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Coordination Cages

Stepwise Halide-Triggered Double and Triple Catenation of Self-Assembled Coordination Cages**

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Abstract: *A simple self-assembled* [$Pd_2\mathbf{L}_4$] *coordination cage consisting of four carbazole-based ligands was found to dimerize into the interpenetrated double cage* [$3X@Pd_4\mathbf{L}_8$] *upon the addition of 1.5 equivalents of halide anions* ($X = Cl^-$, Br^-)*. The halide anions serve as templates, as they are sandwiched by four* Pd^{II} *cations and occupy the three pockets of the entangled cage structure. The subsequent addition of larger amounts of the same halide triggers another structural conversion, now yielding a triply catenated link structure in which each* Pd^{II} *node is trans-coordinated by two pyridine donors and two halide ligands. This simple system demonstrates how molecular complexity can increase upon a gradual change of the relative concentrations of reaction partners that are able to serve different structural roles.*

Concentration-dependent changes of the structural or mechanistic features of complex molecular systems play a major role in catalysis, pharmacology, and many biological regulatory processes. In order to gain a basic understanding of the underlying processes found in such complicated environments, the field of systems chemistry has evolved where networks of interacting molecules can be studied in great detail.[1] Such artificial model systems are often based on supramolecular self-assembly which utilizes the formation of complex structures from simple building blocks containing a preprogrammed connectivity.[2] Current research foci include the implementation of functions such as selective sensing[3] and catalysis.[4] The realization of advanced topologies such as knots and links in the form of self-assembled architectures is another subtopic in this area.[5] Furthermore, the temporal and spatial control of structural rearrangements and encapsulation processes by the addition of external triggers,[6] a change in pH[7] or electrochemical potential,[8] and irradiation with light[9] is of high current interest.

With regard to self-assembled coordination cages,[10] we and others have provided first examples implementing controllable elements such as light-switchable ligands[11] and redox-active functionalities[12] within the last couple of years. In one particular strategy, we realized the self-assembly of a series of interpenetrated double cages [$3BF_4@Pd_4\mathbf{L}'_8$] based on banana-shaped bis(pyridyl) ligands **L**′ and the tetrafluoroborate salt of square-planar-coordinated Pd^{II}.[12a,13,14] All structures were found to carry three tetrafluoroborate anions in their one central and two outer pockets. The outer two BF_4^- ions could be replaced by halide ions following an allosteric binding mechanism.[13b–e] By using bulky ligands, we further showed that the choice of an added anionic template residing in the central pocket controls the selectivity for the subsequent binding of further anionic guests in the two outer pockets of these mechanically coupled double-cage systems.[13g]

Here, we demonstrate that structurally related but slightly shorter bis-pyridyl ligands based on a carbazole backbone react with the palladium salt [$Pd(CH_3CN)_4$](BF_4)$_2$ to give stable monomeric cages [$Pd_2\mathbf{L}_4$] that show no tendency to dimerize in the presence of tetrafluoroborate anions (Figure 1). The subsequent addition of stoichiometric amounts of halide ions was found to lead to the formation of interpenetrated double cages. Excess amounts of the same anionic trigger, however, induced a second structural transition leading to a triply catenated link structure.

Ligand **L** was synthesized in three steps starting from carbazole by the Sonogashira cross-coupling reaction of 3,6-dibromo-9-hexylcarbazole[15] and 3-ethynylpyridine (Figure 1a). After a 2:1 mixture of ligand **L** and [$Pd(CH_3CN)_4$](BF_4)$_2$ in CD_3CN had been heated at 70 °C for 5 h, the monomeric cage [$Pd_2\mathbf{L}_4$] was obtained quantitatively as indicated by ^1H NMR spectroscopy (Figure 2a,b) and ESI mass spectrometry (Figure 3a). The structure of [$Pd_2\mathbf{L}_4$] was unambiguously confirmed by the result of a single-crystal X-ray structure determination (Figure 4a and the Supporting Information). In contrast to our previous reports on the formation of cages from slightly longer bis(byridyl) ligands based on tricyclic dibenzosuberone or phenothiazine backbones,[12a,13b,f] no dimerization to give interpenetrated double cages was observed at this point. We would like to emphasize that we were able to predict this behavior based on our collection of X-ray structures[12a,13b,f] and the dimensions (separation of the pyridine N atoms) of the newly designed carbazole ligand **L** that were extracted from a molecular model (DFT B3LYP/6-31G*). This deviating behavior can be explained by the fact that the shorter carbazole-based ligand

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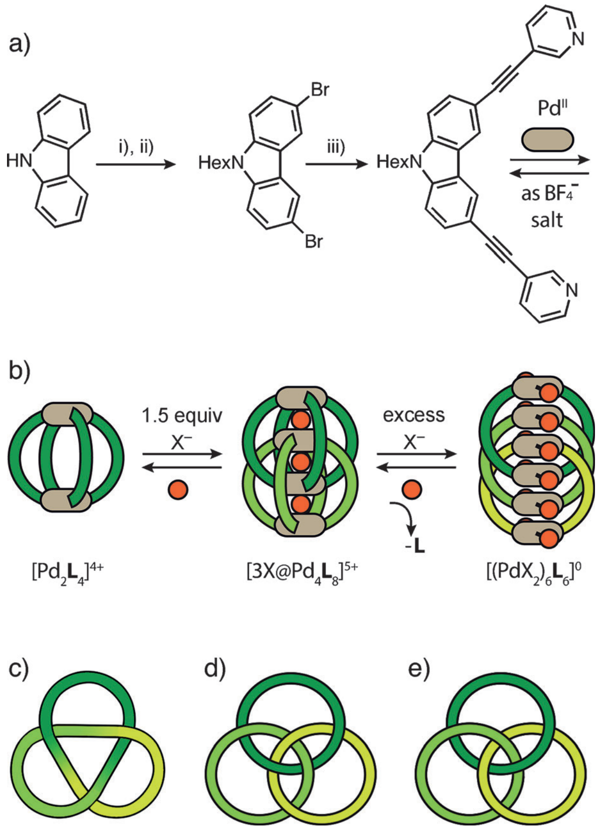

Figure 1. a) Synthesis of the ligand: i) NBS, DMF, 0°C; ii) 1-bromohexane, 50% NaOH, DMSO; iii) 3-ethynylpyridine, CuI, $Pd(PPh_3)_2Cl_2$, NEt_3, 90°C. b) Stepwise assembly of the monomeric cage [Pd_2**L**$_4$], the halide-templated double cage [3X@Pd_4**L**$_8$] (X = Cl^-, Br^-), and the triple catenane {*trans*-[$(PdX_2)_2$**L**$_2$]}$_3$ (X = Br^-). c–e) Schematic depiction of the topologies of a trefoil knot (c), the Borromean rings (d), and the L6n1 link (e) that describes the molecular structure of the triple catenane {*trans*-[$(PdBr_2)_2$**L**$_2$]}$_3$.

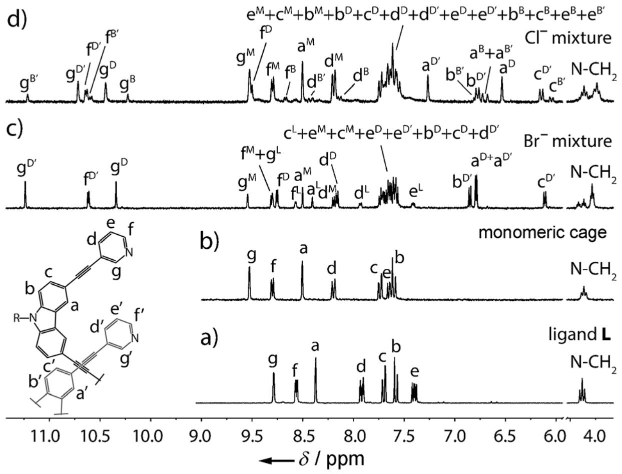

Figure 2. ^1H NMR spectra of a) ligand **L**, b) the monomeric cage [Pd_2**L**$_4$], and mixtures resulting from the reaction of 0.7 mM [Pd_2**L**$_4$] with c) 1.5 equiv of bromide and d) 1.0 equiv of chloride (298 K, 500 MHz, $NnBu_4^+$ signals at 0.7–3.1 ppm omitted, L = ligand, M = monomeric cage, D = major double cage, B = minor double cage [2Cl + Br@Pd_4**L**$_8$]).

L gives rise to a smaller cavity which does not allow for the inclusion of two relatively large tetrafluoroborate counter anions sandwiching the $Pd(pyridine)_4$ plane of a second, interpenetrating cage unit. A comparison of the length of ligand **L** with the lengths of the previously studied systems is discussed in the Supporting Information. Furthermore, previously gathered knowledge about the ideal distance between the $Pd(pyridine)_4$ planes and tetrafluoroborate or halide anions allowed us to predict the dimerization of the carbazole monomeric cages in the presence of smaller anions such as chloride or bromide.[13c,e]

Indeed, after 1.5 equivalents of bromide or chloride anions had been added to a solution of monomeric cage [Pd_2**L**$_4$] and the reaction mixture had been heated for 5 h, NMR spectroscopy (Figure 2c,d) and ESI mass spectrometry (Figure 3b,c) indicated the formation of an interpenetrated species [3X@Pd_4**L**$_8$] with three halide anions inside its pockets. In accordance with our previous reports, double-cage formation is indicated by a twofold splitting of all NMR signals and characteristic signal shifts of the pyridine protons pointing inside the cage's three cavities. In the high-resolution ESI mass spectra, the double cage can be unambiguously identified by the signals for the species [3X@Pd_4**L**$_8$]$^{5+}$, {[3X@Pd_4**L**$_8$] + BF_4}$^{4+}$, and {[3X@Pd_4**L**$_8$] + 2BF_4}$^{3+}$.

Since an X-ray structure could not be obtained in this case, a DFT model of the chloride-containing assembly was prepared based on the spectroscopic results obtained for [3Cl@Pd_4**L**$_8$] and the crystal structures of the reported double cages by performing a geometry optimization on the ωB97XD/def2-SVP level of theory (Figure 4b and the Supporting Information). In terms of the Pd^{2+}–Cl^-–Pd^{2+}

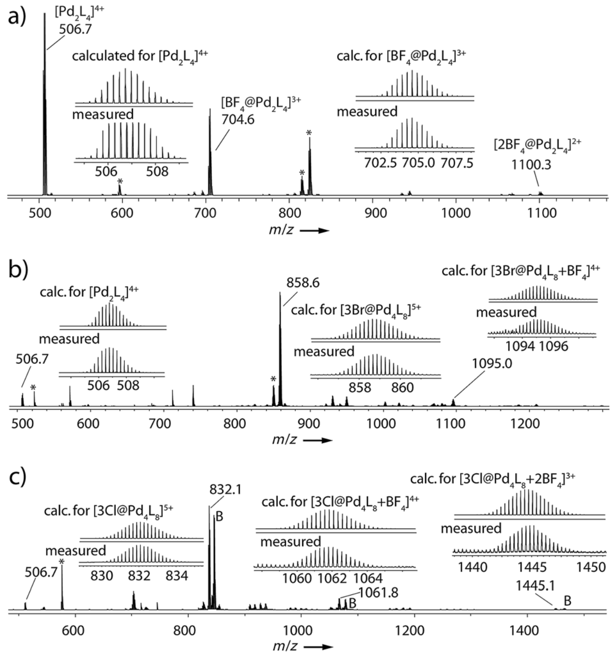

Figure 3. ESI-FTICR mass spectra of a) monomeric cage [$n$$BF_4$@$Pd_2$**L**$_4$]$^{(4-n)+}$ with n = 0–2, b) double cage {[3Br@Pd_4**L**$_8$]-$(BF_4)_n$}$^{(5-n)+}$ with n = 0, 1 and c) double cage {[3Cl@Pd_4**L**$_8$]$(BF_4)_n$}$^{(5-n)+}$ with n = 0–2 (* = adducts with impurities, **B** = double cage [2Cl + Br@Pd_4**L**$_8$]$^{5+}$).

distances, the results of this calculation are in good agreement with our previously published theoretical and experimental studies of related double-cage structures.[12a,13]

As can be seen from the NMR spectral analysis, however, the double cages are in equilibrium with the monomeric cage and the free ligand (Figure 2c,d). The ratio of the species $[3\,\mathrm{X@Pd_4}\mathbf{L}_8]/[\mathrm{Pd_2}\mathbf{L}_4]/\mathbf{L}$ was determined to be 5:3:10 for bromide and 5:5:2 for chloride[16] by NMR spectroscopy. The spectrum resulting from the chloride titration reproducibly showed a minor contamination of a further double cage which could be identified as the mixed chloride/bromide species $[2\,\mathrm{Cl}+\mathrm{Br@Pd_4}\mathbf{L}_8]$ (=**B**) by high-resolution mass spectrometry (see the Supporting Information).

Since no free ligand was present in the solution of the monomeric cage, the formation of the major component $[3\,\mathrm{X@Pd_4}\mathbf{L}_8]$ must be accompanied by a partial release of the ligands by decomplexation, even when stoichiometric amounts of halide were added. This behavior is in accordance with our previously reported observations which showed that also other halide-binding (but tetrafluoroborate-templated) double cages release the free ligand upon addition of excess amounts of halide anions.[13b,e] A plausible explanation is the competition of halide binding inside the cage's pockets with the direct coordination to the square-planar Pd$^{\mathrm{II}}$ cations under displacement of up to two of the pyridine donors. The resulting PdX$_2$(pyridine)$_2$ motif is well known in supramolecular self-assembly.[17] Probable self-assembled components apart from the $[\mathrm{Pd_2}\mathbf{L}_4]$ and $[3\,\mathrm{X@Pd_4}\mathbf{L}_8]$ cages are the macrocycle *trans*-$[(\mathrm{PdX_2})_2\mathbf{L}_2]$ and the [2]-catenane {*trans*-$[(\mathrm{PdX_2})_2\mathbf{L}_2]\}_2$ which are formally obtained by replacing two and four ligands of the monomeric and dimeric cages with halide substituents, respectively. These neutral species are expected to be poorly soluble in the polar medium acetonitrile and thus account at least in part for the observed precipitates.

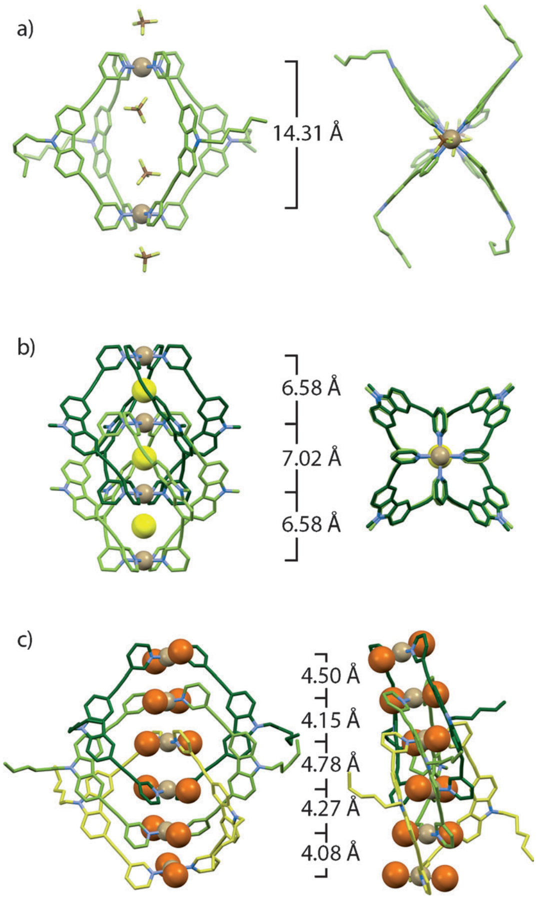

Figure 4. a) Single-crystal X-ray structure of the monomeric cage $[\mathrm{Pd_2}\mathbf{L}_4]^{4+}$ (counter anions = $\mathrm{BF_4}^-$), b) DFT-optimized structure of $[3\,\mathrm{Cl@Pd_4}\mathbf{L}_8]^{5+}$, and c) X-ray structure of the triple catenane {*trans*-$[(\mathrm{PdBr_2})_2\mathbf{L}_2]\}_3$.

To our surprise, however, a triply catenated compound {*trans*-$[(\mathrm{PdBr_2})_2\mathbf{L}_2]\}_3$ was isolated and a single crystal was structurally characterized by X-ray diffraction analysis (Figure 4c). In contrast to the cage structures, the halide-coordinated Pd$^{\mathrm{II}}$ nodes in the triply catenated assembly carry no net charge.[18] Consequently, no further counter anions are associated with the structure and the palladium atoms are able to approach each other much closer than in the charged double cages. The intermetallic distances within the structures of $[3\,\mathrm{X@Pd_4}\mathbf{L}_8]$ and {*trans*-$[(\mathrm{PdBr_2})_2\mathbf{L}_2]\}_3$ are given in Figure 4 in order to illustrate this effect. The average Pd–Pd distance in the chloride-templated double cage amounts to 6.73 Å, whereas the average distance in the triple catenane is 4.36 Å. Since the latter distance is significantly greater than twice the van der Waals radius of Pd (1.63 Å), direct contacts between the metal centers are not expected to control the formation of this peculiar product. Nevertheless, the observation of an almost linear stack of six Pd atoms around which the bromide substituents are arranged in a helical fashion indicates that this arrangement is favored over other conformations in which the metal centers are not aligned in this fashion. In our interpretation, the main explanation for the observed structure is the maximization of the stabilizing π–π interactions between the ligand backbones in this arrangement. For five of the six ligands, close π-stacking with the neighboring carbazole moieties is observed in the X-ray structure. One ligand is twisted away from its nearest neighbor, which is a packing effect caused by the adjacent catenane (for a depiction of the crystal packing see the Supporting Information).

From a topological point of view, this triply catenated structure is an L6n1 link according to the Thistlethwaite link table.[19] Figure 1 compares the topologies of the well-known trefoil knot (Figure 1c) and Borromean rings (Figure 1d), both of which have been realized in a supramolecular context before,[5] with the structure of the triple catenane {*trans*-$[(\mathrm{PdBr_2})_2\mathbf{L}_2]\}_3$ obtained here (Figure 1e). Whereas the trefoil knot consists of only one ring, both other topologies consist of three individual rings. In the Borromean rings, when one single ring is removed the other two rings become unlinked. In the case of the triply catenated structure here, however, all three rings are interlinked. To the best of our knowledge, this topology has never been realized by metal-mediated self-assembly in which the metal centers are components of the macrocycles.[20]

At different concentrations, the halide trigger has two distinct roles in this system: First, it mediates the formation of interpenetrated double cages by templating the dimerization of the monomeric precursor cages. In this role, three halide anions are encapsulated in the three equal-sized pockets of the double cage, and are thus tightly sandwiched between the four dicationic palladium centers by Coulomb interactions yielding an alternating Pd^{2+}-X^{-}-Pd^{2+}-X^{-}-Pd^{2+}-X^{-}-Pd^{2+} stack. At a higher concentration of the halide anions, a further structural conversion kicks in. Under disassembly of the double cages and partial release of the free ligand, a triply interdigitated catenane is formed. Here, the halide anions directly bind to the Pd^{II} centers as part of their square-planar coordination sphere along with displacement of two pyridine donors.

It should be noted that the palladium halides $PdCl_2$ or $PdBr_2$ cannot be used to assemble the interpenetrated double cages $[3X@Pd_4\mathbf{L}_8]$ directly, since these salts would introduce too much halide into the system right from the start. Consequently, this situation would be comparable to a “halide-overtitrated” state of the previous experiment, which, assuming that the system is in thermodynamic equilibrium, should not contain double cages. Indeed, the direct reaction of acetonitrile adducts of the palladium halides ($PdCl_2$ or $PdBr_2$) with ligand **L** was found to yield nonpolar products, which were found to have a much higher solubility in chloroform than the charged single and double cages. According to their simple NMR spectra (no signal splitting) these products are most probably the uncharged macrocycles *trans*-$[(PdX_2)_2\mathbf{L}_2]$ ($X = Cl^-, Br^-$; see the Supporting Information).

In conclusion, we have presented an interconverting system of three self-assembled structures all based on the same bis(pyridyl) ligand and varying Pd/halide ratios from 1:0 in the case of the monomeric cage $[Pd_2\mathbf{L}_4]$, to 4:3 in the case of the interpenetrated double cage $[3X@Pd_4\mathbf{L}_8]$, and up to 1:2 in the case of the triple catenane {*trans*-$[(PdBr_2)_2\mathbf{L}_2]\}_3$.

Interestingly, the role of the halide anions in the self-assembly of the double cages described here differs significantly from the function of the halides in our previously reported double-cage systems: the cages based on dibenzosuberone and phenothiazine backbones were found to assemble into interpenetrated dimers with BF_4^- as the templating counter anion. Halide binding was not required for dimerization but was found to occur in the outer two pockets of the pre-assembled double cages with tremendous affinity.[12a,13b]

In a second type of system based on sterically more demanding ligands, halide anions were indeed needed to template the formation of double cages but not because the ligands were too short for the accommodation of three BF_4^- anions sandwiched between four Pd^{II} centers. Instead, halide anions were needed because the steric crowding around the ligand backbones only allowed for double-cage formation when a small template was available.[13g] Here, in contrast, the steric demand of the ligand backbones is not responsible for the peculiar dimerization behavior; instead, the somewhat shorter carbazole ligands allow for the formation of an interpenetrated double cage only when all three pockets can be satisfied by the uptake of small halide anions.

The addition of further amounts of the same halide then leads to the formation of a triple catenane whose unique topology was determined by X-ray analysis. The observation that three different self-assembled products are formed by variation of the concentration of a small anionic additive shows that the use of one multifunctional trigger can be sufficient to create a notable degree of complexity in a supramolecular system. The experiments described in this work required nothing but a simple organic ligand, a palladium source, and a halide salt. In our opinion, this serves as a prime example of the promising potential of systems chemistry.[1]

Experimental Section

The synthesis of ligand **L** is described in the Supporting Information. Cage $[Pd_2\mathbf{L}_4]$ was obtained from ligand **L** by adding 0.5 equiv of $[Pd(CH_3CN)_4](BF_4)_2$ in CD_3CN and heating the mixture to 70 °C for 5 h. The halide anions were added as acetonitrile solutions of their tetrabutylammonium salts and the samples were heated to 70 °C for 5 h after each titration step before the measurement of the NMR and ESI mass spectra. Single crystals suitable for X-ray crystal structure analysis were grown by slow evaporation of solutions of the self-assemblies in acetonitrile. CCDC-1011498 and -1011499 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[18] This complicated the mass spectrometric analysis and obviously caused low solubility in the polar solvent acetonitrile. Due to the intricate equilibrium situation, presumably also including the formation of the macrocycle *trans*-$[(PdX_2)_2\mathbf{L}_2]$ and the [2]catenane $\{trans\text{-}[(PdX_2)_2\mathbf{L}_2]\}_2$, no yield for the triple-catenated $\{trans\text{-}[(PdX_2)_2\mathbf{L}_2]\}_3$ reaction product could be determined. An overall yield for the formation of all $\{trans\text{-}[(PdBr_2)_2\mathbf{L}_2]\}_n$ ($n = 1.3$) species by halide-induced precipitation, however, was estimated based on elemental analysis (see the Supporting Information).

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