

raised to a temperature of $627 \pm 3^\circ$ and fluorine passed over the sample at a flow rate of 3–4 cm³/min. The flow was continued at that temperature for at least 12 hr. Then the furnace was cooled and the fluorine shut off while helium was again passed over the chamber to drive the fluorine out of the chamber. A snow white product (~3 g) was then removed from the nickel boat. *Anal.* Calcd C, 35.98; F, 61.11. Found: C, 36.01; F, 63.57. Calculated empirical formula, CF_{1.12±0.03}.

A high resolution infrared spectrum revealed a strong band at 1217 cm⁻¹ which may be assigned to the C–F stretching vibrations for tertiary carbon atoms. Previously Rudorff and Brodersen⁶ had reported only a single band at 1215 cm⁻¹. Two medium bands were observed at 1342 and 1072 cm⁻¹, presumably due to asymmetric and symmetric stretching vibrations, respectively, of the peripheral CF₂ groups. A 332-cm⁻¹ far-infrared band was observed and is probably due to bending in CF₂ groups.

X-Ray powder pattern analysis with copper radiation yielded interplanar "d" spacings of 5.80 (s), 2.89 (m), 2.22 (s), and 1.29 (s) Å. Interplanar spacings of 6.0, 2.23, and 1.30 have been previously reported by Palin and Wadsworth.⁷

To produce (CF_x)_n of the highest fluorine content and whitest color, it was necessary to maintain a temperature of $627 \pm 3^\circ$. This six-degree range was very critical. In the previous work this was not recognized and consequently the process for production of (CF_x)_n gained a reputation for being very irreproducible. (CF_x)_n is formed from about 540 to 630° at atmospheric fluorine pressure. It has been found that at higher pressures the critical reaction temperatures decrease.⁸ At the 540° temperature the empirical formula is CF_{0.68} and the product is black. One may observe this effect experimentally in the reaction boat. If the furnace has a "hot" zone within this 6° range smaller than the length of the boat, only the central region of the boat produces white (CF_x)_n and on either side the color ranges from gray to black. At temperatures over 630° the compound is unstable in fluorine and burns to produce CF₄ and a black soot. (CF_x)_{1.1} is therefore a solid subfluoride of carbon which should be considered metastable with respect to CF₄. These observations of reaction variations with temperature can be explained by consequent changes in fluorine atom concentrations and subsequent kinetics.

As a result of the discovery of the critical nature of the temperature control, the limiting stoichiometry of (CF_x)_n has been found to be CF_{1.12±0.03}. Other maximum values have been reported previously in the CF_{0.98} region, *i.e.*, the *x* in (CF_x)_n approaches one. The stoichiometry CF_{1.12±0.03}, implies extra fluorine atoms and these fluorines occur as CF₂ groups around the edge of the ring. Rudorff's CF_{0.95} empirical formula does not provide evidence for these peripheral CF₂ groups and even indicates some fluorine deficiencies on the tertiary carbon atoms in the graphite plane. It is also possible that Rudorff's particle size may have been large enough to make this excess negligible stoichiometrically. The peripheral CF₂ groups would have fluorine atoms in

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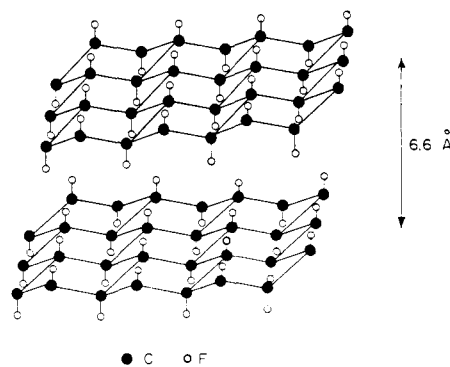


Figure 1. Rudorff (CF_x)_n structure.

axial and equatorial positions. The side bands at 1342 and 1072 cm⁻¹ are due to the asymmetric and symmetric stretching of these groups and provide evidence of their presence. The CF₂ bending at 332 cm⁻¹ also supports this conclusion.

Recently, studies by the Lewis Research Center of the National Aeronautics and Space Administration⁹ and by the Frankford Arsenal of the U. S. Army¹⁰ have shown that poly(carbon monofluoride) is a superior solid lubricant under heavy loads, high temperatures, in oxidizing atmospheres, and under other such extreme conditions. Workers at the U. S. Army Electronics Command at Ft. Monmouth, N. J.¹¹ and industrial workers in Japan have concurrently demonstrated a high potential for carbon monofluoride for use as a cathode material in high energy batteries.

Acknowledgment. Support for this work was received from the Army Research Office (Durham).

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A Paramagnetic Dioxygen Complex of Iron(II) Derived from a "Picket Fence" Porphyrin. Further Models for Hemoproteins

Sir:

Recently attention has been given to models for the dioxygen binding hemoproteins, myoglobin (Mb), and hemoglobin (Hb).¹⁻⁴ We have demonstrated that iron(II) complexes constructed from "picket fence" porphyrins,¹ having steric shielding on one side of the

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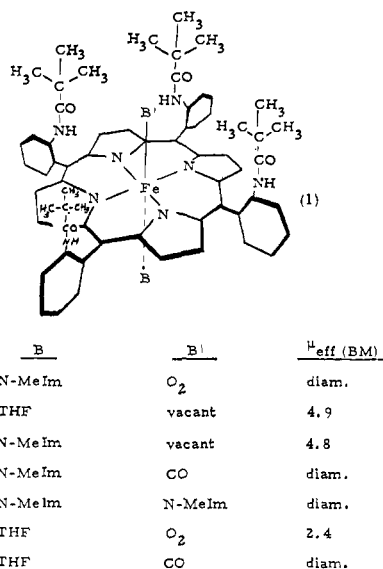


Figure 1. Fe(II) complexes of $\alpha, \alpha, \alpha, \alpha$ -H₂TpivPP.

porphyrin, reversibly oxygenate in solution at 25°—provided that an axial base is present to retard irreversible oxidation. Such bases prevent coordination of dioxygen on the unprotected side of the porphyrin. From one picket fence porphyrin a crystalline *diamagnetic* dioxygen complex, Fe($\alpha, \alpha, \alpha, \alpha$ -TpivPP)(N-MeIm)(O₂)⁵ (**1**), has been fully characterized—including a full X-ray structure.² Herein we report the use of other ligands as axial bases supporting reversible oxygenation and the use of solid-gas reactions to prepare a crystalline *paramagnetic* dioxygen complex!

Reduction of Fe($\alpha, \alpha, \alpha, \alpha$ -TpivPP)Br in THF¹ afforded crystalline Fe($\alpha, \alpha, \alpha, \alpha$ -TpivPP)(THF)₂ (**2**) ($\mu = 4.9$ BM,⁶ 25°) (Figure 1). The high magnetic moment of **2** is indicative of five-coordinate high spin iron(II), and we suppose one THF is coordinated to iron—the other acting as a crystal solvate.⁷ Dilute (5×10^{-5} M) THF solutions of **2** exhibit reversible spectral changes at 25° when alternately exposed to oxygen and then flushed with nitrogen (Figure 2). Several cycles of oxygenation-deoxygenation were carried out with very minor decomposition, but continuous exposure to oxygen for 24 hr resulted in ~50% oxidation. Attempts to isolate this supposed dioxygen complex by treating saturated THF solutions of **2** with air were unsuccessful—yielding mostly the oxidized complex [Fe($\alpha, \alpha, \alpha, \alpha$ -TpivPP)]₂O. The greater rate of oxidation in concentrated solutions of **2** is not surprising in view of the supposed bimolecular nature of the irreversible oxidation but this case serves to emphasize the difficulty in crystallizing such dioxygen complexes even when spectral evidence can be obtained for reversible oxygenation in dilute solutions.

In contrast to studies with another porphyrin system,^{4d} pyridine and also piperidine support reversible oxygenation in benzene solution. However, all attempts to isolate the corresponding dioxygen complexes

(5) Abbreviations: $\alpha, \alpha, \alpha, \alpha$ -H₂TpivPP = *meso*-tetra($\alpha, \alpha, \alpha, \alpha$ -*o*-pivalamidophenyl)porphyrin; N-MeIm = N-methylimidazole; THF = tetrahydrofuran. All compounds described herein have acceptable elemental analyses which have been provided to the referees.

(6) Magnetic susceptibilities were measured by the Faraday method and corrected for diamagnetic contributions.

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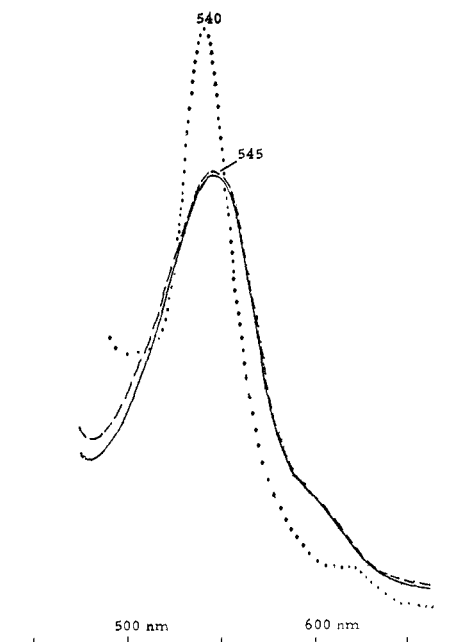


Figure 2. Visible spectrum of 5×10^{-5} M Fe($\alpha, \alpha, \alpha, \alpha$ -TpivPP) in THF: (—) under nitrogen, (·····) under oxygen (1 atm), (----) under nitrogen after two oxygenation-deoxygenation cycles.

lead to the Fe(II) complexes with two equivalents of the axial base, a phenomenon discussed previously.¹

Apparently the crystalline lattice of these "picket fence" porphyrins is highly porous permitting facile gas-solid reactions. For example, the solid dioxygen complex **1** loses O₂ *in vacuo* (25°, 12 hr, powdered sample) affording a high spin complex, Fe($\alpha, \alpha, \alpha, \alpha$ -TpivPP)(N-MeIm)₂ (**3**) ($\mu = 4.8$ BM, 25°).⁸ which upon exposure to dry air or O₂ re-forms the diamagnetic starting material **1**. Treatment of either solid **1** or **3** with CO affords the diamagnetic carbonyl complex Fe($\alpha, \alpha, \alpha, \alpha$ -TpivPP)(N-MeIm)(CO), **4** ($\nu_{\text{CO}} = 1965$ cm⁻¹), identical with that isolated from solution.⁹ Similarly CO reacts with the solid diamagnetic Fe($\alpha, \alpha, \alpha, \alpha$ -TpivPP)(N-MeIm)₂, **5**, affording diamagnetic Fe($\alpha, \alpha, \alpha, \alpha$ -TpivPP)(N-MeIm)₂CO ($\nu_{\text{CO}} = 1965$ cm⁻¹), in which one N-MeIm would seem not to be coordinated. However, **5** does not react with O₂—apparently because of an unfavorable equilibrium.

Crystals of the THF complex, **2**, rapidly oxygenated in air (>90% reaction in 3 hr) affording the *paramagnetic* dioxygen complex Fe($\alpha, \alpha, \alpha, \alpha$ -TpivPP)(THF)₂O₂, **6** ($\mu = 2.4$ BM). This *reversible* solid-state oxygenation was followed through several cycles by monitoring changes in magnetic susceptibility. The possibility of irreversible oxidation was eliminated by quantitative conversion of **2** and **6** to the diamagnetic carbonyl complex Fe($\alpha, \alpha, \alpha, \alpha$ -TpivPP)(THF)₂(CO), **7** ($\nu_{\text{CO}} = 1955$ cm⁻¹), by treating the solids with dry CO (1 atm, 6 hr). Moreover addition of pyridine to solid **6**, quantitatively liberated oxygen (0.96 ± 0.05 mol O₂ per mol **6**). Hence the magnetic moment of **6** cannot be explained by partial oxidation or oxygenation. Preliminary Mössbauer spectra for **6** show different isomer shifts δ

(8) A full X-ray analysis has confirmed our early supposition concerning a high spin five-coordinate iron(II) porphyrin having 2-methylimidazole as an axial base: J. P. Collman, J. L. Hoard, G. Lang, T. J. Radonovich, and C. A. Reed, unpublished results.

(9) An X-ray structural analysis by J. L. Hoard is in progress.

(0.33 mm sec⁻¹, 77°K; 0.27, 298°K) and quadrupole splitting ΔE_Q (2.18 mm sec⁻¹, 77°K; 1.90, 298°K) from those found for our diamagnetic dioxygen complex **1**.¹ The major difference between the Mössbauer parameters was the larger ΔE_Q values found for **6**.

Single crystals of **2** were treated with pure O₂ (1 atm, 24 hr) affording **6**. X-Ray analysis showed the complex to retain its crystallinity during oxygenation—the crystals of **2** and **6** having the same cell constants within experimental error ($a = 18.74$, $b = 19.12$, $c = 18.69$ Å, $\beta = 91.6^\circ$, $d_{\text{measd}} = 1.22$, $Z = 4$, $M_{\text{calcd}} = 1240$, $M_{\text{found}} = 1228$). Full crystallographic analyses of the series **2**, **6**, and **7** are planned.

The nature of dioxygen coordination and the role of the two THF groups in the paramagnetic dioxygen complex **6** remains to be clarified by structural analysis and more detailed physical measurements. The structure and physical properties of **6** are of potential significance as they may be related to the dioxygen binding site in the P₄₅₀ cytochrome based monohydroxylases. The latter is thought to have a sulfur base rather than an imidazole as the axial base.¹⁰ Further, these porous crystalline lattices may prove better models for the active hemoprotein sites, in contrast to solution studies, as solvent effects which are not important in the natural systems are eliminated with these solids.

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Iron Carbonyl Complexes from Vinylcyclopropane¹

Sir:

Polycyclic^{2a} and bicyclic^{2b} hydrocarbons containing vinylcyclopropane systems react with iron carbonyl to give both iron carbonyl complexes possessing an intact cyclopropane ring^{2b,3} and compounds resulting from cleavage of a C–C bond of the cyclopropane ring.^{2,3} The thermally unstable iron carbonyl compounds derived from parent vinylcyclopropane (I) in which rotation at the C³–C⁴ bond is possible have so far escaped synthesis. I wish to report the synthesis and successful isolation of these compounds using low temperature techniques. Irradiation of a 1% ether solution of vinylcyclopropane (I) and two equivalents of iron pentacarbonyl with a high-pressure mercury lamp (125 W, 4 hr, filter of Duran glass) at -50° results in the formation of a 10:1 mixture of 4,5- η -vinylcyclopropaneiron

(1) Paper 7 of the series Reactions of Strained C–C bonds with Transition Metals. Paper 6: R. Aumann, K. Froehlich, and H. Ring, *Angew. Chem.*, in press.

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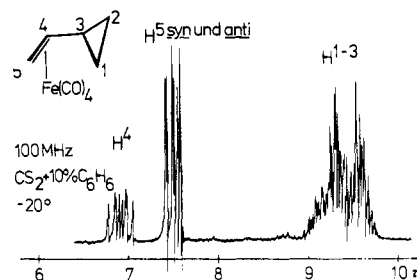


Figure 1. The 100-MHz spectrum of II.

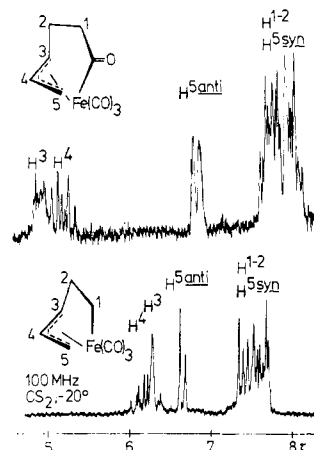
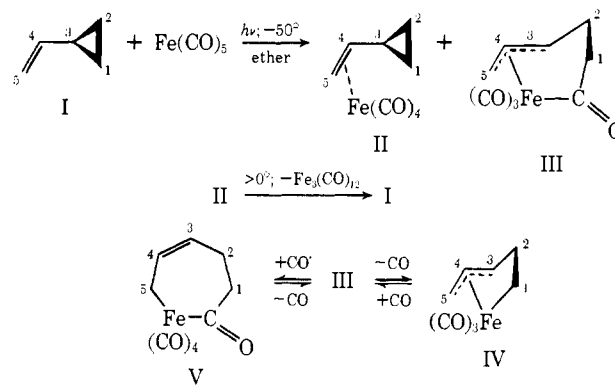


Figure 2. The 100-MHz spectra of III and IV.



tetracarbonyl (II) and 3,4,5,6- η -hex-4-en-3,6-yl-6-one-iron tricarbonyl (III) (total yield 89%). II and III were separated by chromatography under nitrogen atmosphere on a short silica (Woelm neutral) column at -20° using pentane to elute II (80%; yellow oil; decomposition $T > 0^\circ$ to I and $\text{Fe}_3(\text{CO})_{12}$; m/e 236; ir (hexane) $\nu(\text{M})\text{—C}\equiv\text{O}$ 2080, 1999, 1986 cm^{-1} ; nmr⁴ (Figure 1, $\text{CS}_2 + 10\% \text{C}_6\text{H}_6$, -20°) δ 3.10 (m, H-4), 2.6–2.4 (m, H-5 syn, H-5 anti), 1.0–0.3 (m, H-1, H-2, H-3). *Anal.* Calcd for $\text{C}_9\text{H}_8\text{FeO}_4$: C, 45.80; H, 3.42. Found: C, 45.92; H, 3.55.) and ether to elute III (9%; yellow crystals; gradual decomposition on warming; m/e 236; ir $\nu(\text{M})\text{—C}\equiv\text{O}$ (hexane) 2064, 2005 cm^{-1} ; $\nu(\text{C}=\text{O})$ (CH_2Cl_2) 1665 cm^{-1} ; nmr⁴ (Figure 2, CS_2 , -20°) δ 5.15 (m, H-3), 4.89 (ddd, $J = 8.5, 8.5, 12.5$ Hz; H-4), 3.25 (d, H-5 syn), 2.5–2.1 (m, H-5 anti, H-1, H-2). *Anal.* Calcd for $\text{C}_9\text{H}_8\text{FeO}_4$: C, 45.80; H, 3.42. Found: C, 45.69; H, 3.50.)

III can be recrystallized from pentane at -70° and is

(4) Assignments deduced from decoupling experiments and comparison of chemical shifts of related compounds, ref 2 and 3.