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Chair−Boat Form Transformation of Piperazine-Containing Ligand toward the Preparation of Dirhenium Metallacycles

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A new generation of a flexible bipyridine-based ligand, 1,4-bis(4-pyridyl)-piperazine, with two main stable states (chair and twist-boat forms) was employed in the construction of unusual dirhenium metallacycles.

Self-assemblies of discrete metallacycles with nanoscopic dimensions have attracted great attention for more than a decade. Supramolecular metallacycles, including triangles, squares, rectangles, pentagons, hexagons, etc., have the potential to act as selective receptors, catalysts, and model compounds that mimic natural systems.[1−5] Nitrogen-containing heterocycles are frequently used as building blocks in the construction of supramolecules. In particular, bipyridines (4,4′, 3,3′, and 2,2′) have been regarded as the most widely used ligands for this purpose.[6] The incorporation of flexible units into metallacycles has recently received increasing attention because they offer several potential advantages, such as adaptive recognition properties and breathing ability in the solid state.[7] Conjugated bipyridines are, however, rather rigid. Derivatives such as dipyridylpropane, dipyridylethane, and dipyridylmethane have been used to modulate the flexibility of the bipyridines.[8] Nevertheless, the lack of a controllable element, due to the freedom of the C−C single-bond connection, between the two pyridine units prevents the ligands from serving as useful building blocks.

Herein, we describe the selection and use of 1,4-bis(4-pyridyl)piperazine (bpp)[9] as a flexible ligand with a limited number of conformations for constructing metallacycles (Scheme 1). The bpp ligand not only is flexible but also possesses two main stable states, chair and twist-boat forms, which can be used as a 0−1 switch for the construction of metallacycles (Scheme 2). A novel class of dinuclear

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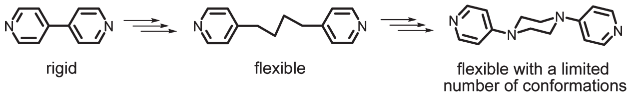
Scheme 1. Development of a Flexible Pyridine-Based Ligand with a Limited Number of Conformations



Scheme 2. Chair–Boat Form Transformation of the bpp Ligand

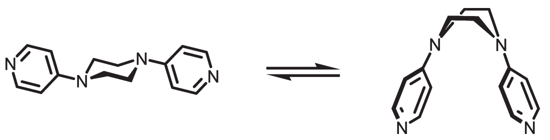


Figure 1. ORTEP diagram of **1** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity.

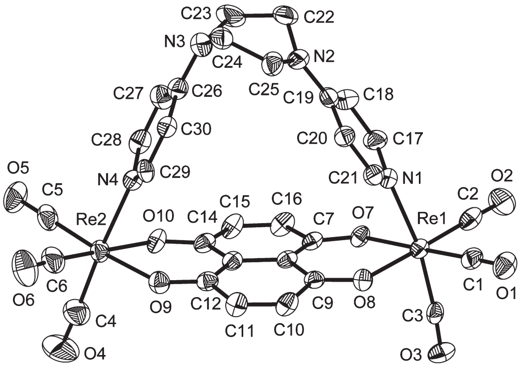
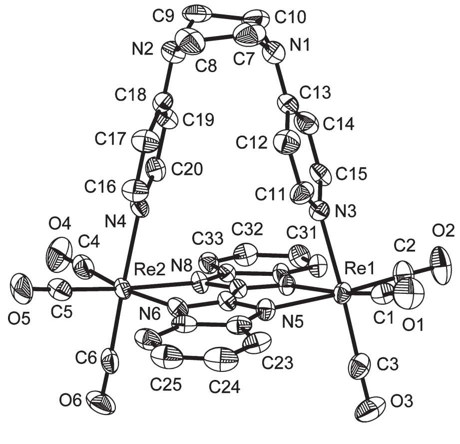
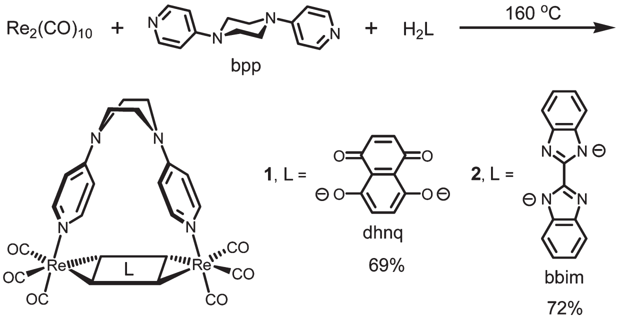


Figure 2. ORTEP diagram of **2** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity.



Scheme 3. Synthesis of Dirhenium Metallacycles **1** and **2**



metallacycles, containing two rhenium centers, one bis(chelating) dianion, and one bpp adopting a twist-boat form, was assembled in high yields (Scheme 3).

Treatment of $Re_2(CO)_{10}$ with bpp and either 5,8-dihydroxy-1,4-naphthoquinone (H_2dhnq) or 2,2′-bis(benzimidazole) (H_2bbim)[10] in a 1:1:1 ratio under hydrothermal conditions afforded dirhenium metallacycles **1** and **2**, respectively.[11] The ^{1}H NMR spectrum of **1** indicated the presence of bpp and dhnq ligands; the chemical shifts of the pyridyl protons appeared at 7.68 and 6.60 ppm. Significantly, the piperazine moiety revealed two doublet proton signals (3.78 and 3.44 ppm) in contrast to one singlet (3.48 ppm) in the free ligand. This indicates that the piperazine unit may adopt a boat or a twist-boat conformation. The fast atom bombardment mass spectrometry (FAB-MS) spectrum of **1** showed a molecular ion at *m*/*z* 968.1, with the experimental isotope pattern matching the simulated mass.

A single-crystal X-ray diffraction analysis[12] revealed that **1** adopts a dinuclear architecture (Figure 1). The two Re^I ions are bridged by one dhnq moiety through four oxygen atoms. The bpp ligand with a twist-boat form of piperazine unit bridges two Re^I centers, thereby constituting the third apex of the triangle, with each rhenium center possessing a distorted octahedral geometry. The Re$\cdots$Re distance is 8.48 Å, and the angles of N2–Re1–Re2 and N3–Re2–Re1 are 59.6 and 65.1°, respectively, leading to the formation of a near-regular triangle. Complex **2** adopts a dinuclear molecular structure (Figure 2). In addition to a bridging bbim moiety, the two Re^I centers are also coordinated by a boat-shaped piperazine unit, as the third apex of the triangle, in which the Re$\cdots$Re distance (5.73 Å) is much shorter than that for **1**. The N1–Re1–Re2 and N2–Re2–Re1 angles are 75.0 and 76.2°, respectively, and thus a roughly isosceles triangle is produced. Interestingly, because of the shorter Re$\cdots$Re distance, the bpp ligand adopts a more bent conformation with strong π–π stacking interactions between the pyridyl

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(11) Synthesis for **1**: A mixture of $Re_2(CO)_{10}$ (65.3 mg, 0.10 mmol), bpp (24.0 mg, 0.10 mmol), and H_2dhnq (19.0 mg, 0.10 mmol) in toluene (6 mL) in a 20 mL Teflon flask was placed in a steel bomb. The bomb was placed in an oven maintained at 160 °C for 72 h and then cooled to 25 °C. Compound **1** was contained as black crystals and powder that were filtered off, washed with butanol and *n*-hexane, and then air-dried. Yield: 73.0 mg (69%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.68 (d, 4H, $J = 4.5$ Hz, H_α-Py), 7.07 (s, 4H, dhnq), 6.60 (d, 4H, $J = 4.5$ Hz, H_β-Py), 3.78 (d, 4H, $J = 8.4$ Hz, piperazine), 3.44 (d, 4H, $J = 8.4$ Hz, piperazine). IR (THF, cm^{-1}): ν(C≡O) 2016 (sh), 2010 (vs), 1910 (vs), 1890 (vs). FAB-MS: *m*/*z* 968.1 (M^+). Anal. Calcd for $C_{37}H_{28}N_4O_{10}Re_2$ (**1**·toluene): C, 41.88; H, 2.66; N, 5.28. Found: C, 41.43; H, 2.71; N, 5.28. Synthesis for **2**: The yellow compound **2** was prepared in a manner similar to that of **1** but with the substitution of H_2bbim for H_2dhnq in mesitylene. Yield: 95.0 mg (72%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.72 (dd, 4H, $J = 6.0$ and 3.0 Hz, bbim), 7.45 (dd, 4H, $J = 6.0$ and 3.0 Hz, bbim), 7.30 (d, 4H, $J = 6.0$ Hz, H_α-Py), 6.27 (d, 4H, $J = 6.0$ Hz, H_β-Py), 3.70 (d, 4H, $J = 8.2$ Hz, piperazine), 3.15 ppm (d, 4H, $J = 8.2$ Hz, piperazine). IR (THF, cm^{-1}): ν(C≡O) 2024 (s), 2018 (vs), 1914 (vs), 1900 (vs). FAB-MS: *m*/*z* 1012.6 (M^+). Anal. Calcd for $C_{56.5}H_{54}N_8O_6Re_2$ (**2**·2.5mesitylene): C, 51.66; H, 4.14; N, 8.53. Found: C, 51.33; H, 4.34; N, 8.44.

(12) Crystal data for **1**·toluene and **2**·2.5mesitylene at 200 K with Mo Kα ($\lambda = 0.710\,73$ Å) radiation. **1**·toluene: $C_{37}H_{28}N_4O_{10}Re_2$, $M = 1061.03$, monoclinic, $P2_1/n$, $a = 12.6190(2)$ Å, $b = 11.7120(2)$ Å, $c = 24.5400(4)$ Å, $\beta = 97.3410(10)°$, $V = 3597.13(10)$ Å^3, $Z = 4$. R1 = 0.0494 [$I > 2\sigma(I)$], wR2 = 0.1359 for all data. **2**·2.5mesitylene: $C_{56.5}H_{54}N_8O_6Re_2$, $M = 1313.48$, triclinic, $P1$, $a = 11.285(2)$ Å, $b = 13.528(3)$ Å, $c = 17.562(4)$ Å, $\alpha = 89.21(3)°$, $\beta = 88.11(3)°$, $\gamma = 85.64(3)°$, $V = 2671.8(9)$ Å^3, $Z = 2$. R1 = 0.0383 [$I > 2\sigma(I)$], wR2 = 0.1042 for all data.

moieties. The distances of the two face-to-face pyridyl rings are in the range of 3.23–4.67 Å. The ^{1}H NMR spectrum of compound **2** showed a distinct upfield shift in the pyridine region (7.30 and 6.27 ppm), compared with those of compound **1** (7.68 and 6.60 ppm), which also is indicative of $\pi-\pi$ stacking of the pyridine ring.[13]

It is likely that the lengths of the bischelating units provide the potential for directing the conformation of the bpp ligand.[7d] Entropy effects, however, in the formation of the metallacycles **1** and **2** during the hydrothermal process, cannot be excluded.[4a,4c,4f,4g,5j–5l] In particular, the extent of bending of the twist-boat form of the bpp ligand is adjustable depending on the length of either the dhnq or bbim spacer. Hosseini and co-workers reported on a tripalladium metallacycle containing bpp ligands, which was characterized by NMR spectroscopy and FAB-MS spectrometry.[9a] Our previous results show that a derivative of the bpp ligand adopts a chair conformation.[9c] In addition to the lengths of the bischelating units, the relatively limited number of conformations, i.e., chair and boat forms of the piperazine moiety of the bpp ligand, is also an important factor in tuning the formation of **1** and **2**.

The UV–vis spectrum of **1** in tetrahydrofuran (THF) showed two sharp absorption peaks at 229 and 273 nm and a broad band at 457 nm. The UV–vis spectrum of **2** in THF showed absorption peaks at 231, 284, and 328–370 nm bands. In compounds **1** and **2**, the absorptions from 229 to 284 nm are assigned to the $\pi-\pi^*$ transition of the bridging ligands. In **1**, the broad absorption at 457 nm may have arisen from the intraligand transition of the dhnq unit. The weak band at 550–700 nm can be attributed to the intraligand transition of the quinone moiety.[14] In **2**, the absorption in the 328–370 nm range is associated with the bbim bridging ligand in line with the relative rhenium complexes.[15] The emission spectrum of **2** in THF at room temperature exhibited a set of structured bands centered at 444 nm when excited at 349 nm. These emission bands are due to the decay of the $\pi-\pi^*$ excited state of the bbim ligand.

The bpp ligand not only modulates the rigidity of the traditional bipyridine derivatives but also avoids an unlimited number of conformations of other flexible ligands. Although only a few reports related to the ligand and its coordination chemistry can be found in the literature,[9] the utilization of a flexible ligand with two main stable states, namely, chair and twist-boat forms, in the construction of metallacycles has never been addressed. The successful isolation of the dirhenium metallacycles proves the applicability of the concept of self-adaptation and switching of the title unit.

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Supporting Information Available: X-ray crystallographic files for **1** and **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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