

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

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To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201814359 Angew. Chem. 10.1002/ange.201814359

Link to VoR: http://dx.doi.org/10.1002/anie.201814359 http://dx.doi.org/10.1002/ange.201814359

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Unusual Attractive Au-π Interactions in Diacetylene-modified Small Gold Clusters

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Abstract: It is well known that alkynes serve as π -acid to form metal complexes through strong π -coordination bonds. In this work, we highlight unprecedented "attractive" Au-π interactions found in diacetylene-modified [core+exo]-type $[Au_8]^{4+}$ clusters (2). The 4-phenyl-1,3-butadiynyl-modified cluster (2a) showed unusually short $Au-C_{\alpha}$ distances in the crystal structure, revealing the presence of attractive interactions of the coordinating C=C moieties with the neighboring bitetrahedral Au₆ core, which was further supported by IR and NMR spectra. To note is the fact that such weak interactions were not found in mono-acetylene-modified clusters (1), indicating they are specific for diacetylenic ligands. The Au- π attractive interactions are likely associated with the low π^* energy level of the diacetylenic moieties, to which the valence electrons in the gold core may be donated in a backdonation-like manner. 2 showed clear red shifts of > 10 nm with respect to the corresponding mono-acetylenic clusters (1) for the visible absorption bands, indicating the substantial electronic perturbation effects of the Au- π interactions. This work implies potential utility of diacetylenic ligand for the emergence of unique binding motif and cluster structures.

Ligand-protected gold clusters with defined nuclearity and geometrical structure have attracted considerable interests in relation to the applications in optoelectronic materials and catalysis.^[1-6] Thiolates^[1-3] and phosphines^[6-10] have been frequently used as protecting ligands, while alkynyl (acetylide) ligands have recently emerged as unique and suitable ligands stabilizing gold clusters.^[4] Unlike thiolates and phosphines having only σ -bonding coordination characters, π -electron functionalities of acetylide ligands serve as both σ - and π -donors to interact gold atoms, enabling the formation various coordination motifs on the cluster surface. The first example of such alkynyl-protected gold clusters is Au₅₄(C≡CPh)₂₆ reported by Tsukuda et al in 2012,^[11] but the crystal structure determination has not been achieved. We have also introduced alkynyl ligands in Au₈ and Au₁₃ clusters as coligands and showed the substantial perturbation effects of particular π electron systems on the electronic properties of the gold clusters.^[12-15] In addition, Q.-M. Wang et al have recently reported numerous homoleptic and heteroleptic alkynylprotected gold clusters, demonstrating the formation of various surface Au(I)-acetylide motifs such as -C≡C-Au-C≡C- and -C≡C-

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http://dx.doi.org/10.1002/xxx

Au-C=C-Au-C=C-.^[16-20] These motifs are analogous to the staple units found in the thiolate-protected clusters but to note is the capability to accommodate additional gold atoms through π coordination. Such diverse coordination modes of alkynyl ligands are unique features that are not found for conventional σ -only type ligands, which expand the scope and aspects of molecular gold clusters.

In the examples mentioned above, mono-acetylenic ligands, such as phenylethynyl, have been used as the protecting ligands. Herein we show that diacetylenic (1,3-diynyl) ligands (C=C-C=CR) have unusual interaction activities with gold frameworks, which were firmly identified by X-ray crystal structures, IR spectra, and solution NMR spectra. The attractive interaction affected HOMO-LUMO gap energies, causing substantial red shifts of the visible absorptions. The present finding demonstrates that diacetylenic ligands offer opportunities to create novel structures / properties that cannot be achieved by the use of simple mono-acetylenic ligands.

4-Aryl-1,3-butadiynes (aryl = phenyl or 4-pyridyl) were synthesized by organic syntheses and introduced at the two *exo* positions of dppp (Ph₂P(CH₂)₃PPh₂)-coordinated [core+*exo*]-type Au₈ cluster ([Au₈(dppp)₄R₂]²⁺) in a similar manner to that reported for the synthesis of mono-acetylenic-ligated clusters (**1**, Fig. 1).^[12] Thus, the reaction of [Au₈(dppp)₄]²⁺ with the alkynyl anions proceeded smoothly at ambient conditions. The product clusters with two diacetylenic fragments were isolated as nitrate salts (**2**), which were characterized by electrospray ionization (ESI) mass (Fig. S3) and NMR spectra.





X-ray crystallography was successfully performed for the 4phenyl-1,3-butadiynyl-modified cluster (**2a**), whose structure was compared with a mono-acetylenic analogue (**1a**).^[12] As shown in Fig. 2, **1a** and **2a** both had similar [core+*exo*]-type Au₈ frameworks composed of a bitetrahedral Au₆ core and two attached gold atoms at *exo* positions. The Au₆ cores gave almost same structural parameters (Table S3), but marked differences were found around the coordinating C=C moieties. Thus, as shown in Fig. 2b, the diacetylenic units of **2a** are substantially tilted from the terminal Au₃ triangles (Au_{edge}-Au_{exo}-C_a angle: 65.7 and 77.5°, Table 1), which is contrastive to the almost perpendicular orientation of the ethynyl units of **1a** (Fig. 2a) with Au_{edge}-Au_{exo}-C_a angles of 84.8 and 86.7° (Table 1). It should be noted that the coordinating carbon atoms (C_a) of **2a**

are located in proximity to the gold atoms on the exo-bridged edges of the bitetrahedron (Au_{edge}). The Au_{edge}-C_{α} distances are 2.98 and 3.26 Å (Table 1) which are longer than the distance of normal Au-C bonds but shorter than the sum of the van der Waals radii (3.36 Å). Thus, in addition to the conventional atop σ -coordination of terminal alkynyl units, the α -carbon atoms (C $_{\alpha}$) of 2a have attractive interaction with neighboring gold atoms. On the other hand, the corresponding distances of 1a (3.41 and 3.53 Å, Table 1) were sufficiently above the distance of van der Waals contacts, indicating the absence of the attractive interactions. Since the distances of the Au_{exo} - C_{α} coordination bonds of the two clusters were similar to each other (2.02 and 2.00 Å, respectively) (Table 1), the unusually short Au_{edge} -C_a distances in 2a are likely solely due to the attractive force with the bitetrahedral Au₆ core, rather than the enhancement of the σ -coordination of C_{α} to Au_{exo}. The intramolecular interactions appeared to be correlated with the substantial distortion of the Au₈ framework. The terminal Au₃ triangles of 2a were tilted from the mean plane of the four Au_{edge} atoms by ~14.2°, whereas in 1a they are almost in plane (angle: ~2.0°) (Table 1). Accordingly, 2a showed longer Auedae-Auexo distances (3.05 and 3.18 Å) than 1a (2.93 and 3.02 Å) (Table 1).

As mentioned, the diacetylenic cluster (2a) had intramolecular interactions involving the C_{α} atoms, which were not found in the mono-acetylenic cluster (1a). One of the possible factors to contribute to this difference is the steric hindrance of the Ph groups attached to the ethynyl ligands of 1a, which may hamper the access of the $C_{\alpha}\equiv C$ moiety to the Au_{edge} atoms owing to the repulsion with the neighboring P-Ph groups (Fig. 1(i)). However, such steric effects seem not critical since no substantial interactions were observed in the 1-hexynyl-modified

Table 1. Selected Structural Parameters of 1	a, 1c and 2a.ª
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	1a	1c	2a
Au _{edge} —Au _{exo}	2.93, 3.02 Å	2.94, 3.03 Å	3.05, 3.18 Å
$Au_{edge}-C_{\alpha}$	3.41, 3.53 Å	3.24, 3.44 Å	2.98, 3.26 Å
Au _{exo} –C _α	2.02 Å	2.02 Å	2.00 Å
Au _{edge} –Au _{exo} –C _a	84.8, 86.7°	79.2, 83.4°	65.7, 77.5°
Tilt angle ^b	2.0 °	5.1 °	14.2 °

 a For atom labeling, see Figure 2. b Angles between the terminal Au_3 triangles and the mean plane composed of four Au_{edge} atoms.

cluster (1c).^[12] When compared with 1a, the $C_{\alpha} \equiv C$ units of 1c were slightly oriented towards the Au_{6} core (Fig. S4), suggesting the presence of some degree of steric hindrance in 1a. Accordingly, the Au_{edge} - C_{α} distances of 1c were shorter than 1a, but they are around the distance of the van der Waals contact (Table 1). Thus, the $C_{\alpha} \equiv C$ -mediated attractive interactions in 1c seem negligible, similarly to 1a. The similarity of the structural features of 1a and 1c was further supported by the IR and NMR spectra (*vide infra*). Therefore, it is likely that electronic factors, rather than the steric effects, primarily responsible for the diacetylenic-specific attractive interaction.

The unusual interaction between the Au₆ core and the C_α atoms of **2a** is considered to be associated with the π-systems of the diacetylenic moieties. To obtain further insights into this point, we measured IR spectra of **2a** and also the 4-pyridyl-substituted analogue (**2b**) in order to check the generality. As shown in Table 2 (entry 4) and Fig. S5, **2a** (KBr pellet) gave two vibration bands at 2054 and 2179 cm⁻¹. A related σ -gold(I) complex of 4-phenyl-1,3-butadiyne (Ph₃PAuC₄Ph) was reported to show vibrations at 2134 and 2181 cm⁻¹, but the assignments



Figure 2. X-ray crystal structures of (a) 1a and (b) 2a. (i) Entire and (ii) (iii) partial structures of the cationic moieties with hydrogen atoms omitted for clarity.

were not given.^[21] If the lower-energy bands are tentatively assigned due to the terminal coordinating $C_{\alpha}\equiv C$ bonds, the red shifts of the vibrations of **2a** from the above reference complex are evaluated 80 and 2 cm⁻¹ for the coordinating and distal C≡C moieties, respectively. This assignment seems reasonable considering that the C_{α} atoms of **2a** are involved in additional interactions in the crystal structure. **2b** also showed two bands at similar wavenumbers (2060 and 2182 cm⁻¹, entry 5). On the other hand, their mono-acetylenic analogues (**1a** – **1c**) gave C≡C vibrations at ~2100 cm⁻¹ (entries 1 - 3) (Fig. S5a-c). Accordingly, vibration bands of the coordinating $C_{\alpha}\equiv C$ bonds of the diacetylenic clusters (**2**) were red-shifted by ~50 cm⁻¹ from those of corresponding mono-acetylenic counterparts (**1**), which appears to be concerned with the attractive interaction found in the crystal structure of **2a**.

 $\ensuremath{\textit{Table 2}}$. IR and UV-vis Absorption Data of Alkynyl-ligated Au_8 Clusters.

entry	cluster	$v_{C \equiv C} (cm^{-1})^{a}$	λ (nm) ^ь
1	1a	2101	509
2	1b	2107	512
3	1c	2113	509
4	2a	2054, 2179	520
5	2b	2060, 2182	524

^a In KBr pellet at room temperature. ^b In methanol at 25°C.

The above crystallographic and IR profiles implied that the σcoordinated $C_{\alpha} \equiv C$ bonds of the diacetylenic Au₈ clusters (2) are weakened as a result of the additional interaction with the neighboring gold atoms in the Au₆ framework. Such a bond weakening has been well established in many alkyne mcomplexes^[22-23] and also found in phenylethynyl-capped gold clusters.^[11, 17, 24] In the present case, one can also postulate the possibility of σ - and π -complexation for the additional interaction. Actually, recent crystallographic studies of phenylethynyl-capped gold clusters have shown diverse binding motifs, some of which contain σ -bonded Au-C=C- moieties that simultaneously bind neighboring gold atoms via σ - or π -coordination.^[4] However, such $\sigma\text{-}$ or $\pi\text{-}\text{bonding}$ is unlikely in 2, considering the long distances and relative orientation between the $C_{\alpha}\equiv C$ and Au_6 framework in the crystal structure (Fig. 2b). Furthermore, as mentioned, the additional interaction is specifically observed for diacetylenic clusters (2), not for the mono-acetylenic clusters (1). In this relation, the energy level of π^* orbital of 1,3-butadiynyl anion was shown to be substantially lower than that of the corresponding ethynyl anion.[25-26] On the basis of this information, we would propose the involvement of "backdonation-type" mechanism for the attractive interaction, as illustrated in Fig. 3. Thus, the low energy level of π^* orbital of the conjugated diacetylenic system may facilitate the through-space electron donation from the bitetrahedral Au₆ core. For the electron donation from the gold core, our previous theoretical and experimental studies on a series of [core+exo]-type gold clusters demonstrated that the HOMO is localized around the exo-bridged edges of the polyhedral core,^[27] and the core serves as an electron pool to induce unique behaviors.^[14, 28] Thus, the electron-donating capability of the Au₆ core, as well as the diacetylene π^* orbital level, is likely responsible for the unusual attractive Au- π interaction in **2**.



Figure 3. Schematic illustration of a possible mechanism of the Au- π interaction. Back-bonding-like electron donation from the Au₆ core to the σ -bonded C=C unit in **2**.

To obtain further insights into the attractive Au- π interactions specific in the diacetylenic clusters (2), we conducted DFT calculation studies of 1a and 2a. As shown in Fig. S6, orbital distribution features of 1a and 2a were similar to each other for HOMO and LUMO, but notable differences were found in the lower-energy occupied orbitals. Specifically, in 2a, two bonding interactions between the superatomic cluster orbitals located around the Au_{edge} atoms and C_q=C units were explicitly found in the HOMO-2 and HOMO-4, which respectively involve each of the two orthogonally oriented $C_{\alpha} \equiv C \pi$ orbitals (e.g., π_{2py} , π_{2pz}) (Fig. 4). Therefore, the attractive interaction found in the diacetylenic cluster appears to be augmented by dual interactions of the cluster valence electrons with the two π orbitals. In contrast, for 1a, there were no signs of bonding interactions between the molecular orbitals of the gold cluster units and the C_α≡C moieties in the lower-energy orbitals as far as inspected to HOMO-8 (Fig. S6a). In this relation, natural bond orbital (NBO) analyses revealed that 2a has more positive charges on the Au_{edge} atoms and negative charges on the C_{α} =C units than 1a (Fig. S7). These results may reflect the preference of the back-donation character of the electronic interaction of the Au₆ core with the diacetylenic moieties.



Figure 4. DFT molecular orbital plots for (a) HOMO-2 and (b) HOMO-4 of **2a**.

As described, crystallographic and IR studies have clearly revealed the [core+exo]-type Au₈ clusters bearing mono- (1) and di-acetylenic units (2) attached to the exo gold atoms were structurally different, which are associated with the intramolecular attractive Au- π interaction. Based on these structural features in solid states, we next measured NMR spectra to investigate the solution structures. The ³¹P NMR spectra of the four clusters all displayed three signals with an integrated intensity ratio of 1 : 2 : 1, in agreement with the

[core+exo]-type Au₈ framework decorated by four dppp ligands. However, the careful comparison revealed that there is a marked trend to discriminate 1 and 2 in terms of the chemical shifts of the signals assignable to the phosphorus atoms bonded to the Auedge and Aucenter atoms (Pedge and Pcenter) (Fig. S8). The P_{center} signals of the **2a** and **2b** were observed at $\delta = \sim 54.9$, which were upfield from those of the mono-acetylenic clusters (1a - 1c) (δ = ~55.6). On the contrary, P_{edge} signals appeared at a lower magnetic field for **2** (δ = ~51.6) than for **1** (δ = ~51.0). Such a difference between 1 and 2 was also observed in the ¹H NMR spectra for some protons of phenyl groups of dppp ligands (Fig. 5 and Table S4). The signals of o-protons of Ph2 of 2a and **2b** are observed at $\delta = -8.0$ ((c) and (d)), which are upfield from corresponding signals of **1a**, **1b** and **1c** (δ = ~8.1, (a - c)). Since the Ph2 groups are located closed to the coordinating C≡C moieties, the observed NMR profiles may reflect the presence/absence of the Au-m attractive interaction. On the other hand, the *m*- and *p*-protons of Ph1 of **1a** and **1b** were observed upfield from those of 1c, 2a, and 2b (Fig. 5), suggesting the spatial proximity of the Ph1 groups to the terminal aryl groups of the acetylide ligands of 1a and 1b.



Figure 5. Aromatic region of ¹H NMR spectra of (a) **1a**, (b) **1b**, (c) **1c**, (d) **2a**, and (e) **2b** in CD₂Cl₂ / CD₃OD (1/1) at 25 °C. The asterisks indicate the signals assignable to *p*-Ph1 (δ = ~7.0) and *m*-Ph1 (δ = ~6.8). Structure with Ph-group labeling is also shown.

Finally, we accessed the electronic properties to investigate the perturbation effects of the intramolecular Au- π interactions. We have previously reported that the [core+exo]-type Au₈ clusters exhibit single absorption bands at 500-550 nm due to the HOMO-LUMO transitions within the gold framework, and the positions (wavelengths) sensitively reflect band the electronic/attractive interactions with the proximal ligand moieties. As summarized in Table 2, the diacetylenic clusters (2a and 2b) showed red shifts of > 10 nm with respect to the corresponding mono-acetylenic clusters (1a and 1b) (Fig. S9). Such red shifts have been reported when specific heteroatoms undergo attractive interaction with the gold core.^[14] Therefore, the red shift of the HOMO-LUMO transitions appears to be a result of the perturbation effect caused by additional interactions.

In conclusion, we have demonstrated that C=C ligands and gold frameworks of diacetylene-modified Au₈ clusters undergo not only atop-type σ -bonding but also additional Au- π attractive interaction. Such interactions were not found in simple mono-acetylene-modified analogues and hence are specific for the diacetylenic clusters. The involvement of back-bonding type electron donation from the cluster core to π^* orbital of diacetylenic units was proposed. With respect to the bonding patterns of C=C units in protected gold clusters, there are numerous configurations involving well-known σ - / π -bonding, such as Au-C-Au bridging. The present interaction does not fall into these categories, and, rather may be related to the hollow-site adsorption found in the interactions on substrate surface.^[29-30] The unique capability of diacetylenic ligands would endow intriguing structures and properties in metal cluster chemistry.

Experimental Section

Diynes were prepared by organic synthesis (see Supporting Information) and were reacted with $[Au_8(dppp)_4](NO_3)_2$ according to the method reported for the synthesis of mono-acetylenic clusters (1).^[8] 2a: To a methanolic solution (20 mL) of [Au₈(dppp)₄](NO₃)₂ (20.0 mg, 5.47 µmol) was added buta-1,3-diyn-1ylbenzene (3.0 mg, 23.9 µmol) and sodium methoxide (6.4 mg, 119 µmol), and the mixture was stirred for 13 h at room temperature under nitrogen and room light. The product was further purified by vapor diffusion of ether into a cluster solution in methanol to give 2a as pink crystals (6.5 mg, 59%). CCDC 1834911 (2a) and 1885501 (1c) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif. 2b was prepared in a similar manner to the preparation of 2a. Characterization data (ESI-MS and NMR) are given in Supporting Information.

Acknowledgements

This work was supported by MEXT/JSPS Grants-in-Aid (KAKENHI 18H01987 to K.K., 16H05961 to Y.S., and 18J11586 to M.I) and Mitsubishi Foundation. We thank the help of Dr. K. Yoza of Bruker AXS in the crystal data refinement.

Keywords: cluster compounds \cdot gold \cdot diyne $\cdot \pi$ -complex \cdot ligand effect

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