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Structural Characterization of a Sterically Encumbered Iron(II) Porphyrin CO Complex

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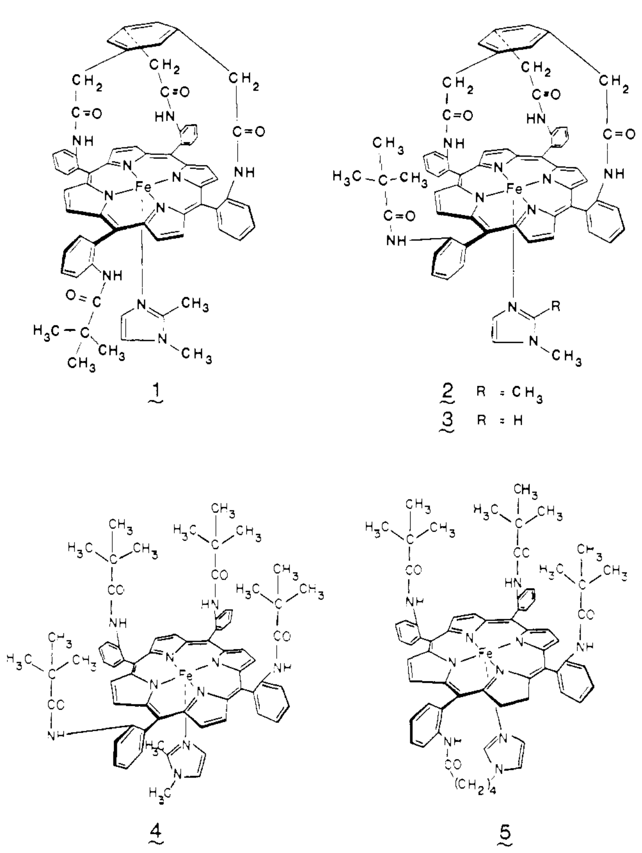

Figure 1. Five-coordinate "pocket" and "picket fence" porphyrins. These are abbreviated as follows: 1, Fe(β-PocPivP)(1,2-Me_2Im); 2, Fe(PocPivP)(1,2-Me_2Im); 3, Fe(PocPivP)(1-MeIm); 4, FeTpivP(1,2-Me_2Im); 5, $FePiv_35CImP$.

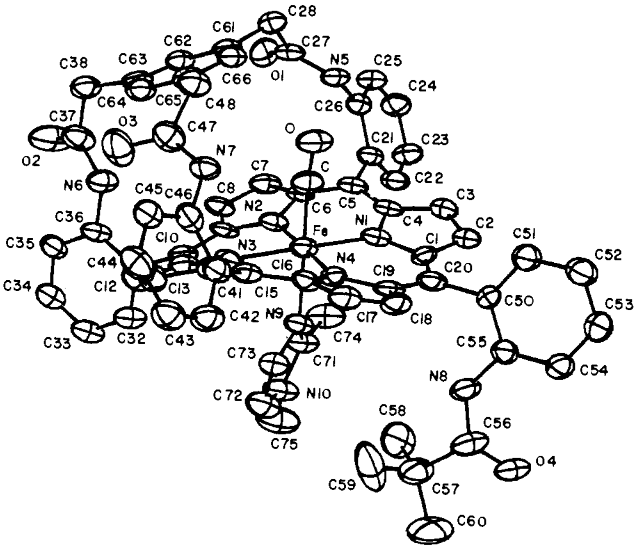

Figure 2. ORTEP representation of Fe(β-PocPivP)(1,2-Me_2Im)(CO), the CO complex of 1. Ellipsoids are scaled to 50% probability level. Important bond lengths and angles are the following: Fe–C = 1.768 (7) Å, C–O = 1.148 (7) Å, Fe–C–O = 172.5 (6)°, Fe–N_{Im} = 2.079 (5) Å, Fe–N = 1.973 (8) Å, C–Fe–N_{Im} = 176.3 (3)°. The Fe atom is 0.001 Å out of the 24-atom least-squares plane toward the CO ligand.

In protein-free CO complexes of simple iron(II) porphyrins crystallographic analyses indicate that the Fe–C–O unit is essentially linear and normal to the mean porphyrin plane.[1-3] In contrast, there are several reasonably well characterized protein crystal structures where the O atom of the bound CO ligand deviates significantly from the normal to the heme plane.[4-11] This deviation has been modeled either as a tilt at the Fe atom or as a bend of the Fe–C–O group at the C atom. At the resolution available for protein structures of this complexity, it is not possible to distinguish between these two alternatives, especially since in some instances, e.g., sperm whale carbonmonoxy myoglobin (Mb(CO)),[6,11] the carbonyl subunit is disordered. These finer points of ligand binding, however, may be important in the sense of O_2/CO discrimination.[7,8,12-17] As a result, in recent years a number of encumbered iron(II) porphyrin model systems have been prepared in an effort to delineate the structural details of small ligand binding.[18-30] Unfortunately, as yet, little accurate X-ray structural information is available for these encumbered model systems.[31,32] We report here the crystal structure of

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Fe(β-PocPivP)(1,2-Me_2Im)(CO), a six-coordinate CO complex derived from **1**, an atropisomer[33] of the five-coordinate "pocket" porphyrin system **2**, prepared[19b] and studied[19c] earlier. The CO ligand is found to be slightly but detectably distorted from linearity. This result, which is in apparent conflict with that obtained from earlier EXAFS work on a closely related complex,[34] provides a structural basis for interpreting the CO binding behavior of the sterically encumbered "pocket" porphyrin model complexes.[19]

The iron(II) "pocket" porphyrin complexes **2** and **3**, first reported in 1981,[19a] were prepared in an effort to probe further the possible role of distal-side steric effects in influencing O_2/CO discrimination. While the "picket fence" porphyrins **4** and **5** present no encumbrance to either CO or O_2 binding,[2,35,36] the "pocket" system was specifically designed to favor the binding of an intrinsically bent group, e.g., Fe–O–O. Analysis of CPK models suggested that the covalently attached benzene ring would be constrained to lie above the plane of the porphyrin macrocycle. Thus O_2 was expected to bind to **2** and **3** in its usual bent fashion while CO would sustain appreciable interactions with the benzene "cap" and be forced to bend or tilt off axis. Considerable discrimination in favor of O_2 was found in these "pocket" systems. As compared to the appropriate "picket fence" control compounds (**4** and **5**),[13,37] the absolute CO affinities, in toluene solution at STP, were reduced by a factor of 7.5 and 70 in the *T* and *R* state "pocket" porphyrin models **2** and **3**, respectively, while the O_2 affinities remained largely unchanged among the pairs **2** and **4**, and **3** and **5**.[19c] Under these conditions, the CO affinity of the "picket down" complex **1** is the same within experimental error (±18%) as that of the "picket up" atropisomer **2**. The "pocket" in **1** thus provides a roughly 1.2 kcal/mol lowering in energy for CO binding as compared to the "picket fence" control **4**.

A drawing of the CO complex of **1** is shown in Figure 2.[38] This structure reveals the bound carbonyl ligand to be slightly but detectably distorted from linearity, being both bent and tilted off the axis normal to the porphyrin plane. The Fe–C–O bond angle is 172.5 (6)° and the off-axis displacements for the C and O atoms of the carbonyl are 0.18 and 0.38 Å, respectively. The modest distortion of the carbonyl subunit is accompanied by considerable ruffling of the porphyrin periphery and significant shifting of the benzene "cap" away from the bound carbonyl ligand.[39] Taken together, these results suggest that the lower CO affinities observed for the encumbered "pocket" porphyrins[19] as compared to the unhindered "picket fence" control systems[13,37] reflect a combination of structural changes involving both localized ligand distortions and overall porphyrin skeletal deformations. These results could have significant implications for the interpretation of protein structures of carbonylated heme systems.

The key structural parameters reported here for the *T* state model Fe(β-PocPivP)(1,2-Me_2Im)(CO) are very different from those obtained from an EXAFS analysis of the *R* state model Fe(PocPivP)(1-MeIm)(CO) and of sperm whale Mb(CO).[34] For instance, from the EXAFS data, the following values were calculated in the model system for the Fe–C–O angle and the Fe–C and Fe–O bond lengths, respectively: 127 ± 4°, 1.94 Å, 2.79 Å;[34] the corresponding values obtained in the present X-ray diffraction study of Fe(β-PocPivP)(1,2-Me_2Im)(CO) are 172.5 (6)°, 1.768 (7) Å, 2.910 (7) Å. We consider these discrepancies to be significant, even though the experiments are not strictly comparable. They were run at different temperatures (4 K vs 110 K), with different atropisomers ("picket" up vs "picket" down), in different phases (glass vs crystalline), and with different axial bases (1-methylimidazole vs 1,2-dimethylimidazole). The first three factors are not likely to be significant; however, differences in the axial base may be important. If distortion is related to lower CO affinity then the *R*-state model could be more distorted. Nevertheless, we consider the differences too great to be accounted for by this argument. In short, we do not find a compelling explanation for the conflict between the EXAFS and X-ray diffraction analyses. We therefore suggest that the EXAFS results[34] on the "pocket" system as well as EXAFS[34] and XANES[41] results on Mb(CO) together with the bent carbonylated heme structures based in part on these results warrant reinterpretation. From available vibrational spectroscopic data a similar suggestion has recently been made.[42]

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(38) Crystal data for Fe(β-PocPivP)(1,2-Me_2Im)(CO)·C_7H_8·0.5C_7H_{16}·2CH_3OH: Monoclinic, $P2_1/n$, a = 17.274 (2) Å, b = 15.315 (2) Å, c = 25.718 (3) Å, β = 95.13 (1)°; T = 110 K. CAD4 diffractometer, Cu radiation, $R(F^2)$ = 0.133 for 8839 observations, 871 variables; $R(F)$ = 0.083 for 5129 with $F_o^2 > 3\sigma(F_o^2)$.

(39) The porphyrin core is S_4-ruffled, with an average deviation of 0.27 Å of atoms from the 24-atom least-squares plane. The average C_m deviation is 0.53 Å while the C_b average is 0.20 Å. Such ruffling is not extraordinarily large.[40]

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Supplementary Material Available: Table S1 giving positional and thermal parameters (3 pages). Ordering information is given on any current masthead page.

Thermal Synthesis and Structural Characterization of $Re(CO)_3(PCy_3)_2$, a Rhenium(0) Radical

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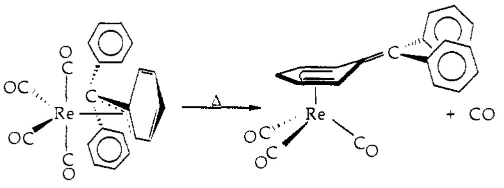
There is considerable interest in radicals of the general type $M(CO)_{5-n}(L)_n$ (M = Mn, Re; L = phosphorus donor ligand) particularly with regard to their structure and reactivity. While the reactivity of these species has been extensively studied, structural data for this class of radicals is limited to inferences from spectroscopic observations. Consistent with theoretical predictions,[1] a C_{4v} square-pyramidal structure for the parent $M(CO)_5$ radicals (M = Mn,[2] Re[3]) has been assigned based on matrix isolation IR studies. In contrast to the facile dimerization of the parent radicals, persistent radicals have been prepared by replacement of two carbonyl groups with bulky phosphine ligands to give the species $M(CO)_3(PR_3)_2$ (M = Mn,[4] Re;[5] PR_3 = bulky phosphine). Such persistent radicals have been well charcterized in solution but have so far not been isolated, presumably due to limitations of the photochemical syntheses employed. We now report an efficient thermal method for the preparation of Re(0) radicals of the type $Re(CO)_3(PR_3)_2$ (PR_3 = bulky phosphine).

We have previously reported the synthesis and properties of $(\eta^3\text{-}CPh_3)Re(CO)_4$ (**1**). Compound **1** reacts with CO to cleanly generate $Re(CO)_5$ radical and triphenylmethyl radical, presumably via the highly unstable σ-bonded intermediate $(CO)_5Re\text{-}CPh_3$.[6] Unfortunately, reaction of **1** with phosphines is limited to those with cone angles[7] less than that of PPh_3 and leads only to diamagnetic products.[8] A more suitable precursor for generating stable radicals can be prepared by thermal decarbonylation of **1** to give $(\eta^5\text{-}CPh_3)Re(CO)_3$ (**2**), which has been fully characterized (eq 1).[9]



1 **2**

(1)

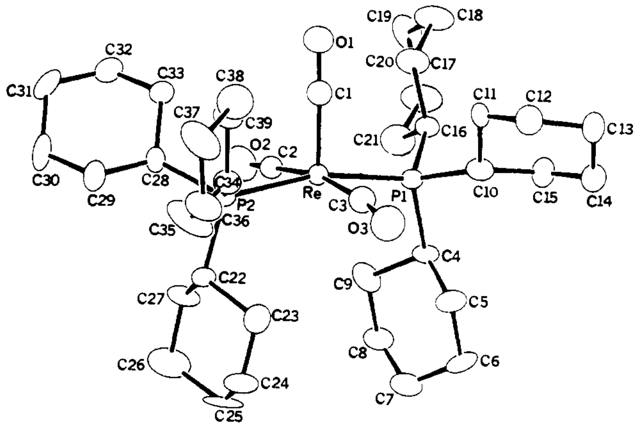


Figure 1. ORTEP projection and labeling scheme for **3**. Atoms are depicted as 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

Compound **2** reacts with excess PCy_3 or $P(i\text{-}Pr)_3$ (benzene, room temperature) to give deep blue solutions of the $Re(CO)_3L_2$ radicals (L = PCy_3, **3**; $P(i\text{-}Pr)_3$,**4**). In each case the presence of radicals was detectable by EPR spectroscopy; the spectra obtained for both complexes were identical with that reported earlier for $Re(CO)_3(PCy_3)_2$.[5] Well formed deep blue needles of **3** suitable for X-ray study precipitated from solution upon standing for several days.[10] The structure of **3** is a distorted square pyramid with $CO_{\text{apical}}\text{-}M\text{-}L_{\text{basal}}$ angles of 95–98° (see Figure 1).[11] Relevant bond angles are C(1)–Re–P(1) = 97.0 (4)°, C(1)–Re–P(2) = 97.3 (4)°, C(1)–Re–C(2) = 95.1 (6)°, C(1)–Re–C(3) = 98.1 (6)°.

Spetroscopic data for **3** are also consistent with the square-pyramidal structure. The infrared spectrum of **3** exhibits one band in the CO stretching region (ν_{CO}(benzene) 1849 (s) cm^{-1}).[12] The electronic spectrum (benzene solution) shows three bands (λ_{max}

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[8] The results of experiments involving reaction of **1** with a variety of phosphines will be reported separately.

[9] A THF solution (4 mL) of **1** (380 mg, 0.702 mmol) was degassed in a tube equipped with a high-vacuum Teflon stopcock and heated in a 90 °C oil bath for 24 h. The product, upon recrystallization from heptane, was isolated in 78% yield (280 mg). Anal. Calcd for $C_{22}H_{15}O_3Re$: C, 51.36; H, 2.92. Found: C, 51.28; H, 3.07. IR (heptane) ν(CO): 2033 (m), 1956 (s), 1944 (s) cm^{-1}. ^1H NMR (acetone-d_6, 298 K, 250 MHz) δ 7.35–7.27 (m, 4 H, free ortho), 7.16–7.06 (m, 6 H, free meta, para) 5.98 (tt, J = 6, 1 Hz, 1 H, coord. para), 5.70 (m, 2 H, coord. meta), 4.89 (dd, J = 8, 1 Hz, 2 H, coord. ortho). An X-ray study of **2** confirmed the structure suggested by the spectroscopic data.

[10] The magnetic susceptibility, measured using the method of Evans (Evans, D. F. *J. Chem. Soc.* **1959**, 2003–2005), corresponds to one unpaired electron.

[11] Summary of X-ray analysis: The structure of **3** was determined by X-ray crystallography using a crystal that measured 0.50 × 0.25 × 0.13 mm. The crystal was mounted in a sealed capillary in a glovebox and care was taken to ensure that the sample did not come into contact with air. Data collection was done at –75 °C. Diffraction measurements were made on a Rigaku AFC5S fully automated diffractometer using graphite monochromated Cu Kα radiation (λ = 1.54178 Å). Preliminary indications of the unit cell based on 25 randomly selected reflections revealed monoclinic symmetry. The data were processed with the high angle cell with the following lattice parameters: a = 10.011 (2) Å, b = 20.277 (4) Å, c = 21.094 (2) Å, β = 92.923 (9)°. The space group, based on the systematic absences: $0k0$, $k = 2n + 1$; $h01$, $h + 1 = 2n + 1$ was uniquely assigned as $P2_1/n$ with one molecule of composition $C_{39}H_{66}ReO_3P_2$ and one molecule of the solvent of crystallization, benzene, forming the asymmetric unit. The volume was 4276 (1) $Å^3$ and the calculated density was 1.41 g/cm^3. There were 6786 unique reflections collected with $2\theta \leq 120°$, of those reflections 3894 (57%) with $I \geq 3\sigma(I)$ were adjudged observed. The data were corrected for Lorentz factor, polarization, and absorption using DIFABS. Correction for absorption by the psi scan method was also tried but the R factor was less satisfactory (R = 0.074 and R_w = 0.089). The structure was solved by locating the position of the rhenium atom using the Patterson function. Iterative use of the WFOURIER option in DIRDIF revealed the entire non-hydrogen structure. The hydrogens were input at their calculated locations. The full-matrix refinement of the non-hydrogen atoms, with the exception of the carbonyl carbons which remained isotropic (the carbonyl carbons C1, C2, and C3 go non-positive definite upon anisotropic refinement), and input of the hydrogen scattering factors resulted in convergence of the crystallographic reliability factor to an unweighted residual of 0.053 and a weighted residual of 0.065. All intramolecular bond distances and angles are within normal ranges.

[12] Previously reported IR spectral data for **3**:[5] ν_{CO}(benzene) 1849 cm^{-1}.

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