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Platinum(II) Molecular Triangle with a Deep Intramolecular Cavity

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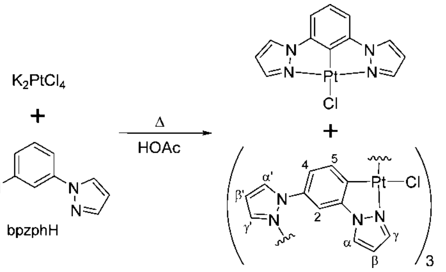
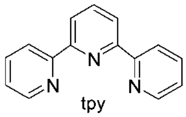
Depending on the conditions, the reaction of K_2PtCl_4 with 1,3-bis(*N*-pyrazolyl)benzene (bpzphH) yields either Pt(bpzph)Cl, [Pt(μ-bpzph)Cl]$_3$, or a mixture of these products. In the case of the C_3-symmetric trimer, each bpzph$^-$ ligand is bidentate with the metal bonded to a pyrazolyl group and to the phenyl group at the 6 position; the remaining pyrazolyl group bridges to an adjacent platinum center. The crystal structure confirms that each complex is chiral with an unusually deep (∼8 Å) intramolecular cavity; enantiomeric pairs of trimers encapsulate the diethyl ether solvate. NMR studies establish that the trimer exhibits excellent thermal and kinetic stability. Substitution of the chloride ligands provides a strategy for elaborating the macrocycle.

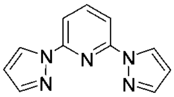
Considerable effort is currently directed toward the self-assembly of supramolecular macrocyclic architectures using platinum(II)-containing subunits because of the metal center's predictable square-planar coordination geometry and kinetic stability. The prevailing strategy focuses on cyclic structures in which trans coordination of linker groups is used to extend edge units and cis coordination is used to create vertices.[1] Already this approach has generated a wide variety of macrocycles with varying cavity shapes and sizes.[2] A limitation of this chemistry is that the resulting molecules tend to have annulus-like structures often characterized by low barriers to rotation of edge groups[3] and shallow cavities with limited surface area available for interaction with an encapsulated guest. Typically, chemical elaboration by substitution of nonbridging ligands is not practical because of the kinetic lability of the linker groups, and unless chiral ligands are employed,[4] the structures are achiral.

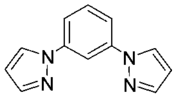
Scheme 1. Synthetic Scheme for Pt(bpzph)Cl and [Pt(μ-bpzph)Cl]$_3$



The use of bridging ligands capable of chelating one or both metal centers can be expected to produce more rigid macrocycles. In this regard, conventional meridional tridentate chelates such as tpy and bpp would appear to be unlikely bridging groups because of their tendency to favor tridentate coordination. However, it may be anticipated that the relative geometric constraints of the five-membered pyrazolyl rings of bpp, as compared to six-membered pyridyl rings, will tend to destabilize tridentate coordination.[5] In support of this view, we have discovered that bpzph$^-$ favors bidentate coordination of platinum(II), allowing a second pyrazolyl group to bridge to another metal center. Here we report the one-pot synthesis of the resulting remarkably stable chiral molecular triangle, which has an unusually deep intramolecular cavity.


tpy


bpp


bpzphH

The reaction of $K_2[PtCl_4]$ and bpzphH in refluxing acetic acid yielded a tan solid, which upon washing with methylene chloride was found to contain Pt(bpzph)Cl, [Pt(μ-bpzph)Cl]$_3$, or a mixture of these products in overall high yield (typically 50–90%; Scheme 1). The identities of both products were confirmed by single-crystal X-ray diffraction studies (Figure 1). For the C_{2v}-symmetric monomer, the bpzph$^-$ ligand is tridentate with the platinum bonded at the 2 position of the

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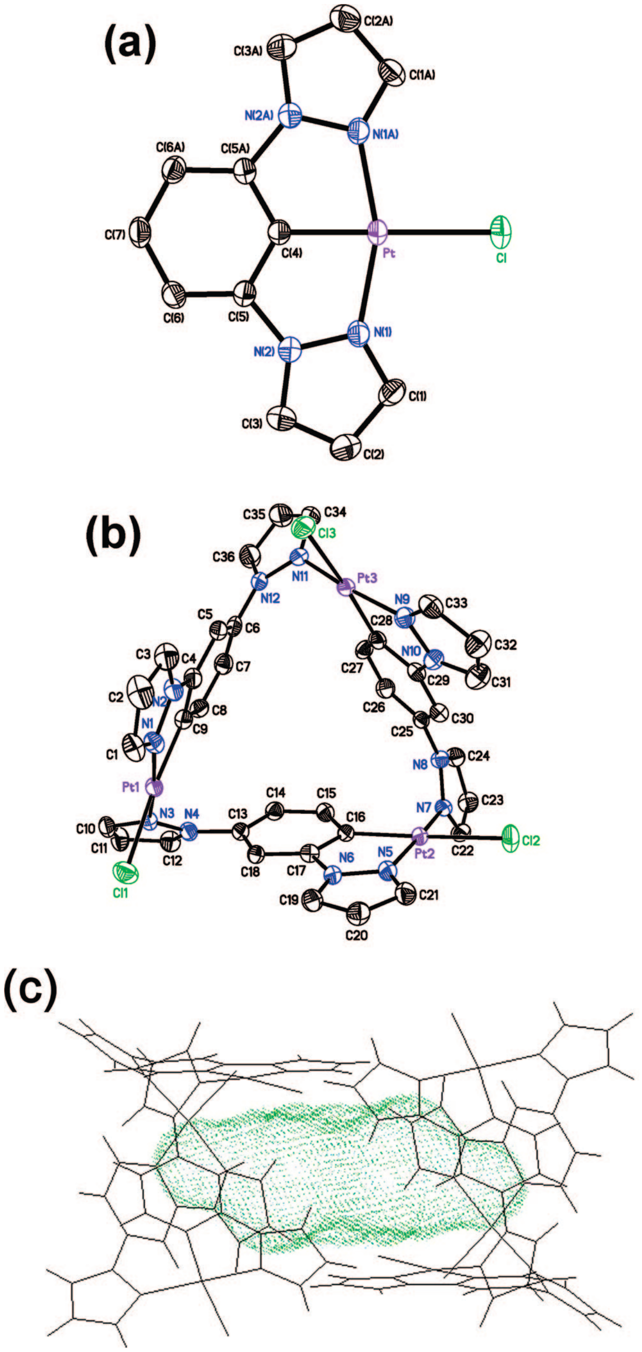

Figure 1. ORTEP diagrams of (a) Pt(bpzph)Cl and (b) the complex in crystals of [Pt(μ-bpzph)Cl]$_3$•DMF•0.5Et$_2$O. Hydrogen atoms are omitted for clarity. (c) Void space occupied by the Et$_2$O molecule in the cavities of a pair of [Pt(μ-bpzph)Cl]$_3$ complexes.

phenyl group; the fourth coordination site of the metal is occupied by a chloride ligand. In the case of the C_3-symmetric trimer, each bpzph$^-$ ligand is bidentate with the metal bonded to a pyrazolyl group (pz) and to the phenyl group at the 6 position; the remaining pyrazolyl group (pz′) is bonded to a different platinum center, resulting in a trans arrangement of the two nitrogen-donor pyrazolyl groups bonded to each platinum. The two products are readily distinguished by their electrospray ionization mass spectrometry (ESI-MS) and ^{1}H NMR spectra. It is noteworthy that the highest sample peaks in the ESI-MS spectra of [Pt(μ-bpzph)Cl]$_3$ are consistent with the loss of one chloride, and there is no evidence of tetramers or higher-order aggregates.

Each complex can be selectively prepared by controlling the initial concentration of the platinum starting material and the duration of the reaction. Although the concentration/time parameter space was not fully explored, a series of 18 reactions employing different initial platinum concentrations ([Pt], 8–220 mM) and reaction times (t, 2–14 days) were performed. The results showed that exclusively trimer is isolated for [Pt] $\geq$ 50 mM and $t \geq 9$ days; shorter reaction times yielded monomer/trimer mixtures. However, for [Pt] < 15 mM and $t \leq 14$ days, only the monomer was isolated. Product mixtures were readily purified by fractional crystallization from *N*,*N*-dimethylformamide (DMF); the trimer crystallizes as plates, leaving a supernatant enriched in the monomer product. The accumulated observations are consistent with the initial formation of the monomer, as expected for coordination of the pyrazolyl nitrogen-donor groups driving C–H activation.[6] Subsequent conversion of the monomer to the trimer involves an unusual [1,3]-metallotropic shift accompanied by a [3,1]-proton shift. From studies of the cis and trans isomers of Pt(phpy)(py)Cl,[7] (phpyH = 2-phenylpyridine), we infer that the resulting trans disposition of the halide and phenyl groups is thermodynamically more stable than the alternative cis arrangement.

The crystal structure of Pt(bpzph)Cl shows that the entire Pt(bpzph)Cl unit is planar with root-mean-square deviation from a best-fit plane of 0.0066 Å for 18 non-hydrogen atoms (Figure 1a).[8] Despite a short Pt–C bond distance [1.924(5) Å], the N–Pt–N bite angle [158.89(14)°] is significantly smaller than that found for Pt(bpp)Cl$^+$ [161.3(2)°][5] and eight Pt(tpy)Cl$^+$ salts [162.0(6)°],[9] which may, in part, account for the tendency of the monomer to convert to the trimer. By contrast, the average Pt–C distance [1.990(5) Å] is somewhat longer for crystals of [Pt(μ-bpzph)Cl]$_3$•DMF•0.5Et$_2$O, with the average N(pz)–Pt–N(pz′) angle [173(1)°] approaching the idealized 180° angle. The adjoining phenyl and pz′ groups form a dihedral angle ranging from 41.4(3) to 47.9(3)°, and the N–N–Pt–Cl torsion angles involving pz′ range from 101.3(4) to 110.6(4)°. When viewed perpendicularly to the plane defined by the three platinum atoms, [Pt(μ-bpzph)Cl]$_3$ has a triangular shape, with the pz′

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(8) Pt(bpzph)Cl: $C_{12}H_9N_4ClPt$, $T = 173$ K, $\lambda = 0.7750$ Å, monoclinic, $C2/c$, $a = 10.4065(7)$ Å, $b = 14.7195(9)$ Å, $c = 7.8539(5)$ Å, $\beta = 99.944(2)°$, $V = 1184.97(13)$ Å^3, R1 = 0.0208, CCDC-656112. [Pt(μ-bpzph)Cl]$_3$: $C_{36}H_{27}N_{12}Cl_3Pt_3$•DMF•0.5Et$_2$O, $T = 150$ K, $\lambda = 1.54178$ Å, triclinic, $P\bar{1}$, $a = 11.8105(4)$ Å, $b = 14.1236(5)$ Å, $c = 14.6980(5)$ Å, $\alpha = 68.355(1)°$, $\beta = 73.082(1)°$, $\delta = 82.618(2)°$, $V = 2179.61(13)$ Å^3, R1 = 0.0311, CCDC-656113.

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groups and chlorine atoms at the vertices (Figure 1b). However, in contrast to conventional platinum(II) molecular polygons, the intramolecular cavity is unusually deep (~8 Å), with the metal coordination planes lining its walls. The intramolecular Pt···Pt distances range from 6.669(1) to 6.897(1) Å, and half of a diethyl ether molecule occupies ~65 Å^3 of the interior volume of the cavity (Figure 1c). Because of the trans arrangement of the pyrazolyl groups, each complex is chiral, having a cyclodextrin-like structure. Thus, the chloride and pz groups are situated at one opening of the molecular cavity, and the phenyl−pz′ groups lie at the other opening. However, each coordination plane forms a ~79° angle with the plane defined by the three platinum atoms, and, consequently, the cavity is somewhat narrower at the phenyl−pz′ end, with estimated shortest interligand phenyl H···H contacts ranging from 2.89 to 3.07 Å. Molecular models suggest that small bond rotations can slightly open the narrower end of the cavity, but the polygon is too sterically hindered to fully invert and thereby switch chirality. Enantiomeric pairs of complexes, related by an inversion center, come together at the more open end of their cavities to encapsulate a disordered diethyl ether molecule (Figure 1c). DMF molecules lie at either end of the trimer pairs near the narrower openings to the molecular cavities. Thus, when viewed along the [111] direction, the complexes give the appearance of forming channels containing solvate (Figure S6 in the Supporting Information).

The monomer and trimer are both stable in a DMF solution, as determined by NMR spectroscopy. The ^{1}H NMR spectrum of Pt(bpzph)Cl exhibits four resonances with coincidental overlap of the pyrazolyl α proton and solvent resonances at 8.0 ppm. As expected from studies of 1-phenylpyrazole complexes,[7,10] the pyrazolyl resonances are shifted slightly downfield from those of the free ligand ($\Delta\delta$, 0.2–0.3 ppm), whereas the phenyl resonances are shifted slightly upfield ($\Delta\delta$, −0.2 ppm). The spectrum of [Pt(μ-bpzph)Cl]$_3$ consists of nine sharp resonances, which were fully assigned using COSY and NOESY techniques. The α′, γ', α, and γ proton pyrazolyl resonances fall between 8.55 and 8.05 ppm along with the 2-phenyl proton resonance of bpzph$^-$; the β and β' resonances occur slightly downfield from those of the free ligand. Interestingly, the resonances for the protons at the 4 and 5 positions on the phenyl group are strongly shifted upfield by 0.8 and 1.6 ppm, respectively, from those of the free ligand. These observations are consistent with strong transannular interactions between the ligand phenyl rings.[11] The large shift for the 4-phenyl proton is in agreement with the crystal structure, which suggests that the hydrogen atom is directed toward one face of the pz′ five-membered ring, resulting in shortest H(4-phenyl)···N(pz′) contacts ranging from 2.64 to 2.77 Å. Strong inter-ring NOE signals between the α′-pyrazoyl and 4-phenyl protons, as well as between the 2-phenyl and α-pyrazoyl protons, confirm the connectivity observed in the solid state.

To investigate its thermal stability, [Pt(μ-bpzph)Cl]$_3$ was heated for 30 min periods in DMF-d_7 at a series of progressively higher temperatures (100, 120, 135, 140, 150, and 158 °C), and the room-temperature spectrum was recorded between each period. The spectrum was unchanged after heating at 120 °C. At higher temperatures, a small amount of black precipitate was detected, and resonances due to bpzphH were observed in the NMR spectrum. However, the decomposition was slow, as indicated by the persistence of trimer proton resonances throughout the experiment, and no resonances associated with the monomer or other complexes were detected. Similarly, heating of mixtures of Pt(bpzph)Cl and [Pt(μ-bpzph)Cl]$_3$ in DMF did not result in new products or a change in the ratio of the monomer to the trimer. Stirring the trimer with 6 equiv of NaBr in DMF also did not result in any reaction. It seems likely that coordination of pz′ trans to pz in the trimer, rather than trans to the labilizing phenyl group, contributes to the observed stability. On the other hand, treatment of a room-temperature solution of [Pt(μ-bpzph)Cl]$_3$ in DMF with 3 equiv of $TlPF_6$, followed by the addition of 3.5 equiv of NaBr, gave two new products, Pt(bpzph)Br and [Pt(μ-bpzph)Br]$_3$. The MS spectrum shows a peak at 1372.8 ppm, corresponding to $Pt_3(bpzph)_3Br_2^+$; no chloride-containing products were detected (Figure S5 in the Supporting Information). The ^{1}H NMR spectrum in DMF-d_7 is consistent with clean conversion to the monomer and trimer in a 1:1 ratio. As expected for halide substitution, the trimer resonances are shifted slightly downfield relative to the chloro adduct, with the γ-pyrazolyl and 2-phenyl proton resonances being the most affected ($\Delta\delta$, ~0.15 ppm).

The results presented here show that a conventional meridional tridentate chelate can support the assembly of platinum(II) centers to give a comparatively rigid molecular polygon. The product in this case is a racemic mixture of enantiomers that exhibit remarkable thermodynamic and kinetic stability. Moreover, the complex possesses an unusually deep molecular cavity. The chloride groups at one opening of the molecular cavity afford the opportunity to elaborate on the structure by ligand substitution in order to expand the cavity, introduce functionalities, or couple trimers to form larger molecular containers.

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Supporting Information Available: Preparative details for bpzphH and the complexes, two-dimensional NMR and mass spectra, details of the crystallographic data acquisition and analysis, a packing diagram for [Pt(μ-bpzph)Cl]$_3$·DMF·0.5Et$_2$O, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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