On the Chemical Bonding of Gold in Auro-Boron Oxide Clusters Au_nBO^- (n = 1-3)

Dmitry Yu. Zubarev and Alexander I. Boldyrev*
Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300

Jun Li*
W. R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory MS K8-91, P. O. Box 999, Richland, WA 99352

Hua-Jin Zhai and Lai-Sheng Wang*
Department of Physics, Washington State University, 2710 University Drive, Richland, WA 99354 and Chemical Sciences Division, Pacific Northwest National Laboratory, MS K8-88, P. O. Box 999, Richland, WA 99352

Supporting Information

Table S1. NBO analysis of AuBO $C_{\infty v}$ ($^1\Sigma^+$) at the geometry of $AuBO^-$ $C_{\infty v}$ ($^2\Sigma^+$) at the B3LYP/Au/Stuttgart/B,O/aug-cc-pvTZ level of theory.

	Natural Charge, |e|			Natural Configuration		
O	-0.84			$2s^{1.76}\ 2p^{5.05}\ 3d^{0.03}$		
B	0.70			$2s^{0.82}\ 2p^{1.44}\ 3s^{0.01}\ 3p^{0.02}\ 4p^{0.01}$		
Au	0.14			$6s^{1.06}\ 5d^{9.80}$		
Bonding				Lone Pairs		
Occ.	Center	%	Hybridization, %	Occ.	Center	Hybridization
2.00	B	20.4	$s^{42.8}\ p^{57.2}\ d^{0.1}$	2.00	Au	$s^{0.0}\ p^{0.0}\ d^{100}$
	O	79.6	$s^{55.6}\ p^{43.6}\ d^{0.7}$	2.00		$s^{0.0}\ p^{0.0}\ d^{100}$
2.00	B	18.6	$s^{0.0}\ p^{99.8}\ d^{0.2}$	2.00		$s^{12.4}\ p^{0.0}\ d^{87.6}$
	O	81.4	$s^{0.0}\ p^{99.6}\ d^{0.4}$	1.97		$s^{0.0}\ p^{0.0}\ d^{100}$
2.00	B	18.6	$s^{0.0}\ p^{99.8}\ d^{0.2}$	1.97		$s^{0.0}\ p^{0.0}\ d^{100}$
	O	81.4	$s^{0.0}\ p^{99.6}\ d^{0.4}$			
2.00	Au	46.3	$s^{87.5}\ p^{0.2}\ d^{12.3}$	1.98	O	$s^{44.3}\ p^{55.5}\ d^{0.3}$
	B	53.7	$s^{56.4}\ p^{43.0}\ d^{0.2}\ f^{0.4}$			

Table S2. NBO analysis of $AuBO^-$ $C_{\infty v}$ ($^2\Sigma^+$) at the B3LYP/Au/Stuttgart/B,O/aug-cc-pvTZ level of theory.

	Natural Charge, |e|			Natural Configuration		
O	-0.96			$2s^{1.76}\ 2p^{5.16}\ 3d^{0.03}$		
B	0.35			$2s^{1.14}\ 2p^{1.42}\ 3s^{0.04}\ 3p^{0.04}\ 4p^{0.01}$		
Au	-0.39			$6s^{1.46}\ 5d^{9.79}\ 6p^{0.10}\ 7s^{0.03}\ 6d^{0.02}$		
Bonding (α)				Lone Pairs (α)		
Occ.	Center	%	Hybridization, %	Occ.	Center	Hybridization
1.00	B	16.9	$s^{0.0}\ p^{98.0}\ d^{0.2}$	1.00	Au	$s^{0.0}\ p^{0.0}\ d^{100}$
	O	83.1	$s^{0.0}\ p^{99.6}\ d^{0.4}$	1.00		$s^{0.0}\ p^{0.0}\ d^{100}$
1.00	B	16.9	$s^{0.0}\ p^{98.0}\ d^{0.2}$	1.00		$s^{28.2}\ p^{0.2}\ d^{71.7}$

	O	83.1	$s^{0.0}\ p^{99.6}\ d^{0.4}$	0.98		$s^{0.0}\ p^{0.0}\ d^{100}$
1.00	B O	19.5 80.5	$s^{29.6}\ p^{70.4}\ d^{0.1}$ $s^{60.6}\ p^{38.7}\ d^{0.7}$	0.98 0.95		$s^{0.0}\ p^{0.0}\ d^{100}$ $s^{66.6}\ p^{5.3}\ d^{28.1}$
				0.92	B	$s^{71.9}\ p^{27.9}\ d^{0.1}\ f^{0.1}$
				0.99	O	$s^{39.3}\ p^{60.4}\ d^{0.3}$
Bonding (β)				Lone Pairs (β)		
Occ.	Center	%	Hybridization, %	Occ.	Center	Hybridization
1.00	B O	16.9 83.1	$s^{0.0}\ p^{99.8}\ d^{0.3}$ $s^{0.0}\ p^{99.6}\ d^{0.4}$	1.00 1.00 1.00 0.98 0.98	Au	$s^{0.0}\ p^{0.0}\ d^{100}$ $s^{0.0}\ p^{0.0}\ d^{100}$ $s^{17.0}\ p^{0.0}\ d^{83.0}$ $s^{0.0}\ p^{0.0}\ d^{100}$ $s^{0.0}\ p^{0.0}\ d^{100}$
1.00	B O	16.9 83.1	$s^{0.0}\ p^{99.8}\ d^{0.3}$ $s^{0.0}\ p^{99.6}\ d^{0.4}$			
1.00	B O	19.5 80.5	$s^{40.9}\ p^{59.0}\ d^{0.1}$ $s^{58.9}\ p^{40.4}\ d^{0.7}$			
1.00	Au B	45.2 54.8	$s^{82.7}\ p^{0.2}\ d^{17.1}$ $s^{58.9}\ p^{40.6}\ d^{0.2}\ f^{0.3}$	0.99	O	$s^{41.0}\ p^{58.8}\ d^{0.3}$

Table S3. NBO analysis of Au_2BO^+ C_{2v} ($^1A_1$) at the B3LYP/Au/Stuttgart/B,O/aug-cc-pvTZ level of theory.

	Natural Charge, |e|			Natural Configuration		
O1	-0.63			$2s^{1.74}\ 2p^{4.85}\ 3d^{0.03}$		
B2	0.37			$2s^{0.80}\ 2p^{1.76}\ 3s^{0.01}\ 3p^{0.03}\ 3d0.01\ 4d^{0.01}\ 4f^{0.01}\ 5d^{0.01}$		
Au3	0.63			$6s^{0.57}\ 5d^{9.81}$		
Au4	0.63			$6s^{0.57}\ 5d^{9.81}$		
Bonding				Lone Pairs		
Occ.	Center	%	Hybridization, %	Occ.	Center	Hybridization
2.00	O1	78.7	$s^{58.7}\ p^{40.6}\ d^{0.7}$	1.98	O1	$s^{41.2}\ p^{58.5}\ d^{0.3}$
	B2	21.3	$s^{41.5}\ p^{58.5}\ d^{0.0}$	2.00	Au3	$s^{0.0}\ p^{0.0}\ d^{100}$
2.00	O1	78.9	$s^{0.0}\ p^{99.6}\ d^{0.4}$	2.00		$s^{0.6}\ p^{0.0}\ d^{99.4}$
	B2	21.1	$s^{0.0}\ p^{99.0}\ d^{1.0}$	1.99		$s^{1.3}\ p^{0.0}\ d^{98.7}$
1.95	O1	74.5	$s^{0.0}\ p^{99.7}\ d^{0.3}$	1.97		$s^{0.0}\ p^{0.0}\ d^{100}$
	B2	25.5	$s^{0.0}\ p^{99.3}\ d^{0.7}$	1.88		$s^{0.6}\ p^{0.0}\ d^{99.4}$
2.00	B2	54.0	$s^{56.8}\ p^{42.2}\ d^{0.8}$	2.00	Au4	$s^{0.0}\ p^{0.0}\ d^{100}$
	Au3	23.0	$s^{96.9}\ p^{0.3}\ d^{2.7}$	2.00		$s^{0.6}\ p^{0.0}\ d^{99.4}$
	Au4	23.0	$s^{96.9}\ p^{0.3}\ d^{2.7}$	1.99		$s^{1.3}\ p^{0.0}\ d^{98.7}$
				1.97		$s^{0.0}\ p^{0.0}\ d^{100}$
				1.88		$s^{0.6}\ p^{0.0}\ d^{99.4}$

Table S4. NBO analysis of Au_2BO^- C_{2v} ($^1A_1$) structure V at the B3LYP/Au/Stuttgart /B,O/aug-cc-pvTZ level of theory.

	Natural Charge, |e|			Natural Configuration		
O1	-0.93			$2s^{1.75}\ 2p^{5.15}\ 3p^{0.01}3d^{0.03}$		
B2	0.49			$2s^{0.80}\ 2p^{1.66}\ 3s^{0.01}\ 4p^{0.02}\ 4f^{0.01}$		
Au3	-0.28			$6s^{1.46}\ 5d^{9.81}\ 7s^{0.01}$		
Au4	-0.28			$6s^{1.46}\ 5d^{9.81}\ 7s^{0.01}$		
Bonding				Lone Pairs		
Occ.	Center	%	Hybridization, %	Occ.	Center	Hybridization
2.00	O1	80.7	$s^{63.5}\ p^{35.8}\ d^{0.8}$	1.98	O1	$s^{36.4}\ p^{63.3}\ d^{0.3}$
	B2	19.3	$s^{35.4}\ p^{64.5}\ d^{0.1}$	2.00	Au3	$s^{0.0}\ p^{0.0}\ d^{100}$
2.00	O1	80.9	$s^{0.0}\ p^{99.6}\ d^{0.4}$	2.00		$s^{0.0}\ p^{0.0}\ d^{100}$
	B2	19.1	$s^{0.0}\ p^{99.7}\ d^{0.3}$	2.00		$s^{19.6}\ p^{0.0}\ d^{80.4}$
1.92	O1	86.8	$s^{0.0}\ p^{99.8}\ d^{0.3}$	1.98		$s^{0.0}\ p^{0.0}\ d^{100}$
	B2	13.2	$s^{0.0}\ p^{79.8}\ d^{10.1}\ f^{10.1}$	1.97		$s^{0.0}\ p^{0.0}\ d^{100}$
1.74	B2	26.6	$s^{31.9}\ p^{40.6}\ d^{12.3}\ f^{15.2}$	2.00	Au3	$s^{0.0}\ p^{0.0}\ d^{100}$
	Au3	73.4	$s^{79.8}\ p^{0.0}\ d^{20.1}\ f^{0.0}$	2.00		$s^{0.0}\ p^{0.0}\ d^{100}$
1.74	B2	26.6	$s^{31.9}\ p^{40.6}\ d^{12.3}\ f^{15.2}$	2.00		$s^{19.6}\ p^{0.0}\ d^{80.4}$
	Au4	73.4	$s^{79.8}\ p^{0.0}\ d^{20.1}\ f^{0.0}$	1.98		$s^{0.0}\ p^{0.0}\ d^{100}$
				1.97		$s^{0.0}\ p^{0.0}\ d^{100}$

Table S5. NBO analysis of Au_2BO^- C_{2v} ($^1A_1$) second-order saddle point, where $7a_1$ LUMO+1 of Au_2BO^+ C_{2v} ($^1A_1$) is occupied instead of $5b_2$ LUMO (B3LYP/Au/Stuttgart /B,O/aug-cc-pvTZ level of theory).

	Natural Charge, |e|			Natural Configuration		
O1	-1.03			$2s^{1.78}\ 2p^{5.22}\ 3d^{0.03}$		
B2	0.07			$2s^{1.55}\ 2p^{1.31}\ 3s^{0.04}\ 3p^{0.02}\ 4p^{0.01}$		
Au3	-0.02			$6s^{1.02}\ 5d^{9.95}\ 6p^{0.04}\ 7p^{0.01}$		
Au4	-0.02			$6s^{1.02}\ 5d^{9.95}\ 6p^{0.04}\ 7p^{0.01}$		
Bonding				Lone Pairs		
Occ.	Center	%	Hybridization, %	Occ.	Center	Hybridization
2.00	O1	85.1	$s^{0.0}\ p^{99.6}\ d^{0.4}$	1.99	O1	$s^{39.1}\ p^{60.6}\ d^{0.3}$
	B2	14.9	$s^{0.0}\ p^{99.7}\ d^{0.3}$	2.00	Au3	$s^{0.0}\ p^{0.0}\ d^{100}$
2.00	O1	82.2	$s^{60.8}\ p^{38.5}\ d^{0.8}$	2.00		$s^{0.9}\ p^{0.0}\ d^{99.1}$
	B2	17.8	$s^{26.9}\ p^{73.0}\ d^{0.1}$	2.00		$s^{0.0}\ p^{0.0}\ d^{100}$
2.00	O1	84.8	$s^{0.0}\ p^{99.6}\ d^{0.4}$	2.00		$s^{0.1}\ p^{0.0}\ d^{99.8}$
	B2	15.2	$s^{0.0}\ p^{99.7}\ d^{0.3}$	1.99		$s^{2.5}\ p^{0.0}\ d^{97.4}$
1.97	Au3	50	$s^{95.8}\ p^{0.6}\ d^{3.6}$	2.00	Au4	$s^{0.0}\ p^{0.0}\ d^{100}$
	Au4	50	$s^{95.8}\ p^{0.6}\ d^{3.6}$	2.00		$s^{0.9}\ p^{0.0}\ d^{99.1}$
				2.00		$s^{0.0}\ p^{0.0}\ d^{100}$
				2.00		$s^{0.1}\ p^{0.0}\ d^{99.8}$
				1.99		$s^{2.5}\ p^{0.0}\ d^{97.4}$
				1.92	B2	$s^{76.1}\ p^{23.9}$

Table S6. NBO analysis of Au_2BO^- $C_{\infty v}$ ($^1\Sigma^+$) structure IV at the B3LYP/Au/Stuttgart /B,O/aug-cc-pvTZ level of theory.

	Natural Charge, |e|			Natural Configuration		
O1	-0.94			$2s^{1.75}\ 2p^{5.15}\ 3d^{0.03}$		
B2	0.52			$2s^{1.00}\ 2p^{1.44}\ 4s^{0.02}\ 4p^{0.02}$		
Au3	0.06			$6s^{1.16}\ 5d^{9.77}\ 7p^{0.01}$		
Au4	-0.64			$6s^{1.69}\ 5d^{9.94}$		
Bonding				Lone Pairs		
Occ.	Center	%	Hybridization, %	Occ.	Center	Hybridization
2.00	O1	79.9	$s^{59.6}\ p^{39.7}\ d^{0.7}$	1.98	O1	$s^{40.3}\ p^{59.5}\ d^{0.2}$
	B2	20.1	$s^{39.2}\ p^{60.7}\ d^{0.1}$	2.00	Au3	$s^{0.0}\ p^{0.0}\ d^{100}$
2.00	O1	83.4	$s^{0.0}\ p^{99.6}\ d^{0.4}$	2.00		$s^{0.0}\ p^{0.0}\ d^{100}$
	B2	16.6	$s^{0.0}\ p^{99.8}\ d^{0.2}$	2.00		$s^{13.2}\ p^{0.0}\ d^{86.7}$
2.00	O1	83.4	$s^{0.0}\ p^{99.6}\ d^{0.4}$	1.95		$s^{0.0}\ p^{0.0}\ d^{100}$
	B2	16.6	$s^{0.0}\ p^{99.8}\ d^{0.2}$	1.95		$s^{0.0}\ p^{0.0}\ d^{100}$
2.00	B2	58.2	$s^{60.4}\ p^{39.2}\ d^{0.2}\ f^{0.2}$	2.00	Au4	$s^{0.0}\ p^{0.0}\ d^{100}$
	Au3	41.8	$s^{86.7}\ p^{0.1}\ d^{13.2}$	2.00		$s^{0.0}\ p^{0.0}\ d^{100}$
0.34*	B2	41.8	$s^{60.4}\ p^{39.2}\ d^{0.2}\ f^{0.2}$	2.00		$s^{14.1}\ p^{0.0}\ d^{85.9}$
	Au3	58.2	$s^{86.7}\ p^{0.1}\ d^{13.2}$	2.00		$s^{0.0}\ p^{0.0}\ d^{100}$
				2.00		$s^{0.0}\ p^{0.0}\ d^{100}$
				1.64		$s^{85.7}\ p^{0.1}\ d^{14.2}$

* - low-occupancy bonding orbitals produced during NBO analysis.

Table S7. NBO analysis of Au_3BO C_{2v} ($^1A_1$) at the geometry of Au_3BO^- C_{2v} ($^2B_2$) structure IV (B3LYP/Au/Stuttgart /B,O/aug-cc-pvTZ level of theory).

	Natural Charge, |e|			Natural Configuration		
O1	-0.85			$2s^{1.75}\ 2p^{5.06}\ 3d^{0.03}$		
B2	0.58			$2s^{0.90}\ 2p^{1.48}\ 3s^{0.01}\ 4p^{0.02}$		
Au3	0.01			$6s^{1.17}\ 5d^{9.78}\ 6d^{0.02}$		
Au4	0.13			$6s^{0.92}\ 5d^{9.95}\ 6d^{0.01}$		
Au5	0.13			$6s^{0.92}\ 5d^{9.95}\ 6d^{0.01}$		
Bonding				Lone Pairs		
Occ.	Center	%	Hybridization, %	Occ.	Center	Hybridization
2.00	O1	79.4	$s^{57.6}\ p^{41.7}\ d^{0.7}$	1.98	O1	$s^{42.3}\ p^{57.5}\ d^{0.3}$
	B2	20.6	$s^{41.0}\ p^{58.9}\ d^{0.1}$	2.00	Au3	$s^{0.0}\ p^{0.0}\ d^{100}$
2.00	O1	81.9	$s^{0.0}\ p^{99.6}\ d^{0.4}$	2.00		$s^{0.2}\ p^{0.0}\ d^{99.8}$
	B2	18.1	$s^{0.0}\ p^{99.8}\ d^{0.2}$	1.99		$s^{11.3}\ p^{0.0}\ d^{88.7}$
2.00	O1	81.6	$s^{0.0}\ p^{99.6}\ d^{0.4}$	1.97		$s^{0.0}\ p^{0.0}\ d^{100}$
	B2	18.4	$s^{0.0}\ p^{99.8}\ d^{0.2}$	1.93		$s^{0.0}\ p^{0.0}\ d^{100}$
2.00	B2	53.9	$s^{58.2}\ p^{41.3}\ d^{0.2}\ f^{0.3}$	2.00	Au4	$s^{0.0}\ p^{0.0}\ d^{100}$
	Au3	46.1	$s^{86.7}\ p^{0.1}\ d^{13.2}$	2.00		$s^{0.7}\ p^{0.0}\ d^{99.3}$
1.76	Au3	41.8	$s^{60.4}\ p^{39.2}\ d^{0.2}\ f^{0.2}$	2.00		$s^{0.0}\ p^{0.0}\ d^{100}$
	Au4	58.2	$s^{88.3}\ p^{0.1}\ d^{11.6}$	2.00		$s^{1.2}\ p^{0.0}\ d^{98.8}$
				1.97		$s^{0.3}\ p^{0.0}\ d^{99.7}$
				2.00	Au5	$s^{0.0}\ p^{0.0}\ d^{100}$
				2.00		$s^{0.7}\ p^{0.0}\ d^{99.3}$
				2.00		$s^{0.0}\ p^{0.0}\ d^{100}$
				2.00		$s^{1.2}\ p^{0.0}\ d^{98.8}$
				1.97		$s^{0.3}\ p^{0.0}\ d^{99.7}$

Table S8. NBO analysis of Au_3BO^- C_{2v} ($^2B_2$) at the B3LYP/Au/Stuttgart /B,O/aug-cc-pvTZ level of theory.

	Natural Charge, |e|			Natural Configuration		
O1	-0.91			$2s^{1.75}\ 2p^{5.12}\ 3d^{0.03}$		
B2	0.55			$2s^{0.95}\ 2p^{1.46}\ 3s^{0.01}\ 3p^{0.02}$		
Au3	0.07			$6s^{1.12}\ 5d^{9.79}\ 6p^{0.01}\ 7s^{0.01}\ 6d^{0.01}$		
Au4	-0.36			$6s^{1.39}\ 5d^{9.94}\ 6p^{0.01}\ 7s^{0.01}$		
Au5	-0.36			$6s^{1.39}\ 5d^{9.94}\ 6p^{0.01}\ 7s^{0.01}$		
Bonding (α)				Lone Pairs (α)		
Occ.	Center	%	Hybridization, %	Occ.	Center	Hybridization
1.00	O1	79.8	$s^{59.2}\ p^{40.1}\ d^{0.7}$	0.99	O1	$s^{40.7}\ p^{59.0}\ d^{0.3}$
	B2	20.2	$s^{39.8}\ p^{60.2}\ d^{0.1}$	1.00	Au3	$s^{0.0}\ p^{0.0}\ d^{100}$
1.00	O1	83.2	$s^{0.0}\ p^{99.6}\ d^{0.4}$	1.00		$s^{0.2}\ p^{0.0}\ d^{99.8}$
	B2	16.8	$s^{0.0}\ p^{99.8}\ d^{0.2}$	1.00		$s^{11.3}\ p^{0.0}\ d^{88.7}$
1.00	O1	82.8	$s^{0.0}\ p^{99.6}\ d^{0.4}$	0.98		$s^{0.0}\ p^{0.0}\ d^{100}$
	B2	17.2	$s^{0.0}\ p^{99.8}\ d^{0.2}$	0.98		$s^{0.0}\ p^{0.0}\ d^{100}$
1.00	B2	56.5	$s^{59.7}\ p^{39.9}\ d^{0.2}\ f^{0.3}$	1.00	Au4	$s^{3.1}\ p^{0.0}\ d^{96.9}$
	Au3	43.5	$s^{88.5}\ p^{0.1}\ d^{11.4}$	1.00		$s^{0.0}\ p^{0.0}\ d^{100}$
0.12*	B2	43.5	$s^{59.7}\ p^{40.0}\ d^{0.2}\ f^{0.3}$	1.00		$s^{0.0}\ p^{0.0}\ d^{100}$
	Au3	56.5	$s^{88.5}\ p^{0.1}\ d^{11.4}$	1.00		$s^{2.7}\ p^{0.0}\ d^{97.3}$
				1.00		$s^{8.6}\ p^{0.0}\ d^{91.4}$
				0.92		$s^{85.4}\ p^{0.0}\ d^{14.5}$
				1.00	Au5	$s^{3.1}\ p^{0.0}\ d^{96.9}$
				1.00		$s^{0.0}\ p^{0.0}\ d^{100}$
				1.00		$s^{0.0}\ p^{0.0}\ d^{100}$
				1.00		$s^{2.7}\ p^{0.0}\ d^{97.3}$
				1.00		$s^{8.6}\ p^{0.0}\ d^{91.4}$
				0.92		$s^{85.4}\ p^{0.0}\ d^{14.5}$
Bonding (β)				Lone Pairs (β)		
1.00	O1	79.7	$s^{59.2}\ p^{40.1}\ d^{0.7}$	0.99	O1	$s^{40.7}\ p^{59.0}\ d^{0.3}$
	B2	20.3	$s^{39.8}\ p^{60.2}\ d^{0.1}$	1.00	Au3	$s^{0.0}\ p^{0.0}\ d^{100}$
1.00	B2	57.1	$s^{59.9}\ p^{39.7}\ d^{0.2}\ f^{0.3}$	1.00		$s^{0.1}\ p^{0.0}\ d^{99.9}$
	Au3	42.9	$s^{88.6}\ p^{0.1}\ d^{11.3}$	1.00		$s^{11.2}\ p^{0.0}\ d^{88.8}$
0.88	Au4	50	$s^{94.5}\ p^{0.9}\ d^{4.6}$	0.98		$s^{0.0}\ p^{0.0}\ d^{100}$
	Au5	50	$s^{94.5}\ p^{0.9}\ d^{4.6}$	0.97		$s^{0.0}\ p^{0.0}\ d^{100}$
0.14*	B2	42.9	$s^{59.9}\ p^{39.7}\ d^{0.2}\ f^{0.3}$	1.00	Au4	$s^{1.2}\ p^{0.0}\ d^{98.8}$
	Au3	57.1	$s^{88.6}\ p^{0.1}\ d^{11.3}$	1.00		$s^{0.0}\ p^{0.0}\ d^{100}$
				1.00		$s^{0.0}\ p^{0.0}\ d^{100}$
0.83**	O1		$s^{0.0}\ p^{99.6}\ d^{0.4}$	1.00		$s^{2.1}\ p^{0.0}\ d^{97.9}$
0.19**	B2		$s^{0.0}\ p^{99.9}\ d^{0.1}$	0.98		$s^{1.1}\ p^{0.0}\ d^{98.9}$
0.83**	O1		$s^{0.0}\ p^{99.6}\ d^{0.4}$	1.00	Au5	$s^{1.2}\ p^{0.0}\ d^{98.8}$
0.19**	B2		$s^{0.0}\ p^{99.9}\ d^{0.1}$	1.00		$s^{0.0}\ p^{0.0}\ d^{100}$
				1.00		$s^{0.0}\ p^{0.0}\ d^{100}$
				1.00		$s^{2.1}\ p^{0.0}\ d^{97.9}$
				0.98		$s^{1.1}\ p^{0.0}\ d^{98.9}$

* - low-occupancy bonding orbitals produced during NBO analysis.

** - in the original NBO output these orbitals are regarded as low-occupation lone pairs. It is possible though, that they actually represent two B-O π-bonds.

Table S9. NBO analysis of Au_3BO^- C_s ($^2A'$) at the B3LYP/Au/Stuttgart /B,O/aug-cc-pvTZ level of theory.

	Natural Charge, |e|	Natural Configuration
O1	-0.92	$2s^{1.75}\ 2p^{5.13}\ 3d^{0.03}$
B2	0.54	$2s^{0.97}\ 2p^{1.44}\ 3s^{0.02}\ 3p^{0.02}$
Au3	0.02	$6s^{1.19}\ 5d^{9.78}\ 6p^{0.01}\ 6d^{0.01}$
Au4	-0.32	$6s^{1.37}\ 5d^{9.93}\ 6p^{0.01}\ 6d^{0.01}$
Au5	-0.33	$6s^{1.36}\ 5d^{9.96}\ 7s^{0.01}$

Bonding (α)				Lone Pairs (α)		
Occ.	Center	%	Hybridization, %	Occ.	Center	Hybridization
1.00	O1	79.9	$s^{59.7}\ p^{39.6}\ d^{0.7}$	1.00	O1	$s^{40.2}\ p^{59.5}\ d^{0.3}$
	B2	20.1	$s^{38.9}\ p^{61.0}\ d^{0.1}$	1.00	Au3	$s^{0.0}\ p^{0.0}\ d^{100}$
1.00	O1	82.7	$s^{0.0}\ p^{99.6}\ d^{0.4}$	1.00		$s^{0.0}\ p^{0.0}\ d^{100}$
	B2	17.3	$s^{0.0}\ p^{99.8}\ d^{0.2}$	1.00		$s^{12.4}\ p^{0.0}\ d^{87.6}$
1.00	O1	82.7	$s^{0.0}\ p^{99.6}\ d^{0.4}$	0.98		$s^{0.0}\ p^{0.0}\ d^{100}$
	B2	17.3	$s^{0.0}\ p^{99.8}\ d^{0.2}$	0.98		$s^{0.0}\ p^{0.0}\ d^{100}$
1.00	B2	60.0	$s^{60.9}\ p^{38.7}\ d^{0.2}$	1.00	Au4	$s^{0.2}\ p^{0.0}\ d^{99.8}$
	Au3	40.0	$s^{87.5}\ p^{0.1}\ d^{12.4}$	1.00		$s^{0.0}\ p^{0.0}\ d^{100}$
0.28*	B2	40.0	$s^{60.9}\ p^{38.7}\ d^{0.2}\ f^{0.2}$	1.00		$s^{9.9}\ p^{0.0}\ d^{90.1}$
	Au3	60.0	$s^{87.5}\ p^{0.1}\ d^{12.4}$	1.00		$s^{0.0}\ p^{0.0}\ d^{100}$
				1.00		$s^{0.0}\ p^{0.0}\ d^{100}$
				0.76		$s^{89.4}\ p^{0.3}\ d^{10.3}$
				1.00	Au5	$s^{0.0}\ p^{0.0}\ d^{100}$
				1.00		$s^{0.0}\ p^{0.0}\ d^{100}$
				1.00		$s^{12.7}\ p^{0.0}\ d^{87.3}$
				1.00		$s^{0.0}\ p^{0.0}\ d^{100}$
				1.00		$s^{0.0}\ p^{0.0}\ d^{100}$
				0.92		$s^{87.2}\ p^{0.0}\ d^{12.8}$

Bonding (β)				Lone Pairs (β)		
1.00	O1	80.1	$s^{52.7}\ p^{46.7}\ d^{0.6}$	0.99	O1	$s^{41.2}\ p^{58.6}\ d^{0.2}$
	B2	19.9	$s^{36.4}\ p^{63.5}\ d^{0.1}$	1.00	Au3	$s^{0.0}\ p^{0.0}\ d^{100}$
1.00	O1	83.3	$s^{0.0}\ p^{99.6}\ d^{0.4}$	1.00		$s^{0.0}\ p^{0.0}\ d^{100}$
	B2	16.7	$s^{0.0}\ p^{99.8}\ d^{0.2}$	1.00		$s^{14.0}\ p^{0.0}\ d^{86.0}$
1.00	O1	82.9	$s^{6.0}\ p^{93.6}\ d^{0.4}$	0.98		$s^{0.0}\ p^{0.0}\ d^{100}$
	B2	17.1	$s^{4.5}\ p^{95.3}\ d^{0.2}$	0.98		$s^{0.0}\ p^{0.0}\ d^{100}$
0.99	B2	52.7	$s^{58.7}\ p^{40.9}\ d^{0.2}$	1.00	Au4	$s^{0.0}\ p^{0.0}\ d^{100}$
	Au3	47.3	$s^{86.0}\ p^{0.1}\ d^{14.0}$	1.00		$s^{0.0}\ p^{0.0}\ d^{100}$
0.97	Au4	58.5	$s^{95.6}\ p^{0.2}\ d^{4.2}$	1.00		$s^{3.9}\ p^{0.0}\ d^{96.1}$
	Au5	41.5	$s^{96.2}\ p^{0.2}\ d^{3.5}$	1.00		$s^{0.0}\ p^{0.0}\ d^{100}$
				0.98		$s^{0.0}\ p^{0.0}\ d^{100}$
				1.00	Au5	$s^{0.0}\ p^{0.0}\ d^{100}$
				1.00		$s^{0.0}\ p^{0.0}\ d^{100}$
				1.00		$s^{0.0}\ p^{0.0}\ d^{100}$
				1.00		$s^{1.2}\ p^{0.0}\ d^{98.8}$
				1.00		$s^{2.2}\ p^{0.0}\ d^{97.8}$

* - low-occupancy bonding orbitals produced during NBO analysis.