### SUPPLEMENTARY INFORMATION

Application of the aza-Wittig reaction for the synthesis of carboranyl Schiff bases, benzothiazoles and benzoselenazolines.

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1. Crystallography. Intensity data sets for compounds SB1, SB2, SB4, SB7, nido-SB3, amine-SB3 and nido-benzothiazole-SB4, were collected using a Bruker X8 Kappa APEXII diffractometer and for compounds SB3 and SB5 were collected using a Smart-CCD-1000 BRUKER diffractometer, both of them using Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Compound **IB3** was collected using a Rigaku XtaLAB Synergy-S diffractometer using Cu-K $\alpha$  radiation ( $\lambda$  = 1.54184 Å). The  $\omega$  and  $\phi$  scan technique was employed to measure the intensities. All compounds were measured at 100 K. Decomposition of the crystals did not occur during data collection. The intensities of all data sets were corrected for Lorentz and polarization effects. Absorption effects in all compounds were corrected using the program SADABS,<sup>[C1]</sup> except for **IB3**, in which they were corrected using the program SCALE3 ABSPACK. The crystal structures of all compounds were solved by direct methods using SHELXT.<sup>[C2]</sup> All structures were refined using SHELXL 2019/2.<sup>[C3]</sup> Scattering factors were those provided with the SHELX program system. Missing atoms were located in the difference Fourier map and included in subsequent refinement cycles. The structures were refined by full-matrix least-squares refinement on F<sup>2</sup>, using anisotropic displacement parameters for all non-hydrogen atoms. The positions of hydrogen atoms of NH, OH and C<sub>cluster</sub>H groups and the bridging hydrogen atoms of the C<sub>2</sub>B<sub>3</sub> open face of the nido derivatives were located in the difference Fourier maps. The positions of the rest hydrogen atoms were placed geometrically and refined using a riding model with Uiso constrained at 1.2 times U<sub>eq</sub> of the carrier C or B atom, except for methyl groups, whose hydrogen atoms were constrained at 1.5 times U<sub>eq</sub> of the carrier C atom. In the last cycles of refinement of all structures a weighting scheme was used, with weights calculated using the following formula w =  $1/[\sigma^2(F_0^2)+(aP)^2+bP]$ , where P=  $(F_0^2+2F_c^2)/3$ . ORTEP3 drawings<sup>[C4]</sup> were produced for all structures.

The crystal structure of **amine-SB3** presents a 50% disorder of the thioether group (-SMe) and the crystal structure of **nido-benzothiazole-SB4** presents a 50% disorder of some atoms of the  $C_2B_3$  open face (C-H,  $H_{bridge}$ ). In both cases the disorder was handled by introducing split positions for the disordered atoms in the refinement with the 50% occupancies. The crystal structures of **SB7**, **nido-benzothiazole-SB4** and **IB3** present no merohedral twinning and were refined as 2-component perfect twins.

CCDC reference numbers: 2393159-2393168.

[C1] G. M. Sheldrick, SADABS: Program for absorption correction using area detector data. University of Göttingen, Germany, 1996.

[C2] G. M. Sheldrick, SHELXT-Integrated Space-Group and Crystal-Structure Determination.ActaCrystallographicaSectionA,2015,A71,3-8.https://doi.org/10.1107/S2053273314026370

[C3] G. M. Sheldrick, Crystal Structure Refinement with SHELXL, *Acta Crystallographica C*, 2015, **C71**, 3-8. http://dx.doi.org/10.1107/S2053229614024218

[C4] (a) L. J. Farrugia, WinGX and ORTEP for Windows: an update, *J. Appl. Cryst.*, 2012, **45**, 849-854. https://doi.org/10.1107/S0021889812029111; (b) L. J. Farrugia, ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI), *J. Appl. Cryst.*, 1997, **30**, 565. https://doi.org/10.1107/S0021889897003117

	SB1	SB2	SB3	SB4	SB5
Empirical Formula	$C_{10}H_{19}B_{10}NO$	$C_9H_{17}B_{10}NO$	$C_{10}H_{19}B_{10}NS$	$C_{18}H_{32}B_{20}N_2S_2$	C <sub>10</sub> H <sub>19</sub> B <sub>10</sub> NSe
Formula weight	277.36	263.33	293.42	556.77	340.32
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystalline system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> /n	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	Pbca	P2 <sub>1</sub> /n
Cell Constants (Å, °)	a = 8.7742(9)	a = 10.2765(6)	a = 10.231(2)	a = 12.0591(9)	a = 6.7117(13)
	b = 22.4893(19)	b = 21.3974(16)	b = 11.712(3)	b = 10.8146(9)	b = 17.891(3)
	c = 7.9927(8)	c = 13.8904(10)	c = 13.304(3)	c = 45.473(3)	c = 13.374(3)
	α = 90	α = 90	α = 90	α = 90	α = 90
	$\beta$ = 103.148(3)	β = 108.800(3)	β <b>= 90</b>	β <b>= 90</b>	β = 92.059(3)
	γ <b>=</b> 90	γ = 90	γ = 90	γ = 90	γ <b>= 90</b>
Volume (ų)	1535.8(3)	2891.4(3)	1594.1(6)	5930.3(8)	1604.9(5)
Z	4	8	4	8	4
Absorption coefficient (mm <sup>-1</sup> )	0.064	0.064	0.187	0.197	2.324
F(000)	576	1088	608	2288	680
Theta range for data collection (°)	1.811-26.402	1.818-25.350	2.317-26.018	1.912-24.404	1.902-25.679
Size (mm)	0.35 x 0.31 x 0.20	0.50 x 0.25 x 0.20	0.33 x 0.28 x 0.23	0.70 x 0.32 x 0.02	0.35 x 0.30 x 0.20
Collected reflections	15737	34944	11314	27179	13829
Independent reflections	3105 [R(int) = 0.0714]	5277 [R(int) = 0.0719]	3137 [R(int) = 0.0300]	4877 [R(int) = 0.1474]	3052 [R(int) = 0.0349]
Data/ restraints/ parameters	3105 / 0 / 204	5277 / 0 / 395	3137 / 0 / 204	4877 / 0 / 387	3052 / 0 / 204
Goodness-on-fit (F <sup>2</sup> )	1.052	1.039	1.062	1.034	1.047
Final R indices [I>2s(I)] <sup>[a]</sup>	$R_1 = 0.0640$	$R_1 = 0.0560$	$R_1 = 0.0349$	$R_1 = 0.0695$	$R_1 = 0.0262$
	$wR_2 = 0.1505$	$wR_2 = 0.1273$	$wR_2 = 0.0887$	$wR_2 = 0.1413$	$wR_2 = 0.0621$
R indices (all data)	$R_1 = 0.1093$	R <sub>1</sub> = 0.0822	R <sub>1</sub> = 0.0397	R <sub>1</sub> = 0.1227	$R_1 = 0.0348$
	$wR_2 = 0.1686$	$wR_2 = 0.1398$	wR <sub>2</sub> = 0.0924	$wR_2 = 0.1673$	$wR_2 = 0.0661$
Largest diff. peak and hole (e <sup>.</sup> Å <sup>-3</sup> )	0.303 and -0.367	0.365 and -0.313	0.253 and -0.234	0.601 and -0.349	0.320 and -0.306

2. Table S1. Summary of crystal and refinement data for the crystal structures.

<sup>[a]</sup>  $R_1 = \sum [|F_o| - |F_c| / \Sigma |F_o]; wR_2 = [|\Sigma (F_o^2 - F_c^2) / \Sigma (F_o^2)]^{1/2}$ 

	2(SB7) <sup>.</sup> hexane	nido-SB3	Amine-SB3	(nido-BT-SB4) <sup>.</sup> MeOH	IB3
Empirical Formula	$C_{38}H_{62}B_{20}N_4O_4S_2$	$C_{10}H_{20}B_9NS$	$C_{10}H_{21}B_{10}NS$	C <sub>10</sub> H <sub>20</sub> B <sub>9</sub> NOS	C <sub>20</sub> H <sub>26</sub> B <sub>10</sub> NP
Formula weight	919.23	283.62	295.44	299.62	419.49
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	1.54184
Crystalline system	Triclinic	Monoclinic	Orthorhombic	Triclinic	Triclinic
Space group	P-1	P2 <sub>1</sub> /c	Pbca	P-1	P-1
Cell Constants (Å, °)	a = 10.2795(9)	a = 9.9493(5)	a = 11.1107(11)	a = 7.0558(8)	a = 15.1375(1)
	b = 15.2051(13)	b = 11.5647(6)	b = 11.3129(11)	b = 10.3528(11)	b = 16.6265(1)
	c = 17.1951(14)	c = 13.7718(7)	c = 26.083(2)	c = 11.3035(18)	c = 16.7014(1))
	$\alpha$ = 90.720(4)	α = 90	α = 90	α = 69.599(3)	$\alpha$ = 79.222(1)
	$\beta = 100.394(4)$	β <b>= 93.242(2)</b>	β = 90	β <b>= 87.608(5)</b>	β <b>= 67.177(1)</b>
	γ = 105.753(4)	γ <b>= 90</b>	γ <b>= 90</b>	γ = 88.140(3)	γ = 63.665(1)
Volume (ų)	2538.8(4)	1582.06(14)	3278.4(5)	773.08(17)	3471.70(5)
Z	2	4	8	2	6
Absorption coefficient (mm <sup>-1</sup> )	0.148	0.187	0.182	0.199	1.086
F(000)	964	592	1232	312	1308
Theta range for data collection (°)	1.207-26.384	2.050-26.391	2.408-26.019	1.923-26.416	2.871-70.230
Size (mm)	0.62 x 0.32 x 0.08	0.37 x 0.34 x 0.04	0.43 x 0.25 x 0.14	0.42 x 0.20 x 0.04	0.11 x 0.09 x 0.06
Collected reflections	50828	11860	16962	31780	164572
Independent reflections	16590 [R(int) = 0.0614]	3245 [R(int) = 0.0698]	3223 [R(int) = 0.0432]	27371 [R(int) = 0.0850]	23827 [R(int) = 0.0429]
Data/ restraints/ parameters	16590 / 0 / 633	3245 / 0 / 203	3223 / 4 / 227	27371/0/231	23827 / 0 / 889
Goodness-on-fit (F <sup>2</sup> )	1.018	1.033	1.030	0.994	1.327
Final R indices [I>2s(I)] <sup>[a]</sup>	$R_1 = 0.0716$	$R_1 = 0.0623$	$R_1 = 0.0554$	$R_1 = 0.0638$	$R_1 = 0.1031$
	$wR_2 = 0.1812$	$wR_2 = 0.1380$	$wR_2 = 0.1403$	$wR_2 = 0.1391$	wR <sub>2</sub> = 0.2696
R indices (all data)	$R_1 = 0.1007$	$R_1 = 0.1050$	$R_1 = 0.0745$	$R_1 = 0.1230$	$R_1 = 0.1050$
	wR <sub>2</sub> = 0.2029	$wR_2 = 0.1612$	$wR_2 = 0.1561$	$wR_2 = 0.1648$	wR <sub>2</sub> = 0.2735
Largest diff. peak and hole (e <sup>.</sup> Å <sup>-3</sup> )	1.212 and -0.571	0.445 and -0.524	0.416 and -0.488	0.508 and -0.390	1.331 and -0.484

 Table S1 (cont.).
 Summary of crystal and refinement data for the crystal structures.

<sup>[a]</sup>  $R_1 = \sum [|F_o| - |F_c| / \Sigma |F_o]; wR_2 = [|\Sigma (F_o^2 - F_c^2) / \Sigma (F_o^2)]^{1/2}$ 

	$C_{cage}$ - $C_{cage}$	C-B range	B-B range	C <sub>cage</sub> -C	C-N	N-C <sub>Ph</sub>	C <sub>Ph</sub> -X	Other
SB1	1.635(3)	1.693(4)-1.732(3)	1.763(4)-1.792(4)	1.489(3)	1.268(3)	1.422(3)	0: 1.373(3)	O-Me: 1.426(3)
SB2	1.626(3)	1.693(3)-1.731(3)	1.762(4)-1.795(3)	1.485(3)	1.259(3)	1.419(3)	0: 1.372(2)	
	1.622(3)	1.692(3)-1.735(3)	1.760(3)-1.791(3)	1.490(3)	1.266(3)	1.420(3)	0: 1.371(2)	
SB3	1.637(2)	1.691(3)-1.730(3)	1.760(3)-1.793(3)	1.492(3)	1.259(3)	1.418(2)	S: 1.7630(17)	S-Me: 1.786(2)
SB4	1.629(6)	1.686(7)-1.731(7)	1.745(7)-1.795(7)	1.493(6)	1.248(5)	1.419(5)	S: 1.785(4)	S-S: 2.0331(16)
	1.625(6)	1.698(7)-1.732(6)	1.757(7)-1.797(7)	1.491(6)	1.272(5)	1.421(6)	S: 1.782(5)	
SB5	1.623(3)	1.692(3)-1.734(3)	1.764(3)-1.786(4)	1.494(3)	1.251(3)	1.417(3)	Se: 1.910(2)	Se-Me: 1.941(2)
SB7	1.630(4)	1.690(5)-1.735(4)	1.758(5)-1.793(6)	1.488(4)	1.259(4)	1.426(4)	N: 1.437(4)	N-S: 1.633(3)
	1.624(4)	1.691(5)-1.733(5)	1.760(5)-1.802(5)	1.494(4)	1.263(4)	1.420(4)	N: 1.429(4)	S=O: 1.439(2)
								S=O: 1.433(2)
								S-C <sub>Ph</sub> : 1.767(3)
nido-SB3	1.568(4)	1.620(5)-1.748(5)	1.748(5)-1.836(5)	1.437(4)	1.286(4)	1.428(4)	S: 1.771(3	S-Me: 1.803(3)
Amine-SB3	1.633(3)	1.691(4)-1.730(3)	1.746(4)-1.783(4)	1.541(3)	1.444(3)	1.375(3)	S: 1.774(3)	S-Me: 1.851(5)
(nido-BT-SB4)	1.568(10)	1.588(11)-1.745(11)	1.756(7)-1.816(7)	1.313(5)	1.313(5)	1.394(5)	S: 1.739(4)	S-Me: 1.710(4)

3. Table S2. Selected bond lengths (Å) for SB1-SB5, SB7, nido-SB3, Amine-SB3 and (nido-BT-SB4).

	$C_{cage}$ - $C_{cage}$ - $C$	C <sub>cage</sub> -C-N	C-N-C <sub>Ph</sub>	Tors[C <sub>cage</sub> -C <sub>cage</sub> -C-N]	$Tors[C_{cage}\text{-}C\text{-}N\text{-}C_{Ph}]$
SB1	116.34(18)	119.9(2)	119.8(2)	19.4(3)	176.26(19)
SB2	117.83(17)	120.89(19)	121.72(18)	17.8(3)	178.41(17)
	117.57(17)	120.44(18)	120.56(18)	4.8(3)	177.08(17)
SB3	117.09(15)	120.78(17)	119.61(16)	14.3(4)	178.2(2)
SB4	116.8(4)	119.6(4)	122.6(4)	0.3(6)	179.4(4)
	117.2(4)	119.4(4)	120.4(4)	0.2(6)	174.6(4)
SB5	116.32(17)	119.59(19)	122.84(19)	7.6(3)	176.35(18)
SB7	116.9(2)	119.2(3)	122.7(3)	3.5(5)	176.5(3)
	117.4(2)	119.7(3)	121.9(3)	6.7(5)	176.6(3)
nido-SB3	117.5(3)	122.3(3)	128.3(3)	166.0(3)	178.9(3)
Amine-SB3	120.02(16)	114.67(18)	125.3(2)	36.6(3)	93.6(3)
(nido-BT-SB4)	118.4(5)	124.4(4)	115.2(4)	36.1(7)	178.2(4)

4. Table S3. Selected angles (<sup>o</sup>) for SB1-SB5, SB7, nido-SB3, Amine-SB3 and (nido-BT-SB4).



**5. Figure S1**. Molecular structure of iminophosphorane **IB3**, Thermal ellipsoids are shown at the 40% probability level.

**6. Table S4.** Selected bond lengths (Å) and angles (<sup>o</sup>) for **IB3** (three molecules per asymmetric unit).

Molecule (1)						
C(1)-C(2)	1.606(3)	C(1)-B(3)-N(1)	122.3(2)			
C-B Range	1.669(3)-1.830(3)	C(2)-B(3)-N(1)	126.5(2)			
B-B Range	1.761(3)-1.816(3)	B(3)-N(1)-P(1)	139.90(17)			
N(1)-B(3)	1.385(3)	N(1)-P(1)-C(3)	113.28(11)			
P(1)-N(1)	1.5543(18)	N(1)-P(1)-C(9)	109.20(10)			
P(1)-C(3)	1.811(2)	N(1)-P(1)-C(15)	114.59(10)			
P(1)-C(9)	1.808(2)					
P(1)-C(15)	1.805(2)					
	Molecule (2)	_				
C(101)-C(102)	1.620(3)	C(101)-B(103)-N(2)	122.8(2)			
C-B Range	1.703(3)-1.833(4)	C(102)-B(103)-N(2)	124.83(19)			
B-B Range	1.752(4)-1.807(3)	B(103)-N(2)-P(2)	135.55(16)			
N(2)-B(103)	1.383(3)	N(2)-P(2)-C(103)	114.24(10)			
P(2)-N(2)	1.5608(18)	N(2)-P(2)-C(109)	108.13(9)			
P(2)-C(103)	1.805(2)	N(2)-P(2)-C(115)	113.52(10)			
P(2)-C(109)	1.804(2)					
P(2)-C(115)	1.803(2)					
Molecule (3)						
C(201)-C(202)	01)-C(202) 1.605(3)		123.71(19)			
C-B Range	1.685(3)-1.832(3)	C(202)-B(203)-N(3)	125.91(19)			
B-B Range	1.768(4)-1.822(3)	B(203)-N(3)-P(3)	141.13(17)			
N(3)-B(203)	1.383(3)	N(3)-P(3)-C(203)	111.81(10)			
P(3)-N(3)	1.5532(18)	N(3)-P(3)-C(209)	110.35(10)			
P(3)-C(203)	1.818(2)	N(3)-P(3)-C(215)	115.13(10)			
P(3)-C(209)	1.809(2)					
P(3)-C(215)	1.805(2)					

# 7. <sup>1</sup>H NMR spectra.







**Figure S4**. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of **I7**.



Figure S5. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of iminophosporane IB3.







Figure S7. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of SB2.























Figure S13. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of SB8.



Figure S14. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of *nido*-SB3.



Figure S15. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of amine-SB3.



Figure S16. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of benzothiazole-SB4.



Figure S17. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of benzoselenazoline-SB6.

8. <sup>31</sup>P{<sup>1</sup>H} NMR spectra.



Figure S18.  ${}^{31}P{}^{1}H$  NMR spectrum (CDCl<sub>3</sub>) of I5.



Figure S19.  ${}^{31}P{}^{1}H$  NMR spectrum (CDCl<sub>3</sub>) of I6.



Figure S20.  ${}^{31}P{}^{1}H$  NMR spectrum (CDCl<sub>3</sub>) of I7.



**Figure S21**. <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (CDCl<sub>3</sub>) of **iminophosporane IB3**.

## 9. <sup>13</sup>C{<sup>1</sup>H} NMR spectra.





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Figure S25.  ${}^{13}C{}^{1}H$  NMR spectrum (CDCl<sub>3</sub>) of SB3.



Figure S26. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (CDCl<sub>3</sub>) of SB4.



Figure S27.  $^{13}\text{C}\{^{1}\text{H}\}$  NMR spectrum (CDCl<sub>3</sub>) of SB5.











Figure S30.  $^{13}\text{C}\{^{1}\text{H}\}$  NMR spectrum (CDCl<sub>3</sub>) of SB8.



Figure S31. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (CDCl<sub>3</sub>) of amine-SB3.



Figure S32. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (CDCl<sub>3</sub>) of benzothiazole-SB4.



Figure S33. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (CDCl<sub>3</sub>) of benzoselenazoline-SB6.

### 10. <sup>11</sup>B NMR spectra.









Figure S37.  $^{11}\text{B}\{^{1}\text{H}\}$  and  $^{11}\text{B}$  NMR spectra (CDCl3) of SB3.



Figure S38.  $^{11}B{^1H}$  and  $^{11}B$  NMR spectra (CDCl<sub>3</sub>) of SB4.



Figure S39.  $^{11}B{^1H}$  and  $^{11}B$  NMR spectra (CDCl<sub>3</sub>) of SB5.



Figure S40.  ${}^{11}B{}^{1}H{}$  and  ${}^{11}B$  NMR spectra (CDCl<sub>3</sub>) of SB6.



Figure S41.  ${}^{11}B{}^{1}H{}$  and  ${}^{11}B$  NMR spectra (CDCl<sub>3</sub>) of SB7.



Figure S42.  ${}^{11}B{}^{1}H{}$  and  ${}^{11}B$  NMR spectra (CDCl<sub>3</sub>) of SB8.







Figure S44. <sup>11</sup>B{<sup>1</sup>H} and <sup>11</sup>B NMR spectra (CDCl<sub>3</sub>) of amine-SB3.



Figure S45. <sup>11</sup>B{<sup>1</sup>H} and <sup>11</sup>B NMR spectra (CDCl<sub>3</sub>) of benzothiazole-SB4.



Figure S46. <sup>11</sup>B{<sup>1</sup>H} and <sup>11</sup>B NMR spectra (CDCl<sub>3</sub>) of benzoselenazoline-SB6.



Figure S47. <sup>11</sup>B{<sup>1</sup>H} and <sup>11</sup>B NMR spectra (CDCl<sub>3</sub>) of *nido*-(benzothiazole-SB4).