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Perspective

# Evolution of Triangular All-Metal Aromatic Complexes from Bonding Quandaries to Powerful Catalytic Platforms

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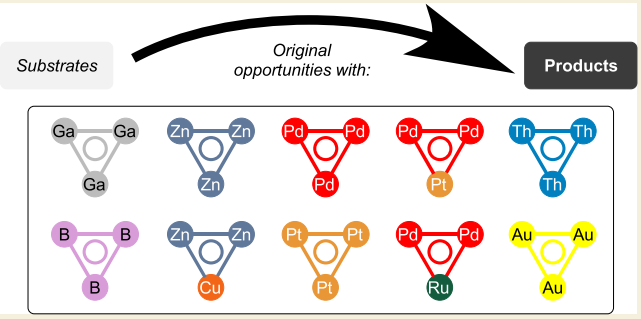
**ABSTRACT:** This manuscript describes an overview on the literature detailing the observation of trinuclear complexes that present delocalized metal−metal bonds similar to those of regular aromatics, which are formed combining main group elements. A particular emphasis is given to the structural and electronic features of aromatic clusters that are sufficiently stable to allow their isolation. In parallel to the description of their key bonding properties, the work presents reported catalytic applications of these complexes, which already span from elaborated C−C-forming cascades to highly efficient cross-coupling methods. These examples present peculiar aspects of the unique reactivity exerted by all-metal aromatic complexes, which can often be superior to their established, popular mononuclear peers in terms of chemoselectivity and chemical robustness.




**KEYWORDS:** *aromaticity, cluster compounds, cross-couplings, DFT, domino reactions, homogeneous catalysis*

Aromaticity is a chemical concept that owns many guises, as Hoffmann brilliantly wrote.[1] Its enduring charm in the chemical community is indeed most likely due to its multifaceted nature. The concept of aromaticity is routinely introduced to chemists, physicists, and biologists at the early stages of their academic journey; like many other cornerstones of basic organic chemistry, such as the concepts of polarity or chemical kinetics, it is tremendously useful and yet elusive at the same time. Indeed, while the result of strong efforts by several research groups has allowed the community to coalesce on a relatively short set of criteria to describe an aromatic bonding pattern,[2] no single analytic technique can provide the *aromatic* label nor can any physical unit[3] precisely[4] measure *aromaticity*. The dual nature of the concept, both simple and useful on one hand, yet fleeting to fully grasp, was pretty much on display at the beginning of this century, when pioneering reports on the observation of all-metal aromaticity started to appear, and also roughly a decade ago, when some of us begun to study this issue on bench-stable molecular objects.

This manuscript will provide a brief overview of the field of metal aromaticity, providing brief notes on aspects that are already covered by recent reviews. The main focus of the first part of this work is on the structural and bonding features displayed by stable trinuclear all-metal aromatics. In this context, the term stable is taken from the jargon of synthetic chemists and thus refers to molecular objects that can be, at least, prepared, purified, and analyzed without altering their stereoelectronic features. In parallel, the catalytic activity of these cluster compounds will be presented, with the aim of stressing their complementary nature with respect to that of their more common mononuclear peers.

## SEMINAL STUDIES

All-metal aromatics are compounds that present a cyclic core involving only metal nuclei and have a delocalized bonding pattern in analogy to regular aromatics. As mentioned above, the main effects of electronic delocalization are the following: (i) bond length equalization; (ii) large HOMO/LUMO (highest occupied molecular orbital/lowest unoccupied molecular orbital) gaps; (iii) unusual chemical shifts; (iv) large diamagnetic susceptibilities.

The combination of one or more of these points has been postulated for cyclic molecules that also involve metal atoms since at least 1979.[5] Soon after,[6] the preparation of the first osmabenzene was reported.[7] However, the synthesis of the first all-metal aromatic derivative took much longer. This milestone

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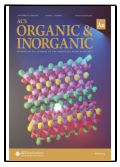

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was accomplished by Robinson's group in 1995, during the course of his studies on organogallium derivatives (Figure 1a).

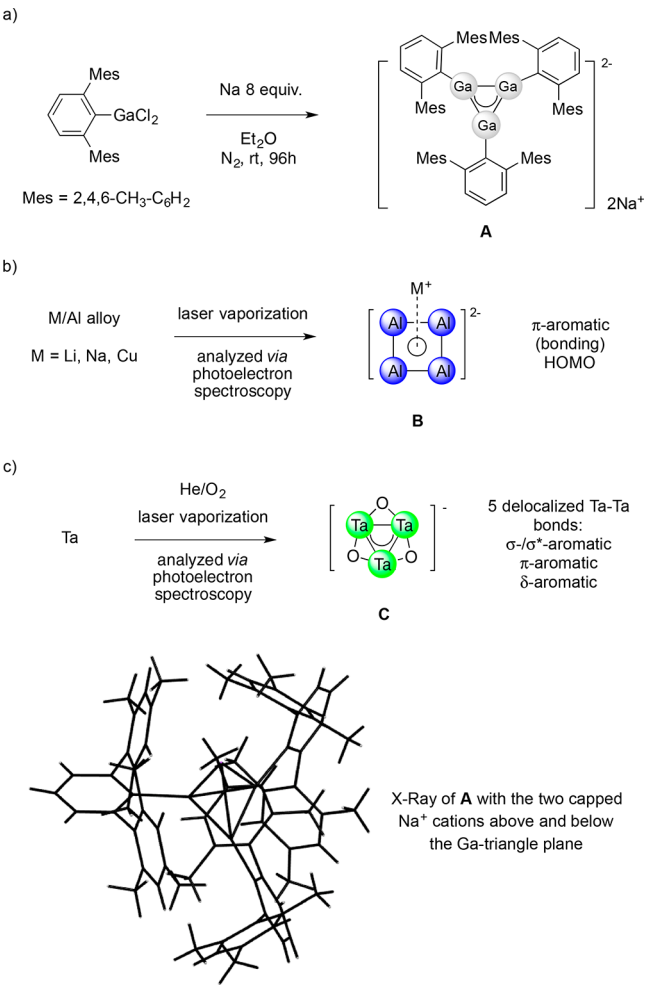


**Figure 1.** Synthesis of the first stable triangular all-metal aromatic complex (a) and selected milestones on the observation of delocalized metal−metal bonds in tetra- (b) and trinuclear (c) clusters.

The work introduced the first cyclogallene, $Na_2[(Mes_2C_6H_3)Ga]_3$ (**A**), which was a trinuclear system that showed aromatic properties.[8] The group was investigating the behavior of aryl-based ligands for heavier group 13 elements, and it found that 2,6-dimesitylphenyl was an excellent ligand to obtain gallium and indium dichloride complexes, such as $(Mes_2C_6H_3)_2GaCl_2$.[9] The latter can undergo reduction by means of an alkali metal affording cluster **A**. The trinuclear compound has a planar core that presents an equalized Ga−Ga bond distance (2.441 Å) and a single Ga−Ga−Ga angle (60.0°). These features make the triangle equilateral. The metal core of the cluster is decorated by two sodium cations that are almost evenly centered above and below the triangular plane. The five nuclei thus form a regular trigonal bipyramidal structure with a single Na−Ga distance (3.220 Å). The triangular core of the complex has very short Ga−Ga distances compared to that of known tetranuclear[10] gallium compounds. This was even more surprising considering the steric hindrance of the organic ligands surrounding the metal core itself, and it encouraged the group to gain more insight into the origin of the peculiar structure.

The authors proposed a 2$\pi$-electron system in which two sodium atoms donated one electron each to the unoccupied $p_z$-type orbitals of the gallium nuclei. Overall, this would result in a perfectly delocalized molecular orbital that would render the metal core isoelectronic with the cyclopropenium cation. A modeling confirmation was provided by nucleus-independent chemical shifts (NICS) calculation,[11] which is an often-used tool to assess magnetic anisotropies, such as those induced by ring currents in aromatic systems.

These results promoted the creativity of several groups in the next 2 decades, as brilliantly witnessed by the first computational study in which the potential aromaticity of trinuclear clusters of group III elements was discussed.[12] Analysis on the bonding arrangement of $M_3^-$ clusters (M is B, Al, Ga) allowed the authors to propose the presence of a delocalized molecular orbital on these trinuclear complexes that is due to the presence of two $\pi$-electrons and that could be prone to interact with alkali cations. These observations were soon followed by additional studies,[13] in which the concept of $\sigma$-aromaticity in all-metal clusters was initially introduced. In contrast to main group based aromatics, which have delocalized molecular orbitals (MOs) of $\pi$-symmetry only, the variety of atomic orbitals (AOs) of metal nuclei could indeed lead to the generation of delocalized bonds that have different shapes, depending on the symmetry of the MO. The main results presented in these works[12,13] will have a large impact on the development of the field, as presented in several points throughout the next sections.

The next major breakthrough was reported at the beginning of the century by the groups of Boldyrev and Wang, which showed that delocalized bonding patterns could be observed in all-metal species.[14]

The groups used a laser vaporization source to produce anionic clusters of the $MAl_4^-$ series (M is Li, Na, Cu), which were then analyzed by means of photoelectron spectroscopy and various computational tools (**B**, Figure 1b). The joint experimental and theoretical approach allowed them to rationalized the structure of these clusters, which have a pyramidal structure. Their cationic M atom caps the pyramid, which has a square planar base formed by the four aluminum nuclei. In all cases, the base has a single Al−Al distance (between 2.60 and 2.65 Å) and its internal angles are equal to 90°. According to ab initio calculations, both clusters **B** and the isolated $[Al_4]^{2-}$ subunit present a HOMO that is a fully delocalized molecular orbital of $\pi$-like symmetry.

By taking advantage of similar experimental setups, Boldyrev and Wang were able to report the observation of several other families[15] of all-metal aromatic clusters and rationalize their bonding pattern.[16] This work led to significant advances, in particular with respect to the chemistry of boron clusters.[17]

As a brief but meaningful selection, it appears relevant to mention the observation of triangular anionic Ta clusters, which was reported in 2007.[18]

According to computational studies on $Hf_3$ clusters,[19] all-metal aromatic system could in principle involve several delocalized MOs of different symmetries, which would be a bonding feature not accessible by combining the AOs of main group elements. This original hypothesis was soon confirmed by experimental results. Through vapor laser generation, cluster **C** ($[Ta_3O_3]^-$, Figure 1c) was formed and analyzed by photoelectron spectroscopy.[18] The compound was also analyzed through various computational tools including population analysis ones. Both experimental and modeling


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results pointed to a highly symmetrical geometry for the complex, which resulted from the presence of several delocalized bonding orbitals between its transition metal centers. The three more relevant achievements of the work are the following. This cluster was a proof of concept that all-metal aromatic species could be made by combining transition metal atoms and not just main group metals. Multiple types of delocalized metal−metal bonds, depending on the symmetry of the involved molecular orbital, could be present in the same molecule giving, in principle, rise to multiple aromaticities. One of these delocalized MOs had a $\delta$-like symmetry, which is a feature not accessible by combining main group elements because they lack any d-type atomic orbitals.

This brief selection of key findings in the field allows one to grasp their relevance with respect to the ample body of research that has been carried out in the last 2 decades.[20−25] In particular, several original research lines were reported, focusing both on the observation of new bonding modes and on the preparation of either small clusters[26,27] or extended materials[27,28] that present delocalized metal−metal bonds. Several high-level recent reviews already extensively cover these areas of research,[29−34] highlighting both the structural/synthetic aspects[35] as well as the physicochemical features of their peculiar chemical bonds.[36] We thus recall the attention of readers to these studies and focus the next sections of the present work to the chemistry of stable trinuclear all-metal aromatics only.

## ■ DEVELOPMENTS OF THE LAST DECADE

During the past decade, several major advances in the field of aromatic trinuclear clusters have been reported. This part will present these studies following an increasing order in the atomic number of the element involved in the complex.

The group of Braunschweig reported the preparation of aromatic triangular boron clusters (Figure 2a).[37] The dianionic complex **D** can be prepared by reduction of a dichloroamino-borane using sodium sand as an electron source. The process allows for the synthesis of the desired cluster, whose boron-based core can be regarded as the lightest possible end of prototypical Hückel 2$\pi$-aromatic systems. The complex was characterized by various NMR techniques and in the solid state. The latter highlights its most peculiar structural features, namely, a nearly equilateral triangular core, with essentially degenerate boron distances and angles (around 1.62 Å and 60 °C, respectively). In particular, the B−B distance is considerably shorter than a usual single bond (ca. 1.75 Å), strongly suggesting a higher bond order. This is confirmed by rather elongated B−N distances, which are ca. 0.18 Å longer than usual, that could be ascribed to the increased electronic density on the central dianionic core. In the solid state, the complex is organized in columns, whose repeating unit is represented by two triangular clusters and four sodium cations. The aromatic character of the complex was supported by density functional theory (DFT) modeling, which showed the presence of delocalized MOs of $\pi$-like symmetry. This electronic behavior was further confirmed by cyclic voltammetry, which revealed a largely negative potential for the oxidation of the anionic cluster (−2.42 V relative to ferrocene/ferrocenium), in agreement with the large HOMO/LUMO gap expected for aromatic compounds.

Frenking and Fischer's groups reported the synthesis and characterization of triangular monocationic zinc cluster **E** (Figure 2b).[38] The complex can be prepared by reaction of a

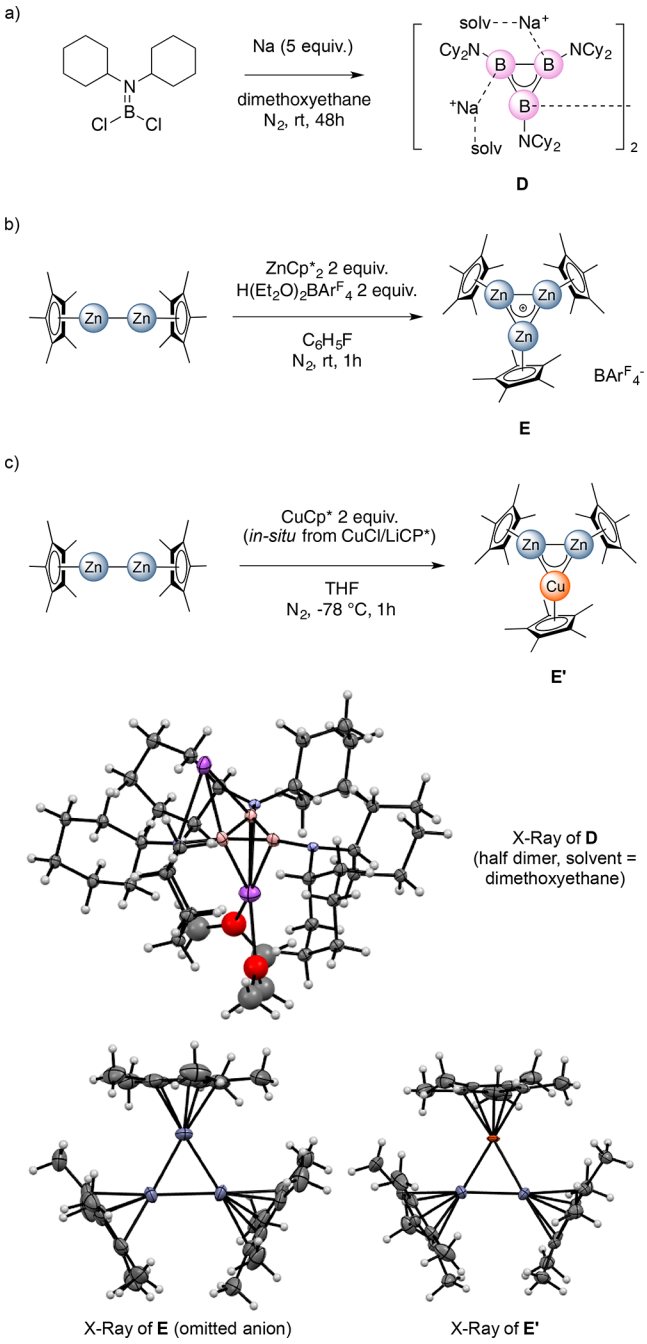


**Figure 2.** Synthesis of stable aromatic trinuclear complexes involving boron (a), zinc (homonuclear, b) and copper/zinc (heterobimetallic, c) nuclei in their core.

Zn(I) dimer with a cationic monomeric zinc fragment. The triangular species has a metal core with three Cp* ligands that coordinate the zinc nuclei. In the solid state, the structure of **E** shows the presence of a nearly equilateral triangular core, with angles close to 60° and metal−metal distances that are essentially degenerate (ca. 2.43 Å). Remarkably, by switching the cationic precursor that reacts with the Zn(I) dimer, the authors were able to prepare the corresponding heterobimetallic $[Zn_2Cu]^+$ complex **E′** (Figure 2c), whose metal core can be regarded as the basic building block of brass at the molecular level. The structure of this cluster closely resembles that of its homonuclear peer, with three nearly identical angles and just slightly different metal−metal distances (Zn−Cu and


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Zn−Zn being 2.38 and 2.36 Å, respectively). The analysis of the bonding pattern of **E** and **E′** was carried out using various modeling tools, and the choice of the proper model proved nontrivial, especially to properly describe the heterobimetallic cluster. The best correspondence with the X-ray structure was achieved using a generalized gradient approximation (GGA) functional, rather than the more commonly used meta-GGA ones, and considering correction for dispersion forces. This showed the aromatic character of the cluster, which is due to the presence of a delocalized three-center−two-electron bond of sigmoid symmetry.

This feature was further confirmed by NICS analyses, which supported the presence of a magnetic ring current due to the metal kernel. Additional developments were later reported and showed the feasibility to extend the nuclearity of the heterobimetallic cluster,[39] affording various heptanuclear complexes that have a trigonal bipyramidal core and still present exotic delocalized metal−metal bonds.

The synthesis of the first highly symmetric 44-core valence electrons (CVE) tripalladium cluster was reported in 2014.[40] Complex **F** was formed by reacting an *N*-acyl isothiourea with a palladium(0) precursor in dichloromethane in the presence of a tertiary phosphine (Figure 3a). Crystals suitable for X-ray diffraction could be achieved by anion metathesis using a silver(I) salt that has a noncoordinating counteranion. The method allowed one to prepare various clusters with different ancillary phosphines and bridging aryl thiolates in good to excellent yields. These clusters are stable under air in the solid state for months and could be fully characterized by various spectroscopic techniques. Their structures present a flat core in which metal nuclei and heteroatoms fulfilling their first coordination sphere remain essentially coplanar. The triangular kernel is an equilateral triangle with a single metal−metal distance (between 2.82 and 2.92 Å, depending on the organic fragments) and identical angles.

DFT analyses of their bonding showed that the combination of the $d_{x2-y2}$ AOs of palladium formed the bonding HOMO and two nearly degenerate empty MOs (LUMO and $LUMO_{+1}$). The former is fully delocalized among the three metal nuclei and has a $\sigma$-like symmetry that makes the cluster aromatic. This feature was confirmed by NICS analyses and proved experimentally by measuring significant magnetic susceptibility by analyzing **F** via superconducting quantum interference device (SQUID) experiments.

Soon after, an improved synthetic method was reported.[41] By switching the solvent to chloroform, it was possible to replace the organic precursor, which needed a three-step synthesis limited to the incorporation of *S*-aryl fragments, with commercially available disulfides (Figure 3b). Interestingly, this modification allowed one not just to form clusters **F** in good to excellent yields but also to extend the method to the incorporation of alkyl thiolates and selenides as bridging ligands. The desired clusters could be purified by either crystallization or column chromatography on silica gel, further showing the strong chemical stability of these trinuclear complexes. Moreover, through this protocol it was possible to synthesize the corresponding isolobal platinum complex **F′** and, furthermore, the heterobimetallic Pd/Pt clusters **F″**. The latter share the same stereoelectronic features as their homonuclear peers discussed above. Complexes **F″**, thanks to the lanthanide contraction that essentially equalizes the atomic radii of Pd and Pt, maintain a perfectly equilateral metal core. Interestingly, this structural feature is not accessible

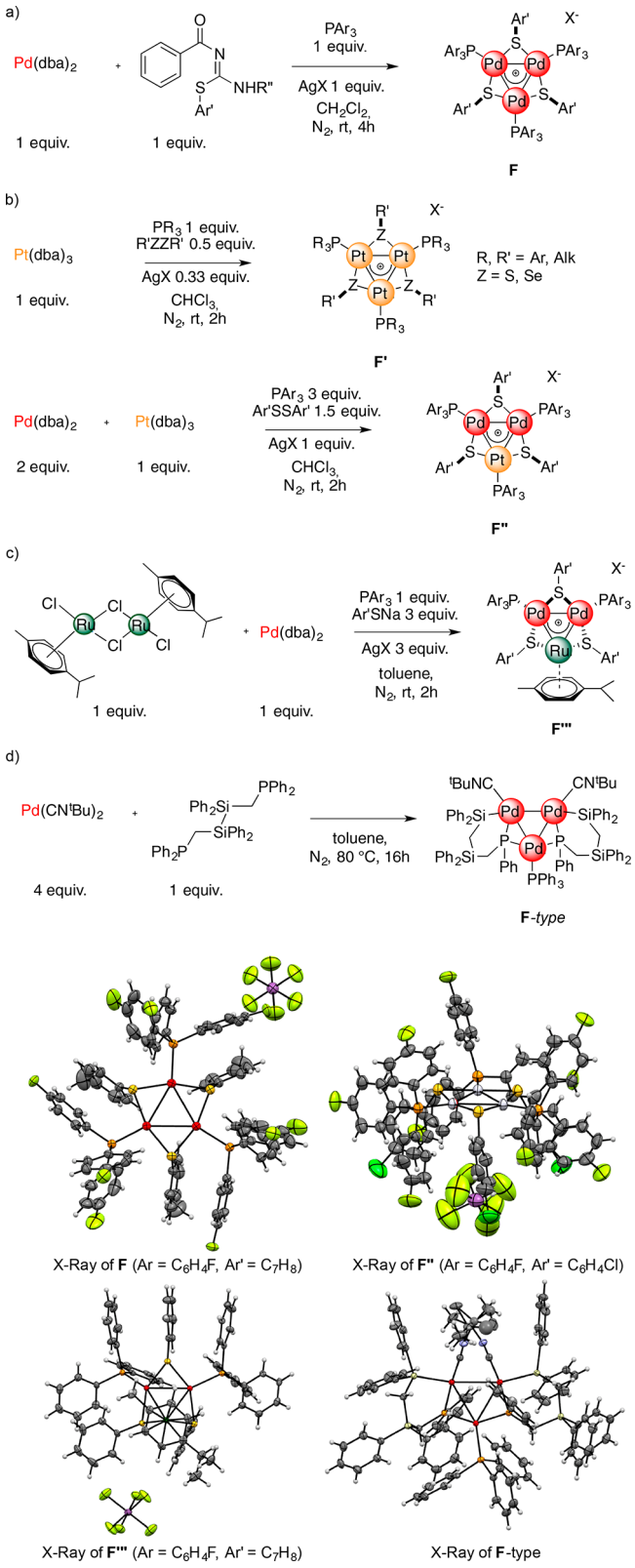


**Figure 3.** Synthesis of homo- and heterobimetallic all-metal aromatic trinuclear clusters involving palladium (a), platinum (b), and ruthenium (c) nuclei and via activation of disilanes (d).

regarding regular heteroaromatics made through the combination of main group elements, such as furans or pyridines, for which the difference in their respective atomic radii prevents an actual equalization of bond lengths, which is otherwise


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considered a hallmark signature of aromaticity. Magnetic measures on homonuclear complexes gave similar results, while lower susceptibilities were observed when analyzing heterobimetallic ones, in agreement with the usually lower susceptibility of heteroaromatics.[42] It is worth noting that an isolobal analogue of the $[Pt_3]^+$ complex **F′** was independently prepared through a different synthetic route by Steinborn's group in 2007.[43] In this case, the authors did not elaborate on the likely aromatic character of the cluster.

An additional extension was recently reported through the incorporation in a triangular aromatic cluster of two nonneighboring elements of the periodic table.[44] The reaction of a palladium(0) precursor with a ruthenium(II) dimer in the presence of a silver(I) salt and sodium thiolates allowed one to isolate the corresponding heterobimetallic $[Pd_2Ru]^+$ cluster **F‴** in low to moderate yields (Figure 3c). The complex had a quasi-equilateral core, with angles and metal−metal distances ranging between 59.5° and 60.7° and 2.74−2.77 Å, respectively. The latter is ca. 0.15 Å shorter than distances observed in the family of clusters **F**. It is worth noting that the difference in the atomic radii of Ru and Pd is much narrower (ca. 0.03 Å) and could thus not account for the observed shrinkage in the size of the metal triangle. In **F‴**, the ancillary and bridging ligands are no longer coplanar with the central kernel. According to various modeling tools, these structural differences stem from the delocalized metal−metal bond that makes the complex $\sigma$-aromatic, which in this case results from the combination of a Ru $d_{z^2}$ AO with Pd AOs that have a different angular momentum. Moreover, the ruthenium nucleus is in this case engaged in two different types aromatic bonding, being part of both a $\sigma$ and a $\pi$ aromatic kernel. This makes this heteronuclear cluster the transition metal analogue of the stable, main group element based double-aromatic molecules that were reported in pioneering works by Saito's group.[45]

The group of Sunada recently reported the synthesis of a tripalladium cluster from the reaction of a suitable Pd(0) precursor with a disilane bearing two tertiary phosphine arms (Figure 3d).[46] The resulting complex has metal−metal distances comparable with those of **F**-type clusters and a quasi-equilateral core. The authors did not elaborate on the possible aromatic character of this cluster, although its stereoelectronic features could suggest that each metal center should have four d-type lone pairs and participate in one delocalized metal−metal bond, thus paralleling the pattern of **F**. The cluster reported in this case has two bridging diphenylphosphino ligands. As already established for palladium clusters of different nuclearity and/or CVE count,[47] this shows that bridging units in tripalladium clusters are not limited to thiolates and selenides. The next part of the manuscript dedicated to catalytic applications will mention similar examples in which aromatic tripalladium clusters isolobal with the **F**-type one could feature different bridging ligands, too.

The extensive modeling analyses carried out on clusters **F** and their heterobimetallic variants showed that these cationic complexes had largely negative quadrupolar moments perpendicular to their metal cores (Figure 4). This was rather surprising because this feature is usually found for electron-rich, neutral, or anionic aromatics instead. The feature usually allows one to coordinate cations using these electron-rich, $\pi$-donating arenes. It was thus challenging to try to probe experimentally the feasibility to use an all-metal-based cationic

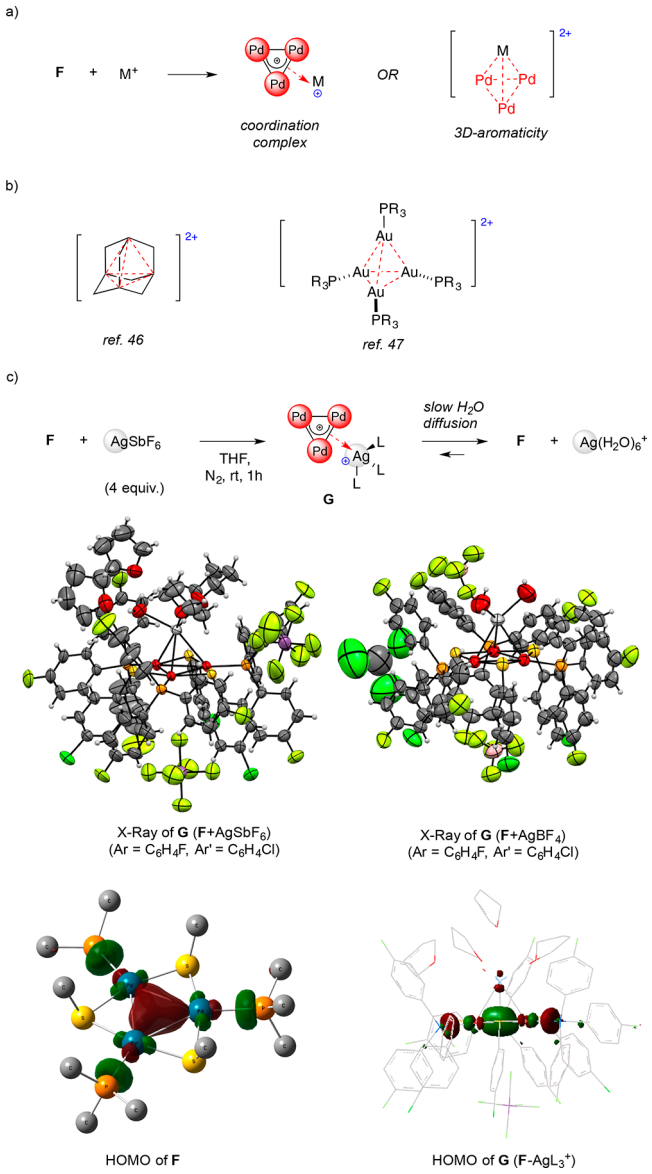


**Figure 4.** Complementary nature between coordination complexes and 3D aromaticity (a). Examples of dications featuring 3D aromaticity (b) and the ligand-like behavior of aromatic clusters **F** with Lewis acids (c).

platform as a mimic of a traditional electron-donating ligand, hoping to overcome electrostatic repulsion (Figure 4a). The concept was proved for several group 11 cations,[48] as unambiguously evidenced by various NMR, mass spectrometry (MS), and X-ray analyses. The latter were performed on $[Pd_3Ag]^{2+}$ complexes **G** and showed that the structure of the parent Pd triangle remained essentially unaltered upon coordination to an unsaturated silver(I) cation. Metal−metal distances and angles on the triangle remained indeed very similar to those of the parent cluster **F**. Various modeling tools, including DFT, electron localization function (ELF), and noncovalent interactions (NCI) methods, confirmed the initial working hypothesis on a coordination-like bonding mode. This make these clusters complementary to the reported examples of three-dimensional aromatics, which present delocalized four-center−two-electron bonds, such as the adamantyl dication[49] or isolobal tetranuclear gold clusters (Figure 4b).[50] Beside NICS analyses confirming this difference,


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conclusive experimental evidence was observed by NMR titrations (Figure 4c). A competition experiment indeed showed a shifting of the coordination equilibrium thanks to increasing amounts of water, which played the role of a ligand for the silver(I) cations disfavoring their binding by the donating $[Pd_3]^+$ cluster.

Saito's group reported the synthesis of an original heterobimetallic complex featuring a $[TiSn_2]$ core (Figure 5a).[51] The compound was prepared by treating at room temperature a Sn-containing cyclopentadienoate with a Ti(IV) complex. The resulting compound has a nearly isosceles triangular core characterized by two similar Ti−Sn distances (ca. 2.69 and 2.72 Å, respectively) and a Sn−Sn one of ca. 3.06 Å. Interestingly, the former are shorter than previously reported Ti−Sn single bonds (by more than 0.12 Å) while the latter is longer than typical Sn−Sn double bonds (by at least 0.2 Å). These unusual structural features could be rationalized on the basis of a delocalized metal−metal bond, which would make this complex a $\sigma$-aromatic cluster.[52] This hypothesis was backed by various modeling tools, including DFT, natural population analysis, and NICS, which strongly pointed to the presence of a delocalized bonding interaction between the three metal nuclei.

The group of Sadighi reported the preparation of $[Au_3]^+$ clusters **I** that have a delocalized metal−metal bond of sigmoid symmetry (Figure 5b).[53] The work involved the preparation of cationic Au(I) carbonate, bearing one bulky *N*-heterocyclic carbene (NHC) ligand for each metal nucleus, that could be reduced to the desired cluster in the presence of CO (1 atm). The aromatic complex has no bridging species and presents a quasi-equilateral core with nearly degenerate Au−Au distances (varying between 2.64 and 2.66 Å in the solid state). The combination of an s-type AO of each gold atom results in the generation of the bonding HOMO and of two degenerates LUMOs, which lie at a fairly high energy level (gap of +5.42 eV). This is a confirming hint for the aromaticity of the complex, and the modeling result was confirmed by cyclic voltammograms, which showed the reluctant tendency of **I** to undergo redox events.

An isolobal analogue of **I**, in which cyclicalkylaminocarbenes (CAAC) replaced the NHCs ligands, was reported soon after by Bertrand's group.[54] In this case, the aromatic cluster was assembled through a complementary strategy, which is reminiscent of that described for the synthesis of **E** (Figure 5c). A suitable Au(0) dimer that has a covalent Au−Au bond could react with a cationic Au(I) fragment that features a sufficiently noncoordinating counteranion. The driving force of the process could be potentially ascribed to the formation of the delocalized metal−metal bond. Although the strong prowess of gold atoms to display aurophilic interactions might blur a clear distinction between these two bonding phenomena, it is worth noting that weaker aurophilic interactions usually led to longer Au−Au distances, up to well above 3 Å, which are significantly longer than those observed in clusters **I**. Both this trigold cluster and related analogues will be mentioned in the next section dedicated to catalytic applications.

The heaviest trinuclear all-metal aromatic cluster reported to date has been synthesized by the group of Liddle.[55] The thorium complex **J** has a dianionic core, composed of a metal triangle with six bridging chloride ligands and three ancillary cyclooctatetraenyl ones (Figure 5d). X-ray analysis showed that **J** has an essentially equilateral triangular core, with nearly degenerate angles and metal−metal distances (ca. 3.99 Å), which are significantly below the sum of van der Waals radii of thorium (4.74 Å). According to various DFT, population analysis, and NICS experiments, the authors proposed that the HOMO of the cluster has a bonding character and represents a

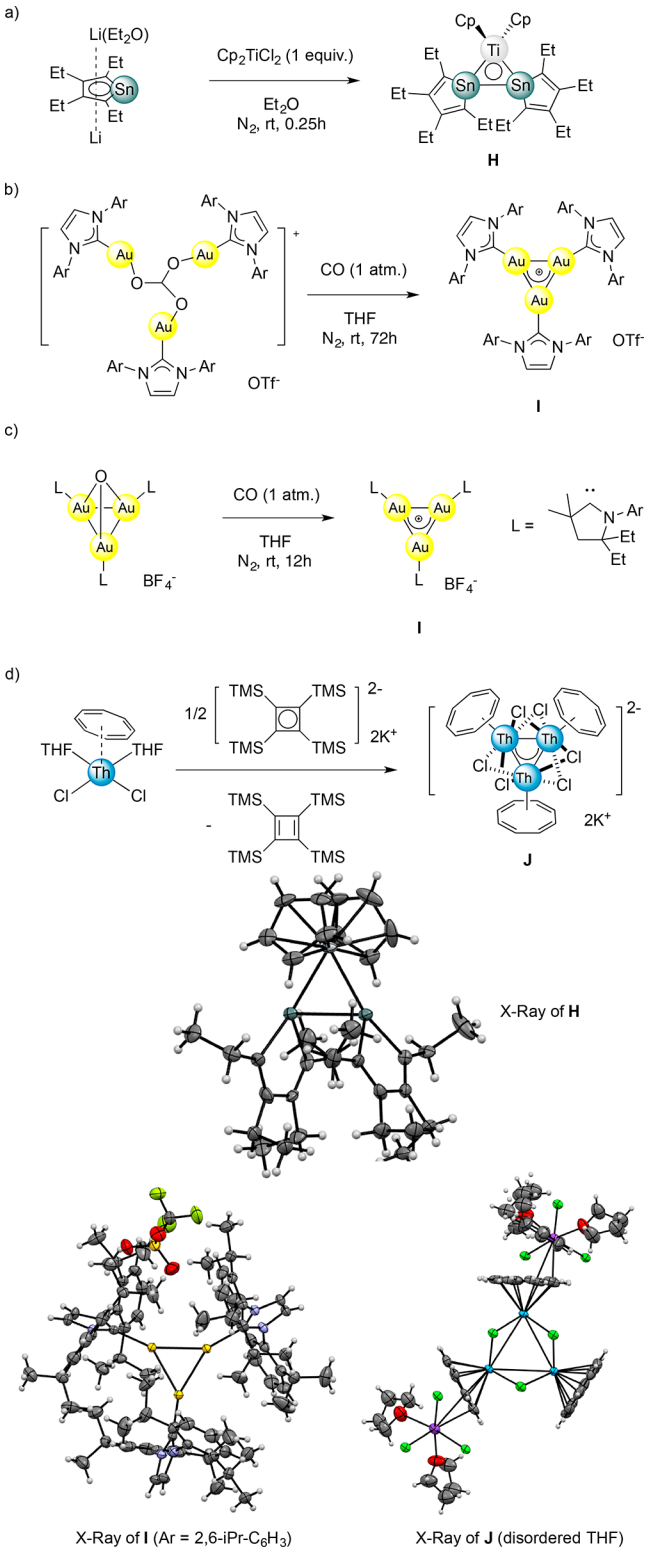


**Figure 5.** Synthesis of a heterobimetallic Sn/Ti complex (a), alternative syntheses of aromatic trigold clusters (b and c), and preparation of a triangular thorium cluster (d).


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three-center−two-electron delocalized metal−metal bond of sigmoid symmetry, hence claiming the aromatic character of **J**.

The interpretation of the relevance of some modeling results, particularly NICS ones, and, consequentially, the aromaticity of the cluster **J**, was later questioned[56] and resulted in an exchange with the authors of the original synthesis. Without commenting on the soundness of each orthogonal claim, the discussion seems to us both scientifically healthy and didactic, because it shows two relevant and general points for research activity at large. First, almost always no single analytic tool, either experimental or computational, could on its own provide conclusive and clear-cut evidence. Last, but not least, the observation of aromaticity is rarely, by itself, a meaningful end for research activity; it might, however, become a key point once it could rationalize either new molecular architectures or unexpected reactivities. This opinion is, incidentally, the best way to introduce the next part of the work, which deals with the catalytic applications of aromatic trinuclear clusters.

## ■ CATALYTIC APPLICATIONS

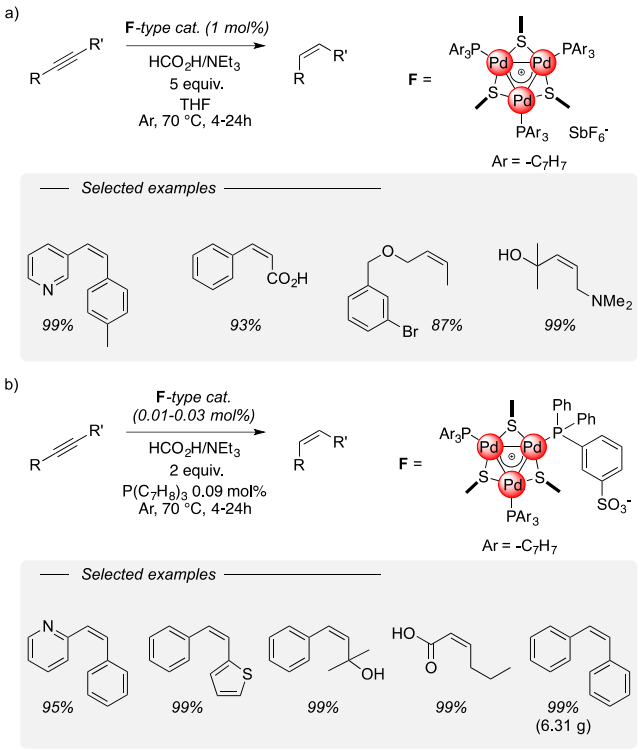
In stark contrast with the vast majority of reported trinuclear metal clusters, for which catalytic applications are often limited at best, most of the above-mentioned aromatic species already showed promising results in catalysis. Moreover, in many cases their behavior is complementary to those of mononuclear catalysts, either from a mechanistic or a reactivity-oriented point of view.

The catalytic semireduction of alkynes to *Z*-alkenes was the first reaction developed using tripalladium clusters **F**.[57] The reaction can be performed under transfer hydrogenation conditions, using ammonium formate as a reducing source, in order to avoid the requirement of hydrogen gas, which is hazardous and explosive (Scheme 1a). The use of catalyst loadings down to 1 mol %, which is the literature benchmark among homogeneous, Pd-based, reduction catalysts, allows one to achieve full conversion of the starting alkyne in a few hours (4−24 h) over an ample range of substrates, affording desired products in yields that are usually above 90%. The best results were obtained employing a cluster with relatively small methyl thiolates as bridging units, showing that the reaction is quite sensitive to steric hindrance around the metal core. Interestingly, although the reactions were performed with an excess of donor (5 equiv), no traces of over-reduction occurred.

This feature highlights the complete chemoselectivity of the system for the reduction of alkynes over alkenes, and it is usually not observed using most mononuclear homogeneous catalysts instead.[58] Mass spectrometry analyses on samples taken from reaction mixtures showed the signature isotopic peaks of the $[Pd_3]^+$ cluster throughout these experiments, strongly suggesting their actual role as catalysts. The use of deuterated formic acids led to the observation that the transfer of both the acidic proton and the hydride showed a significant primary kinetic isotope effect. This finding is not observed using mononuclear reduction catalysts under transfer hydrogenation conditions, for which just one of these two steps had a meaningful kinetic isotopic effect.

A second-generation method was later reported thanks to the preparation of zwitterionic analogues of **F**, in which one ancillary tertiary phosphine is replaced by one bearing an aryl sulfonate group (Scheme 1b).[59] The resulting cluster proved significantly more active than its peer, although more prone to

**Scheme 1. Catalytic Semireduction of Internal Alkynes Using Cationic (a) and Zwitterionic (b) Aromatic $[Pd_3]^+$ Clusters, with Selected Synthetic Examples**




decomposition prior to accomplishing full conversion of the starting material. However, addition of a catalytic amount of a tertiary phosphine proved decisive to strike a positive balance between the activity and the chemical stability of the cluster. This allowed one to reduce the catalytic loading by up to 2 orders of magnitude by keeping relatively short reaction times for an ample range of substrates.[60] Monitoring the reaction progress by means of UV−vis spectroscopy showed that the key bands due to the cluster in the visible region remained unaltered throughout the reaction, highlighting its chemical stability. The use of deuterium-enriched ammonium formates led to the formation of *Z*-alkenes in which the allylic position showed extensive *d*-labeling (up to 50%). This result indicated that the reaction likely involves the isomerization of the alkyne group into the corresponding allene. Under optimized conditions, the semireduction method allowed one to recover the desired products usually in >95% yield, and the functional group tolerance of the catalytic system includes aryl bromides, alcohols, amines, and heterocycles such as thiophenes and pyridines. The practical viability of the method is further witnessed by the possibility to perform the semireduction up to a 6 g scale, without hampering the rate of the reaction or its selectivity. Moreover, the alkyne/reducing mixture could be employed as solvent/reagents in this case, minimizing the formation of wastes. To the best of our knowledge, this alkyne semireduction method is still the most active (in terms of turnover frequency, TOF), chemically robust (in terms of turnover number, TON), and selective among those reported in the literature based on a palladium catalyst.[61]

The chemical activity of aromatic $[Pd_3]^+$ clusters in alkyne reductions has been recently shown by Ma's group to be preserved incorporating these complexes into metal organic frameworks (MOFs).[62] By taking advantage of the cationic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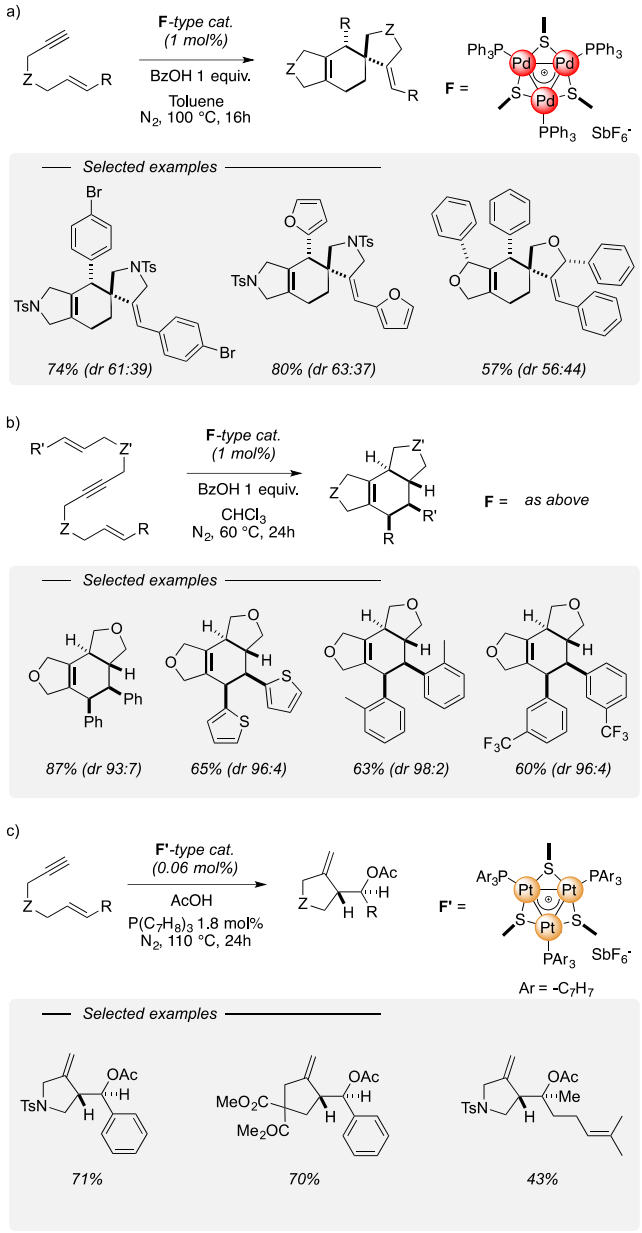
core of **F**, it is possible to trigger a cation exchange with small counterions of the MOF and induce the desired derivatization. The resulting hybrid material can be readily characterized spectroscopically and showed promising catalytic properties in the above-mentioned alkyne reduction.

The tripalladium cluster **F** could also be used in C−C-forming sequences (Scheme 2a).[63] In the presence of mild carboxylic acid cocatalysts, it is indeed possible to activate the terminal triple bond of 1,6-enynes and induce their cycloisomerization to form the corresponding cyclic 1,3-dienes. These species could further react *in situ* to afford tricyclic derivatives in which a central cyclohexene unit is decorated by a spiro carbon via catalytic [4 + 2] cycloaddition. This unusual structure could be found in a few natural products, such as ramonanins.[64]

**Scheme 2. Examples of C−C-Forming Cascades of Enynes (a), Dienynes (b), and Enynes with Carboxylic Acids (c) Catalyzed by Aromatic $[M_3]^+$ Clusters, Presenting Meaningful Synthetic Examples**




The method proved tolerant to several functional groups, including cyano groups, esters, chlorides, and bromides, and relatively insensitive to electronic factors. The chemoselectivity of the cycloaddition is complete, while the diastereoselectivity is lower for the intermolecular step. The sequence could be monitored by $^{31}$P NMR to study the fate of cluster **F** throughout the reaction. At the initial stages, the key singlet resonance of the cluster (ca. 15 ppm) disappears, with the concomitant appearance of a new one in the Pd(II)−P region (ca. 30 ppm). Once the concentration of the starting reagent begins to fade, the intensity of this new peak recedes, and the signal of the trinuclear complex starts to come back. Once conversion is complete, the peak due to the original cluster is essentially restored, in agreement with the possibility to recover the complex by column chromatography at the end of the reaction (up to ca. 70% recovery). According to extensive modeling studies, the reaction proceeds through a series of endoergonic intermediates in which the aromaticity of the starting complex **F** is no longer present.[65] This, in turn, paves the way for the straightforward regeneration of the complex at the end of the catalytic cycle, thus greatly contributing to its overall chemical stability. These findings could be regarded as a consequence of the aromaticity of **F** itself, which induces a strong driving force toward its generation/regeneration. Besides the present examples, this effect is potentially much more widely present in the huge field of palladium catalysis than currently realized.[66]

The alkyne activation could take place as well using internal triple bonds (Scheme 2b).[67] This possibility has been exploited for the synthesis of fused tricycles by preparing the corresponding linear dienynes. In this case, the combination of cluster **F** (1 mol %) with a carboxylic acid allows one to obtain the polycyclization delivering up to four contiguous stereocenters in the final product. The reaction likely proceeds in a similar way to that of 1,6-enynes, leading to the intermediate formation of a monocyclic triene, in which the conjugated diene arm and the isolated double bond could readily undergo an intramolecular [4 + 2] cyclization. As observed in the previous case, the electronic mismatch of this Diels−Alder reaction is overcome thanks to the cluster itself, which likely impoverishes the electronic density of the 1,3-diene unit via coordination. Remarkably, the product of this intermolecular cascade is retrieved with very high diastereocontrol (dr > 9:1) over an ample range of substrates. In contrast to alkyne semireductions, these C−C-forming sequences are rather insensitive to the steric hindrance of bridging thiolates.

The triplatinum analogue **F′** could be competent in cyclization sequences, too (Scheme 2c).[68] In this case, 1,6-enynes could be activated by the cluster using acetic acid as a solvent/reagent. Under mild conditions and low catalyst loadings (0.3−0.6 mol %), it is possible to induce the sequential substrate cyclization/incorporation of a carboxylate unit to deliver the final product in moderate to good yields. Preliminary mechanistic investigations, which included deuterium-labeled species, suggest a mechanism in which the cluster induces the electrophilic activation of the alkyne, leading to the nucleophilic attack by the alkene. The resulting intermediate carbocation is then eventually quenched by a carboxylate species, affording the desired product.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The use of trinuclear palladium clusters that are isolobal to **F** could represent a tool to trigger efficient Suzuki-type cross-coupling reactions (Scheme 3a).[69]

The complex used in this case features different bridging ligands compared to those discussed above for other C−C bond-forming sequences. In particular, the cluster has two diphenylphosphino units and a chloride anion, which is believed to be easily replaceable within the catalytic manifold. The complex is prepared in a one-pot, two-step fashion starting from palladium dichloride and displays stereoelectronic features that makes it similar to its **F** peers. A nearly equilateral triangle is present in its core, and various bonding analyses point to the presence of a delocalized three-center−two-electron Pd−Pd bond that makes this species $\sigma$-aromatic. The use of this cluster in reactions involving aryl bromides and aryl boronic acids leads to the recovery of the corresponding biaryl products in very good to excellent yields over an ample range of substituents.

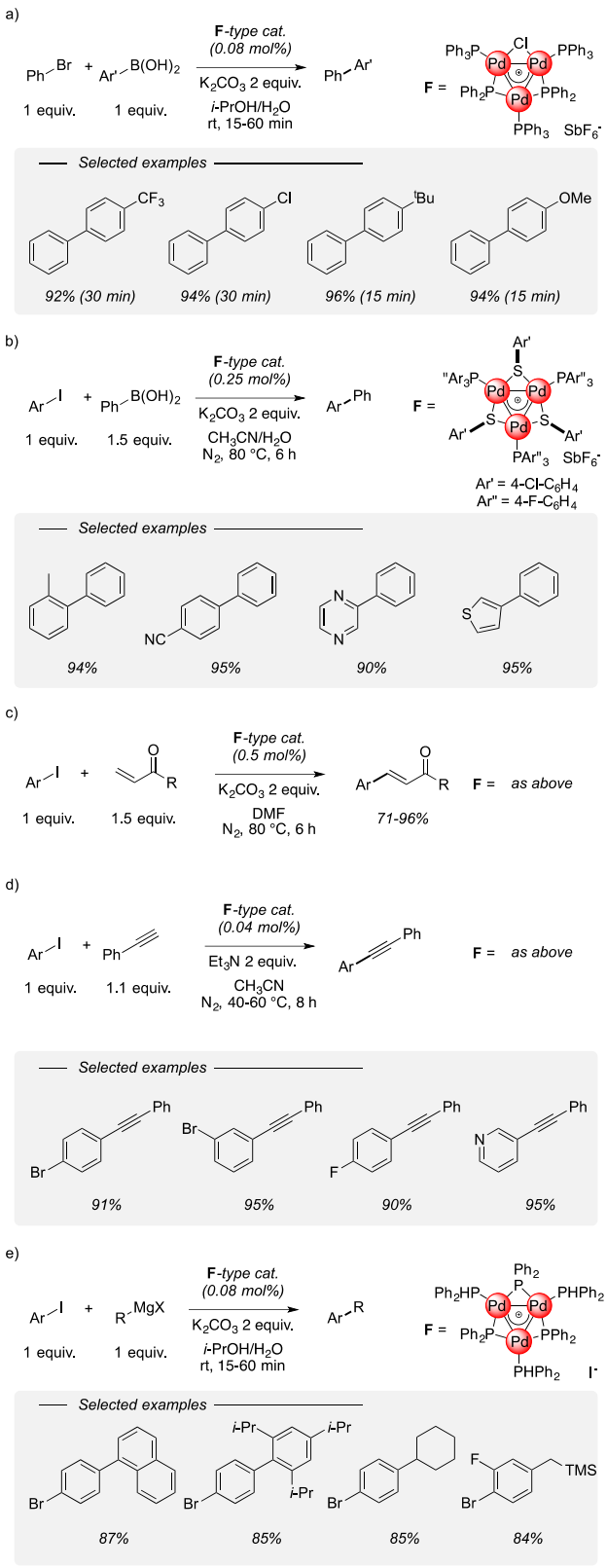
Moreover, reactions can be conveniently performed at room temperature, allowing one to achieve complete conversion of the substrate usually in less than 1 h even employing low catalyst loadings (down to 0.08 mol % of the tripalladium clusters). According to MS studies on the most favorable reaction mechanisms, the authors have proposed that the formation of products involved in this case usually neglected a transmetalation step rather than the most often invoked boronate-based one. It is indeed proposed that, in the presence of hydroxide anions, the activation of boronic acids occurs by means of Pd−OH fragments, in which an oxygen lone pair acts as a base to fulfill the unoccupied boron orbital. The so-formed association complex would then pave the way for a smooth transmetalation step, which transfers the aryl arm to the palladium nucleus. The resulting aryl palladium fragment would then react with the aryl halide, regenerating the initial cluster with a bridging bromide and with the concomitant liberation of a product molecule. The actual elementary step through which this C−C coupling event took place was not elaborated further.

A more recent alternative method involves the use of a cluster **F**-type catalyst, with bridging aryl sulfide ligands, to trigger the efficient Suzuki coupling of aryl iodides with aryl boronic acids (Scheme 3b).[70] Reactions are performed in the presence of potassium carbonate as the base, and the solvent is an acetonitrile/water mixture. Once again, low catalyst loadings can be employed (down to 0.25 mol %), although the method requires heating in order to deliver the target biaryl products (80 °C).

Reactions afford the latter in good to excellent yield over an ample range of functionalities, which are usually well-tolerated even using sterically hindered, ortho-substituted aromatic derivatives. The scope of the reaction includes several heterocyclic derivatives, such as thiophenes, pyridines, and unprotected pyrazoles. The method was also tested for the preparation of a selective cyclooxygenase 2 inhibitor, namely, 2-[1,1′-biphenyl]-2-ylbenzothiazole, which could be retrieved in up to 94% yield.

An interesting difference between the two catalytic systems that were shown to promote the Suzuki coupling lies in their halo-selectivity. The phosphino-bridged cluster is highly active in the activation of C(sp$^2$)−Br bonds,[69] while the thiolate-bridged variant is highly selective for the functionalization of C(sp$^2$)−I ones.[70] Indeed, different C(sp$^2$)−Br and C(sp$^2$)−Cl functions remain untouched in this case, even if these reactions

**Scheme 3. Cross-Coupling Methods for the Synthesis of Polyfunctionalized Arenes Catalyzed by Aromatic $[Pd_3]^+$ Clusters, Including Suzuki- (a and b), Heck- (c), Sonogashira- (d), and Kumada-Type Reactions (e), Highlighting Key Synthetic Examples**





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are performed at 80 °C. It is worth noting that the vast majority of popular mononuclear Pd-based cross-coupling catalysts show limited competence with respect to the selective functionalization of polyhalogenated substrates. According to recent studies by the group of Fairlamb, the nuclearity of the active species could play a decisive role in this context.[71]

Heck-type coupling, too, can be efficiently accomplished using 0.5 mol % of cluster **F** as the catalyst (Scheme 3c).[72] Reactions can be performed in dimethylformamide (DMF), at 80 °C, using a carbonate salt as the base. The reaction affords the desired vinylarenes in good to excellent yields employing several functionalized aryl iodides. In general, those substituted with electron-withdrawing groups performed slightly better than those using electron-rich reagents. Similarly, various acrylates and acrylamides can be employed. In analogy to the observation made for the Suzuki coupling method, the use of polyhalogenated arenes allows one to form selectively monofunctionalized products, preserving both C(sp$^2$)−Br and C(sp$^2$)−Cl functions as convenient synthetic handles for further derivatization. Under optimized conditions, the reaction of 4-bromoiodobenzene was remarkable to this end, because the use of cluster **F** as a catalyst quantitatively provided the monovinylated product, while several mononuclear Pd-based species afforded exclusively the difunctionalized derivative.

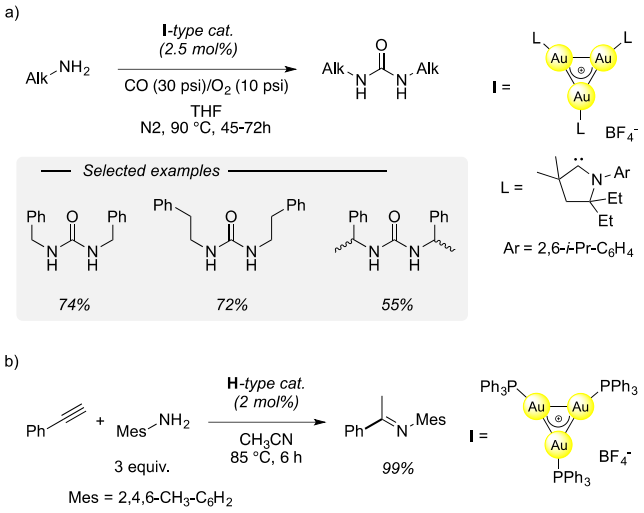
The catalytic system is also amenable for triggering copper-free Sonogashira couplings. In this case, reaction mixtures could be heated at lower temperatures (40−60 °C) and the catalyst loading could be reduced to 0.04 mol % (Scheme 3d).[72] Once more, a complete chemoselectivity for the activation of C(sp$^2$)−I bonds was observed. A variety of biarylacetylene derivatives could be prepared through this method, and products were recovered in good to excellent yields across an ample spectrum of functional groups. In general, the best results were achieved with the least-hindered aryl iodides, which feature either meta or para substituents.

The first observation of the potential displayed by aromatic tripalladium clusters with respect to their halo-selectivity was reported by the group of Schoenebeck in 2019 (Scheme 3e).[73]

The group reported a simple synthesis of diphenylphosphino-bridged **F**-type clusters, which could be recovered as iodide salts and featured diphenylphosphines as ancillary ligands. These complexes can be formed in nearly quantitative yields from the corresponding Pd(I) dimers. Moreover, the resulting trinuclear cluster proved to be highly active for Kumada-type cross-coupling reactions. The method allows one to react aryl iodides with Grignard reagents at room temperature, and the corresponding products could be obtained in good to excellent yields. An ample range of interesting functionalities could decorate the targets, including thiophenes, pyrimidines, vinyl groups, cyclopropyl rings, and bulky arenes such as a 2,4,6-triisopropyl phenyl ring. Several aryl, alkenyl, and alkyl magnesium reagents can be readily coupled. In stark contrast to several mono- and dimeric palladium precursors, the use of the trinuclear complex as the catalyst enabled the selective monofunctionalization of polyhalogenated reagents, as witnessed over an ample range of substrates featuring both C(sp$^2$)−Br and C(sp$^2$)−Cl bonds. According to preliminary modeling results, the origin of this remarkable chemoselectivity has been assigned to the significant difference between barriers relative to the oxidative addition of a C(sp$^2$)−X bond on a palladium nucleus of the triangular cluster. While the barrier found for the activation of a C(sp$^2$)−I bond could still allow the reaction to take place under ambient conditions, the process becomes highly unfavorable for aryl bromides and chlorides.

The group of Bertrand reported the application of trigold cluster **I**, in which each metal nucleus is coordinated by a CAAC ligand, for the preparation of ureas through the carbonylation of primary amines (Scheme 4a).[54] Several

**Scheme 4. Catalytic Applications of Aromatic $[Au_3]^+$ Clusters Showing Their Prowess Towards Synthesis of Ureas (a) and Alkyne Hydroaminations (b)**




aliphatic and aromatic amines could be employed, affording the corresponding ureas in moderate to good yields. The reaction requires relatively moderate pressures and the presence of molecular oxygen (30 and 10 psi for CO and $O_2$, respectively). The catalytic system proved to be sensitive to steric hindrance, and the worst results were indeed achieved employing 1-adamantyl amine as the substrate. According to preliminary evidence on the reaction mechanism, the authors proposed that the catalytic cycle proceeds with the cleavage of the delocalized gold−gold bond, giving rise to a gold dimer with a bridging aminyl unit, which was characterized by X-ray analysis. The insertion of CO into the Au−N bond would then lead to the elimination of an intermediate isocyanate, allowing the regeneration of the trigold cluster **I**. The desired product is eventually formed via nucleophilic attack of a second amine molecule on the isocyanate.

Recently, an interesting development was reported showing that the hydroamination of terminal alkynes could be accomplished using trigold clusters (Scheme 4b).[74] The active complex is isolobal to **I**, and it has triphenylphosphine as the ligand instead of a carbene. This species could be prepared by CO-mediated reduction of its parent oxo complex, through a strategy that is reminiscent to that adopted by Sadighi for the synthesis of **I**. The aromatic trigold cluster is then able to convert a variety of phenylacetylene derivatives into the corresponding imines with excellent yields. The reaction can be performed employing several anilines as nucleophiles, and their attack on the alkyne partner is always shown to occur onto the most hindered C(sp) nucleus. Remarkably, steric hindrance on the aniline partner is well-tolerated, and 2,6-disubstituted derivatives still allow one to recover the desired product in very good yields.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## CONCLUSIONS

This manuscript presented an overview of the studies on the chemistry of stable trinuclear all-metal aromatic clusters. Thanks to pioneering works that were carried out nearly 20 years ago, these fascinating structures have evolved from a computational-based curiosity, for which experimental proofs were deemed very challenging at best, into solid synthetic tools. This process has been possible through the research activity of several groups, which enabled the preparation of highly elaborate organometallic architectures, these days incorporating a large palette of different elements from the periodic table. Furthermore, the chemical robustness of most of these clusters allowed one to probe their behavior in catalysis. Reported methods are already abundant and represent a strong proof of the potential efficiency of these clusters in several fields, including reductions, C−C-forming cascades, and various cross-coupling methods. In most cases, trinuclear complexes emerged as efficient alternatives to popular mononuclear catalysts, often revealing complementary traits that might be further exploited in the future. We hope that this present overview will further push studies on the frontiers of this chemistry by showing that already reported evidence strongly suggests that ample room for future developments is ready to be attained.

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Franca Bigi** writing-review & editing (supporting); **Daniele Cauzzi** writing-review & editing (supporting); **Nicola Della Ca'** writing-review & editing (supporting); **Max Malacria** writing-review & editing (supporting); **Raimondo Maggi** writing-review & editing (supporting); **Elena Motti** writing-review & editing (supporting); **Yanlan Wang** writing-review & editing (supporting); **Giovanni Maestri** conceptualization (lead), writing-review & editing (lead).

### Notes

The authors declare no competing financial interest.

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