

and hydrazine, formed were measured quantitatively.²² The evolved gas consisted of N₂ together with some H₂. We have not detected the presence of H₂ in similar reactions carried out with *trans*-Mo(N₂)₂(triphos)(PPh₃). The yields of NH₃ and N₂H₄ are given in Table I. In all cases the total nitrogen balance (including N₂ gas) exceeded 78%.

It is interesting to note that the highest yield of ammonia was obtained from the reaction with **1F**, the iron-containing phosphine ligand complex. This is the first Fe-Mo-N₂ complex to produce either ammonia or hydrazine under any conditions. The highest

yield of hydrazine was obtained when **1A** was treated with HCl (40 mol)/toluene at 70 °C for 39 h: 0.36 (NH₃), 0.48 (N₂H₄). The highest overall conversion to reduced nitrogen (in the combined form of NH₃ and N₂H₄) was also in this latter reaction. In tetrahydrofuran solution **1A** (HBr) and **1E** (HCl) gave little ammonia and no hydrazine, and **1D** (HCl) afforded all nitrogen as N₂.

Further work is in progress to expand the range of mono-N₂ complexes and isolate intermediates in the ammonia- and hydrazine-forming reactions.

Acknowledgment. This work was supported by the National Science Foundation through Grant CHE83-05478.

(22) For details of analytical procedures see ref 5a.

Artificial Allosteric Systems. 3. Cooperative Carbon Monoxide Binding to Diiron(II)-Gable Porphyrin-Diimidazolylmethane Complexes

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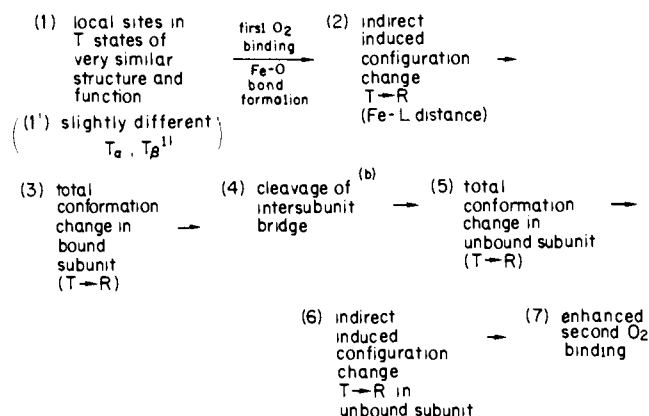
Abstract: A gable porphyrin-diiron(II)-bridging ligand complex was investigated as an artificial allosteric system of a hemoglobin type, to which CO binds cooperatively. For bridging ligand concentration ranging from 7.7×10^{-5} to 7.7×10^{-3} M, CO binds to the complex with remarkable cooperativity. The maximum Hill coefficient observed was 1.9, with *N,N'*-diimidazolylmethane as a bridging ligand, while with 4,4'-dipyridylmethane the maximum Hill coefficient was observed to be 1.4. This cooperativity can be interpreted by a model in which binding of a first CO molecule converts the artificial system from a hexacoordinate T-T state to a hexacoordinate R-R state with one free and one CO bound subunit. However, at low ligand concentration, cooperativity was not observed, suggesting that CO binding proceeded with retention of the T-T structure. At the ligand concentration of 0.15 M, cooperativity was not observed due to the fact that the CO free artificial system is present in the hexacoordinate R-R state. We interpreted the observed allosteric effect by a sequence of events characteristic of the native allosteric binding system—T-T states for the free system, direct structure change caused by the first CO binding, indirect induced structure change, intersubunit bond cleavage, transmission of induced structure change, and enhancement of the second CO binding.

The concept of allosterism¹ in biological phenomena is now reasonably well understood, although detailed studies have been limited to a few cases such as cooperative O₂ or CO binding to hemoglobin.² The simplest mechanistic interpretation of the cooperative O₂ binding is as follows: a conformational change induced at one of the subunits in the tetrasubunit-protein by the first O₂ binding causes a remarkable structure change in the unit linking two (or more) active sites of very similar local structures. Then the structure change is further transferred to the second (and/or third, fourth) active site(s) to increase the second (etc.) O₂ binding capacity.^{1,2} The mechanistic profile is depicted in a somewhat specific and detailed fashion in Scheme I. Interestingly, it was recently found that the generalized mechanism also operates in certain entirely artificial systems³⁻⁷ as shown in Table I. Thus, design of *artificial allosteric molecules or systems* is emerging as a new concept.⁵ However, only very limited examples are available at present, and further study is necessary to understand allosterism in detail.

In this article, cooperativity in CO binding to Fe(II)-gable porphyrin-bridging ligand complex is described as the first

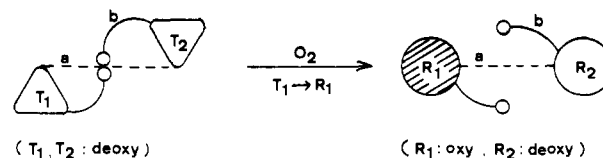
well-defined example of artificial allosteric CO binding compounds.^{4a}

Scheme I. Analysis of Allosteric O₂ Binding by Hemoglobin¹⁰



^a Concerning only "homotropic effects";¹ heterotropic effect,

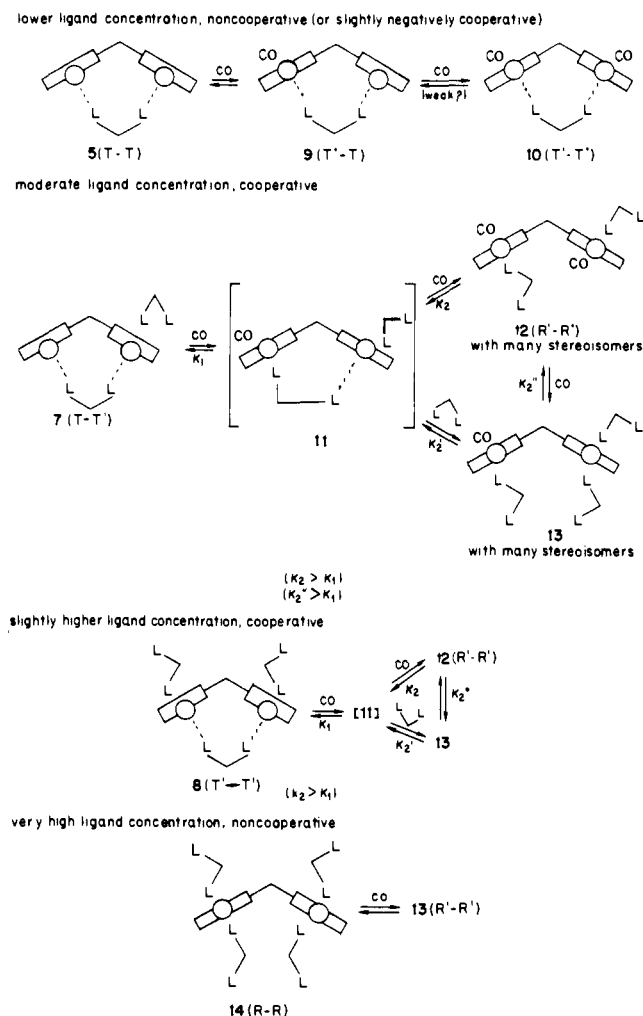
allosteric system A $\xrightarrow{\text{effector}}$ allosteric system B, is not discussed here. ^b Schematic representation may be as follows;



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Table I. Artificial Allosteric Systems

system	no. of sites interacting	n_{max}	function	subunit	type of information transmittance	allosteric requirements (Scheme I) satisfied
Rebek	2	1.15	metal binding	crown ether	change of dihedral angle of biaryl group	1, 3, 5, 7
Traylor	2	2.1(?)	CN ⁻ binding	Fe(II)-porphyrin	aggregation of monomer	1, 5, 7
Tabushi	2	1.5	O ₂ binding	Co(II)-porphyrin	cleavage of bridging ligation	1, 2, 4, 6, 7

Scheme II

Results and Discussion

Cooperative CO Binding to Gable Porphyrin-Fe(II)-Bridging Ligand Complexes. Gable porphyrin-iron(II) complex, **2a**, was prepared from gable porphyrin⁶ **1**, as reported elsewhere.⁷ Appropriate difunctional bases such as **3** and **4** were found to bind to the metal complexes strongly and stereospecifically (as seen in the previous system)^{3,6,7} to form *artificial allosteric molecules*. In contrast to ordinary Fe(II)-porphyrin complexes, formation of the pentacoordinate complex (**5**) from **2a** and a bridging ligand is favored over the hexacoordinate complex (**6**) at a bridging ligand concentration of 4×10^{-5} – 6×10^{-5} M. Due to the entropically enhanced bridging ligation, K_{penta}/K_{hexa} is 25 for gable-Fe but 0.11 for TPP-Fe; in the latter, the hexacoordinate complex is formed predominantly even at low ligand concentrations.⁸ Therefore, the predominant species in the present system are **5**, **7**, and **8** (see Scheme II at a bridging ligand concentration of 4 – 6×10^{-5} , 1 – 3×10^{-4} , and 1×10^{-3} – 0.01 M, respectively). Binding of CO to the artificial allosteric molecules **5**, **7**, and **8** was studied by measuring changes in electronic spectra. Sigmoid curves are

Table II. Observed Hill Coefficients for CO Binding^a

[DIM] (M)	6.0×10^{-6}	7.7×10^{-5}	7.7×10^{-4}	7.7×10^{-3}	0.15
n (± 0.1)	0.9	1.9	1.8	1.16	1.0
P_{50} (± 0.02) (mmHg)	0.12	0.29	0.40	0.66	7.60

^a [Fe(II)₂-gable] = 6.0×10^{-6} M, 18 °C in DMF. See ref 15.

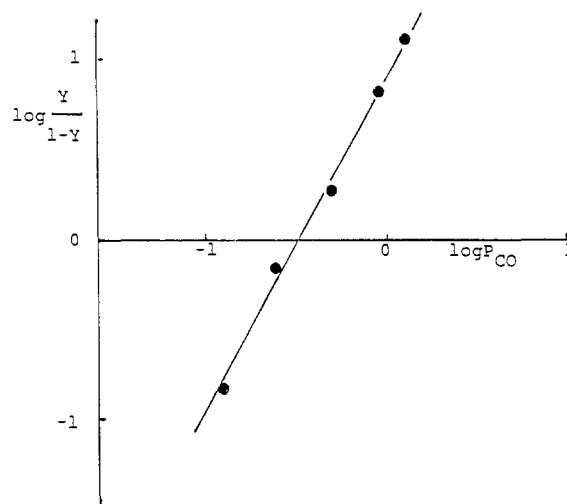


Figure 1. Hill plot for CO binding to Fe^{II}₂-gable porphyrin. Conditions: [Fe(II)₂-gable] = 6.0×10^{-6} M, [DIM] = 7.7×10^{-5} M at 18 °C in DMF.

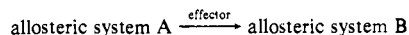
obtained by plotting CO bound vs. CO pressure. From the observed sigmoid relationship, Hill coefficient n and half saturation pressure P_{50} are estimated (Table II) by plotting $\log Y/(1-Y)$ against $\log P_{CO}$ (see Figure 1).

Effect of Ligand Concentration on Cooperativity. The observed sigmoidness of the CO adsorption curves (and the Hill coefficient) is highly dependent on the bridging ligand concentration. As shown in Table II at the very low concentration of the bridging ligand, cooperativity disappears ($n \approx 1$) or even becomes slightly negative.⁹ In the region, the predominant species is **5**, assigned by the electronic spectrum titration⁷ (at 5×10^{-5} M of the bridging ligand concentration, population of **5** is calculated as 71%). At the higher ligand concentrations, observed cooperativity slowly increases with the ligand concentration until a rather flat maximum is attained ($n = 1.9$ at 7.7×10^{-5} M ligand concentration). At the high ligand concentration (0.15 M), cooperativity actually disappears.

The observed dependence of the cooperativity on the bridging ligand concentration is similar to that for O₂ binding to gable porphyrin-Co(II) complex,³ in spite of the fact that pentacoordinate is predominant for the Co(II) complex while hexa-

(9) Considering experimental errors involved, observed slightly negative cooperativity is not quite certain.

(10) Concerning "homotropic effects"; heterotropic effect



are not discussed here.

(11) This makes allosteric effect much larger.¹²

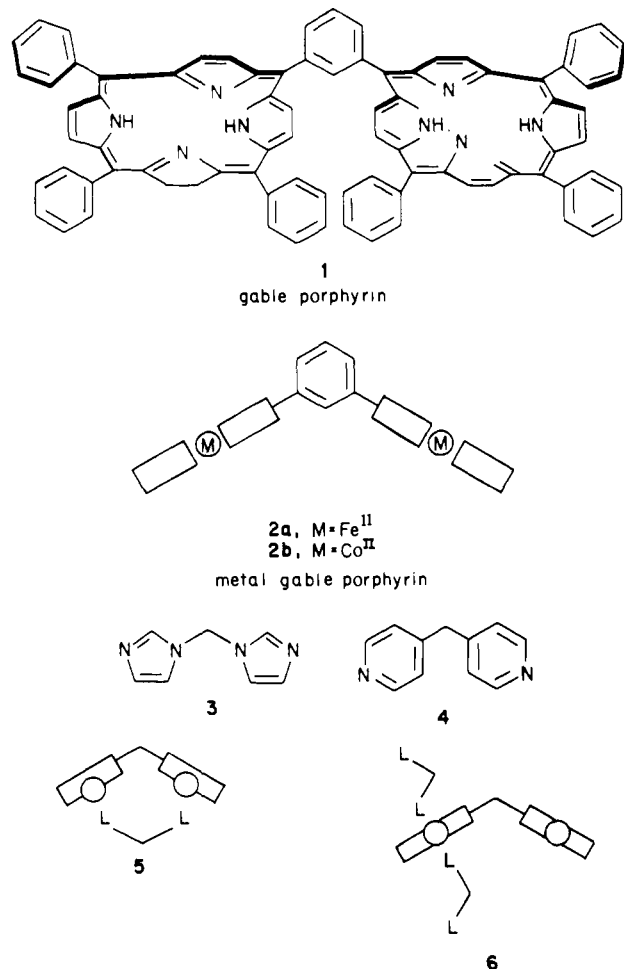
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coordination is competitive to pentacoordination for the Fe(II) complex. This fact suggests that the common structural unit, a metal-gable-bridging ligand complex, is responsible for the cooperative binding of O₂ and CO in both cases.

Nature of CO Complexes. Evidence Supporting Formation of T-Structure. By use of X-ray, EXAFS, MCD, NMR, and Raman spectra,¹⁴ it is well established that a bulky ligand such as 1,2-dimethylimidazole binds to a porphyrin-Fe(II) to form a stable pentacoordinate complex in T-structure. The present bridging ligand-gable porphyrin-Fe(II) complex shows a blue shift in electronic spectra similar to (even larger than) 1,2-Me₂Im from normal absorption of Fe(II)-porphyrin-ligand complexes (in the R-structure). These observations strongly suggest that the present bridging complex is in a T-structure. The CO binding to gable-Fe(II)-bridging ligand complex, forming the hexacoordinate complex, is demonstrated by the appearance of a strong new characteristic absorption at 419 nm, together with moderate absorptions at 508–512 and 539–543 nm when 38 mmHg of CO is applied to the complex (Figure 2). This characteristic absorption of the gable-CO complex shows a blue shift (6–8 nm) from the corresponding R-state models (see Table III), strongly suggesting that it is still in the T-state. Porphyrin-Fe(II)-1,2-Me₂Im-CO also shows a remarkable blue shift compared with the corresponding less bulky base complexes as shown in Table III. Therefore, "tension" in the gable-CO complex seems to be

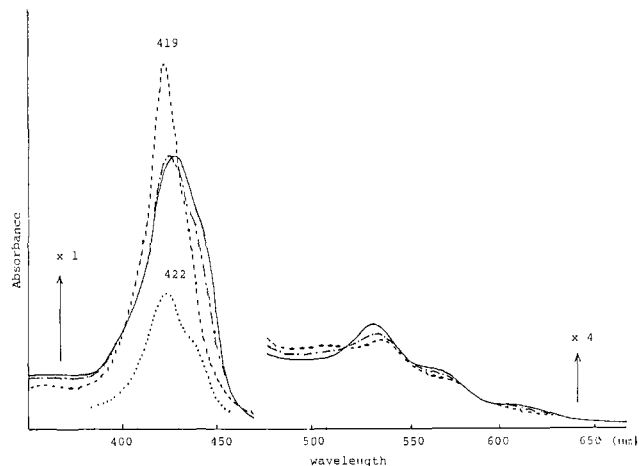


Figure 2. Visible spectral change for CO binding to Fe^{II}₂-gable (DIM) complex in benzene. P_{CO} (mmHg); (—) 0; (---) 0.12; (···) 38; (-·-·) Difference spectrum (---) - 1/2 (—). Conditions: [DIM] = 6.0×10^{-6} M, [Fe(II)₂-gable] = 6.0×10^{-6} M.

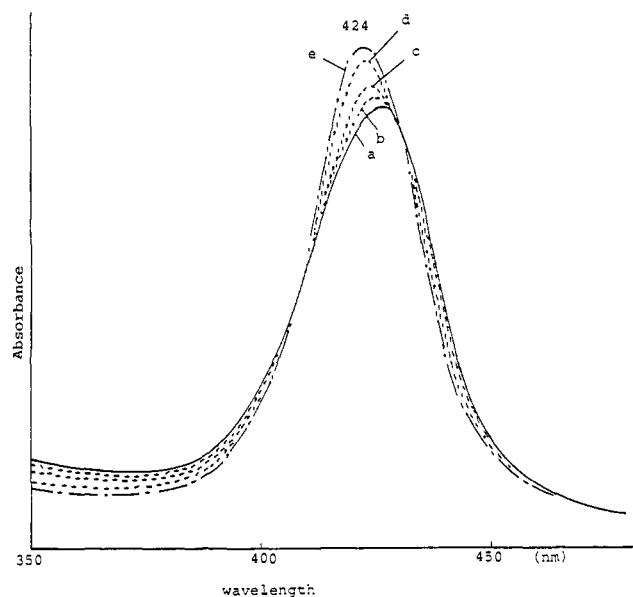


Figure 3. Visible spectral change for CO binding to T-state hexacoordinate complex 8. Conditions: [DIM] = 4.5×10^{-3} M, [Fe(II)₂-gable] = 6.0×10^{-6} M. P_{CO} (mmHg): a. 0.12 b. 0.36 c. 0.52 d. 1.4 e. 2.8.

Table III. Visible Maxima of Fe(II)-Porphyrin-Carbonyl Complexes of T- and R-State Model in Benzene

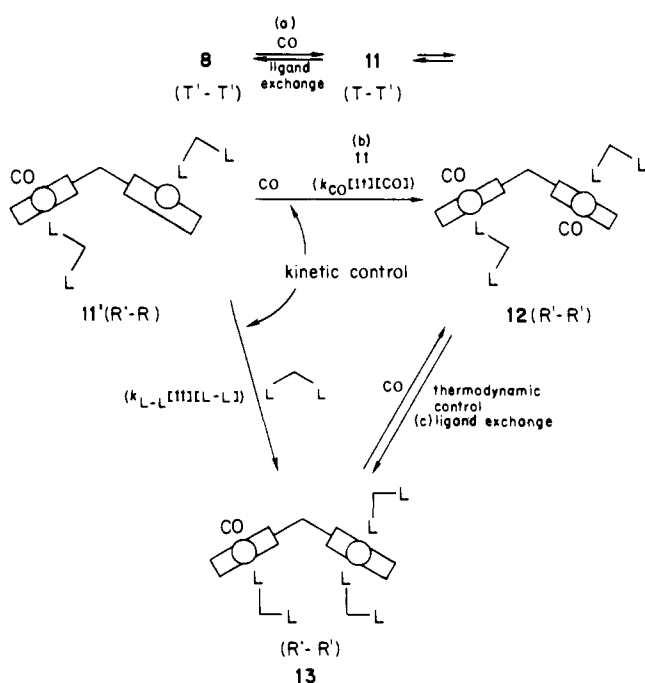
porphyrin	axial ligand	Soret	Q	ref
TPP	—, CO	418	516, 551, 590, 608	13
	1-MeIm, CO	427	542, 580	13
	1,2-Me ₂ Im, CO	424	543, 582	this work
gable	—, CO	417	514, 551, 589, 609	this work
	1-MeIm, CO	425	544, 579	this work
	1,2-Me ₂ Im, CO	422	538, 582	this work
	DIM, CO	419	512, 542, 590	this work
	(6.0×10^{-6} M)			
	DIM, CO	424	545, 580	this work
	(4.5×10^{-3} M)			

stronger than that induced by 1,2-dimethylimidazole based as estimated from electronic spectroscopy (see Table III).

At low DIM concentration ($4-9 \times 10^{-6}$ M) where the pentacoordinate state 5 is predominant, the first CO binding ($P_{CO} = 0.19-0.40$ mmHg) caused a remarkable decrease in the concentration of the T-state five-coordinate complex (427, 435, 534, 566, and 609 nm) together with a remarkable increase in the absorptions at 420–425, 508, and ca. 540 nm (see Figure 2). The

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Scheme III



^a Key: (a) strain increase, (c) strain free [(c) is more favorable than (a)]; (b) no cleavage M-L bond, strain free [(b) is much more favorable than (a)].

latter two new absorptions are ascribed to the T-state CO hexacoordinate complex. The new band in the Soret region is also ascribed to the T-state CO complex by taking the difference spectrum (Figure 2). Therefore, it is concluded that free T-state complex gives the T-state-CO complex in spite of the fact that "tension" in the latter may be increased. It is mainly due to the entropically enhanced ligation capacity of the present bridging ligand. The T-state CO-ligand hexacoordinate complex is still more stable than the ligand free CO pentacoordinate complex. And under this condition, second CO binding is not enhanced by the first CO binding.

However, at the moderate ligand concentrations where cooperativity in the CO binding is remarkable, structure change from the T- to the R-form is strongly suggested by the electronic spectroscopy. In the absence of CO, the predominant form, hexacoordinate complex **8** (ca. 96% at 4.5×10^{-3} M ligand concentration), shows a clear blue shift of 4.5 nm (424.5 compared with the corresponding R-state hexacoordinate complex with *N*-methylimidazole absorbing at 429 nm), suggesting that **8** is in the T form. In the presence of 150 mmHg CO, hexacoordinate CO-ligand complex absorbs at 424 and 545 nm, very similar to the gable-Fe(II)-CO-1-MeImd R-state complex¹³ (see Table III). These observations indicate that the hexacoordinate CO ligand complex takes the R-form as shown in **12** (or other stereoisomers). This contrasts with the CO binding to pentacoordination ligand complex **5** discussed above. At intermediate CO pressures (0.2–5 mmHg), continuous spectral change from **8** to **12** is observed (see Figure 3). Where **7** is the most populated (50% at 2×10^{-4} M ligand concentration), similar spectral change is observed, again suggesting that the structure change from the T- and the R-form takes place.

The dramatic change in the CO binding mechanism from the low ligand concentration (T → T) to the moderate ligand concentration (T → R), as discussed above, may be due to the presence of the ligand in excess capable of ligand exchange with the bridging ligand which is experiencing increased tension by CO binding via Fe(II) movement to planar position. Thus, the first CO binding leads to the cleavage of the "intersubunit" bond (bridging ligation) to give the stable R-form (see Scheme III).

Total Mechanism Interpreting Cooperative CO Binding to Gable-Fe(II)-Bridging Ligand Complexes. The above model thus

correlates the cooperativity observed for CO binding to the gable-Fe(II)-bridging ligand complex with the local structure change in the "subunits" of the total molecular system. At the moderate to high concentration (7.7×10^{-5} – 7.7×10^{-3} M) of *N,N'*-diimidazolymethane, the original local T-structure is converted to the R-structure on CO binding as discussed above. In the ligand concentration range, the observed cooperativity coefficient *n* changes depending on the original population of T-deoxy local structure (see Table III). At too high ligand concentration, *n* approaches unity (no cooperativity), because the population of subunit in the deoxy T-form decreases due to predominant formation of R-state complex **14** with 4:1 ligand/gable ratio. At low concentration of the ligand, bridging structure (via "intersubunit" bond in Scheme II) is not cleaved on the CO binding, resulting in noncooperative CO binding (T to T). These mechanisms of cooperative and noncooperative CO binding are summarized in Scheme II.

Local structure change from T to R in the "subunit" on the CO binding in the presence of the reasonably large excess ligand is in an interesting contrast to the structure retention of the bridging on CO binding at the low ligand concentration. This situation may be interpreted by the favorable ligand exchange at the subunit (Scheme II). The proposed kinetically competitive CO/ligand binding may be supported by the reported rate constants¹⁴ for CO/ligand binding to deuteroporphyrin-Fe(II)-L, where $k_{\text{CO}} = 5.7 \times 10^8 \text{ s}^{-1} \text{ M}^{-1}$ and $k_{\text{ligand}} = 9 \times 10^8 \text{ s}^{-1} \text{ M}^{-1}$, which gives the expected rate ratio, $V_{\text{ligand}}/V_{\text{CO}} = 6$, at 2 mmHg CO and 7.7×10^{-5} M of the ligand.¹⁴

The present allosteric system is the first well-defined example of cooperative CO binding to Fe(II)-porphyrin moiety, in which the possibility of hexacoordination makes the situation much more complex than the Co(II)-gable-O₂ system. Nevertheless, a sequence of events characteristic of allosteric binding as shown in Scheme II are successfully modeled: (1) two subunits in the T-states (the first CO binding induces direct structure change) (L₆-M to CO-M), (2) indirect induced structure change (in CO L₅, T → R), (4) cleavage of the "intersubunit" bridge, (6) indirect induced structure change (M-L₅ change in the other subunit, T → R), (7) enhanced second CO binding (see Scheme II). However, other important interactions especially conformation changes ((3) and (5)) are not modeled here. We are now studying a new allosteric system involving conformational change.

Experimental Section

Instruments and Apparatus. Electronic spectra, infrared, and H NMR spectra were recorded with a Union SM-401 spectrophotometer, a Hitachi 215 infrared spectrophotometer, and a JEOL PMX-60 spectrometer, respectively.

The amounts of O₂, N₂, and CO were determined by gas chromatography (Shimadzu GC-4C), by using a molecular sieve 13X column (Yanagimoto, 1 m) with He as a carrier gas at 35 °C.

Materials, General. Commercially available chemicals were used directly unless otherwise noted. DMF was stirred over powdered BaO (5 g/1 L) for 12 h and fractionally distilled under reduced pressure (a glass helix column; 1 cm o.d. × 30 cm, reflux ratio 4:1, 16–17 °C/5 mmHg) just before use. 1-MeIm and picoline were dried over KOH, distilled under vacuum, and stored under Ar. *N,N'*-Diimidazolymethane and γ,γ' -dipyridylmethane were prepared according to the literature.^{15,16}

Co(II)₂-gable and Fe(III)₂-gable porphyrins were prepared by the methods described before.⁷ Fe(II)-gable porphyrin was prepared by the reduction of the corresponding Fe(III) complex as described previously.⁷ N₂ and Ar gas were of high-quality grades (Kyoto-Teisan, containing less than 2.0 ppm oxygen). Gaseous oxygen was purchased from Kyoto-Teisan. Gaseous CO was purchased from Kyoto-Teisan and was passed through a Na₂S₂O₄-KOH-anthraquinonesulfonate mixture or MnO column to remove dioxygen.

All manipulations of air-unstable compounds such as Fe(II)-gable and Co(II)-gable porphyrins were performed in the Vacuum Atmospheres drybox filled with oxygen-free (MnO treatment) dry argon.

Base Equilibria Measurements. Equilibrium constants were determined by spectrophotometric titration spectra. An aliquot of deoxy-

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generated DIM, either neat or diluted with DMF, was added to a DMF solution (1 mL) of the metalloporphyrin under Ar and the total volume was adjusted to 5 mL. The temperature of the porphyrin solution was maintained at 18 ± 0.5 °C. In general, the spectra were recorded at the 350–750 nm range.

Carbon Monoxide Affinity Measurements. The experimental procedures used for these studies were similar to those described before for oxygen affinity measurements, but special precautions were necessary to avoid air-oxidation of the Fe(II)-porphyrins. Because of the very high oxygen affinity of the Fe(II)-porphyrins in solution, Fe(II)-porphyrins were freshly prepared in a carefully deaerated condition and used immediately. In a typical experiment, a mixture of a 5 mL benzene solution of 2.0 mg (1.6×10^{-6} mol) of Fe(III)₂-gable-Cl₂ and 0.5 mL of aqueous buffer solution (0.1 M phosphate, pH 6.86) was deoxygenated by three freeze-pump-thaw cycles (2×10^{-6} torr). To the mixture 20 mg (1.1×10^{-4} mol) of solid Na₂S₂O₄ was added, and the mixture was stirred vigorously for 30 min. The resulting orange-red solution of crude bisferrous gable porphyrin was dried over anhydrous Na₂SO₄ and applied to a specially prepared alumina column (vide infra). The column was eluted with oxygen-free methanol (1%) in benzene to afford the fractions containing Fe(II)₂-gable alone. The fractions were combined and evaporated to dryness, and the residue was redissolved in 10 mL of deoxygenated DMF. Into the 1-cm quartz cell was placed 0.1 mL of the stock solution of Fe(II)₂-gable. To the solution, 3 mL of deoxygenated DMF containing an appropriate amount of an axial ligand was added. Into the quartz cell was introduced by means of a vacuum line a premixed Ar-CO gas, deoxygenated by either procedure A or procedure B described below, by a vacuum line into the quartz cell. Then the mixture was kept standing at the fixed temperature until the equilibrium was attained, as indicated by reaching constant absorbance. This procedure was repeated several times under different CO partial pressure. The slow equilibration is inevitably accompanied with some minor O₂ oxidation, leading to the Fe(III)-porphyrins. Concentration of Fe(III) species was determined spectrophotometrically at 630 nm absorption. Data were only recorded when less than 5% of total Fe-porphyrin was converted to the corresponding Fe(III) complex.

Deoxygenation Procedure A. MnO¹⁷ was freshly prepared by pyrolysis of Mn(C₂O₄) at 350 °C, 1×10^{-2} torr. The freshly prepared MnO was packed into a column (1 cm o.d. \times 20 cm) and a mixed Ar-CO gas was introduced.

Deoxygenation Procedure B. A THF solution of sodium anthracenide (0.01 M) was prepared¹⁸ in a vacuum line. Mixed Ar-CO gas was bubbled through the solution by applying a vacuum.

For the present deoxygenation purpose, the MnO method was found more effective than the sodium anthracenide method.

Preparation of Alumina Column. A suspension of 4 g of neutral alumina (Wolem activity I) and 0.15 g of Na₂S₂O₄ in 20 mL of deoxygenated H₂O was stirred for 30 min under Ar. Alumina was collected by decantation, washed with deoxygenated H₂O (6×10 mL), and dried in vacuo (1×10^{-3} torr, at room temperature) for 12 h. The pretreated alumina was placed into a column and used for the purification of bisferrous gable porphyrin. To remove trace oxygen adsorbed on alumina, 1 mL (ca. 1×10^{-4} M) of benzene solution of bisferrous gable porphyrin was passed through the column by use of benzene-methanol (100:1) as an eluent, just before use. All of the procedures above were carried out in a carefully deoxygenated glovebox.

Acknowledgment. We are grateful to Professor J. Sessler for his helpful discussion. We are also grateful to Mr. Mano for his kind assistance in some of the spectroscopic measurements.

Registry No. Fe(TPP)(1,2-Me₂Im)(CO), 80975-58-2; (gable)[Fe(CO)]₂, 97467-40-8; (gable)[Fe(1-MeIm)(CO)]₂, 97467-41-9; (gable)[Fe(1,2-Me₂Im)(CO)]₂, 97467-42-0; (gable)[Fe(CO)]₂(μ-DIM), 97486-02-7; (gable)Fe₂, 96481-89-9; (gable)[Fe(1-MeIm)]₂, 97486-03-8; (gable)[Fe(1,2-Me₂Im)]₂, 97467-43-1; (gable)Fe₂(μ-DIM), 97467-44-2; CO, 630-08-0.

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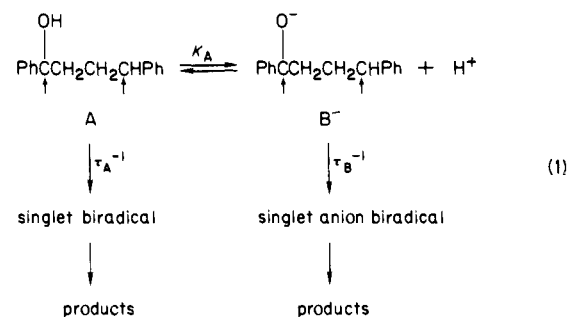
pH Dependence of the Lifetime of a Norrish II Biradical

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Abstract: The transient spectroscopy of γ-phenylbutyrophenone in a 2:1 (v/v) methanol:water mixture has been studied as a function of pH. The lifetime of the Norrish II 1,4-biradical shows an excellent titration curve. The moderately strongly absorbing acidic form of the biradical has a lifetime of 125 ns, with λ_{max} of the difference spectrum with starting material at 320 nm. The strongly absorbing basic form has a lifetime of 62 ns and λ_{max} 325 nm. The pK_a in the mixed solvent is 11.8. The pK_a in pure water, based on solvent dependence of pK_a values for phenols of similar acidity, is estimated as 10.2 ± 0.2, essentially identical with a value reported for the acetophenone ketyl monoradical.

The spectra, lifetimes, and properties of Norrish II biradicals are increasingly well known.¹⁻⁴ The OH group of the triplet biradical appears to be quite important in determining its lifetime. For example, solvent dependence of lifetime correlates with H-bond accepting ability of the solvent,⁵ with the biradical showing much longer lifetimes in more basic solvents such as methanol, pyridine, and HMPA than in, e.g., hydrocarbons. We now report the pK_a of the biradical derived from γ-phenylbutyrophenone and the effect of deprotonation of the OH group on the lifetime of the biradical.



Experimental Section

The laser flash photolysis studies were performed on a Q-switched Nd-YAG laser (fourth harmonic, 266 nm, attenuated to ca. 10 mJ per pulse, 10 ns fwhm) at the Center for Fast Kinetics Research at UT-

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