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Metallo-supramolecular assembly of protic pincer-type complexes: encapsulation of dinitrogen and carbon disulfide into multiproton-responsive diruthenium cage

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Metallo-supramolecular assembly of protic pincer-type complexes: encapsulation of dinitrogen and carbon disulfide into multiproton-responsive diruthenium cage†

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Partial dehydrobromination of a diprotic pincer-type ruthenium complex in the presence of a rigid 1,3-bis(diphenylphosphino)benzene linker provided a dinuclear cage containing a guest template KBr surrounded by hydrogen bonds and electrostatic interactions. Dinitrogen and carbon disulfide were encapsulated into the cage with proton channels formed by the pyrazole arms in the pincer ligands.

Integration of noncovalent interactions typified by hydrogen bonds (H-bonds) and electrostatic attraction in a metal coordination sphere has become an area of intensive research. These weak interactions can have pivotal roles in molecular recognition, bond activation and catalysis by the metal center.[1] Proton transfer events in metalloenzymes are also accomplished by the outer sphere H-bond network involving a chain of water and peptide residues.[2] In one manifestation, nitrogenases have a proton channel from the protein surface to the buried active site with an $MoFe_7S_9C$ cluster core.[3] The proton transfer path would allow regulated provision of protons to dinitrogen on the multimetallic active site, which, along with a sophisticated electron transfer system, appears a key to the efficient reduction to ammonia associated with only a minimum loss of protons as dihydrogen (obligatory H_2 evolution).[4] However, most of the modeling studies so far focused on the metal center,[5] and H-bond networks in the second coordination sphere has attracted much less attention.[6]

Polyprotic, multidentate ligands have been used as a tool to mimic the H-bond-rich coordination environment,[7] as illustrated by pincer-type ligands furnished with two protic pyrazole arms.[8–12] We considered that the higher order architecture in globular metalloproteins featuring multitude of functional groups for weak interactions and proton channels around the metal cofactor may be modeled by accumulation
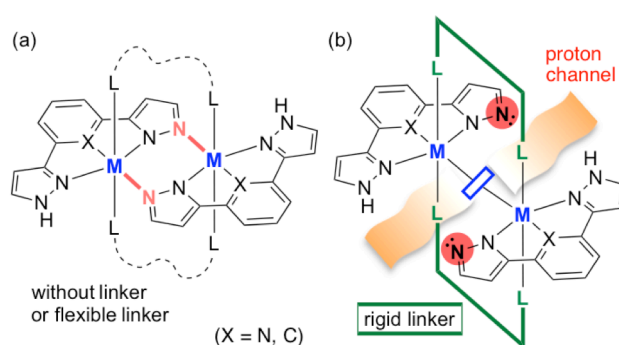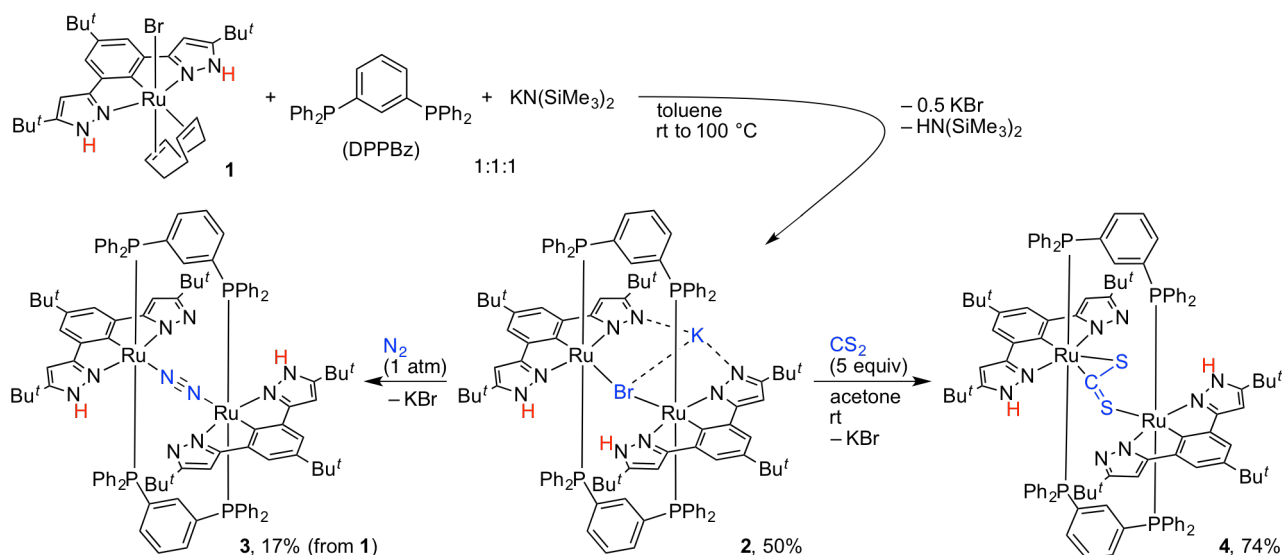

Fig. 1 Assembly of two proton-responsive pincer-type pyrazole–pyrazolato complexes with linker ligands L. (a) Self-quenching of the Lewis acidic metal and pyrazolato site in the two pincer units. (b) Preservation of the metal–pyrazolato bifunctionality in the dinuclear complex by virtue of rigid linkers.

of the preorganized protic pincer-type complexes (Fig. 1). A problem to be resolved here is rigorous control of the relative orientation of the pincer-type units to avoid self-quenching of the functional groups (Fig. 1a).[11–13] We describe here a metallo-supramolecular synthetic approach[14] with judicious choice of the linker to craft a dimetallic cage structure (Fig. 1b) and uptake of dinitrogen and carbon disulfide molecules into the central cavity surrounded by proton-responsive sites.

We selected 1,3-bis(diphenylphosphino)benzene (DPPBz)[15] bearing two phosphorus donors separated by an appropriate distance as a rigid linker to accumulate the protic NCN pincer-type ruthenium complex [RuBr(cod)(LH$_2$)] (1; LH$_2$ is the NCN pincer ligand)‡ without self-quenching shown in Fig. 1a. The reaction of 1 with an equimolar amount of DPPBz and a base in toluene led to the formation of the dinuclear pyrazole–pyrazolato complex K[{Ru(LH)(μ-dppbz)}$_2$(μ-Br)] (2) in 50% isolation yield (Scheme 1). Fig. 2 depicts the crystal structure of 2,§ comprised of two partially-deprotonated pincer-type Ru(LH) units bridged by two DPPBz and a bromido ligand. The potassium cation is further bound to the uncoordinated nitrogen atoms in the pyrazolato arms (N3 and N7)[10,11] as well as the bromido ligand. In addition, close contacts between the cation and the phenylene rings in the DPPBz linkers (K···C:

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Scheme 1 Assembly of the mononuclear pincer-type complex **1** with DPPBz and subsequent encapsulation of dinitrogen and carbon disulfide.

3.150(3)–3.347(3) Å) suggest electrostatic cation–π interaction; the interplane angle of the two phenylene groups is 14.3°. These integrated noncovalent interactions obviously contribute efficient metallo-supramolecular assembly in the non-polar solvent, and make the two pincer units almost coplanar. The Ru–Br distances of 2.9580(5) and 2.8566(6) Å are much longer than that in the mononuclear complex **1** (2.5796(7) Å) even if taking account of the strong trans influence of the NCN pincer-type ligand.[9] The weak Ru–Br coordination is also suggested by the trans Br–Ru–C angles of 159.77(8) and 162.93(9)°, which are far from the linearity. The K–Br distance of 3.2269(8) Å is comparable with the sum of the ionic radii of potassium and bromine (3.29 Å).[16] Meanwhile, the short NH···Br distances (2.84 and 2.95 Å) may imply intramolecular hydrogen bonding although the estimated N–H···Br angles of 121.4 and 119.3° are considerably small. Complex **2** can thus be regarded as a molecular host carrying KBr in the cavity surrounded by functional groups for polarized bonding.

The ^1H NMR spectrum of **2** exhibits three singlets arising from the t-butyl groups as well as a 2H-intensity signal for the NH groups at δ 10.01, indicating no rapid site exchange of the NH protons and potassium cation. The CH resonance at the 2-

position of the DPPBz phenylene group appears a quintet due to virtual coupling with the four phosphorous nuclei. The $^{31}P\{^1H\}$ NMR, showing only one singlet at δ 30.5, reveals C_{2v} symmetry of **2** in solution.

When the synthesis of **2** was carried out under dinitrogen atmosphere, the guest template KBr was lost to give the N_2-bridged dinuclear complex [{Ru(LH)(μ-dppbz)}$_2$(μ-η^1:η^1-N_2)] (**3**) as shown in Scheme 1. Dinitrogen binding has been confirmed by the Raman spectrum showing an N–N stretching at 2083 cm^{-1}, which shifted to 2016 cm^{-1} upon ^{15}N labeling. Fig. 3 depicts the structure of **3** with crystallographic C_i symmetry.[§] Loss of the potassium–π electron interactions in **2** led to a flip of one of the DPPBz linkers. The linker still enforces the two pincer ligands coplanar, which contrasts with most of N_2-bridged dinuclear pincer-type complexes.[17] The pyrazole and pyrazolato arms are bridged by a co-crystalized water molecule with H-bonds (H1···O1: 1.90, N1···O1: 2.653(6), O1···N3*: 2.651(4) Å). In addition, the water molecules are close to the bridging dinitrogen ligand (O1···N5/N5*: 3.065(4)/3.034(3) Å), providing a proton channel connecting the cavity and the hydrophobic surface of the cage complex. The short N5–N5* distance of 1.124(5) Å and linear coordination (Ru1–N5–N5* angle: 179.3(4)°) are commonly observed in the related diruthenium(II) complexes bearing a weakly activated N_2 ligand.[18] The two pyrazole arms in the pincer ligand appear equivalent in the ^1H NMR criteria, indicating rapid proton shifts in the H-bond network.

Carbon disulfide, a versatile small molecule often used in modeling CO_2 reactivity,[19] was also encapsulated in the multi-proton-responsive cavity in **2** (Scheme 1). The crystal structure of the product [{Ru(LH)(μ-dppbz)}$_2$(μ-η^1:η^2-CS_2)] (**4**) is shown in Fig. 4.[§] Despite of the disorder due to the crystallographically imposed inversion center, the position of the bridging CS_2 ligand has been refined reasonably. The in-plane coordinated CS_2 is strongly bent with the S–C–S angle of 140.7(5)°. The C–S distances (C25–S1: 1.647(8), C25–S2: 1.638(8) Å) are elongated in comparison to free CS_2 (1.5526 Å; gas phase).[20] These structural features are common with the related μ-η^1:η^2-CS_2
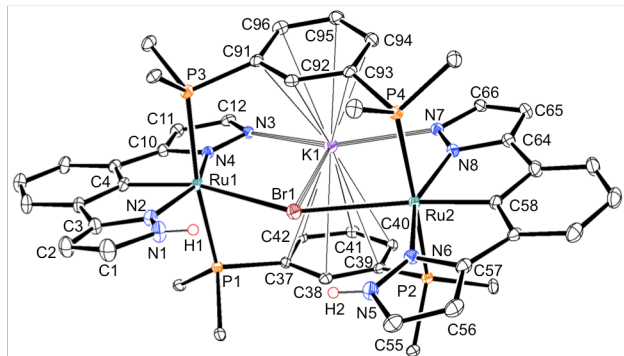

Fig. 2 Crystal structure of **2**·benzene·0.5(pentane). The t-butyl and phenyl groups except for the ipso carbons, CH hydrogen atoms and co-crystallized benzene molecule are omitted for clarity. Ellipsoids are drawn at the 30% probability level.
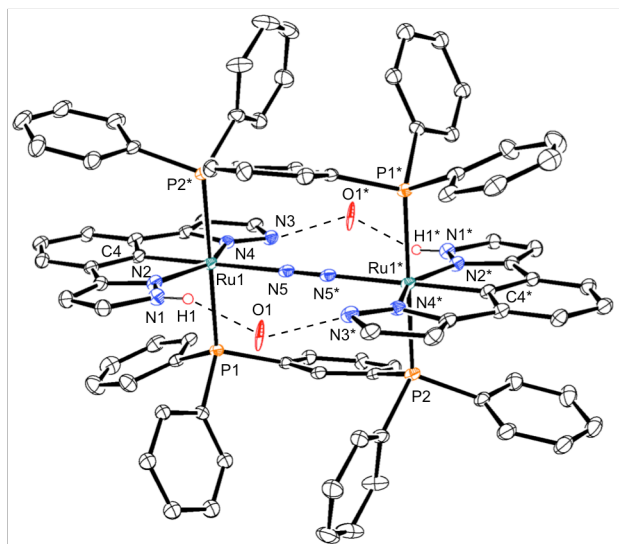
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Fig. 3 Crystal structure of **3**·2H₂O·1.5(toluene). The *t*-butyl groups and CH hydrogen atoms are omitted for clarity. The hydrogen atoms in co-crystalized water molecules could not be located. Asterisks denote atoms generated by a symmetry operation ($1 - x$, $1 - y$, $1 - z$). Ellipsoids are drawn at the 30% probability level.
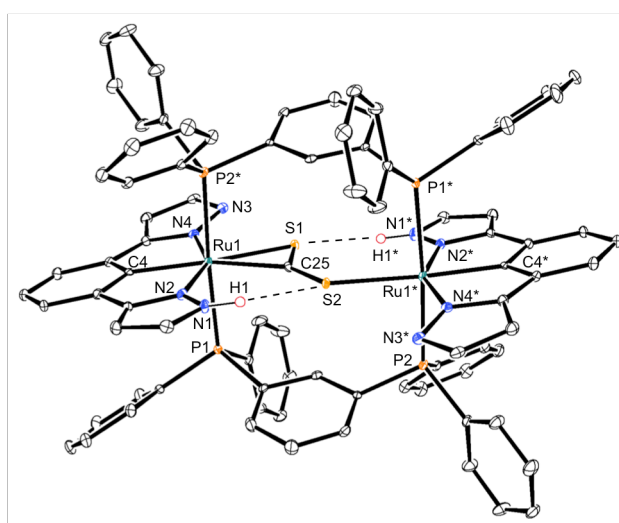

Fig. 4 Crystal structure of **4**·2THF. The *t*-butyl groups, CH hydrogen atoms and the co-crystallized THF molecules are omitted for clarity. Only one set of the atoms in the disordered CS₂ ligand is shown. Asterisks denote atoms generated by a symmetry operation ($-x$, $1 - y$, $2 - z$). Ellipsoids are drawn at the 30% probability level.

complexes.[21] The reactions of ruthenium complexes with carbon disulfide generally involve the co-ligands therein,[22] and the η^1:η^2-coordination of carbon disulfide is novel for ruthenium. The CS₂ ligand is further engaged in hydrogen bonding network within the pincer plane (S1···H1*: 2.36, S1···N1*: 3.186(4), S2···H1: 2.45, S2···N1: 3.187(4) Å). The Ru···Ru distances in **3** and **4** (5.340(1) and 5.658(3) Å, respectively) vary from that in the bromido complex **2** (5.5525(9) Å), showing restricted fluctuation of the DPPBz-bridged dinuclear core. The ¹H NMR resonances of **4** are resolved at −40 °C in line with the C_s symmetry. Broadening of the signals at room temperature suggests fluxional behavior of the CS₂ ligand in the cage.

In summary, a bioinspired, multiproton-responsive molecular host with acid–base bifunctionality in close proximity inside the cavity has been synthesized by dehydrohalogena-tion-induced assembly of mononuclear protic pincer-type complexes and DPPBz. Accumulation with the suitable linker successfully evaded spoiling of the reactive Lewis acid–base pairs, which may provide insights into the chemistry of frustrated Lewis pairs[23] and metal–ligand cooperating catalysts.[1] Despite of the multitude of surrounding interactions, the KBr guest template in the metallo-supramolecular cage **2** was smoothly replaced by non-polar dinitrogen and carbon disulfide molecules, which enjoy the H-bond network in **3** and **4**. The network can be regarded as a proton channel penetrating the hydrophobic shell, which would be utilized for selective proton-coupled conversion of the guest molecules in the confined dinuclear coordination space. Further studies to elaborate the supramolecular approach are ongoing in our group.

Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ See the ESI† for the details.
§ *Crystal data* for **2**·benzene·0.5(pentane): C₁₁₆.₅H₁₂₄BrKN₈P₄Ru₂, $M = 2081.35$, triclinic, $a = 14.936(3)$, $b = 16.296(3)$, $c = 22.411(4)$ Å, $\alpha = 92.417(2)$, $\beta = 101.754(2)$, $\gamma = 104.9134(18)°$, $U = 5134.7(16)$ Å³, $T = 93$ K, space group $P\bar{1}$ (no. 2), $Z = 2$, 57664 reflection measured, 22894 unique ($R_{int} = 0.0415$), $R1 = 0.0503$ [$I > 2\sigma(I)$], w$R2 = 0.1357$ (all data). For **3**·2H₂O·1.5(toluene): C₁₁₈.₅H₁₂₈N₁₀O₂P₄Ru₂, $M = 2050.42$, trigonal, $a = 47.685(5)$, $c = 12.1985(16)$ Å, $U = 24021(5)$ Å³, $T = 93$ K, space group $R\bar{3}$ (no. 148), $Z = 9$, 88358 reflection measured, 11981 unique ($R_{int} = 0.0706$), $R1 = 0.0649$ [$I > 2\sigma(I)$], w$R2 = 0.1914$ (all data). For **4**·2THF: C₁₁₇H₁₂₈N₈O₂P₄Ru₂S₂, $M = 2068.51$, triclinic, $a = 12.341(9)$, $b = 13.779(9)$, $c = 17.827(12)$ Å, $\alpha = 98.921(4)$, $\beta = 108.772(10)$, $\gamma = 110.878(8)°$, $U = 2554(3)$ Å³, $T = 93$ K, space group $P\bar{1}$ (no. 2), $Z = 1$, 21006 reflection measured, 11175 unique ($R_{int} = 0.0639$), $R1 = 0.0477$ [$I > 2\sigma(I)$], w$R2 = 0.1276$ (all data).

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A protic pincer complex and rigid diphosphine linker formed a cage, which incorporated N_2 and CS_2 into the multiproton-responsive cavity.