

Stoichiometrically Controlled Revocable Self-Assembled “Spiro” versus Quadruple-Stranded “Double-Decker” Type Co...

Garry Hanan


Chemistry - A European Journal

Cite this paper

Downloaded from [Academia.edu](#) 

[Get the citation in MLA, APA, or Chicago styles](#)

Related papers

[Download a PDF Pack](#) of the best related papers 



[Light-Triggered Guest Uptake and Release by a Photochromic Coordination Cage](#)

Michael John

[Classification of coordination polygons and polyhedra according to their mode of self-assembly. 2. Re...](#)

Gerhard f. Swiegers

[NMR-Based Structure Determination of an Intertwined Coordination Cage Resembling a Double Trefoi...](#)

Michael John

Self-Assembly

Stoichiometrically Controlled Revocable Self-Assembled "Spiro" versus Quadruple-Stranded "Double-Decker" Type Coordination Cages

Sreenivasulu Bandi,^[a, b] Amlan K. Pal,^[b] Garry S. Hanan,^{*,[b]} and Dillip Kumar Chand^{*,[a]}

Dedicated to Professor Makoto Fujita on the silver jubilee of his molecular square

Abstract: The simple combination of Pd^{II} with the tris-monodentate ligand bis(pyridin-3-ylmethyl) pyridine-3,5-dicarboxylate, **L**, at ratios of 1:2 and 3:4 demonstrated the stoichiometrically controlled exclusive formation of the "spiro-type" Pd₁L₂ macrocycle, **1**, and the quadruple-stranded Pd₃L₄ cage, **2**, respectively. The architecture of **2** is elaborated with two compartments that can accommodate two units of fluoride, chloride, or bromide ions, one in each of the enclosures. However, the entry of iodide is altogether restricted. Complexes **1** and **2** are interconvertible under suitable conditions.

Combination of Pd^{II} with suitable nonchelating bis-monodentate ligands is an established strategy for the preparation of a variety of discrete coordination complexes of the general formula Pd_mL_{2m}.^[1] Mononuclear "spiro-type" complexes of Pd₁L₂ formulation are rarely reported;^[2] however, the family of self-assembled quadruple-stranded binuclear "cage-type" complexes of Pd₂L₄ formulation^[1c,3-9] (Figure 1) is arguably the most reported Pd_mL_{2m}-type compound. Among the Pd₂L₄ type of complexes, only a few are helicates^[3] or of the homochiral type^[7] and the rest are symmetrical/propeller shaped.^[4-6,8-9] Their applications include the binding of guests such as inorganic/organic anions,^[4,5] metal complexes,^[4c-f] neutral organic molecules,^[5b,f] fullerenes,^[8] among others. The functionalization^[6] and fluorescence^[8] behavior of some cages have also been studied. Two units of the Pd₂L₄ cages in some specific cases are catenated to form three-dimensional [2]-catenanes^[9] with anion-binding capabilities.^[9b,e] Considering the overwhelming success of Pd₂L₄-type complexes, the next generation "double-decker" cages of general formula Pd₃L₄ (Figure 1) is envisioned as a fresh design using Pd^{II} and a judiciously de-

signed "E-shaped" tris-monodentate ligand, **L** (Scheme 1). In this work, ligand **L** is bis(pyridin-3-ylmethyl) pyridine-3,5-dicarboxylate.

Structural variation of the coordination cages by simply varying the solvent,^[10] counter anion, or the templating guest molecules^[11] is known in the literature. However, the variation of metal-to-ligand ratios during the complexation reactions could potentially lead to variation in the empirical formula of the cages and naturally the architectures. This phenomenon is reported for the preparation of discrete coordination cages by using the variable coordination number of metal ions, for example, Ag^I and Hg^{II}.^[12] We propose to conceptualize the differential coordination ability of ligand **L** with a metal ion of fixed coordination number, for example, Pd^{II}, without the use of a template/guest, and to validate this phenomenon by varying the metal-to-ligand ratio.

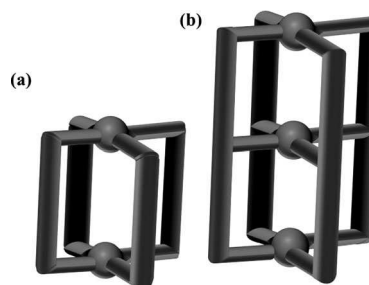


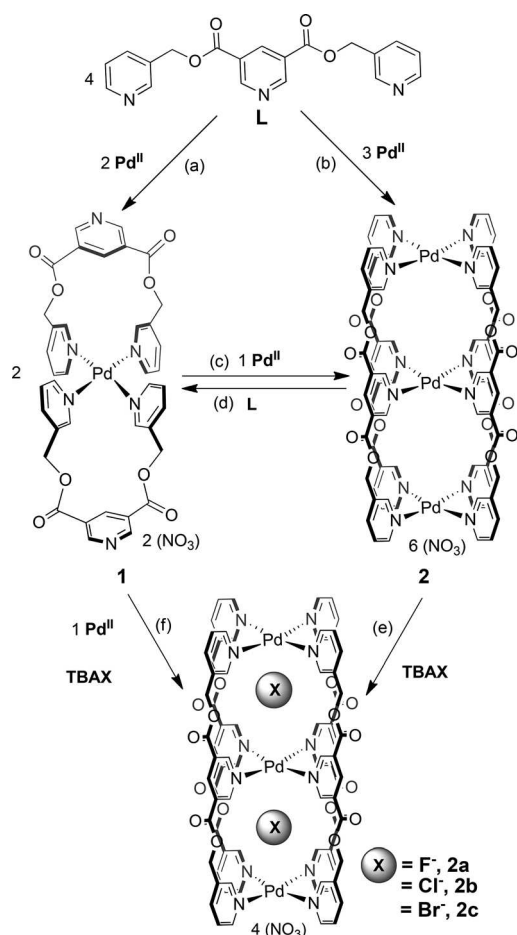
Figure 1. Cartoon representation of the self-assembled discrete coordination complexes of the (a) well-explored cage-type Pd₂L₄, and (b) the new double-decker Pd₃L₄ architectures.

Herein, we demonstrate the exclusive synthesis of a "spiro-type" complex, [Pd(L)₂](NO₃)₂ (**1**) and a molecular "double-decker" coordination cage [Pd₃(L)₄](NO₃)₆ (**2**) in a stoichiometrically controlled manner by the combination of Pd(NO₃)₂ with the new tris-monodentate ligand, **L**, at ratios of 1:2 and 3:4, respectively (Scheme 1). The differential coordination abilities of the two terminal pyridine groups versus the internal pyridine are successfully exploited for the variation of the architectures by simply controlling the metal-to-ligand ratios. Complex **2** is further used for the encapsulation of two units of halide ions, one in each of the compartments. Although fluoride, chloride, and bromide ions could be encapsulated very easily to prepare

[a] S. Bandi, Prof. Dr. D. K. Chand
Department of Chemistry, Indian Institute of Technology Madras
Chennai 600036 (India)
E-mail: dillip@iitm.ac.in

[b] S. Bandi, Dr. A. K. Pal, Prof. Dr. G. S. Hanan
Department of Chemistry
University of Montreal, Montreal QC H3T-1J4 (Canada)
E-mail: garry.hanan@umontreal.ca

Supporting information for this article is available on the WWW under
<http://dx.doi.org/10.1002/chem.201403808>.



Scheme 1. Metal-to-ligand stoichiometrically controlled exclusive synthesis of self-assembled (a) "spiro-type" Pd₁L₂, **1**, and (b) "double-decker" Pd₃L₄, **2**. Synthesis of (c) complex **2** from **1**, and (d) complex **1** from **2**, using additional amounts of Pd^{II} or ligand through dynamic reorganization processes. Preparation of [(X)₂CpD₃(L)₄](NO₃)₄, **2 a–2 c** (X = fluoride, chloride, or bromide) by (e) encapsulation of two units of the halide ions in cage **2** or (f) further complexation of **1** with Pd^{II} followed by halide encapsulation. (Note: in step (d), 2 equivalents of L are added to 1 equivalent of **2** to afford 3 equivalents of **1**. The abbreviation TBAX stands for tetrabutylammonium halide, that is, nBu₄NX).

the corresponding [(X)₂CpD₃(L)₄](NO₃)₄ complexes, **2 a–2 c** (Scheme 1), iodide was not accommodated in the compartments.

The new tris-monodentate ligand bis(pyridin-3-ylmethyl) pyridine-3,5-dicarboxylate, **L**, was prepared by reacting 3,5-pyridinedicarbonyl chloride with 3-hydroxymethyl pyridine in dry dichloromethane in the presence of triethylamine. A detailed description of the synthesis and characterization of the ligand is provided in the Supporting Information. The ¹H NMR spectra of the ligand, **1**, and **2** in [D₆]DMSO are shown in the Figure 2.

The self-assembled spiro-type complex [Pd(L)₂](NO₃)₂, **1**, with Pd^{II} as the spiro-atom, was synthesized by the combination of Pd(NO₃)₂ with **L** at a ratio of 1:2 in DMSO (Scheme 1). The clear solution obtained by mixing the participating components was stirred at r.t. for 10 min. Complex **1** was isolated from this solution as a white solid by addition of excess ethyl acetate. In contrast, the double-decker coordination cage [Pd₃(L)₄](NO₃)₆, **2**,

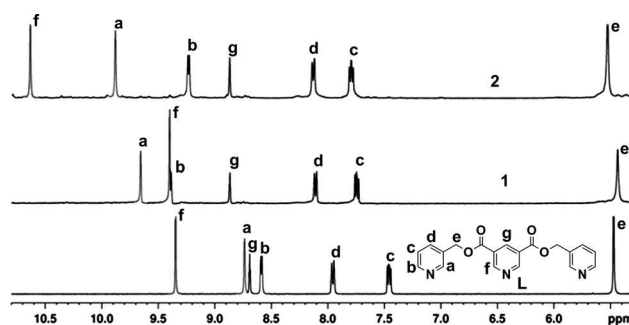


Figure 2. ¹H NMR spectra in [D₆]DMSO (residual solvent as internal standard) for the ligand **L**, [Pd(L)₂](NO₃)₂, **1**, and [Pd₃(L)₄](NO₃)₆, **2**.

was prepared by the combination of Pd(NO₃)₂ with **L** at a ratio of 3:4 in DMSO (Scheme 1). The clear solution was heated at 90 °C for 2 h, and then cooled down to r.t. The cage **2** was precipitated from the solution as a white solid by addition of excess ethyl acetate. The single discrete nature of the complexes were ascertained by recording their ¹H NMR spectra in [D₆]DMSO (Figure 2). The mononuclear Pd₁L₂ (for **1**) and the trinuclear Pd₃L₄ (for **2**) compositions were confirmed by ESI-MS (Figure in Supporting Information).

The ESI-MS spectrum of the pure compound **1** showed a set of peaks at *m/z* = 402.05 assignable to the fragment [1–2NO₃]²⁺ that corresponds to the loss of two nitrate ions from **1**. This set shows the isotopic pattern for a fragment containing one unit of palladium and was found to be in good agreement with the calculated data. The ESI-MS spectrum of compound **2** showed peaks at *m/z* = 982.73, 634.35, and 460.23, which correspond to the fragments [2–2NO₃]³⁺, [2–3NO₃]⁴⁺, and [2–4NO₃]⁵⁺, respectively. The peaks show isotopic patterns for fragments containing three palladium units and are in good agreement with the calculated data.

The appreciable downfield shift of the signals of H_a (Δδ = 0.93 ppm) and H_b (Δδ = 0.81 ppm), and at the same time a very small downfield shift for that of H_f (Δδ = 0.06 ppm), in the ¹H NMR spectrum of compound **1** as compared to the free ligand **L** is noteworthy. This behavior could be considered as a signature for the ligation of the terminal pyridine atoms and free (no ligation) internal pyridine nitrogen atom in complex **1**. This priority of coordination by the terminal pyridine is expected because these pyridines are comparatively electron-rich as compared to the diester-substituted internal pyridine. Furthermore, the ideal metal-to-ligand ratio of 1:2 facilitated the Pd₁L₂ composition. On the other hand, the signals of H_a, H_b, and H_f are all shifted downfield appreciably (Δδ = 1.16, 0.66, and 1.30 ppm, respectively) in complex **2** as compared to the free ligand, indicating the engagement of the terminal as well as the internal pyridine nitrogen atoms for metal–ligand interactions. The calculated electron density at the terminal and internal pyridine nitrogen atoms found by using DFT method (Figure S64 of the Supporting Information) support the observed differential coordination ability of the ligand **L**.^[13] The downfield shift of hydrogen atoms H_g and H_d, located at positions remote from the metal-binding sites, and those of H_c, which are somewhat nearer, are all marginally

downfield shifted for complexes **1** and **2** as compared to ligand **L** ($\Delta\delta$ for H_g , H_d , and H_c = 0.18, 0.15, and 0.29 for **1**; and 0.18, 0.18, and 0.33 for **2**). In fact, the signals of these protons are located in comparable positions for both complexes **1** and **2** with $\Delta\Delta\delta$ of 0.01, 0.02, and 0.04 ppm for H_g , H_d , and H_c , respectively.

The complexation reactions were also carried out in situ by using deuterated DMSO as the solvent system. The quantitative formation of single discrete products was confirmed by changes in the ^1H NMR spectra of the reaction mixtures under appropriate conditions. Although compound **1** self-assembled spontaneously at r.t., the organization of the components to form **2** required either a longer reaction time or elevated temperatures (Figures S24 and S25 of the Supporting Information). When the synthesis of **2** was monitored by recording the ^1H NMR spectra at r.t., initially only **1** was observed as a single product and the unutilized Pd^{II} remained in solution. The reaction mixture was stirred at r.t., giving a mixture of **1** and **2** over time, with additional signals probably corresponding to some intermediate products. Eventually, over a period of 15 days, quantitative formation of **2** was observed. Alternatively, the self-assembly process to build **2** from a mixture of **L** and $\text{Pd}(\text{NO}_3)_2$ could be completed within 2 h when stirred at an elevated temperature of 90°C . The ^1H NMR spectra of the isolated and in situ prepared complexes are found to be closely comparable. Thus, by simple variation of the metal-to-ligand ratios, complexes **1** and **2** could be prepared, amazingly, in a quantitative manner.

Pure compound **1** could also be completely converted to **2** by the addition of $\text{Pd}(\text{NO}_3)_2$ to effect the reorganization of the assemblies. The reorganization of **1** to **2** happened smoothly within 2 h when the mixture was heated at 90°C (Scheme 1, and Figure S26 in the Supporting Information). However, the synthesis of **2** from **1** has no kinetic advantage over its preparation from the subcomponents, that is, the ligand **L** and Pd^{II} . The conversion of the trinuclear cage **2** to the mononuclear cage **1** was also possible when the required amount of the ligand **L** was added to **2** and the solution was stirred at r.t. for 24 h (Scheme 1, Figure S27 in the Supporting Information).

In addition to the positive charges of the metal centers and suitable pocket sizes, the inner walls of the two cavities of the cage **2** are also delineated with several electron deficient pyridine- α protons and hence the cage could be considered as a suitable host for anionic guests. There is a growing demand for the study of molecular recognition/binding of anionic moieties by a variety of host molecules.^[14] It was planned to encapsulate spherical halide ions as guest molecules by combining **2** with $n\text{Bu}_4\text{NX}$ (X = fluoride, chloride, bromide, or iodide). In a typical experiment, a solution of $n\text{Bu}_4\text{NX}$ in $[\text{D}_6]\text{DMSO}$ was added to a solution of **2** in $[\text{D}_6]\text{DMSO}$ in a portion-wise manner. The changes in the ^1H NMR spectra of the system were monitored as a function of the amount of the added guest component. To our satisfaction, one unit of the cage **2** could encapsulate two units of the halide ions, one in each of the two compartments (Scheme 1). Although fluoride, chloride, and bromide are accommodated, no entry was extended to iodide ions. The formation of $[(X)_2\text{C}\text{Pd}_3(\text{L})_4](\text{NO}_3)_4$, **2a–2c** (X =

fluoride, **2a**; chloride, **2b**; bromide, **2c**), is confirmed on the basis of detailed ^1H NMR studies and the single-crystal X-ray structure of $[(\text{Cl})_2\text{C}\text{Pd}_3(\text{L})_4](\text{PF}_6)_4$, **2b'**. Also the ESI-MS of **2b**, **2b'**, and **2c** further supported the claim. All these host–guest complexes were also prepared in DMSO and were precipitated with ethyl acetate. Although **2b** and **2c** could be isolated and characterized, complex **2a** decomposed during isolation. Compound **2b'** was prepared from a solution of **2b** in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ by anion exchange using NH_4PF_6 . The ^1H NMR spectra of **2b** and **2b'** are in fact closely comparable. As a representative case, the required amount of the two reagents, that is, $\text{Pd}(\text{NO}_3)_2$ and $n\text{Bu}_4\text{NCl}$ were added to a solution of **1** in $[\text{D}_6]\text{DMSO}$, where upon compound **2b** was formed within 2 h at 90°C (Scheme 1).

The ^1H NMR data corresponding to the portion-wise addition of halide ions indicated that during the initial stages a mixture of the mono-halide complex $[(X)\text{C}\text{Pd}_3(\text{L})_4](\text{NO}_3)_5$, and the di-halide complex $[(X)_2\text{C}\text{Pd}_3(\text{L})_4](\text{NO}_3)_4$ was formed along with some proportion of unutilized free cage **2**. Upon further addition of the halide components, no free cage remained and a mixture of mono- and di-halide complexes were seen. Subsequently, the reaction mixture showed exclusive formation of the di-halide complex $[(X)_2\text{C}\text{Pd}_3(\text{L})_4](\text{NO}_3)_4$, denoting that some dynamic behavior of the slightly flexible cage occurs with halide encapsulation during the self-assembly process as noted in other systems.^[15] The ^1H NMR spectra of halide encapsulation at each stage of guest addition are given in the Supporting Information (Figures S29, S37, and S47). The final ^1H NMR spectra of the di-halide complexes $[(X)_2\text{C}\text{Pd}_3(\text{L})_4](\text{NO}_3)_4$, **2a–2c**, are shown in Figure 3 along with the NMR spectrum of free

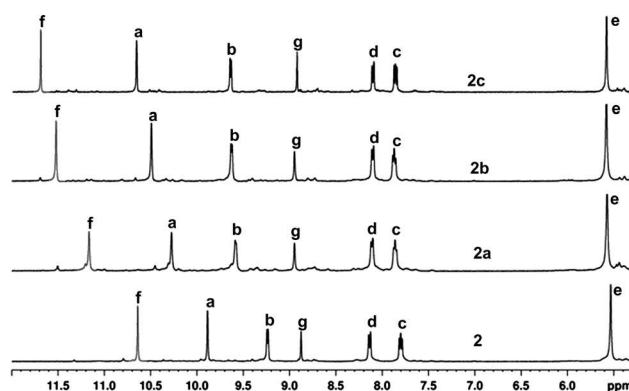


Figure 3. ^1H NMR spectra in $[\text{D}_6]\text{DMSO}$ (residual solvent as internal standard) for **2**, **2a**, **2b**, and **2c** (see the inset in Figure 2 for the designation of protons).

cage **2**. The downfield shift of the relevant protons in the ^1H NMR spectra of the di-halide complexes as compared to the free cage are: **2a** (H_f = 0.51, H_a = 0.38, and H_b = 0.31 ppm); **2b** (H_f = 0.87, H_a = 0.60 and H_b = 0.37 ppm); and **2c** (H_f = 1.05, H_a = 0.77 and H_b = 0.39 ppm) as compared to **2**. The $\Delta\delta$ values observed are quite supportive of guest encapsulation.

The ESI-MS spectrum of compound **2b** showed peak patterns at m/z = 955.67, 616.13, and 446.58, corresponding to the

fragments $[2b-2NO_3]^{2+}$, $[2b-3NO_3]^{3+}$, and $[2b-4NO_3]^{4+}$, respectively. The ESI-MS data for $2b'$ also showed the required peaks at $m/z = 1039.00$, 644.34 , and 446.76 , corresponding to the fragments $[2b'-2PF_6]^{2+}$, $[2b'-3PF_6]^{3+}$, and $[2b'-4PF_6]^{4+}$, respectively. As per theoretical calculations, the two encapsulated chloride ions are retained in the formula of all these fragments. Similarly, compound $2c$ displayed peak patterns at $m/z = 645.99$ and 468.98 , corresponding to the fragments $[2c-3NO_3]^{3+}$ and $[2c-4NO_3]^{4+}$. Here also, the two encapsulated bromide ions are accounted for in the formula of the fragments. The calculated and observed isotopic distribution patterns of the peaks corresponding to the abovementioned fragments are found to be comparable (see the Supporting Information).

Single crystals suitable for data collection from X-ray diffraction (XRD) were obtained for complex **1** (Figure 4 and the Supporting Information) by layering a solution of $Pd(NO_3)_2$ in acetonitrile over a solution of ligand **L** in chloroform. The com-

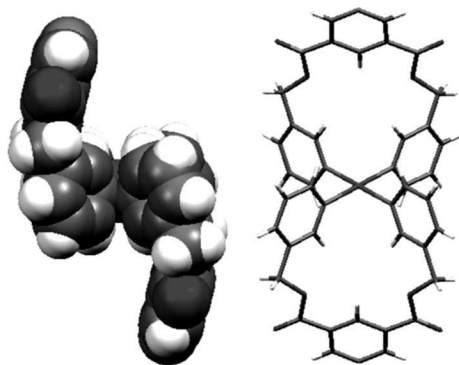


Figure 4. Crystal structure of $[Pd(L)_2](NO_3)_2 \cdot 2CHCl_3$, $1 \cdot 2CHCl_3$. Anions and solvents are omitted for clarity.

pound crystallized as $1 \cdot 2CHCl_3$. The coordination environment of the square-planar Pd^{II} center is completed by two units of the ligand **L**. The ligand adopts a "U-shape" and metallo-macrocyclic rings are formed to create the "spiro-type" complex of Pd_1L_2 formulation. Each of the two strands of the ligand occupy the *cis*-positions of the Pd^{II} center, where the individual ligand loops are oriented in an alternate manner one above and the other below the coordination square plane. The Pd–N bond lengths in the complex are in the range 2.027–2.038 Å, and the *cis*-N–Pd–N bond angles span the range 87.33–92.67°.

Single crystals suitable for data collection by XRD were obtained for $[(Cl)_2CpPd_3L_4](PF_6)_4$, $2b'$ (Figure 5 and the Supporting Information). The crystals of $2b' \cdot n(\text{solvent})$ were grown by slow diffusion of toluene into a DMF solution of $2b'$. The structure showed a double-decker arrangement with two compartments. These compartments lodge one chloride ion in each, whereas the hexafluorophosphate counter anions are located outside the cavity. The Pd–N bond lengths involving the terminal and internal pyridine nitrogen atoms span the ranges 2.013–2.030 and 2.066–2.067 Å, respectively. The *cis*-N–Pd–N bond angles of the two outer Pd^{II} and the lone inner Pd^{II} centers span the ranges 88.83–91.06° and 88.36–91.64°, respec-

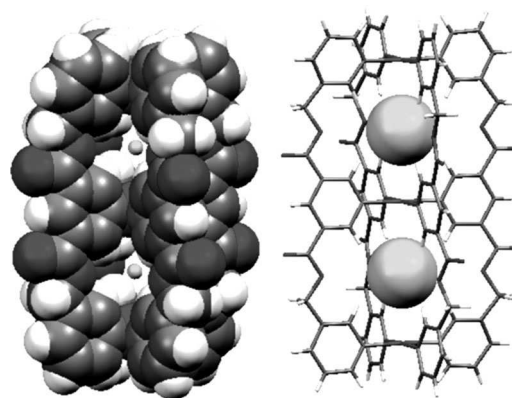


Figure 5. Crystal structure of $[(Cl)_2CpPd_3L_4](PF_6)_4$, $2b'$, depicting chloride encapsulation in the enclosures. The counter anions outside the cavity are omitted for clarity.

tively. The Pd–Pd nonbonded separation in a given compartment and between the two extreme Pd^{II} centers are 6.970 and 13.940 Å, respectively. The encapsulated chloride ions are in short contact with the inwardly pointed protons of the ligand strands (i.e., H_a and H_f as designated in Figure 2) of the double-decker cage. The calculated distances of $H(\text{py})\text{--}Cl$ span the range 2.731–2.807 Å,^[16] which is indicative of a hydrogen-bonding interaction.

In summary, we have demonstrated stoichiometry-controlled self-assembly of a tris-monodentate ligand, **L**, with Pd^{II} to prepare a "spiro-type" complex, $[Pd(L)_2](NO_3)_2$ (**1**) and a "molecular double-decker" coordination cage, $[Pd_3(L)_4](NO_3)_6$ (**2**). Complexes **1** and **2** are interconvertible under suitable conditions when suitable amounts of Pd^{II} or **L** are added. The double-decker cage, **2**, could encapsulate two halide ions (fluoride, chloride, or bromide), one unit in each of the enclosures, with no entry permitted for iodide. In particular, a new avenue is opened by the fresh architecture of **2**. In this context, the design and synthesis of several other double-decker cages and utilization of their isolated cavities is likely to contribute to the progress of supramolecular coordination chemistry.

Acknowledgements

S.B. thanks UGC, India, and the Commonwealth Foundation for fellowships. D.K.C. thanks DST, India (SB/S₁/IC-05/2014), and IIT Madras for financial support. G.S.H. thanks DFAIT, Canada, the NSERC of Canada, and the University of Montreal for financial support. The authors also thank the Shastri Indo-Canadian Institute for financial support covering a visit of D.K.C. to Montreal.

Keywords: anions · metal-to-ligand ratios · molecular double-decker · palladium · self-assembly

[1] a) N. B. Debata, D. Tripathy, D. K. Chand, *Coord. Chem. Rev.* **2012**, *256*, 1831–1945; b) T. R. Cook, Y.-R. Zheng, P. J. Stang, *Chem. Rev.* **2013**, *113*, 734–777; c) M. Han, D. M. Engelhard, G. H. Clever, *Chem. Soc. Rev.* **2014**, *43*, 1848–1860.

- [2] a) L. Pirondini, A. G. Stendardo, S. Geremia, M. Campagnolo, P. Samor, J. P. Rabe, R. Fokkens, E. Dalcanale, *Angew. Chem.* **2003**, *115*, 1422–1425; *Angew. Chem. Int. Ed.* **2003**, *42*, 1384–1387; b) A. Hori, K.-i. Yamashita, T. Kusukawa, A. Akasaka, K. Biradha, M. Fujita, *Chem. Commun.* **2004**, 1798–1799; c) A. Boixassa, J. Pons, X. Solans, M. Font-bardia, J. Ros, *Inorg. Chim. Acta* **2004**, *357*, 827–833; d) H. S. Sahoo, D. Tripathy, S. Chakraborty, S. Bhat, A. Kumbhar, D. K. Chand, *Inorg. Chim. Acta* **2013**, *400*, 42–50; e) M. D. Johnstone, M. Frank, G. H. Clever, F. M. Pfeffer, *Eur. J. Org. Chem.* **2013**, 5848–5853.
- [3] a) D. A. McMorran, P. J. Steel, *Angew. Chem.* **1998**, *110*, 3495–3497; *Angew. Chem. Int. Ed.* **1998**, *37*, 3295–3297; b) H. S. Sahoo, D. K. Chand, *Dalton Trans.* **2010**, 39, 7223–7225; c) D. Tripathy, A. K. Pal, G. S. Hanan, D. K. Chand, *Dalton Trans.* **2012**, *41*, 11273–11275.
- [4] a) D. K. Chand, K. Biradha, M. Fujita, *Chem. Commun.* **2001**, 1652–1653; b) N. L. S. Yue, D. J. Eisler, M. C. Jennings, R. J. Puddephatt, *Inorg. Chem.* **2004**, *43*, 7671–7681; c) G. H. Clever, S. Tashiro, M. Shionoya, *Angew. Chem.* **2009**, *121*, 7144–7146; *Angew. Chem. Int. Ed.* **2009**, *48*, 7010–7012; d) J. D. Crowley, E. L. Gavey, *Dalton Trans.* **2010**, 39, 4035–4037; e) G. H. Clever, W. Kawamura, S. Tashiro, M. Shiro, M. Shionoya, *Angew. Chem.* **2012**, *124*, 2660–2663; *Angew. Chem. Int. Ed.* **2012**, *51*, 2606–2609; f) J. E. M. Lewis, E. L. Gavey, S. A. Cameron, J. D. Crowley, *Chem. Sci.* **2012**, *3*, 778–784; g) M. Han, J. Hey, W. Kawamura, D. Stalke, M. Shionoya, G. H. Clever, *Inorg. Chem.* **2012**, *51*, 9574–9576; h) M. Han, R. Michel, B. He, Y.-S. Chen, D. Stalke, M. John, G. H. Clever, *Angew. Chem.* **2013**, *125*, 1358–1362; *Angew. Chem. Int. Ed.* **2013**, *52*, 1319–1323; i) J. E. M. Lewis, C. J. McAdam, M. G. Gardiner, J. D. Crowley, *Chem. Commun.* **2013**, 49, 3398–3400.
- [5] a) G. H. Clever, S. Tashiro, M. Shionoya, *J. Am. Chem. Soc.* **2010**, *132*, 9973–9975; b) P. Liao, B. W. Langloss, A. M. Johnson, E. R. Knudsen, F. S. Tham, R. R. Julian, R. J. Hooley, *Chem. Commun.* **2010**, 46, 4932–4934; c) G. H. Clever, M. Shionoya, *Chem. Eur. J.* **2010**, *16*, 11792–11796; d) R. Sekiya, R. Kuroda, *Chem. Commun.* **2011**, 47, 12346–12348; e) G. H. Clever, W. Kawamura, M. Shionoya, *Inorg. Chem.* **2011**, *50*, 4689–4691; f) N. Kishi, Z. Li, Y. Sei, M. Akita, K. Yoza, J. S. Siegel, M. Yoshizawa, *Chem. Eur. J.* **2013**, *19*, 6313–6320.
- [6] a) A. M. Johnson, R. J. Hooley, *Inorg. Chem.* **2011**, *50*, 4671–4673; b) J. E. M. Lewis, A. B. S. Elliott, C. J. McAdam, K. C. Gordon, J. D. Crowley, *Chem. Sci.* **2014**, *5*, 1833–1843.
- [7] C. Gütz, R. Hovorka, G. Schnakenburg, A. Lützen, *Chem. Eur. J.* **2013**, *19*, 10890–10894.
- [8] a) N. Kishi, Z. Li, K. Yoza, M. Akita, M. Yoshizawa, *J. Am. Chem. Soc.* **2011**, *133*, 11438–11441; b) Z. Li, N. Kishi, K. Yoza, M. Akita, M. Yoshizawa, *Chem. Eur. J.* **2012**, *18*, 8358–8365.
- [9] a) M. Fukuda, R. Sekiya, R. Kuroda, *Angew. Chem.* **2008**, *120*, 718–722; *Angew. Chem. Int. Ed.* **2008**, *47*, 706–710; b) S. Freye, J. Hey, A. Torras-Galan, D. Stalke, R. Herbst-Irmer, M. John, G. H. Clever, *Angew. Chem.* **2012**, *124*, 2233–2237; *Angew. Chem. Int. Ed.* **2012**, *51*, 2191–2194; c) R. Sekiya, M. Fukuda, R. Kuroda, *J. Am. Chem. Soc.* **2012**, *134*, 10987–10997; d) M. Frank, J. Hey, I. Balcioglu, Y.-S. Chen, D. Stalke, T. Suenobu, S. Fukuzumi, H. Frauendorf, G. H. Clever, *Angew. Chem.* **2013**, *125*, 10288–10293; *Angew. Chem. Int. Ed.* **2013**, *52*, 10102–10106; e) S. Freye, R. Michel, D. Stalke, M. Pawliczek, H. Frauendorf, G. H. Clever, *J. Am. Chem. Soc.* **2013**, *135*, 8476–8479; f) M. Frank, J. M. Dieterich, S. Freye, R. A. Mata, G. H. Clever, *Dalton Trans.* **2013**, 42, 15906–15910; g) M. Frank, L. Krause, R. Herbst-Irmer, D. Stalke, G. H. Clever, *Dalton Trans.* **2014**, 43, 4587–4592.
- [10] a) K. Suzuki, M. Kawano, M. Fujita, *Angew. Chem.* **2007**, *119*, 2877–2880; *Angew. Chem. Int. Ed.* **2007**, *46*, 2819–2822; b) S. Zarra, J. K. Clegg, J. R. Nitschke, *Angew. Chem.* **2013**, *125*, 4937–4940; *Angew. Chem. Int. Ed.* **2013**, *52*, 4837–4840.
- [11] a) M. Scherer, D. L. Caulder, D. W. Johnson, K. N. Raymond, *Angew. Chem.* **1999**, *111*, 1689–1694; *Angew. Chem. Int. Ed.* **1999**, *38*, 1587–1592; b) K. Umemoto, K. Yamaguchi, M. Fujita, *J. Am. Chem. Soc.* **2000**, *122*, 7150–7151; c) D. K. Chand, K. Biradha, M. Kawano, S. Sakamoto, K. Yamaguchi, M. Fujita, *Chem. Asian J.* **2006**, *1*, 82–90; d) I. A. Riddell, M. M. J. Smulders, J. K. Clegg, Y. R. Hristova, B. Breiner, J. D. Thoburn, J. R. Nitschke, *Nat. Chem.* **2012**, *4*, 751–756; e) I. A. Riddell, Y. R. Hristova, J. K. Clegg, C. S. Wood, B. Breiner, J. R. Nitschke, *J. Am. Chem. Soc.* **2013**, *135*, 2723–2733.
- [12] a) S. Hiraoka, T. Yi, M. Shiro, M. Shionoya, *J. Am. Chem. Soc.* **2002**, *124*, 14510–14511; b) S. Hiraoka, K. Harano, M. Shiro, M. Shionoya, *Angew. Chem.* **2005**, *117*, 2787–2791; *Angew. Chem. Int. Ed.* **2005**, *44*, 2727–2731; c) K. Harano, S. Hiraoka, M. Shionoya, *J. Am. Chem. Soc.* **2007**, *129*, 5300–5301; d) N. Kishi, M. Akita, M. Yoshizawa, *Angew. Chem.* **2014**, *126*, 3678–3681; *Angew. Chem. Int. Ed.* **2014**, *53*, 3604–3607.
- [13] a) V. M. Williamson, M. Hegarty, G. Deslongchamps, K. C. Williamson, III, M. J. Shultz, *J. Chem. Educ.* **2013**, *90*, 159–164; b) S. R. Hinze, V. M. Williamson, G. Deslongchamps, M. J. Shultz, K. C. Williamson, D. N. Rapp, *J. Chem. Educ.* **2013**, *90*, 1275–1281.
- [14] a) D. J. Mercer, S. J. Loeb, *Chem. Soc. Rev.* **2010**, *39*, 3612–3620; b) S. Freye, D. M. Engelhard, M. John, G. H. Clever, *Chem. Eur. J.* **2013**, *19*, 2114–2121; c) A. Caballero, F. Zapata, P. D. Beer, *Coord. Chem. Rev.* **2013**, *257*, 2434–2455; d) A. Bessette, S. Nag, A. K. Pal, S. Derossi, G. S. Hanan, *Supramol. Chem.* **2012**, *24*, 595–603.
- [15] A. J. Baer, B. D. Koivisto, A. P. Cote, N. J. Taylor, G. S. Hanan, H. Nierengarten, A. Van Dorsselaer, *Inorg. Chem.* **2002**, *41*, 4987–4989.
- [16] a) J.-F. Ayme, J. E. Beves 1, D. A. Leigh, R. T. McBurney, K. Rissanen, D. Schultz, *Nat. Chem.* **2012**, *4*, 15–20; b) J.-F. Ayme, J. E. Beves 1, D. A. Leigh, R. T. McBurney, K. Rissanen, D. Schultz, *J. Am. Chem. Soc.* **2012**, *134*, 9488–9497.

Received: June 4, 2014

Published online on August 19, 2014