Pergamon

Tetrahedron Letters 40 (1999) 2753–2756

TETRAHEDRON LETTERS

Synthesis and Characterisation of a New Chiral Ruthenium Picket-Fence Porphyrin and its Use in Chiral Recognition of Racemic Isocyanides

Erwan Galardon, Michael Lukas, Paul Le Maux and Gérard Simonneaux*

Laboratoire de Chimie Organométallique et Biologique, CNRS et Université de Rennes 1, 35042 Rennes cedex, France.

Received 14 December 1998; accepted 5 February 1999

Abstract: The preparation of a new chiral porphyrin bearing eight optically active pickets, four on each side of the porphyrin plane is described. Chiral recognition in the complexation of racemic isocyanide to the ruthenium compound leads to the formation of three stereoisomers with low stereoselectivity (15%). © 1999 Elsevier Science Ltd. All rights reserved.

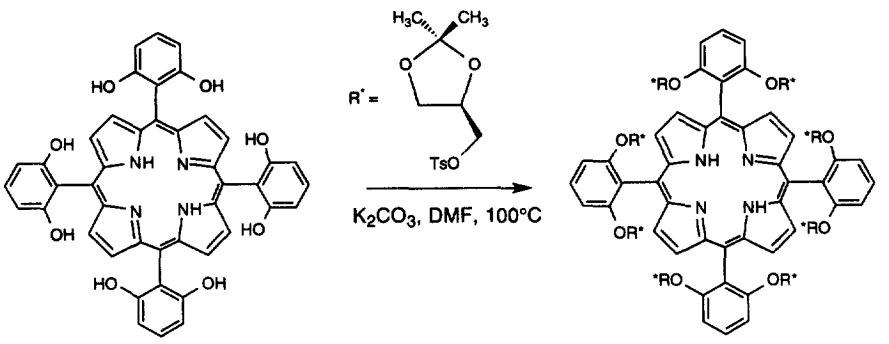
The design of chiral porphyrins is of fundamental interest, as well as of potential economic value. Chiral ruthenium porphyrins have been recently used for catalytic epoxidation of alkenes[1,2] and for reactions involving diazo compounds.[3-6] Chiral metalloporphyrins are also potentially useful framework for selective receptors of natural or synthetic substrates.[7,8,9] As part of our continuing effort to develop chiral ruthenium porphyrins,[9-10] we now wish to report a new chiral system containing eight D-α-β-isopropylideneglycerol residues linked to the ortho *meso*-phenyl positions via ether bonds, as well as its use for the chiral recognition of isocyanides.

To be effective, chirality centres of metalloporphyrins need to be close to the coordination centre. To built such a cavity, chiral entities should be either linked directly on the *meso* position of the ring,[11] or linked on the ortho phenyl positions of the porphyrin ring. For the purpose of molecular recognition, it was decided that the later possibility offered the greater synthetic simplicity. Thus we used 5,10,15,20 tetrakis(2,6-dihydroxyphenyl)porphyrin as precursor. It is easily available from the commercial 2,6-dimethoxybenzaldehyde,[12] and was successfully used by Tsuchida[13] to synthesise porphyrins bearing eight non chiral groups, and by Gross to prepare a homochiral macrocycle.[14] The synthesis of the new porphyrin was achieved following the procedure recently reported by Collman.[15] The coupling of the porphyrin with commercially available D-α-β-isopropylideneglycerol-γ-tosylate in dimethylformamide in the presence of potassium carbonate leads to **1** in 26 % yield (Figure 1). As expected for a D_4 symmetry, all the pickets are equivalent in ^1H NMR spectroscopy, and thus only one singlet is observed for the pyrrole protons (δ = 8.66 ppm) of **1**. Fixation of the eight chiral blocks was definitely confirmed by mass spectrometry.[16]

Fax: 02 99 28 16 46 E-mail: simonnea@univ-rennes1.fr

PII: S0040-4039(99)00289-0

Figure 1.



1

Addition of Ru_3CO_{12} in *o*-dichlorobenzene[17] at 170° yields the new compound **2** (P*)Ru(CO)[18] in fairly good yield (69%), without destruction of the porphyrin ring. In this case, the ^1H NMR spectrum displays two doublets instead of a singlet for the pyrrole protons due to a lower symmetry. Coordination of the carbon monoxide was confirmed by IR spectroscopy with a strong absorption at 1924 cm^{-1} which is typical of porphyrin ruthenium carbonyl complexes.[19]

$$\underset{\mathbf{2}}{(P^*)Ru(CO)} + 2\,(Ph)CH(Me)NC \longrightarrow \underset{\mathbf{3}}{(P^*)Ru[(CNCH(Me)(Ph)]_2} + CO \qquad (1)$$

Complexation of racemic 1-phenyl-ethyl-isocyanide to the chiral ruthenium porphyrin **2** (equation 1) leads to the compound (P*)Ru[CNCH(Me)(Ph)]$_2$ with chiral recognition. In a typical experiment, reaction of **2** with the isocyanide (8 equiv.) at 25 °C for 15 min in dichloromethane under inert atmosphere gave **3** as a 32 : 51 : 17 mixture of the three diastereoisomers (RR / RS / SS, respectively). As expected, signals due to the isocyanide methyl groups are split in the bis-isocyanide complex. Moreover, these resonances in ^1H NMR are shifted upfield ($\delta \sim -1.9$ ppm), as a result of the strong porphyrin ring current effect. The integration of the NMR signals indicates the preference for a particular configuration (R) (preference per binding site: R / S = 1.35). A pure diastereoisomer **3**(RR) has been synthesised by a separate experiment, involving complexation of pure (R)-1-phenyl-ethyl-isocyanide to **2**, to assign the major diastereoisomer. Except for **3**(RR)[20], details of identification and spectral characteristics of these isomers will be described elsewhere. The selectivity observed (15 %) is under kinetic control, the isocyanide-ruthenium bond being quite strong (for example, no exchange was detected after addition of 8 equivalents of racemic isocyanide to **3**(R,R) in dichloromethane). The weak

enantioselectivity by this chiral ruthenium porphyrin is at first surprising, given the high enantioselectivity observed (>95 %) for the chiral recognition in the complexation of racemic benzylmethylphenylphosphine to the ruthenium picket-fence porphyrins bearing optically active α-methoxy-α-(trifluoromethyl)phenylacetyl residues on both sides of the porphyrin plane (α,β,α,β isomer).[9] Both chiral porphyrin complexes have the potential of discriminating chiral axial ligands. The source of the high stereoselectivity observed in the latter reaction is mainly attibuted to steric effect. It is the preferred mode of the binding of the chiral phosphine to the ruthenium porphyrin that determines the chiral recognition. Thus the present result confirms our previous work showing that enantioselective complexation can be obtained under kinetic control. In the latter case, the observed steroselectivity was however much higher because the chiral center was bound to the metal atom. The long distance Ru-isocyanide chiral centre and the absence of any intramolecular hydrogen bond between the chiral picket and the chiral ligand may also explained this weak selectivity. It should be noted that negligible enantioselection was recently observed with amine adducts to chiral cobalt porphyrins.[21]

Further implications of this work, including cyclopropanation and oxidation reactions catalysed by **1** are currently under studies in our laboratory.

Acknowledgements. We gratefully acknowledge the financial support of the MESR for a grant to E. G.

References and Notes.

1) Gross, Z.; Ini, S.; Kapon, M.; Cohen, S. *Tetrahedron Lett.* **1996**, *37*, 7325.
2) Gross, Z.; Ini, S. *J. Org. Chem.* **1997**, *62*, 5514.
3) Galardon, E.; Le Maux, P.; Simonneaux, G. *J. Chem. Soc., Chem. Commun.* **1997**, 927.
4) Galardon, E.; Roué, S.; Le Maux, P.; Simonneaux, G. *Tetrahedron Lett.* **1998**, *39*, 2333.
5) Lo, W. C.; Che, C. M.; Cheng, K. F.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1997**, 1205.
6) Frauenkron, M.; Berkessel, A. *Tetrahedron Lett.* **1997**, *38*, 7175.
7) Ogoshi, H.; Mizutani, T. *Acc. Chem. Res.* **1998**, *31*, 81.
8) Simonato, J. P.; Pécaut, J.; Marchon, J. C. *J. Am. Chem. Soc.* **1998**, *120*, 7363.
9) Le Maux, P.; Bahri, H.; Simonneaux, G. *J. Chem. Soc., Chem. Commun.* **1991**, 1350.
10) Le Maux, P.; Bahri, H.; Simonneaux, G. *J. Chem. Soc., Chem. Commun.* **1994**, 1287.
11) Marchon, J. C.; Mazzanti, M.; Veyrat, M.; Ramasseul, R. *Inorg. Chem.* **1996**, *35*, 3733.
12) Momenteau, M.; Mispelter, J.; Loock, B.; Bisagni, E. *J. Chem. Soc., Perkins Trans. 1* **1983**, 189.
13) Tsuchida, E.; Hasegawa, E.; Komatsu, T.; Nakata, T.; Nishide, H. *Chem. Letters* **1990**, *3*, 389.
14) Ini, S.; Kapon, M.; Cohen, S.; Gross, Z. *Tetrahedron Asym.* **1996**, *7*, 659.
15) Collman, J. P.; Lee, V. J.; Kellen-Yuen, C. J.; Zhang, X.; Ibers, J. A.; Brauman, J. I. *J. Am. Chem. Soc.* **1995**, *117*, 692.

16) Potassium carbonate (457 mg, 3.3 mmol) was added to a solution of 5,10,15,20 tetrakis(2,6-dihydroxyphenyl)porphyrin (138 mg, 0.18 mmol) in DMF at 100°. After 18 hours of stirring, the solution was cooled, DMF evaporated and the crude product dissolved in diethylether. After filtration, the porphyrin was purified by chromatography on basic alumina (CH_2Cl_2 / EtOAc / NEt_3: 50 / 49 / 1). 78 mg of **1** is obtained (26% yield). ^1H NMR (200 MHz, $CDCl_3$): δ = 8.66 (s, 8H); 7.69 (t, 4H, J = 8.2 Hz); 7.03 (d, 8H, J = 8.6 Hz); 3.97 (dd, 8H, J = 4.0 Hz, J = 9.4 Hz); 3.73 (t, 8H, J = 8.7 Hz); 3.47 (m, 8H); 2.84 (dd, 8H, J = 5.0 Hz, J = 9.0 Hz); 2.67 (dd, 8H, J = 5.8 Hz, J = 8.8 Hz); 0.85 (s, 24H); 0.81 (s, 24H); -2.60 (s, 2H); λ_{max} (CH_2Cl_2, nm): 417 (Soret), 512, 588, 644; FAB MS: m / z: Calc. for $C_{92}H_{110}N_4O_{24}$: 1655.7543; Found: 1655.7581. Anal: Calc. for $C_{93}H_{108}N_4O_{25}Ru$: C, 66.76; H, 6.79; N, 3.56; Found: C, 66.73; H, 6.70; N, 3.38.

17) Collman, J. P.; Brauman, J. I.; Fitzgerald, J. P.; Hampton, P. D.; Naruta, Y.; Sparapany, J. W.; Ibers, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 3477.

18) Ru_3CO_{12} (63 mg, 0,097 mmol) was slowly added (1 h) to a solution of 65 mg (0,039 mmol) of **1** in *o*-dichlorobenzene at 170°. After an hour of stirring, the solvant was evaporated, and the residu purified by chromatography on neutral alumina (pentane / Et_2O: 90 / 10, then Et_2O). 48 mg (69%) of **2** were obtained as a red powder. ^1H NMR (200 MHz, $CDCl_3$): δ = 8.61 (d, 4H, J = 4.7 Hz); 8.47 (d, 4H, J = 8.0 Hz, J = 4.7 Hz); 7.64 (t, 4H, J = 8.3 Hz); 6.99 (d, 4H, J = 8.1 Hz); 6.91 (d, 4H, J = 8.0 Hz); 3.95 (m, 8H); 3.69 (m, 4H); 3.49 (t, 8H, J = 7.4 Hz); 3.11 (m, 4H); 2.70 (d, 8H, J = 5.6 Hz); 2.38 (dd, 4H, J = 4.7 Hz, J = 9.1 Hz); 1.93 (dd, 4H, J = 6.3 Hz, J = 8.9 Hz); 1.03 (s, 12H); 0.58 (s, 12H); 0.50 (s, 12H); 0.40 (s, 12H); λ_{max} (CH_2Cl_2, nm): 413 (Soret), 530; IR (KBr, cm^{-1}): 1924; FAB MS: m / z: Calc. for $C_{93}H_{108}N_4O_{25}Ru$: 1782.6346; Found: 1782.6388.

19) Eaton, G. R.; Eaton, S. S. *J. Am. Chem. Soc.* **1975**, *97*, 235.

20) ^1H NMR (200 MHz, $CDCl_3$): δ = 8.30 (s, 8H); 7.58 (t, 4H, J = 8.2 Hz); 6.95 (d, 8H, J = 8.5 Hz); 6.82 (m, 6H); 4.85 (d, 4H, J = 5.2 Hz); 3.79 (dd, 8H, J = 4.1 Hz, J = 8.7 Hz); 3.48 (t, 8H, J = 9.7 Hz); 3.03 (m, 8H); 2.78 (dd, 8H, J = 6.2 Hz, J = 9.0 Hz); 2.59 (q, 2H, J = 6.8 Hz); 2.46 (dd, 8H, J = 6.0 Hz, J = 9.0 Hz); 1.00 (s, 24H); 0.81 (s, 24H); -0.20 (d, 6H, J = 6.7 Hz). λ_{max} (CH_2Cl_2, nm): 398, 418 (Soret), 533. IR (KBr, cm^{-1}): 2113.

21) Toronto, D.; Sarrazin, F.; Pecaut, J.; Marchon, J. C.; Shang, M.; Scheidt, W. R. *Inorg. Chem.* **1998**, *37*, 526.