Bridging Gold: B-Au-B Three-Center-Two-Electron Bonds in Electron-Deficient B$_2$Au$_{n-1}^-$ (n = 1, 3, 5) and Mixed Analogues

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Abstract: A systematic density functional theory and wave function theory investigation on the geometrical and electronic structures of the electron-deficient diboron aurides B$_2$Au$_{n-1}^-$ (n = 1, 3, 5) and their mixed analogues B$_n$H$_m$Au$_n^-$(m + n = 3, 5) has been performed in this work. Ab initio theoretical evidences strongly suggest that bridging gold atoms exist in the ground states of C$_{2n}$ B$_2$Au$_n^-$(1A), C$_2$ B$_2$Au$_1^-$(1A), C$_{2n}$ B$_2$Au$_n^-$(1B$_1$), C$_{2n}$ B$_2$Au$_n^-$(1A$_1$), and C$_n$ B$_2$Au$_n^-$(1A), which all prove to possess a B–Au–B three-center-two-electron (3c-2e) bond. For B$_n$H$_m$Au$_n^-$ (m + n = 3, 5) mixed anions, bridging B–Au–B units appear to be favored in energy over bridging B–H–B, as demonstrated by the fact that the Au-bridged C$_{2n}$ B$_2$H$_2$Au$_n^-$(1A), C$_2$ B$_2$H$_2$Au$_n^-$(1A), and C$_n$ B$_2$H$_2$Au$_n^-$(1A) lie clearly lower than their H-bridged counterparts C$_n$ B$_2$H$_2$Au$_n^-$(1A), C$_n$ B$_2$H$_2$Au$_n^-$(1A), and C$_n$ B$_2$H$_2$Au$_n^-$(1A), respectively. Orbital analyses indicate that Au 6s makes about 92–96% contribution to the Au-based orbitals of the concerned anions have been calculated to facilitate their future experimental characterizations. The results obtained in this work establish an interesting 3c-2e bonding model (B–Au–B) for electron-deficient systems in which Au 6s plays a major role with non-negligible contribution from Au 5d.

Key words: diboron aurides; bridging gold; 3c-2e bonds; ab initio calculations; structures; properties

Introduction

Gold differs dramatically from other coinage metals (Cu and Ag) mainly because of its strong relativistic effects: the stabilization and contraction of Au 6s and the concomitant destabilization and expansion of Au 5d.$^{1,2}$ This gives rise to the high-electronic affinity of Au that behaves like halogens in alkaline metal and transition metal aurides.$^{1,4}$ Au also possesses the highest electronegativity (2.4) in all metals, which is comparable with that of H (2.2). Au/H similarity is well supported by the surprising experimental discovery of H/AuPR$_3$ analogy$^3$ and, more recently, the joint experimental and theoretical confirmation of the H/Au isobal relationship in silicon aurides T$_d$ SiAu($^{18}$S,$^{18}$N, C$_{2n}$, Si$_2$Au($^{16}$S,$^{18}$N, C$_{2n}$C$_{2n}$, Si$_2$Au($^{16}$S,$^{18}$N, and C$_{2n}$) and heptaboron auride C$_{2n}$ B$_7$Au($^{16}$S) cage-like B$_n$Au$_n^-$(1A).$^{5}$ with the Au terminals in the n-Au terminals were predicted stable recently in theory.$^9$ Relativistic pseudopotential calculations on the X-centered XAu$_{m}^+$ cluster cations (X = B–N, Al–S, n = 4–6)$^{10}$ and Au-bridged X–Au–Y Lewis acid-base pairs$^{11}$ were also reported. However, to the best of our knowledge, there have been no investigations reported in literature on bridging gold atoms in electron-deficient systems possessing three-center-two-electron (3c-2e) bonds. In this work, we choose diboron aurides B$_2$Au$_{n-1}^-$ (n = 1, 3, 5) and their mixed analogues B$_n$H$_m$Au$_n^-$(m + n = 3, 5) as typical examples to investigate the possibility of electron-deficient B-Au-B 3c-2e bonds. Theoretical evidences at both density functional theory (DFT) and wave function theory levels strongly suggest that bridging Au atoms exist in the ground states of C$_{2n}$ B$_2$Au$_n^-$(1A$_1$), C$_2$ B$_2$H$_2$Au$_n^-$(1A$_1$), and C$_n$ B$_2$H$_2$Au$_n^-$(1A$_1$), respectively. Orbital analyses indicate that Au 6s makes about 92–96% contribution to the Au-based orbitals of the concerned anions have been calculated to facilitate their future experimental characterizations. The results obtained in this work establish an interesting 3c-2e bonding model (B–Au–B) for electron-deficient systems in which Au 6s plays a major role with non-negligible contribution from Au 5d.

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Bridging Gold

219

electron detachment energies (VDEs) of $B_2Au^-$ and $B_2H_4Au^-$
anions have been calculated to aid their photoelectron spectroscopy
(PES) characterizations. The results achieved in this work establish
an interesting 3c-2e bonding model ($B-Au-B$) for electron-deficient systems and present the possibilities of new gold-rich compounds, which may possess novel catalytic and chemical properties.\textsuperscript{11}

Theoretical Methods

Intensive structural searches were performed using a DFT-based
random structure-generating program (GXZY).\textsuperscript{12} Further structural optimizations, frequency analyses, and natural-localized molecular orbital (NLOMO) analyses were carried out on low lying isomers using the hybrid B3LYP\textsuperscript{13} method and the second-order Moller-Plesset approach with the frozen core approximation
(MP2(FC)).\textsuperscript{14} MP2 produced similar ground-state structures and
order Møller-Plesset approach with the frozen core approximation
(C0/C0)

electron detachment energies (VDEs) of $B_2Au$\textsuperscript{(4)} and $C_n$, $B_2Au$\textsuperscript{(4)} possesses the same geometry as linear $B_2H_4$ in $C_n$, $B_2Au^-$ (A\textsubscript{1}) (I). $Au$ 6s overlaps with one of the two half-filled $\pi_n$ orbitals of $B_2H_4$\textsuperscript{(2)}\textsuperscript{15} and the extra electron of the anion enters the other half-filled B-B $\pi_n$ orbital perpendicular to the molecular plane. The bond order increase from $WBI_{B-Au} = 1.96$ in 3 to $WBI_{B-Au} = 2.77$ in 1, and the bond length decrease from $r_{B-Au} = 1.65$ Å in 3 to $r_{B-Au} = 1.60$ Å in 1 also indicates that the extra electron of the anion has been totally localized between $B-B$, and the bridging $B-Au-B$ 3c-2e interaction is mainly covalent.

Detailed NLOMO analyses quantitatively reveal the existence of a bridging $B-Au-B$ 3c-2e bond (t) bond in both $C_2v$, $B_2Au^-$ (I) and $C_n$, $B_2Au$ (3), as clearly shown in their 3c-2e orbital pictures, contour plots, and orbital hybridizations in Figure 5. With the orbital hybridization of $WBI_{B-Au-B} = 0.50(sp^{2.72})B$ + 0.71(sd$^{0.09}$)Au + 0.50(sp$^{1.17}$)B and the corresponding atomic contribution of 25%B + 50%Au + 25%B for the 3c-2e bond in $C_2v$, $B_2Au^-$ (I), $Au$ 6s makes 91.9% and $Au$ 5d makes 8.0% contribution to the Au-based orbital, whereas $B$ 2p contributes 94.8% and $B$ 2s contributes 4.3% to the $B$-based orbital. Obviously, $Au$ 6s and $B$ 2p make the major contributions to the $B-Au-B$ bridging bond in $C_2v$, $B_2Au^-$ (I). This agrees with the qualitative discussion presented earlier. However, the 8% contribution from $Au$ 5d is not negligible due to the strong relativistic effects of $Au$. Thus, the 3c-2e bond of $C_n$, $B_2Au^-$ can be practically approximated as $r_{B-Au-B} = 0.50(p_n) + 0.71(sd^{0.09})Au + 0.50(p_m)$, as shown in Figure 5. As a local minimum, neutral $C_2v$, $B_2Au$ (3) possesses a similar $B-Au-B$ bond with $C_2v$, $B_2Au^-$ (I).

$B_2Au^-$, $B_2H_4Au^-$, and $B_2H_4Au^+$

Adding one-$Au$ terminally to each $B$ center in $C_n$, $B_2Au^-$ (I) produces the ground state of the slightly distorted T-shaped $C_2v$ $B_2Au^+$ (A\textsuperscript{1}) (5) ($C_2$ 5 has the exact symmetry of $C_2$ at MP2), which proves to be 0.35, 1.50, and 1.68 eV more stable than the Y-shaped transition state of $C_2v$, $B_2Au^-$ (A\textsuperscript{1}) (6) (which has one small imaginary frequency at 151 cm$^{-1}$ vibrationally leading to $C_2$ 5), the slightly distorted chain $C_2v$, $B_2Au^+$ (A\textsuperscript{1}) (7), and the slightly off-planed $C_1$, $B_2Au^+$ (A\textsuperscript{1}) (8) at CCSD(T), respectively. The Au-bridged $C_2v$, $B_2Au^+$ (5) with the $B-B$ distance of $r_{B-Au-B} = 1.53$ Å is the diboron auride analogue of the H-bridged $C_2v$, $B_2H_4^-$ in which $r_{B-Au-B} = 1.466$ Å at MP2(full)/6-311G**\textsuperscript{22,21}. The terminal (t) and bridging (b) bonds in $C_2v$, $B_2Au^+$ (5) have the bond lengths of $r_{B-Auth} = 1.98$ Å and $r_{B-Au(b)} = 2.18$ Å, and the corresponding bond orders of $WBI_{B-Au(t)} = 1.05$ and $WBI_{B-Au(b)} = 0.62$, respectively. The atomic charges of $q_{Auth} = -0.68$ and $q_{Auth(a)} = +0.22$e, and $q_{Auth} = +0.07$e, and the $B-Au$ binding bond orders of $WBI_{B-Au(b)} = 0.62$ in 5 indicate again that the extra electron of the anion is totally localized in the $B-B$ $\pi_n$ orbital perpendicular to the molecular plane, and the $B-Au-B$ 3c-2e bond is basically covalent. Different from $B_2H_4$ that favors a non-bridged $C_2v$, $B_2H_4$ (B\textsubscript{1}) (similar to $C_2v$, $B_2Au^-$) neutral favors

Results and Discussion

$B_2Au^-$ and $B_2Au$

We started from $B_2Au^-$ and $B_2Au$, the smallest diboron aurides possible to contain a bridging $B-Au-B$ unit. As shown in Figure 1, the Au-bridged $C_2v$, $B_2Au$ (A\textsuperscript{1}) (I) is indeed the ground state of $B_2Au$: it lies 1.12 and 0.12 eV lower than the non-bridged $C_2$, $B_2Au$ (A\textsuperscript{1}) (2) at MP2 and CCSD(T), respectively (though it is 0.64 eV less stable than $C_2$ at B3LYP). However, the Au-bridged $C_2v$, $B_2Au$ (B\textsubscript{1}) neutral (3) proves to be a local minimum lying 0.63, 0.06, and 0.15 eV higher than the non-bridged $C_{nv}$, $B_2Au$ (A\textsubscript{2}) (4) at B3LYP, MP2, and CCSD(T), respectively. $B_2Au$ neutral has the same number of valence electrons as $B_2$ (A\textsubscript{2})\textsuperscript{19} and $C_n$, $B_2Au$ (4) possesses the same geometry as linear $B_2H_4$ in $C_n$, $B_2Au^-$ (A\textsubscript{1}) (I). $Au$ 6s overlaps with one of the two half-filled $\pi_n$ orbitals of $B_2H_4$ (A\textsubscript{2})\textsuperscript{19} and the extra electron of the anion enters the other half-filled B-B $\pi_n$ orbital perpendicular to the molecular plane. The bond order increase from $WBI_{B-Au} = 1.96$ in 3 to $WBI_{B-Au} = 2.77$ in 1, and the bond length decrease from $r_{B-Au} = 1.65$ Å in 3 to $r_{B-Au} = 1.60$ Å in 1 support this bonding mode. The natural atomic charges of $q_{B} = -0.58$ le and $q_{A(G)} = +0.16$e, and the $B$-$Au$ bridging bond orders of $WBI_{B-Au(b)} = 0.76$ in $C_2v$, $B_2Au^-$ (I) also indicates that the extra electron of the anion has been totally localized between $B-B$, and the bridging $B-Au-B$ 3c-2e interaction is mainly covalent.

Table 2. All the calculations in this work were performed using
indexes of $B_2Au$ and $B_2H_3$, which may possess novel catalytic and chemical properties.5–11

.. figure:: images/binding_energy.png

Figure 5, with the natural atomic charges and Wiberg bond
devices discussed in this work are shown in

.. figure:: images/bond_orders.png

- The low lying isomers obtained are depicted in Figures 1–4 with relative energies at $B_3LYP$, MP2, and CCSD(T)/B3LYP indicated. The molecular orbital (MO) pictures, contour plots, and orbital hybridizations of the $B-Au-B$ 3c-2e $\tau$ bonds discussed in this work are shown in Figure 5, with the natural atomic charges and Wiberg bond indexes of $B_2Au$\textsuperscript{(20)} ($n = 1, 3, 5$) tabulated in Table 1 and ADEs and VDEs of the $B_2Au^-$ and $B_2H_4Au^-$ anions summarized in Table 2. All the calculations in this work were performed using the Gaussian 03 program.\textsuperscript{18}

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Figure 1. Two lowest lying isomers of (a) B$_2$Au$^+$ and (b) B$_2$Au at B3LYP, with the relative energies $\Delta E$ (eV) at B3LYP//B3LYP, MP2//MP2, and CCSD(T)//B3LYP indicated.

<table>
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<th>3. C$_{2v}$ ($^1B_1$)</th>
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Figure 2. Four lowest lying isomers of (a) B$_2$Au$_3^-$, (b) B$_2$H$_2$Au$_2^-$, and (c) B$_2$HAu$_2^-$ at B3LYP, with relative energies $\Delta E$ (eV) at B3LYP//B3LYP, MP2//MP2, and CCSD(T)//B3LYP indicated.

|   | 5. C$_2$ ($^1A'$) | 6. C$_6$ ($^1A'$) | 7. C$_s$ ($^1A'$) | 8. C$_1$ ($^1A'$) | 9. C$_{2v}$ ($^1A_1'$) | 10. C$_s$ ($^1A_1'$) | 11. C$_{2v}$ ($^1A_1'$) | 12. C$_s$ ($^1A_1'$) | 13. C$_s$ ($^1A'$) | 14. C$_2$ ($^1A'$) | 15. C$_1$ ($^1A'$) | 16. C$_s$ ($^1A'$) |
|---|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| ΔE/B3LYP | 0.00            | +0.17           | +0.91           | +1.35           | 0.00            | +0.53           | +0.47           | +1.92           | 0.00            | +0.57           | +0.65           | +1.91           |
| MP2      | 0.00            | +0.64           | +2.38           | +1.27           | 0.00            | +0.76           | +0.99           | +2.45           | 0.00            | +0.62           | +1.55           | +1.79           |
| CCSD(T)  | 0.00            | +0.35           | +1.50           | +1.68           | 0.00            | +0.76           | +0.99           | +2.45           | 0.00            | +0.69           | +1.77           | +1.89           |
the Au-bridged $C_{2v}$ B$_2$Au$_3$ ($^1B_1$) (25), which lies 0.39 eV lower than the nonbridged $C_{2v}$ B$_2$Au$_3$ ($^1B_1$) (26).

It is interesting to compare the 3c-2e bonds in the slightly distorted C$_2$ B$_2$Au$_3$ ($C_{2v}$) [\(0.52\)sp\(^{10}\)B $+ 0.67$sd\(^{0.06}\)Au $+ 0.52$lpH] and C$_2$ B$_2$H$_3$ ($C_{2v}$) [\(0.52\)sp\(^{10}\)B $+ 0.67$lpH $+ 0.52$lpH] at B3LYP level. Surprisingly, bridging Au (sd\(^{0.06}\)) in B$_2$Au$_3$ and bridging H (s) in B$_2$H$_3$ make exactly the same contribution (45%) to the 3c-2e interactions in these T-shaped monoanions! However, there exist obvious differences between them in orbital hybridizations. First, the 27% contribution from each B center is different: B 2s orbital in B$_2$H$_3$ makes about 10% contribution to the B sp hybridization, whereas B 2s in B$_2$Au$_3$ contributes $\leq 3\%$, which has been omitted in Figure 5. Second, the Au-based orbital in B$_2$Au$_3$ contains 94.2% contribution from Au 6s.

![Diagram](image)

**Figure 3.** Four lowest lying isomers of (a) B$_2$Au$_3^-$, (b) B$_2$HAu$_4^-$ at B3LYP, with relative energies $\Delta E$ (eV) at B3LYP//B3LYP, MP2//MP2, and CCSD(T)//B3LYP indicated.

![Diagram](image)

**Figure 4.** Two lowest lying isomers of (a) B$_2$Au$_3$ and (b) B$_2$Au$_5$ neutrals obtained at B3LYP, with relative energies $\Delta E$ (eV) at B3LYP//B3LYP, MP2//MP2, and CCSD(T)//B3LYP indicated.
and 5.8% from Au 5d, whereas the H-based orbital in B₂H₅⁻ contains contribution purely from H 1s.

As typical diboron mixed clusters, $\text{B}_2\text{H}_2\text{Au}^-$ and $\text{B}_2\text{H}_2\text{Au}_5^-$ provide two good candidates to compare bridging $\text{B}–\text{Au}–\text{B}$ interaction with bridging $\text{B}–\text{H}–\text{B}$ in one molecule. As shown in Figures 2b and 2c, at CCSD(T) level, the Au-bridged $\text{C}_2\text{v}$ $\text{B}_2\text{H}_2\text{Au}^-$ ($\text{1}^\text{A}$) (9) is 0.57 eV more stable than the H-bridged $\text{C}_2\text{v}$ $\text{B}_2\text{H}_2\text{Au}^-$ ($\text{1}^\text{A}$) (10), with $\text{C}_2\text{v}$ $\text{B}_2\text{H}_2\text{Au}^-$ ($\text{1}^\text{A}$) (11) and $\text{C}_2\text{v}$ $\text{B}_2\text{H}_2\text{Au}_5^-$ ($\text{1}^\text{A}$) (12) lying 0.65 eV and 1.91 eV higher than $\text{C}_2\text{v}$ 9, respectively. Similarly, the Au-bridged $\text{Cs}$ $\text{B}_2\text{H}_2\text{Au}^-$ ($\text{1}^\text{A}$) (13) lies 0.69 eV lower than the H-bridged $\text{Cs}$ $\text{B}_2\text{H}_2\text{Au}^-$ ($\text{1}^\text{A}$) (14), with $\text{Cs}$ $\text{B}_2\text{H}_2\text{Au}^-$ ($\text{1}^\text{A}$) (15) and $\text{Cs}$ $\text{B}_2\text{H}_2\text{Au}_5^-$ ($\text{1}^\text{A}$) (16) lying 1.77 and 1.89 eV above the ground state. The bridging $\text{B}–\text{Au}–\text{B}$ 3c-2e bonds in $\text{C}_2\text{v}$ $\text{B}_2\text{H}_2\text{Au}^-$ (9) and $\text{Cs}$ $\text{B}_2\text{H}_2\text{Au}_5^-$ (13) possess the orbital hybridizations of $\tau_{\text{B–Au–B}} = 0.49(\text{p}_\text{B}) + 0.72(\text{sd})_{\text{Au}} + 0.49(\text{p}_\text{B})$ and $\tau_{\text{B–Au–B}} = 0.48(\text{p}_\text{B}) + 0.69(\text{sd})_{\text{Au}} + 0.54(\text{p}_\text{B})$, respectively. Similar to $\text{Cs}$ $\text{B}_2\text{H}_2\text{Au}^-$. As indicated in Figure 2, the calculated B–B bond distances in the Au-bridged $\text{C}_2\text{v}$ 9 (1.51 Å) and $\text{Cs}$ 13 (1.51 Å), all prove to be obviously longer than B–B distances in the corresponding H-bridged $\text{C}_2\text{v}$ 10 (1.46 Å) and $\text{Cs}$ 14 (1.47 Å), respectively, well in line with the fact that the $\text{B}_2\text{H}_3^-$ (similar to $\text{C}_2\text{v}$ 5) was obviously shorter than the unbridged $\text{B}–\text{H}–\text{B}$ ($\tau_{\text{B–H–B}} = 1.56$ Å) in a $\text{C}_2\text{v}$ local minimum (analogous to $\text{C}_2\text{v}$ 6). This situation can be qualitatively explained in terms of the atomic size difference between Au and H: a bridging Au (6s5d) is much bigger than a bridging H(1s) in size, and, therefore, to form a stable $\text{B}–\text{Au}–\text{B}$ bridge in $\text{C}_2\text{v}$ $\text{B}_2\text{H}_2\text{Au}_5^-$ (5), the B–B bond is obviously elongated by about 0.07 Å to reduce the geometrical strains. This B–B bond length elongation agrees with the Wiberg bond order decreasing from WBI = 2.29 in the H-bridged $\text{C}_2\text{v}$ $\text{B}_2\text{H}_2^-$ ($\text{1}^\text{A}$) to WBI = 2.15 in the Au-bridged $\text{C}_2\text{v}$ $\text{B}_2\text{H}_2\text{Au}_5^-$ ($\text{1}^\text{A}$). As indicated in Figure 2, the calculated B–B distances in the Au-bridged $\text{C}_2\text{v}$ 9 (1.51 Å) and $\text{Cs}$ 13 (1.51 Å), all prove to be obviously longer than B–B distances in the corresponding H-bridged $\text{C}_2\text{v}$ 10 (1.46 Å) and $\text{Cs}$ 14 (1.47 Å), respectively, well in line with the fact that the

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$^a$The final state corresponds to $\text{C}_2\text{v}$ $\text{B}_2\text{H}_2\text{Au}_5^-$ (25).
$^b$The final state corresponds to $\text{Cs}$ $\text{B}_2\text{H}_2\text{Au}^-$ (13).
$^c$CCSD(T) calculations on doublet $\text{Cs}$ $\text{B}_2\text{H}_2\text{Au}^-$ neutral are beyond the reach of available computing resources.
Wiberg bond orders of \( \text{C}_2 \) (2.16) and \( \text{C}_3 \) (2.17) are systematically lower than that of \( \text{Cs} \) (2.24) and \( \text{C}_2 \) (2.20). On the other hand, an \(-\text{Au}\) terminal proves to cause only minor changes to the attached \( \text{B} - \text{B} \) units in bond lengths, as shown in the typical cases of the Au-terminated \( \text{C}_5 \) and \( \text{C}_6 \), which have very similar \( \text{B} - \text{B} \) bond lengths with the H-terminated \( \text{B} - \text{B} \) bond in \( \text{C}_3 \). The two factors work together to make the \( \text{B} - \text{B} \) bond length in the bridged \( \text{C}_2 \) \( \text{B}_2\text{Au}^- \) (5) only slightly shorter than \( \text{B} - \text{B} \) bond in the unbridged \( \text{C}_5 \) \( \text{B}_2\text{Au}^- \) (6). Similar situations happen to the Au-bridged \( \text{B}_2\text{Au}^- \) discussed earlier and \( \text{B}_3\text{Au}^- \) detailed in the next section. The B3LYP results obtained above well parallel the results previously reported for the corresponding boron hydrides\(^{20-23}\) and invite experimental and more accurate theoretical confirmations.

**Figure 5.** Three-dimensional views, contour plots, and orbital hybridizations of the 3c-2e \( \tau \) bonds in \( \text{B}_2\text{Au}^- \) (1), \( \text{B}_2\text{Au}^- \) (3), \( \text{B}_2\text{Au}^- \) (5), \( \text{B}_2\text{H}_3\text{Au}^- \) (9), \( \text{B}_2\text{H}_5\text{Au}^- \) (13), \( \text{B}_2\text{H}_7\text{Au}^- \) (17), and \( \text{B}_2\text{H}_9\text{Au}^- \) (21) discussed in this work. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
We now turn to \(B_2Au^-\) and its mixed analogue \(B_2HAu^-=\). \(B_2Au^-\) has the high-symmetry ground state of the Au-bridged \(C_{2v}\) \(B_2Au^-(\text{A}_1)\) that lies 0.64, 0.62, and 1.42 eV lower than \(C_i B_2Au^-(\text{A}')\) (18), \(C_i B_2Au^-(\text{A}'\text{A})\) (19), and \(D_{2d} B_2Au^-(\text{A}_1)\) (20) at CCSD(T), respectively. \(C_n B_2Au^-(\text{A}_1)\) is the diboron auride analogue of the H-bridged \(C_n B_n H_{2}\). The \(r_{\beta-Au-B}\) bond in \(B_2Au^-\) possesses the orbital hybridization of \(r_{\beta-Au-B} = 0.54(p_H) + 0.65(s(\delta^0(Au)) + 0.54(p_H)\). The two sp\(^2\)-hybridized B atoms in \(C_n B_2Au^-(\text{A}_1)\) form a \(B-B\) \(\sigma\) bond with \(r_{\beta-B} = 1.65\ \AA\) in the \(Au-B-B-Au^-\) plane, whereas the \(Au\) 6s\(^1\) electron and the extra electron of the anion form the bridging \(-Au-B\) 3c-2e interaction with \(r_{\beta-Au-B}(A) = 2.25\ \AA\). Similar to the H-bridged \(C_n B_n H_{2}\), \(B_2Au^-\) neutral favors the Au-bridged \(C_i B_2Au^-(\text{A}'')\) (27) over the slightly off-planed \(C_i B_2Au^-(\text{A}'')\) (28) by 0.85 eV. It is interesting to notice that bridging \(Au\) atoms in the whole \(B_2Au^-(n)\) series \((n = 1, 3, 5)\) have considerably high total bond orders between \(WBI_{\text{ab}}(Au)\) 1.30–1.52 (Table 1), indicating that effective multi-center interactions (3c-2e) exist in these diboron auride clusters. Similar situation exists in their mixed analogues.

The Au-bridged \(C_3 B_2HAu^-(\text{A}'')\) (21) appears to lie 0.71 eV lower than the H-bridged \(C_3 B_2H_{2}\), \(B_2HAu^-(\text{A}_1)\) (23) and 0.43 eV and 0.88 eV lower than \(C_1 B_2HAu^-(\text{A})\) (22) and \(C_3 B_2HAu^-\) (\(\text{A}'\text{A}\)) (24) at CCSD(T), respectively, indicating again that a bridging \(-Au-B\) unit is favored over a bridging \(-H-B\) in mixed anions. With two unsymmetrical B centers, \(C_i B_2HAu^-\) (21) with \(r_{\beta-B} = 1.65\ \AA\) possesses the 3c-2e bond of \(r_{\beta-Au-B} = 0.49(p_H) + 0.68(s(\delta^0(Au)) + 0.54(p_H)\). There exists a general trend to notice that, in the orbital hybridizations of the 3c-2e bonds shown in Figure 5, the \(B'\) centers directly connected to H-terminals have slightly lower orbital coefficients (0.48–0.49) and, therefore, less contribution to the multi-center interactions than B centers directly bonded to Au-terminals (0.50–0.54).

### Thermodynamic Stabilities and Electron Detachment Energies

Concerning the thermodynamic stabilities of the diboron auride clusters studied in this work, at CCSD(T)/B3LYP level, we calculate the atomization energies (AEs) of the low lying \(B_2Au_n\) neutral isomers compared with that of the corresponding \(B_2H_n\) \((n = 1, 3, 5)\). Table 8 shows the electron binding energies of these clusters be thermodynamically stable. Removing the bridging \(Au\) of the ground state \(B_2Au^-\) plus a \(B_2Au_n\) neutral to produce the lowest fragmentation energies in various processes, with \(FE = 81.2\) kcal/mol for \(C_n B_2Au^- (1)\), \(77.1\) kcal/mol for \(C_2 B_2Au^- (5)\), and \(79.1\) kcal/mol for \(C_n B_2Au^- (17)\). Fragmentations in \(B_2Au^- (C_n A) = B_2(S) + Au^- (2)\) with \(FE = 146.0\) kcal/mol, \(B_2Au^- (C_i A) = B_2(S) + Au^- (2)\) with \(FE = 195.9\) kcal/mol, and other processes involving the breakdown of the \(-B-B\) bonds appear to be much less favorable in energies.

We also calculate the ADE and VDE values of the anions possible to be measured in PES experiments. As can be seen from Table 2, B3LYP and CCSD(T)/B3LYP methods agree well in producing the one-electron detachment energies of these anions. For \(B_2H_{n}Au^-\) with \(m + n = 1\) and 3, the calculated ADEs and VDEs lie between 1.47 and 1.89 eV, whereas for \(m + n = 5\), the corresponding values seem to be obviously higher (2.86–3.39 eV). The high-electron detachment energies of \(B_2Au^-\) and \(B_2HAu^-\) anions may be related with the fact that they have the same number of valence electrons as the well-known diborane \(B_2H_6\). The electron binding energies of these anions fall within the energy range of the conventional excitation laser (266 nm, 4.661 eV) in PES measurements.6–8

### Table 8

<table>
<thead>
<tr>
<th>(n)</th>
<th>(FE) (kcal/mol)</th>
</tr>
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<tr>
<td>1</td>
<td>81.2</td>
</tr>
<tr>
<td>3</td>
<td>77.1</td>
</tr>
<tr>
<td>5</td>
<td>79.1</td>
</tr>
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Summary

Ab initio theoretical evidences obtained in this work strongly suggest that bridging gold atoms exist in diboron aurides B2Au\textsubscript{n} (n = 1, 3, 5) and their B2H\textsubscript{m}Au\textsubscript{n} mixed analogues (m + n = 3, 5) that all prove to possess a B–Au–B 3c-2e bond. Bridging B–Au–B units appear to be favored in energy over B–H–B in mixed clusters. B–B units with the B–B distances of 1.46–1.68 Å are well maintained in most of the low lying isomers obtained in this work (except D2h\textsubscript{20}). Detailed orbital analyses indicate that Au 6s makes 92–96% and Au 5d makes 8–4% contribution to the Au-based orbitals in bridging B–Au–B units, partially reflecting the relativistic effect of gold. Diboron auride clusters and their mixed analogues are thermodynamically stable and possible to be produced by laser ablation of B2Au binary targets and characterized with PES spectra. The concept of B–Au–B 3c-2e bonds proposed in this work provides an interesting bonding mode for electron-deficient systems and helps to design new materials and catalysts with highly dispersed Au atoms.6–9 Initial investigations indicate that both the double Au-bridged D2h B2Au6 and D2h B2Au6\textsuperscript{2} similar to the double H-bridged D2h B2H6 are true minima of the systems and Al2Au\textsubscript{n} \textsuperscript{2} and Ga2Au\textsubscript{n} \textsuperscript{2} clusters (n = 1–6) possess certain similarities and differences with B2Au\textsubscript{n} \textsuperscript{2}.

References