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Metal-Directed Formation of Three-Dimensional M_3L_2 Trigonal-Bipyramidal Cages

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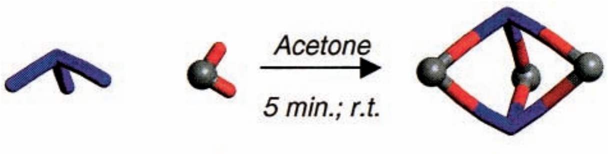
ABSTRACT



1 **2** **3**

The simple combination of two angular tritopic pyridine donor linkers (109° bond angle) with three ditopic platinum acceptors (90° bond angle) leads to essentially quantitative formation of self-assembled M_3L_2 trigonal-bipyramidal (TBP) supramolecular species.

Metal-directed supramolecular self-assembly is a rapidly growing field, and recent years have witnessed enormous research activity in this area.[1] This methodology has allowed the preparation of structurally well-defined grids, honeycombs, and cages.[1] Among these, cages have attracted much attention as a result of their important properties such as molecular recognition, inclusion phenomena, and catalysis.[2]

In metal-directed self-assembly, the simple combination of tritopic linkers with ~90° linkers in a 2:3 ratio is known to give either "double squares" or M_3L_2 cage molecules depending upon the size, bond angles, and rigidity of the building blocks.[3−7] For example, treatment of the *rigid* tris-4-pyridylmethane (tritopic 109° linker) with metal containing ~90° acceptor linkers is known to give a double-square.[3] Likewise, a variety of flexible tritopic linkers with metal complexes of Pd,[4,5] Zn,[6] and Ag[7] resulted in the formation of M_3L_2 cages. However, there is no report on the preparation of M_3L_2 cages using tritopic 109° linkers. Herein, we report the synthesis of a new tritopic linker **1** and the preparation of unique platinum containing trigonal bipyramidal (TBP) structure **3** via self-assembly.

The tritopic pyridine linker **1** was prepared as shown in Scheme 1. The tribromoadamantane[8] **4** was treated with vinyl bromide and $AlCl_3$, followed by reaction with $KOBu^t$ in

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(1) (a) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (b) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*(11), 975. (c) Chambron, J.-C.; Dietrich-Buchecker, C.; Sauvage, J.-P. Transition Metals as Assembling and Templating Species. In *Comprehensive Supramolecular Chemistry*; Lehn, J.-M., Chair Ed., Atwood, J. L., Davis, J. E. D., MacNicol, D. D., Vögtle, F., Exec. Eds., Pergamon Press: Oxford, 1996; Vol. 9, Chapter 2, p 43. (d) Baxter, P. N. W. Metal Ion Directed Assembly of Complex Molecular Architectures and Nanostructures. In *Comprehensive Supramolecular Chemistry*; Lehn, J.-M., Chair Ed., Atwood, J. L., Davis, J. E. D., MacNicol, D. D., Vögtle, F., Exec. Eds., Pergamon Press: Oxford, 1996; Vol. 9, Chapter 5, p 165. (e) Fujita, M. *Chem. Soc. Rev.* **1998**, *6*, 417. (f) Saalfrank, R. W.; Bernt, I.; Uller, E.; Hampel, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2482. (g) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502.

(2) (a) Fujita, M.; Ogura, D.; Miyazawa, M.; Oka, H.; Yamaguchi, K.; Ogura, K. *Nature* **1995**, *378*, 469. (b) Cram, D. J.; Cram, J. M. *Container Molecules and Their Guests*; Royal Society of Chemistry: Cambridge, 1994. (c) Meissner, R. S.; Mendoza, J. D.; Rebek, J. *Science* **1995**, *270*, 1485. (d) Kang, J.; Rebek, J. *Nature* **1997**, *385*, 50.

(3) Fujita, M.; Yu, S.-Y.; Kusukawa, T.; Funaki, H.; Ogura, K.; Yamaguchi, K. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2082.

(4) Ikeda, A.; Udzu, H.; Zhong, Z.; Shinkai, S.; Sakamoto, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **2001**, *123*, 3872.

(5) (a) Fujita, M.; Fujita, N.; Ogura, K.; Yamaguchi, K. *Nature* **1999**, *400*, 52. (b) Hiraoka, S.; Fujita, M. *J. Am. Chem. Soc.* **1999**, *121*, 10239. (c) Fujita, M.; Nagao, S.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 1649.

(6) Liu, H.-K.; Sun, W.-Y.; Ma, D.-J.; Yu, K.-B.; Tang, W.-X. *J. Chem. Soc., Chem. Commun.* **2000**, 591.

(7) Sun, W.-Y.; Fan, J.; Okamura, T.; Xie, J.; Yu, K. B.; Ueyama, N. *Chem. Eur. J.* **2001**, *7*, 2557.

(8) Stang, P. J.; Cao, D. H.; Saito, S.; Arif, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 6273.

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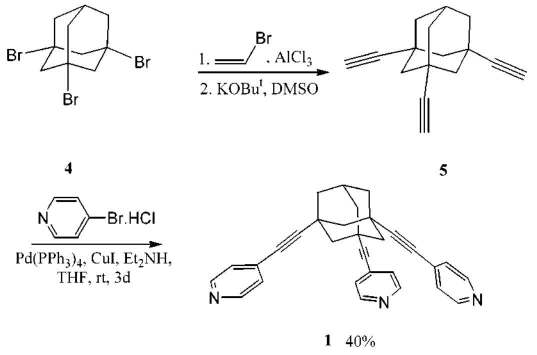
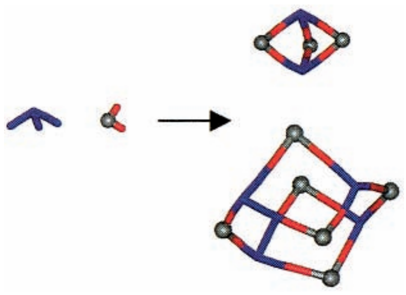
Scheme 1. Preparation of Tritopic Linker **1**



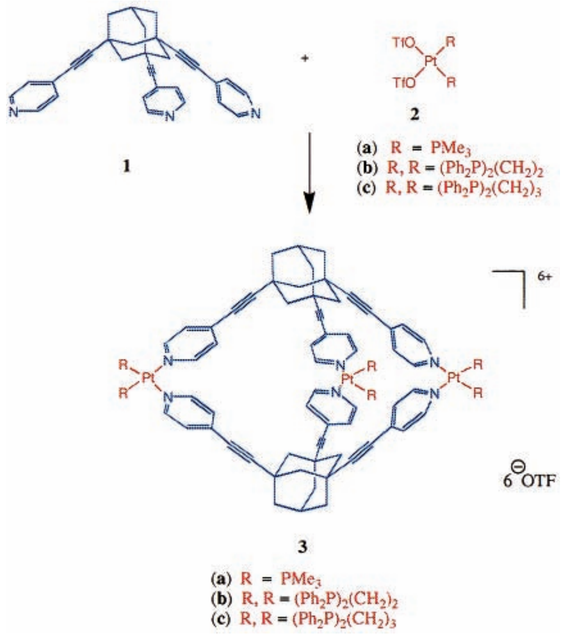
DMSO to give the triethynyladamantane **5** (54%).[9] This species was then coupled with bromopyridine in the presence of Pd(0)/CuI catalysts to provide the required tritopic pyridine linker **1**.

A trigonal bipyramidal framework **3** can be prepared via edge-directed assembly from 2 equiv of tritopic 109° angular units and 3 equiv of ditopic 90° angular units such as *cis*-Pt$(PMe_3)_2(OTf)_2$ (**2a**), *cis*-Pt(dppe)$(OTf)_2$ (**2b**), and *cis*-Pt-(dppp)$(OTf)_2$ (**2c**),[10] but as mentioned previously, there is the possibility of forming double squares and/or TBPs when reacting tritopic linkers and 90° ditopic linkers in a 2:3 ratio, as shown in Scheme 2. However, the double square and TBP can be distinguished using NMR spectroscopy. In double squares two inequivalent pyridyl moieties are present in a 2:1 ratio, resulting in the appearance of four doublets for the pyridine signals in the proton spectra.[3] Likewise, for double squares a doublet appears in the ^{31}P NMR due to the presence of two inequivalent phosphorus nuclei in a 2:1 ratio.

Scheme 2. Self-Assembly of TBP and/or Double Square



Scheme 3. Self-Assembly of Trigonal Bipyramidal Species **3**



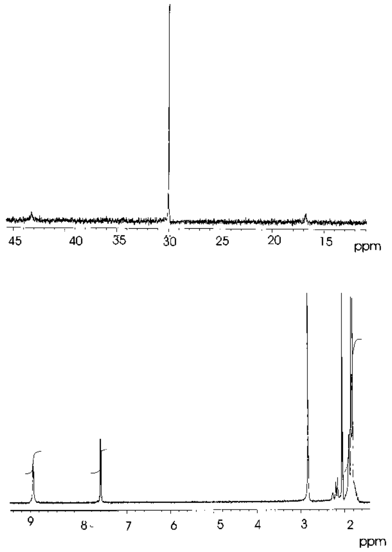


Figure 1. ^{31}P NMR and ^{1}H NMR of **3a**.

The self-assembly was carried out by the slow addition of an acetone solution of the ditopic tecton **2a** to an acetone solution of tritopic linker **1** at 25 °C. This combination resulted in the immediate, quantitative formation of a single, highly symmetrical entity **3a (**Scheme 3). Two additional ensembles (**3b** and **3c**) were assembled using the ditopic linkers *cis*-Pt(dppe)$(OTf)_2$ **2b** and *cis*-Pt(dppp)$(OTf)_2$ **2c** with the pyridine linker **1** via a procedure similar to that followed for **3a** (Scheme 3). The ^{31}P NMR spectrum of these assemblies exhibited a singlet indicating the formation of a single, highly symmetrical species (Figure 1). Moreover, two doublets appeared for the pyridyl protons in the ^{1}H NMR spectra, and the α-pyridyl protons exhibit a downfield shift (0.2−0.6 ppm) due to the loss of electron density upon coordination (Figure 1). The multinuclear NMR and physical

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[9] Delimaskij, R. E.; Rodionov, V. N. Yurchenko, A. G. *Ukr. Khim. J.* **1988**, *54*, 437.

[10] (a) Malik, A. A.; Archibald, T. G.; Baum, K.; Unroe, M. R. *J. Polym. Sci.; Part A: Polym. Chem.* **1992**, *30*, 1747. (b) Rukavishnikov, A. V.; Phadke, A.; Lee, M. D.; Lamunyon, D. H.; Petukhov, P. A.; Keana, J. F. W. *Tetrahedron Lett.* **1999**, *40*, 6353.

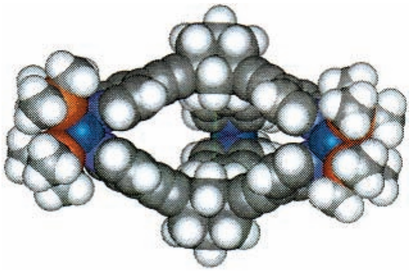

Figure 2. Force field simulation of TBP **3a**.

data of each assembly are consistent with the design-based TBP structure.

Further proof of the TBP structure is obtained using mass spectrometry. Electrospray ionization mass spectrometry (ESI/MS) was used to identify the respective compositions of **3a**, **3b**, and **3c**. In the mass spectrum of **3b** and **3c**, the 2+ species resulting from the loss of two triflates, with a mass-to-charge ratio (*m*/*z*) of 1625.3 for **3b** (calcd 1626.04) and 1648.2 for **3c** (calcd 1648.04), were observed. Compound **3a** was analyzed using ESI/MS after exchanging two of the triflate anions with cobalticarborane anions ($^{-}B_{18}C_4CoH_{22}$). In the mass spectrum of this compound, a peak attributable to the loss of two triflate anions [M − 2OTf] {*m*/*z* 1432.2 (calcd 1430.14)} and a peak due to the loss of two cobalticarborane anions with an *m*/*z* ratio of 1257.7 (calcd 1256.39) were observed.

A molecular model obtained using MM2 force field simulation to visualize the size and shape of the three-dimensional cage **3a** is presented in Figure 2.[11] The diameter of the inner cavity of the cage is about 2.7 nm.

Apart from the size, bond angles, and flexibility of linkers, thermodynamics is an important factor in determining the size of macrocycles, and it has been concluded that small cycles or cages are favored over larger ones for entropic reasons.[12] This may likely account for the essentially exclusive formation of the smaller TBP cages, instead of the larger double squares in these experiments.

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Supporting Information Available: Detailed descriptions of experimental procedures and physical and spectral data for compounds **3a**, **3b**, and **3c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] *Chem3D Pro 3.5.2*; CambridgeSoft Corporation: Cambridge, MA, 1996.

[12] Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483.