

A Density Functional Investigation on $C_2Au_n^+$ ($n = 1, 3, 5$) and C_2Au_n ($n = 2, 4, 6$): from Gold Terminals, Gold Bridges, to Gold Triangles

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Abstract A systematic density functional theory investigation on $C_2Au_n^+$ ($n = 1, 3, 5$) and C_2Au_n ($n = 2, 4, 6$) indicates that gold atoms serve as terminals ($-Au$) in the chain-like $C_s C_2Au^+$ ($C \equiv C-Au^+$) and $D_{\infty h} C_2Au_2$ ($Au-C \equiv C-Au$) and as bridges ($-Au-$) in the side-on coordinated $C_{2v} C_2Au_3^+$ ($[Au-C \equiv C-Au]Au^+$) and $C_s C_2HAu_2^+$ ($[H-C \equiv C-Au]Au^+$). However, when the number of gold atoms reaches four, they form stable gold triangles ($-Au_3$) in the head-on coordinated $C_{2v} C_2Au_4$ ($Au-C \equiv C-Au_3$) and the side-on coordinated $C_{2v} C_2Au_5^+$ ($[Au-C \equiv C-Au]Au_3^+$). Similar $-Au_3$ triangular units exist in the head-on coordinated $C_{2v} C_2HAu_3$ ($H-C \equiv C-Au_3$) and $D_{2d} C_2Au_6$ ($Au_3-C \equiv C-Au_3$). The existence of stable $-Au_3$ triangular units in small dicarbon aurides is significant and intriguing. The high stability of Au_3 triangles originates from the fact that an equilateral $D_{3h} Au_3^+$ cation possesses a completely delocalized three-center-two-electron ($3c-2e$) σ bond and therefore is σ -aromatic in nature. The extension from H/Au analogy to H/ Au_3 analogy established in this work may have important implications in designing new gold-containing catalysts and nano-materials.

Keywords Dicarbon aurides · Structures · DFT · Gold triangles · $3c-2e$ bonds

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Introduction

Gold differs substantially from other coinage metals mainly because of its strong relativistic effect which decreases the energy difference between 6s and 5d orbitals and as a consequence Au 5d electrons are expected to participate in chemical bonding, whereas the 4d and 5s orbitals in silver stay energetically well separated [1–23]. Au possesses the highest electronegativity (2.4) in all metals which is comparable with that of H (2.2). Various compounds with C–Au, N–Au and B–Au σ bonds have been reported [8–16] since the discovery of the H/AuPPh₃ analogy [5–7]. More recently, a series of compounds such as T_d SiAu₄^{0/−} [17] C_{2v} Si₂Au₂^{0/−}, and C_{2h}/C_{2v} Si₂Au₄[−] [18, 19] and heptaboron auride C_{2v} B₇Au₂^{0/−} [20] have been characterized by joint photoelectron spectroscopy and density functional theory (DFT) investigations, further confirming the H/Au isolobal relationship. An Au-bridged X...Au–Y Lewis acid–base pair has also been reported in literature [21]. Very recently, our group presented an ab initio investigation on BAu_n^{0/−} ($n = 1–4$) [22] and B₂Au_n^{−/0} ($n = 1, 3, 5$) diboron aurides and their B₂H_mAu_n[−] mixed analogues ($m + n = 3, 5$) which contain gold terminals and gold bridges [23]. In this work, we perform a systematic density functional theory investigation on the geometrical and electronic structures of small dicarbon aurides C₂Au_n⁺ ($n = 1, 3, 5$) and C₂Au_n ($n = 2, 4, 6$). Surprisingly, in addition to gold terminals (–Au) in the chain-like C_s C₂Au⁺ (1) and D_{∞h} C₂Au₂ (3) and gold bridges in the side-on coordinated C_{2v} C₂Au₃⁺ (5) and C_s C₂HAu₂⁺ (7), gold triangular units (–Au₃) were found to exist stably in the ground-state structures of the head-on coordinated C_{2v} C₂Au₄ (10) and the side-on coordinated C_{2v} C₂Au₅⁺ (14). Both Au⁺ cations and Au₃⁺ triangles serve as Lewis acids side-on coordinated to an Au–C≡C–Au chain in structures 5, 7, and 14. Head-on coordinated Au₃ triangles also exist in C_{2v} C₂HAu₃ (20) and D_{2d} C₂Au₆ (21). The existence of the highly stable Au₃ triangles in dicarbon aurides can be understood based on the fact that an equilateral D_{3h} Au₃⁺ cation possesses a completely delocalized 3c–2e σ bond and therefore is σ -aromatic in nature (satisfying the $4n + 2$ Huckel rule with $n = 0$). The prediction of –Au₃ triangles in small carbon auride clusters invites future experimental characterizations which may shed insight into the unique structures and unusual catalytic properties of gold-containing clusters and nanomaterials.

Theoretical Methods

A comprehensive global minimum search was performed for dicarbon auride clusters using a DFT-based random structure-generating program (GXYZ) [24]. Further structural optimizations, vibrational analyses, and natural localized molecular orbital (NLMO) analyses were comparatively carried out on low-lying isomers using the hybrid B3LYP [25, 26] and PBE1PBE [27] methods. PBE1PBE and B3LYP produced similar ground-state structures and relative energies with slightly different bond parameters. Energies relative to the ground-state structures were further refined for low-lying isomers using the coupled cluster method with triple excitations (CCSD(T)) [28–30] at B3LYP structures. The Stuttgart quasi-relativistic

pseudo-potential and basis set augmented with two f -type polarization functions and one g -type polarization function (Stuttgart_rsc_1997_ecp + 2f1g ($\alpha(f) = 0.498$, $\alpha(f) = 1.464$, and $\alpha(g) = 1.218$) [31, 32] were employed for Au and the augmented Dunning's correlation consistent basis sets of aug-cc-pVTZ [33] used for C and H throughout this work.

The most important low-lying isomers obtained for the concerned clusters are depicted in Figs. 1, 2, 3, 4, 5, and 6, with their relative energies at B3LYP, PBE1PBE, and CCSD(T)//B3LYP levels indicated. The pictures and contour plots of the 3c–2e σ molecular orbitals of D_{3h} Au_3^+ , C_{2v} $C_2Au_5^+$, and C_{2v} C_2Au_4 are shown in Fig. 5b. The calculated Wiberg bond orders, net atomic charges and HOMO–LUMO energy gaps are summarized in Table 1. The widely used nucleus independent chemical shift (NICS) values tabulated in Table 2 were calculated at points 0.0, 0.5 and 1.0 Å above the geometrical centers of the Au_3 triangular units using the gauge-independent atomic orbital (GIAO) method [34]. Natural bonding orbital (NBO) analyses were performed using the NBO5.0 program [35]. All the calculations in this work have been done using the Gaussian 03 program [36].

Results and Discussions

As the main body of the paper, the following discussions on C_2Au_n dicarbon aurides are organized in an order with increasing number of gold atoms ($n = 1–6$), in which Au atoms forming terminals, bridges, and finally triangles when the number of gold atoms reaches four. The high stability of a gold triangular unit in dicarbon aurides has been explained in terms of its 3c–2e σ aromatic bonding and highly negative NICS values.

C_2Au^+ and C_2Au_2

We start from C_2Au^+ , the smallest dicarbon auride. As can be seen from Fig. 1, the Au-terminated C_s C_2Au^+ (**1**, $^3A''$) with the bond lengths of $r_{C=C} = 1.32$ Å and $r_{C-Au} = 1.89$ Å is the ground state of the triatomic cation which lies 0.33, 0.28 and 0.22 eV lower than the Au-bridged C_{2v} C_2Au^+ (**2**, 3A_1) at B3LYP, PBE1PBE,

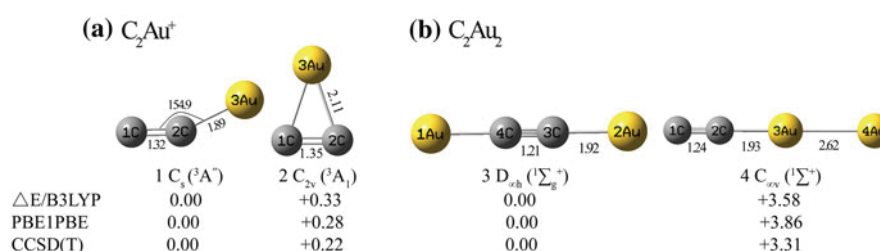


Fig. 1 Two Low-lying isomers of **a** C_2Au^+ and **b** C_2Au_2 at B3LYP, with their relative energies ΔE (eV) at B3LYP, PBE1PBE, and CCSD(T)//B3LYP indicated. Bond lengths are in angstroms, bond angles in degree

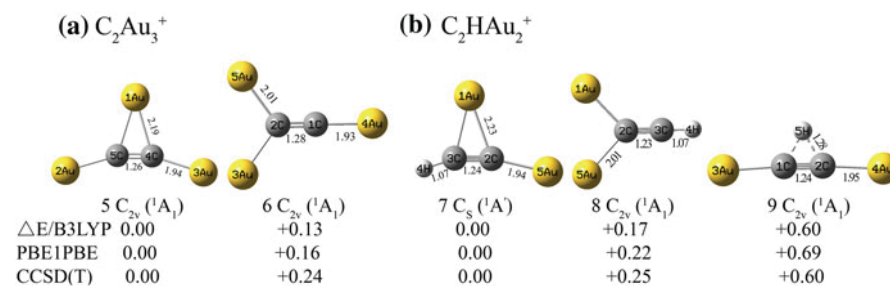


Fig. 2 Low-lying isomers of **a** $C_2Au_3^+$ and **b** $C_2HAu_2^+$ at B3LYP, with their relative energies ΔE (eV) at B3LYP, PBE1PBE, and CCSD(T)//B3LYP indicated. Bond lengths are in angstroms

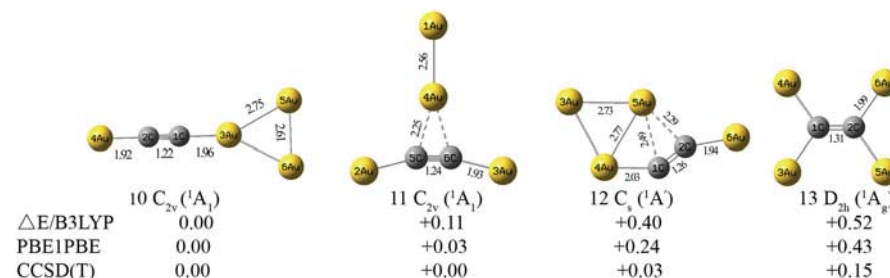


Fig. 3 Four low-lying isomers of C_2Au_4 at B3LYP, with their relative energies ΔE (eV) indicated at B3LYP, PBE1PBE, and CCSD(T)//B3LYP. Bond lengths are in angstroms

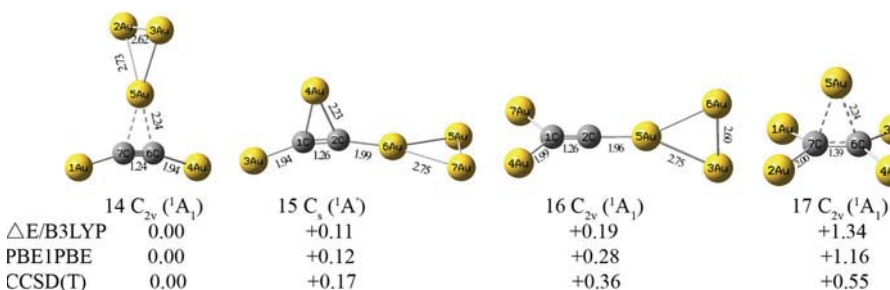


Fig. 4 Four low-lying isomers of $C_2Au_5^+$ with their relative energies ΔE (eV) indicated at B3LYP, PBE1PBE, and CCSD(T)//B3LYP. Bond lengths are in angstroms

and CCSD(T)//B3LYP levels, respectively. The slightly bent C_2Au^+ (**1**) with a bond angle of 154.9° proves to be similar with linear C_2H^+ [37] in geometry which lies 25.3 kcal/mol lower than the perfectly linear $C_{\infty v}$ C_2Au^+ ($^1\Sigma_g$) at B3LYP. As expected and confirmed in Table 1, the positive charge of the C_2Au^+ cation is mainly concentrated on the gold terminal which carries the high net atomic charge of $q_{Au} = +0.84$ *lel*. NBO analyses indicate that the C–Au interaction in C_s $C=C-Au^+$ (**1**) is mainly ionic (67%).

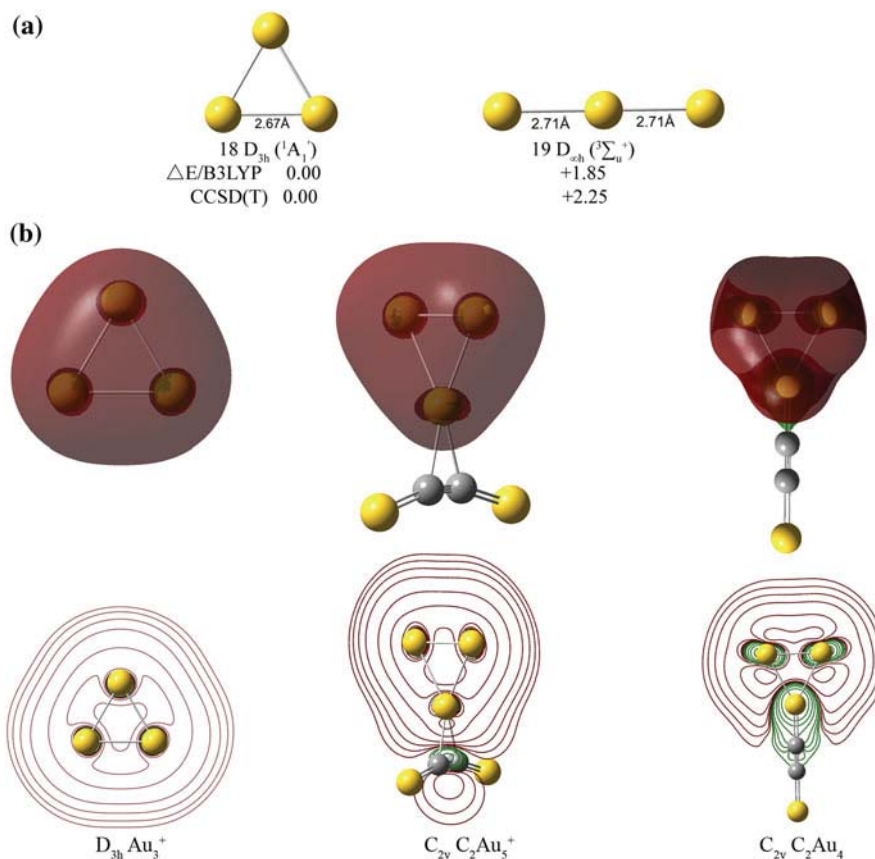


Fig. 5 **a** Two Lowest-lying isomers of Au_3^+ with their relative energies ΔE (eV) indicated at B3LYP and CCSD(T)//B3LYP and **b** orbital pictures and contour plots of the 3c–2e bonds in $D_{3h} Au_3^+$ (**18**), $C_{2v} C_2Au_5^+$ (**14**), and $C_{2v} C_2Au_4$ (**10**)

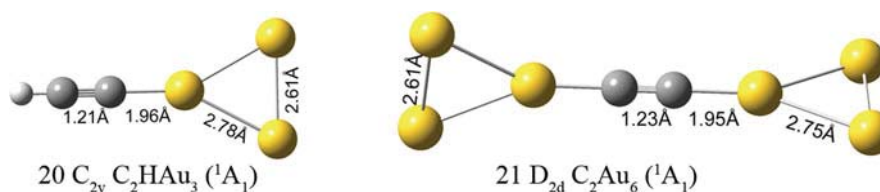


Fig. 6 Optimized structures of Au_3 -containing $C_{2v} C_2HAu_3$ and $D_{2d} C_2Au_6$ at B3LYP

The H/Au analogy is best demonstrated in the perfect linear $D_{\infty h}$ C_2Au_2 (**3**, $^1\Sigma_g^+$) which has exactly the same symmetry as an acetylene $D_{\infty h}$ C_2H_2 . $D_{\infty h}$ $Au-C\equiv C-Au$ (**3**) is a deep global minimum lying 3.58, 3.86, and 3.31 eV lower than the second lowest-lying isomer $C_{\infty v}$ C_2Au_2 (**4**, $^1\Sigma^+$) at B3LYP, PBE1PBE and CCSD(T)//B3LYP, respectively. The calculated HOMO–LUMO energy gap of 3.40 eV (see Table 1) well supports the high stability of this perfectly linear

Table 1 Calculated Wiberg bond indexes (WBI) and natural atomic charges (q_{el}) of the lowest-lying structures of C_2Au^+ ($n = 1, 3, 5$), C_2Au ($n = 2, 4$), and $\text{D}_{3h} \text{Au}_3^+$ (**18**) at B3LYP

Isomers	WBI		q		$\Delta E_{\text{HOMO-LUMO}}$
1 C_2Au^+ C_s ($3A''$)	C2–Au3	0.95	C1	0.39	5.19(α)
	C1–C2	1.90	C2	−0.23	2.41(β)
			Au3	0.84	
3 C_2Au_2 $\text{D}_{\infty h}$ ($1\Sigma_g^+$)	Au1–C4	0.92	Au1	0.44	3.40
	C3–C4	2.90	C3	−0.44	
			C4	−0.44	
5 C_2Au_3^+ C_{2v} ($1A_1$)	C4–Au3	0.76	Au1	0.75	3.93
	C4–Au1	0.39	Au2	0.67	
	C4–C5	2.50	C4	−0.54	2.09
10 C_2Au_4 C_{2v} ($1A_1$)	Au3–C1	0.67	C1	−0.52	
	Au4–C2	0.93	C2	−0.43	
	Au3–Au5	0.26	Au3	0.33	
	Au5–Au6	0.68	Au4	0.42	
	C1–C2	2.85	Au5	0.10	
14 C_2Au_5^+ C_{2v} ($1A_1$)	Au5–C6	0.25	Au1	0.62	3.25
	Au5–Au2	0.36	Au2	0.21	
	Au3–Au2	0.62	Au5	0.42	
	Au4–C6	0.78	C6	−0.55	
	C6–C7	2.59			
18 Au_3^+ D_{3h} ($1A_1''$)	Au–Au	0.47	Au	0.33	4.05

Calculated HOMO–LUMO energy gaps ($\Delta E_{\text{HOMO-LUMO}}$ /eV) at the same theoretical level have also been tabulated

Table 2 Calculated NICS (ppm) values for the Au_3 triangles in structures 10, 14–16, 18, 20, and 21 at B3LYP level

	NICS (0.0)	NICS (0.5)	NICS (1.0)
$\text{C}_{2v} \text{C}_2\text{Au}_4$ (10)	−27.9	−22.3	−13.4
$\text{C}_{2v} \text{C}_2\text{Au}_5^+$ (14)	−27.9	−22.6	−13.8
$\text{C}_1 \text{C}_2\text{Au}_5^+$ (15)	−29.2	−23.6	−14.1
$\text{C}_{2v} \text{C}_2\text{Au}_5^+$ (16)	−28.7	−22.1	−12.9
$\text{D}_{3h} \text{Au}_3^+$ (18)	−29.8	−24.4	−15.0
$\text{C}_{2v} \text{C}_2\text{HAu}_3$ (20)	−27.9	−22.3	−12.7
$\text{D}_{2d} \text{C}_2\text{Au}_6$ (21)	−27.5	−22.1	−13.2

molecule which contains a $\text{C}\equiv\text{C}$ triple bond with $r_{\text{C}\equiv\text{C}} = 1.21 \text{ \AA}$ and two equivalent C–Au σ -bonds with $r_{\text{C–Au}} = 1.92 \text{ \AA}$ (the two terminal C–Au σ -bonds prove to be mainly covalent (60%)). Our calculated Au–C and C–C bond lengths in linear $\text{D}_{\infty h} \text{C}_2\text{Au}_2$ (**3**, $1\Sigma_g^+$) agree well with the corresponding values obtained by Pyykko et al. [16]. The two Au terminals in this head-on coordinated neutral molecule carry the net atomic charges of $q_{\text{Au}} = +0.44 \text{ |el|}$.

$C_2Au_3^+$ and $C_2HAu_2^+$

Similar to the H-bridged $C_{2v} C_2H_3^+$, [38] a $C_2Au_3^+$ cation possesses the ground-state geometry of the Au-bridged $C_{2v} C_2Au_3^+$ (**5**, 1A_1) which lies 0.13, 0.16, and 0.24 eV lower in energy than the Au-terminated $C_{2v} C_2Au_3^+$ (**6**, 1A_1) at B3LYP, PBE1PBE and CCSD(T)//B3LYP, respectively. $C_2Au_3^+$ (**5**) possesses a considerably wide HOMO–LUMO energy gap (3.93 eV) and appears to be analogous in geometry to the Au-bridged $C_{2v} B_2Au_3^-$ at the same theoretical level [23]. However, a major difference occurs at the nature of the C–Au–C bridge bonding: with the bridging Au in $C_{2v} C_2Au_3^+$ (**5**) carrying the high positive charge of $q_{Au} = +0.75$ |e| and the two equivalent carbon atoms in the Au–C≡C–Au unit carrying the negative atomic charge of $q_C = -0.54$ |e|, $C_{2v} C_2Au_3^+$ (**5**) can be viewed as a side-on coordinated Lewis acid–base pair ($[Au-C\equiv C-Au]Au^+$) in which the bridging Au with an empty Au 6s orbital serves as an electron acceptor (Lewis acid) while the Au–C≡C–Au chain with two perpendicularly occupied π orbitals serves as an electron donor (Lewis base). Detailed NBO analyses indicate that the side-on coordination interaction with the Au–C bond length of $r_{Au-C} = 2.19$ Å in $C_{2v} C_2Au_3^+$ (**5**) is mainly ionic (89.9%). The coordination energy with respect to the reaction of $Au^+ + Au-C\equiv C-Au(D_{\infty h}) = [Au-C\equiv C-Au]Au^+(C_{2v})$ is estimated to be $\Delta E = -92.6$ kcal/mol at CCSD(T)//B3LYP level. Interestingly, an Au-bridge is favored over an H-bridge in a $C_2HAu_2^+$ mixed cluster: the Au-bridged $C_s C_2HAu_2^+$ (**7**, $^1A'$) proves to be about 0.60 eV more stable than the H-bridged $C_{2v} C_2HAu_2^+$ (**9**, 1A_1), similar to the situation on $B_2HAu_2^-$ [23].

 C_2Au_4 and $C_2Au_5^+$

Given the H/Au analogy, it is easy to design an ethylene-like $D_{2h} C_2Au_4$ (**13**, 1A_g) for C_2Au_4 [16]. However, as shown in Fig. 3, $D_{2h} C_2Au_4$ (**13**) turns out to be only a local minimum lying 0.52, 0.43, and 0.15 eV higher in energy than the head-on coordinated $C_{2v} C_2Au_4$ (**10**, 1A_1) at B3LYP, PBE1PBE, and CCSD(T)//B3LYP, respectively. The ground state $C_{2v} Au-C\equiv C-Au_3$ (**10**) is the first lowest-lying structure obtained which contains a head-on coordinating $-Au_3$ triangular unit. An Au_3 triangular unit was indeed experimentally observed in the ground state of Au_3BO^- [39]. NBO analyses indicate that the AuCC– Au_3 σ bond in $C_{2v} C_2Au_4$ (**10**) with the bond length of $r_{Au-C} = 1.96$ Å and the Wiberg bond order of $WBI_{Au-C} = 0.67$ is mainly covalent. Both the high symmetry $C_{2v} C_2Au_4$ (**11**, 1A_1) and the distorted $C_s C_2Au_4$ (**12**, $^1A'$) contain an $-Au_2$ unit somehow side-on coordinated to an Au–C≡C–Au chain and lie slightly higher than $C_{2v} C_2Au_4$ (**10**). Interestingly, an Au_3 triangle has also been formed in $C_s C_2Au_4$ (**12**) in the molecular plane. The appearance of a stable Au_3 triangle in the low-lying C_2Au_4 isomers with four gold atoms (**10** and **12**) is significant and intriguing. It represents a new kind of structural unit in gold-containing systems and presents the possibility of H/ Au_3 analogy in carbon auride clusters.

$C_2Au_5^+$ corresponds to $B_2Au_5^-$ [23] and $C_2H_5^+$ [38] in valence electron counts. However, much different from the H-bridged $C_{2v} C_2H_5^+$ [38] and the Au-bridged $C_{2v} B_2Au_5^+$ [23], the ground state of $C_2Au_5^+$ is the side-on coordinated $C_{2v} C_2Au_5^+$

(**14**, 1A_1) which lies 0.17 eV, 0.36 eV and 0.55 eV lower than the Au-bridged C_s $C_2Au_5^+$ (**15**, $^1A'$), the head-on coordinated C_{2v} $C_2Au_5^+$ (**16**, 1A_1), and Au-bridged C_{2v} $C_2Au_5^+$ (**17**, 1A_1) at CCSD(T)//B3LYP, respectively. The ground-state C_{2v} $C_2Au_5^+$ (**14**) is characterized with a side-on coordinating Au_3 triangle and can be obtained by substituting the bridging Au^+ cation in C_{2v} $C_2Au_3^+$ (**5**) or the bridging H^+ in C_{2v} $C_2HAu_3^+$ (**9**) with an Au_3^+ triangular unit, further supporting the H/ Au_3 analogy observed above in C_{2v} C_2Au_4 (**10**). Interestingly, the second lowest-lying C_s $C_2Au_5^+$ (**15**) and the third lowest-lying C_{2v} $C_2Au_5^+$ (**16**) also possesses head-on coordinated Au_3 triangles. The total net atomic charges of the $-Au_3$ triangles in C_{2v} $C_2Au_5^+$ (**14**), C_s $C_2Au_5^+$ (**15**), and C_{2v} $C_2Au_5^+$ (**16**) are calculated to be +0.86 |e|, +0.78 |e| and +0.80 |e|, respectively, quite close to the value (+1) of a unitary positive charge, indicating that the Au_3 triangles in these low-lying isomers behave like an Au_3^+ cation. It is also noticed that the Wiberg bond order of the Au–C coordination interaction is relatively low (WBI = 0.25) in C_{2v} $C_2Au_5^+$ (**14**). Thus, C_{2v} $C_2Au_5^+$ (1A_1) (**14**) can be practically viewed as an Lewis acid–base pair ($[Au-C \equiv C-Au]Au_3^+$) between an Au_3^+ cation and an $Au-C \equiv C-Au$ chain. The coordination bond length of $r_{C-Au} = 2.24$ Å in this complex appear to be obviously longer than the head-on coordinated covalent Au–C bond lengths of 1.99 Å in C_s $C_2Au_5^+$ (**15**) and 1.96 Å in C_{2v} $C_2Au_5^+$ (**16**). The head-on coordination in C_{2v} $C_2Au_5^+$ (1A_1) (**14**) is maintained by the estimated interaction energy of $\Delta E = -71.9$ kcal/mol with respect to $Au_3^+(D_{3h}) + Au-C \equiv C-Au(D_{\infty h}) = [Au-C \equiv C-Au]Au_3^+(C_{2v})$ at CCSD(T)//B3LYP.

Then, why Au_3 triangular units? What is the driving force to maintain the integrity of the gold triangles in small dicarbon aurides? We will try to answer these questions in the following parts.

3c–2e Bonds in Au_3^+ Triangular Units

To simplify the discussion, we compare the low-lying isomers of a free Au_3^+ in Fig. 5a. The equilateral triangle D_{3h} Au_3^+ (**18**, $^1A_1'$), which has the electronic configuration of $1a_1'^2 1e'^4 2a_1'^2 2e'^8 1a_2'^2 1a_2''^2 1e''^4 3a_1'^2 3e'^4 2a_2''^2$, the bond length of $r_{Au-Au} = 2.67$ Å, and the Wiberg bond order of $WBI_{Au-Au} = 0.47$, appears to be the ground state of Au_3^+ lying 2.25 eV lower than the linear triplet $D_{\infty h}$ Au_3^+ (**19**, $^3\Sigma_u^+$) at CCSD(T) level. Our D_{3h} Au_3^+ (**18**) agrees well with the D_{3h} Au_3^+ structures proposed by Zhao [40] and Stefan and coworkers [41] which have the bond lengths of $r_{Au-Au} = 2.67$ and 2.64 Å, respectively. The calculated Au–Au bond length (2.67 Å) is obviously shorter than Ag–Ag distance in triangular D_{3h} Ag_3^+ (2.74 and 2.75 Å obtained by Klacar [42] and Tian [43], respectively) due to much stronger relativistic effects in gold. This bond lengths stand well in line with the calculated Au–Au distances of 2.60–2.78 Å in the Au_3 -containing structures shown Figs. 3, 4, and 6.

As shown in Fig. 5b, D_{3h} Au_3^+ (**18**) possesses a completely delocalized 3c–2e σ -bond (τ bond) with the orbital hybridization of $\tau_{Au-Au-Au} = 0.58(sp^{0.04}-d^{0.01})_{Au} + 0.58(sp^{0.04}-d^{0.01})_{Au} + 0.58(sp^{0.04}-d^{0.01})_{Au}$. The three equivalent Au atoms contribute equally to the 3c–2e bond in the cation, with Au 6s, Au 6p, and Au 5d contributing about 95%, 4%, and 1% to the Au-based orbital, respectively. With two

delocalized σ electrons in the valence shell, D_{3h} Au_3^+ (**18**) satisfies the $4n + 2$ Huckel aromatic rule with $n = 0$ and therefore is σ -aromatic in nature, making it a highly stable structural unit head-on or side-on coordinated to a $X-C\equiv C-X'$ unit in small dicarbon aurides with only slight structural distortions. For example, as shown in Fig. 5b, the side-on coordinated C_{2v} $C_2Au_5^+$ (**14**) contains such a 3c–2e bond over the $-Au_3^+$ triangle which has the orbital hybridization of $\tau_{Au-Au-Au} = 0.61(sd^{0.02})_{Au} + 0.50(sd^{0.07})_{Au'} + 0.61(sd^{0.02})_{Au}$ (Au' stands for the Au atom coordinated to two C atoms) (see Fig. 5b). There exists also a similar 3c–2e bond over the $-Au_3$ triangle in the head-on coordinated C_{2v} C_2Au_4 (**10**).

It is interesting to compare Au_3^+ with H_3^+ at this stage. It is true that an H_3^+ cation has an equilateral triangle (D_{3h} , $^1A_1'$) ground state which is also σ -aromatic in nature [44, 45]. However, an H_3^+ triangle proves to be not robust enough to exist in the ground state of the H-bridged C_{2v} $C_2H_5^+$ [38]. The Au–Au metallic bonding and the unique relativistic effect in gold help to maintain the integrity of Au_3 triangular units in dicarbon aurides. Gold triangles can serve as a Lewis acid head-on or side-on coordinated to a Lewis base (like the $Au-C\equiv C-Au$ unit mainly concerned is this work) through $\sigma \rightarrow \sigma$ or $\pi \rightarrow \sigma$ back-donation.

As shown in Fig. 6, Au_3 triangular units can serve as substituents to replace one H atom in C_2H_2 to form the head-on coordinated C_{2v} C_2HAu_3 (1A_1) (**20**) or two H atoms in C_2H_2 to produce the doubly head-on coordinated D_{2d} C_2Au_6 (1A_1) (**21**). These structures all prove to be true minima of the corresponding systems, strongly supporting the H/ Au_3 analogy presented in this work.

NICS Values of the Au_3 Triangles

NICS values have been shown to serve as effective indicators of aromaticity for various molecules in explaining their structures, stabilities and reactivities [46, 47]. For D_{3h} Au_3^+ (**18**), the calculated negative NICS values of $NICS(0.0) = -29.8$ ppm, $NICS(0.5) = -24.4$ ppm, and $NICS(1.0) = -15.0$ ppm strongly support its global σ -aromaticity. Furthermore, as indicated in Table 2, all the concerned dicarbon aurides possess highly negative NICS(0.0) values at the geometrical centers of the Au_3 triangles they contain, indicating again the strong local σ -aromaticity of these clusters. It is the σ -aromaticity of these Au_3 triangles that keeps the triangular structural units stable in dicarbon aurides and introduces extra stabilities to the clusters as a whole. The highly electronegative carbon atoms strongly withdraw electrons from Au atoms to form stable Au_3^+ triangular units in dicarbon aurides. However, such Au_3 triangles do not exist in small diboron aurides $B_2Au_n^-$ and their mixed analogues $B_2H_xAu_y^-$ [23] for the reason that B atoms are not electronegative enough to form stable Au_3^+ triangles in such systems.

Summary

We have presented a structural pattern for $C_2Au_n^+$ ($n = 1, 3, 5$) and C_2Au_n ($n = 2, 4, 6$) dicarbon aurides at DFT levels in this work. As the size of the clusters increases, gold atoms serve as terminals and bridges in small dicarbon aurides, and

form triangles when the number of gold atoms reaches four. H/Au analogy has been extended to H/Au₃ analogy in this work. The high stability of Au₃ triangles in small dicarbon aurides originates from the completely delocalized 3c–2e σ bonds of the Au₃⁺ triangles which renders high local σ -aromaticity to the concerned clusters. This observation in C–Au binary systems reminds us the fact that small gold clusters Au_n are all built up with Au₃ triangular units [40], as exemplified by the well-known tetrahedral Au₂₀ cage which is covered solely with Au₃ triangles [48]. It is reasonable to expect that, through a side-on or head-on [X–C $\equiv$ C–X'] $\rightarrow$ Au₃ back-donation ($\pi \rightarrow \sigma$ or $\sigma \rightarrow \sigma$), medium-sized and nano-scaled gold clusters with Au₃ triangles on surfaces may serve as effective catalysts to catalyze C $\equiv$ C involved chemical reactions.

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