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Authors: Jiaxin Chen, Lu Huang, Lifang Wu, Yichi Zhang, Rong Zhang, Yinhuan Li, Yunqing Zhao, Liliang Wang, Dewei Feng, Mitsuo Kira, Zhenyang Lin, and Zhifang Li

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Isolable Tetrargold(0) Clusters with Polarity-Tunable exo-Au–Au Bond via Intramolecular σ-Aromatization


[a] J. Chen, L. Huang, L. Wu, R. Zhang, Y. Li, Y. Zhao, Prof. Dr. L. Wang, D. Feng, Prof. Dr. M. Kira, Prof. Dr. Z. Li
College of Material Chemistry and Chemical Engineering, Key Laboratory of Organosilicon Chemistry and Material Technology, Ministry of Education, Key Laboratory of Organosilicon Material Technology of Zhejiang Province, Hangzhou Normal University
Hangzhou (China)
E-mail: twang@hznu.edu.cn; zhifanglee@hznu.edu.cn
[b] J. Chen, Y Zhang, Prof. Dr. Z. Lin
Department of Chemistry, The Hong Kong University of Science & Technology
Clear Water Bay, Kowloon, Hong Kong (China)
E-mail: chzlin@ust.hk
† These authors contributed equally to this work.

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Abstract: Intramolecular π-aromatization is a trait of many organic compounds that enhances the stability of their structures and polarizes related C–C π bonds. In contrast, rare study is focused on this phenomenon in metal clusters. Many existing homometallic clusters exhibit aromaticity, often characterized by nonpolar metal-metal bonds and a high degree of symmetry. However, synthesizing low-symmetric homometallic clusters with high-polar metal-metal bonds is challenging due to their limited thermodynamic stability. Herein, we report a facile strategy for the synthesis of [Au(μ3-ER2)]2−AuPMe3 (E = Ge, Sn; R2 = 1,1,4,4-tetrais(trimethylsilyl)butane-1,4-diy) clusters and reveal a novel stabilization mode, intramolecular σ-aromatization. Our electronic structure analyses show that these low-symmetric clusters possess a ten-electron σ-aromatic system, which is achieved via intramolecular σ-aromatization. Moreover, the strength of σ-aromaticity gives rise to a polarity-tunable exo-Au–Au bond.

In 1825, Faraday’s discovery of benzene paved the foundation for Hofmann to introduce the concept of aromaticity in 1856.[1] Since then, aromaticity has expanded to include a wide range of compounds, ranging from organic to inorganic, with descriptors evolving into four criteria: geometric, energetic, magnetic, and electronic. Nowadays, new types of aromaticity have emerged, including heteroaromaticity, Möbius aromaticity, three-dimensional aromaticity, and excited state aromaticity.[2] In recent decades, various planar homometallic clusters have been synthesized and have often been discovered with aromaticity and high symmetry. For example, Wang and co-workers invoked σ-aromaticity to explain the stability of the square planar [Au4]4− cluster, which was later demonstrated by Islas et al. as doubly aromatic with both σ and π electrons being delocalized.[3] Afterwards, the concept of σ-aromaticity was extended to the designing and synthesis of other triangular clusters subsequently, such as [L[Au3]]n− (L = N-heterocyclic carbene and cyclic-(alkyl)-(amino) carbenes).[4][5][6] [R2(EAu)3]− (E = Si, Ge, and Sn; R2 = 1,1,4,4-tetrais(trimethylsilyl)butane-1,4-diy),[7] [Zn3(Cp*)3]− (Cp* = η3-C5Me5),[8] anionic metal Ta2O7,[9] and [Th(C6H5)2Cl2]2+ cluster.[8]

As above, existing homometallic clusters with aromaticity usually consist of nonpolar metal-metal bonds due to their stable aromatic non-polarized Lewis structures, restricting the development of homometallic clusters in the aspect of structural varieties. In contrast, the intramolecular π-aromatization can enhance the stability of planar organic compounds having various structural features, accompanying the polarization of C–C π-bonds over a conjugated system in organic chemistry. Examples of such compounds include methylenecyclopropane (I),[9] fulvene (II),[10] calicene (III),[11] and azulene (IV).[12] Figure 1a), which would undergo intramolecular π-aromatization, giving rise to more stable aromatic zwiterionic Lewis structures.[13] This behavior has seldom been reported in metal clusters. As aromaticity can significantly contribute to the stability and reactivity control of homometallic clusters,[14] we naturally assumed that intramolecular aromatization will also carve out a place in constructing unprecedented homometallic clusters.

Based on these considerations and our previous work,[5] we herein designed and synthesized [Au(μ3-ER2)]2−AuPMe3 clusters. The cyclic-[Au(μ3-ER2)]3+ moiety contributes nine in-plane electrons (three 6s Au electrons and six in-plane electrons from the three μ3-ER2 bridging units), whereas the exo-AuPMe3 moiety provides another electron. This enables intramolecular σ-aromatization to occur in the planar accompanying the formation of a highly polarized exo-Au–Au σ bond toward the cyclic-[Au(μ3-ER2)]3+ moiety, even allowing the formation of an aromatic zwiterionic Lewis structure (Figure 1b). To the best of our knowledge, the neutral Au4 cluster has not yet been isolated in the laboratory, but theoretical chemists have predicted that it could have two possible molecular geometries: a C2v Y-shape or a D2h rhombus.[15] This uncertainty underscores the importance of precise synthesis of the Au4 cluster at atomic-level, meanwhile, which is also a great challenge for synthetic chemists.[16] Here, we report the synthesis of (R2E Au)3−AuPMe3 (E = Ge (2a), and Sn (2b); R2 = 1,1,4,4-tetrais(trimethylsilyl)butane-1,4-diy) clusters through the rarely nucleophilic substitution reaction of (R2E Au)3+ anion with Me3PAuCl, and demonstrate that the polarity of the exo-Au–Au bond can be tuned by the strength of σ-aromaticity, even resulting in a distinct ionization behavior of the two clusters in solution (Figure 1b).
COMMUNICATION

a. Polarization of C-C σ bond via intramolecular π-aromatization

I. Methylene cyclopropane

II. Fulvene

III. Calicene

IV. Azulene

b. Polarization of exo-Au-Au σ bond via intramolecular α-aromatization

This work

Figure 1. Molecules involving different types of intramolecular aromatization. a) Organic molecules stabilized through intramolecular π-aromatization. b) (R(2)EAu)-AuPM3 stabilized through intramolecular α-aromatization in solid state and the distinct ionization behavior of (R(2)EAu)-AuPM3 in solution state tuned by α-aromaticity.

Scheme 1. Synthesis of 2a and 2b.

The synthesis of ligand-enveloped Au4 clusters 2a and 2b was achieved through a metathesis reaction, in which an excess amount of Me3PAuCl was added to a tetrahydrofuran (THF) solution of cyclic-[Au(μ2-ER)2]K (1a and 1b) at room temperature to yield, respectively, the tetracold(0) complexes 2a (34%) and 2b (51%) as green solids (Scheme 1). The tetracold(0) clusters 2a and 2b were stable under inert conditions and exhibited poor solubility in nonpolar hydrocarbons but decomposed in chlorinated solvents and acetonitrile. Single crystals of these complexes were obtained by volatilizing the THF solutions in a glovebox at ~30 °C. The structures of 2a and 2b were characterized using single-crystal X-ray diffraction, multinuclear NMR spectroscopy, and high-resolution mass spectrometry. The experimental details are provided in the Supporting Information (SI).

Single-crystal X-ray diffraction analysis revealed that both molecular structures 2a and 2b in the solid state exhibited nearly reflective symmetry, with the exo-Au atom located almost on the reflection symmetry plane (Figure 2). The Au2–Au3 bond adopted a coplanar configuration with a cyclic-Au3 ring in both structures. The Ge1–Au2 bond length in 2a (2.5334(9) Å) was considerably longer than that for Ge1–Au1 (2.4807(9) Å) and known Ge–Au bond lengths (2.3271–2.4277 Å).[16] On the other hand, the Au1–Au4 bond length in 2a (2.7188(6) Å) was significantly shorter than those of Au1–Au2 (2.8471(5) Å) and 1a (average 2.8498 Å), where the shortest Au–Au distance was 2.5932(6) Å, which was assigned to the Au2–Au3 bond. In contrast to the structural parameters of 2a, the three Ge–Au bonds in 1a (average 2.4780 Å) were almost equal.[14] In 2b, the intranuclear Au–Au bond distances were slightly longer than those in 2a; however, the exocyclic Au2–Au3 bond length was 0.02 Å shorter. The three intranuclear gold atoms remained in an isosceles triangular coordination environment, with the Au1–Au2–Au4 angle being 57.04° for 2a and 57.67° for 2b, and the Au4–Au1–Au2 angle being 61.48° for 2a and 61.75° for 2b. In contrast to the trigold anions 1a and 1b, the cyclic-[R(2)EAu3] moiety was distorted in both 2a and 2b, which could be attributed to the presence of the exo-Au–Au bond.

Figure 2. Molecular structures of 2a and 2b. Hydrogen atoms were omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Trimethylsilyl and methyl groups are depicted in a wireframe model.

In the 1H NMR spectrum of 2a at room temperature in C6D6, the signals of the methylene and trimethylsilyl (TMS) protons in 1,1,4,4-tetraakis(trimethylsilyl)butane-1,4-diy1 appeared at 2.16 and 0.47 ppm, respectively, as sharp singlets (Figure S1), indicating that the three dialkylgermylene ligands were equivalent in solution. However, the solid structure shows that the three dialkylgermylene ligands have different chemical environments (Figure 2a). The other sharp doublet at 0.62 ppm with a coupling constant of 12 Hz was assigned to the methyl protons of PMe3. In contrast, the 1H NMR spectrum of 2b displayed broadening of the TMS proton signals at 0.19, 0.22, and 0.24 ppm, and two singlet peaks at the chemical shift at 2.75 and 2.78 ppm (intensity ratio 2:1), which were assigned to the ring methylene protons (Figure S5). In other words, unlike those in 2a, the three dialkylstannylene ligands in 2b were not equivalent and can be divided into two types at a ratio of 1:2. Trimethylphosphine ligated to the exo-Au
atom exhibited a doublet signal in the $^1$H NMR at 1.69 ppm with a coupling constant of 12 Hz and a signal in the $^{31}$P NMR at 7.71 ppm (Figure S8). The $^{1}$C and $^{29}$Si spectra of 2b at room temperature were also consistent with those of the solid structures determined by X-ray crystallography (Figure 2b).

To obtain a concise and deep insight into the structure and bonding of these clusters, we first performed the geometry optimizations of 2a and 2b at the PBE0-D3/def2-svp level of theory (See SI for computational details). Overall, our optimized structures closely reproduced the crystal structures, with only a minor discrepancy in the relative position between the exo-Au atom and the cyclic-(AuGe)$_2$ moiety for 2a (see Figure S25 and accompanying remarks for a detailed comparison and explanation). We then employed an orbital alignment procedure to construct the net skeletal bonding molecular orbitals (Skeletal MOs) for the Au–Au and Au–E bonding interactions in 2a, which was achieved by subtracting the electron densities of Au, R$_2$E, and phosphine from the total density matrix of the overall clusters.[19] From this, the alignment frontier molecular orbitals (Alignment FMOs) were obtained to visualize the bonding interactions among the skeletal gold/germanium (or tin) atoms. The top row of Figure 3 shows the plots of the five alignment FMOs that accommodate the ten in-plane electrons, which demonstrate that these electrons are delocalized along the cyclic-(AuE)$_2$ moiety with participation of the exo-Au atom.

To better understand the five alignment FMOs discussed above, we presented a schematic orbital diagram in Figure S13a for the cyclic-[Au($\mu_2$-ER)$_2$], anion fragment, illustrating the orbital interaction between the inner Au$_3$ triangle and outer ($\mu_2$-ER)$_2$ triangle. Each ($\mu_2$-ER)$_2$ bridging unit in this diagram contributed two in-plane fragment orbitals (one sp$^2$ hybrid orbital and one in-plane p orbital), whereas each Au orbital contributed one 6s orbital. The resulting bonding orbitals for cyclic-[Au($\mu_2$-ER)$_2$] corresponded to 1a', 1e', and 2e' Mulliken symbols. Subsequently, the orbital interactions between cyclic-[Au($\mu_2$-ER)$_2$] anion and the exo-(AuPM$_2$)$_2$ cation fragments, as shown in Figure S13b, results in five skeletal bonding MOs (1a', 2a, 1b', 3a', and 2b') for the entire cluster molecule [Au($\mu_2$-ER)$_2$]$_2$-AuPM$_2$. Sketches of these five occupied Skeletal MOs correlated well with the above-discussed five alignment FMOs (Figure 3). Overall, these results reveal the indispensable role of the in-plane 4p(Ge)/5p(Sn) and sp$^3$(Ge/Sn) orbitals in the construction of ten-electron delocalization systems of Au$_4$ clusters.

We then performed additional electronic structure analyses to gain further insight into the properties of the exo-Au–Au bond in 2a and 2b. The calculated Mulliken charges for 2a and 2b have been compared in Figure 4a, in which the exo-Au–Au bond in 2a was more polar, with a more negative Mulliken charge (−2.53) on cyclic-(AuGe)$_2$, moiety. Natural bond orbital (NBO) analysis was consistent with these results, showing that the cyclic-(AuGe)$_2$ moiety possessed a more negative NBO charge than the cyclic-(AuSn)$_2$ moiety by 0.42 e$^-$. From the $^1$H NMR data discussed above, we conclude that the ionization of 2a to cyclic-[R$_2$GeAu]$^-$ and [AuPM$_2$]$^+$ occurs in solution. This is consistent with the findings from the Mulliken charge and NBO analysis, which indicate 2a has a highly polarized exo-Au–Au bond. In contrast, 2b remains neutral in solution due to the relatively lower polarity of its exo-Au–Au bond (Figure 4b).

The significant differences observed experimentally in ionization between 2a and 2b can be attributed to their varying levels of $\sigma$-aromaticity. The high-polar exo-Au–Au bond of 2a and 2b allowed electron transfer from the exo-Au atom to the cyclic-(AuE)$_2$ moiety, leading to intramolecular $\sigma$-aromatization. Nucleus-independent chemical shift (NICS) calculations were performed to verify the intramolecular $\sigma$-aromatization of 2a and 2b. The NICS(0) and NICS(1) values at the center of cyclic-(AuGe)$_2$, moiety for 2a were calculated to be −22.97 and −12.74 ppm, those for 2b were −21.52 and −12.41 ppm, respectively. 2a, therefore, has a stronger $\sigma$-aromaticity in its cyclic-(R$_2$GeAu)$_2$ moiety, resulting in a greater degree of exo-Au–Au bond polarization and even plausible ionization in solution.

Since the magnetically induced local paratropic current on the Au atoms could potentially taint the NICS values and the core-electron contributions to the molecular magnetic response might contaminate the NICS values as well, to precisely determine the relative aromaticity and identify the intrinsic reasons for tunability of the polarity of the exo-Au–Au bond, the electron...
density of the delocalized bonds (EDDB) was calculated.\cite{26} \(2a\) has an EDBD(r) at 5.01e in the cyclic-(AuGe)\(_3\) moiety, while \(2b\) cluster possesses an EDBD(r) at 4.46e in the cyclic-(AuSn)\(_3\) moiety (Figure 4c). These quantitative results indicate that the strength of the aromaticity in \(2a\) is approximately 12% greater than that in \(2b\), which represents a stronger intramolecular \(\alpha\)-aromatization and results in a higher polarity of exo-Au–Au bond in \(2a\). For comparison, the EDBD(r) of \(1a\) was also calculated to be 6.07e (Table S2). This value is comparable to that of \(2a\), confirming that cyclic-[Au(\(\mu_2\)-ER)]\(_2\)-[Au(PMe)\(_3\)]\(_2\) is a more efficient form for electron delocalization.

To get closer to the truth of electron delocalization and aromaticity, we conducted further analyses on the simplified cyclic-[Au(EH)]\(_2\)-[Au(\(\mu_2\)-ER)]\(_2\)-[Au(PMe)\(_3\)]\(_2\) anion (\(2a\)), which revealed the presence of a magnetically induced ring current. Figure 5b is the corresponding modulus density plot showing the presence of a local paratropic current (indicated in red) along the cyclic-(AuGe)\(_2\) moiety (See the GIMIC plots of \(2b\), benzene, and H\(_2\)\(_2\) in Figures S14-18). To quantify the strength of the ring currents in \(2a\) and \(2b\), two integration planes were investigated including plane-1 and plane-2 (Figure S19 shows the integration planes). As depicted in Figure 5b, strong local paratropic currents on the Au atoms can significantly affect the integral current densities calculated on plane-1, leading to inaccurate values. In contrast, the influence of these local currents on the values obtained from integration plane-2 was negligible. Thus, the net ring current densities obtained for plane-2 are at +14.2 nA/T in \(2a\) and +14.1 nA/T in \(2b\), further supporting the stronger aromaticity in \(2a\). For comparison, the induced ring density of benzene was +12.2 nA/T, whereas that of H\(_2\)\(_2\) was +4.5 nA/T (Figures S20 and S21 show the corresponding integration planes).

Natural resonance theory (NRT),\cite{27} and block-localized wavefunction analyses (BLW)\cite{28} were also conducted to verify primary resonance mode of the cyclic-[Au(EH)]\(_2\)-[Au(\(\mu_2\)-ER)]\(_2\)-[Au(PMe)\(_3\)]\(_2\) anion fragment (\(2a\) and \(2b\)) and extra cyclic resonance energy (62.9 kcal/mol for \(2a\) and 57.8 kcal/mol for \(2b\)), which further confirmed the aromaticity within the cyclic-[Au(E)]\(_2\) moiety and the relatively higher level of aromaticity in \(2a\). (Figure S22 and Figure S23) These results further prove that aromatic zwitserionic Lewis structures, cyclic-[Au(\(\mu_2\)-ER)]\(_2\)-[Au(PMe)\(_3\)]\(_2\), are more stable than their non-polarized Lewis structures.

In conclusion, we have demonstrated an unprecedented nucleophilic substitution reaction of Au\(_3\), anionic building block with PMe\(_{6}\)AuCl resulting in the precise synthesis of ligand-enveloped Au\(_k\) clusters, where the isolable and non-highly symmetric homometallic clusters \(2a\) and \(2b\) possessing exo-gold tails have been successfully synthesized at ambient conditions. Moreover, by referring to the commonly intramolecular \(\pi\)-aromatization in organic chemistry, we introduce a novel stabilization mode, intramolecular \(\alpha\)-aromatization, which facilitates the construction of metal clusters with unusual topologies and helps construct the high-polar exo-metal-metal bond. Notably, the polarity of the exo-Au–Au bonds can be tuned via the strength of \(\alpha\)-aromatization. Consequently, cluster \(2a\) exhibits abnormal ionization behavior of the exo-Au–Au bond in solution due to its stronger \(\alpha\)-aromatization. Overall, the Au\(_3\), anionic cluster acts as a building block for the construction of novel oligomeric gold(0) clusters, thus unveiling new reactivity and electronic properties of these species which are currently under active investigation in our laboratory.

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**Conflict of interest**

Authors declare no competing interests.

**Data Availability Statement**

The data that support the findings of this study are available in the Supporting material of this article.

**Keywords:** metal-metal bond • electronic structure • homometallic clusters • intramolecular \(\alpha\)-aromatization • gold clusters

Ligand-enveloped tetragold(0) clusters have been successfully synthesized via a nucleophilic substitution reaction between an Au$_3$ anionic cluster and PM$_2$AuCl. A novel stabilization mode, intramolecular σ-aromatization, has been discovered, in which the intramolecular σ-aromatization has now been observed for the first time in homometallic clusters, and the polarity of the exo-Au-Au bonds can be tuned via the strength of σ-aromaticity.