

Articles

Biphenyl-Strapped Diphenylporphyrins: Synthesis and Spectroscopic Characterization of a Series of Porphyrins with Ether-Linked Straps. Preliminary CO Binding Properties of Their Iron(II) Derivatives

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The synthesis of a series of *meso*-5,15-diphenylporphyrins strapped by 2,2'-disubstituted biphenyl units (**6H₂**, **7H₂**, **8H₂**) is described. The biphenyl straps used are linked via their 3,3'-positions by CH₂O groups to ortho-positions of the phenyl rings of the 5,15-diphenylporphyrins. The straps of these porphyrins have their 2,2'-positions occupied by H (**6H₂**), Me (**7H₂**), and OMe (**8H₂**). The electronic spectral properties of these strapped porphyrins are given, and their conformational properties, which have been studied by ¹H NMR spectroscopy, are described. The synthesis and spectroscopic characterization of several iron(II) and iron(III) derivatives of these porphyrins with different axial bases are also presented. The X-ray structure of the chloroiron(III) derivative of the diphenylporphyrin dianion **6** has been determined. Violet crystals of composition **6**·FeCl·CH₃OH·CH₂Cl₂ have been obtained by slow evaporation of CH₂Cl₂/MeOH solutions of **6**·FeCl. These crystals belong to the monoclinic system, space group *P*2₁/*c*, with *a* = 10.164(3) Å, *b* = 28.977(9) Å, *c* = 14.283(4) Å, β = 106.22(2)°, and *Z* = 4. The iron atom of **6**·FeCl is five-coordinate, high-spin. The axial chloride ligand lies opposite to the strap. The average Fe–N_p bond distance is 2.046(6) Å, and the Fe–Cl bond length equals 2.234(2) Å. The porphyrin is slightly domed and ruffled with the iron atom lying at 0.45(1) Å out of the 4N_p mean-plane and 0.49(1) Å out of the 24-atom core mean-plane of the porphyrin ring. Ferrous carbonyl adducts of these porphyrins have been obtained in various solvents in the presence or absence of nitrogenous bases. Their structures have been studied by ¹H NMR and IR spectroscopy. Two CO stretching vibrations differing by 20 cm^{−1} occur in the IR spectra of **6**·Fe(CO)(B) (*B* = py, ImH, NMeIm). The possible origin of these two ν_{CO} bands is discussed.

Introduction

The binding of small molecules to iron(II) porphyrins modeling the active sites of oxygen-carrying hemoproteins has aroused considerable interest during the last 20 years. Numerous “capped” and “strapped” porphyrins have been synthesized in an attempt to discriminate between CO and O₂ binding.^{1–4} For a long period, it was assumed that CO/O₂ discrimination is based

mainly on distal steric constraints.⁵ As a result, most of the model porphyrins which were synthesized had alkyl chains containing bulky groups as straps with the aim of sterically impeding linear upright binding of CO.⁶ More recently, emphasis has shifted on the stabilization of O₂ binding by distal polar interactions and destabilization of CO binding by porphyrin buckling.^{7–10}

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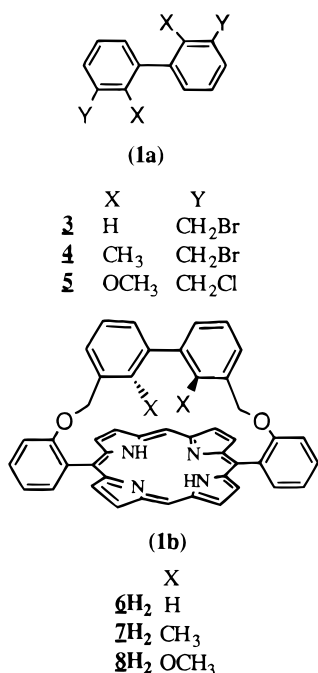


Figure 1. Schematic representations of the 2,2'-disubstituted biphenyl straps (a) and of the biphenyl-strapped 5,15-diphenylporphyrins (b).

To study CO/O₂ discrimination by iron(II) porphyrins, we have synthesized several diphenylporphyrins strapped with biphenyl units which carry H (**6H₂**), CH₃ (**7H₂**), OCH₃ (**8H₂**) groups at their 2,2'-positions and are covalently linked by two CH₂O groups to the ortho-positions of the porphyrin phenyl groups (see Figure 1). The functions of the 2,2'-substituents of the biphenyl strap were 2-fold: (i) introduction of different polar groups into the distal porphyrin cavity; (ii) upholding, by steric interactions with the porphyrin cores, of the straps in central position over the metal center. The X-ray structure of the chloroiron(III) complex of such a biphenyl-strapped porphyrin is also described. The synthesis, structures, and properties of ferrous carbonyl adducts of these porphyrins, obtained in various solvents in the presence or absence of nitrogenous bases, are presented and discussed.

Experimental Section

General Methods. Toluene, ether, and THF were distilled from their purple sodium benzophenone ketyl solutions. Dichloromethane was distilled from CaH₂. Dry solvents used for iron(II) complexes were subsequently degassed on a vacuum line using freeze-pump-thaw cycles. Other chemicals were obtained from Aldrich or Lancaster and used without further purification. Melting points are uncorrected and were measured on a Büchi SMP-20. UV-visible data were obtained using a Cary 5E spectrometer. ¹H NMR spectra were recorded on a Bruker WP 200 SY (200 MHz), chemical shifts δ are expressed in ppm relative to deuterated chloroform (7.26 ppm) or other NMR solvents (THF-*d*₈, acetone-*d*₆), and the coupling constants *J* are given in hertz. IR spectra were obtained on a Bruker ISF 25 instrument. Elemental analyses were performed in the Laboratoire de Recherche Appliquée et de Transfert de Technologie (IUT-Strasbourg sud). Chromatography columns were run on Merck No. 7734 silica gel and Merck No. 1097 alumina.

Synthesis. 5,15-Bis(phenyl)porphyrin (1H₂). This compound was

prepared as described by Manka et al. by condensation of benzaldehyde with 2,2'-dipyrromethane.^{11,12}

5,15-Bis(2-hydroxyphenyl)porphyrin (2H₂). To a mixture of 500 mg of 5,15-bis(2-methoxyphenyl)porphyrin¹² and 20 mL of dichloromethane was added 6 mL of BBr₃ (1 M in CH₂Cl₂) at -78 °C. The mixture was allowed to warm at room temperature and stirred under argon overnight. A solution of MeOH/H₂O (1:1 v/v, 10 mL) was slowly added to the green solution. The mixture was then extracted with 5% ether/dichloromethane (200 mL), washed with aqueous saturated NaHCO₃ and water, and dried over MgSO₄. The solvent was removed, and the residue was recrystallized from a dichloromethane/hexane mixture to yield 380 mg of the title compound (80%). ¹H NMR (CDCl₃): δ -3.19 (s, 2H, NH), 5.04 (s, 2H, OH), 7.40 (m, 4H, Ar H), 7.77 (t, 2H, *J* = 7.7, Ar H), 8.05 (d, 2H, *J* = 7.7, Ar H), 9.1 (d, 4H, *J* = 4.6, β -H), 9.43 (d, 4H, *J* = 4.6, β -H), 10.35 (s, 2H). Anal. Calcd (found) for C₃₄H₂₂N₄O₂: C, 77.72 (75.6); H, 4.48 (4.4); N, 11.3 (11.1). UV/vis (ϵ , 10⁻⁴ L mol⁻¹ cm⁻¹) (CH₂Cl₂): 406 (29.6), 501 (1.95), 534 (0.82), 574 (0.86), 627 (0.48) nm.

3,3'-Bis(bromomethyl)biphenyl (3). This compound was prepared by bromination with *N*-bromosuccinimide of commercial 3,3'-dimethylbiphenyl; it had a melting point of 112 °C (lit.¹³ mp 115–117 °C). ¹H NMR (CDCl₃): δ 4.56 (s, 4H, CH₂Br), 7.47 (m, 6H), 7.61 (s, 2H).

2,2'-Dimethyl-3,3'-bis(bromomethyl)biphenyl (4). This compound was obtained by a multistep synthesis via 2,2'-dimethyl-3,3'-diiodobiphenyl (**4a**), 2,2'-dimethyl-3,3'-diformylbiphenyl (**4b**), and 2,2'-dimethyl-3,3'-bis(hydroxymethyl)biphenyl (**4c**).

4a. To a suspension of 1.5 g (7.1 mmol) of 2,2'-dimethyl-3,3'-diaminobiphenyl,¹⁴ in concentrated HCl (15 mL) and water (10 mL), cooled to -5 °C, was added a solution of sodium nitrite (1.12 g, 2.2 equiv) in water (6 mL). The resulting solution was stirred for 30 min at 0/5 °C. At this time a saturated aqueous solution of potassium iodide (7.8 g, 47 mmol) was added and the mixture was stirred overnight at 50 °C. The solution was poured into dichloromethane. The resulting organic phase was washed with water, saturated aqueous NaHCO₃, saturated aqueous NaHSO₃, and water, and the solvent was removed under vacuum. The residue was purified by chromatography on a SiO₂ column, eluted with CH₂Cl₂ to give 1.0 g of **4a** (33%). ¹H NMR (CDCl₃): δ 2.16 (s, 6H, Me), 6.90 (t, 2H, *J* = 7.7), 7.05 (d, 2H, *J* = 7.5), 7.85 (d, 2H, *J* = 7.7).

4b. To a stirred solution of **4a** (0.8 g, 1.8 mmol) in dry ether (25 mL) at -15 °C under argon was added *n*-butyllithium (2.2 equiv, 2.5 mL, 1.6 M in hexane). After 1 h, 1 mL of anhydrous DMF was added and the solution allowed to warm to room temperature. After 3 h, 20 mL of aqueous hydrochloric acid (2 M) was added and the mixture stirred for an additional 30 min. The organic layer was separated and washed with saturated aqueous NaHCO₃ and water, and the solvent was removed under vacuum. The residue was purified by chromatography on a SiO₂ column, eluted with CH₂Cl₂. Yield: 250 mg, 57%. Mp: 149 °C. ¹H NMR (CDCl₃): δ 2.35 (s, 6H, Me), 7.40 (m, 4H), 7.87 (dd, 2H, *J* = 7.6), 10.37 (s, 2H, CHO).

4c. A solution containing **4b** (250 mg, 1.11 mmol), NaBH₄ (25 mg, 0.65 mmol), and 10 mL of absolute ethanol was stirred for 1 h at 40 °C. The mixture was combined with water (100 mL) and extracted with ether (2 $\times$ 50 mL). The organic layer was washed with water twice and removed under vacuum. The biphenyl **4c** was recrystallized from hexane (210 mg, 84%), mp 136–137 °C. ¹H NMR (CDCl₃): δ 2.03 (s, 6H, Me), 4.77 (d, 4H, *J* = 5.1, CH₂ OH), 7.07 (d, 2H, *J* = 7.7), 7.25 (t, 2H, *J* = 7.5), 7.39 (d, 2H, *J* = 7.5). Anal. Calcd (found) for C₁₆H₁₈O₂, 0.5 H₂O: C, 76.47 (76.6); H, 7.49 (7.5).

4. A solution containing **4c** (200 mg, 0.83 mmol) and 10 mL of 33% HBr in AcOH was warmed at 50 °C for 12 h. After cooling, water was added (100 mL) and the mixture was extracted with dichloromethane (100 mL). The organic layer was washed with water, saturated aqueous NaHCO₃, and water and dried over MgSO₄. The

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solvent was removed under vacuum to give a brown oil which was purified by chromatography on a SiO₂ column, eluted with a mixture of CH₂Cl₂/hexane (2:1) to give 225 mg (74%) of pure **4**, mp 122–123 °C. ¹H NMR (CDCl₃): δ 2.09 (s, 6H, Me), 4.59 (s, 4H, CH₂Br), 7.08 (d, 2H, *J* = 7.5), 7.21 (t, 2H, *J* = 7.5), 7.34 (d, 2H, *J* = 7.5). Anal. Calcd (found) for C₁₆H₁₆Br₂: C, 52.21 (52.1); H, 4.38 (4.3).

2,2'-Dimethoxy-3,3'-bis(chloromethyl)biphenyl (5). This derivative was synthesized via 2,2'-dimethoxy-3,3'-diformylbiphenyl (**5a**) and 2,2'-dimethoxy-3,3'-bis(hydroxymethyl)biphenyl (**5b**). **5a.** 2,2'-Dimethoxydilitiobiphenyl was prepared in refluxing ether under Gillman's conditions on 20 g (93 mmol) of 2,2'-dimethoxybiphenyl in the presence of 2.2 equiv of *n*-butyllithium (130 mL, 1.6 M in hexane).¹⁵ After cooling of the mixture to 0 °C, 25 mL of anhydrous DMF was slowly added. The mixture was allowed to warm to room temperature while being stirred under argon overnight and then hydrolyzed with 400 mL of 2 M aqueous hydrochloric acid. Stirring was maintained for 30 min. The organic layer was filtered, washed with saturated aqueous NaHCO₃ and water, and removed under vacuum to give a brown oil, **5a**, which was recrystallized twice from ethanol. Yield: 5.5 g, 25%. Mp: 145–146 °C. ¹H NMR (CDCl₃): δ 3.58 (s, 6H, OMe), 7.33 (t, 2H, *J* = 7.7), 7.64 (dd, 2H, *J* = 7.5, *J* = 1.8), 7.93 (dd, 2H, *J* = 7.7, *J* = 1.9), 10.47 (s, 2H, CHO). Anal. Calcd (found) for C₁₆H₁₄O₄: C, 71.10 (70.84); H, 5.22 (5.05).

5b. Following the same procedure described for **4c**, the reaction of **5a** (3.0 g, 11 mmol) with NaBH₄ (250 mg, 6.6 mmol) afforded 2.9 g (95%) of **5b**, mp 91 °C. ¹H NMR (CDCl₃): δ 2.4 (m, 2H, OH), 3.43 (s, 6H, OMe), 4.78 (d, 4H, *J* = 5.9, CH₂OH), 7.21 (t, 2H, *J* = 7.5), 7.32 (dd, 2H, *J* = 7.6, *J* = 1.8), 7.39 (dd, 2H, *J* = 7.5, *J* = 1.5). ¹H NMR (CDCl₃ + D₂O): δ 4.77 (s, 4H, CH₂OH). Anal. Calcd (found) for C₁₆H₁₈O₄: C, 70.06 (69.85); H, 6.61 (6.47).

5. A solution containing **5b** (2.0 g, 7.3 mmol), 5 mL of SOCl₂, and 10 mL of anhydrous CH₂Cl₂ was stirred overnight at room temperature. The solvents were removed under vacuum, and the crude product was recrystallized from *n*-hexane (2.05 g, 90%), mp 142–143 °C. ¹H NMR (CDCl₃): δ 3.47 (s, 6H, OMe), 4.74 (s, 4H, CH₂Cl), 7.18 (t, 2H, *J* = 7.7), 7.37 (dd, 2H, *J* = 7.6, *J* = 1.8), 7.44 (dd, 2H, *J* = 7.5, *J* = 1.8). Anal. Calcd (found) for C₁₆H₁₆Cl₂O₂: C, 61.75 (61.69); H, 5.18 (5.13).

General Procedure Used for the Preparation of the Porphyrins with Straps Attached via CH₂O Linkages (6H₂–8H₂). A 200 mg amount of porphyrin 2H₂, 1.5 equiv of 3,3'-dihalogenomethylbiphenyl (**3-5**) (0.61 mmol) and 3 equiv of anhydrous K₂CO₃ (220 mg) were mixed. This powder was added in little portions over a 12-h period to a solution of 100 mL of anhydrous acetone refluxing under inert atmosphere. After completion of the addition, refluxing was maintained for 12 h. The mixture was then poured in 200 mL of water and then extracted twice with methylene chloride (2 × 100 mL). The organic layers were washed with water and removed under vacuum. The residue was purified by column chromatography (SiO₂, CH₂Cl₂). Compounds **6H₂–8H₂** were recrystallized from CH₂Cl₂/*n*-hexane.

5,15-[o,o'-((3,3'-Biphenyldiyl)dimethylene)dioxy]diphenylene]porphyrin (6H₂). A 200 mg amount of biphenyl **3** was used for the preparation of **6H₂** (150 mg, 53%). ¹H NMR (CDCl₃): δ -3.96 (s, 2H, NH), 3.36 (s, 2H, 2,2'-H), 4.42 (s, 4H, OCH₂), 4.77 (d, 2H, *J* = 7.6, H_a), 5.90 (t, 2H, *J* = 7.6, H_b), 6.23 (d, 2H, *J* = 7.5, H_c), 7.52 (d, 2H, *J* = 7.9, Ar H), 7.62 (t, 2H, *J* = 7.7, Ar H), 7.83 (t, 2H, *J* = 7.7, Ar H), 8.46 (d, 2H, *J* = 7.7, Ar H), 8.98 (d, 4H, *J* = 4.5, β-H), 9.22 (d, 4H, *J* = 4.5, β-H), 10.01 (s, 2H). UV/vis (CH₂Cl₂): 411, 506, 538, 577, 632 nm. Anal. Calcd (found) for C₄₆H₃₂N₄O₂: C, 82.12 (81.6); H, 4.79 (4.7); N, 8.33 (7.9).

5,15-[o,o'-((2,2'-dimethyl-3,3'-biphenyldiyl)dimethylene)dioxy]diphenylene]porphyrin (7H₂). Following the general procedure, the condensation of biphenyl precursor **4** (140 mg) with 2H₂ afforded compound **7H₂**, which contained after column chromatography bis-(porphyrin) impurities. These impurities were removed by repeated crystallizations in dichloromethane/hexane mixtures to give pure **7H₂** (135 mg, 35%). ¹H NMR (CDCl₃): δ -3.03 (s, 2H, NH), -2.36 (s, 6H, Me), 3.89 (d, 2H, *J* = 9.8, OCH₂), 3.97 (d, 2H, *J* = 9.8, OCH₂), 5.92 (d, 2H, *J* = 7.4, H_a), 6.45 (t, 2H, *J* = 7.5, H_b), 6.64 (d, 2H, *J* =

7.5, H_c), 7.33 (d, 2H, Ar H), 7.67 (t, 2H, Ar H), 7.82 (t, 2H, Ar H), 8.83 (d, 2H, Ar H), 8.94 (d, 2H, *J* = 4.6, β-H), 9.0 (d, 2H, *J* = 4.6, β-H), 9.21 (d, 2H, *J* = 4.6, β-H), 9.24 (d, 2H, *J* = 4.6, β-H), 10.06 (s, 2H). UV/vis (CH₂Cl₂): 408, 502, 534, 576, 630 nm. Treatment of the mother liquor with an excess of ZnCl₂ in refluxing THF yielded the zinc(II) complex, which was purified by chromatography on silica gel to yield a second crop of porphyrin **7-Zn** (50 mg, 13%). No demetalation occurred after several days by dissolution of **7-Zn** in pure trifluoroacetic acid.

7-Zn. ¹H NMR (CDCl₃ + 1 drop of THF-*d*₄): δ -2.72 (s, 6H, Me), 3.62 (d, 2H, *J* = 9.9, OCH₂), 3.80 (d, 2H, *J* = 9.8, OCH₂), 5.75 (d, 2H, *J* = 7.5, H_a), 6.29 (t, 2H, *J* = 7.5, H_b), 6.50 (d, 2H, *J* = 7.5, H_c), 7.22 (d, 2H, *J* = 8.1, Ar H), 7.54 (t, 2H, *J* = 7.4, Ar H), 7.68 (t, 2H, *J* = 7.7, Ar H), 8.71 (d, 2H, *J* = 7.9, Ar H), 8.81 (d, 2H, *J* = 4.6, β-H), 8.88 (d, 2H, *J* = 4.6, β-H), 9.10 (d, 2H, *J* = 4.6, β-H), 9.14 (d, 2H, *J* = 4.6, β-H), 9.90 (s, 2H). UV/vis (10⁻⁴ε, L mol⁻¹ cm⁻¹) (THF): 393 (sh), 414 (57.3), 545 (2.45), 580 (0.41) nm. Anal. Calcd (found) for C₄₈H₃₄N₄O₂Zn: C, 75.24 (75.7); H, 4.74 (4.6); N, 7.31 (7.5).

5,15-[o,o'-((2,2'-dimethoxy-3,3'-biphenyldiyl)dimethylene)dioxy]diphenylene]porphyrin (8H₂). A 160 mg amount of biphenyl **5** were used for the preparation of **8H₂** (120 mg, 41%). ¹H NMR (CDCl₃): δ -3.26 (s, 2H, NH), -2.09 (s, 6H, OMe), 4.34 (m, 4H, OCH₂), 6.28 (m, 4H, H_a + H_b), 6.57 (d, 2H, H_c), 7.18 (d, 2H, Ar H), 7.59 (t, 2H, *J* = 7.4, Ar H), 7.81 (t, 2H, *J* = 7.6, Ar H), 8.83 (d, 2H, *J* = 7.2, Ar H), 8.92 (m, 4H, β-H), 9.18 (m, 4H, β-H), 9.98 (s, 2H). FABMS (*m/e*): calcd for C₄₈H₃₆N₄O₄, 732.84; found, 733.1 (100, M⁺). UV/vis (CH₂Cl₂): 408, 502, 532, 575, 628 nm.

Iron Insertion into Porphyrins 1H₂ and 6H₂–8H₂. Iron insertion was performed with an excess of anhydrous ferrous chloride in refluxing THF in the presence of 2,6-dimethylpyridine under an argon atmosphere. The disappearance of the metal-free porphyrin was monitored by TLC (SiO₂, 5:95 ether/CH₂Cl₂). When the metalation was ended, methylene chloride was added to the reaction mixture which was then poured into aqueous hydrochloric acid. After workup, the iron(III) chloride complexes were purified by chromatography on an alumina column (basic grade I). Elution with MeOH/CH₂Cl₂ (5:95 v/v) gave the red (μ-oxo)iron(III) dimers which were recrystallized in CH₂Cl₂–hexane and isolated in 70–80% yields. These (μ-oxo)iron(III) dimers showed typical UV/vis spectral bands in THF (λ_{max} = 403, 565 nm). Elemental analyses were performed on these μ-oxo dimers. Indeed, the metalloporphyrins were not isolated as iron(III) chloride complexes owing to the difficulties to resolubilize them in all usual organic solvents, except DMSO. Nevertheless, these chloroiron(III) complexes were easily generated on bubbling HCl vapors from an opened bottle containing concentrated HCl into the μ-oxo-dimer solutions.

1-FeCl. ¹H NMR (CDCl₃): δ 77.3 (s, β-H), 80.1 (s, β-H). UV/vis (10⁻⁴ε L mol⁻¹ cm⁻¹) (CH₂Cl₂): 373 (5.8), 406 (8.6), 501 (1.4), 572 (0.43), 662 (0.41) nm. Anal. Calcd (found) for C₆₄H₄₀N₈OFe₂, 1.5 H₂O: C, 71.5 (71.4); H, 4.03 (4.1); N, 10.4 (10.3).

6-FeCl. ¹H NMR (CDCl₃): δ 75.9 (s, β-H), 83.4 (s, β-H). UV/vis (10⁻⁴ε L mol⁻¹ cm⁻¹) (THF): 371 (4.7), 408 (8.8), 499 (1.5), 571 (0.80), 636 (0.72) nm. Anal. Calcd (found) for C₉₂H₆₀N₈O₅Fe₂·4H₂O: C, 71.7 (71.5); H, 4.45 (4.6); N, 7.27 (7.2).

7-FeCl. ¹H NMR (CDCl₃): δ 74.4 (d, β-H), 82.9 (d, β-H). UV/vis (10⁻⁴ε L mol⁻¹ cm⁻¹) (THF): 370 (6.1), 406 (8.2), 498 (1.6), 570 (0.69), 634 (0.60) nm. Anal. Calcd (found) for C₉₆H₆₈N₈O₅Fe₂·5H₂O: C, 71.4 (71.1); H, 4.87 (4.80); N, 6.84 (6.7).

8-FeCl. ¹H NMR (CDCl₃): δ 76.8 (d, β-H), 86.6 (d, β-H). UV/vis (10⁻⁴ε L mol⁻¹ cm⁻¹) (THF): 376 (5.7), 405 (8.3), 497 (1.5), 572 (0.7), 634 (0.66) nm. Anal. Calcd (found) for C₉₆H₆₈N₈O₉Fe₂·2.5H₂O: C, 70.55 (70.5); H, 4.50 (4.5); N, 6.86 (6.7).

Crystallographic Data Collection and Structure Determination. Violet prismatic single crystals of composition **6-FeCl**·MeOH·CH₂Cl₂ were obtained by slow evaporation of CH₂Cl₂/MeOH solutions of **6-FeCl**. Crystal data were collected at -100 °C in the θ/2θ flying step-scan mode with a crystal of 0.40 × 0.20 × 0.10 mm³ dimensions on a Philips PW1100/16 diffractometer using graphite-monochromated Cu Kα radiation. X-ray experimental data are given in Table 1. The unit cell parameters have been refined using 24 high-angle reflections. A total of 4886 independent reflections were collected in the range 3 < θ < 52.5° (limit imposed by the cooling device, -10 ≤ *h* ≤ 10, 0

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Table 1. Crystallographic Data for **6**-FeCl $\cdot$ CH $_3$ OH $\cdot$ CH $_2$ Cl $_2$

formula: C $_{48}$ H $_{36}$ N $_4$ O $_3$ Cl $_3$ Fe	fw: 879.05
$a = 10.164(3)$ Å	space group: $P2_1/c$ (No. 14)
$b = 28.977(9)$ Å	$T = -100$ °C
$c = 14.283(4)$ Å	$\lambda = 1.54184$ Å
$\beta = 106.22(2)^\circ$	$\rho_{\text{calc}} = 1.45$ g cm $^{-3}$
$\mu = 5.261$ mm $^{-1}$	transm coeff = 0.61–1.00
$V = 4039(3)$ Å 3	$R(F_o) = 0.056$
$Z = 4$	$R_w(F_o) = 0.087$

$\leq k \leq 29$, $0 \leq l \leq 14$) from which 3161 had $I > 3\sigma(I)$. These latter reflections were used to determine the structure by direct methods and to refine it. After isotropic refinements, a difference map showed maxima close to the positions expected for hydrogen atoms. These atoms, with the exception of the methanol protons, were included at their idealized positions as fixed contributors in structure factor calculations with a C–H = 0.95 Å and isotropic temperature factors such as $B(\text{H}) = 1.3B_{\text{eqv}}(\text{C})$ Å 2 . At this stage, absorption corrections, using DIFABS, were applied (min/max transmission coefficients = 0.61–1.00). Anisotropic refinements of all non-hydrogen atoms, with the exception of the methanol C and O atoms, on $|F|$, with weights given by $w = 4F_o^2/(\sigma^2(F_o) + 0.0064F_o^4)$, converged to $R(F_o) = 0.056$, $R_w(F_o) = 0.087$, and GOF = 1.887. No extinction corrections were applied. A nonresolved electron-density residue of 1.4 e/Å 3 remains near the methanol molecule, indicating some disorder in the region around this solvent. All calculations were performed using the OpenMoleN package on a DEC Alpha work station.^{19a} Scattering factors and anomalous dispersion coefficients were taken from Cromer and Waber.^{19b}

Results

Conformational Properties of the Biphenyl-Strapped Porphyrins in Solution. The electronic absorption spectra of these metal-free strapped porphyrins **6H $_2$ –8H $_2$** showed only minor changes relative to that of the precursor porphyrin **2H $_2$** . The Soret bands are slightly red-shifted from 1 to 5 nm, the largest shift of this band (5 nm) being observed for porphyrin **6H $_2$** in which the 2,2'-positions of the biphenyl strap are not substituted. The small shifts of the Soret bands indicate that, relative to the precursor porphyrin **2H $_2$** , the rings of **6H $_2$ –8H $_2$** are somewhat more distorted and less planar.¹⁶ The slight supplementary distortions of the porphyrin rings are, most probably, induced by the covalently attached biphenyl straps. However, because the Soret band is most shifted for **6H $_2$** , in which the 2,2'-positions of the biphenyl strap are not substituted, the observed band shifts of 1–5 nm cannot be directly related to steric interactions of the 2,2'-substituents with the porphyrin rings.

The free-base porphyrins were also studied by ^1H NMR spectroscopy. Figure 2a displays the ^1H NMR spectrum (CDCl $_3$) of the metal-free porphyrin **7H $_2$** . As illustrated by this spectrum, the methine proton signals of these strapped porphyrins **6H $_2$ –8H $_2$** , which appear between 9.98 and 10.06 ppm (Table 2), are weakly upfield shifted by 0.29–0.37 ppm relative to these proton signals in the precursor porphyrin **2H $_2$** . These

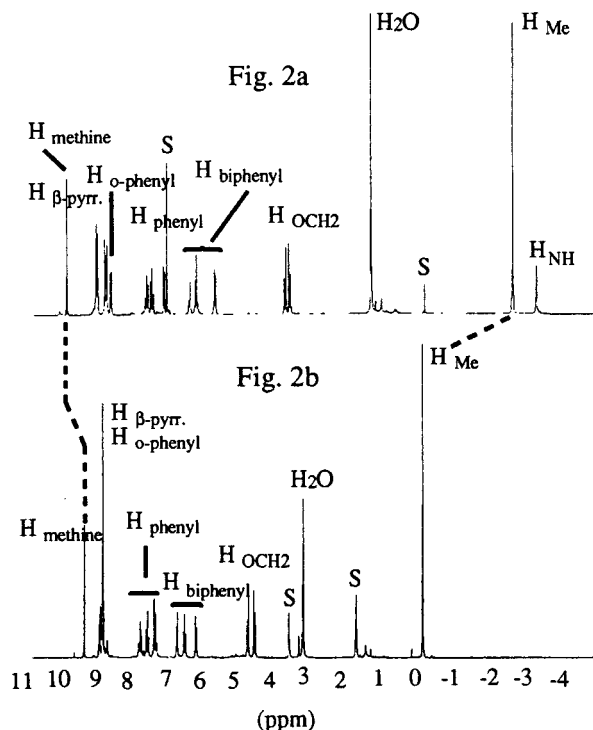


Figure 2. (a) ^1H NMR spectra of metal-free base **7** in CDCl $_3$ at room temperature. (b) **7-Fe(CO)(py-d $_5$)** in THF- d_8 at room temperature.

Table 2. $^1\text{H}_{\text{NH}}$ and $^1\text{H}_{\text{methine}}$ Chemical Shifts (ppm) in the ^1H NMR Spectra (in CDCl $_3$) of (Figure 1a) the Metal-Free Porphyrin **2H $_2$** and the CH $_2$ O-Linked Biphenyl-Strapped Metal-Free Porphyrins **6H $_2$ –8H $_2$**

	H_{NH}	$\text{H}_{\text{methine}}$	Δ^a		H_{NH}	$\text{H}_{\text{methine}}$	Δ^a
2H$_2$	-3.19	10.35		7H$_2$	-3.03	10.06	-0.29
6H$_2$	-3.96	10.01	-0.34	8H$_2$	-3.26	9.98	-0.37

^a Δ = differences in the $\text{H}_{\text{methine}}$ chemical shifts for **6H $_2$ –8H $_2$** relative to the shift in **2H $_2$** .

small shifts confirm that small distortions occur in **6H $_2$ –8H $_2$** , relative to **2H $_2$** .¹⁷ However again, because one of the largest shifts of the methine proton resonances is observed for **6H $_2$** , these distortions cannot be directly related to steric interactions exerted by the 2,2'-substituents on the porphyrin rings.

The large upfield shifts observed for the 2,2'-substituent singlets indicate that these groups are facing the porphyrin macrocycle. The methyl and methoxy group resonances of porphyrins **7H $_2$** and **8H $_2$** are upfield shifted by 4.45 and 5.56 ppm relative to the biphenyl precursors **4** and **5**, respectively. These orientations of the methyl and methoxy 2,2'-substituents have been confirmed by the X-ray structures of the metal-free porphyrins **7H $_2$** and **8H $_2$** .¹⁸

Specific assignments of the β -pyrrole resonances are somewhat ambiguous. For porphyrin **6H $_2$** , the β -pyrrole signals appear as two doublets integrating as four protons. This apparent C_{2v} symmetry indicates that a dynamic exchange process is occurring. Interconversion of the two chiral atropisomers of this strapped porphyrin must proceed via a coplanar conformation of the 2,2'-unsubstituted biphenyl strap. On the other hand, the four doublets lying between 8.81 and 9.18 ppm in the spectra of porphyrins **7H $_2$** (Figure 2a) and **8H $_2$** , which have been assigned to the four different types of β -pyrrolic protons, show an actual C_2 symmetry. An increase in temperature to 60 °C does not produce significant variations in the spectrum of **8H $_2$** , confirming that the dynamic exchange process

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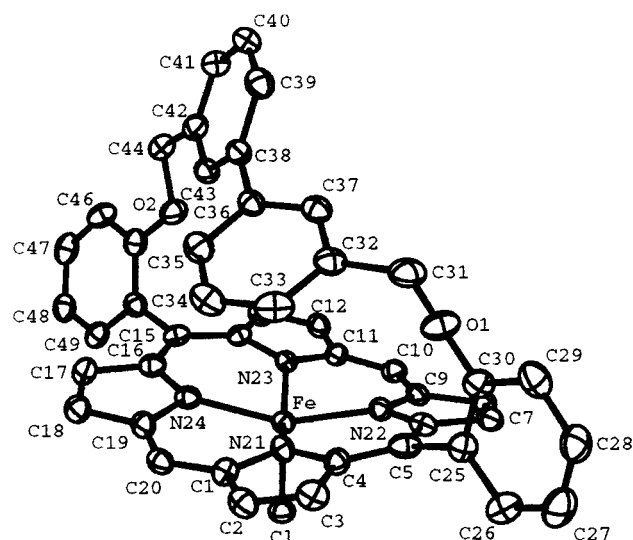


Figure 3. ORTEP plot of **6-FeCl**. Ellipsoids are scaled to enclose 50% of the electronic density. Hydrogen atoms are omitted.

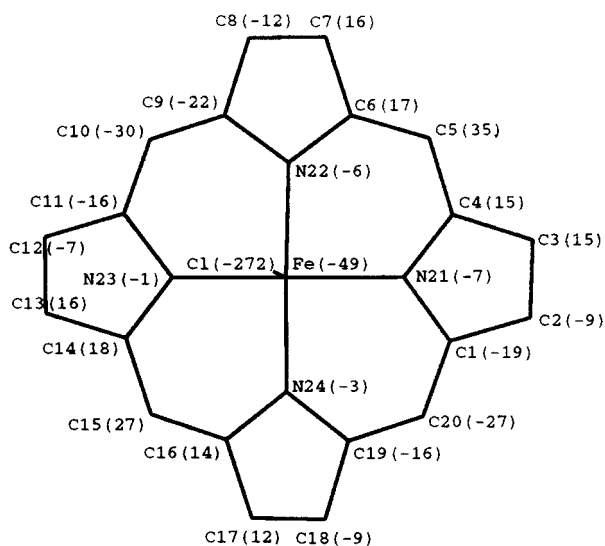


Figure 4. Pluto plot of the porphyrin core of **6-FeCl**. Numbers in parentheses indicate the deviations in 0.01 Å relative to the mean plane porphyrin ring.

of the strap occurring in **6H₂** is prevented in **8H₂** and in **7H₂** by the bulkiness of the 2,2'-substituents. Furthermore, the methylene protons of the CH₂O links, which are diastereotopic in nature due to the chirality of these strapped porphyrins, give two well-defined doublets in the case of porphyrin **7H₂** ($J = 9.8$ Hz) (Figure 2a), an apparent quartet in case of porphyrin **8H₂**, but only a singlet integrating as four protons in the spectrum of porphyrin **6H₂**. This again shows that the strap interconversion occurring in **6H₂** is blocked in **7H₂** and **8H₂**.

Crystal Structure of 6-FeCl·CH₃OH·CH₂Cl₂. The molecular structure of **6-FeCl** is displayed in Figure 3 together with a part of the labeling scheme used. Figure 4 shows the perpendicular displacements (in 0.01 Å units) of the porphyrin-core atoms and the FeCl unit relative to the porphyrin-core mean-plane. Selected average bond distances and bond angles occurring in **6-FeCl** are assembled in Table 3.

The iron atom of **6-FeCl** is five-coordinate, high-spin. The axial chloride ligand lies opposite to the strap. The coordination geometry of the iron center is similar to that in other five-

Table 3. Selected Averaged Bond Distances and Bond Angles and Out-of-Mean-Plane Displacements in **6-FeCl**

$\langle \text{Fe}-\text{N} \rangle$ (Å)	$\text{Fe}-\text{Cl}$ (Å)	$\langle \text{N}-\text{Fe}-\text{N} \rangle$ (deg)	$\langle \text{N}-\text{Fe}-\text{Cl} \rangle$ (deg)
2.046(6)	2.234(2)	87.2(2)	102.7(2)
$\Delta(\text{Fe})/4\text{N}_p$ (Å):	0.45(1)	$\Delta(\text{Fe})/24\text{-core}$ (Å):	0.49(1)

coordinate systems of the FeCl(Porph) type.²⁰ The perpendicular displacements of the porphyrin-core atoms of **6-FeCl** relative to their mean-plane indicate that the macrocycle is slightly domed and ruffled (Figure 4). The doming, which is characterized by a separation of 0.04(1) Å between the 4N_p and porphyrin-core mean-planes, moves the 4N_p mean-plane in the opposite direction relative to the strap and thus increases slightly the space between the strap and the porphyrin core. It is related to the pentacoordination and out-of-plane displacement of 0.45(1) Å of the iron center relative to the four pyrrole nitrogen mean-plane. The ruffling is characterized by a mean displacement of 0.32(1) Å above the porphyrin core mean-plane of the C5 and C15 *meso*-carbons, which lie on the same side of the porphyrin ring as the strap. It is connected to the presence of a strap covalently linked to an ortho position of both phenyl rings of the 5,15-diphenylporphyrin. The distortions of the porphyrin ring in **6-FeCl** are more severe than those occurring in the sterically protected chloroiron(III) porphyrin derivatives, [Fe^{III}Cl(C2-cap)] and [Fe^{III}Cl(C4-Cap)].²⁰ The average displacements of the porphyrin core atoms relative to their mean-plane is 0.15(1) Å in **6-FeCl**, the largest deviation being 0.35(1) Å. In contrast, in the chloroiron(III) complexes of the capped tetraphenylporphyrins H₂(C2-Cap) and H₂(C4-Cap), the average deviations from the porphyrin mean-planes are only 0.08 and 0.04 Å, respectively. The dihedral angle between the two phenyl rings forming the biphenyl strap is 133.7(2)°. Thus, this angle is slightly larger than 120°, a value known to occur in one of the thermodynamically stable conformations of the free 2,2'-disubstituted biphenyls.²¹ The dihedral angles between the two phenyl rings forming the strap and the porphyrin-core mean-plane are 32.4(2) (C32–C37) and 108.8(2)° (C38–C43). The cavity height occurring in **6-FeCl** defined as the distance between the centroid of the strap and the porphyrin-core mean-plane is 4.817(7) Å. The lateral shift of the strap determined as the distance between the centroid of the strap and the normal to the porphyrin-core mean-plane passing through the center C_t of the porphyrin ring is 1.002(7) Å.

Synthesis and Spectroscopic Characterization of Iron(II) Biphenyl-Strapped Porphyrins and Their CO Adducts. The reduction of the ferric into ferrous porphyrin derivatives was achieved by zinc/Hg amalgam in dry degassed solvents (THF, toluene, dichloromethane). Addition of deoxygenated nitrogenous aromatic bases (imidazoles, pyridine) yielded pure high-spin, five-coordinate complexes, except for porphyrin **6H₂**, which formed, under these conditions, a low-spin six-coordinate iron(II) complex. The five-coordinate iron(II) complexes were characterized by UV/vis and ¹H NMR spectroscopy. In THF, these compounds exhibited typical UV/vis spectra with bands lying between 359 and 363, 423 and 425 (Soret), and 526 and 549 nm. The characteristic band lying in the range 359–363 nm, indicating the presence of pentacoordinated, high-spin derivatives, does not appear in the electronic spectrum of **6-Fe(II)** by addition of an aromatic base and disappears in all the derivatives upon addition of CO. In THF, the six-coordinate Fe^{II}(CO)(nitrogenous base) derivatives of porphyrins **7H₂** and

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Table 4. Chemical Shifts (ppm) of the 2,2'-Biphenyl Substituent Group Resonances and the Biphenyl Proton and Porphyrin Methine Proton Signals Observed in the ^1H NMR Spectra of **1**-Fe(CO)(py- d_5) (in CDCl_3) and for **6**-, **7**-, and **8**-Fe(CO)(py- d_5) (in $\text{THF}-d_8$)^a

compd	H(substituents)	H(biphenyl)	H(methine)
1 -Fe(CO)(py- d_5)			9.82 (s, -0.48)
6 -Fe(CO)(py- d_5)			9.26 (s, -0.75)
7 -Fe(CO)(py- d_5)	-0.07 (s, 2.29)	6.32 (d, +0.78) 6.63 (t, -0.18) 6.84 (d, +0.20)	9.45 (s, -0.61)
8 -Fe(CO)(py- d_5)	1.16 (s, +3.25)	6.40 (s, +0.12) 6.78 (m, +0.15; +0.44)	9.39 (s, -0.59)

^a The nature of the signal and the difference in chemical shift relative to the metal-free porphyrin are indicated in parentheses.

8H₂ show UV/vis bands ranging between 416 and 419 (Soret) and 511 and 523 nm.

The ^1H NMR spectra of the pentacoordinated, high-spin, ferrous species were measured in $\text{THF}-d_8$ or CDCl_3 solutions containing the iron(II) porphyrins ($c \approx 10$ mM) and pyridine- d_5 ($c \approx 2.5$ M). Their pyrrole resonances appear downfield between 45 and 55 ppm and show C_2 symmetry. The methine proton signals lie upfield between -10 and -15 ppm. A signal lying at 17.1 ppm in the spectrum of **7**-Fe^{II}(py- d_5) has been attributed to the 2,2'-methyl substituents on the basis of its integration. The 2,2'-methoxy group resonances appear at 15.6 ppm in the spectrum of **8**-Fe^{II}(py- d_5).

Addition of CO to the Fe^{II}(py- d_5) NMR samples of porphyrin dianions **7** and **8** yielded the corresponding six-coordinate, low-spin, carbonyl adducts. Figure 2b displays the ^1H NMR spectrum of **7**-Fe^{II}(CO)(py- d_5).

As shown in Table 4, the methine proton signals are slightly upfield shifted in the ^1H NMR spectra of **6**-, **7**-, and **8**-Fe(CO)(py- d_5) with respect to the methine proton signal of **1**-Fe(CO)(py- d_5). These upfield shifts are compatible with a slight increase in distortion of the porphyrin cores upon CO binding. However, since the largest shift occurs in the spectrum of **6**-Fe(CO)(py- d_5) in which the strap is not substituted, the distortions of the porphyrin cores in **6**-, **7**-, and **8**-Fe(CO)(py- d_5) relative to that present in **1**-Fe(CO)(py- d_5) are, again, not directly related to the size of the 2,2'-substituents.

Binding of CO within the cavity formed by the porphyrin core and the strap (distal side) results in large downfield shifts of the proton resonances of the 2,2'-substituents in the ^1H NMR spectra of the carbonyl adducts relative to the resonances of these groups in the spectra of the corresponding metal-free porphyrins (Table 4). For instance, in the ^1H NMR spectrum of **7**-Fe(CO)(py- d_5) (Figure 2b), shifts ranging from 2.5 to 3.5 ppm are observed relative to the resonances of these substituents in the metal-free base **7**H₂ (Figure 2a) or zinc(II) derivative **7**-Zn (see Experimental Section).

In THF, in the absence of any nitrogenous base, complex **7**-Fe(THF) seems to yield the regioisomer **7**-Fe(CO)_{in}(THF) in which CO lies within the cavity (distal side). The main UV/vis spectral bands (THF) of this complex lie at 410 and 513 nm, and the CO stretching vibration lies at 1983 cm^{-1} . In contrast, **8**-Fe seems to yield in THF the regioisomer in which CO lies outside the cavity (proximal side). Indeed, the downfield shift of the methoxy group resonances, relative to the metal free base, is very small (0.14 ppm) precluding the hypothesis of CO lying inside the cavity. Furthermore, the main bands in the UV/vis spectrum (THF) appear at 398 and 502 nm and the CO stretching vibration lies at 1955 cm^{-1} in the IR spectrum.

Table 5. CO Stretching Vibrations (cm^{-1}) in **1**-, **6**-, **7**-, and **8**-Fe(CO)(L) in THF and in the Presence of a Nitrogenous Base L (L = Pyridine (py), Imidazole (ImH), and *N*-Methylimidazole (N-Melm))

compd	L = Py	L = ImH	L = N-Melm
1 -Fe(CO)(L)	1976	1969	
6 -Fe(CO)(L)	1993	1985	1987
7 -Fe(CO)(L)	1992		1987
8 -Fe(CO)(L)	2006, 1986	1999, 1981	2000, 1981

Table 6. CO Stretching Vibrations (cm^{-1}) in **1**-, **6**-, and **8**-Fe(CO)(py) in CH_2Cl_2 and Toluene

compd	CH_2Cl_2	toluene
1 -Fe(CO)(py)	1975	1980
6 -Fe(CO)(py)	1983	1994
8 -Fe(CO)(py)	1999, 1983	2006, 1988

In noncoordinating solvents such as CH_2Cl_2 and in the absence of any nitrogenous base, **1**-Fe, **6**-Fe, and **7**-Fe form two carbonyl adducts showing one ν_{CO} band at 2029 cm^{-1} and the other ranging between 1966 (**1**-Fe), 1962 (**6**-Fe), and 1954 cm^{-1} (**7**-Fe). Since, the dicarbonyl adduct of iron(II) tetraphenylporphyrin ($[\text{Fe}(\text{CO})_2(\text{TPP})]$) is characterized by a ν_{CO} band located at 2042 cm^{-1} ,²² the 2029 cm^{-1} band, most probably, corresponds to the ferrous bis-CO complexes of the porphyrin dianions **1**, **6**, and **7**. The second band ranging between 1966 and 1954 cm^{-1} corresponds probably to the ν_{CO} band of the monocarbonylated (CO)_{out} regioisomer. Under similar conditions **8**-Fe yields only one CO adduct characterized by a ν_{CO} band at 1956 cm^{-1} , which corresponds to the (CO)_{out} regioisomer.

Table 5 gives the CO stretching vibrations observed for **1**-, **6**-, **7**-, and **8**-Fe(CO)(B) in THF and in the presence of an axial nitrogenous base B (B = pyridine, imidazole, *N*-methylimidazole). The ν_{CO} bands shift to smaller wavenumbers when the axial ligand strength increases from pyridine to imidazole and *N*-methylimidazole.²³ Table 6 gives the CO stretching vibrations observed for **1**-, **6**-, and **8**-Fe(CO)(py) as a function of solvent. The 2,2'-disubstituted straps do not shield completely the bound CO from the solvent. Indeed, upshifts of the ν_{CO} bands are observed between CH_2Cl_2 and the less polar toluene. The CO stretching vibrations of the carbonyl adducts obtained with these strapped porphyrins in the presence of a nitrogenous axial base lie often between 1980 and 2000 cm^{-1} and, thus, are quite elevated. The elevated ν_{CO} values, lying close to 2000 cm^{-1} , indicate a close interaction of the carbonyl oxygen with the π -cloud of an aromatic ring as in $[\text{FeCO}(\text{1-Melm})(\text{C2-Cap})]$.^{25b}

In non- or weakly coordinating solvents and in the presence of a nitrogenous base, the carbonyl adduct of **8**-Fe always exhibits two ν_{CO} bands (Figure 5) which, by reaction with O₂ disappear, simultaneously, while keeping an identical intensity ratio.

Table 7 compares the CO pressures needed for half-saturation

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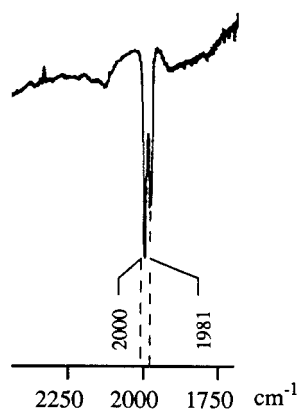


Figure 5. Infrared spectrum of **8-Fe(CO)(NMeIm)** in THF in the CO band region.

Table 7. CO Pressures in Torr for Half-Saturation ($P_{1/2}$) and Stability Constants $K_{\text{B}}\text{CO}$ in Toluene for **7-** and **8-Fe** in the Presence of N-MeIm (0.3 M) and Comparison with the Half-Saturation CO Pressures and $K_{\text{B}}\text{CO}$ Values Known for Sperm-Whale Mb (H_2O , pH = 7.0–7.5) and Several Model Porphyrins

compd	$P_{1/2}$	$K_{\text{B}}\text{CO}$	ref
7-Fe	9×10^{-2}	8.3×10^5	^a
8-Fe	3.4×10^1	3.0×10^3	^a
Mb	$(1.2\text{--}2.8) \times 10^{-2}$		30
Fe(PocPiv)	1.5×10^{-3}	6.7×10^7	6b
Fe(piv ₂ -C ₈)	1.1×10^{-2}	9.4×10^6	27
Fe-SP-13 ^b	1.2×10^1	8.3×10^3	26
Fe(OC ₂ O)	10^2	1.0×10^3	25b

^a This work. ^b Benzene, 0.2 M N-MeIm.

($P_{1/2}$)²⁶ of **7-** and **8-Fe^{II}(N-MeIm)** in toluene with the $P_{1/2}$ values known for sperm-whale Mb and several model porphyrins. This table shows that **8-Fe(N-MeIm)** displays a reduced affinity in comparison with **7-Fe(N-MeIm)**.

Discussion

The synthetic methods used to prepare these biphenyl-strapped diphenylporphyrins **6H₂**–**8H₂** allow the modification of the distal periphery of the porphyrins via a systematic variation of the size, polarity, and degree of freedom of the 2,2'-biphenyl substituents. The size of the substituents is an important parameter: (i) It controls the access of the bases and solvents to the distal cavity. (ii) It should limit the lateral displacement of the straps from their central positions. As a consequence, our 2,2'-substituted biphenyl-strapped porphyrins yield, even in the presence of a large excess of aromatic nitrogenous bases (larger than 2000 equiv), pure high-spin, five-coordinate, iron(II) species.

Earlier studies have shown that in the metal-free porphyrins **7H₂** and **8H₂** the mean-value of the cavity heights, defined as the distance between the centroid of the straps and the porphyrin mean-planes, is 5.293(4) Å.¹⁸ Upright binding of CO seems not probable in such a small cavity. However, recent structural data obtained on several five-coordinate iron(II) derivatives and six-coordinate iron(II)–CO adducts of mixed picket basket-handle,²⁷ pocket, and capped porphyrins²⁵ have shown that CO binding increases the ruffling of the porphyrin core or/and

induces large lateral and vertical movements of the handle, pocket, or cap. Both these effects lead to a considerable expansion of the distal cavities allowing the accommodation of a non- or weakly tilted and linear or quasi-linear Fe–C–O unit (Fe–C–O angles larger than 172°). Similar linear or quasi-linear Fe–C–O conformations are probably also present in the iron(II)–CO adducts of the 2,2'-substituted biphenyl-strapped porphyrins **7H₂** and **8H₂**, although the ¹H NMR data seem to indicate that the distortions of the porphyrin cores present in these CO adducts relative to those present in the metal-free macrocycles are small.

One important conformational rearrangement resulting from the distal binding of CO involves the opening of the dihedral angle of the phenyl moieties forming the biphenyl strap in order to minimize the peripheral interaction with the 2,2'-substituents. These steric effects, which are not strongly affected by the expansion and/or distortion of the porphyrinic cores, depend on the intrinsic nature of the substituents. Thus, in THF, in the absence of a nitrogenous base, **7-Fe(THF)** yields only the regioisomer **7-Fe(CO)_{in}(THF)_{out}**, despite the low affinity of THF as axial base;²⁸ whereas, under identical conditions, **8-Fe(THF)** forms only the **8-Fe(CO)_{out}** regioisomer. The large difference in affinity observed for CO in toluene between **7-Fe(py)** and **8-Fe(py)** (Table 7) also illustrates the effects of the 2,2'-substituents on the binding properties of these porphyrins. Despite that porphyrin **8H₂** possesses a distal symmetrical cavity, the FTIR spectra of **8-Fe(CO)(B)** (B = Py, ImH, 1-MeIm) show two ν_{CO} bands ranging in THF respectively from 2006 to 1999 cm⁻¹ and from 1986 to 1981 cm⁻¹ with intensity ratios of ca. 2:1. An equilibrium of the type **8-Fe(CO)₂** and **8-Fe(CO)(py)** seems excluded here, since **8-Fe(II)** does not form a bis-CO adduct, even in noncoordinating solvents and in absence of any nitrogenous base. Thus, the two CO bands indicate that two linear or quasi-linear Fe–C–O units having slightly different orientations are present in these compounds. The shift of 20 cm⁻¹ in THF between the two ν_{CO} bands is, most probably, due to a change in polarity around one CO within the cavity of porphyrin dianion **8**.²³ Furthermore, as seen before, elevated ν_{CO} bands indicate a negative polar environment around CO.^{10,25b,29} Since, one of the ν_{CO} bands of the CO adducts **8-Fe(CO)(B)** (B = Py, ImH, 1-MeIm) has always a very high stretching frequency (2006–1999 cm⁻¹), most probably, due to steric crowding within the cavity, the Fe–C–O orientation displaying the more elevated ν_{CO} band interacts more strongly than the other with the π -cloud of a benzene ring belonging to the biphenyl strap. Thus, the 20 cm⁻¹ difference observed between the two ν_{CO} stretching vibrations is probably mainly due to a stronger interaction of one of the Fe–C–O orientations with one of the benzene rings of the biphenyl strap. However, despite the occurrence of two ν_{CO} bands in the infrared spectrum of the carbonyl adduct **8-Fe(CO)(py-d₅)** (B = py-d₅) and only one in that of **7-Fe(CO)(py-d₅)**, the ¹H NMR spectra of these two complexes are very similar, even at low temperature (–70 °C). This is also consistent with the presence in **8-Fe(CO)(B)** (B = py, ImH, NMeIm) of two linear or quasi-linear Fe–C–O groups which are oriented slightly differently and which are interconverting more rapidly than the NMR time scale. While several ν_{CO} stretching vibrations ascribed to different Fe–C–O orientations or conformers (substates) are commonly observed in carbonyl adducts of hemeproteins,³⁰ the observation of more than one ν_{CO} band in the IR spectra of model porphyrin

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complexes is less common. We have obtained, recently, several carbonyl adducts of unsymmetrically 2,2'-substituted biphenyl-strapped diphenylporphyrins exhibiting two ν_{CO} bands which differ by more than 20 cm^{-1} in their IR spectra.³¹ Occurrence of two such bands indicates again that two Fe—C—O units adopting two slightly different orientations are present in these compounds. Moreover, like the CO adducts of several hemoproteins,³² the CO adducts of these biphenyl-strapped model porphyrins enriched with ^{13}C display only one ^{13}C NMR signal

indicating that the two Fe—C—O orientations giving rise to the two ν_{CO} bands interconvert more rapidly than the NMR time scale.³¹

Supporting Information Available: Tables S1–S6, listing X-ray experimental data, atomic coordinates and equivalent thermal parameters for all non-hydrogen atoms, atomic coordinates and thermal parameters for hydrogen atoms, thermal parameters for anisotropic atoms, bond lengths in Å, and bond angles in deg (14 pages). Ordering information is given on any current masthead page.

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