

with particular success to C-H bond activation where the formation of stable $\text{Ir}^{\text{III}}\text{-H}$ bonds acts as an additional driving force.⁴⁰ Much remains to be learned about the intimate mechanisms and scope of such reactions, and studies are ongoing in our laboratory which should clarify these questions.

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The "Pocket" Porphyrin: A Hemoprotein Model with Lowered CO Affinity

James P. Collman,* John I. Brauman,* Terrence J. Collins, Brent Iverson, and Jonathan L. Sessler

Department of Chemistry, Stanford University
Stanford, California 94305

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The role of the heme cavity in causing discrimination in the binding of small ligands to hemoproteins is an area of active interest.^{1,2} We report here the synthesis and preliminary binding studies of a new model compound, the "pocket" porphyrin $\text{H}_2\text{PocPivP}$ (Ia). This compound has been specifically designed to investigate the effect of steric interaction on O_2 and CO binding in ferrous porphyrins. Our findings indicate that, compared with open-cavity models such as the "picket fence",^{3,4} the added steric encumbrance of the pocket reduces the CO affinity without substantially changing that⁵ of O_2 .

Structural analyses in carbonylated hemoproteins reveal that the CO unit is bent and/or tilted from the perpendicular to the porphyrin plane owing to interaction with the distal residues⁶ (histidine,^{6a} valine,^{6b} and leucine^{6c} or isoleucine^{6d}). In simple model compounds, the linear FeCO group is normal to the porphyrin plane.⁷ We^{4,5} and others^{8a,9} have proposed that in hemoproteins distortion of the FeCO unit reduces the CO affinity without affecting the O_2 affinity of the intrinsically bent FeO_2 group.^{2a,10,11}

Mutant hemoglobins such as HbZh ($\beta 63\text{His} \rightarrow \text{Arg}$), for which structural studies reveal a more open binding pocket,^{8a} have been investigated as a means of assessing distal steric effects.^{8,12} The

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(3) Abbreviations: $P_{1/2}$ = partial pressure of gas at half-saturation; $M = P_{1/2}^{\text{O}_2}/P_{1/2}^{\text{CO}}$; K_B = equilibrium constant for the binding of a single axial ligand to the four-coordinate heme; 1-MeIm = 1-methylimidazole; 1,2-Me₂Im = 1,2-dimethylimidazole; TPivPP = picket-fence, meso- $\alpha,\alpha,\alpha,\alpha$ -tetrakis[*o*-(pivalamido)phenyl]porphyrinato; $\text{Fe}[\text{Piv}_3(5\text{ClImP})\text{Por}] = \text{meso-}\alpha,\alpha,\alpha$ -tris[*o*-(β -pivalamido)phenyl]- β -[*o*-[5-(*N*-imidazolyl)valeramido]phenyl]porphyrinatoiron(II); Hb (R), Hb (T) = relaxed and tense hemoglobin (human), respectively; Mb = myoglobin (human); HbZh = hemoglobin Zurich.

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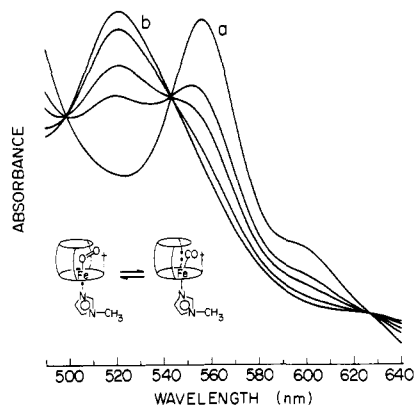
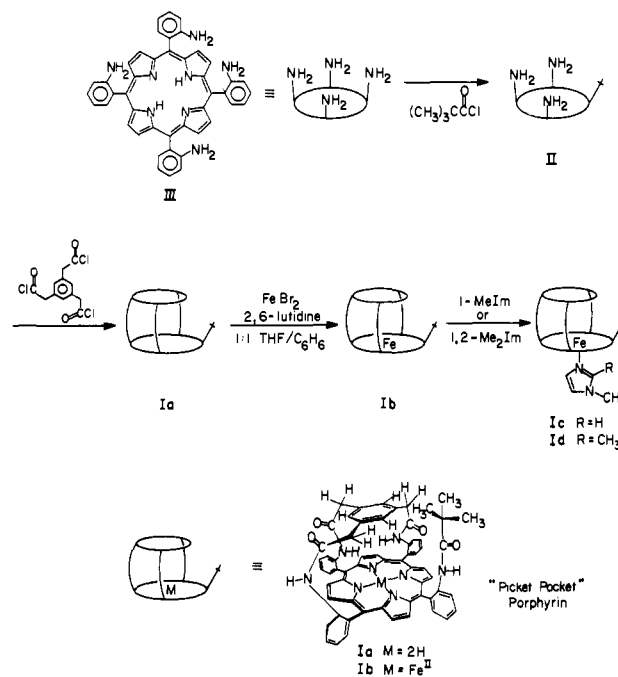


Figure 1. Determination of M value for $\text{Fe}(\text{PocPivP})(1\text{-MeIm})$ (Ic). Ic; ca. 5×10^{-5} M in toluene, 1.0 M 1-methylimidazole, 25.0 ± 0.1 °C. Curve a; under 1 atm of O_2 ; curve b; under 1 atm of CO. Intermediate curves obtained by diluting O_2 with increased quantities of 4.95% CO/N_2 .

Scheme I



CO affinities of this mutant apparently have not yet been directly determined; however, HbZh appears to bind CO more tenaciously than does normal HbA.^{12b,13} Investigations in hemoproteins can be complemented by carefully designed model porphyrin systems which explore particular aspects of ligand-heme binding.^{15,16}

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(13) The O_2 affinity and CO "on" rate have been kinetically determined for isolated mutant chains of HbZh (see ref 12d). An M value for the tetrameric form has also been reported⁸ (Table I). It has been suggested¹⁴ that the lower O_2 affinity could account for the higher M value of HbZh. However, studies with this mutant, in general, and comparisons between single chain and tetramer data, in particular, are complicated by cooperativity, its heterogeneity, and sensitivity toward oxidation. The 10-fold higher CO "on" rate for monomeric mutant chains^{12d} may indicate a higher CO affinity for HbZh. Importantly, the blood of a "patient with HbZh disease was found to contain the abnormal β subunits saturated with CO under conditions where the α subunit and normal β subunits were only occupied to a normal extent by CO " (ref 12a, p 2).

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Table I. O₂ and CO Affinities of Iron Porphyrins and Hemoproteins

| system | $P_{1/2}^{O_2}$ (25 °C), torr | M | $P_{1/2}^{CO}$ (25 °C), torr | ref |
|------------------------------------------------------------|-------------------------------|------------|-------------------------------------------|--------------|
| Mb ^a | 0.65–0.72 | 25–40 | $1.2 \times 10^{-2} - 2.8 \times 10^{-2}$ | 32 |
| Hb (R) ^{a,b,c} | 0.15–1.5 | 200–250 | $1 \times 10^{-3} - 4 \times 10^{-3}$ | 33, 34 |
| Hb (T) ^{a,b,c} | 9–160 | 32–1600 | $1 \times 10^{-1} - 2.8 \times 10^{-1}$ | 33, 34a, 34b |
| Hb Zurich ($\beta 63$ His \rightarrow Arg) ^d | 0.31 ^{c,e} | ≥ 500 | | 8a, 12d |
| FePiv ₃ (SCImP)Por ^d | 0.58 | 26600 | 2.2×10^{-5} | 5 |
| FeTPivPP(Me ₂ Im) ^d | 38 | 4280 | 8.9×10^{-3} | 5 |
| FePocPivP(1-MeIm) ^d | 0.36 | 270 | 1.5×10^{-3} | this work |
| FePocPivP(Me ₂ Im) ^d | 12.6 | 216 | 6.7×10^{-2} | this work |

^a Aqueous, pH 7. ^b Various combinations of 0.1 M NaCl, 0.1 M phosphate, 2 mM inositol hexaphosphate, and 2 mM 2,3-diphosphoglycerate were used. ^c Calculated from reported K (mol⁻¹ L) by using Henry's law constants. ^d Toluene. ^e Abnormal isolated chains, β_{SH}^{ZH} (20 °C).

Iron(II), picket-fence porphyrins mimic the O₂ affinities of Mb, Hb (R), and Hb (T);⁵ however, the binding cavities in these models are not expected to distort CO, and, indeed, their CO affinities are substantially higher than those of⁴ Hb and Mb (Table I). Although solvation and other media effects may play a role in accounting for this difference, we believe that steric effects are primarily responsible.⁵ In benzene or toluene other simple hemes, such as deuteroheme¹⁷ ($P_{1/2}^{CO} = 0.0004$) and "chelated mesoheme"¹⁸ ($P_{1/2}^{CO} = 0.0002$), have CO affinities that are an order of magnitude higher than that of Hb (R). Recently, Romberg and Kassner¹⁹ investigated the NO and CO affinities of horse myoglobin and "chelated protoheme"¹⁸ and found evidence for steric interaction of the bound CO. However, Traylor and Berzins, using the same data, have suggested that distal side effects do not play a substantial role in regulating CO binding in hemoglobin(R): "bending of the FeCO bond does not correlate with CO affinities".¹⁴

Sterically hindered model systems offer the potential for evaluating what effect distortion of the FeCO unit has upon the CO affinity. A Schiff-base model, developed by Busch and co-workers, shows that a tilting and bending of the FeCO structure leads to lowered CO affinity.²⁰ Other model porphyrins designed to simulate a distal steric effect have been reported.^{21,22} To our knowledge, however, the pocket porphyrin Ib is the first *sterically constrained* porphyrin model for which CO and O₂ equilibrium binding data have been reported.

The pocket in I is designed to allow binding of an unhindered, bent FeO₂ unit but to provide steric encumbrance sufficient (as suggested from CPK models) to prevent formation of a linear FeCO moiety. The pocket polarity approximates that of the picket-fence systems, thus allowing useful comparisons to be made.

The synthesis of Ia and Ib is shown in Scheme I.²³ MCD indicates that Ic remains five-coordinate in dilute toluene solutions

(ca. 50 μ M) in the presence of an overwhelming excess (2 M) of nonhindered axial base 1-methylimidazole (1-MeIm),²⁶ demonstrating a steric effect of the pocket ($\mu_{eff} = 5.03 \mu_B$,²⁷ $S = 2$; $\log K_B = 4.5$). While simple ferrous porphyrins are six-coordinated under these conditions,²⁹ the previously reported "capped" heme of Baldwin et al. is likewise five-coordinated.³⁰

In toluene solutions containing the axial base 1,2-Me₂Im, Id is obtained ($\mu_{eff} = \mu_B$, $S = 2$; $\log K_B = 4.7$) from Ib. When excess base (0.1–1.0 M) is present, the oxygen complex of Id is sufficiently stable to allow direct independent determinations of the $P_{1/2}^{CO}$, $P_{1/2}^{O_2}$, and M ($P_{1/2}^{O_2}/P_{1/2}^{CO} = M$) values at 25 °C under equilibrium conditions.³¹ (Experiments were performed using methods reported earlier.^{4,5}) It is gratifying that the three interdependent, but independently measured, determinations of two values (O₂ and CO affinity) match within our current error estimate of 15% (Figure 1.) Binding values of $P_{1/2}^{O_2}$ and M have also been obtained for Fe(PocPivP)(1-MeIm) (Ic) (Table I).

Table I allows a comparison of the $P_{1/2}^{CO}$, $P_{1/2}^{O_2}$, and M values for the picket-fence and pocket porphyrin systems. In the Hb (T) state models the Fe(PocPivP)(1,2-MeIm) (Id) shows a sevenfold lower CO affinity than does Fe(TPivP)(1,2-MeIm). The O₂ affinities are comparable; in fact, that for the pocket porphyrin is somewhat higher. A comparison between the Hb (R) models,

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(31) The formation of these systems is reversible and interchangeable. For instance, under these conditions, bubbling O₂ through the six-coordinate carbonyl complex of Id, Fe(PocPivP)(1,2-Me₂Im)(CO), yields Fe(PocPivP)(1,2-Me₂Im)(O₂); this, in turn, when treated with N₂, yields the five-coordinate complex Id. Similar observations are made with derivatives of the 1-MeIm (Ic) system, concurrent with oxidation. Since axial bases can bind only to the unencumbered side of the pocket heme Ib, sufficiently large concentrations of axial base serve to (i) reduce the concentration of the rapidly oxidized, four-coordinate species^{30b} and (ii) effect regioselective gaseous ligand binding within the pocket, as the axial base competitively inhibits O₂ or CO from binding on the unencumbered side. (Under these conditions, the gaseous ligand affinities of Ic and Id are virtually independent of axial base concentration.) Although extremely sensitive to the presence of impurities (e.g., H₂O or MeOH) which accelerate autoxidation, the half-lives of dilute solutions of Ic and Id in oxygenated solutions of dry toluene (0.1 M in axial base) are ca. 7 and 24 h, respectively, at 25 °C. Even with rigorously purified 1-MeIm (1.0 M), where the formation of μ -oxo is completely suppressed, the half-life of Ic increases to only 36 h. The difference in longevity of Id compared to Ic is not yet understood.

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the "imidazole tailed picket-fence" porphyrin,^{5,35} Fe[Piv₃-(5CImP)Por], and Fe(PocPivP)(1-Melm) (Ic) shows that the CO affinity of the pocket porphyrin is smaller by almost two orders of magnitude. The oxygen affinities are quite similar. These results dramatically illustrate the effect that steric encumbrance can play in regulating CO binding in otherwise similar ferrous porphyrins.

It is tempting to compare the M , $P_{1/2}^{CO}$, and $P_{1/2}^{O_2}$ values for the pocket porphyrin models with those for hemoproteins. The O₂ affinities of both the picket-fence and pocket models are similar to that of myoglobin, but only the sterically encumbered pocket porphyrin has a CO affinity approaching that³⁶ of Hb and Mb. Our findings strongly suggest that distal side steric effects play a role in regulating CO-binding affinities in hemoproteins. We hope to augment this study with structural determinations, allowing us to assess to what degree the observed reductions in CO binding are reflected in tilting and/or bending of the FeCO unit.

Acknowledgment. We thank Kenneth Doxsee for helpful discussions and Professor Daryle Busch (Ohio State) for communicating results prior to publication. Mass spectral data were obtained at the Midwest Center for Mass Spectrometry, The University of Nebraska—Lincoln, and at the Middle Atlantic Mass Spectrometry Laboratory, The Johns Hopkins University, Baltimore, Maryland. Both facilities are supported under the National Science Foundation Regional Instrumentation Facilities Program. Our work was supported by the National Institutes of Health (Grant CM17880) and the National Science Foundation (Grants CHE78-09443 and CHE77-22722).

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(36) The roughly 10-fold higher CO affinity of Hb (R) vs. Mb can make these comparisons difficult. For example, on the basis of model compound behavior Romberg and Kassner¹⁹ infer a distal steric effect in Mb; Traylor and Berzins¹⁴ claim the same data show no steric effect in Hb (R). We hypothesize that the essentials of binding in Hb and Mb are the same, and because of complexities introduced by pH, salts, etc., in Hb, we generally prefer comparisons with Mb. An advantage of model studies such as ours is that they can focus on the effect of one specific variable and yield results without requiring comparisons to natural systems.

Theoretical Challenge to the Experimentally Determined Geometrical Structure of Dimethylsilaethylene

Yasunori Yoshioka, John D. Goddard,[†] and Henry F. Schaefer, III*

Department of Chemistry
and Institute for Theoretical Chemistry
University of Texas, Austin, Texas 78712
and Department of Chemistry
and Lawrence Berkeley Laboratory
University of California, Berkeley, California 94720

Received October 10, 1980

In a recent communication to this journal, Mahaffy, Gutowsky, and Montgomery¹ (MGM) presented an experimental molecular structure for 1,1-dimethylsilaethylene (DMSE), on the basis of their electron diffraction data. Their work was of particular interest, inasmuch as it represented the first experimental structural study of any molecule containing a carbon-silicon double bond.² The most significant finding of MGM was an extremely long Si=C double bond, namely, $1.83 \pm 0.04 \text{ \AA}$, or only 0.08 \AA shorter than their observed Si-C single bond, $1.91 \pm 0.02 \text{ \AA}$. For comparison, the typical C=C double bond (1.35 \AA) is 0.19 \AA

* Address correspondence to Department of Chemistry, University of California, Berkeley, CA 94720.

[†] Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R6.

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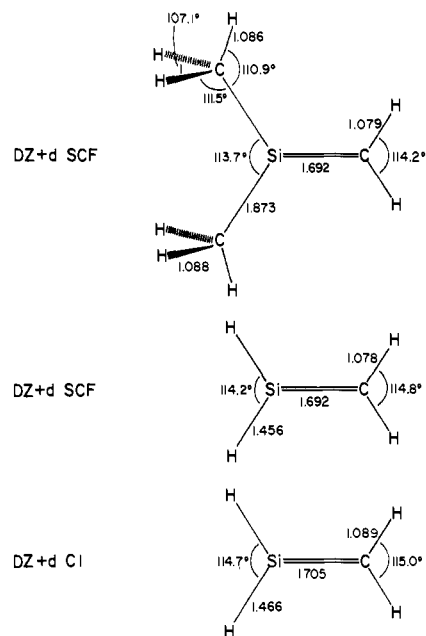


Figure 1. Theoretical equilibrium geometries for 1,1-dimethylsilaethylene (DMSE) and the parent unsubstituted silaethylene.

shorter than the typical C-C single bond (1.54 \AA). If this long Si=C distance of 1.83 \AA is correct, one would likely infer that the π bond in DMSE is exceptionally weak.

MGM noted an apparent discrepancy between theory and experiment. For the parent unsubstituted silaethylene $H_2Si=CH_2$, MGM cited about a dozen quantum mechanical predications^{3,4} of the Si=C bond distance, and these vary from 1.63 \AA to 1.75 \AA . Of these the most complete study⁴ was carried out at the self-consistent-field (SCF) level of theory and employed a double-zeta (DZ) basis set of contracted Gaussian functions. Since the predicted Si=C bond distance of 1.715 \AA is so much less than the experimental DMSE value of 1.83 \AA , one is logically left with three alternatives: (a) the two methyl substituents greatly increase the Si=C distance in DMSE relative to the parent $H_2Si=CH_2$; (b) the theoretical predictions for the Si=C bond distance in $H_2Si=CH_2$ are all incorrect; (c) the experimental Si=C distance is DMSE is in error. Of course it is also possible that some superposition of these three effects might lead to the 0.115-\AA gap between theory for $H_2Si=CH_2$ and experiment for DMSE.

In the present communication we report results which drastically reduce the possibility that points (a) or (b) above could be responsible for the discrepancy between theory and experiment. First, an explicit optimization of the geometrical structure of DMSE has been completed. Furthermore, this equilibrium geometry was determined at a level of theory higher than any previous structural optimization of even the parent $H_2Si=CH_2$. To the double-zeta (DZ) basis⁵ used by Hood and Schaefer⁴ was added a set of d functions on each heavy atom. These polarization functions were assigned orbital exponents $\alpha = 0.75$ (carbon) and $\alpha = 0.60$ (silicon). The designation of this DZ + d basis set is then Si(11s7p1d/6s4p1d), C(9s5p1d/4s2p1d), and H(4s/2s).

The predicted theoretical structure for DMSE is seen in Figure 1. The relative orientations of the two methyl groups was arbitrarily chosen to maintain point group C_{2v} , but the barriers to

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