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Neutral heteroleptic rhenium-based M_3L_3L' type metallacycles: Synthesis, structural characterization and DFT/TDDFT studies

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ABSTRACT

Three new M_3L_3L'-type metallacycles (**2**–**4**) based of *fac*-$Re(CO)_3$ core (M), three rigid anionic ditopic bridging ligands (L = imidazolate for **2**; benzimidazolate for **3**; benzotriazolate for **4**), and flexible tripodal N-donors (L′ = 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene for **2** and **3**; 1,3,5-tris(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene for **4**) have been synthesized and structurally characterized by elemental analysis, FT-IR, and ^1H NMR spectroscopy. The structure of metallacycle **4** was confirmed by single crystal X-ray diffraction analysis. The crystal structure of **1**·DMSO (**1** = M_3L_3L'; L = benzimidazolate, and L′ = 1,3,5-tris(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene) was discussed. The absorption and emission properties of complexes have been investigated and were assigned using time-dependent density functional theory calculations.

1. Introduction

In the past three decades, metallacycles have attracted much attention in various fields of chemistry such as molecular recognition, photo- and electro-chemical sensing, cavity-controlled catalysis, and molecular biology [1–20]. The synthesis of metallacycles by coordination-driven self-assembly using predesigned metal acceptors and organic donors is well established. Efforts are being directed towards the design of new functional metallacycles because of their potential applications in several fields [1–20]. We are particularly interested in neutral and heteroleptic *fac*-$Re(CO)_3$-core-based metallacycles because of their properties and potential applications in host–guest chemistry, catalysis, probes for photoluminescence quenching, anticancer agents, and photo- and electro-chemical sensing [21–44]. Many types of rhenium(I)-based cyclic molecules of various shapes and sizes are known, including dinuclear M_2LL', M_2L_2; trinuclear M_3L_3; tetranuclear squares M_4L_4; rectangles $M_4L_4L'_2$, $M_4L_2L'_2$; gondolas $M_4L_2L'_2$; metallacalix[4]arenes $M_4L_2L'_2$; bowls M_4L; hexanuclear prisms $M_6L_6L'_2$, $M_6L_3L'_2$; and octanuclear cycles $M_8L_8L'_2$, $M_8L_4L'_2$ [21–42]. We recently reported a capped metallacalix[3]arene-shaped M_3L_3L'-type metallacycle (**1**, Scheme 1) [34], which was self-assembled in one-step using new bonding combinations, i.e. orthogonal tritopic metal acceptors [*fac*-$Re(CO)_3$], rigid anionic angular ditopic bridging benzimidazolate nitrogen donors (~120°), and neutral flexible tri(monodentate) tripodal nitrogen donors (Scheme 1). The molecular structures of known organic and ionic metallacycles based on the tripodal nitrogen donors used to construct metallacycle **1** indicate that metallacycle **1** possesses two types of hydrogen bonding donors sites, denoted by A and B in Fig. 1. The coordination of the flexible tripodal nitrogen donor ligand organizes the three benzimidazolium rings in such a way that a set of three endo C–H bonds can act as hydrogen-bond donors to anions in **1**. In contrast, the cone-shaped metallacalix[3]arene in **1** provides a set of three exo C–H bonds from three benzimidazolate units, which can act as hydrogen-bond donors to anions [45–49].

As a continuation of our previous work on metallacycle **1**, we thought that replacing a neutral benzimidazolyl and/or anionic benzimidazolate moiety on the ligands by other suitable heterocyclic units would result in similar metallacycles with different functional properties. In this paper, three new M_3L_3L'-type metallacycles (**2**–**4**; **2**, H-L = imidazole (H-IMZ) and L′ = 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (timz); **3**, H-L = benzimidazole (H-BENZ) and L′ = timz; **4**, H-L = benzotriazole (H-BTZ) and L′ = 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (tbimz)) with different building blocks are

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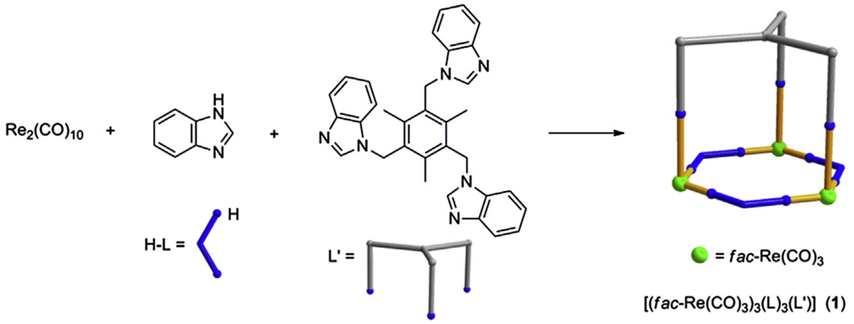

Scheme 1. Synthesis of metallacycle **1**.

reported. Self-assembly of the metallacycles was achieved using $Re_2(CO)_{10}$, imidazole/benzimidazole/benzotriazole, and tripodal nitrogen donors timz/tbimz in a one-step process. The metallacycles were characterized by elemental analysis, and Fourier-transform infrared (FT-IR), ^1H nuclear magnetic resonance (NMR), absorption and emission spectroscopies. The molecular structures of **1**·DMSO (DMSO: dimethyl sulfoxide) and **4** were further confirmed using single-crystal X-ray diffraction (XRD) analysis. The molecular structures of **2** and **3** were optimized using density functional theory (DFT) calculations. The absorption and emission properties of complexes **1**–**4** were also investigated and assigned using time-dependent DFT (TDDFT) calculations.

2. Results and discussion

2.1. Synthesis and characterization of *2*–*4*

The solvothermal reaction of $Re_2(CO)_{10}$, rigid nitrogen donors (H-IMZ for **2**, H-BENZ for **3**, and H-BTZ for **4**) and tripodal ligand (timz for **2**–**3**, and tbimz for **4**) in toluene resulted in the formation of complexes (Scheme 2). The resulting products are air and moisture stable, and soluble in polar organic solvents. The FT-IR spectra of complexes **2**–**4** showed strong bands, characteristic of *fac*-$Re(CO)_3$ unit in an asymmetric environment [34–44]. The ^1H NMR spectra of complexes **2**–**4** exhibited one set of well-separated signals for the ligands (Fig. 2–4). The assignments of all protons were based on spin–spin splitting structure, ^1H–^1H COSY spectroscopy (Figs. S1–S3). The COSY spectrum of **2** showed correlation between the imidazolyl H^{4-5} protons and the imidazolyl H^2 proton, confirming the assignment of the imidazolyl protons in the metallacycle. Similarly, correlations were also observed between the imidazolate H^b protons and the imidazolate H^a proton in **2**. A similar correlations for the imidazolyl protons ($H^{4,5} \leftrightarrow H^2$) was known [50,51]. The H^{4-5} chemical resonance of the imidazolyl unit was shifted downfield, whereas the H^2, $-CH_2-$, and CH_3 proton resonances were shifted upfield relative to those of free tripodal timz ligand. These results clearly indicate that the imidazolyl units in timz are coordinated to metal ions. The large upfield shift observed for the H^2 proton ($\Delta\delta = -2.2$ ppm) in complex **2** relative to the free ligand suggests that timz adopts a head-to-head *syn* conformation, i.e. all three imidazolyl units are at the same side and the three 2-imidazolyl protons directly face each other. A similar upfield shift for the imidazolyl H^2 proton of the tritopic ligand 1,3,5-tris(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene was also observed in the case of ionic metallacycles $[M_3(L')_2]$ (M = Cu, Ag) and complex **1** [52,53]. Similarly, significant chemical shifts were observed for both the H^a and H^b protons of the bridging imidazolate in **2**. A large downfield shift ($\Delta\delta = 0.92$ ppm) was observed for H^a of the bridging imidazolate in **2**, due to its close proximity to the bridging nitrogen atoms (Re–N–CH^a–N–Re), which lose electron density on coordination. The chemical resonance of H^b of the imidazolate, which is also adjacent to coordinated nitrogen atoms (Re–N–CH^b–CH^b–N–Re), was shifted upfield by δ 1.13 ppm relative to the proton of free imidazole. This is possible only if the H^b proton lies close to the π-cloud of the aromatic unit. The methylene (CH_2) and methyl (CH_3) protons of timz in complex also shifted upfield relative to those of free timz ligand, suggesting that the CH_2 and CH_3 protons also experience a ring-current effect from the adjacent imidazolate π-cloud. These chemical resonance data support the suggestion that complex **2** adopts a metallacyclic

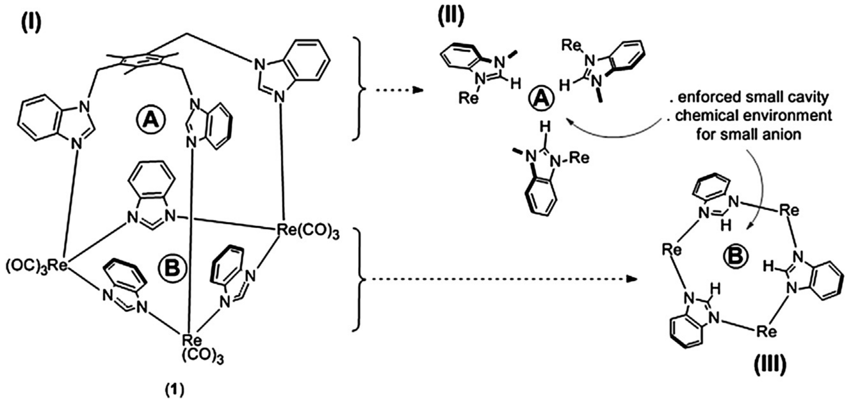

Fig. 1. Molecular structure of metallacycle **1** (A = metallacyclic cavity, and B = exocyclic cavity) (I). Stereochemical arrangement of three benzimidazolyl units (II) and three benzimidazolate units (III).