

## Electronic supplementary information

### Systematic examination of classical and multi-center bonding in heteroborane clusters

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**Table S1** The summarized IBO data for various *closo*-heteroboranes. For the sake of clarity, the multicenter B-B-H and B-B-B bonds are not included.

Compound	Bonding	
	Multicenter	Classical
<i>11</i> -vertex		
<i>closo</i> -2-CB <sub>10</sub> H <sub>11</sub> <sup>-</sup>	2 × B-C-B; 1 × B-C-B-B	--
<i>closo</i> -2,3-C <sub>2</sub> B <sub>9</sub> H <sub>11</sub>	4 × B-C-B	2 × B-C
<i>9</i> -vertex		
<i>closo</i> -4-CB <sub>8</sub> H <sub>9</sub> <sup>-</sup>	3 × B-C-B	--
<i>closo</i> -1,7-C <sub>2</sub> B <sub>7</sub> H <sub>9</sub>	6 × B-C-B	--
<i>7</i> -vertex		
<i>closo</i> -2-CB <sub>6</sub> H <sub>7</sub> <sup>-</sup>	2 × B-C-B; 1 × B-C-B-B	1 × B-C
<i>closo</i> -2,4-C <sub>2</sub> B <sub>5</sub> H <sub>7</sub>	6 × B-C-B	--

**Table S2.** Comparison of IBO with NBO results.

Compound	IBO		NBO	
	Multicenter	Classical	Multicenter	Classical
<i>closo</i> -1-SB <sub>11</sub> H <sub>11</sub>	1 × B-S-B; 1 × B-S-B-B	--	1 × B-S-B	1 × B-S
<i>closo</i> -1-NB <sub>11</sub> H <sub>12</sub>	2 × B-N-B	1 × B-N	2 × B-N-B	1 × B-N
<i>closo</i> -1,7-C <sub>2</sub> B <sub>10</sub> H <sub>12</sub>	6 × B-C-B	--	6 × B-C-B	--
<i>closo</i> -1,7-P <sub>2</sub> B <sub>10</sub> H <sub>10</sub>	3 × B-P-B; 3 × B-B-P-B	--	5 × B-P-B	--
<i>closo</i> -1,2-C <sub>2</sub> B <sub>10</sub> H <sub>12</sub>	4 × B-C-B	1 × C-C	--	4 × B-C, 1 × C-C
<i>closo</i> -1,2-P <sub>2</sub> B <sub>10</sub> H <sub>10</sub>	4 × B-P-B; 1 × B-P-P-B	--	4 × B-P-B; 1 × P-B-P	--
<i>closo</i> -1,2-C <sub>2</sub> B <sub>8</sub> H <sub>10</sub>	4 × B-C-B	1 × C-C	4 × B-C-B	1 × C-C
<i>closo</i> -1,6-C <sub>2</sub> B <sub>8</sub> H <sub>10</sub>	5 × B-C-B; 1 × B-C-B-B	--	5 × B-C-B	1 × C-B
<i>closo</i> -2,1-PCB <sub>8</sub> H <sub>9</sub>	2 × B-P-B; 2 × B-C-B	1 × C-P	1 × B-C-B	1 × P-C; 2 × B-C
<i>closo</i> -6,1-PCB <sub>8</sub> H <sub>9</sub>	3 × B-C-B; 2 × B-P-B; 1 × B-P-B-B	--	2 × B-P-B	3 × B-C
<i>closo</i> -1-SB <sub>9</sub> H <sub>9</sub>	2 × B-S-B	1 × B-S	2 × B-S-B	--
<i>closo</i> -1,5-C <sub>2</sub> B <sub>3</sub> H <sub>5</sub>	--	6 × B-C	--	6 × B-C
<i>closo</i> -2,3-C <sub>2</sub> B <sub>3</sub> H <sub>5</sub>	2 × B-C-B; 1 × B-C-C-B	2 × B-C; 2 × B-B	1 × B-C-B; 1 × C-B-C	2 × B-C, 1 × B-B
<i>closo</i> -1,2-C <sub>2</sub> B <sub>3</sub> H <sub>5</sub>	2 × B-C-B	1 × C-C; 2 × B-C	1 × B-C-B	3 × B-C; 1 × C-C
<i>nido</i> -7,8,10-C <sub>2</sub> SB <sub>8</sub> H <sub>10</sub>	1 × B-S-B	2 × B-S; 2 × B-C; 1 × C-C	2 × B-C-B	2 × C-B; 1 × C-C; 3 × S-B
<i>nido</i> -7,11,8,9-C <sub>2</sub> P <sub>2</sub> B <sub>7</sub> H <sub>9</sub>	2 × B-P-B; 2 × B-C-B	1 × P-P; 1 × C-C; 1 × C-P; 1 × B-C; 1 × P-B	1 × B-P-C; 1 × B-P-B; 1 × B-C-B	1 × P-P; 1 × C-C; 1 × C-P; 1 × B-C; 1 × P-B
<i>nido</i> -7,8,9,10-P <sub>3</sub> CB <sub>7</sub> H <sub>8</sub>	3 × B-P-B; 1 × B-C-B	2 × P-P; 1 × P-C; 1 × B-C; 1 × B-P	1 × B-C-B; 1 × B-P-B	2 × P-P; 1 × P-C; 1 × B-C; 1 × P-P