observed during the photolysis of ^{17}O-labeled ketones, which produce a radical pair that can recombine to form ^{17}O-enriched starting ketone. An absolute enrichment of ^{17}O-labeled recovered starting ketone[37] is as high as 21% (from 34.2% ± 0.5 to 41.5% ± 0.5), corresponding to $S(f) = 1.36$.

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Synthesis, Characterization, and X-ray Structure of the Ruthenium "Picnic-Basket" Porphyrins

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Abstract: The synthesis and characterization of a new class of sterically protected porphyrins, the "picnic-basket" porphyrins, are presented. These tetraarylporphyrins, which were prepared as cytochrome P-450 active-site analogues, bear a rigid superstructure on one face of the porphyrin macrocycle. The cavity defined by the appended superstructure may be readily varied in size, chirality, and functionality. In addition, the synthesis and characterization, including an X-ray structure, of several ruthenium picnic-basket porphyrin carbonyl complexes are reported. The regiochemistry of axial ligation in these ruthenium derivatives has been determined by ^1H NMR spectroscopy.

The relevance of synthetic iron porphyrins as hemoglobin and myoglobin active-site analogues has been amply demonstrated during the past 15 years. Elegant syntheses of sterically protected iron porphyrins that reversibly bind molecular oxygen have been reported. Some examples include the "capped" porphyrins of Baldwin and co-workers,[1] the "bridged" porphyrins of Battersby and associates,[2] the "picket fence"[3] and "pocket"[4] porphyrins of Collman and co-workers, the "basket-handle" porphyrins of Momenteau[5a-c] and associates, the "gyroscope" porphyrins of Rose and co-workers,[5d,e] the "cyclophane" porphyrins of Traylor and associates,[6] and the related but nonporphyrinic "lacunar" complexes of Busch and co-workers.[7] These porphyrins bear peripheral appendages that mimic the apoprotein in (1) controlling axial ligand coordination at the iron center and (2) preventing irreversible oxidative dimerization on interaction with dioxygen. Such model compounds have made possible systematic investigations into structural and mechanistic features of dioxygen transport and storage by hemoglobin and myoglobin.

Synthetic porphyrins have also been used to probe dioxygen activation as exhibited by the cytochrome P-450 enzymes. These ubiquitous hemoprotein monooxygenases bind and convert dioxygen into a powerful oxygenating agent capable of hydroxylating unactivated alkanes, epoxidizing alkenes, and oxygenating heteroatoms.[8] Reductive activation of molecular oxygen by simple manganese porphyrins has been achieved with the use of a variety of reducing agents and activating groups.[9] This chemistry has also been extended to iron porphyrins.[10] However, in the presence of dioxygen simple iron(II) porphyrins are thermodynamically unstable and undergo irreversible oxidation to catalytically inactive μ-oxo dimers.[11] In addition, the high affinities of both Fe(II) and Fe(III) porphyrins for axial ligands results in the formation of catalytically inactive bis-ligand species.[12] For these reasons Tabushi et al. have studied iron picket-fence porphyrin as a cy-

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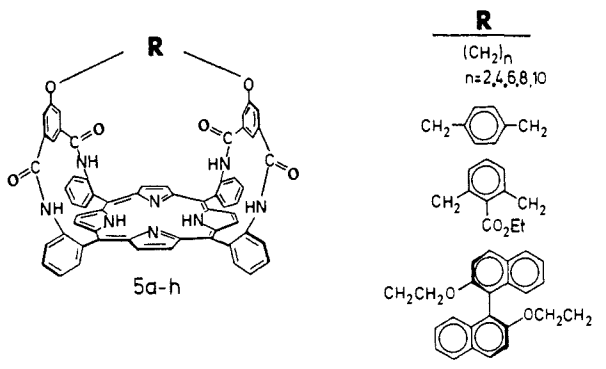


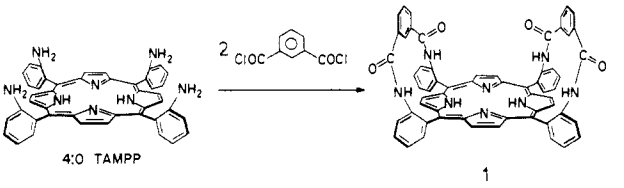
Figure 1. The "picnic-basket" porphyrins.

tochrome P-450 active-site analogue.[13] We report herein our efforts to develop a cytochrome P-450 active-site analogue.

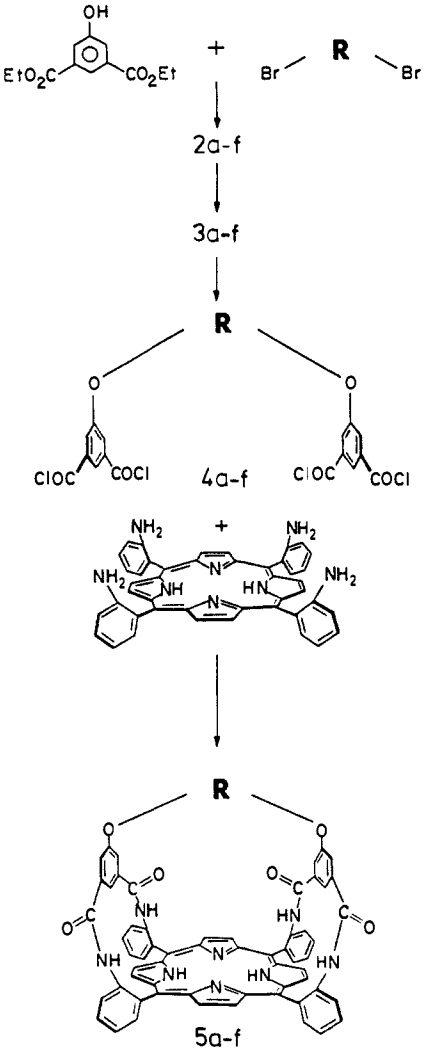
In our ongoing study of cytochrome P-450 model compounds, we are interested in synthesizing a metalloporphyrin capable of binding and activating dioxygen in a manner similar to the enzyme. Such a model, since it also must reversibly bind dioxygen, will incorporate the same structural features found in the hemoglobin and myoglobin models mentioned above. These models, however, bind dioxygen within tight cavities.[14-16] The pockets were designed to hinder coordination of ligands as small as 1-methylimidazole and in some cases carbon monoxide. For example, a crystal structure of a capped porphyrin shows a separation of less than 4 Å between the phenyl "cap" and the porphyrin ring.[14] Such hemoglobin/myoglobin models could limit substrate accessibility to the active site, making them unsuitable as cytochrome P-450 model compounds.

In addition to the size of the cavity, the rigidity and stability of the superstructure are also important in the design of a P-450 model. Groves et al.[17] and Chang and Kuo[18] have demonstrated that alkyl groups on the porphyrin periphery that can approach the active site of a P-450 model may be oxidized. Furthermore, study of heavy-metal P-450 analogues requires that the superstructure must also be stable to porphyrin metalation conditions;

Scheme I. Coupling of α,α,α,α-Tetrakis(*o*-aminophenyl)porphyrin and Isophthaloyl Chloride



Scheme II. Synthesis of the Picnic-Basket Porphyrins



this eliminates the picket-fence porphyrin, the pickets of which isomerize at the high temperatures (>150 °C) and long reaction times necessary for the insertion of ruthenium. Thus, an ideal cytochrome P-450 active-site analogue should contain a rigid superstructure that (1) is stable to metalation conditions, (2) is inaccessible to the active site, (3) provides a cavity within which dioxygen can be bound and activated, and (4) does not exclude substrate from the active site.

In this paper we describe a new class of sterically protected porphyrins, shown in Figure 1, that meet the above criteria and whose synthesis is both convergent and general. The molecules have been given the trivial name "picnic-basket" porphyrins. These tetraarylporphyrins bear a rigid superstructure, which defines a molecular cavity of variable volume on one face of the porphyrin macrocycle. The cavity may be functionalized or made chiral. Several ruthenium carbonyl derivatives of these picnic-basket porphyrins have been prepared; their synthesis and characterization, including a single-crystal X-ray structure, are described. In addition, NMR criteria that indicate the regiochemistry of axial ligation in these complexes are presented.

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Results and Discussion

Synthesis. Among the many syntheses of sterically protected porphyrins several approaches have been taken. Condensations of covalently linked benzaldehydes with pyrrole have produced families of capped and strapped porphyrins in low yields. While the work of Lindsey et al.[19d] has improved yields for porphyrin condensations, the linear nature of this synthetic route makes it less efficient.[19] A second approach to protected porphyrins involves building a superstructure from a preformed porphyrin ring.[5a-d,20] This strategy also suffers from being a linear synthesis. We have found that a convergent coupling of an intact superstructure to a preformed porphyrin is the most efficient route to a family of protected porphyrins with systematic structural variation.

We previously reported[3] good yields for the high-dilution coupling of 2 equiv of isophthaloyl chloride and the 4:0 atropisomer of TAMPP, as shown in Scheme I. This high yield was attributed to the complementary geometries of the isophthalate bridge and the aminophenyl groups on adjacent meso positions. While the iron(II) dioxygen complex of **1** is not stable to oxidative dimerization, the porphyrin possesses many of the features desired in a P-450 model. We proposed that by linking the 5,5′ positions of the isophthalamido walls, we could form a porphyrin with a large, rigid cavity. Scheme II outlines the synthesis of the picnic-basket porphyrins from two covalently linked isophthaloyl chlorides and the 4:0 atropisomer of tetrakis(*o*-aminophenyl)-porphyrin (4:0 TAMPP). The synthesis is general; various derivatives of these picnic-basket porphyrins are specified by the notation $M(R\text{-}PBP)(L)_{in}(L')_{out}$, where M = metal or H_2 for unmetalated porphyrins, R = bridging group (C*n* = *n*-methylene alkane, PXY = *p*-xylyl, DMB = 2,6-dimethylbenzoate, BN = binaphthyl), PBP = picnic-basket porphyrin, $(L)_{in}$ = ligand within the protected cavity, and $(L')_{out}$ = ligand bound on unencumbered porphyrin face.

The more elaborate picnic-basket porphyrins, H_2(DMB-PBP) (**5g**) and H_2(BN-PBP) (**5h**), were synthesized for specific applications. The 2,6-dimethylbenzoate-bridged porphyrin, **5g**, was designed to hold a carboxyl group so that it could interact with coordinated dioxygen. Studies of model compounds[9,10] and P-450 itself[21] suggest that activation of coordinated dioxygen requires acylation of the terminal oxygen atom. Chang and Kondylis have demonstrated unusually high dioxygen affinities for synthetic cobalt porphyrins that can hydrogen bond to the terminal oxygen atom of coordinated O_2.[22] The binaphthyl-bridged picnic-basket porphyrin, **5h**, was prepared as a potential enantioselective oxygenation catalyst.

Multigram quantities of the tetraacid chlorides **4a–f** may be synthesized as outlined in Scheme II. Diethyl isophthalate esters, **2a–f**, linked by simple alkyl straps are readily available via alkylation of diethyl 5-hydroxyisophthalate with any of a series of alkyl dibromides. On treatment with basic aqueous ethanol, these tetraesters are saponified to tetraacids, **3a–f**, which are then converted to the corresponding tetraacid chlorides, **4a–f**, with thionyl chloride.

Tetraacid chlorides containing a 2,6-dimethylbenzoate bridge, **4g**, or a binaphthyl bridge, **4h**, are prepared via slightly modified routes as illustrated in Scheme III. Ethyl 2,6-dimethylbenzoate (**6**), prepared from the acid, is converted to the bis(methyl bromide), **7**, via a free radical halogenation. Bromide displacement by the anion of bis(diphenylmethyl) 5-hydroxyisophthalate gives the mixed pentaester, **2g**. The diphenylmethyl groups of **2g** are selectively cleaved on treatment with trifluoroacetic acid, leaving the ethyl ester intact. Conversion to the ethyl benzoate bridged tetraacid chloride, **4g**, is effected with thionyl chloride as before. In preparing the binaphthyl-bridged tetraacid chloride, **4h**, diethyl 5-hydroxyisophthalate is treated with a large excess of 1,2-dibromoethane to give the bromide, **8**. Double alkylation of 1,1′-binaphth-2-ol (racemic or chiral) by the bromide, **8**, gives the tetraester, **2h**, which is converted to the tetraacid chloride, **4h**, as before.

The yields for the final high-dilution coupling reaction between a tetraacid chloride and 4:0 TAMPP are consistently greater than 40% even as the bridging group, R, is varied from two to ten methylene units. Over 600 mg of **5c** can be obtained from a single condensation reaction. As expected for a reaction in which four amide bonds must form intramolecularly, the only side products are polymeric and are easily removed upon chromatography.

Characterization. Each of the unmetalated picnic-basket porphyrins has been characterized by ^{1}H NMR spectroscopy, visible spectroscopy, mass spectrometry, and elemental analysis.

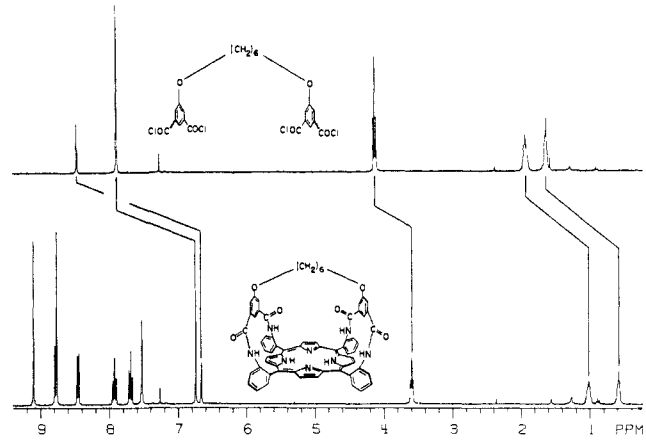
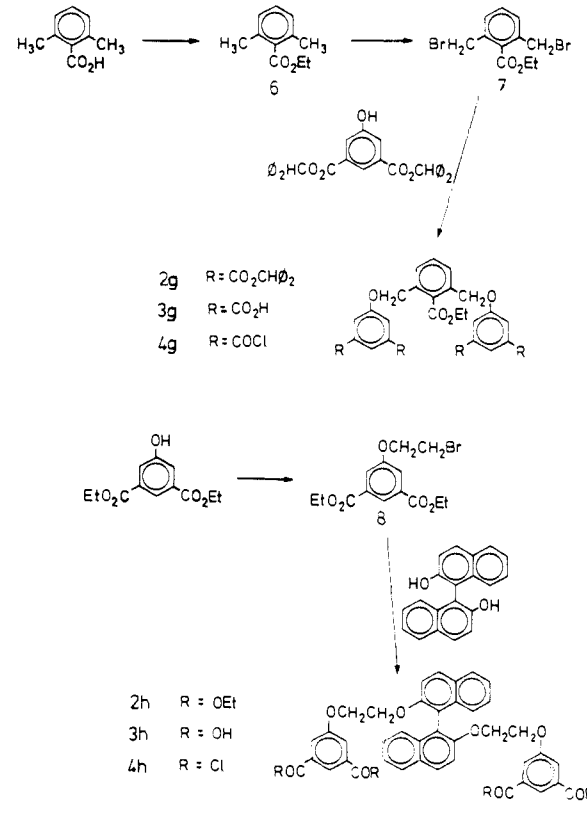


Figure 2. 300-MHz proton NMR spectrum of the hexyl-bridged picnic-basket porphyrin and precursor tetraacid chloride.

Scheme III. Synthesis of the 2,6-Dimethylbenzoate and Binaphthyl-Bridged Tetraacid Chlorides



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Mass spectroscopy shows no evidence of oligomers. The molecular ion peak corresponds to the mass of the product of coupling one tetraacid chloride and one tetraamine. Elemental analyses have been obtained for most derivatives as the half-chloroform solvate. The presence of a chloroform solvate has been confirmed by ^{1}H NMR spectroscopy.

The ^{1}H NMR spectrum of H_2(C6-PBP) (**5c**), is plotted with its tetraacid chloride precursor in Figure 2. From signal integrals, multiplicities, and exchange with deuterium oxide, most signals can be assigned. Specific assignments of the β-pyrrolic and meso-phenyl signals remain ambiguous. The two low-field singlets at 9.10 and 8.76 ppm are assigned to the two different types of β-pyrrolic protons. The two doublets, 8.78 and 8.45 ppm, and two triplets, 7.93 and 7.69 ppm, are due to the four meso-phenyl protons. The singlet at 7.53 ppm is exchangeable with deuterium oxide and therefore is unambiguously assigned to the amide protons. The two singlets at 6.74 and 6.66 ppm, in a 2:1 ratio, are assigned to the two types of protons on the isophthalamide rings. In the high-field region, the triplet at 3.59 ppm and the two broad signals at 1.02 and 0.59 ppm are due to the three types of protons in the hexyl strap. The signal for the porphyrin internal N–H protons at a chemical shift of −2.78 ppm is not shown.

The lines connecting the two spectra in Figure 2 illustrate the upfield shift in signals assigned to superstructure protons. The observed shifts, which are due to the magnetic field anisotropy of the porphyrin ring, support the assigned structure.

Conformational averaging of the porphyrin superstructure on the NMR time scale results in effective C_{2v} symmetry for the picnic-basket porphyrins except for the binaphthyl-bridged porphyrin, H_2(BN-PBP) (5h), whose chiral center results in effective C_2 symmetry. The binaphthyl-bridged porphyrin derivative has its C_2 axis normal to the porphyrin plane, and this is evident in the ^{1}H NMR spectrum. Although complicated, this spectrum can be assigned with the use of D_2O exchange and homonuclear decoupling experiments. These assignments indicate that signals due to equivalent protons in the picnic-basket porphyrins of C_{2v} symmetry are split into two signals on lowering to C_2 symmetry. For example, the signals for the two types of amide protons in H_2(BN-PBP) are separated by more than 0.30 ppm.

Since chiral 1,1′-binaphth-2-ol shows little racemization under the reaction conditions employed, no attempt was made to measure the enantiomeric purity of **5h**. That **5h** could be prepared in an optically active form was demonstrated by the presence of a circular dichroism spectrum for **5h** prepared from (*R*)-(+)-binaphthol; no signal was observed for **5h** derived from racemic binaphthol.[23]

The visible spectra of all picnic-basket porphyrins, recorded in methylene chloride, shows absorbances at the same wavelengths and of similar relative intensities, independent of bridging group. Dolphin and Einstein and co-workers[24a] and Walker and co-workers[24b] have demonstrated that deformation of the porphyrin ring from planarity causes shifts in wavelengths and relative intensities of absorbances in the visible spectrum. This suggests that shortening the superstructure bridging group in the picnic-basket porphyrins induces no significant distortion of the porphyrin ring. This has been confirmed by a crystal structure determination.

Ruthenium Insertion. The picnic-basket porphyrins have been metalated with manganese, iron, cobalt, nickel, and ruthenium. Modification of a literature procedure (higher boiling solvent, inert-atmosphere purge) gives a general method for metalating any picnic-basket porphyrin with ruthenium.[25] All reported methods for inserting ruthenium into a porphyrin give a six-co-

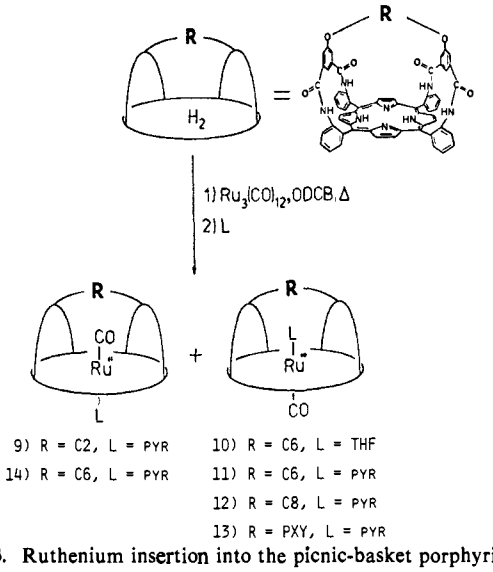
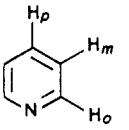


Figure 3. Ruthenium insertion into the picnic-basket porphyrins.

Table I. Chemical Shifts of Pyridine Protons in Some Ruthenium Porphyrin Pyridine Carbonyl Complexes



	H_o	H_m	H_p
Ru(C6-PBP)(CO)$_{out}$(pyr)$_{in}$	0.55	4.12	4.67
Ru(C6-PBP)(CO)$_{in}$(pyr)$_{out}$	1.99	5.42	6.29
Ru(TPP)(CO)(pyr)	1.53	5.20	6.09

ordinate, ruthenium carbonyl mono-L adduct, where L is a neutral σ-donating ligand. Ruthenium carbonyl derivatives of C2-PBP (**5a**), C6-PBP (**5c**), C8-PBP (**5d**), and PXY-PBP (**5f**) have been prepared with L = THF or pyridine. These complexes are air stable, are readily soluble in polar organic solvents, and are stable to silica gel chromatography. These picnic-basket porphyrins are the first ruthenium porphyrin monomers that contain a protecting superstructure. A cofacial dimer of ruthenium porphyrins has recently been reported.[26] There are several reports of synthetic porphyrins bearing chelating appendages that can form heterobimetallic complexes. Derivatives where ruthenium is bound in the nonporphyrinic site have been described.[27]

Two regioisomers are possible for the ruthenium insertion product due to asymmetry of the picnic-basket porphyrin. In one regioisomer, CO is coordinated within the cavity, and in the other regioisomer, it is coordinated on the unhindered side of the porphyrin, as illustrated in Figure 3. The relative amount of each regioisomer obtained on insertion of ruthenium depends dramatically on steric interactions between the porphyrin superstructure and the coordinated ligand and on the reaction conditions. For example, insertion of ruthenium into H_2(C2-PBP) (**5a**) gives only Ru(C2-PBP)(CO)$_{in}$(pyr)$_{out}$ independent of reaction time. CPK models demonstrate that pyridine is sterically prevented from binding within the ethyl-bridged pocket yet CO can bind without destabilizing steric interactions. For ruthenium insertion into the larger hexyl-bridged picnic-basket porphyrin (**5c**) both regioisomers are observed at early reaction times. For longer reaction times, however, only Ru(C6-PBP)(CO)$_{out}$(pyr)$_{in}$ is observed. This is the opposite regioisomer from that found in the H_2(C2-PBP) metalation.

For Ru(C6-PBP)(CO)(pyr), both regioisomers have been isolated and unambiguously identified by their ^{1}H NMR spectra and, in the case of Ru(C6-PBP)(CO)$_{in}$(pyr)$_{out}$, by a crystal

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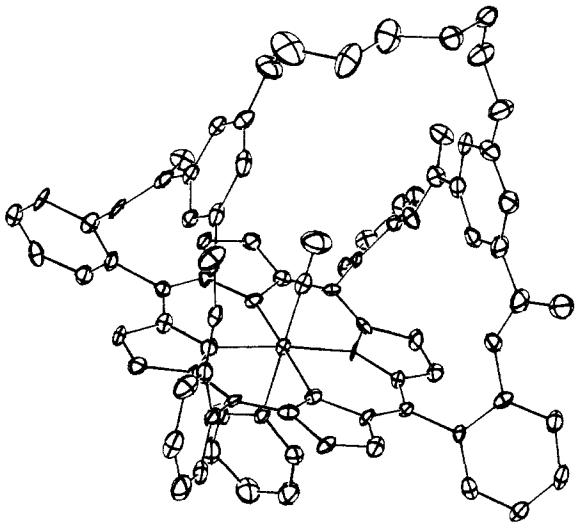

Figure 4. Molecular structure of Ru(C6-PBP)$(CO)_{in}(pyr)_{out}$. The 50% ellipsoids are shown.

structure determination (see below). Measurement of the infrared CO stretching frequencies of the two regioisomers shows only a slight difference; for the more stable Ru(C6-PBP)$(CO)_{out}(pyr)_{in}$, ν_{CO} = 1958 cm^{-1}, and for Ru(C6-PBP)$(CO)_{in}(pyr)_{out}$, ν_{CO} = 1951 cm^{-1}. We do not consider this 7-cm^{-1} difference significant.

Regioisomer Assignment. Proton NMR spectroscopy has been used to determine the regiochemistry of axial ligation in these ruthenium picnic-basket porphyrin complexes. Ligands coordinated within the protected cavity are in the shielding region of the two isophthalamido walls and therefore have ^1H NMR signals at higher field than ligands bound on the unhindered side of the porphyrin. The chemical shifts of coordinated pyridine for both Ru(C6-PBP)(CO)(pyr) regioisomers and for the related tetraphenylporphyrin complex are listed in Table I. The ortho, meta, and para pyridine protons are identified by their different multiplicities and integrals.

The pyridines in the two picnic-basket porphyrin regioisomers experience different magnetic environments. The pyridine environment in one regioisomer is similar to that of Ru(TPP)(CO)(pyr). This regioisomer is therefore assigned to have pyridine coordinated on the unhindered face of the picnic-basket porphyrin, which is structurally similar to tetraphenylporphyrin. Pyridine signals for the other regioisomer are shifted approximately 1.5 ppm upfield, as expected for pyridine coordinated within the protected cavity. These assignments have been confirmed by an X-ray crystal structure determination on Ru(C6-PBP)$(CO)_{in}(pyr)_{out}$.

X-ray Structure of Ru(C6-PBP)$(CO)_{in}(pyr)_{out}$. The structural assignments of the two Ru(C6-PBP)(CO)(pyr) regioisomers by pyridine chemical shifts have been verified by an X-ray structure determination of isomerically pure Ru(C6-PBP)$(CO)_{in}(pyr)_{out}$. Diffraction-quality crystals were obtained by diffusion of *n*-hexane into a pyridine solution of the porphyrin complex at room temperature. NMR analysis of a solution of the crystalline material from which the diffraction-quality crystal was selected showed no regioisomerization had occurred during crystal growth. The material crystallizes with four pyridine solvent molecules per porphyrin. Crystal data and collection procedures are listed in Table II. The structure is illustrated in Figure 4 and the atomic numbering scheme in Figure 5. Several key bond distances and angles for Ru(C6-PBP)$(CO)_{in}(pyr)_{out}$ and related ruthenium porphyrin complexes that have been structurally characterized[28,29] are listed in Table III. More complete tables of bond distances and bond angles are given in Tables 1S and 2S.[30]

Regiospecific coordination of CO and pyridine, consistent with our previous assignments based on pyridine chemical shifts, is evident from Figure 4. A comparison of Ru(C6-PBP)$(CO)_{in}(pyr)_{out}$ and the analogous tetraphenylporphyrin complex is particularly informative. The metal atom environment in both complexes is an axially distorted octahedron, and the data in Table

Table II. Crystallographic Data for Ru(C6-PBP)$(CO)_{in}(pyr)_{out}$ (6)

formula	$RuC_{72}H_{51}N_9O_7 \cdot 4C_5H_5N$
formula wt, amu	1571.7
space group	C_{2h}^5-$P2_1/n$
a, Å	16.112 (7)
b, Å	18.687 (7)
c, Å	24.750 (7)
β, deg	92.83 (2)
V, Å^3	7443
Z	4
temp, °C	−150 (1)[a]
radiation	Mo Kα, $\lambda(K\alpha_1)$ = 0.7093 Å graphite monochromator
linear absorp coeff, cm^{-1}	2.72
transmission factors	0.963–0.969[b]
density (calcd), g/cm^3	1.402
crystal vol, mm^3	0.0069
detector aperture	4.8 mm wide × 4.5 mm high 32 cm from crystal
take-off angle, deg	2.5
scan mode	ω–2θ
scan speed	2°/min in 2θ
scan range, deg	0.75 below Kα_1 to 0.75 above Kα_2
2θ limits, deg	3.0 ≤ 2θ ≤ 47.5
background counts	10 s at each end of scan with rescan option[c]
data collected	$+h,+k,\pm l$
standard reflections	6 in diverse regions of reciprocal space remeasured every 3.0 h of X-ray exposure time
unique data (including $F_o^2 < 0$)	11324
unique data ($F_o^2 > 3\sigma(F_o^2)$)	5508
final no. of variables	1018
p factor for $\sigma(F_o^2)$	0.03
$R(F)$ ($F_o^2 > 3\sigma(F_o^2)$)	0.069
$R_w(F)$ ($F_o^2 > 3\sigma(F_o^2)$)	0.066
$R(F^2)$	0.137[d]
$R_w(F^2)$	0.159
error in observation of unit weight, e^2	1.141

[a] The low-temperature system is based on a design by Huffman (Huffman, J. C. Ph.D. Thesis, Indiana University, 1974). [b] The analytical method as employed in Northwestern Absorption program *AGNOST* was used, but no correction was applied (de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014–1018). [c] The diffractometer was run under the Vanderbilt disk-oriented system (Lenhert, P. G. *J. Appl. Crystallogr.* **1975**, *8*, 568–570). [d] Final refinement on F^2, using all the unique data.

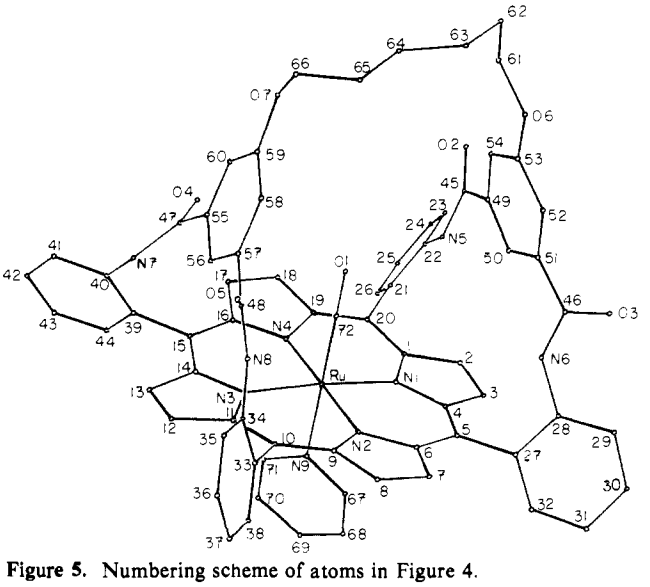

Figure 5. Numbering scheme of atoms in Figure 4.

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Table III. Averaged Bond Lengths (Å) and Angles (Deg) for Some Ruthenium Porphyrin Carbonyl Complexes

	Ru(C6-PBP)-$(CO)_{in}(pyr)_{out}$	Ru(TPP)-(CO)(pyr)[28]	Ru(TPP)-(CO)(EtOH)[29]
Ru–N(pyr)	2.173 (6)[a]	2.193 (4)[c]	
Ru–C(CO)	1.836 (8)	1.838 (9)	1.77 (2)[c]
C(CO–O(CO)	1.147 (9)	1.141 (10)	1.16 (3)
Ru–N(porphy)	2.052 (6)[b]	2.052 (9)	2.049 (5)
$N–C_a$	1.369 (16)	1.370 (9)	1.374 (8)
$C_a–C_m$	1.402 (15)	1.395 (10)	1.393 (10)
$C_a–C_b$	1.444 (10)	1.446 (11)	1.437 (13)
$C_b–C_b$	1.344 (9)	1.333 (11)	1.327 (12)
$C_a–N–C_a$	107.4 (13)	107.8 (6)	107.4 (6)
$N–C_a–C_b$	109.0 (8)	108.3 (8)	108.3 (6)
$N–C_a–C_m$	125.8 (9)	126.4 (7)	125.6 (6)
$C_a–C_b–C_b$	107.3 (9)	107.8 (8)	108.0 (8)
$C_a–C_m–C_a$	125.3 (7)	125.0 (7)	126.1 (6)
Ru–C(CO)–O(CO)	174.3 (7)	178.4 (7)	175.8 (19)
N(pyr)–Ru–C(CO)	174.0 (3)	178.9 (3)	

[a] Data collected at −150 °C. [b] This error on a mean value is the larger of the unweighted estimated standard deviation of a single observation as estimated from the values averaged or as estimated from the least-squares inverse matrix. [c] Data collected at room temperature.

III indicate very similar Ru–N(py) and Ru–CO bond distances. The Ru–N(py) bond length in the picnic-basket porphyrin derivative, 2.173 (6) Å, is slightly shorter than the 2.193 (4) Å reported for the tetraphenylporphyrin complex. However, this remains a long bond, consistent with the strong trans effect of the carbonyl ligand. The pyridine ring of Ru(C6-PBP)$(CO)_{in}$-$(pyr)_{out}$ is tipped slightly relative to the porphyrin plane, the dihedral angle between these planes being 78.4°. The pyridine ring is oriented such that its normal makes an angle of 54° with the N1–N3 vector. In contrast, the pyridine and porphyrin rings of Ru(TPP)(CO)(pyr) are essentially perpendicular (dihedral angle 87.9°). The porphyrin ring of Ru(C6-PBP)$(CO)_{in}(pyr)_{out}$ is puckered (Table 3S);[30] the puckering has a C_2 distribution, with individual atoms deviating by up to 0.33 Å from the mean porphyrin plane (Table 4S).[30] The displacements of individual porphyrin atoms from the mean porphyrin plane, however, indicate this distortion is not caused by the superstructure. For example, the pyrrole rings that lie underneath the isophthalamide walls are displaced toward the isophthalamido bridges and not away as would be expected if the superstructure were causing the distortion. We believe crystal packing forces are responsible for the ruffled picnic-basket porphyrin. Although the displacements observed in the picnic-basket porphyrin derivative are 5 times those seen in Ru(TPP)(CO)(pyr), they are well within the range exhibited by other structurally characterized metalloporphyrins.[31]

The hexyl-bridged picnic-basket porphyrin cavity is surprisingly large. Approximately 7 Å separates the nearly planar isophthalamido walls. The closest approach of any carbon atom of the strap to the carbonyl oxygen atom is over 6 Å (Table 5S).[30] The four solvated pyridine molecules do not lie directly inside the picnic-basket porphyrin pocket but flank CO on either side of the pocket.

Regioisomer Equilibration. That both Ru(C6-PBP)(CO)(pyr) regioisomers were observed early in the metalation reaction but only the $(CO)_{out}$ isomer later suggests that the initially produced mixture slowly equilibrates to the thermodynamically more stable isomer. We examined this hypothesis by preparing each pure regioisomer and attempting their interconversion. While it is possible to separate the two Ru(C6-PBP)(CO)(pyr) regioisomers by chromatography, this method is tedious. For this reason, a procedure to prepare the proposed kinetic regioisomer, Ru(C6-PBP)$(CO)_{in}(pyr)_{out}$, from pyrolyzed Ru(C6-PBP)$(THF)_2$ was developed (see Experimental Section). This procedure may involve

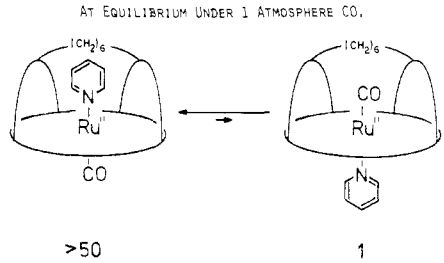

Figure 6. Equilibration of the Ru(C6-PBP)(CO)(pyr) regioisomers.

the intermediacy of a four-coordinate ruthenium porphyrin.[32]

Upon heating a $CDCl_3$ solution of the proposed kinetic isomer, Ru(C6-PBP)$(CO)_{in}(pyr)_{out}$, at reflux under a CO atmosphere, as would be present during the metalation reaction, we find complete conversion to the $(CO)_{out}$ isomer within 1 h (Figure 6). Similar treatment of Ru(C6-PBP)$(CO)_{out}(L)_{in}$ (L = THF or pyridine) showed no change. Since no $(CO)_{in}$ regioisomer is observed at equilibrium by ^1H NMR spectroscopy, the $(CO)_{out}$ regioisomer is favored over the $(CO)_{in}$ regioisomer by at least 50:1, the detection limit of the NMR measurement. From this ratio it is determined that Ru(C6-PBP)$(CO)_{out}(pyr)_{in}$ is at least 2 kcal/mol more stable than Ru(C6-PBP)$(CO)_{in}(pyr)_{out}$. Isomerization may involve the intermediacy of the bis(carbonyl) adduct; if such a species exists it was not detected by ^1H NMR spectroscopy.

Even though X-ray crystallography has shown the hexyl-bridged pocket is large enough to accommodate pyridine, one might expect the regioisomer with the sterically less demanding ligand within the pocket to be more stable; however, this is not the case. The ground-state energy difference between these two regioisomers most likely arises from subtle dipolar interactions with the porphyrin superstructure or solvent. Increased ligand affinities of protected porphyrins versus simple porphyrins have previously been attributed to dipolar effects[33] of the amide linkages in the superstructure and to solvation effects.[34]

Experimental Section

Materials. All solvents and materials were of reagent grade quality, purchased commercially, and used without further purification, except as noted below. Methylene chloride was dried by distillation from CaH_2 or P_2O_5 under a dinitrogen atmosphere. Dry DMF was obtained by reduced-pressure distillation from BaO onto 4-Å molecular sieves. Thionyl chloride was distilled from triphenyl phosphite just prior to its use. Ruthenium dodecacarbonyl was recrystallized from hexanes. Diphenyldiazomethane,[35] diethyl 5-hydroxyisophthalate,[36] tetrakis(*o*-aminophenyl)porphyrin,[37] and Ru(TPP)(CO)(pyr)[38] were prepared by published methods. The $\alpha,\alpha,\alpha,\alpha$ atropisomer of TAMPP was enriched by equilibration in the presence of silica gel.[39,40] Silica gel for flash chromatography was Type 7736, manufactured by E. M. Science and distributed by VWR Inc. For TLC, commercially prepared silica plates were purchased from Analtech Inc.

Physical Methods. Electronic spectra were recorded on a Cary 219 spectrophotometer. Infrared spectra were measured on an IBM Instruments, Inc., IR/98 spectrometer as either methylene chloride solutions or Nujol mulls. A Nicolet NMC-300 spectrometer was used to obtain

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the NMR spectra. Mass spectra were recorded at the Mass Spectrometry Resource, School of Pharmacy, University of California at San Francisco, San Francisco, CA, and elemental analyses were obtained from Chemical Analytical Services, Berkeley, CA.

X-ray Data Collection and Structure Solution of Ru(C6-PBP)-$(CO)_{in}(pyr)_{out}$. Suitable crystals of $Ru(C6\text{-}PBP)(CO)_{in}(pyr)_{out}$ were obtained by vapor diffusion of *n*-hexane into a pyridine solution of the porphyrin at room temperature. The dark red crystal selected for data collection had dimensions 0.33 × 0.30 × 0.36 mm. It was mounted in the cold stream of an Enraf-Nonius CAD-4 diffractometer. Initial searching and indexing showed symmetry and systematic absences consistent with the monoclinic space group C_{2h}^5-$P2_1/n$. The crystal was then transferred to the cold stream of a Picker FACS-1 diffractometer for data collection. The ruthenium atom and four pyrrolic nitrogen atoms were located from the Patterson function and the rest of the molecule from DIRDIF.[41] Hydrogen atom positions were idealized (C–H = 0.95 Å, $B_H = B_{C,N} + 1.0$ Å^2) and were not varied. Final refinement, with techniques standard in this laboratory,[42] was on F^2 with all the data. This final refinement involved an anisotropic model for the non-hydrogen atoms; there were 1018 variables and 11 324 observations. Analysis of $\sum w(F_o^2 - F_c^2)^2$ as a function of F_o^2, setting angles, and Miller indices showed no unusual trends. Additional crystal data and refinement procedures are listed in Table II. Table 6S[30] lists the final positional parameters of the non-hydrogen atoms. Table 7S[30] lists the positional parameters of the hydrogen atoms; Table 8S[30] lists the anisotropic thermal parameters of the non-hydrogen atoms; Table 9S[30] gives values of $10|F_o|$ vs $10|F_c|$.

Tetraester Precursors. Diethyl 5-Hydroxyisophthalate. In a 500-mL three-neck round-bottom flash fitted with a magnetic stirrer, N_2 inlet, condenser, and gas dispersion tube was placed 25.0 g (0.137 mol) of 5-hydroxyisophthalic acid dissolved in 250 mL of absolute ethanol. While the solution was stirred under an N_2 atmosphere, HCl gas was slowly bubbled into the solution through the gas dispersion tube for 10 min. The solution was stirred an additional 2 h and then poured into 1.5 L of H_2O. The resultant white precipitate was collected by vacuum filtration, washed 3 times with 150 mL of H_2O, and dried under vacuum. Mp 104–106 °C (lit. mp 103 °C). Yield = 31.0 g (95%).[36]

^{1}H NMR ($CDCl_3$): δ 8.25 (s, 1 H), 7.81 (s, 2 H), 6.36 (s, 1 H), 4.41 (q, 4 H), 1.42 (t, 6 H).

Bis(diphenylmethyl) 5-Hydroxyisophthalate. To a solution of 4.0 g (22 mmol) of 5-hydroxyisophthalic acid in 350 mL of acetone maintained at 0 °C in the dark was added dropwise a solution of 9.39 g (48.0 mmol) of diphenyldiazomethane in 20 mL of acetone over 1 h. The mixture was stirred at 0 °C for 5 h and then stored at 0 °C for 1 day. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 and loaded onto a silica flash chromatography column (4.5-cm diameter × 20 cm) prepared from CH_2Cl_2 slurry. Elution with CH_2Cl_2 and then 10/1 CH_2Cl_2/Et_2O afforded the pure tetraester after drying in vacuo. Yield = 11.29 g (100%).

^{1}H NMR ($CDCl_3$): δ 8.47 (s, 1 H), 7.86 (s, 2 H), 7.69 (s, 1 H), 7.16–7.48 (m, 20 H), 7.08 (s, 2 H).

Ethyl 2,6-dimethylbenzoate (6). Into a 25-mL three-neck round-bottom flask with a stir bar were placed 7.72 g (51.4 mmol) of 2,6-dimethylbenzoic acid, 5.6 mL of thionyl chloride, and 1 drop of DMF. This mixture was stirred for 4 h at room temperature under a dinitrogen atmosphere, after which time the excess $SOCl_2$ was removed under vacuum. To the residue, dissolved in 50 mL of dry CH_2Cl_2 containing 1 mL of dry Et_3N, was added 6.0 mL of ethanol, dropwise. This solution was stirred for 1 h, the solvent was removed on a rotovap, and a benzene solution of the residue was filtered through a 3-cm pad of gravity silica gel. Removal of the solvent from the filtrate gave the pure ethyl ester. Yield = 8.7 g (95%).

^{1}H NMR (CCl_4): δ 6.9–7.2 (m, 3 H), 4.30 (q, 2 H), 2.30 (s, 6 H), 1.36 (t, 3 H).

Ethyl 2,6-Bis(bromomethyl)benzoate (7). A 100-mL round-bottom flask was charged with 3.0 g (16.8 mmol) of ethyl 2,6-dimethylbenzoate, 6.28 g (35.2 mmol) of *N*-bromosuccinimide, approximately 30 mg of benzoyl peroxide, and 30 mL of CCl_4. This was heated at reflux for 3 h, cooled to room temperature, and filtered. The collected precipitate was washed with CCl_4, and the washings were combined with the filtrate. The CCl_4 solution was concentrated and crystallized in a freezer (−20 °C). The product was recrystallized twice from 5% Et_2O–hexane to give the pure dibromide. Yield = 1.3 g (23%).

^{1}H NMR (CCl_4): δ 7.38 (s, 3 H), 4.59 (s, 4 H), 4.46 (q, 2 H), 1.47 (t, 3 H).

Diethyl 5-(2-Bromoethoxy)isophthalate (8). A 250-mL three-neck round-bottom flask fitted with a magnetic stirrer, N_2 inlet, dropping funnel, and condenser was charged with 18.0 mL (44.0 mmol) of 1,2-dibromoethane, 14.0 g of K_2CO_3, and 120 mL of DMF. This stirred mixture was heated to 80 °C when 5.0 g (21.0 mmol) of diethyl 5-hydroxyisophthalate dissolved in 50 mL of DMF was added dropwise over 3 h. The reaction was stirred at 80 °C for an additional 24 h and examined by TLC (SiO_2, CH_2Cl_2), which showed a small amount of unreacted starting material. An additional 2.0 g of K_2CO_3 and 3.0 mL of 1,2-dibromoethane were added and the reaction was continued an additional 24 h. Workup required pouring the reaction mixture into 300 mL of 2% aqueous HCl and extracting this solution twice with 100 mL of CH_2Cl_2. The combined CH_2Cl_2 fractions were washed 3 times with 60 mL of 5% aqueous NaOH and once with 100 mL of H_2O, dried over $MgSO_4$, filtered, and reduced on a rotovap to a golden oil, which was further dried under vacuum. The oil, dissolved in 25 mL of CH_2Cl_2, was loaded onto a silica flash column (4.5-cm diameter × 10 cm) and eluted with CH_2Cl_2, separating the desired product from the less mobile impurities. Removal of solvent left a waxy white solid that was dried under vacuum. Mp 55–56 °C. Yield = 3.85 g (53%).

^{1}H NMR ($CDCl_3$): δ 8.31 (s, 1 H), 7.75 (s, 2 H), 4.40 (m, 6 H), 3.67 (t, 2 H), 1.41 (t, 6 H).

Tetraester Synthesis. 1,2-Bis(3,5-dicarbethoxyphenoxy)ethane (2a). In a 100-mL round-bottom flask under an N_2 atmosphere were stirred 9.50 g (40.0 mmol) of diethyl 5-hydroxyisophthalate, 3.50 g (18.6 mmol) of 1,2-dibromoethane, and 10.0 g of K_2CO_3 in 50 mL of dry DMF maintained at 60 °C for 12 h. The reaction was monitored by TLC (SiO_2 10/1 CH_2Cl_2/Et_2O). Six 1.0-g aliquots of 1,2-dibromoethane were added to the reaction mixture every 12 h over 3 days until TLC indicated the reaction was complete. Workup required pouring the reaction mixture into 400 mL of H_2O and stirring vigorously for 15 min, collecting the white precipitate by vacuum filtration, and washing 3 times with 100 mL of H_2O. The precipitate, dissolved in 400 mL of CH_2Cl_2, was washed 3 times with 100 mL of 5% aqueous NaOH in a separatory funnel. The CH_2Cl_2 solution was then dried over $MgSO_4$, filtered, and reduced on a rotovap to a white solid that was dried under vacuum. Yield = 5.7 g (57%).

^{1}H NMR ($CDCl_3$): δ 8.31 (s, 2 H), 7.81 (s, 4 H), 4.46 (s, 4 H), 4.40 (q, 8 H), 1.41 (t, 12 H).

General Procedure (2b–f). In a 50-mL round-bottom flask under an N_2 atmosphere were stirred 23.1 mmol of diethyl 5-hydroxyisophthalate, 10.0 mmol of α,ω-dibromoalkane, and 5.0 g of K_2CO_3 in 25 mL of dry DMF for 48 h. The reaction mixture was poured into 400 mL of H_2O and stirred vigorously for 15 min. The resulting white precipitate was collected by vacuum filtration and washed 3 times with 100 mL of H_2O. The precipitate, dissolved in 400 mL of CH_2Cl_2, was washed 3 times with 100 mL of 5% aqueous NaOH in a separatory funnel. The CH_2Cl_2 solution was then dried over $MgSO_4$, filtered, and reduced on a rotovap to a white solid that was dried under vacuum. Yield = 80–85%.

Butane Derivative (2b). ^{1}H NMR ($CDCl_3$): δ 8.27 (s, 2 H), 7.74 (s, 4 H), 4.40 (q, 8 H), 4.14 (m, 4 H), 2.05 (m, 4 H), 1.41 (t, 12 H).

Hexane Derivative (2c). ^{1}H NMR ($CDCl_3$): δ 8.26 (s, 2 H), 7.75 (s, 4 H), 4.40 (q, 8 H), 4.05 (t, 4 H), 1.85 (m, 4 H), 1.60 (m, 4 H), 1.40 (t, 12 H).

Octane Derivative (2d). ^{1}H NMR ($CDCl_3$): δ 8.26 (s, 2 H), 7.75 (s, 4 H), 4.40 (q, 8 H), 4.05 (t, 4 H), 1.83 (m, 4 H), 1.50 (m, 4 H), 1.41 (t, 16 H).

Decane Derivative (2e). ^{1}H NMR ($CDCl_3$): δ 8.26 (s, 2 H), 7.75 (s, 4 H), 4.40 (q, 8 H), 4.05 (t, 4 H), 1.82 (m, 4 H), 1.30–1.55 (m), 1.41 (t).

***p*-Xylene Derivative (2f).** ^{1}H NMR ($CDCl_3$): δ 8.30 (s, 2 H), 7.84 (s, 4 H), 7.50 (s, 4 H), 5.16 (s, 4 H), 4.40 (q, 8 H), 1.41 (t, 12 H).

Ethyl 2,6-Bis((3,5-bis((diphenylmethoxy)carbonyl)phenoxy)methyl)-benzoate (2g). Bis(diphenylmethyl) 5-hydroxyisophthalate (0.40 g, 1.30 mmol), ethyl 2,6-bis(bromomethyl)benzoate (1.40 g, 2.74 mmol), and 0.6 g of K_2CO_3 were stirred in 50 mL of DMF under an N_2 atmosphere for 4 h. This mixture was then poured into 200 mL of H_2O, the aqueous solution was extracted 3 times with 75 mL of Et_2O, and the combined Et_2O layers were washed once with 100 mL of H_2O and once with saturated aqueous NaCl. After removal of the ether the residue was chromatographed on silica gel with hexanes/Et_2O as eluent to give the pure pentaester. Yield = 1.45 g (95%).

^{1}H NMR ($CDCl_3$): δ 8.54 (s, 2 H), 8.03 (s, 3 H), 7.90 (s, 4 H), 7.40 (m, 40 H), 7.12 (s, 2 H), 5.18 (s, 4 H), 4.10 (q, 2 H), 1.09 (t, 3 H).

2,2′-Bis(2-(3,5-dicarbethoxyphenoxy)ethoxy)-1,1′-binaphthyl (2h). In a 50-mL round-bottom flask under an N_2 atmosphere 0.510 g (1.48 mmol) of diethyl 5-(2-bromoethoxy)isophthalate, 0.210 g (0.73 mmol) of 1,1′-binaphth-2-ol, and 2.0 g of K_2CO_3 were stirred in 20 mL of dry DMF. The reaction was monitored by TLC (SiO_2 1/1 hexanes/Et_2O). After 18 h, an additional 2.0 g of K_2CO_3 was added, and stirring was

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continued for 24 h. Workup required pouring the reaction mixture into 200 mL of 2% aqueous HCl and extracting this solution 2 times with 75 mL of CH_2Cl_2. The combined CH_2Cl_2 layers were washed 3 times with 50 mL of aqueous NaOH, dried over $MgSO_4$, filtered, and reduced to an oil on a rotovap. The oil, dissolved in CH_2Cl_2, was loaded onto a silica flash column (4.5-cm diameter × 10 cm) and eluted with CH_2Cl_2 and then 10/1 CH_2Cl_2/Et_2O. Removal of solvent and drying gave the desired product. Yield = 0.469 g (78%).

^1H NMR ($CDCl_3$): δ 8.18 (s, 2 H), 7.89 (d, 2 H), 7.78 (d, 2 H), 7.42 (m, 6 H), 7.05–7.20 (m, 6 H), 4.37 (q, 8 H), 4.27 (q, 4 H), 3.96 (m, 4 H), 1.41 (t, 12 H).

Tetraacid Synthesis. General Procedure (3a–f). In a 250-mL round-bottom flask fitted with a magnetic stirrer, heating mantle, and condenser was suspended 10.75 mmol of tetraester in 100 mL of 95% aqueous ethanol. This stirred mixture was warmed to 65 °C when a solution of 2.5 g (62.5 mmol) of NaOH dissolved in 10 mL of water was added. After being stirred an additional 12 h at 65 °C, the mixture was allowed to cool and then vacuum filtered through a large Büchner funnel. The white precipitate that was collected was washed once with 100 mL of cold ethanol and then dissolved in 300 mL of H_2O. This solution was filtered and then treated with 6 mL of concentrated HCl to precipitate the tetraacid, which was collected by vacuum filtration through a large Büchner funnel, washed with water, and dried at 50 °C under vacuum. Yield = 90–95%.

Ethane Derivative (3a). ^1H NMR (D_2O/K_2CO_3): δ 7.73 (s, 2 H), 7.40 (s, 4 H), 4.32 (s, 4 H).

Butane Derivative (3b). ^1H NMR (D_2O/K_2CO_3): δ 7.72 (s, 2 H), 7.39 (s, 4 H), 4.05 (m, 4 H), 1.83 (m, 4 H).

Hexane Derivative (3c). ^1H NMR (D_2O/K_2CO_3): δ 7.80 (s, 2 H), 7.46 (s, 4 H), 4.05 (t, 4 H), 1.74 (m, 4 H), 1.45 (m, 4 H).

Octane Derivative (3d). ^1H NMR (D_2O/K_2CO_3): δ 7.73 (s, 2 H), 7.39 (s, 4 H), 3.96 (t, 4 H), 1.65 (q, 4 H), 1.15–1.35 (m, 8 H).

Decane Derivative (3e). ^1H NMR (D_2O/K_2CO_3): δ 7.73 (s, 2 H), 7.40 (s, 4 H), 3.99 (t, 4 H), 1.64 (q, 4 H), 1.10–1.40 (m, 12 H).

***p*-Xylene Derivative (3f).** ^1H NMR (D_2O/K_2CO_3): 7.84 (s, 2 H), 7.54 (s, 4 H), 7.50 (s, 4 H), 5.16 (s, 4 H).

Ethyl 2,6-Bis((3,5-dicarboxyphenoxy)methyl)benzoate (3g). To 3.25 g (2.8 mmol) of pentaester precursor in 20 mL of CH_2Cl_2 was added 3.0 mL of CF_3CO_2H at room temperature with stirring. The reaction was allowed to proceed for 4 h, during which time a white precipitate gradually formed. The solvent and acid were removed under vacuum, and the residue was washed 4 times with dry CH_2Cl_2 to remove any diphenylmethane. The pure white solid was then dried under vacuum. Yield = 1.43 g (95%).

^1H NMR (D_2O/K_2CO_3): δ 7.74 (s, 2 H), 7.43 (s, 3 H), 7.36 (s, 4 H), 5.13 (s, 4 H), 3.87 (q, 2 H), 0.83 (t, 3 H).

2,2′-Bis(2-(3,5-dicarboxyphenoxy)ethoxy)-1,1′-binaphthyl (3h). In a 50-mL round-bottom flask were combined 0.71 g (0.87 mmol) of the precursor tetraester, 1.0 g (18.0 mmol) of KOH, 10 mL of H_2O, and 20 mL of ethanol. These were heated at reflux for 6 h, cooled to room temperature, and then acidified with concentrated HCl. The flocculent white precipitate was collected by filtering through a packed Celite pad and was washed with cold ethanol. The desired tetraacid was then extracted from the Celite with hot THF. Removal of the THF under vacuum gave the pure product. Yield = 0.57 g (94%).

^1H NMR (D_2O/K_2CO_3): δ 7.97 (m, 4 H), 7.86 (d, 2 H), 7.60 (d, 2 H), 7.32 (s, 4 H), 7.26 (t, 2 H), 7.13 (t, 2 H), 6.87 (d, 2 H), 4.34 (m, 4 H), 4.03 (m, 4 H).

Tetraacid Chloride Synthesis. General Procedure (4a–g). In a 50-mL flask fitted with a magnetic stirrer and condenser were placed 4.48 mmol of precursor tetraacid, 30 mL of thionyl chloride (freshly distilled from triphenyl phosphite), and 3 drops of DMF. This stirred mixture was heated at reflux under argon for 8 h to give a clear, slightly yellow solution. The excess $SOCl_2$ was removed from the cooled solution under vacuum to give the desired product as a light tan solid. Yield = 85–90%.

Ethane Derivative (4a). ^1H NMR ($CDCl_3$): δ 8.51 (s, 2 H), 7.96 (s, 4 H), 4.53 (s, 4 H).

Butane Derivative (4b). ^1H NMR ($CDCl_3$): δ 8.46 (s, 2 H), 7.88 (s, 4 H), 4.19 (m, 4 H), 2.09 (m, 4 H).

Hexane Derivative (4c). ^1H NMR ($CDCl_3$): δ 8.46 (s, 2 H), 7.88 (s, 4 H), 4.13 (t, 4 H), 1.92 (m, 4 H), 1.61 (m, 4 H).

Octane Derivative (4d). ^1H NMR ($CDCl_3$): δ 8.45 (s, 2 H), 7.88 (s, 4 H), 4.00 (t, 4 H), 1.87 (q, 4 H), 1.40–1.65 (m, 8 H).

Decane Derivative (4e). ^1H NMR ($CDCl_3$): δ 8.46 (s, 2 H), 7.88 (s, 4 H), 4.08 (t, 4 H), 1.85 (q, 4 H), 1.30–1.55 (m, 12 H).

***p*-Xylene Derivative (4f).** ^1H NMR ($CDCl_3$): δ 8.49 (s, 2 H), 7.96 (s, 4 H), 7.50 (s, 4 H), 5.23 (s, 4 H).

Ethyl 2,6-Dimethylbenzoate Derivative (4g). ^1H NMR ($CDCl_3$): δ 8.47 (s, 2 H), 7.93 (s, 4 H), 7.57 (m, 3 H), 5.36 (s, 4 H), 4.32 (q, 2 H), 1.30 (t, 3 H).

2,2′-Bis(2-(3,5-bis(chlorocarbonyl)phenoxy)ethoxy)-1,1′-binaphthyl (4h). The precursor tetraacid (0.364 g, 0.51 mmol) was heated at reflux in 4.0 mL of $SOCl_2$ (distilled from triphenyl phosphite) under an N_2 atmosphere for 8 h. After removal of the excess thionyl chloride from the cooled solution, the residue was transferred into the inert-atmosphere box where it was dissolved in 10 mL of dry CH_2Cl_2 and passed through basic alumina. Removal of solvent gave the desired pure product as a foamy solid that was further dried under vacuum. Yield = 0.219 (55%).

^1H NMR ($CDCl_3$): δ 8.30 (s, 2 H), 7.78 (d, 2 H), 7.65 (d, 2 H), 7.39 (s, 4 H), 7.33 (d, 2 H), 7.20 (t, 2 H), 7.08 (t, 2 H), 6.93 (d, 2 H), 3.95–4.45 (m, 8 H).

H_2(PBP) Synthesis. Procedure 1 (5a–h). The following was done under rigorously dry conditions in oven-dried glassware that was allowed to cool in a drybox. 4:0-Tetrakis(*o*-aminophenyl)porphyrin (270 μmol), dissolved in 30 mL of CH_2Cl_2 (distilled from P_2O_5 or CaH_2), was stirred with 3.0 g of 4-Å molecular sieve pellets for 3 h (removes CH_3OH trapped in the crystal structure). A tetraacid chloride (270 μmol) was dissolved in 50 mL of CH_2Cl_2. Each of these solutions was drawn into a separate gastight syringe. With a syringe pump, both reactant solutions were added to a stirred solution of 2 mL of triethylamine (distilled from Na) in 50 mL of CH_2Cl_2 maintained at 0 °C under an N_2 atmosphere. Addition of reactants required 10 h after which time the solution was stirred an additional 12 h at room temperature. Workup required washing the reaction solution once with 100 mL of saturated aqueous $NaHCO_3$ and once with 100 mL of aqueous NaCl in a separatory funnel. The solvent was removed from the organic layer under vacuum and the residue further dried under vacuum. The residue, dissolved in 20 mL of CH_2Cl_2, was loaded onto a silica gel flash column (4-cm diameter × 10 cm) prepared from CH_2Cl_2 slurry and eluted as described below. Removal of solvent gave the desired H_2(PBP); it was further dried under vacuum.

Procedure 2. This scaled-up version of procedure 1 was done under rigorously dry conditions. 4:0-Tetrakis(*o*-aminophenyl)porphyrin (1.35 mmol), dissolved in 125 mL of dry CH_2Cl_2, was gently stirred over 5 g of 4-Å molecular sieves under an inert atmosphere for 3 h. A tetraacid chloride (1.35 mmol) was dissolved in 250 mL of dry CH_2Cl_2. While these solutions stirred, a 1-L three-neck round-bottom flask containing 5 mL of dry triethylamine, 5 g of 4-Å molecular sieves, a magnetic stir bar, and 50 mL of dry CH_2Cl_2 was fitted with an Ar bubbler, a 125-mL addition funnel, and a 250-mL addition funnel. After the 4:0 solution had stirred the necessary 3 h, it and the tetraacid chloride solution were transferred by cannula into the 125-mL and 250-mL addition funnels, respectively. The two reactants were added dropwise in equimolar aliquots over the course of 6 h to the 1-L reaction flask maintained at 0 °C under an Ar atmosphere. After the addition was complete, the solution was stirred at room temperature for 12 h. Workup and product isolation were done as in procedure 1.

H_2(C2-PBP) (5a). Procedure 1 was followed, using 695 μmol of each reactant. The pure product was obtained by flash chromatography on silica gel with CH_2Cl_2 and then 20% acetone/CH_2Cl_2 as eluent. Yield = 298 mg (43%).

^1H NMR ($CDCl_3$): δ 9.06 (s, 4 H), 8.77 (s, 4 H), 8.65 (d, 4 H), 8.40 (d, 4 H), 7.89 (t, 4 H), 7.65 (t, 4 H), 6.31 (s, 4 H), 6.28 (s, 4 H) D_2O exchangeable, 5.94 (s, 2 H), 3.60 (s, 4 H), −3.05 (s, 2 H) D_2O exchangeable. UV–vis (CH_2Cl_2): λ 405 (sh), 424 (Soret), 486 (sh), 518, 549 (sh), 589, 646 nm. MS: *m/e* 993 $(M + H)^+$ for $C_{62}H_{40}N_8O_6$ (LSIMS+). Anal. Calcd for $C_{62}H_{40}N_8O_6 \cdot 0.5CHCl_3$: C, 71.31; H, 3.88; N, 10.64. Found: C, 71.19; H, 3.73; N, 10.62.

H_2(C4-PBP) (5b). Procedure 1 was followed, but because of reactant solubilities 160 μmol of each reactant was used. The product was obtained by flash chromatography on silica gel with CH_2Cl_2 and then 10% acetone/CH_2Cl_2 as eluent. Yield = 33.3 mg (22%, unoptimized).

^1H NMR ($CDCl_3$): δ 9.08 (s, 4 H), 8.80 (s, 4 H), 8.59 (d, 4 H), 8.54 (d, 4 H), 7.91 (t, 4 H), 7.72 (t, 4 H), 7.06 (s, 4 H) D_2O exchangeable, 6.57 (s, 4 H), 6.40 (s, 2 H), 3.32 (t, 4 H), 1.16 (t, 4 H), −2.90 (s, 2 H) D_2O exchangeable. UV–vis (CH_2Cl_2): λ 405 (sh), 424 (Soret), 488 (sh), 520, 555 (sh), 592, 650 nm. MS: *m/e* 1021 $(M + H)^+$ for $C_{64}H_{44}N_8O_6$ (LSIMS+). Anal. Calcd for $C_{64}H_{44}N_8O_6 \cdot 0.5CHCl_3$: C, 71.68; H, 4.15; N, 10.37. Found: C, 71.70; H, 3.98; N, 10.23.

H_2(C6-PBP) (5c). Procedure 1 was followed; 270 μmol of each reactant was used. The pure product was obtained by silica gel flash chromatography with CH_2Cl_2 and then 10% Et_2O/CH_2Cl_2 as eluent. Yield = 113 mg (41%). Alternatively, procedure 2 was followed, with 1.35 mmol of tetraacid chloride and tetraamine being used. Yield = 600 mg (44%).

^1H NMR ($CDCl_3$): δ 9.10 (s, 4 H), 8.78 (d, 4 H), 8.76 (s, 4 H), 8.45 (d, 4 H), 7.93 (t, 4 H), 7.69 (t, 4 H), 7.53 (s, 4 H) D_2O exchangeable, 6.74 (s, 4 H), 6.66 (s, 2 H), 3.59 (t, 4 H), 1.02 (m, 4 H), 0.59 (m, 4 H), −2.78 (s, 2 H) D_2O exchangeable. UV–vis (CH_2Cl_2): λ 405 (sh), 425 (Soret), 486 (sh), 521, 556 (sh), 592, 649 nm. MS: *m/e* 1049 (M +

H)$^+$ for $C_{66}H_{48}N_8O_6$ (LSIMS+). Anal. Calcd for $C_{66}H_{48}N_8O_6 \cdot 0.5CHCl_3$: C, 72.03; H, 4.41; N, 10.11. Found: C, 71.92; H, 4.34; N, 10.15.

H_2(C8-PBP) (5d). Procedure 1 was used on the same scale as with the hexane derivative. The product was obtained by flash chromatography on silica gel with $CHCl_3$ as eluent. Yield = 125 mg (45%).

^{1}H NMR ($CDCl_3$): δ 9.08 (s, 4 H), 8.83 (d, 4 H), 8.79 (s, 4 H), 8.42 d, 4 H), 7.92 (t, 4 H), 7.77 (s, 4 H) D_2O exchangeable, 7.68 (t, 4 H), 6.89 (s, 4 H), 6.71 (s, 2 H), 3.59 (t, 4 H), 1.26 (m, 4 H), 0.60–0.85 (m, 8 H), –2.70 (s, 2 H) D_2O exchangeable. UV–vis (CH_2Cl_2): λ 405 (sh), 425 (Soret), 488 (sh), 521, 558, 594, 651 nm. MS: *m/e* 1077 (M + H)$^+$ for $C_{68}H_{52}N_8O_6$ (LSIMS+). Anal. Calcd for $C_{68}H_{52}N_8O_6 \cdot 0.5CHCl_3$: C, 72.37; H, 4.65; N, 9.86. Found: C, 73.47; H, 4.64; N, 9.58.

H_2(C10-PBP) (5e). Procedure 1 was used on the same scale as with the hexane derivative. The pure product was obtained by flash chromatography on silica gel with $CHCl_3$ as eluent. Yield = 150 mg (53%).

^{1}H NMR ($CDCl_3$): δ 9.08 (s, 4 H), 8.89 (d, 4 H), 8.80 (s, 4 H), 8.40 (d, 4 H), 7.85–8.0 (m, 8 H) D_2O exchangeable to triplet, 7.67 (t, 4 H), 6.96 (s, 4 H), 6.77 (s, 2 H), 3.59 (t, 4 H), 1.39 (q, 4 H), 0.80–1.10 (m, 12 H), –2.66 (s, 2 H) D_2O exchangeable. UV–vis (CH_2Cl_3): λ 405 (sh), 425 (Soret), 486 (sh), 521, 556, 594, 650 nm. MS: *m/e* 1105 (M + H)$^+$ for $C_{70}H_{56}N_8O_6$ (LSIMS+).

H_2(PXY-PBP) (5f). Procedure 1 was used but owing to the solubility of the tetraacid chloride, 220 μmol of each reactant was used. The product was isolated after flash chromatography on silica gel with $CHCl_3$ as eluent. Yield = 82 mg (35%).

^{1}H NMR ($CDCl_3$): δ 9.08 (s, 4 H), 8.76 (d, 4 H), 8.71 (s, 4 H), 8.44 (d, 4 H), 7.90 (t, 4 H), 7.68 (t, 4 H), 7.39 (s, 4 H) D_2O exchangeable, 6.90 (s, 4 H), 6.56 (s, 2 H), 6.54 (s, 4 H), 4.83 (s, 4 H), –2.88 (s, 2 H) D_2O exchangeable. UV–vis (CH_2Cl_2): λ 405 (sh), 424 (Soret), 488 (sh), 520, 553, 593, 649 nm. MS: *m/e* 1069 (M + H)$^+$ for $C_{68}H_{44}N_8O_6$ (LSIMS+). Anal. Calcd for $C_{68}H_{44}N_8O_6 \cdot 0.5CHCl_3$: C, 72.88; H, 3.97; N, 9.93. Found: C, 73.13; H, 3.76; N, 9.89.

H_2(DMB-PBP) (5g). Procedure 1 was followed; 300 μmol of each reactant was used. The product was isolated after chromatography on silica gel with CH_2Cl_2 and then 10% Et_2O/CH_2Cl_2 as eluent. Yield = 127 mg (37%, unoptimized).

^{1}H NMR ($CDCl_3$): δ 9.07 (s, 4 H), 8.75 (m, 8 H), 8.54 (d, 4 H), 7.93 (t, 4 H), 7.69 (t, 4 H), 7.36 (s, 4 H) D_2O exchangeable, 6.94 (m, 2 H), 6.87 (m, 1 H), 6.80 (s, 4 H), 6.65 (s, 2 H), 4.78 (s, 4 H), 3.22 (q, 2 H), 0.33 (t, 3 H), –2.89 (s, 2 H) D_2O exchangeable. UV–vis (CH_2Cl_2): λ 405 (sh), 423 (Soret), 488 (sh), 519, 552, 591, 648 nm. MS: *m/e* 1141 (M + H)$^+$ for $C_{71}H_{48}N_8O_8$ (LSIMS+). Anal. Calcd for $C_{71}H_{48}N_8O_8 \cdot 0.5CHCl_3$: C, 73.47; H, 4.18; N, 9.59. Found: C, 73.23; H, 3.91; N, 9.41.

H_2(BN-PBP) (5h). Procedure 1 was carried out on 72 μmol of each reactant in 10 mL of CH_2Cl_2. The pure product was separated from a closely preceding impurity by flash chromatography on silica gel with CH_2Cl_2 and then 5% Et_2O/CH_2Cl_2 as eluent. Yield = 42 mg (24%).

^{1}H NMR ($CDCl_3$): δ 9.09 (s, 4 H), 8.70–8.90 (m, 8 H), 8.51 (d, 2 H), 8.40 (d, 2 H), 7.93 (m, 4 H), 7.60–7.80 (m, 8 H), 7.52 (s, 2 H) D_2O exchangeable, 7.49 (d, 2 H), 7.19 (s, 2 H) D_2O exchangeable, 7.10 (t, 2 H), 6.95 (d, 2 H), 6.88 (m, 4 H), 6.68 (s, 2 H), 6.47 (s, 2 H), 3.2–3.8 (m, 8 H), –2.73 (s, 2 H) D_2O exchangeable. UV–vis (CH_2Cl_2): λ 405 (sh), 425 (Soret), 492 (sh), 525, 555, 593, 650 nm. MS: *m/e* 1304 M$^+$ for $C_{84}H_{56}N_8O_8$ (FD). No satisfactory elemental analysis was obtained for this compound.

Ruthenium Insertion. General Procedure (9–14). Unmetalated picnic-basket porphyrin (286 μmol) was suspended in 120 mL of *o*-dichlorobenzene in a 250-mL two-neck round-bottom flask that was fitted with a magnetic stirrer, a glass pipet extending into the solution, and a condenser. Argon was gently bubbled through the stirred solution as the flask was slowly warmed in an oil bath to 190 °C and held at that temperature for 1 h. After this time all the porphyrin had dissolved and the solution was thoroughly degassed. While Ar was bubbled through the solution, 500 mg (782 μmol) of crystalline $Ru_3(CO)_{12}$ was added in 10 equal aliquots over 2.5 h. The solution was stirred at 190 °C an additional 5 h when examination by visible spectroscopy indicated that metalation was complete. The solvent was removed from the cooled solution under mechanical pump vacuum, and the resulting residue was suspended in 100 mL of a 4/1 CH_2Cl_2/THF solution and filtered through packed Celite to remove ruthenium metal. The Celite pad was washed with 50 mL of the CH_2Cl_2/THF solution, and the washings were combined with the original filtrate. The solvent was removed from this solution under reduced pressure, and the residue was dissolved in 100 mL of CH_2Cl_2 that contained 2 mL of CF_3CO_2H. After being stirred at room temperature for 1.5 h, the solution was transferred to a separatory funnel, 10 mL of THF was added, and the resulting solution was washed twice with 100 mL of water. The solvent was then removed from the organic layer, and the residue was dissolved in 10 mL of CH_2Cl_2 that contained 2 drops of coordinating solvent (tetrahydrofuran or pyridine). This solution was then flash chromatographed on a silica gel column (4-cm diameter × 10 cm) with the solvent system described below. The desired product, Ru(PBP)CO·L (L = tetrahydrofuran or pyridine), was removed from the column as a deep red solution, 20 mL of hexanes was added, and the solvent was slowly removed on a rotovap. The pure product, obtained as microcrystals, was washed with hexanes and dried under vacuum. Yield = 65–85%.

Ru(C2-PBP)(CO)$_{in}$(pyr)$_{out}$ (9). Chromatography on silica gel, using CH_2Cl_2 to load and a solvent mixture of 100/50/2 CH_2Cl_2/Et_2O/THF to elute the column, gave the pure product.

^{1}H NMR ($CDCl_3$): δ 8.88 (s, 4 H), 8.54 (d, 4 H), 8.45 (s + d, 8 H), 7.82 (t, 4 H), 7.65 (t, 4 H), 6.36 (s, 4 H), 6.26 (s + t, 5 H), 5.97 (s, 2 H), 5.44 (t, 2 H), 3.64 (s, 4 H), 2.04 (d, 2 H). UV–vis (CH_2Cl_2): λ 416 (Soret), 536, 569 nm. IR (CH_2Cl_2): CO stretch 1955 cm^{-1}. Anal. Calcd for $C_{68}H_{43}N_9O_7Ru \cdot CH_2Cl_2$: C, 64.53; H, 3.54; N, 9.82. Found: C, 64.56; H, 3.91; N, 9.25.

Ru(C6-PBP)(CO)$_{out}$(THF)$_{in}$ (10). Chromatography on silica gel, using CH_2Cl_2 to load and a solvent mixture of 100/10/1 CH_2Cl_2/Et_2O/THF to elute the column, gave the pure product.

^{1}H NMR ($CDCl_3$): δ 9.04 (s, 4 H), 8.65 (d, 4 H), 8.49 (m, 8 H), 7.89 (t, 4 H), 7.71 (t, 4 H), 7.63 (s, 4 H), 6.80 (s, 4 H), 6.49 (s, 2 H), 3.60 (t, 4 H), 1.12 (br m, 4 H), 0.70 (br m, 4 H), –2.15 (br m, 4 H), –2.94 (br m, 4 H). UV–vis (THF): λ 415 (Soret), 532, 564 nm. IR (CH_2Cl_2): CO stretch 1949 cm^{-1}. MS: *m/e* 1177 (M + H – THF)$^+$ for $C_{71}H_{54}N_8O_8Ru$ (LSIMS+). Anal. Calcd for $C_{71}H_{54}N_8O_8Ru \cdot CH_2Cl_2$: C, 64.85; H, 4.24; N, 8.41. Found: C, 64.84; H, 4.16; N, 8.26. The CH_2Cl_2 solvate was quantified by ^{1}H NMR spectroscopy.

Ru(C6-PBP)(CO)$_{out}$(pyr)$_{in}$ (11). Chromatography on silica gel, using CH_2Cl_2 to load and a solvent mixture of 100/10 CH_2Cl_2/Et_2O to elute the column, gave the pure product.

^{1}H NMR ($CDCl_3$): δ 8.86 (s, 4 H), 8.60 (s, 4 H), 8.575 (d, 4 H), 8.525 (d, 4 H), 7.70 (t, 4 H), 6.64 (s, 4 H), 6.55 (s, 4 H), 5.53 (s, 2 H), 4.67 (t, 1 H), 4.12 (t, 2 H), 3.52 (t, 4 H), 1.45 (br m, 4 H), 1.09 (br m, 4 H), 0.55 (d, 2 H). UV–vis (CH_2Cl_2): λ 416 (Soret), 534, 568 nm. IR (CH_2Cl_2): CO stretch 1958 cm^{-1}. MS: *m/e* 1256 (M + H)$^+$, 1227 (M – CO)$^+$, 1177 (M – pyr) for $C_{72}H_{51}N_9O_7Ru$ (LSIMS+). Anal. Calcd for $C_{72}H_{51}N_9O_7Ru \cdot CH_2Cl_2$: C, 65.41; H, 3.99; N, 9.41. Found: C, 65.93; H, 4.04; N, 9.20. The CH_2Cl_2 solvate was quantified by ^{1}H NMR spectroscopy.

Ru(C8-PBP)(CO)$_{out}$(pyr)$_{in}$ (12). Chromatography on silica gel, using CH_2Cl_2 to load and a solvent mixture of 100/10 CH_2Cl_2/Et_2O to elute the column, gave the pure product.

^{1}H NMR ($CDCl_3$): δ 8.88 (s, 4 H), 8.58 (d, 4 H), 8.55 (s, 4 H), 8.50 (d, 4 H), 7.84 (t, 4 H), 7.58 (t, 4 H), 7.32 (s, 4 H), 6.74 (s, 4 H), 5.93 (s, 2 H), 2.79 (t, 1 H), 4.01 (t, 2 H), 3.54 (t, 4 H), 1.43 (br m, 4 H), 0.90–1.10 (br m, 8 H), 0.80 (d, 2 H). UV–vis (CH_2Cl_2): λ 416 (Soret), 534, 567 nm. IR (CH_2Cl_2): CO stretch 1960 cm^{-1}. Anal. Calcd for $C_{74}H_{55}N_9O_7Ru$: C, 69.26; H, 4.32; N, 9.82. Found: C, 68.36; H, 4.19; N, 9.50.

Ru(PXY-PBP)(CO)$_{out}$(pyr)$_{in}$ (13). Chromatography on silica gel, using CH_2Cl_2 to load and a solvent mixture of 100/10 CH_2Cl_2/Et_2O to elute the column, gave the pure product.

^{1}H NMR ($CDCl_3$): δ 8.84 (s, 4 H), 8.52–8.55 (m, 12 H), 7.83 (t, 4 H), 7.69 (t, 4 H), 6.94 (s, 4 H), 6.83 (s, 4 H), 6.74 (s, 4 H), 5.45 (s, 2 H), 4.84 (s, 4 H), 3.54 (t, 2 H), 2.51 (s, 1 H), 0.44 (d, 2 H). UV–vis (CH_2Cl_2): λ 416 (Soret), 534, 567 nm. Anal. Calcd $C_{74}H_{47}N_9O_7Ru \cdot CH_2Cl_2$: C, 66.22; H, 3.64; N, 9.27. Found: C, 65.31; H, 3.44; N, 8.79.

Ru(C6-PBP)(CO)$_{in}$(pyr)$_{out}$ (14). In a drybox, 20 mg (155 μmol) of Ru(C6-PBP)(THF)$_2$ (preparation of this compound is described in the following paper),[43] dissolved in 2 mL of THF, was added to 50 mL of benzene in a 100-mL lyophilization flask. The sealed flask was removed from the box and lyophilized to give a fluffy brown powder. In an inert-atmosphere box, this material was transferred to a pyrolysis tube and placed under high vacuum (1×10^{-5} Torr). The sample was heated to 250 °C in a silicone oil bath for 18 h. No dramatic color change was observed. When the resulting red-brown powder was exposed to 1 atm of CO, it immediately turned cherry red. After 1 h under a CO atmosphere the excess CO was removed under high vacuum (1×10^{-5} Torr, 250 °C, 10 h). The powder was then exposed to air and dissolved in 5 mL of CH_2Cl_2 containing 5 drops of pyridine. Chromatography on silica gel using CH_2Cl_2 and then 10% Et_2O/CH_2Cl_2 as eluent afforded the pure product. Yield = 13 mg (65%).

^{1}H NMR ($CDCl_3$): δ 9.92 (s, 4 H), 8.68 (d, 4 H), 8.43 (d, 4 H), 7.84 (t, 4 H), 7.63 (t, 4 H), 7.16 (s, 4 H), 6.76 (s, 4 H), 6.29 (s + t, 3 H), 5.42 (t, 2 H), 3.48 (t, 4 H), 1.99 (d, 2 H), 1.30 (br m, 4 H), 0.86 (br

(43) Collman, J. P.; Brauman, J. I.; Fitzgerald, J. P.; Sparapany, J. W.; Ibers, J. A. *J. Am. Chem. Soc.*, following paper in this issue.

m, 4 H). UV-vis (CH_2Cl_2): λ 416 (Soret), 535, 567 nm. IR (CH_2Cl_2): CO stretch 1951 cm^{-1}.

Summary

The picnic-basket porphyrins are readily available via a convergent, general synthesis. These tetraarylporphyrins bear rigid organic appendages that define a molecular cavity on one face of the porphyrin macrocycle. The large cavity volume of the hexyl-bridged picnic-basket porphyrin has been confirmed by X-ray crystallographic analysis and by ligand-binding studies. The utility of these protected porphyrins as cytochrome P-450 active-site analogues is currently being explored.

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Registry No. 2a, 113585-29-8; **2b**, 52739-96-5; **2c**, 113585-30-1; **2d**, 113585-31-2; **2e**, 113585-32-3; **2f**, 113585-33-4; **2g**, 113597-93-6; **2h**, 113585-34-5; **3a**, 52739-95-4; **3b**, 113585-35-6; **3c**, 22937-73-1; **3d**, 113585-36-7; **3e**, 22937-74-2; **3f**, 22937-70-8; **3g**, 113585-37-8; **3h**, 113585-38-9; **4a**, 113585-39-0; **4b**, 113585-40-3; **4c**, 113597-94-7; **4d**, 113597-95-8; **4e**, 113597-96-9; **4f**, 113585-41-4; **4g**, 113585-42-5; **4h**, 113585-43-6; **5a**, 113597-97-0; **5b**, 113597-98-1; **5c**, 113585-44-7; **5d**, 113585-45-8; **5e**, 113585-46-9; **5f**, 113585-47-0; **5g**, 113585-48-1; **5h**, 113585-49-2; **6**, 36596-67-5; **7**, 113585-50-5; **8**, 113597-99-2; **9**, 113598-00-8; **10**, 113585-10-7; **11**, 113585-11-8; **12**, 113585-12-9; **13**, 113585-13-0; **14**·$4C_5H_5N$, 113666-12-9; 4:0 TAMPP, 52199-35-6; $Br(CH_2)_2Br$, 106-93-4; $Br(CH_2)_4Br$, 110-52-1; $Br(CH_2)_6Br$, 124-09-4; $Br(CH_2)_8Br$, 373-44-4; $Br(CH_2)_{10}Br$, 646-25-3; $Ru_3(CO)_{12}$, 15243-33-1; 1,4-bis(bromomethyl)benzene, 623-24-5; diethyl 5-hydroxyisophthalate, 39630-68-7; 5-hydroxyisophthalic acid, 618-83-7; bis(diphenylmethyl) 5-hydroxyisophthalate, 113585-51-6; diphenyldiazomethane, 883-40-9; 2,6-dimethylbenzoic acid, 632-46-2; 1,1'-binaphth-2-ol, 602-09-5.

Supplementary Material Available: Bond distances (Table 1S), bond angles (Table 2S), dihedral angles (Table 3S), displacements from the mean porphyrin plane (Table 4S), distances between O (of CO) and the basket atoms (Table 5S), positional and thermal parameters for the non-hydrogen atoms (Table 6S), positional and thermal parameters of the hydrogen atoms (Table 7S), anisotropic thermal parameters (Table 8S) (16 pages); structural amplitudes (Table 9S) (46 pages). Ordering information is given on any current masthead page.

Reversible Binding of Dinitrogen and Dioxygen by a Ruthenium "Picnic-Basket" Porphyrin

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Abstract: We recently reported the synthesis and characterization of ruthenium "picnic-basket" porphyrin carbonyl complexes. These synthetic tetraarylporphyrins bear a rigid superstructure that defines a molecular cavity on one face of the porphyrin macrocycle. Photolysis of these carbonyl complexes in a coordinating solvent results in formation of bis-solvent complexes. The bis(pyridine) complex has been structurally characterized. General methods to control axial ligation in these ruthenium picnic-basket porphyrins are presented. A transient pentacoordinate ruthenium picnic-basket porphyrin, which reversibly binds both dinitrogen and dioxygen within the protected cavity, has been prepared. The N_2 and O_2 complexes have been characterized by UV-visible, ^1H NMR, and IR spectroscopies. The diamagnetic dioxygen complex shows $\nu(^{16}O-^{16}O)$ at 1103 cm^{-1} and thus is described as containing coordinated superoxide ion. A correlation between dioxygen binding and the Ru(III/II) potential was observed.

Interactions between molecular oxygen and low-valent metalloporphyrins have received considerable attention because of their relevance to the biological transport and activation of oxygen by hemoproteins.[1] The periodic relationship of ruthenium to iron, the metal found in hemoproteins, has stimulated considerable interest in the interactions of ruthenium porphyrins and molecular oxygen. To date, however, no example of a well-characterized ruthenium porphyrin dioxygen adduct has been reported.

The first ruthenium porphyrin reported to bind dioxygen reversibly was a five-coordinate ruthenium(II) porphyrin pyridine complex, stabilized within a lipid monolayer.[2] Hopf and Whitten formed this species by photochemical ejection of CO from the six-coordinate carbonyl adduct that had already been incorporated in the monolayer. Prior to this, all known ruthenium(II) porphyrins were six-coordinate and contained strong π-acceptor ligands that render the ruthenium(II) center inert to dioxygen.[3] The five-coordinate species was also reported to bind dinitrogen reversibly. Unfortunately, because of the lipid matrix the only

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