Cite this: Dalton Trans., 2012, 41, 9154

## COMMUNICATION

## **Cooperation between metal and ligand in oxygen atom transport by N-confused porphyrin oxorhenium(v) complexes**<sup>†</sup>

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*Received 24th April 2012, Accepted 25th May 2012* DOI: 10.1039/c2dt30885a

N-Confused porphyrin oxorhenium(v) complexes were prepared and their X-ray structures were elucidated. The oxorhenium(v) complexes can transfer oxygen atom from pyridine *N*-oxide to triphenylphosphine, in which unique cooperation between metal and ligand was observed.

The properties of a transition metal complex are governed by the interaction between the metal centre and its surrounding ligands. When a metal complex operates a substrate, the role of surrounding ligands is to tune electronic state of the centre metal as well as the steric environment, in which the ligand itself does not participate in substrate or atom transport.<sup>1</sup> Representative examples of atom transport by the ligand are found in nature. The galactose oxidase converts primary alcohol into aldehyde efficiently, in which abstraction of a hydrogen atom by a tyrosyl radical ligand and electron abstraction by copper(II) metal play a critical role.<sup>2</sup> Artificial examples on such cooperation between metal and ligand have been developed in the last decade.<sup>3</sup> Nevertheless, in most cases, only hydrogen atoms are transported by the ligands and transport of heavy atoms has been seldom reported. This time we have succeeded to transport an oxygen atom of pyridine N-oxide to PPh<sub>3</sub> by the N-confused porphyrin rhenium(v) complexes, where unique cooperation between metal and ligand was observed.

The rhenium(v) complexes of N-confused porphyrin were prepared by the oxidation of the corresponding rhenium(1) complex (Scheme 1). When the parent N-confused porphyrin (NCP, 1)<sup>4,5</sup> was treated with Re<sub>2</sub>(CO)<sub>10</sub> or Re(CO)<sub>5</sub>Br, a skeletal rearrangement readily occurred to give the N-fused porphyrin rhenium(1) complex (2).<sup>6</sup> Thus, *N*-methyl-NCP (3) was used to prepare the NCP rhenium(1) tricarbonyl complex (4),<sup>7,8</sup> which was oxidized by *t*-BuOOH. After purification, the oxorhenium(v) complex (5) was obtained in 7% yield and the oxorhenium(v) complex (6) was obtained in trace yield. Significant improvement of the product yields (5: 48%, 6: 2%) was achieved when 4 was oxidized by 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) in



Scheme 1 Preparation of NCP rhenium complexes.



Fig. 1 The ORTEP drawings of (a) 5 and (b) 6.

the presence of  $K_2CO_3$ .<sup>9</sup> Alternatively, the oxorhenium(v) complexes **5** and **6** could be prepared directly from **3** in comparable yields. This is the first example of N-confused porphyrin oxometal complexes as well as rhenium(v) complexes.

The structures of **5** and **6** were elucidated by X-ray crystallographic analysis (Fig. 1 and Table 1).‡ The N-confused pyrrole ring (gray-colored) was oxidized and became the amide-like form. In **6**, the rhenium metal was placed inside the NNNC core and was further coordinated by the oxo ligand, forming a typical square pyramidal geometry. The structure of **5** was similar to that of **6** except for the carbon atom of the NNNC core being oxidized to form a unique Re–O3–C1 metalaoxirane. The Re–O2 lengths for **5** and **6** are around 1.67 Å, which is typical for oxo-rhenium(v) complexes.<sup>10</sup> The Re–C1 length of **6** is 2.070(4) Å, which is comparable to the Re–N bond lengths (avg. 2.073 Å). Meanwhile, the Re–C1 lengths of **5** are 2.241 Å (avg.), which are significantly longer than that of **6**. The C1–O3

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<sup>†</sup>Electronic supplementary information (ESI) available: All the experimental and calculation details. CCDC 867528 and 867529. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30885a

Selected bond lengths in Å for 5 and 6 Table 1 **5-1**<sup>*a*</sup> 5-2<sup>a</sup> 6 Re-C1 2.245(9)2.237(19)2.070(4)Re-N2 2.113(5)2.161(6)2.076(4)2.080(4)Re-N3 2.032(5)2.073(5)Re-N4 2.110(3)2.05(4)2.064(4)Re-O2 1.671(5)1.684(16) 1.668(4)2.014(15) Re-O3 2.031(5)C1-O3 1.415(11) 1.423(19)1.256(6) C2-O1 1.234(11)1.229(19)

<sup>a</sup> Two disordered structures were observed in the solid state.



**Scheme 2** Coordination environment of NCP derivatives. The number and type of detachable hydrogen atoms inside the macrocycle are shown in the brackets.

lengths are 1.419 Å (avg.), which is similar to paraffinic carbon– oxygen single bonds (1.43 Å) but shorter than oxirane carbon– oxygen single bonds (1.45 Å).<sup>11</sup>

Before discussing the valency of the rhenium metals in **5** and **6**, coordination environment of NCP ligands should be mentioned (Scheme 2). The *N*-methyl-NCP has one CH and one NH inside the core and can be mono-negative or di-negative. When the  $\alpha$ -position of N-confused pyrrole is oxidized, an amide-type *N*-methyl-NCP ligand (NCPO) is obtained. The NCPO ligand has one CH and two NHs inside the core and can be di-negative or tri-negative. Importantly, NCPO can be further oxidized at the inner CH moiety to give an oxo-NCPO ligand. The oxo-NCPO ligand would be under equilibrium between the enol and keto forms, both of which can be tri-negative.

According to the coordination environment of NCPO and oxo-NCPO ligands, the formal charge of rhenium metal in **5** and **6** is determined to be +5. The rhenium metal of **6** is surrounded by one tri-negative NCPO ligand and one oxo ligand. Then it can be described as Re<sup>V</sup>O(NCPO). In an analogous fashion, the complex **5** can be described as Re<sup>V</sup>O(oxo-NCPO). The <sup>1</sup>H NMR spectra in CDCl<sub>3</sub> illustrated diamagnetic character of rhenium complexes **5** and **6**, which is consistent with their oxidation state of +5. The  $\beta$ -pyrrolic protons appeared in the region of  $\delta$  8.6–9.0 and 8.9–9.1 ppm for **5** and **6**, respectively. Observation of those signals in the typical aromatic region suggests negligible contribution of intramolecular charge separation and strong aromaticity both in **5** and **6**.

Absorption spectra of **5** and **6** in  $CH_2Cl_2$  and pyridine are shown in Fig. 2. In the absorption spectrum of **5** in  $CH_2Cl_2$ , a sharp Soret-type band was observed at 506 nm. Essentially the same spectrum was obtained in pyridine, indicating no coordination site was left in **5**. By contrast, absorption spectra of **6** are strongly dependent on solvents. A Soret-type band of **6** was observed at 484 nm in  $CH_2Cl_2$  and 539 nm in pyridine. This solvatochromism would be explained by the coordination of



Fig. 2 Absorption spectra of (a) 5 and (b) 6.



Scheme 3 Interconversion between 5 and 6.

pyridine to the vacant site of rhenium metal, forming the hexacoordinate rhenium(v) complex 7 (Scheme 3). Correlation between solvent polarity and absorption wavelengths is low, which would negate the possibility of intramolecular charge transfer for solvatochromism (Fig. S4 and S5†).

Interestingly, interconversion between **5** and **6** could be achieved with PPh<sub>3</sub> as reductant and pyridine *N*-oxide as oxidant (Scheme 3). Thus, treatment of **5** with PPh<sub>3</sub> afforded **6** in 81% yield and oxidation of **6** with pyridine *N*-oxide afforded **5** in 90% yield. The presumable dioxorhenium(VII) complex **8** was not observed. Importantly, the formal charge of rhenium metal does not change in this oxidation/reduction process, indicating the unique non-innocent character of NCPO ligands.<sup>12</sup> In turn, the NCPO ligand of **5** was oxidized by pyridine *N*-oxide and the oxygen atom of the oxo-NCPO ligand in **6** was taken by PPh<sub>3</sub>, formally. Thus, this interconversion can be regarded as oxygen atom transport from pyridine *N*-oxide to PPh<sub>3</sub> by the NCPO ligand. These conversion processes were carried out under inert atmosphere and thus molecular oxygen did not participate in any reactions.

A possible oxygen atom transfer (OAT) reaction pathway for the interconversion between **5** and **6** is proposed as shown in Scheme 4. First, coordination of pyridine *N*-oxide to **6** gives **9**. The absorption spectrum of **6** changed largely by adding an excess of pyridine *N*-oxide, which would support formation of **9** in solution (Fig. S6†). Second, the inner carbon atom of the NCPO core is oxidized by pyridine *N*-oxide to give **5** and pyridine. Third, the oxo-rhenium(v) moiety is reduced by PPh<sub>3</sub> to form Re<sup>III</sup>(oxo-NCPO) **10**. Finally, the oxygen atom is moved from the oxo-NCPO ligand to the rhenium metal, giving back to **6**. Isomerization from **10** to **6** can be regarded as an intramolecular oxidation reaction of the rhenium metal by the oxo-NCPO



Scheme 4 Plausible mechanism for the catalytic OAT reaction.



Fig. 3 HOMO and LUMO of 5 and 6.

ligand. Such cooperation between the rhenium metal and the NCPO ligand would be a noticeable example among cooperating ligands.

The above reaction mechanism was supported by DFT calculations.<sup>†</sup> All the calculations were achieved on the corresponding meso-free derivatives. The HOMO and LUMO of 5 and 6 are shown in Fig. 3. First of all, both the HOMO and LUMO of 5 and 6 are similar to each other. The HOMO of 6 is exclusively composed of the NCPO  $\pi$ -orbitals and thus oxidation of 6 would not occur at the rhenium metal but at the NCPO ligand. Contrastingly, significant contribution of the oxo-rhenium moiety is observed in the LUMO of 5, which indicates that the reduction would occur at the oxo-rhenium moiety to give 10. Formation of 6 directly from 5 is unlikely to occur, since trivial contribution at the C-O bond moiety was observed. Besides, no C-O bond cleavage has been reported in the reported oxo-NCP metal complexes.<sup>13</sup> The rhenium(III) complex **10** is energetically less stable than the isomeric rhenium(v) complex 6 by 69.2 kcal  $mol^{-1}$  and no transition state was found between 10 and 6 in DFT calculations. Hence this transformation is supposed to be fast. The relative stability for the other possible intermediates is also consistent with the plausible reaction mechanism (see ESI<sup>+</sup>).

To validate the efficiency of interconversion between **5** and **6**, oxygen atom transport from pyridine *N*-oxide to PPh<sub>3</sub> was examined with a catalytic amount of **5** or **6**.<sup>14</sup> Satisfactory, the reaction proceeded quantitatively at 80 °C for 24 h with 1 mol% of **6** (Scheme 5). The reaction proceeded even in the presence of 0.01 mol% of **6** in 55% yield (TON = 5500). Similarly, the



Scheme 5 Oxygen atom transport catalyzed by 6.

reaction proceeded in 97% yield with 1 mol% of **5**. When the same reaction was achieved with 1 mol% of triphenylcorrole oxo-rhenium(v) complex ( $\text{Re}^{VO}(\text{COR})$ ),<sup>15</sup> only 9.8% yield was observed. Accordingly, the existence of Re–C bond like **5** and **6** would be important for efficient oxygen atom transport. It should be noted that oxygen atom transport without any metal complexes required elevated temperature above 230 °C.<sup>16</sup>

In conclusion, the N-confused porphyrin oxorhenium(v) complexes **5** and **6** were prepared for the first time and their structures were elucidated by X-ray crystallographic analysis. These complexes can transport oxygen atom efficiently from pyridine *N*-oxide to PPh<sub>3</sub>, in which cooperation between the metal centre and the NCPO ligand would be expected. Further study on the application of this unique cooperation to catalysis is now underway. Development of cooperative ligands based on N-confused porphyrin would be also expected in the near future.<sup>17</sup>

The present work was supported by the Grant-in-Aid for Scientific Research (22350020, 22655044) from the MEXT.

## Notes and references

‡*Crystallographic data* 5·2MeOH: C<sub>47</sub>H<sub>37</sub>N<sub>4</sub>O<sub>5</sub>Re,  $M_W$  924.04, triclinic, space group  $P\bar{1}$  (No. 2), a = 11.231(3), b = 13.123(4), c = 14.134(5) Å, V = 1870.9(10) Å<sup>3</sup>, Z = 2, T = 123 K, R = 0.0646 ( $I > 2\sigma(I)$ ),  $R_W = 0.1473$  (all data), GOF on  $F^2 = 0.992$  (all data), CCDC reference number 867528; 6·1/2C<sub>6</sub>H<sub>6</sub>: C<sub>48</sub>H<sub>32</sub>N<sub>4</sub>O<sub>2</sub>Re,  $M_W$  882.98, triclinic, space group  $P\bar{1}$  (No. 2), a = 11.841(6), b = 12.438(7), c = 14.373(7) Å, V = 1795.6(16) Å<sup>3</sup>, Z = 2, T = 123 K, R = 0.0432 ( $I > 2\sigma(I)$ ),  $R_W = 0.0826$  (all data), GOF on  $F^2 = 1.030$  (all data), CCDC reference number 867529.

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