Tetraphenylbenziporphyrin—A Ligand for Organometallic Chemistry

Marcin Stępień and Lechosław Latos-Grażyński*[a]

Abstract: 6,11,16,21-Tetraphenylbenziporphyrin (TPBPH)H, an analogue of tetraphenylporphyrin with one of the pyrrole groups replaced by a benzene ring, is formed in good yield in the condensation of the appropriate precursor with pyrrole and benzaldehyde. (TPBPH)H gives organometallic complexes with palladium(II) and platinum(II), [(TPBP)Pd^{II}] and [(TPBP)Pt^{II}], in which the metal ion is bound in the macrocyclic cavity by three pyrrolic nitrogen atoms and a carbon atom of the benzene ring. In the reaction with silver(I) acetate benziporphyrin does not yield a stable complex but undergoes selective acetoxylation at the internal carbon atom. (TPBPH)H is reversibly reduced to 6-benziphlorin and reacts with a water or methanol molecule to give 6-hydroxy- or 6-methoxy-6-benziphlorin, respectively.

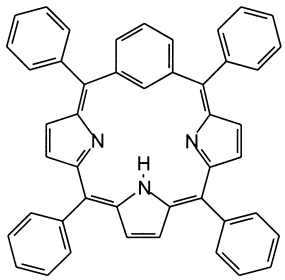
Keywords: porphyrinoids · macrocyclic ligands · NMR spectroscopy · platinum · palladium

Introduction

Modifications of the porphyrin core involving the introduction of a CH unit in place of one of the nitrogen atoms have led to the preparation of a series of monocarbaporphyrinoids that may have interesting properties both in terms of their aromatic character and their potential ability to bind metal ions.[1–4] Such a replacement preserves three regular pyrrole moieties, while the CNNN core becomes the denominator of monocarbaporphyrinoid structure.[5, 6] These macrocycles bear functional resemblance to certain polydentate ligands, which, by virtue of a favorably oriented carbon donor, afforded rare organometallic compounds of transition elements, often stabilizing untypical oxidation states or unusual coordination geometries.[7–10] The structure of carbaporphyrinoids suggests their prospective use as nontrivial ligands and consequently their coordination properties have aroused particular interest. Thus the inverted porphyrin (2-aza-21-carba-5,10,15,20-tetraarylporphyrin) and its methylated derivatives revealed a remarkable tendency to stabilize peculiar organometallic compounds containing nickel(I), paramagnetic nickel(II) (including a high-spin species with two Ni–C bonds), nickel(III), copper(II), palladium(II), and silver(III).[1, 11–16]

8,19-Dimethyl-9,13,14,18-tetraethylbenziporphyrin was synthesized previously,[3, 13] and it was demonstrated that a hydroxy substituent, suitably placed to form 2-hydroxybenziporphyrin, offers access to the aromatic oxybenziporphyrin through an enol–keto tautomerization.[4, 13]

In light of these we have synthesized 6,11,16,21-tetraphenylbenziporphyrin (**1**). Formally this macrocycle has been



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constructed by replacement of one of the pyrrole rings of 5,10,15,20-tetraphenylporphyrin ($TPPH_2$) with a benzene moiety. To indicate the chemical difference between the 22-C and 24-N protons we will use the symbol (TPBPH)H for **1**.

6,11,16,21-Tetraphenylbenziporphyrin has a relationship to 8,9,13,14,18,19-hexaalkylbenziporphyrin similar to that of tetraarylporphyrins to octaalkylporphyrins since identical substituents at β- and *meso*-positions are present in both pairs.

Results and Discussion

Tetraphenylbenziporphyrin **1** has been synthesized (Scheme 1) in a condensation of pyrrole, benzaldehyde, and 1,3-bis(phenylhydroxymethyl)benzene (**2**), which was ob-

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Supporting information (1D ^{13}C NMR spectra for compounds **1**, **1**-NO_2, **3**, **4**, **7**, and **8**) for this article is available on the WWW under http://www.wiley-vch.de/home/chemistry/ or from the author.

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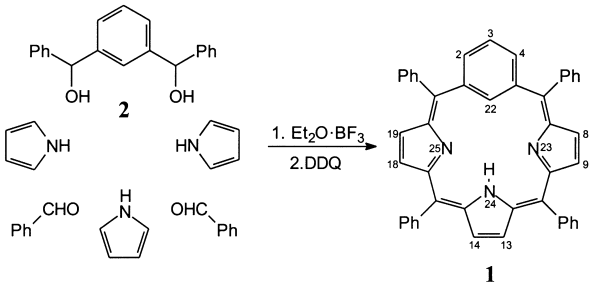


Scheme 1. Synthesis of **1**.

tained in the reaction of phenylmagnesium bromide with isophtalaldehyde. The procedure follows the methodology previously utilized for the synthesis of heteroporphyrins.[5] After chromatographic workup the compound was obtained in 15% yield. The electronic spectrum of **1** and its dication $[\mathbf{1}\text{-}H_2]^{2+}$ is shown in Figure 1.

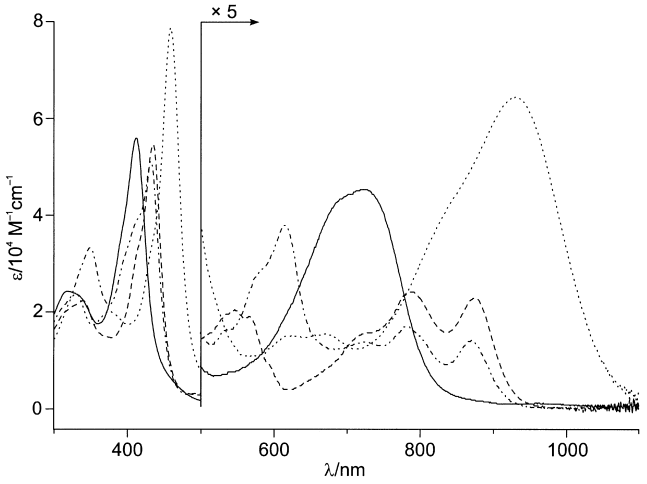
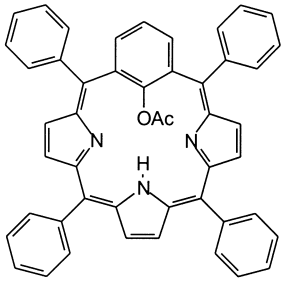


Figure 1. The electronic spectra of **1** (——, green), $[\mathbf{1}\text{-}H_2]^{2+}$ (····, brownish yellow), **7** (····, orange-brown), and **8** (----, green) in CH_2Cl_2 (298 K).

For topological reasons the molecule **1** cannot retain the macrocyclic aromaticity typical of porphyrins. The ^{1}H NMR spectrum of **1** presents the resonances at positions consistent with a nonaromatic structure. Thus the aromatic ring current is absent, as clearly illustrated by the downfield shift of the 24-NH resonance ($\delta = 10.30$) (Trace A, Figure 2). Scalar coupling detected between 24-NH and 13,14-H pyrrole protons is consistent with the prevalence of the symmetrical tautomer **1**.

Treatment of (TPBPH)H with two equivalents of silver acetate produced 21-acetoxy-6,11,16,21-tetraphenylbenziporphyrin (**3**). This oxidative acetoxylation proceeds cleanly and selectively under mild conditions according to reaction (1).

$$\mathbf{1} + 2\,Ag(OAc) \longrightarrow \mathbf{3} + 2\,Ag + AcOH \quad (1)$$



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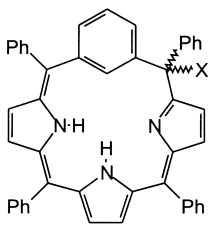
The structure of **3** was determined in an X-ray diffraction study (Figure 3).[14] The six-membered ring is sharply tipped out of the N(23)-N(24)-N(25) plane, making room for the 6,21-phenyl groups, which are almost coplanar with the macrocycle. The π bonds within the tripyrrane subunit are largely localized in the manner indicated by valence structure **3**. On the other hand, the bond lengths in the six-membered ring are almost equal and benzene-like. The C(21)–C(1) and C(5)–C(6) distances (1.476(2) Å and 1.474(2) Å) approach the single-bond limit for $C(sp^2)$–$C(sp^2)$. These structural features confirm that the benzene ring incorporated in the framework of **3** completely blocks macrocyclic delocalization while retaining unperturbed [6]annulene aromaticity. In the crystal acetoxybenziporphyrin acts as an acceptor of one molecule of water, which is coordinated through two hydrogen bonds to N(23) and N(25). The water molecule is situated above the macrocyclic plane on the opposite side to the acetoxy substituent.

The ^{1}H NMR spectrum of **3** (see Experimental Section) closely resembles that of **1**. Presumably the remarkable differentiation of the 8,19-H and 9,18-H resonances seen for **1** and **3** is related to the location of 8,19-H in the deshielding instead of shielding zone of the neighboring *meso* phenyl groups.

Benziporphyrin **1** reacts with sodium borohydride to produce 6,11,16,21-tetraphenyl-6-benziphlorin (**4**, one of the



4: X = H; **5**: X = OH; **6**: X = OMe

Abstract in Polish: *6,11,16,21-Tetrafenylobenziporfiryna TPBP, analog tetrafenyloporfiryny, w którym jeden z pierścieni pirolowych zastąpiony jest benzenowym, powstaje z dobrą wydajnością w kondensacji odpowiedniego prekursora z pirolem i benzaldehydem. TPBP tworzy metaloorganiczne połączenia z palladem(II) i platyną(II), (TPBP)Pd^{II} i (TPBP)Pt^{II}, w których jon metalu związany jest we wnęce makrocyklicznej poprzez trzy pirolowe atomy azotu i atom węgla pierścienia benzenowego. W reakcji z octanem srebra(I) benziporfiryna nie tworzy trwałego kompleksu, natomiast ulega selektywnej acetoksylacji na wewnętrznym atomie węgla. TPBP ulega odwracalnej redukcji do 6-benzifloryny a także przyłą,cza cząsteczkę wody bądź metanolu dając odpowiednio 6-hydroksy- i 6-metoksy-6-benziflorynę.*

0947-6539/01/0723-5114 $ 17.50+.50/0 *Chem. Eur. J.* **2001**, *7*, No. 23

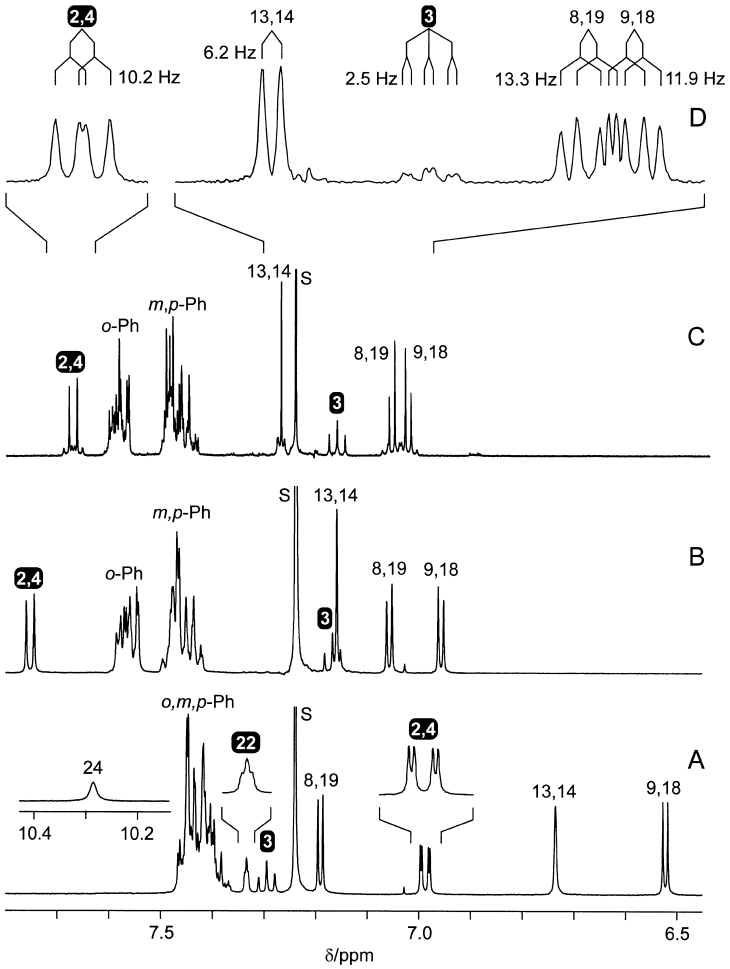


Figure 2. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of A) **1**, B) **7**, C) **8**. D) The ^{195}Pt-edited spectrum of **8**, which exposes the patterns of Pt satellites. Resonance assignments (obtained from COSY and NOESY maps) follow the numbering scheme given for **1** in Scheme 1.

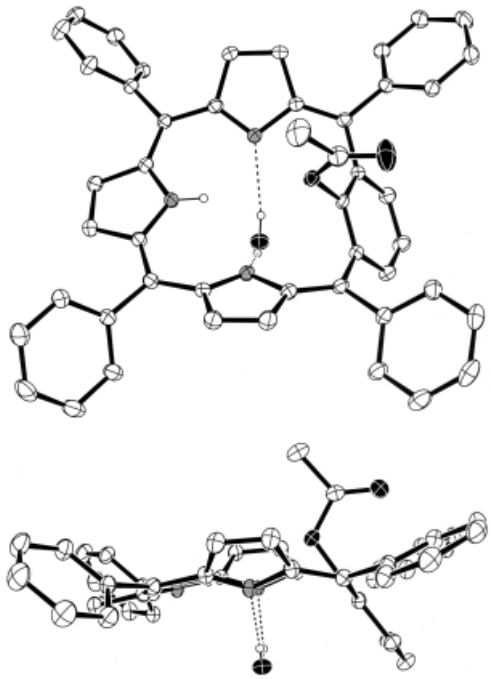
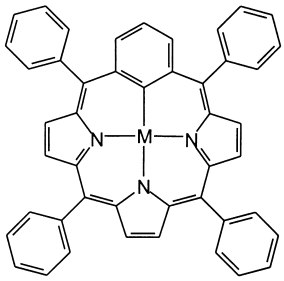


Figure 3. Crystal structure of **3** (thermal ellipsoids at 50% probability level). O atoms are shown in black, N atoms in gray, and selected H atoms are represented by small circles.

three possible tautomers), which structurally resembles porphyrin-derived phlorins and is analogous to an alkyl-substituted benziphlorin reported previously.[3] The reaction is selective as the saturation at the 6-position was solely observed. The ^{1}H NMR spectrum reflects symmetry lowering of **4** in comparison to **1**. The three pyrrolic AB patterns, two inner NH signals, and 6-H resonance can easily be identified. The C(6) carbon atom of **4** produces a resonance at $\delta =$ 51.5, which is consistent with a tetrahedral geometry. The reaction with $NaBH_4$ can be considered a special case of the typical reactivity of **1** with respect to nucleophiles. For example, the reaction of **1** with water or methanol yields 6-hydroxy-6,11,16,21-tetraphenyl-6-benziphlorin (**5**) and 6-methoxy-6,11,16,21-tetraphenyl-6-benziphlorin (**6**), respectively. This reactivity resembles the nucleophilic *meso*-addition of hydride or hydroxide to [(TPP)Au^{III}Cl] (TPP = tetraphenylporphyrin) to yield phlorin or hydroxyphlorin complexes.[15] Addition of gaseous HCl to **5** or **6** resulted in water or alcohol elimination, respectively, and quantitative recovery of **1**. The easy accessibility of phlorins **4**–**6** is related to the loss of aromaticity suffered by **1**.

Insertion of palladium(II) or platinum(II) into **1** yields [(TPBP)Pd^{II}] **7** (orange-brown) and [(TPBP)Pt^{II}] **8** (green),



7: M = Pd; **8**: M = Pt

whose electronic spectra differ essentially from that of **1** (Figure 1). The most notable feature of **7** and **8** is the coordination through the unprotonated C(22) carbon atom of the benzene ring as inferred from the disappearance of the 22-

H resonance in the ^{1}H NMR spectra (Figure 2, Traces B and C). A chemical shift of $\delta = 145.5$ ($\delta = 139.3$), typical for sp^2 hybridization, has been detected for the coordinated C(22) atom in the ^{13}C NMR spectra of **7** (**8**). In addition the ^{1}H-^{15}N HMBC spectrum of **8** gave the assignments of three pyrrole nitrogen atoms at $\delta = -226$ (23,25-N) and $\delta = -216$ (24-N), that is upfield with respect to the signal for [(TPP)Pt^{II}] ($\delta = -252$ vs. $MeNO_2$). The ^{195}Pt resonance of **8** ($\delta = 560$) is shifted upfield relative to that of [(TPP)Pt^{II}] ($\delta = 1235$[16]) reflecting the presence of a different donor in the coordination core.

Owing to the coordination of a metal ion the pyrrole and benzene resonances of **7** and **8** are downfield shifted with respect to their positions for the free base **1**. In **7** or **8** the metal ion is located in the CNNN plane, which forces a coplanar position of the benzene ring. The effectively orthogonal position of the *meso*-phenyl groups removes the source of shift differentiation for 8,19-H and 9,18-H resonances seen for **1** and **3**. The ^{1}H NMR spectrum of **8** displays four-bond ^{1}H–^{195}Pt scalar couplings to pyrrole β-protons and, consistent with the formation of a Pt-C(22) bond, to 2,4-benzene protons (Figure 2, Trace D).

In conclusion, the nonaromatic tetraphenylbenziporphyrin **1** may serve as a valuable ligand for organometallic investigations of benzene reactivity by efficiently protecting the metal–carbon σ bond through the encapsulation of the metal center in the CNNN coordination core.

Experimental Section

1: 1,3-Bis(phenylhydroxymethyl)benzene (**2**; 290 mg, 1 mmol), pyrrole (208 μL, 3 mmol), and benzaldehyde (204 μL, 2 mmol) were added to dry CH_2Cl_2 (900 mL) under nitrogen. $Et_2O \cdot BF_3$ (100 μL) was then added and the reaction mixture was protected from light and stirred for 2 h. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 750 mg, 3 mmol) was subsequently added and the mixture evaporated under reduced pressure. The residue was subjected to chromatography (grade II basic alumina, CH_2Cl_2). The desired product eluted as a green band following a trace of H_2TPP. Recrystallization from CH_2Cl_2/hexane yielded deep blue crystals. The filtrates contained sizable amounts of hydroxybenziphlorin **5**, which was dehydrated to give a second batch of the product. Total yield 93 mg (15%). ^{1}H NMR (298 K): $\delta = 10.29$ (s; 24-NH); 7.37–7.46 (m; 6,11,16,21-Ph); 7.33, 7.29, 6.99 (ABC$_2$: $^4J_{A,C} = 1.7$ Hz, $^3J_{B,C} = 7.8$ Hz; 22-H, 3-H, 2,4-H); 7.19, 6.52 (AB: $^3J = 4.8$ Hz; 8,19-H, 9,18-H), 6.74 (s; 13,14-H); ^{13}C NMR (partial data, 298 K): $\delta = 172.0$, 156.6 (7,20,10,17-C); 147.7 (12,15-C); 144.5 (6,21-C); 138.1 (1,5-C); 136.6 (8,19-C); 133.4 (2,4-C); 130.5 (9,18-C); 129.8 (13,14-C); 128.8 (3-C); 109.4 (22-C); UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 319 (4.53), 411 (4.89), 723 nm (4.09); HRMS (ESI): m/z: 626.2646 (626.2591 for $C_{46}H_{31}N_3$ + H$^+$); elemental analysis (%) calcd for $C_{46}H_{31}N_3$: C 88.32, H 4.96, N 6.72; found (sample dried at 150 °C for 24 h): C 88.08, H 4.82, N 6.98.

6,21-Diphenyl-11,16-bis(4-nitrophenyl)benziporphyrin (1-NO$_2$): Compound **1**-NO_2 was obtained analogously to **1**, by using 4-nitrobenzaldehyde (302 mg, 2 mmol) instead of benzaldehyde. Yield 126 mg (17%). ^{1}H NMR (298 K): $\delta = 10.30$ (s; 24-NH); 8.31, 7.64 (AA′BB′: $^3J_{A,B} = 9.7$ Hz; 11,16-*m*-Ph, 11,16-*o*-Ph); 7.40–7.50 (m; 6,21-Ph); 7.33, 7.31, 7.01 (ABC$_2$: $^3J_{A,C} = 7.7$ Hz, $^4J_{B,C} = 1.7$ Hz; 3-H, 22-H, 2,4-H); 7.27, 6.46 (AB: $^3J = 4.8$ Hz; 8,19-H, 9,18-H), 6.76 (s; 13,14-H); HRMS (ESI): m/z: 716.2302 (716.2292 for $C_{46}H_{29}N_5O_4$ + H$^+$).

2: Isophthalaldehyde (1 g, 7.46 mmol) was dissolved in dry degassed THF (250 mL). PhMgBr (3 mL of a 3 M solution in Et_2O, 9 mmol) was added, which caused the reaction mixture to turn blue-violet. After the mixture had been stirred for 1 h, the solution was heated and refluxed for an additional 0.5 h. The reaction mixture was hydrolyzed with aqueous ammonium chloride and extracted with CH_2Cl_2. The extracts were washed twice with water and the solvent was removed under reduced pressure. The residue was recrystallized from CH_2Cl_2/*n*-hexane to afford several batches of the product (white solid). Yield (first batch): $\delta = 1.21$ g (56%). ^{1}H NMR (298 K, mixture of stereoisomers): $\delta = 7.47$, 7.45 (2 t, $J \approx 2$ Hz; 2-H); 7.21–7.36 (m, 13 H, remaining aryl protons); 5.81, 2.18 (AB: $J \approx 3$ Hz; C*H*OH, CHO*H*).

3: (TPBP)H (58 mg) and Ag(OAc) (30 mg, 2.16 equiv) were refluxed for 15 min in a mixture of $CHCl_3$ and MeCN (15 + 15 mL). The solution was then evaporated to dryness and the residue chromatographed (grade II basic alumina, CH_2Cl_2) to yield **3** (42 mg; 66% after a recrystallization from CH_2Cl_2/MeOH). ^{1}H NMR (298 K): $\delta = 9.51$ (s; 24-NH); ~7.55 (m, 4 H; 6,21-*o*-Ph); ~7.48 (m, 4 H; 11,16-*o*-Ph); 7.39–7.45 (m, 12 H; 6,21,11,16-*m*,*p*-Ph); 7.16, 7.07 (AB$_2$: $^3J = 7.6$ Hz; 3-H, 2,4-H); 7.29, 6.52 (AB: $^3J = 4.8$ Hz; 8,19-H, 9,18-H); 6.83 (s; 13,14-H), 1.31 (s; CH_3); ^{13}C NMR (partial data, 298 K): $\delta = 169.9$ (O–C=O); 170.2, 156.6 (10,17;7,20-C); 140.5 (1,6-C); 134.8 (8,19-C); 133.8 (1,5-C); 131.2 (9,18-C); 131.2 (2,4-C); 130.2 (13,14-C); 126.5 (3-C); 118.1 (22-C); 20.3 (CH_3); UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 310 (4.48), 409 (4.84), 702 nm (4.28); HRMS (ESI): m/z: 684.2658 (684.2646 for $C_{48}H_{33}N_3O_2$ + H$^+$); elemental analysis (%) calcd for $C_{46}H_{33}N_3O_2 \cdot 0.4\,CH_2Cl_2$: C 80.90, H 4.75, N 5.85; found: C 80.80, H 4.96, N 5.76.

4: (TPBP)H (2.5 mg) was dissolved in a small volume of $CHCl_3$ and reduced with a solution of $NaBH_4$ in EtOH. The reaction was monitored spectrophotometrically. The solvents were removed at room temperature under reduced pressure. The residue was extracted with CH_2Cl_2, filtered, and evaporated to dryness. Alternatively, **4** was obtained directly in the condensation reaction, if *p*-chloranil (520 mg, 2.1 equiv) was used in place of DDQ. ^{1}H NMR (333 K): $\delta = 9.79$, 7.87 (2 b, 2 H; NH); 7.89, 7.22, 6.92, 6.22 (ABCD: $^3J_{A,B} = 7.8$ Hz, $^3J_{B,C} = 7.9$ Hz, $^4J_{A,D} = 1.1$ Hz, $^4J_{C,D} = 1.2$ Hz; 4-H, 3-H, 2-H, 22-H); 7.0–7.6 (m, 10 H; 6,11,16,21-Ph), 6.92, 6.67 (AB: $^3J = 5.6$ Hz; 19 H, 18-H); 6.78, 6.40 (AB: $^3J = 4.8$ Hz; 13-H, 14-H); 6.63, 6.48 (AB: $^3J = 3.9$ Hz; 8-H, 9-H); 5.69 (s; 6-H); ^{13}C NMR (partial data, 333 K): $\delta = 126.5$ (4-C), 128.3 (2-C), 129.4 (19-C), 128.1 (3-C), 135.0 (13-C), 128.8 (18-C), 111.0 (8-C), 120.8 (9-C), 128.1 (14-C), 51.5 (6-C); UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 300 (4.41), 399 (4.74), 666 nm (4.54); electronic spectra of the remaining phlorins are virtually indistinguishable; HRMS (ESI): m/z: 628.2738 (628.2747 for $C_{46}H_{33}N_3$ + H$^+$).

5: (TPBP)H (2.5 mg) was added to THF (10 mL) containing water (1%) and a trace of HCl. The mixture was stirred until the starting material had dissolved. The resultant blue solution was neutralized and dried with anhydrous K_2CO_3 and evaporated to dryness under reduced pressure. ^{1}H NMR (298 K): $\delta = 9.42$, 7.79 (2 b, 2 H; NH); 8.26 (d, 4-H); 7.3–7.6 (m, 20 H; 6,11,16,21-Ph); 7.23 (t; 3-H); 7.00, 6.75; 6.87, 6.50; 6.81, 6.45 (3 AB: 8,9-H; 13,14-H; 18,19-H); 6.94 (d; 2-H); 6.16 (b; 22-H), 2.53 (b; OH); HRMS (ESI): m/z: 644.2685 (644.2696 for $C_{46}H_{33}N_3O$ + H$^+$).

6: (TPBP)H (10 mg) was dissolved in $CHCl_3$ (5 mL) and transformed into the dication with gaseous HCl. MeOH (30 mL) was then added and the mixture cooled in the freezer (−20 °C). The cold mixture was neutralized with anhydrous K_2CO_3 (ca. 50 mg), filtered, and the filtrate evaporated to dryness under reduced pressure. The deep blue product was too unstable to be chromatographed but the conversion was close to quantitative. ^{1}H NMR (CD_3OD, 273 K, monocation): $\delta = 8.13$ (d; 4-H); 7.41–7.91 (m, 20 H; 6,11,16,21-Ph); 7.40, 6.82, 7.26, 6.72, 6.99, 6.67 (3 AB: 8,9,13,14,18,19-H); 7.34 (3-H), 7.00 (2-H); NH signals and the CH_3 peak cannot be observed due to deuteration. In other solvents the spectrum is dynamically broadened.

7: (TPBP)H (15 mg) and $PdCl_2$ (4.5 mg, 1.2 equiv) were added to dry MeCN (20 mL) and the mixture was refluxed for 2 h. The solution was allowed to cool down, the violet precipitate was filtered off, washed with MeCN, and dried in air. Yield 8.5 mg (49%). ^{1}H NMR (298 K): $\delta = 7.75$, 7.17 (A$_2$B: $^3J_{A,B} = 7.7$ Hz; 2,4-H, 3-H); 7.54–7.59 (m; 6,11,16,21-*o*-Ph); 7.42–7.50 (m; 6,11,16,21-*m*,*p*-Ph); 7.16 (s; 13,14-H); 7.06, 6.96 (AB: $^3J = 5.2$ Hz; 8,19-H, 9,18-H); ^{13}C NMR (partial data, 298 K): $\delta = 157.6$, 145.5 (8,19;9,18-C); 152.6 (12,15-C); 145.5 (22-C); 144.1 (6,21-C); 142.3 (2,4-C); 135.3 (8,19-C); 134.2 (1,5-C); 133.6 (13,14-C); 126.4 (9,18-C); 124.8 (3-C); UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 349 (4.34), 434 (4.74), 546 (3.61), 787 (3.68), 875 nm (3.65); HRMS (ESI): m/z: 730.1589 (730.1469 for $C_{46}H_{29}N_3Pd^+$).

Palladium 6,21-diphenyl-11,16-bis(4-nitrophenyl)benziporphyrin (7-NO$_2$): Compound **7**-NO_2 was obtained analogously to **7** by using **1**-NO_2 as the ligand. ^{1}H NMR (298 K): $\delta = 8.38$, 7.78 (AA′BB′: $^3J_{A,B} = 8.8$ Hz; 11,16-*m*-Ph, 11,16-*o*-Ph); 7.77, 7.19 (A$_2$B: $^3J_{A,B} = 7.8$ Hz; 2,4-H, 3-H,); 7.45–7.55 (m,

0947-6539/01/0723-5116 $ 17.50+.50/0 *Chem. Eur. J.* **2001**, *7*, No. 23

10H; 6,21-Ph); 7.15, 6.88 (AB: $^3J = 5.2$ Hz; 8,19-H, 9,18-H), 7.12 (s; 13,14-H).

8: (TPBP)H (50 mg) and $PtCl_2$ (22 mg, 1 equiv) were refluxed in benzonitrile (20 mL) for 4 h under nitrogen. The solvent was removed in a stream of nitrogen at about 100 °C. The solid residue was chromatographed (CH_2Cl_2, grade II basic alumina), the green product **8** was eluted as the first band. Yield after recrystallization (CH_2Cl_2/MeOH) 11.5 mg (20%). ^{1}H NMR (298 K): $\delta = 7.67$, 7.16 (A_2B: $^3J_{A,B} = 7.6$ Hz; 2,4-H, 3-H); 7.43–7.60 (m; 6,11,16,21-Ph); 7.27 (s; 13,14-H); 7.05, 7.02 (AB: $^3J = 5.3$ Hz; 8,19-H, 9,18-H); ^{13}C NMR (partial data, 298 K): $\delta = 157.7$, 142.9 (7,20; 10,17-C); 151.5 (12,15-C); 147.5 (6,21-C); 144.3 (2,4-C); 139.3 (22-C); 136.6 (8,19-C); 133.7 (13,14-C); 131.5 (1,5-C); 127.3 (9,18-C); 123.0 (3-C); UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 349 (4.52), 432 (4.71), 615 (3.88), 726 (3.45), 782 nm (3.53); HRMS (ESI): m/z: 818.2016 (818.2004 for $C_{46}H_{29}N_3Pt^+$).

Instrumentation: NMR spectra were recorded on a 500 MHz Bruker Avance spectrometer equipped with a broadband inverse gradient probehead. Proton data are referenced to the residual $CHCl_3$ signal ($\delta = 7.24$). Data for heteronuclei were obtained from ^{1}H-detected correlation spectra. ^{13}C shifts are referenced to $^{13}CDCl_3$ ($\delta = 77.0$), ^{15}N to neat external $MeNO_2$ ($\delta = 0$), and ^{195}Pt to external [Pt(TPP)] in $CDCl_3$ ($\delta = 1235$,[16] Ξ-scale). The ^{1}H–^{195}Pt 1D HMQC experiment used an evolution time of 50 ms and was processed in the magnitude mode.

Acknowledgements

Financial support from the State Committee for Scientific Research KBN of Poland (Grant 3 T09A 155 15) and the Foundation for Polish Science is kindly acknowledged. We thank Prof. Tadeusz Lis for valuable discussions.

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[14] Crystal data for **3** (100 K): Crystals obtained by slow evaporation of a $CHCl_3$ solution, $C_{48}H_{33}N_3O_2 \cdot CHCl_3 \cdot H_2O$, rhombic plate, $0.25 \times 0.25 \times 0.10$ mm, triclinic $P\bar{1}$, $a = 9.977(1)$, $b = 13.268(1)$, $c = 17.184(1)$ Å, $\alpha = 67.97(1)$, $\beta = 80.89(1)$, $\gamma = 76.53(1)^\circ$, $V = 2044.3(3)$ Å^3, $Z = 2$, $\lambda = 0.71073$ Å. Structure solved with SHELXS-97 and refined against $|F|^2$ using SHELXL-97 (G. M. Sheldrick, University of Göttingen, Germany, **1997**): $R1 = 0.0643$, $wR2 = 0.1270$, $S = 1.084$ for 10949 reflections with $I > 2\sigma(I)$ and 625 parameters; max./min residual electron density $+0.42/-0.47$ e Å^{-3}. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-156372. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Received: June 19, 2001 [F3352]