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Heteroligand Molecular “Stirrups” Using Conformationally Flexible Ditopic Pyridyl–Pyrazolyl Ligands

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Heteroligand molecular “stirrups” form by the self-assembly of flexible ditopic ligands in combination with 4,4′-bipyridine and [(dppp)Pd]²⁺. Crystallographic analysis shows that the ligands, bis[3-(4-pyridyl)pyrazolyl]-*m*-xylene (**mXy**^{4py3pz}) and bis[4-(4-pyridyl)pyrazolyl]-*p*-xylene (**pXy**^{4py4pz}) form complexes of the type [(dppp)Pd]₂(4,4′-bipy)(**L**)·4OTf (1·4OTf and 2·4OTf, respectively) in the solid state, with remarkably similar structures considering the differences in substitution patterns between the two ligands. The self-assembly of both **1**⁴⁺ and **2**⁴⁺ is assisted by face-to-face π interactions on the exterior of the macrocycle between the phenyl rings of the dppp ligands and the pyridyl groups of the ditopic ligands.

The synthesis of molecular polygons using a self-assembly approach is garnering a significant amount of research interest as a route toward nanoscale devices.¹ The combination of metal-containing species with predictable coordination geometries, most commonly cis-protected Pd^{II}/Pt^{II}, with

a rigid organic ligand is able to yield a remarkable array of complexes.^{1c} Metal–organic polygons have been reported of triangles,² squares and rectangles,³ and pentagons,⁴ showing the versatility of a self-assembly approach in forming a range of geometric targets. The vast majority of discrete metal–organic polyhedra contain only a single type of bridging ligand, often a symmetrical species, with perhaps the most notable exception being the catenated mixed bipyridine/bis-(pyridyl)biphenyl system of Fujita et al.⁵ Herein we report two novel “stirrup” complexes that form by the self-assembly of a combination of ditopic ligands, the rigid 4,4′-bipyridine and flexible pyridyl–pyrazolyl species, with cis-protected Pd^{II}.

The flexible ditopic ligands bis[3-(4-pyridyl)pyrazolyl]-*m*-xylene (**mXy**^{4py3pz}) and bis[4-(4-pyridyl)pyrazolyl]-*p*-xylene (**pXy**^{4py4pz}) contain meta- and para-substituted xylene cores, respectively (Figure 1). On either side of the core unit are rigid pyridyl–pyrazolyl arms, with substitution at the pyrazolyl ring differing between the two ligands. The two ligands are synthesized in approximately 30–40% yield by phase-transfer reactions of the pyridyl–pyrazolyl precursors with the respective α,α' -dibromoxylene in the presence of potassium hydroxide (see the Supporting Information). While the arms of these ditopic ligands are relatively rigid, there is a significant degree of conformational flexibility arising from the methylene spacers between the arms and the central aromatic ring. In principle, the arms are able to position themselves on opposing sides of the core group, to coordinate in a divergent manner, or on the same side, allowing convergent coordination. Similar ligands that contain alkyl spacers have previously been used to form coordination polymers and, more recently, a π -stacked [2]-catenane.⁶

The combination of the ditopic pyridyl–pyrazolyl ligands with 4,4′-bipyridine (4,4′-bipy) and [(dppp)Pd(OTf)₂] in a

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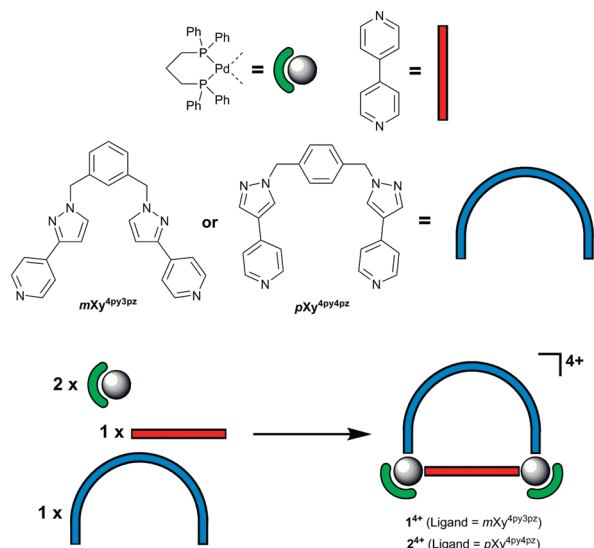


Figure 1. Five-component self-assembly of the molecular “stirrup” complexes 1^{4+} and 2^{4+} using the flexible ditopic pyridyl–pyrazolyl ligands mXy^{4py3pz} and pXy^{4py4pz} .

1:1:2 ratio at room temperature in dichloromethane yields complexes of the general formula $[(\{(\text{dppp})\text{Pd}\}_2(4,4'\text{-bipy})(\text{L})]\cdot 4\text{OTf}$ (where L = either mXy^{4py3pz} or pXy^{4py4pz} , giving $1\cdot 4\text{OTf}$ and $2\cdot 4\text{OTf}$, respectively; Figure 1). The two complexes, despite containing significantly different ligands, both form molecular “stirrups” that have been characterized by X-ray crystallography, multinuclear NMR, and mass spectrometry.

The molecular complex containing the meta-substituted ligand, $[(\{(\text{dppp})\text{Pd}\}_2(4,4'\text{-bipy})(mXy^{4py3pz}))(\text{OTf})_4]$ ($1\cdot 4\text{OTf}$), crystallizes from a dichloromethane/toluene solution in the orthorhombic space group $Pca2_1$.⁷ The asymmetric unit contains one complete 1^{4+} complex and four associated triflate counteranions, although there are no noteworthy intermolecular interactions between the complex and the anions. The complex takes the form of a molecular “stirrup”, with the mXy^{4py3pz} ligand adopting a “horseshoe” geometry and the 4,4'-bipy ligand acting as the rigid linear bridge (Figure 2). The Pd atoms adopt slightly distorted square-planar geometries with P–Pd–P angles of 92.0 and 91.5° and associated N–Pd–N angles of 85.8 and 84.0°, respectively, although there is very little deviation from planarity (the average out-of-plane P/N distance is approximately 0.06 Å with the Pd atom removed from the N_2P_2 plane by only 0.01 Å). The metallomacrocycle adopts a slightly concave geometry, with the *m*-xylene spacer group lying out of the “plane” of the rest of the ligand and 4,4'-bipy (Figure 2).

It appears that the dppp ligands may play more of a structural role than simply providing the cis-blocked Pd atom. Four of the phenyl groups form face-to-face π interactions with pyridyl rings from both the mXy^{4py3pz} and 4,4'-bipy ligands. The rings involved in the π interactions are not coplanar because of the steric demands of the complex with ring centroid distances in the range 3.79–4.00 Å. The closest interatomic distances ($\text{C}\cdots\text{N}$) are in the range 3.07–3.16 Å,

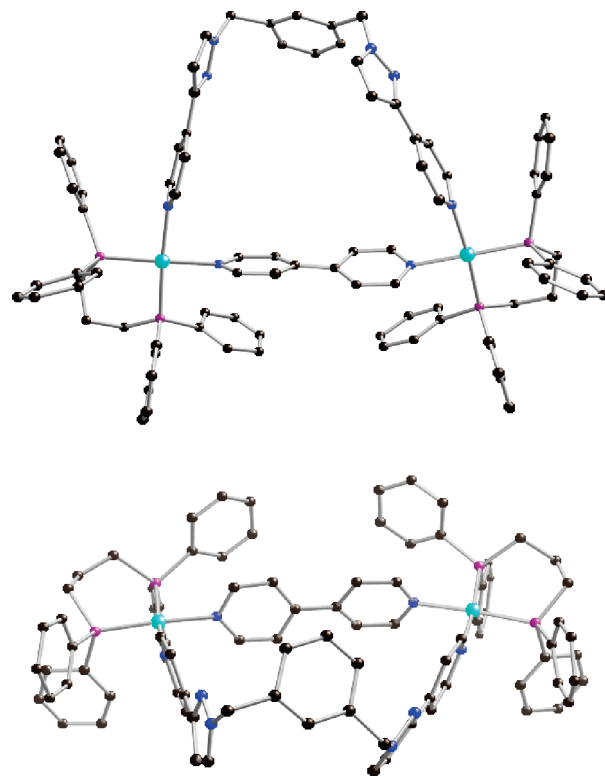


Figure 2. Two views of the molecular “stirrup” complex 1^{4+} from the crystal structure of $1\cdot 4\text{OTf}$ showing the π -stacking interactions between the dppp ligands and the exterior of the macrocycle. Triflate counteranions and H atoms omitted for clarity.

close to the sum of the van der Waals radii (3.25 Å).⁸ We have previously observed the phenyl groups of the dppp ligands playing a significant role from the exterior of a π -stacked catenane.^{6c} It is interesting to observe a similar effect in the “stirrup” complex, although the distances between the π rings and their nonparallel alignment suggest that this may be a secondary stabilization effect rather than a primary structure-directing role (full geometric parameters for $\pi\cdots\pi$ interactions are given in the Supporting Information). The complexes pack poorly, and the structure contains significant solvent-accessible voids.

The complex $[(\{(\text{dppp})\text{Pd}\}_2(4,4'\text{-bipy})(pXy^{4py4pz}))(\text{OTf})_4]$ ($2\cdot 4\text{OTf}$) crystallizes from an *n*-pentane/dichloromethane mixture in the monoclinic space group $C2/m$ (Figure 3).⁷ The asymmetric unit contains half of the cationic complex and two triflate anions, with the complex forming a “stirrup-like” geometry similar to that of 1^{4+} . The molecule possesses a mirror plane along the center of the stirrup (i.e., bisecting the 4,4'-bipy ligands and the *p*-xylene spacer group). The coordination environment around the Pd atoms is very similar to those in 1^{4+} (P–Pd–P = 91.4° and N–Pd–N = 84.6°). These measurements indicate that the degree of strain within the ring, i.e., the “horseshoe” ligand pulling the geometry of the metal away from an idealized square-planar geometry, is not remarkably different between 1^{4+} and 2^{4+} . This is quite surprising considering the differing nature of both the spacer group and the substitution position of the pyridine at the pyrazole ring. The π interactions between the dppp ligands and the pyridyl rings that were observed in 1^{4+} are again present, although the dppp phenyl groups close to the bipyridine ligand are disordered over two sites. It is not clear whether this is an artifact of the

(7) $1\cdot 4\text{OTf}$: orthorhombic, $Pca2_1$, $a = 31.7475(8)$ Å, $b = 13.1008(4)$ Å, $c = 27.9322(9)$ Å, $R1 = 0.0920$. $2\cdot 4\text{OTf}$: monoclinic, $C2/m$, $a = 28.0643(8)$ Å, $b = 23.5338(6)$ Å, $c = 18.5747(6)$ Å, $\beta = 93.262(2)^\circ$, $R1 = 0.0733$. Full crystallographic details are supplied in the Supporting Information.

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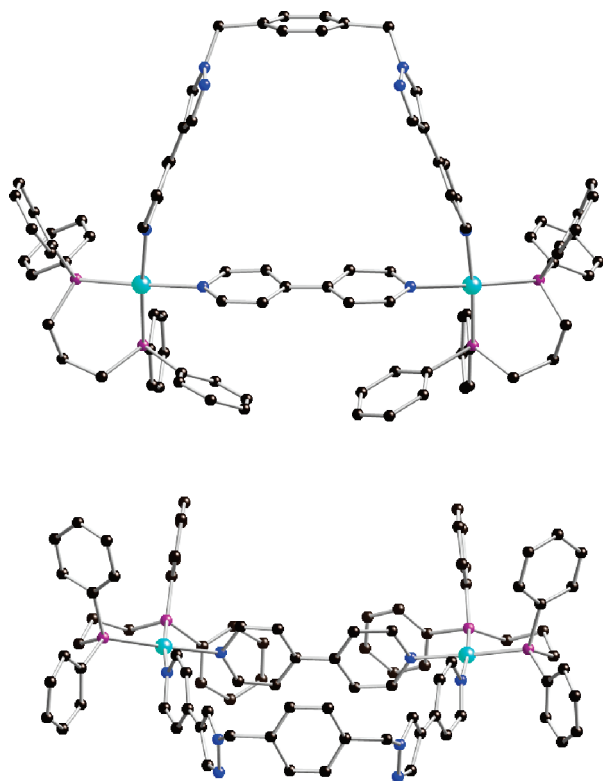


Figure 3. Two views of the “stirrup” complex 2^{4+} from the crystal structure of $2 \cdot 4OTf$. H atoms and counteranions are omitted for clarity.

crystallographic symmetry in the complex (two superimposed preferred orientations) or the dynamic disorder that has been frozen into two apparent conformations. The distances between the ring centroids are comparable to those observed in 1^{4+} with overlap of the van der Waals radii for the pivot atoms of the aromatic rings (see the Supporting Information).

While the two complexes 1^{4+} and 2^{4+} adopt remarkably similar geometries in the solid state, preliminary studies of their solution behavior show differences. Both the 1H and ^{31}P NMR spectra of $1 \cdot 4OTf$ display broad, overlapping signals that are indicative of several species coexisting in solution (see the Supporting Information). However, electrospray ionization mass spectrometry (ESI-MS) indicates that the “stirrup” complex does persist in solution, with the molecular ion observed alongside a number of other aggregate species. A signal is observed that corresponds to $\{1 \cdot 3OTf\}^+$, with calculated and experimental isotopic patterns in agreement with an overlapping signal corresponding to a fragment with double the formula, although the exact nature of this species cannot be deduced (i.e., large macrocycle vs catenane). Peaks relating to a number of different ligand/metal ratios were also noted (see the Supporting Information).

In contrast, 1H and ^{31}P NMR spectra of $2 \cdot 4OTf$ (Figure 4) show the presence of only a single, symmetric species in

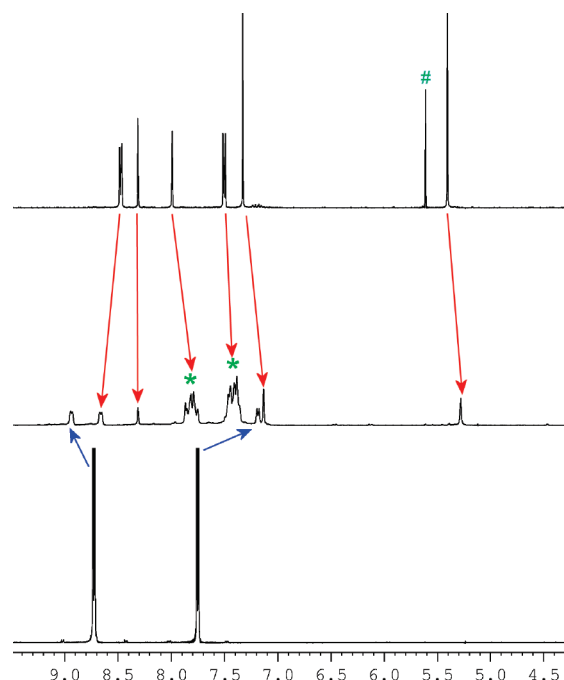


Figure 4. Partial 1H NMR spectra of pXy^{4py4pz} (top), 4,4'-bipy (bottom), and the “stirrup” complex $2 \cdot 4OTf$ (middle) in acetone- d_6 (* indicates signals from the phenyl groups of the dppp ligands; # indicates residual CH_2Cl_2).

solution with assignments supported by 2D NMR (see the Supporting Information). The $^{31}P\{^1H\}$ NMR displays two doublet peaks at 8.00 and 7.14 ppm ($^2J_{P-P} = 33$ Hz). This supports the formation of the heteroligand complex in which two magnetically inequivalent phosphorus nuclei are bound to the same Pd atom. The difference in solution behavior between the two complexes suggests that 1^{4+} may be more sterically strained. ESI-MS studies give further confirmation that 2^{4+} exists in solution, with an isotopically resolved peak corresponding to $\{2 \cdot 3OTf\}^+$ overlapped with a doubly charged species.

In conclusion, we have demonstrated the formation of two molecular “stirrups” that form through the combination of two different ditopic ligands rather than forming homoligand compounds. Despite substitutional differences between the two pyridyl–pyrazolyl ligands, there are remarkable similarities between their complexes; however, preliminary studies show that their solution behavior is markedly different.

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Supporting Information Available: Crystallographic data (CIF) for **1** and **2**, full crystallographic refinement information, synthetic details, NMR spectra, and ESI-MS results. This material is available free of charge via the Internet at <http://pubs.acs.org>.