Synthesis of Binuclear Palladium(II) Complexes of Bidentate N(21),N(22)-Bridged Porphyrins

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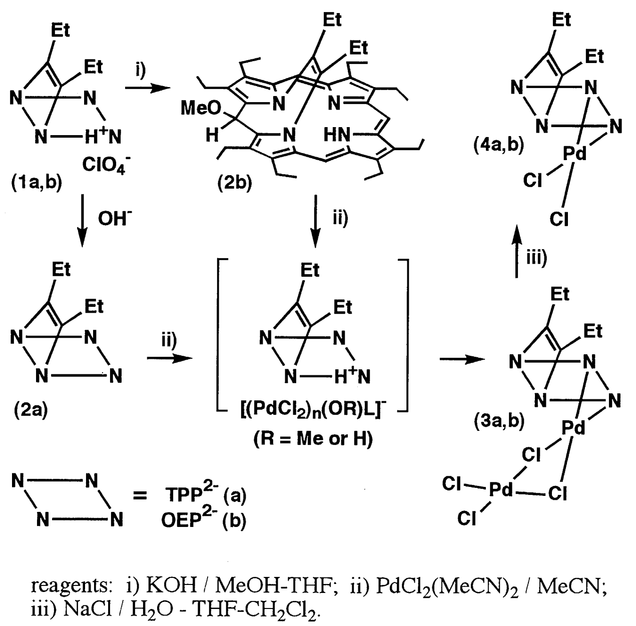
N(21),N(22)-(etheno)-bridged porphyrins were metallated with $PdCl_2$ to give binuclear porphyrin complexes with (μ-dichloro)dipalladium(II) structure in which the terminal $PdCl_2$ moiety is coming close to the porphyrin plane.

Since palladium(II) is strongly coordinated by the four nitrogens of porphyrin ligand in Pd(II) porphyrins, studies on Pd(II) porphyrins have so far been limited to photo and redox chemistry.[1] Palladium complexes, however, with a bidentate nitrogen base ligand have recently been shown to be applicable for a number of organic transformations as catalysts in place of classical Pd complexes having phosphine ligands.[2] N(21),N(22)-bridged porphyrins are of interest in the sense that they can serve as bidentate nitrogen base ligands because two pyrrolic nitrogens of porphyrin core are alkylated and not used for coordination to the metal. Furthermore, the basicity of the porphyrin nitrogens is increased by the N-substitution and the N(21),N(22)-bridged structure renders the unsubstituted pyrrole rings to cant towards the opposite side of the N(21),N(22)-bridge.[3] Thus, two imine-type nitrogens, N(23) and N(24), serve as a bidentate ligand. There have been only two reports of Pd complexes of N(21),N(22)-bridged porphyrins,[4,5] in which two adjacent nitrogens of porphyrin core are bridged by a one-carbon bridge such as $CH(CO_2Et)$ and CH(OBn). The X-ray crystal structure of the latter Pd complex showed that two imine-type nitrogens and two bromine atoms occupy square planar coordination sites.[5] This type of square planar Pd(II) complexes are of great interest not only in view of the steric factor of the porphyrin ligand moiety but also in view of the unique photochemical and redox activity of N(21),N(22)-bridged porphyrins.[6,7] Since the reported Pd(II) complexes tend to lose the bridge moieties giving ordinary Pd(II) porphyrins on standing even as crystals, we are interested in developing stable Pd complexes of N(21),N(22)-bridged porphyrins. In this study are reported the synthesis of stable Pd(II) porphyrins with a two-carbon (etheno) bridge between N(21) and N(22) and also the X-ray crystal structure of the newly formed (μ-dichloro)dipalladium(II) complex.

There have been reported a few examples of metallation reaction of N(21),N(22)-bridged porphyrins.[4,5,8,9] Balch and co-workers have successfully used a monoprotonated form as well as a free base form of N(21),N(22)-(1,1-diarylvinylidene)-bridged porphyrin in the metallation reaction with $Ru_3(CO)_{12}$.[9] Although monoprotonated forms of N(21),N(22)-(1,2-diethyl-etheno)-bridged porphyrins, N(21),N(22)-(EtC=CEt)(TPP[10])H-ClO_4 (**1a**) and N(21),N(22)-(EtC=CEt)(OEP)$HClO_4$ (**1b**), did not react with $PdCl_2(MeCN)_2$ (4 equivalents) in acetonitrile at room temperature, the corresponding TPP free base, N(21),N(22)-(EtC=CEt)(TPP) (**2a**), reacted under the same reaction conditions with showing color change from brown to reddish green in 30 min at room temperature. The UV-Vis spectrum at this stage (Soret band at 428 nm) is characteristic of monoprotonated N(21),N(22)-bridged porphyrins. Therefore, the initial product does not seem to have strong coordination of porphyrin nitrogens to Pd(II). Then, inorganic salts were removed by passing this solution through a silica gel column and the porphyrin residue was allowed to stand in a $CHCl_3$ solution. The conversion from the initial product to a green Pd complex (**3a**)[11] was completed in 3 days to give 79% yield. The CHN elemental analysis of **3a** was in agreement with inclusion of two $PdCl_2$ units per porphyrin. A vigorous stirring of a two-phase mixture of a THF-CH_2Cl_2 solution of **3a** and a saturated aqueous NaCl solution gave a mononuclear Pd complex (**4a**)[11] in 80% yield. These Pd complexes **3a** and **4a** showed a Soret band at 466 and 479 nm, respectively. The UV-Vis spectral pattern of **3a** and **4a** was similar to that of N(21),N(22)-[CH(OBn)](TPP)$PdCl_2$ (**4c**).[5] When the initial ratio of **2a** and $PdCl_2(MeCN)_2$ was 1 : 1, a mixture of **3a** and **4a** was obtained directly with a ratio of 3 : 2. This is indicative of the relative stability of the binuclear complexes to the mononuclear complexes.

While the TPP free base form **2a** was readily obtained by the treatment of a CH_2Cl_2 solution of the monoprotonated form **1a** with a 10% KOH solution,[12] the monoprotonated form of the OEP analogue **1b** was not deprotonated due to the higher basicity of OEP nitrogens. But, a methoxide ion attacked on the 5-meso position of **1b** to give 5-methoxy-5*H*-phlorin (**2b**) in 81% yield when **1b** was treated with KOH in MeOH.[6] The addition of $PdCl_2(MeCN)_2$ (4 equivalents) to a MeCN solution of **2b**



reagents: i) KOH / MeOH-THF; ii) $PdCl_2(MeCN)_2$ / MeCN; iii) NaCl / H_2O - THF-CH_2Cl_2.

Scheme 1.

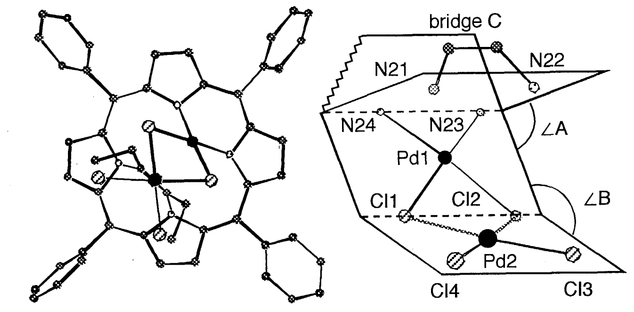


Figure 1. X-ray structure of **3a** (left); diagram of two square planes of Pd coordination and the porphyrin 4N mean plane of **3a** with showing the dihedral angles ∠A and ∠B (right).

Table 1. Selected distances (Å) and angles (deg) with their estimated standard deviations for **3a** and **4c**[a]

distances	3a	4c	angles	3a	4c
Pd1-X1	2.324(4)	2.395(1)	X1-Pd1-X2	84.6(2)	93.1(1)
Pd1-X2	2.333(4)	2.429(1)	N23-Pd-N24	87.0(5)	79.0(2)
Pd1-N23	2.02(1)	2.071(7)	X1-Pd-N23	175.0(4)	170.9(2)
Pd1-N24	2.01(1)	2.010(7)	X1-Pd-N24	93.6(4)	93.9(2)
N21-N22	2.81(2)	2.36(1)	X2-Pd-N23	94.4(4)	93.8(2)
N22-N23	3.21(2)	3.42(1)	X2-Pd-N24	175.9(4)	172.8(2)
N23-N24	2.77(2)	2.59(1)	∠A[b]	69	67
N24-N21	3.20(2)	3.40(1)	∠B[b]	142	-

[a]The structure data of **4c** were taken from reference 5. Atom numberings are shown in Figure 1. X stands for Cl (**3a**) and Br (**4c**). [b]∠A and ∠B are dihedral angles shown in Figure 1.

resulted in the formation of an initial product, which showed virtually the same UV-Vis spectrum as that of **1b**. This suggests that $PdCl_2$ as a Lewis acid would abstract a methoxy anion from **2b** to give a monoprotonated porphyrin product probably with $[(PdCl_2)_n(OMe)L]^-$ as a counter anion. This initial product was converted into the binuclear Pd complex (**3b**)[11] (78% yield) and further into the mononuclear Pd complex (**4b**)[11] (40% yield) by a similar procedure to that described for **3a** and **4a**.

In the single crystal X-ray structure of the binuclear complex **3a** as shown in Figure 1 (left),[13] two adjacent imine nitrogens, N(23) and N(24), of the porphyrin are coordinating to the proximal Pd(1) as the terminal ligands with the dihedral angle (∠A) of 69° between the 4N mean plane of porphyrin and the square plane of the Pd(1) coordination sphere. The most salient feature in the molecular structure of **3a** is the (μ-dichloro)-dipalladium core in which the distal Pd(2) is forced to come close to the porphyrin ring with the dihedral angle (∠B) of 142° between the two square planes of Pd coordination (see Figure 1 (right)). This endo type conformation seems to be retained also in solution as suggested by the ^1H NMR data.[11] That is, one of four β-pyrrole signals of **3a** (9.20 ppm) and one of three meso-H signals of **3b** (10.92 ppm with 1H integral) are specifically shifted to the lower magnetic fields by 0.34 ppm and 0.66 ppm, respectively, upon going from the mononuclear to the binuclear complexes. These downfield shifts are ascribable to the direct influence of the distal Pd(2) on the 3(pyrrole-β)-, 5(meso)-, and 7(pyrrole-β)-positions of the porphyrin ring.

It was shown that the N(21),N(22)-methano bridge of **4c** makes the porphyrin 4N core to distort greatly from square to rectangle.[5] The very short distance (2.59 Å) between N(23) and N(24) of **4c** induces the distorted geometry (∠N(23)-Pd(1)-N(24) = 79.0°) in the Pd coordination sphere and this may be responsible for its labile nature. In contrast, the two-carbon bridge in the case of **3a** does not deform the porphyrin 4N core (N(23)-N(24) distance = 2.77 Å) so extraordinarily as the one-carbon bridge and therefore allows Pd to take undistorted geometry (∠N(23)-Pd(1)-N(24) = 87.0°) for the square planar coordination as summarized in Table 1. Thus, the present Pd(II) complexes are not demetallated and N-dealkylated at all in solution, which will allow extensive study on their chemical reactivity.

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References and Notes

1 J. A. Mercer-smith, C. R. Sutcliffe, R. H. Schmehl, and D. G. Whitten, *J. Am. Chem. Soc.*, **101**, 3995 (1979); J. L. Karas, C. M. Lieber, and H. B. Gray, *J. Am. Chem. Soc.*, **110**, 599 (1988); E. M. McGhee, B. M. Hoffman, and J. A. Ibers, *Inorg. Chem.*, **30**, 2162 (1991); A. M. Stolzenberg and L. L. Schussel, *Inorg. Chem.*, **30**, 3205 (1991).

2 A. Togni and L. M. Venanzi, *Angew. Chem., Int. Ed. Engl.*, **33**, 497 (1994).

3 H. J. Callot, R. Cromer, A. Louati, B. Metz, and B. Chevrier, *J. Am. Chem. Soc.*, **109**, 2946 (1987).

4 A. W. Johnson, D. Ward, P. Batten, A. L. Hamilton, G. Schelton, and C. M. Elson, *J. Chem. Soc., Perkin Trans. 1*, **1975**, 2076.

5 H. J. Callot, J. Fischer, and R. Weiss, *J. Am. Chem. Soc.*, **104**, 1272 (1982).

6 J. Setsune, M. Ikeda, T. Iida, and T. Kitao, *J. Am. Chem. Soc.*, **110**, 6572 (1988); J. Setsune, H. Yamaji, and T. Kitao, *Tetrahedron Lett.*, **31**, 5057 (1990).

7 J. Setsune, K. Wada, and H. Higashino, *Chem. Lett.*, **1994**, 213.

8 Y. W. Chan, M. W. Renner, and A. L. Balch, *Organometallics*, **2**, 1888 (1983).

9 A. L. Balch, Y. W. Chan, M. M. Olmstead, M. W. Renner, and F. E. Wood, *J. Am. Chem. Soc.*, **110**, 3897 (1988).

10 Abbreviations: TPP = 5,10,15,20-tetraphenylporphyrin dianion; OEP = 2,3,7,8,12,13,17,18-octaethylporphyrin dianion.

11 ^1H NMR data (δ-value in $CDCl_3$, 270MHz) **3a**: 9.20, 8.75, 8.70, 8.52 (dx4, 2Hx4, pyrrole-β-H), 8.67~7.66 (m, 20H, phenyl-H), -1.27 (t, 6H, CH_3), -2.71, -4.14 (dqx2, 2Hx2, CH_2, J_{gem} = 15Hz); **4a**: 8.86, 8.66, 8.49, 8.37 (dx4, 2Hx4, pyrrole-β-H), 8.31~7.74 (m, 20H, phenyl-H), -1.41 (t, 6H, CH_3), -2.91, -4.23 (dqx2, 2Hx2, CH_2, J_{gem} = 15Hz); **3b:** 10.92, 10.23 (sx2, 1Hx2, meso-H), 10.51 (s, 2H, meso-H), 4.39~3.89 (m, 16H, CH_2), 2.24, 1.94, 1.70, 1.70 (tx4, 6Hx4, CH_3), -1.68 (t, 6H, bridge-CH_3), -3.10, -4.61 (dqx2, 2Hx2, bridge-CH_2, J_{gem} = 15Hz); **4b:** 10.26, 10.15 (sx2, 1Hx2, meso-H), 10.51 (s, 2H, meso-H), 4.13~3.79 (m, 16H, CH_2), 2.05, 1.88, 1.63, 1.60 (tx4, 6Hx4, CH_3), -1.79 (t, 6H, bridge-CH_3), -3.24, -4.66 (dqx2, 2Hx2, bridge-CH_2, J_{gem} = 15Hz);

12 J. Setsune, Y. Ishimaru, and T. Kitao, *Chem. Lett.*, **1990**, 1351.

13 Crystal data for **3a**•(H_2O)(CH_2Cl_2): $Pd_2Cl_6ON_4C_{51}H_{42}$, M = 1152.44, triclinic, space group $P\bar{1}$, a = 19.941(8), b = 20.251(6), c = 13.103(4) Å, α = 96.028(26), β = 105.012(29), γ = 79.322(42)°, V = 5013.1(3) $Å^3$, Z = 4, D_{calc} = 1.527 g/cm^3, D_{obs} = 1.54 g/cm^3, μ(Mo-Kα) = 7.89 cm^{-1}, T = 296 K, crystal size 0.20 x 0.10 x 0.50 mm. A total of 18145 unique reflections were collected on a Rigaku AFC5R diffractometer using graphite-monochromated Mo-Kα radiation; 7550 reflections with I > 3.00σ(I) were observed. The structure was solved by Patterson method and refined by the full-matrix least-squares method. The refinement converged at R = 0.071, R_w = 0.069.