

Rhenium(I)-based Double-heterostranded Helicates

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Abstract: Rhenium(I)-based supramolecular coordination complexes were obtained using $\text{Re}_2(\text{CO})_{10}$, (2-hydroxyphenyl)benzimidazole-derived bis-chelating N/O donors and a benzimidazolyl-derived ditopic monodentate N-donor possessing Troger's base spacer in a one-pot approach.

Keywords: Complex · Helicate · Rhenium · Supramolecule · Troger's base

Supramolecular coordination complexes (SCCs) are functionally important molecules due to their wide applications as sensors, catalysts, in dye-sensitized solar-cells, as electroluminescent devices, and biomolecular imaging.^[1] Among the several metal ion-based SCCs, the *fac*- $\text{Re}(\text{CO})_3$ -based complexes are in general kinetically inert, neutral, and display interesting photophysical properties.^[2–4] The Re-based SCCs are generally assembled using anionic bis-chelating N/O–/O/O–/N/O– donors and neutral N donor ligands. Recently, the focus was shifted to use functionalized benzimidazolyl coordinating units incorporating di-/tri-/tetra-topic ligands to construct various sizes of Re-SCCs because the nature of the donor unit, the spacer moiety, and the substituents on both units influence the resulting architecture and properties of SCCs.^[3] Although the incorporation of furan/thiophene/SH/SMe functions on the benzimidazolyl core is now well established, attempts to change/modulate the central phenylene spacer by other functional spacer are rare in Re-based SCCs.^[2–4] In an attempt to modulate the phenylene spacer in the ditopic benzimidazolyl donors, Troger's base (TB) was chosen due to its C_2 -symmetric heterocyclic nature with relatively rigid backbone, hydrophobic cavity, concave conformation, and the applications of its derivatives in molecular recognition, catalysis, bio-imaging and sensing (Fig. 1).^[5,6] To the best of our knowledge, there is no report of Re(I)-based complexes or Re-based SCCs containing a Troger's base moiety. However, there are a few reports of

homoleptic and ionic SCCs based on other metal ions and Troger's base derivatives.^[6] Herein we report on the first examples of Re(I)-based SCCs possessing Troger's base as a spacer unit.

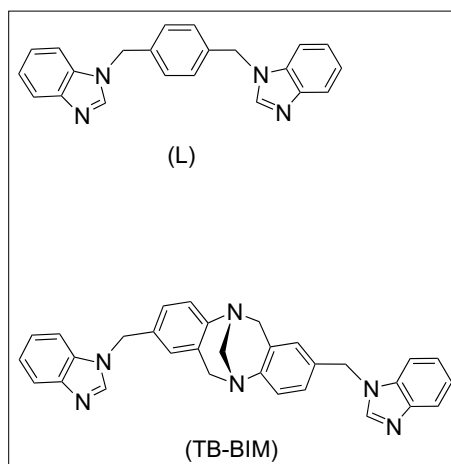


Fig. 1. Benzimidazolyl based N-donor ligands with phenylene (top) and Troger's base (bottom) spacer.

The treatment of $\text{Re}_2(\text{CO})_{10}$ with 1,4-bis(2-(2-hydroxyphenyl)benzimid-

azol-1-ylmethyl)benzene (H_2 -pBC) or 1,3-bis(2-(2-hydroxyphenyl)benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene (H_2 -mBC)^[3c] and Troger's base incorporated bis(benzimidazolyl) (TB-BIM)^[7] in toluene resulted in the formation of **1** and **2**, respectively (Scheme 1). The products are air and moisture stable. Complex **1** is insoluble in organic solvents. Complex **2** is sparingly soluble in polar organic solvents. The FT-IR spectra of complexes **1** and **2** showed three strong bands at 2012, 1898, 1868 and 2012, 1901, 1867 cm^{-1} , respectively characteristic of *fac*- $\text{Re}(\text{CO})_3$ units in an asymmetric environment.^[2,3] Proton NMR spectrum of **2** in d_6 -DMSO showed multiple peaks (Supplementary data; Fig. S1). The ratio of methyl unit and remaining protons of the complex is 9:43, which suggests the formation of complex **2**. In addition, upfield shifts were observed for few aromatic protons in the aliphatic region indicating that complex **2** retains its metallacyclic structure in solution. The electrospray ionization mass spectra of **1** and **2** showed molecular-ion peaks (m/z 1544.3028 for $[\mathbf{1}]^+$ and 1586.3430 for $[\mathbf{2}]^+$) that match the theoretical values (Fig. 2).

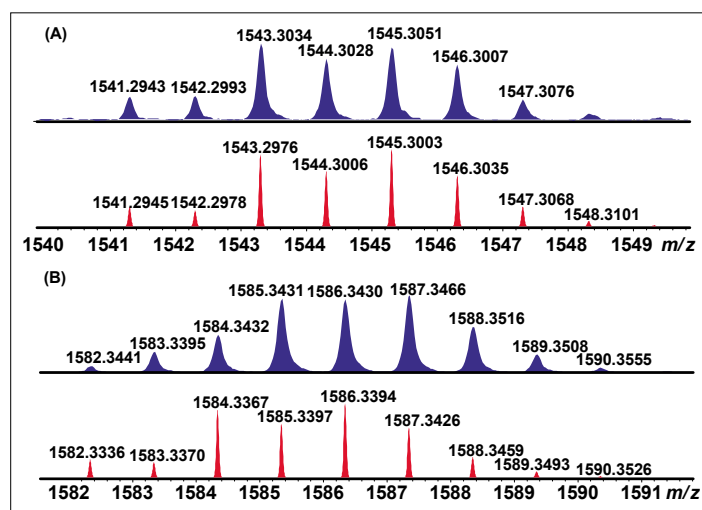


Fig. 2. Experimental (blue) and calculated (red) ESI-TOF-MS spectra of $[\mathbf{1} + \text{H}]^+$ (A), and $[\mathbf{2}]^+$ (B).

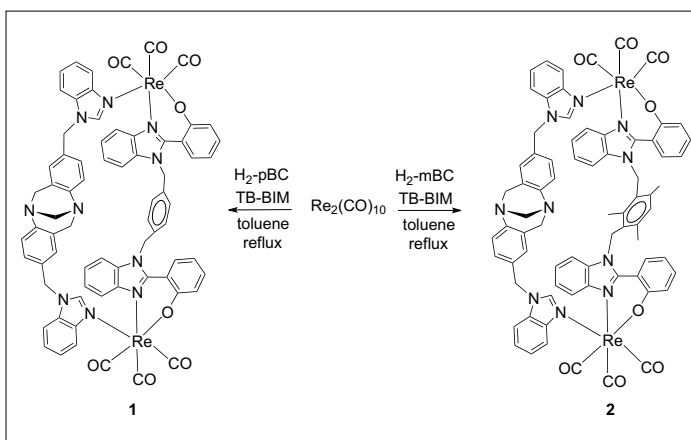
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The single-crystal X-ray structure analysis of complex **1** revealed an unsaturated heterostranded dinuclear double helicate structure, which is made of two *fac*-Re(CO)₃ cores, one dianionic pBC strand and one neutral TB-BIM strand (Fig. 3). The Re(I) adopts a distorted octahedral arrangement and is surrounded by a N \curvearrowright O⁻ donor from the chelating unit of pBC, a N donor atom from the benzimidazolyl unit of TB-BIM and three carbonyl groups. Both pBC and TB-BIM-strands wrap around the Re...Re axis in a helical manner. The length of the helix, as defined by the intramolecular Re...Re distance is ~13 Å. The twist angle, *i.e.* the angle between the planes of the two Re–O–N_(pBC) units is 83°. Two types of very weak intramolecular C–H... π interactions were found between the two strands (pBC...TB-BIM, central phenylene unit of pBC to one of the Troger's phenylene ring, distance C3/C4...centroid (C51, C52, C54, C55, C56, C57) = 4.225/4.117 Å; C1(CH2)...C44(phenylene) = 4.041 Å). The (pBC)²⁻ strand takes an *anti*-conformation with co-facial arrangement of the two (2-hydroxyphenyl)benzimidazole units. The TB-BIM ligand adopts an *anti*-conformation as identified by opposite orientations of the two benzimidazolyl groups with respect to the plane passing through two methylene connectors. The distance between the centres of the two phenylene rings of the Tröger's base in **1** (4.8 Å) and the dihedral angle between the phenylene rings (84°) indicates strained arrangement of Tröger's base in **1**.^[5,6]

In the crystal structure of **1**, each helicate molecule interacts with adjacent helicate molecules *via* the various non-covalent interactions including aryl edge-to-face-, alkyl C–H... π -, face-to-face π – π stacking-, and C=O...H hydrogen bonding interactions (Fig. 4). A strong intermolecular π – π stacking (distance = ~3.35 Å) and C–H... π -interactions (C42(CH2)...C37(phenylene) = 3.528 Å) was found between the two neighbouring methylenebenzimidazolyl units of TB-BIM (Supplementary data; Fig. S2 and S3).

Conclusions

Flexible bis(bidentate) N \curvearrowright O derived dianionic donors and Troger's base derived ditopic ligand were used to assemble rhenium(I)-double heterostranded helicates containing a Troger's base derivative. The replacement of the phenylene spacer by a TB unit, introduced potential donor groups in the form of bridgehead nitrogens for post-synthetic modifications. Our future work will focus on the photo-physical properties of the complexes and their biological applications.



Scheme 1. Synthesis of complexes **1** and **2**.

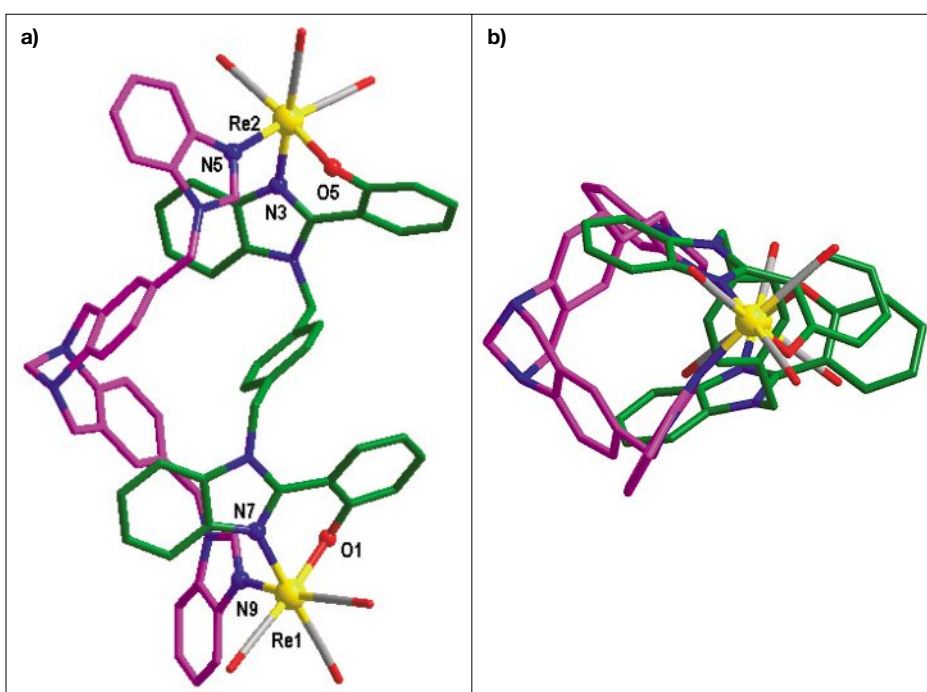


Fig. 3. (a) Perspective view of **1**; (b) Axial view; the carbon atoms of the two strands TB-BIM and dianionic pBC are differently colored for clarity. Green = Rose = Gray = C, White = H, Blue = N, Red = O, Yellow = Re. Hydrogen atoms are omitted for clarity.

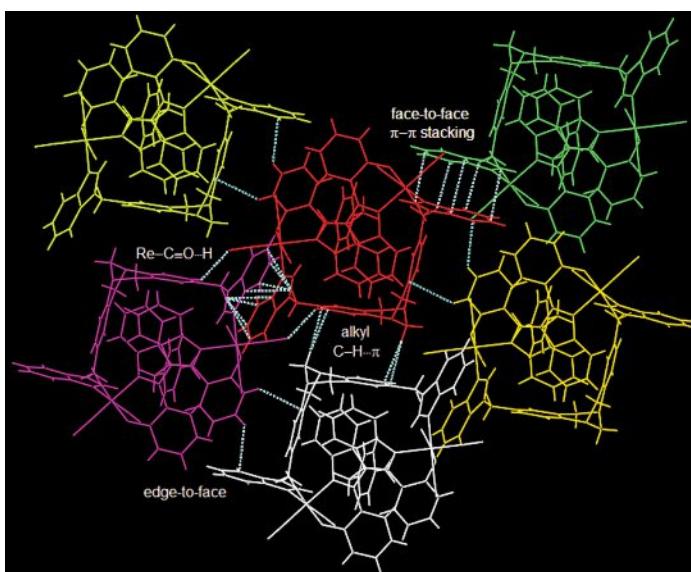


Fig. 4. The partial packing diagram of **1**.

Experimental Section

Synthesis of $[\{\text{Re}(\text{CO})_3\}_2(\text{pBC})(\text{TB-BIM})]$ (1)

$\text{Re}_2(\text{CO})_{10}$ (200.0 mg, 0.3064 mmol), $\text{H}_2\text{-pBC}$ (160.1, 0.3064 mmol), TB-BIM (149.9 mg, 0.3065 mmol), and toluene (12 mL) were taken in a Teflon vessel, which was placed in a steel bomb. The bomb was kept in an oven maintained at 160 °C for 48 h and then cooled to 25 °C. Yellow crystals were obtained and separated by filtration. The product was washed with distilled hexane and air-dried. Yield: 31% (146 mg, 0.0946 mmol). Anal. calcd for $\text{C}_{71}\text{H}_{50}\text{N}_{10}\text{O}_8\text{Re}_2 \cdot 1/4\text{C}_7\text{H}_8$ (Mw: 1543.65 + 23.03): C, 55.77; H, 3.35; N, 8.94. Found: C, 55.97; H, 3.08; N, 8.68. IR (KBr, cm^{-1}): $\nu(\text{C}\equiv\text{O})$ 2012 (s), 1898 (vs), 1868 (vs).

Synthesis of $[\{\text{Re}(\text{CO})_3\}_2(\text{mBC})(\text{TB-BIM})]$ (2)

$\text{Re}_2(\text{CO})_{10}$ (100.0 mg, 0.1532 mmol), $\text{H}_2\text{-mBC}$ (86.5 mg, 0.1532 mmol), TB-BIM (73.9, 0.1532 mmol), and toluene (10 mL) were taken in a Teflon flask, which was placed in a steel bomb. The bomb was placed in an oven maintained at 160 °C for 48 h and then cooled to 25 °C. Yellow crystals were obtained and separated by filtration. The product was washed with distilled hexane and air-dried. Yield: 44% (108 mg, 0.0681 mmol). Anal. calcd for $\text{C}_{74}\text{H}_{56}\text{N}_{10}\text{O}_8\text{Re}_2 \cdot 1/2\text{C}_7\text{H}_8$ (Mw: 1585.73 + 46.07): C, 57.05; H, 3.71; N, 8.58. Found: C, 56.80; H, 4.30; N, 8.55. IR (KBr, cm^{-1}): $\nu(\text{C}\equiv\text{O})$ 2012 (s), 1901 (vs), 1867 (vs).

Supplementary Data

Supplementary data is available: Experimental section, and CIF data (CCDC 1019399 for 1).

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