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Facial discrimination in monoarylporphyrins: Synthesis and stereochemical behaviour of bis(ligated) monospirobifluorenylporphyrin ruthenium complexes

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Abstract

Condensation of dipyrromethane, pyrrole-2-carbaldehyde with either 9,9′-spirobifluorene or fluorene aldehyde yields new *meso*-monosubstituted, β-unsubstituted porphyrins. The large size of spirobifluorene hinders the rotation around the C_{meso}–C_{aryl} bond to give, for bis-ligated complexes, two different topological faces.

Keywords: Monoarylporphyrin; Spirobifluorene; Fluorene; Ruthenium; Atropisomer; Nuclear magnetic resonance

Restricted rotation of phenyl rings resulting from steric interactions with neighbouring groups is an area of intense investigation [1]. The phenomenon of atropisomerism in porphyrins with *meso* aryl substituents was first described by Gottwald and Ullman [2]. Since then, studies of rotational processes in porphyrins and metalloporphyrins have enormously expanded in the intervening 20 years [3]. Thus, restricted rotations have been reported for tetra-*meso* [4,5] as well as di-*meso* [6–8] substituted porphyrins, mainly with substituents in *ortho* position of the phenyl ring. A few examples of atropisomerism in *meta* position have also been described with bulky substituents such as fullerenes or carboranes [9–11]. In principle, facial discrimination is also possible in monoarylporphyrins due to a possible interaction between pyrrole hydrogens and phenyl *ortho* hydrogens. Such interactions in monosubstituted porphyrin lead to the formation of two different topological faces. In this report, we described our stereochemical investigations in an unprecedented monoporphyrin substituted in *meso* position with a bulky spirobifluorenyl group showing such a case. Indeed, the large size of the spirobifluorene (which can be considered as a phenyl ring substituted in *meta* position) hinders the rotation around the C_{meso}–C_{aryl} bond to give, for bis ligated ruthenium complexes, two different topological faces. Syntheses and stereochemical studies of less hindered *meso* monofluorenylporphyrin were also developed in order to ascertain this phenomenon.

A simple and straightforward method that provides an access to *meso*-monosubstituted, β-unsubstituted porphyrins has been recently reported [12]. This procedure offers *meso*-monosubstituted porphyrins with moderate yields (2–12%) by condensation of aldehydes with dipyrromethane and pyrrole-2-carbaldehyde (Scheme 1). Accordingly, in a typical experimental procedure, dipyrromethane (2.06 mmol), pyrrole-2-carbaldehyde and 9,9′-spirobifluorene-2-carbaldehyde [13] or fluorene-2-carbaldehyde (2.06 mmol) dissolved in 1 L of distilled dichloromethane were stirred with 100 μl of trifluoroacetic acid, under an

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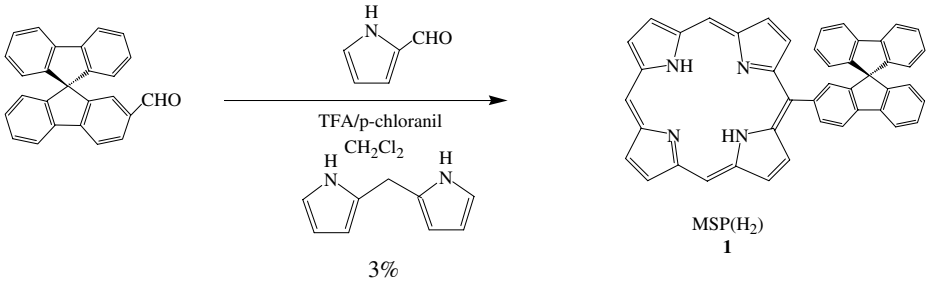


Scheme 1. Synthesis of MSP(H_2) **1**.

argon atmosphere, for 16 h. After addition of chloranil (5.78 mmol), and 1 h more stirring, 1.5 mL of triethylamine was added and the solvent was removed. During this condensation, the disubstituted porphyrin is also obtained as a by-product. However, the *meso*-monoporphyrin with either fluorene (6% yield, called MFP for monofluorenylporphyrin) or spirobifluorene (3% yield, called MSP for monospirobifluorenylporphyrin) [14] can be easily separated from the reaction mixture, by simple filtration followed by column chromatography, due to the low solubility of the 5,15-disubstituted derivative, i.e. 5,15-difluoren-2-yl-porphyrin and 5,15-dispirobifluoren-2-yl-porphyrin. The ^{1}H NMR spectrum of 5-(9,9′-spirobifluoren-2-yl)porphyrin (**1**) is presented in Fig. 1. Due to the local symmetry of the molecule, two sets of *meso* hydrogens are observed, one for the *meso* hydrogens in position 10 and 20 (10.26 ppm) and one for the *meso* hydrogen in position 15 (10.22 ppm).

The UV–Visible spectrum of **1** is shown in Fig. 2. The Q bands allow to determined that this porphyrin is a phyllo type porphyrin as usually observed for *meso*-monosubstituted derivatives [15]. Indeed, the *meso*-monosubstitution with an electrodonating group, i.e. spirobifluorene induces a dissymmetry of the π electronic cloud of the porphyrin which lead to this type of electronic structure.

To detect a possible facial discrimination with a bulky spirobifluorene group in *meso* position [16], the ruthenium complex (MSP)Ru^{II}(CO) (**2**) was first prepared by treatment of **1** with $Ru_3(CO)_{12}$ in *o*-dichlorobenzene at 160 °C (2 h) (see Scheme 2). Then, it was decided that complexation of methyldiphenylphosphine or *t*-butylisocyanide offered the greater simplicity and efficiency because these bis-ligated complexes can provide, depending of the symmetry, a porphyrin ring with two topologically different faces. These complexes were prepared by adding an excess of the free ligand (methyldiphenylphosphine or *t*-butylisocyanide) to the Ru(CO) precursor **2** [17,18]. The ^{1}H NMR spectrum of the bis(*t*-butylisocyanide) complex (MSP)Ru^{II}(*t*-BuCN)$_2$ (**3**), displayed two identical high field singlets at −0.65 and −0.83 ppm (each corresponding to nine hydrogens) for the methyl resonances of the *t*-butyl group (Fig. 3a). This result clearly showed the presence of two different methyl sets and thus two different topological porphyrin faces. This phenomenon has been attributed to the large size of the bulky spirobifluorene group and is due to the slow rotation of spirobifluorene group around the C_{meso}–C_{aryl} bond.

To ascertain this interpretation, we decided to study the complexation of methyldiphenylphosphine and again, the bis-ligated complex exhibits two different topological faces. Thus, the ^{1}H NMR spectrum of the bis(methyldiphenylphosphine) adduct (MSP)Ru(II)($PMePh_2$)$_2$ (**4**) displayed two identical triplets at $\delta = -2.57$ and −2.71 ppm (each corresponding to six hydrogens) for the methyl resonance of the phosphine ligands (Fig. 4a). It should be noted that the multiplicity of these signals, i.e. triplets are due to virtual coupling [19] with phosphorus as previously reported for similar complexes [16].

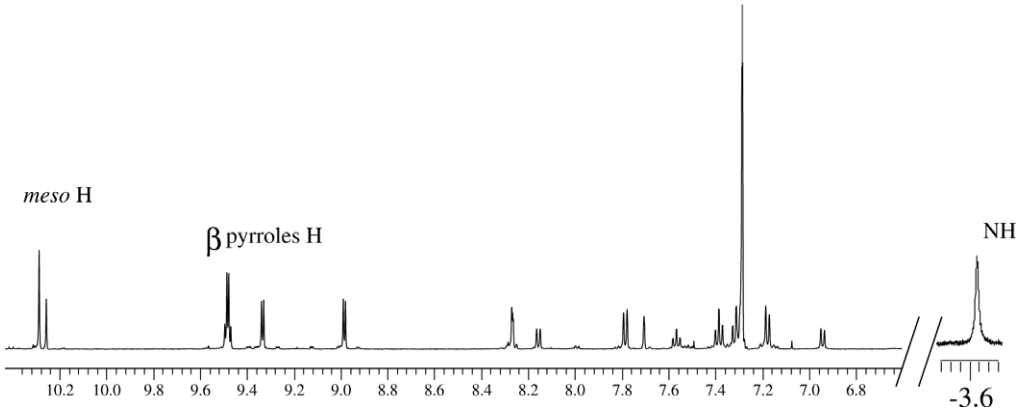


Fig. 1. ^{1}H NMR spectrum of MSP(H_2) **1** ($CDCl_3$).

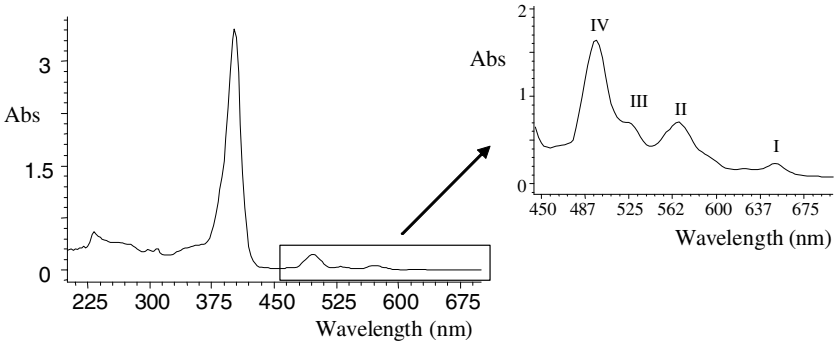


Fig. 2. UV–Visible spectrum of MSP(H_2) **1** (CH_2Cl_2).

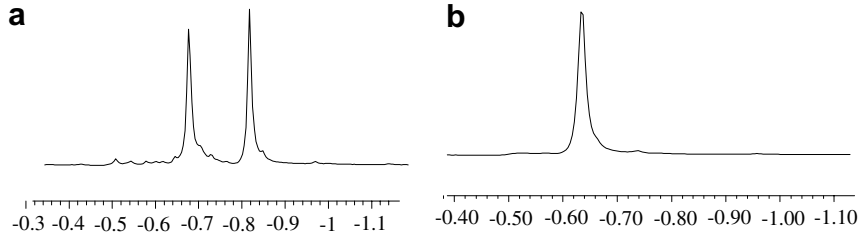
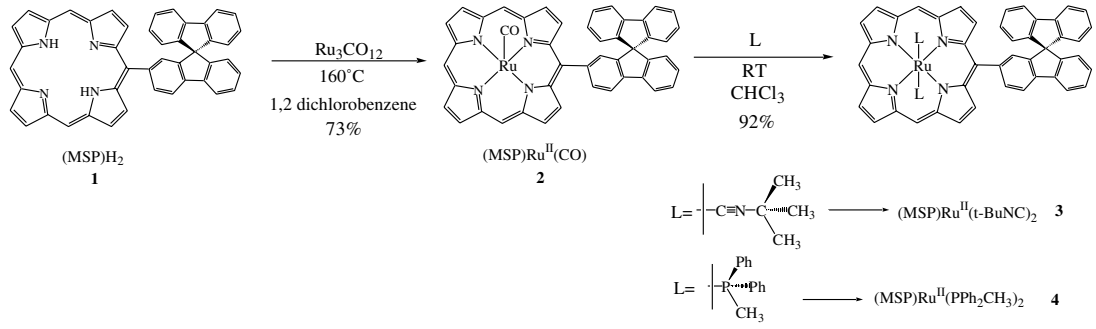


Fig. 3. High field portion of the ^{1}H NMR spectrum ($CDCl_3$) of (a) (MSP)Ru^{II}(*t*-BuCN)$_2$ (**3**) and (b) (MFP)Ru^{II}(*t*-BuCN)$_2$ (**7**).



Scheme 2. Synthesis of ruthenium complexes of 5-(9,9′-spirobifluoren-2-yl) porphyrin.

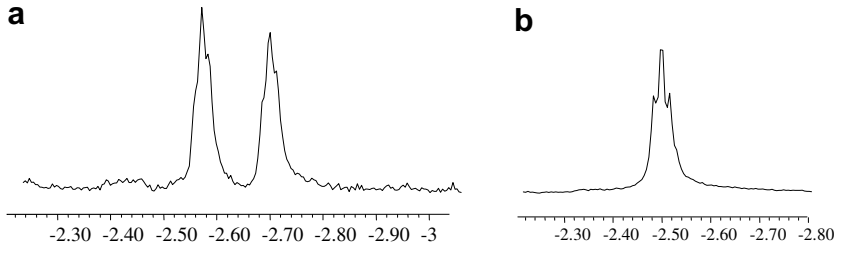
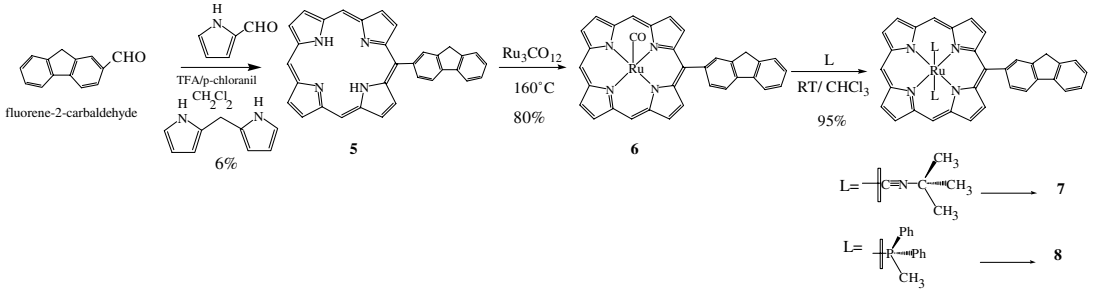


Fig. 4. High field portion of the ^{1}H NMR spectrum ($CDCl_3$) of (a) (MSP)Ru^{II}(PMePh$_2$)$_2$ (**4**) and (b) (MFP)Ru^{II}(PMePh$_2$)$_2$ (**8**).

In order to study the influence of the *meso* substituent, we also prepared 5-fluoren-2-yl-porphyrin (MFP) (**5**) and their ruthenium complexes **6**–**8** following the same route (Scheme 3). As described for **3**, the (MFP)Ru^{II}(*t*-BuCN)$_2$ (**7**) adduct (Scheme 3) should also theoretically exhibited two signals for the methyl resonances due to the two different topological faces of this complex. In contrast, only one resonance ($\delta = -0.63$ ppm) for the isocyanide groups was detected in ^{1}H NMR (Fig. 3b). Indeed, in this case the methyl groups of the isocyanide ligand are too far away from the methylene C9 of the *meso* fluorene substituent and thus do not allow to distinguish the different faces of the porphyrin ring. The same behaviour is also observed in the ^{1}H NMR spectrum of (MFP)Ru^{II}(PMePh$_2$)$_2$ (**8**), which showed only one resonance for the methyl resonance of the phosphine ligands ($\delta = -2.50$ ppm, Fig. 4b).



Scheme 3. Synthesis of 5-fluoren-2-yl-porphyrin derivatives.

In conclusion, we have prepared new bis ligated ruthenium monoporphyrin complexes bearing in *meso* position either a spirobifluorene or a fluorene group and investigated their stereochemical properties. The fluorene ring can be considered as a *meta* substituted phenyl ring. In this case, bis-ligated ruthenium monofluorenylporphyrin complexes do not display any facial discrimination in ^{1}H NMR spectrum. The large size of the spirobifluorene group that hinders the rotation around the C_{meso}–C_{aryl} bond, allows us to detect two different topological faces, after ruthenium complexation. Such atropisomerisation phenomenon is usually observed for *ortho* substituted phenyl rings but rarely with *meta* substituted phenyl rings such as spirobifluorene. Porphyrins of this type, bearing only one substituent, are of special interest because they offer valuable reference derivatives for polymerisation studies and appear to be efficient catalysts for oxidation reactions [14].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007.02.006.

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