Preparation, Characterization and Reaction of the First Dioxoruthenium(VI) Complexes of Chiral Picket-fence Porphyrins

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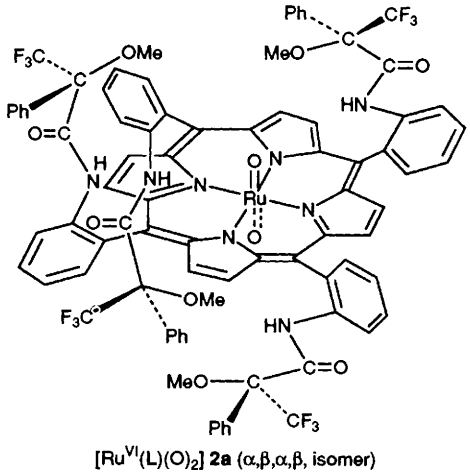
Preparation and characterization of dioxoruthenium(VI) picket-fence complexes bearing optically active α-methoxy-α(trifluoromethyl)phenylacetyl residues on both sides of the porphyrin plane (α,β,α,β and α,α,β,β isomers) are described; oxidation of racemic benzyl(methyl)(phenyl)phosphine by the α,β,α,β isomer leads to the formation of optically active phosphine oxide (enantiomeric excess 41%) and proceeds with retention of the configuration of the phosphorus atom.

High-valent oxoruthenium complexes of porphyrins have received recent attention because of their relevance to the biological activation of oxygen by haemoproteins.[1,2] By using a sterically encumbered porphyrin (tetramesitylporphyrin, TMP), Groves and Quinn isolated the first monomeric dioxoruthenium(VI),[1a] whereas more recently, dioxo ruthenium(VI) complexes with non-sterically encumbered porphyrins were prepared in good yields in coordinating solvents (methanol and ethanol).[2] In connection with our studies on molecular recognition by chiral ruthenium porphyrins,[3,4] we describe here the isolation and the characterization of the first optically active *trans*-dioxoruthenium(VI) porphyrin complexes. Further, the oxidation of racemic benzyl(methyl)-(phenyl)phosphine is investigated in order to examine the mechanism of oxygen transfer.

Oxidation of [Ru(**L**)(CO)(THF)] **1a** (α,β,α,β isomer)[3] {**L** = 5,10,15,20-tetrakis[*o*-(2-methoxy-2-phenyl-3,3,3-trifluoropropanoylamino)phenyl]porphyrin} was carried out by introducing a small excess of *m*-chloroperbenzoic acid (*m*CPBA) (2.2 equiv.) in dry methylene chloride at room temperature under argon to yield a new species **2a** (λ 422 and 516 nm).† Complex **2a** could be isolated by addition of hexane in 80% yield and the solid sample was stable in air for hours. The IR spectrum of **2** shows a strong band at 823 cm^{-1} and the disappearance of the CO band which was observed for **1a** at 1950 cm^{-1}. The IR spectroscopic properties are similar to those for previously reported examples: assignments for O=Ru=O stretching vibration, both for Ru(TMP)$(O)_2$[1a] and for Ru(OEP)$(O)_2$,[3a] (OEP = octaethylporphyrin) at 821 cm^{-1}. Accordingly, we have assigned the band at 823 cm^{-1} to the Ru=O stretching bands in **2a** and **2b** (*vide infra*). The ^1H NMR spectrum of **2a** shows resonances characteristic of diamagnetic metalloporphyrins (Fig. 1). The ^{19}F NMR spectrum shows only one peak for the CF_3 groups at δ −69.5 ($CDCl_3$), indicating that the four CF_3 groups are identical, defined by a D_2 symmetry as expected in this α,β,α,β isomer. A similar result was previously reported with the unmetalled porphyrin.[3] Oxidation of the α,α,β,β isomer,[3] using the previous experimental conditions, followed the same way. With this isomer, α,α,β,β [Ru(**L**)$(O)_2$] **2b**† was obtained with 76% yield (λ 420 and 514 nm, $\nu_{R=O}$ 823 cm^{-1}). The ^1H NMR spectrum of **2b** shows resonances characteristic of a diamagnetic metalloporphyrin (Fig. 1). Moreover, the ^{19}F NMR spectrum shows two resonances as expected with a C_2 symmetry.†



[Ru^{VI}(**L**)$(O)_2$] **2a** (α,β,α,β, isomer)

The presence of two oxo ligands was also demonstrated by reaction of **2a** with racemic benzyl(methyl)(phenyl)phosphine. Addition of 4 equivalents of this phosphine yielded 2 equivalents of optically active (+)-(*S*)-benzyl(methyl)-(phenyl)phosphine oxide with 41% enantiomeric excess (*S* : *R* = 2.4) (Scheme 1). Moreover, complexation of the other 2 equivalents of the phosphine to the ruthenium leads to the compound [Ru(**L**){P(Me)(CH_2Ph)(Ph)$\}_2$][3] with chiral recognition. In a typical experiment, reaction of **2a** with the phosphine at 25 °C for 1 h in CH_2Cl_2 (10 ml) under nitrogen gave a 37.5 : 53.5 : 9 mixture of the three diastereoisomers (*SS* : *RS* : *RR*, respectively) (preference per binding site *S* : *R* = 2.3). The stereochemical course of the oxidation was

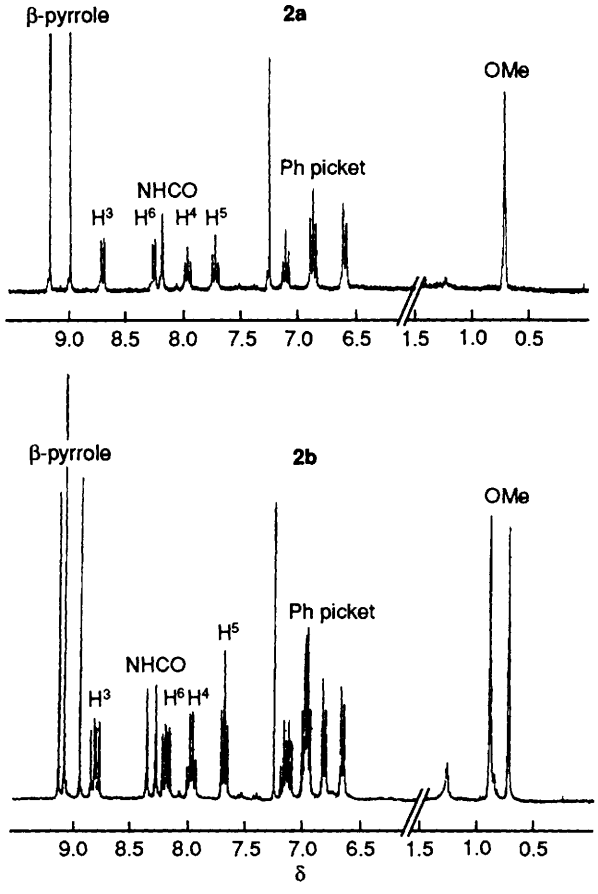
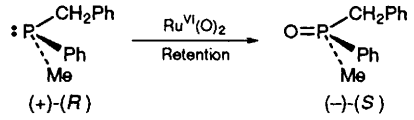


Fig. 1 ^1H NMR spectra ($CDCl_3$) of dioxoruthenium(VI) complexes **2a** (α,β,α,β isomer) and **2b** (α,α,β,β isomer)



Scheme 1

deduced from configurational correlations, previously reported by Mislow[5a] and Kyba.[5b] Thus the configuration and optical rotation of the phosphine and the phosphine oxide are well established. Consequently, it should be noted that there is a very good correlation between the preference of the ruthenium binding site and the enantiomeric excess (e.e.) of the phosphine oxide. This is necessarily related to an oxygen transfer which proceeds with retention of phosphorus configuration (Scheme 1).

In order to obtain additional information on the mechanism of oxygen transfer from ruthenium to phosphorus, we have performed e.e. measurements on reactions between **2a** and various amounts of the phosphine. The results show that addition of an excess of the racemic phosphine leads to a decrease in the e.e. of the phosphine oxide, but with the same *S* configuration. The e.e.s are 25 and 12% with 6 and 10 equivalents of racemic phosphine, respectively. The source of the stereoselectivity observed in the oxidation reaction is attributed mainly to the preferred mode of the initial binding of the chiral phosphine to a possible oxoruthenium(IV) porphyrin intermediate, similar to that previously reported with ruthenium tetramesitylporphyrin.[1c] Thus the oxygen transfer seems weakly selective and further the stereoselectivity of the oxidation (phosphine *R*) and the stereoselectivity of the complexation (phosphine *S*) are inverted. A similar kinetic resolution was also obtained using **2b** as oxidant but with a lower e.e. Addition of 4 equivalents of racemic (benzyl)(methyl)(phenyl)phosphine to **2b** yielded 2 equivalents of optically active (+)-(*S*)-(benzyl)(methyl)(phenyl)phosphine oxide with 26% e.e. (*S*:*R* = 1.7) and 2 equivalents of the ruthenium diastereoisomers. The details of the mechanism and the nature of the catalytic intermediate are under study.

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† *Selected spectroscopic data* for **2a**, ^{1}H: δ 0.73 (s, 12 H, OMe), 6.60 (d, 8 H, *J* 7.8 Hz, *o*-H Ph picket), 6.87 (t, 8 H, *J* 7.5 Hz, *m*-H Ph picket), 7.11 (t, 4 H, *J* 7.4 Hz, *p*-H Ph picket), 8.70 (d, 4 H, *J* 8.3 Hz, H-3), 7.96 (t, 4 H, *J* 7.5 Hz, H-4), 7.72 (t, 4 H, *J* 7.5 Hz, H-5), 8.02 (d, 4 H, *J* 7.6 Hz, H-6), 8.17 (s, 4 H, NHCO), 8.97, 9.14 (2s, 8 H, β-pyrrole). ^{19}F: δ −69.53 (s, 4 CF_3). VIS (CH_2Cl_2): λ_{max}/nm 422 (ε 100 dm^3 $mmol^{-1}$ cm^{-1}), 516 (ε 12). IR (CH_2Cl_2): ν/cm^{-1} 823 (O=Ru=O).

For **2b**, ^{1}H: δ 0.73, 0.89 (2s, 12 H, OMe), 6.66, 6.82 (2d, 8 H, *J* 7.7 Hz, *o*-H Ph picket), 6.97, 6.98 (2t, 8 H, *J* 7.5 Hz, *m*-H Ph picket), 7.12, 7.19 (2t, 4 H, *J* 7.4 Hz, *p*-H Ph picket), 8.78, 8.82 (2d, 4 H, *J* 8.3 Hz, H-3), 7.95, 7.98 (2t, 4 H, *J* 7.8 Hz, H-4), 7.68 (1t, 4 H, *J* 7.5 Hz, H-5), 8.17, 8.20 (2d, 4 H, *J* 7.6 Hz, H-6), 8.27, 8.35 (2s, 4 H, NHCO), 8.93, 9.12 (2s, 4 H, β-pyrrole), 9.06 (1s, 4 H, β-pyrrole). ^{19}F: δ −69.62, −69.72 (2s, 4 CF_3). VIS (CH_2Cl_2): λ_{max}/nm 420 (ε 143 dm^3 $mmol^{-1}$ cm^{-1}), 5.14 (ε 9.9). IR (CH_2Cl_2): ν/cm^{-1} 823 (O=Ru=O).

NMR spectra were recorded on a Bruker AC 300P spectrometer in $CDCl_3$ at 300 MHz (^{1}H), 282 MHz (^{19}F). Visible spectra were measured on a Uvikon 941 spectrometer in dichloromethane. IR spectra were taken on a Nicolet 205 FT-IR spectrometer in dichloromethane. Satisfactory elemental analyses were obtained for **2a** and **2b**.

References

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