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Synthesis and Stereochemical Studies of Chiral Ruthenium Porphyrins.

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Abstract The synthesis and NMR characterization of chiral picket-fence porphyrins bearing α-methoxy-α-(trifluoromethyl) phenylacetyl residues and, the regiochemistry of axial ligation after ruthenium insertion are described.

INTRODUCTION

The phenomenon of atropisomerism in porphyrins with meso aryl substituents was first reported by Gottwald and Ullman, who separated the four isomers of 5,10,15,20-tetrakis (2-hydroxyphenyl)-porphyrin[1]. Since then the restricted rotation which results for example, when an amido substituent[2] is placed onto the ortho positions of the meso aryl rings, has been exploited in the design and synthesis of a number of chemical models for heme-containing biological systems. Thus the recent development of chirally modified metalloporphyrins provided important model compounds for oxygen transfer in cytochrome P-450[3]. On the basis of these studies it seems that porphyrin systems with chiral ortho substituents on the meso aryl rings could prove very useful precursors for chiral recognition. We recently reported such a recognition of racemic phosphines by a chiral ruthenium porphyrin[4]

However the symmetry properties of these porphyrins are affected both by the chiral substituents in the ortho positions of the four aryl units and by atropisomerism The four atropisomers that contain four identical optically active units in their ortho positions are represented in figure 1. Obviously, all the atropisomers are dissymmetric and hence optically active Of these compounds, only the isomer $\alpha\alpha\alpha\beta$ is asymmetric since this molecule does not possess a Cn rotation axis . The other atropisomers contain one or several Cn axes. In particular, the α,β,α,β isomer contains three mutually perpendicular C_2 axes to give the molecule D_2 symmetry whereas the α,α,β,β isomer contains an in plane C_2 axis In both cases, the two faces are stereochemically equivalent. The two cavities on each face are different for the two other compounds Finally, the α,α,α,α isomer contains a C_4 axis which is perpendicular to the porphyrin plane These considerations are very important when the topic of nuclear magnetic resonance is discussed, for, under favorable conditions, non-equivalent atoms give rise to separate peaks in the spectrum.

In order to overcome the severe problems which attend the resolution and assignment of proton nmr signals from complex materials such as chiral porphyrins, the presence of an nmr probe in the system is needed. Of particular interest is the judicious introduction of fluorine into the chiral pickets Thus, fluorine signals will be easier to detect than proton resonances and, because the fluorines are different for the four atropisomers, identification of each isomer will be facilited. We describe first the synthesis and characterization of chiral picket-fence porphyrins bearing α-methoxy-α-(trifluoromethyl)phenylacetyl residues and then the regiochemistry of axial ligation after ruthenium insertion The chiral pickets have been prepared by coupling of the four atropisomers of meso-tetra(o-aminophenyl)porphyrin with Mosher's reagent[5]

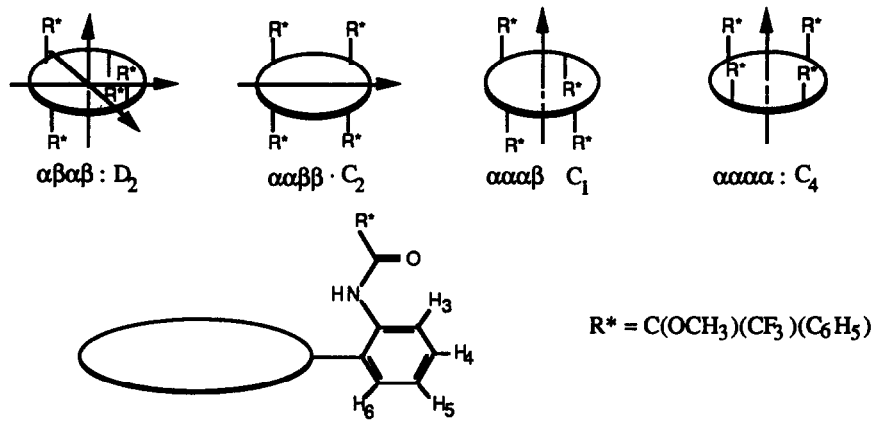


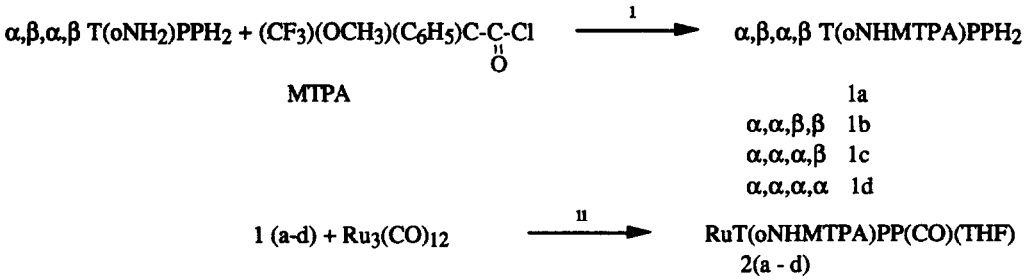
Figure 1 Symmetries of chiral picket-fence porphyrins bearing α-methoxy-α-(trifluoromethyl)phenylacetyl residues

RESULTS AND DISCUSSION

Synthesis of chiral picket-fence porphyrins

Collman et al have described the synthesis and the isolation of all the rotational atropisomers of 5,10,15,20 tetrakis (o-aminophenyl)porphyrin[2]. For the purpose of general stereochemical studies of chiral porphyrins, it was decided that all the four atropisomers bearing optically active residues must be prepared. Because the risk of racemization of the chiral centers must be avoided, Mosher's reagent was chosen The α-methoxy-α-(trifluoromethyl)phenylacetyl group as a potential porphyrin appendage has the property of wearing a CF_3 group useful for the NMR study and to be stereochemically stable. This latter is due to the absence of carbon-hydrogen bond onto the chiral center Synthesis of the four chiral porphyrins was achieved by stirring (R)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride and each of the four atropisomers in methylene chloride at room temperature. This procedure gave good yields of each isomer respectively for **1a** (80 %), **1b** (65 %), **1c** (55 %) and **1d** (44 %).

The synthetic pathway for the preparation of chiral porphyrins is depicted in scheme 1. We have also prepared the chiral porphyrins as a mixture of **1a-d**, starting directly from the thermodynamic mixture of the tetrakis (o-aminophenyl)porphyrins Four bands were observed by TLC but the Rf of each atropisomer being not enough different, isolation of the pure compound by chromatography on preparative silica gel plates or column failed.



Scheme 1 i CH_2Cl_2, Argon, 25°C, 30 minutes. ii a) o-dichlorobenzene, Argon, 180°C, 18 hours ; b) THF

Structural assignment of atropisomers

^{19}F NMR spectroscopy of porphyrins **1** The ^{19}F NMR spectra of **1a**, **1b**, **1c** and **1d** are presented in figure 2 The spectra of **1a** and **1d** show one peak for the CF_3 groups respectively at -70.00 and -70 68 ppm This indicated that the four CF_3 groups in each compound are identical defined by a D_2 symmetry in the α,β,α,β

isomer and by a C_4 symmetry in the α,α,α,α isomer For the atropisomer α,α,β,β, the spectrum shows two peaks at -69.92 and -70 19 corresponding to two groups of two identical CF_3 defined by a C_2 symmetry. The C_2 axis is in the porphyrin plane which implicates that the two equivalent CF_3 are adjacent but on different side The α,α,α,β atropisomer spectrum gives four peaks at -69.81, -69.99, -70.07 and -70.81 with the same intensity. This can be explained by the absence of any element of symmetry in the molecule (C_1 group) and consequently, the four CF_3 are magnetically inequivalent.

Fluorine NMR investigations of the atropisomers of tetraarylporphyrins, when a fluorine[6] (or a CF_2 group)[7] is placed on to the ortho positions, have been previously reported. In these cases, the ^{19}F spectrum of a mixture of the four atropisomers exhibited six magnetically inequivalent fluorine groups By its planar symmetry, the ^{19}F NMR spectrum of α,α,α,β isomer has three types of fluorine groups. All these molecules have, at least, one mirror plane, which is obviously absent when the pickets are chiral This explains the increase number of signals for α,α,β,β and α,α,α,β atropisomers that we observe with the chiral pickets

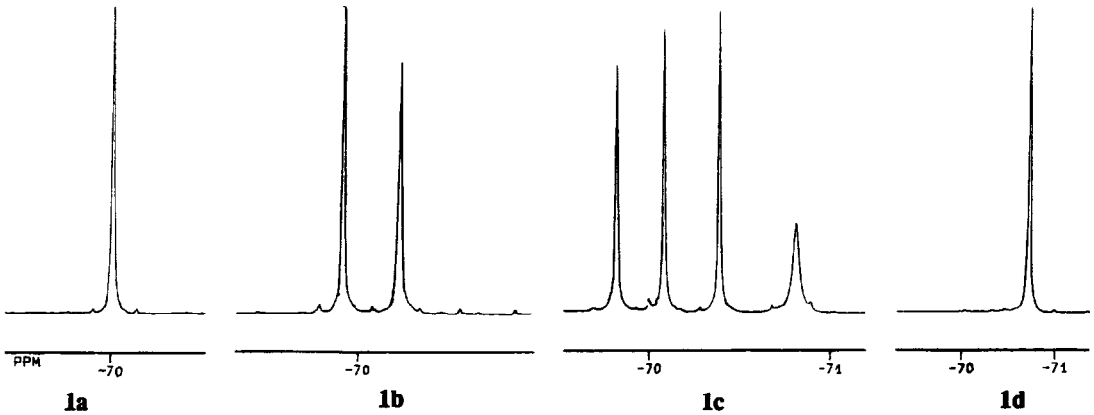


Figure 2 ^{19}F NMR spectra of porphyrins **1a, 1b, 1c** and **1d.**

^1H NMR spectroscopy of porphyrins **1.** The data are listed in table 1. Picket methoxy resonances have upfield shifts (1 2-1.6 ppm) compared to MTPA (3 71 ppm) which are due to the magnetic field anisotropy of the porphyrin ring. The spectra of the compounds **1a** and **1d** show one singlet. Two and four singlets are observed, respectively for **1b** and **1c** These results are consistent with the symmetry attributed to each atropisomer and ^{19}F NMR spectroscopy

The picket phenyl signals are found in the 6 5-7 ppm range We observe one broad singlet in the spectrum of **1a** and a multitude of peaks in the spectra of **1b, 1c** and **1d** These observations may suggest that only the α,β,α,β isomer allows no steric hindrance between the pickets

Amide NH protons give broad singlets between 8-9 ppm · a single broad singlet in the spectra of **1a,b,d** and four broad singlets for the asymmetric atropisomer **1c**

The multiplicity of the pyrrolic protons will also reflect the symmetry of the chiral porphyrin. This property has been previously used as a single proof of absence of racemization during the synthesis of chiral α,β,α,β atropisomer[8,9] to confirm the α,β,α,β structure[3a,e] However, investigation of the three other atropisomers has not been reported This is crucial since it allows discrimination between α,β,α,β and α,α,α,α atropisomers Only those two possibilities have four identical pickets (vide supra). The results are summarized in table 1 The spectrum of the α,β,α,β exhibited two singlets for the pyrrolic protons as expected for two sets of four magnetically equivalent nuclei In the case of the α,α,β,β atropisomer, the spectrum exhibited two singlets and two doublets In α,α,α,β atropisomer, the signal splitting of β-pyrrolic protons should give two singlets and four doublets Unfortunately, assignment is rendered difficult by peak superposition between 8 76 and 8 86 ppm. The remaining atropisomer α,α,α,α would have exhibited two doublets but the spectrum gave only a

broad multiplet at 8.85 ppm. The pyrrole NH protons give one singlet in the -2.5 -2.8 ppm range with deshielding from **1a** to **1d**.

Identification of meso-phenyl protons was also based on symmetry consideration. The H_3 proton signals (fig. 1) occur at the lowest field, in the 8.6-8.8 ppm range. The signals are well resolved doublets due to the coupling with H_4 proton The multiplicity is in agreement with the atropisomer symmetry : one doublet for **1a** and **1d**, two doublets for **1b** and four doublets for **1c** One can also remark a long-range coupling due to H_3-H_5 coupling constant of J ≈ 1 Hz. In **1c**, three doublets of doublet are well assigned at 8.60, 8.67 and 8.75 ppm, the fourth is hided by the multiplet between 8.76-8.86 ppm. The H_4 protons resonate at about the same field (≈ 7 9 ppm) in the four atropisomers. The signal is composed of one triplet in **1a** and **1d**, two triplets in **1b**. However, in **1c**, signal superimposition renders their assignment difficult. With the H_5 protons , the signal multiplicity is the same as with H_4 for every atropisomer and is found in the 7.55-7.65 ppm range The H_6 protons give a doublet of doublet for **1a** and **1d** at 8.07 and 7 85 ppm respectively For **1b**, the signal splits into two doublets of doublet at 7.98 and 8.03 ppm. In the spectrum of **1c**, three doublets of doublet are distinguishable at 7.96, 8.04 and 8.09 ppm, integrating for 3H, the fourth is localized in the multiplet between 7 85-7.90 ppm.

Table 1. ^1H RMN ($CDCl_3$) Data of Porphyrins **1a**, **1b**, **1c** and **1d**

	Porphyrin		Meso-phenyl				Picket		
	H pyrrole	NH pyrrole	H_3	H_4	H_5	H_6	NHCO	C_6H_5	OCH_3
1a	8.65-8.83 8H, 2s	-2 76 2H, s	8.58 4H, d J=8 1 Hz	7 90 4H, td 7 9,1.3 Hz	7 65 4H, td 7.5, 1 0 Hz	8 07 4H, dd 6.3, 1 3 Hz	8 02 4H, brs	6 48 20H, brs	1 40 12H, s
1b	8-6,5,8 80 4H, 2s 8 79,8 32 4H, 2d J=4.8 Hz	-2 70 2H, s	8 68, 8 77 4H, 2dd, J=8 2,≈1Hz	7 89-7 91 4H, 2td 7 9,1.5 Hz	7 60, 7 61 4H, 2td 7 5,1 3 Hz	7 98-8 03 4H, 2dd 7 6,1 4 Hz	8 15-8 17 4H, 2s	6 61-6 97 20H, brm	1 20, 1 54 12H, 2s
1c*	8 76-8.86 8H, m	-2 66 2H, s	8 60,8 67 8 75 3H, 3dd J=8 3,1 Hz	7 85-7 90 4H, m	7 54-7 65 4H, m	7 96,8 04 8 09 3H, 3dd 7 5,1 4 Hz	8 01,8.17 8 24.8 49 4H, 4brs	6 50-7 02 20H,brm	1 22,1 43 1 49,1 62 12H, 4s
1d	8.85 8H, s	-2 54 2H, s	8 83 4H, d J=8 5 Hz	7 87 4H, td 7 6,1 5 Hz	7 53 4H, td 7 5,1 1 Hz	7 85 4H, dd 7 7, 1 2 Hz	8 80 4H, brs	7 00-7 15 20H, m	1 25 12H, s

*In **1c**, the fourth H_3 and H_6 are in the multiplet corresponding to β-pyrrole protons and H_4 protons respectively

Table 2. ^{19}F NMR chemical shifts of atropisomers **2a-d** ($CDCl_3$)

α,β,α,β (**2a**)	α,α,β,β (**2b**)	α,α,α,β (**2c**)	α,α,α,α (**2d**)
-69,36, -71 05	-69 26, -69 52, -70 14, -71 14	-69 51, -69 64, -69 70, -70 44	-70,17
		-36 32, -70 40, -70 79, -72 05	-70 20

Ruthenium insertion into the chiral picket-fence porphyrins (scheme 1, ii) and atropisomer separation.

A literature procedure was used for inserting ruthenium[11] The reaction conditions are depicted in scheme 1. The starting chiral picket-fence porphyrin is a mixture of the four atropisomers 1 since pure atropisomers isomerize in these conditions. The reaction is controlled by thin layer chromatography and visible spectroscopy After 18 hours, the reaction mixture is composed of four red complexes, typical of ruthenium porphyrins, excess of unreacted $Ru_3(CO)_{12}$ and relatively small amounts of unidentified blue-gray products. These complexes are air-stable and have the following visible spectrum : 410 (Soret), 530, 605nm. The presence of ruthenium carbonyl is confirmed by the ir spectrum at 1970 cm^{-1}. Tetrahydrofuran (THF) was added in the resulting solution before separation of the isomers in order to obtain a six coordinate ruthenium carbonyl mono L adduct (L = THF). Chromatography on preparative silica gel plates using diethyl ether-hexane-THF (100:100:1) as eluent gives separation of the atropisomers. In order of elution they were obtained in the approximate ratio of 2:1.5:4: < 0.5 and were assigned in order of increasing polarity as α,β,α,β **2a**, α,α,β,β **2b**, α,α,α,β **2c** and α,α,α,α **2d** respectively with Rf = 5.2, 4 6, 4 and 2.5. These assignments were confirmed by NMR spectroscopy (see below).

Structural assignment of ruthenium atropisomers.

^{19}F NMR spectroscopy. The presence of a CO axial ligation in these atropisomers increases the multiplicity of the fluorine signals. The signal due to equivalent CF_3 groups in the chiral unmetallated porphyrin **1a** (D_2 symmetry) is split into two signals on lowering to C_2 symmetry in **2a** with the C_2 axis normal to the porphyrin plane. In the case of **2b**, the disappearance of the C_2 symmetry renders the CF_3 groups inequivalent. Both **2a** and **2b** have two different faces due to the CO ligation. With the remaining isomers **2c** and **2d**, two regioisomers are possible for the ruthenium product due to asymmetry of the two faces. In one regioisomer, CO is coordinated within the three pickets, and in the other regioisomer, CO is on the unhindered side. Both regioisomers **2c** (α,α,α,β-Ru) and **2d** (α,α,α,α-Ru) are present at the end of insertion reaction (18 hours) (see fig. 3). In each case, one isomer is approximately two-fold excess. This result is different from that previously reported by Collman et al. in Ruthenium "Picnic-Basket" Porphyrins[11] In our case, the presence of carbonyl out and inside the pocket is due to inversion of pickets that is not possible with the rigid structure of "Picnic-basket" Porphyrins. For longer reaction time (> 24 hours), the regioisomer ratio for **2c** is almost unchanged but is inverted for **2d**. The fluorine chemical shifts of the CF_3 groups of all these isomers are summarized in table 2. One can also observed that each atropisomer has a number of peaks corresponding to the well-defined configuration of the four chiral centres. This confirms that no racemization of the chiral centres has occured during ruthenium insertion

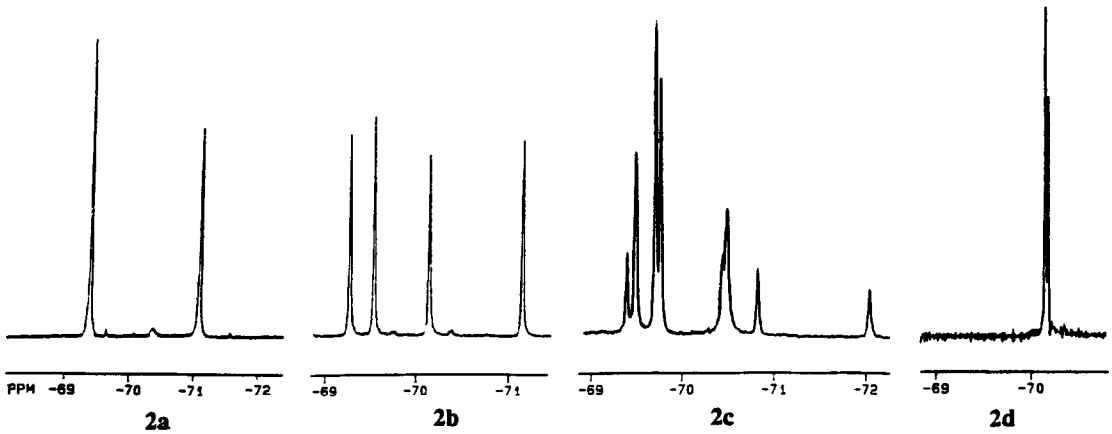


Figure 3 ^{19}F NMR spectra of ruthenium porphyrins **2a, 2b, 2c** and **2d** after ruthenium insertion (18 hours)

Table 3. ^{1}H NMR Data of Ruthenium Porphyrins 2.

	Porphyrin	Meso-phenyl				Picket		
	H pyrrole	H_3	H_4	H_5	H_6	NHCO	OCH_3	Phényl
2a	8.39, 8 42, 8.59, 8 62, 8H, 2d, J = 5 Hz	8 63, 8 72, 4H, 2dd, J = 8 2,1Hz	7 81, 7 90, 4H, 2td, J=7 7,1.5Hz	7.50, 7 90, 4H, 2td, J=7 5,1 Hz	7 68, 8 35, 4H, 2dd, J=7 5,1.5 Hz	7 42, 8.51, 4H, 2s	1.52, 1 79, 12H, 2s	H_o 6 60,6.90,8H,2d, J=7 8 Hz H_m 6 85,7 02,8H,2t, J=7 6 Hz H_p 7.05,7 20,4H,2t, J=7.3 Hz
2b	4d centered at 8 43, 8 64, 4H 8.55, 8.56, 8 60, 8 65, 4H, 4d	8 47, 8 67, 8 80, 8 82 4H, 4d J = 8.3 Hz	7 81-7 89 4H, m	7.51, 7.54, 7 61, 7 66, 4H, 4t, J = 7 5 Hz	7 96, 8 09, 8.22, 3H, 3d, J=7 6 Hz 7 8-7 89, 1H	8 08, 2H, 1brs, 8 48, 8.53, 2H, 4s	1 62,1 70, 1 77, 1 87, 12H, 4s	6,69-7 19, 20H, m
2c	8 44, 8 46, 8.58, 8.59, 8 60, 8 61, 8 62, 8 64, 8H, 8d, J = 5Hz	8 71, 8 73, 8 81, 8 84, 4H, 4d, J = 7 2 Hz	7 78-7 92, 4H, m	7 49, 7.51, 7 63, 7 66, 4H, 4td, J = 6 3,1Hz	7 78-7 92, 3H, 8 16, 1H, 1d,J = 7 1Hz	8.57-8 65, 3H, 8 73, 1H, 1brs	1 57, 1 64, 1 71, 1 76, 12H, 4s	6 51-7.31, 20H, m
2d	8 65, 8H, 1t, J=4 2 Hz	8 94, 4H, 1d, J=8 3 Hz	7 82, 4H, 1t, J=7 6 Hz	7 46, 4H, 1t, J=7 6 Hz	7 71, 4H, 1d, J=7 Hz	9 12, 4H, 1brs	1 61, 12H, 1brs	Ho, 7 13, 8H, 1d, J=7.3Hz Hm,7.22, 8H, 1td, J=7 4,1.5Hz Hp,7 28, 4H, 1td, J=6.5,1.5Hz

^{1}H NMR spectroscopy The data are listed in table 3. Only one regioisomer is represented in the case of **2c** and **2d.** As a general rule, the ruthenium insertion induced a splitting of all the porphyrin protons : for instance, the pyrrolic singlets of porphyrin **1a** split into two doublets. With **2d**, the overlapping of the two doublets gives a triplet. Only these two ruthenium atropisomers have a symmetry axis normal to the porphyrin plane. With **2b** and **2c**, the absence of symmetry axis makes the eight pyrrolic protons different and consequently gives rise to eight doublets For the picket methoxy protons (1 5-2 ppm range), splitting of the signals in each atropisomers is identical to that has already seen with CF_3. For the other protons (meso-phenyl, amide and picket phenyl), they appear as a limited number of well defined signals in symmetrical **2a** and **2d.** Each kind of protons has one and two resonances while with **2b** and **2c**, the four different chiral pickets lead for the same type of protons to four sets of peaks which are originally of the increasing splitting of signals and render the assignment more difficult.

Regioisomer assignment. Diphenylmethylphosphine has been used to determine the regioselectivity of axial ligation in these ruthenium chiral picket fence porphyrins It was supposed that bulky ligand complexation within the protected cavity was prevented by the chiral pickets The two different **2d** ($\alpha,\alpha,\alpha,\alpha$-Ru) regioisomers reacted differently with diphenylmethylphosphine

Reaction with a regioisomer mixture leads to the mono-phosphine adduct **3 d** RuT(oNHMTPA)PP(CO)($PMePh_2$) and unreacted RuT(oNHMTPA)PP(CO)(THF) ^{19}F NMR identification of the unreacted regioisomer shows one peak at -70 20 From this result, it is proposed that only RuT(oNHMTPA)$(CO)_{in}$ reacts with the phosphine Starting with **2c** ($\alpha,\alpha,\alpha,\beta$–Ru) , the same reaction leads to a mixture of mono and bis phosphine adducts The spectra recorded without phosphine excess show decoordination of the ligand In these conditions, it has not been possible to determine the assignments of regioisomers

CONCLUSION

The detailed analysis of symmetry on chiral picket-fence porphyrins for various atropisomers is a useful source of information. This example underlines the interest of using fluorine labelling for elimination of ambiguities of proton assignments in the crowded region of the ^1H NMR spectrum. In addition, assignment of the pyrrole protons leads to the univocal identification of all the chiral atropisomers. This analysis can be applied to a large number of chiral picket porphyrins.

EXPERIMENTAL

Visible spectra were measured on a JOBIN YVON HITACHI 100-60 spectrometer in dichloromethane solutions Infrared spectra were taken on a NICOLET 205 FT-IR spectrometer in dichloromethane solutions NMR spectra were recorded on a BRUKER AC 300P spectrometer in $CDCl_3$ at 300 MHz (^1H, $CDCl_3$) and 280 MHz (^{19}F, $CFCl_3$) Elemental analysis were performed by the Service Central d'Analyses (CNRS) at Vernaison (France) Melting points were not determined because the products decompose. Silica gel 60G (Merck) was used for preparative chromatography Dichloromethane and ortho dichloro-benzene were distilled under argon immediately before use

α,β,α,β-T(oNHMTPA)PPH$_2$ **1a.**

In a two necked flask under argon, 200 mg (296 μmol) of atropisomer α,β,α,β tetrakis (o-aminophenyl) porphyrin was dissolved in 20 ml dry CH_2Cl_2 and 378 mg (150 μmol) of (R)-(+)-α-methoxy-α-trifluoromethyl phenylacetyl chloride and 0.2 ml of pyridine were then added The reaction mixture was stirred at room temperature for 2 hours. After removal of solvent, the residue was purified by chromatography on silica gel plates (eluted with hexane followed by dichloromethane-hexane, 4·1) to give **1a** as blue-purple needles (364 mg, 236 μmol, 80 % yield) . VIS (CH_2Cl_2) · λmax/nm 421 (ε 290 dm^3 $mmol^{-1}$ cm^{-1}), 513 (ε 40), 545 (ε 22), 589 (ε 23), 649 (ε 18) ; ^{19}F NMR ($CDCl_3$) δ -70 00 , ^1H NMR ($CDCl_3$) see table 1 , El. Anal calcd for $C_{84}H_{62}N_8O_8F_{12}$, C 65 53, H 4 03, N 7 28, F 14 82, found C 65 39, H 4 12, N 7 11, F 14 71

This protocol was repeated for the other three atropisomers **1b**, **1c** and **1d** and the mixture **1a-d** The visible spectra were identical to **1a**.

α,β,α,β–α,α,β,β–α,α,α,β–α,α,α,α-RuT(oNHMTPA)PP(CO) **2a,b,c,d**

250 mg (162 μmol) of unmetalated atropisomer mixture was dissolved in 40 ml of ortho dichlorobenzene freshly distilled and heated at 180°C under argon for one hour After, 311 mg (487 μmol) of $Ru_3(CO)_{12}$ was added in eight aliquots over two hours The ruthenium insertion was followed by visible spectroscopy and thin layer chromatography until complete metallation (15 hours) The solvent was removed under pump vacuum. The resulting residue was dissolved in CH_2Cl_2-THF (5 1) and flash chromatography on a silica gel column eluted with the same solvent mixture to remove decomposition and ruthenium metal After solvent evaporation and redissolution in CH_2Cl_2, the four ruthenium isomers were separated on preparative silica gel plates eluted with diethyl ether-hexane-THF (100 100 1) and assigned as previously described in the text. Each atropisomer still contained blue-gray products which were eliminated by chromatography under the same conditions The total yield was approximately 32 % The spectral characteristics, visible and infrared, are identical for the four isomers . VIS (CH_2Cl_2) · λ max/nm 410 (ε 187 dm^3 $mmol^{-1}$ cm^{-1}), 530 (ε 24) , IR ν, cm^{-1} (CH_2Cl_2) 1970 (RuCO), 1705 (NHCO) , ^{19}F NMR ($CDCl_3$) see table 2 , ^1H NMR ($CDCl_3$) see table 3 , El Anal calcd for $C_{85}H_{60}N_8O_9F_{12}Ru$, C 61 26, H 3 72, N 6 72, F 13 69, Ru 6 06, found C 60 93, H 3 88, N 6 67, F 12 52, Ru 6.46

α,α,α,α RuT(oNHMTPA)PP(CO)(PMePh$_2$) **3d.**

Reaction of a regioisomer mixture **2d** obtained after isomerisation (35 mg, 21 μmol) with the phosphine $PMePh_2$ (20 mg, 100 μmol) at 25°C for 3 hours in CH_2Cl_2 (10 ml) under argon gave a mixture of RuT(oNHMTPA)PP(CO)($PMePh_2$) and RuT(oNHMTPA)(CO). Separation of the products on silica gel plates eluted with hexane-ether (3:2) gave 18 mg (9 μmol) of monophosphine adduct and 15 mg (9 μmol) of unreacted starting product with the carbonyl out of the pocket. **3d** · VIS (CH_2Cl_2) : λ max/nm 424, 545 ; IR ν/cm^{-1} (CH_2Cl_2) : 1970 (RuCO), 1706 (NHCO) , ^{19}F NMR ($CDCl_3$) δ -70.22 ($4CF_3$, s) , ^{31}P NMR ($CDCl_3$) δ -26.18 (s) ; ^{1}H NMR ($CDCl_3$) -2 31 (3H, d, J = 6 Hz, MeP), 1.60 (12H, s, OCH_3), 4.11 (4H, t, J = 9 Hz, Ho Ph phosphine), 6.55 (4H, td, J = 8.4, 1.9 Hz, Hm Ph phosphine), 6 85, 6 86 (2H, 2td, J = 9.2, 2 1 Hz, Hp Ph phosphine, 7.11-7 27 (20 H, m), 7.36 (4H, dd, J = 7 5, 1.6 Hz, H_6), 7 43 (4H, td, J = 7.4, 1 Hz, H_5), 7.78 (4H, td, J = 7.7, 1.6 Hz, H_4), 8.90 (4H, dd, J = 7 6, 1 Hz, H_3), 8.46, 8 52 (8H, 2d, J = 5 Hz, β-pyrrole), 9 05 (4H, s, NHCO).

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