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Synthesis of Triangular Tripalladium Cations as Noble-Metal Analogues of the Cyclopropenyl Cation**

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In memory of Gian Paolo Chiusoli

Abstract: *The first C_3-symmetric 44-core-valence-electron triangular palladium clusters, $[\{(SAr')(PAr_3)Pd\}_3]^+$, have been synthesized by activation of the C–S bond of isothioureas. Owing to delocalized metal–metal bonding, these stable complexes are the first noble-metal analogues of the π-aromatic cyclopropenyl cation $[C_3H_3]^+$, with their all-metal aromaticity involving d-type atomic orbitals.*

The concept of aromaticity has fascinated chemists since the early days of chemistry. It still represents a great tool for understanding, describing, and predicting the properties of molecules and materials.[1] The concept of metal aromaticity has been developed to describe similar bonding properties involving main-group elements.[1c–e] However, while organic aromatic molecules, both naturally occurring or artificial, are ubiquitous, most metal aromatic clusters remain elusive compounds and are often observed in the gas phase.[2] This elusiveness has limited their exploitation despite the obvious potential that their unique stereoelectronic properties hold for applications from materials chemistry to catalysis.

The first example of a metal aromatic cluster characterized by X-ray was reported in 1995 for a main-group metal. Robertson et al. reported a triangular organogallium bisanionic cluster featuring a D_{3h}-symmetric triangular core with π-aromatic properties.[3] Then in 2012, Sadighi et al. introduced a quasisymmetric trigold monocation as a noble metal isolobal analogue of the σ-aromatic $[H_3]^+$ cation (Figure 1, top).[4] This all-gold analogue of the simplest three-center, two-electron bond is a significant breakthrough in noble-metal cluster chemistry. Relativistic effects make its delocalized metal–metal bond a combination of gold 6s atomic orbitals. In contrast, transition metals with larger 4d/5s gaps might be good candidates to generate an aromatic bonding pattern involving unfilled d orbitals.

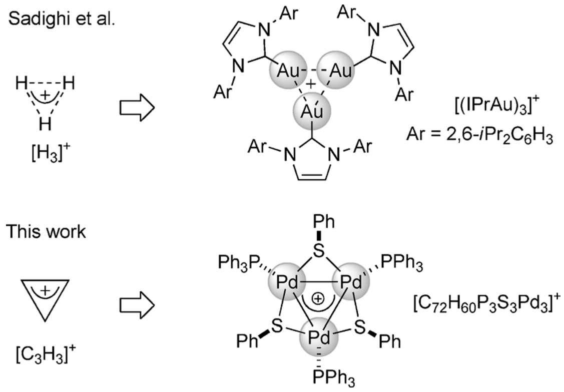
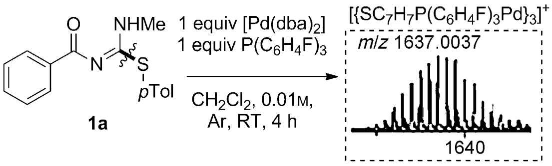


Figure 1. Noble-metal analogues of the smallest aromatic cycles.

We report herein a family of triangular, 44-core-valence-electron (cve) palladium clusters showing overall C_3 symmetry, and that their nearly D_{3h}-symmetric tripalladium core is the first noble-metal analogue of the cyclopropenyl cation (Figure 1, bottom).

The first such cluster was serendipitously obtained upon the reaction of the isothiourea **1a**[5] with one equivalent of $[Pd(dba)_2]$ in the presence of an equimolar amount of tris(p-fluorophenyl)phosphine in degassed dichloromethane at room temperature (Scheme 1). A deep-red powder was isolated in high mass return, and exhibited the peculiar isotopic pattern expected for a tripalladium cluster by ESI^+/TOF. The mass peaks corresponded to the cation $[\{SC_7H_7P(C_6H_4F)_3Pd\}_3]^+$ (**2**), which exhibits the fingerprint of the thiol component, but not that of the rest of the isothiourea, thus suggesting that the C–S bond has been activated during the reaction.



Scheme 1. Activation of C–S bond by Pd^0. dba = dibenzylideneacetone.

Addition of one equivalent of $AgSbF_6$ upon full conversion of **1a** allowed the growth of monoclinic red crystals of

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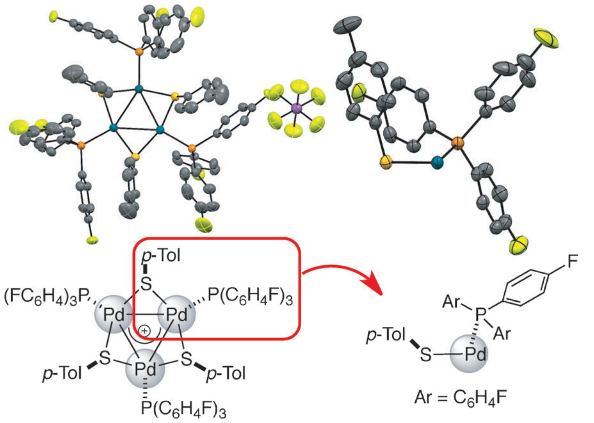


Figure 2. X-ray structure and asymmetric unit side view of complex **2**. Hydrogen atoms omitted for clarity. Thermal ellipsoids are shown at 50% probability.

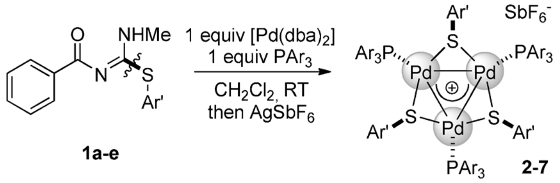
2 (Figure 2). The crystals proved very stable to oxygen and moisture at room temperature, and could be handled in air without any precaution. A structure was obtained using X-ray diffraction, which confirmed that **2** is a triangular cluster exhibiting C_3 symmetry. The three metal–metal distances in **2** are exactly equal at 2.8872(1) Å, which is below the sum of their van der Waals radii (3.26 Å). This distance is comparable to that reported for 44 cve tripalladium clusters[6a] and to that of some palladium(II) dimers showing d^8–d^8 bonding interactions.[7] The three angles of the palladium triangle are 60.0°, thus making the triangle perfectly equilateral. The Pd-S-Pd and S-Pd-S angles are 78.40(3)° and 161.38(4)°, respectively, and these six atoms (3 Pd/3 S) are coplanar (largest dihedral angle is below 2°). The Pd–S and Pd–P distances are 2.284(2) and 2.306(2) Å, respectively, with the first sphere of coordination thus displaying near D_{3h} symmetry. The phosphines point slightly out of the plane, as indicated by the corresponding dihedral angle of 8.2(1)°, while the aryl groups of the thiolates fragment are nearly perpendicular to the plane containing the metals (112.3(1)°). Their *ortho* hydrogens are 2.89 Å above the plane itself. Finally, all the phosphines on the palladium centers point in the same direction, and all the sulfur substituents point in the opposite direction, with a perfect alternation (*trans* 1,2 relationships relative to the Pd_3 cycle).

About 78 trinuclear palladium solid-state structures exist, most of which have either 42 or 44 cve.[8] Only eight have 44 cve and just two feature the formal +4/3 metal oxidation state found in **2**.[6b,c] While there are some quasisymmetric structures among 44 cve clusters, only our system displays a perfectly equilateral triangular core and an overall C_3 symmetry.

Multinuclear NMR analyses of **2** only show a single pattern of signals for each thiolate and phosphine fragment and no peak splitting resulting from inhibition of the dynamic processes was detected at −80 °C. These observations indicate that the highly symmetric arrangement found in the solid state is maintained in solution. Also, ^{1}H NMR chemical shifts of the S-aryl fragments were unusually shifted upfield, which is in sharp contrast with palladium thiolate complexes.[9] For example the signal for the *ortho* protons H_a resonates at around $\delta = 6.2$ ppm versus the usual $\delta = 7.5$ ppm region.[9]

To examine the scope of the reaction, various isothioureas and phosphines have been reacted with [Pd(dba)$_2$]. The clusters **2**–**7** were isolated (Table 1). They all contain aromatic phosphines and sulfide moieties. Full conversion was observed within one hour in chloroform, although partial degradation occurred, as shown by multiple phosphorus signals in the ^{31}P NMR spectra of the crude residue. The reaction is almost instantaneous in CCl_4. However, the desired complexes spontaneously decomposed within a few minutes and could be isolated in trace amounts only. The low concentration (0.01 M) proved equally important to minimize the formation of polymeric clusters.[10] Try as we might, we could not isolate any amidine-containing intermediates, so the fate of those fragments in **1** remains unknown. Finally, alkyl phosphines led to intractable mixtures.

Table 1: Synthesis of clusters **2** from isothioureas.



Entry	Substrate	Ar′	Ar	Product Yield [%][a]
1	**1a**	4-MeC$_6$H$_4$	4-FC$_6$H$_4$	**2**: 93
2	**1a**	4-MeC$_6$H$_4$	4-MeC$_6$H$_4$	**3**: 84
3	**1b**	4-NH$_2$C$_6$H$_4$	4-FC$_6$H$_4$	**4**: 75
4	**1c**	Ph	Ph	**5**: 88
5	**1d**	4-OMeC$_6$H$_4$	Ph	**6**: 81
6	**1e**	4-ClC$_6$H$_4$	4-MeC$_6$H$_4$	**7**: 91

[a] Yield is that of isolated product.

Overall, the observations suggest that π–π interactions play a crucial role in the stabilization of the cationic clusters. We were intrigued by the unique symmetry of the core of these clusters. Such a high symmetry is often a telltale sign of aromaticity, and we wondered whether aromaticity was the origin of the former. We thus tried to gain better understanding of the bonding pattern through various theoretical and experimental analyses.

We used the crystalline structure of **2** as the starting geometry with different DFT functionals (BP86, B3LYP, and M06). To exclude any bias from *para* substituents on aryls, the same study was carried out on complex **5**. The optimizations were then performed without any symmetry constraint. No matter which linear or cyclic combination of fragments was used as an initial geometry, the optimization led invariably to the same, quasisymmetric triangular structure, thus suggesting it has a global-minimum character. Indeed all the calculated atomic charges of the same elements were nearly identical and the largest differences in bond lengths were in the ppm range in all cases. The geometry calculated at the M06/def2-svp level of theory provided the best correlation with the solid-state structure, with only slightly elongated bonds (Pd-

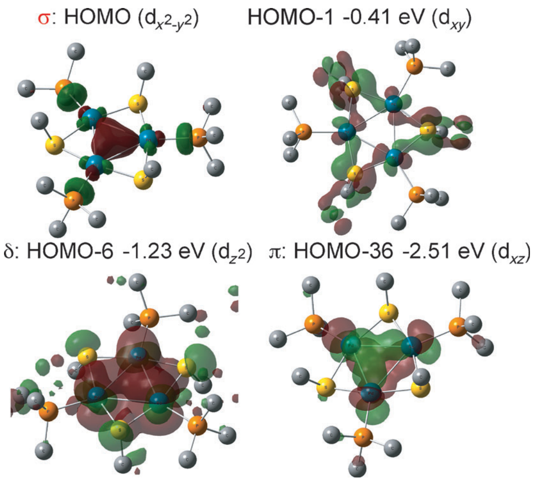


Figure 3. Selected molecular orbitals of **5**. The orbitals evenly involve the three metal atoms. Energies are given relative to the HOMO, and atomic orbital contribution is indicated within brackets. Phenyl groups are omitted for clarity.

Pd, Pd-S, and Pd-P deviations by 0.04, 0.07, and 0.03 Å, respectively).

Figure 3 highlights the most interesting molecular orbitals of **5**, which evenly involve all the three metal atoms. The HOMO is clearly a delocalized, three-center, two-electron bond. This molecular orbital arises from the combination of $d_{x^2-y^2}$ atomic orbitals (top left) and its symmetry makes it a σ-molecular orbital. The other valence d orbitals are mainly engaged in back donation to the sulfur atoms. For example, HOMO−1 (top right, −0.41 eV) originates from d_{xy} metal orbitals. The antibonding repulsion in the C_3-symmetric framework is minimized by their combination with sulfur p orbitals in a hexagonal array. The same features are observed when modeling complex **2** (see the Supporting Information).

Singularly, the HOMO−6 (Figure 3; bottom left) results from the overlap of the d_{z^2} orbital of each metal atom, thus lying far below the HOMO at −1.23 eV. This interaction is in sharp contrast with the resulting d_{z^2} bonding one in palladium(II) dimers,[7] where in most cases the metal square-planar coordination imposes a limited axial overlap of d_{z^2} orbitals in clamshell or paddlewheel structures. Indeed the resulting partially bonding molecular orbital is often the HOMO of these complexes. In a symmetric triangle the overlap is instead maximized and the HOMO−6 contributes to metal–metal bonding in our case. Most excitingly, HOMO−6 is a *δ* orbital, characterized by a) two nodal surfaces perpendicular to the C_3 axis of the molecule and b) a plane of symmetry (that of the triangle). A similar outcome occurs for modeling complex **2**, where the calculated Pd-Pd distance is 2.90 Å (0.02 Å shorter than in **5**) and the molecular orbital displaying d_{z^2} overlap becomes the HOMO−9, which is 1.24 eV below the HOMO of **2**.

The HOMO−36 of **5** (Figure 3; bottom right) results from the partial overlap of d_{xz} atomic orbitals instead. It lies −2.51 eV below the HOMO and its symmetry makes it a π-molecular orbital (in complex **2** this MO is again HOMO−36, at −2.57 eV).

Single-point calculations at the MP2 and B2PLYP levels provided molecular orbitals comparable to those obtained by DFT. Indeed, HOMO, HOMO−6, and HOMO−36 closely resemble the molecular orbitals calculated for d-orbital and δ-aromatic early-transition-metal oxo clusters produced by laser vaporization and investigated in situ.[2] In our 44 cve clusters the cyclic delocalization makes the three palladium atoms equivalent, and thus explains the structural observations (one bond length and one angle for the Pd_3 triangle).

Natural bond orbital analyses on **2** and **5** were performed to confirm the original atomic orbital contribution to the delocalized bond responsible for aromaticity. Both complexes present a delocalized bonding HOMO resulting from a combination of atomic orbitals having a main d-type character (between 49 and 94 % using different basis sets), together with a smaller p-type hybridization (between 4 and 27 %). These results confirm that clusters show d-orbital aromaticity.

AdNDP analysis is another useful tool to assess the presence of aromaticity.[11] On the model cluster, $(PdSHPH_3)_3^+$, in which aromatic rings were replaced by hydrogen atoms, this method confirmed the presence of a multicenter, delocalized, three-center, two-electron bond between the three palladium atoms with a σ-like symmetry.[12]

These different theoretical analyses together indicate that the core of these cationic Pd_3 clusters features three equivalent palladium atoms and a fully delocalized three-center, two-electron bond between them, a bond which originates from d-type atomic orbitals. They are thus aromatic noble-metal analogues of the π-aromatic, D_{3h}-symmetric cyclopropenyl cation $[C_3H_3]^+$. To the best of our knowledge, d-orbital aromaticity in stable triangular clusters of transition metals has not been reported to date.[13] In contrast to this, the same theoretical analyses on two models of representative 42 and 44 cve tripalladium clusters, which are commonly considered non-aromatic ($[\{Pd(CO)PPh_3\}_3]$ and $[Pd_3(CO)_2dppm_3]^{2+}$), did not reveal any delocalized orbital among their three metal atoms (see the Supporting Information for details).

We used nucleus-independent chemical shift (NICS) analyses[14] to confirm the presence of an aromatic ring in our clusters. This theoretical tool is routinely used to evaluate the aromaticity of cyclic molecules by calculating the absolute magnetic shielding of a series of relevant points of the space around the cycle of interest. Thus, for an aromatic system, negative shifts should be measured along the perpendicular axis.

Figure 4 shows plots of the calculated $NICS_{zz}$ as a function of the distance from the center of the palladium triangle. This probe represents the component of the magnetic tensor perpendicular to the plane of interest (thus called "zz").[14] The chemical shifts for complex **5** are always negative up to 5 Å above the metal triangle, in perfect agreement with the presence of an aromatic ring.

We then considered the theoretical tricationic analogue **5**-NO, where the two delocalized electrons responsible for the metal aromaticity have been formally removed. $NICS_{zz}$ values in **5**-NO are always positive, either using the geometry of **5** or that obtained upon full reoptimization of **5**-NO.[15] This behavior is exactly expected for a non-aromatic molecule.

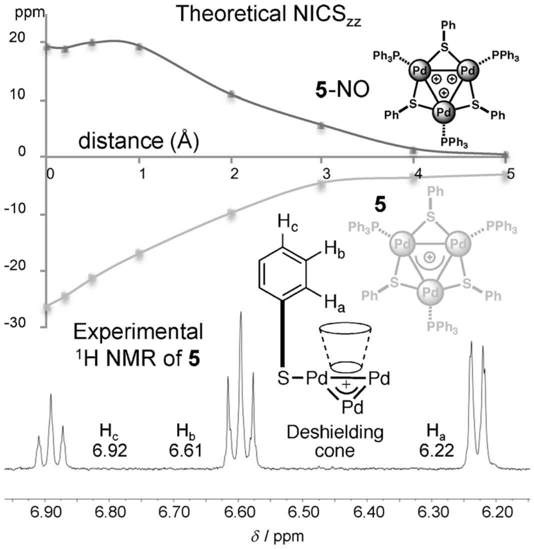


Figure 4. Plot of calculated NICS$_{zz}$ and experimental NMR data.

The isotropic values NICS(1) were $\delta = -9.68$ ppm for aromatic cation **5** and $\delta = +1.95$ ppm for the non-aromatic trication **5**-NO, thus following the same trend as NICS$_{zz}$. Furthermore, the negative NICS$_{zz}$ value ($\delta = -4.5$ ppm) obtained for **5** at 3.0 Å above the plane matches the experimentally observed ^{1}H NMR signals of the *ortho* protons on the sulfide substituent, positioned nearly perpendicular to the palladium triangle, at a distance of 2.89 Å. They resonate at $\delta = 6.22$ ppm, thus 1.4 ppm below the resonances usually observed in Pd-S-Ar fragments. Their experimental upfield shifts are consistent with the presence of an aromatic ring as they would lie in its deshielding cone.[16]

The aromatic delocalization should also lead to an experimentally measurable intense diamagnetic susceptibility.[17] We measured the magnetic susceptibility of selected clusters by SQUID experiments. The complex **4** exhibited a χT of 0.41 emu K mol^{-1} at 300 K, while the trinuclear cluster $[\{Pd(CO)PPh_3\}_3]$ has a χT value roughly one order of magnitude lower at 0.031 emu K mol^{-1} at 300 K (see the Supporting Information). For comparison, a value around 0.5 emu K mol^{-1} at room temperature is expected for a paramagnetic molecule with spin $^1\!/_2$ (such as 2,2,6,6-tetramethylpiperidin-1-oxyl, TEMPO), while regular, non-aromatic diamagnetic derivatives shows no significant susceptibility at all. These experimental observations thus support the aromaticity of **4** and the non-aromaticity of $[\{Pd(CO)PPh_3\}_3]$. In addition, the susceptibility of **4** is nearly independent from temperature in the 20–300 K range, and in perfect agreement with the presence of a ring current in an otherwise diamagnetic molecule.[18]

To conclude, the activation of the C–S bond of isothioureas generates unprecedented aromatic C_3-symmetric 44 cve triangular palladium clusters. The d orbital metal aromatic core of these complexes is the first noble-metal analogue of the D_{3h}-symmetric, π-aromatic cyclopropenyl cation $[C_3H_3]^+$. Our report opens a new branch in the bench-stable aromatic triangular metal cluster family, after $[Au_3]^+$ [4a] and $[Ga_3]^{2-}$ [3], whose aromaticity involve s- and p-atomic orbitals, respectively. Further work will examine the consequences of this new mode of bonding on reactivity.

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[15] The geometry and molecular orbitals of **5**-NO remained similar to those of **5**, with just an expected slight elongation of the Pd–Pd bond to 3.0 Å, and the obvious absence of the HOMO of **5** for **5**-NO.

[16] As suggested by one reviewer, we cannot rule out the fact that simple proximity of metal d orbitals causes ^{1}H NMR upfield shifts. However, this shielding is usually small at distances above 4 Å owing to the spatially contracted nature of nonbonding metal d orbitals (see for instance the ^{1}H NMR spectra of the complexes in Ref. [8–10]). However, it can persist for field currents induced by aromaticity. In **5** *meta* and *para* protons lie far away from the triangle plane, at 5.5 and 7.4 Å, respectively. However, they are still shifted upfield ($\delta = 6.61$ and 6.92 ppm, respectively). In addition, the deshielding contribution resulting from the proximity of a metal on an aryl fragment generally acts as an inductive effect, thus providing resonances following the *ortho, para, meta* order. In **5**, the ^{1}H NMR resonances follow the *ortho, meta, para* order instead. Taken together these data are more consistent with a magnetic (counter)field generated by electron delocalization, whose effects slowly fade away over distance.

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