Re(VII) complex of N-fused tetraphenylporphyrin†

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By treatment of N-fused tetraphenylporphyrin rhenium(I) tricarbonyl complex with trimethylamine *N*-oxide, oxidation of the metal center proceeded to afford N-fused tetraphenylporphyrin rhenium(VII) trioxo complex, which was quite stable against air, light and heat.

Porphyrinoid ligands with a small cavity continue to gather considerable attention, since they often show the great ability to stabilize metal atoms in high oxidation states.[1,2] For example, corroles can stabilize Cr(V)[3] and Co(IV)[4] oxidation states. Formation of stable Cu(III) complexes with N-confused porphyrins[5] or doubly N-confused porphyrins (N_2CP)[6] is also noteworthy (Chart 1). In these complexes, the four coordinating atoms (N or C) are placed in proper positions and strongly lock the high oxidation state metal centers with small ionic radii.[7] Meanwhile, the number of additional ligands on the metal centers is highly limited.[1]

We have recently developed a unique monovalent 6-electron donor ligand, N-fused tetraphenylporphyrinato (NFp), which is isoelectronic as Cp and hydrotris(1-pyrazolyl)borato (Tp) ligands.[8,9] Since the NFp ligand has only three coordinating nitrogen atoms as well as a fairly small cavity, it would be a good alternative to corroles and related macrocyclic compounds, where the metal center could have more additional ligands. This time, we have demostrated the impressive ability of NFp to stabilize high oxidation state metal complexes through the synthesis of a Re(VII) trioxo complex, $NFpReO_3$ (**2**), by oxidation of the corresponding Re(I) complex, $NFpRe(CO)_3$ (**1**).[9] Note that Re(VII) trioxo complexes have been widely used as versatile starting materials for structurally interesting metal complexes and played important roles in many catalytic reactions.[10,11]

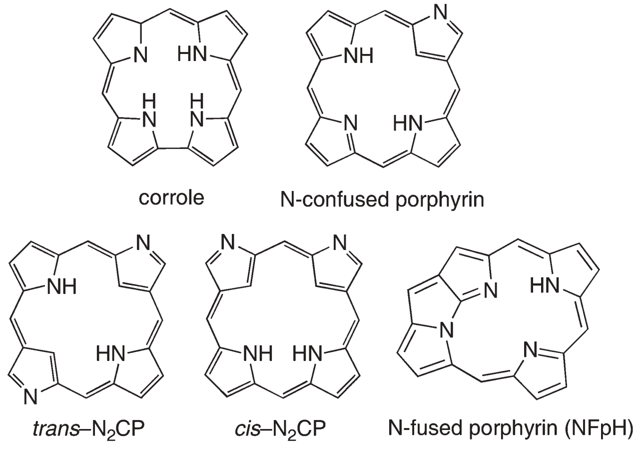
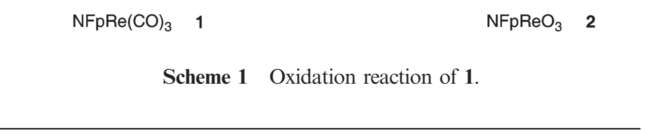


Chart 1 Structures of porphyrinoid ligands.

When $NFpRe(CO)_3$ (**1**) was treated with an excess amount of $Me_3NO{\cdot}2H_2O$ in 1,2-$Cl_2C_6H_4$ at 140 °C for 30 min, oxidation proceeded to afford $NFpReO_3$ (**2**) in 32% yield (Scheme 1). Hydrated Me_3NO was important in this reaction, since the reaction with anhydrous Me_3NO resulted in much lower yield. The presence of light and oxygen practically gave no change in isolated yields. Reactions with other amine *N*-oxides auch as 4-methylmorpholine *N*-oxide did not give acceptable results. Since the reaction proceeded even under a N_2 atmosphere, the oxygen atoms on the rhenium center should be supplied from Me_3NO. To the best of our knowledge, this is the first example of Re(VII) complexes bearing a porphyrinoid ligand.[12]

Usage of Me_3NO as oxidant was essential for preparation of **2**. When **1** was treated with typical oxidants such as *t*-BuOOH, only highly polar compounds were produced possibly due to direct oxidation of the NFp skeleton and **2** was not obtained at all. A theoretical study on the electronic state of **1** revealed that HOMO of **1** was mostly composed of the NFp moiety and only a trivial contribution from the rhenium metal was observed (Fig. 1).[13] Hence simple oxidation of **1** would occur firstly at the NFp ligand and result in decomposition of the NFp skeleton. Contrastingly, the reaction of $Cp^*Re(CO)_3$ with *t*-BuOOH in benzene successfully gave Cp^*ReO_3,[14] while Me_3NO oxidation was not effective.[15] Though the specific role of Me_3NO is unclear yet, it might be related to its ability to oxidize carbonyl ligands selectively to carbon dioxides.[16]

The structure of **2** was elucidated by NMR, IR and mass spectra, and was subsequently confirmed by X-ray crystallographic analysis. In the ^1H NMR spectrum, the signals were observed in the region of δ 7.4–9.4 ppm, which was similar to those of **1** but showed slight low-field shift in *ca.* 0.1 ppm. The characteristic signals due to Re=O stretching were distinctively observed at



Scheme 1 Oxidation reaction of **1**.

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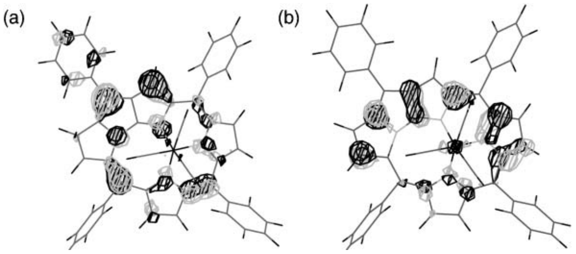


Fig. 1 Kohn–Sham orbitals of **1**; (a) HOMO (b) HOMO-1.

932 (s) and 908 (vs) cm^{-1} in the IR spectrum. The molecular ion peaks corresponding to $[M]^+$, $[M–O]^+$, and $[M–2O]^+$ were observed in MALDI-TOF mass spectra at *m*/*z* = 844, 828, and 812, respectively.

Recrystallization of **2** from CH_2Cl_2/MeOH with vapor diffusion technique gave purple crystals, which were analyzed by X-ray diffraction.‡ The molecular structure of **2** is shown in Fig. 2. The rhenium metal is placed above the center of three nitrogen atoms and three oxygen atoms are directly connected to the metal center. The Re=O bond lengths (average 1.720 Å) are almost identical with those of $TpReO_3$ (average 1.712 Å).[17] The Re–N bond lengths (average 2.189 Å) are shorter than those of $TpReO_3$ (average 2.231 Å), implying strong connectivity between the Re(VII) center and the NFp ligand. The tilt angle between the phenyl group at the C5 position and the tri-pentacyclic moiety (2.9°) is significantly smaller than that of **1** (32.1°).[9]

Oxidation of the metal center caused significant red-shift in the absorption spectrum as shown in Fig. 3. The Soret-like band of **2** was observed at 520 nm, which showed a red-shift of 24 nm as compared to **1**. The maximum absorption wavelength of **2** appeared even at 995 nm and the absorption edge reached as far as 1100 nm. This change was mainly due to lowering of the LUMO level, which was exemplified by electrochemical measurements (Table 1). While the first oxidation potentials (M^+/M) of **1** and **2** were similar to each other, the first reduction potential (M/M^-) of **2** was distinctly more positive than that of **1** in 0.26 V.

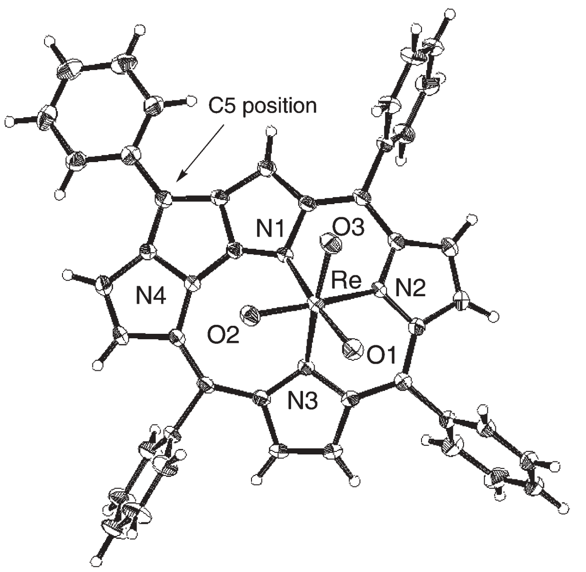


Fig. 2 Crystal structure of **2**: Solvent molecules are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths in Å: Re–O1 1.715(5), Re–O2 1.733(4), Re–O3 1.713(4), Re–N1 2.213(4), Re–N2 2.139(5), Re–N3 2.212(4).

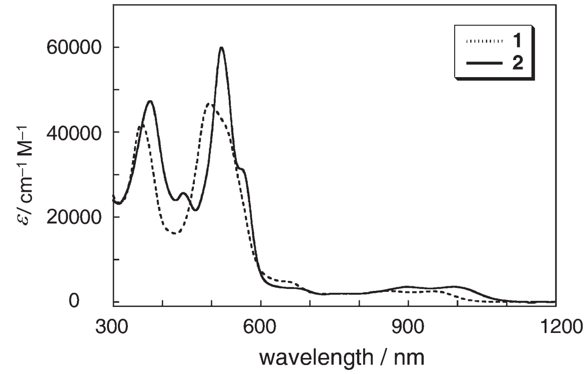


Fig. 3 Absorption spectra of **1** and **2** in CH_2Cl_2.

Table 1 Electrochemical data of **1** and **2** (V *vs.* Fc^+/Fc)[a]

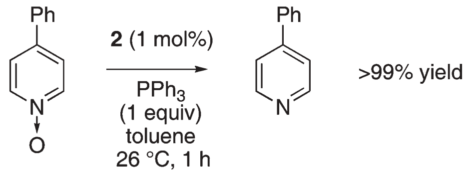
	M^+/M	M/M^-	M^-/M^{2-}
1	0.47	−1.22	−1.67
2	(0.53)	−0.96	(−1.51)

[a] Conditions: 0.1 M Bu_4NPF_6 in CH_2Cl_2 at 24 °C with a Pt working electrode. The parentheses mean irreversible waves in cyclic voltammetry measurements and the values were obtained by differential pulse voltammetry. The other waves were reversible and the values were obtained by cyclic voltammetry.

Capability of NFp ligands to stabilize the metal complexes with high oxidation states was elucidated by heating experiments. When **2** was heated at 230 °C for 2 h in a sealed tube, no change was observed at all. Only slight decomposition was observed by prolonged heating at 250 °C. Furthermore **2** did not decompose on exposure to air and sunlight even in a CH_2Cl_2 solution over three weeks. Such stability is astonishing when it is compared to the related Re(VII) trioxo complexes such as $CpReO_3$ and $TpReO_3$.[10]

A preliminary study on catalytic activity of **2** revealed that it was an effective catalyst for an oxygen transfer reaction of pyridine *N*-oxides (Scheme 2).[18] When 4-phenylpyridine *N*-oxide was treated with PPh_3 in the presence of a catalytic amount of **2**, the reaction proceeded cleanly at ambient temperature to give 4-phenylpyridine essentially in a quantitative yield. After the reaction, PPh_3 was reasonably transformed to $O{=}PPh_3$ and hence PPh_3 should receive the oxygen atom of 4-phenylpyridine *N*-oxide.

In conclusion, we have found unique oxidation conditions of $NFpRe(CO)_3$ (**1**) to give $NFpReO_3$ (**2**) and demonstrated the ability of the NFp ligand to stabilize high oxidation state metal complexes. Further studies on coordination chemistry of the NFp ligand and application of **2** as an oxygen transfer catalyst are now underway.



Scheme 2 Oxygen transfer reaction catalyzed by **2**.

Notes and references

‡ Crystal data: **1**, Violet prism, $C_{44}H_{27}N_4O_3Re{\cdot}CH_2Cl_2{\cdot}H_2O$, M_W 948.88, triclinic, space group $P\bar{1}$ (No. 2), a = 9.4652(5), b = 12.3800(6), c = 17.0943(8) Å, α = 79.190(1), β = 83.834(1), γ = 75.902(1)°, V = 1904.3(2) Å^3, Z = 2, T = 223 K, R = 0.0445 ($I > 2\sigma(I)$), R_W = 0.0806 (all data), GOF on F^2 = 1.239 (all data). CCDC 274093. See http://dx.doi.org/10.1039/b508208k for crystallographic data in CIF or other electronic format.

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