B}_{11}\text{Cl}_{11}$ in CDCl_3 .

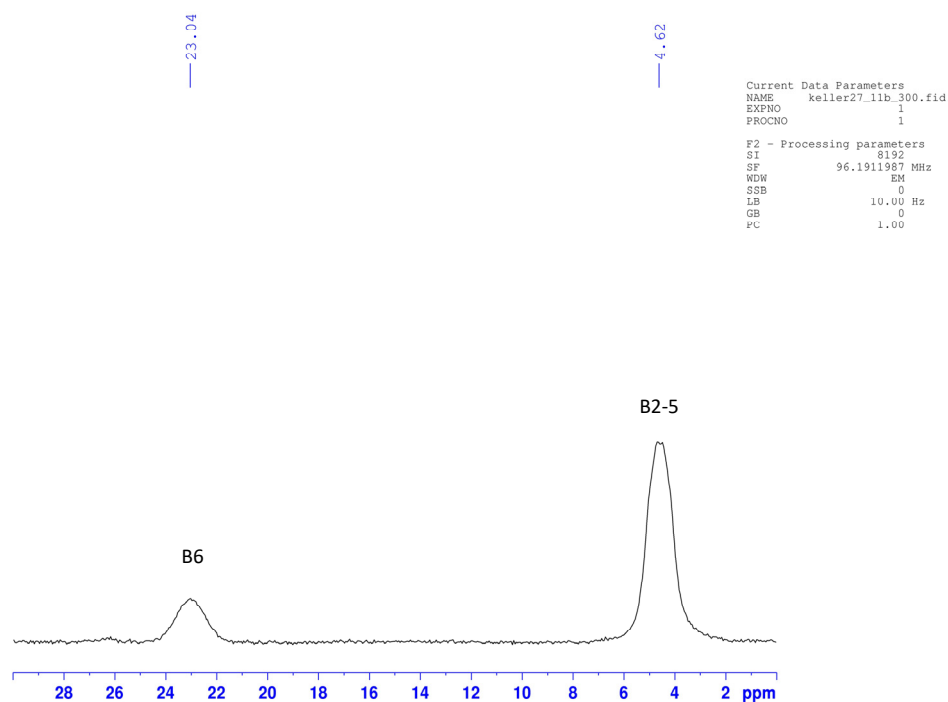


Figure S3: 96.19 MHz ^{11}B NMR spectrum of *closo*- SeB_5Cl_5 (**1a**) in CDCl_3 .

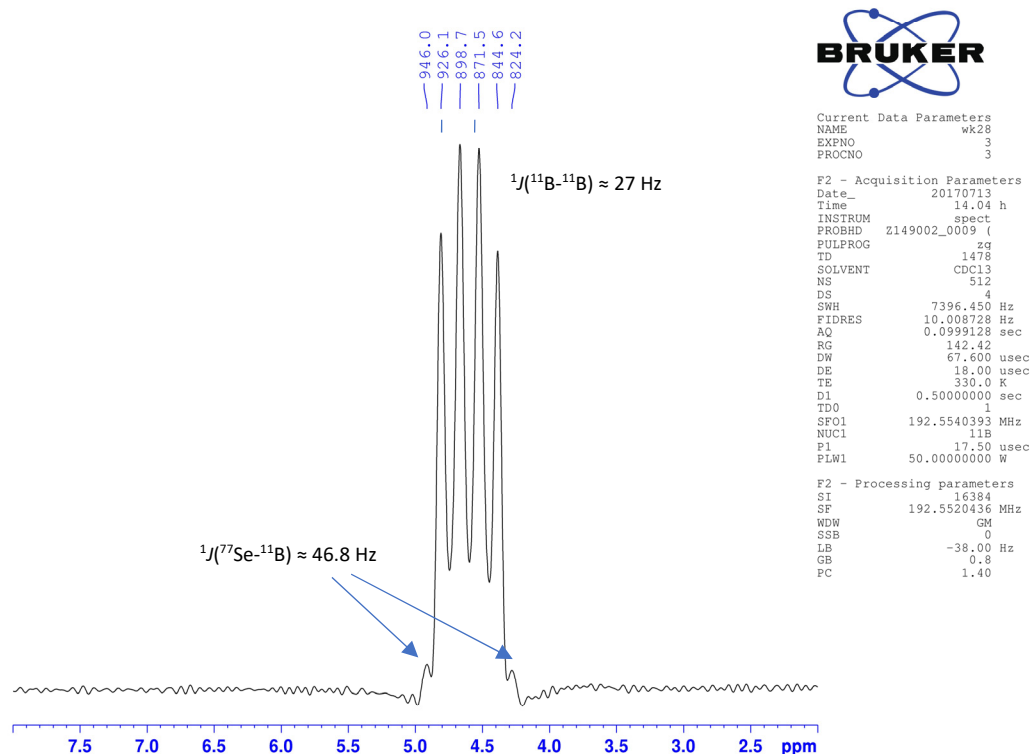


Figure S4. Cutout of the signal of B2-B5 (coupled to Se1 and B6) of *closo*- SeB_5Cl_5 (**1a**), ^{11}B NMR 192.6 MHz in CDCl_3 . Gauss multiplication ($\text{LB} = -38\text{Hz}$, $\text{GB} = 0.8$) was applied in order to resolve the coupling $^1J(^{11}\text{B}-^{11}\text{B}) = 27 \text{ Hz}$ and the coupling $^1J(^{11}\text{B}-^{77}\text{Se}) = 46.8 \text{ Hz}$.

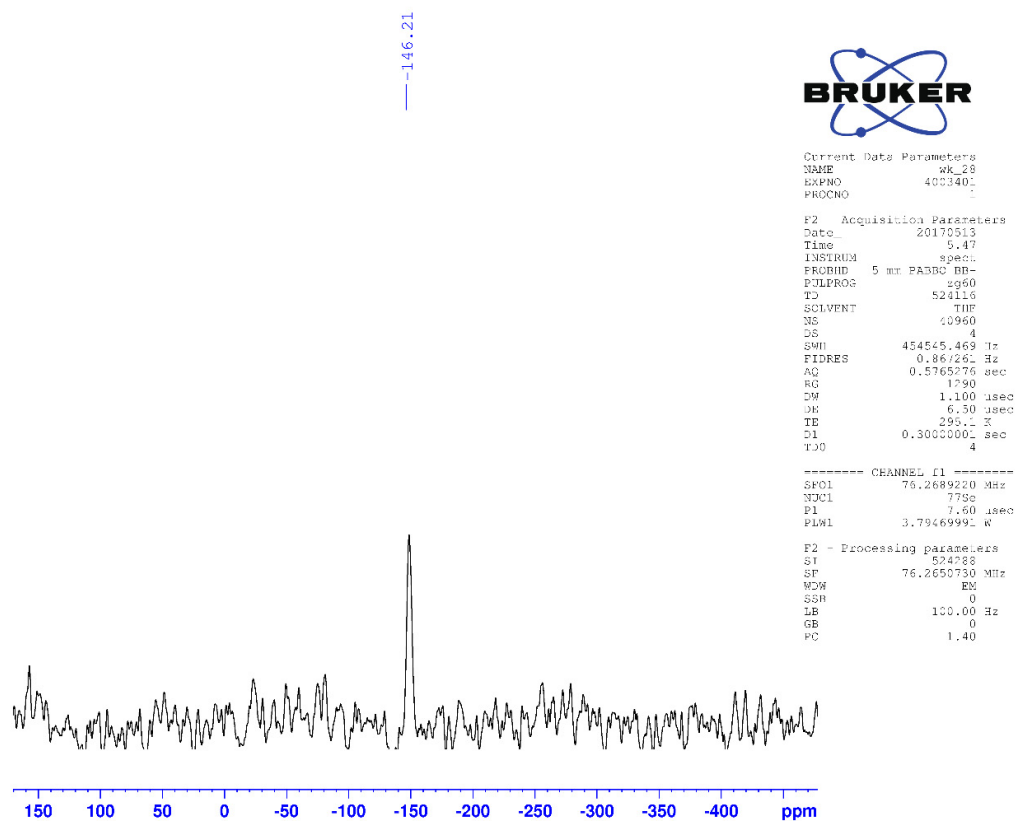


Figure S5. 76.27 MHz ^{77}Se NMR spectrum of *closo*- SeB_5Cl_5 (**1a**) in CDCl_3 .

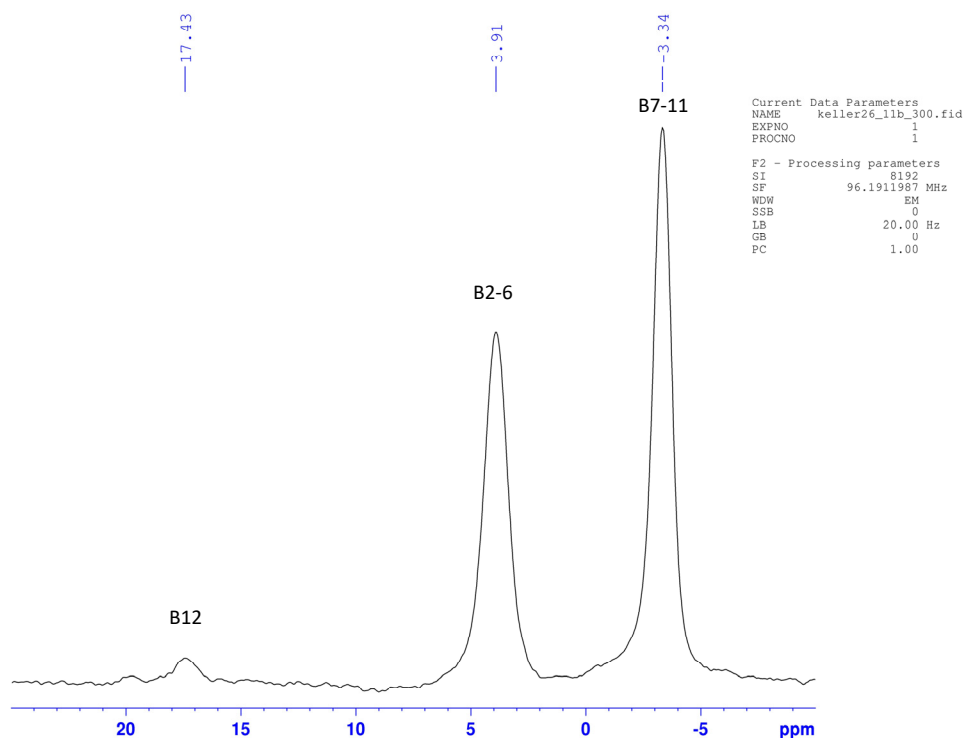


Figure S6. 96.19 MHz ^{11}B NMR spectrum of *closo*- $\text{SeB}_{11}\text{Cl}_{11}$ (**1b**) in CDCl_3 .

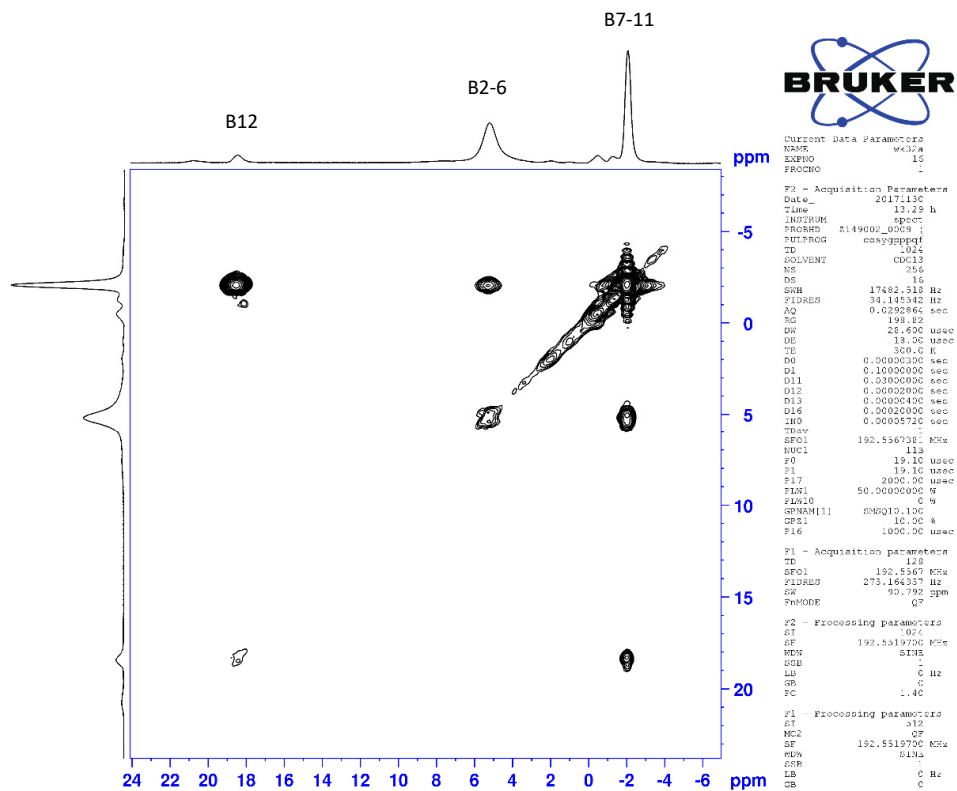


Figure S7. 192.55 MHz $^{11}\text{B}^{11}\text{B}$ COSY NMR spectrum of *closo*-SeB₁₁Cl₁₁ (**1b**) in C₂D₂Cl₄.

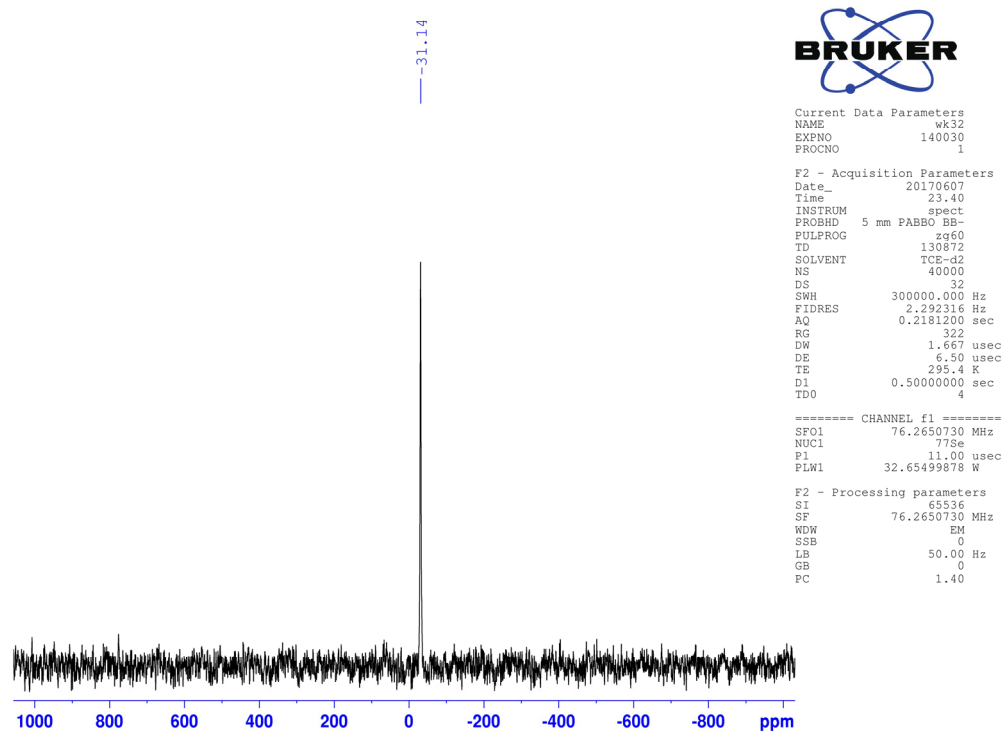


Figure S8. 76.27 MHz ^{77}Se NMR spectrum of *closo*-SeB₁₁Cl₁₁ (**1b**) in C₂D₂Cl₄.

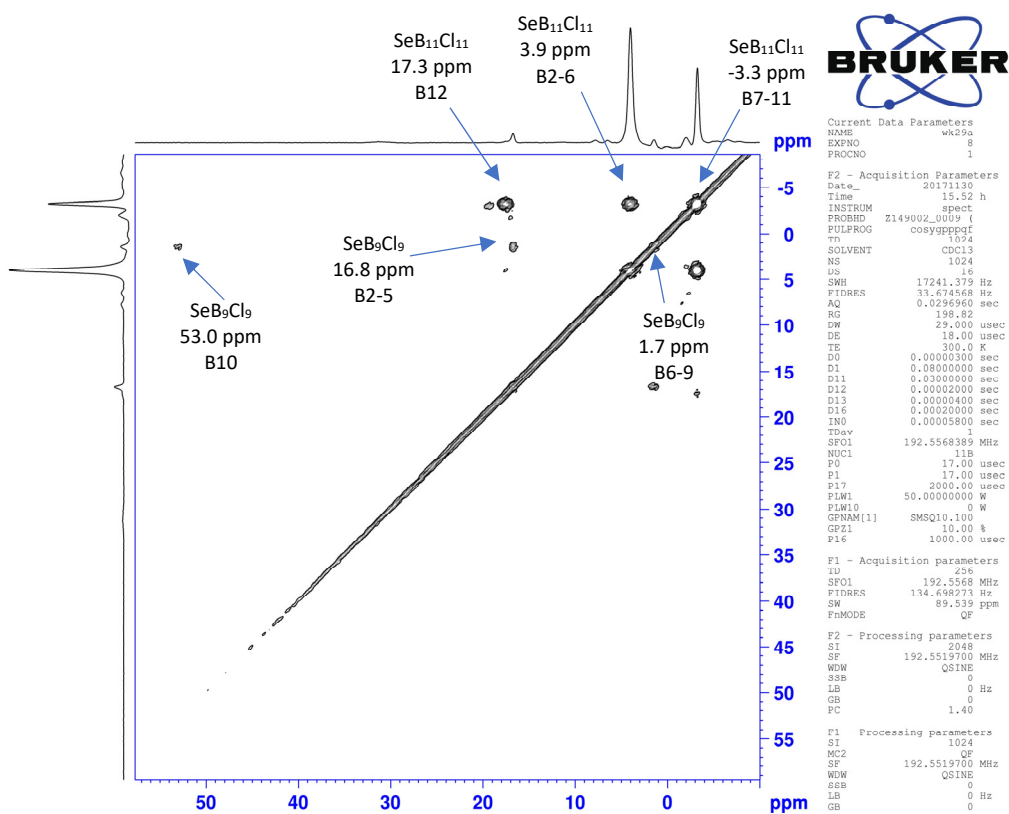


Figure S9. 192.55 MHz $^{11}\text{B}^{11}\text{B}$ COSY NMR spectrum of a mixture containing the selenaboranes *closo*-1- SeB_9Cl_9 (**2**) and conglomerate *closo*- $\text{SeB}_{11}\text{Cl}_{11}$ (**1b**) in CDCl_3 .

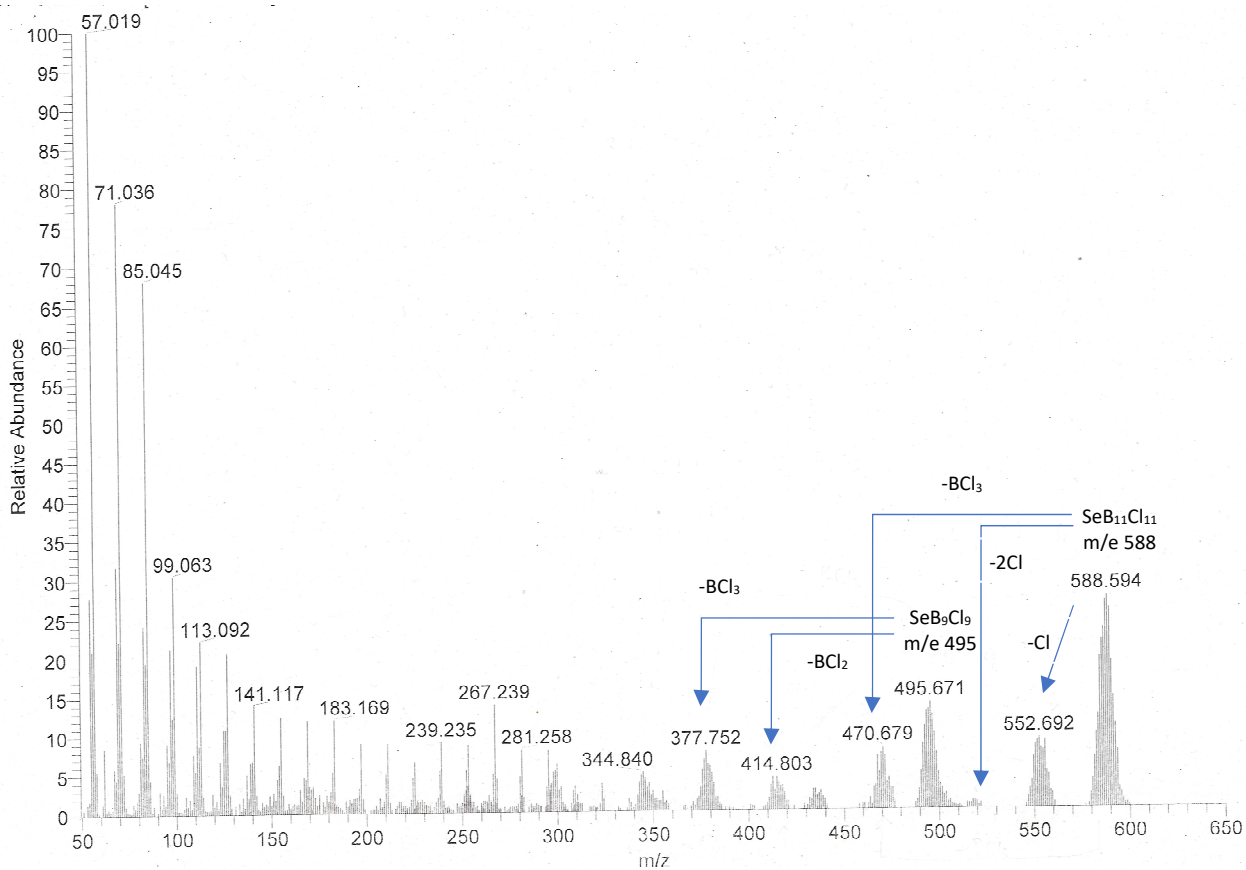


Figure S10: Full EI- mass spectrum of a sample containing SeB_9Cl_9 (**2**) and $\text{SeB}_{11}\text{Cl}_{11}$ (**1b**).

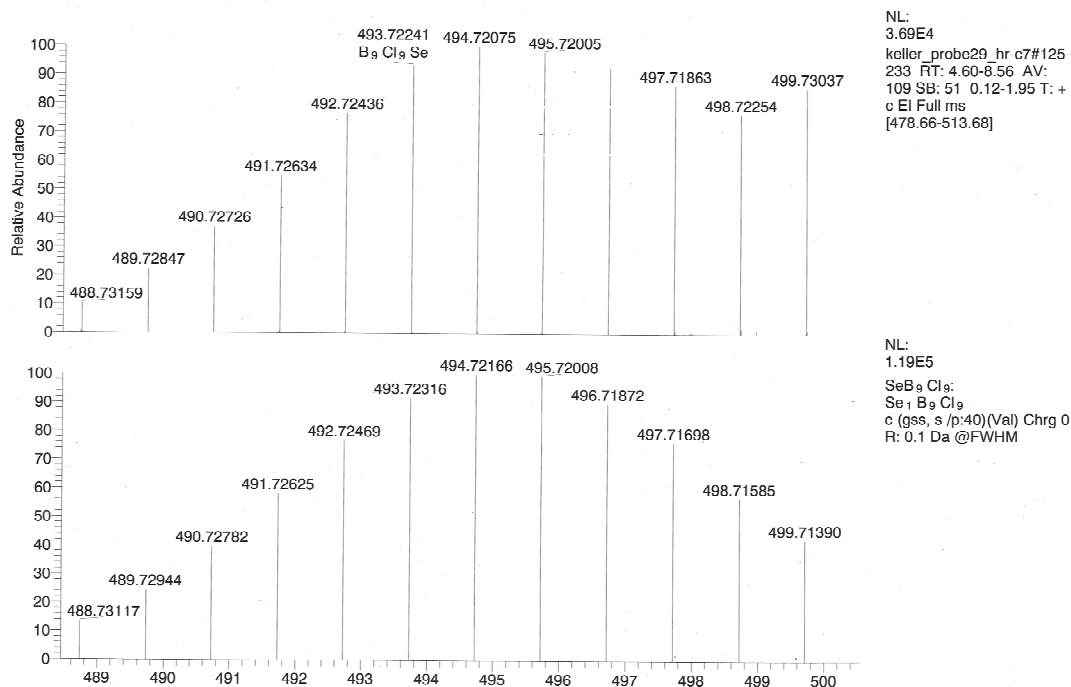


Figure S11: High resolution EI-MS of *closo*-1- SeB_9Cl_9 (**2**).



Fig. S12: Sealed pyrolysis double-flask after reaction before work-up.

References

- 1 D. F. Shriver and M. A. Drezdon in *The Manipulation of Air-Sensitive Compounds*, 2nd ed., John Wiley & Sons, New York, 1986.
- 2 P. L. Timms, *Adv. Inorg. Chem. Radiochem.*, 1972, **14**, 121.
- 3 W. Keller and M. Hofmann, *Z. Anorg. Allg. Chem.*, 2017, **643**, 729.
- 4 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09*, revision D.01, Gaussian, Inc., Wallingford CT, **2009**.
- 5 G. Knizia, *J. Chem. Theory Comput.*, 2013, **9**, 4834.

- 6 *TURBOMOLE*, Version 7.3, 2018, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2017, TURBOMOLE GmbH, 2007.
- 7 P. Flükiger, H. P. Lüthi, S. Portmann and J. Weber, MOLEKEL 4.3, Swiss Center for Scientific Computing: Manno, Switzerland, 2000.
- 8 S. Portmann and H. P. Lüthi, MOLEKEL: An Interactive Molecular Graphic Tool, *Chimia*, 2000, **54**, 766.
- 9 J. Řezáč, *J. Comput. Chem.*, 2016, **37**, 1230.
- 10 T. M. Parker, L. A. Burns, R. M. Parrish, A. G. Ryno and C. D. Sherrill, *J. Chem. Phys.* 2014, **140**, 094106.
- 11 B. Jeziorski, R. Moszynski and K. Szalewicz, *Chem. Rev.*, 1994, **94**, 1887.
- 12 J. M. Turney, A. C. Simmonett, R. M. Parrish, E. G. Hohenstein, F. Evangelista, J. T. Fermann, B. J. Mintz, L. A. Burns, J. J. Wilke, M. L. Abrams et al., *WIREs Comput. Mol. Sci.*, 2012, **2**, 556.
- 13 K. Kabsch, in: M. G. Rossmann, ed. E. Arnold, *International Tables for Crystallography*, Vol. F, Ch. 11.3, Kluwer Academic Publishers, Dordrecht, 2001.
- 14 CrysAlisPro, Agilent Technologies UK Ltd., Oxford, UK 2011–2014 and Rigaku Oxford Diffraction, Rigaku Polska Sp.z o.o., Wrocław, Poland, 2015–2018.
- 15 SCALE3 ABSPACK, CrysAlisPro, Agilent Technologies UK Ltd., Oxford, UK 2011–2014 and Rigaku Oxford Diffraction, Rigaku Polska Sp.z o.o., Wrocław, Poland 2015–2018.
- 16 R. H. Blessing, *Acta Cryst.*, 1995, **A51**, 33.
- 17 W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.
- 18 (a) L. Palatinus, SUPERFLIP, EPF Lausanne, Switzerland and Fyzikální ústav AV ČR, v. v. i., Prague, Czech Republic, 2007–2014; (b) L. Palatinus and G. Chapuis, *J. Appl. Cryst.*, 2007, **40**, 786.
- 19 (a) G. M. Sheldrick, SHELXL–20xx, University of Göttingen and Bruker AXS GmbH, Karlsruhe, Germany 2012–2018; (b) G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112; (c) G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3.