Synthesis of an oxorhenium(V) corrolate from porphyrin with detrifluoromethylation and ring contraction

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Metallation of highly electron deficient 5,10,15,20-tetrakis(trifluoromethyl)porphyrin 1 with [Re$_2$(CO)$_{10}$] in refluxing PhCN resulted in a novel synthesis of oxorhenium(V) 5,10,15-tris(trifluoromethyl)corrolate 2 characterized by single crystal X-ray crystallography.

A new family of porphyrins having highly electron deficient perfluoroalkyl groups in the *meso*-positions has been efficiently synthesized recently by the acid-catalyzed condensation of perfluoro-1-(2′-pyrrolyl)alkan-1-ols.[1] Metallo-perfluoroalkylporphyrins have attracted considerable interest owing to their special non-planar conformation,[1] unusual electronic features,[2] and catalytic properties.[3] In order to explore the chemistry of these electron deficient metalloporphyrins, we have prepared the metal complexes of the porphyrin 5,10,15,20-tetrakis(trifluoromethyl)porphyrin (H$_2$TCF$_3$P, **1**). In the course of metallation of **1** with [Re$_2$(CO)$_{10}$], we have discovered a novel oxorhenium(V) corrolate **2**, [Re(TCF$_3$C)(O)], with concomitant detrifluoromethylation and ring contraction of the porphyrin **1** (Scheme 1).

When **1** was refluxed with [Re$_2$(CO)$_{10}$] in benzonitrile in N$_2$ for 1 h, the brown solution changed to pink. After cooling in air for 1 h, the solution turned to a muddy green suspension. A diamagnetic red product **2** was obtained in *ca.* 9% yield after chromatographic separation in air, together with other uncharacterized side products. The diamagnetic ^{1}H NMR spectrum of **2** showed a doublet at δ 9.88 (J 4.8 Hz) and a multiplet at δ 10.09 with integration ratio of 1 to 3, respectively. The β-pyrrolic protons were therefore non-equivalent. Moreover, the molecular ion appeared at 702 in the mass spectrum and was too low for any expected carbonyl or oxorhenium porphyrin.‡

The structure of **2** was obtained from a single crystal X-ray study.§ The structure was shown to be an oxorhenium corrolate **2** [Fig. 1(*a*)] with detrifluoromethylation and ring contraction having taken place at one of the *meso*-carbons of **1**. C(1) and C(19) of **1** were bonded together with a distance of 1.417(4) Å to form a corrole skeleton. The distances between the opposite nitrogens N(1)···N(3) and N(2)···N(4) were 3.751 and 3.754 Å, respectively, and were shorter than that of the free base porphyrin **1** by *ca.* 30%.¶ The central rhenium lay in a square pyramidal environment in which the corrolate trianion constructed the basal square and the oxygen acted as the axial ligand with Re=O bond length of 1.662(2) Å.[4] The characteristic Re=O stretching frequency appeared at about 994 cm^{-1} in the IR spectrum.[5] Owing to the contraction of the porphyrin to corrole, the large central rhenium deviated from the mean plane of the nitrogens by 0.701 Å [Fig. 1(*b*)] toward the oxygen to accommodate the typical Re–N bond distance of 2 Å.[5] To the best of our knowledge, it is the first oxorhenium porphyrin like macrocycle to be characterized by X-ray crystallography.

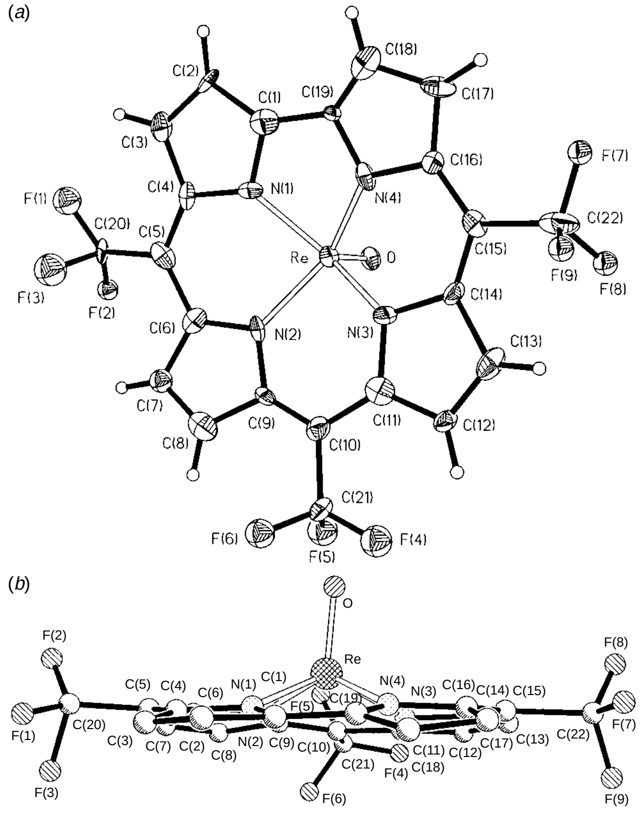
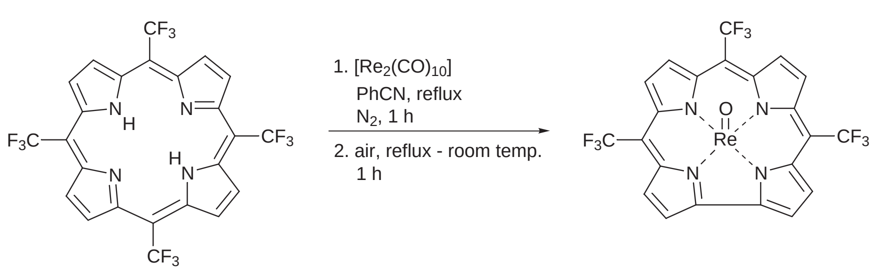


Fig. 1 (*a*) ORTEP view of [Re(TCF$_3$C)(O)] showing the atom labelling. The thermal ellipsoids are drawn at a 35% probability level and hydrogen atoms have been omitted for clarity. (*b*) Simplified diagram of the side view of [Re(TCF$_3$C)(O)].



1

2 9 %

Scheme 1

The novel oxorhenium corrole likely arose from the reduction of **1** by $[Re_2(CO)_{10}]$ *via* a cyclopropane intermediate. The formation of cyclopropane product has been reported in the reaction of octaethylporphyrinogen with transition metals.[6] The driving force for corrole formation is probably due to the release of steric hindrance in this and other non-planar porphyrin-like macrocycles.[7] However, the mechanism of novel detrifluoromethylation and ring contraction to form a corrole from a porphyrin remains unclear. Further studies of the electron deficient corrole are in progress.

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Notes and References

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‡ The molecular ion of [*meso*-tetrakis(trifluoromethyl)porphyrinato] rhenium, $[ReTCF_3P]^+$ occurs at *m/z* 767. UV–VIS (CH_2Cl_2): λ_{max}/nm (log ε) 429 (4.64), 549 (3.71), 589 (3.87).

§ Single crystals suitable for X-ray crystallographic studies were obtained by slow evaporation of a $CHCl_3$–MeOH solution of **2**. *Crystal data* for oxorhenium(V) 5,10,15-tris(trifluoromethyl)corrolate **2**, $C_{22}H_8F_9N_4ReO$: red prism, monoclinic, space group C_2, a = 19.219(4), b = 13.798(3), c = 8.112(2) Å, β = 111.59(3)°, Z = 4, μ = 6.186 mm^{-1}, 2465 reflections collected [T = 293(2) K], 2396 independent reflections (R_{int} = 0.0315) observed. The structure was solved by direct methods and refinement was by full-matrix least squares. In the final refinement, calculated H atom positions were included using a riding model with fixed isotropic *U*. R_1 [$I > 2\sigma(I)$] = 0.0388, wR_2 = 0.1101. Programs used: Siemens SHELXTL PLUS (PC Version). CCDC 182/857.

¶ The distances between opposite nitrogens of **1** were found to be 4.159 and 4.180 Å. The crystal structure of **1** will be published elsewhere.

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