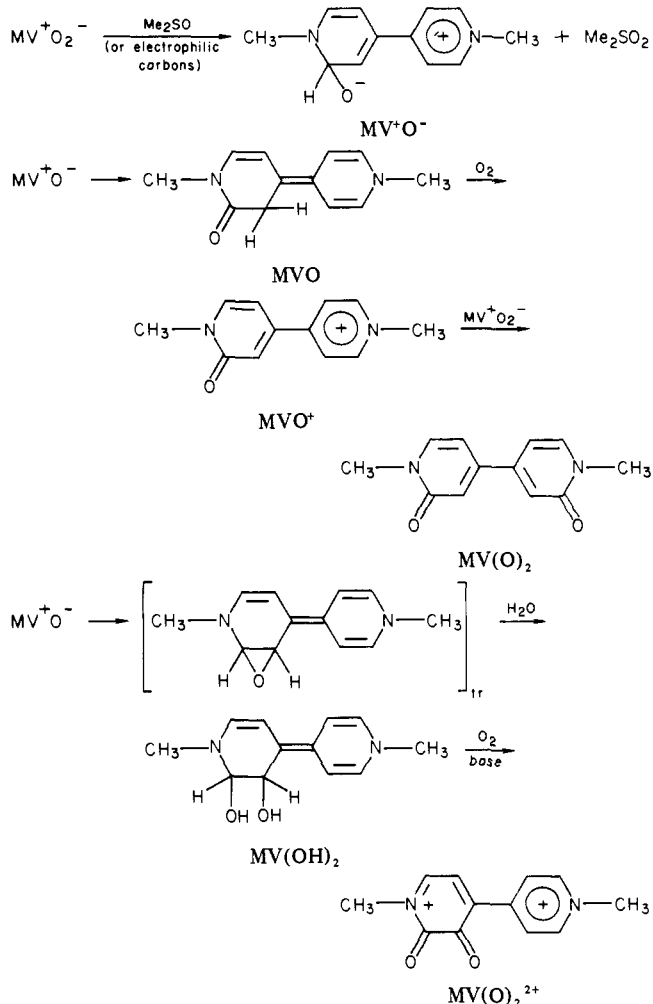


Scheme II



While the direct coupling of O₂⁻ to cation radicals has been previously proposed,^{33,34} we believe that this is one of the first observations of a stoichiometric process.³⁵ Similar radical-radical coupling between O₂⁻ and N⁵-ethyl-3-methylflavin radical to yield a 4a-peroxide anion (an effective oxygenase) has been observed in our laboratories.³⁶ Hence, the MV⁺O₂⁻ peroxide from the primary coupling reaction and its degradation products (Scheme II) may be highly reactive with biological substrates.

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(31) That the system is basic is confirmed by the anodic peak at +0.88 V vs. SCE (Figure 1) in DMF, which is characteristic of OH⁻.³² The anodic wave does not appear in the experiments carried out in Me₂SO, which indicates that the peroxide anion (MV⁺O₂⁻) rapidly reacts with the solvent to give the monoperoxide anion (MV⁺O⁻) and dimethyl sulfone (the reaction of Me₂SO with peroxide anion, HO₂⁻, produces Me₂SO₂).³²

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Reversible Migration of an Axial Carbene Ligand into an Iron-Nitrogen Bond of a Porphyrin. Implications for High Oxidation States of Heme Enzymes and Heme Catabolism

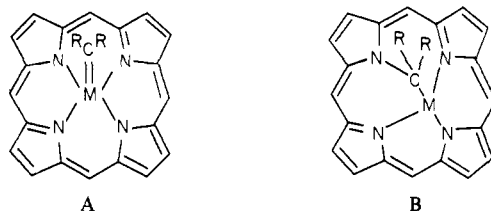
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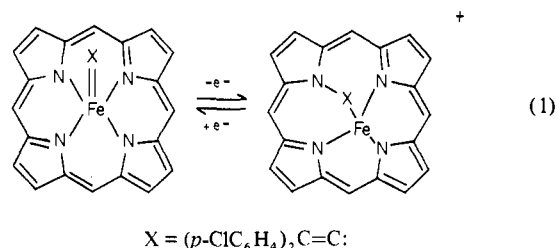
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Two types of carbene adducts of metalloporphyrins are known in which the carbene is bound to the metal. One, A, involves a carbene axially coordinated to the metal¹ while the other, B, involves a carbene which has been inserted into the metal-nitrogen bond.²⁻⁵ Carbenes are also known to add to the porphyrin ring



itself to form homoporphyrins, N-alkylated porphyrins, meso-substituted porphyrins, and cyclopropanic chlorins.³⁻⁹ Related complexes of type B are known in which a nitrene has been inserted into a metal-nitrogen bond.¹⁰ Mansuy and co-workers have recently reported the synthesis of the vinylidene carbene complexes [(p-ClC₆H₄)₂C=C:]FeTPP (1) (where TPP is the dianion of meso-tetraphenylporphyrin)¹¹ and have shown that these are oxidized to the species of composition [(p-ClC₆H₄)₂C=C:]⁺FeTPPY (2).¹⁰ The oxidized form 2 may be readily reduced to re-form 1. Here we demonstrate that this involves reversible carbene migration coupled to the redox reaction as shown in eq 1.



The ¹H NMR spectrum of 1, both alone and in the presence of excess 1-methylimidazole, is characteristic of a diamagnetic metalloporphyrin with full fourfold symmetry. Consequently 1 has been assigned the axial carbene structure A¹¹ and is similar

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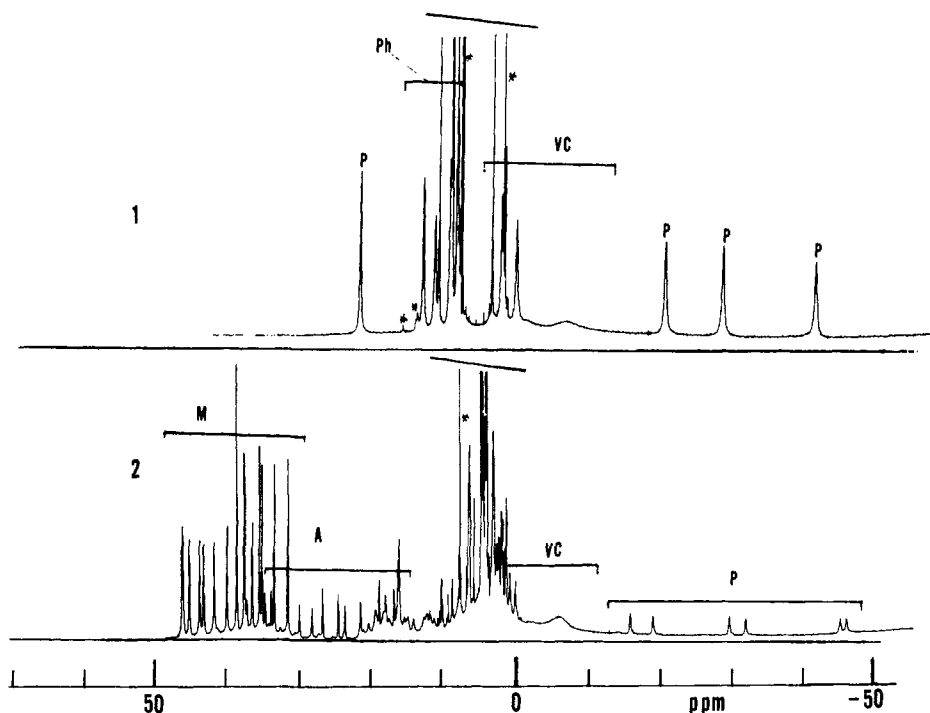
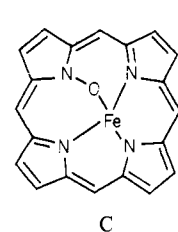


Figure 1. 360-MHz ^1H NMR spectra of (1) $[(p\text{-ClC}_6\text{H}_4)_2\text{C}=\text{C}](\text{TPP})\text{FeI}$ and (2) $[(p\text{-ClC}_6\text{H}_4)_2\text{C}=\text{C}](\text{DPDMe})\text{FeI}$ (DPDMe = dianion of deuteroporphyrin dimethyl ester) in CDCl_3 at 298 K. The resonance assignments are M, methyl; P, pyrrole; A, α -methylene of propionic acid residues; VC, phenyl of vinylidene carbene ligand; Ph, phenyl of TPP. The resonance assignments for **1** were verified by selective deuteration of the vinylidene carbene and the phenyl groups of the porphyrin.

to the isoelectronic Cl_2CFeTPP which has been structurally characterized.¹

In contrast, the ^1H NMR spectrum of paramagnetic **2** shows a distinct lack of fourfold symmetry. The spectrum of **2** ($\text{Y} = \text{I}$) is shown in Figure 1. Four pyrrole resonances have been identified. Particularly anomalous is the observation of a single, downfield, hyperfine-shifted pyrrole resonance and three upfield, hyperfine-shifted pyrrole resonances. This pattern, along with the ^{13}C NMR spectrum of **1** ($\text{Y} = \text{Cl}$) enriched with ^{13}C at the meso carbon,¹³ which shows two resonances at -100 and -67.3 ppm, indicates that the porphyrin has suffered major perturbation and attack at a pyrrole ring. The ^1H NMR spectrum of the analogous vinylidene carbene complex obtained by using deuteroporphyrin IX dimethyl ester shows that the four possible isomeric insertion products are formed in nearly equivalent amounts. Thus 16 methyl resonances have been identified in the region $50\text{--}30$ ppm, and 6 upfield-shifted pyrrole resonances are clearly seen. Two other pyrrole resonances may lie in the cluttered region between $10\text{--}30$ ppm. These data are consistent with assigning structure **B** to **2**, and this assignment has been confirmed by an X-ray crystallographic study.¹⁴ Consequently **2** is best considered as an Fe(III) , $S = 3/2$ complex. The magnetic susceptibility and ESR spectrum previously reported¹² are entirely in accord with the properties of other iron complexes having this oxidation and spin state.^{15,16}

These results have implications involving the nature of intermediates of heme enzymes, with high formal oxidation states of iron and the mechanism of heme catabolism. The relationship between metal oxo and carbene species has been previously noted.¹² The carbene complex **1** is formally isoelectronic to a porphyrin complex of an FeO^{2+} unit, and **2** is isoelectronic with a similar complex of FeO^{3+} . Intermediates at the FeO^{3+} level of oxidation are encountered as detectable species in horseradish peroxidase (HRP),¹⁷ and **2** has been proposed as a model for HRP-compound I.^{12,18} These FeO^{3+} intermediates are also speculated¹⁹ to occur in the mechanism of action of cytochrome P-450. The observation of carbene and nitrene insertion into the metal–nitrogen bonds of metalloporphyrins raises the possibility that metalloporphyrins with an oxene inserted into a metal–nitrogen bond (structure **C**)



may be involved in the chemistry of enzymatic intermediates containing the FeO^{3+} or FeO^{2+} unit. In this context, the observation that amine oxides under light irradiation can mimic certain oxygen–atom transfer reactions of cytochrome P-450 takes on added significance.²⁰ Carbene ligands are suspected to be formed during the reductive metabolism of a variety of substances by

(13) The porphyrin was obtained by condensation of pyrrole with benzaldehyde- $\alpha\text{-}^{13}\text{C}$.

(14) (a) The complex $\text{TpTP}[(p\text{-ClC}_6\text{H}_4)_2\text{C}=\text{C}]\text{FeCl}_2\text{CH}_2\text{Cl}_2$ (where TpTP is the dianion of *meso*-tetra-*p*-tolylporphyrin), prepared as described previously,¹² crystallizes in the space group $P2_1/n$ with $a = 19.654$ (5), $b = 12.418$ (2), $c = 23.453$ (5) Å, $\beta = 103.10$ (2) $^\circ$ at 140 K. The iron is five-coordinate with approximate trigonal-bipyramidal geometry. The iron is bound to three of the four pyrrole nitrogens, the carbene carbons, and the chloride. The fourth pyrrole nitrogen is 2.529 (8) Å from the iron and is uncoordinated. The Fe–C(carbene) distance is 1.92 (1) Å, N–C(carbene) distance is 1.41 (1) Å and the Fe–C–N angle is 97.8 $^\circ$. Olmstead, M. M.; Cheng, R. J.; Balch, A. L., to be published. (b) Note Added in Proof. An independent determination of the structure of a different solvated form of this compound has recently been reported: Chevrier, B.; Weiss, R.; Lange, M.; Chottard, J.-C.; Mansuy, D. *J. Am. Chem. Soc.* **1981**, *103*, 2899–2901.

(15) The g values of 4.4 and 2.03 reported for **2** at 77 K¹² are reasonably similar to the g values of 4.75 and 2.03 reported¹⁴ for $\text{Fe}(\text{TPP})\text{ClO}_4$, $S = 3/2$, at 10 K.

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cytochrome P-450.²¹ The transfer of a carbene ligand from iron to pyrrole nitrogen may offer a pathway for the destruction of cytochrome P-450 which produces green porphyrins with similar features of N-alkylated porphyrins.²² Shifts of an oxene unit from metal to nitrogen by reaction 1 followed by further migration analogous to the N-alkylporphyrin-homoporphyrin conversion⁸ could also be involved in heme oxygenase activity.²³

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Synthesis and Molecular Structure of an Aminophosphanide Transition-Metal Adduct. First Transition-Metal Derivative Having a Cyclic N-P-M Arrangement

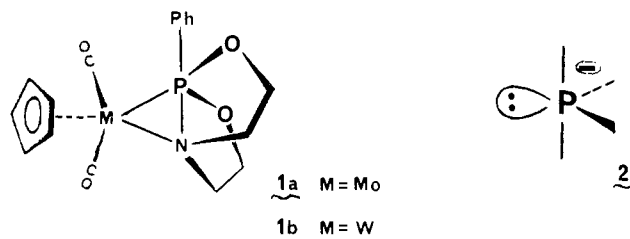
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A novel structural arrangement has been found in compounds **1**, which exhibit two remarkable features: (1) the metal atom is bound to a pentacoordinated phosphorus atom, which thus acts as a *phosphanide* ligand **2**, and (2) the metal is bound to a nitrogen atom to form a hitherto unknown N-P-M cycle, which is all the more surprising in view of the low basicity expected from a P-bound nitrogen atom. Also very unusual is the location of the oxygen atoms in equatorial sites and of the phenyl group in an apical site of the bipyramidal phosphorus atom.

The aminophosphanidemolybdenum adduct **1a** was obtained by allowing 1 molar equiv of LiMe to react with the cationic adduct **3a**¹ in a THF/ether solution (3:1) at -20 °C. Infrared



monitoring of the reaction showed that the $\nu(\text{CO})$ vibrations of **3a** at 1850 and 1978 cm^{-1} had completely disappeared after 30 min, while two new absorptions had developed at 1855 and 1945 cm^{-1} . The evolution of methane was ascertained by IR spectroscopy. The insoluble LiBPh_4 salt, precipitated, was filtered off, and **1** was isolated in 66% yield as yellow crystals, moderately air-sensitive, soluble in THF, CHCl_3 , acetone, ether, and benzene. It is indefinitely stable at room temperature and melts (with decomposition) at ~ 145 °C.

Compound **1** exhibits a single resonance in the proton decoupled ^{31}P NMR spectrum at 43.9 ppm, which is an unusual location

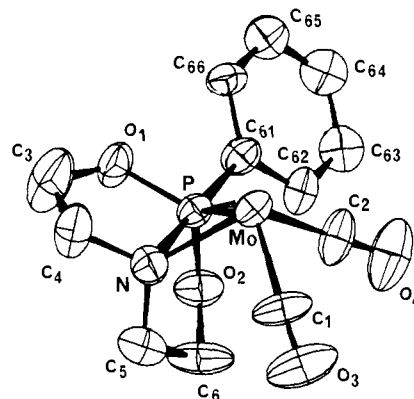
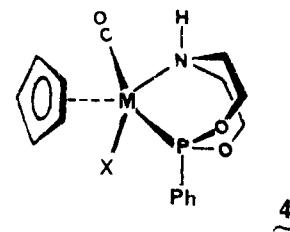


Figure 1. Molecular structure of $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mo}[\text{PhP}(\text{OCH}_2\text{CH}_2)_2\text{N}]$. The $\eta^5\text{-C}_5\text{H}_5$ ring has been omitted for clarity. Selected bond lengths (average): P-Mo 2.382 (4), P-N 1.908 (12), P-O₁ 1.625 (10), P-O₂ 1.624 (10), P-C₆₁ 1.856 (12), N-Mo 2.227 (10). Angles: Mo-P-N 61.7 (3), Mo-P-O₁ 119.4 (4), Mo-P-O₂ 118.4 (4), O₁-P-O₂ 115.8 (5), C₆₁-P-N 176.4 (5), O₁-P-C₆₁ 92.1 (5), O₂-P-C₆₁ 93.4 (5), Mo-N-P 69.7 (4), P-Mo-N 48.7 (3).

when compared to the 185-200-ppm range found for Mo-P^{III} adducts of type **3** or **4**.¹ The ^1H spectrum shows a single sharp



signal for the C_5H_5 protons at 5.32 ppm in CDCl_3 . The $\nu(\text{N-H})$ vibration at 3205 cm^{-1} in **3** has disappeared.

The structure of **1** was established by X-ray diffraction. It forms triclinic crystals [space group $P\bar{1}$ with unit cell parameters $a = 11.156$ (1) $b = 11.593$ (3) $c = 14.554$ (1) Å; $\alpha = 101.55$ (1), $\beta = 111.35$ (1), $\gamma = 90.52$ (2)°; $v = 1710.53$ Å³; $Z = 4$]. The triclinical system was determined and confirmed by Weissenberg films and powder diffraction spectra. The centrosymmetrical $P\bar{1}$ space group was established by statistical tests. The Patterson function showed the presence of four Mo atoms in the unit cell; all the nonhydrogen atoms were located by Fourier difference maps and showed the presence of two types of molecules of slightly different conformation. From 6760 measured reflections ($2 < \theta < 25^\circ$; Mo $K\alpha$ radiation, Ge monochromator) 4681 were used for the preliminary refinement of the structure (R value = 8%).

The most prominent features (Figure 1) of the molecule are the five-connected character of the phosphorus atom, i.e., the presence of the original phosphanide ligand; the shortest Mo^{II}-P bond found so far (average 2.38 Å), 0.07-0.14 Å shorter than those found in complexes having the $\text{CpMo}^{\text{II}}\text{PR}_3$ pattern ($R = \text{OCH}_3$, C_6H_5);² the presence of the new N-P-Mo cycle (average Mo-N 2.23 Å); one of the longest P-N bonds known (average 1.91 Å);³ an almost perfect bipyramidal arrangement of the substituents on phosphorus, with the two Mo-P-O and one O-P-O angles all close to 120° and the NPC(phenyl) atoms almost aligned (average 176°) perpendicular to the equatorial plane formed by the other substituents of P.

While phosphanides were postulated as reaction intermediates by Wittig as early as 1967,⁴ it was only in 1978 that direct evidence was provided by Granoth and Martin for the existence of an ionic lithium phosphanide.⁵ Still more recently, the first transi-

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