

# A size-flexible organometallic box for the encapsulation of fullerenes

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We would like to dedicate this article to Javier A. Cabeza, on the occasion of his 60<sup>th</sup> birthday

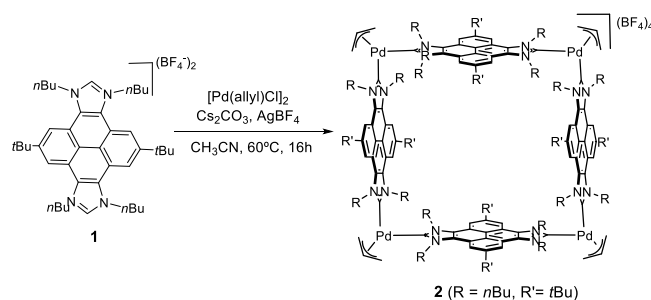
**Abstract:** A palladium-conjoined molecular square obtained by using a pyrene-bis-imidazolylidene ligand is described. This “three-dimensional” metallo-polygon is suitable for the encapsulation of C<sub>60</sub> and C<sub>70</sub>. The X-ray diffraction structures of the empty and complexed cage with both fullerenes are described. The encapsulation of the fullerenes produces perturbations in the structural parameters of the metallo-square, showing that it can adapt the shape of its cavity to the size of each fullerene.

Over the last three decades, coordination self-assembly evolved as the most effective strategy for the rational construction of discrete supramolecular coordination complexes (SSCs).<sup>[1]</sup> The directional bonding approach allows that the outcome of the self-assembly process is guided by the information provided by the building units (coordination angles, number of coordination sites, shape and length of connecting ligands), so that the outcome of the self-assembly process can be predicted with a high level of certainty. Arguably, the presence of cavities with well-defined sizes and shapes able to encapsulate selected substrates is the most important property of a self-assembled structure, because most of the properties that can derive in applications are directly related to the host-guest chemistry of the supramolecular assembly.<sup>[1f, 1j, 2]</sup> It should be noted that this field of research is dominated by Werner-type coordination complexes, wherein the supramolecular assemblies are connected via oxygen or nitrogen donors from multidentate ligands, with very few organometallic-based carbon donor ligands reported in the literature.<sup>[3]</sup>

We were recently interested in preparing organometallic hosts based on N-heterocyclic carbene ligands (NHC) for the selective recognition of organic substrates. In particular, by combining a pyrene-bisimidazolylidene and di-pyridine ligands, we obtained a series of nickel-cornered molecular rectangles that served as receptors and scavengers of a series of polycyclic aromatic hydrocarbons (PAHs).<sup>[4]</sup> More recently, by using the same bis-

NHC and a tris-pyridyl ligand, we prepared a hexa-nickel three-dimensional cage that acted as a selective receptor for C<sub>70</sub> over C<sub>60</sub>, and even facilitated the separation of the former from a mixture of the two.<sup>[5]</sup> Related to this type of research, in a recent contribution Hahn and co-workers described two Ir- and Pd-based metallo-squares<sup>[6]</sup> using a benzo-bis-imidazolylidene ligand.<sup>[7]</sup> Despite the structural interest of these two tetrametallic architectures, the dimensions of these structures (side length ≈ 10 Å) made them unsuitable for the encapsulation of most common organic substrates, due to the small void volume of the internal cavity. Because we thought that metallo-squares based on (only) N-heterocyclic carbene bridging ligands should render highly stable supramolecular architectures, with very well-defined internal cavities, we pursued to obtain a similar type of molecule but using a longer pyrene-imidazolylidene ligand (13 Å).<sup>[8]</sup> This should facilitate the preparation of a metallo-supramolecular architecture with a larger cavity, therefore able to trap organic guest molecules. By following this idea, herein we describe the preparation of a palladium-cornered metallo-square for the encapsulation of fullerenes C<sub>60</sub> and C<sub>70</sub>.

The reaction between the pyrene-bisimidazolium salt, **1**, and [Pd(allyl)Cl]<sub>2</sub> in acetonitrile in the presence of AgBF<sub>4</sub> and Cs<sub>2</sub>CO<sub>3</sub>, afforded the air-stable palladium-cornered metallo-square **2** in 50% yield after purification (Scheme 1). The complex was characterized by NMR spectroscopy, mass spectrometry and elemental analysis. The tetrametallic nature of the supramolecular assembly was confirmed by ESI-TOF-MS measurements, which showed peaks at 766.42 and 1050.57, assigned to [M-4BF<sub>4</sub>]<sup>4+</sup> and [M-3BF<sub>4</sub>]<sup>3+</sup>, respectively. The diffusion-ordered NMR spectroscopy (DOSY), showed that all proton resonances display the same diffusion coefficient in deuterated acetonitrile (7.5x10<sup>-10</sup> m<sup>2</sup>s<sup>-1</sup>, see SI for details), indicating the presence of a single assembly.

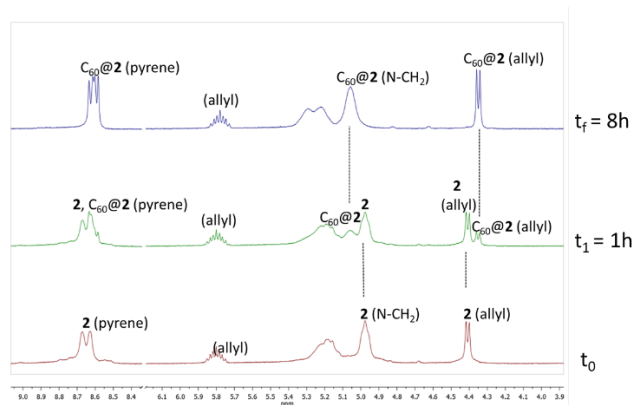


**Scheme 1.** Preparation of metallo-square **2**

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## COMMUNICATION

Although complex **2** may be described as a metallo-square, the flat polyaromatic surface of the four pyrene moieties generates a "three-dimensional", rather than a "two-dimensional" macrocyclic cubic box. Given the large size of the internal cavity, we envisioned that complex **2** could be a suitable receptor for large 3-dimensional guests, such as fullerenes  $C_{60}$  and  $C_{70}$ . Besides, the flexibility of the torsional angles about the Pd- $C_{NHC}$  bond, should facilitate that the open window is modulated for facilitating the encapsulation of these guest molecules, whose van der Waals diameters are in the 10.1-11.0 Å range.

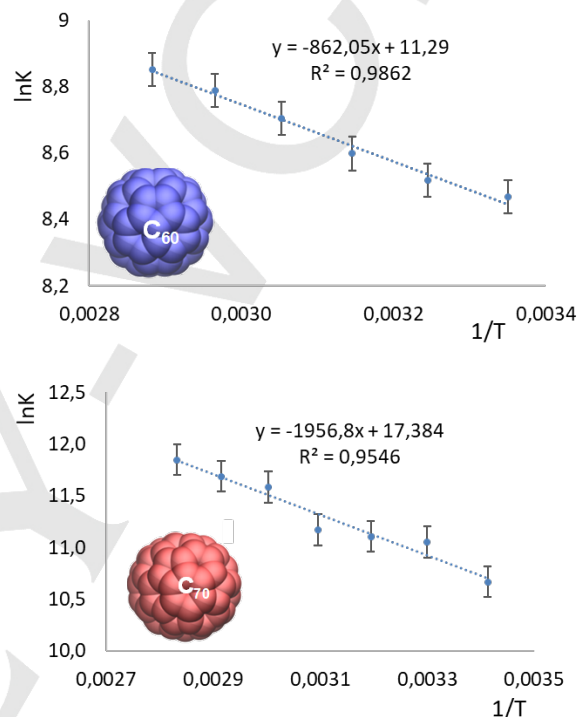


**Figure 1.** Selected region of the  $^1\text{H}$  NMR spectra of a mixture of **2** with  $C_{60}$  in  $\text{CD}_3\text{CN}$ . The spectra were recorded immediately after mixing, and after 1 and 8 hours.

The encapsulation of fullerenes can be performed by dissolving **2** in  $\text{CD}_3\text{CN}$ , in the presence of a suspension of  $C_{60}$  (or  $C_{70}$ ), in an NMR tube. Then the mixture is sonicated, and the formation of the host:guest adducts may be monitored by  $^1\text{H}$  NMR spectroscopy. As can be observed from the series of spectra shown in Figure 1, after one hour of sonication in the presence of  $C_{60}$ , the  $^1\text{H}$  NMR spectrum shows the appearance of new signals which are attributed to the formation of the  $C_{60}@2$  host:guest complex. The signals due to the protons of the pyrene moiety are slightly downfield shifted, and the two singlets observed for **2** give rise to two well-resolved doublets (clearly observed after 8h of sonication). The signal due to one of the diastereotopic protons of the N- $\text{CH}_2$  groups from the *n*butyls is slightly downfield shifted. Finally, one of the doublets due to the protons of the allyl group is shifted upfield by 0.05 ppm, with respect to the same resonance in **2**. The spectrum recorded after 8h showed only the signals due to  $C_{60}@2$ , therefore indicating that the reaction was complete. The experiment performed using  $C_{70}$  afforded similar results, indicating the formation of the  $C_{70}@2$  complex (see SI for more details). These experiments allowed the isolation and full characterization of  $C_{60}@2$  and  $C_{70}@2$ . The  $^{13}\text{C}$  NMR spectrum of  $C_{60}@2$  displayed the signal due to the sixty equivalent carbons of the encapsulated fullerene at 141.1 ppm, while the spectrum of  $C_{70}@2$  showed four resonances due to  $C_{70}$ . At this point, it is important to mention that both fullerenes are completely insoluble in  $\text{CD}_3\text{CN}$ , so the NMR-observable signals are a clear indication of their encapsulation in the metallo-square. The mass spectra of the solutions containing  $C_{60}@2$  and  $C_{70}@2$ , showed peaks at  $m/z$  946.1 and 1290.8 (assigned to  $[C_{60}@2-4\text{BF}_4]^{4+}$  and  $[C_{60}@2-$

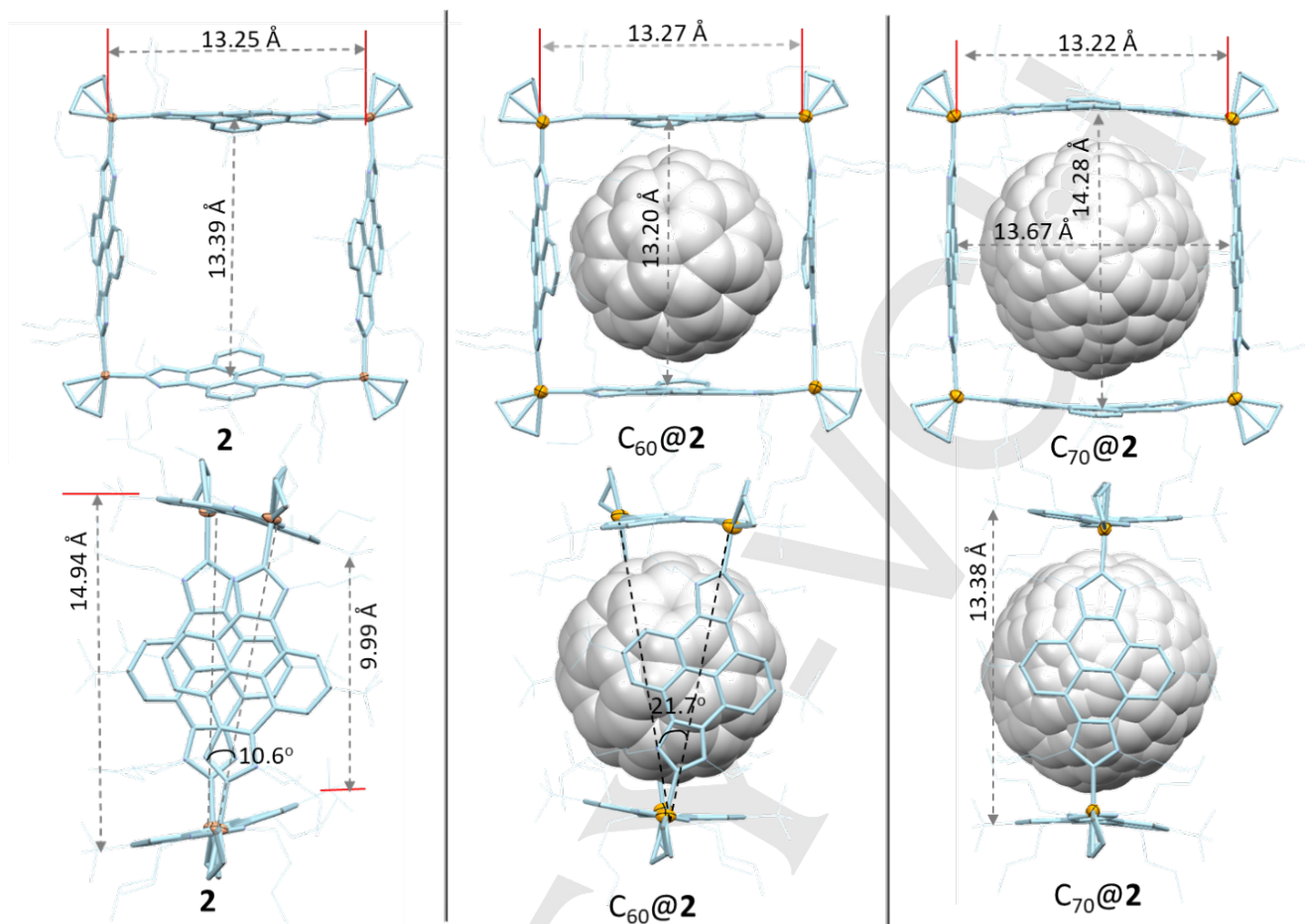
$3\text{BF}_4]^{3+}$ , respectively), and at 976.2 and 1330.9 (for  $[C_{70}@2-4\text{BF}_4]^{4+}$  and  $[C_{70}@2-3\text{BF}_4]^{3+}$ ).

For the determination of the association constants we took advantage that the exchange between the host and the host:guest complexes was slow on the  $^1\text{H}$  NMR timescale, so that the constants could be determined by simply integrating the signals associated to each of the species present in solution. We found that a mixture of acetonitrile:*o*-dichlorobenzene (1:4) provided the best solubilities for both, the metallo-square and the fullerenes.



**Figure 2.** Plots of  $\ln K$  vs.  $1/T$ . The plots were built by using the binding constants obtained from the  $^1\text{H}$  NMR spectra taken at different temperatures, from equimolar solutions (0.3 mM) of **2** and fullerene in  $\text{CD}_3\text{CN}$ :*o*-dichlorobenzene- $d_4$  1:4. Error bands assume uncertainties of 10% in binding constant values.

The constants were calculated at different **2**/fullerene ratios, and at different temperatures, by using the integration of the signals due to the terminal protons of the allyl groups, which were the ones to show the best conditions for an accurate integration. By doing this, the constants that we obtained at room temperature were  $5.4 \times 10^3 \text{ M}^{-1}$  and  $7.1 \times 10^4 \text{ M}^{-1}$ , for the formation of  $C_{60}@2$  and  $C_{70}@2$ , respectively. The determination of the equilibrium constants at different temperatures allowed us determining the thermodynamic parameters by using corresponding Van't Hoff plots (Figure 2). The thermodynamic values found for the encapsulation of  $C_{60}$  were  $\Delta H = 1.7 \text{ kcal/mol}$  and  $\Delta S = 22 \text{ cal/molK}$ . For the encapsulation of  $C_{70}$ , the values obtained were  $\Delta H = 3.9 \text{ kcal/mol}$  and  $\Delta S = 34 \text{ cal/molK}$ . The small and positive values of the association enthalpies can be explained due to the large solvation enthalpies of the fullerenes in *o*-dichlorobenzene (the reported experimental solvation enthalpies in *o*-dichlorobenzene are  $-30.5$  and  $-35.3 \text{ kcal/mol}$  for  $C_{60}$  and  $C_{70}$ , respectively).<sup>[9]</sup>



**Figure 3.** X-ray diffraction structures of **2** (left),  $C_{60}@2$  (middle), and  $C_{70}@2$  (right), showing some selected dimensions. Hydrogen atoms, counteranions ( $BF_4^-$ ) and solvent molecules have been omitted for clarity. Two molecules of  $C_{70}$  (0.5 occupancy each) are shown in the structure of  $C_{70}@2$ .

The large and positive entropy values indicate that the process is entropically driven. The larger entropy value found for the encapsulation of  $C_{70}$  is due to its larger surface area, which leads to the presence of a greater number of solvent molecules bound compared to  $C_{60}$ . It is important to mention that these thermodynamic parameters are almost identical to the ones that we obtained in a previous work in which we used a nickel-cornered trigonal prismatic supramolecular assembly for the encapsulation of the two same fullerene guests.<sup>[5]</sup> This may indicate that the electronic nature of the box has a minor importance, since the encapsulation of the three-dimensional guests is dominated by desolvation, rather than to intrinsic interactions between the electron-deficient fullerenes and the electron-rich faces of the pyrene moieties of the metallo-square. Given the higher affinity of **2** for the encapsulation of  $C_{70}$ , we designed a competing experiment in which we dissolved the metallo-square in acetonitrile and added an equimolar mixture of  $C_{60}$  and  $C_{70}$ . Then the mixture was sonicated for 2h. The analysis of the solution by  $^{13}C$  NMR and mass spectrometry indicated that only  $C_{70}$  was encapsulated in **2**.

The molecular structures of **2**,  $C_{60}@2$ , and  $C_{70}@2$  were unambiguously confirmed by means of single crystal X-ray diffraction studies (Figure 3). The comparison of these three structures provides an excellent opportunity for demonstrating experimentally the important structural perturbations produced by the encapsulation of the fullerene guests inside the cavity of the  $Pd_4$  metallo-square. The molecular structure of **2** consists of a square-shaped molecule containing four palladium atoms connected by four pyrene-di-imidazolylidene ligands (Figure 4, left). The coordination sphere about each palladium atom is completed by one allyl ligand. The average distance between the palladium atoms is 13.25 Å. The planes formed by the opposite panels formed by the pyrene-di-NHC ligands of the cage are disposed at an average angle of 28.25°. This makes that the quaternary carbons of the tert-butyl groups at opposite pyrene moieties are separated by two closer distances at 9.99 and 11.31 Å, and two longer ones at 14.94 and 15.34 Å (only two of these distances are displayed in Figure 3). These measures are important, because they define the limits of the “open window” of the box.

The molecular structure of  $C_{60}@2$  (Figure 3, middle) shows a molecule of  $C_{60}$  trapped inside the cavity of the  $Pd_4$  metallo-square. All four pyrene moieties of the pyrene-di-imidazolylidene ligands are curved, adapting their shapes for a maximum face-to-face interaction with the surface of the fullerene. The metallo-square is twisted, and therefore slightly compressed, in order to adapt its size to the size of  $C_{60}$  (see side-on view of the structure). This is reflected by the slight shortening of the distances between the central points of opposite pyrene moieties (13.20 Å in  $C_{60}@2$ ; 13.39 Å in **2**), and by the torsion angles formed by the two Pd-Pd axis [defined by the Pd(1)-Pd(2)-Pd(3)-Pd(4) dihedral angles], which is 10.6° for **2** and 21.7° for  $C_{60}@2$ . The molecular structure of  $C_{70}@2$  (Figure 3, right), shows that the encapsulation of the molecule of  $C_{70}$  produces an expansion of the structure of the metallo-square, which looks as 'inflated', compared to the structures of the cage in **2** and in  $C_{60}@2$ . This is reflected by a significant bending of the pyrene moieties, which renders expanded distances of 13.67 and 14.28 Å at the central part of the pyrene fragments. Interestingly, two out of the four *N*-butyl groups at each pyrene-bis-imidazolylidene ligand are wrapped around the  $C_{70}$  molecule, very likely contributing to enhance the encapsulating abilities of the  $Pd_4$  cage.

The determination of the guest-available volume of the cavity of **2**,  $C_{60}@2$  and  $C_{70}@2$  (710, 650 and 696 Å<sup>3</sup>, respectively, after removing the molecules of  $C_{60}$  and  $C_{70}$ ), shows that there is an important shrinkage (8.5%) of the volume of the molecule from **2** to  $C_{60}@2$  (see ESI for details regarding the calculation of the cavity volumes).<sup>[10]</sup> Examples of guest-induced size-adaptable metallocages have been reported previously.<sup>[11]</sup>

In summary, we obtained and characterized a NHC-based palladium-cornered metallo-square by using the metal-directed self-assembly strategy. Our organometallic metallo-square is significantly different compared to the most widely used supramolecular assemblies for the encapsulation of fullerenes, which are dominated by structures with Werner-type porphyrin-containing ligands,<sup>[12]</sup> or structures with curved conjugated networks.<sup>[13]</sup> This observation is not trivial, because the presence of the four bis-imidazolylidene bridging ligands in our host provides a greater stability to the structure, which remains intact in solution for days without any sign of decomposition. The 'cubic' cage possesses a cavity that makes it suitable for the encapsulation of fullerenes  $C_{60}$  and  $C_{70}$ . The cage molecule exhibits higher affinity towards the larger fullerene over the smaller one, an observation that allowed designing a simple experiment for the selective extraction of  $C_{70}$  from a mixture of  $C_{60}/C_{70}$ . The metallo-square is size-flexible, and therefore able to adapt its shape to the size of the encapsulated fullerene. This is achieved by compressing or expanding the structure and by bending the pyrene moieties in order to maximize the face-to-face overlap with the convex surface of the fullerenes. This bending of the pyrene moiety is counterintuitive, because pyrene and other polyaromatic hydrocarbons are traditionally considered as a rigid flat structures, so our observations may be used for future applications in the design of surface-adaptable supramolecular receptors.

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**Keywords:** N-heterocyclic carbenes • Palladium • Self-assembly • host-guest • fullerenes

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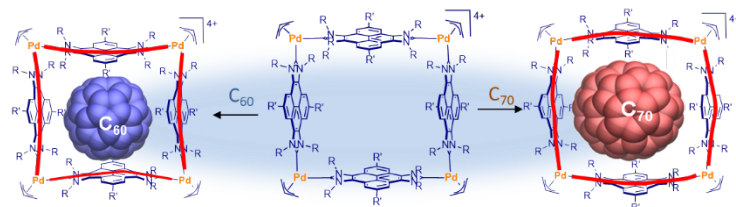
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A palladium-conjoined cubic box with four pyrene-di-imidazolylidene bridging ligands behaves as a surface-adaptable receptor of fullerenes.

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