

# Structural Characterization of OC<sub>3</sub>OPor Capped Porphyrins: H<sub>2</sub>(OC<sub>3</sub>OPor), Fe(OC<sub>3</sub>OPor)(Cl), Fe(OC<sub>3</sub>OPor)(CO)(1-MeIm), and Fe(OC<sub>3</sub>OPor)(CO)(1,2-Me<sub>2</sub>Im)

Carla Slebodnick, Michelle L. Duval, and James A. Ibers\*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

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The sterically encumbered OC<sub>3</sub>OPor system consists of a 1,2,4,5-substituted benzene cap with five-atom arms of the type –O(CH<sub>2</sub>)<sub>3</sub>O– linking the benzene cap to the ortho positions of 5,10,15,20-tetraphenylporphyrin. The structures of the following compounds have been determined by single-crystal X-ray diffraction methods: H<sub>2</sub>(OC<sub>3</sub>OPor) (**1**), Fe(OC<sub>3</sub>OPor)(Cl) (**2**), Fe(OC<sub>3</sub>OPor)(CO)(1-MeIm) (**3**), and Fe(OC<sub>3</sub>OPor)(CO)(1,2-Me<sub>2</sub>Im) (**4**). Structures **1–3** pack as one crystallographically independent porphyrin with solvate molecules, whereas structure **4** packs with half of a crystallographically independent porphyrin molecule and a solvate molecule. In compound **2** the Cl ligand is bound to the Fe center on the unprotected side of the porphyrin. In **3** and **4**, which represent R-state (relaxed) and T-state (tense) models for hemoglobin, respectively, CO is bound underneath the cap and either 1-MeIm (**3**) or 1,2-Me<sub>2</sub>Im (**4**) is bound to the sixth coordination site, opposite the CO and outside the cap. The bulkier 1,2-Me<sub>2</sub>Im in **4** forces the Fe atom 0.10 Å out of the mean nitrogen plane toward the 1,2-Me<sub>2</sub>Im ligand. In **3**, where the base is less bulky, the Fe atom lies 0.06 Å out of the plane toward the CO ligand. The cap-to-porphyrin distance increases approximately 0.8 Å to accommodate CO, from 4.74 and 4.65 Å in **1** and **2**, respectively, to 5.55 and 5.59 Å in **3** and **4**, respectively. The Fe–C–O angle is 173.9(7)° in **3** and is constrained by symmetry to be 180° in **4**.

## Introduction

The use of model porphyrin systems to probe structure–function relationships in the hemoproteins hemoglobin (Hb) and myoglobin (Mb) has been an active field of research over the past quarter century.<sup>1–5</sup> In most forms of Hb and Mb values of M (M = P<sub>1/2</sub>O<sub>2</sub>/P<sub>1/2</sub>CO)<sup>6</sup> are small compared with those for nonbiological systems.<sup>4</sup> Thus, Hb and Mb discriminate against the binding of CO. How this discrimination comes about is unclear. One explanation is that because the roles of Hb and Mb are O<sub>2</sub> transport and storage, the cavity where O<sub>2</sub> binds is shaped to accommodate O<sub>2</sub> in its preferred Fe–O–O bent geometry but not CO in its preferred Fe–C–O linear geometry.<sup>7</sup> Therefore, for CO to bind, the porphyrin must distort, the protein must distort, or the Fe–C–O linkage must tilt or bend, all energetically unfavorable processes. The report of bent Fe–C–O angles of 120–140° in protein crystal structures<sup>8,9</sup> has been used to support this explanation for discrimination against CO binding. However, these values are unreliable owing to the limited accuracy of protein structure determinations.<sup>4,10</sup> It is important and necessary to use models, where much higher

accuracy is obtainable, to address the issue of steric discrimination against CO binding.<sup>5,10</sup>

The synthesis and binding properties for many types of sterically protected model systems have been reported. These include “strapped”,<sup>11–17</sup> “picnic basket”,<sup>18–22</sup> “picket fence”,<sup>23–26</sup> “pocket”,<sup>26–28</sup> and “capped”<sup>29–36</sup> porphyrins as well as hybrids

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of these different classifications.<sup>37,38</sup> However, for most of these systems structural data are very limited; yet structural data are essential in the elucidation of structure–function relationships. Notable exceptions are found in the POCpivP,<sup>39–43</sup> Piv<sub>2</sub>C<sub>n</sub>,<sup>19,38,39</sup> and C<sub>n</sub>–Cap systems,<sup>43–47</sup> and especially in the TPivP<sup>39</sup> system, the only one for which structures of both a five-coordinate Fe<sup>II</sup>(base)<sup>48</sup> and a six-coordinate Fe<sup>II</sup>(O<sub>2</sub>)(base)<sup>48,49</sup> have been reported.

Herein, we present one of the most complete structural studies to date of a sterically encumbered heme model system. The following structures for the five-atom linked capped porphyrin system OC<sub>3</sub>OPor have been determined by single-crystal X-ray diffraction methods: H<sub>2</sub>(OC<sub>3</sub>OPor) (**1**), Fe(OC<sub>3</sub>OPor)(Cl) (**2**),

Fe(OC<sub>3</sub>OPor)(CO)(1-MeIm) (**3**), and Fe(OC<sub>3</sub>OPor)(CO)(1,2-Me<sub>2</sub>Im) (**4**). Comparison of the structures of **1** and **2** with those of **3** and **4** allows for analysis of the types and amounts of distortion that take place upon CO ligation under the cap. Structures **3** and **4** represent models for the R- and T-states of Hb and Mb, respectively, and structural differences at the Fe center will be used to address how the bulkier 1,2-Me<sub>2</sub>Im affects the structure and consequent ligand binding properties. In addition, these structures in the OC<sub>3</sub>OPor system will be compared with the related structures of the five-atom linked C<sub>2</sub>–Cap porphyrin system H<sub>2</sub>(C<sub>2</sub>–Cap),<sup>44</sup> Fe(C<sub>2</sub>–Cap)(Cl),<sup>45</sup> and Fe(C<sub>2</sub>–Cap)(CO)(1-MeIm).<sup>46</sup>

## Experimental Section

**Materials.** All solvents and reagents were used as purchased, except toluene and *n*-hexane which were dried over Na. H<sub>2</sub>(OC<sub>3</sub>OPor) was prepared according to the literature procedure.<sup>50</sup> UV–visible spectra were obtained on a Cary 1E spectrophotometer, IR spectra were obtained on a Nicolet 520SX infrared spectrometer, and mass spectra were recorded on a VG Analytical 70 SE quadrupole mass spectrometer.

**H<sub>2</sub>(OC<sub>3</sub>OPor)·C<sub>7</sub>H<sub>8</sub> Crystal Growth.** Crystals of H<sub>2</sub>(OC<sub>3</sub>OPor)·C<sub>7</sub>H<sub>8</sub> were grown by the slow diffusion of *n*-hexane (~8 mL) into a toluene solution (~1 mL) of **1** (~4 mg) at 4 °C.

**Preparation of Fe<sup>II</sup>(OC<sub>3</sub>OPor).** Fe<sup>II</sup>(OC<sub>3</sub>OPor) was prepared by the use of a literature procedure for Fe insertion.<sup>25</sup> H<sub>2</sub>(OC<sub>3</sub>OPor) (~50 mg), K<sub>2</sub>CO<sub>3</sub> (~75 mg), and FeBr<sub>2</sub> (~75 mg) were stirred in a 1:1 THF/toluene solution for 24 h in an inert atmosphere glovebox. The solvent was pumped off under vacuum, and the product was chromatographed through silica with 1:1:10 THF:CH<sub>3</sub>OH:toluene. After removal of the solvent the solid product was stored in a glovebox for further use. An alternative method for the preparation of Fe<sup>II</sup>(OC<sub>3</sub>OPor) is through the reduction of a THF solution of Fe<sup>III</sup>(OC<sub>3</sub>OPor)(Cl); the solution is stirred with Zn powder for ~18 h and filtered, and then the THF is pumped off under vacuum in a glovebox. UV–vis (THF), λ<sub>max</sub>: 525, 540 nm.

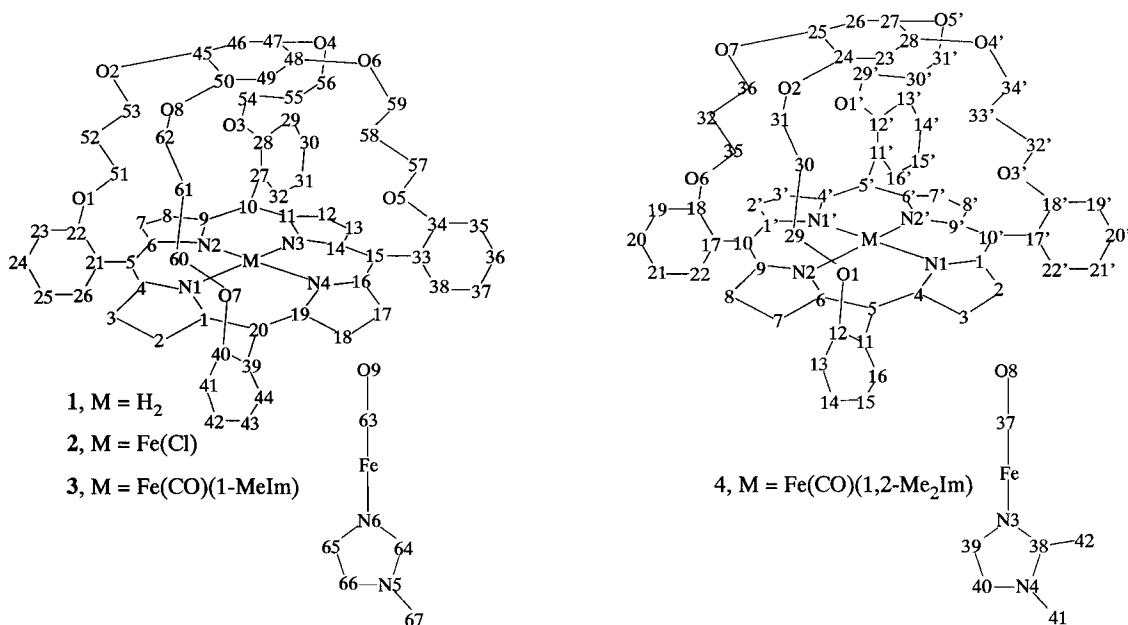
**Preparation of Fe(OC<sub>3</sub>OPor)(Cl)·CHCl<sub>3</sub> and Crystal Growth.** Upon exposure of a CHCl<sub>3</sub> solution of Fe<sup>II</sup>(OC<sub>3</sub>OPor) to air, [Fe<sup>III</sup>(OC<sub>3</sub>OPor)]<sub>2</sub>(μ-O) immediately forms. The solution was extracted three times with 1 M HCl and once with water. The CHCl<sub>3</sub> layer was isolated, dried over Na<sub>2</sub>SO<sub>4</sub>, and filtered. X-ray quality crystals of Fe(OC<sub>3</sub>OPor)(Cl)·CHCl<sub>3</sub> were isolated by layering CH<sub>3</sub>OH over the CHCl<sub>3</sub> solution and allowing diffusion to occur over 3 days at 25 °C. UV–vis (CHCl<sub>3</sub>), λ<sub>max</sub> (log ε): 380 (4.78), 417 (5.01), 512 (4.13), 583 (3.54) nm. MS. Calcd for C<sub>62</sub>H<sub>50</sub>N<sub>4</sub>O<sub>8</sub>Fe (parent – Cl). *m/z* 1034.7. Found. *m/z* 1034.3.

**Preparation of Fe(OC<sub>3</sub>OPor)(CO)(1-MeIm)·1.5C<sub>7</sub>H<sub>8</sub> and Crystal Growth.** Fe(OC<sub>3</sub>OPor) (~4 mg) was transferred to a diffusion tube and dissolved in a CO-saturated 1-MeIm/toluene solution (~1 mL, 0.5 M). CO-saturated *n*-hexane (~8 mL) was layered over the toluene solution and allowed to diffuse into the solution at 4 °C. X-ray quality crystals were obtained in about 2 months. UV–vis (toluene), λ<sub>max</sub>: 427, 543 nm. IR (Nujol): ν(CO) 1978 cm<sup>-1</sup>. MS. Calcd for C<sub>67</sub>H<sub>60</sub>FeN<sub>6</sub>O<sub>9</sub> (parent peak – CO and 1-MeIm). *m/z* 1034.5. Found. *m/z* 1034.8.

**Preparation of Fe(OC<sub>3</sub>OPor)(CO)(1,2-Me<sub>2</sub>Im)·2CHCl<sub>3</sub> and Crystal Growth.** The same procedures used in the preparation of **3** were followed in preparing **4** except a CO-saturated 1,2-Me<sub>2</sub>Im/CHCl<sub>3</sub> solution (~1 mL, 0.2 M) was used in place of the 1-MeIm/toluene solution. X-ray quality crystals

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- (39) Abbreviations: POCpivP = a porphyrin with three –CH<sub>2</sub>(CO)NH– linkages connecting the 1,3,5–positions of a benzene cap to the ortho positions of 5,10,15,20-tetraphenylporphyrin (TPP) and a pivalamido arm extending from the ortho position of the fourth phenyl group of TPP in either the α (toward the cap) or β (away from the cap) direction; C<sub>n</sub>–Cap = a capped porphyrin with four –(CO)O(CH<sub>2</sub>)<sub>n</sub>O– linkages connecting the 1,2,4,5 positions of a benzene cap to the ortho positions of TPP; 1-MeIm = 1-methylimidazole; 2-MeIm = 2-methylimidazole; 1,2-Me<sub>2</sub>Im = 1,2-dimethylimidazole; Py = pyridine; 1,5-DCIm = 1,5-dicyclohexylimidazole; Deut = deuteroporphyrinato dianion; Proto = protoporphyrin IX dimethyl ester dianion; TTOMePP = *meso*-tetra-(3,4,5-trimethoxyphenyl)porphyrinato dianion; Piv<sub>2</sub>C<sub>n</sub> (*n* = 6–10) = porphyrinato dianion with a straps of the type –NH(CO)(CH<sub>2</sub>)<sub>n</sub>(CO)–NH– linking the ortho positions of opposite phenyl groups of TPP and pivalamido groups extending from the ortho positions of the remaining two phenyl groups in the α direction; Ph<sub>5,5</sub>–BHP = basket handle porphyrinato dianion with two straps of the type –O(CH<sub>2</sub>)<sub>4</sub>– linking the 1,4 positions of a benzene cap to opposite phenyl groups of TPP, one strap on each face of the porphyrin; Durene–*n/n* = a strapped porphyrin with a 1,4-substituted 2,3,5,6-tetramethylbenzene cap containing –(CH<sub>2</sub>)<sub>n</sub>– chains bonded to the trans pyrrole rings of a porphyrin that is alkylated with methyl or ethyl groups at the other β-pyrrolic positions; TPivP = the picket-fence porphyrin = *meso*-tetrakis(α,α,α,α-o-pivalamidophenyl)porphyrinato dianion; Piv<sub>3</sub>SCIm = the picket fence porphyrin *meso*-α,α,α,α-tris(o-pivalamidophenyl)-β-(o-5-N-imidazoylevaleramido)phenylporphyrin.
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**Figure 1.** Labeling schemes for H<sub>2</sub>(OC<sub>3</sub>OPor) (1), Fe(OC<sub>3</sub>OPor)(Cl) (2), Fe(OC<sub>3</sub>OPor)(CO)(1-MeIm) (3), and Fe(OC<sub>3</sub>OPor)(CO)(1,2-Me<sub>2</sub>Im) (4).

**Table 1.** Selected Crystallographic Data

	H <sub>2</sub> (OC <sub>3</sub> OPor) (1)	Fe(OC <sub>3</sub> OPor)(Cl) (2)	Fe(OC <sub>3</sub> OPor)(CO)(1-MeIm) (3)	Fe(OC <sub>3</sub> OPor)(CO)(1,2-Me <sub>2</sub> Im) (4)
chem form	C <sub>62</sub> H <sub>52</sub> N <sub>4</sub> O <sub>8</sub> ·C <sub>7</sub> H <sub>8</sub>	C <sub>62</sub> H <sub>50</sub> FeN <sub>4</sub> O <sub>8</sub> Cl·CHCl <sub>3</sub>	C <sub>67</sub> H <sub>56</sub> FeN <sub>6</sub> O <sub>9</sub> ·1.5C <sub>7</sub> H <sub>8</sub>	C <sub>68</sub> H <sub>58</sub> FeN <sub>6</sub> O <sub>9</sub> ·2CHCl <sub>3</sub>
fw	1073	1190	1283	1398
space group	C <sub>2h</sub> -P2 <sub>1</sub> /n	C <sub>2h</sub> <sup>s</sup> -P2 <sub>1</sub> /c	C <sub>2h</sub> <sup>s</sup> -P2 <sub>1</sub> /n	C <sub>2h</sub> <sup>s</sup> -C2/c
a, Å	16.964(2)	13.110(4)	16.221(7)	12.983(2)
b, Å	18.000(2)	16.306(4)	22.763(10)	33.705(6)
c, Å	18.109(2)	25.838(13)	17.133(6)	15.387(4)
β, deg	95.26(1)	90.96(3)	92.70(3)	105.27(2)
V, Å <sup>3</sup>	5506.3(9)	5523(4)	6319(5)	6496(2)
Z	4	4	4	4
density (calc), g/cm <sup>3</sup>	1.295	1.431	1.349	1.429
μ, cm <sup>-1</sup>	7	45	25	47
T, °C	-167(2)	-167(2)	-167(2)	-167(2)
transm factor	0.813–0.894	0.449–0.636	0.296–0.716	
R(F)	0.076	0.13	0.087	0.12
R <sub>w</sub> (F <sup>2</sup> )	0.171	0.275	0.209	0.265

were obtained in about 1 month. UV–vis (toluene), λ<sub>max</sub>: 423, 539 nm. IR (Krytox<sup>51</sup>): ν(CO) 1974 cm<sup>-1</sup>. MS: Calcd for C<sub>68</sub>H<sub>58</sub>FeN<sub>6</sub>O<sub>9</sub> (parent peak – CO and 1,2-Me<sub>2</sub>Im). *m/z* 1034.5. Found. *m/z* 1035.

**X-ray Crystal Structure Determinations.** To prevent solvent evaporation, the chosen crystals of each compound were coated with Krytox<sup>51</sup> oil and mounted in the cold stream (–167 °C) of an Enraf Nonius CAD4 diffractometer. Unit cell parameters were determined by the least-squares refinement of 25 reflections that had been automatically centered on the diffractometer. Profile intensity data were collected, processed,<sup>52</sup> and corrected for absorption.<sup>53</sup> Crystallographic details for the structures are given in Table 1. The direct methods program SHELXS<sup>54</sup> was used for structure solution and the program SHELXL-93<sup>55</sup> for structure development. The program package SHELXTL PC<sup>54</sup> was used for the ensuing molecular graphics generation.

**H<sub>2</sub>(OC<sub>3</sub>OPor)·C<sub>7</sub>H<sub>8</sub>.** The observed Laue symmetry and systematic absences are consistent with the monoclinic space

group C<sub>2h</sub><sup>s</sup>-P2<sub>1</sub>/n. The final refinement on F<sup>2</sup> involved an anisotropic model for all non-hydrogen atoms and fixed positions for the hydrogen atoms. There were 9274 independent observations and 731 variables. The refinement converged to the R indices given in Table 1. The atom-labeling scheme is given in Figure 1. Table 2 provides selected bond lengths and angles. Additional crystallographic data, atomic coordinates, and equivalent isotropic displacement parameters, additional bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates and isotropic displacement parameters are available in Tables SI–SV.<sup>56</sup>

**Fe(OC<sub>3</sub>OPor)(Cl)·CHCl<sub>3</sub>.** The observed Laue symmetry and systematic absences are consistent with the monoclinic space group C<sub>2h</sub><sup>s</sup>-P2<sub>1</sub>/c. The final refinement on F<sup>2</sup> involved an anisotropic model for all non-hydrogen atoms. The final refinement of 721 variables and 8492 independent observations converged to the R indices given in Table 1. The atom-labeling scheme is given in Figure 1. Selected bond lengths and angles are given in Table 2. Additional crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, additional bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates and isotropic displacement parameters are available in Tables SVI–SX.<sup>56</sup>

**Fe(OC<sub>3</sub>OPor)(CO)(1-MeIm)·1.5C<sub>7</sub>H<sub>8</sub>.** The observed Laue

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(56) Supporting Information.

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for **2–4**

	Fe(OC <sub>3</sub> OPor)- Fe(OC <sub>3</sub> OPor)- (Cl) ( <b>2</b> )	Fe(OC <sub>3</sub> OPor)- (CO)(1-MeIm) ( <b>3</b> )	Fe(OC <sub>3</sub> OPor)- (CO)(1,2-Me <sub>2</sub> Im) ( <b>4</b> )
Fe–C(CO)		1.748(7)	1.713(8)
C–O(CO)		1.171(8)	1.161(10)
Fe–L <sub>ax</sub> <sup>a</sup>	2.232(3)	2.027(5)	2.102(6)
Fe–N(1)	2.064(7)	1.999(5)	1.985(4)
Fe–N(2)	2.051(7)	1.990(4)	2.014(4)
Fe–N(3) <sup>b</sup>	2.070(7)	1.983(5)	1.985(4)
Fe–N(4) <sup>b</sup>	2.060(7)	2.010(5)	2.014(4)
av Fe–N <sub>eq</sub>	2.061(8)	1.996(12)	2.00(2)
av N–C <sub>a</sub> <sup>c</sup>	1.376(9)	1.38(2)	1.388(5)
av C <sub>a</sub> –C <sub>b</sub>	1.429(13)	1.433(11)	1.430(6)
av C <sub>b</sub> –C <sub>b</sub>	1.350(16)	1.338(18)	1.361(2)
av C <sub>a</sub> –C <sub>m</sub>	1.403(11)	1.394(13)	1.383(11)
Fe–C–O		173.9(7)	180
C(CO)–Fe–N(1)		95.1(3)	89.97(12)
C(CO)–Fe–N(2)		92.0(2)	88.16(12)
C(CO)–Fe–N(3)		83.4(3)	89.98(12)
C(CO)–Fe–N(4)		88.9(2)	88.16(12)
C(CO)–Fe–L <sub>ax</sub> <sup>a</sup>		174.5(3)	173.0(2)
L <sub>ax</sub> –Fe–N(1)	102.5(2)	90.3(2)	86.3(3)
L <sub>ax</sub> –Fe–N(2)	100.4(2)	89.5(2)	85.9(3)
L <sub>ax</sub> –Fe–N(3)	105.7(2)	91.3(2)	93.7(3)
L <sub>ax</sub> –Fe–N(4)	103.8(2)	89.7(2)	97.7(3)
N(1)–Fe–N(2)	86.9(3)	89.4(2)	89.9(2)
N(1)–Fe–N(3)	151.7(3)	178.4(2)	179.9(2)
N(1)–Fe–N(4)	86.9(2)	89.8(2)	90.1(2)
N(2)–Fe–N(3)	87.2(3)	90.7(2)	90.1(2)
N(2)–Fe–N(4)	155.9(3)	178.8(2)	176.3(2)
N(3)–Fe–N(4)	87.3(3)	90.1(2)	89.9(2)

<sup>a</sup> L<sub>ax</sub> = Cl for **2**, L<sub>ax</sub> = N (1-MeIm) for **3**, L<sub>ax</sub> = N (1,2-Me<sub>2</sub>Im) for **4**. <sup>b</sup> For purposes of clarity, N(3) in this table refers to N(1)' and N(4) refers to N(2)' of porphyrin **4**. <sup>c</sup> Selected bond distances (Å) for H<sub>2</sub>(OC<sub>3</sub>OPor) are av N–C<sub>a</sub> = 1.369(9), av C<sub>a</sub>–C<sub>b</sub> = 1.443(10), av C<sub>b</sub>–C<sub>b</sub> = 1.349(5), av C<sub>a</sub>–C<sub>m</sub> = 1.400(7).

symmetry and systematic absences are consistent with the monoclinic space group  $C_{2h}^5-P2_1/n$ . The crystallographically independent solvent molecules appeared to be a combination of toluene and 1-MeIm disordered over the same site. In the final refinement the solvents were modeled as toluene molecules, occupying two positions with occupancies that refined to 0.578(12) and 0.422(12) for the first solvent site and were fixed at 0.5 for the toluene molecule located at the inversion center. The final refinement on  $F^2$ , which involved 810 variables and 7459 independent observations, converged to the  $R$  indices given in Table 1. The atom-labeling scheme is given in Figure 1. Selected bond lengths and angles are given in Table 2. Additional crystallographic data, atomic coordinates, equivalent isotropic displacement parameters and occupancies for all atoms (including hydrogen atoms), additional bond lengths and angles, and anisotropic displacement parameters are available in Tables SXI–SXIV.<sup>56</sup>

**Fe(OC<sub>3</sub>OPor)(CO)(1,2-Me<sub>2</sub>Im)·2CHCl<sub>3</sub>.** The observed Laue symmetry and systematic absences are consistent with the monoclinic space groups  $C_{2h}^6-C2/c$  and  $C_s^4-Cc$ . A structure consisting of one porphyrin and two CHCl<sub>3</sub> molecules was solved in the space group  $Cc$ , but it refined poorly. The MISSYM<sup>57</sup> algorithm, as implemented in the PLATON<sup>58</sup> suite of programs, indicated that 80% of the resultant atoms were related by a 2-fold axis of symmetry. The 20% that were not related by symmetry encompassed the six atoms of the benzene cap, five atoms in the arms, and the 1,2-Me<sub>2</sub>Im ligand. A preferable model is thus one involving a slightly disordered

Fe(OC<sub>3</sub>OPor)(CO)(1,2-Me<sub>2</sub>Im) molecule with a crystallographically imposed 2-fold axis and one CHCl<sub>3</sub> molecule in the centrosymmetric space group  $C2/c$ . In the final refinement the cap, parts of the arms, and the 1,2-Me<sub>2</sub>Im ligand were modeled as occupying two positions at 50% occupancy. The atoms of the cap were restrained to fit a hexagon, and the oxygen atoms bonded to the benzene cap were restrained to lie in the same plane as the cap. Atom C(29) was modeled as being disordered over two positions with occupancies that refined to 0.50(6) and 0.50(6). Hydrogen-atom positions were only generated for atoms not involved in disorder. The final refinement on  $F^2$ , which used an anisotropic model for all non-hydrogen atoms except N(3), involved 488 variables, 6 restraints, and 5728 independent observations; it converged to the  $R$  indices given in Table 1. The atom-labeling scheme is given in Figure 1. Selected bond lengths and angles are given in Table 2. Additional crystallographic data, atomic coordinates, equivalent isotropic displacement parameters, occupancies for all atoms (including hydrogen atoms), additional bond lengths and angles, and anisotropic displacement parameters are available in Tables SXV–SXXVIII.<sup>56</sup>

## Results and Discussion

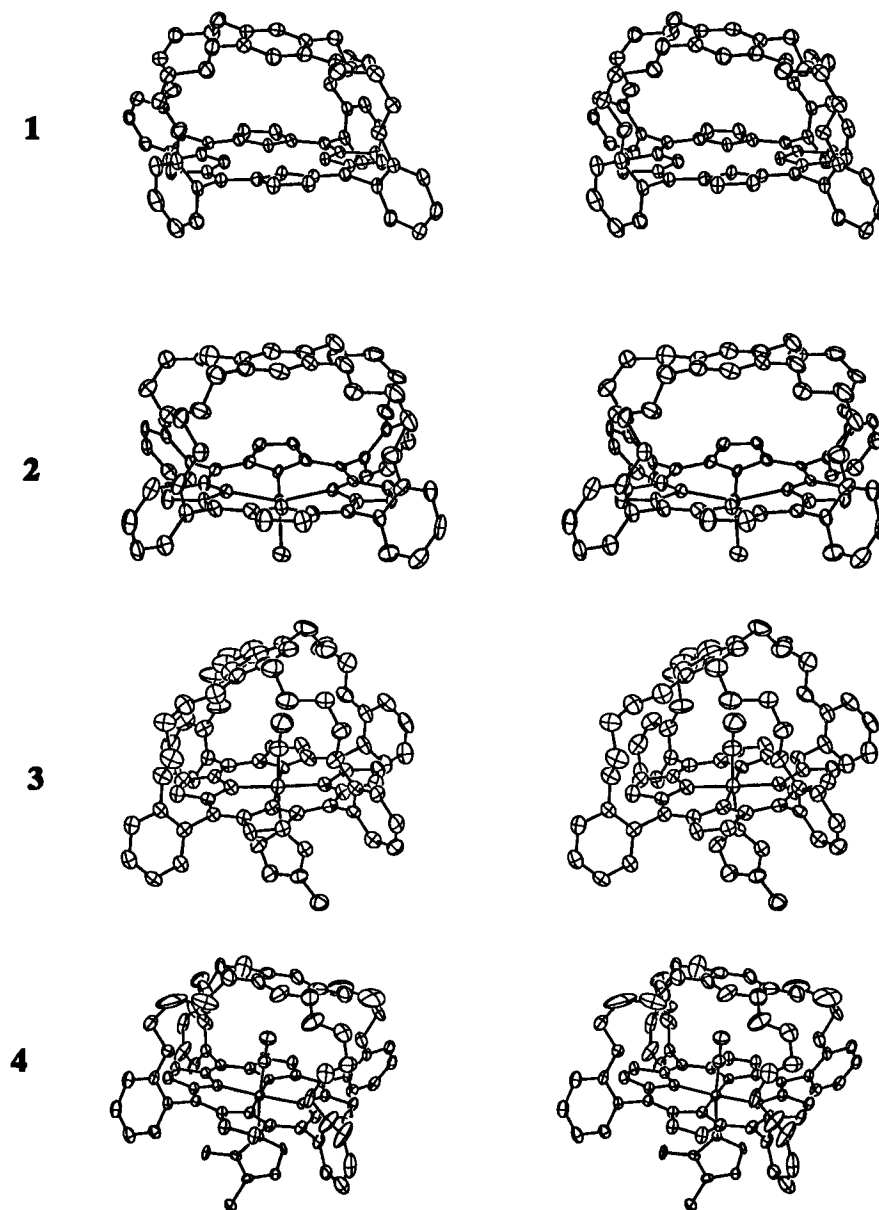
**Syntheses.** The insertion of Fe into **1** was accomplished by stirring a solution of FeBr<sub>2</sub> and the porphyrin in the presence of K<sub>2</sub>CO<sub>3</sub>, followed by purification by column chromatography. An alternative method for the preparation of Fe<sup>II</sup>(OC<sub>3</sub>OPor) is reduction of Fe<sup>III</sup>(OC<sub>3</sub>OPor) by Zn. Exposure of this Fe<sup>II</sup> product to air leads to the rapid formation of the  $\mu$ -oxo dimer [Fe(OC<sub>3</sub>OPor)]<sub>2</sub>( $\mu$ -O); extraction of a solution of the dimer with 1 M HCl yields the five-coordinate species **2**. Solvation of Fe<sup>II</sup>(OC<sub>3</sub>OPor) in a base solution under a CO atmosphere yields the six-coordinate species **3** (base = 1-MeIm) and **4** (base = 1,2-Me<sub>2</sub>Im).

**Description of the Structures.** Stereoviews of the porphyrin parts (**1–4**) of H<sub>2</sub>(OC<sub>3</sub>OPor)·C<sub>7</sub>H<sub>8</sub>, Fe(OC<sub>3</sub>OPor)(Cl)·CHCl<sub>3</sub>, Fe(OC<sub>3</sub>OPor)(CO)(1-MeIm)·1.5C<sub>7</sub>H<sub>8</sub>, and Fe(OC<sub>3</sub>OPor)(CO)(1,2-Me<sub>2</sub>Im)·2CHCl<sub>3</sub> are presented in Figure 2. The OC<sub>3</sub>OPor molecule consists of four five-atom arms of the type –O(CH<sub>2</sub>)<sub>3</sub>O– linking the 1,2,4,5 positions of a benzene cap to the ortho positions of 5,10,15,20-tetraphenylporphyrin. The crystal structures of H<sub>2</sub>(OC<sub>3</sub>OPor)·C<sub>7</sub>H<sub>8</sub>, Fe(OC<sub>3</sub>OPor)(Cl)·CHCl<sub>3</sub>, and Fe(OC<sub>3</sub>OPor)(CO)(1-MeIm)·1.5C<sub>7</sub>H<sub>8</sub> consist of the packing of one crystallographically independent porphyrin molecule and solvate molecules in the unit cell. Fe(OC<sub>3</sub>OPor)(CO)(1,2-Me<sub>2</sub>Im)·2CHCl<sub>3</sub> packs with half of a crystallographically independent porphyrin and a CHCl<sub>3</sub> solvate in the unit cell. The Fe(OC<sub>3</sub>OPor)(CO)(1,2-Me<sub>2</sub>Im) molecule thus has a crystallographically imposed 2-fold axis, and there is some resultant disorder in the cap, arms, and base that were modeled over two positions at 50% occupancy. The stereoview of **4** in Figure 2 does not show this disorder. Porphyrins **1** and **2** have no ligands bound beneath the cap. Porphyrin **1** is unmetalated, whereas porphyrin **2** is the Fe<sup>III</sup> chloride with the chloro ligand outside the cap. The coordination geometry about the Fe atom is similar to that of other five-coordinate high-spin systems of the type Fe(Por)(Cl) (Table 3). There is nothing unusual about compound **2**.

It is useful to discuss the disposition of the cap relative to the porphyrin in terms of several parameters, including the vertical displacement of the cap, which is the perpendicular distance from cap centroid to the porphyrin plane, the lateral displacement of the cap, which is the distance from porphyrin centroid to the above perpendicular, and the interplanar angle between the cap and the porphyrin planes. The amounts and

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**Figure 2.** Stereoviews of **1**–**4**. Ellipsoids are drawn at the 50% probability level for **1**–**3** and at the 30% probability level for **4**. Hydrogen atoms are omitted.

**Table 3.** Metrical Data for Selected Fe(Por)(Cl) Systems

compd	av Fe–N, Å	Fe–Cl, Å	av N–Fe–N, deg	av N–Fe–Cl, deg	Fe dev from N <sub>4</sub> plane	Fe dev from 24-atom plane	ref
Fe(TPP)(Cl) <sup>a</sup>	2.049(9)	2.192(12)			0.38	0.38	60
Fe(TPP)(Cl) <sup>b</sup>	2.070(9)	2.211(1)	86.8	103.6	0.49	0.57	61
Fe(Proto)(Cl) <sup>39</sup>	2.062(10)	2.218(6)	87.0	103.3	0.48	0.55	62
Fe(Ph <sub>5,5</sub> -BHP)(Cl) <sup>39</sup>	2.060(2)	2.207(2)	87.25(5)	102.6(5)	0.46	0.45	12
Fe(TTOMePP)(Cl) <sup>39</sup>	2.079	2.207(20)	86.2	106	0.53	0.58	63
Fe(Durene)(Cl) <sup>39</sup>	2.054	2.232(1)	86.8	103.6	0.49	0.64	16
Fe(C <sub>2</sub> –Cap)(Cl)	2.063(3)	2.242(1)	87.2(4)	102.8	0.46	0.47	45
Fe(OC <sub>3</sub> OPor)(Cl)	2.064(7)	2.232(3)	87.1(2)	103(2)	0.47	0.52	this work
Fe(C <sub>4</sub> –Cap)(Cl)	2.07(2)	2.243(3)	87.2(4)	103(1)	0.46	0.43	43
	2.071(7)	2.226(3)	87.5(5)	102(1)	0.49	0.46	

<sup>a</sup> Tetragonal form. <sup>b</sup> Monoclinic form.

types of distortions that take place in these and other encumbered porphyrin systems are summarized in Table 4. The vertical displacement of 4.74 and 4.65 Å respectively for porphyrins **1** and **2** is significantly greater than that of 3.96 and 4.01 Å in the five-atom linked porphyrins H<sub>2</sub>(C<sub>2</sub>–Cap)<sup>44</sup> and Fe(C<sub>2</sub>–Cap)(Cl).<sup>45</sup> Presumably the ester linkage in the C<sub>2</sub>–Cap allows more efficient folding of the arms than does the ether linkage in the OC<sub>3</sub>OPor system. Whereas the displacements and interplanar

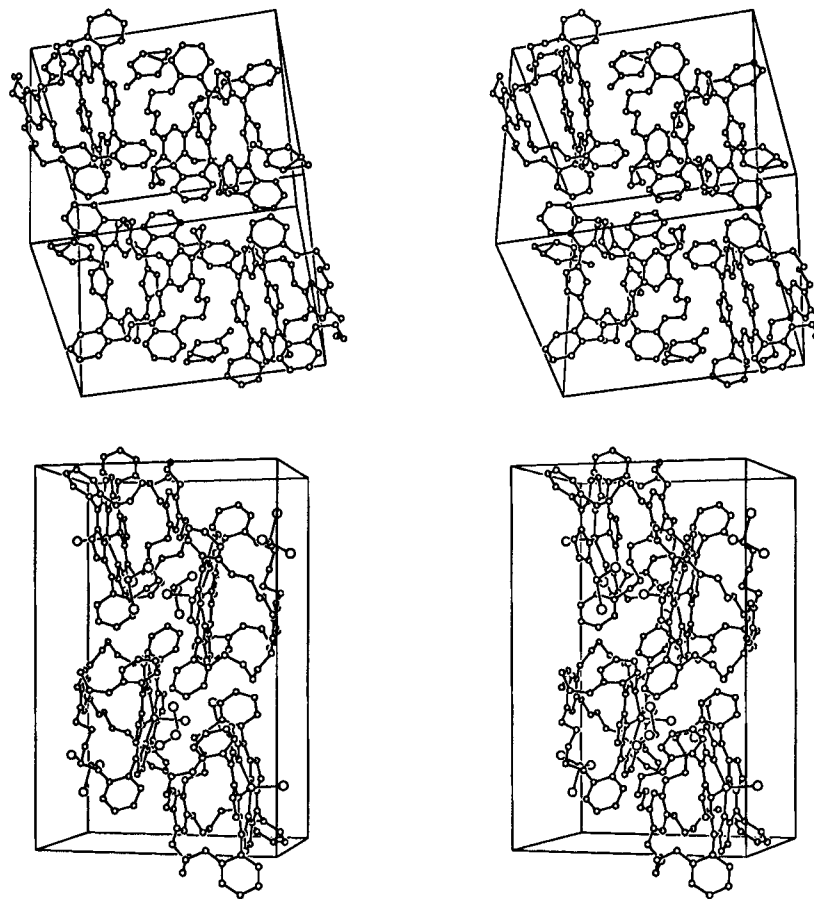
angles in H<sub>2</sub>(C<sub>2</sub>–Cap) and Fe(C<sub>2</sub>–Cap)(Cl) are similar, the lateral displacements and interplanar angles of **1** and **2** are very different from one another. As can be seen from the stereoviews of the unit cells (Figure 3), the disposition of solvent molecules relative to the porphyrins is very different in H<sub>2</sub>(OC<sub>3</sub>OPor)·C<sub>7</sub>H<sub>8</sub> and Fe(OC<sub>3</sub>OPor)(Cl)·CHCl<sub>3</sub>.

Comparison of the structures of **3** and **4** with those of **1** and **2** provides an indication of the types and amounts of distortion

**Table 4.** Porphyrin Distortions

structure	dihedral angle <sup>a</sup>	av dev from 24-atom plane, Å	Fe dev from 24-atom plane, <sup>b</sup> Å	vertical displacement of cap, <sup>c</sup> Å	lateral displacement of cap, Å <sup>d</sup>	Fe–C–O, deg	ref
H <sub>2</sub> (C <sub>2</sub> –Cap)	0.0	0.134		3.96	0.12		44
Fe(C <sub>2</sub> –Cap)(Cl)	3.2	0.08	0.47	4.01	0.24		45
Fe(C <sub>2</sub> –Cap)(CO)(1-MeIm)	15.5	0.08	0.02	5.57	0.30	172.9(6)	46
	11.5	0.08	–0.01	5.67	0.00	175.9(6)	
H <sub>2</sub> (OC <sub>3</sub> OPor) ( <b>1</b> )	14.3	0.07		4.74	0.54		this work
Fe(OC <sub>3</sub> OPor)(Cl) ( <b>2</b> )	3.9	0.15	0.52	4.65	1.35		this work
Fe(OC <sub>3</sub> OPor)(CO)(1-MeIm) ( <b>3</b> )	20.3	0.08	0.06	5.55	0.21	173.9(7)	this work
Fe(OC <sub>3</sub> OPor)(CO)(1,2-Me <sub>2</sub> Im) ( <b>4</b> )	5.3	0.07	–0.10	5.59	0.66	180.0 <sup>e</sup>	this work

<sup>a</sup> The dihedral angle is the interplanar angle between the cap and the 24-atom porphyrin plane. <sup>b</sup> A positive value indicates displacement toward the chloride ligand or toward the CO group. <sup>c</sup> The vertical displacement of the cap is the perpendicular distance from cap centroid to porphyrin plane. <sup>d</sup> The lateral displacement of the cap is the distance from porphyrin centroid to the above perpendicular. <sup>e</sup> By symmetry.

**Figure 3.** Stereoviews of the unit cells of H<sub>2</sub>(OC<sub>3</sub>OPor)·C<sub>7</sub>H<sub>8</sub> (top) and Fe(OC<sub>3</sub>OPor)(Cl)·CHCl<sub>3</sub> (bottom).

that take place in the cap and arms to accommodate the binding of CO under the cap. In **3** and **4** the cap expands  $\sim 0.9$  Å, from 4.74 Å (**1**) and 4.65 Å (**2**) to 5.55 Å (**3**) and 5.59 Å (**4**). The vertical displacements in these OC<sub>3</sub>OPor carbonyl structures are remarkably close to those of 5.57 and 5.67 Å in the two crystallographically independent molecules of Fe(C<sub>2</sub>–Cap)(CO)(1-MeIm). It is thus clear that a vertical displacement of  $\sim 5.6$  Å is necessary to accommodate an essentially linear Fe–C–O linkage under the cap. Analysis of torsion and interplanar angles about the cap, arms, and phenyl rings of each porphyrin does not reveal any obvious trends in the expansion process. The cap in **3** is significantly tilted, with an interplanar angle of 20.3°. The CO group is slightly tilted and bent toward the higher portion of the cap, with a tilt angle of 5.7° and an Fe–C–O angle of 173.9(7)°. In contrast, in **4** the interplanar angle is only 5.3°; the Fe–C–O angle is constrained to be 180° by symmetry. Generally Fe(C<sub>2</sub>–Cap)(CO)(1-MeIm) shows values similar to these (Table 4).

To the best of our knowledge, **3** and **4** permit the first comparison of high-affinity R- and low-affinity T-state carbonyl structures in model systems. The only other R- and T-state structures reported for a single model porphyrin system are for the O<sub>2</sub> complex of the picket-fence porphyrin TPivP, namely, Fe(TPivP)(O<sub>2</sub>)(1-MeIm)<sup>49</sup> and Fe(TPivP)(O<sub>2</sub>)(2-MeIm).<sup>48</sup> The steric effects of the T-state systems involving the bulky bases are obvious: in **4** the Fe atom lies 0.10 Å out of the mean nitrogen plane toward the 1,2-Me<sub>2</sub>Im ligand, whereas in Fe(TPivP)(O<sub>2</sub>)(2-MeIm) it lies 0.086 Å toward the 2-MeIm base. In **3** and in Fe(TPivP)(O<sub>2</sub>)(1-MeIm) the Fe atom lies 0.06 or 0.03 Å, respectively, out of the plane toward the CO or O<sub>2</sub> ligand.

Further comparisons among these four structures, as well as other selected Fe<sup>II</sup> porphyrin systems, are presented in Table 5. Unfortunately, the comparisons one would like to make, namely, Fe–base and Fe–L distances in the two T- and R-state systems, are suspect owing to disorder of the O<sub>2</sub> molecules in the TPivP

**Table 5.** Metrical Data for Selected Porphyrins of the Type Fe(Por)(L)(Base) (L = CO or O<sub>2</sub>)

	av Fe–N, Å	Fe–L, Å	L–O, Å	Fe–L–O, deg	Fe–base, Å	Fe dev from mean N plane <sup>a</sup>	ref
Fe(TPP)(Py)(CO) <sup>39</sup>	2.02(3)	1.77(2)	1.12(2)	179(2)	2.10(1)	0.02	64
Fe(Deut)(CO)(THF) <sup>39</sup>	1.98(3)	1.706(5)	1.144(5)	178.3(14)	2.127(4)	0.08	65
Fe(Piv <sub>2</sub> C <sub>6</sub> )(CO)(1-MeIm) <sup>39</sup>	1.981(3)	1.733(4)	1.149(5)	178.3(5)	2.045(2)		38
Fe(Piv <sub>2</sub> C <sub>8</sub> )(CO)(1-MeIm) <sup>39</sup>	1.991(4)	1.752(4)	1.149(6)	178.0(5)	2.039(3)		38
Fe(Piv <sub>2</sub> C <sub>10</sub> )(CO)(1-MeIm) <sup>39</sup>	1.999(3)	1.728(6)	1.149(6)	180.0 <sup>b</sup>	2.062(5)	0.02	19
Fe(PocPivP)(CO)(1,2-MeIm)	1.973(8)	1.768(7)	1.148(7)	172.5(6)	2.079(5)	0.02	40
Fe(OC <sub>3</sub> OPor)(CO)(1-MeIm)	1.996(12)	1.748(7)	1.171(8)	173.9(7)	2.027(5)	0.06	this work
Fe(OC <sub>3</sub> OPor)(CO)(1,2-Me <sub>2</sub> Im)	2.00(2)	1.713(8)	1.161(10)	180.0 <sup>b</sup>	2.102(6)	–0.10	this work
Fe(C <sub>2</sub> –Cap)(CO)(1-MeIm)							46
molecule 1	1.990(7)	1.742(7)	1.161(8)	172.9(6)	2.043(6)	0.01	
molecule 2	1.988(13)	1.748(7)	1.158(8)	175.9(6)	2.041(5)	0.02	
Fe(C <sub>3</sub> –Cap)(CO)(1-MeIm)	1.992(21)	1.800(13)	1.107(13)	178.0(13)	2.046(10)	0.04	43
Fe(TPivP)(O <sub>2</sub> )(1-MeIm)	1.98(1)	1.75(2)	1.17(4) <sup>c</sup>	129(2)	2.07(2)	0.03	49
			1.15(4)	133(2)			
Fe(TPivP)(O <sub>2</sub> )(2-MeIm)	1.996(4)	1.898(7)	1.205(16) <sup>c</sup>	129.0(12)	2.107(4)	–0.09	48
			1.232(22)	128.5(18)			

<sup>a</sup> Positive value indicates displacement toward the CO group. <sup>b</sup> By symmetry. <sup>c</sup> The dioxygen is disordered over two sites.

systems and of the 1,2-Me<sub>2</sub>Im base in **4**. Nevertheless, the Fe–base distances in these systems are self-consistent, being significantly longer in the T-state molecules. The difference between the Fe–C(CO) bond length of 1.748(7) Å in **3** and 1.713(8) Å in **4** is significant and in the expected direction from trends in  $\nu(\text{Fe–C(CO)})$  for R-state models compared with T-state models (Table 6).<sup>59</sup> The CO stretching frequency decreases from 1978 cm<sup>–1</sup> in **3** to 1974 cm<sup>–1</sup> in **4**, indicating at least a slight decrease in CO bond order; a corresponding increase in Fe–C bond order would be expected. Whether the magnitude of the differences in Fe–C bond lengths is real or an artifact of the disorder in the structure of **4** is another question. Comparison of Fe–C stretching frequencies (Table 6) and binding affinities<sup>3,15,26,31,38</sup> for R- and T-state models of other porphyrin systems reveals that factors in addition to the Fe–C bond strength contribute to the energetics of binding. Indeed an inverse trend between Fe–C bond strength and bonding affinity is seen.<sup>59</sup>

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**Table 6.** Fe–CO Stretching Frequencies for R- and T-state Model Compounds<sup>a</sup>

compd	base	$\nu(\text{Fe–C}),$ cm <sup>–1</sup>	$\nu(\text{CO}),$ cm <sup>–1</sup>	ref
Fe(OC <sub>3</sub> OPor)(CO)	1-MeIm <sup>b</sup>		1978	this work
	1,2-Me <sub>2</sub> Im <sup>c</sup>		1974	this work
Fe(TPivP)(CO)	1-MeIm	489	1966–9	7, 59
	1,2-Me <sub>2</sub> Im	496	1962	59
Fe(C <sub>2</sub> –Cap)(CO)	1-MeIm	497	2002 <sup>d</sup>	10, 31
	1,2-Me <sub>2</sub> Im		1999	31
Fe(PocPivP)(CO)	1-MeIm	500	1964	10, 27
	1,2-Me <sub>2</sub> Im	502		10
Fe(TPP)(CO)	1-MeIm	486		59
	1,2-Me <sub>2</sub> Im	494	1970	31, 59

<sup>a</sup> Spectra were obtained in benzene unless otherwise noted. <sup>b</sup> Nujol. <sup>c</sup> Krytox oil.<sup>51</sup> <sup>d</sup> Toluene gives the same stretching frequency.

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**Supporting Information Available:** Tables SI–SV and SVI–SX, giving crystallographic data, atomic coordinates, equivalent isotropic displacement parameters, additional bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates and isotropic displacement parameters for **1** and **2**, respectively, and Tables SXI–SXIV and SXV–SXVIII, giving crystallographic data, atomic coordinates, equivalent isotropic displacement parameters, occupancies for all atoms (including hydrogen atoms), additional bond lengths and angles, and anisotropic displacement parameters for **3** and **4**, respectively (43 pages). Ordering information is given on any current masthead page.

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