

Apparent π -Allyl Rotation in the π -(Allyl)palladium(II) Complexes of N^{21}, N^{22} -Bridged Porphyrins

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Received December 8, 1998

Summary: Reaction of (dichloro)palladium(II) complexes of N^{21}, N^{22} -(etheno) bridged porphyrins with $AgClO_4$ gave bis(perchlorato)Pd(II) porphyrins via (chloro)(perchlorato)Pd(II) porphyrins. While the latter as a dimeric μ -(dichloro)dipalladium(II) form was not reactive, the former reacted with allyltributyltins to afford a mixture of trans and cis isomers of π -(allyl)Pd(II) porphyrins. A trans isomer of π -(C_3H_5)Pd(II) porphyrin preferentially formed by the reaction of $(\eta^1-C_3H_5)SnBu_3$ gradually isomerized to a cis isomer, reaching an equilibrium state with a trans/cis ratio of 3:7. The single-crystal X-ray analysis of the cis isomer showed an average Pd–C bond distance of 2.119(3) Å. The N3–Pd–N4 plane is canted by 53.4° from the porphyrin plane defined by four meso-carbons, C5, C10, C15, and C20. The π -(allyl) plane has dihedral angles of 106.8° and 53.5° relative to the N3–Pd–N4 plane and the porphyrin plane, respectively.

While a large number of organopalladium complexes with various amine and phosphine ligands have been known, efforts in their ligand design are focused mostly on the stereochemical aspect. In view of the rich photochemistry and electrochemistry of porphyrins,¹ it is of great interest to generate organopalladium complexes of porphyrin. A coordination site for an organo ligand, however, is not available for ordinary palladium porphyrins because of the tetradentate nature of porphyrin. We have recently shown that N^{21}, N^{22} -etheno bridged porphyrin serves as a bidentate nitrogen base ligand for stable coordination to palladium.² Organopalladium complexes with bidentate nitrogen base ligands instead of classical phosphine ligands have

recently been recognized as useful in enantioselective organic transformations and polymerizations.^{3,4} Thus, organopalladium complexes of N^{21}, N^{22} -bridged porphyrins are of particular significance. Here we describe the first example of organopalladium(II) porphyrins: preparation of π -(allyl)Pd(II) complexes by the reaction of dicationic Pd(II) complexes with allyltributyltin derivatives and their trans–cis isomerization behavior.

(Dichloro)[(1,2-diphenylethene- N^{21}, N^{22})-meso-tetraphenylporphyrinato- N^{23}, N^{24}]palladium(II), N^{21}, N^{22} -(PhC=CPh)(TPP)Pd^{II}Cl₂ (**1a**), and its analogues, N^{21}, N^{22} -(EtC=Ct)(TPP)Pd^{II}Cl₂ (**1b**) and N^{21}, N^{22} -(PhC=CPh)-(OEP⁵)Pd^{II}Cl₂ (**1c**), did not undergo displacement reaction of the coordinated chloride by using allylsilanes and allyltins. To increase reactivity of Pd, **1a–1c** were treated with an equimolar amount of $AgClO_4$ in CH_2Cl_2 to give **2a–2c**, respectively, in a quantitative yield. The upfield shifts of the ¹H NMR signals due to the porphyrin periphery of **2a–2c** as compared with **1a–1c** are indicative of the μ -(dichloro)dipalladium(II) bisporphyrin structure (see Scheme 1).⁶ This is supported by the MS peak at $m/e = 1772$ (M – ClO₄) observed for **2b**. On the other hand, treatment of **1a** and **1b** with 2-fold molar amounts of $AgClO_4$ quantitatively gave the bis(perchlorate)s, **3a** and **3b**, respectively. The monomeric nature of **3b** is indicated by the MS peak at $m/e = 899$ (M – ClO₄) and by the similarity of the ¹H NMR chemical shifts to those of **1b**.

Although the mono(perchlorate) **2a** did not react with allyltributyltin, addition of allyltributyltin (1.1 equiv)

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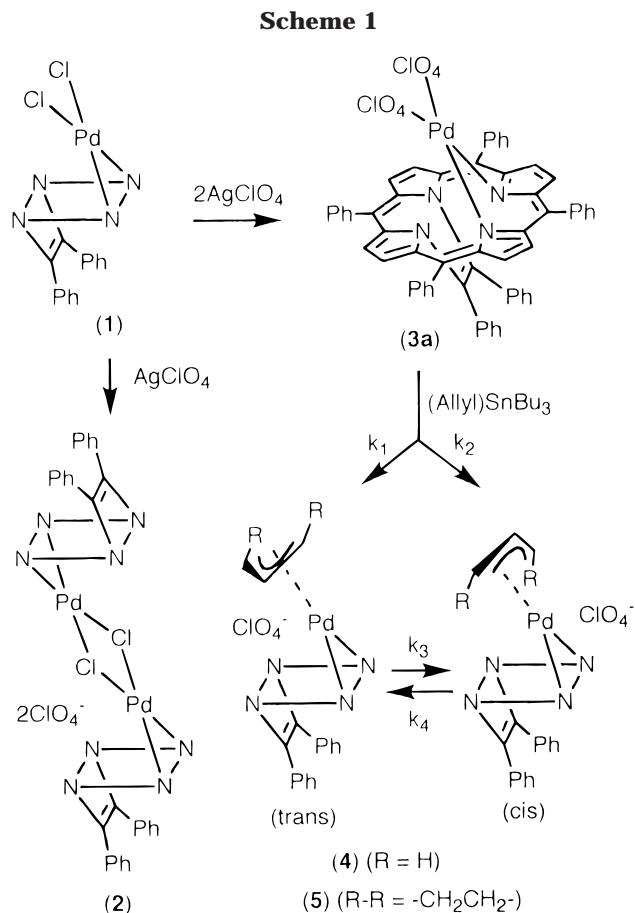
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(5) Abbreviations. OEP (octaethylporphyrin dianion).

(6) ¹H NMR (300 MHz, CDCl₃): **2a**, δ 9.41, 8.49, 8.47, 7.69 (d \times 4, 2H \times 4, β -Py–H), 8.39–7.03 (m, 20H, meso-Ph–H), 5.98 (t, 2H, bridge-Ph p-H), 5.49 (br, 4H, bridge-Ph m-H); **3a**, δ 9.35, 8.91, 8.68, 8.20 (d \times 4, 2H \times 4, β -Py–H), 8.66–7.31 (m, 20H, meso-Ph–H), 6.22 (t, 2H, bridge-Ph p-H), 5.77 (br, 4H, bridge-Ph m-H); *trans-4*, δ –1.06 (d, $J_{anti} = 10.9$ Hz, 2H, allyl terminal CH), –1.25 (m, 1H, allyl central CH), –1.37 (d, $J_{syn} = 5.9$ Hz, 2H, allyl terminal CH); *cis-4*, δ 2.14 (m, 1H, allyl central CH), –0.28 (d, $J_{syn} = 6.9$ Hz, 2H, allyl terminal CH), –4.55 (d, $J_{anti} = 11.9$ Hz, 2H, allyl terminal CH); *trans-5*, δ 0.27 (s, 2H, allyl terminal CH), –0.91, –1.19 (d \times 2, $J_{gem} = 13.9$ Hz, 2H \times 2, CH₂), –1.68 (s, 1H, allyl central CH); *cis-5*, δ 2.64 (s, 1H, allyl central CH), 1.10 (s, 2H, allyl terminal CH), –1.69, –5.38 (d \times 2, $J_{gem} = 12.9$ Hz, 2H \times 2, CH₂).



to the bis(perchlorate) **3a** in CH₂Cl₂ at room temperature resulted in the formation of π -(allyl)Pd(II) complex **4** of N²¹,N²²-bridged porphyrin in a 93% isolated yield. ¹H NMR spectrum of the product after chromatographic purification on silica gel showed two sets of C_s-symmetric π -allyl signals at high magnetic fields with a ratio of 3:7. The major component shows the π -allyl terminal methylene protons at -4.55 (*J*_{anti} = 11.9 Hz) and -0.28 ppm (*J*_{syn} = 6.9 Hz) and the π -allyl central methine proton at 2.14 ppm, while the minor component shows the corresponding protons at -1.06 (*J*_{anti} = 10.9 Hz) and -1.37 ppm (*J*_{syn} = 5.9 Hz) and at -1.25 ppm. Since the proton chemical shifts of the π -allyl group greatly depend on the ring current effect of porphyrin, the major isomer is associated with a *cis* isomer in which the terminal methylene protons anti to the central methine proton are very close to the porphyrin plane as shown in Scheme 1. On the other hand, the minor isomer should be a *trans* isomer in which the central methine proton comes closer to the porphyrin plane than the terminal methylene protons.

The progress of the reaction of **3a** (0.013 mM) with allyltributyltin (0.019 mM) in CDCl₃ (0.50 mL) at 25 °C was monitored by ¹H NMR. Most of **3a** has reacted in 3 min, whereupon ¹H NMR analysis shows a molar ratio of 0.03:0.62:0.35 for **3a**/*trans*-**4**/*cis*-**4**. The kinetically favored *trans*-**4** was then gradually isomerized to

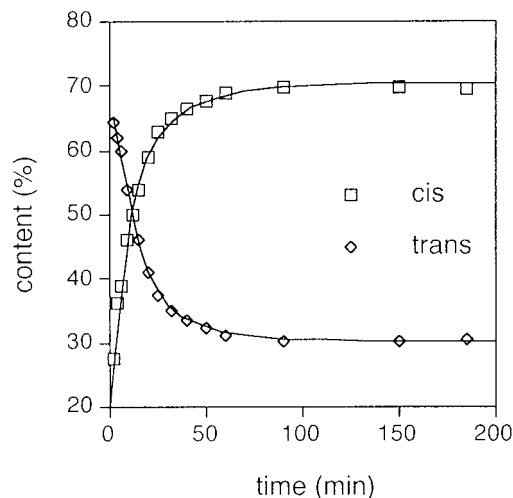


Figure 1. Change in the product distribution (*trans*-**4** and *cis*-**4**) with time at 25 °C after addition of (η^1 -C₃H₅)₃SnBu₃ (0.019 mM) to **3a** (0.013 mM) in CDCl₃ (0.5 mL).

the thermodynamically more stable *cis*-**4** until the equilibrium state (*K*_{eq} = 2.3) was reached, as shown in Figure 1. The rate constant *k*₃ for the isomerization from *trans*-**4** to *cis*-**4** was estimated as 7.1 × 10⁻⁴ s⁻¹ at 25 °C. The phase-sensitive 2D NOESY experiment of the mixture of *trans*-**4** and *cis*-**4** in tetrachloroethane-*d*₂ at 80 °C showed cross-peaks due to chemical exchange between signals at -1.06 (*trans*-**4**) and -4.55 (*cis*-**4**) ppm and between signals at -1.37 (*trans*-**4**) and -0.28 (*cis*-**4**) ppm. This is consistent with the mechanism involving dissociation of one Pd-N bond and rotation around the other Pd-N bond.⁷ Since there are no positive cross-peaks between the syn and anti π -allyl terminal methylene protons, a η^3 - η^1 type isomerization mechanism is excluded.⁸ This isomerization could be neglected up to 1 h after the addition of allyltributyltin to **3a** at -5 °C, and the second-order rate constants *k*₁ and *k*₂ for the formation of *trans*-**4** and *cis*-**4** from **3a** were determined at -5 °C as 3.2 × 10⁻² and 1.2 × 10⁻² L mol⁻¹ s⁻¹, respectively. (Cyclopent-2-enyl)tributyltin reacted with **3a** more slowly than allyltributyltin to give the corresponding π -(allyl)Pd(II) complex **5**.⁶ The molar ratio at 3 min after the addition of the tin reagent (1.5 equiv) to **3a** in CDCl₃ at 25 °C is 0.71:0.15:0.14 for **3a**/*trans*-**5**/*cis*-**5**. This *trans*/*cis* isomer ratio was not changed

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(9) Crystallographic data for *cis*-**4**: C₆₁H₄₅N₄ClPd·2(H₂O), M = 1009.92, monoclinic, space group P2₁/n (No. 14), a = 16.518(1) Å, b = 16.287(3) Å, c = 18.134(2) Å, β = 92.706(7)°, V = 4873(1) Å³, Z = 4, D_{calc} = 1.376 g/cm³, μ(Mo Kα) = 4.85 cm⁻¹, T = 299 K, crystal size 0.4 × 0.4 × 0.1 mm (purple plates recrystallized from CH₂Cl₂-Et₂O). A total of 11988 reflections were collected (4° < 2θ < 55°) and 11598 were unique. The 4853 reflections with I > 3σ(I) were used for structure solution and refinement. No decay was observed over the course of data collection. The data were corrected for Lorentz and polarization effects, and the absorption was based on azimuthal scans. The structure was solved by the direct method and refined by the full-matrix least-squares method. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at standard positions (C-H = 0.95 Å) but not refined. The refinement converged at R = 0.059, R_w = 0.041, and GOF = 1.52.

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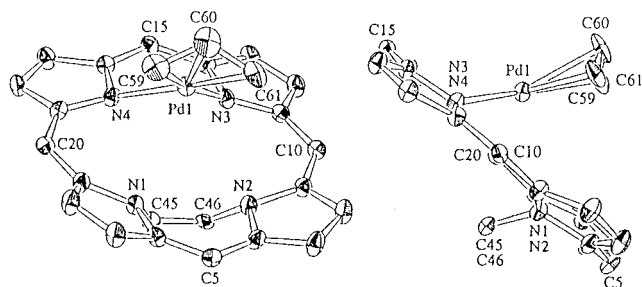


Figure 2. ORTEP drawings of *cis-4'* showing 30% probability thermal ellipsoids and atom-numbering scheme. Six phenyl groups (at C5, C10, C15, C20, C45, and C46), disordered chloride counteranions, and water solvates were omitted for clarity. Side-on view is shown on the right. Selected distances (Å) and angles (deg): Pd–N3, 2.118(5); Pd–N4, 2.106(5); Pd–C59, 2.125(7); Pd–C60, 2.085(7); Pd–C61, 2.147(7); C59–C60, 1.37(1); C60–C61, 1.40(1); N3–Pd–N4, 83.4(2); N3–Pd–C61, 104.8(3); N4–Pd–C59, 103.2(3); C59–Pd–C61, 68.7(3); C59–C60–C61, 121.2(9).

greatly when **3a** was allowed to react with the tin reagent (1.8 equiv) for 3 h in CH_2Cl_2 and then chromatographed to afford **5** in a 90% yield.

Recrystallization of a *trans/cis* (3:7) mixture of [(1,2-diphenylethene- N^{21},N^{22})-*meso*-tetraphenylporphyrinato- N^{23},N^{24}](η^3 -allyl)palladium(II) chloride (**4**) from CH_2Cl_2 – Et_2O gave crystals of *cis-4'* only. This is probably due to the effect of crystal packing. X-ray molecular structure of *cis-4'* is shown in Figure 2.⁹ The Pd–N (2.106–2.118 Å) and Pd–C (2.085–2.147 Å) bond lengths as well as the N3–Pd–N4 (83.4°) and C59–Pd–C61 (68.7°) bite angles are similar to those of the π -(allyl)-palladium complex of bipyridine.¹⁰ The N3–Pd–N4 plane is canted by 53.4° from the porphyrin plane defined by four meso-carbons, C5, C10, C15, and C20. The dihedral angle (106.8°) between the π -(allyl) plane and the N3–Pd–N4 plane is in the range frequently

observed for π -(allyl)palladium complexes. If this angle is retained in the *trans* isomer, the π -(allyl) plane is presumed to tilt by 19.8° with respect to the porphyrin plane in the *trans* isomer, while the corresponding tilt angle in the *cis* isomer is 53.5°. This relatively parallel orientation of the π -(allyl) plane with respect to the porphyrin plane in the *trans* isomer is consistent with the small difference in the ^1H NMR chemical shifts between the π -(allyl) protons.

It was pointed out that either the (chelating ligand)–Pd or the (π -allyl)–Pd part has to be nonsymmetric with respect to a mirror plane perpendicular to the palladium coordination plane, to detect the π -allyl ligand rotation.^{7b} The present study shows for the first time that two rotational isomers can be differentiated despite the presence of such a mirror plane (C_s -symmetry). Moreover, the porphyrin ring current effect helps identify the conformation of the π -allyl ligand in solution. The unique structure of the present π -(allyl)palladium porphyrins in which an organopalladium moiety is sitting closely over a large porphyrin plane illustrates the potential of N^{21},N^{22} -bridged porphyrin as a ligand for controlling the reactivity of an organo ligand and also characterizing its dynamic behavior by ^1H NMR.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture, Japan. We are grateful to Dr. H. Miyake (Kobe University) for the gift of allyltins, Ms. S. Nomura (Institute for Molecular Science, Okazaki, Japan) for FAB MS analysis, and Ms. M. Nishinaka (Kobe University) for microanalysis.

Supporting Information Available: Preparation procedures and spectroscopic and analytical data for compounds **2a**, **3a**, **4**, and **5** and listings of the details in the structure determination for *cis-4'*, including crystallographic data, atomic coordinates, thermal parameters, bond lengths, bond angles, torsion angles, least-squares planes, and an ORTEP drawing. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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