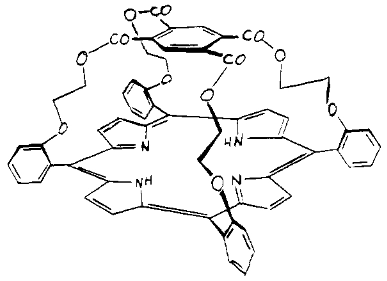
4.74 (8 H, m), 7.05 (8 H, m), 7.31-7.91 (8 H, m), 8.03 (2 H, s), 10,47 (4 H, s). Condensation of **3** with pyrrole (1 equiv) for 1.5 hr in propionic acid at reflux[4] gave a black mixture. After filtration from a black granular polymer the chloroform solubles were chromatographed on silica gel. The resultant crude porphyrin was treated with dichlorodicyanobenzoquinone in methylene chloride-benzene to oxidize traces of chlorin.[5] A single chromatography over silica gel gave pure porphyrin, **5**, as lustrous violet crystals, recrystallized from methylene chloride-methanol (2%, based on aldehyde **3**).

The structure assigned to **5** is based on its constitution (*Anal.* Calcd: C, 71.5; H, 4.47; N, 5.6; mol wt, 1036. Found: C, 71.8; H, 4.25; N, 5.4; mol wt (osmometric) 985, $C_{62}H_{44}N_4O_{12}$.) and spectral properties: ν_{max} ($CHCl_3$) 3450, 1740 cm^{-1}; λ_{max} ($CHCl_3$) 422 nm (305,000), 517 (15,800), 548 (4200), 591 (5000), 647 (2100); nmr ($CDCl_3$) (Fig. 2) NH, δ −3.32 (2 H), aliphatic 3.65-4.71 (16 H, m), aromatic 7.68-7.91 (16 H, m) and a sharp singlet at δ 5.41 (2 H) which we attributed to the two protons on the "capping" benzene ring, shifted upfield (relative to **3**) by the diamagnetic anisotropy of the suspended porphyrin. Furthermore the C_2 symmetry implicit in structure **5** was clearly indicated by the pyrrole resonances of **5** which appear as a sharp doublet centered at δ 8.70 (8 H). The same compound **5** could be obtained from the isomeric mixture of porphyrins **6**[6] by esterification with pyromellitoyl chloride in boiling phenol in 15% yield, based on **6**. However, the difficulty in obtaining **6** renders the first method the preferred one. Attempts to condense the homologous aldehyde, derived from the ether **7**, with pyrrole in propionic acid were unsuccessful.



5

Even more hindered porphyrins are available by the tetraaldehyde approach. Thus when tetraether **8** (R = H)[7] was formylated by the Vilsmeier procedure, aldehyde **8** (R = CHO) was produced in 70% yield. Condensation with pyrrole in propionic acid over 10 hr, followed by the above work-up, gave the naphthalene analog of **5** (0.4%, based on **8** (R = CHO)), the lower yield reflecting the increased hindrance in the precursor.

Acknowledgment. We thank the National Science Foundation, The Petroleum Research Fund, administered by the American Chemical Society, Eli Lilly & Co., and Hoffmann-La Roche for generous financial support.

References and Notes

(1) A multistep synthesis of a cyclophane porphyrin has been described in a preliminary communication; *cf.* H. Diekmann, C. K. Chang, and T. G. Traylor, *J. Amer. Chem. Soc.*, **93**, 4068 (1971).

(2) A "picket fence" porphyrin has been synthesized by a route involving the separation of an isomeric mixture of tetra(O-substituted phenyl)porphins; *cf.* J. P. Collman, R. R. Gagne, T. R. Halbert, J. C. Marchon, and C. A. Reed, *J. Amer. Chem. Soc.*, **95**, 7868 (1973).

(3) All new compounds have given satisfactory combustion analysis.

(4) A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assouri, and L. Karsakoff, *J. Org. Chem.*, **32**, 476 (1967).

(5) Oxidation of chlorin to porphyrin was followed by the disappearance of the 655-nm band and appearance of a 647-nm band; *cf.* G. H. Barrett, M. F. Hudson, and K. M. Smith, *Tetrahedron Lett.*, 2887 (1973).

(6) This mixture of diphenyl-type isomers, results from condensation of **4** with pyrrole in propionic acid; *cf.* L. K. Gottwald and E. F. Ullman, *Tetrahedron Lett.*, 3071 (1969).

(7) This compound was readily obtained (73%) by condensation of β-naphthol with ethylene oxide.

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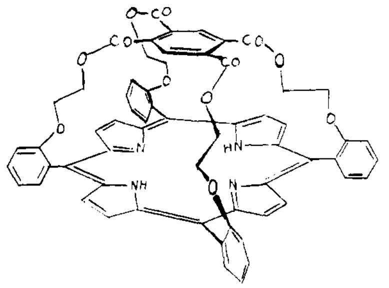
Reversible Oxygenation and Autoxidation of a "Capped" Porphyrin Iron(II) Complex

Sir:

Recently we reported that steric inhibition of an irreversible bimolecular process between an iron(II) dioxygen complex and an iron(II) species, eq 1, enabled observation of reversible oxygen binding in a solution of a ferrous octaazamacrocycle at low temperatures.[1] Similar low temperature behavior was observed for unhindered iron(II) porphyrins,[2,3] whereas a sterically hindered, so-called "picket fence" porphyrin bound oxygen reversibly at room temperature and gave a crystalline complex.[4] In an accompanying report[5] we describe a method for the direct formation of "capped" porphyrins and here we describe its conversion to an iron(II) complex and its reaction with oxygen.

$$Fe^{II}(O_2) + Fe(II) \longrightarrow Fe(III) \tag{1}$$

Reaction of porphyrin **1**[5] with anhydrous ferrous chloride in tetrahydrofuran under nitrogen provided a good yield (95%) of crystalline ferric porphine chloride, λ_{max} ($CHCl_3$) 513 nm,[6] μ 5.98 *M.*[7] Following the procedure of Collman[8] this iron(III) complex was reduced with chromous bis(acetylacetonate) in benzene to the crystalline ferrous porphine, represented schematically as **2:** λ_{max} (benzene) 420, 447, 537 nm; (pyridine) 535, 565 nm; μ 4.10 BM. Exposure of a pyridine solution of **2** to oxygen at 25° was accompanied by an immediate change in the spectrum, to λ_{max} 434, 545, and 580 nm.[10] Deaeration by freeze-thawing restored the spectrum of the ferrous complex, Figure 1. Hardly any deterioration of the complex was observed, even after several such cycles; the lifetime of the dioxygen adduct **4** in pyridine being *ca.* 20 hr. After this time only the spectrum of an iron(III) species can be observed. Similarly, benzene solutions of **2**, containing 5% 1-methylimidazole showed identical reversible spectral behavior at 25°, but the lifetime of the dioxygen adduct decreased to 5 hr. The crystalline product of autoxidation in both solvents was the μ-oxo dimer **5:** λ_{max} (pyridine) 424, 575; (benzene) 424, 580 nm.[11] At



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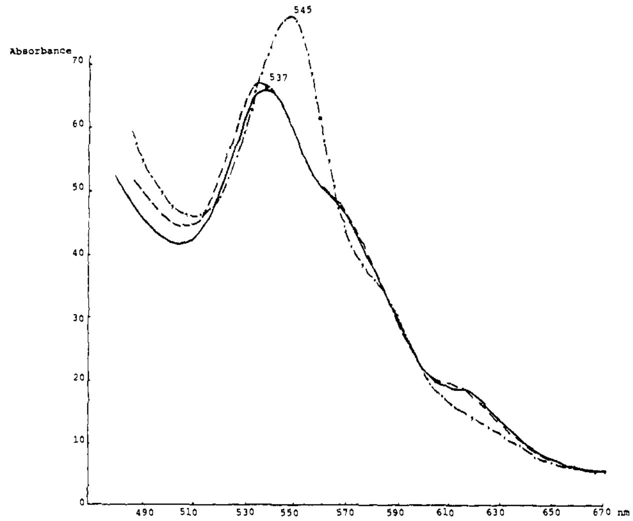
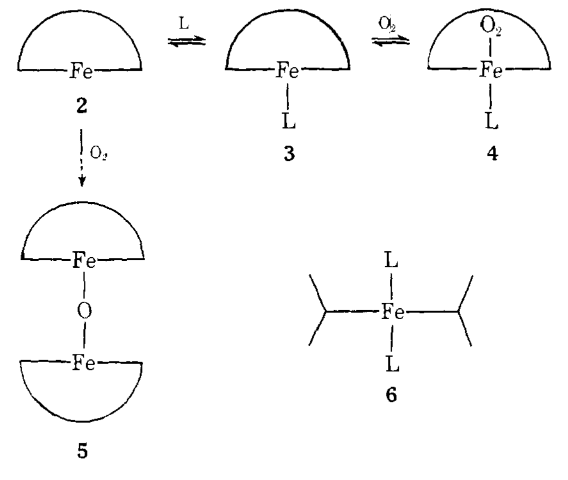


Figure 1. Visible spectrum of the Fe^{II} porphyrin in dry pyridine: (——) under argon, (- •- •) under oxygen, (- - -) under argon after three oxygenation-deoxygenation cycles.

−20° pyridine solutions of adduct **4** are stable for several days.[12]

In this system the stability of the dioxygen adduct **4** is largely dependent on the nature[13] and concentration of the coordinating base, L. Thus a 5% concentration of 1-methylimidazole in benzene provides a 5-hr lifetime (25°) whereas rapid autoxidation occurs in a solution of 5% pyridine in benzene. A rationale for these observations is presented in Scheme I. Assuming that the predominant species in anaerobic solution is the pentacoordinate complex **3**, it may react with oxygen reversibly to octahedral adduct **4** or it may dissociate to square planar complex **2.** Experiment has shown that in benzene solution, in the absence of ligand L, the species **2** is instantaneously autoxidized, most certainly by oxygenation of the unprotected face. A large excess of L shifts the equilibrium toward pentacoordinate complex **3** and consequently reduces the rate of autoxidation. In the previously described system[4] the presence of an octahedral species, **6,** results in a lower concentration of the sensitive square planar species, such as **2.** Consequently in our system, Scheme I, the absence of octahedral species, such as **6,** which are geometrically impossible renders this system much more sensitive toward irreversible autoxidation.[14] An analogous explanation can be offered for the rapid autoxidation of an extremely hindered porphine prepared by Collman,[4] which also forms a pentacoordinate ferrous complex with nitrogenous ligands.

Scheme I



In agreement with this general Scheme I, we have shown that decay of **4,** over two half-lives follows clean first-order kinetics (25°, benzene, 5% 1-methylimidazole). Such behavior is in complete accord with dissociation of **4** to the autoxidizable square planar species **2.**

In summary these results support the thesis that steric inhibition of the bimolecular process, eq 1, provides a means of stabilizing ferrous dioxygen complexes of porphyrins. However, they also indicate that the position of the equilibria is important in determining the lifetimes of such species.

Acknowledgments. We thank the National Science Foundation, the Petroleum Research Fund, administered by the American Chemical Society, Eli Lilly & Co., and Hofmann-La Roche for their generous financial support.

References and Notes

(1) J. E. Baldwin and J. Huff, *J. Amer. Chem. Soc.*, **95**, 5757 (1973).
(2) C. K. Chang and T. G. Traylor, *J. Amer. Chem. Soc.*, **95**, 5810, 8477, 8475 (1973).
(3) (a) J. Almog, J. E. Baldwin, R. L. Dyer, J. Huff, and C. J. Wilkerson, *J. Amer. Chem. Soc.*, **96**, 5600 (1974); (b) D. L. Anderson, C. J. Weschler, and F. Basolo, *ibid.*, **96**, 5599 (1974).
(4) J. P. Collman, R. R. Gagne, T. R. Halbert, J. C. Marchon, and C. A. Reed, *J. Amer. Chem. Soc.*, **95**, 7868 (1973); J. P. Collman, R. R. Gagne, and C. A. Reed, *ibid.*, **96**, 2629 (1974).
(5) J. Almog, J. E. Baldwin, R. L. Dyer, and M. Peters, preceding communication.
(6) The analogous mesotetraphenylporphineiron(III) chloride has λ_{max} ($CHCl_3$) 509.5 nm, μ 5.87BM; E. B. Fleischer and T. S. Srivastava, *J. Amer. Chem. Soc.*, **91**, 2404 (1969).
(7) All magnetic moments were determined in the solid state at 25° unless otherwise stated. We thank Mr. S. Koch for these determinations.
(8) J. P. Collman and C. A. Reed, *J. Amer. Chem. Soc.*, **95**, 2048 (1973).
(9) The analogous mesotetraphenylporphineiron(II) has λ_{max} 534, and 563 nm (in toluene with *N*-methylimidazole).[8]
(10) Manometric determination[7] revealed an uptake of 0.9 ± 0.1 mol of dioxygen per mole of complex. We thank Dr. R. L. Dyer for this measurement. The solution so obtained is diamagnetic; *cf.* J. Löliger and R. Scheffold, *J. Chem. Educ.*, **49**, 646 (1972).
(11) (a) The μ-oxo dimer of *meso*-tetraphenylporphineiron(III) complex has λ_{max} ($CHCl_3$) 408 and 571 nm: (b) Compound **5** could be reconverted to the ferric chloro species by treatment with hydrogen chloride in chloroform.
(12) We have made many attempts to crystallize the adduct **4**; however, to date all our efforts have only produced the less soluble precursor **2** as a crystallizable species.
(13) Use of a 5% solution of imidazole in benzene results in instantaneous autoxidation; *cf.* (a) V. Stynes, H. C. Stynes, J. A. Ibers, and B. R. James, *J. Amer. Chem. Soc.*, **95**, 1142 (1973); also ref 3a.
(14) Accurate models of I show that nitrogen ligands, such as pyridine or 1-methylimidazole cannot enter the cavity of **1**.

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Hydrozirconation, II, Oxidative Homologation of Olefins *via* Carbon Monoxide Insertion into the Carbon-Zirconium Bond

Sir:

We have recently reported[1] the preparation of di(η^5-cyclopentadienyl)(chloro)alkylzirconium(IV) complexes, $(\eta^5\text{-}C_5H_5)_2Zr(Cl)R$ (**1**), which are inexpensively and conveniently produced by reaction of the corresponding hydride,[2] **2,** with olefins (hydrozirconation). These alkylzirconium compounds are versatile intermediates for organic synthesis in that they react with a variety of electrophilic reagents to generate organic products in high yield and under mild conditions. We now wish to report our results concerning another aspect of the chemistry of **1** which expands in scope the utility of these complexes as reagents for organic synthesis. We have found that **1** undergoes a clean and high yield insertion of CO into the C-Zr bond[3] to pro-