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The first bis-Rh(I) metal complex of *N*-confused porphyrin†

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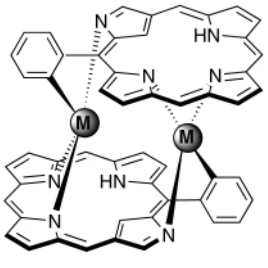
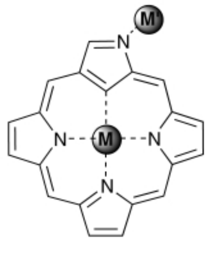
An inner- and outer-*N* coordinated bis-Rh(I) metal complex was obtained from the reaction of *N*-confused porphyrin and [Rh(CO)$_2$Cl]$_2$ in CH$_2$Cl$_2$ and the structure was confirmed by a single crystal X-ray analysis.

N-Confused porphyrin (NCP) is a porphyrin isomer in which one of the pyrrole rings is *confused* or *inverted*.[1,2] Because of the unique NCP structure, which has peripheral nitrogen and inner core carbon atoms, entirely different coordination chemistry from the parent porphyrin system has been expected and revealed gradually.[3–5] Recently, we reported a new type of double-decker Pd NCP dimer complex that used both the inner- and outer-N coordination sites with the help of a carbon–metal bond from an *ortho*-position of a *meso*-aryl ring (**A**).[6] At that point, it was really a question whether outer-*N* coordination was general and whether the complex formed could be stabilized without any assistance from the surroundings (**B**). Such coordination, if manipulated easily, would be of particular interest for potential use in metal catalysts.[7] Herein, we report the X-ray structure of a bis-Rh(I) NCP complex where the Rh(I) metal atoms are coordinated to the inner- and the outer-nitrogen atoms. For comparison, the X-ray structure of the bis-Rh(I) tetraphenylporphyrin (TPP) complex is also presented.[8] To the best of our knowledge, the structures are the first examples of bis-Rh(I) complexes of *meso*-phenylporphyrin and NCP.

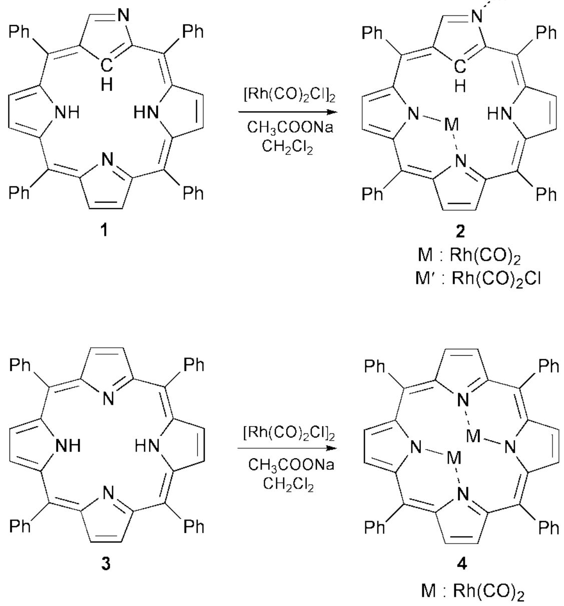


A



B

When *N*-confused tetraphenylporphyrin (NCTPP, **1**) was treated with 1 equiv. of [Rh(CO)$_2$Cl]$_2$ in the presence of 10 equiv. of sodium acetate in refluxing CH$_2$Cl$_2$ for 2 h, bis-Rh(I) NCTPP complex **2** was obtained as a blue-greenish solid in 53% yield. Using the same procedure with TPP (**3**), bis-Rh(I) TPP complex **4** was obtained as a purple solid in 36% yield (Scheme 1). FAB mass spectra of **2** and **4** showed molecular ion peaks at *m/z* 967.5 and 930.6, respectively, indicating the presence of two Rh metal ions connected with a chloride and four carbonyl ligands in **2** and the absence of the chloride ligand in **4**. ^{1}H NMR spectral peaks of complex **2** in CDCl$_3$ appeared distinctly in the region from −4 ppm to 9 ppm. The appearance of peaks corresponding to inner β-CH, outer α-CH and an inner NH at −3.83, 8.89 and 1.06 ppm, respectively, proved that they do not participate in the metal coordination and further confirms that only two pyrrolic nitrogens are coordinated to the Rh metal in the cavity. Relative to NCTPP (**1**), there is significant shielding of the inner α-CH and the outer β-CH signals ($\Delta\delta$ = 1.28 and 0.11 ppm) suggesting that the peripheral nitrogen also participates in the metal coordination. In contrast, the absence of NH signals for complex **4** inferrs that all four nitrogens are involved in the metal coordination.



Scheme 1 Syntheses of bis-Rh(I) metal complexes.

The absorption spectrum of **2** in CH$_2$Cl$_2$ displays a Soret-like band at 488 nm and four Q-type bands in the region of 545–780 nm (Fig. 1). In general, the metal complexation is accompanied by a red-shift of both the Soret and Q-type bands.[9] The bis-metallic complex of **2** also shows 50 nm and 44 nm red-shifts of the Soret and the Q-type bands, respectively, as compared to **1**. This proves that the peripheral nitrogen coordination should not perturb the π electron delocalization much, while the Rh coordinated inside the cavity is expected to perturb the

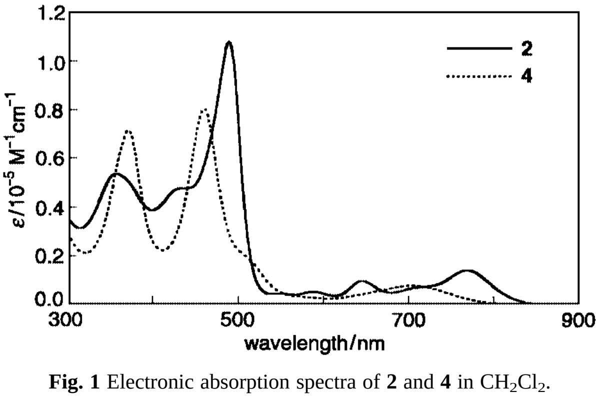


Fig. 1 Electronic absorption spectra of **2** and **4** in CH$_2$Cl$_2$.

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† Electronic supplementary information (ESI) available: synthetic procedures and X-ray structure information for **2** and **4**. See http://www.rsc.org/suppdata/cc/b1/b104004a/

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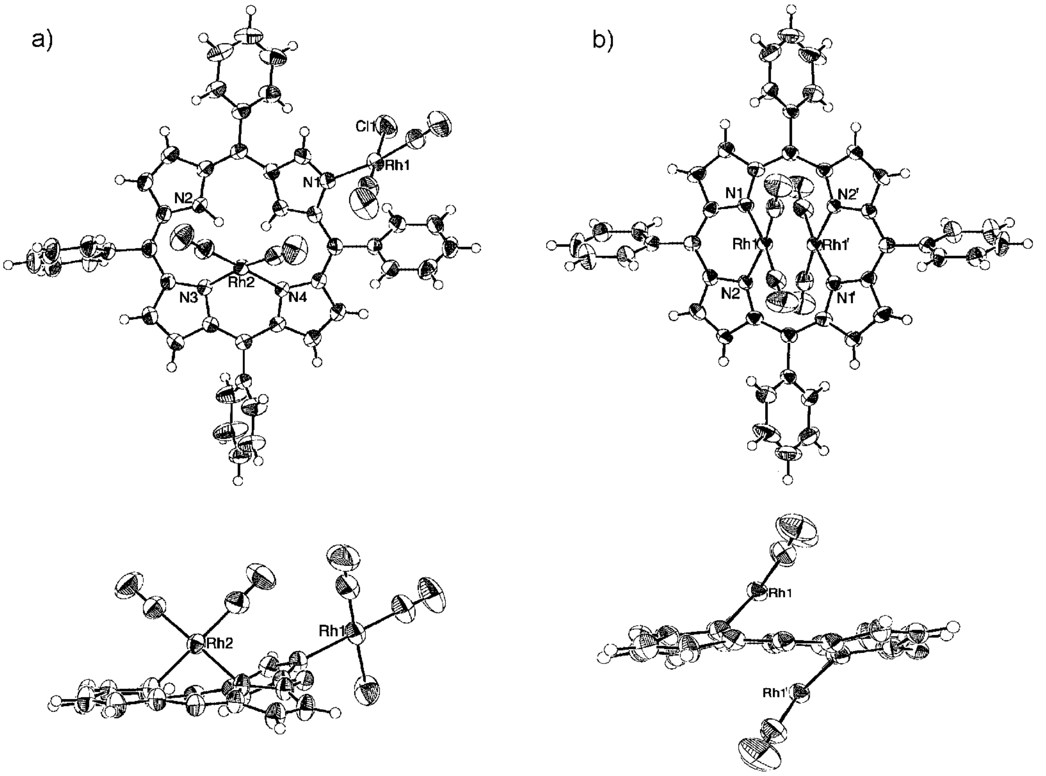

Fig. 2 X-Ray structures of (a) **2** and (b) **4**. The *meso*-aryl rings are omitted for clarity in the side views (bottom). Selected bond lengths (Å) for **2**: Cl1–Rh1, 2.349(3); Rh1–N1, 2.104(6); Rh2–N3, 2.099(6); Rh2–N4, 2.0877(6); and for **4**: Rh1–N1, 2.067(6), Rh1–N2, 2.074(6).

delocalization pathway, and this is reflected in the larger optical absorption band shifts. This trend is further confirmed by the absorption spectrum of **4** where both the Rh are coordinated inside the cavity leading to strong distortion of the molecule and resulting in bands at 371, 460 and 704 nm (Fig. 1).

The explicit structural details of the bis-Rh(I) complexes **2** and **4** were derived from the single crystal X-ray diffraction analyses (Fig. 2).[10] As predicted from the above observations, in the bis-metallic complex of **2**, there are two Rh atoms attached in the NCP skeleton. One imino (N3) and one amino (N4) nitrogen of the macrocycle are coordinated to the Rh2 ion and the other two coordination sites are occupied by the carbonyl ligands. The other Rh1 ion is coordinated to the periphery nitrogen (N1) and the remaining coordination sites are occupied by a chloride and the two carbonyl ligands. Both the Rh(I) ions are located above the NCP plane and the geometry around the metal centers is close to square planar (Cl1–Rh1–N1, 87.6(2)°; N3–Rh2–N4, 85.7(2)°). The angles between the planes containing the Rh1 and the Rh2 with their coordinated atoms and the mean NCP plane are 117.29° and 61.30°, respectively, and the distance between the two Rh metal centers is 6.286 Å.

On the other hand, the metalloporphyrin of **4** is centrosymmetric and the two Rh(I) metal ions are bonded to two dipyrromethene units, one above and one below the macrocyclic plane. Like **2**, the geometry around the metal centers is close to square planar (N1–Rh1–N2, 84.9(2)°). The angle between the plane containing the Rh(1) with its coordinated atoms and the mean TPP plane is 131.59° and the distance between the two metal centers is 3.166 Å, which is considerably longer than the Rh(I)–Rh(I) single bond (2.617–2.705 Å).[11] These results are comparable with the bis-Rh(I) octaethylporphyrin (OEP) complex.[8]

In conclusion, we have synthesized two new bis-Rh(I) metal complexes and disclosed their solid state structures. Inner- and outer-metallation is characteristic of NCP ligands, thus, for **2**, rich and diverse coordination chemistry similar to the parent porphyrin (**1**) can be expected. The present study has also exploited the interaction of only Rh(I) metal ions, but other metal ions are likely to interact with the macrocycle, especially at the peripheral nitrogen. Studies on the synthesis of such hetero bis-metal NCP complexes are currently underway.

Notes and references

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