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N,N′-Bridged Porphyrins. Novel Synthesis, Metal Complexes, and Conversion into N-Monosubstituted Porphyrins. Crystal Structure of (*N*,*N*′-((Benzyloxy)methylene)tetraphenylporphyrin-*N*″,*N*‴)-dibromopalladium(II)

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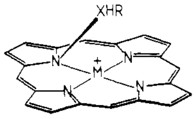
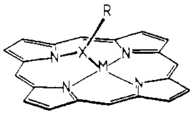
Abstract: Formation of a one-carbon bridge between vicinal pyrrolic nitrogen atoms of porphyrins was easily achieved by using $CHCl_3/NaOH/ROH$ in the presence of a phase-transfer agent. Alkylation of a third nitrogen atom of the resulting bases and acid-catalyzed hydrolysis of the bridge allowed the preparation of various N-monosubstituted porphyrins. The bridged bases acted as a bidentate ligand toward palladium(II) and mercury(II) to give sitting-atop metal complexes. The crystal and molecular structures of (*N*,*N*′-((benzyloxy)methylene)tetraphenylporphyrin-*N*″,*N*‴)dibromopalladium(II), $PdBr_2(N_4OC_{52}H_{36})\cdot CH_2Cl_2$, have been determined from three-dimensional single-crystal X-ray diffraction data, collected by counter techniques. The dark purple crystals are triclinic of space group $P1$ (No. 1) with one formula unit in the unit cell of dimensions a = 10.591 (2) Å, b = 10.706 (1) Å, c = 12.560 (1) Å, α = 118.82 (1)°, β = 114.63 (1)°, and γ = 77.68 (1)°. The structure has been refined by least-squares methods to R = 0.051 (R_w = 0.067) for 3569 unique reflections having $F^2 > 3\sigma(F^2)$. The (benzyloxy)methylene moiety bridges two adjacent nitrogen atoms and the $PdBr_2$ group bridges the two other nitrogen atoms leading to a very distorted prophyrin ring. The palladium atom is out of the 4N mean plane by 1.460 Å, and the individual pyrrole rings make dihedral angles with the 4N plane between 8.2 and 21.3°.

Coordination of porphyrins involve the stepwise replacement of the metal ligands with pyrrolic nitrogen atoms. To study the likely intermediates of the reaction (one to three coordinated N atoms), one must rely on models. Two approaches are available: one may either use second- and third-row metals whose reaction with porphyins is known to proceed via sitting-atop complexes[3] (rhodium,[4] rhenium,[5] mercury,[6] platinum,[7] for example) or block one to three pyrrolic nitrogen atoms with alkyl or amino groups. Monoalkylated (or aminated porphyrins) form a series of metal complexes in which the metal is four-coordinated to the four porphyrinic N atoms (**1**)[8] or to three porphyrinic N atoms plus one side-chain C or N atom (**2**).[9] However in certain cases the metal may coordinate with only three porphyrinic N atoms: we recently described the preparation and crystal structure of such a mercury(II) derivative, **3**.[10]

Metal complexes of N,N′-dialkylated porphyrins are unknown, except in the case of a N,N′ one carbon bridged porphyrin (**4**).[11] The corresponding base was obtained in low yield on rearrangement of **2** (M = Co(III), XR = $CHCO_2Et$, OEP series), while another bridged porphyrin, **5**, resulted from the direct interaction of CH_2I_2 with octaethylporphyrin. The $PdCl_2$ complex of **4** was isolated although the X-ray crystal structure was not determined.[12]



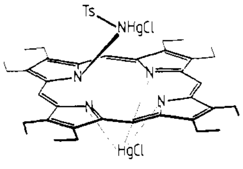
1



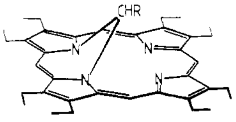
2

divalent metal ion, peripheral substituents omitted

1 X = CH   2 X = CH or N



3



4 R = COOEt
5 R = H
7 R = OCH_3

In this paper we wish to describe the easy preparation of a series of stable N,N′-bridged porphyrins, the reactions and metalation of the bases, and the crystal structure of a palladium(II) complex.

Synthesis of the Ligands and Metal Complexes

Treatment of *meso*-tetraphenylporphyrin (H_2TPP) with chloroform and base under phase-transfer conditions (NaOH, H_2O, ROH, triethylbenzylammonium chloride = TEBA) rapidly gave a series of bridged porphyrins **6a–e**. (Under the same conditions, octaethylporphyrin gave a bridged base **7** in low yield.) Yields

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[12] The proposed structure for this $PdCl_2$ complex does not agree with our findings.

0002-7863/82/1504-1272$01.25/0

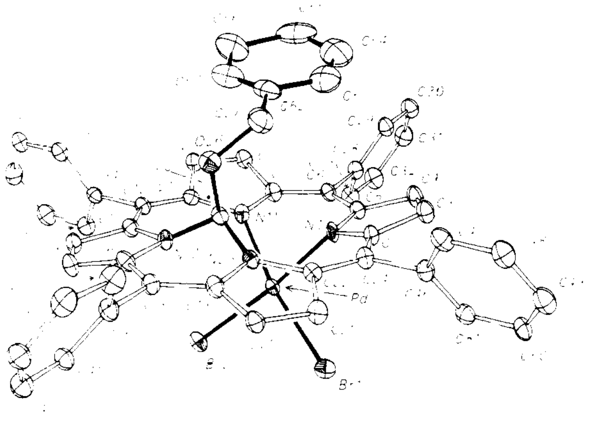
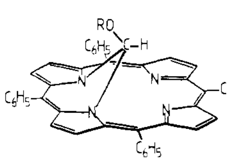
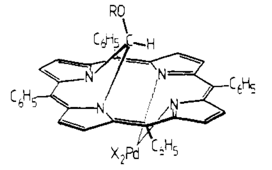


Figure 1.

vary from 16 to 25% (33 to 53% if one takes into account the recovered starting material).



6a R = CH_3
6b R = CH_2CH_3
6c R = $CH(CH_3)_2$
6d R = $(CH_2)_2OCH_3$
6e R = $CH_2C_6H_5$



8a R = CH_3 X = Cl
8b R = C_2H_5 X = Cl
8c R = $CH_2C_6H_5$ X = Cl
8d R = $CH_2C_6H_5$ X = Br

The similarities of the NMR spectra demonstrated that all bases (**6a–e**) belonged to the same series. The pyrrolic signals appeared two AB systems, thus indicating a plane of symmetry containing two opposite meso carbons. Very large upfield shifts characterized the signals of the bridge and side-chain protons (−0.93 to −1.30 ppm for the bridge proton). At this stage it was difficult to specify the relative positions of the bridge substituents.

The treatment of the bases with $PdCl_2$ in CH_3CN/CH_2Cl_2 (or $PdCl_2$ + LiBr in the same solvent system) gave the corresponding $PdCl_2$ complexes (respectively $PdBr_2$) formulated as **8a–d**. A similar $HgCl_2$ complex was prepared from **6b** but could not be purified from excess $HgCl_2$. Preparation of $PtCl_2$ complex, for comparison with the known $PtCl_2$–porphyrin complexes,[7] failed since decomposition of **6b** to give H_2TPP occurred faster than the metalation.

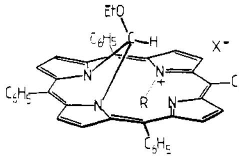
The $PdCl_2$ complexes were stable enough to give good quality NMR spectra but on standing (even as crystals) decomposed to PdTPP. Only compounds **8c** and **8d** (benzyloxy side chain) gave stable crystals. The NMR spectra showed the same symmetry but large shift differences compared to those of the bases: in particular the bridge proton signal was shifted upfield ($\Delta\delta = -1.73$ to -2.47) while the alkoxy side chain remained less affected. Since in the vicinity of the electrophilic $PdCl_2$ group one would expect downfield shifts[13] (as exemplified by the downfield shift of some ortho phenyl protons, see Experimental Section), these data indicate that (a) the $PdCl_2$ group is placed on the side of the macrocycle opposite to the carbon bridge, (b) Pd is bound with the N″ and N‴ atoms (same symmetry as the bases), and (c) complexation with $PdCl_2$ will pull the corresponding N atoms and fold the π system toward the carbon bridge. Since the most affected group should point toward the center of the molecule the stereochemistry of the carbon bridge should be that depicted. the X-ray crystal structure of **8d** fully confirmed this interpretation (see second part of this paper). The NMR data available for the corresponding $HgCl_2$ complex (see Experimental Section) suggest a similar mode of coordination to the macrocycle.

Table I. Selected Bond Lengths (Å) and Angles (Deg) with Their Estimated Standard Deviations

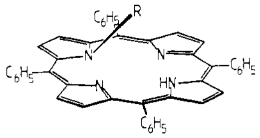
	Bond Lengths		
Pd-Br1	2.395 (1)	C21-C22	1.42 (1)
Pd-Br2	2.429 (1)	C3-C4	1.35 (1)
Pd-N1	2.010 (7)	C8-C9	1.37 (1)
Pd-N11	2.071 (7)	C14-C15	1.34 (1)
Pd-H25	2.58	C20-C21	1.38 (1)
N1-N11	2.59 (1)	C6-C5	1.40 (1)
N11-N17	3.42 (1)	C6-C7	1.39 (1)
N17-N23	2.36 (1)	C12-C10	1.42 (1)
N23-N1	3.40 (1)	C12-C13	1.38 (1)
N1-C2	1.381 (9)	C18-C16	1.39 (1)
N1-C5	1.34 (1)	C18-C19	1.40 (1)
N11-C7	1.40 (1)	C24-C2	1.41 (1)
N11-C10	1.37 (1)	C24-C22	1.40 (1)
N17-C13	1.42 (1)	C6-C28	1.49 (1)
N17-C16	1.38 (1)	C12-C34	1.52 (1)
N23-C19	1.41 (1)	C18-C40	1.50 (1)
N23-C22	1.40 (1)	C24-C46	1.51 (1)
C2-C3	1.43 (1)	N17-C25	1.45 (1)
C4-C5	1.45 (1)	N23-C25	1.46 (1)
C7-C8	1.44 (1)	C25-O26	1.40 (1)
C9-C10	1.45 (1)	O26-C27	1.43 (1)
C13-C14	1.41 (1)	C27-C52	1.58 (2)
C15-C16	1.37 (1)	mean C⋯C (phenyl rings)	1.375 (3)
C19-C20	1.38 (1)		

	Bond Angles		
Br1-Pd-Br2	93.14 (4)	N17-C13-C12	133.0 (7)
N1-Pd-N11	79.0 (2)	N17-C16-C18	119.2 (7)
Br1-Pd-N1	93.9 (2)	N23-C19-C18	120.3 (8)
Br1-Pd-N11	170.9 (2)	N23-C22-C24	133.3 (7)
Br2-Pd-N1	172.8 (2)	Pd-N1-C2	127.8 (5)
Br2-Pd-N11	93.8 (2)	Pd-N1-C5	116.5 (5)
C2-N1-C5	106.3 (6)	Pd-N11-C7	114.9 (5)
C7-N11-C10	105.8 (6)	Pd-N11-C10	134.7 (5)
C13-N17-C16	107.0 (6)	C13-N17-C25	130.3 (6)
C19-N23-C22	106.8 (6)	C22-N23-C25	134.5 (6)
C5-C6-C7	121.5 (7)	N17-C25-N23	107.6 (6)
C10-C12-C13	133.0 (7)	C16-N17-C25	117.1 (6)
C16-C18-C19	118.3 (7)	C19-N23-C25	115.6 (6)
C22-C24-C2	131.7 (7)	N17-C25-O26	107.9 (6)
N1-C5-C6	121.6 (6)	N23-C25-O26	109.1 (6)
N1-C2-C24	127.0 (6)	C25-O26-C27	117.2 (7)
N11-C7-C6	122.4 (7)	O26-C27-C52	107.9 (9)
N11-C10-C12	126.9 (7)		

Alkylation of base **6b** (CH_3I, C_2H_5I, p-$NO_2C_6H_4CH_2Br$) gave trialkylated salts, tentatively formulated as **9** in nearly quantitative yield. Acid treatment of the salts caused the loss of the bridge and the formation, on neutralization, of the N-monoalkylated porphyrins **10a–c** in good yields. This reaction sequence represents a versatile method for the N-monoalkylation of H_2TPP since direct alkylation usually leads to mixtures.[8,14] (Only N-methylation could so far be achieved with reasonable selectivity and yields by using either $CF_3SO_3CH_3$[15] or $N_2CHCO_2Et/ZnTPP$ followed by decarboxylation[16].)



9a R = CH_3
9b R = C_2H_5
9c R = $CH_2C_6H_4$-p-NO_2



10a R = CH_3
10b R = C_2H_5
10c R = $CH_2C_6H_4$-p-NO_2

Structure of Compound 8d

Figure 1 shows the molecule as it exists in the crystal together with the labeling scheme used, and Figure 2 shows a stereoview. Individual bond lengths and angles are given in Table I and least-square mean planes in Table II. The (benzyloxy)methylene moiety bridges the two adjacent nitrogen atoms N17 and N23

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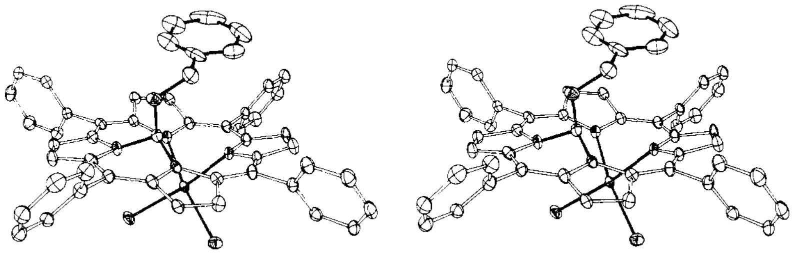

Figure 2.

of the tetraphenylporphyrin. The two other adjacent nitrogen atoms N1 and N11 are bridged by the palladium atom, and the $PdBr_2$ group is on the opposite side of the porphyrin plane with regard to the (benzyloxy)methylene moiety. The coordination polyhedron of the palladium atom is completed by the hydrogen atom H25 (Pd–H25 = 2.58 Å) and is a deformed square prism.

Whereas in classical porphyrins, the pyrrole rings are nearly coplanar with the 4N plane, the porphyrin macrocycle is here very distorted. As shown in Table II, the four nitrogen atoms are approximately coplanar and the palladium atom is out of the mean plane PL1 by −1.460 Å. The individual pyrrole rings are planar within experimental errors (PL2 to PL6) and make dihedral angles of 17.4, 21.3, 8.2, and 12.7° with mean plane PL2 containing the meso-carbon atoms (C6/C12/C18/C24). The distorsion is such that pyrrole rings N1 and N11 are rotated around the α–α carbon atom axis toward the palladium atom and pyrrole rings N17 and N23 are rotated toward the (benzyloxy)methylene moiety; these deformations are obviously due to the two bridges on N1/N11 and N17/N23, the first one inducing more important rotation than the second.

These different rotations in turn fix the orientations of the phenyl rings with respect to mean plane PL2: the pyrrole ring N1 makes a dihedral angle of 17.4° with PL2 while for the pyrrole ring N11, this angle is 21.3°; the orientations of phenyl rings Ph4 (C46–C51), Ph1 (C28–C33), and Ph2 (C34–C39) is such to minimize the interactions with the pyrrole β-carbon hydrogens. The same situation occurs for rings N17 and N23. The dihedral angles between the phenyl rings Ph1, Ph2, Ph3, Ph4, and PL2 are respectively 116.5, 68.0, 68.3, and 120.8°. The bridges introduce a great asymmetry on the N–N bond distances and in the N–C–C bond angles as shown in Table I; the four nitrogen atoms are not as usually at the corners of a square. The observed deformations are much more pronounced than those observed in other distorted porphyrin skeletons.[4,8,17–19]

Using C_a and C_b to denote the α- and β-carbon atoms of a pyrrole ring, C_m for the methine carbon and C_p for the phenyl carbon atom bonded to the core, the average bond lengths in the porphyrin skeleton are as follows: $N–C_a$ = 1.388 (3), $C_a–C_b$ = 1.421 (4), $C_b–C_b$ = 1.362 (6), $C_a–C_m$ = 1.403 (4), and $C_m–C_p$ = 1.508 (5) Å. Despite the important deformation of the porphyrin skeleton, these mean value averages remain in the ranges found in normal planar porphyrins,[20] illustrating the important flexibility of porphyrin rings, but as already mentioned, the bond angles are very sensitive to this deformations.

The (benzyloxy)methylene moiety has a normal geometry, with the phenyl ring mean plane making an angle of 15.3° with PL2; this ring is located over the porphyrin ring. The carbon atom C25 points toward the center of the 4N plane and the hydrogen atom H25 is 0.71 Å out of the mean plane PL1 opposite to the palladium atom.

The average values of internal angle in the phenyl rings is 119.9 (2)°, and the average value of the C–C bond distances is 1.375 (3) Å.

Table II. Least-Squares Mean Planes

no.	dist,ª Å		equations^b
PL1	N1°	0.013 (9)	$a = -0.7604, b = -0.6077,$
	N11°	−0.015 (9)	$c = -0.2293, d = 1.4605$
	N17°	0.015 (9)	
	N23°	−0.013 (9)	
	Pd	−1.460 (0)	
PL2	C6°	−0.043 (11)	$a = -0.7597, b = -0.5598,$
	C12°	0.042 (11)	$c = -0.3308, d = 1.6716$
	C18°	−0.045 (11)	
	C24°	0.047 (12)	
	N1	−0.237 (9)	
	N11	−0.336 (9)	
	N17	0.068 (9)	
	N23	0.102 (9)	
PL3	N1°	−0.007 (9)	$a = -0.9100, b = -0.3025,$
	C2°	0.008 (12)	$c = -0.2834, d = 0.9574$
	C3°	−0.005 (14)	
	C4°	−0.003 (14)	
	C5°	0.008 (12)	
PL4	N11°	−0.003 (9)	$a = -0.5364, b = -0.5669,$
	C7°	−0.005 (11)	$c = -0.6252, d = 0.6767$
	C8°	0.013 (11)	
	C9°	−0.016 (11)	
	C10°	0.012 (10)	
PL5	N17°	−0.013 (9)	$a = -0.8343, b = -0.4374,$
	C13°	0.018 (11)	$c = -0.3356, d = 2.1141$
	C14°	−0.012 (12)	
	C15°	−0.002 (12)	
	C16°	0.015 (12)	
PL6	N23°	−0.014 (8)	$a = -0.6446, b = -0.5615,$
	C19°	0.024 (11)	$c = -0.5189, d = 2.2796$
	C20°	−0.012 (11)	
	C21°	−0.004 (12)	
	C22°	0.016 (11)	

Dihedral Angles, Deg

PL1/PL2	6.4	PL2/PL5	8.2
PL2/PL3	17.4	PL2/PL6	12.7
PL2/PL4	21.3		

[a] Atoms with a degree sign are used to compute equation of planes. [b] Least-squares mean planes computed according to: Blow, D. M. *Acta Crystallogr.* 1960, *13*, 168–170.

The molecule crystallizes with a dichloromethane molecule which links different molecules together. Selected contact distances are given in Table III.

Experimental Section

Visible spectra were recorded on a Cary 118 spectrophotometer. Proton magnetic resonance spectra were recorded on a Perkin-Elmer model R12 (60-MHz) and a Cameca (250-MHz) spectrometers. The chemical shifts are expressed in δ values (ppm) relative to tetramethylsilane and the coupling constants in hertz (s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet). Combustion analyses were performed by the Service de Microanalyse de l'Institut de Chimie de Strasbourg. All analyses agree with the calculated values within ±0.4%, except when the figures are given in full. Separation and purification of the products were obtained by using Merck standardized alumina (II-III).

Preparation of Bases 6a-e. General Procedure. A mixture of H_2TPP (0.5 g), triethylbenzylammonium chloride (TEBA) (50 mg), NaOH (0.5 g), H_2O (0.5 g), alcohol ROH (0.5 mL), and $CHCl_3$ (30 mL, freshly distilled from P_2O_5) was vigorously stirred under N_2 for 2 h. To the brown suspension was added Na_2SO_4 (5 g), and the mixture was filtered through a sintered glass. The solid was extracted with CH_2Cl_2, and the

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(20) Among recent example: Scheidt, W. R.; Kastner, M. E.; Hatano, K. *Inorg. Chem.* **1978**, *17*, 708–710. Scheidt, W. R.; Reed, C. A. *Ibid.* **1978**, *17*, 710–714.

Table III. Contacts Less Than 3.1 Å

A B	dist, Å	equiv code[a]
Br1···H35	3.00	1/100
Br1···H43	2.95	1/101
Br1···H58	2.92	1/00$\bar{1}$
Br2···H36	3.10	1/100
C5···H44	3.09	1/101
C7···H48	3.00	1/011
C8···H48	2.89	1/011
C9···H48	2.90	1/011
C10···H48	3.07	1/011
C20···H38	2.82	1/0$\bar{1}\bar{1}$
C21···H38	2.95	1/0$\bar{1}\bar{1}$
O26···H32	3.10	1/$\bar{1}$0$\bar{1}$
C30···H21	2.79	1/001
C30···H37	2.91	1/1$\bar{1}$0
C31···H21	2.99	1/001
C31···H37	2.98	1/1$\bar{1}$0
C35···H43	2.96	1/001
C36···H4	2.99	1/$\bar{1}$10
C36···H42	3.08	1/001
C36···H43	2.96	1/001
C37···H42	3.00	1/001
C41···H49	3.07	1/$\bar{1}$10
C42···H9	2.87	1/00$\bar{1}$
C42···H49	2.74	1/$\bar{1}$10
C43···H9	3.08	1/00$\bar{1}$
C43···H49	2.93	1/$\bar{1}$10
C44···H56	3.03	1/00$\bar{1}$
C50···H15	2.91	1/1$\bar{1}$0
C50···H31	2.98	1/00$\bar{1}$
C51···H31	2.97	1/00$\bar{1}$
Cl 1···H3	2.75	1/011
Cl 2···H41	2.98	1/001

[a] The relative coordinates of the atoms in column A are listed in Table IV. The atoms in column B have their atomic coordinates specified by *I/uvw* which denotes how the parameters can be derived from the corresponding atoms in the crystal unit: 1, x, y, z. U, v, and w code a lattice translation as $u\vec{a} + v\vec{b} + w\vec{c}$.

organic phases were evaporated to dryness under vacuum. Chromatography (alumina, 150 g in CH_2Cl_2) gave the unchanged starting material followed by base **6** (crystallized from CH_2Cl_2–hexane).

Base 6a (16%, recovered H_2TPP, 70%): NMR ($CDCl_3$) δ -1.87 (s, 3, CH_3), -1.18 (s, 1, bridge H), 7.8 and 8.3 (2 m, 20, phenyl), 8.35 and 8.67 (2 d AB, 2 + 2, J = 4.3 Hz, pyrrolic H), 8.96 and 9.22 (2 d AB, 2 + 2, J = 5.1 Hz, pyrrolic H); visible (toluene) λ_{max} 432 nm (ϵ 183 000), 532 (15 700), 565 sh (6200), 608 (8800). Anal. ($C_{46}H_{32}N_4O$): C, H, N.

Base 6b (25%; recovered H_2TPP, 24%): NMR ($CDCl_3$) δ ca. -2.0 (m, 5, CH_2CH_3), -1.22 (s, 1, bridge H), 7.8 and 8.3 (2 m, 20, phenyl), 8.32 and 8.62 (2 d AB, 2 + 2, J = 4.4 Hz, pyrrolic H), 8.90 and 9.14 (2 d AB, 2 + 2, J = 5.0 Hz, pyrrolic H); visible (toluene) λ_{max} 434 nm (ϵ 187 000), 533 (15 400), 565 sh (6400), 608 (9100). Anal. ($C_{47}H_{34}N_4O$): C, H, N.

Base 6c (18%; recovered H_2TPP, 60%): NMR ($CDCl_3$) δ -2.92 (septet, 1, isopropyl H), -2.15 (d, 6, isopropyl), -1.30 (s, 1, bridge H), 7.8 and 8.3 (2 m, 20, phenyl), 8.26 and 8.58 (2 d AB, 2 + 2, J = 4.3 Hz), 8.85 and 9.11 (2 d AB, 2 + 2, J = 5.2 Hz); visible (toluene) λ_{max} 435 nm (ϵ 151 000), 533 (13 500), 567 sh (5900), 608 (8200). Anal. ($C_{48}H_{36}N_4O$): C, H, N.

Base 6d (22%; recovered H_2TPP, 44%) NMR ($CDCl_3$) δ -2.02 (t, 2, J = 5.5 Hz, O-CH_2), -1.20 (s, 1, bridge H), -0.12 (t, 2, J = 5.5 Hz, O-CH_2), 1.6 (s, 3, OCH_3), 7.8 and 8.3 (2 m, 20, phenyl), 8.33 and 8.64 (2 d AB, 2 + 2, J = 4.4 Hz, pyrrolic H), 8.90 and 9.17 (2 d AB, 2 + 2, J = 5.1 Hz, pyrrolic H); visible (toluene) λ_{max} 435 nm (ϵ 136 000), 533 (12 000) 565 sh (5500), 608 (7700). Anal. ($C_{48}H_{36}N_4O_2$): C, H, N.

Base 6e (24%; recovered H_2TPP, 31%): NMR ($CDCl_3$) -1.10 (s, 2, CH_2), -0.93 (s, 1, bridge H), 4.43 (d, 2, ortho H of side-chain phenyl), ca. 6.50 (m, 3, meta + para of side-chain phenyl), 7.8 and 8.3 (2 m, 20, phenyl), 8.34 and 8.67 (2 d AB, 2 + 2, J = 4.1 Hz, pyrrolic H), 8.94 and 9.19 (2 d AB, 2 + 2, J = 5.0 Hz, pyrrolic H); visible (toluene) λ_{max} 437 nm (ϵ 136 000), 535 (12 500), 566 sh (5300), 610 (7300). Anal. ($C_{52}H_{36}N_4O$ + 0.5 CH_2Cl_2 NMR detected): C, H, N.

Palladium Complexes. A suspension of palladium(II) chloride (300 mg) in acetonitrile (20 mL) was stirred at 20 °C for 2 h and filtered. This solution was added to a solution of base **6** (200 mg) in CH_2Cl_2 (15 mL) and the mixture kept in the dark. Slow evaporation gave complexes **8a–c**. The complex **8d** was obtained by using the same procedure but with the addition of 1 g of LiBr to the $PdCl_2$/acetonitrile suspension. The resulting crystals were washed (acetonitrile) and dried (10^{-2} torr at 20 °C). Only **8c** and **8d** proved to be stable and gave satisfactory analyses. Average yields: 70–75%.

$PdCl_2$ Complex 8a: NMR ($CDCl_3$) δ -3.00 (s, 1, bridge H), -1.76 (s, 3, CH_3), 7.9 and 8.3–8.8 (2 m, 20, phenyl), 8.18 and 8.73 (2 d AB, 2 + 2, J = 4.8 Hz, pyrrolic H), 9.09 and 9.18 (2 d AB, 2 + 2, J = 6.0 Hz, pyrrolic H).

$PdCl_2$ Complex 8b: NMR (CDl_3) δ -2.95 (s, 1, bridge H), -2.35 (t, 3, J = 7 Hz, CH_3), -2.02 (q, 2, J = 7 Hz, CH_2), 7.9 and 8.2–8.8 (2 m, 20, phenyl), 8.16 and 8.70 (2 d AB, 2 + 2, J = 5.0 Hz, pyrrolic H), 9.06 and 9.16 (2 d AB, 2 + 2, J = 6.2 Hz, pyrrolic H).

$PdCl_2$ Complex 8c: NMR ($CDCl_3$) δ -3.40 (s, 1, bridge H), -0.03 (s, 2, CH_2), 3.28 (d, 2, ortho H of side-chain phenyl), 5.53 (t, 2, meta H of side-chain phenyl), 6.06 (t, 1, para H of side-chain phenyl), 7.9 and 8.3–8.8 (2 m, 20, phenyl), 8.13 and 8.65 (2 d AB, 2 + 2, J = 4.9 Hz, pyrrolic H), 9.08 and 9.16 (2 d AB, 2 + 2, J = 5.4 Hz, pyrrolic H); visible (CH_2Cl_2) λ_{max} 408 nm (ϵ 51 200), 468 (53 200), 550 sh (3700), 602 (6600), 628 (9200). Anal. ($C_{52}H_{36}N_4OPdCl_2$ + 2 $CHCl_3$, NMR detected): C, H, N.

$PdBr_2$ Complex 8d: NMR ($CDCl_3$) δ -3.50 (s, 1, bridge H), -0.02 (s, 2, CH_2), 3.30 (d, 2, ortho H of side-chain phenyl), 5.30 (CH_2Cl_2), 5.56 (t, 2, meta H of side-chain phenyl), 6.08 (t, 1, para H of side-chain phenyl), 7.9 and 8.3–8.8 (2 m, 20, phenyl), 8.14 and 8.66 (2 d AB, 2 + 2, J = 4.9 Hz, pyrrolic H), 9.08 and 9.16 (2 d AB, 2 + 2, J = 5.4 Hz, pyrrolic H). Anal. ($C_{52}H_{36}N_4OPdBr_2$ + CH_2Cl_2, NMR detected): H, N, C (calcd, 59.60; found, 58.88).

$HgCl_2$ Complex. Base **6b** was dissolved in CH_2Cl_2 and solid $HgCl_2$ added until completion of the reaction (green solution; followed by silica gel TLC). The product was precipitated three times from CH_2Cl_2–hexane but did not crystallize. The NMR spectrum indicated only one product but combustion analysis and TLC demonstrated the presence of $HgCl_2$: NMR ($CDCl_3$) -3.70 (s, 1, bridge H), ca. -2.0 (m, 5, CH_2CH_3), 7.9 and 8.2–8.5 (2 m, 20, phenyl), 8.44 and 8.85 (2 d AB, 2 + 2, J = 4.7 Hz, pyrrolic H), 9.14 and 9.33 (2 d AB, 2 + 2, J = 5.2 Hz, pyrrolic H).

***N*-Methyl TPP (10a) from 6b.** A solution of base **6b** (50 mg) and CH_3I (0.5 mL) in CH_2Cl_2 (8 mL) was left at 20 °C for 12 h. The solvent was evaporated and the product showed the following (NMR in $CDCl_3$): δ -3.45 (s, 3, N-CH_3), -3.10 (s, 1, bridge H), ca. -2.1 (m, 5, CH_2CH_3), 7.6–9.3 (m, 28, phenyl + pyrrolic H).

The crude iodide was dissolved in CH_2Cl_2 (10 mL), TsOH·H_2O (0.1 g) added, and the green solution kept for 4 h at 20 °C; afterward it was washed with aqueous Na_2CO_3, dried (Na_2SO_4), filtered, and evaporated. The product (35 mg, 76%) was crystallized from CH_2Cl_2–MeOH and was identical (NMR, TLC) with an authentic sample of *N*-methyl TPP.[15,16]

***N*-Ethyl TPP (10b) from 6b.** A solution of base **6b** (50 mg) and EtI (2 mL) in CH_2Cl_2 was kept at 20 °C for 72 h. The same treatment as above (TsOH) gave *N*-ethyl TPP (**10b**) (41 mg, 85%), identical (NMR, TLC) with an authentic sample.[16]

***N*-*p*-Nitrobenzyl TPP (10c) from 6b.** A solution of base **6b** (50 mg) and *p*-nitrobenzyl bromide (100 mg) in CH_2Cl_2 (3 mL) was kept at 20 °C for 48 h. The solvent was evaporated and the residue extracted with 3 × 5 mL Et_2O to separate excess *p*-nitrobenzyl bromide. Treatment of the remaining solid as above gave *N*-p-nitrobenzyl TPP (**10c**) (44 mg, 79%). The product **10c** was independently prepared by direct alkylation of H_2TPP (0.6 g H_2TPP; 3 g of bromide; 150 °C; 1 h) albeit in low yield (2.5% + numerous other products): NMR ($CDCl_3$) δ -3.38 (s, 2, CH_2), ca. 0 (br s, 1, NH), 4.67 (d, 2, side-chain phenyl), 7.48 (d, 2, side-chain phenyl), 7.66 (s, 2, pyrrolic H), 7.8 and 8.0–8.3 (2 m, 20, phenyl), 8.56 and 8.72 (2 d AB, 2 + 2, J = 4.8 Hz, pyrrolic H), 8.96 (s, 2, pyrrolic H); visible (toluene) λ_{max} 432 nm (ϵ 290 000), 495 sh (4700), 527 (11 000), 568 (16 000), 614 (4500), 676 (5000). Anal. ($C_{51}H_{35}N_5O_2$): C, H, N.

Preparation of Base 7. With use of the general procedure (see above) base **7** was obtained in 5.5% yield (recovered H_2OEP, 71%): NMR ($CDCl_3$) δ -2.5 (s, 4, OCH_3 + bridge H), 1.84, 1.88, and 1.92 (3 t, 12 + 6 + 6, CH_3), 3.7–4.6 (m, 16, CH_2), 9.96 (s, 1, meso), 10.00 (s, 1, meso), 10.42 (s, 2, meso); visible (toluene) λ_{max} 415 nm (ϵ 70 800), 518 (10 500), 545 (5900), 588 (6800), 640 (5000). Anal. ($C_{38}H_{48}N_4O$): H, N. No satisfactory value for C could be obtained.

$PdCl_2$ Complex from 7 (General Procedure): NMR ($CDCl_3$) -3.83 (s, 1, bridge H), -2.46 (s, 3, OCH_3), 1.54, 1.86, and 1.99 (3 t, 6 + 12 + 6, CH_3), 3.7–4.4 (m, 16, CH_2), 10.35 (s, 1, meso), 10.68 (s, 2, meso). Like **8a,b** this complex is unstable and did not give satisfactory analytical results.

X-ray Crystallographic Data. Crystal data: $PdBr_2C_{52}H_{36}N_4O·CH_2Cl_2$; mol. wt. 1084.04; triclinic; a = 10.591(2), b = 10.706(1), c =

12.560(1), $\alpha = 118.82(1)$, $\beta = 114.63(1)$, $\gamma = 77.68(1)$; U = 1134.1 Å^3, Z = 1; $F_{000} = 542$; $d_{calc} = 1.587$, $d_{obs} = 1.56 \pm 0.02$ g.cm^{-3}; space group P1 (N° 1); CuKα (1.54184 Å) radiation for cell dimensions and intensity measurements; $\mu = 71.52$ cm^{-1}.

Preliminary X-ray examination established a one-molecule triclinic unit cell. Precise lattice constants and diffracted intensities were derived from measurements carried out on a Enraf-Nonius CAD4F automatic diffractometer using a crystal of dimensions 0.20 × 0.16 × 0.08 mm. The setting angles of 25 reflections with θ values in the range 9-20° were determined. Least-squares refinement of these reflections led to the lattice constants reported above. The measured density reported was obtained by flotation in aqueous zinc chloride solution.

Intensity data were collected by using the $\theta/2\theta$ scan technique and graphite-monochromated Cu Kα radiation. The intensities of 4058 unique reflections were measured within $0.045 < (\sin\theta)/\lambda < 0.587$. the prescan speed was 2° min^{-1}, and all reflections having $I < \sigma(I)$ during the prescan were flagged unobserved and not measured. The final scan speed was adjusted to have at least $\sigma(I)/I < 0.4$. The total ω scan angle was 1.20 + (Cu K$\alpha_1\alpha_2$ splitting)°.

The intensities of three standard reflections were monitored throughout the data collection period and measured every 2 h; no significant trend appeared. The intensity data were reduced to relative square amplitudes by application of the standard Lorentz and polarization factors. Absorption factors were computed by using the numerical integration method of Busing Levy.[21] For each reflection, a standard deviation was attached as $\sigma^2(F_o^2) = \sigma_{count}^2 + (pI)^2$ with a p value of 0.08.

For all computations, the Enraf-Nonius SDP/V17 package[22] was used.

The structure was solved by the heavy-atom method and refined by full-matrix least-squares technique using the 3569 reflections having $F^2 \geq 3\sigma(F^2)$. All nonhydrogen atoms were refined by assuming anisotropic thermal motion. Hydrogen atoms were introduced in structure factor calculations with their computed coordinates (C-H = 0.95 Å) and isotropic thermal factors ($B_H = 7$ Å^2) but not refined. The final values of $R_1(F)$ and $R_2(F)$ are 0.051 and 0.067, respectively, after determination of the absolute configuration. The estimated standard deviation of a unit weight observation is 1.33. A final difference map showed no significant peaks.

Tables IV and V list the final atomic positional and thermal parameters.[23]

Acknowledgment. We wish to thank Louis Ricard[2] for useful discussions and André Mitschler[2] for X-ray data collection.

Supplementary Material Available: Tables of positional and thermal parameters and general temperature factor expressions and a listing of structure factors (21 pages). Ordering information is given on any current masthead page.

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[23] See paragraph at end of paper regarding supplementary material.

The Effects of Solvent on Axial Ligation Constants of a Cobalt(II) Porphyrin

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Abstract: Axial ligation constants for the reaction of Co(T(p-CH$_3$O)PP) with pyridine, piperidine, and N-methylimidazole in several solvents, 1,2 dichloroethane, methylene chloride, chlorobenzene, chloroform, toluene, dimethylformamide, and o-nitrotoluene/toluene mixtures, were found to be nearly constant at room temperature. This was attributed to the fact that reactions were carried out near the isoequilibrium temperature (320 ± 24 K) as determined from plots of ΔH vs. ΔS. The solvent was found to affect the enthalpy and entropy changes of the ligation reaction in three ways. In low dielectric constant media, the change of ΔH and ΔS with the dielectric constants of the solvents was linear and "gas-phase" enthalpy and entropy changes for the reactions were obtained by extrapolation. The values of ΔH(g) and ΔS(g) for pyridine, piperidine, and N-methylimidazole reactions were respectively -5.5 ± 0.8 kcal/mol and -7 ± 2 eu, -8.0 ± 0.3 kcal/mol and -13 ± 1 eu, and -7.5 ± 0.6 kcal/mol and -12 ± 2 eu. The difference between ΔH(g) and ΔH was related to the enthalpy of solvation which had the effect of stabilizing the adduct linearly with respect to the dielectric constant of the solvent. Reactions in the higher dielectric medium of dimethylformamide required the displacement of coordinated solvent prior to reaction of the complex with base, and this resulted in near constant and more positive values of ΔH (-7 ± 0.5 kcal/mol) and ΔS (-11 ± 1 eu) than expected on the basis of the linear relationship found in low dielectric media. The enthalpy and entropy change for reactions in solvent mixtures of o-nitrotoluene and toluene were nearly constant, and this was attributed to the ability of the solvent to form π complexes with the cobalt porphyrin adduct.

The importance of solvent in affecting the stability of dioxygen adducts of cobalt and iron porphyrin complexes has appeared in several reports in the literature[1] but a systematic study regarding the fundamental properties causing the effect has not been published. We decided to carry out an investigation of this type by first defining the solvent interactions occurring in the forming of the precursor complex. The particular system chosen was (5,10,15,20-tetrakis(p-methoxyphenyl)porphinato)cobalt(II) (Co(T(p-CH$_3$O)PP). The electronic, axial ligation, and reversible oxygenation properties were previously studied by Walker[2] and her reports were used as a basis for this study.

Thermodynamic values for the axial ligation of cobalt porphyrin complexes were also determined in other studies. Most of these were concerned with protoporphyrin IX dimethyl ester (PP(IX)DME) compounds,[3-5] picket fence porphyrins,[6] and capped

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