Synthesis and Structure of Palladium(II) Complexes with N(21),N(22)-Bridged Porphyrin Ligands

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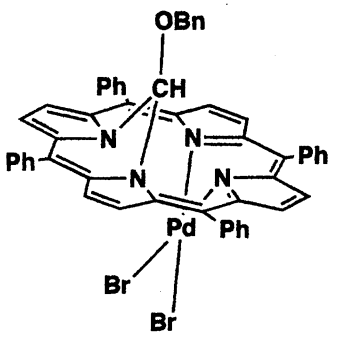
Palladium complexes of N(21),N(22)-(etheno)-bridged porphyrins were synthesized by the reaction of palladium(II) chloride and N(21),N(22)-(etheno)-tetraphenylporphyrins or N(21),N(22)-(etheno)-octaethyl-5,22-dihydroporphyrins. The metallation proceeded via an initially produced monoprotonated porphyrin with a palladate anion. Dinuclear complexes including two $PdCl_2$ units were preferentially produced and were converted into mononuclear complexes by a treatment with a saturated aqueous NaCl solution. Single-crystal X-ray diffraction shows the di-μ-chlorodipalladium(II) structure of the dinuclear complex, N(21),N(22)-(EtC=CEt)(TPP)$(PdCl_2)_2 \cdot CH_2Cl_2 \cdot H_2O$ (TPP = 5,10,15,20-tetraphenylporphyrin dianion). Pd(1) is coordinated by two adjacent imine nitrogens of the porphyrin as the terminal ligands and placed out of the porphyrin 4N mean plane by 1.32 Å. The distal Pd(2) is placed at a distance of 3.78 Å from the porphyrin 4N mean plane and comes close to the porphyrin ring with a dihedral angle of 139.8° between the two square planes of the Pd coordination. The NMR spectrum in solution indicated the influence of the distal Pd(2) on the porphyrin ring. The etheno bridge keeps the geometry of the 4N core of the porphyrin relatively undeformed in comparison with the previously reported methano bridge, which accounts for the enhanced stability of Pd(II) complexes.

Palladium complexes with a bidentate nitrogen base ligand have recently been applied to a number of organic transformations as catalysts as well as conventional Pd complexes with phosphine ligands.[1] On the other hand, ordinary palladium(II) porphyrins are coordinatively saturated by the four pyrrole nitrogens of a porphyrin ligand, and thus Pd(II) porphyrins have been studied so far only in the fields of photo and redox chemistry.[2] There have been reported metalloporphyrins in which metals are coordinated by porphyrins as bidentate or tridentate ligands and positioned out of the plane of porphyrin rings.[3,4] Those structures are, however, unstable and readily converted to usual metalloporphyrins coordinated by four pyrrole nitrogens. In this context, N(21),N(22)-bridged porphyrins are of interest in the sense that they can act as bidentate nitrogen base ligands, like 2,2′-bipyridine, because two alkylated pyrrole nitrogens are not used for coordination to metals. Two unsubstituted pyrrole nitrogens are basic and canted towards the opposite side of the N(21),N(22)-bridge, which is appropriate for coordination to metals.[5] It has been shown that the reactions of N(21),N(22)-vinylideno-bridged porphyrin and metal carbonyls result in the formation of metalloporphyrins with the elimination of the N(21),N(22)-bridge.[6] However, Pd complexes of N(21),N(22)-bridged porphyrins with a one-carbon (methano) bridge were isolated by Callot and co-workers.[7] They showed that two imine-type nitrogens and two bromine atoms of N(21),N(22)-[CH(OBn)](TPP)$\cdot PdBr_2$ (**4c**) (CH(OBn) = (benzyloxy)methylene, TPP = 5,10,15,20-tetraphenylporphyrin dianion) occupy square-planar coordination sites (Chart 1). Those Pd(II) complexes also tend to lose the bridge moiety, yielding ordinary Pd(II) porphyrins upon standing, even as crystals. This type of square-planar Pd(II) complex is of great interest not only in view of the stereochemical influence of the porphyrin ligand moiety on the coordination chemistry of Pd(II), but also in view of the unique photochemical and redox activity of N(21),N(22)-bridged porphyrins.[8,9] Hence, it seems worthy to develop stable Pd complexes of N(21),N(22)-bridged porphyrins. The present report is concerned with the synthesis and structure of stable Pd(II) porphyrins with a two-carbon (etheno) bridge.[10]



(4c)

Chart 1.

Experimental

N(21),N(22)-etheno-bridged porphyrins (**1**) were prepared by a method from the literature.[11] $[PdCl_2(MeCN)_2]$ was prepared by a modification of a literature method.[12] Dichloromethane, methanol, *n*-hexane, and acetonitrile were dried over calcium chloride. Diethyl ether was dried over benzophenoneketyl. Acetone was dried over drielite and THF was passed through basic Al_2O_3. They were then distilled before use. Other chemicals were of reagent grade. Wakogel C-200 silica gel (Wako Junyaku) was used for column chromatography. The UV-visible spectra were measured on a Hitachi U-3210 spectrophotometer. ^{1}H NMR and ^{13}C NMR were recorded on a JEOL EX-270 spectrometer in $CDCl_3$. ^{1}H and ^{13}C chemical shifts are referenced with respect to $(CH_3)_4Si$ (0 ppm) and $CDCl_3$ (77.00 ppm), respectively, as internal standards. Elemental analyses of C, H, and N were made with a Yanaco MT-3 CHN corder.

Preparation of N(21),N(22)-(RC=CR)TPP Free Bases (2a, 2a′). **2a′** was prepared according to a literature method,[13] and **2a** was synthesized analogously.

N(21),N(22)-(EtC=CEt)TPP (2a). Yield 55%. ^{1}H NMR δ = 8.45, 8.17, 8.04, 7.91, (d×4, 2H×4, pyrrole-β-H), 8.5—7.3 (m, 20H, phenyl-H), −1.38 (t, 6H, CH_3), −2.45, −3.57 (dq×2, 2H×2, CH_2, J_{gem} = 15 Hz). UV-vis (diethyl ether) λ_{max} 430, 540, 572, 618, 673 nm.

Preparation of N(21),N(22)-Etheno-bridged Octaethyl-5-methoxy-5,22-dihydroporphyrins (2b, 2b′). **2b** and **2b′** were prepared by a modified method from the literature.[8] 20 mL of a 10% KOH solution in methanol was added dropwise to a solution of N(21),N(22)-etheno-bridged $OEPHClO_4$ (75 mg) in a mixture of THF (5 mL) and methanol (20 mL). The solution was stirred for 30 min, and the organic solvents were evaporated after the addition of 50 mL of water. Formed purple precipitates were collected by a filter and washed with water. The dried precipitates were extracted with hexane and the solution was evaporated to afford crude N(21),N(22)-bridged octaethyl-5-methoxy-5,22-dihydroporphyrin. Further purification was not attempted due to its labile nature.

N(21),N(22)-(EtC=CEt)-Octaethyl-5-methoxy-5,22-dihydroporphyrin (2b). Yield 81%. ^{1}H NMR ($CDCl_3$) δ = 7.01, 6.86 (s×2, 1H×2, *meso*-H), 7.73 (s, 2H, *meso*-H), 6.41 (s, 1H, NH), 3.26 (s, 3H, OCH_3), 3.2—2.9 (m, 16H, CH_2), 1.42 (t, 12H, CH_3), 1.24, 1.12 (t×2, 6H×2, CH_3), 0.48, 0.28 (dq×2, 2H×2, bridge-CH_2, J_{gem} = 16 Hz), −0.14 (t, 6H, bridge-CH_3). UV-vis (hexane) λ_{max} 388, 572, 617 nm.

N(21),N(22)-(PhC=CPh)-Octaethyl-5-methoxy-5,22-dihydroporphyrin (2b′). Yield 97%. ^{1}H NMR (C_6D_6) δ = 7.37, 7.31 (s×2, 1H×2, *meso*-H), 7.47 (s, 2H, *meso*-H), 3.2—2.8 (m, 16H, CH_2), 1.50, 1.42, 1.18, 1.05 (t×4, 6H×4, CH_3), 6.44 (t, 2H, bridge phenyl *p*-H), 5.92 (t, 4H, bridge phenyl *m*-H), 5.01 (br, 4H, bridge phenyl *o*-H), 3.51 (s, 3H, OCH_3). UV-vis (hexane) λ_{max} 388, 565, 608 nm.

Synthesis of Dinuclear Pd(II) Complexes of N(21),N(22)-Etheno Bridged Porphyrins (3a, 3a′, 3b, 3b′). A mixture of $[PdCl_2(MeCN)_2]$ (80 mg) and **2** (70 mg) in acetonitrile (10 mL) were stirred at room temperature under aerobic conditions. After the UV-vis spectrum was changed to that of typical monocationic porphyrins **1**, the solution was evaporated and the residue was extracted with $CHCl_3$. The solution was allowed to stand at room temperature under aerobic conditions in the dark for 3 d. After the color of the solution turned green, the solvent was removed. Column chromatography of the residue on silica gel with CH_2Cl_2–acetone (10 : 1—5 : 1), followed by recrystallization of the main fraction from CH_2Cl_2–hexane, gave a crystalline material.

N(21),N(22)-(EtC=CEt)(TPP)$(PdCl_2)_2$ (3a). Yield 79% based on **2a**. Anal. Calcd for $C_{50}H_{38}N_4$ $(PdCl_2)_2 \cdot CH_2Cl_2 \cdot H_2O$: C, 53.15; H, 3.67; N, 4.86%. Found: C, 53.29; H, 3.60; N, 4.59%. ^{1}H NMR δ = 9.20, 8.75, 8.70, 8.52 (d×4, 2H×4, pyrrole-β-H), 8.67—7.66 (m, 20H, phenyl-H), −1.27 (t, 6H, CH_3), −2.71, −4.14 (dq×2, 2H×2, CH_2, J_{gem} = 15 Hz). UV-vis (CH_2Cl_2) λ_{max} (log ε) 400 (4.76), 466 (5.15), 561 (sh) (3.86), 603 (4.11), 656 (4.36) nm.

N(21),N(22)-(PhC=CPh)(TPP)$(PdCl_2)_2$ (3a′). Yield 87% based on **2a′**. Anal. Calcd for $C_{58}H_{38}N_4$ $(PdCl_2)_2$: C, 60.81; H, 3.34; N, 4.89%. Found: C, 61.13; H, 3.51; N, 4.89%. ^{1}H NMR δ = 9.41, 8.83, 8.66, 8.17 (d×4, 2H×4, pyrrole-β-H), 9.0—7.1 (m, 20H, phenyl-H), 6.22 (t, 2H, bridge phenyl-*p*-H), 5.77 (t, 4H, bridge phenyl *m*-H), 2.23 (br, 4H, bridge phenyl *o*-H). UV-vis (CH_2Cl_2) λ_{max} (log ε) 402 (4.89), 469 (5.30), 555 (sh) (4.15), 603 (4.35), 656 (4.54) nm.

N(21),N(22)-(EtC=CEt)(OEP)$(PdCl_2)_2$ (3b). Yield 78% based on **2b**. Anal. Calcd for $C_{42}H_{54}N_4$ $(PdCl_2)_2$: C, 52.03; H, 5.61; N, 5.78%. Found: C, 52.55; H, 5.73; N, 5.92%. ^{1}H NMR δ = 10.92, 10.23 (s×2, 1H×2, *meso*-H), 10.51 (s, 2H, *meso*-H), 4.37 (dq, 2H, CH_2), 4.09—3.89 (m, 14H, CH_2), 2.24, 1.94, 1.70, 1.70 (t×4, 6H×4, CH_3), −1.68 (t, 6H, bridge-CH_3), −3.10, −4.61 (dq×2 2H×2, bridge-CH_2, J_{gem} = 15 Hz). ^{13}C NMR δ = 150.44, 149.58, 148.66, 145.77, 144.71, 144.13, 141.80, 138.67 (pyrrole-C), 124.42 (bridge vinyl-C), 15.35, 8.43 (bridge ethyl-C), 109.29, 103.59, 103.00 (*meso*-C). UV-vis (CH_2Cl_2) λ_{max} (log ε) 399 (4.76), 442 (4.63), 565 (sh) (3.90), 579 (4.00), 604 (3.88) nm.

N(21),N(22)-(PhC=CPh)(OEP)$(PdCl_2)_2$ (3b′). Yield 51% based on **2b′**. Anal. Calcd for $C_{50}H_{54}N_4$ $(PdCl_2)_2 \cdot 2H_2O$: C, 54.51; H, 5.31; N, 5.09%. Found: C, 54.50; H, 4.89; N, 5.50%. ^{1}H NMR δ = 11.35, 10.52 (s×2, 1H×2, *meso*-H), 10.06 (s, 2H, *meso*-H), 4.56 (dq, 2H, CH_2), 4.18—3.51 (m, 14H, CH_2), 2.39, 1.91, 1.58, 1.25 (t×4, 6H×4, CH_3), 6.03 (t, 2H, bridge phenyl *p*-H), 5.56 (t, 4H, bridge phenyl *m*-H). ^{13}C NMR δ = 151.45, 149.81, 148.12, 146.67, 145.82, 145.04, 142.60, 140.52 (pyrrole-C), 126.79, 126.37, 125.12, 124.35, 124.32 (bridge-C), 109.71, 103.88, 103.03 (*meso*-C). UV-vis (CH_2Cl_2) λ_{max} (log ε) 404 (4.80), 444 (4.73), 564 (sh) (3.99), 582 (4.08), 600 (sh) (3.96), 625 (sh) (3.81) nm.

Conversion to Mononuclear Pd(II) Complexes (4a, 4a′, 4b, 4b′). A saturated NaCl aqueous solution (20 mL) was added to a THF–CH_2Cl_2 (1 : 3) solution (40 mL) of the dinuclear Pd(II) complexes **3** (17 mg); the mixture was then stirred at room temperature for 1 h. After evaporation of the solvent, the product was extracted with CH_2Cl_2, dried over Na_2SO_4, and evaporated to dryness. The residue was then chromatographed on silica gel with CH_2Cl_2–acetone (10 : 1). The main green fraction was recrystallized from CH_2Cl_2–hexane to afford mononuclear complexes.

N(21),N(22)-(EtC=CEt)(TPP)$PdCl_2$ (4a). Yield 80% based on **3a**. Anal. Calcd for $C_{50}H_{38}Cl_2N_4Pd \cdot H_2O$: C, 67.46; H, 4.52; N, 6.29%. Found: C, 67.82; H, 4.66; N, 6.22%. ^{1}H NMR δ = 8.86, 8.66, 8.49, 8.37 (d×4, 2H×4, pyrrole-β-H), 8.31—7.74 (m, 20H, phenyl-H), −1.41 (t, 6H, CH_3), −2.91, −4.23 (dq×2, 2H×2, CH_2, J_{gem} = 15 Hz). UV-vis (CH_2Cl_2) λ_{max} (log ε) 409 (4.73), 479 (4.92), 555 (sh) (3.79), 673 (4.17) nm.

N(21),N(22)-(PhC=CPh)(TPP)$PdCl_2$ (4a′). Yield 85% based on **3a′**. Anal. Calcd for $C_{58}H_{38}Cl_2N_4Pd \cdot CH_2Cl_2$: C, 67.28; H, 3.83; N, 5.32%. Found: C, 67.99; H, 3.67; N, 5.11%. ^{1}H NMR δ = 9.06, 8.67, 8.56, 8.04 (d×4, 2H×4, pyrrole-β-H), 8.6—7.3 (m, 20H, phenyl-H), 6.17 (t, 2H, bridge phenyl *p*-H), 5.75 (t, 4H, bridge phenyl *m*-H), 2.20 (br, 4H, bridge phenyl *o*-H). UV-vis (CH_2Cl_2) λ_{max} (log ε) 411 (4.73), 485 (4.89), 555 (sh) (3.74), 595 (sh) (3.85), 646 (4.04), 673 (4.09) nm.

N(21),N(22)-(EtC=CEt)(OEP)PdCl$_2$ (4b). Yield 40% based on **3b**. Anal. Calcd for $C_{42}H_{54}Cl_2N_4Pd\cdot0.5H_2O$: C, 62.96; H, 6.92; N, 6.99%. Found: C, 62.99; H, 6.89; N, 6.95%. ^{1}H NMR δ = 10.26, 10.15 (s×2, 1H×2, *meso*-H), 10.51 (s, 2H, *meso*-H), 4.13—3.79 (m, 16H, CH_2), 2.05, 1.88, 1.63, 1.60 (t×4, 6H×4, CH_3), −1.79 (t, 6H, bridge-CH_3), −3.24, −4.66 (dq×2, 2H×2, bridge-CH_2, J_{gem} = 15 Hz). ^{13}C NMR δ = 151.73, 141.23, 147.33, 144.71, 143.22, 142.91, 140.63, 135.49 (pyrrole-C), 124.19 (bridge vinyl-C), 14.97, 8.47 (bridge ethyl-C), 110.49, 105.16, 98.73 (*meso*-C). UV-vis (CH_2Cl_2) λ_{max} (log ε) 403 (4.61), 463 (4.37), 566 (sh) (3.69), 592 (3.80), 610 (sh) (3.73) nm.

N(21),N(22)-(PhC=CPh)(OEP)PdCl$_2$ (4b′). Yield 44% based on **3b′**. Anal. Calcd for $C_{50}H_{54}Cl_2N_4Pd\cdot0.5H_2O$: C, 66.93; H, 6.18; N, 6.24%. Found: C, 67.08; H, 6.37; N, 6.28%. ^{1}H NMR δ = 10.71, 10.49 (s×2, 1H×2, *meso*-H), 10.07 (s, 2H, *meso*-H), 4.30—3.44 (m, 16H, CH_2), 2.17, 1.86, 1.54, 1.14 (t×4, 6H×4, CH_3), 6.00 (t, 2H, bridge phenyl *p*-H), 5.33 (t, 4H, bridge phenyl *m*-H). ^{13}C NMR δ = 152.81, 141.70, 146.65, 146.00, 144.71, 144.03, 141.31, 137.02 (pyrrole-C), 127.51, 126.25, 124.82, 124.51, 124.26 (bridge-C), 110.21, 105.27, 99.49 (*meso*-C). UV-vis (CH_2Cl_2) λ_{max} (log ε) 406 (4.68), 463 (4.43), 571 (sh) (3.81), 594 (3.85), 635 (sh) (3.45) nm.

X-Ray Analysis of 3a. A black prismatic crystal of **3a**·(CH_2Cl_2)(H_2O) was obtained by recrystallization through the slow diffusion of diethyl ether into a CH_2Cl_2 solution of **3a** in a refrigerator. It was mounted on a Rigaku AFC5R diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The crystallographic data are listed in Table 1. The cell constants and orientation matrix, obtained from a least-squares refinement using the setting angles of 25 reflections ($22.04 < 2\theta < 25.72°$), corresponded to a triclinic cell. The space group $P\bar{1}$ was determined based on a successful solution and refinement of the structure. The data were collected using the ω–2θ scan technique. Scans of $(1.37+0.35\tan\theta)°$ were made at a speed of 16.0° min^{-1} (in omega).

Table 1. Crystallographic Data

Formula	$C_{51}H_{42}Cl_6N_4OPd_2$
Fw	1152.44
Space group	$P\bar{1}$
a/Å	19.941(8)
b/Å	20.251(6)
c/Å	13.103(4)
α/deg	96.03(3)
β/deg	105.01(3)
γ/deg	79.32(4)
V/Å^3	5013(2)
Z	4
D_{calcd}/g cm^{-3}	1.527
D_{obsd}/g cm^{-3}	1.543[a]
Crystal system	Triclinic
Crystal dimensions	0.20 × 0.10 × 0.50 mm
Diffractometer	Rigaku AFC5R
μ(Mo $K\alpha$)/cm^{-1}	10.78
Scan type	ω–2θ
t/°C	23.0
Scan width/deg	1.37+0.35 tan θ
$2\theta_{max}$/deg	55.0
No. of collcd data	18686
No. of unique data	18145
No. of data, $I > 3.00\sigma(I)$	7555
No. of refined	1153
Refln/param ratio	6.6
R[b]	0.070
R_w[c]	0.068

a) Flotation in a mixed solution of carbon tetrachloride and hexane. b) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
c) $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

The intensities of three standard reflections were measured after every 100 reflections, and no decay was observed. An absorption correction based on azimuthal scans was applied. The data were corrected for Lorentz and polarization effects. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques.[14] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at standard positions (C–H = 0.95 Å), but not refined. The final cycle of a full-matrix least-squares refinement converged to values of *R* and R_w of 0.071 and 0.069, respectively. The standard deviation of the unit weight was 2.23. Neutral atom-scattering factors were taken from Cromer and Waber.[15] The values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[16] The values for the mass attenuation coefficients are those of Creagh and Hubbel.[17] All of the calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.[18]

Tables of atomic coordinates, thermal parameters and least-squares planes are deposited as Document No. 71027 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Semiempirical MO Calculation. Theoretical calculations were performed with the SPARTAN package version 4.0 (Wavefunction, Inc., Irvine, CA). The MNDO/d MO calculation using a PM3(tm) MO method[19] afforded a heat of formation (567 kcal mol^{-1}) for **3a** on the basis of the atomic coordinates for the X-ray structure. Starting from the original X-ray structure, the Pd(2) square plane was rotated around an axis passing through the bridging chlorine atoms, Cl(1) and Cl(2), in the opposite direction to the N(21),N(22)-bridge until the dihedral angle between PL(Pd1) and PL(Pd2) was set to −140°. A single point energy (heat of formation) for this hypothetical structure, calculated in the same manner as noted above, is 586 kcal mol^{-1}. A further structure optimization for this hypothetical structure was performed by allowing three atoms (Pd(2), Cl(3), and Cl(4)) to move with the rest of the molecule being locked. The energy minimum (576 kcal) was reached without a significant changes in the structural parameters.

Results and Discussion

Synthesis. Although the free base forms are suitable for the metallation reaction of N-substituted porphyrins, N(21),N(22)-bridged porphyrins exist as the monoprotonated forms due to their basic nature. Of a few examples of the metallation reaction of N(21),N(22)-bridged porphyrins previously reported,[6,7,20,21] Balch and co-workers successfully used a monoprotonated form as well as a free base form of the N(21),N(22)-(1,1-diarylvinylideno)-bridged porphyrin in a metallation reaction with [$Ru_3(CO)_{12}$].[21] However, the monoprotonated forms of N(21),N(22)-ethenobridged porphyrins, N(21),N(22)-(RC=CR)(TPP)$HClO_4$ (**1a**: R=ethyl, **1a′**: R=phenyl) and N(21),N(22)-(RC=CR)(OEP)-$HClO_4$ (**1b**: R = ethyl, **1b′**: R = phenyl) (OEP = 2,3,7,8, 12,13,17,18-octaethylporphyrin dianion), did not react with [$PdCl_2(MeCN)_2$] in MeCN at room temperature. Then, the corresponding TPP free base forms, N(21),N(22)-(RC=CR)-(TPP) (**2a**, **2a′**), were prepared at first by the treatment of a CH_2Cl_2 solution of the monoprotonated form **1a** and **1a′**

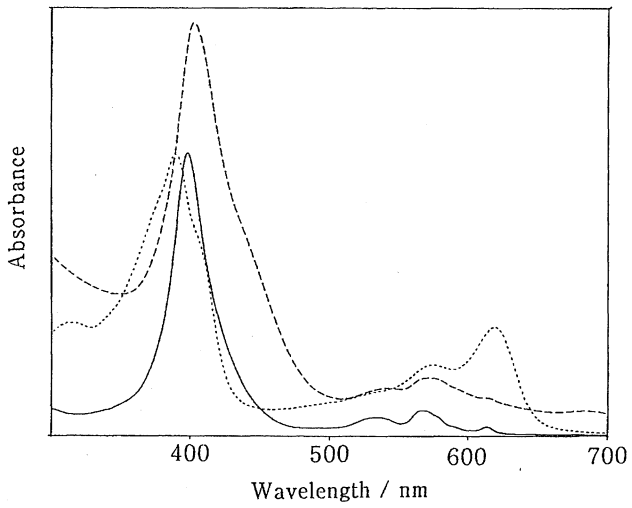


Fig. 1. UV-vis spectra of **1b** in CH_2Cl_2 (solid line), **2b** in hexane (dotted line), and initial product in CH_3CN (dashed line). The ordinate for the absorbance is arbitrarily.

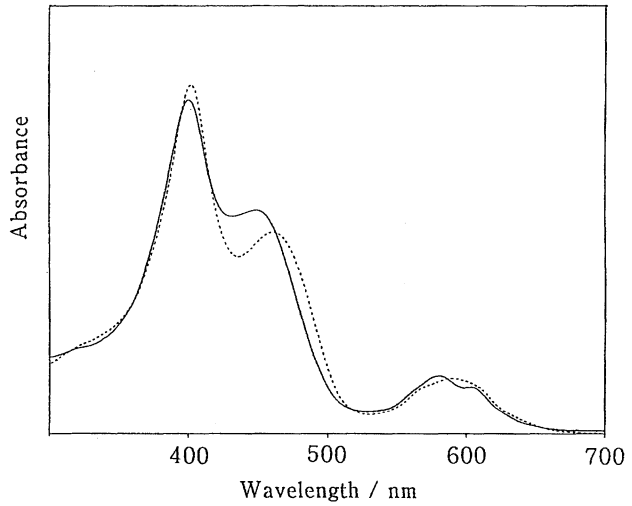


Fig. 2. UV-vis spectra of **3b** (solid line) and **4b** (dotted line) in CH_2Cl_2. The ordinate for the absorbance is arbitrarily.

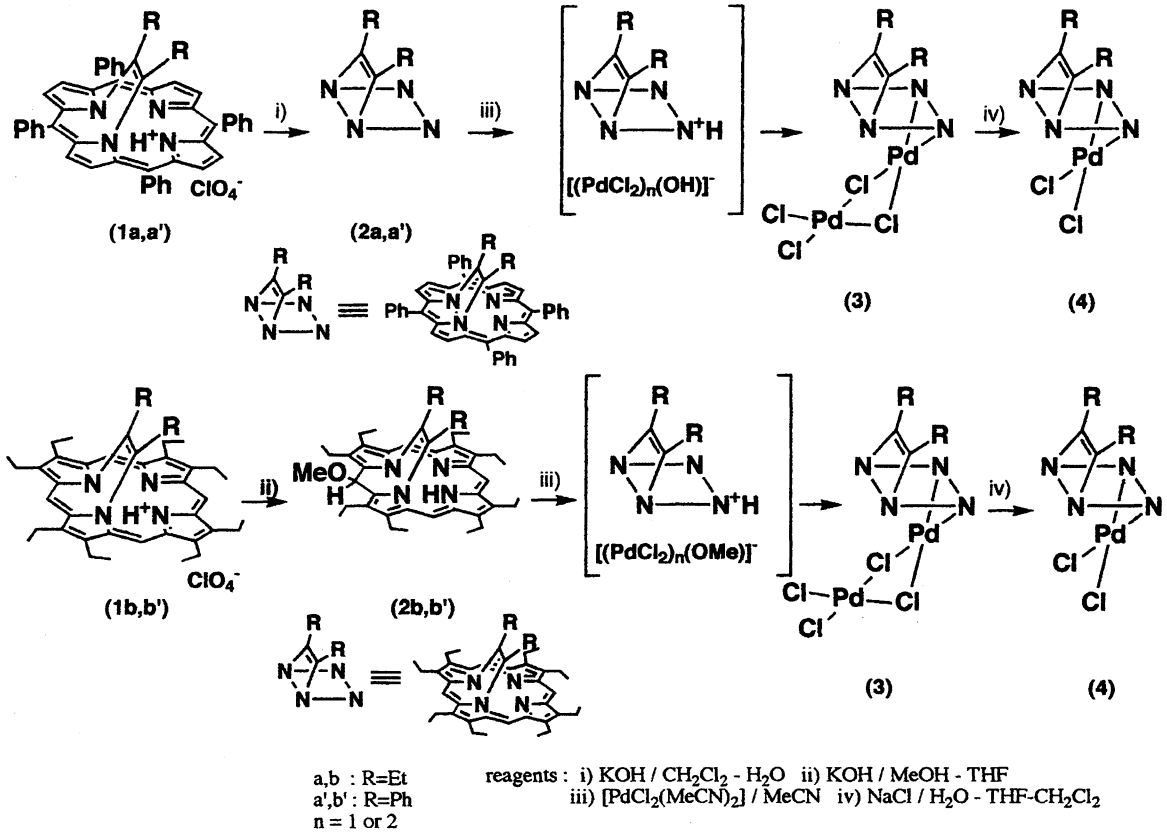
with a 10% KOH solution.[13] When **2a** was allowed to react with $[PdCl_2(MeCN)_2]$ (3—4 molar amounts) in acetonitrile, the brown color of the free base porphyrin changed to reddish green in 30 min at room temperature to form an initial product (**Ia**), whose UV-vis spectrum is substantially the same as that of the monoprotonated porphyrin **1a**. This initial product gradually changed to a green Pd complex (**3a**) in $CHCl_3$ in 3 d to give a 79% yield based on **2a**, after evaporation of acetonitrile and extraction of the initial product with $CHCl_3$ under aerobic conditions. The complex **3a′** was obtained in a 87% yield within 17 h through the initial product (**Ia′**).[22] The Pd complexes, **3a** and **3a′**, include two $PdCl_2$ units per porphyrin on the basis of a CHN elemental analysis. Vigorous stirring of a two-phase mixture of a THF–CH_2Cl_2 solution of **3a** or **3a′** and a saturated aqueous NaCl solution resulted in the formation of the mononuclear Pd complexes (**4a**, **4a′**) in quantitative yields.

Since the basicity of OEP pyrrole nitrogens is higher than that of TPP pyrrole nitrogens, the monoprotonated OEP analogues, **1b** and **1b′**, could not be deprotonated. A methoxide ion attacked on the 5-*mso* position of **1b** and **1b′** gave 5-methoxy-5,22-dihydroporphyrins (**2b**, **2b′**) when **1b** and **1b′** were treated with KOH in methanol.[8] The addition of $[PdCl_2(MeCN)_2]$ (3—4 molar amounts) to blue solutions of **2b** and **2b′** in MeCN resulted in the formation of red initial products; these were converted into green dinuclear Pd complexes (**3b**, **3b′**). The mononuclear Pd complexes (**4b**, **4b′**) were obtained by the same procedure as in the case of the TPP analogues. The reaction of equimolar amounts of **2a** and $[PdCl_2(MeCN)_2]$ resulted in the formation of a mixture of **3a** and **4a** with a ratio of 3 : 2. In the case of **2b**, the product ratio of **3b** and **4b** was 5 : 2. This is indicative of the relatively higher stability of the dinuclear complexes than the mononuclear complexes.

Table 2. Selected Bond Distances (Å) and Angles (deg) of **3a** with Their Estimated Standard Deviations[a]

	Molecule A	Molecule B
Pd(1)–Cl(1)	2.324(4)	2.334(5)
Pd(1)–Cl(2)	2.333(4)	2.332(5)
Pd(1)–N(3)	2.02(1)	2.03(1)
Pd(1)–N(4)	2.01(1)	2.03(1)
Pd(2)–Cl(1)	2.353(5)	2.359(5)
Pd(2)–Cl(2)	2.325(4)	2.228(5)
Pd(2)–Cl(3)	2.265(5)	2.259(5)
Pd(2)–Cl(4)	2.251(5)	2.264(5)
C(45)–N(1)	1.43(2)	1.44(2)
C(46)–N(2)	1.43(2)	1.45(2)
C(45)–C(46)	1.34(2)	1.32(2)
Cl(1)–Pd(1)–Cl(2)	84.6(2)	84.7(2)
N(23)–Pd(1)–N(24)	87.0(5)	86.4(5)
Cl(1)–Pd(1)–N(3)	175.0(4)	176.1(4)
Cl(1)–Pd(1)–N(4)	93.6(4)	95.1(4)
Cl(2)–Pd(1)–N(3)	94.4(4)	93.5(4)
Cl(2)–Pd(1)–N(4)	175.9(4)	173.4(4)
Pd(1)–Cl(1)–Pd(2)	87.7(2)	89.2(2)
Pd(1)–Cl(2)–Pd(2)	88.2(2)	89.7(2)
Cl(1)–Pd(2)–Cl(2)	84.2(2)	84.0(2)
Cl(3)–Pd(2)–Cl(4)	92.1(2)	91.0(2)
Cl(1)–Pd(2)–Cl(3)	92.2(2)	93.0(2)
Cl(2)–Pd(2)–Cl(4)	91.5(2)	92.0(2)
Cl(1)–Pd(2)–Cl(4)	175.3(2)	175.9(2)
Cl(2)–Pd(2)–Cl(3)	175.5(2)	176.3(2)
C(16)–N(4)–Pd(1)	117(1)	116(1)
C(19)–N(4)–Pd(1)	130(1)	130(1)
C(16)–N(4)–C(19)	108(1)	107(1)
C(11)–N(3)–Pd(1)	129(1)	130(1)
C(14)–N(3)–Pd(1)	116(1)	117(1)
C(11)–N(3)–C(14)	108(1)	108(1)
N(1)–C(45)–C(46)	120(1)	121(1)
N(1)–C(45)–C(47)	115(1)	113(1)
C(46)–C(45)–C(47)	123(1)	125(1)
N(2)–C(46)–C(45)	121(1)	119(1)
N(2)–C(45)–C(49)	115(1)	116(1)
C(45)–C(46)–C(49)	122(1)	122(1)

a) Atoms related by symmetry operations. Atom numberings are shown in Fig. 5.



Scheme 1.

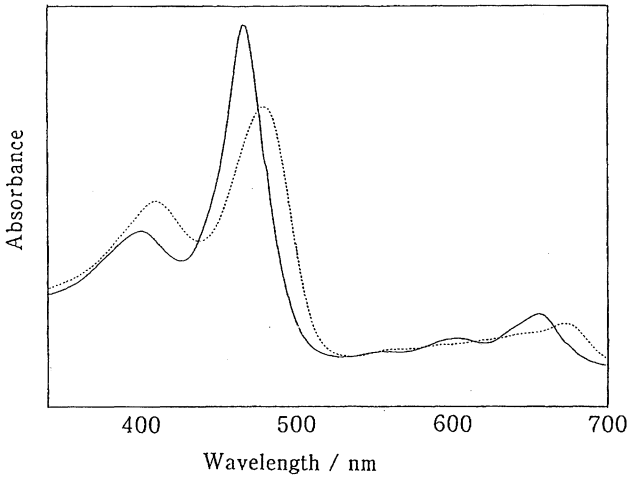


Fig. 3. UV-vis spectra of **3a** (solid line) and **4a** (dotted line) in CH_2Cl_2. The ordinate for the absorbance is arbitrarily.

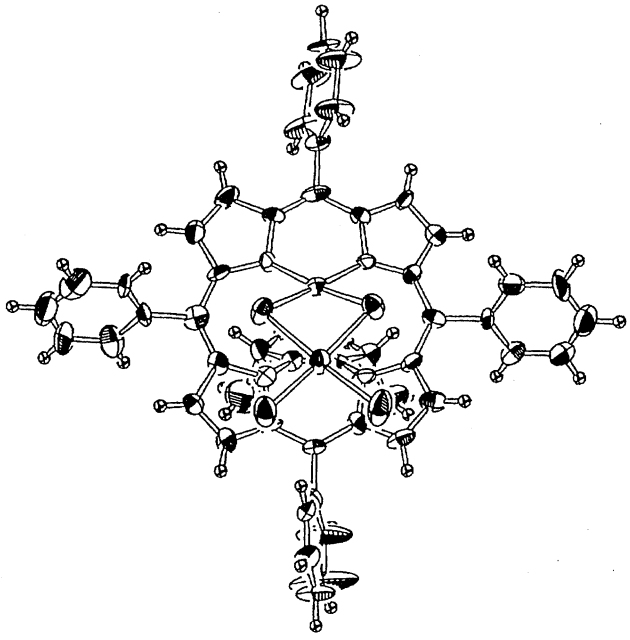


Fig. 4. An ORTEP drawing of **3a**.

A series of reactions described above were monitored by UV-vis spectroscopy. The spectral changes in the reactions from **1b** to **4b** are shown in Figs. 1 and 2. The UV-vis spectra of the initial products generated from **2** and $PdCl_2(MeCN)_2$ were virtually the same as those of **1** and they were characteristic of monoprotonated N(21),N(22)-bridged porphyrins. This suggests that the initial products are monoprotonated porphyrin compounds, which do not have strong coordination of pyrrole nitrogens to Pd(II). In the reaction of OEP analogues, $PdCl_2$ as a Lewis acid seems to abstract a methoxide anion from the basic dihydroporphyrins, **2b** and **2b'**, to give monoprotonated porphyrins probably with $[(PdCl_2)(OMe)]^-$ (n=1 or 2) as a counter anion as shown in Scheme 1. The UV-vis spectra of the obtained Pd complexes of N(21),N(22)-bridged porphyrins show that the Soret bands are split into two absorptions in the 400—480 nm region. As shown in Fig. 3, the Soret bands of the Pd complexes of N(21),N(22)-bridged TPP (**3a**, **3a'**, **4a**, and **4a'**) are also split into

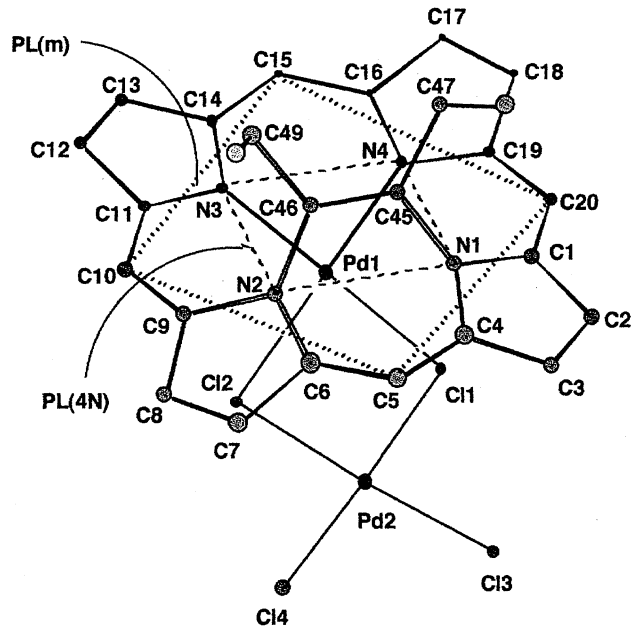


Fig. 5. Diagram of a porphyrin mean plane (PL(m)) containing four *meso* carbons, a 4N mean plane (PL(4N)), and two square planes of Pd coordination of **3a** with showing the atom numbering scheme. *meso*-Phenyl groups are omitted for clarity.

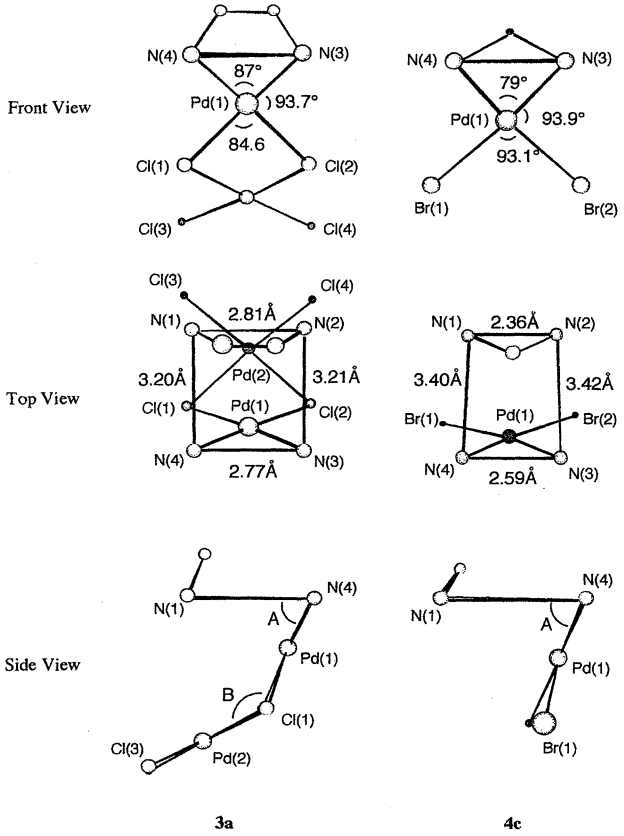


Fig. 6. Comparison of the coordination structures for **3a** and **4c**.

two bands, the longer wavelength absorptions of which have a higher intensity. This UV-vis spectral pattern is similar to that of N(21),N(22)-[CH(OBn)](TPP)$PdBr_2$ (**4c**).[7] Each Soret band moved to longer wavelength regions upon going from the dinuclear Pd complexes to the mononuclear ones.

Structure of N(21),N(22)-(EtC=CEt)(TPP)($PdCl_2$)$_2$ (3a). Although the crystal of **3a** contains two independent molecules, A and B, in an asymmetric unit, there are no significant differences in the structural parameters for these two chemically equivalent molecules. The selected interatomic distances and angles are given in Table 2 and an ORTEP drawing of the molecule A is illustrated in Fig. 4. Two CH_2Cl_2 and two H_2O molecules are present in the vicinity of molecule B. The structure of **3a** has a C_s symmetry and contains a folded di-μ-chlorodipalladium core. The atom-numbering scheme for **3a** is shown in Fig. 5. Pd(1) is coordinated by two adjacent imine nitrogens, N(3) and N(4), of the porphyrin as the terminal ligand. Pd(1) is placed out of the porphyrin 4N mean plane, PL(4N), by 1.32 Å towards the opposite side to the etheno bridge. The dihedral angle (A) is 69.3° between the 4N mean plane of the porphyrin and the square plane of the Pd(1) coordination sphere. The distal Pd(2) is placed at a distance of 3.78 Å from the 4N mean plane and two square planes of Pd coordination, PL(Pd1) and PL(Pd2), are folded along the axis passing through Cl(1) and Cl(2) with a dihedral angle (B) of 139.8° (see Fig. 5).

Although the Pd–Cl distances and the Cl–Pd–Cl angles are similar to those found in other di-μ-chlorodipalladium complexes, the Pd(1)–Cl–Pd(2) bond angles of **3a** are smaller and the Pd(1)–Pd(2) distance is relatively shorter due to the folding of the two Pd square planes (see Table 3).[22] This folding of Pd_2Cl_4 core toward the porphyrin plane may arise from an electronic repulsion between the lone-pair electrons of two bridging chlorides and the porphyrin π-electrons, because the distances between the bridging chlorides (Cl1 and Cl2) and some of porphyrin atoms (N1, C1, C20, C19, N2, C9, C10, C11) in the X-ray structure of **3a** are within van der Waals contacts (see Table 4). Since the distance between the terminal $PdCl_2$ unit and the porphyrin plane is longer than 3.5 Å, the interaction between these two moieties is not important. Therefore, the terminal $PdCl_2$ prefers the folded conformation, where the lone-pair electrons of the bridging chlorides get away from the porphyrin plane. Indeed, the heat of formation of this folded conformation (PL(Pd1)/PL(Pd2) = 139.8°), calculated by a semi-empirical molecular orbital method (PM3), is lower by 19 kcal mol^{-1} than that for a reversed conformation of the terminal $PdCl_2$, in which the dihedral angle between PL(Pd1) and PL(Pd2) is set to −140° with other structural parameters being unchanged. This result may support the idea that the original molecular structure in which Pd(2) comes close to the porphyrin ring relieves electronic repulsion between the bridging chlorides and the porphyrin ring. This *endo*-type conformation also seems to be retained in solution, as suggested by the NMR spectra (see Table 5). One of four β-pyrrolic-H signals of **3a** (9.20 ppm) is specifically shifted to a lower magnetic fields by 0.34 ppm upon going from a mononuclear complex to a dinuclear complex, whereas the chemical shift changes for the other β-pyrrole protons are less than 0.2 ppm. Fur-

Table 3. The Structural Parameters of Some Di-μ-chlorodipalladium(II) Complexes

Complex	Pd–Cl (Å)[a]	Cl–Pd–Cl (degree)[b]	Pd–Cl–Pd (degree)[c]	Pd–Pd (Å)	Ref.
3a	2.31	84.4	88.0	3.24	
$[PdCl\{CH_2CMe_2CMe{=}N(OH)\}]_2$	2.44			2.99	23(a)[d]
$[PdCl\{C_6H_3(OMe)NMe_2\}]_2$	2.41	85.5	94.5	3.54	23(b)
				3.51	
				3.50	
$[PdCl\{CH(CHO)CMe_2CH_2NMe_2\}]_2$	2.41	87.7	92.3		23(c)
$[PdCl\{P(mesityl)_2C_6H_2Me_2CH_2\}]_2$	2.44	85.7	94.4		23(d)

a) Averaged distances of the four Pd–Cl distances. b) Averaged angles of two Cl–Pd–Cl angles. c) Averaged angles of two Pd–Cl–Pd angles. d) $(PdCl)_2$ core is folded.

Table 4. Selected Distances between the Pd_2Cl_4 Unit and Porphyrin Atoms

Atoms	Distances (Å)	Atoms	Distances (Å)
Cl(1)–N(1)	3.50(2)	Cl(2)–N(2)	3.46(1)
Cl(1)–C(1)	3.23(2)	Cl(2)–C(9)	3.25(2)
Cl(1)–C(20)	3.31(2)	Cl(2)–C(10)	3.36(2)
Cl(1)–C(19)	3.41(2)	Cl(2)–C(11)	3.45(2)
Cl(3)–C(22)	4.18(2)	Cl(4)–C(22)	3.83(2)
Cl(3)–C(3)	3.69(2)	Cl(4)–C(7)	4.00(2)
Pd(2)–C(4)	3.85(2)	Pd(2)–C(6)	4.08(2)
Pd(2)–C(5)	4.02(2)		

Table 5. ^1H and ^{13}C NMR Chemical Shifts (δ) for Dinuclear Pd Complexes (**3**) and Mononuclear Pd Complexes (**4**) of *N,N′*-Etheno-Bridged Porphyrins

Compd	Pyrrole β-H			
3a	9.20 8.75 8.69 8.53			
4a	8.86 8.66 8.49 8.37			
3a′	9.41 8.83 8.66 8.17			
4a′	9.07 8.67 8.58 8.04			
	meso H		methylene H	*meso* C
3b	10.92	10.51[a] 10.23	4.37 4.09—3.89	109.29 103.59[a] 103.00
4b	10.51[a]	10.26 10.15	4.13—3.78	110.49 105.16[a] 98.73
3b′	11.35	10.52 10.06[a]	4.56 4.18—3.51	109.71 103.88[a] 103.03
4b′	10.71	10.49 10.07[a]	4.30—3.44	110.21 105.27[a] 99.49

a) Signals of two *meso* protons or carbons assigned to 10- and 20-positions.

Table 6. Selected Distances (Å) and Angles (deg) for **3a**, **4c**, and **1d**

Bridge Porphyrin	**3a** EtC=CEt $(TPP)Pd_2Cl_4$	**4c** CH(OBn) $(TPP)PdBr_2$	**1d** PhC=CPh $(TPP)HClO_4$
N(1)–N(2)	2.81(2)	2.36(1)	2.797(5)
N(1)–N(4)	3.21(2)	3.40(1)	3.131(7)
N(2)–N(3)	3.20(2)	3.42(1)	3.114(6)
N(3)–N(4)	2.77(2)	2.59(1)	2.776(6)
N(3)–Pd–N(4)	87.0(5)	79.0(2)	—
C(1)–N(1)–C(45)	125(1)	134.5(6)	123.9(4)
C(4)–N(1)–C(45)	119(1)	115.6(6)	118.1(3)
C(6)–N(2)–C(46)	120(1)	117.1(6)	118.2(5)
C(9)–N(2)–C(46)	124(1)	130.3(6)	122.0(4)
PL(4N)/PL(m)[a]	10.5	6.4	—
PL(N1)/PL(m)	22.9	12.7	18.83
Pl(N2)/PL(m)	18.6	8.2	15.15
PL(N3)/PL(m)	16.7	21.3	13.40
PL(N4)/PL(m)	14.7	17.4	4.44
PL(Pd1)/PL(4N)[b]	69.3	67	

a) PL is the least-squares mean plane: PL(4N) contains four pyrrole nitrogens. PL(m) contains four *meso* carbons. PL(N1–N4) are the pyrrole planes. b) Designated as A in Fig. 6.

thermore, one of three *meso*-H signals (10.92 ppm with 1H integral) and one of three *meso*-C signals (103.00 ppm) of **3b** are shifted downfield by 0.66 and 4.27 ppm, respectively, relative to the corresponding signals of **4b**, though the chemical-shift differences for the other *meso* protons and *meso* carbons are less than 0.1 and 1.6 ppm, respectively. And one methylene-H signal of **3b** (4.37 ppm with a 2H integral) is also shifted to a lower magnetic field. The other peripheral methylene proton signals of **3b** appear in a similar magnetic field (4.13—3.78 ppm) to those of **4b**. Similar shifts are observed in the NMR data of **3a′** and **3b′**, as shown in Table 4. These downfield shifts are ascribable to a magnetic deshielding effect of the distal Pd(2) on the 3(pyrrole-β)-, 5(*meso*)-, and 7(pyrrole-β)-positions of the porphyrin ring.

Although the bond lengths of the etheno moiety have normal values, the seven-membered ring, including the etheno bridge, is folded along the axis passing through N(1) and N(2) due to a repulsion between the etheno bridge and the porphyrin plane. The angle between the mean plane, PL(C5), containing N(1), C(4), C(5), C(6), and N(2) and the mean plane, PL(B), containing N(1), C(45), C(46), and N(2) is 49.5°. The C(47) and C(49) atoms attached to the bridge olefin carbons are not contained in the plane of the bridge and the dihedral angle between PL(B) and PL(Et) containing C(45), C(46), C(47), and C(49) is 169.5°. This structural feature is indicative of steric constraints between the bridge moiety and the N-unsubstituted pyrrole rings. The distances between the bridge moiety and N(3) or N(4), (N(3)–C(46), N(4)–C(45), N(3)–C(49), and N(4)–C(47)), are 3.09(2), 3.09(2), 3.49(2), and 3.54(2) Å, respectively. Some of them are within the van der Waals contacts.

The structure of **3a** is compared with those of N(21),N-(22)-(etheno)-bridged (TPP)$HClO_4$ (**1d**) and the Pd complex (**4c**) of N(21),N(22)-(methano)-bridged TPP in Table 6.[5,7] The methano bridge of **4c** makes the porphyrin 4N core to distort from a square to a rectangle more seriously than the etheno bridges of **3a** and **1d**. Figure 6 shows the structure of a 4N core with bridge carbons and a Pd coordination sphere. The methano bridge shortens the distance between two pyrrole nitrogens and makes an angle strain on the pyrrole rings. This is seen by a larger difference (18.9°) in the angles between C1–N1–C45 and C4–N1–C45 in the case of **4c** than in **3a** (6°) and **1d** (5.8°). The very short distance (2.59 Å) between N(3) and N(4) of **4c** induces the distorted geometry (N(3)–Pd(1)–N(4) = 79.0°) in the Pd coordination sphere, while the etheno bridge of **3a** does not deform the porphyrin 4N core (N(3)–N(4) distance = 2.77 Å) so extraordinarily, and therefore allows Pd to take an undistorted geometry (N(3)–Pd(1)–N(4) = 87.0°). Since the N(21),N(22)-bridge is forced to get out of the porphyrin plane, the N-substituted pyrrole ring is required to rotate around the axis passing through C1 and C4 or the axis passing through C6 and C9. This is shown by the dihedral angles between PL-(N1) and PL(m) (22.9°) and between PL(N2) and PL(m) (18.6°) for **3a**. (PL(N1), PL(N2), PL(N3), and PL(N4) are the pyrrole mean planes containing each pyrrole nitrogen, N(1), N(2), N(3), and N(4), respectively. PL(m) is the mean plane containing four meso carbons.) On the other hand, the N-unsubstituted pyrroles are rotated in the opposite direction to relieve the steric constraint from the N(21),N(22)-bridge, as is seen in the dihedral angles between PL(N3) and PL-(m) (16.7°) and between PL(N4) and PL(m) (14.7°) for **3a**. Since N-substituted pyrroles bridged by one carbon in **4c** are not allowed to rotate so much as the pyrroles in **3a**, due to an increase in the angle strain on N1–C(bridge)–N2, the cant of N-substituted pyrroles (dihedral angles are 12.7° for PL-(N1)/PL(m) and 8.2° for PL(N2)/PL(m)) in **4c** is smaller than that in **3a**. Thus, the porphyrin ring of **3a** is distorted more greatly than **4c** (dihedral angles between PL(4N) and PL(m) are 10.5° for **3a** and 6.4° for **4c**). The distance between the methylene proton of the methano bridge moiety and Pd is no longer than 2.58 Å. The close proximity of the Pd atom to the bridge moiety may induce strained bondings of the methano bridge to be cleaved, leading to decomposition into PdTPP. Thus, the unstrained geometries in the porphyrin 4N core, bridged nitrogen, the bridges and the square planar Pd coordination sphere of **3a** seem to be responsible for its more stable nature than **4c**.

Conclusion

The reaction of N(21),N(22)-etheno-bridged porphyrins with $PdCl_2$ preferentially afforded dinuclear complexes which can be converted to mononuclear complexes by ligand exchange. The X-ray structure showed that **3a** is di-μ-chlorodipalladium(II) complex coordinated by the porphyrin as the terminal ligand with the distal Pd(2) coming close to the porphyrin ring. The etheno substitution of **3a** makes the pyrrole rings to cant, and two pyrrole rings are favorably situated for the coordination to the Pd atom. After all, the present Pd complexes are not demetallated and N-dealkylated at all in solution, which will allow an extensive study on their chemical reactivity.

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22) One of the referees suggested that this initial product **Ia′** may not be related to the formation of **3** and **4**. Since addition of

$PdCl_2(MeCN)_2$ to the acetonitrile solution of **2a′** containing triethylamine (10 equivalents) also gave **Ia′**, a direct metallation of the free base **2a′** with $PdCl_2$ to give **3a′** or **4a′** is not plausible. The initial product **Ia′** was separated by column chromatography on silica gel and recrystallized from CH_2Cl_2–*n*-hexane. The elemental analysis indicates that **Ia′** is a mixture of monoprotonated porphyrins having different number of the $PdCl_2$ unit (one or two) in the counter anion. The ^1H NMR spectrum of **Ia′** shows only one set of signals due to the porphyrin protons, the chemical shifts of which are substantially the same as those of **1a′**. (NMR data of **Ia′** in $CDCl_3$: $\delta = 9.26$, 9.10, 8.85, 8.73 (d×4, 2H×4, pyrrole-β-H), 8.49—7.08 (m, 20H, phenyl-H), 6.31 (t, 2H, bridge phenyl-*p*-H), 5.91 (t, 4H, bridge phenyl *m*-H), 2.6 (br, 4H, bridge phenyl *o*-H), 2.63 (s, 1H, OH)). A 1H-singlet at 2.63 ppm may be assigned to the coordinated OH proton in the counter anion. The largest mass peak in the FAB MS spectrum of **Ia′** is 791 which corresponds to the porphyrin cation. We have confirmed that the isolated initial product **Ia′** is converted into the dinuclear Pd complex **3a′** and that this transformation does not occur by way of the mononuclear Pd complex **4a′**. Thus, we would like to propose the stepwise pathway for the ligation.

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