tion products were more favored than the insertion products. This might appear to indicate that triplet carbene reacts with the double bond in preference to the sulfur atom. However, since the triplet bis(carbomethoxy)carbene formed by the benzophenone-photosensitized reaction does not interact with the sulfur atom, the insertion product may probably be considered to be formed through other pathways than those involving ylide intermediates.

Table I. Yield of Products from Dimethyl Diazomalonate

		Yield, %		
Sulfide	Product	Direct	Sens.	Thermal[a]
Allyl *n*-butyl	Ii	57	28	93
	Ia	11	55	0
Allyl *t*-butyl	IIi	34	Trace	13
	IIa	14	50	0
β-Methylallyl *n*-butyl	IIIi	54	*b*	100
	IIIa	12	*b*	0
Allyl phenyl	IVi	32	0.34[c]	90
	IVa	7		0
γ-Methylallyl phenyl	Vi	47	0.13[c]	92
	Va	10		0

[a] Copper sulfate catalyzed thermal reaction at 90°. [b] The products could not be separated from benzophenone in the gas chromatograph. [c] The yields of insertion and addition products were very low, and only the molar ratio of the products, i/a, was determined from their peak area in gas chromatography.

A possible pathway is proposed involving addition of the triplet carbene to the unsaturated carbon. The biradical thus formed undergoes homolytic transfer of the thiyl group through the cyclic transition state as well as cyclopropane ring formation.

In the addition of triplet carbene to olefin involving two bond-forming processes, spin inversion is required in the intermediate step. During the step, internal rotations which gives the conformation leading to the cyclic structure illustrated in Scheme I may occur. This situation is reminiscent of nonstereospecific addition of a triplet to olefins.[1]

Copper salt or copper metal powder catalyzed thermal decompositions of diazo compounds in allyl sulfides yield insertion products in high yield. No addition product was obtained (Table I).[11] This high selectivity can be explained in terms of a copper complex of carbene. This is to be expected since the possible back-donation from the copper to the vacant p_z orbital of the carbenic carbon may contribute to stabilize the complex.[12]

It is hoped that the control over product formation demonstrated in the preceding examples will be useful in synthesis and be capable of extension to the reactions of carbenes with molecules containing hetero atoms.

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[11] Copper-catalyzed thermal reaction of dimethyl diazomalonate in an equimolar solution of cyclohexene and dimethyl sulfide gave only dimethylsulfonium bis(carbomethoxy)methylide; no adduct to cyclohexene was observed.

[12] H. Nozaki, H. Takya, S. Moriuti, and R. Noyori, *Tetrahedron*, **24**, 3655 (1968).

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Stereochemistry of the Low-Spin Iron Porphyrin, Bis(imidazole)-α,β,γ,δ-tetraphenylporphinatoiron(III) Chloride[1]

Sir:

Recent structure determinations for high-spin iron porphyrins demonstrate that the iron atom lies 0.40–0.50 Å out-of-plane from the four porphine-nitrogen atoms, that it forms rather long bonds, 2.06–2.07 Å, with these atoms, and that it generally forms one short bond with a single axial ligand to complete square-pyramidal five-coordination.[2,3] The coordination group within the high-spin heme of ferrimyoglobin has the iron atom displaced ~0.30 Å out-of-plane toward the tightly bound axial ligand (imidazole nitrogen), has five Fe–N bonds all estimated as ~1.9 Å in length, and has as a sixth ligand a weakly coordinated water molecule that is partially stabilized in this position by hydrogen bonding.[4–7] (This water molecule is lacking in the heme of deoxymyoglobin.[7]) From application of the protein structure analyst's version of Fourier difference synthesis[5–7] in its lowest order of approximation[2a] to the structural study of various myoglobin derivatives, the Cambridge workers seem to infer that the out-of-plane displacement of the iron atom and Fe–N bond parameters which characterize the heme in ferrimyoglobin are essentially maintained in the several myoglobin derivatives, changes in oxidation state, coordination number, and spin state of the iron atom notwithstanding.[5–7] The chemical implausibility of this sweeping inference and the quantitatively severe limitations on the approximate procedures from which it derives are treated in detail elsewhere.[2a] We report herein the results of an X-ray analysis of crystalline structure for bis(imidazole)-α,β,γ,δ-tetraphenylporphinatoiron(III) chloride (written as $Im_2FeTPP^+Cl^-$), the first low-spin iron porphyrin to be thus analyzed.

$Im_2FeTPP^+Cl^-$, prepared by the procedure of Epstein, *et al.*,[8] was obtained as monoclinic crystals of the 1:1 solvate by recrystallization from methanol. Preliminary X-ray study by photographic techniques established a four-molecule unit corresponding to calculated and measured densities of 1.365 and 1.36 g cm^{-3}, respectively, and $P2_1/n$ as the uniquely probable space group. Intensity measurements from the largest crystal, 0.10 × 0.13 × 0.23 mm, obtainable from controlled recrystallizations utilized nickel-filtered Cu Kα radiation on an automated Picker four-circle diffractometer at an ambient laboratory temperature of 19 ± 1°; of the

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[1] This investigation was supported in part by Grant 2-RO1-GM09370 from the National Institutes of Health, General Medical Sciences, by National Science Foundation Grant GP-6710X, and by the Advanced Research Projects Agency.

[2] (a) J. L. Hoard in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman and Co., San Francisco, Calif., 1968, pp 573–594; (b) J. L. Hoard, G. H. Cohen, and M. D. Glick, *J. Amer. Chem. Soc.*, **89**, 1992 (1967); (c) J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughey, *ibid.*, **87**, 2312 (1965).

[3] D. F. Koenig, *Acta Cryst.*, **18**, 663 (1965).

[4] J. C. Kendrew, R. E. Dickerson, B. E. Strandberg, R. G. Hart, D. R. Davies, D. C. Phillips, and V. C. Shore, *Nature*, **185**, 422 (1960).

[5] L. Stryer, J. C. Kendrew, and H. C. Watson, *J. Mol. Biol.*, **8**, 96 (1964).

[6] H. C. Watson in "Hemes and Hemoproteins," B. Chance, R. W. Estabrook, and T. Yonetani, Ed., Academic Press, New York, N. Y., 1966, pp 63–66.

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

[8] L. M. Epstein, D. K. Straub, and C. Marcondi, *Inorg. Chem.*, **6**, 1721 (1967).

practicable alternatives, Cu Kα radiation clearly afforded the optimum combination of range with sensitivity of measurement. Precision lattice constants of $a = 14.265\ (3)$, $b = 16.390\ (4)$, $c = 18.121\ (5)$ Å, and cos $\beta = -0.01451\ (30)$ giving $\beta = 90° 50'$, were calculated ($\bar{\lambda}$ 1.54178 Å) from a least-squares treatment of the diffractometer setting data for 43 reflections. The θ–2θ scanning of each reflection included a 2.0° range for the estimated base width at $2\theta = 0°$ plus a variable increment to take account of spectral dispersion; a scanning rate of 1°/min and background counts of 40-sec duration at both limits were employed. Some 5551 independent reflections of the total of 6833 having $(\sin \theta)/\lambda < 0.572$ (the limit imposed by the diffractometer geometry) were retained as observed from consideration of the counting statistics and were used for the determination and refinement of the 559-parameter structure (hydrogen parameters not counted). Structure determination was achieved by the heavy-atom technique with initial phasing of the Fourier coefficients determined by the contribution of the iron atoms. Concentrations of electron density indicative of hydrogen atoms, excluding only those in the methanol molecule, were well developed in the later difference syntheses at positions in good agreement with those calculated using an apparent C–H bond length of 0.98 Å. Refinement[9] of the atomic coordinates, anisotropic except for the hydrogen positions, utilized block-diagonal[10] least-squares minimization of the function, $\Sigma w(|F_o| - k|F_c|)^2$, with $w = 1$; a conventional R, computed for the 5551 data, of 0.077 was obtained.

A diagram in perspective[11] of the Im_2FeTPP^+ cation is shown in Figure 1. The slightly ruffled porphine skeleton observes quasi-fourfold symmetry, and the averaged bond lengths for the several chemical types that are entered on Figure 1 fit well into the general pattern for metalloporphyrins as discussed elsewhere.[12] It is, however, the octahedral coordination group of this low-spin iron porphyrin that commands attention. The averaged length of the four complexing bonds to porphine-nitrogen atoms is 1.989 (5; 4) Å,[13] some 0.08 Å shorter than the corresponding bond lengths in high-spin iron porphyrins. The lengths of the axial Fe–N bonds to imidazole-nitrogen atoms, 1.957 (4) and 1.991 (5) Å, are objectively somewhat different for reasons outlined below. The equatorial array of four porphine-nitrogen atoms is very slightly ruffled so that one pair of diagonally opposite atoms is displaced an apparent 0.009 (5) Å above, the other pair the same distance below, the mean plane of the quartet; the iron atom also is displaced 0.009 (3) Å from this plane, but toward the more distant (1.991 Å) axial ligand. Reference to Figure 1 shows that imidazole A, the more closely bound (1.957 Å) axial ligand, is much more favorably oriented for minimizing the steric interference of its critical pair of hydrogen atoms (those of the C–H bonds adjacent to the complexed nitrogen atom) with any part of the porphine ring system than is imidazole B. Indeed, the critical hydrogen atoms of imidazole B are each about 2.60 Å from porphine-nitrogen atoms, well below the 2.9 Å estimated from the van der Waals radii.[14] The responsibility for this unfavorable orientation of imidazole B and, consequently, for the stretched (1.991 Å) Fe–N bond must rest with the packing constraints in the crystal.

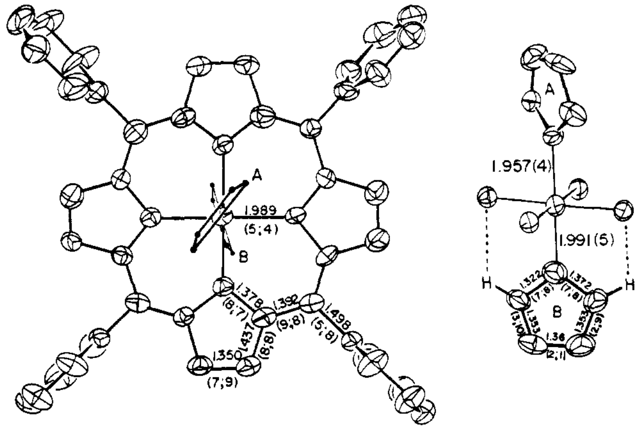

Figure 1. The configurations of (at left) the Im_2FeTPP^+ cation and (at right) the coordination group and axial imidazole ligands therein. Only the two hydrogen atoms that are presumably responsible for the significantly different lengths of the axial complexing bonds are shown. The averaged length entered on the diagram for each chemical type of bond carries, in parentheses, the mean deviation from the average followed by the estimated standard deviation of an individual bond length (both in the last significant figure of the datum). The averaged C–C bond length in the peripheral phenyl substituents is 1.381 (12; 11) Å.

These considerations, including the slight out-of-plane displacement (0.009 Å) of the iron atom, suggest that equatorial and axial Fe–N bond lengths of 1.99 and 1.95–1.96 Å, respectively, are appropriate to the Im_2FeTPP^+ cation when it is relieved of asymmetric environmental constraints. The greater length of the equatorial bonds is largely or wholly to be assigned to the marked resistance of the porphine skeleton to undue radial contraction, as most fully displayed in low-spin square-planar nickel(II) porphyrins.[12] These bond lengths require eight N···N distances of only 2.79 Å and four (within the porphine skeleton) of 2.81 Å, a tightness of packing quite matching that observed in low-spin cobalt(III) complexes that carry six monodentate nitrogen ligands. Further studies of low-spin iron porphyrins that utilize chemically unsymmetrical pairings of biologically interesting axial ligands are in prospect.

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(9) Atomic form factors were from D. T. Cromer and J. B. Mann, *Acta Cryst.*, **A24**, 321 (1968), with corrections, real and imaginary, for anomalous dispersion in the iron form factor from D. T. Cromer, *ibid.*, **18**, 17 (1965).

(10) One complete cycle of the standard Busing–Martin–Levy full-matrix anisotropic refinement of the $Im_2FeTPP^+Cl^-$ structural parameters on the IBM 360/65 computer must be approximated by a three-stage sequential refinement by parts (at nearly prohibitive cost). Our block-diagonal program REFINE, written by Dr. J. J. Park, has consistently given results that differ insignificantly from those given by the standard full-matrix refinement when applied to data sets in which (a) the ratio of independent amplitudes to structural parameters ranges upward from eight and (b) the refinement is dominated by the higher resolution Fourier coefficients from beyond the chromium Kα sphere.

(11) C. K. Johnson, "ORTEP, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(12) D. M. Collins and J. L. Hoard, *J. Amer. Chem. Soc.*, in press.

(13) The figures in parentheses are, respectively, the mean deviation from the average and the estimated standard deviation of an individual bond length in the last significant figure of the datum. This same notation is employed in Figure 1.

(14) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260. The "aromatic" 1.70-Å radius is appropriate for nitrogen.

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