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Cage-to-Cage Cascade Transformations

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Dedicated to Prof. P. K. Bharadwaj on the occasion of his retirement

Abstract: A series of Pd_2L_4-type binuclear self-assembled coordination cages (**1**–**4**), where **L** stands for a nonchelating bidentate ligand, were prepared. The strategies adopted for the synthesis of the cages were: combination of Pd^{II} with 1) a selected ligand or 2) subcomponents of the ligand. Highly efficient cage-to-cage transformation reactions are demonstrated by suitable covalent modification (from **1** to **2** or **3** or **4**) or ligand-exchange reactions (from **1** to **2** or **3** or **4**; from **2** to **3** or **4**). Thus, new cascade transformations (from **1** to **2** to **3**; from **1** to **2** to **4**) are achieved beautifully.

Coordination-driven self-assembly has been well recognized as an efficient strategy for the construction of a vast range of metallo-supramolecular architectures. The well-established classical self-assembly[1] and relatively new subcomponent self-assembly[2,3] routes are typically adopted for preparation of such architectures. Thermodynamically favored self-assembled coordination cages are often the final products of these complexation reactions, because self-healing of incorrectly formed bonds is facilitated by the dynamic nature of metal–ligand interactions.[1] Post-self-assembly modification[4–9] of already self-assembled coordination cages has been a recent trend of considerable significance in the realm of supramolecular coordination chemistry.

The classical self-assembly route involves combination of a chosen ligand with a suitable metal component under appropriate reaction conditions to afford the targeted assembly.[1] In the subcomponent self-assembly route, in situ synthesis of the ligand is carried out in presence of the metal component so that the self-assembly phenomenon could take place in one-pot. Thus, the steps involved in the synthesis and isolation of the ligand is avoided.[2,3] In the post-self-assembly modification route, a suitably fabricated pre-prepared self-assembled compound is subjected to alteration. The most studied phenomenon among the post-modification strategies has been covalent modification of the back-bone of a self-assembled coordination complex. For such modifications, it is necessary to have suitable functional groups anchored at the ligand back-bone; these can be derivatized with a chosen organic fragment.[4] However, alterations/exchange of the metal, ligand, counter anion or guest molecule are more commonly used for post-modification.[4–9]

In some cases of ligand-exchange reactions the bound ligand units of a coordination complex are replaced with a required number of a suitable incoming ligand[5] or a coordinating fragment of the already coordinated ligand is covalently replaced by an incoming fragment of similar functionality in a dynamic covalent space (defined as subcomponent self-assembly by Nitschke).[2–3] Transmetallation is another dynamic process that could be considered a post-modification.[6] Transmetallation with or without structural change of a chosen self-assembled compound is well known[6d] and included under disruptive or direct exchange. Exchange of the counter anion of a self-assembled cage is known to either retain the core architecture or induce structural change, forming yet another cage of higher or lower nuclearity.[7] Post-modification induced by a suitable guest[8] or stimuli, such as light,[9] has also been shown successfully. The dynamic nature of the metal–ligand interactions helps only when there is a requirement of metal–ligand bond breaking and making. However, pure covalent modifications or rearrangement without touching the metal–ligand bonds does not really require the dynamic nature of the metal–ligand bonds. Most of the post-modification phenomena described above could be defined as cage-to-cage transformations.

Complexation of Pd^{II} with suitably designed bidentate nonchelating ligands is known to afford binuclear Pd_2L_4-type self-assembled coordination-cage molecules.[1,10] The ligands with coordination vectors almost parallel to each other and pointing in the same direction are ideal designs for the construction of these binuclear architectures.

In this work we have used Pd_2L_4-type coordination-cage molecules to study the cage-to-cage transformation phenomenon (Figure 1 and Scheme 1). We have conceptualized the phenomenon of covalent modification of a coordination cage by a direct condensation reaction of the coordinating atoms of the cage with a chosen incoming organic functionality in such a manner that the ligation loyalty is either retained (Figure 1 a and Scheme 1 a) or transferred (Figure 1 c,e and Scheme 1 c,e). In consequence, the size of the cavity is either retained or expanded. Ligand-exchange reactions were also performed by choosing suitable incoming ligands so that the cavity size is either retained (Figure 1 b and Scheme 1 b) or expanded (Figure 1 d,f and Scheme 1 d,f). The cage-to-cage transformations in the steps (a) and (b) could be continued further in a cascade

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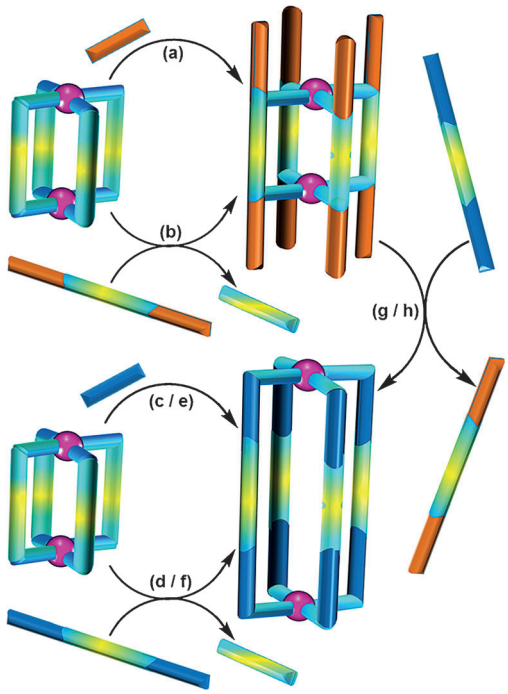


Figure 1. Cartoon diagram showing the cage-to-cage transformations in a one-step manner through covalent modifications (a)/(c)/(e), or ligand-exchange reactions (b)/(d)/(f)/(g)/(h). The two-step cascade transformations are represented as step (a) followed by step (g) or (h), and step (b) followed by step (g) or (h). Steps (a)–(h) are comparable to the same in Scheme 1.

fashion, for example, through ligand-exchange reactions as shown in the step (g) or (h).

Ligands **L1**–**L4** considered for complexation reactions with Pd^{II}, to prepare Pd_2L_4-type cages, are shown in Figure 2. Another relevant compound **L2a** (not a ligand) and two other monodentate ligands **L5** and **L6** are also shown in Figure 2. Ligands **L2**–**L4** are crafted with a pair of arms that are shown extended and wide open (Figure 2). Ligands **L2**–**L4** and compound **L2a** were prepared from commercially available bis(4-aminophenyl)methane, **L1**, and other appropriate reagents either by using literature methods,[11] sometimes with slight modifications. Thus, condensation of **L1** with benzaldehyde, benzoyl chloride, nicotinaldehyde, or nicotinoyl chloride resulted in **L2**, **L2a**, **L3**, and **L4**, respectively. Nicotinoyl azide can be used instead of nicotinoyl chloride for the preparation of **L4**. The experimental details of the synthesis are provided in the Supporting Information (see Section S1). The energy-minimized structures of ligands **L1**–**L4** are shown in the Figure 3; these were calculated with the Gaussian 09 software package.[12] The ligands adopt an overall bent shape with one of the arms in an extended conformation and the other somewhat retracted as shown in the chemical drawing of **L4** in Figure 3. The conformations of the ligands in the corresponding Pd_2L_4 complexes are worthy of comparison and discussed in a later section.

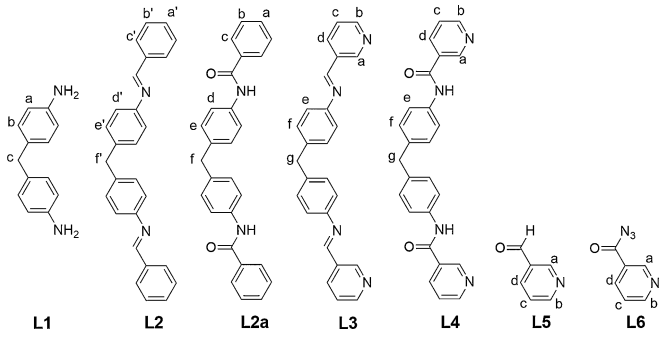


Figure 2. Ligands **L1**–**L6** and compound **L2a**.

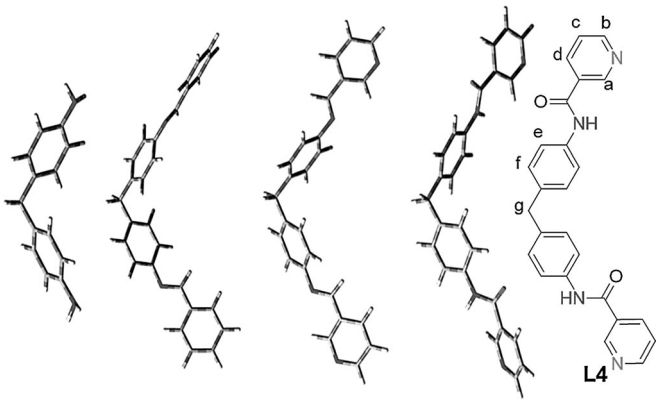
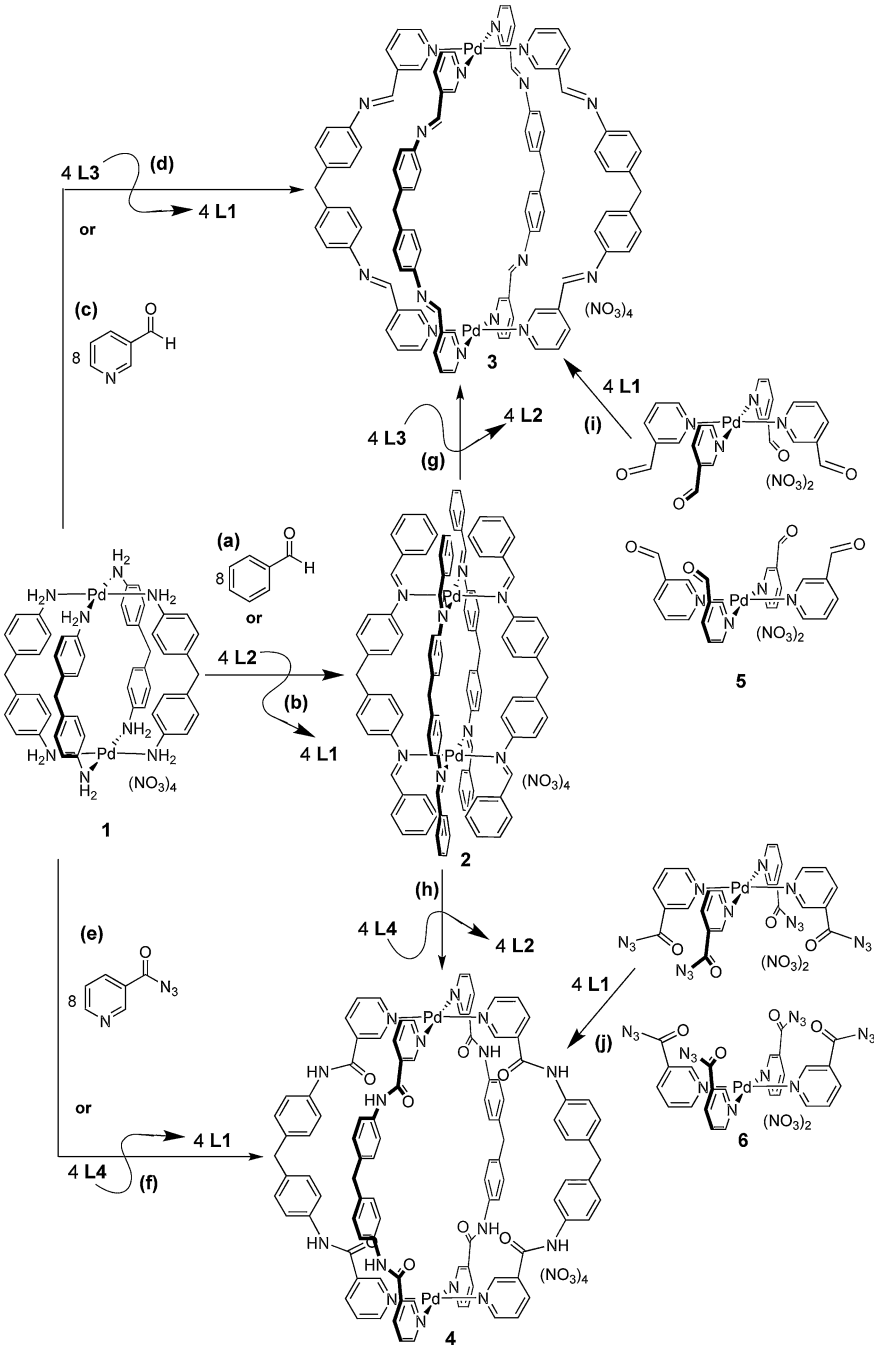


Figure 3. Energy-minimized structures of the ligands **L1**–**L4** (from left to right) showing the bent conformations and structure of **L4** in the comparable conformation.

Although **L1** is commercially available and the crystal structure of **L3** has been reported recently,[13] both of these compounds have not been explored for complexation with metal ions. Ligand **L2** displays C–H activation when reacted with $Fe_2(CO)_9$ to form organometallic complexes,[14] whereas ligand **L4** has been used for complexation with $Cu(NO_3)_2$ for preparation of 1D coordination polymers.[15] The smaller ligands, **L5** and **L6**, have not been explored for complexation with metal ions. Compounds **L1, L2**, and **L4** are typical bidentate nonchelating ligands for which the coordinating atoms are a pair of well-separated amine, imine, and pyridine nitrogen centers, respectively. Ligand **L3** has four binding sites, that is, two imine and two terminal pyridine nitrogen centers. Thus **L3** could act as a bidentate nonchelating ligand by utilizing either the imine pair or the pyridine pair; actually the pyridine set is found to coordinate with Pd^{II}.

Complexation of $Pd(NO_3)_2$ with ligands **L1**–**L4** at a ratio of 2:4 resulted in the quantitative formation of the Pd_2L_4-type cages **1**–**4**, respectively. The general formula of these complexes is $[Pd_2(L)_4](NO_3)_4$, where **L** stands for the ligand. Similarly, complexation of $Pd(NO_3)_2$ with the monodentate ligands **L5** and **L6** at a ratio of 1:4 resulted in the Pd_1L_4-type complexes **5**–**6**, with the general formula $[Pd(L)_4](NO_3)_2$. The chemical structures of complexes **1**–**6** can be seen in the Scheme 1. Schemes outlining the syntheses, through the above-mentioned classical self-assembly protocol, are provided in the Supporting Information (Supporting Information Schemes S1–S6).

All six complexes (**1**–**6**) were characterized by recording their ^1H NMR, ^{13}C NMR, H-H COSY, C-H COSY, DOSY, and ESI-MS data (see the Supporting Information Figures S1–S24, and S44–



Scheme 1. Transformation of cage **1** by covalent modification/ligand-exchange reactions to form: (a)/(b) cage **2**, (c)/(d) cage **3** and (e)/(f) cage **4**. Transformation of cage **2** by ligand-exchange reactions to form: (g) cage **3** and (h) cage **4**. Covalent modification of **5** and **6** to form: (i) cage **3** and (j) cage **4**, respectively. The cascade transformation reactions are represented by the conversion of cage **1** to **2** to **3** (or **4**).

S48). The ^{1}H NMR spectra of ligands **L1**–**L4** and complexes **1**–**4** are provided in Figure 4. The energy-minimized structures of complexes **1**–**4** are shown in Figure 5; these were obtained by DFT methods by using the Gaussian 09 software package.[12] The conformations of ligands **L2**–**L4** in the free and bound states (i.e., in complexes **2**–**4**) are worth noting. Whereas **L2** moieties adopted a fully extended conformation in the structure of complex **2**, albeit with a slim cavity, the arms of **L3** and **L4** are fully retracted, resulting in wider cavities of **3** and **4**. The single crystal X-ray structure of complex **4** unequivocally confirmed the Pd_2L_4 architecture of the molecule with retracted arms (Figure 6) in line with the energy-minimized structure of **4**.

The ^{1}H NMR spectra of complexes **1**–**6** are compared with the corresponding free ligands **L1**–**L6** (Figure 4, and Figures S1, S5, S9, S13, S17, and S21 in the Supporting Information). Complexation-induced changes in the chemical shifts of the decisive signals are summarized here. The downfield and upfield shifts are designated with plus (+) and minus (−) signs, respectively. The NH_2 protons in **1** are shifted by 2.1 ppm, indi-

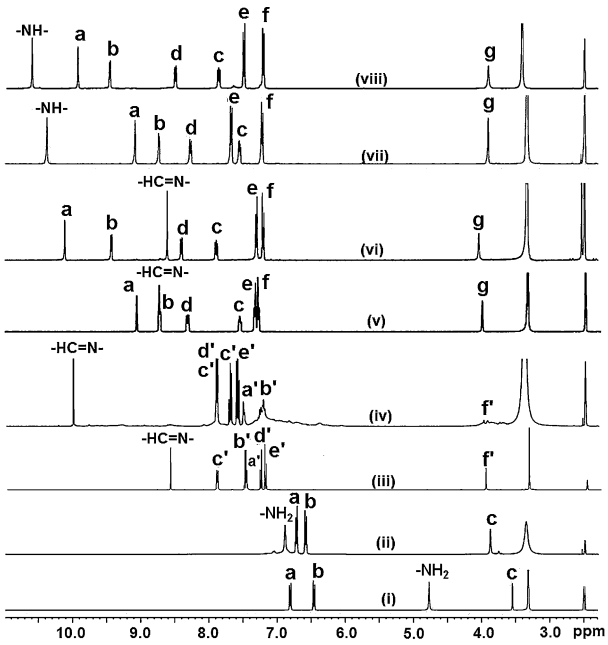


Figure 4. 400 MHz ^{1}H NMR spectra in [D$_6$]DMSO for (i) **L1**; (ii) [Pd$_2$(**L1**)$_4$](NO$_3$)$_4$, **1**; (iii) **L2**; (iv) [Pd$_2$(**L2**)$_4$](NO$_3$)$_4$, **2**; (v) **L3**; (vi) [Pd$_2$(**L3**)$_4$](NO$_3$)$_4$, **3**; (vii) **L4**; and (viii) [Pd$_2$(**L4**)$_4$](NO$_3$)$_4$, **4**.

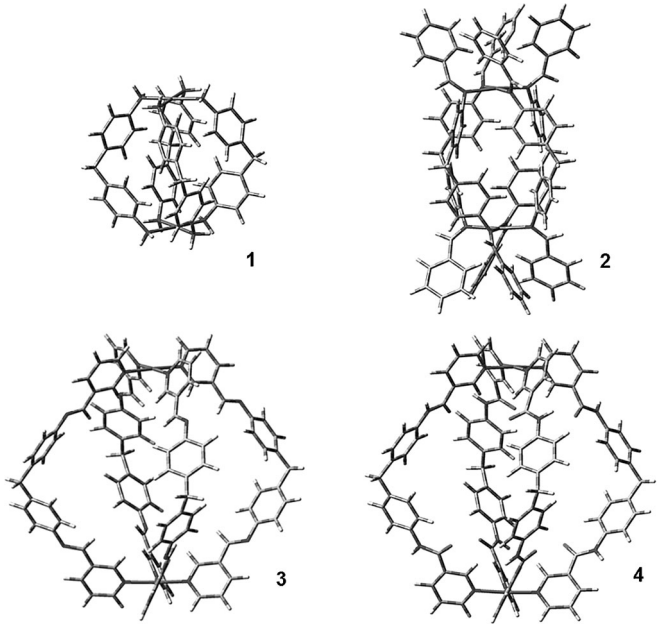


Figure 5. Energy-minimized structures of the complexes **1**–**4**.

cating the coordination of an amine nitrogen atom to the metal center. The CH=N protons in **2** are shifted by 1.4 ppm, indicating the coordination of a Schiff base nitrogen atom to the metal center. The CH=N protons in **3** are marginally shifted by −0.1 ppm, indicating that there is no interaction between the Schiff base nitrogen atom and the metal center. However, the pyridine-ring protons of **3** showed a very common complexation-induced shift, that is, 1.0 ppm for H$_a$ protons. Similarly, the shift of the pyridine-ring protons in **4** also supports complexation of the pyridine units, that is, 0.8 ppm shift for H$_a$ protons. Complexes **5** and **6** showed similar complexation-induced shifts of the pyridine protons.

The DOSY spectra of complexes **1**, **2**, **3**, and **4** showed single bands in each case, corresponding to single species. The diffusion coefficient, *D*, for compounds **1**–**4** are 1.115×10^{-10}, 1.752×10^{-10}, 9.723×10^{-11}, and 8.280×10^{-11} m^2 s^{-1}, respectively. The radius of the solvated cages (often referred to as hydrodynamic radius) **1**, **2**, **3**, and **4** were calculated. The shapes of **1**, **3**, and **4** were considered spherical and that of **2** as spheroidal. Accordingly, suitable equations[16] were used for the calculation of the radius of the molecules. The calculated radiuses of **1**–**4** are 9.84, 9.47, 11.28, and 13.25 Å, respectively. Thus, the sizes of cages **1** and **2** are comparable, and so are those of **3** and **4** as well. However, the sizes of **1** and **2** are smaller than those of **3** and **4**. The DOSY spectra and detailed calculations are provided in the Supporting Information (Figures S44–S48 and Section S3).

ESI-MS data of complexes **1**–**4**, support the Pd$_2$**L**$_4$ formulations of the architectures (see the Supporting Information, Figures S4, S8, S12, S16), whereas the same data for **5** and **6** indicate mononuclear Pd$_1$**L**$_4$-type complexes (see the Supporting Information, Figures S20, S24). The peak patterns at *m/z* = 564.59 for the fragment [**1**−2NO$_3$]$^{2+}$; *m/z* = 917.06 for the fragment [**2**−2NO$_3$]$^{2+}$; *m/z* = 593.49 and 429.62 corresponding to the fragments [**3**−3NO$_3$]$^{3+}$and [**3**−4NO$_3$]$^{4+}$; *m/z* = 985.31, 636.26 and 461.68 corresponding to the fragments [**4**−2NO$_3$]$^{2+}$, [**4**−3NO$_3$]$^{3+}$ and [**4**−4NO$_3$]$^{4+}$; *m/z* = 267.08 and 349.03 corresponding to the fragments [**5**−2NO$_3$]$^{2+}$ and [**6**−2NO$_3$]$^{2+}$ are found to be comparable to the theoretically calculated isotopic peak patterns (see the Supporting Information, Figures S4a, S8a, S12a, S16a).

We have devised domino reaction conditions by utilizing the concept of the dynamic subcomponent self-assembly process to prepare complexes **2**–**4**. Thus, the ligands (**L2**–**L4**) were synthesized in the presence of Pd(NO$_3$)$_2$ to afford the targeted complexes (see the Supporting Information, Schemes S7–S9). For instance, a mixture of Pd(NO$_3$)$_2$, **L1**, and benzaldehyde at a ratio of 2:4:8 resulted in complex **2**. The use of nicotinaldehyde or nicotinoyl azide instead of benzaldehyde resulted in complexes **3** or **4**, respectively. The progress of the domino reactions were monitored by ^{1}H NMR spectroscopy. No major differences can be seen between the ^{1}H NMR spectra of complexes **2**–**4** prepared by the domino methods (see the Supporting Information, Figures S25–S27) and the same complexes prepared by usual self-assembly methods.

After characterization of the complexes, the cage-to-cage transformations through the covalent modifications and ligand-exchange reaction routes were probed (Scheme 1). In the covalent-modification method, the pre-prepared cage **1**, with the amine nitrogen atoms coordinated to the Pd^{II} centers, was allowed to react with eight equivalents of benzaldehyde, nicotinaldehyde, or nicotinoyl azide to exclusively prepare the corresponding complexes **2**–**4** (Figure 1 and Scheme 1). The schematic representation and ^{1}H NMR spectra of the complexes are given in the Supporting Information (Schemes S10–S12, Figures S28–S30). The amine functionality of **1** was cova-

lently modified to form a Schiff base or an amide group by reaction with suitable functional groups. Simultaneous reorganization also happened during the covalent modifications. The nitrogen center of **L1**, which is responsible for coordination in **1**, retained the ligation loyalty even after complex **1** was reacted with benzaldehyde, because no other coordination sites are available in the covalently modified ligand moiety. Thus, the imine functionality was involved in coordination and formation of complex **2**. However, upon reaction of **1** with nicotinaldehyde, the coordination site got shifted in favor of the pyridine nitrogen atoms (and not the imine nitrogens) to form **3**. When complex **1** was reacted with nicotinoyl azide, the coordination site was shifted to the only possible pyridine nitrogen atoms to form **4**, because the amide groups formed were inefficient for complexation with Pd^{II}. Thus, the ligation loyalty was either retained or transferred, depending on the nature of the functional group generated via covalent modification. Reaction of **1** with benzoyl azide, however eliminated the ensuing compound **L2a** due to concomitant decomplexation (see the Supporting Information, Scheme S13, Figure S31).

Complexes **1**–**4** were probed for the ligand-exchange reactions by combining a given complex with four equivalents of ligands of another variety (Figure 1 and Scheme 1). The schematic representation and ^{1}H NMR spectra of the complexes are given in the Supporting Information (Schemes S14–S18, Figures S32–S36). Cage **1** was allowed to react with four equivalents of **L2**, **L3**, or **L4** where upon complexes **2**–**4** are formed, respectively. This could happen smoothly as ligand **L1** was released in each experiment in favor of the incoming ligands. Likewise, combination of complex **2** with four equivalents of **L3** or **L4** lead to the release of **L2** in both cases and made way for complexes **3** and **4**, respectively. However, combination of **3** with **L4** (see the Supporting Information, Scheme S19, Figure S37) or **4** with **L3** resulted in a mixture of products. Thus, the order of binding abilities of the ligands with Pd^{II} can be considered as **L1** < **L2** < **L3** ≈ **L4**. A mixture of $Pd(NO_3)_2$, **L1**, and **L2** (or **L3**, or **L4**) at a ratio of 2:4:4 resulted complex **2** (or **3**, or **4**) and **L1** remained free. Similarly, combination of $Pd(NO_3)_2$, **L2**, and **L3** (or **L4**) at a ratio of 2:4:4 resulted complex **3** (or **4**) and **L2** remained free (see the Supporting Information, Scheme S20, Figure S38). However, a combination of $Pd(NO_3)_2$, **L3**, and **L4** at a ratio of 2:4:4 resulted in a mixture of products with no particular preference to any of the ligands (see the Supporting Information, Scheme S21, Figure S39). An equimolar mixture of **3** and **4** also resulted in a mixture of products (see the Supporting Information, Scheme S22, Figure S40). Thus, the cavity size of the cage before and after the ligand-exchange reactions are either unchanged or changed, depending on the nature of incoming ligand.

Covalent modification of the mononuclear complexes **5** and **6** were probed by using ligand **L1**. Complexes **3** and **4** were thus prepared by this alternative route by combining four equivalents of **L1** with two equivalents of **5** and **6** to afford complexes **3** and **4**, respectively (Scheme 1, and in the Supporting Information, Schemes S23–S24, Figures S41–S42). During the covalent-modification routes, in situ formations of ligand moieties **L3** and **L4** occur. One such case was achieved by simply combining **L1** with nicotinoyl azide, where upon ligand **L4** was formed (see the Supporting Information, Scheme S25, Figure S43).

The geometries of the reactant and product molecules were optimized and the frequencies were calculated at the B3LYP/6-31G* level of theory (see the Supporting Information, Figure S53). The overall Gibbs free energies (ΔG) and the enthalpies (ΔH) for the formation were also calculated and support the formation of all experimental products (see the Supporting Information, Table S3), except for the formation of **2**. A brief discussion is provided in the Supporting Information (Section S5). The energy-minimized structures of the complexes can be seen in Figure 5.

Single crystals of compound **4** suitable for X-ray diffraction data collection were grown by slow diffusion of ethyl acetate into a dimethyl sulfoxide solution of **4**. The crystal structure of **4** reveals that four units of the ligand is coordinated with two units of Pd^{II} ions in a square planar geometry. The carbonyl groups point towards the inner side of the cavity of **4**. The Pd–N bond lengths in the complex span the range of 2.009–2.035 Å and the *cis*-*N*-Pd–N bond angles span the range of 88.03–91.24° (Figure 6a). Further details on the crystal structure are briefly discussed in the Supporting Information (Section S6).

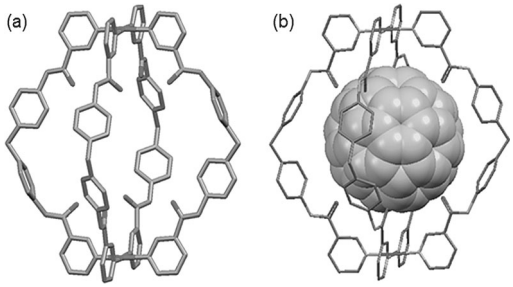


Figure 6. (a) Crystal structure of **4** (the counter anions and solvent molecules are omitted for clarity) and (b) energy-minimized structure of $[C_{60}\subset Pd_2(\mathbf{L4})_4]^{4+}$.

Cages **3** and **4** were considered suitable, for encapsulation of C_{60}. This was presumed on the basis of the size, shape, and internal chemical environment of the cages. Preliminary investigation by ^{1}H and ^{13}C NMR techniques (see the Supporting Information, Figures S48–S51) indicates the intended host–guest interactions. The ^{1}H NMR signals of the host molecules are found to be shifted upfield. The sole ^{13}C NMR signal of the guest molecule was also found to be shifted upfield. These changes are in line with the literature,[17] where binding of C_{60} in the cavity of 2D and 3D metallocages were successfully demonstrated. The energy-minimized structure of the host–guest complexes are shown in Figure 6b and in the Supporting Information, Figure S52.

In summary, a series of $Pd_2\mathbf{L}_4$-type, binuclear, self-assembled, coordination cages were prepared by metal–ligand complexation through classical self-assembly or domino routes through subcomponent self-assembly. Cage-to-cage transformations of these cages were carried out by covalent modifications or

ligand-exchange reactions of the pre-prepared complexes. The covalent modifications were performed directly at the metal binding site; this led to ligation-loyalty retention or ligation-loyalty transfer, depending on the nature of the modification. In the ligand-exchange-reaction processes (also covalent modifications) the size of the cavity of the cages are either unchanged or changed, depending on the nature of the incoming ligand.

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Keywords: cage-to-cage transformation · palladium · reorganization · self-assembly · subcomponents

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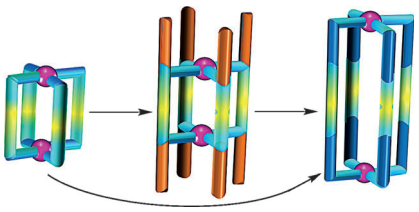
Let's cascade! Cage-to-cage transformation reactions of Pd_2L_4-type (**L** is a non-chelating bidentate ligand) coordination cages are achieved by covalent modifications or ligand-exchange reactions of suitable pre-prepared complexes. The palladium atoms retain their positions or move away to increase the cavity size depending on the nature of the modification/exchange.



Reorganization Reactions

*S. Bandi, D. K. Chand**

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Cage-to-Cage Cascade Transformations