Neutral metallacyclic rotors†

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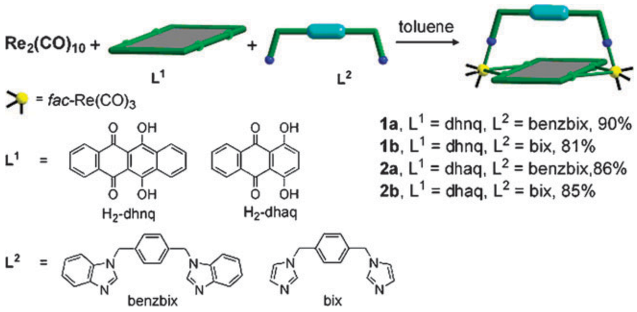
A prototype of a neutral Re-based metallacyclic rotor, assembled in a one-step process, possesses a *para*-phenylene rotor that rotates in solution with respect to the stator.

The intriguing design, synthesis and characterization of various types of molecular rotors has attracted great interest because rotating units are ubiquitous in natural systems, *e.g.* F1-ATPase, kinesin and the dynein family, DNA motors, motor proteins from myosin, and man-made machines.[1] Examples of molecular-sized mechanical analogues are gears, brakes, turnstiles, compasses, gyroscopes, cogwheels, ratchets, shuttles, scissors, walkers and switches.[2–6] Among these, discrete metallacyclic-based molecular rotors are rare.[5,6] Recently, research has been directed to the design of elegant ionic metallacyclic molecular rotors,[6,7] whereas the neutral metallacyclic rotor has remained elusive. This study reports on an efficient approach, *i.e.* the simple combination of *fac*-$Re(CO)_3$-cores and bis(chelating) dianion with *para*-phenylene-incorporated semi-rigid ditopic ligands, to neutral metallacyclic rotors. This metallacycle contains a *para*-phenylene unit that rapidly rotates within the metallacycle.

Compound **1a** was assembled by reacting equimolar amounts of $Re_2(CO)_{10}$, 6,11-dihydroxy-5,12-naphthacenedione (H_2-dhnq) and α,α′-bis(benzimidazole-1-yl)-*para*-xylene (benzbix) in a one-pot procedure (Scheme 1).‡ The resulting dark green products are air-and moisture-stable and soluble in polar organic solvents. The IR spectrum of **1a** exhibited strong bands at 2010, 1907 and 1883 cm^{-1}, characteristic of *fac*-$Re(CO)_3$ in an asymmetric environment.[8] The FAB-MS analysis showed a molecular ion peak at m/z 1168.4, with the experimental isotope pattern matching calculated values and corresponding to a dirhenium metallacyclic structure. Following a similar procedure as for **1a**, metallacycles **1b** and **2a,b** were also synthesized.

A single-crystal X-ray diffraction analysis§ at 150(1) K showed that metallacycle **1a** adopts a dinuclear chair-shaped structure (Fig. 1) and can be regarded as a molecular rotor, in which the dianionic dhnq unit is related to the stator, the *para*-xylene unit is related to the axle and the *para*-phenylene group is related to the rotor. The coordination sphere around the Re centers is a distorted *fac*-C_3NO_2 octahedral geometry. The dianionic dhnq unit acts as a doubly-bridging unit using the chelating oxygen atoms. The benzbix ligand adopts a *syn*-conformation mode. The nearly face-to-face opposite benzimidazole units have separations ranging from 6.9 to 8.3 Å. The distance between the axle and the dhnq mean plane is 5.3 Å. The length of the dhnq stator is 11.38 Å. The dhnq unit and *para*-phenylene group of the benzbix unit are arranged in an almost edge-to-face arrangement, and the short distances between them (C34···C10 3.73 Å and C35···C15 3.80 Å) indicate the existence of C–H···π interactions (Fig. S1, ESI†).[9a] The lattice toluene molecules interact with both the dhnq and *para*-phenylene groups in the same molecule, similar to "benzene ring trimer" interactions (Fig. S1, ESI†).[9b] When the diffraction analysis of **1a** was performed at 295(2) K using different single crystals, no lattice solvent molecules were present and the benzbix ligand was site-disordered over two positions, with a site-of-occupancy of 0.5 (Fig. S3, ESI†). The molecular structures of **1b** and **2b** (Fig. S4 and S5, ESI†) are analogous to that of metallacycle **1a**.

The ^1H NMR spectrum of **1a** at room temperature shows well-separated signals for the ligands (Fig. 2). The H^2, H^4 and H^7 proton signals are shifted downfield, which is normally observed for protons adjacent to coordinated nitrogens.[10] In particular, a single resonance at δ 6.50 for the *para*-phenylene protons, about δ 0.75 upfield from the free benzbix (δ 7.25), was observed. Considering the solid-state structure, the *para*-phenylene protons should give two sets of peaks: a singlet with an upfield signal for the two adjacent protons (H–C34 and H–C35 in Fig. 1 or $H^{9'}$ in Fig. 2) located directly above the shielding zone of the dhnq and a singlet with a downfield (or no significant shift) signal for the remaining two protons (H–C37 and H–C38 in Fig. 1 or H^9 in Fig. 2). Hence, the single resonance for the *para*-phenylene protons in **1a** suggests that the phenylene ring is rotating in solution and that metallacycle **1a** can be depicted as a molecular rotor (Chart 1).[11,12]



Scheme 1 The self-assembly of molecular rotors **1a,b** and **2a,b**.

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† Electronic supplementary information (ESI) available: Synthesis and characterisation details of **2a,b**. Crystallographic and spectral data of **1a,b** and **2a,b**. CCDC 717894–717897. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b901535c

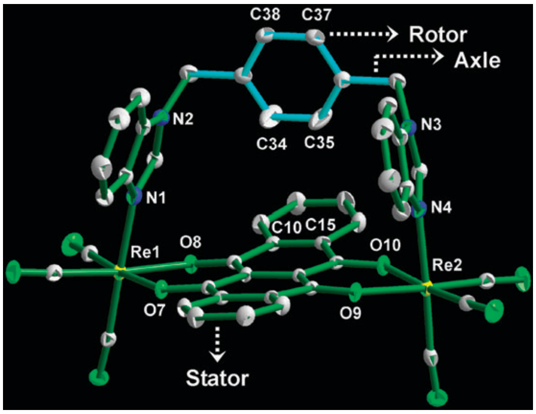

Fig. 1 An ORTEP plot (50% probability) of **1a** measured at 150(1) K. Axle and rotor bonds are indicated by cyan lines. Hydrogen atoms and guest toluene molecules are omitted for clarity.

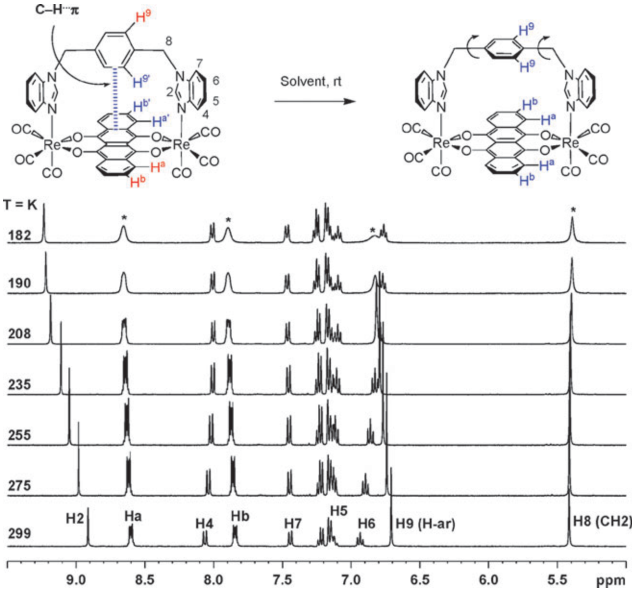

Fig. 2 A schematic representation of **1a** in the solid (left, top) and solution (right, top) state. Variable temperature ^{1}H NMR spectra of **1a** (bottom).

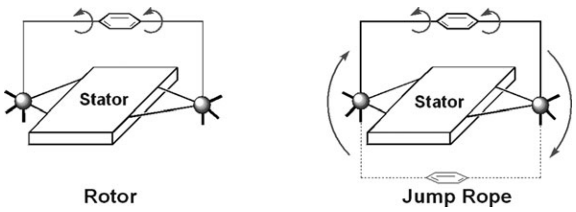

Chart 1 Models of a rotor and a jump rope.

Furthermore, the NOESY spectrum revealed NOEs from H^9 to the H$^{7–8}$ and H^2 protons, and no NOEs to the dhnq protons.

The dynamic behavior of **1a** was further probed by variable temperature ^{1}H NMR spectroscopy. A solution of **1a** in acetone-d_6 was cooled from 299 to 182 K (Fig. 2). Below 208 K, the proton signals corresponding to the *para*-phenylene unit (H^9), the methylene protons (H^8) and the dhnq protons (H^{a,b}) started to broaden. This indicates that at low temperature, the *para*-phenylene rotation was slowed. Complete decoalescence of the *para*-phenylene protons' signals could not be observed at an accessible temperature (182 K). The free energy of activation ($\Delta G^{\neq}$ = 13.7 kcal mol^{-1}) of **1a** was evaluated at a coalescence temperature of 208 K with a chemical shift difference of the resonances ($\Delta\nu$ = 12.4 Hz) calculated using an approximate method (Table S2, ESI†). The energy barrier for *para*-phenylene rotation in **1a** obtained experimentally was closely matched with a complete line-shape analysis (14.5 kcal mol^{-1}; Table S2, ESI†) corresponding to the H^9 peak utilized in the calculation. The energy barrier to *para*-phenylene rotation was slightly higher than that observed for *para*-phenylene rotation (9.3–10.4 kcal mol^{-1}) in some other reports.[6b,13] It is suggested that the C–H···π interactions between the dhnq and *para*-phenylene groups may play a role as an intrinsic brake function in mediating the restricted rotation of the rotor at low temperature, as indicated by the higher energy barrier of rotation. When a solution of **1a** was warmed from 299 to 378 K in DMSO-d_6 (Fig. S7, ESI†), no additional peaks were observed, which suggested thermal stability of the metallacycle. The proton signals of the benzimidazole units were shifted during the cooling and heating of the sample. This indicates that the benzimidazolyl units are flexible. Therefore, a *syn*/*anti* conformational exchange/equilibrium process is possible. The more downfield shift observed for the imidazolyl proton (H^2) indicates that this proton is moving away from the shielding zone when the temperature is lowered. Compared to the imidazolyl proton, the fused arene of the benzimidazolyl unit (H$^{4–7}$) is at the other end and shows the opposite effect, with less significant chemical shift changes. The two benzimidazolyl units are coordinated onto the axial sites of the two rhenium centers; it is impossible for the benzbix ligand to rotate around the two Re centers. Furthermore, swinging of the benzbix rope around the dhnq seems unlikely because of steric hindrance (the half-length of the dhnq (5.69 Å) is longer than the width of the rope (5.45 Å; Fig. S2, ESI†)). Hence, metallacycle **1a** is not a jump rope[12] and is best depicted as a rotor (Chart 1). The ^{1}H NMR spectra of **1b** and **2a,b** indicate that their *para*-phenylene groups rotate similarly to that in **1a**.

In conclusion, neutral, Re-based metallacyclic rotors were assembled in a one-step synthesis in high yields. The metallacycles possess *para*-phenylene rotors that rotate in solution. These rotors can be considered a prototype of a neutral altitudinal rotor, and are almost the first such rotors to be reported. A key feature is the very easy assembly of the system and the use of some unique elements, which are promising for expansion to more complex structures.

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Notes and references

‡ *Synthesis and characterisation details*

1a: A suspension consisting of a mixture of $Re_2(CO)_{10}$ (217 mg, 0.33 mmol), benzbix (113 mg, 0.30 mmol) and H_2-dhnq (97 mg, 0.33 mmol) in toluene (16 mL) in a Teflon flask 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. Good quality, dark green-colored single crystals of **1a** were obtained. The crystals were separated by filtration and washed with hexane. Yield: 90% (363 mg). Anal. calc. for

$C_{46}H_{26}N_4O_{10}Re_2\cdot(C_7H_8)_{0.5}$: C, 49.00; H, 2.49; N, 4.62. Found: C, 48.73; H, 2.24; N, 4.49%. IR (CH_3COCH_3/cm^{-1}): 2010 ($C{\equiv}O$), 1907 ($C{\equiv}O$) and 1883 ($C{\equiv}O$). MS-FAB (*m*/*z*): 1168.4 [M^+]. ^1H NMR (DMSO-d_6): δ 8.88 (s, 2H, H^2, benzbix), 8.45 (m, 4H, H^1, dhnq), 7.95 (d, J = 8.1 Hz, 2H, H^4, benzbix), 7.85 (m, 4H, H^2, dhnq), 7.62 (d, J = 8.1 Hz, 2H, H^7, benzbix), 7.22 (m, 6.5H, H^{5-6}, benzbix, toluene), 6.50 (s, 4H, H^9, benzbix), 5.35 (s, 4H, CH_2, benzbix) and 2.29 (s, 1.5H, CH_3, toluene).

1b: Dark green crystals of **1b** were obtained by following a similar procedure to that for **1a**, using $Re_2(CO)_{10}$ (217 mg, 0.33 mmol), α,α'-bis(imidazole-1-yl)-*para*-xylene (bix) (89 mg, 0.34 mmol) and H_2-dhnq (99 mg, 0.34 mmol) in toluene (16 mL). Yield: 81% (287 mg). Anal. calc. for $C_{38}H_{22}N_4O_{10}Re_2$: C, 42.77; H, 2.08; N, 5.25. Found: C, 42.99; H, 2.14; N, 5.30%. IR (CH_3COCH_3/cm^{-1}): 2009 ($C{\equiv}O$), 1901 ($C{\equiv}O$) and 1886 ($C{\equiv}O$). MS-FAB (*m*/*z*): 1066.13 [M^+]. ^1H NMR (DMSO-d_6): δ 8.44 (m, 4H, H^1, dhnq), 8.29 (s, 2H, H^2, bix), 7.90 (m, 4H, H^2, dhnq), 7.04 (t, J = 1.23 Hz, 2H, H^4, bix), 6.90 (s, 2H, H^5, bix), 6.44 (s, 4H, H^7, bix) and 5.01 (s, 4H, CH_2, bix).

§ Crystal data for **1a**: $C_{46}H_{26}N_4O_{10}Re_2$, M_r = 1167.11, orthorhombic, a = 12.7711(2), b = 19.6190(3), c = 17.1168(3) Å, U = 4288.72(12) Å^3, T = 295(2) K, space group *Pnma*, Z = 4, 24 620 reflections measured, 5246 unique (R_{int} = 0.0732), which were used in all calculations. Final R indices: $R1$ = 0.0669 and w$R2$ = 0.1338 for 3793 reflections [$I > 2\sigma(I)$]; $R1$ = 0.0896 and w$R2$ = 0.1431 for all data. GOF = 1.159. CCDC 717894.†

Crystal data for $\mathbf{1a}\cdot 0.5C_7H_8$: $C_{49.50}H_{30}N_4O_{10}Re_2$, M_r = 1213.17, monoclinic, a = 9.9194(3), b = 21.3024(8), c = 21.7617(8) Å, β = 96.463(1)°, U = 4569.2(3) Å^3, T = 150(1) K, space group $P2_1/n$, Z = 4, 45 222 reflections measured, 10 488 unique (R_{int} = 0.0357), which were used in all calculations. Final R indices: $R1$ = 0.0313 and w$R2$ = 0.0826 for 9496 reflections [$I > 2\sigma(I)$]; $R1$ = 0.0369 and w$R2$ = 0.0886 for all data. GOF = 1.197. CCDC 717895.†

Crystal data for **1b**: $C_{38}H_{22}N_4O_{10}Re_2$, M_r = 1067.00, orthorhombic, a = 23.8693(6), b = 25.9927(7), c = 10.8655(3) Å, U = 6741.3(3) Å^3, T = 150(1) K, space group *Cmca*, Z = 8, 32 508 reflections measured, 3959 unique (R_{int} = 0.0367), which were used in all calculations. Final R indices: $R1$ = 0.0222 and w$R2$ = 0.0451 for 3610 reflections [$I > 2\sigma(I)$]; $R1$ = 0.0260 and w$R2$ = 0.0464 for all data. GOF = 1.111. CCDC 717896.†

Crystal data for $\mathbf{2b}\cdot C_3H_6O$: $C_{37}H_{26}N_4O_{11}Re_2$, M_r = 1075.02, monoclinic, a = 22.3424(8), b = 20.9297(7), c = 7.9283(3) Å, β = 98.913(1)°, U = 3662.7(2) Å^3, T = 150(1) K, space group $C2/m$, Z = 4, 17 827 reflections measured, 4325 unique (R_{int} = 0.0561), which were used in all calculations. Final R indices: $R1$ = 0.0460 and w$R2$ = 0.1081 for 3497 reflections [$I > 2\sigma(I)$]; $R1$ = 0.0627 and w$R2$ = 0.1224 for all data. GOF = 1.189. CCDC 717897.†

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