context it is also interesting to note that the ratio $J_{Pt(II)}/J_{Pt(IV)}$ (see Table I) is found to be 1.41 between compounds **1** and **5** and 1.50 between compounds **3** and **6**, values which compare very favorably with the ratio calculated on the basis of a change of hybridization from dsp^2 to d^{2}sp^3 and with that of *ca.* 1.5 obtained for some related phosphine complexes.[6] The major influence of changes in s character on coupling constants does not appear to be restricted to those arising from directly bonded atoms as it is also found that the values of ${}^{3}|J_{^{195}Pt-N-C-H}|$ in complexes [Pt(en)$_2$]Cl$_2$ and [PtCl$_2$(en)$_2$]Cl$_2$ give a ratio of $J_{Pt(II)}/J_{Pt(IV)}$ of 1.60.[14]

As found previously in complexes *cis-* and *trans-*[PtX$_2$(R$_3$P)$_2$], the J_{Pt-N} values for complexes *cis*-[PtX$_2$A$_2$] are larger than those found for the corresponding trans complexes (see Table I), although in the former case $J_{Pt(II)}/J_{Pt(IV)}$ is *ca.* 1.5 and in the latter case, it is *ca.* 1.2. Thus, as found in the case of the phosphine complexes, *isomerization in complexes [PtX$_2$A$_2$] is accompanied by a significant amount of rehybridization which can only be due to σ effects.* On the other hand, because of the nature of the equations used to express ${}^{1}|J_{^{195}Pt-^{15}N}|$ and ${}^{1}|J_{^{195}Pt-^{31}P}|$ the difference in cis/trans ratios between amine and phosphine complexes cannot be taken as an indication that rehybridization occurs to a different extent in the complexes of the two ligands.

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[14] T. G. Appleton and J. R. Hall, *Inorg. Chem.*, **10**, 1717 (1971).

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Syntheses of Ferrous–Porphyrin Complexes. A Hypothetical Model for Deoxymyoglobin

Sir:

Intense, sustained interest in simple models for oxy- and deoxymyoglobin and hemoglobin has resulted in many reports concerned with iron porphyrins. However, few of these describe experimentally well characterized iron(II) porphyrins. Only low-spin complexes of the type Fe(porphyrin)L$_2$ for L = pyridine[1,2] and piperidine[3] appear to be well documented, and the crystal structure of Fe(TPP)(piperidine)$_2$ (TPP = *meso*-tetraphenylporphyrin) has been determined.[4] Herein we describe a clean high-yield preparation of unsubstituted Fe(TPP) and the conversion of this isolated complex into a series of Fe(II)–TPP derivatives including a five-coordinate high-spin complex which appears to be a model for deoxymyoglobin.

Reduction of FeCl(TPP) with Cr(acac)$_2$[5] in rigorously degassed benzene, followed by precipitation with ethanol and recrystallization from benzene–ethanol (using Schlenk tube techniques within an inert atmosphere chamber), affords an 80% yield of purple crystalline Fe(TPP) (**1**). *Anal.* Calcd for C$_{44}$H$_{28}$N$_4$Fe: C, 79.05; H, 4.2; N, 8.4; Fe, 8.4. Found: C, 79.0; H, 4.45; N, 8.65; Fe, 8.4. The postulated four-coordinate nature of **1** cannot be verified without a crystallographic study or a molecular weight determination and so far our measurement of the latter has been frustrated by its meager solubility and extreme solution air sensitivity. Four-coordinate d^6 complexes are rare and none have been characterized by X-ray crystallographic analysis. Phthalocyanineiron(II)—a good model for **1**—has an unusual magnetic moment (μ = 3.71 BM at 25°) and has been extensively studied.[6] The moment observed for **1** (μ = 4.4 BM at 25°)[7] is intermediate between that expected for high- and low-spin Fe(II). It should be noted that most four-coordinate iron complexes are tetrahedral so that the constrictions imposed by the essentially planar porphyrin may force an unusual electronic state upon the iron in **1**. Conversely the iron(II) may tend to maximize distortion from planarity of the porphyrin making the crystallographic analysis of **1** a paramount objective.

As expected Fe(TPP) reacts rapidly with strong field nitrogen donors L, affording diamagnetic low-spin complexes Fe(TPP)L$_2$ (L = imidazole, pyridine, piperidine).[7] Tetrahydrofuran (THF) affords the high-spin complex FeTPP(THF)$_2$, μ = 5.1 BM at 25°. *Anal.* Calcd for C$_{52}$H$_{44}$N$_4$O$_2$Fe: C, 76.85; H, 5.45; N, 6.9; Fe, 6.9. Found: C, 76.7; H, 5.6; N, 7.2; Fe, 7.0. While this work was in progress a different preparation of Fe(TPP) and Fe(TPP)(THF)$_2$ was published,[2] but elemental analyses were poor and the reported magnetic moments differ from this work.

X-Ray diffraction studies of myoglobin (Mb)[8] and hemoglobin (Hb)[9] and predictions advanced by Hoard[10] suggest the high-spin deoxy–heme geometry to be five-coordinate square pyramidal with the iron atom displaced 0.5–0.8 Å above the porphyrin plane toward the axial histidyl imidazole. In all low-spin six-coordinate complexes such as Fe(TPP)(piperidine)$_2$[4] and probably oxyhemoglobin,[11] the iron is thought to occupy an in-plane position.

The absence of simple models for deoxymyoglobin undoubtedly results from the affinity of five-coordinate iron(II) to bind another imidazole forming low-spin six-coordinate complexes. In the natural system the shape of the globin protein pocket enforces five-coordination. Using a simple concept of nonbonded steric inter-

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[1] J. O. Alben, W. H. Fuchsman, C. A. Beaudreau, and W. S. Caughey, *Biochemistry*, 7, 624 (1968).

[2] H. Kobayashi and Y. Yanagawa, *Bull. Chem. Soc. Jap.*, **45**, 450 (1972).

[3] L. M. Epstein, D. K. Straub, and C. Maricondi, *Inorg. Chem.*, **6**, 1970 (1967).

[4] L. J. Radonovich, A. Bloom, and J. L. Hoard, *J. Amer. Chem. Soc.*, **94**, 2073 (1972).

[5] An inner-sphere atom transfer mechanism has been shown to operate in this reduction: I. A. Cohen, C. Jung, and T. Governo, *J. Amer. Chem. Soc.*, **94**, 3003 (1972).

[6] B. W. Dale, R. J. P. Williams, C. E. Johnson, and T. L. Thorp, *J. Chem. Phys.*, **49**, 3441 (1968); C. G. Barraclough, R. L. Martin, S. Mitra, and R. C. Sherwood, *J. Chem. Phys.*, **53**, 1643 (1970).

[7] Magnetic measurements were done in air using a Cahn Faraday balance—these well-formed crystalline solids appear to be air stable. Crystalline materials having good elemental analyses have been obtained in all cases. Adducts are also formed with CO and activated acetylenes—these will be the subject of a future publication.

[8] C. L. Nobbs, H. C. Watson, and J. C. Kendrew, *Nature (London)*, **209**, 339 (1966).

[9] M. F. Perutz, H. Muirhead, J. M. Cox, and L. C. G. Goaman, *Nature (London)*, **219**, 139 (1968).

[10] J. L. Hoard, *Science*, **174**, 1295 (1971).

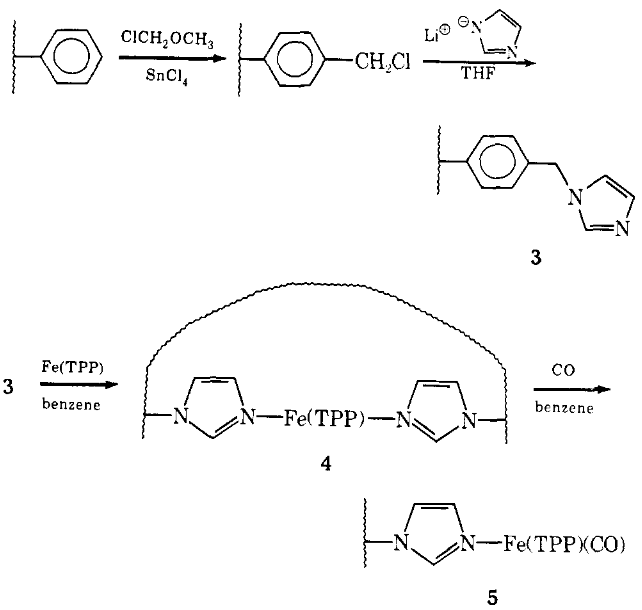
[11] M. F. Perutz, *Nature (London)*, **228**, 726 (1970).

actions, we have forced iron into a situation which appears to minic the coordination in deoxymyoglobin. This was based on our hypothesis that 2-methylimidazole (2-Me-imid) should be unable to form a strong coordinate bond with an in-plane iron porphyrin because of severe nonbonded repulsive interactions between the hydrogen atoms on the methyl group and the electrons of the porphyrin ring so that coordination of two 2-Me-imid groups is improbable. Thus reaction between 2-methylimidazole and Fe(TPP) in benzene–ethanol afforded well formed single crystals of Fe(TPP)(2-Me-imid)$\cdot C_2H_5OH$ (**2**). [*Anal.* Calcd for $C_{50}H_{40}N_6OFe$: C, 75.4; H, 5.05; N, 10.55; Fe, 7.0. Found: C, 75.65; H, 5.15; N, 10.2; Fe, 7.5. Crystal data: $M_{\mathrm{calcd}} = 797$; monoclinic C_c from systematic absences hkl, $h + k = 2n + 1$, and $h0l$, $l = 2n + 1$ on precession films; $a = 17.10$, $b = 16.51$, and $c = 14.71$ Å; $\beta = 98.7°$; $d_{\mathrm{measd}} = 1.295$ by flotation in aqueous $ZnBr_2$, $Z = 4$; $d_{\mathrm{calcd}} = 1.29$. The density agreement gives an unequivocal proof of the formulation.] Like deoxyhemoglobin ($\mu = 5.1$ BM)[12] **2** is high spin ($\mu = 5.2$ BM at 25°), and we suspect **2** has a similar square-pyramidal coordination with a large out of plane displacement of the iron atom toward the axial 2-Me-imid ligand.

The possibility that **2** is in fact six-coordinate with an ethanol molecule in the sixth position cannot be rigorously excluded in the absence of a full crystallographic study, but three observations are inconsistent with six-coordination. Firstly, the predicted "out of plane" position of the iron away from a sixth ligand makes this site very unfavorable for coordination by what is already a very poor ligand. Secondly, addition of ethanol to a benzene solution of Fe(TPP) in the presence of 2-Me-imid does not significantly perturb its visible spectrum.[12] Thirdly, it should be noted that recrystallization from benzene–methanol affords only four-coordinate Fe(TPP) even in the presence of a large excess of 2-Me-imid. Apparently the ethanol molecule stabilizes the lattice of **2** as a solvate. Otherwise the lattice of Fe(TPP) is more stable (less soluble).

X-Ray crystallographic studies are planned to test the hypotheses advanced in this paper. Such detailed structural data should be useful in assessing the Perutz[11] model for cooperative oxygen binding in hemoglobin.

Scheme I



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Reversible oxygenation of myoglobin appears to result from a five-coordinate high-spin iron(II) porphyrin immobilized within a hydrophobic pocket.[13] Our attempts to prepare a model for oxygenated myoglobin by treating Fe(TPP) with resin-bonded imidazole, **3**, afforded **4** whose diamagnetism and electronic spectrum suggest six-coordinate Fe(II) (Scheme I). Treatment of **4** with CO yielded the diamagnetic carbonyl **5** (ν_{CO} 1970 cm^{-1}) but prolonged heating of **5** under vacuum afforded only slight paramagnetism. These results are consistent with our earlier report concerning the mobility of cross-linked polystyrene ligands.[15] Treatment of either **4** or **5** with O_2 in benzene caused leaching of the oxidized product O[FeTPP]$_2$.

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(12) $\lambda_{\max}$: Fe(TPP) in benzene, 540; Fe(TPP)(imid)$_2$ in benzene, 535, 560, 610; Fe(TPP) with excess 2-Me-imid in benzene–ethanol, 530, 570, 610 nm.

(13) Apparently irreversible oxygenation of iron results from either an interaction involving two Fe(II) complexes and one O_2 molecule,[14] or protonation affording H_2O_2 which subsequently reacts with the Fe(II). Coordinatively unsaturated Fe(II) seems to be necessary for reaction with O_2.

(14) G. S. Hammond and C. S. Wu, *Advan. Chem. Ser.*, **No.** 77, 186 (1968).

(15) J. P. Collman, L. S. Hegedus, M. P. Cooke, J. R. Norton, G. Dolcetti, and D. N. Marquardt, *J. Amer. Chem. Soc.*, **94**, 1789 (1972).

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Optical Activity Associated with Isolated Olefinic Bonds. I. The Allylic Bond Polarization (ABP) Model and Its Extension to Homoconjugated Systems

Sir:

Although a definitive theoretical understanding of the electronic spectra of substituted ethylenes has yet to emerge,[1] the optical activity associated with nonconjugated olefinic linkages has come under increased scrutiny now that circular dichroism can be determined down to 185 nm routinely, and a number of empirical rules have been advanced.[2,6] The reversed octant rule of Scott and Wrixon[2] (SW rule) offers the most consistent explanation for the reported data for the λ_2

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(1) Three transitions from the π_x state (to the π_y^*, π_x^*, and σ^* states, in decreasing order of energy) have been considered (see ref 2b and 3 and references cited therein). The latter, a Rydberg-like transition, appears to account for the low-energy tail of the electronic spectra, but is not expected to be optically active.[4] Yogev, Sagiv, and Mazur[5] have recently demonstrated that the major olefin uv band is a composite of two transitions ($\lambda_1 \sim 185$–190 and $\lambda_2 \sim 200$–210 nm) of comparable intensity but differing polarization. In many of the cyclohexenes examined[2b,c] two CD extrema of opposite sign are observed in the 185–220-nm energy span, again reflecting the composite nature of the electronic spectrum.

(2) (a) A. I. Scott and A. D. Wrixon, *Chem. Commun.*, 1182 (1969); (b) *Tetrahedron*, **26**, 3695 (1970); (c) *Tetrahedron*, **27**, 4787 (1971).

(3) C. C. Levin and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 3446 (1972).

(4) M. Yaris, A. Moscowitz, and R. S. Berry, *J. Chem. Phys.*, **49**, 3150 (1968); S. F. Mason and G. W. Vane, *Chem. Commun.*, 540 (1965).

(5) A. Yogev, J. Sagiv, and Y. Mazur, *J. Chem. Soc., Chem. Commun.*, 411 (1972).