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Self-Assembly of Nanoscopic Coordination Cages Using a Flexible Tripodal Amide Containing Linker

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Flexible, nanoscopic 3D cages containing the amide functionality were prepared via coordination-driven self-assembly from palladium(II) based 90° ditopic acceptor units and a tripod *N*,*N*′,*N*″-tris(3-pyridyl)trimesic amide. Both cages were characterized by NMR (^{31}P, ^{1}H) and electrospray ionization mass spectrometry. An MM2 force field simulation of one cage showed that the shape is likely pseudo trigonal bipyramidal with the diameter of the inner cavity of the cage about 1.9 nm.

Introduction

Formation of discrete, supramolecular entities via coordination-driven self-assembly is an advanced area of investigation at the forefront of supramolecular chemistry.[1] Square planar platinum(II) and palladium(II) have long been the favorite metals in this area. A wide variety of 2D and 3D architectures have been reported with these metals.[1a−c,e,k] Much of this chemistry has been based on the use of rigid linkers to control the geometry and symmetry of the final ensembles.[1] This type of ligand usually maintains bonding directionality. The use of flexible donor linkers is less common in the construction of Pt(II) and Pd(II) self-assemblies.[2] Flexible organic components are generally less predictable during self-assembly and have a tendency to generate catenanes, helicates, or oligomeric product upon their reactions with metals.[2e−i] Incorporating flexible spacers in supramolecular systems may generate flexible ensembles in which the bridging ligands could potentially obtain a more thermodynamically stable conformation for host−guest interactions. Moreover, introduction of functionality in the nanostructure to guide the properties of the resulting ensembles is of current interest. For example, Lewis base receptor sites,[3] porphyrin,[4] and calixarene[5] units among others have been incorporated into self-assemblies. However, incorporation of an amide function in Pt(II)- and Pd(II)-based finite assemblies is rare. Only a few 2D examples were reported recently.[6] The amide functional group can form strong H-bonds (both H-bonding acceptor and donor group); thus, the assemblies may be templated with a guest molecule to form discrete species even with flexible linkers. Hence, it was of interest whether the self-assembly of flexible, amide-containing donors with the readily available, widely employed, Pd(II) and Pt(II) acceptor units would afford discrete supramolecular assemblies.

To introduce both the amide functionality and flexibility into supramolecular ensembles we have selected *N*,*N*′,*N*″-tris(3-pyridyl)trimesic amide (**1**) as a tritopic donor linker in combination with Pd(II)-based 90° acceptor units (**2**) to construct 3D pseudo trigonal bipyramidal cages (**3**). Characterization of these newly synthesized cages was achieved with NMR (^{31}P and ^{1}H), IR, and ESI-mass spectrometry.

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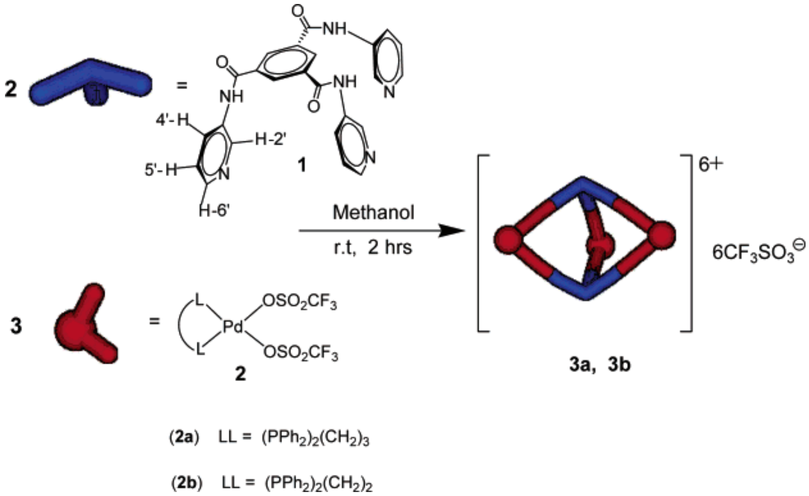
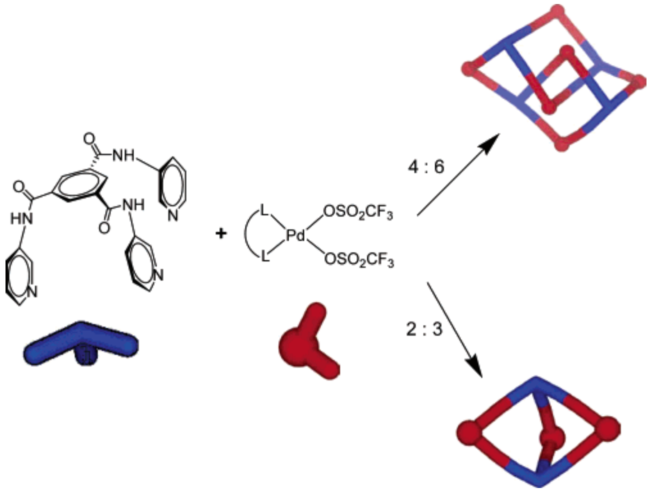
SCHEME 1. Self-Assembly of Flexible Molecular Trigonal Bipyramidal Cages 3



SCHEME 2. Self-Assembly of Trigonal Bipyramid and/or Double Square



Result and Discussion

The formation of 3-D cages **3** is shown in Scheme 1. They are prepared via self-assembly from a 2:3 combination of tripodal angular unit (**1**) and 90° angular units such as *cis*-Pd(dppp)(OTf)$_2$ (**2a**) and *cis*-Pd(dppe)(OTf)$_2$ (**2b**). However, there is also the possibility of forming double squares when reacting tripod linkers and 90° ditopic units in a 2:3 ratio as shown by Fujita et al. (Scheme 2).[7a] The double square and trigonal bipyramid can be easily distinguished by NMR spectroscopy. For a double square, two signals (1:2 ratio) appear in the ^{31}P NMR spectrum due to the presence of two inequivalent phosphorus nuclei.[7a] In the case of a trigonal bipyramid, only a single peak is expected as all phosphorus nuclei are equivalent.[7b] Moreover, a double square is formed by the combination of four tritopic and six ditopic units. Hence, the molecular weight of a trigonal bipyramidal cage will be half of that of a double square. Thus, these two possible geometries can also be distinguished by mass spectrometry.

The self-assembly was performed in methanol solution at room temperature for 2 h. The resulting colorless, microcrystalline precipitates were isolated and identified as the products **3**. The ^{31}P spectrum of each assembly displayed a sharp singlet (13. 7 ppm **3a**, 67.0 ppm **3b**) shifted upfield from the starting 90° linkers by 6−7 ppm, indicating the formation of a single, highly symmetrical species. The shift of these phosphorus signals is an indication of nitrogen-to-palladium coordination.[8] The ^{1}H NMR spectra of these cages are also indicative of symmetrical structures and displayed spectroscopic differences from the precursor building blocks. Satisfactory elemental analyses of **3a**,**b** as the triflate salts was obtained. Attempts to prepare the corresponding Pt(II) complexes were unsuccessful; only an intractable mixture of compounds including oligomers was obtained. The stronger Pt−N bond compared to the Pd−N bond, the poor kinetic lability of Pt(II), as well as the larger radius of Pt(II) compared to Pd(II) may be responsible for the formation of a mixture of products in the case of Pt(II) rather than a single, discrete product. More specifically, the stronger Pt−N dative bond makes reversibility and “self-healing” less likely than in the case of the weaker Pd−N bond.

In the IR spectrum of each cage, absorptions arising from the amide group were observed. The carbonyl stretching frequency of the starting **1** appeared at 1675 cm^{-1}, whereas the corresponding cages showed the carbonyl absorption at 1692 cm^{-1} for **3a** and 1689 cm^{-1} for **3b**. This shift of the C═O to higher frequency is consistent with complexing of **1** and the loss of electron density from this ligand to the Pd metal via the dative Pd−N bond.

Electrospray ionization mass spectrometry has proven to be an indispensable tool in the corroboration of structural assignments for self-assembled aggregates of this nature.[9] The ESI-mass spectrum of **3a** (Figure 1) showed signals attributable to the consecutive loss of triflate counterions, [M − OTf]$^+$, [M − 2OTf]$^{2+}$, and [M − 3OTf]$^{3+}$. The ESI-mass spectrum for **3a** is presented

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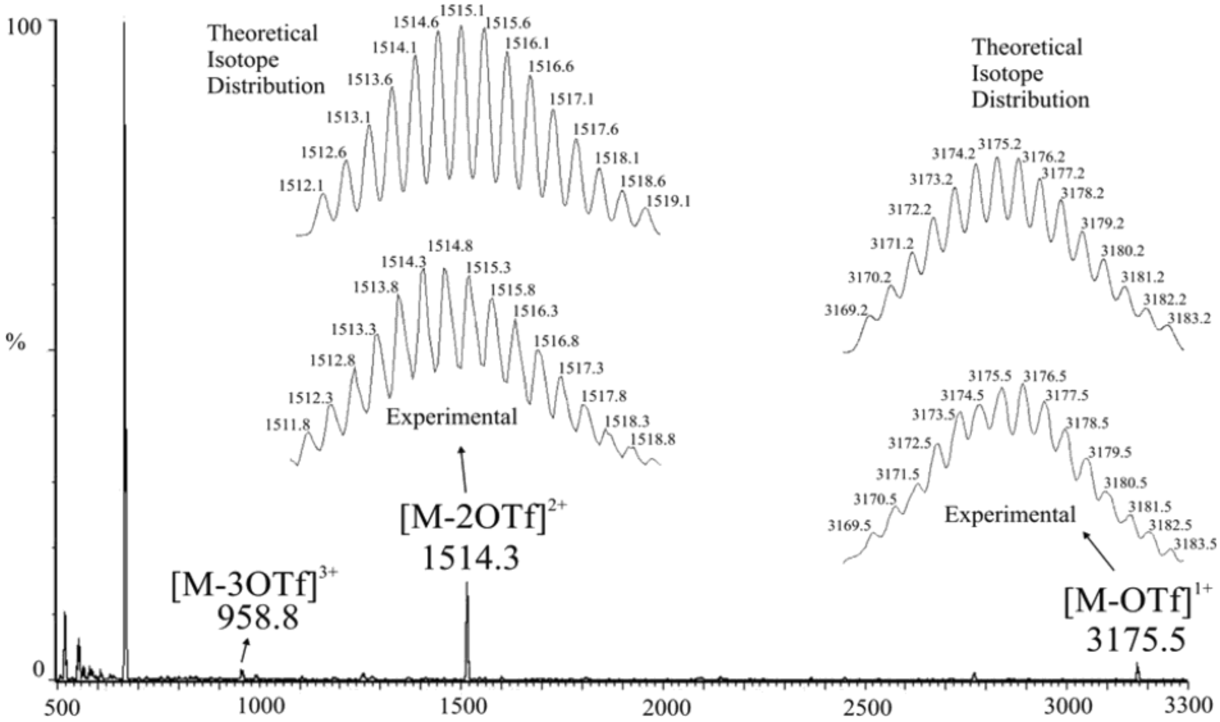

FIGURE 1. ESI-mass spectrum of the assembly **3a**.

in Figure 1. For **3a**, [M − OTf]$^+$ [m/z = 3175.5 (calcd 3175.4)], [M − 2OTf]$^{2+}$ [m/z = 1514.3 (calcd 1513.2)], and [M − 3OTf]$^{3+}$ [m/z = 958.8 (calcd 959.1)], where M represents the intact trigonal bipyramidal cage with six triflate counterions, were detected. The [M − OTf]$^+$ and [M − 2OTf]$^{2+}$ peaks were isotopically resolved and match the theoretical distribution very well (Figure 1). Similarly for **3b**, [M − 2OTf]$^{2+}$ [m/z = 1492.6 (calcd 1491.6)], and [M − 3OTf]$^{3+}$ [m/z = 945.8 (calcd 945.1)] peaks were observed. The former was isotopically resolved and matches the theoretical distribution.[10] The multinuclear NMR and physical data of each assembly are consistent with the trigonal bipyramidal structure (**3**).

As suitable X-ray quality crystals for **3** could not be obtained, MM2 force field simulations[11] were employed to visualize the shape and size of **3a**. The simulated structure of cage **3a** represents a pseudo trigonal bipyramidal shape (Figure 2). The internal cavity size is 1.9 nm as measured by the Pd−Pd distance. No hydrogen bonding was found between the amide groups in the cage.

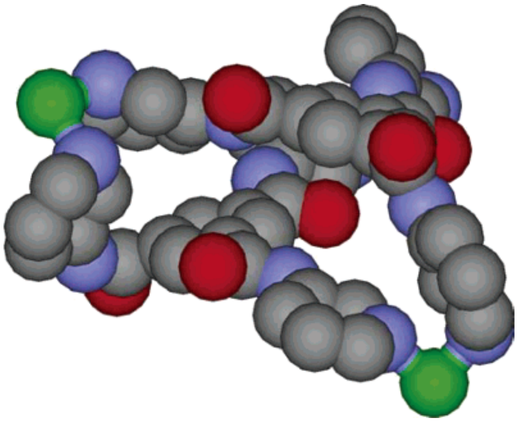

FIGURE 2. MM2 force field simulation of trigonal bipyramidal cage **3a** (C = gray, O = red, N = blue, Pd = green). Phosphine ligands are omitted for clarity.

In conclusion, we report the first finite, nanoscopic Pd(II)-based self-assembled 3D cages incorporating both an amide functionality and flexibility using ligand **1**. Despite its ability to form oligomeric products by varying its bonding directionality, ligand **1** prefers to self-assemble into closed discrete ensembles. This provides further evidence of thermodynamic control favoring formation of discrete entities over oligomeric networks. Among the two possible discrete geometries, the exclusive formation of trigonal bipyramidal cages **3a** and **3b**, instead of the larger double squares is presumably controlled by entropy factors.[12] The use of carboxamide containing flexible linkers in conjugation with Pd(II)- or Pt(II)-acceptor units and formation of flexible ensembles has the potential to expand the directional bonding paradigm in self-assembly.

Experimental Section

Methods and Materials. (dppp)Pd((OTf)$_2$ **2a**,[13] (dppe)Pd(H_2O)$_2$(OTf)$_2$ **2b**,[14] and N,N',N''-tris(3-pyridyl)trimesic amide **1**[15] were all prepared as previously reported. The $^{31}P\{^1H\}$ chemical shifts are reported relative to an external, unlocked sample of H_3PO_4 (δ 0.0 ppm). IR spectra were recorded in KBr pellets. The mass spectra were obtained under electrospray

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[10] See the Supporting Information.

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ionization conditions using a dichloromethane and methanol (1:3) mixture solution of the products **3**.

General Procedures for the Preparation of Cages 3. To a 2 mL methanol solution containing 4.380 mg (0.010 mmol) of amide linker **1** was added a methanol solution (2 mL) of either **2a** or **2b** (0.015 mmol) drop-by-drop with continuous stirring. The colorless microcrystalline products (**3**), which precipitated after 2 h of stirring, were filtered and washed with ether.

3a. Yield: 97%. Mp: 242−245 °C dec. Anal. Calcd for $C_{135}H_{114}F_{18}N_{12}O_{24}P_6Pd_3S_6$: C, 48.72; H, 3.450; N, 5.050. Found: C, 48.53; H, 3.770; N, 4.710. $^{31}P\{^1H\}$ NMR (DMSO-d_6, 121.4 MHz): δ 13.7 (s). ^1H NMR (DMSO-d_6, 300 MHz): δ 10.9 (s, 6H, NH), 9.06 (d, 6H, H-2′), 8.86 (s, 6H, H-2,4,6), 8.40 (d, 6H, H-6′), 8.31 (d, 6H, H-4′), 7.80 (m, 24H, phenyl-P H-2,6), 7.55 (m, 42H, phenyl-P H-3,4,5 plus H-5′), 2.70 (m, 12H, CH_2-P), 1.74 (m, 6H, CH_2CH_2-P). IR (KBr): ν(C═O) 1692 cm^{-1}; ν(NH) 3082 cm^{-1}.

3b. Yield: 95%. Mp: 308−310 °C dec. Anal. Calcd for $C_{132}H_{108}F_{18}N_{12}O_{24}P_6Pd_3S_6$: C, 48.25; H, 3.31; N, 5.120. Found: C, 48.62; H, 3.670; N, 4.820. $^{31}P\{^1H\}$ NMR (DMSO-d_6, 121.4 MHz): δ 67.0 (s). ^1H NMR (DMSO-d_6, 300 MHz): δ 10.9 (s, 6H, NH), 9.00 (d, 6H, H-2′), 8.80 (s, 6H, H-2,4,6), 8.36 (d, 6H, H-6′), 8.23 (d, 6H, H-4′), 7.87 (m, 24H, phenyl-P H-2,6), 7.55 (m, 36H, phenyl-P H-3,4,5), 7.42 (m, 6H, H-5′), 2.68 (broad d, 12H, CH_2-P). IR (KBr): ν(C═O) 1689 cm^{-1}; ν(NH) 3080 cm^{-1}.

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Supporting Information Available: ^{31}P and ^1H NMR spectra of **3a** and **3b** (four figures), ESI-mass spectrum of **3b** (one figure). This material is available free of charge via the Internet at http://pubs.acs.org.

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