

Coordination of Amines to Palladium(II) Complexes of N^{21},N^{22}-Bridged Porphyrins

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Pyridine and ethylenediamine reacted with Pd(II) complexes of N^{21},N^{22}-bridged porphyrins to give mixed-ligand Pd(II) complexes. The UV-vis and ^{1}H NMR spectral features of the porphyrin ligand provide information regarding the nature of the coexisting ligands and Pd(II) coordination geometry in the products. That is, the splitting pattern in the Soret region of the UV-vis spectra was dependent on whether porphyrinatopalladium(II) was coordinated by neutral ligands or anionic ligands. In the ^{1}H NMR spectra of ethylenediamine complexes of porphyrinatopalladium(II), signal broadening of porphyrin β-pyrrole protons and a chemical shift change of ethylenediamine protons were seen in the dichloride in comparison with the bis(perchlorate). These phenomena indicate the equilibrium of the coordination and dissociation of chloride and amine at the apical and basal sites in the square pyramid. The H–D exchange in the ethylenediamine ligand was promoted by the presence of chloride.

We have recently shown that N^{21},N^{22}-etheno bridged porphyrin serves as a bidentate nitrogen base ligand for stable coordination to palladium.[1] We have also reported the preparation of (η^3-allyl)(porphyrinato)palladium(II) as examples of organopalladium porphyrins.[2] This bidentate porphyrin ligand is not only interesting in view of its stereochemical, electrochemical, and photochemical properties, but also valuable as an NMR shift reagent. The X-ray crystal structures of these porphyrinatopalladium(II) complexes indicate that two Pd–N bonds are tilted by 21.8 and 23.7 degree from the corresponding pyrrole planes.[1,2] In spite of their bent Pd–N bondings, these porphyrinatopalladium(II) complexes seem to be quite stable. There are many reports on Pd complexes of bidentate nitrogen base ligands, such as 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen), where an inter-ligand steric hindrance causes distortion on the coordination geometry and the ligand structure.[3–6] In the case of [Pd^{II}(bpy)$_2$] complexes, two bidentate ligands can not assume a coplanar arrangement due to a steric repulsion between the hydrogen atoms. Thus, the coordination geometry of Pd is tetrahedrally distorted from square planarity with two bpy ligands in a twisted orientation. A different way to alleviate the steric hindrance between two bpy ligands is to put them in a step-like conformation with some dihedral angle between the Pd square plane and the mean bpy plane. This step-like conformation is accompanied by a bowing of two pyridine rings within one chelating bpy ligand.[7,8] A similar bowing of two pyrrole rings within a chelating dipyrrylmethene unit is observed in the structure of Pd complexes of N^{21},N^{22}-etheno bridged porphyrin.[1,2] It is known that heteroaromatic bidentate ligands, such as bpy and phen, are readily replaced by ethylenediamine in mixed-ligand Pd complexes with ethylenediamine and heteroaromatic bidentate ligand.[9–11] This paper describes the ligand substitution reaction of porphyrinatopalladium(II) complexes with amines in order to see how strong their bent Pd–N bondings are. Furthermore, the dynamic behaviors of the porphyrinatopalladium(II) complexes ligated by ethylenediamine are discussed based on their spectroscopic properties.

Results and Discussion

Dichloropalladium(II) complex (**1a**), (μ-dichloro)dipalladium(II) complexes (**2a**, **2b**), and bis(aqua)palladium(II) complexes (**3a**, **3c**) of N^{21},N^{22}-etheno-bridged porphyrin were used as starting materials. The μ-dichloro complexes and bis(aqua) complexes have perchlorate ions as counter anions. Amine adducts (**4a**–**10a**, **5b**, **6c**) of these starting complexes were prepared in good yields (70–100%) as shown in Scheme 1. The reaction of **1a** with excess pyridine (4 equiv) in CH_2Cl_2 at room temperature caused the replacement of only one chloride to give **4a**. Similar mono(pyridine) adducts (**5a**, **5b**) were obtained from **2a** and **2b**, and bis(pyridine) adducts (**6a**, **6c**) were readily obtained from **3a** and **3c**. It took 11.2 h for half amounts of **1a** to be converted to **4a** by the addition of pyridine (0.040 mol dm^{-3}) to **1a** (0.010 mol dm^{-3}) in $CDCl_3$ at room temperature, while the formation of **5a** and **6a** occurred almost instantly. The addition of excess ethylenediamine (1.2–2.5 equiv) to **1a**, **2a**, and **3a** resulted in the formation of ethylenediamine chelate complexes, (**7a**–**9a**), respectively, without any dissociation of the porphyrin ligand. The time required for the conversion of half amounts of **1a** by ethylenediamine (0.040 mol dm^{-3}) to **1a** (0.010 mol dm^{-3}) was much shorter (23 min) than that by pyridine under the same conditions as indicated above.

UV-vis spectra of Pd complexes of N^{21},N^{22}-bridged porphyrin show split Soret bands of the porphyrin chromophore at around 410 nm and 440 nm. The intensity ratio of the latter band relative to the former band is much greater for the bis(pyridine) adduct (**6a**) than for the mono(pyridine) adducts

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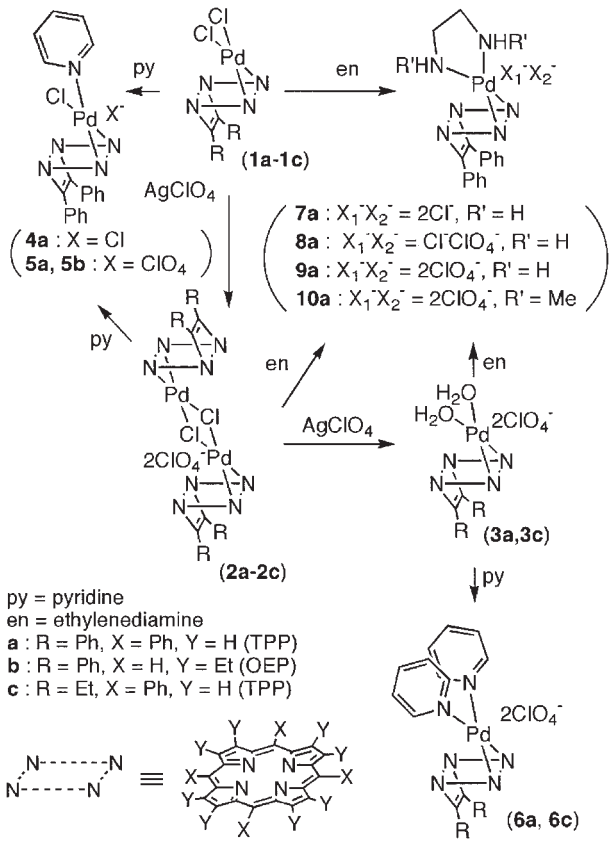


Scheme 1.

(**4a**, **5a**) (see Fig. 1; middle). This Soret band splitting may be diagnostic of whether porphyrinatopalladium(II) is ligated by at least one anionic ligand. In fact, the shape of the Soret band of **6a** is very similar to that of bis(perchlorate) (**3a**), while the Soret bands of **4a** and **5a** look like that of dichloride (**1a**) (see Fig. 1; top). The C_s symmetric chelating molecular structure is indicated for all of the ethylenediamine complexes, (**7a**–**9a**), by their ^{1}H NMR spectra. However, their UV-vis spectra indicate that the structure of bis(perchlorate) (**9a**) is very similar to that of **6a**, but different from those of **7a** and **8a**. (See Fig. 1; bottom). The splitting pattern of the Soret bands of **7a** and **8a** is similar to that of mono(pyridine) adducts (**4a**, **5a**). This observation suggests that the coordination of the chloride anion occurs in the complexes of **7a** and **8a**.

The ^{1}H NMR spectra of **7a**, **8a**, and **9a** show four broad 2H-signals due to the chelated ethylenediamine protons in the chemical shift range between 0.4 and −2.6 ppm, as shown in Fig. 2. One of the amino proton signals (−1.50, −2.48, and −2.53 ppm for **7a**, **8a**, and **9a**, respectively) is greatly shifted to a lower frequency region than TMS due to the porphyrin ring current effect, and is thus associated with the proton very close (syn) to the porphyrin plane, as depicted in Scheme 2. The chemical shift of H_{syn} moves toward the higher frequency region upon going from **9a** to **8a** and **7a** and also upon going from −15 °C to 5 °C and then 25 °C, as summarized in Table 1. Since the amino protons at the apical site would experience a smaller ring-current effect of the porphyrin than at the basal site, these chemical shift changes of H_{syn} may be induced through the ligation of chloride to Pd followed by

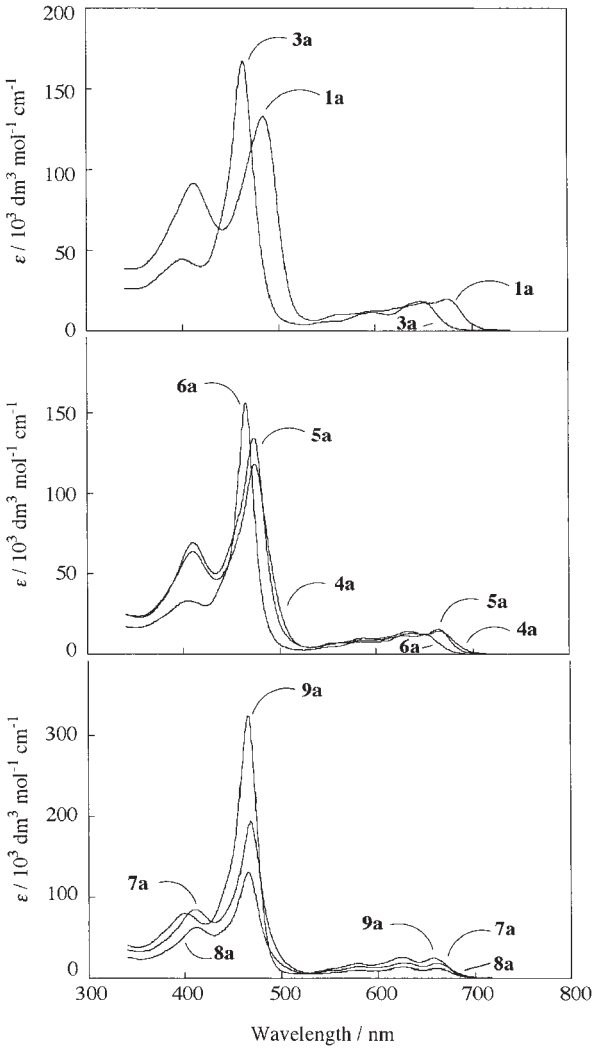


Fig. 1. UV-vis spectra of porphyrinatopalladium(II) complexes (top: **1a** and **3a**), pyridine complexes (middle: **4a**–**6a**), and ethylenediamine complexes (bottom: **7a**–**9a**) in CH_2Cl_2.

transposition of the amino ligand from the basal site (structure **A**) to the apical site (structure **B**). It is reasonable to assume that such a change in the coordination geometry is promoted by the presence of a greater amount of chloride anion and at a higher temperature. As a matter of fact, the addition of $Me_4N^+Cl^-$ (3 molar eq.) to a $CDCl_3$ solution of **9a** caused a change in the ^{1}H NMR chemical shift of H_{syn} from −2.53 to −1.50 ppm. Signals due to ethylenediamine protons of **7a**, **8a**, and **9a** are broad with half-height linewidths in the range of 22.15–24.80 Hz. The flipping motion of the five-membered metallacycle may be responsible for this line broadening. However, the linewidths of signals due to β-pyrrole protons are more sensitive to the counter anion and the temperature. The half-height linewidths of the β-pyrrole protons at around 9.4 ppm of **7a**, **8a**, and **9a** are 12.83, 8.60, and 2.45 Hz, respectively, in $CDCl_3$, as can be seen in Fig. 2 and that of **7a** at 9.37 ppm becomes smaller from 12.83 to 9.69, and then to 3.44 Hz with decreasing temperature from 25 °C to 5 °C and then to −15 °C. These phenomena may also be explained in terms

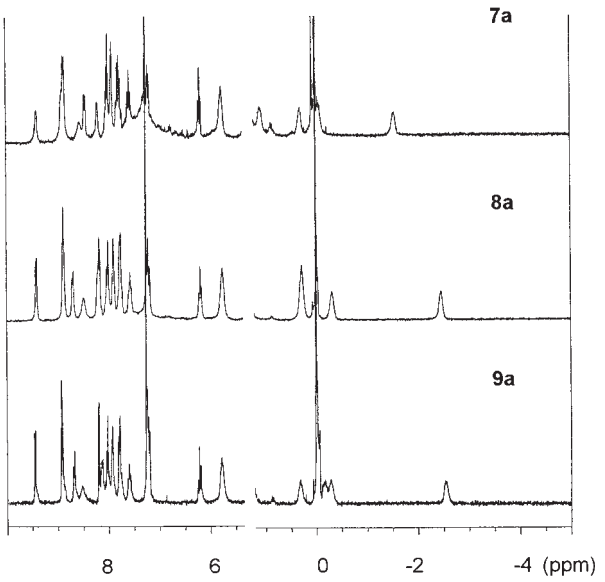


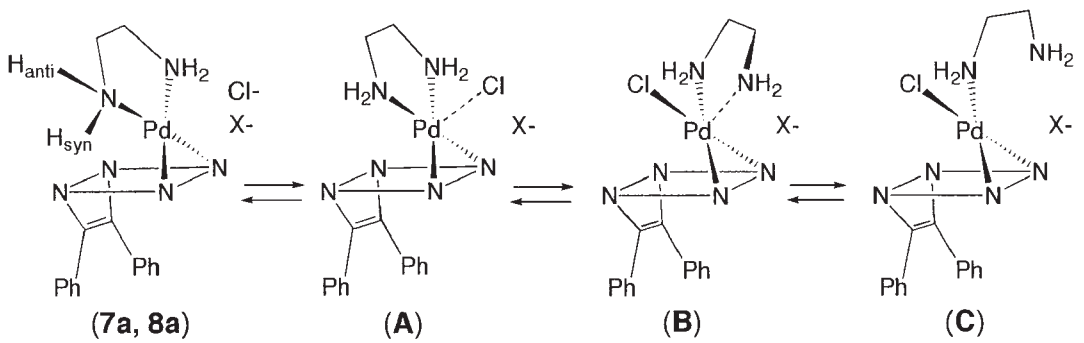
Fig. 2. ^{1}H NMR spectra of ethylenediamine complexes (**7a**–**9a**) in $CDCl_3$ at 25 °C (270 MHz).

Table 1. ^{1}H NMR[a)] Data of Porphyrinatopalladium(II) Complexes

Comp.	Temp.	Chemical shift/ppm		
	°C	pyridine-α	pyridine-β	pyridine-γ
4a	25	3.62	6.23	7.09
5a	25	3.63	5.80	7.01
5b	25	—[b)]	6.03	7.25
6a	25	—[c)]	6.34	6.88
6c	25	—[c)]	6.32	6.85

Comp.	Temp.	Chemical shift/ppm		Line width/Hz
	°C	en-CH_2	en-NH_2	pyrrole-β[d)]
7a	25	0.32, −0.05	1.09, −1.50	12.83
7a	5	0.28, −0.05	1.06, −1.61	9.69
7a	−15	0.26, −0.14	1.06, −1.74	3.44
8a	25	0.33, −0.22	0.00, −2.48	8.60
9a	25	0.32, −0.27	−0.13, −2.53	2.45
9a[e)]	25	−0.13, −0.89	1.35, −2.09	12.94

a) 270 MHz. b) Overlapped. c) Not detected. d) Half height width. e) In DMSO-d_6.



Scheme 2.

of the coordination–dissociation equilibrium of chloride and transposition of the coordinated chloride between the apical site and the basal site as shown in Scheme 2. Although the bis(perchlorate) (**9a**) shows sharp NMR signals in $CDCl_3$, as noted above, the β-pyrrole proton signal of **9a** become much broader in DMSO, where the half-height linewidth is 12.94 Hz. This is well explained in terms of the coordinating ability of DMSO.

The NH_2 signals of ethylenediamine were assigned based on the H–D exchange. Both signals assigned to the amine H_{syn} (−1.50 ppm) and the amine H_{anti} (1.09 ppm) of **7a** disappeared rapidly in $CDCl_3$ upon the addition of D_2O, while the amine H_{syn} (−2.53 ppm) of **9a** exchanged with D_2O much more slowly than the amine H_{anti} (−0.13 ppm), as shown in Fig. 3. Since the Pd-ligand bonding is weaker in five-coordinated complexes than in four-coordinated complexes, rapid H–D exchange in the complex (**7a**) would take place after the dissociation of an amino group from Pd (structure **C**). The difference in the H–D exchange kinetics between H_{syn} and H_{anti} in the case of **9a** is remarkable, which suggests that the H–D exchange of the amino protons occurs without dissociation of the amino group. The D_2O molecule is not easily accessible to the amino H_{syn} proton of **9a** due to the steric hindrance of the porphyrin ligand, if the amino groups do not dissociate.

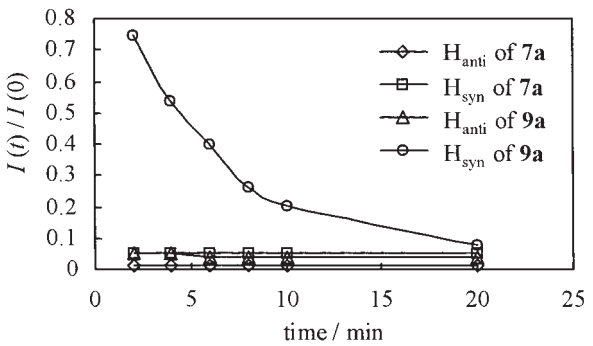
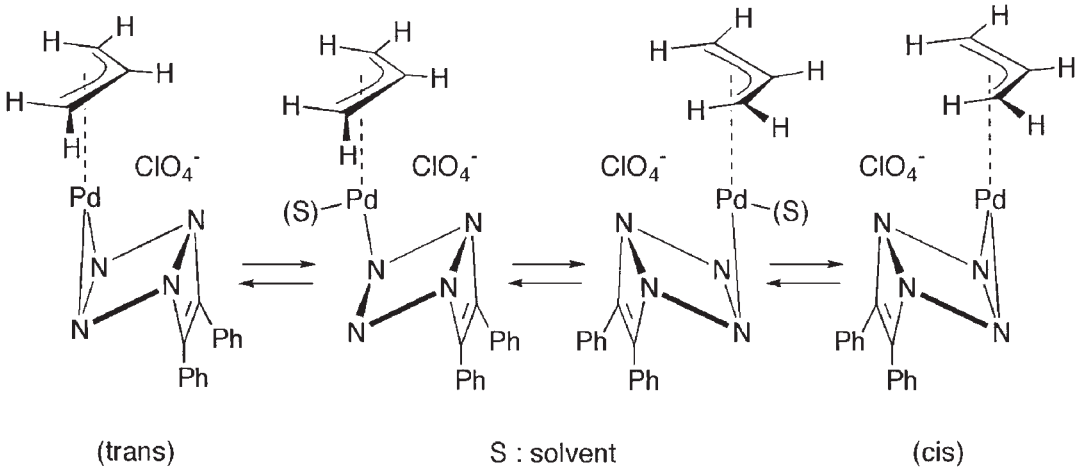


Fig. 3. Decay of ^{1}H NMR signals due to amino protons (H_{syn} and H_{anti}) of **7a** and **9a** with time by exchange to D_2O in $CDCl_3$ at 25 °C. $I(t)$: Signal intensity at the time t.

We have already reported that (η^3-allyl)Pd complexes of N^{21},N^{22}-bridged porphyrin undergo isomerization through bond dissociation between Pd and a porphyrin nitrogen, followed by the rotation around the remaining Pd–N bonding and then remaking of the Pd–N bonding, as shown in



Scheme 3.

Scheme 3.[2] This type of dynamic behavior should cause an exchange between the amine H_{syn} and the amine H_{anti} of the ethylenediamine ligand. Since the linewidths of the coordinated ethylenediamine protons do not depend on the counter anion and temperature, we think that the bond dissociation between Pd and a porphyrin nitrogen is not occurring in these complexes. This is in agreement with the fact that the half-lives for the substitution of the porphyrin ligand of **7a** and **9a** under pseudo first-order conditions by ethylenediamine (0.5 mol dm^{-3}) in MeOH at 25 °C are 2.90×10^3 s and 2.94×10^3 s, although bpy ligand of [Pd(en)(bpy)]Cl_2 is replaced by ethylenediamine under the same conditions within a few seconds.[10]

We have shown that the N^{21},N^{22}-bridged porphyrin ligand strongly coordinates to Pd and influences the dynamic behavior of the coexisting ligand in the same coordination sphere and that the changes in the metal coordination structure are sensitively detected by the spectroscopic properties of the porphyrin ligand.

Experimental

Preparation Procedures and Spectroscopic and Analytical Data for Compounds (4a, 5a, 5b, 6a, 6c, and 7a–10a). A mixture of **1a–c** (0.05 mmol), $AgClO_4$ (0.05 mmol for **2** and 0.2 mmol for **3**), and CH_2Cl_2 (5 cm^3) was stirred vigorously for 3 h at room temperature. **2a**, **b** and **3a**, **c** were given after filtration to remove AgCl and precipitation from CH_2Cl_2–hexane.

To a CH_2Cl_2 solution containing 0.02 mmol of **1a–3a**, **2b**, and **3c** were added the amines (4 equiv of pyridine for **4a–6a**, **5b**, and **6c**, 1.2 equiv of ethylenediamine for **7a**, 2.5 equiv of ethylenediamine for **8a** and **9a**, and 2.5 equiv of dimethylethylenediamine for **10a**). The mixture was stirred overnight at room temperature, the products were then deposited from CH_2Cl_2–hexane as a green solid and washed with ether. **4a**: Yield 76%. ^{1}H NMR (300 MHz, at 25 °C in $CDCl_3$) δ 3.62 (br, 2H, py-α-H), 6.23 (br, 2H, py-β-H), 7.09 (t, 1H, py-γ-H), 9.34, 9.20, 9.04, 9.01, 8.83, 8.73, 8.66, 8.20 (d × 8, 1H × 8, β-pyrrole-H), 8.57–6.83 (m, 20H, *meso*-Ph-H), 6.17 (m, 2H, bridge-Ph *p*-H), 5.76 (br, 4H, bridge-Ph *m*-H), *o*-H is not detected. Anal. Calcd for $C_{63}H_{43}N_5Cl_2Pd \cdot 3H_2O$: C, 68.70; H, 4.48; N, 6.36%. Found: C, 68.30; H, 4.01; N, 5.85%. UV-vis (CH_2Cl_2): $\lambda_{max}(\log \varepsilon)$ 410 (4.80), 474 (5.07), 591 (3.95), 637 (4.12), 665 (4.16) nm. MS (ESI in MeOH) *m*/*z* 1010.2351 (calcd for $C_{63}H_{43}N_5ClPd$ (M − Cl): 1010.2254). **5a**: Yield 90%. ^{1}H NMR δ 3.63 (br, 2H, py-α-H), 5.80 (br, 2H, py-β-H), 7.01 (t, 1H, py-γ-H), 9.46, 9.18, 9.02, 8.83, 8.72, 8.26, 8.21 8.17 (d × 8, 1H × 8, β-pyrrole-H), 8.58–6.83 (m, 20H, *meso*-Ph-H), 6.18 (m, 2H, bridge-Ph *p*-H), 5.80 (br, 4H, bridge-Ph *m*-H), *o*-H is not detected. Anal. Calcd for $C_{63}H_{43}N_5Cl_2O_4Pd \cdot H_2O$: C, 67.00; H, 4.02; N, 6.20%. Found: C, 67.09; H, 4.13; N, 6.28%. UV-vis (CH_2Cl_2): $\lambda_{max}(\log \varepsilon)$ 410 (4.84), 473 (5.13), 587 (3.99), 634 (4.16), 665 (4.19) nm. MS (ESI in MeOH) *m*/*z* 1010.1200 (calcd for $C_{63}H_{43}N_5ClPd$ (M − ClO_4): 1010.2254). **5b**: Yield 81%. ^{1}H NMR δ 6.01 (br, 2H, py-β-H), 7.25 (t, 1H, py-γ-H), α-H is not detected, 11.09, 10.69, 10.28, 9.59 (s × 4, 1H × 4, *meso*-H), 4.68–3.32 (m, 16H, CH_2), 2.15, 2.03 (t × 2, 3H × 2, CH_3) 1.92, 1.56, 1.22 (t × 3, 6H × 3, CH_3), 6.03 (m, 2H, bridge-Ph *p*-H), 5.57 (br, 4H, bridge-Ph *m*-H), *o*-H is not detected. Anal. Calcd for $C_{55}H_{59}N_5Cl_2O_4Pd$: C, 64.05; H, 5.77; N, 6.79%. Found: C, 63.79; H, 5.57; N, 6.50%. MS (ESI in MeOH) *m*/*z* 930.2750 (calcd for $C_{55}H_{59}N_5ClPd$ (M − ClO_4): 930.3504). **6a**: Yield 94%. ^{1}H NMR δ 6.34 (br, 4H, py-β-H), 6.88 (t, 2H, py-γ-H), α-H is not detected, 9.73, 9.03, 8.44, 8.05, (d × 4, 2H × 4, β-pyrrole-H), 8.99–6.88 (m, 20H, *meso*-Ph-H), 6.20 (t, 2H, bridge-Ph *p*-H), 5.76 (br, 4H, bridge-Ph *m*-H), *o*-H is not detected. Anal. Calcd for $C_{68}H_{48}N_6Cl_2O_8Pd \cdot H_2O$: C, 64.18; H, 3.96; N, 6.60%. Found: C, 64.37; H, 3.55; N, 6.36%. UV-vis (CH_2Cl_2): $\lambda_{max}(\log \varepsilon)$ 406 (4.52), 465 (5.19), 585 (3.90), 629 (4.07), 650 (4.09) nm. MS (ESI in MeOH) *m*/*z* 527.1230 (calcd for $C_{68}H_{48}N_6Pd$ ((M − 2ClO_4)/2): 527.1493). **6c**: Yield 85%. ^{1}H NMR δ 6.32 (br, 4H, py-β-H), 6.85 (t, 2H, py-γ-H), α-H is not detected, 9.52, 8.85, 8.53, 8.39, (d × 4, 2H × 4, β-pyrrole-H), 8.73–7.65 (m, 20H, *meso*-Ph-H), −1.44 (t, 6H, bridge-CH_3), −2.97, −4.46 (dq × 2, 2H × 2, bridge-CH_2, $J_{gem} = 15.0$ Hz). Anal. Calcd for $C_{60}H_{48}N_6Cl_2O_8Pd \cdot 2H_2O$: C, 60.33; H, 4.39; N, 7.04%. Found: C, 60.01; H, 4.50; N, 6.55%. MS (ESI in MeOH) *m*/*z* 479.1073 (calcd for $C_{60}H_{48}N_6Pd$ ((M − 2ClO_4)/2): 479.1492). **7a**: Yield 91%. ^{1}H NMR δ 1.09, −1.50 (br × 2, 2H × 2, en-NH_2), 0.32, −0.05 (br × 2, 2H × 2, en-CH_2), 9.37, 8.87, 8.85, 8.17, (br × 4, 2H × 4, β-pyrr.-H), 8.55–7.19 (m, 20H, *meso*-Ph-H), 6.18 (t, 2H, bridge-Ph *p*-H), 5.75 (br, 4H, bridge-Ph *m*-H), *o*-H is not detected. Anal. Calcd for $C_{60}H_{46}N_6Cl_2Pd \cdot 3H_2O$: C, 66.58; H, 4.84; N, 7.76%. Found: C, 66.18; H, 4.50; N, 8.14%. UV-vis (CH_2Cl_2): $\lambda_{max}(\log \varepsilon)$ 411 (4.93), 468 (5.29), 582 (4.14), 628 (4.27), 661 (4.25) nm. MS

(ESI in MeOH) m/z 478.1552 (calcd for $C_{60}H_{46}N_6Pd$ ((M − 2Cl)/2): 478.1414). **8a**: Yield 85%. ^{1}H NMR δ 0.00, −2.48 (br × 2, 2H × 2, en-NH_2), 0.33, −0.22 (br × 2, 2H × 2, en-CH_2), 9.38, 8.86, 8.18 (br × 3, 2H + 4H + 2H, β-pyrr.-H), 8.72–7.21 (m, 20H, *meso*-Ph-H), 6.20 (t, 2H, bridge-Ph *p*-H), 5.77 (br, 4H, bridge-Ph *m*-H), *o*-H is not detected. Anal. Calcd for $C_{60}H_{46}N_6Cl_2O_4Pd\cdot0.5Pd(C_2H_8N_2)Cl(ClO_4)$: C, 58.94; H, 4.05; N, 7.89%. Found: C, 59.19; H, 3.67; N, 7.85%. UV-vis (CH_2Cl_2): $\lambda_{max}(\log\varepsilon)$ 412 (4.80), 466 (5.12), 581 (4.00), 626 (4.13), 661 (4.08) nm. MS (ESI in MeOH) m/z 478.1044 (calcd for $C_{60}H_{46}N_6Pd$ ((M − Cl-ClO_4)/2): 478.1414). **9a**: Yield 100%. ^{1}H NMR δ −0.13, −2.53 (br × 2, 2H × 2, en-NH_2), 0.32, −0.27 (br × 2, 2H × 2, en-CH_2), 9.44, 8.91, 8.90, 8.18 (d × 4, 2H × 4, β-pyrr.-H), 8.68–7.20 (m, 20H, *meso*-Ph-H), 5.90 (t, 2H, bridge-Ph *p*-H), 5.42 (br, 4H, bridge-Ph *m*-H), *o*-H is not detected. Anal. Calcd for $C_{60}H_{46}N_6Cl_2O_8Pd\cdot H_2O$: C, 60.44; H, 4.23; N, 7.05%. Found: C, 60.82; H, 4.21; N, 7.04%. UV-vis (CH_2Cl_2): $\lambda_{max}(\log\varepsilon)$ 400 (4.90), 466 (5.51), 579 (4.24), 625 (4.41), 658 (4.39) nm. MS (ESI in MeOH) m/z 478.1136 (calcd for $C_{60}H_{46}N_6Pd$ ((M − 2ClO_4)/2): 478.1414). **10a**: Yield 70%. ^{1}H NMR δ 0.06 (d, 6H, NCH_3), −0.65, −2.05 (br × 2, 2H × 2, en-CH_2), 9.38, 9.03, 8.97, 8.24 (d × 4, 2H × 4, β-pyrr.-H), 8.53–6.87 (m, 20H, *meso*-Ph-H), 6.18 (t, 2H, bridge-Ph *p*-H), 5.74 (br, 4H, bridge-Ph *m*-H), *o*-H is not detected. Anal. Calcd for $C_{62}H_{50}N_6Cl_2O_8Pd\cdot H_2O$: C, 61.93; H, 4.36; N, 6.99%. Found: C, 61.66; H, 4.57; N, 7.22%. MS (ESI in CH_3CN) m/z 1085.38 (calcd for $C_{62}H_{50}N_6PdClO_4$ (M − ClO_4): 1085.25), 492.44 (calcd for $C_{62}H_{50}N_6Pd$ ((M − 2ClO_4)/2): 492.15).

H–D exchange. The H-D exchanges of the amino protons of ethylenediamine complexes (**7a** and **9a**) were monitored by ^{1}H NMR. After adding 3.5 mm^3 of D_2O to a 0.5 cm^3 $CDCl_3$ solution of **7a** or **9a** (3 μmol) in a NMR tube and shaking the sample tube for 20 s, the tube was transferred to a NMR spectrometer at 25 °C. The progress of the H–D exchange of each amino proton was measured by ^{1}H NMR integrations with time.

Kinetics. The substitution of porphyrin ligand of **7a** and **9a** by ethylenediamine was studied under pseudo first-order conditions with respect to the Pd complex. To a 3 cm^3 MeOH solution of **7a** or **9a** (2.0×10^{-5} and 8.4×10^{-6} mol dm^{-3}) in a photometric cell was added 100 mm^3 (1.5×10^{-3} mol) of ethylenediamine, just after which the cell was transferred to a UV-vis spectrophotometer at 25 °C. The absorbance of the Soret band at 463 nm of N^{21},N^{22}-bridged porphyrin ligand of the palladium(II) complex decreased with time. The half life period of this pseudo first-order reaction was estimated based on the decay curve.

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