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Notes

Self-Assembly of a Nanoscopic Platinum(II) Double Square Cage

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Summary: Self-assembly of a rigid tripyridyl linker with a bidentate 90° Pt(II) acceptor yielded a somewhat unusual double square cage, representing the first example of Pt(II) cage of such shape. Multinuclear NMR as well as single-crystal structure analysis characterized the cage.

Introduction

Self-assembly of metallosupramolecular structures by the directional bonding approach is a subject of current research; special attention has focused on the formation of species with nanometer size.[1] The major requirement for this directional self-assembly approach is the use of rigid precursors of appropriate sizes and shapes. The structure, conformation, and topology of these supramolecules mainly depend on the nature of the organic backbone and also on the nature of the metal−ligand interaction.[1] Square-planar Pt(II) and Pd(II) have long been used as favorite metals in this area because of their rigid square-planar environment.[2] A few recent examples are known where flexibility is also introduced into discrete assemblies by introducing organic ligands with arms containing flexible ester/amide functional groups. We and others have shown that the self-assembly of a *cis*-blocked Pt(II)-based 90° acceptor (M) and a tripodal donor linker (L) in a 3:2 molar ratio leads to the exclusive formation of either a trigonal-bipyramidal cage (M_3L_2) or a truncated tetrahedron type cage (M_6L_4) despite the possibility of the formation of an alternative double square cage with the same empirical formula.[3] No example is known where a Pt(II) double square cage was formed as product. A recent result from our group established the exclusive formation of a Pt(II) trigonal-bipyramidal (TBP) cage upon treatment of a Pt(II) 90° acceptor with a tripodal ligand containing an ester functionality.[4] The formation of a Pt(II) TBP cage in this case is due to the flexibility of the donor arms of the ligand due to the presence of a flexible ester functional group. In continuation of this work we have designed a rigid tripodal ligand (**1**) with an ester cap [**1** = 1,1,1-tris(4-pyridyl)COOR, where R = Ph−CH(C_2H_5)]. A 2:3 self-assembly of **1** with *cis*-$(PEt_3)_2Pt(OTf)_2$ as a 90° ditopic acceptor unit (**2**) yielded a somewhat unusual 3D cage (**3**), representing the first example of Pt(II) double square.

Results and Discussion

To prepare the double square we have used a tripodal linker (**1**) in combination with a *cis*-$(PEt_3)_2Pt(OTf)_2$ as a 90° acceptor unit (**2**). The ligand **1** used in this study was prepared by simple esterification of 1,1,1-tris(4-pyridyl)methanol with the appropriate acid chloride (Scheme 1).

When 2 equiv of the ligand **1** was treated with 3 equiv of *cis*-$(PEt_3)_2Pt(OTf)_2$ [where PEt_3 = triethylphosphine, OTf = $CF_3SO_3^-$] in acetone for 2 h, the self-assembly of a double square cage (Scheme 2) as a single product occurred.

A similar treatment could also give a M_3L_2 trigonal-bipyramidal (TBP) cage (Scheme 3), which is common in the literature.[3] These two geometries can be easily distinguished by ^{31}P NMR spectroscopy. Although all the pyridyl moieties in ligand **1** were identical, interestingly, in complex **3** two different kinds of pyridyl moieties are expected due to the different connectivity to Pt centers. The eight pyridyl groups connected to four (bold) Pt centers (Scheme 2) are different from the other four pyridyl moieties connected to the other two Pt centers. Thus 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 forms

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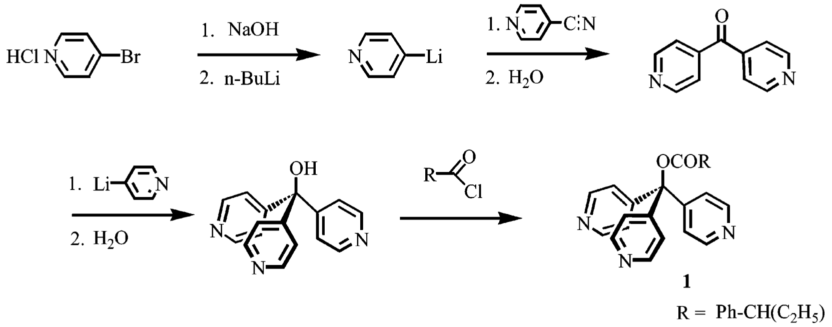
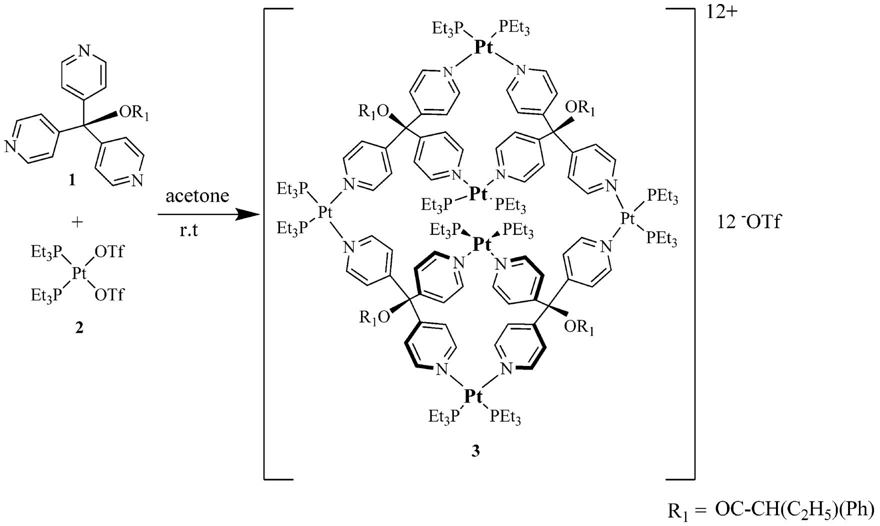
Scheme 1. Synthesis of the Donor Ligand 1

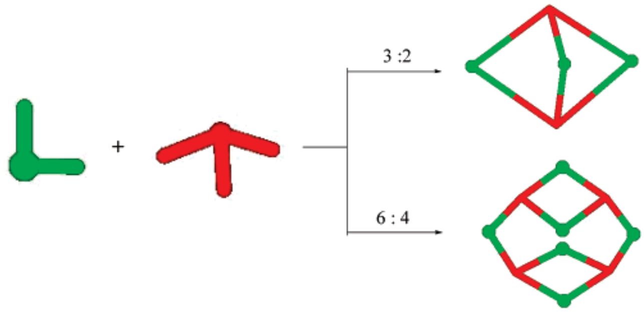


Scheme 2. Synthesis of Cage 3[a]



[a] The four Pt centers shown by bold letters are different from the other two Pt centers due to different connectivity.

Scheme 3. Self-Assembly of the TBP and the Double Square



from 10 components with M_6L_4 composition (where M = ditopic unit and L = tritopic ligand), while a TBP cage results from five components with M_3L_2 composition. Hence, the molecular weight of the double square will be twice that of the TBP analogue. Thus, mass spectrometry can also very easily distinguish these two geometries.

The self-assembly reaction was performed in acetone at ambient temperature for 2 h. The product was isolated as a white powder by adding diethyl ether. The ^{31}P spectrum of the precipitate showed two very closely spaced sharp singlets with expected concomitant Pt satellites corresponding to both the peaks. An upfield shift of 6 ppm of the phosphorus peak in the product from the starting **2** was a clear indication of ligand to metal coordination. Two closely spaced peaks in the ^{31}P NMR as well two sets of α- and β-protons (2:1) in the ^1H NMR of the product also indicated the formation of a double square cage as a single product. Electrospray ionization mass spectrometry also confirmed the M_6L_4 composition by the appearance of signals corresponding to the consecutive loss of triflate anions, $[M - 4CF_3SO_3]^{4+}$and $[M - 6CF_3SO_3]^{6+}$.

Finally, X-ray single-crystal structure analysis unambiguously established this somewhat unusual double square cage structure. Several attempts to get good-quality single crystals failed. Highly solvent-dependent poor-quality single crystals were obtained by slow diffusion of diethyl ether into an acetone solution of the product at 10 °C. The diffraction pattern, although collected at 150 K, was not good because of the nonavailability of good-quality crystals even after several attempts. However, despite the relatively poor figure of merit, the structural characterization of this complex is conclusive as to the general shape of the molecule and the results are better than having to rely only upon various sorts of indirect evidence (NMR, mass spectra). A view of the molecular structure is presented in Figure 1. It consists of a 10-component, three-dimensional metallo-supramolecular cage comprised of six 90° *cis*-$Pt(PEt_3)_2(OTf)_2$ acceptor units (**2**) bridged by four molecules of tripodal rigid donor linker **1**.

The structure can also be considered as a macrotricyclic cage, where two small squares are again linked by two Pt centers to form a larger rhomboid. The longest Pt−Pt distance is 17.3 Å, while the dimension of the smaller squares is 9.8 × 8.1 $Å^2$. The geometry around each Pt is close to square planar. From the top view of **3**, a roughly rhomboidal cavity (17.3 × 9.0 $Å^2$) can be seen [Figure 2 (left)]. This cavity encapsulates a disordered $CF_3SO_3^-$ anion. A side view represents [Figure 2 (right)] the existence of a pseudosquare-shape cavity.

In conclusion, we have presented the reaction of a rigid tripodal ligand having an ester functionality with a 90° Pt(II)

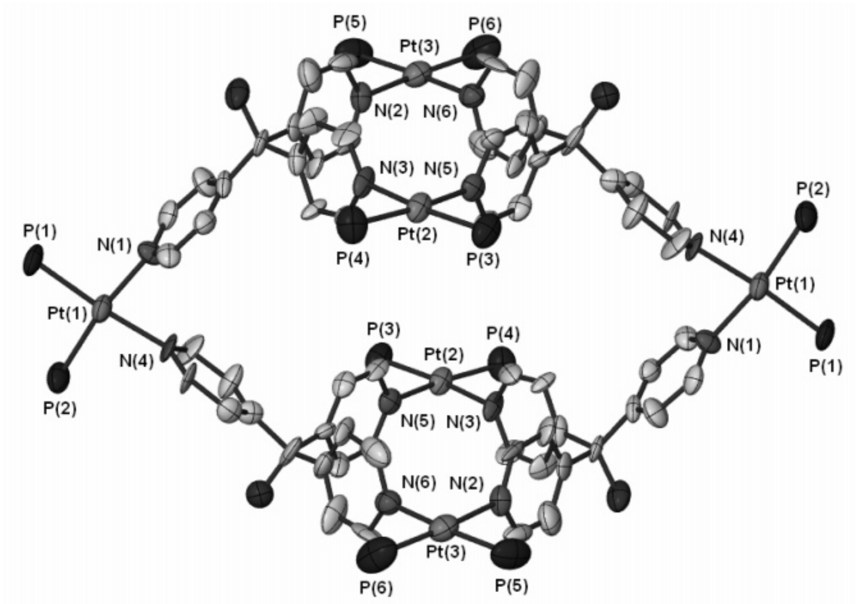


Figure 1. View of the molecular structure of cage **3**. Ethyl groups of the PEt_3 and CO−CH(Ph)(C_2H_5) part of the organic ligand are omitted for the sake of clarity. Selected bond lengths (Å): Pt(1)−P(1) = 2.291(5), Pt(1)−P(2) = 2.325(6), Pt(1)−N(1) = 2.092 (11), Pt(1)−N(4) = 2.084(11), Pt(2)−N(5) = 2.146(12), Pt(2)−N(3) = 2.151(12), Pt(2)−P(4) = 2.266(6), Pt(2)−P(4) = 2.268(7), Pt(3)−N(6) = 2.151(13), Pt(3)−N(2) = 2.216(11), Pt(3)−P(5) = 2.300(8), Pt(3)−P(6) = 2.307(9). Angles (deg): N(4)−Pt(1)−N(1) = 84.2(5), N(4)−Pt(1)−P(1) = 173.8(4), N(1)−Pt(1)−P(1) = 90.0 (4), N(4)−Pt(1)−P(2) = 87.6(4), N(1)−Pt(1)−P(2) = 171.4(6), P(1)−Pt(1)−P(2) = 98.2(2).

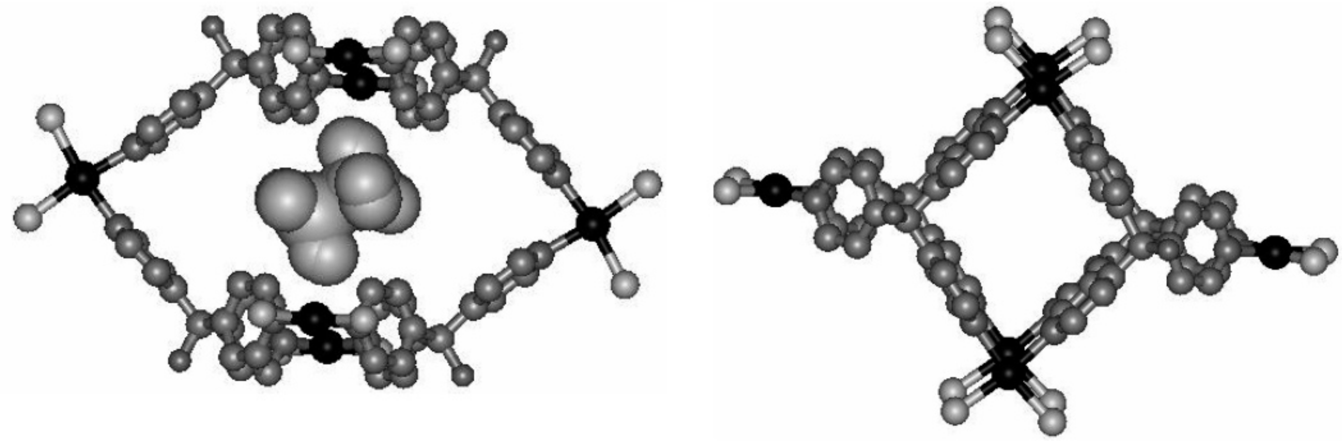


Figure 2. Top view of cage **3**; the encapsulated disordered $CF_3SO_3^-$ anion is shown by the CPK model (left); side view of cage **3** (right).

acceptor to obtain a somewhat unusual double square cage of nanoscopic dimension. A few examples are known in the literature where tridentate donor linkers have been used in the self-assembly reaction with 90° Pt(II)acceptor units. In all the previous cases, either trigonal-bipyramidal or truncated tetrahedral cages[6] were obtained. Our present result discloses the first example of formation of a Pt(II) double square cage. Previous results showed the exclusive formation of a TBP cage using a flexible tripodal ligand,[3d,4] and our present result clearly demonstrates that a completely different geometry with the same empirical formula can be obtained by simply changing the rigidity of the ligand while keeping the donor moieties unchanged. The use of rigid tripyridyl linkers containing other functionalities in conjunction 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 materials of unusual shapes.

Experimental Section

Methods and Materials. Deuterated solvents, the hydrochloride salt of 4-bromopyridine, and 4-cyanaopyridine were purchased from Aldrich Chemical Co. and used without further purification. Metal-based linker **2** was prepared from its chloride analogue by treating with $AgCF_3SO_3$. ^1H NMR and ^{31}P spectra were recorded in a Bruker 400 MHz machine. ^1H chemical shifts are reported relative to the residual protons of deuterated chloroform (δ 7.26 ppm). $^{31}P\{H\}$ chemical shifts are reported relative to an external, unlocked sample of H_3PO_4 ($\delta = 0.0$ ppm). Elemental analyses were performed using a Perkin-Elmer CHN analyzer.

X-ray Structure Determination and Refinements. The structure contains large voids that are occupied by extremely disordered anions and solvent molecules. This reduces the overall precision of the model and limits refinement of the structure to a significant extent. While the connectivity of the Pt_6 cage is unambiguous, the

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disorder has a pronounced effect on many of the peripheral ligand groups. Only nine CF_3SO_3 anions could be accurately located, and the ethyl groups of eight PEt_3 ligands could not be reasonably modeled. The chiral group of one of the crystallographically unique ligands could also not be resolved. The SQUEEZE routine of PLATON was therefore applied to the data.[5] A void volume of 6705.3 Å^3 was calculated to contain 2778 electrons per unit cell. This value represents 1389 electrons per Pt_6 cluster. The missing groups (anions, ethyl groups, and chiral substituent) calculate to be 491 electrons per cluster, leaving 892 electrons worth of solvent disordered in the lattice. Pyridyl rings were constrained with FLAT and SADI restraints where needed. Trifluoromethylsulfonate anions were restrained with DFIX and DANG commands due to apparent disorder and consequently have large anisotropic parameters. One CF_3SO_3 anion could not be satisfactorily refined anisotropically and therefore has been refined using an isotropic model.

Synthesis of 1. To a 3 mmol n-BuLi solution in 20 mL of dry diethyl ether cooled to −60 °C was added freshly prepared 4-bromopyridine (3 mmol) in 20 mL of dry ether with continuous stirring. The light yellow slurry was stirred for another 20 min maintaining the temperature below −50 °C. 4-Cyanopyridine (3 mmol) in 20 mL of dry THF was added slowly to the above cold solution. The mixture was allowed to warm to rt, and following hydrolysis with 40 mL of water, the ether part was extracted with 6% H_2SO_4 several times. The combined acid parts were heated to remove ether and made basic with dilute KOH solution. The slurry was extracted with chloroform, dried over magnesium sulfate, and evaporated to obtain di(4-pyridyl) ketone. This ketone was treated with 4-pyridyllithum in dry ether at −60 °C and temperature raised to rt. The product was diluted with water and extracted with ethyl acetate to obtain tris(4-pyridyl)methanol. Tris(4-pyridyl)methanol (1 mmol) and 20 mL of THF were added to a Schlenk flask under N_2. The reaction was cooled to −60 °C in an acetone/liquid nitrogen bath. *n*-Butyllithium in THF (1 mmol) was added slowly to the stirred mixture. The reaction was warmed to −30 °C. 2-Phenylbutyryl chloride (1 mmol) was added at one time, and the reaction was then allowed to warm to room temperature. The solvent was removed *in vacuo* and the residue chromatographed on silica gel (ethanol/acetone). The product **1** was initially obtained as a light brown paste. Addition of an ethylacetate/hexane mixture (1:1) yielded **1** as a white powder. ^{1}H NMR (CD_3OD, 300 MHz): δ 8.41 (d, 6H, H_α-Py), 7.31−7.48 (m, 11H, H_β-Py and H-phenyl), 3.96 (t, 1H, C(O)−CH), 2.06−1.86 (m, 2H, C(O)−CH(Ph)−C*H*H) and C(O)−CH(Ph)−CH*H*), 0.78 (d, 3H, $-CH_3$).

Table 1. Crystal Data and Structure Refinement Parameters of 3

cryst syst	monoclinic
T/K	123(2)
space group	$P2_1/n$
a/Å	20.769(4)
b/Å	32.173(6)
c/Å	22.143(6)
α/deg	90.00
β/deg	110.07(3)
γ/deg	90.00
V/Å^3	13897(5)
Z	2
μ(Mo Kα)/mm^{-1}	3.205
λ/Å	0.71073
R_w[a]	0.2912
R[a]	0.1150
D/Mg m^{-3}	1.521

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{1/2}$.

Synthesis of 3. To a 2 mL acetone solution containing 4.1 mg (0.010 mmol) of ester linker **1** was added an acetone solution (2 mL) of **2** (0.015 mmol) drop-by-drop with continuous stirring. The colorless product (**3**) was isolated as a precipitate by adding ether to the acetone solution. Yield: 91%. Anal. Calcd for $Pt_6C_{188}H_{272}N_{12}O_{44}F_{12}S_{12}P_{12}S_{12}$: C, 37.54; H, 4.52; N, 2.79. Found: C, 37.22; H, 4.82; N, 2.53. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.85, 8.76 (2d, 24H, $H_{\alpha-Py}$); 7.82, 7.78 (2 d, 24H, $H_{\beta-Py}$); 7.48−7.6 (m, 20H, H_{phenyl}); 4.18 (t, 4H, C(O)−CH); 2.10 (m, 8H, C(O)−CH(Ph)−C*H*$_2$); 1.42 (m, 72H, P−C*H*$_2$−); 0.86 (m, 120H, P−CH_2−C*H*$_3$ and C(O)−CH(Ph)−CH_2−C*H*$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz): δ 8.3, 8.1 (s, s).

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Supporting Information Available: CIF file giving X-ray data for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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