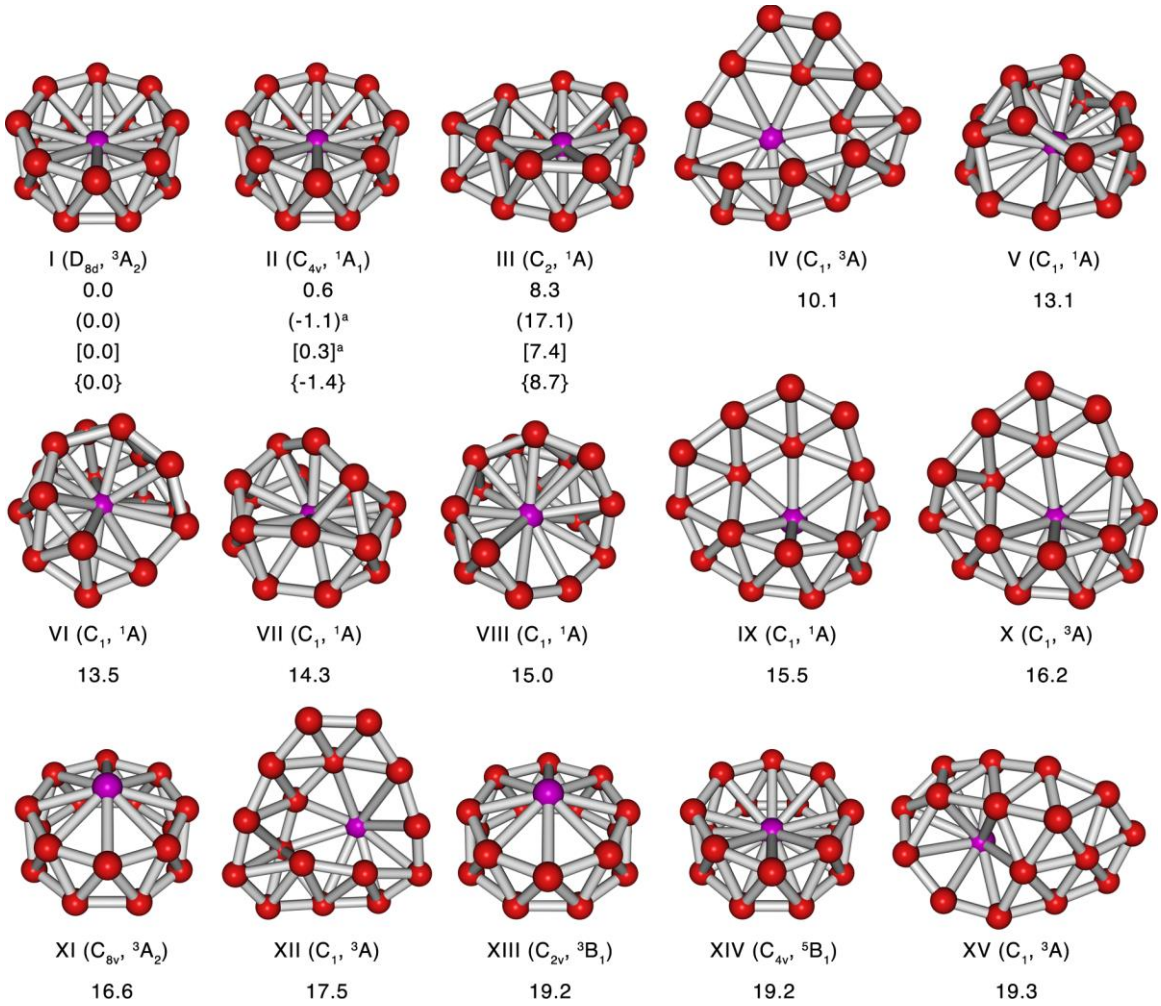
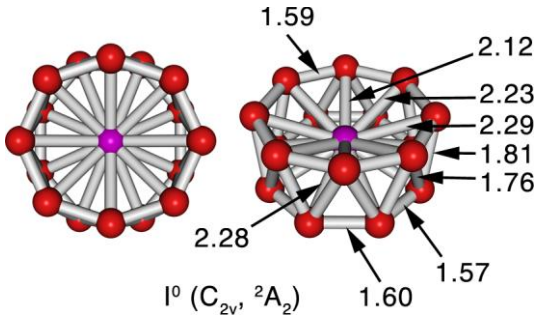
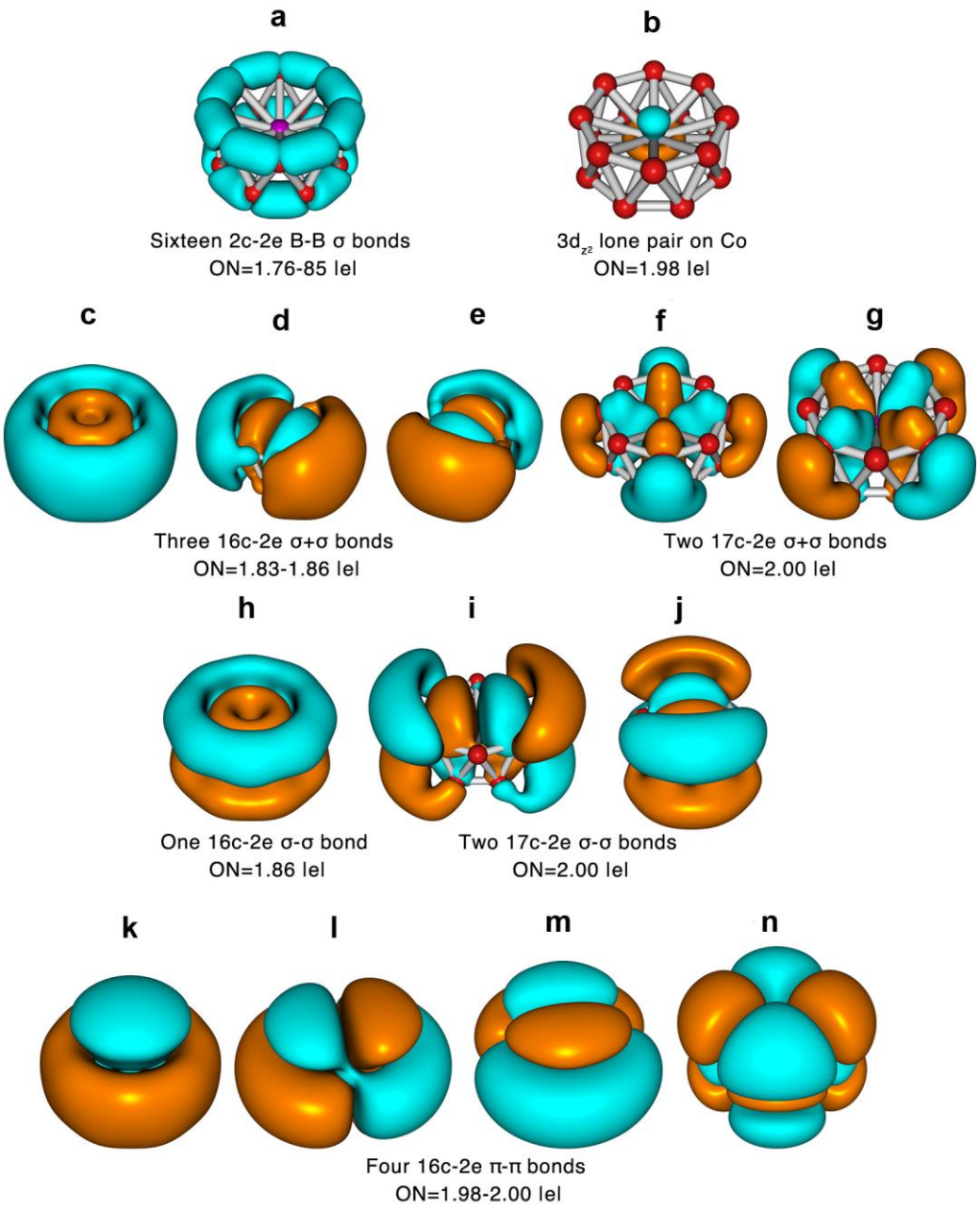


Supplementary Figure 1. Relative energies (in kcal/mol) of the lowest lying (<20 kcal/mol above the global minimum) isomers of CoB_{16}^- at the PBE0/Def2-TZVP level of theory.

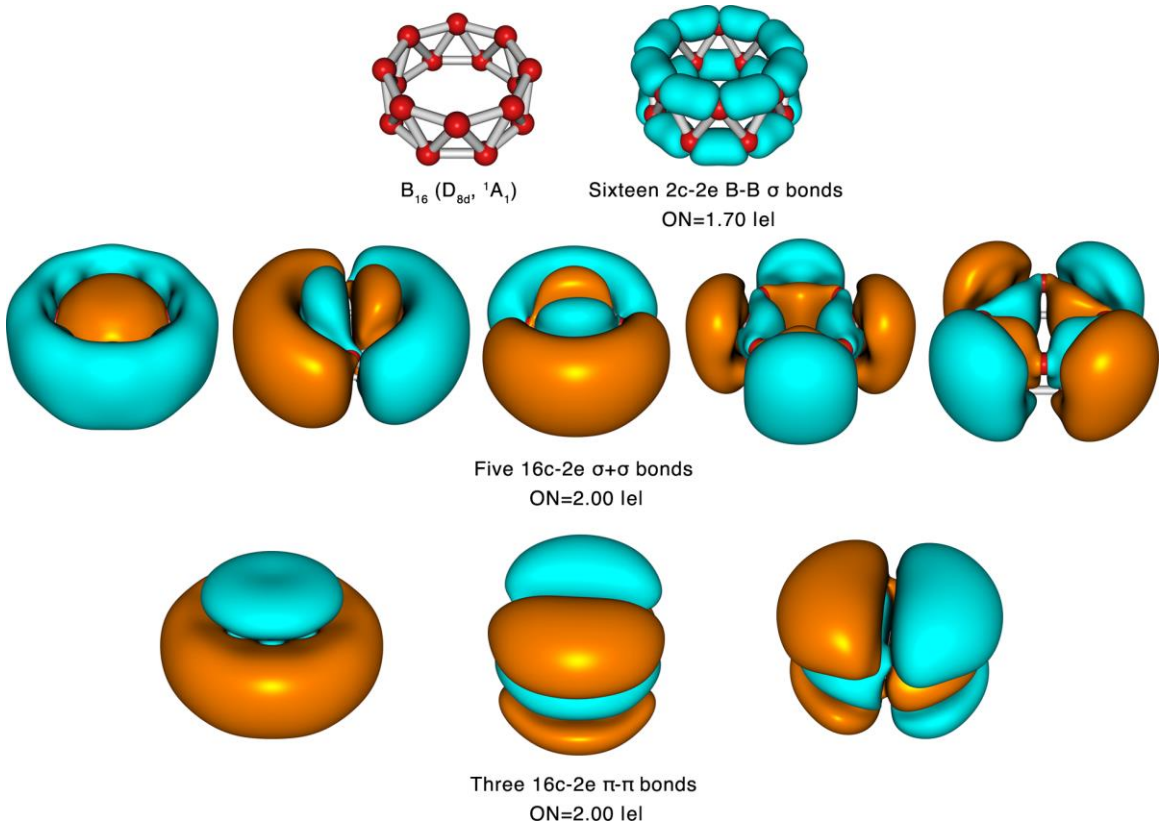
B3LYP/Def2-TZVP, TPSSh/Def2-TZVP, and ROCCSD(T)/6-311+G(2df)//PBE0/Def2-TZVP relative energies for the three lowest energy isomers **I, II,** and **III** are shown in parenthesis, square brackets, and curly brackets, respectively. All energies are corrected for zero-point energies (ZPE) at their respective levels of theory aside from single-point coupled-cluster calculations, which are ZPE corrected at PBE0/Def2-TZVP. The C_{4V} structure (isomer **II**) has one imaginary frequency at this level of theory. Geometry optimization following the imaginary frequency leads to the local minimum structure possessing C_4 symmetry. However, including ZPE corrections the vibrationally averaged structure has effectively C_{4V} symmetry.



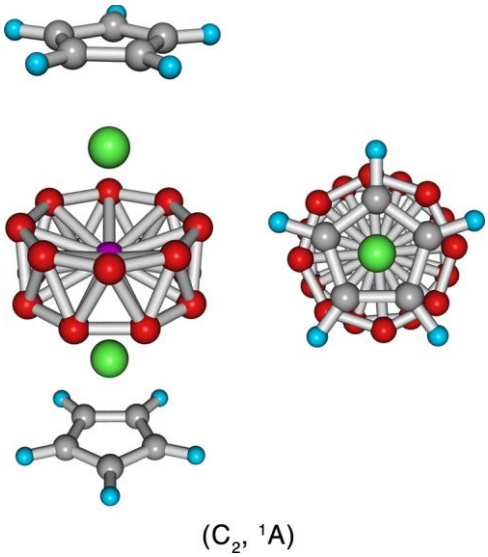
Supplementary Figure 2. Two views of the neutral CoB_{16} isomer I^0.
Its point group symmetries and spectroscopic states are shown in parenthesis. All distances are in Å.



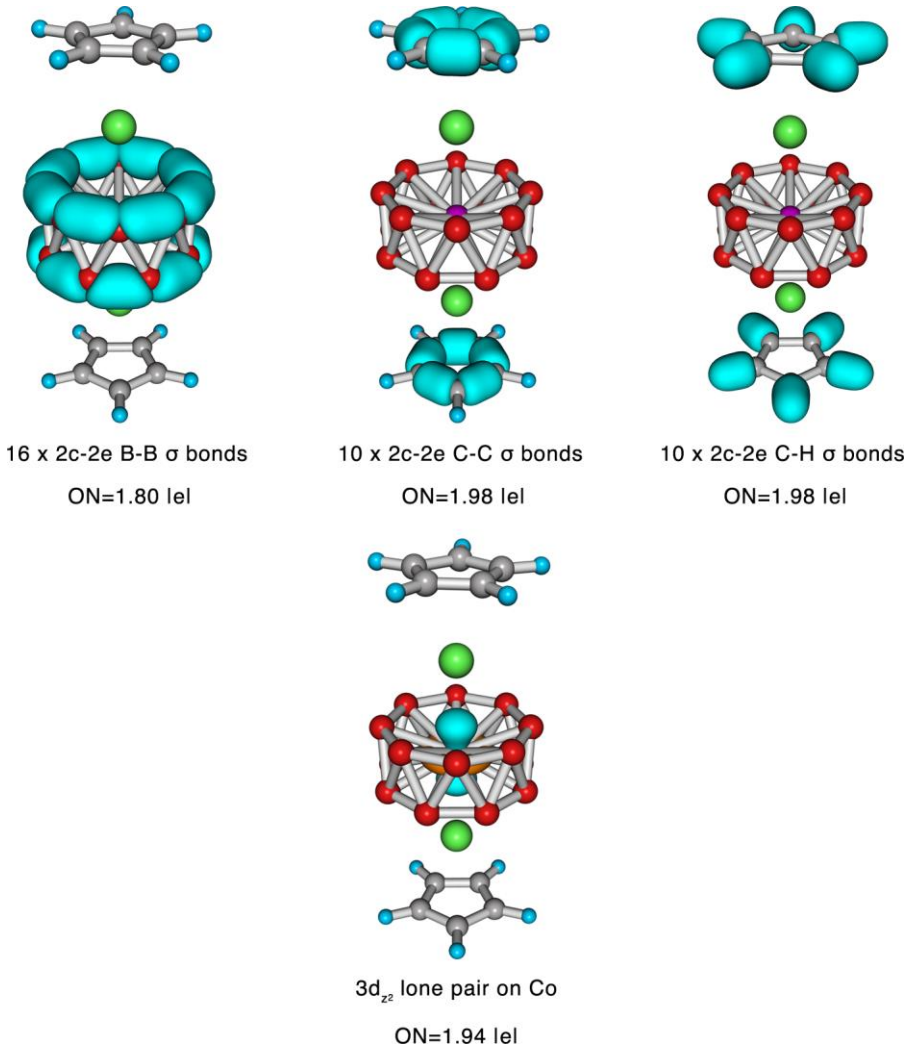
Supplementary Figure 3. The AdNDP chemical bonding picture obtained for isomer II (C_{4v}, $^1A_1$) of CoB_{16}^-.



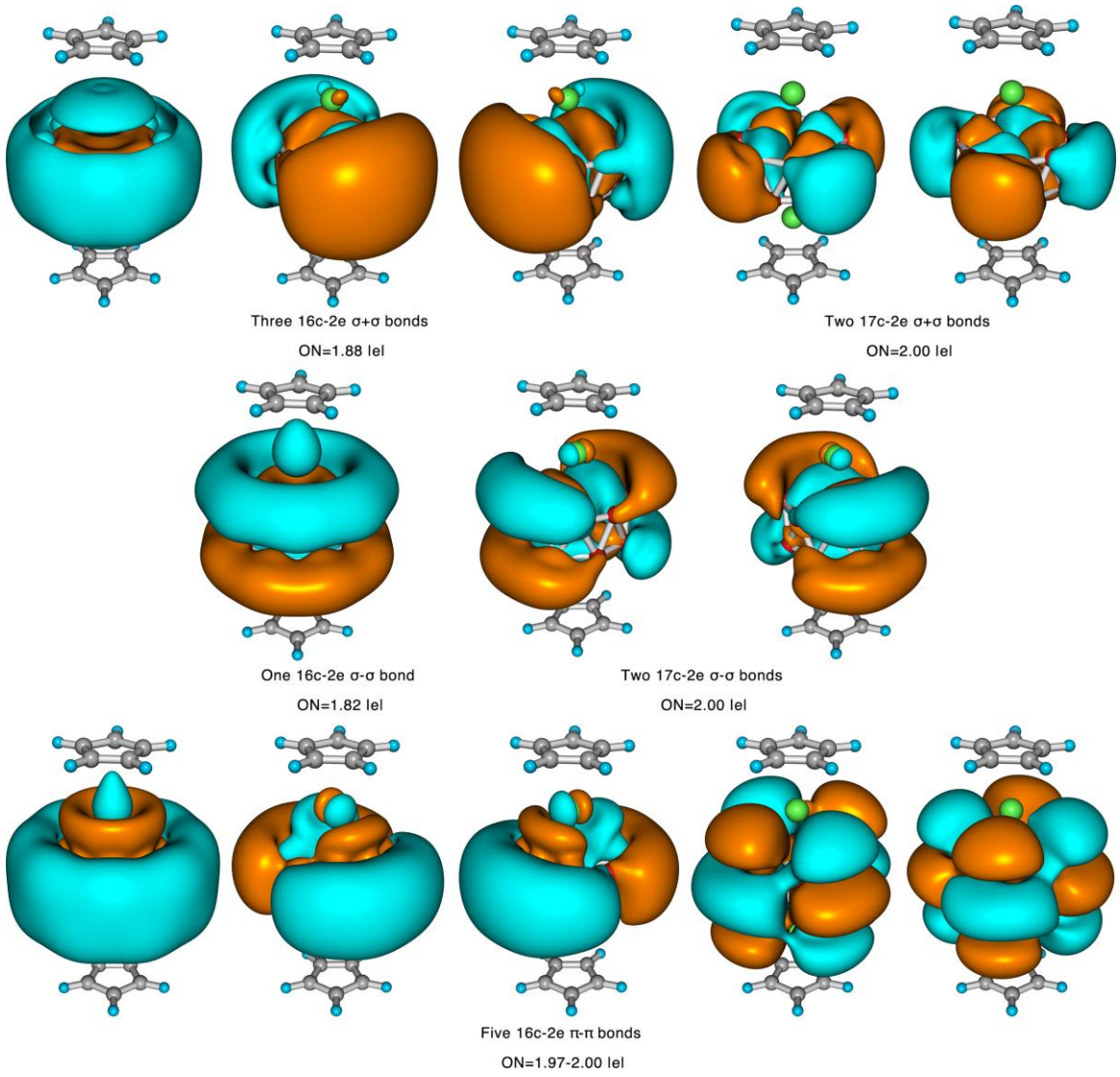
Supplementary Figure 4. The AdNDP chemical bonding picture obtained for the tubular isomer of the B_{16} cluster.



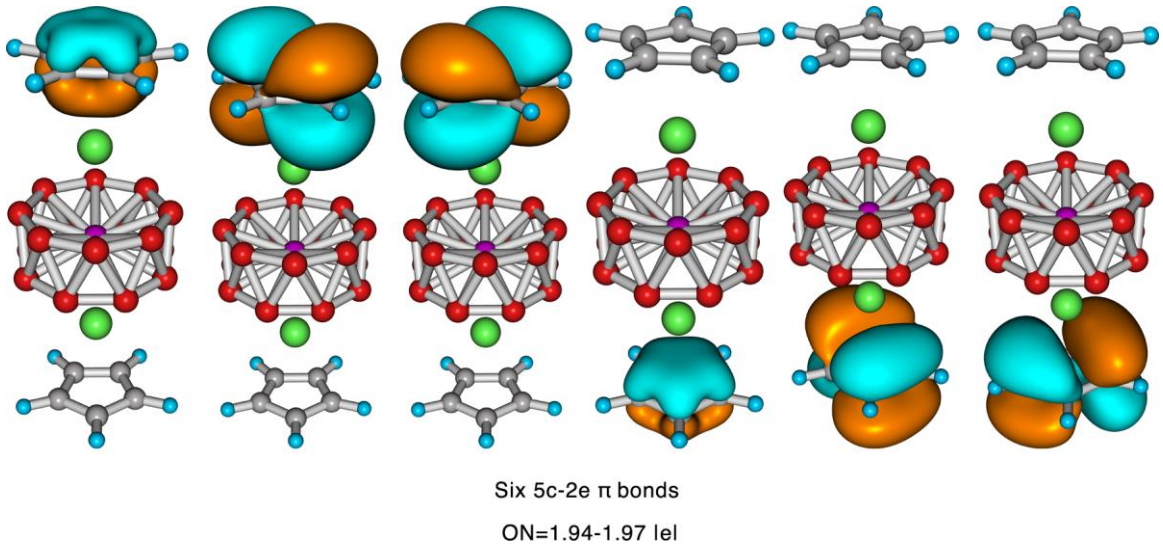
Supplementary Figure 5. Two views of the triple-decked $[CoB_{16}(CaCp)_2]^-$ cluster.
Its point group symmetry and spectroscopic state are shown in parenthesis. Color scheme: Ca is green, C is grey, H is blue, B is red, and Co is magenta.



Supplementary Figure 6. Localized elements of chemical bonding: 1c-2e (lone pairs) and 2c-2e (classical two-center two-electron) bonds found on both the CoB_{16}^{3-} and $C_5H_5^-$ fragments.



Supplementary Figure 7. Delocalized elements of chemical bonding found on the CoB_{16}^{3-} fragment in $[CoB_{16}(CaCp)_2]^-$.



Supplementary Figure 8. Delocalized elements of chemical bonding found on the $C_5H_5^-$ fragments in $[CoB_{16}(CaCp)_2]^-$.

Supplementary Table 1.
Cartesian coordinates of the three lowest energy isomers of the CoB_{16}^- cluster (I-III), neutral CoB_{16} isomer I^0, and the triple-decked $[CoB_{16}(CaCp)_2]^-$ sandwich compound at the PBE0/Def2-TZVP level of theory.

I	5	0.000000000	2.072443000	0.806679000
	27	0.000000000	0.000000000	0.000000000
	5	-1.465438000	-1.465438000	0.806679000
	5	1.465438000	-1.465438000	0.806679000
	5	2.072443000	0.000000000	0.806679000
	5	-2.072443000	0.000000000	0.806679000
	5	-1.465438000	1.465438000	0.806679000
	5	1.465438000	1.465438000	0.806679000
	5	0.000000000	-2.072443000	0.806679000
	5	-1.914687000	0.793089000	-0.806679000
	5	0.793089000	1.914687000	-0.806679000
	5	0.793089000	-1.914687000	-0.806679000
	5	1.914687000	-0.793089000	-0.806679000
	5	-0.793089000	1.914687000	-0.806679000
	5	1.914687000	0.793089000	-0.806679000
	5	-0.793089000	-1.914687000	-0.806679000
	5	-1.914687000	-0.793089000	-0.806679000
II	5	-1.926102000	0.772790000	-0.817317000
	27	0.000000000	0.000000000	-0.003007000
	5	1.926102000	0.772790000	-0.817317000
	5	0.772790000	-1.926102000	-0.817317000
	5	-0.772790000	-1.926102000	-0.817317000
	5	0.772790000	1.926102000	-0.817317000
	5	-0.772790000	1.926102000	-0.817317000
	5	-1.926102000	-0.772790000	-0.817317000
	5	1.926102000	-0.772790000	-0.817317000
	5	0.000000000	2.103180000	0.773458000
	5	-2.103180000	0.000000000	0.773458000
	5	1.423652000	-1.423652000	0.865236000
	5	0.000000000	-2.103180000	0.773458000
	5	-1.423652000	1.423652000	0.865236000
	5	-1.423652000	-1.423652000	0.865236000
	5	2.103180000	0.000000000	0.773458000
	5	1.423652000	1.423652000	0.865236000

III	27	0.000000000	0.000000000	0.254632000
	5	-1.598686000	-0.027003000	-1.298828000
	5	1.376226000	0.157703000	1.718441000
	5	-0.769403000	-0.124147000	-2.723566000
	5	-0.095219000	1.023694000	-1.533573000
	5	-1.376226000	-0.157703000	1.718441000
	5	0.000000000	-0.906301000	2.116848000
	5	0.769403000	0.124147000	-2.723566000
	5	1.063171000	-1.616745000	-0.411190000
	5	-1.063171000	1.616745000	-0.411190000
	5	-1.181627000	1.489917000	1.183241000
	5	2.033584000	-0.232101000	0.261119000
	5	1.598686000	0.027003000	-1.298828000
	5	1.181627000	-1.489917000	1.183241000
	5	-2.033584000	0.232101000	0.261119000
	5	0.095219000	-1.023694000	-1.533573000
	5	0.000000000	0.906301000	2.116848000
I^0	5	1.448199000	1.506481000	-0.788339000
	27	0.000000000	0.000000000	0.000385000
	5	0.000000000	-2.162238000	-0.768730000
	5	-1.949398000	0.000000000	-0.836223000
	5	-1.448199000	1.506481000	-0.788339000
	5	1.448199000	-1.506481000	-0.788339000
	5	1.949398000	0.000000000	-0.836223000
	5	0.000000000	2.162238000	-0.768730000
	5	-1.448199000	-1.506481000	-0.788339000
	5	1.990339000	-0.802304000	0.769780000
	5	0.801384000	1.832645000	0.820516000
	5	-1.990339000	-0.802304000	0.769780000
	5	-1.990339000	0.802304000	0.769780000
	5	1.990339000	0.802304000	0.769780000
	5	-0.801384000	1.832645000	0.820516000
	5	-0.801384000	-1.832645000	0.820516000
	5	0.801384000	-1.832645000	0.820516000
$[CoB_{16}(CaCp)_2]^-$	5	0.407037000	-0.804126000	-2.040487000
	27	0.000000000	0.000000000	0.006130000
	5	1.158948000	-0.803673000	1.740415000
	5	-1.734320000	-0.803739000	1.164948000
	5	-2.046524000	-0.804227000	-0.400973000
	5	2.046585000	-0.804103000	0.413103000
	5	1.734263000	-0.803804000	-1.152792000
	5	-1.158844000	-0.803729000	-1.728218000
	5	-0.407004000	-0.804265000	2.052622000
	5	2.046524000	0.804227000	-0.400973000
	5	-0.407037000	0.804126000	-2.040487000
	5	-1.158948000	0.803673000	1.740415000

	5	-2.046585000	0.804103000	0.413103000
	5	1.158844000	0.803729000	-1.728218000
	5	-1.734263000	0.803804000	-1.152792000
	5	0.407004000	0.804265000	2.052622000
	5	1.734320000	0.803739000	1.164948000
	20	0.000000000	2.821886000	0.007190000
	20	0.000000000	-2.821886000	0.007190000
	6	0.330494000	5.286924000	1.144656000
	6	1.201179000	5.277963000	0.026871000
	6	0.407202000	5.266431000	-1.146524000
	6	-0.954154000	5.268140000	-0.753962000
	6	-1.001663000	5.280773000	0.661969000
	6	0.954154000	-5.268140000	-0.753962000
	6	1.001663000	-5.280773000	0.661969000
	6	-0.407202000	-5.266431000	-1.146524000
	6	-1.201179000	-5.277963000	0.026871000
	6	-0.330494000	-5.286924000	1.144656000
	1	2.285178000	5.298079000	0.062981000
	1	0.631016000	5.315278000	2.186602000
	1	-1.900047000	5.303272000	1.269566000
	1	-1.809892000	5.277818000	-1.420519000
	1	0.776775000	5.274625000	-2.166339000
	1	-0.631016000	-5.315278000	2.186602000
	1	-2.285178000	-5.298079000	0.062981000
	1	-0.776775000	-5.274625000	-2.166339000
	1	1.809892000	-5.277818000	-1.420519000
	1	1.900047000	-5.303272000	1.269566000

Supplementary Table 2.

The first two calculated VDE values for isomer III (C_2, ^1A) of CoB_{16}^- at three levels of theory.

Isomer **III** ($1a^2 2a^2 1b^2 3a^2 2b^2 4a^2 3b^2 4b^2 5a^2 5b^2 6a^2 6b^2 7a^2 7b^2 8a^2 9a^2 10a^2 8b^2 11a^2 9b^2 12a^2 10b^2 13a^2 14a^2 11b^2 12b^2 15a^2 13b^2 16a^2$)					
UPBE0[a]		UB3LYP[b]		ROCCSD(T)[c]	
MO	VDE	MO	VDE	MO	VDE
16a	3.35	16a	3.32	16a	3.65
13b	3.62	13b	3.53	13b	–[d]

[a] The VDEs were calculated at the UPBE0/6-311+G(2df)//UPBE0/Def2-TZVP level of theory. Spin-contamination was found to be very small.

[b] The VDEs were calculated at the UB3LYP/6-311+G(2df)//UPBE0/Def2-TZVP level of theory. Spin-contamination was found to be very small.

[c] The VDEs were calculated at the ROCCSD(T)/6-311+G(2df)//PBE0/Def2-TZVP level of theory, because the UHF wave function has a very high spin-contamination.

[d] VDE could not be calculated at this level of theory.

Supplementary Table 3.

Comparison of the bond distances in B_{16}, CoB_{16}^- (isomers I and II), and $[CoB_{16}(CaCp)_2]^-$ clusters at the PBE0/Def2-TZVP level of theory. All values are in Å.

	B_{16}	CoB_{16} (structure $\mathbf{I^0}$)	CoB_{16}^- (isomer **I**)	CoB_{16}^- (isomer **II**)	$[CoB_{16}(CaCp)_2]^-$
R(Co-B)	-	2.12-2.29	2.22	2.19-2.24	2.24
R(peripheral B-B)	1.63	1.57-1.60	1.59	1.55-1.63	1.60
R(B-B between the rings)	1.64	1.76-1.81	1.80	1.78-1.87	1.80