

# M@B<sub>9</sub> and M@B<sub>10</sub> molecular wheels containing planar nona- and deca-coordinate heavy group 11, 12, and 13 metals (M=Ag, Au, Cd, Hg, In, Tl)

MIAO ChangQing, GUO JinChang & LI SiDian<sup>†</sup>

Institute of Materials Sciences and Department of Chemistry, Xinzhou Teachers' University, Xinzhou 034000, China

**A density functional and *ab initio* theory investigation on M@B<sub>9</sub> and M@B<sub>10</sub> molecular wheels containing planar nona- and deca-coordinate heavy group 11, 12 and 13 metals (M=Ag, Au, Cd, Hg, In, Tl) has been performed. These unusual clusters all prove to be true minima on the potential energy surfaces of the systems and  $\sigma+\pi$  double aromatic in nature. The first two vertical one-electron detachment energies of M@B<sub>10</sub><sup>-</sup> (M=Ag, Au) anions and first two ionization potentials of M@B<sub>9</sub> (M=Ag, Au) and M@B<sub>10</sub> (M=Cd, Hg) neutrals were calculated to aid future experiments. The cluster complexes designed in this work may expand the domain of planar hyper-coordinate elements to include heavy group 11, 12, and 13 metals and serve as interesting candidates to be targeted in experiments.**

planar hyper-coordinate, heavy metals, density functional theory, *ab initio*, geometries, electronic structures

## 1 Introduction

The discovery of planar or quasi-planar small boron clusters B<sub>n</sub> and B<sub>n</sub><sup>-</sup> (n=3–16) in a series of joint photo-electron spectroscopy (PES) and *ab initio* theory investigations by Wang and coworkers has attracted great attention in chemistry and materials science<sup>[1–5]</sup>. Planar B<sub>n</sub> rings were shown to be effective ligands to hyper-coordinate various elements in the periodical table to form elegant molecular wheels, including the planar hexa-, hepta-, and octa-coordinate B in C<sub>6v</sub> B@B<sub>6</sub><sup>-[3]</sup>, C<sub>2v</sub> B@B<sub>7</sub><sup>-</sup>, and D<sub>8h</sub> B@B<sub>8</sub><sup>-[4]</sup> characterized in PES measurements, planar octa-, nona-, and deca-coordinate group 14 elements in D<sub>8h</sub> Si@B<sub>8</sub><sup>[6]</sup>, D<sub>9h</sub> Ge@B<sub>9</sub><sup>+</sup>, and D<sub>10h</sub> Sn@B<sub>10</sub><sup>2+[7]</sup> designed at density functional theory (DFT), and planar octa- and nona-coordinate first-row transition metals in D<sub>nh</sub> M@B<sub>n</sub> (n=8, 9; M=Fe, Co, Ni) predicted at DFT<sup>[8,9]</sup>. Our group also proposed a universal structural pattern for planar hyper-coordinate Si in B<sub>n</sub>H<sub>2</sub>Si which contained fan-shaped B<sub>n</sub> frames as ligands<sup>[10]</sup>, and predicted the possibility of planar octa- and nona-coor-

dinate group 13 elements centered in D<sub>nh</sub> M@B<sub>8</sub><sup>-</sup> and M@B<sub>9</sub> wheels (M=Al, Ga) at DFT and *ab initio* levels<sup>[11]</sup>. However, to the best of our knowledge, there have been no investigations on planar nona- or deca-coordinate heavy group 11, 12 and 13 metals reported to date. In this work, we aim to design a series of planar M@B<sub>n</sub> molecular wheels (n=9, 10) at DFT and *ab initio* theory levels which contain heavy transition metals (M=Ag, Au, Cd, Hg) and heavy group 13 elements (M=In, Tl).

It is well known that to host a planar hyper-coordinate metal atom (M) at the center of a B<sub>n</sub> ring stably, the less electronegative central atom M and surrounding ring B<sub>n</sub> must match both geometrically and electronically. The M@B<sub>n</sub> complexes thus formed usually possess the delocalized  $\pi$  molecular orbitals (MOs) lying higher in energy than their more effectively overlapped in-plane

Received November 3, 2008; accepted November 25, 2008

doi: 10.1007/s11426-009-0086-z

<sup>†</sup>Corresponding author (email: [mailto:lisidian@yahoo.com](mailto:mailto:lisidian@yahoo.com))

Supported by the National Natural Science Foundation of China (Grant No. 20873117)

radial  $\sigma$  counterparts<sup>[10,12–15]</sup>. The results obtained in this work indicate that planar wheel-shaped  $M@B_9^{2-}$ ,  $M@B_9$ ,  $M@B_{10}^-$  ( $M=Ag, Au$ ),  $M@B_{10}$  ( $M=Cd, Hg$ ), and  $M@B_{10}^+$  ( $M=In, Tl$ ) clusters well follow these principles and all turn out to be true minima on the potential energy surfaces of the systems. They prove to be  $\sigma + \pi$  double aromatic in nature and may serve as interesting candidates to be targeted in future experiments.

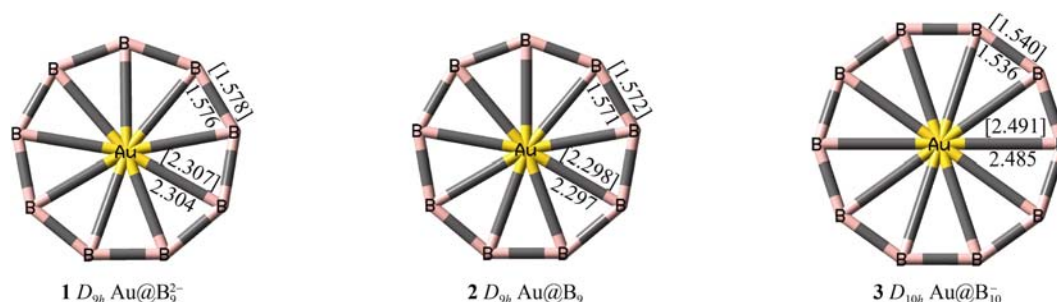
## 2 Theoretical methodology

Structural optimizations, frequency analyses, and natural bonding orbital analyses were performed with the B3LYP<sup>[16,17]</sup> and MP2(full)<sup>[18,19]</sup> procedures implemented in Gaussian 03 program<sup>[20]</sup>, using the basis of aug-cc-pvtz<sup>[21]</sup> for B and aug-cc-pvtz-pp with relativistic pseudo-potentials<sup>[22–25]</sup> for heavy metals. The first two vertical one-electron detachment energies of the anions and neutrals were calculated at OVGF(full) level<sup>[26–28]</sup> and the nucleus independent chemical shifts (NICS)<sup>[29]</sup> obtained with the ghost atoms lying 1.0 Å above the

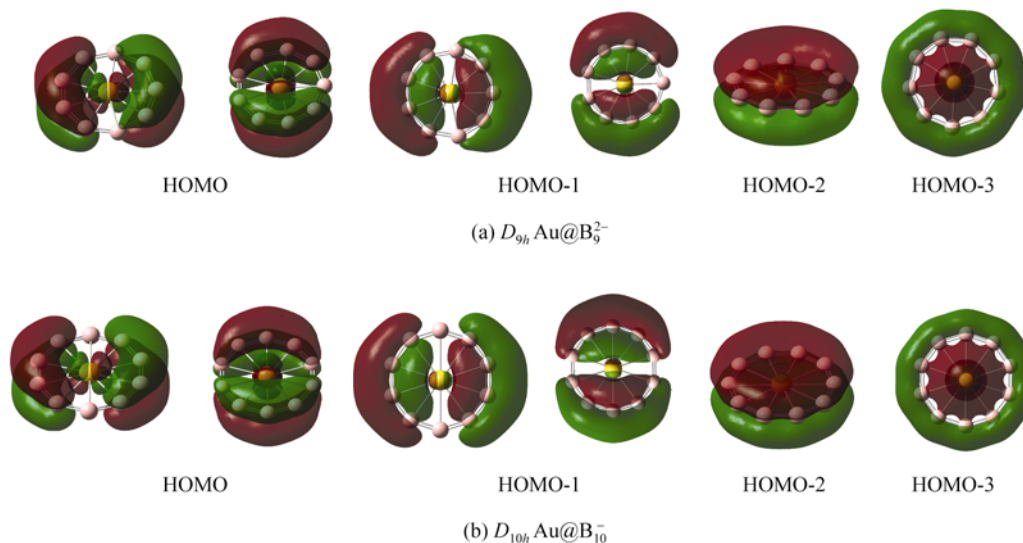
$M@B_n$  planes along the  $n$ th-fold molecular axes (NICS(1)) at B3LYP. The calculated geometrical and electronic properties of the cluster complexes are summarized in Table 1 and, as examples, the structures of  $D_{9h} Au@B_9^{2-}$ ,  $D_{9h} Au@B_9$ ,  $D_{10h} Au@B_{10}^-$  are depicted in Figure 1 and the pictures of the delocalized  $\pi$  and  $\sigma$  MOs of  $D_{9h} Au@B_9^{2-}$  and  $D_{10h} Au@B_{10}^-$  demonstrated in Figure 2.

## 3 Results and discussion

As heavy transition metals, Ag and Au ( $(n-1)d^{10}ns^1$ ) and Cd and Hg ( $(n-1)d^{10}ns^2$ ) all have fully filled  $(n-1)d$  atomic orbitals. Group 13 elements In and Tl ( $(n-1)d^{10}ns^2np^1$ ) possess one more  $np$  electron than their transition metal neighbors. The fully filled  $(n-1)d$  atomic orbitals of these heavy metals greatly simplify the spin multiplicities of the  $M@B_n$  clusters ( $M=Ag, Au, Cd, Hg, In, Tl$ ) which turn out to possess singlet states in most cases except triplet  $Ag@B_9$  and  $Au@B_9$  neutrals.



**Figure 1** Wheel-shaped structures of singlet  $D_{9h} Au@B_9^{2-}$ , triplet  $D_{9h} Au@B_9$ , and singlet  $D_{10h} Au@B_{10}^-$  with bond lengths indicated in Å at B3LYP and [MP2] levels.



**Figure 2** Delocalized MOs of (a)  $D_{9h} Au@B_9^{2-}$  and (b)  $D_{10h} Au@B_{10}^-$ .

A B<sub>9</sub> ring proved to provide a suitable cavity to host a planar nona-coordinate Au at its center in both singlet  $D_{9h}$  Au@B<sub>9</sub><sup>2-</sup> (**1**) and triplet  $D_{9h}$  Au@B<sub>9</sub> (**2**) which were true minima of the systems (Figure 1 and Table 1). However, it was slightly too small for a Ag atom: both singlet  $D_{9h}$  Ag@B<sub>9</sub><sup>2-</sup> and triplet  $D_{9h}$  Ag@B<sub>9</sub> turned out to be transition states with one small imaginary vibrational frequency corresponding to the perpendicular vibration of the central Ag atom along the ninth-fold molecular axis. Relaxations in this imaginary vibrational mode leads to the slightly off-planed C<sub>9v</sub> Ag@B<sub>9</sub><sup>2-</sup> (**4**) and C<sub>9v</sub> Ag@B<sub>9</sub> (**5**) (Table 1). Nevertheless, the energy differences between the C<sub>9v</sub> minima and their  $D_{9h}$  transition states (0.0001 eV for Ag@B<sub>9</sub><sup>2-</sup> and 0.03 eV for Ag@B<sub>9</sub>) are well within the accuracies of the theoretical methods used in this work and much smaller than the zero-point energies of the corresponding clusters. We are inclined to consider them energetically degenerate with practically the same planar wheel-shaped structures.

Perfect planar deca-coordinate group 11, 12, and 13 heavy metals can be achieved in a universal pattern by coordinating them with a B<sub>10</sub> ring to form  $D_{10h}$  M@B<sub>10</sub><sup>-0/+</sup> molecular wheels (Table 1). These high symmetry clusters with different molecular charges all possess the same number of valence electrons as Sn@B<sub>10</sub><sup>2+7</sup> and prove to be true minima on the potential surfaces of the systems without imaginary vibrational frequencies (Table 1). They have the molecular wheel radii (spokes) of  $r_{M-B}=2.48-2.53$  Å and the periphery B—B bond lengths of  $r_{B-B}=1.53-1.57$  Å at B3LYP and MP2(full) levels. As shown in Figure 1, B3LYP and MP2(full) methods produced practically the same bond parameters for these clusters.

Orbital analyses help to understand the electronic stabilities of these clusters. As shown in Figure 2(a), the singlet  $D_{9h}$  Au@B<sub>9</sub><sup>2-</sup> dianion (**1**) possesses three fully occupied delocalized π MOs (the doubly degenerate HOMOs and HOMO-2) with 6 electrons and three fully occupied delocalized radial σ MOs (the degenerate HOMO-1 and HOMO-3) with 6 electrons. This orbital occupation conforms to the 4*n*+2 rule for π and σ aromaticity separately and renders π+σ double aromaticity to Au@B<sub>9</sub><sup>2-</sup> dianion (**1**). Removing two electrons from the degenerate HOMOs of  $D_{9h}$  Au@B<sub>9</sub><sup>2-</sup> produces the triplet  $D_{9h}$  Au@B<sub>9</sub> neutral (**2**) which has two unpaired electrons with parallel spins in the degenerate π -HOMOs.

$D_{9h}$  Au@B<sub>9</sub> (**2**) possesses 4π electrons and 6 σ electrons and therefore follows the 4*n* π aromatic rule for triplet π components and 4*n*+2 aromatic rule for singlet σ components, respectively, rendering π+σ double aromaticity to the triplet Au@B<sub>9</sub> neutral. As clearly indicated in Figure 2(b), singlet  $D_{10h}$  Au@B<sub>10</sub><sup>-</sup> (**3**) also has three well-defined delocalized π MOs (the degenerate HOMOs and HOMO-2) and the three delocalized σ MOs (the degenerate HOMO-1 and HOMO-3). This MO occupation makes  $D_{10h}$  Au@B<sub>10</sub><sup>-</sup> π+σ double aromatic, too. The delocalized π and σ MOs help to maintain the planar wheel structures of these clusters. Orbital analyses indicate that all the M@B<sub>*n*</sub> dianions, anions, neutrals, and cations tabulated in Table 1 are π+σ double aromatic in nature. This judgment is fully supported by the calculated negative NICS(1) values ranging from -29.3 to -54.4 ppm for all the cluster complexes studied in this work (Table 1). Covalent bonding interactions between the (*n*-1)d atomic orbitals (AOs) of the transition metal center M and the 2p AOs of the periphery B atoms also make contribution to stabilize these complexes. For instances, both the bonding HOMO-8 and HOMO-9 of  $D_{9h}$  B<sub>9</sub>Au<sup>2-</sup> (**1**) and  $D_{10h}$  B<sub>10</sub>Au<sup>-</sup> (**3**) mainly involve the AO overlaps between Au 5d and B 2p (see Supporting Information).

NBO analyses indicate that the planar hyper-coordinate metal centers in M@B<sub>9</sub><sup>2-</sup>, M@B<sub>9</sub>, and M@B<sub>10</sub><sup>-</sup> (M=Ag, Au) possess the total Wiberg bond indexes of  $WBI_M=0.99-1.58$  and carry the positive atomic charges of  $q_M=+0.91-+1.02$  |e|. The corresponding values of  $D_{10h}$  Cd@B<sub>10</sub> (**7**) and  $D_{10h}$  Hg@B<sub>10</sub> (**8**) neutrals are between  $WBI_M=0.95-1.33$  and  $q_M=+1.41-+1.58$  |e|. The total bonding orders of the metal centers approximately equal to the sums of individual M-B bonds. For examples, in  $D_{9h}$  Au@B<sub>9</sub><sup>2-</sup>,  $D_{10h}$  Au@B<sub>10</sub><sup>-</sup>,  $D_{10h}$  Tl@B<sub>10</sub><sup>-</sup>, a single M-B interaction has the bond order of 0.17, 0.15, and 0.26, respectively. Obviously, the *ns*<sup>1</sup> and *ns*<sup>2</sup> valence electrons of heavy group 11 and 12 metals have been mostly transferred to their electron-deficient B<sub>*n*</sub> ligands (*n*=9,10) in the corresponding anions and neutrals. Heavy group 13 metals in In@B<sub>10</sub><sup>+</sup> (**9**) and Tl@B<sub>10</sub><sup>+</sup> (**10**), on the other hand, possess the total bond orders of  $WBI_M=2.55-2.60$  and atomic charges of  $q_M=+1.20-+1.32$  |e|. Their *ns*<sup>2</sup>*np*<sup>1</sup> valence electrons are only partially transferred to their electron-deficient B<sub>10</sub> ligands and the bonding interactions between heavy group 13

**Table 1** Calculated bond lengths ( $r_{M-B}$  and  $r_{B-B}/\text{\AA}$ ), HOMO-LUMO energy gaps ( $\Delta E_{\text{gap}}/\text{eV}$ ), natural atomic charges of the hyper-coordinate centers M ( $q_M/|e|$ ), total Wiberg bond indexes of M centers and the periphery B atoms ( $\text{WBI}_M$  and  $\text{WBI}_B$ ), the lowest vibrational frequencies ( $\nu_{\text{min}}/\text{cm}^{-1}$ ), NICS(1) values (NICS(1)/ppm), and the first two vertical one-electron detachment energies (VDEs/eV) (with pole-strengths greater than 0.85) of the  $M@B_n$  ( $n=9,10$ ) clusters obtained at B3LYP/B/aug-cc-pvtz/M/aug-cc-pvtz-pp

	$X@B_n$	$r_{M-B}$	$r_{B-B}$	$\Delta E_{\text{gap}}$	$q_M$	$\text{WBI}_M$	$\text{WBI}_B$	$\nu_{\text{min}}$	NICS(1)	VDEs
1	$D_{9h}$ Au@ $B_9^{2-}$	2.304	1.576	1.20	+0.93	1.58	3.79	+51	-53.3	
2	$D_{9h}$ Au@ $B_9(t)^{3-}$	2.297	1.571	2.61( $\alpha$ ) 2.51( $\beta$ )	+0.95	1.72	3.40	+48	-54.4	8.19, 9.01
3	$D_{10h}$ Au@ $B_{10}^-$	2.485	1.536	2.41	+0.91	1.50	3.70	+99	-49.6	3.70, 4.59
4	$C_{9v}$ Ag@ $B_9^{2-}$	2.302	1.572	1.43	+1.02	1.11	3.79	+14	-42.8	
5	$C_{9v}$ Ag@ $B_9(t)^{3-}$	2.332	1.562	2.96( $\alpha$ ) 2.19( $\beta$ )	+1.00	1.19	3.38	+70	-35.0	8.31, 8.89
6	$D_{10h}$ Ag@ $B_{10}^-$	2.487	1.537	2.61	+0.99	0.99	3.70	+90	-40.8	3.83, 4.63
7	$D_{10h}$ Cd@ $B_{10}$	2.500	1.545	2.84	+1.58	0.95	3.68	+58	-33.9	8.25, 8.96
8	$D_{10h}$ Hg@ $B_{10}$	2.504	1.548	2.69	+1.41	1.33	3.63	+65	-41.5	8.14, 9.04
9	$D_{10h}$ In@ $B_{10}^+$	2.513	1.553	2.95	+1.32	2.55	3.58	+56	-29.3	
10	$D_{10h}$ Tl@ $B_{10}^+$	2.528	1.562	2.82	+1.20	2.60	3.55	+27	-36.4	

a) (t) stands for triplet states. All the others are singlet.

metals and their  $B_{10}$  ligands appear to be mainly covalent. The transferred electrons from the hyper-coordinate metal centers to their  $B_n$  ligands are totally delocalized along the  $B_n$  rings in either  $\pi$  or  $\sigma$  MOs (Figure 2), partially satisfying the bonding requirements of the electron-deficient  $B_n$  ligands. Consequently, the periphery B atoms in these cluster wheels carry the negative atomic charges of  $q_B = -0.03 - 0.36 |e|$  and possess the total bond orders between  $\text{WBI}_B = 3.54 - 3.79$ . The periphery B—B bonds with the calculated bond orders of  $\text{WBI}_{B-B} = 1.37 - 1.52$  exhibit obvious double bond characteristics ( $\pi$  and  $\sigma$ ) in these clusters.

The first one-electron vertical detachment energies of the  $M@B_{10}^-$  anions lie considerably high, with the calculated VDEs of 3.83 eV for  $M = \text{Ag}$  and 3.70 eV for  $M = \text{Au}$ . The first ionization potentials (IPs) of the triplet  $M@B_9$  neutrals turn out to be  $\text{IP} = 8.31$  eV for  $M = \text{Ag}$  and 8.19 eV for  $M = \text{Au}$  and that of the singlet  $M@B_{10}$  neutrals have the corresponding values of  $\text{IP} = 8.25$  eV for  $M = \text{Cd}$  and  $\text{IP} = 8.14$  eV for  $M = \text{Hg}$ . The second VDEs of the anions and second IPs of the neutrals with the pole-strengths greater than 0.85 are also tabulated in

Table 1 to facilitate future spectroscopic studies. As indicated in Table 1, most cluster complexes studied in this work have the HOMO-LUMO gap values greater than 2.40 eV except  $\text{Ag}@B_9^{2-}$  and  $\text{Au}@B_9^{2-}$  dianions, providing further evidences to support their electronic stabilities.

## 4 Summary

We have presented a DFT and *ab initio* theory investigation on planar nona- and deca-coordinate heavy group 11, 12, and 13 metals centered in  $M@B_n$  molecular wheels ( $n=9,10$ ;  $M=\text{Ag}, \text{Au}, \text{Cd}, \text{Hg}, \text{In}, \text{Tl}$ ) in this work. These model clusters all prove to be true minima on the potential energy surfaces of the systems and  $\sigma + \pi$  double aromatic in nature. Similar to the situation in the well-known wheel-shaped  $D_{6h}$   $B_6C^{2-}$  and  $D_{7h}$   $B_7C$  [12,14,15], such high symmetry structures may be local minima on the potential surfaces of the systems and need to be chemically modified to further stabilize them. However, their unique geometrical and bonding characteristics make them interesting enough to be studied further both theoretically and experimentally.

- Sergeeva A P, Zubarev D Y, Zhai H J, Boldyrev A I, Wang L S. A photoelectron spectroscopic and theoretical study of  $B_{16}^-$  and  $B_{16}^{2-}$  An all-boron naphthalene. *J Am Chem Soc*, 2008, 130: 7244–7246[DOI]
- Alexandrova A N, Boldyrev A I, Zhai H J, Wang L S. All-boron aromatic clusters as potential new inorganic ligands and building blocks in chemistry. *Coord Chem Rev*, 2006, 250: 2811–2866[DOI]
- Alexandrova A N, Boldyrev A I, Zhai H J, Wang L S. Electronic structure, isomerism, and chemical bonding in  $B_7^-$  and  $B_7$ . *J Phys Chem A*, 2004, 108(16): 3509–3517
- Zhai H J, Wang L S, Alexandrova A N, Boldyrev A I. Hepta- and octacoordinate boron in molecular wheels of eight- and nine-atom boron clusters: Observation and confirmation. *Angew Chem Int Ed*, 2003, 42(48): 6004–6008[DOI]
- Zhai H J, Boggavarapu K, Li J, Wang L S. Hydrocarbon analogues of boron clusters-planarity, aromaticity and antiaromaticity. *Nature*, 2003, 2: 827–833[DOI]
- Minyaev R M, Griбанова T N, Starikov A G, Minkin V I. Octacoordinated main-group element centers in a planar cyclic  $B_8$  environment:

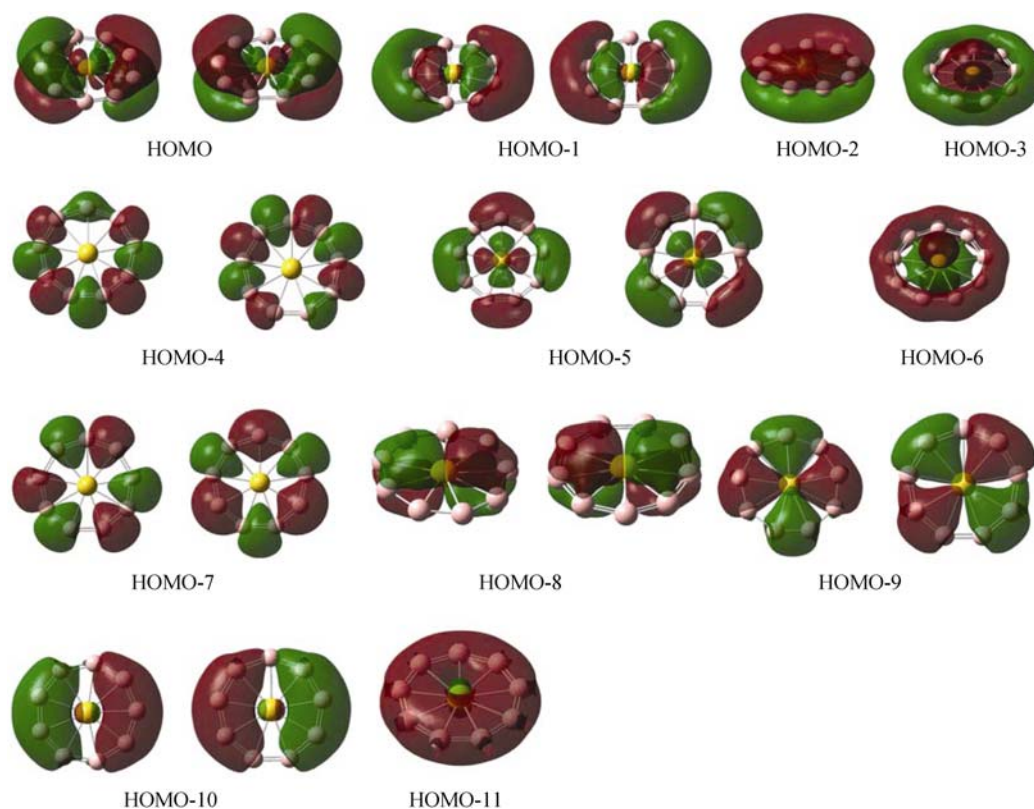
- An *ab initio* study. *Mendeleev Commun*, 2001, (6):1–2
- 7 Islas R, Heine T, Ito K, Schleyer P v R, Merino G. Boron rings enclosing planar hypercoordinate group 14 elements. *J Am Chem Soc*, 2007, 129(47): 14767–14774[DOI]
  - 8 Luo Q. Boron rings containing planar octa- and enneacoordinate cobalt, iron and nickel metal elements. *Sci China Ser B-Chem*, 2008, 51: 607–613[DOI]
  - 9 Luo Q. Theoretical observation of hexatomic molecules containing pentacoordinate planar carbon. *Sci China Ser B-Chem*, 2008, 51(11): 1030–1035[DOI]
  - 10 Li S D, Miao C Q, Guo J C, Ren G M. Planar tetra-, penta-, hexa-, hepta-, and octacoordinate silicons: a universal structural pattern. *J Am Chem Soc*, 2004, 126(49): 16227–16231
  - 11 Guo J C, Yao W Z, Li Z, Li S D. Planar or quasi-planar octa- and ennea-coordinate aluminum and gallium in boron rings. *Sci China Ser B-Chem*, 2009, 52(5): 566–570
  - 12 Exner K, Schleyer P V R. Planar hexacoordinate carbon: A viable possibility. *Science*, 2000, 290: 1937–1940[DOI]
  - 13 Wang Z X, Schleyer P V R. Construction principles of “Hyparenes”: Families of molecules with planar pentacoordinate carbons. *Science*, 2001, 292: 2465–2469[DOI]
  - 14 Wang L M, Huang W, Averkiev B B, Boldyrev A I, Wang L S.  $CB_7^-$ . Experimental and theoretical evidence against hypercoordinate planar carbon. *Angew Chem Int Ed*, 2007, 46: 4550–4553[DOI]
  - 15 Averkiev B B, Zubarev D Y, Wang L M, Huang W, Wang L S, Boldyrev A I. Carbon avoids hypercoordination in  $CB_6^-$ ,  $CB_6^{2-}$ , and  $C_2B_5^-$  planar carbon-boron clusters. *J Am Chem Soc*, 2008, 130: 9248–9250[DOI]
  - 16 Beck A D. Density functional thermochemistry. III. The role of exact exchange. *J Chem Phys*, 1993, 98: 5648–5659[DOI]
  - 17 Lee C, Yang W, Parr R G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys Rev B*, 1988, 37: 785–791[DOI]
  - 18 Head-Gordon M, Pople J A, Frisch M J. Mp2 energy evaluation by direct methods. *Chem Phys Lett*, 1988, 153: 503–506[DOI]
  - 19 Head-Gordon M, Head-Gordon T. Analytic Mp2 frequencies without fifth-order storage. Theory and application to bifurcated hydrogen bonds in the water hexamer. *Chem Phys Lett*, 1994, 220: 122–128[DOI]
  - 20 Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Montgomery J A Jr, Vreven T, Kudin K N, Burant J C, Millam J M, Iyengar S S, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson G A, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox J E, Hratchian H P, Cross J B, Adamo C, Jaramillo J, Gomperts R, Stratmann R E, Yazyev O, Austin A J, Cammi R, Pomelli C, Ochterski J W, Ayala P Y, Morokuma K, Voth G A, Salvador P, Dannenberg J J, Zakrzewski V G, Dapprich S, Daniels A D, Strain M C, Farkas O, Malick D K, Rabuck A D, Raghavachari K, Foresman J B, Ortiz J V, Cui Q, Baboul A G, Clifford S, Cioslowski J, Stefanov B B, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin R L, Fox D J, Keith T, Al-Laham M A, Peng C Y, Nanayakkara A, Challacombe M, Gill P M W, Johnson B, Chen W, Wong M W, Gonzalez C, Pople J A. *Gaussian 03, Revision A.1*. Pittsburgh: Gaussian, Inc., 2003
  - 21 Dunning T H Jr. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J Chem Phys*, 1989, 90: 1007–1023[DOI]
  - 22 Kendall R A, Dunning T H Jr, Harrison R J. Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions. *J Chem Phys*, 1992, 96: 6796–6806[DOI]
  - 23 Peterson K A. Systematically convergent basis sets with relativistic pseudopotentials. I. Correlation consistent basis sets for the post-d group 13–15 elements. *J Chem Phys*, 2003, 119: 11099–11112[DOI]
  - 24 Peterson K A, Puzzarini C. Systematically convergent basis sets for transition metals.II. Pseudopotential-based correlation consistent basis sets for the group 11 (Cu, Ag, Au) and 12 (Zn, Cd, Hg) elements. *Theor Chem Acc*, 2005, 114: 283–296[DOI]
  - 25 Metz B, Stoll H, Dolg M. Small-core multiconfiguration-Dirac-Hartree-Fock-adjusted pseudopotentials for post-d main group elements: Application to PbH and PbO. *J Chem Phys*, 2000, 113: 2563–2569[DOI]
  - 26 von Niessen W, Schirmer J, Cederbaum L S. Computational methods for the one-particle green's function. *Comput Phys Rep*, 1984, 1: 57–125[DOI]
  - 27 Ortiz J V, Zakrzewski V G, Dolgounircheva O. In: Calais J L, Kryachko E, eds. *Conceptual Perspectives in Quantum Chemistry*. Norwell: Kluwer Academic, 1997. 465–518
  - 28 Ortiz J V. Toward an exact one-electron picture of chemical bonding. *Adv Quantum Chem*, 1999, 35: 33–52
  - 29 Schleyer P V R, Maerker C, Dransfeld A, Jiao H, van Eikema Hommes N J R. Nucleus-independent chemical shifts: A simple and efficient aromaticity probe. *J Am Chem Soc*, 1996, 118: 6317–6318[DOI]

## Supplementary materials

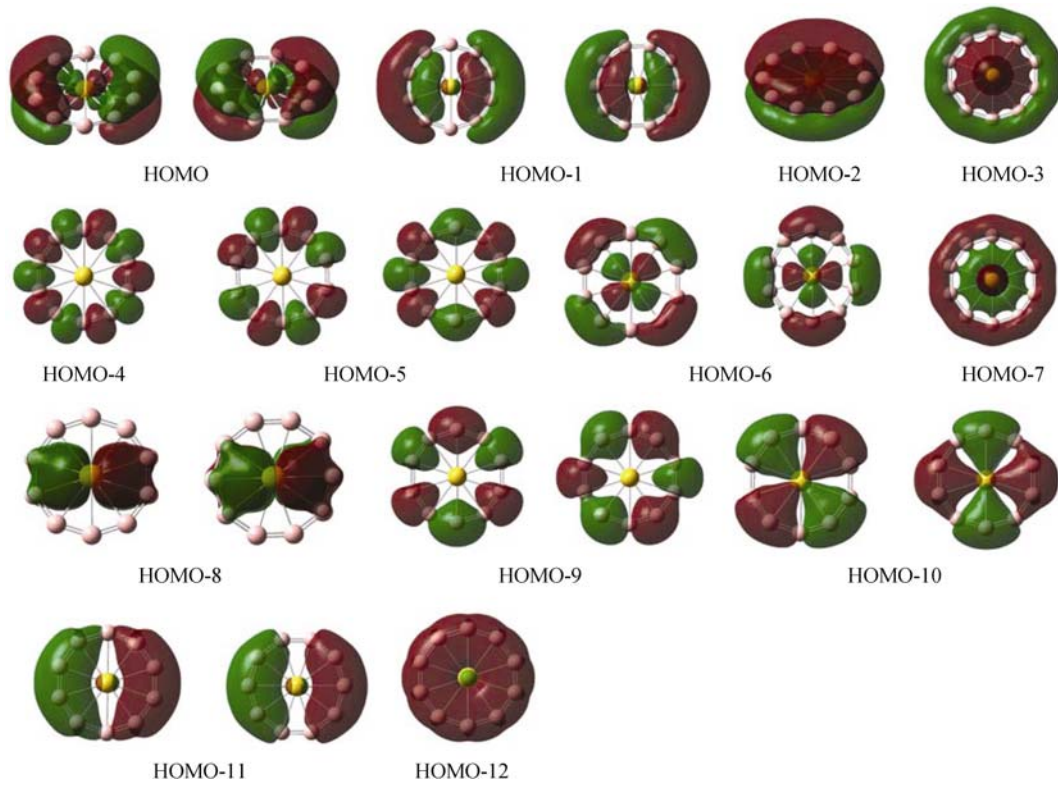
# M@B<sub>9</sub> and M@B<sub>10</sub> molecular wheels containing planar nona- and deca-coordinate heavy group 11, 12, and 13 metals (M = Ag, Au, Cd, Hg, In, Tl)

MIAO ChangQing, GUO JinChang, LI SiDian\*

Institute of Materials Sciences and Department of Chemistry, Xinzhou Teachers' University, Xinzhou 034000, China  
(Email: lisidian@yahoo.com).



**Figure S1** Valence orbital pictures of singlet D<sub>9h</sub> Au@B<sub>9</sub><sup>2-</sup> (1)



**Figure S2** Valence orbital pictures of singlet  $D_{9h}$   $Au@B_{10}^{-}(3)$