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N-Heterocyclic Carbenes: A Door Open to Supramolecular Organometallic Chemistry

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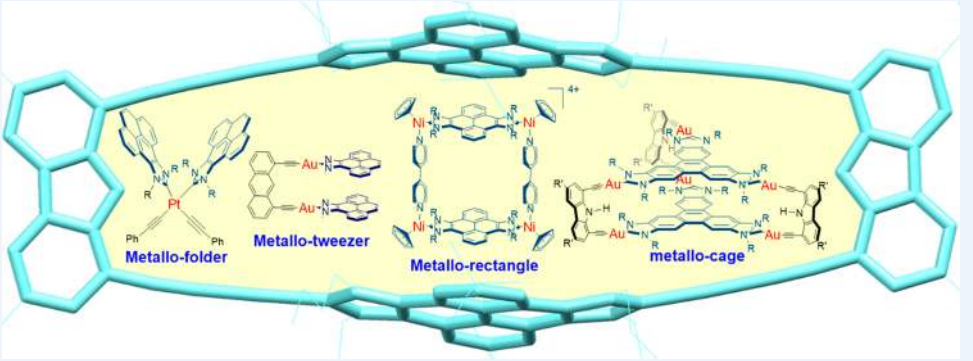

CONSPECTUS: The field of metallosupramolecular chemistry is clearly dominated by the use of O- N-, and P-donor Werner-type polydentate ligands. These molecular architectures are of high interest because of their wide range of applications, which include molecular encapsulation, stabilization of reactive species, supramolecular catalysis, and drug delivery, among others. Only recently, organometallic ligands have allowed the preparation of a variety of supramolecular coordination complexes, and the term supramolecular organometallic complexes (SOCs) is gaining space within the field of metallosupramolecular chemistry. While the early examples of SOCs referred to supramolecular architectures mostly containing bisalkenyl, diphenyl, or bisalkynyl linkers, the development of SOCs during the past decade has been boosted by the parallel development of multidentate N-heterocyclic carbene (NHC) ligands. The first examples of NHC-based SOCs referred to supramolecular assemblies based on polydentate NHC ligands bound to group 11 metals. However, during the last 10 years, several planar poly-NHC ligands containing extended π-conjugated systems have facilitated the formation of a large variety of architectures in which the supramolecular assemblies can contain metals other than Cu, Ag, and Au. Such ligands are Janus di-NHCs and trigonal-planar tris-NHCs—most of them prepared by our research group—which have allowed the preparation of a vast range of NHC-based metallosupramolecular compounds with interesting host–guest chemistry properties. Although the number of SOCs has increased in the past few years, their use for host–guest chemistry purposes is still in its earliest infancy. In this Account, we describe the achievements that we have made during the last 4 years toward broadening the applications of planar extended π-conjugated NHC ligands for the preparation of organometallic-based supramolecular structures, including their use as hosts for some selected organic and inorganic guests, together with the catalytic properties displayed by some selected host–guest inclusion complexes. Our contribution describes the design of several Ni-, Pd-, and Au-based metallorectangles and metalloprisms, which we used for the encapsulation of several organic substrates, such as polycyclic aromatic hydrocarbons (PAHs) and fullerenes. The large binding affinities found are ascribed to the incorporation of two cofacial panels with large π-conjugated systems, which provide the optimum conditions for guest recognition by π–π-stacking interactions. We also describe a series of digold(I) metallotweezers for the recognition of organic and inorganic substrates. These metallotweezers were used for the recognition of "naked" metal cations and polycyclic aromatic hydrocarbons. The recognition properties of these metallotweezers are highly dependent on the nature of the rigid connector and of the ancillary ligands that constitute the arms of the tweezer. A peculiar balance between the self-aggregation properties of the tweezer and its ability to encapsulate organic guests is observed.

1. INTRODUCTION

Metallosupramolecular chemistry refers to the field of research involving the combination of bridging organic ligands with metal units that form discrete or polymeric assemblies of different shapes and sizes.[1] Over the last three decades, coordination-driven self-assembly has become a widespread strategy for the

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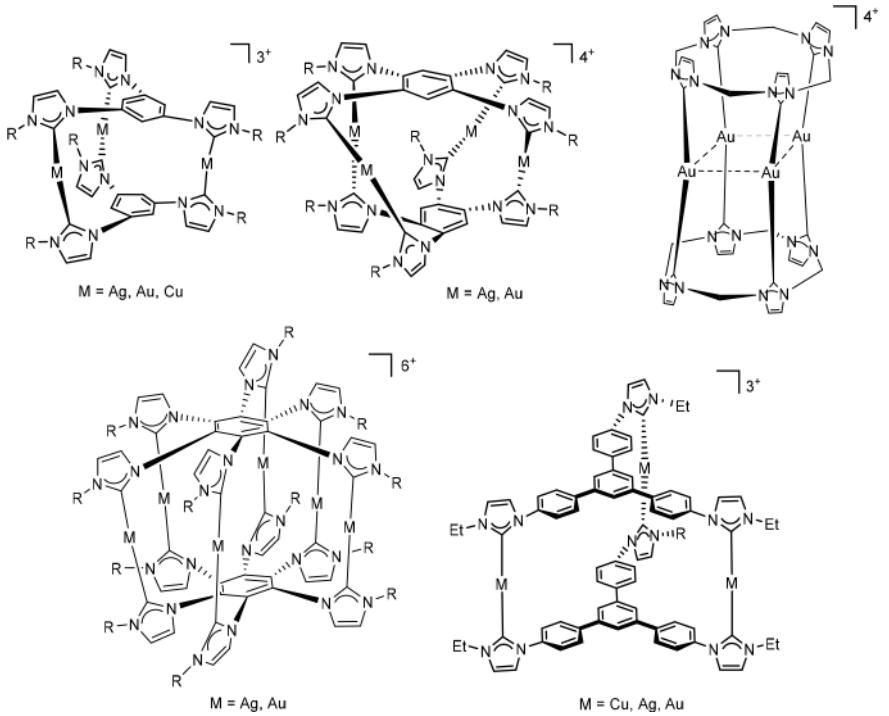
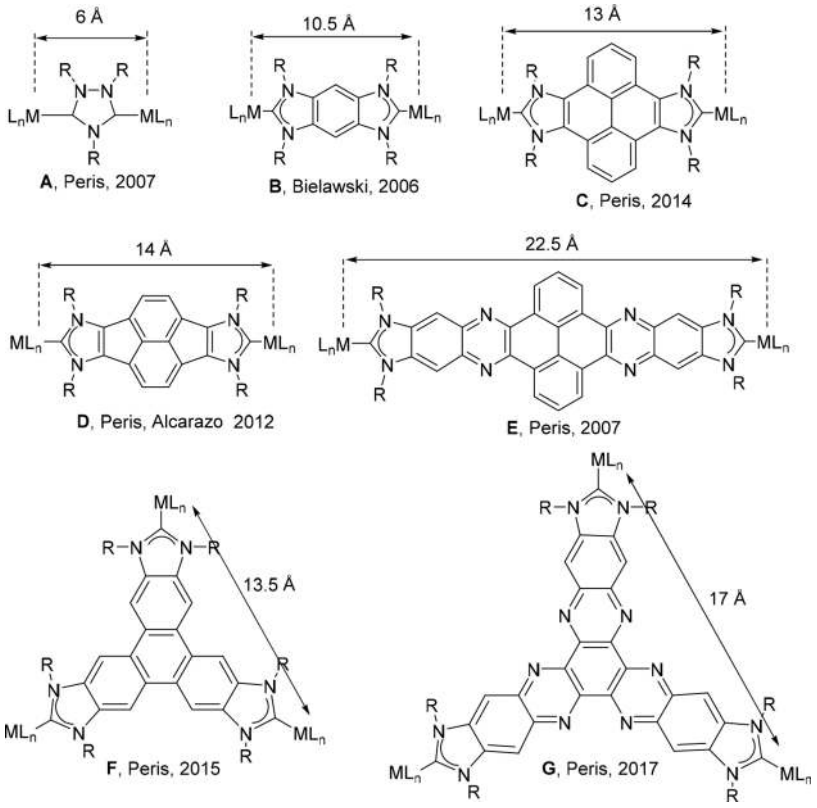
Scheme 1. Some NHC-Based SOCs with Group 11 Metals



Scheme 2. Planar Di- and Tri-NHC Ligands for the Preparation of SOCs



rational construction of discrete supramolecular coordination complexes (SCCs).[1a,2] This technique capitalizes on the directional and predictable nature of the metal−ligand bond, which allows the outcome of the self-assembly process to be predicted with a high level of certainty. Many of the reported SCCs have discrete void areas with well-defined shapes and sizes, and this is why SCCs are often called "molecular flasks".[3] These cavities impart unique properties to the structure that lead to novel functions and applications. For the design of these void spaces, the ligand is arguably the most important building block because its topological features and binding abilities determine the size, geometry, and functionality of the resulting cavities.

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From the ligand perspective, metallosupramolecular chemistry is clearly dominated by the use of O-, N-, and P-donor Werner-type polydentate ligands, while only a few examples of assemblies bearing carbon donor ligands have been reported in the literature. However, during the past decade, the number of organometallic-based supramolecular assemblies has grown fast and parallel to the development of multidentate N-heterocyclic carbene (NHC) ligands,[4] and a number of review articles were published recently.[5] The rapid development of supramolecular assemblies with organometallic ligands is exemplified by the establishment of the term supramolecular organometallic complexes (SOCs), coined by Pöthig and Casini in 2019,[5c] to refer to complexes in which the (organic) linker forms the organometallic bond to the metal node. This means that the carbon−metal bond is structurally crucial for the formation of the architecture of the resulting SOC, in contrast to those assemblies that do not have organometallic-based ligands or those whose organometallic ligands (normally η^5-Cp or η^6-arene) cap the metal nodes.

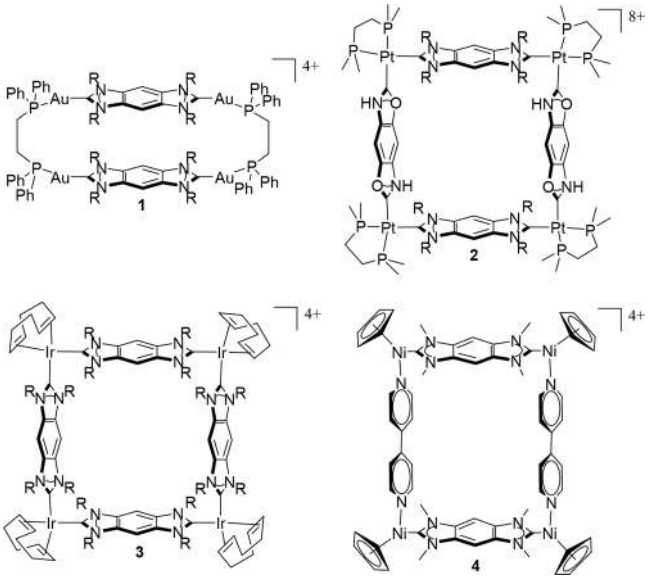
Most NHC-based SOCs are supramolecular assemblies based on polydentate NHC ligands bound to group 11 metals. The reason for this is that these metals often display linear coordination modes that facilitate trans coordination of the NHC ligands, thereby forming assemblies in which the metal atoms are sandwiched between the two polydentate NHC ligands. In addition, the NHC−M bond (M = Cu, Ag, Au) is usually labile, which allows the formation of the thermodynamically most stable assemblies from mixtures of the metal precursors and the poly-NHC. These assemblies include rectangles, triangles,[6] and cylinders,[7] such as the ones shown in Scheme 1.

However, during the last 10 years, several planar poly-conjugated poly-NHC ligands have facilitated the formation of a variety of structures in which the supramolecular assemblies can contain metals other than Cu, Ag, and Au.[8] The use of the Janus di-NHC ligands **A**−**E** (Scheme 2) allows the synthesis of supramolecular assemblies whose dimensions may range from 6 Å as established by triazolylidene ligand **A**[8a] to almost 23 Å when the nanosized di-NHC with the quinoxalinophenanthrophenazine core **E**[8e] is used. Among these, the benzobis(imidazolylidene) ligand **B** described by Bielawski in 2005[9] was the first one to demonstrate its suitability for the preparation of organometallic-based assemblies. Some threefold-symmetric tri-NHCs, such as **F** and **G**, have also been prepared.[8d,f,10]

Hahn's group was the first one to exploit the linear arrangement of **B** for the preparation of a number of square- and rectangular-shaped assemblies that included metals such as gold,[11] iridium,[12] platinum,[13] palladium,[12b] and nickel[14] (Scheme 3). Together with the use of this benzobis(imidazolylidene) ligand, Hahn also used a structurally similar di(NH,O)-NHC ligand for the preparation of a large number of molecular squares.[6a,b] The benzobis(NHC) ligand **B** establishes a metal-to-metal separation of 10.5 Å, which in most cases is too small to build cavities of the appropriate size to host organic guests. This is probably the reason why none of the organometallic assemblies displayed in Scheme 3 were used for host−guest chemistry purposes.

Although the number of SOCs has increased in the past few years, those used for host−guest chemistry purposes are still very few. Some recent relevant examples of SOCs used for the encapsulation of organic substrates were described by Altmann and Pöthig,[15] who developed organometallic-based rotaxanes consisting of Ag_8 and Au_8 pillarplexes, which are highly selective for the encapsulation of linear molecules, such as 1,8-diaminooctane. These metallosupramolecules also showed important antimicrobial activity and anticancer properties.[16]

Scheme 3. NHC-Based Metallosquares Described by Hahn's Group



With all of these precedents in hand, 4 years ago we started a new research line aiming to provide effective synthetic routes to NHC-based SOCs with applications in catalysis and host−guest chemistry. A clear advantage for us is that during the past few years we have prepared a large number of planar di- and tri-NHC ligands bearing π-extended polyconjugated cores such as those shown in Scheme 2, so we thought that this placed us in a privileged position to approach this new research line. In addition, our previous studies on the influence of supramolecular interactions on homogeneously catalyzed reactions[17] had already constituted our initial approach to metallosupramolecular chemistry and thus gave us some expertise in the field. This Account focuses on our achievements in the development of NHC-based SOCs that we prepared during the last 4 years, emphasizing their use as hosts for some selected organic and inorganic guests. The Account thus covers our progress in the development of several Ni-, Pd-, and Au-based metallorectangles, metalloprisms, and metallotweezers together with their respective host−guest chemistry properties.

2. STRUCTURES WITH MONO-NHC LIGANDS: METALLOFOLDERS AND METALLOTWEEZERS

A molecular tweezer is a molecular receptor that contains two identical flat polyaromatic arms at the edges that are connected in a syn conformation by a more-or-less rigid tether (Scheme 4).[18] In order to enable complexation with aromatic substrates by π−π-stacking interactions, the two parallel polyaromatic hands should be ideally separated by ∼7 Å, as aromatic groups stack at an interplanar distance of ≤3.5 Å.

While molecular tweezers were initially based on organic entities, in the past decade some research groups have incorporated metals into the structure of the tweezers, thus introducing a new dimension into the properties of these supramolecular systems.[19] Our first approach to the development of metallotweezers was the preparation of a series of Pt(II) complexes bearing cis-oriented NHC ligands decorated with π-

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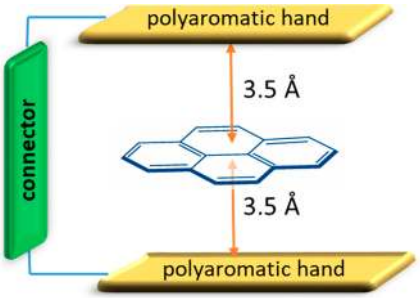
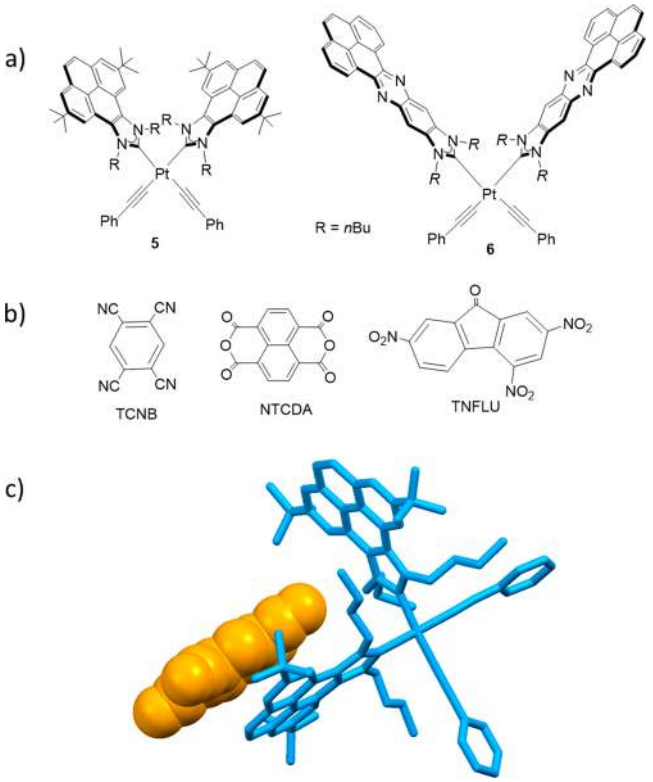
Scheme 4. Schematic Representation of a Molecular Tweezer Trapping a Molecule of Pyrene



s5 extended polyaromatic moieties (Scheme 5a).[20] The orthogonal disposition of the two aromatic hands of the receptor made us consider that the term *metallofolders* would be more accurate to refer to this subclass of metallotweezers. By taking advantage of the void space between the polyaromatic panels, these complexes were used as receptors of electron-deficient organic molecules such as 1,2,4,5-tetracyanobenzene (TCNB), 2,4,7-trinitro-9-fluorenone (TNFLU), and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA). Although the host–guest association constants were low, we observed that the receptors were able to discriminate between electron-rich and electron-deficient aromatic substrates. Besides, we observed that molecule **6** containing the phenanthrophenazine panel was a more effective receptor than molecule **5** containing pyrene, most likely because of the larger surface area provided by the former one, which renders a more effective $\pi-\pi$-stacking interaction with the guests.[20] The relatively low binding affinities shown by these two receptors are due to the orthogonal disposition of the two polyaromatic panels, which prevents their cooperative $\pi-\pi$-stacking interaction with the guests, as would have probably happened if the two panels were disposed in a parallel manner.

Scheme 5. (a) Platinum-Based Metallofolders 5 and 6; (b) Guests Used in the Study; (c) Molecular Structure of TCNB@5



Our next approach for the preparation of metallotweezers was the synthesis of complex **7** (Scheme 6), which contains two s6 Au(I) pyrene–imidazolylidene arms connected by a 1,8-diethynylanthracene linker.[21] In principle, this metallotweezer should show interesting recognition abilities since the two polyaromatic panels are parallel and separated by approximately 7 Å. However, the supramolecular properties of **7** are markedly determined by its tendency to self-aggregate. In a nonpolar solvent such as benzene, **7** self-aggregates to form the duplex complex $(\mathbf{7})_2$ (Scheme 6). This self-complementary duplex complex is formed by the encapsulation of the anthracenyl linker of each tweezer between the two pyrene-functionalized arms of the complementary one. The molecular structure of the complex shows that the four gold atoms form a rectangle displaying strong aurophilic interactions between the pairs of gold atoms of complementary tweezers. In the presence of "naked" metal cations (Cu^+, Ag^+, or Tl^+), the tweezer is able to self-aggregate in CH_2Cl_2, thus forming a similar duplex complex in which the metal cation is trapped inside the small cavity formed by the supramolecular assembly, as shown in Scheme 5 for the case of the addition of Ag^+. The self-aggregated structures formed are stabilized by a combination of $\pi-\pi$-stacking and M–Au metallophilic interactions. Titrations by fluorescence spectroscopy allowed the determination of the large association constants of the resulting inclusion duplex complexes formed by addition of the metal cations.[21]

We were interested in studying how subtle modifications of the structure of **7** would affect the supramolecular properties of the resulting complex. We first obtained the new metallotweezer **8** (Scheme 7) in which we changed the pyrene–imidazolylidene s7 ligand to a smaller benzoimidazolylidene.[22] It was anticipated that this would reduce the ability of the complex to self-aggregate because the π-delocalized surface area of the ligand is smaller than that shown by the pyrene-functionalized ligand in **7**. In fact, we observed that in the absence of an external stimulus, **8** does not show any tendency to self-aggregate. However, the addition of Cu^+, Tl^+, or Ag^+ facilitated the formation of self-aggregated structures in which the metal cations occupied the cavity of the dimer, although the three different species showed very distinctive behaviors. The complex with copper showed an interesting naked-eye-perceivable color change response (orange to yellow) to the presence of acetonitrile or ammonia vapors. This color change reverts after a few minutes upon exposure to air, and the process is fully reversible, as demonstrated through numerous cycles. This reversible vapochromism is explained by the formation of $[Cu(CH_3CN)_4](BF_4)$ or $[Cu(NH_3)_4](BF_4)$ upon exposure of $Cu@(\mathbf{8})_2$ to vapors of acetonitrile and ammonia, respectively, with the concomitant formation of **8**. In addition, while solutions of the thallium-trapped species $Tl@(\mathbf{8})_2$ were stable for days, the compounds containing copper and silver evolved into a polymer (Cu) or an oligomer (Ag) (Scheme 7).[22] The different reactivity patterns shown by **8** and the pyrene-containing tweezer **7** are explained because $\pi-\pi$-stacking interactions are less likely to be produced in **8**, and therefore, the molecule may self-aggregate, but the process is reversible and may also give rise to more complex structures such as oligomers and polymers.

Once we studied the self-aggregation properties of tweezers **7** and **8**, we became interested in studying the cation-triggered

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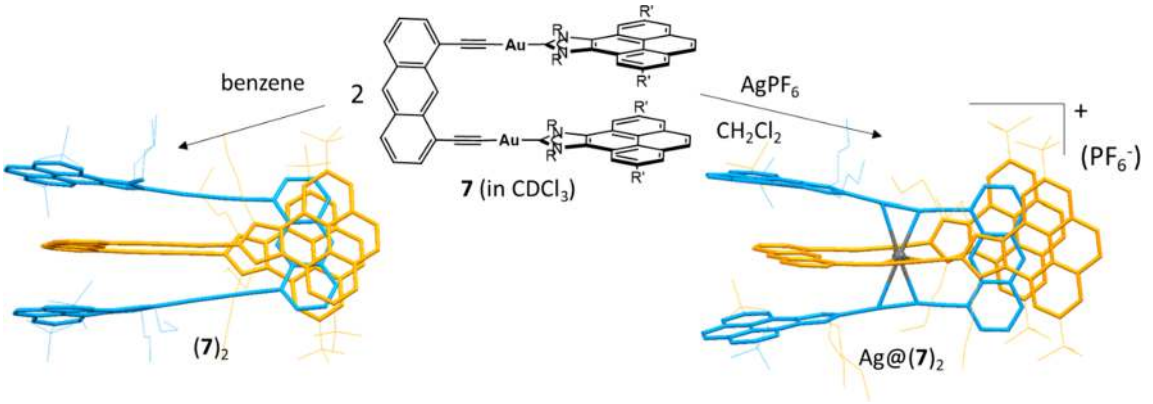
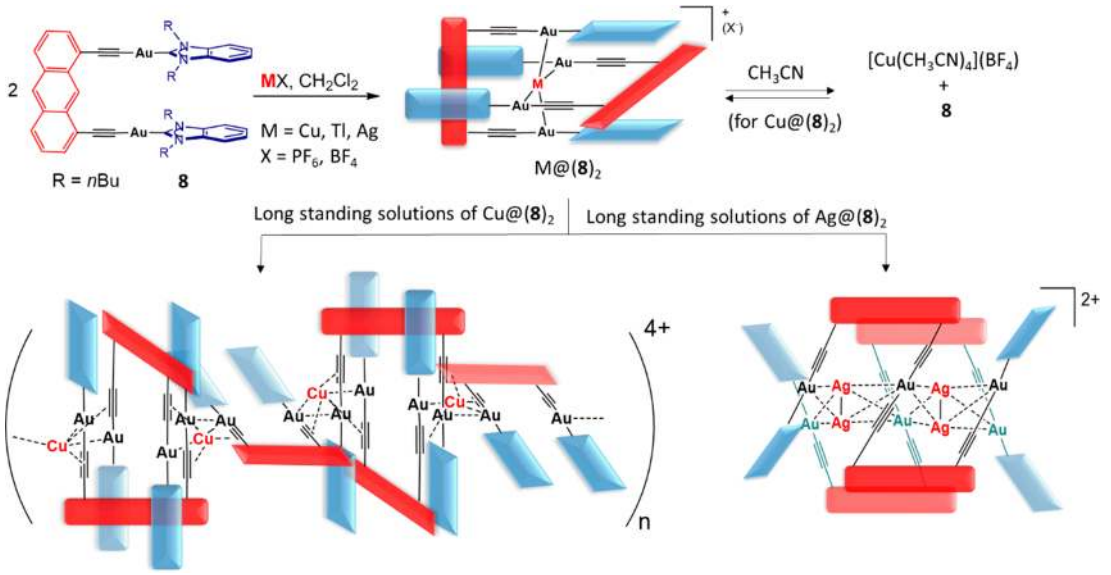
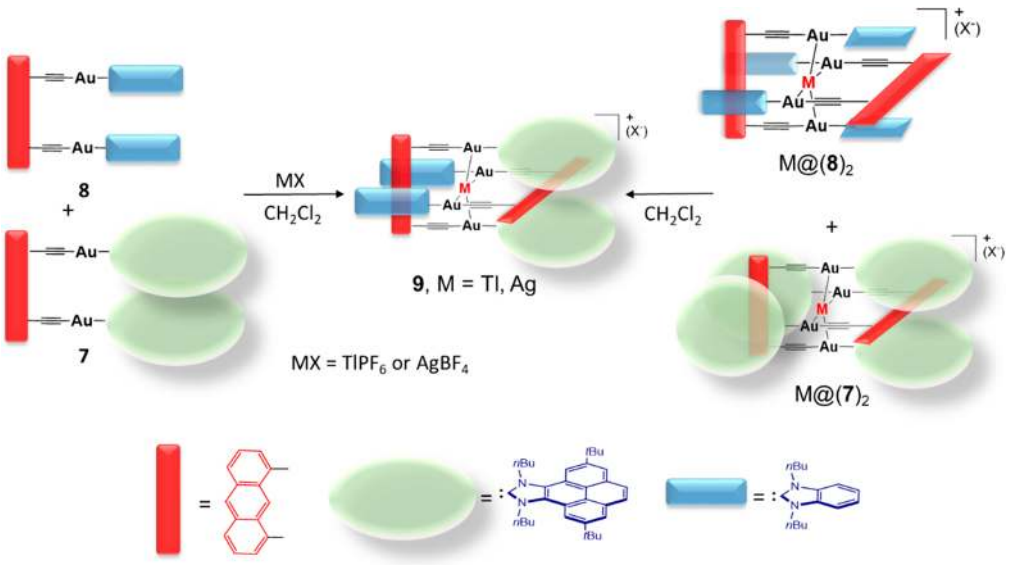
Scheme 6. Self-Aggregation of 7 in Benzene and in the Presence of Ag^+



Scheme 7. Reactivity Shown by 8 upon Addition of Cu^+, Tl^+, or Ag^+



Scheme 8. Social Self-Sorting Involving Mixtures of Complexes 7 and 8



self-association properties of mixtures of these two different metallotweezers in order to determine whether any selectivity was produced in the formation of the resulting molecular aggregates.[23] As depicted in Scheme 8, the reactions of

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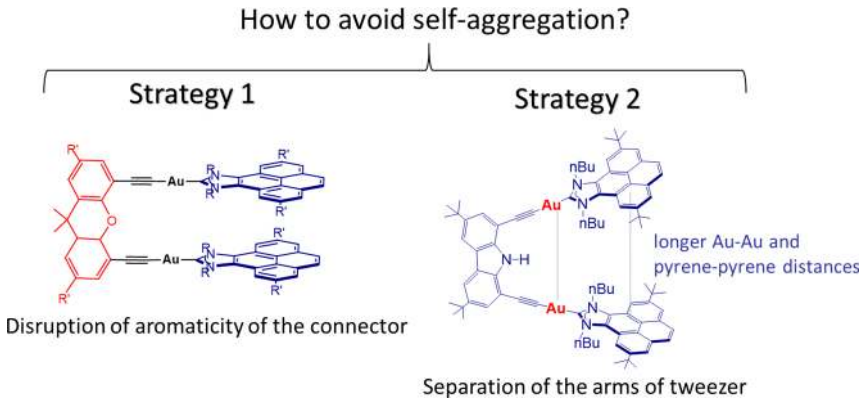
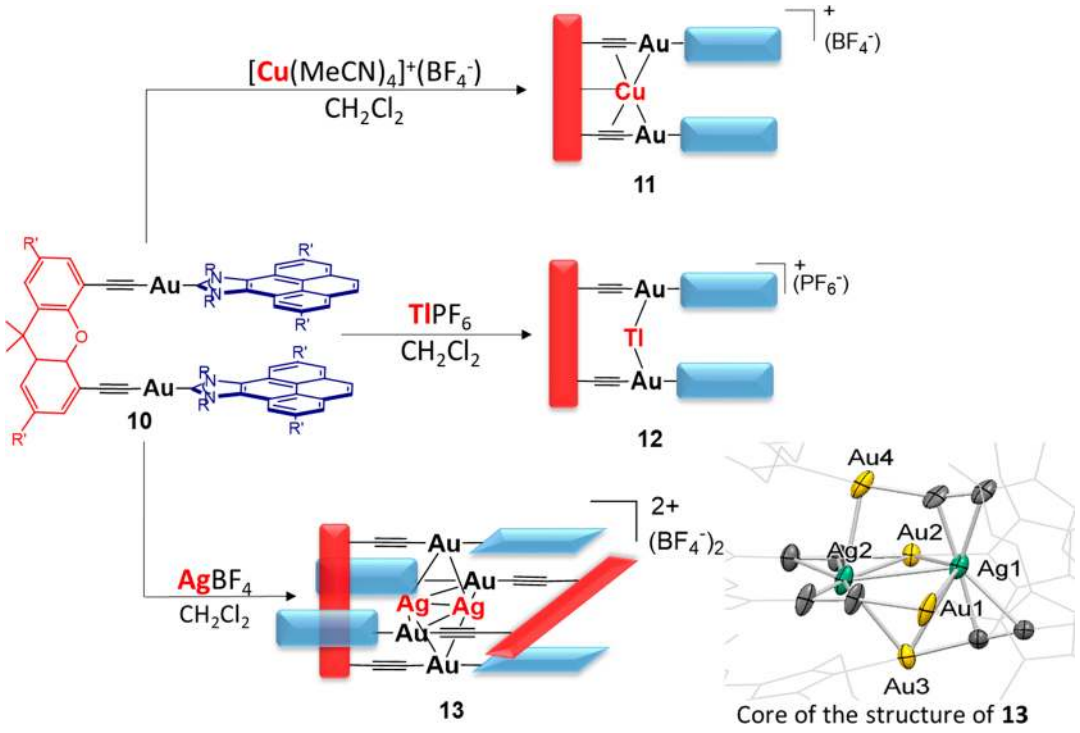
Scheme 9. Strategies for Avoiding the Self-Aggregation of Au(I) Metallotweezers



Scheme 10. Distinct Coordination Modes of 10 with Cu^+, Tl^+, and Ag^+



equimolar mixtures of **7** and **8** with $TlPF_6$ or $AgBF_4$ exclusively yielded the heterocomplexes **9**, in which the two different metallotweezers with the two different NHC-based ligands aggregate, indicating that for this process the product was obtained through a highly selective social self-sorting event. The reactions between the homocomplex dimers containing thallium or silver also evolved to the related mixed-ligand heterocomplexes **9**, thus indicating that **9** is the thermodynamically (rather than kinetically) favored species. The formation of **9** was assumed to be a consequence of the maximization of the $\pi-\pi$-stacking and metallophilic interactions in the aggregated structures.[23] Other examples of self-sorting phenomena shown by NHC-based assemblies have been reported recently.[6c,24]

As can be seen from the description of the properties of **7** and **8**, it became evident that their supramolecular properties are determined by their tendency to self-aggregate. In order to use a metallotweezer for the recognition of aromatic substrates, we needed to minimize the self-aggregation tendency so that the two polyaromatic arms of the receptor would be exclusively used to trap a potential aromatic guest. In order to reduce the self-complementary character of the tweezers, we thought of two different strategies. The first involved designing a new metallotweezer with a linker in which the π-extended system is disrupted, so that its participation in the $\pi-\pi$-stacking event is less likely to occur (Scheme 9, strategy 1). The second strategy consists of using a linker with two diverging alkynyl ligands, so that the two polyaromatic arms of the tweezer are separated by a distance that prevents their participation in the self-aggregation process (Scheme 9, strategy 2).

To implement the first strategy, we prepared U-shaped digold metallotweezer **10** with a bis(alkynyl)xanthene connector (Scheme 10).[25] This metallotweezer acts as metalloligand in the presence of Cu^+, Tl^+, or Ag^+, and we observed that the coordination ability of the metalloligand was highly dependent on the cation used. All of the coordination modes are highly influenced by strong M···Au interactions. Coordination to Cu^+ leads to a complex in which the metalloligand is coordinated in a pincer form (**11**), with the copper atom bound to the two

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alkynyls and to the oxygen of the xanthene linker. In addition, the copper(I) atom is also a very short distance from the Au atoms, indicating strong metallophilic interactions. The reaction of **10** with Tl^+ affords a complex in which the ligand acts as a *trans*-κ^2 chelate ligand through two Tl–Au metallophilic interactions (**12**). The reaction with Ag^+ leads to a self-assembled structure with two silver cations encased inside the cavity of a duplex structure formed by two self-assembled metallotweezers (**13**). The reason for the formation of this structure is found in the core of the molecule, in which it can be observed that the two silver atoms maximize all possible interactions with the binding sites of the metalloligand (alkynyls and gold atoms) with additional stabilization by the formation of a Ag–Ag argentophilic bond (Scheme 10).[25]

The second strategy that we used to avoid the self-association of the metallotweezers was to use a linker with two diverging alkynyl groups. Complex **14** contains a bis(alkynyl)carbazole connector with two pyrene–imidazolylidene–Au(I) arms. As can be observed from the molecular structure of the complex (Figure 1a), the two pyrene moieties are separated by a distance

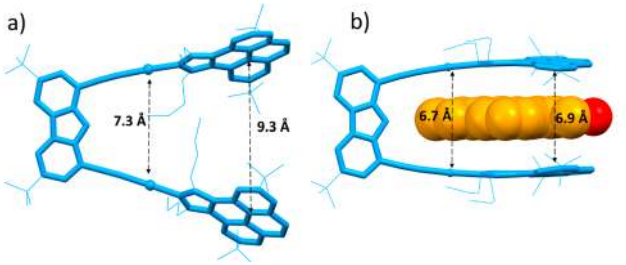


Figure 1. Molecular structures of (a) **14** and (b) 3-perylenylmethanol@**14** (oxygen atom of guest in red).

of 9.3 Å, which is too large to facilitate the self-aggregation of the complex.[26] However, the two arms are flexible enough to reduce this distance to 6.9 Å so that the two pyrene arms can approach the surface of a polyaromatic guest such as 3-perylenylmethanol (Figure 1b), facilitating maximum face-to-face overlap.

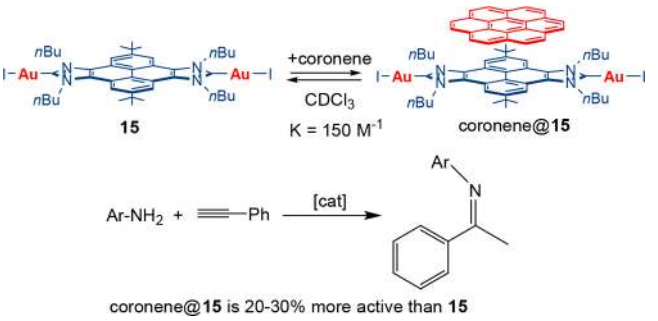
Complex **14** was used for the recognition of a series of polycyclic aromatic hydrocarbons (PAHs). The compound is able to bind these planar polyaromatic guests as a result of the $\pi-\pi$-stacking interactions between the polyaromatic guests and the pyrene moieties of the NHC ligand.[26] In addition, the presence of the NH group in the carbazole tether strengthens the binding of those PAHs functionalized with groups capable of hydrogen bonding, as concluded from our experimental and density functional theory (DFT) studies. The association constants of these guests are up to 1 order of magnitude larger than those shown by unfunctionalized PAHs. For example, the association constant between **14** and pyrene is 10 M^{-1} in toluene, while the constant with 1-pyrenylmethanol is 340 M^{-1}, as shown in Scheme 11. Similarly, the association constant of **14** with perylene is 145 M^{-1}, while the constant with 3-perylenylmethanol is 1350 M^{-1}.[26] These findings demonstrate that the combination of $\pi-\pi$-stacking and hydrogen-bonding interactions can be used for the rational design of more efficient metalloreceptors.

3. STRUCTURES WITH DI- AND TRI-NHC LIGANDS

3.1. Dimetallic Structures with Janus Di-NHCs

In 2018 we studied the binding affinities of **15**, a digold(I) complex with a pyrenebis(imidazolylidene) ligand (Scheme 12),

Scheme 12. Binding of 15 with Coronene and Effect on Catalysis



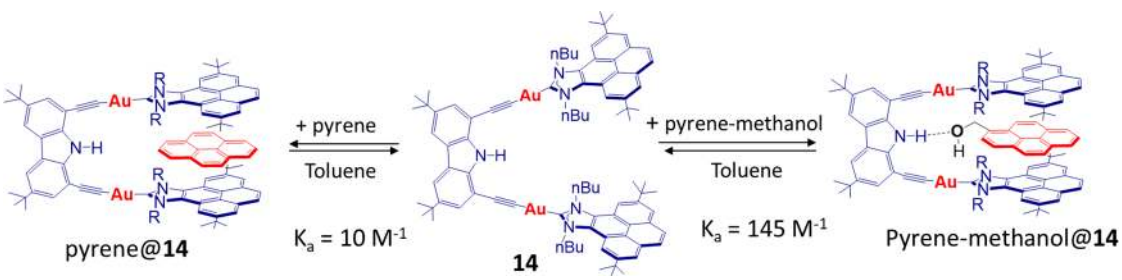
with a series of polycyclic aromatic hydrocarbons.[27] The presence of the pyrene moiety in the complex serves as a $\pi-\pi$-stacking platform for binding of PAHs, and an association constant of 150 M^{-1} was determined for the binding of **15** with coronene in chloroform. Interestingly, the catalytic activity of the complex toward the hydroamination of phenylacetylene with primary amines was improved by 20–30% upon the addition of coronene to the reaction medium. The study demonstrated how the activity of a homogeneous catalyst can be highly influenced by supramolecular interactions with an external additive.[27]

We also prepared a di-NHC ligand connected by a corannulene moiety that we coordinated to gold to afford complex **16** (Scheme 13). We took advantage of the bowl-shaped nature of corannulene to use complex **16** as a receptor for the recognition of fullerene C_{60}. Because of the excellent shape complementarity, **16** and C_{60} showed an excellent binding affinity in toluene solution, producing guest:host complexes with stoichiometries of up to 1:3, as depicted in Scheme 13.

3.2. Au-Based Metallorectangles and Metallocages

The two examples shown in Schemes 12 and 13 constitute good illustrations of how the introduction of extended π-conjugated

Scheme 11. Binding of 14 with Pyrene and 1-Pyrenylmethanol



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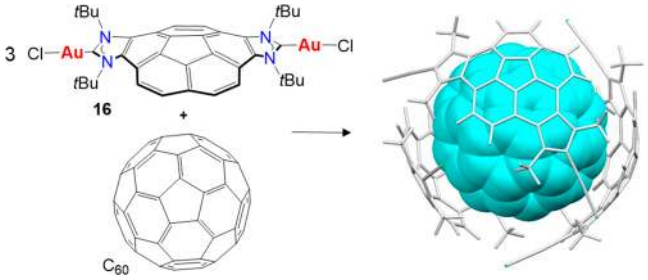
Scheme 13. Reaction of 16 with C_{60}; The DFT-Calculated Structure of the Product Is Shown



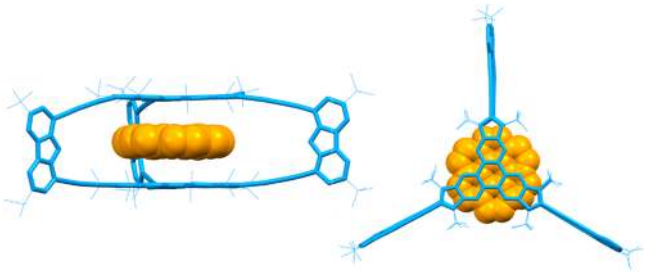
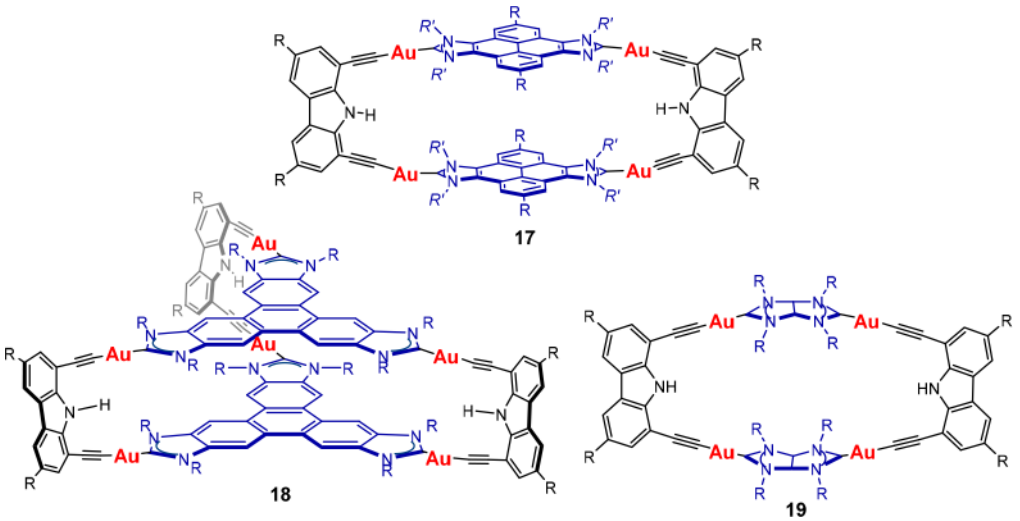


Figure 2. Two perspectives of the molecular structure of coronene@**18**.

systems into the structure of Janus-type di-NHC ligands can bring interesting properties into the resulting complexes due to the establishment of $\pi-\pi$-stacking interactions with polyaromatic guests. The results are even more interesting if we consider that the two examples shown before refer to complexes with open structures lacking well-defined closed cavities. With these results in hand, we thought that the introduction of this type of ligand into the structure of closed metallocages should produce metallosupramolecular assemblies with enhanced host–guest chemistry abilities. Given our previous results on the preparation of gold-based metallotweezers, we aimed to obtain a set of new metallocages by replacing the mono-NHC ligands by di- and tri-NHC ligands connected by extended π-conjugated systems. Using this strategy and the bis(alkynyl)-carbazole linker that we previously used for the preparation of metallotweezer **14**, we prepared metallorectangle **17**,[28] trigonal-prismatic metallocage **18**,[29] and rhombohedral metallocyclophane **19**[30] (Scheme 14). Interestingly, the nanosized nature of the structures shown in Scheme 14, together with the presence of the two cofacial polycyclic-conjugated panels in **17** and **18**, made these two latter assemblies very effective for the encapsulation of polycyclic aromatic hydrocarbons. In particular, the hexagold prismatic cage **18** with the triphenylenetris(NHC) ligand has a "slotlike" cavity with a volume of ~300 Å^3 and a height of 7 Å. This cage shows a very large binding affinity for coronene, which makes it serve as an excellent coronene scavenger in CH_2Cl_2.[29] The perfect dimensional match between **18** and coronene can be visualized in the structure shown in Figure 2. On the other hand, metallorectangle **17** shows very high binding affinities for the encapsulation of planar PAHs in CH_2Cl_2. The binding constants were found to increase exponentially with the number of π electrons of the guest as a consequence of the enhancement of the host–guest face-to-face overlap, ranging from $1.39 < \log K < 6.64$ for naphthalene through coronene.[28] These constants are among the highest found for a metal-containing receptor and compare well with those of the best organic-based cationic hosts.[31] The large binding affinities found for the case of **17** are due to the incorporation of the two cofacial pyrene panels separated by almost exactly 7 Å, thus providing an excellent dimensional match that makes that the encapsulation take place at a minimum energy cost due to the negligible structural distortions suffered by both the host and guest.[28]

A very interesting feature of metallorectangle **17** is that it is able to trap corannulene. As observed from the molecular structure of corannulene@**17** (Figure 3b), the encapsulation of corannulene is accompanied by a significant compression of the bowl-shaped guest (the bowl depth of free corannulene is 0.87 Å, compared with 0.73 Å for the encapsulated one) and concomitant expansion of the host metallocage. The energy cost due to this mutual induced-fit arrangement and the lack of an effective $\pi-\pi$-stacking interaction over the convex surface of the guest in corannulene@**17** explain the reduced binding affinity shown for corannulene compared with its related planar 20-electron PAH, perylene (compare the structures of perylene@**17** and corannulene@**17** in Figure 3).[28]

Scheme 14. Gold-Based Metallosupramolecular Assemblies 17–19



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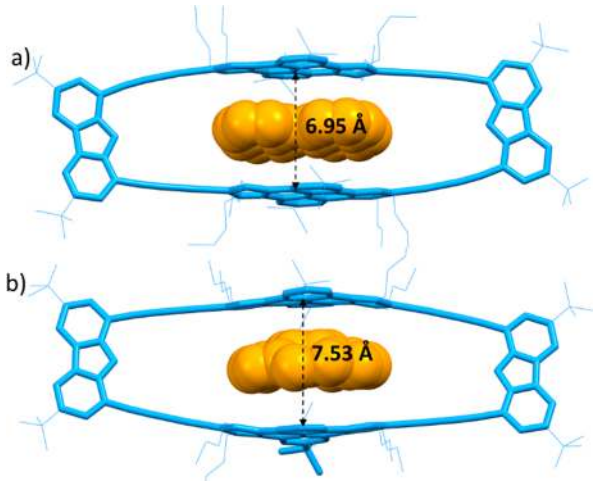


Figure 3. Molecular structures of (a) perylene@**17** and (b) corannulene@**17**.

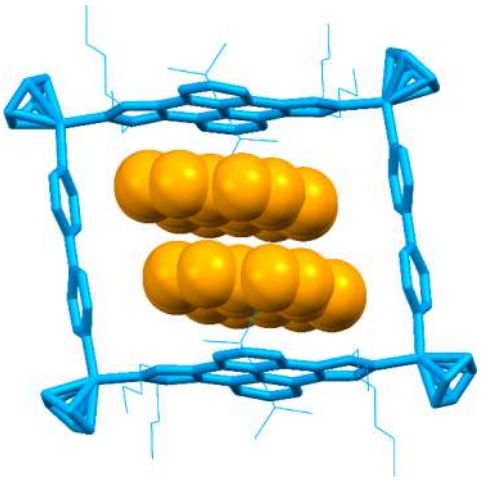


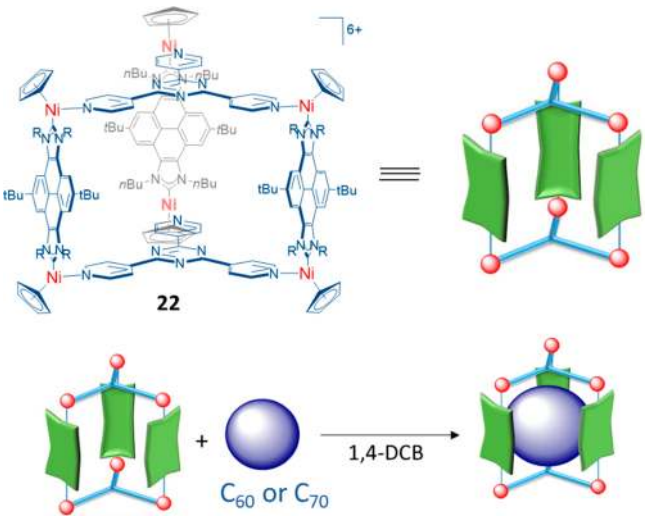
Figure 4. Molecular structure of $(pyrene)_2$@**21**.

3.3. Metallorectangles, Metallosquares, and Metallocages of Ni and Pd

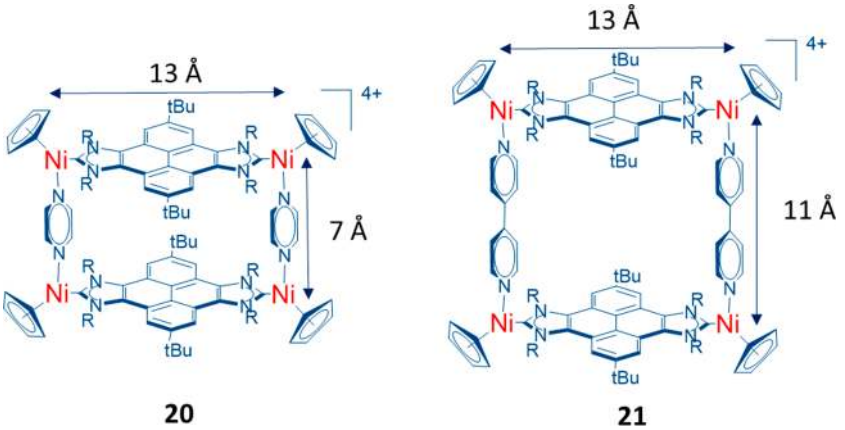
3.3.1. Nickel. Pyrenebis(NHC) ligand **C** (Scheme 2) used in the preparation of tetragold(I) complex **17** turned out to be a very useful synthon for the preparation of metallosupramolecular structures with metals other than gold. By the use of this di-NHC ligand, two nickel-cornered metallorectangles were prepared whose dimensions were modulated by using either pyrazine or 4,4′-bipyridine.[32] The metal-to-metal distance established by the pyrenebis(imidazolylidene) ligands is ∼13 Å, while the distances along the N-donor ligands are 7 and 11 Å for pyrazine and bipyridine, respectively (Scheme 15). These molecular rectangles were used for the encapsulation of PAHs. Because of their dimensions, pyrazine-containing rectangle **20** was able to host only one molecule of the polyaromatic guest, while rectangle **21** containing bipyridine was capable of hosting up to two guest molecules. Figure 4 shows the molecular structure of $(pyrene)_2$@**21**, where it can be observed that effective $\pi-\pi$-stacking interactions are established both between the pyrene guest molecules and between the pyrene guests and the pyrene moieties of the di-NHC ligands. The association constants of the aromatic guests with both receptors were determined in acetone-d_6. The results showed that a good fit between the size of the PAH and the binding constant could be established by correlating the numbers of electrons of the guests with their association constants.[32]

Using tripyridylpyrazine, we obtained trigonal prism **22** (Scheme 16),[33] which was used for the encapsulation of

Scheme 16. Hexanickel Trigonal Prism 22 and Representation of Its Ability to Encapsulate C_{60} and C_{70}



Scheme 15. Nickel-Cornered Metallorectangles 20 and 21



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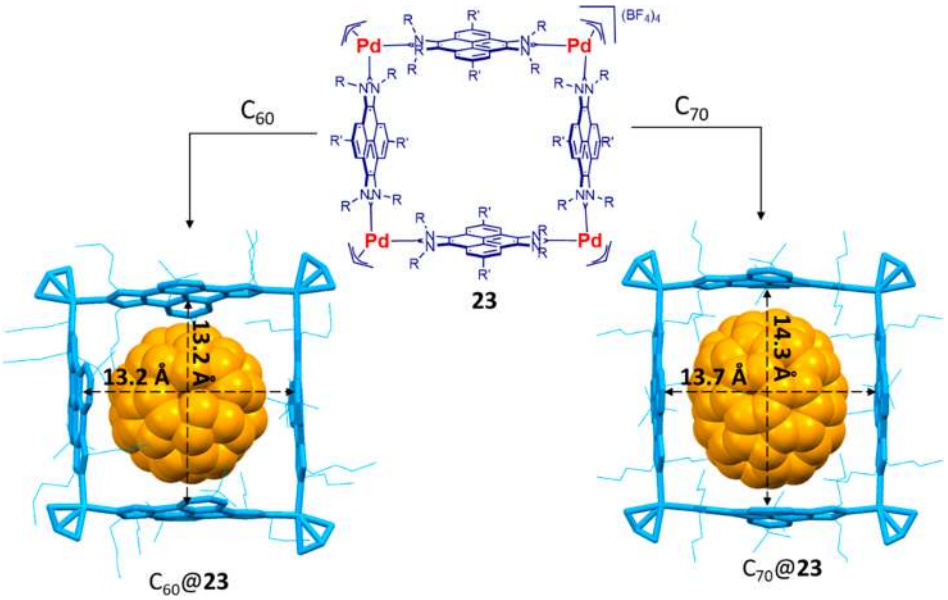
Scheme 17. Palladium-Based Metallosquare 23 Used for the Encapsulation of C_{60} and C_{70}



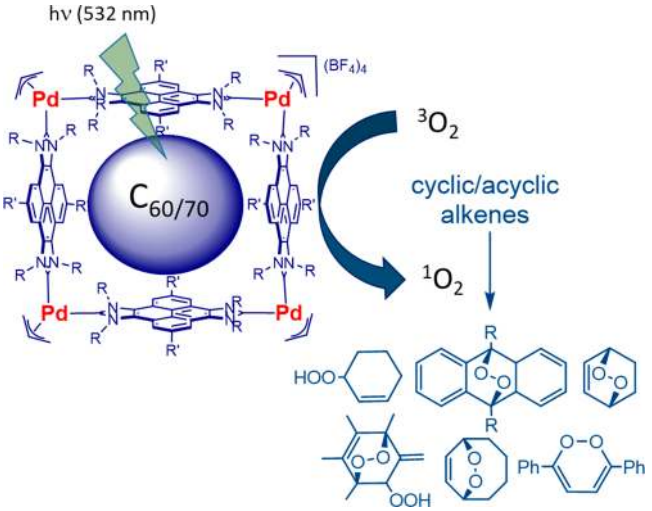
fullerenes C_{60} and C_{70}. The study of the binding affinities showed that the cage exhibits highly selective complexation of C_{70} over C_{60}. The determination of the binding affinities at different temperatures performed by ^{1}H NMR spectroscopy in 1,2-dichlorobenzene allowed the determination of the thermodynamic values associated with the binding process. For the association of C_{60} and C_{70}, it was observed that the enthalpies were low and positive as a consequence of the large solvation enthalpies of both the free host and guests. For both fullerenes, the association entropies were large and positive, thus indicating that the process is entropically driven because of the desolvation of both the host and guests. The higher entropy found for C_{70} with respect to C_{60} is a consequence of the larger surface area of the former, which means that a larger number of solvent molecules are bound to C_{70} relative to C_{60}.[33]

3.3.2. Palladium. The same pyrenebis(imidazolylidene) ligand was used for the preparation of palladium-conjoined molecular square **23** (Scheme 17).[34] The encapsulating properties of this metallosquare are clearly determined by the presence of the four pyrene panels, which endows the compound a three-dimensional shape. This metallosquare was used for the encapsulation of C_{60} and C_{70}. The metallosquare is shape-adaptable in the sense that it can adjust to accommodate the size of the encapsulated fullerene. The pyrene panels bend in order to adapt their shapes to maximize the face-to-face overlap with the convex surface of the fullerene (see Scheme 17), and this also modifies the guest-available volume of the cavity. For example, the distances between the center points of opposite pyrene panels in C_{60}@**23** are significantly shorter than the related distances in C_{70}@**23** (Scheme 17). The cage exhibits a higher affinity for C_{70} over C_{60}, and the thermodynamic parameters obtained from the determination of the association constants at different temperatures show that the binding process is entropically driven, and thus dominated by desolvation rather than intrinsic interactions between the electron-deficient fullerenes and the electron-rich faces of the pyrene moieties of the metallosquare.[34]

An important feature of C_{60}@**23** and C_{70}@**23** is that both host–guest complexes behaved as photochemically stable singlet oxygen photosensitizers.[35] Both host–guest complexes were used for the peroxidation of a series of cyclic and acyclic alkenes at room temperature via visible-light-induced singlet oxygen generation. By measuring the phosphorescence emission spectra of singlet oxygen generated by the two complexes upon irradiation with visible light, $^1O_2$ quantum yields of Φ_Δ = 0.23 and 0.41 were obtained for C_{60}@**23** and C_{70}@**23**, respectively. This explains why the activity shown by C_{70}@**23** in the photocatalytic peroxidations was higher than that shown by C_{60}@**23**.[35] The photosensitizing properties of these two fullerene-containing cages is explained by the excellent spin-converting properties of fullerenes, which make them exceptional agents for singlet oxygen production (Scheme 18). These results are important because they underline the possibility that other fullerene-containing supramolecular systems have the potential to be used for similar catalytic reactions.

Another interesting feature of metallocage **23** is that it displays a metal-to-metal distance of 13 Å, which is approximately 4 times the distance for an effective $\pi-\pi$-stacking interaction and

Scheme 18. C_{60}@23 and C_{70}@23 Used as Photocatalyts for Peroxidation of Alkenes



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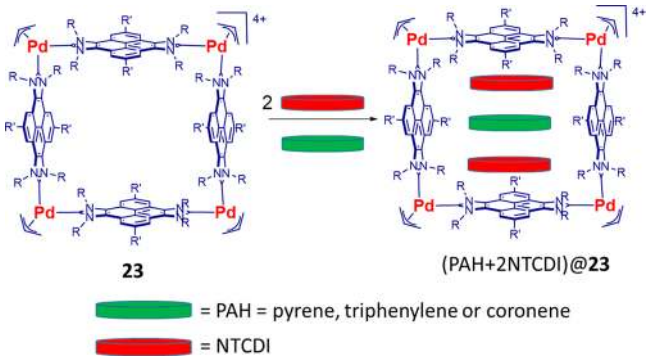
therefore optimum for encapsulating up to three polyaromatic guests. In fact, the complex is able to encapsulate one molecule of an electron-rich polycyclic aromatic hydrocarbon (pyrene, triphenylene, or coronene) and two molecules of electron-deficient *N,N′*-dimethyl-naphthalenetetracarboxydiimide (NTCDI).[36] This forms quintuple π stacks ordered in donor−acceptor−donor−acceptor−donor (D−A−D−A−D) arrays (Scheme 19), with the electron-rich pyrene fragments of the

Scheme 19. Quintuple D−A−D−A−D π Stack Formed by Heteroguest Encapsulation in 23



di-NHC ligand of the cage as bookend donors. The fact that **23** is able to trap large π-conjugated heteroguests to form quintuple π stacks is interesting because most systems previously used for the encapsulation of heteroguests are based on "closed" trigonal-prismatic architectures, while ours is an "open" square structure.

4. CONCLUSIONS AND OUTLOOK

In this Account, we have described our most recent work on the preparation of NHC-based metallosupramolecular assemblies and their host−guest chemistry properties. We have tried to emphasize that NHC ligands bearing planar polyaromatic connectors offer a powerful tool for building hollow organometallic supramolecular receptors, including metallotweezers, metallosquares, metallorectangles, and trigonal-prismatic metallocages. The use of these systems as hosts for organic or inorganic guests is directed by the intentional combination of supramolecular interactions, including $\pi-\pi$-stacking, hydrogen-bonding, and metallophilic interactions.

We once used the term "smart ligands" to refer to NHCs, meaning that NHC chemistry has rapidly adapted to new times and needs for novel reactivities, especially in the design of more effective homogeneous catalysts.[37] The results shown in this Account illustrate how NHC ligands have also adapted to the field of supramolecular chemistry, and therefore, NHC ligands can be also considered smart in this field of chemistry. Probably one of the advantages that needs to be highlighted here is that now there is an extensive library of NHC ligands decorated with rigid polyaromatic moieties that can provide clear advantages over other traditional Werner-type ligands used in metallosupramolecular chemistry, for which the incorporation of these planar polyconjugated fragments is much more difficult to achieve. Another important feature that needs to be considered is that most of the NHC-based supramolecular assemblies described here are remarkably stable and can remain intact in solution for days without signs of decomposition. This obviously widens their potential use for practical applications. In this regard, we expect that further effort will be applied in several directions, for example toward the exploitation of the singlet oxygen generation properties of fullerene-containing supramolecular assemblies, not only from the photocatalytic point of view but also as potential agents for clinical photodynamic therapy (PDT). In addition, on the basis of the biomedical activity shown by other Au- and Ag-containing NHC-based supramolecular assemblies,[16] studies can be directed to prospect the biological applications of this type of system, possibly by including in the NHC scaffolds further functionalities that can target biological units (i.e., peptides), which to date has been mostly explored with small molecules.[38]

Efforts can also be directed toward the reversible encapsulation of homogeneous catalysts, which may be released on demand by the addition of, for example, an additive guest with a higher binding affinity with the receptor. Finally, the possibility that supramolecular organometallic complexes can form stable discrete multiple stacks may have important implications for the design of nanoscale electronic devices because enabling discrete π stacks can facilitate the study of charge transport at the molecular level. In summary, we hope that the findings described in this Account will help advance in the field of supramolecular organometallic host−guest chemistry.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.accounts.0c00312.

Crystallographic data for 3-perylenylmethanol@**14** (CIF)

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Author Contributions

The manuscript was written through contributions of all authors. All of the authors approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Susana Ibáñez graduated in Chemistry in 2001 at the University of Zaragoza. She received her Ph.D. degree with European Doctorate in 2007 at the University of Zaragoza. She then moved to Bari (Italy) as a postdoctoral fellow under the supervision of Prof. Piero Mastrorilli. In 2009 she joined Prof. Bernhard Lippert at Tecnische Universität

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Dortmund, where she stayed for 2 years. In 2014 she joined Prof. Eduardo Peris' group at Universitat Jaume I as an associate researcher.

Macarena Poyatos graduated in Chemistry at Universitat Jaume I (Castellón, Spain). She received her Ph.D. degree in 2005 at Universitat Jaume I under the supervision of Prof. Eduardo Peris. She then moved to Strasbourg, where she joined the group supervised by Prof. Lutz H. Gade and Dr. Stéphane Bellemin-Laponnaz. In 2006 she joined Prof. Robert H. Crabtree's group at Yale University, where she stayed for 2 years. In 2008 she returned to Universitat Jaume I, where she currently holds a position as an associate professor.

Eduardo Peris received his Ph.D. degree in Chemistry in 1991 at the Universidad de Valencia. In 1994 he joined Robert Crabtree's group at Yale University, where he stayed for 2 years. In October 1995 he moved to Universitat Jaume I, where he currently holds a position as a full professor. The current interest of his group is the development of organometallic-based supramolecular systems for the development of host−guest receptors and improved catalysts.

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