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Synthesis and properties of rhenium tricarbonyl complex bearing N-fused tetraphenylporphyrin ligand†

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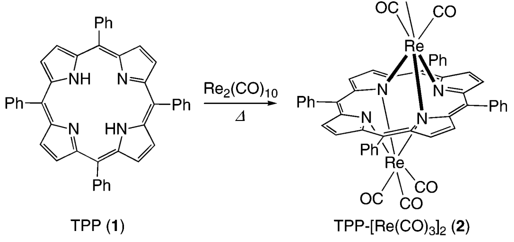
An N-fused porphyrin rhenium complex was synthesized by the thermal reaction of an N-confused porphyrin with $Re_2(CO)_{10}$ and its structure was determined by X-ray crystallographic analysis.

The metal coordination chemistry of porphyrins and their analogues continues to attract the interest of a wide variety of scientists.[1] Among porphyrin metal complexes, a rhenium(I) tricarbonyl complex has a particularly unique structure. Thermal reaction of tetraphenylporphyrin (TPP, **1**) with $Re_2(CO)_{10}$ afforded a bis-rhenium complex (TPP-$[Re(CO)_3]_2$, **2**), where three of the four inner nitrogen atoms coordinate to the metal center (Scheme 1).[2] While rhenium chemistry of porphyrin isomers and expanded porphyrins would also produce unique complexes, studies on such molecules are quite limited.[3,4] Herein we have investigated the reactions of N-confused tetraphenylporphyrin (NCTPP, **3**),[5,6] which is a *confused* isomer of **1**, with rhenium reagents and found that unexpected skeletal conversion from NCTPP to N-fused tetraphenylporphyrin (NFTPP, **7**)[7] took place, together with metal complexation, to afford the NFTPP rhenium complex (NFTPP-$Re(CO)_3$, **4**).

Upon heating of NCTPP (**3**) with $Re_2(CO)_{10}$ at 160 °C in 1,2-dichlorobenzene, polar NCTPP (**3**) was gradually consumed and a much less polar compound was observed in TLC analysis.[8] After 36 h, **3** was completely consumed and then silica gel column separation of the crude product gave the less polar compound as a red-purple solid. Spectral analysis on this solid (*vide infra*) revealed that the product was not an expected NCTPP complex but a rhenium tricarbonyl complex bearing an NFTPP ligand (**4**, 65% yield based on **3**). Alternatively, the rhenium complex **4** was reasonably prepared *via* the intact NFTPP (**7**) using the previously reported stepwise protocol; treatment of **3** with *N*-bromosuccinimide (NBS) gave dibrominated NCTPP (**5**), ring fusion reaction of **5** gave **6**, debromination reaction of **6** gave **7**, and then thermal reaction of **7** with $Re_2(CO)_{10}$ gave the rhenium complex **4** (Scheme 2, 23% yield in 4 steps).[7] Note that this is the first example of an N-fused porphyrin metal complex.

The rhenium complex **4** is extremely stable and easily handled. No decomposition was observed on exposure to air and sunlight in a CH_2Cl_2 solution over two weeks. It was also stable against acids (TFA or H_2SO_4), bases (NaOH or pyridine) and oxidant (H_2O_2) at ambient temperature. Thermal stability is also noteworthy; **4** remained unchanged after heating at 250 °C for 1 h in a sealed tube.

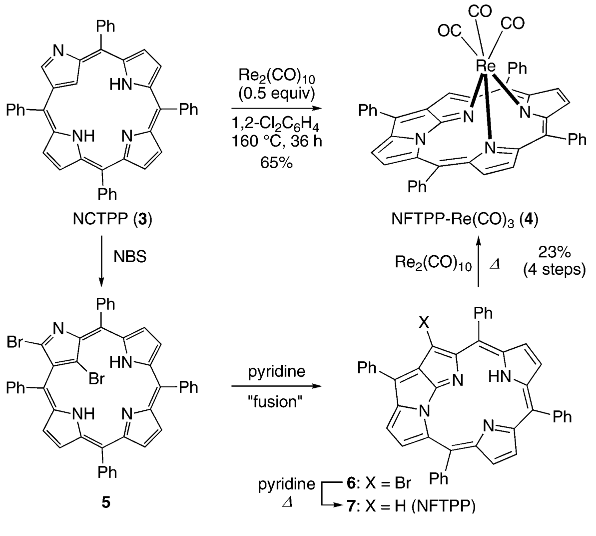


Scheme 1 Preparation of TPP rhenium complex (**2**).

The assigned structure of **4** rested on the ^1H NMR, ^{13}C NMR, mass and IR spectra, and was subsequently confirmed by X-ray analysis. Mass spectra of **4** (ESI: 880 (M^+), MALDI: 796 [M − $3(CO)^+$]) suggested the presence of a rhenium metal as well as three carbonyl groups. In the ^{13}C NMR analysis of **4**, three signals due to three carbonyl groups were observed distinctly at δ 193.24, 193.52 and 193.71 ppm, and the other signals were fully consistent with the assigned structure. Strong absorption at 1999 and 1893 cm^{-1} in the IR spectrum also supported the existence of carbonyl groups coordinated to the metal center. The ^1H NMR spectral peaks of **4** appeared in the region from δ 7.3 ppm to 9.3 ppm, which was similar to that of NFTPP (**7**), with the exception of the singlet peak due to the inner hydrogen atom.

Slow diffusion of hexane into a CH_2Cl_2 solution of **4** gave violet crystals suitable for X-ray crystallographic analysis. The crystal structure of **4** is shown in Fig. 1.[9] The NFTPP skeleton is bowl-shaped and three nitrogen atoms are pointing upward so as to coordinate to the metal center. The rhenium metal is placed above the midst of three nitrogen atoms and all the Re–N bonds are parallel to each carbonyl group. It is noteworthy that the nitrogen atom at the tri-pentacyclic moiety effectively contributes to metal coordination. The bond lengths around the rhenium metal of **4** as well as those of the TPP complex **2**[2] are shown in Fig. 2. The Re–N bonds of **4** are significantly shorter than those of **2** (ave. 2.13 Å, *vs.* 2.32 Å for **2**), while the Re–C bonds are slightly longer (ave. 1.92 Å, *vs.* 1.86 Å for **2**).

The UV-vis spectra of the rhenium complex **4** in CH_2Cl_2 are shown in Fig. 3 together with that of NFTPP (**7**). Soret-like bands



Scheme 2 Preparation of NFTPP rhenium complex (**4**).

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† Electronic supplementary information (ESI) available: experimental details, spectral data and cyclic voltammogram of **4**. See http://www.rsc.org/suppdata/cc/b4/b406234e/

DOI: 10.1039/b406234e

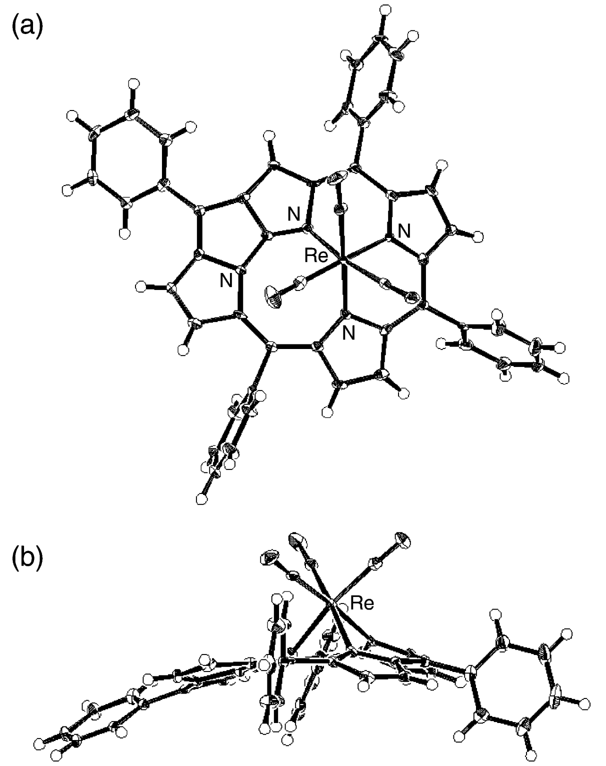

Fig. 1 Crystal structure of the rhenium complex **4**: (a) top view, (b) side view. Solvent molecule was omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

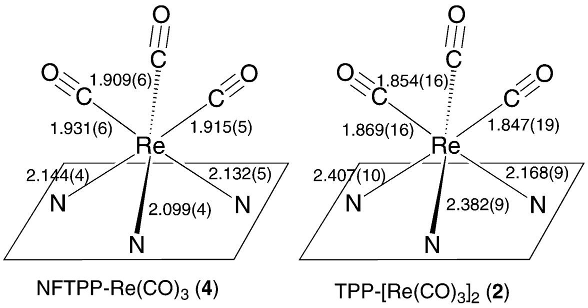

Fig. 2 The bond lengths (Å) around the metal center of **4** and **2**. The data for **2** were taken from ref. 2.

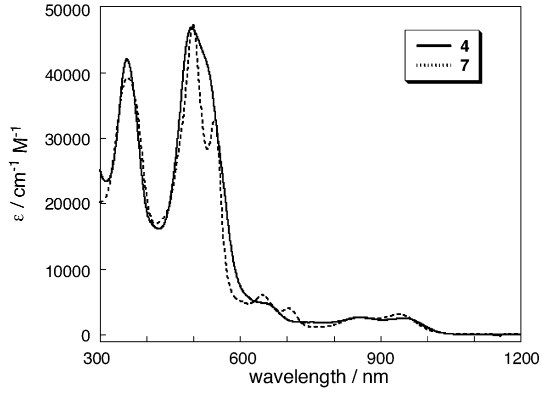

Fig. 3 Absorption spectra of **4** and **7** in CH_2Cl_2.

were observed at 358 and 496 nm, and Q-like bands were observed at 859 and 951 nm. The absorption spectrum of **4** was quite similar to that of **7** and the absorption edge reached to 1000 nm despite the distorted structure of **4**, which is in contrast with the flat structure of **7**.[7]

Cyclic voltammetry measurements revealed that the rhenium complex **4** is robust under redox conditions, allowing the NFTPP complex to be oxidized and reduced without loss of the transition metal atom.[10] In a CH_2Cl_2 solution of the rhenium complex **4**, a reversible one-electron oxidation peak and a reversible one-electron reduction peak were observed at 0.48 V and -1.20 V (*vs.* Fc^+/Fc, 0.1 M Bu_4NPF_6), respectively. The two peaks would not be due to the rhenium metal, but attributable to the NFTPP moiety, since these values were comparable to those of NFTPP (**7**).[11]

While the mechanism of the conversion reaction from NCTPP to NFTPP is unknown, there is some experimental information that gives an insight into the reaction pathway. Firstly, when NCTPP was heated at 160 °C in the absence of $Re_2(CO)_{10}$, no reaction took place. Secondly, in the reaction with a catalytic amount of $Re_2(CO)_{10}$, only the starting NCTPP (**3**) and the NFTPP complex **4** were observed in TLC as well as ^1H NMR analyses. These results suggested that conversion from NCTPP to NFTPP requires the aid of the rhenium metal. Thirdly, when the reaction was carried out with an excess amount of $Re_2(CO)_{10}$ (0.8 equiv.), essentially the same results were obtained (66% yield). Namely, only 0.5 equiv. of $Re_2(CO)_{10}$ was enough for the reaction (**3** : Re = 1 : 1); no rhenium complex was consumed for conversion of NCTPP to NFTPP. Accordingly, a rhenium metal that aided conversion to an NFTPP molecule was most likely identical with a rhenium metal which was introduced to this NFTPP molecule.

In summary, NFTPP Re(I)-complex was synthesized directly from NCTPP in a good yield. A study on the generality and mechanism of this unprecedented reaction is now underway. The NFTPP rhenium complex thus obtained shares important features with the parent NFTPP and shows remarkable stability against a wide variety of chemical and physical conditions. These properties, along with the synergetic effect of N-fused porphyrinoid chemistry[12] and metal complex chemistry, would open up a new area of research in the field of catalysis and materials science.

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8 **3**: $R_f = 0.00$, **4**: $R_f = 0.61$ (silica gel 60, eluent: CH_2Cl_2–hexane = 1 : 1).

9 Crystal data: **4**, Violet prism, $C_{48}H_{29}Cl_2N_4O_3Re$, M_W 966.90, monoclinic, space group $P2_1/c$ (No. 14), $a = 14.8862(8)$, $b = 12.5444(7)$, $c = 21.0094(12)$ Å, $\beta = 101.9270(10)°$, $V = 3838.6(4)$ Å^3, $Z = 4$, $T = 90$ K, $R = 0.0420$, $R_W = 0.0471$ (all data), GOF = 1.155 ($I > 3\sigma(I)$). CCDC 236715. See http://www.rsc.org/suppdata/cc/b4/b406234e/ for crystallographic data in .cif or other electronic format.

10 See Supplementary Information.

11 First oxidation and reduction potentials of NFTPP were 0.16 V and -1.39 V, respectively.

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