

## **Molecular Stereochemistry of a Carbon-bridged Metalloporphyrin: $\mu$ -Carbido-bis(5,10,15,20-tetraphenylporphinatoiron)**

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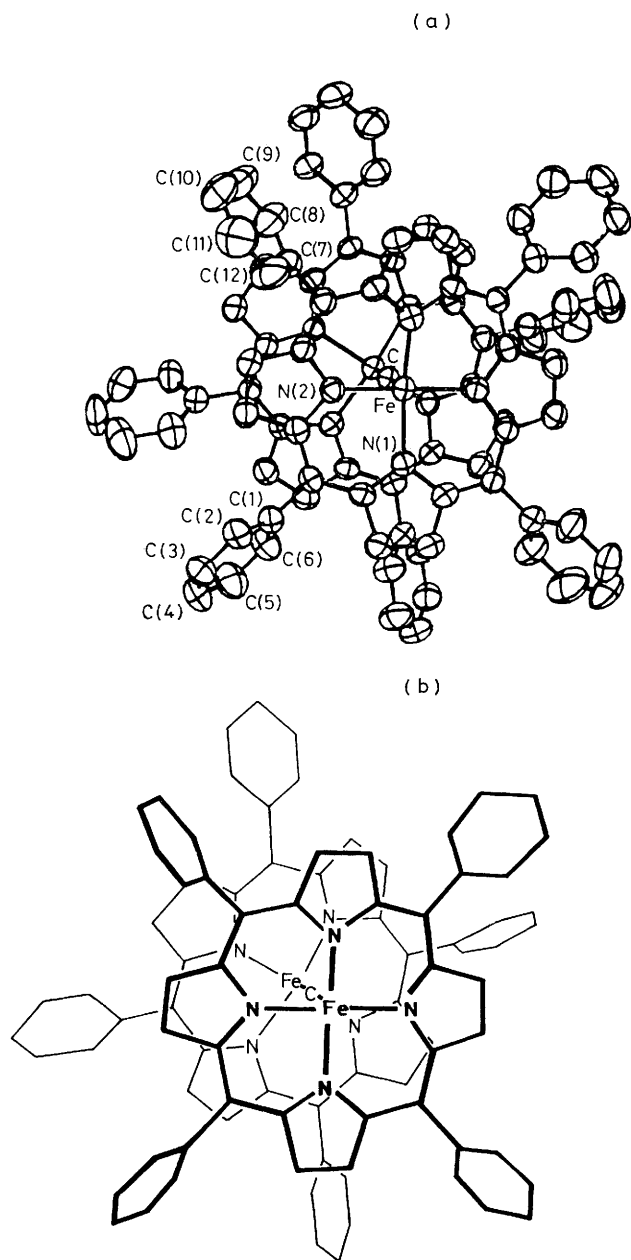
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The X-ray structural determination is reported for the first compound possessing a single carbon atom bridging two first-row transition metals with a linear Fe–C–Fe bond and an Fe–C bond length of only 1.675 Å.

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From the results of their extended Hückel calculations on dimeric metalloporphyrin complexes, Hoffman and co-

workers<sup>1,2</sup> predicted that a simple carbon sandwich of iron tetraphenylporphyrin should be a stable, diamagnetic com-



**Figure 1.** (a) ORTEP and (b) line drawing of the molecular structure of the chloroform solvate of  $[(\text{TPP})\text{Fe}]_2\text{C}$ . Important molecular dimensions are: Fe–C 1.675, Fe–N(1) 1.974, Fe–N(2) 1.986 Å; C–Fe–N(1) 100.0, C–Fe–N(2) 94.9°; the Fe–C–Fe angle is crystallographically constrained to be 180°. In (b), all double bonds have been omitted for clarity.

pound. Mansuy and co-workers<sup>3</sup> have recently reported the successful isolation of  $\mu$ -carbido-bis(5,10,15,20-tetraphenylporphinatoiron),  $[(\text{TPP})\text{Fe}]_2\text{C}$  from the reaction of  $(\text{TPP})\text{Fe}(\text{II})$  with  $\text{Cl}_4$ . To our knowledge, this is the first example of a transition metal complex involving a formally dicarbenic carbon atom bridging two metal centres. The  $\mu$ -carbido-dimer, with its bridging carbon atom, is analogous to the well characterized  $[(\text{TPP})\text{Fe}]_2\text{O}$  and  $[(\text{TPP})\text{Fe}]_2\text{N}$  molecules.

**Crystal data:**  $[(\text{TPP})\text{Fe}]_2\text{C}$  was synthesized in the manner previously described.<sup>3</sup> Single crystals were grown from  $\text{CHCl}_3$  by slow diffusion of hexane vapour;  $[(\text{TPP})\text{Fe}]_2\text{C} \cdot 1/2\text{CHCl}_3$ , orthorhombic, space group  $Fddd$ ,  $a = 22.243(4)$ ,  $b = 30.897(4)$ ,  $c = 22.230(4)$  Å,  $Z = 8$ . The structure was solved and refined from 2722 independent reflections with  $2 < 2\theta$  (Mo- $K\alpha$ )  $< 55^\circ$

**Table 1.** Crystallographic comparisons of single atom-bridged iron tetraphenylporphyrin dimers.

	$\mu$ -carbido	$\mu$ -nitrido <sup>a</sup>	$\mu$ -oxo <sup>a</sup>
Fe out-of-plane distance/Å	0.26	0.32	0.50
Fe-bridging atom bond length/Å	1.675	1.661	1.763
N-Fe-bridging atom angle/°	97.5	99.2	103.7
Fe-bridging atom-Fe angle/°	180	180	174
Mean separation between the porphyrin planes/Å	3.87	3.96	4.53

<sup>a</sup> Taken from reference 4.

and  $I > 2\sigma(I)$  from a total of 4689 reflections collected. At convergence  $R_1 = 7.7\%$ ,  $R_2 = 7.9\%$  for anisotropic thermal vibration parameters for non-hydrogen atoms and fixed contributions for hydrogen atoms.†

Figure 1a is a computer drawn model in perspective of the  $[(\text{TPP})\text{Fe}]_2\text{C}$  molecule as it exists in the crystal. The numbering system used for the structurally unique phenyl groups of the molecule and for the unique carbon and nitrogen atoms of the core is also shown in this figure. This is identical with that routinely used for describing metalloporphyrin molecular stereochemistry.<sup>4</sup> Pertinent crystallographic comparisons for this molecule and the  $\mu$ -oxo- and  $\mu$ -nitrido-analogues are given in Table 1.

As predicted by Hoffman and co-workers<sup>1,2</sup> the  $\mu$ -carbido-dimer has a linear Fe–C–Fe unit. This compares with the linear Fe–N–Fe unit found in the nitrido-dimer and contrasts with the bent Fe–O–Fe unit found in the  $\mu$ -oxo-dimer. Interestingly, the  $\mu$ -carbido-dimer has the smallest out-of-plane displacement of the Fe atoms in this series. This may account for the observed adduct formation in solution when the  $\mu$ -carbido-dimer is exposed to pyridine,<sup>3</sup> whereas no reaction is observed for both the  $\mu$ -oxo- and  $\mu$ -nitrido-dimers. Secondly, the Fe–bridging atom distance is 1.675 Å for the  $\mu$ -carbido-dimer, nearly identical with that of the  $\mu$ -nitrido-dimer. However, this is considerably shorter than that measured for the  $\mu$ -oxo-dimer and that found in an iron carbonyl carbide cluster,<sup>5</sup>  $\text{Fe}_3(\text{CO})_{13}\text{C}$ , where the average Fe–C distance was 1.75 Å. Thirdly, the mean separation between the two porphyrin planes is only 3.87 Å, the smallest interplanar distance of any single atom bridged metalloporphyrin dimer. The short Fe–C bond as well as the close proximity of the two porphyrin planes manifests strong pi-bonding between these two atoms and supports the predicted  $E_3$  ground state assignment.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.