

Metallo-Cryptophanes Decorated with Bis-N-Heterocyclic Carbene Ligands: Self-Assembly and Guest Uptake into a Nonporous Crystalline Lattice

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Supporting Information

ABSTRACT: Pd₃L₂ metallo-cryptophane cages with cyclotrimeratrylene-type L ligands can be stabilized by use of a bis-N-heterocyclic carbene as an auxiliary *cis*-protecting ligand, while use of more common protecting chelating ligands such as ethylenediamine saw a Pd₃L₂ to Pd₆L₈ rearrangement occur in solution. The crystalline Pd₃L₂ complexes act as sponges, taking up 1,2-dichlorobenzene or iodine in a single-crystal-to-single-crystal fashion despite not exhibiting conventional porosity.

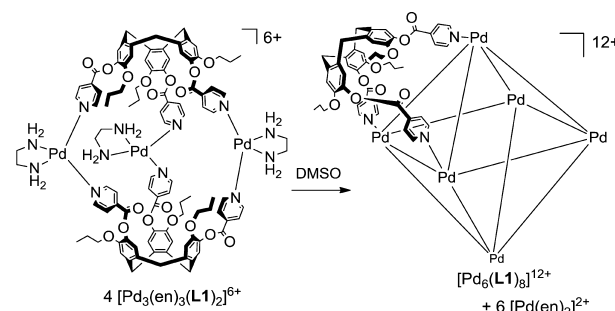
Metallo-cages are discrete 3D polyhedral or prismatic chemical architectures that result from the self-assembly of metal cations with bridging ligands.¹ Cage assemblies have cavities where other molecules may be bound and metallo-cages may behave as nanoscale reaction vessels for chemical applications such as the trapping of reactive species and enabling of unusual reactivities and catalysis.¹ The majority of such studies have been performed in the solution state, however the use of 3D-linked arrays of metallo-cages as solid-state nanovessels is also known.² One of the central tenets in the design of self-assembled metallo-cage species is that the available metal coordination sites can be controlled using a chelating or macrocyclic ligand that will not be easily displaced by bridging monodentate ligands.³ Thus, in complexes such as [Pd(en)(NO₃)₂], where en = ethylenediamine, the square planar Pd(II) is *cis*-protected with two orthogonal binding sites available. Other chelating ligands used for such *cis*-protection include 2,2'-bipyridines and bis-phosphine ligands.¹ We report herein a system where the use of N-donor chelating ligands as *cis*-protection agents fails and introduce instead chelating bis-N-heterocyclic carbene ligands for this purpose.

Our work in metallo-cages focuses on species constructed from chiral tripodal cavitand ligands with a cyclotrimeratrylene scaffold.^{4,5} The simplest of these are M₃L₂ metallo-cryptophanes which are trigonal bipyramidal cages with substantial internal space, first reported by Shinkai and Yamaguchi from the self-assembly of a tris(4-pyridyl)-functionalized cavitand with the *cis*-protected [Pd(PPh₂CH₂CH₂PPh₂)(OTf)₂].⁶ M₃L₂ cages may also form from other classes of tripodal ligands.⁷

The ligands L1–L4 all feature 4-pyridyl donor groups: (±)-L1 and (±)-L2 have been previously reported^{5a,8} and the novel ligands (±)-L3 and (±)-L4 were synthesized from reaction of

cyclotrimeratrylene with the appropriate acid chloride (see SI). Self-assembly of (±)-L1 with [Pd(en)(NO₃)₂] in dimethyl sulfoxide (DMSO) was anticipated to form a [Pd₃(en)₃(L1)₂]⁶⁺ metallo-cryptophane species in accordance with Shinkai and Yamaguchi's work. Initially this was successful. Electrospray mass spectrometry (ES-MS) gave *m/z* peaks at 766.8358 and 1181.2525 corresponding with species {[Pd₃(en)₃(L1)₂]}³⁺ and {[Pd₃(en)₃(L1)₂]}²⁺, respectively. ¹H NMR data were also consistent with formation of the [Pd₃(en)₃(L1)₂]⁶⁺ assembly with a symmetric spectrum showing coordination-induced shifts for L1 and cross-coupling apparent between the en amine and L1 pyridyl (see SI). The [Pd₃(en)₃(L1)₂]⁶⁺ metallo-cryptophane, however, is metastable, and standing the solution at room temperature for 2 weeks results in a complete rearrangement to [Pd₆(L1)₈]¹²⁺ as the metallo-cage species in solution, Scheme 1. We have previously

Scheme 1. Rearrangement of [Pd₃(en)₃(L1)₂]⁶⁺ to [Pd₆(L1)₈]¹²⁺

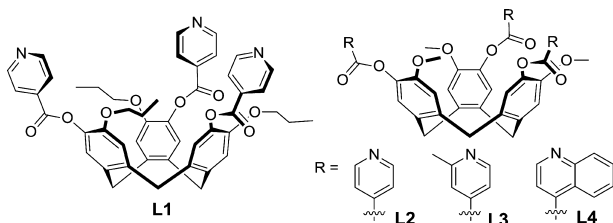


reported [Pd₆(L1)₈]¹²⁺ which has a near spherical, stella octangula architecture,^{5a} whose [Pd₆(L2)₈]¹²⁺ analogue has been shown to bind large surfactant anions.^{5b} Crystallization resulted in isolation of [Pd₆(L1)₈]}¹²⁺·12(NO₃). Similar behavior was observed for L1 with Pd(bpy)(NO₃)₂ (bpy = 2,2'-bipyridine) and with Pt(en)(NO₃)₂. Chand has reported a very similar ligand-exchange process for the trigonal prismatic cage species [Pd₃(en)₃(tpb)₂]⁶⁺ where tpb = 1,3,5-tris(4-pyridylmethyl)benzene.⁹ They reported that heating a DMSO solution of [Pd₃(en)₃(L)₂]⁶⁺ resulted in a complete trans-

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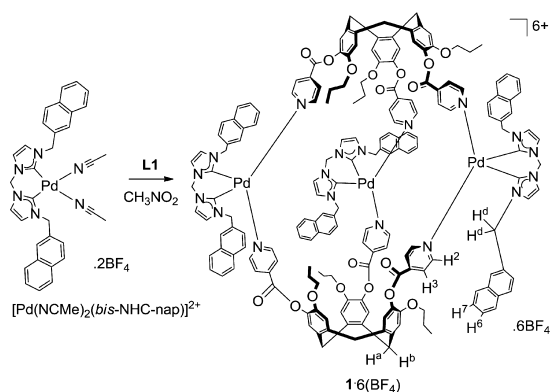
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formation to sphere-like $[\text{Pd}_6(\text{tpb})_8]^{6+}$ and $[\text{Pd}(\text{en})_2]^{2+}$ in solution. These rearrangements may be entropically driven, as there are more cationic species in the rearranged system, and the $[\text{Pd}_6(\text{L1})_8]^{12+}$ species has higher octahedral symmetry consistent with the notions of entropy of symmetry.¹⁰



In order to stabilize the smaller M_3L_2 assembly which features a potential guest binding space more suited to smaller guests, we considered chelating ligands that would be considerably less labile than the N-donor en or bpy, namely bis-N-heterocyclic carbene ligands. Bis-N-heterocyclic carbene ligands are well-known strong σ -donor ligands,¹¹ although their use as protecting ligands for 3D cage assembly has not been previously explored.¹² The palladated precursor $[\text{Pd}(\text{NCMe})_2(\text{bis-NHC-nap})] \cdot 2\text{BF}_4$, where bis-NHC-nap is a 2-naphthylene derived bis-N-heterocyclic carbene, (Scheme 2) was synthesized in three steps from 1,1'-methylenebis-1H-imidazole (see SI).

Scheme 2. Self-Assembly of Cage 1 = $\text{syn-}[\text{Pd}_3(\text{bis-NHC-nap})_3(\text{L1})_2]^{6+}$



Reaction of 3 equiv of $[\text{Pd}(\text{NCMe})_2(\text{bis-NHC-nap})] \cdot 2\text{BF}_4$ with 2 equiv of $(\pm)\text{-L1}$ in nitromethane gives rapid formation of the metallo-cryptophane **1** in solution, Scheme 2, where **1** = $[\text{Pd}_3(\text{bis-NHC-nap})_3(\text{L1})_2]^{6+}$. Peaks in the ES-MS at m/z 848.2383, 1159.9853, and 1783.4759 were attributed to the species $\{1 \cdot 2(\text{BF}_4)\}^{4+}$, $\{1 \cdot 3(\text{BF}_4)\}^{3+}$, and $\{1 \cdot 4(\text{BF}_4)\}^{2+}$ respectively. ^1H NMR in $d_3\text{-MeNO}_2$ showed a slight downfield shift of H^2 of **L1** and significant upfield shift of H^3 from 7.99 to 7.43 ppm. This shielding is indicative of solution-phase $\pi\text{-}\pi$ stacking interactions between the electron-poor and electron-rich π -rings of the pyridyl of **L1** and naphthyl of the bis-NHC-nap groups. The 2D NOESY NMR spectrum shows through space correlation between H^2 of **L1** and one of the diastereotopic H^d protons of the bis-NHC-nap and between H^b of the cyclonatriene core of **L1** and the naphthyl H^6 and H^7 of the bis-NHC-nap ligand. DOSY NMR measurements indicated the presence of a single large species in solution with a hydrodynamic radius of 14.4 Å. Unlike for the metastable $[\text{Pd}_3(\text{en})_3(\text{L1})_2]^{6+}$, there were no changes to the ES-MS and NMR spectra of **1** when

monitored over a time period of several months, and variable temperature NMR measurements indicated no changes to 80 °C.

Comparable reactions of $[\text{Pd}(\text{NCMe})_2(\text{bis-NHC-nap})] \cdot 2\text{BF}_4$ with ligands $(\pm)\text{-L2}$, $(\pm)\text{-L3}$, or $(\pm)\text{-L4}$ led to formation of analogous metallo-cryptophanes species **2** = $[\text{Pd}_3(\text{bis-NHC-nap})_3(\text{L2})_2]^{6+}$, **3** = $[\text{Pd}_3(\text{bis-NHC-nap})_3(\text{L3})_2]^{6+}$, and **4** = $[\text{Pd}_3(\text{bis-NHC-nap})_3(\text{L4})_2]^{6+}$. The inherent chirality of ligands **L1**–**L4** means that chiral *anti* enantiomers and the achiral *syn* diastereomer of metallo-cryptophanes may be formed. The ^1H NMR spectra are indicative of a single isomer in solution, identified as the *syn* metallo-cryptophane from single crystal X-ray structures.

Single crystals of **1**·6(BF_4)·8(CH_3NO_2), **2**·6(BF_4)·8(CH_3NO_2), **3**·6(BF_4)·8(CH_3NO_2), and **4**·6(BF_4)·8(CH_3NO_2) were grown by diffusion of diethyl ether into nitromethane solutions of $[\text{Pd}(\text{NCMe})_2(\text{bis-NHC-nap})] \cdot 2\text{BF}_4$ with the appropriate ligand. The complexes are isostructural, each crystallizing in a hexagonal unit cell with their structures being solved in space group $P6_3/m$. The data obtained for **4**·6(BF_4)·8(CH_3NO_2) were of poor resolution, hence a full structure will not be presented. The cationic cage **2** of **2**·6(BF_4)·8(CH_3NO_2) is shown in Figure 1 and contains both **L2** enantiomers. As

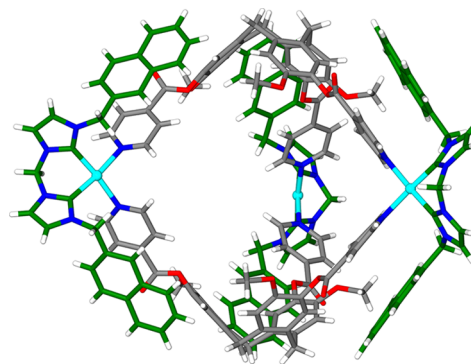


Figure 1. Metallo-cage **2** (= $\text{syn-}[\text{Pd}_3(\text{bis-NHC-nap})_3(\text{L2})_2]^{6+}$) from the crystal structure of **2**·6(BF_4)·8(CH_3NO_2). Carbon atoms of the bis-NHC-nap ligands are shown in green. A second disorder position of the Me group of **L2** is not shown for clarity.

anticipated, each Pd(II) center is coordinated by the chelating bis-NHC-nap ligand with Pd–C distance 1.972(9) Å and by a pyridyl group from each of two symmetry related and enantiomeric **L2** ligands at Pd–N distance 2.107(9) Å. Each **L2** ligand coordinates to all three Pd(II) centers of the metallo-cryptophane. Each naphthyl group of the bis-NHC-nap ligands forms face-to-face $\pi\text{-}\pi$ stacking interactions with a pyridyl group of **L2** at ring centroid separation 3.50 Å. The structures of cage **1** in **1**·6(BF_4)·8(CH_3NO_2) and of cage **3** in **3**·6(BF_4)·8(CH_3NO_2) are essentially the same, although the *iso*-nicotinoyl groups of **L1** are disordered across two positions. In all cases, the **L** ligands align with the naphthyl groups, and the closest $\text{H}\cdots\text{H}$ distances between them in the crystal structures are consistent with the upfield NMR chemical shifts and observed NOE's of the $[\text{Pd}_3(\text{bis-NHC-nap})_3(\text{L})_2]^{6+}$ complexes in solution. Hence the solution- and solid-state structures of the metallo-cryptophane are the same.

The crystal lattice for complex **2**·6(BF_4)·8(CH_3NO_2) is shown in Figure 2. Two BF_4^- anions form second-sphere interactions to Pd(II) at Pd(II) \cdots F separations 3.11 and 3.38 Å. A further BF_4^- anion forms multiple B–F \cdots H–C hydrogen-bonding interactions to the backbone imidazole protons of the bis-NHC-nap

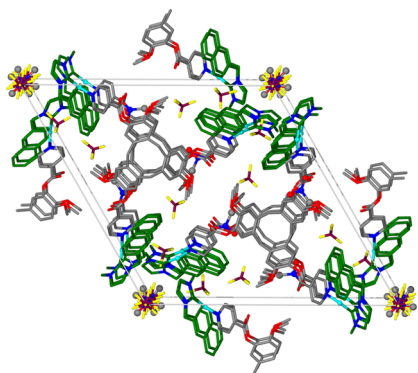


Figure 2. Unit cell of $2\cdot 6(\text{BF}_4)\cdot 8(\text{CH}_3\text{NO}_2)$. CH_3NO_2 molecules shown in ball-and-stick. CH_3NO_2 molecules not located in the structure are assumed to occupy the cage cavities.

ligands of six cages (see SI). Crystallization of the metallo-cryptophane cations did not occur with counter-anions PF_6^- , NO_3^- , ClO_4^- , nor ReO_4^- in place of BF_4^- . Thermogravimetric analysis (TGA) of $1\cdot 6(\text{BF}_4)\cdot 8(\text{CH}_3\text{NO}_2)$ indicates the lattice contains eight molecules of nitromethane per cage, with only four located crystallographically, and none of these are inside the cage. The interior cavity of the cage is 697 \AA^3 , which is sufficient space for the additional solvent to reside inside. This has been taken as the level of solvation for all the isostructural complexes.

Suspension of crystals of $1\cdot 6(\text{BF}_4)\cdot 8(\text{CH}_3\text{NO}_2)$ in 1,2-dichlorobenzene leads to the uptake of 1,2-dichlorobenzene by the crystal lattice despite there being no sizable channels apparent. Crystals were suspended in 1,2-dichlorobenzene for 2 weeks, isolated, washed thoroughly with diethyl ether, and air-dried. ^1H NMR of the crystals redissolved in CD_3NO_2 clearly shows the presence of 1,2-dichlorobenzene and the intact cage **1** in an approximate 3:1 ratio. Similar experiments with crystals of $1\cdot 6(\text{BF}_4)\cdot 8(\text{CH}_3\text{NO}_2)$ that had been heated under vacuum prior to submersion gave similar levels of uptake by NMR. EDX analysis of the crystals also gives a Pd:Cl ratio that is consistent with three molecules of 1,2-dichlorobenzene per cage **1**. TGA is consistent with fewer nitromethane molecules in the lattice compared with the parent $1\cdot 6(\text{BF}_4)\cdot 8(\text{CH}_3\text{NO}_2)$, again supporting solvent exchange of 1,2-dichlorobenzene.

This process occurs in a single crystal-to-single crystal (SCTSC) fashion, and the crystal structure of the daughter complex $1\cdot 6(\text{BF}_4)\cdot 5(\text{CH}_3\text{NO}_2)\cdot 3(\text{C}_6\text{H}_4\text{Cl}_2)$ is isomorphic with the parent complex $1\cdot 6(\text{BF}_4)\cdot 8(\text{CH}_3\text{NO}_2)$. Positions of the absorbed 1,2-dichlorobenzene molecules were located in the crystal structure, and the $[\text{Pd}_3(\text{en})_3(\text{L1})_2]^{6+}$ cage is fully ordered. The 1,2-dichlorobenzene molecules show a 2-fold disorder and are not located inside the metallo-cryptophane but rather in three equivalent positions in the equatorial region outside the cage, Figure 3. The Cl moieties are directed into clefts bounded by pyridyl and propyl groups of two **L1** ligands with closest Cl...C separations ~ 3.28 and 3.37 \AA . One CH_3NO_2 position can be established in the crystal structure and is located in a pocket created by bis-imidazolyl moieties of three adjacent $[\text{Pd}_3(\text{bis-NHC-nap})_3(\text{L1})_2]^{6+}$ cages; solvent was also located in this position in the parent crystal. The presence of four additional CH_3NO_2 per cage was established by TGA, and these are assumed to occupy the internal cavity of the metallo-cryptophane, notably this is the same degree of additional intracage solvation estimated from the TGA of the parent complex $1\cdot 6(\text{BF}_4)\cdot 8(\text{CH}_3\text{NO}_2)$.

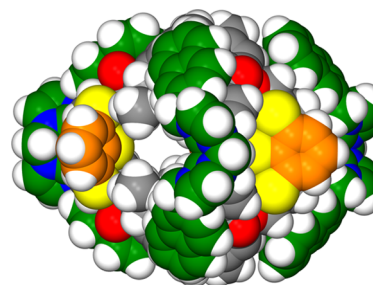


Figure 3. From the crystal structure of $1\cdot 6(\text{BF}_4)\cdot 5(\text{CH}_3\text{NO}_2)\cdot (\text{C}_6\text{H}_4\text{Cl}_2)$ showing disordered 1,2-dichlorobenzene (carbon atoms in orange) *exo* to cage **1**.

The crystalline complex $2\cdot 6(\text{BF}_4)\cdot 8(\text{CH}_3\text{NO}_2)$ also exhibits guest uptake behavior in a SCTSC fashion. Dichlorobenzene uptake was observed by NMR as for $1\cdot 6(\text{BF}_4)\cdot 8(\text{CH}_3\text{NO}_2)$, but the resultant crystals were poorly diffracting, and a crystal structure could not be established. Crystals of $2\cdot 6(\text{BF}_4)\cdot 8(\text{CH}_3\text{NO}_2)$ were soaked in an ethereal solution of iodine for a week to give complex $2\cdot 6(\text{BF}_4)\cdot (\text{H}_2\text{O})\cdot 3(\text{I}_2)$. The level of I_2 uptake was taken from EDX measurements, and Raman spectroscopy was consistent with the presence of iodine species (see SI).¹³ Iodine uptake into a solid-state matrix has relevance in nuclear fuel reprocessing and has been reported with framework materials such as metal-organic frameworks (MOFs)¹⁴ and, more rarely, in porous molecular crystals.¹⁵ The single crystal structure of $2\cdot 6(\text{BF}_4)\cdot (\text{H}_2\text{O})\cdot 3(\text{I}_2)$ is isomorphic with the parent complex. There are three crystallographically distinct and partially occupied sites modeled as included I_2 , Figure 4. One

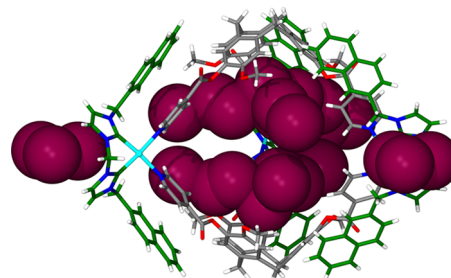


Figure 4. From the crystal structure of complex $2\cdot 6(\text{BF}_4)\cdot (\text{H}_2\text{O})\cdot 3(\text{I}_2)$ showing positions of partially occupied and disordered iodine (shown in space-filling) *exo* and *endo* to the metallo-cryptophane.

partially occupied I_2 molecule is disordered across a 3-fold rotation axis and sits within the tribenzo[*a,d,g*]cyclononatriene cavity of ligand **L2** with each position nearly parallel with an aryl ring at a $\text{I}_2\cdots\text{aryl ring centroid}\cdots\text{centroid}$ separation of 4.197 \AA . This is very similar to $\text{I}_2\cdots\text{aryl}$ separations observed from the uptake of I_2 by a cadmium triazole MOF.^{14a} The parent crystals also absorb iodine from the vapor phase, although at much lower levels of uptake of ~ 1 molecule of I_2 which is absorbed into a lattice rather than intracage site (see complex $2\cdot 6(\text{BF}_4)\cdot (\text{I}_2)$ in SI). The crystals of $2\cdot 6(\text{BF}_4)\cdot (\text{H}_2\text{O})\cdot 3(\text{I}_2)$ do not decolorize on soaking in methanol or diethyl ether or on heating under vacuum at $80 \text{ }^\circ\text{C}$ for 30 min, which removes any surface I_2 deposition. This is consistent with previously reported MOF systems that retain I_2 within their pores on heating.^{14b}

While the crystal lattices contain rigid, although solvent filled, spaces of the metallo-cryptophane, the lattice structure is nonporous. This is because it contains no infinite channels linking these spaces, and gas sorption studies of activated $2\cdot$

6(BF₄) do not show the profiles typical of a material with significant conventional permanent porosity.¹⁶ Permanent porosity and concomitant guest exchange and sorption behavior is well-established for materials, such as MOFs where there are 3D channels in the lattice, and for some coordination cages.¹⁷ There has been considerably less attention, however, directed toward the ability of seemingly nonporous 0D structures to absorb guests as reported here. Atwood, Barbour et al. have shown that nonporous crystals of *p*-tert-butylcalix[4]arene can uptake guests by cooperative van der Waals confinement.¹⁸ Barbour has also reported that an apparently nonporous crystalline lattice of a metallacycle can absorb gaseous guests,¹⁹ and Cooper has demonstrated that Xe and Ra can diffuse through a robust lattice of organic cages despite windows between the cage pores being smaller than the diameter of the gases.²⁰ Interestingly, preliminary experiments also showed a moderate uptake of Xe by complex 2·6(BF₄), which was more pronounced than uptake of the smaller Kr (see SI). Small organic cryptophanes are well-known for binding Xe in solution,²¹ but there are fewer reports of this for molecular materials in the solid state.

In conclusion, we have demonstrated the use of a bis-N-heterocyclic carbene as a *cis*-protecting ligand for the self-assembly of metallo-cages for the first time. The use of the bis-NHC stabilized an otherwise unstable assembly and bis-NHC ligands offers considerably more scope for further *exo* functionalization of these and other metallo-cages than do more commonly used *cis*-protecting ligands. The [Pd₃(bis-NHC-*nap*)₃(L)₂]⁶⁺ cages form as a single *syn* isomer, and examination of the crystal structure indicates that this is likely to be due to the naphthyl groups locking the structure in place through π - π stacking interactions. Despite the apparent nonporosity of the [Pd₃(bis-NHC-*nap*)₃(L)₂]⁶⁺·6(BF₄) crystal structures, the materials are able to absorb the guests dichlorobenzene or molecular I₂. Unlike conventionally porous organic cages,^{17b} once absorbed, the I₂ cannot be easily extracted from the lattice, indicating that these materials have potential as sequestering agents for radioactive I₂. Furthermore, preliminary results indicate an enhanced binding of Xe over Kr, suggesting potential for separations as has recently been demonstrated for a porous lattice of organic cage molecules.²⁰

■ ASSOCIATED CONTENT

■ Supporting Information

Full experimental procedures, spectra, TGA traces, and crystallography. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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