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Transition-Metal-Mediated Rational Design and Self-Assembly of Chiral, Nanoscale Supramolecular Polyhedra with Unique *T* Symmetry[†]

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Summary: A novel family of chiral, discrete, nanoscale-sized supramolecular cages are prepared, via self-assembly and noncovalent interactions from the tridentate ligand 1,3,5-tris[(4-pyridyl)ethynyl]benzene and [(R)-(+)-BINAP]Pd^{II} and -Pt^{II} bis(triflates). The cationic parts of these highly symmetrical species possess large three-dimensional cavities and are rare examples of molecules with T symmetry.

Three-dimensional discrete supramolecular species which possess large void spaces are important in studies of molecular recognition, inclusion phenomena, and catalysis, as they provide unique environments for encapsulating smaller molecules inside their cavity and even stabilize some reactive species.[1−3] Despite the relatively large number of reports concerning self-assembly of chiral transition-metal-based infinite structures and some smaller finite assemblies, such as helices and helicates,[4] no examples of *chiral* three-dimensional discrete species formed via self-assembly using coordination as the motif have been observed to date. Herein, we report the self-assembly and characterization of such optically active coordination-based three-dimensional nanoscopic cages with unique *T* symmetry.

The coordination-based rational design of discrete chiral three-dimensional assemblies in general may be accomplished in a symmetry-driven manner by use of (1) an optically active transition-metal auxiliary in combination with achiral multidentate ligand connectors, (2) a chiral multidentate ligand as connectors in combination with achiral shape-defining metal corners, (3) an inherently chiral octahedral (tris-chelated) metal center with achiral multidentate linkers, or (4) by combination of optically active auxiliaries or chiral metal systems as corner units with chiral multidentate ligands as connectors. The preparation of the assembly itself usually involves simple mixing of the components in the chosen solvent. Since appropriate metal corner units with optically active auxiliaries are more accessible than chiral multidentate ligand connectors or chiral metal systems, we focused on the first approach. Specifically, we chose [(*R*-(+)-BINAP]Pd^{II} and -Pt^{II} bis(triflate) complexes[5] **4** and **5** (BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) as shape-defining corner units due to their high reactivity toward coordination of nitrogen-containing ligands, as well as the significant degree of conformational rigidity of BINAP, which is important, since the loss of conformational entropy is minimized upon binding of these rigid bis(triflate) complexes to the connector ligand. Most important, the rich chemistry of BINAP-based transition-metal complexes has been known for over a decade and has already found a variety of applications in organic synthesis and organometallic catalysis.[6] Moreover, these rigid, chiral complexes were found to be excellent building blocks in the assembly of optically active molecular squares.[7] As connector ligand 1,3,5-tris[(4-pyridyl)-ethynyl]benzene (**3**) was prepared from 1,3,5-triethynylbenzene and 4-bromopyridine via cross-coupling.[8]

Addition of ligand **3** to a dichloromethane or nitromethane solution of the transition-metal bis(triflates) **4** and **5**, respectively, resulted in the formation of a single highly symmetrical entity with a stoichiometry

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[†] Dedicated to Professor Robert W. Parry on the occasion of his 80th birthday.

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(8) For **3**: yield 62%; mp 232−236 °C dec. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 8.62 (d, J = 5.7 Hz, 6H, py H$_\alpha$), 7.77 (s, 3H, Ph), 7.42 (d, J = 6.0, 6H, py H$_\beta$). ^{13}C{^{1}H} NMR (300 MHz, CD$_2$Cl$_2$): δ 150.3 (s), 135.5 (s), 130.7 (s), 125.8 (s), 123.8 (s), 91.5 (s), 88.5 (s). IR (neat, cm^{-1}): 3036, 2217 (C≡C), 1595, 1407, 1215. 989, 881, 819. Anal. Calcd for $C_{27}H_{15}N_3$: C, 85.02; H, 3.96; N, 11.02. Found: C, 85.08; H, 3.99; N, 10.90.

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Scheme 1

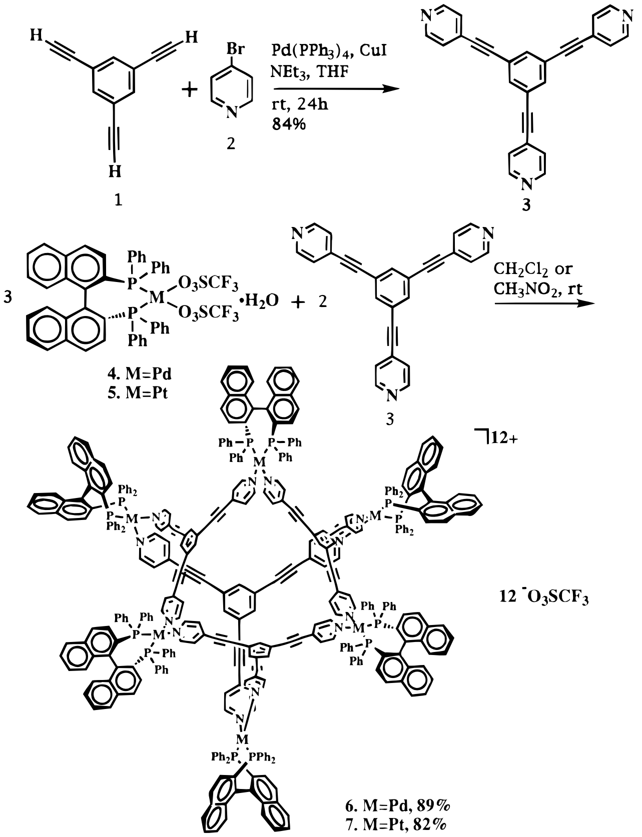
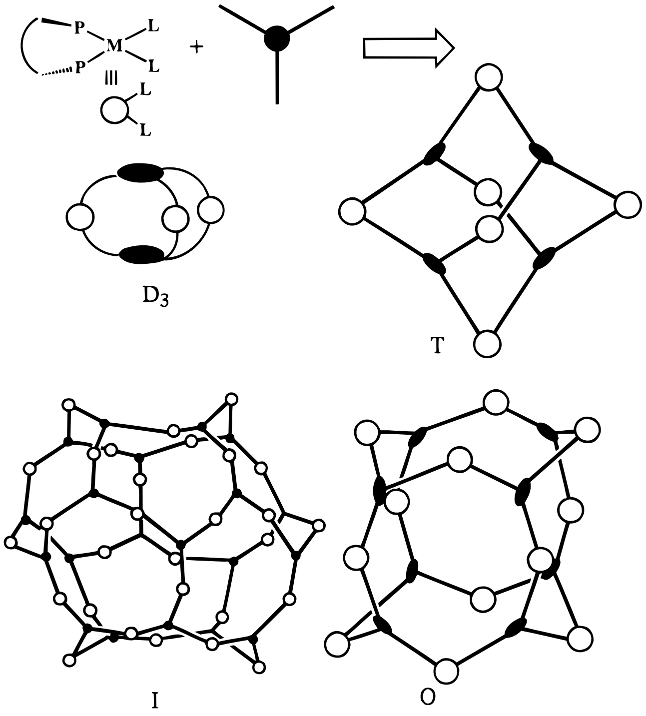


Chart 1



of 3:2 (Scheme 1), as observed by NMR.[9] In particular, the ^{31}P NMR spectrum of **6** exhibited only a sharp singlet. For compound **7** small amounts of oligomer in nitromethane were also observed, but this can be significantly reduced if the reaction is carried out in hot (~90 °C) nitromethane. Oligomer formation in the case of **7** is presumably due to the greater Pt−N vs. Pd−N bond strength that makes reorganization of the ligands in the formation of **7** less favorable. Both products are isolated as robust, although hygroscopic, microcrystalline solids with high decomposition points.[9] The thermodynamic stability of the final products **6** and **7** is quite remarkable: when an excess of metal bis(triflate) is used, only the formation of a complex with a metal corner to connector ligand ratio of 3:2 was observed by NMR and the rest of the starting triflate complex remained unreacted. In contrast, when the *reverse* order of addition was performed, i.e. the metal bis(triflate) was slowly added to a solution of **3** in dichloromethane and hence an excess of coordinating ligand was present, the formation of predominantly oligomeric species was detected. These experiments indicate the complexity of the self-assembly pathways and their dependence on precise reaction conditions.

The structure assignment of **6** and **7** is based upon (a) topology principles relevant to supramolecular chemistry and the self-assembly strategy, (b) spectral data, (c) electrospray-ionization Fourier transform ion cyclotron resonance (ESI-FTICR) mass spectrometry, (d) molecular modeling, and (e) analogy to a related achiral assembly. Specifically, under thermodynamic conditions enthalpy favors formation of discrete macrocyclic systems over oligomers because of the greater number of favorable interactions (dative bonds per connector unit) in the closed system. Although this statement is somewhat simplistic with respect to the formation of polymers, it is applicable in this particular case since a highly charged polymer results in precipitate formation and can also be easily detected by the significant signal broadening in both ^{31}P and ^{1}H NMR. Entropic factors in turn favor a macrocycle with the *minimum* number of subunits, since the energy cost for loss of several degrees of freedom for the components of the assembly will be smaller in the system with the lesser number of units.[10]

Both topology and stereochemistry require that the symmetry elements of the final product be a combination of the symmetries of the starting components, since the symmetry of the individual rigid building units remains unchanged. As the symmetry of the metal corner units **4** and **5** is C_2, and the symmetry of the

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[9] For **6**: yield 89%; mp 58−260 °Cdec. $[\alpha]_D = +319°$ ($c = 0.022$, CH_2Cl_2, 25 °C). ^1H NMR (CD_2Cl_2): δ 8.64 (bs, 24H, py H_α), 8.03 (t, $J = 9.6$ Hz, 12H, BINAP), 7.90 (d, $J = 8.7$, 12H, BINAP), 7.81 (m, 24H, BINAP), 7.73 (d, $J = 8.0$, 12H, BINAP), 7.54 (s, 12H, Ph), 7.47 (t, $J = 7.2$, 12H, BINAP), 7.33 (bm, 24H, BINAP), 7.05 (t, $J = 7.5$, 24H, BINAP), 6.97 (d, $J = 5.1$, 12H, py H_β), 6.43 (d, $J = 8.7$, 12H, BINAP). ^{13}C NMR (CD_2Cl_2): δ 151.5 (s), 140.5 (t), 136.7 (s), 135.2 (s), 133.9 (s), 133.5 (s), 132.3 (s), 132.1 (s), 130.6 (s), 129.7 (s), 129.6 (s), 129.1 (s), 128.7 (s), 127.9 (s), 127.6 (s), 127.5 (t), 127.3 (s), 125.1 (s), 124.6 (s), 124.3 (t), 123.8 (s), 122.8 (s), 121.3 (q), 119.4 (s), 95.2 (s), 87.0 (s). ^{31}P NMR (CD_2Cl_2): δ 27.13 (s). ^{19}F NMR (CD_2Cl_2): δ −76.6 (s, OTf). IR (CCl_4, cm^{-1}): 3047, 2210 (C≡C), 1592, 1435, 1275 (OTf), 1219 (OTf), 1149 (OTf), 1028 (OTf). Anal. Calcd for $C_{384}H_{252}N_{12}S_{12}P_{12}F_{36}O_{36}Pd_6 \cdot 8H_2O$: C, 58.88; H, 3.45; N, 2.15; S, 4.91. Found: C, 58.71; H, 3.61; N, 2.12; S, 4.85. For **7**: yield 82%; mp >278 °C dec; $[\alpha]_D = +145°$ ($c = 0.025$, CD_3NO_2, 25 °C). ^1H NMR (CD_3NO_2): δ 8.50 (bd, 24H, py H_α), 7.99 (t, $J = 9.5$ Hz, 12H, BINAP), 7.79 (d, $J = 8.0$, 12H, BINAP), 7.76 (m, 24H, BINAP), 7.70 (d, $J = 8.0$, 12H, BINAP), 7.68 (s, 12H, Ph), 7.50 (t, $J = 7.1$, 12H, BINAP), 7.40 (bm, 24H, BINAP), 7.12 (t, $J = 7.7$, 24H, BINAP), 7.02 (d, $J = 4.9$, 24H, py H_β), 6.51 (d, $J = 8.9$, 12H, BINAP). ^{13}C NMR (CD_3NO_2): δ 150.0 (s), 142.9 (t), 135.8 (s), 135.0 (s), 134.1 (s), 133.6 (s), 132.5 (s), 132.8 (s), 132.4 (s), 130.4 (s), 126.2 (bm), 129.0 (s), 128.5 (s), 127.3 (s), 127.1 (t), 126.9 (s), 124.91 (s), 124.6 (s), 124.3 (s), 123.4 (s), 121.4 (q), 120.1 (t), 95.6 (s), 87.2 (s). ^{31}P NMR (CD_3NO_2): δ 3.18 (s, ^{195}Pt satellites, $J_{Pt-P} = 3216$ Hz). ^{19}F NMR (CD_3NO_2): δ −76.1 (s, OTf). IR (CCl_4, cm^{-1}): 2212 (C≡C), 1609, 1497, 1436, 1253 (OTf), 1220 (OTf), 1153 (OTf), 1028 (OTf). Anal. Calcd for $C_{384}H_{252}N_{12}S_{12}P_{12}F_{36}O_{36}Pt_6 \cdot 7H_2O$: C, 55.25; H, 3.21; N, 2.01; S, 4.61. Found: C, 55.21; H, 3.23; N, 1.96; S, 4.36.

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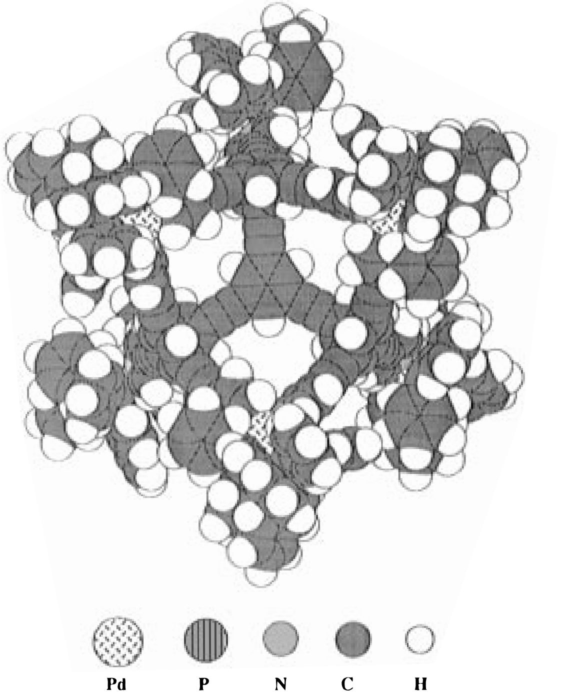

Figure 1. Space-filling model of **6**, obtained from ESFF simulations. The view is parallel to one of the C_3 axes, located along the entrance to the three-dimensional cavity.

tridentate connector ligand **3** is D_{3d}, the conservation of symmetry in a closed spherical-like species requires a minimum of one C_3 and three C_2 axes to be retained. A priori four symmetries satisfy these criteria: molecules with a 3:2 ratio of components may belong to D_3, *T*, *I*, and *O* symmetry groups (Chart 1).[11] However, in this particular case, to achieve D_3 symmetry, the acetylene units of the tridentate linker ligand would have to be significantly bent out of planarity. Similar constraints hold for species with *I* and *O* symmetry groups, where the N−Pt−N and N−Pd−N bond angles would have to be significantly larger than 90° in order to be able to assemble the molecule. Molecular modeling indicates that the overall energy of these molecules with *I* or *O* symmetry would exceed the total bond energy of the dative Pd−N or Pt−N bonds by a considerable margin. The only structure which does not suffer from such angle strain is a molecule with the point group *T*. Both the energy and symmetry considerations are best satisfied in a *T*-symmetrical molecule with a 6:4 ratio of corner units **4** or **5** and linker ligands **3**, as depicted in Scheme 1. Indeed, this 6:4 (i.e. 3:2 by NMR) ratio is observed by integration of the ^{1}H NMR spectra of **6** and **7**. The large number and some overlapping of the signals of the aromatic carbons make the $^{13}C\{^1H\}$ NMR spectra of **6** and **7** quite complex. Careful analysis indicates the presence of 26 unique spin systems: 10 due to the binaphthyl moiety and 8 from the two diastereotopic phenyl rings of BINAP, as well as 7 different signals of the linker ligand and 1 quartet with a coupling constant of 319 Hz from the carbon of the triflate counterions. The $^{31}P\{^1H\}$ NMR spectra of both products exhibit singlets (for **7** it is spin-coupled to ^{195}Pt, resulting in the expected two satellites) and, in the case of **7**, some broad signal near the base line due to the small amount of oligomer. Both singlets are high-field-shifted (6−8 ppm) compared to those of the starting bis(triflate) complexes, confirming nitrogen coordination to the metal centers.[5,7]

The stoichiometry of the proposed chiral cage **6** is firmly proven by mass spectrometry. Electrospray-ionization Fourier transform ion cyclotron resonance (ESI-FTICR) mass spectrometry is an excellent tool to establish the molecular weight of these large and fragile datively bound species. This technique provides gentle ionization of the sample in combination with high-resolution capability.[12] The ESI-FTICR mass spectrum of **6** obtained from a dichloromethane solution resolved the peak centered at *m/z* 1768.19 with an *m/z* peak spacing of $^1/_4$ corresponding to the $[M - 4^{-}OTf]^{4+}$ ion with the 4+ charge state. The observed molecular weight and close match of calculated and observed isotopic distribution patterns of 4+ charge state (7092.76 Da) are in agreement with the theoretical weight of 7092.89 (error 13 ppm), corresponding to the cyclic assembly with loss of four triflate counterions.

Additional evidence for this structure assignment comes from ESFF force field calculations[13] performed with the Biosym/MSI package. The minimum-energy derived structure is indeed the molecule with *T* symmetry, depicted in Figure 1. The simulation data indicate that the transition-metal corners retain a near-square-planar geometry with a N−M−N bond angle of 84.5°, very similar to that observed by Fujita and coworkers in the related achiral product (derived from (ethylenediamine)palladium(II) dinitrate and 2,4,6-tris(4-pyridyl)-1,3,5-triazene), whose structure was unambiguously established by X-ray data.[14]

In conclusion, the first examples of discrete, chiral, three-dimensional macrocyclic cages have been prepared using rational coordination directed self-assembly for the formation of these novel supramolecular species. A unique feature of these optically active supramolecular macrocycles is their symmetry: they are rare examples of molecules belonging to the *T*-symmetrical point group, which to date were found only in a few organic, covalent systems.[15]

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Supporting Information Available: Proton, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR and IR spectra of compounds **3**, **6**, and **7** (11 pages). Ordering information is given on any current masthead page.

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