Supplementary Information

Transition-Metal-Like Bonding Behaviors of Boron Atom in A Boron-Cluster Boronyl Complex $[(\eta^7\text{-}B_7)\text{-}B\text{-}BO]^-$

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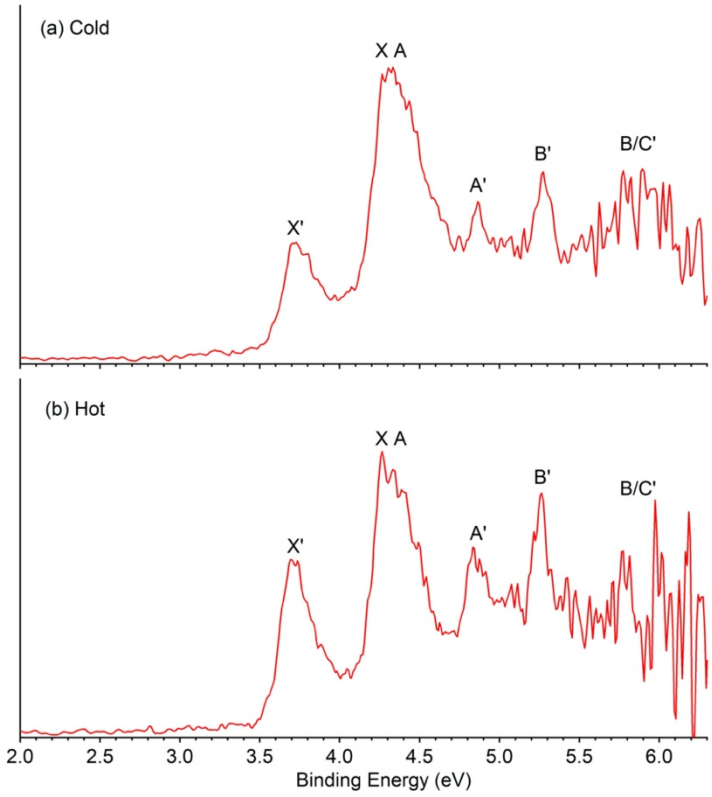

Figure S1. The 193 nm photoelectron spectra of B_9O^- taken at two different experimental conditions. (a) Cold: longer residence time in the nozzle. (b) Hot: short residence time in the nozzle.

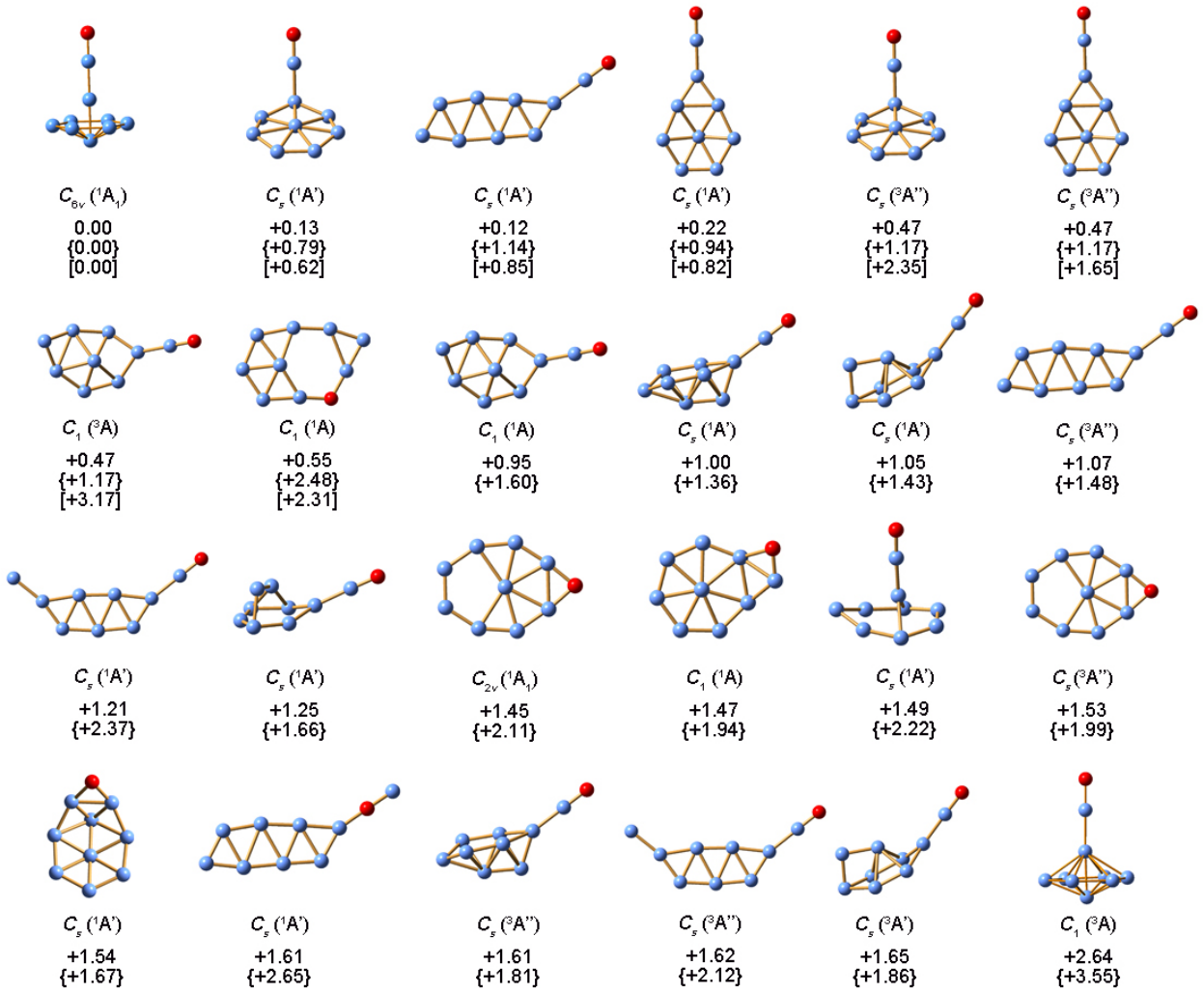

Figure S2. Optimized low-lying structures of the singlet and triplet states of B_9O^- at the B3LYP/6-311++G(d,p) level. Their relative energies are shown in eV at the B3LYP/6-311++G(d,p), PBE0/6-311++G(d,p) (in curly brackets), and single-point CCSD(T)//B3LYP/6-311++G(d,p) (in square brackets) levels.

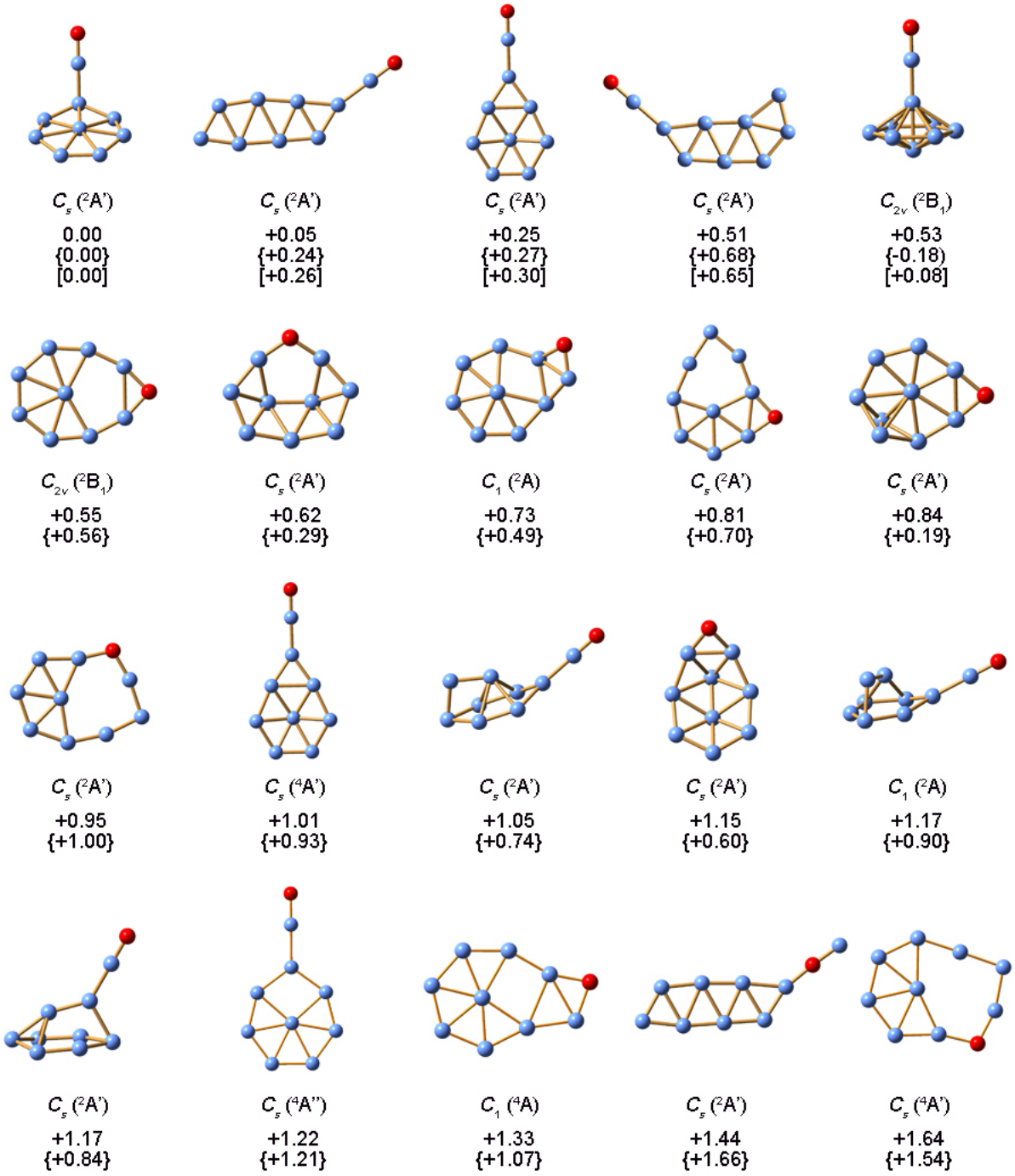

Figure S3. Optimized low-lying structures of the doublet and quartet states of neutral B_9O at the B3LYP/6-311++G(d,p) level. Their relative energies are shown in eV at the B3LYP/6-311++G(d,p), PBE0/6-311++G(d,p) (in curly brackets), and single-point CCSD(T)//B3LYP/6-311++G(d,p) (in square brackets) levels.

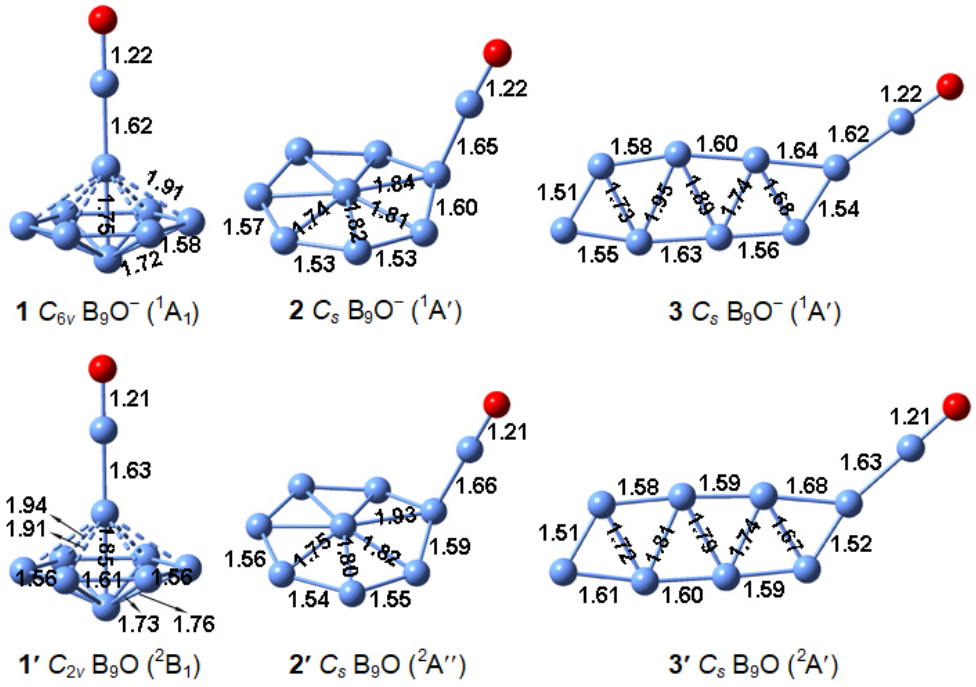

Figure S4. The structural parameters of the three lowest-lying isomers of B_9O^- (**1**-**3**) and B_9O (**1′**-**3′**) at the B3LYP/6-311++G(d,p) level. All bond distances are given in Å.

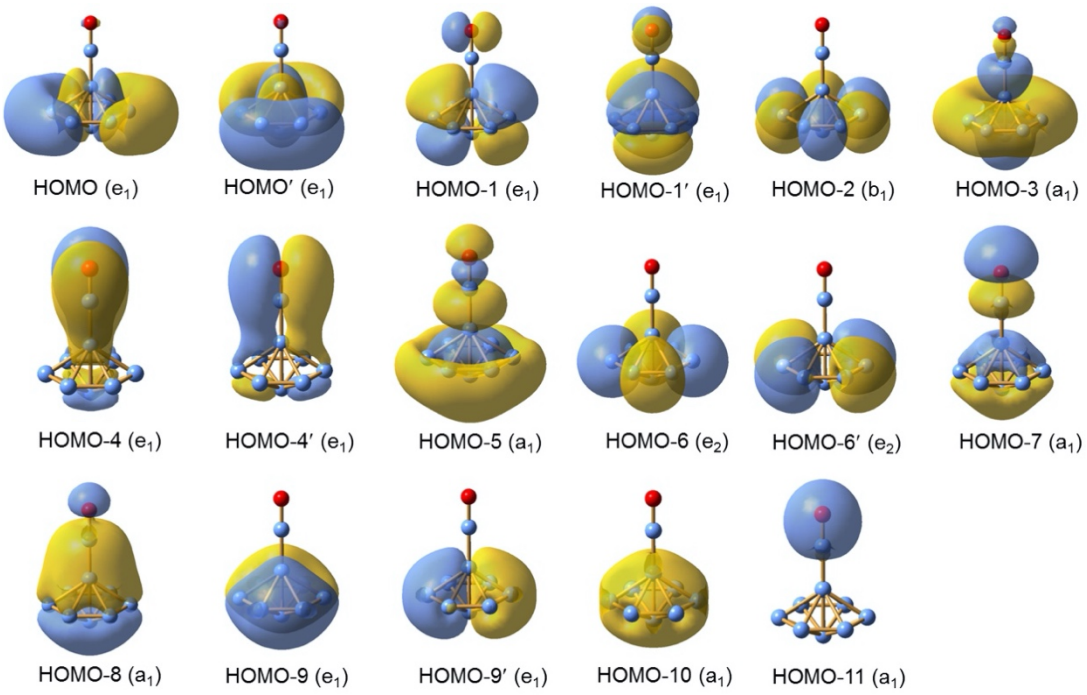

Figure S5. Pictures of the occupied molecular orbitals of the global-minimum C_{6v} B_9O^- (**1**).

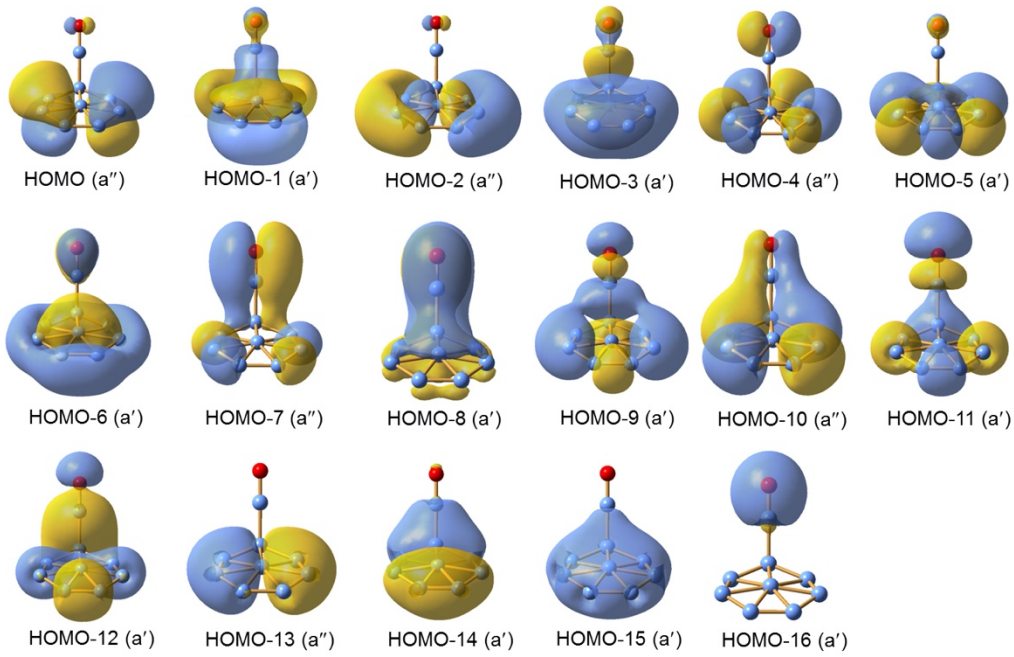

Figure S6. Pictures of the occupied molecular orbitals of the isomer **2** of B_9O^- (C_s).

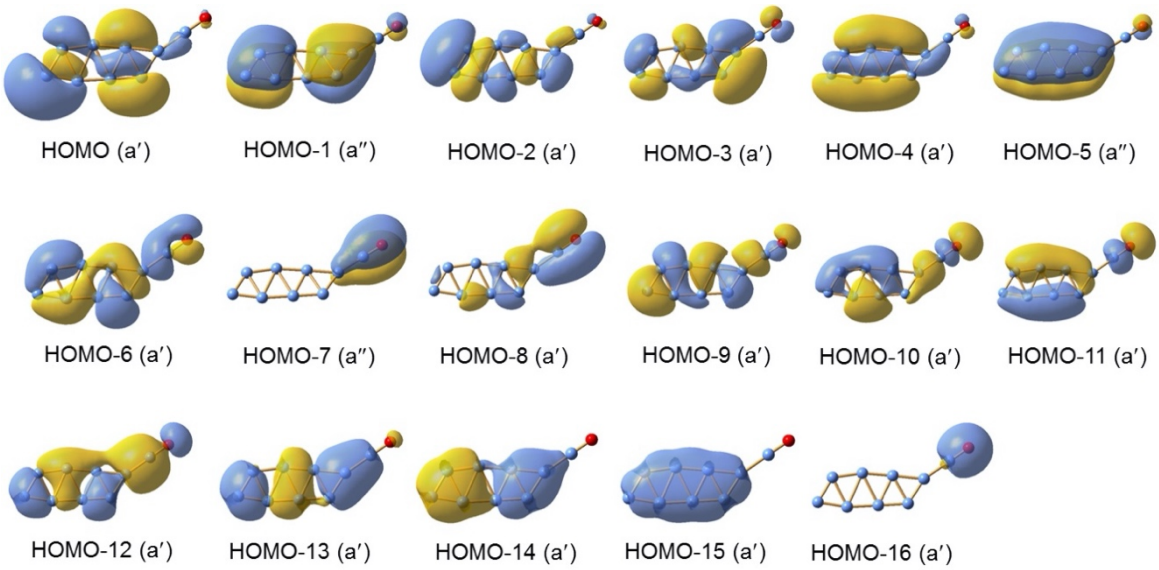

Figure S7. Pictures of the occupied molecular orbitals of the isomer **3** of B_9O^- (C_s).

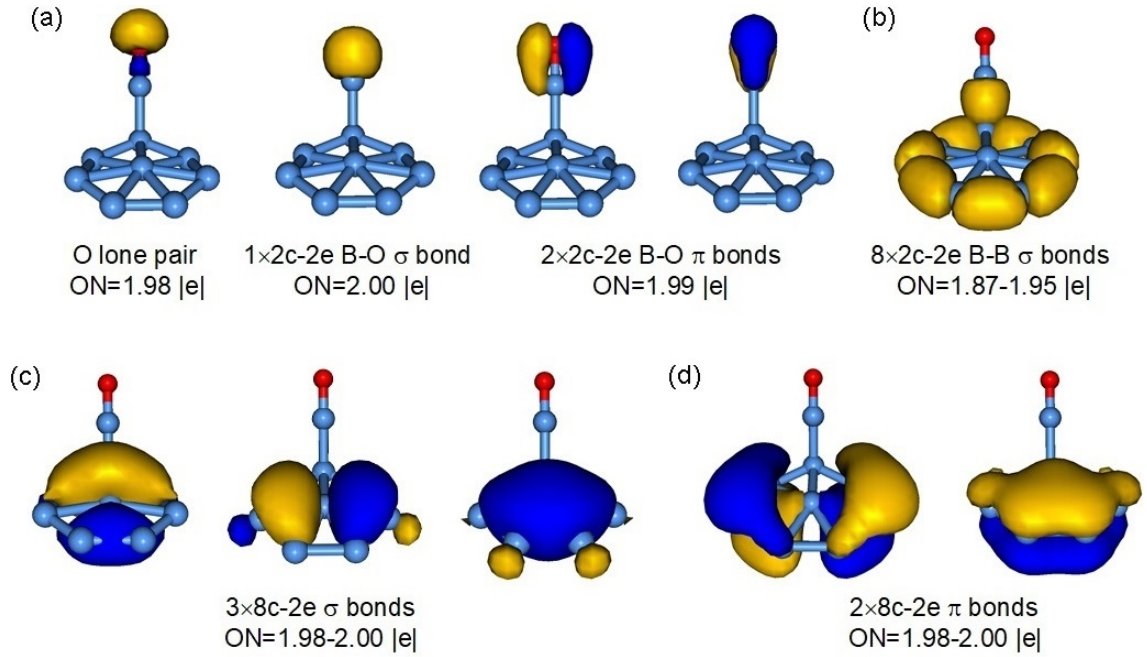

Figure S8. AdNDP analyses for isomer **2** of B_9O^- (C_s). ON is the occupation number.

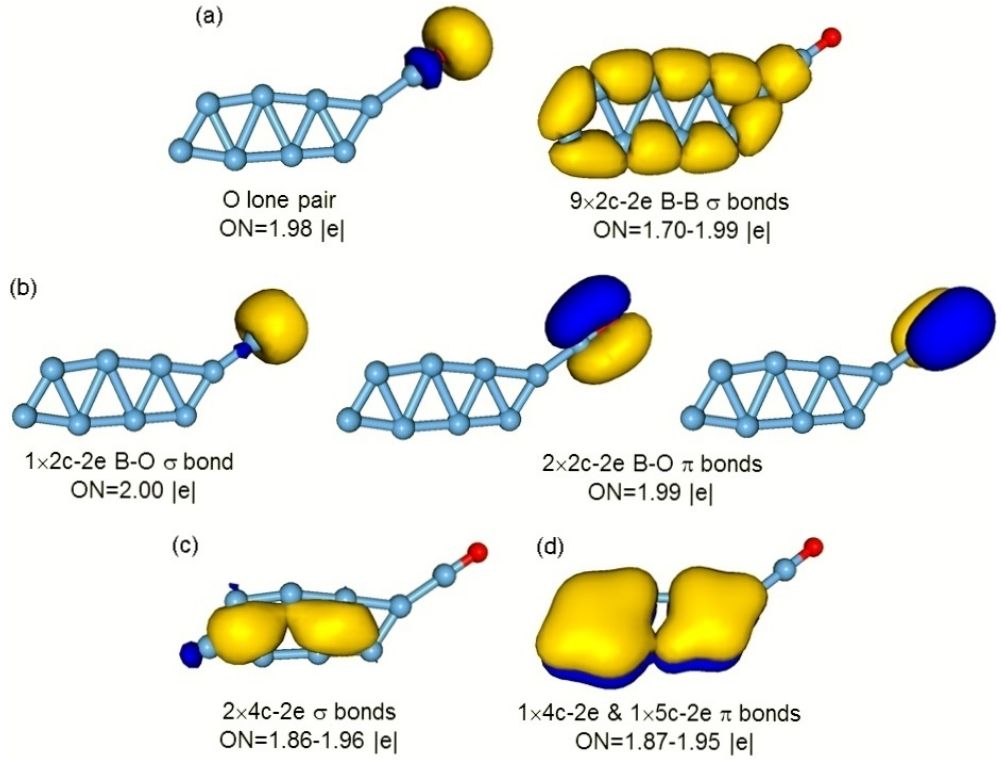

Figure S9. AdNDP analyses for isomer **3** of B_9O^- (C_s). ON is the occupation number.

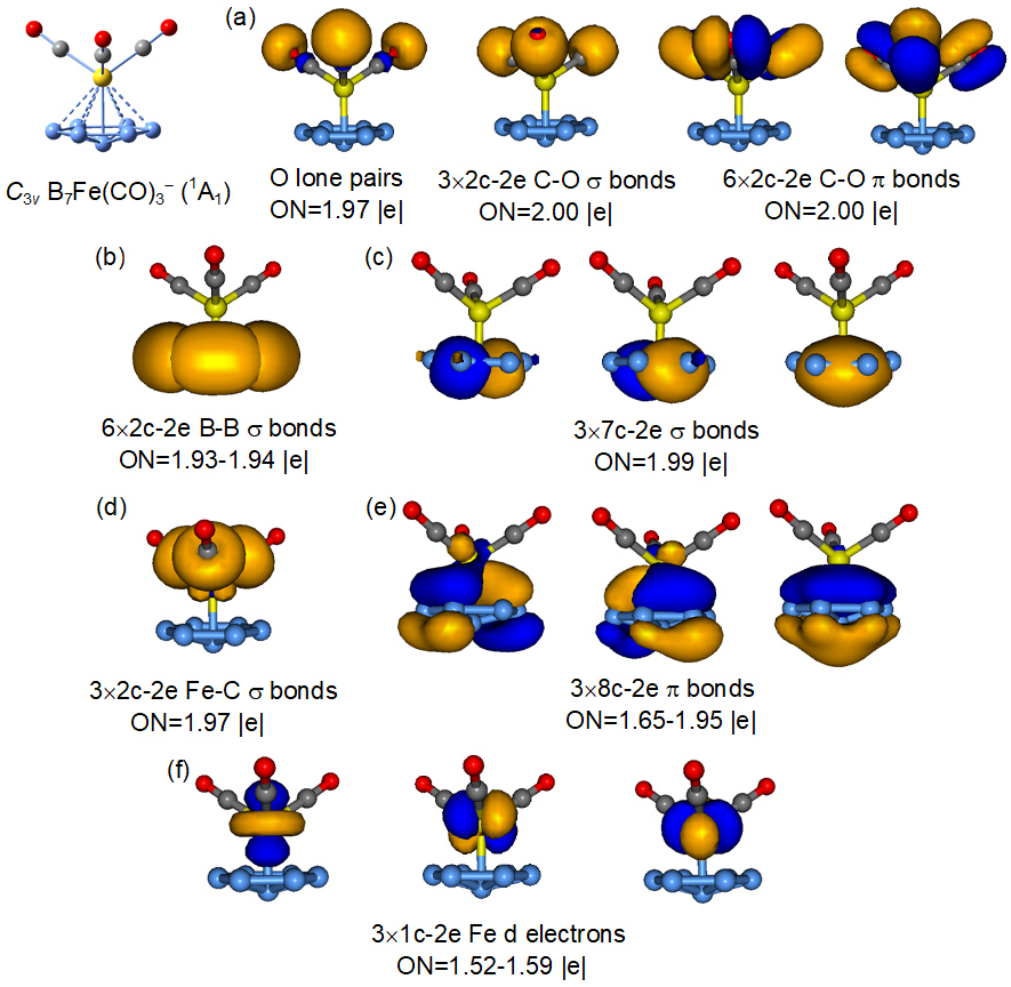

Figure S10. AdNDP analyses for the $B_7Fe(CO)_3^-$ complex. ON is the occupation number.

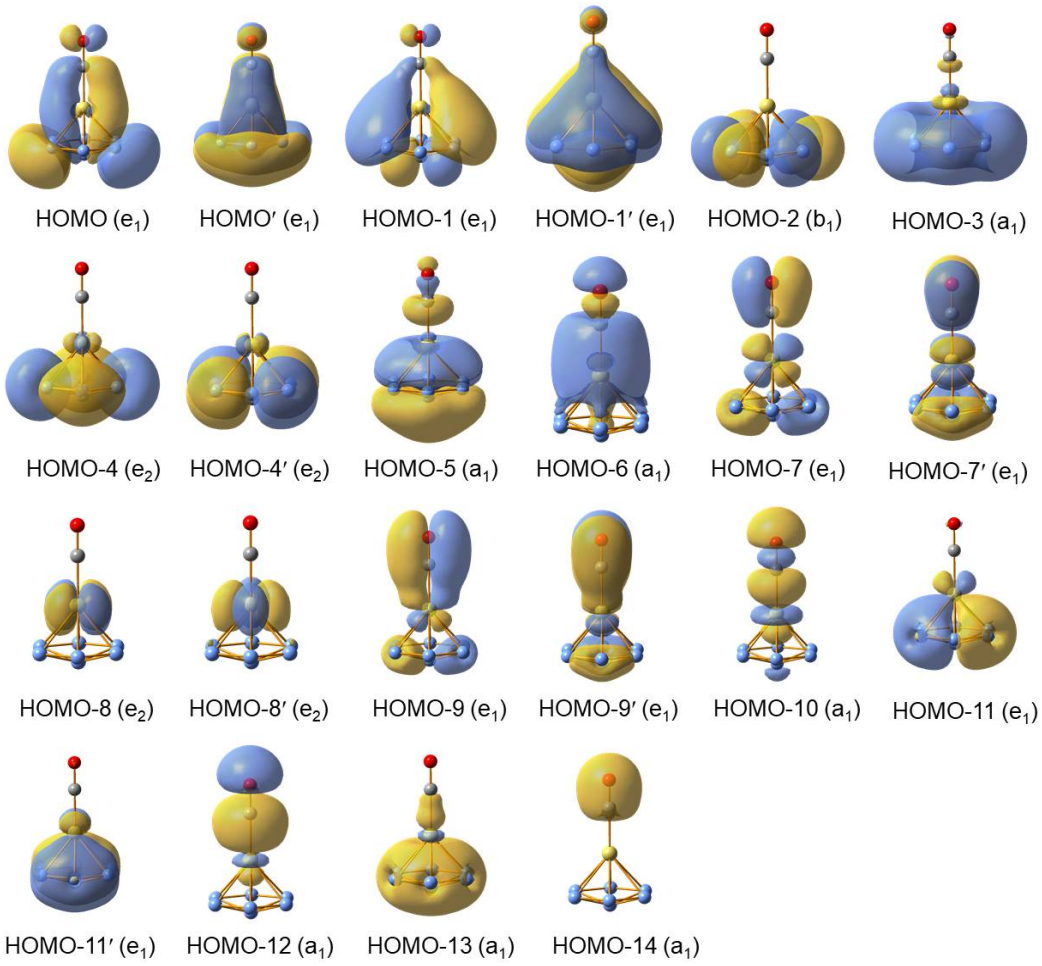

Figure S11. Pictures of the occupied molecular orbitals of $B_7Zn(CO)^-$ complex.

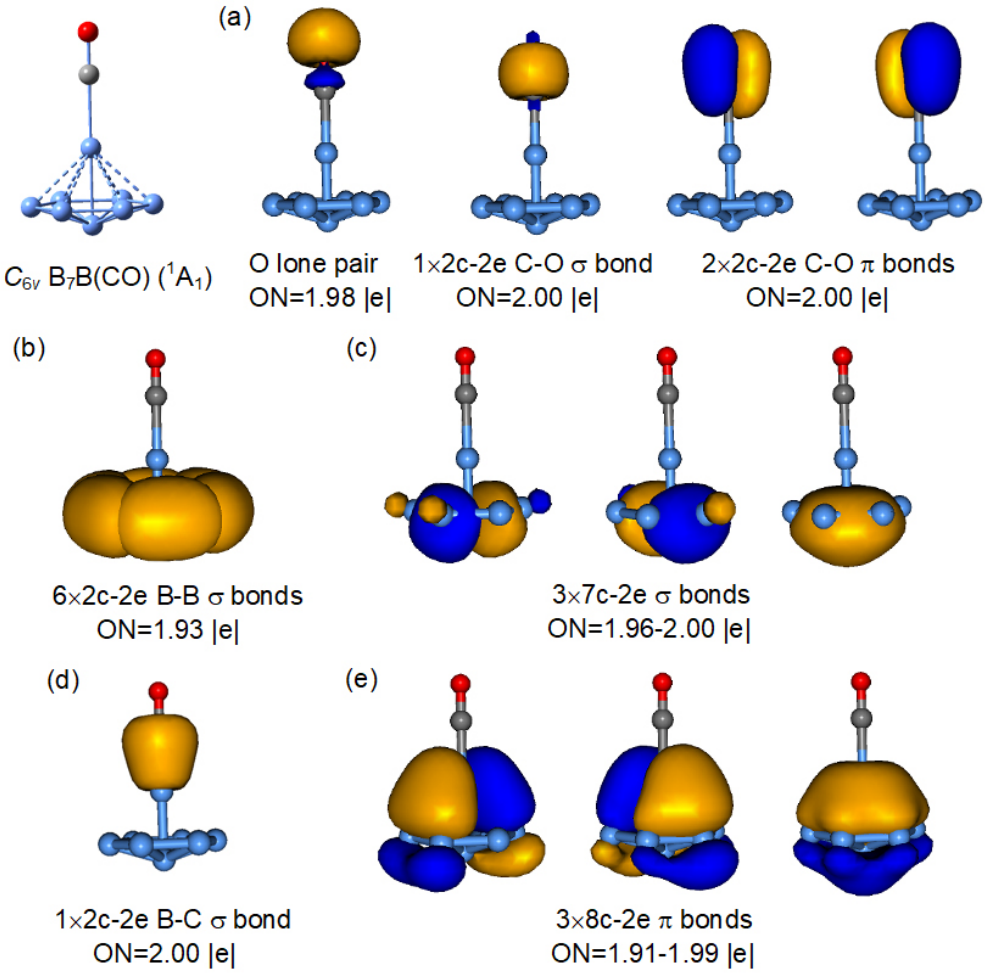

Figure S12. AdNDP analyses for the (η^7-B_7)-B-CO complex. ON is the occupation number.

Table S1. Cartesian coordinates (in Å) of three lowest-lying isomers of B_9O^-, C_{6v} (**1**), C_s (**2**), and C_s (**3**) optimized at the B3LYP/6-311++G(d,p) level.

1. C_{6v} B_9O^-

B	0.00000000	0.00000000	1.81356800
B	0.00000000	1.58018200	-0.88234000
B	0.00000000	0.00000000	-1.55616000
B	0.00000000	0.00000000	0.18923300
B	0.00000000	-1.58018200	-0.88234000
B	-1.36847800	0.79009100	-0.88234000
B	-1.36847800	-0.79009100	-0.88234000
B	1.36847800	-0.79009100	-0.88234000
B	1.36847800	0.79009100	-0.88234000
O	0.00000000	0.00000000	3.02962500

2. C_s B_9O^-

B	-0.90234000	-2.17232700	0.78690200
B	-0.63697600	0.44589900	-1.40099300
B	1.27598000	1.66318400	0.00000000
B	-0.47165600	-0.68495700	0.00000000
B	-0.29219000	1.14364900	0.00000000
B	-0.63697600	-1.03762700	1.77609400
B	-0.63697600	0.44589900	1.40099300
B	-0.90234000	-2.17232700	-0.78690200
B	-0.63697600	-1.03762700	-1.77609400
O	2.40028200	2.12889700	0.00000000

3. C_s B_9O^-

B	2.33602200	-1.43230000	0.00000000
B	0.71073400	-1.29435400	0.00000000
B	0.00000000	0.29384200	0.00000000
B	3.14564200	0.09255000	0.00000000
B	3.86982400	-1.23496400	0.00000000
B	1.59415300	0.37409100	0.00000000
B	-1.63503900	0.17654300	0.00000000
B	-0.84667800	-1.15163900	0.00000000
B	-2.93117000	1.15621900	0.00000000
O	-3.90218100	1.88750700	0.00000000

Table S2. Cartesian coordinates (in Å) of (a) $B_7Zn(CO)^-$ (C_{6v}), (b) $B_7Fe(CO)_3^-$ (C_{3v}), and (c) $B_7B(CO)$ (C_{6v}) optimized at the B3LYP/6-311++G(d,p) level.

(a) C_{6v} $B_7Zn(CO)^-$

B	0.00000000	1.61346600	-1.35331300
B	1.39730300	0.80673300	-1.35331300
B	1.39730300	-0.80673300	-1.35331300
B	0.00000000	-1.61346600	-1.35331300
B	-1.39730300	-0.80673300	-1.35331300
B	-1.39730300	0.80673300	-1.35331300
B	0.00000000	0.00000000	-1.79564600
O	0.00000000	0.00000000	3.34700500
C	0.00000000	0.00000000	2.19885100
Zn	0.00000000	0.00000000	0.32028200

(b) C_{3v} $B_7Fe(CO)_3^-$

B	1.60500300	0.00444400	-1.62275600
B	0.79865300	-1.39219600	-1.62275600
B	-0.79865300	-1.39219600	-1.62275600
B	-1.60500300	0.00444400	-1.62275600
B	-0.80635000	1.38775100	-1.62275600
B	0.80635000	1.38775100	-1.62275600
B	0.00000000	0.00000000	-2.04412700
O	0.00000000	2.52504400	1.59420300
C	0.00000000	1.54698800	0.98469300
O	2.18675300	-1.26252200	1.59420300
C	1.33973100	-0.77349400	0.98469300
Fe	0.00000000	0.00000000	0.11223000
C	-1.33973100	-0.77349400	0.98469300
O	-2.18675300	-1.26252200	1.59420300

(c) C_{6v} $B_7B(CO)$

B	0.00000000	1.61131700	-1.16376870
B	1.39544146	0.80565850	-1.16376870
B	1.39544146	-0.80565850	-1.16376870
B	0.00000000	-1.61131700	-1.16376870
B	-1.39544146	-0.80565850	-1.16376870
B	-1.39544146	0.80565850	-1.16376870
B	0.00000000	0.00000000	-1.68501870
O	0.00000000	0.00000000	3.44789230
C	0.00000000	0.00000000	2.31690830
B	0.00000000	0.00000000	0.37071330