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ScienceDirect
Tetrahedron Letters 47 (2006) 9297–9300
Tetrahedron Letters

Design and synthesis of a Pt(II) nanoscopic trigonal bipyramidal cage using a new tripodal ester-containing ligand

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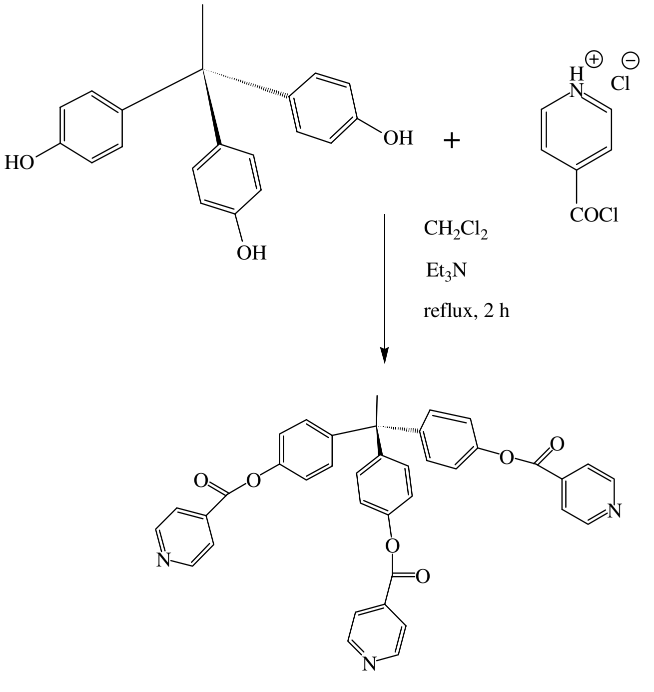
Received 8 September 2006; revised 8 October 2006; accepted 20 October 2006
Available online 9 November 2006

Abstract—The formation of a Pt(II) nanoscopic trigonal bipyramidal cage (TBP) containing a new tripodal linker with ester functionality is achieved by self-assembly. The new tripod ligand and the cage were characterized by multinuclear NMR and electrospray ionization mass spectroscopy. Energy minimized simulation of the cage yielded a pseudo TBP shape with an internal diameter of 2 nm.

Traditional organic synthesis of large molecules needs multi-step reactions and thus generally results in low yields. Coordination driven self-assembly is the most efficient way to construct highly ordered supramolecular structures.[1] Pd(II) and Pt(II) have long been acceptor units of choice because of their very common and rigid square planar coordination environment. It has been well established that the simple combination of the square-planar coordination geometry of palladium/platinum with bridging ligands leads to the quantitative self-assembly of nanometer-sized, discrete metal–organic frameworks such as molecular squares, hexagons, rectangles, and several 3D cages.[1a,2] In the majority of cases rigid nitrogen donor linkers have been utilized with a few recent exceptions where we used oxygen donor linkers.[3] The use of flexible bridging ligands in this field is very rare because of their tendency to form polymers. Flexible ensembles may distort their structure from the expected ideal shape to a thermodynamically stable conformation for a host–guest interaction. Such a distortion is not expected from a rigid ensemble without breaking the framework. On the other hand, the properties of a chemical substance are guided by the nature of the functional group/s present and thus the incorporation of several functional groups into the nanostructure may guide the properties of final supramolecular assemblies. Several functional groups/moieties such as porphyrin, carborane, calixarene and amides have been incorporated into self-assemblies.[4] However, the incorporation of an ester functionality into the nanostructures of Pd(II) and Pt(II) is rare except for a very few recently reported ester-based 2D open frameworks.[5]



1 (Yield = 61%)

Scheme 1. Synthesis of ligand **1**.

Keywords: Supramolecular assemblies; Tripod ligand; TBP cage; Electrospray ionization.

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doi:10.1016/j.tetlet.2006.10.105

To introduce flexibility as well as the ester functionality into a 3D nanostructure we report here the design and synthesis of a new tripodal ester linker **1** and its self-assembly with a cis-protected 90° Pt(II) acceptor to a nanoscopic TBP cage **2**. To the best of our knowledge, **2** represents the first example of a 3D Pt(II) cage (close framework) containing the ester functionalities.

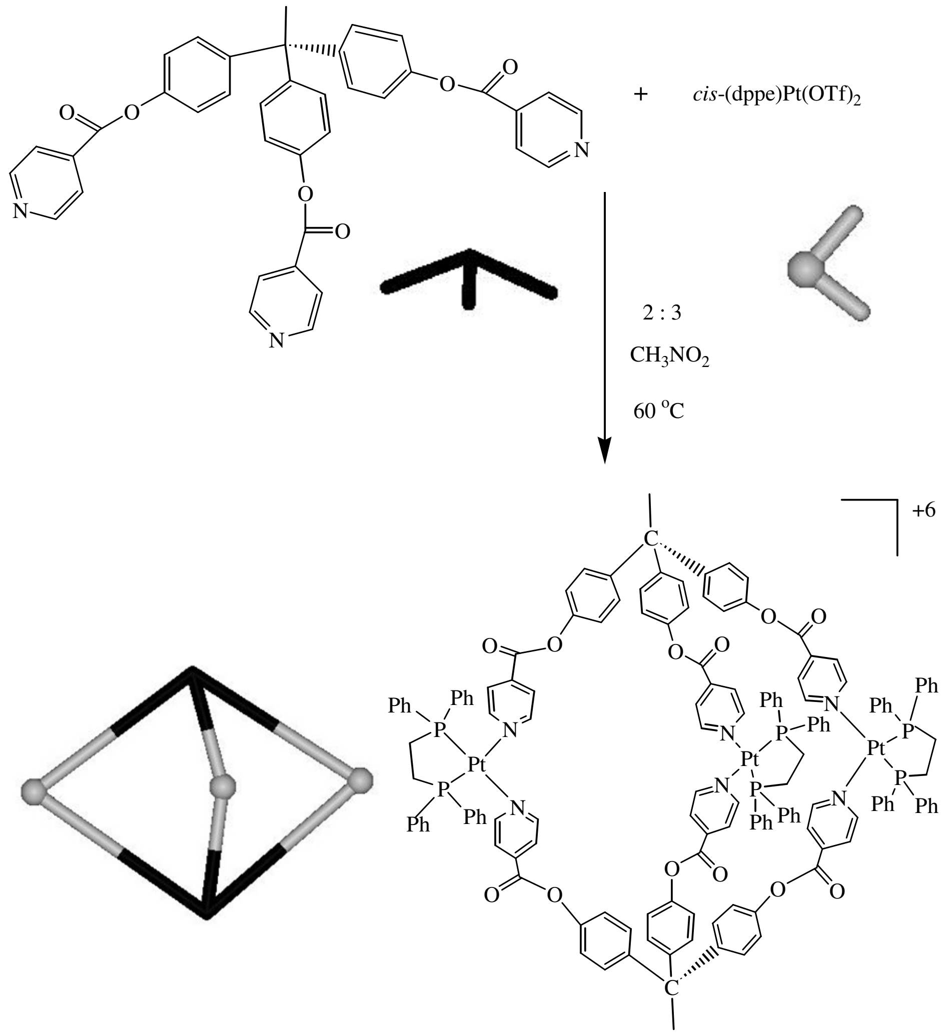
Ligand **1**[6] used in this study was prepared by treating tripodal 1,1,1-tris-(4-hydroxyphenyl)ethane with isonicotinyl chloride hydrochloride in the presence of excess Et_3N as the base under an inert atmosphere (Scheme 1).

When 2 equiv of ligand **1** were treated with 3 equiv of *cis*-Pt(dppe)$(OTf)_2$ [where dppe = 1,2-bis(diphenylphosphino)ethane, OTf = $CF_3\ SO_3^-$] in nitromethane for 2 h, self-assembly of a TBP cage (Scheme 2) as a single product occurred.[7]

A similar treatment might also give a macrotricyclic 'double-square' product with M_6L_4 composition (Scheme 3).

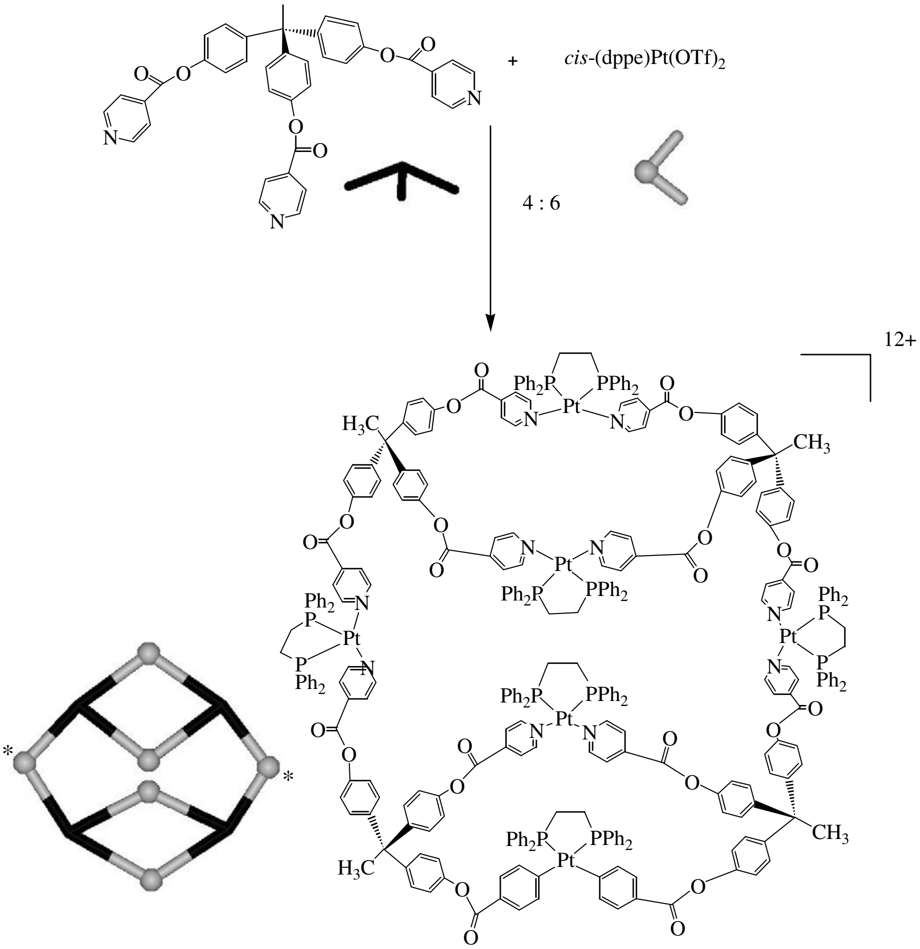
The double-square and trigonal bipyramid can be easily distinguished by ^{31}P NMR spectroscopy. From Scheme 3 it is clear that for a double square, two signals with a 1:2 ratio would be expected in the ^{31}P NMR spectrum due to the presence of two inequivalent phosphorus nuclei. However, in the case of TBP geometry, a single peak was expected. Moreover, a double square is formed with M_6L_4 composition (where M = ditopic unit and L = tritopic ligand) while in a TBP cage the composition is M_3L_2. Hence, the molecular weight of the double-square will be twice that of the TBP analogue. Thus, mass spectrometry can very easily distinguish these two geometries.

The self-assembly reaction was performed in nitromethane at 60 °C for 2 h. The product was isolated as a white powder by adding diethyl ether. The ^{31}P spectrum of the assembly showed a sharp singlet with concomitant Pt satellites (Fig. 1). An upfield shift of 9 ppm of the phosphorus peak in the product from the starting Pt(dppe)$(OTf)_2$ acceptor was a clear indication of ligand-to-metal coordination and the formation of a



2 (Yield = 91%)

Scheme 2. Self-assembly of TBP cage **2**.



Scheme 3. Self-assembly of a double-square. The marked (∗) Pt(II) centers are different from the other four Pt(II) centers.

single product (TBP cage). ^{1}H NMR of the product also indicated the formation of a highly symmetric TBP cage with expected shifts for the proton signals. In the IR spectrum of the cage, the shift of the C=O stretching to a higher frequency was also due to the ligand-to-metal coordination.

Electrospray mass spectroscopy clearly confirmed the M_3L_2 composition ($M = Pt(dppe)(OTf)_2$; $L = \mathbf{1}$) with the molecular weight of 3916.6 Da for **2** (see Supplementry data). The ESI-mass spectrum of **2** showed signals corresponding to consecutive loss of triflate counterions, $[M-2CF_3SO_3]^{2+}$, $[M-3CF_3SO_3]^{3+}$,

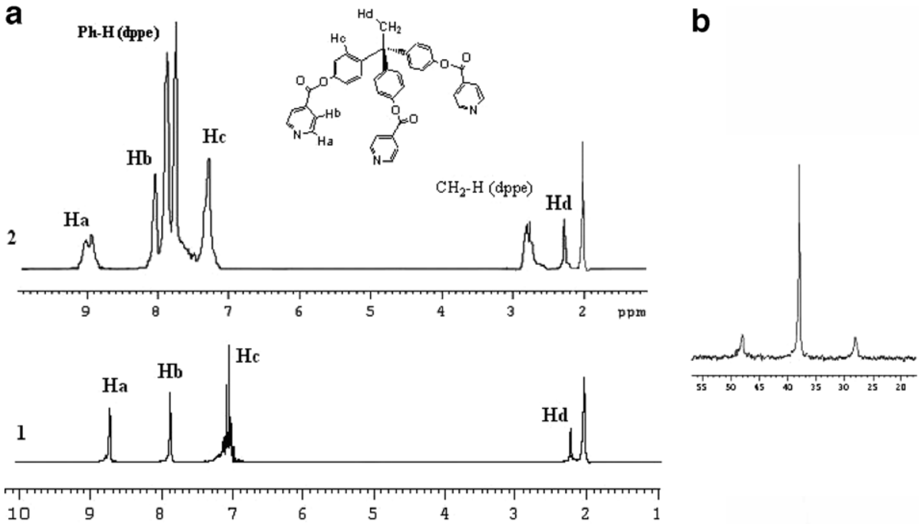


Figure 1. (a) ^{1}H NMR (300 MHz, acetone-d_6) of **1** (bottom) and **2** (top); (b) ^{31}P NMR (121.4 MHz, acetone-d_6) spectrum of **2**.

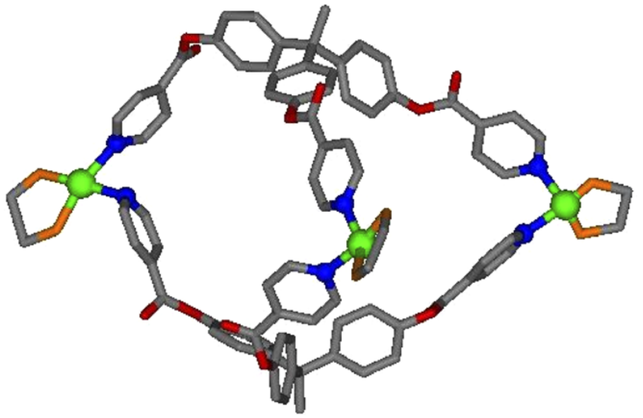


Figure 2. View of the energy minimized TBP cage **2** (green = Pt; blue = N; yellow = P; gray = C). Phenyl rings of the 'dppe' are omitted for the sake of clarity.

and $[M-5CF_3SO_3]^{5+}$; for **2**, $[M-2CF_3SO_3]^{2+}$ [$m/z = 1809.4$ (calcd 1808.7)]; $[M-3CF_3SO_3]^{3+}$ [$m/z = 1157.0$ (calcd 1156.2)] and $[M-5CF_3SO_3]^{5+}$ [$m/z = 634.5$ (calcd 634.04)]. Several attempts to obtain suitable single crystals for an X-ray diffraction failed and thus, energy-minimized simulations were employed to calculate the probable shape and size of cage **2**. The MM2 energy minimized simulation yielded a pseudo trigonal bipyramidal shape with a Pd–Pd distance of 2 nm (Fig. 2).

In conclusion, we have reported a new tripodal ester ligand and its self-assembly with a diphosphine blocked 90° Pt(II) acceptor to a nanoscopic trigonal bypyramidal cage representing the first example of a 3D Pt(II) close framework with the incorporation of ester groups. The use of flexible ester linkers with Pd(II)/Pt(II) metals and the formation of nanocages has the potential to expand the coordination driven self-assembly for the construction of novel materials for practical applications such as gas adsorption, catalysis, and host–guest chemistry.

Acknowledgments

Financial support from the DST, Govt. of India, and the Indian Institute of Science, Bangalore, is gratefully acknowledged. We thank Dr. H. V. Thulasiram of the Department of Chemistry, University of Utah, USA, for his assistance with the electrospray mass analysis.

Supplementary data

The ESI mass spectrum of complex **2** is included. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.10.105.

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6. *Synthesis of* **1**. To a stirred solution of isonicotinyl chloride hydrochloride (0.66 g, 7.5 mmol) in dry dichloromethane (30 mL), triethylamine (1.12 mL, 17 mmol) was added under nitrogen followed by the addition of 1,1,1-tris(4-hydroxyphenyl)ethane (2.5 mmol, 0.82 g). This mixture was then refluxed with stirring for 2 h under nitrogen and washed three times with saturated brine solution. The organic phase was separated and the product was obtained as a white powder after removing the solvent under reduced pressure. Yield: 61%. Anal. Calcd for $C_{38}H_{27}O_6N_3$: C, 73.42; H, 4.38; N, 6.76. Found: C, 73.21; H, 4.52; N, 6.45. ^1H NMR (300 MHz, acetone-d_6): δ 8.75 (d, 6H, *Ha*, $J = 5.2$ Hz); 7.90 (d, 6H, *Hb*, $J = 3.8$ Hz); 7.10 (m, 12H, *Hc*); 2.23 (s, 3H, *Hd*). IR (KBr): ν (C=O), 1742 cm^{-1}; ESI: 622.2 $[M+H^+]$.
7. *Synthesis of* **2**. To a 2 mL CH_3NO_2 solution containing 7.98 mg (0.03 mmol) of (dppe)Pt$(OTf)_2$ was added dropwise a CH_3NO_2 solution (1 mL) of **1** (0.02 mmol) with continuous stirring. The resulting mixture was stirred for 2 h at 60 °C and, after cooling, adding diethyl ether precipitated the product. The pure product was obtained by diffusing diethyl ether into an acetone solution of the precipitate. Yield: 91%. Anal. Calcd for $Pt_3C_{138}H_{126}P_6F_{18}S_6N_6O_{30}$: C, 49.00; H, 3.21; N, 2.14; S, 4.9. Found: C, 49.32; H, 3.42; N, 2.01; S, 4.56. ^1H NMR (300 MHz, acetone-d_6): δ 9.00 (d, 12H, *Ha*, $J = 8.9$ Hz); 8.10 (d, 12H, *Hb*, $J = 5.3$ Hz); 7.70 (dd, 60H, *H–Ph[dppe]*, $J = 11.3$ Hz, 8.6 Hz); 7.25 (d, 24H, *Hc*, $J = 5.2$ Hz); 2.70 (m, 12H, CH_2); 2.28 (s, 6H, *Hd*). ^{31}P $\{^1H\}$ NMR (121.4 MHz, acetone-d_6): δ 37.50. IR (KBr): ν (C=O), 1750 cm^{-1}.