# Unprecedented Pendant Group Exchange of a Porphyrinato Platinum(II) in Benzonitrile

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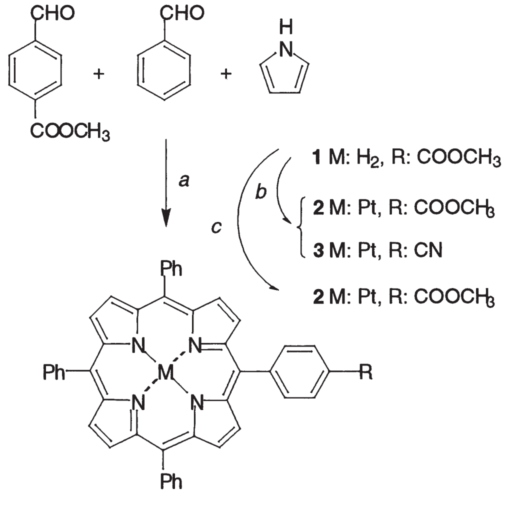
5-(4-cyanophenyl)-10,15,20-triphenylporphyrinato platinum(II) (**3**) and 5-(4-methoxycarbonylphenyl)-10,15,20-triphenylporphyrinato platinum(II) (**2**) were isolated from a reaction of 5-(4-methoxycarbonylphenyl)-10,15,20-triphenyl porphyrin (**1**) with $K_2[PtCl_4]$ in benzonitrile. Seemingly, **3** was generated through the functional group substitution reaction of the phenyl group of tetraphenylporphyrin during platinum ion insertion into **1** and was characterized by $^1H$ NMR, mass spectroscopy, elemental analysis, and X-ray crystallography.

Porphyrin compounds are of great interest in the fields of bioorganic chemistry and material science.[1] The electronic and optical properties of porphyrins can be tuned by metal ion insertion.[2] Recently, platinum porphyrin derivatives have been used for oxygen sensing.[3] In order to improve oxygen sensitivity, considerable effort has been devoted to the synthesis of porphyrinato platinum(II) analogs. In our research on porphyrinato platinum(II) derivatives, we discovered that a unique reaction occurred during the insertion of platinum into a 5,10,15,20-tetraphenylporphyrin derivative in benzonitrile.[4]

Condensation of pyrrole with aldehydes by Lindsey's method afforded 5-(4-methoxycarbonylphenyl)-10,15,20-triphenyl porphyrin (**1**) in 17.7% yield (Scheme 1a).[5] **1** and $K_2[PtCl_4]$ dissolved in anhydrous benzonitrile was heated to 170 °C for 72 h under $N_2$, and the crude product was purified by silica gel column chromatography to afford the 5-(4-methoxycarbonylphenyl)-10,15,20-triphenylporphyrinato platinum(II) (**2**) in 29.8% yield and 5-(4-cyano phenyl)-10,15,20-triphenylporphyrinato platinum(II) (**3**) in 52.7% yield, respectively (Scheme 1b).[6] On the other hand, **2** was obtained as main product from the Scheme 1c in yield 95.4%.[7] When a mixture of **2** and $K_2[PtCl_4]$ dissolved in anhydrous benzonitrile was heated to 170 °C, no **3** was detectable in the $^1H$ NMR spectrum. Thus, **3** was not supposedly generated from **2**. The structure of **3** was established by $^1H$ and $^{13}C$ NMR, mass spectroscopy, elemental analysis, and X-ray crystallography.



**1**

**Scheme 1.** Conditions: *a* (i) $BF_3{\cdot}OEt_2$, $CHCl_3$ (ii) *p*-chloranil; *b* $K_2[PtCl_4]$, Ph-CN; *c* $CH_3COONa$, $K_2[PtCl_4]$, $CH_3COOH$/Ph–Cl.

In the $^1H$ NMR spectrum of **3**, the methyl ester peak at 4.09 ppm (for **2**) was no longer present. However, the peaks in the aromatic region clearly show that **3** is a tetraphenylporphyrin derivative in which one of the four phenyl groups has been replaced by a *p*-substituted phenyl group. In the UV–vis spectrum of **3** (Soret-band at ca. 402.0 nm and two Q-bands at ca. 509.5 and 535.5 nm), the Soret-band is shifted towards shorter wavelength compared with the starting material **1** (ca. 420.0 nm and four Q-bands at ca. 518.5, 550.0, 590.5, and 645.0 nm), and is quite similar to that of **2** (ca. 402.0 nm and two Q-bands at ca. 509.5 and 535.5 nm). This observation suggests that platinum ion was inserted into the porphyrin ring. The shapes of the Soret-band and Q-bands were comparable with those of known normal metalloporphyrins, so it was suggested that the electronic structure of **3** belongs to a normal porphyrin type such as Pt(II)TPP. FAB mass spectroscopy and elemental analysis of **3** supported the formula of 5-(4-cyanophenyl)-10,15,20-triphenylporphinato platinum(II) ($Pt_1C_{45}H_{27}N_5$). Unfortunately, the cyano carbon peak could not be distinguished in the $^{13}C$ NMR spectrum, because it is in the same position as the pyrrole carbon. Recrystallization of **3** from $CH_2Cl_2$–MeOH afforded X-ray quality crystals (Figure 1).[8] The diffraction data revealed a tetragonal crystal system, *I*-42d space group, and $Z = 4$. This indicates that the orientation of the cyano group is statistically disordered to give pseudo four-fold symmetry. The cyano group was found on a differential electron density map, and refined with an isotropic displacement parameter with an occupancy of 1/4. The N(2)–C(12) bond distance was 1.15(3) Å and the N(2)–C(12)–C(9) bond angle was 177(2)°, which resembles that of *meso*-tetrakis(4-cyanophenyl)porphyrinato zinc(II) (C-N triple bond distance, 1.13 Å, and C–C–N bond angle, 176.7°).[9] The crystal of tetraphenylporphirinato platinum(II) (PtTPP) is also tetragonal, *I*-42d space group, and $Z = 4$. The lattice volume of **3** is bigger than that of PtTPP, which reflects the additional volume of the cyano group.[4c] These findings indicate that a novel substitution reaction occurs when the porphyrin ring is heated with $K_2[PtCl_4]$ in benzonitrile.

Recently, many reactions about porphyrins are reported and

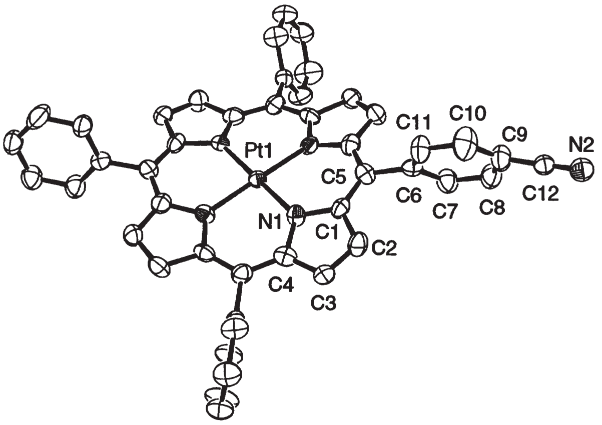


**Figure 1.** ORTEP drawings of **3** showing 50% probability. All hydrogen atoms and other three cyano groups disordered statistically were omitted for clarity.

it is well known that the *meso* position of a porphyrin ring has high reactivity. For example, addition reaction of functional groups to the *meso* position of porphyrins were reported, and the porphyrin which the additional functional group was attached to a *meso* position is called an isoporphyrin.[10] However, to our knowledge, no exchange reaction via an isoporphyrins intermediate was reported, although synthesises of isoporphyrins are realized by means of chemical and electrochemical approaches.[11] Thus, the functional group substitution reaction of the phenyl group of tetraphenylporphyrin is not reported. Therefore, it is suggested that the functional group substitution reaction of porphyrin, which we discovered, should be a new reaction in the field of porphyrin chemistry. This is expected to be a significant result for the synthesis of metal-containing porphyrins. We are now studying the scope of this reaction and are also examining the substitution mechanism.

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5 Pyrrole (4.5 mL, 44.5 mmol) and methyl 4-formylbenzoate (2.01 g, 12.3 mmol) were dissolved in $CHCl_3$ (800 mL). $BF_3{\cdot}OEt_2$ (0.2 mL, 1.60 mmol) was added and the mixture was stirred at room temperature for 19 h under Ar, after which *p*-chloranil (9.65 g, 39.3 mmol) was added. The mixture was maintained at room temperature for 1 day, then the solvent was evaporated. The crude product was purified by silica gel column chromatography eluted with a mixture of $CH_2Cl_2$/acetone (12/1, v/v). Precipitation from $CH_2Cl_2$/methanol afforded a purple powder (1.46 g, 2.18 mmol, 17.7%, $R_f = 0.79$ ($CH_2Cl_2$/acetone 12/1, v/v)) of **1**. $^1H$ NMR ($CDCl_3$): $\delta$ 8.87–8.85 (m, 6H, pyrrole-$\beta$H), 8.78 (d, $^3J = 4.58$ Hz, 2H, pyrrole-$\beta$H), 8.42 (d, $^3J = 8.24$ Hz, 2H, ArH), 8.29 (d, $^3J = 8.55$ Hz, 2H, ArH), 8.23–8.19 (m, 6H, *o*-PhH), 7.77–7.74 (m, 9H, m, *p*-PhH), 4.10 (s, 3H, –$COOCH_3$), −2.78 (s, 2H,–2NH).

6 **1** (0.53 g, 0.80 mmol) and $K_2[PtCl_4]$ (0.78 g, 1.89 mmol) were dissolved in anhydrous benzonitrile (50 mL). The mixture was stirred at 170 °C for 72 h under $N_2$ until no free base was apparent in the UV–vis spectrum. The solvent was removed by vacuum distillation and the crude product was purified by silica gel column chromatography eluted with $CH_2Cl_2$/hexane (15/8, v/v). Two orange bands were separated and precipitated from $CH_2Cl_2$/methanol to afford **2** as a reddish orange solid (0.20 g, 0.24 mmol, 29.8%, $R_f = 0.67$ ($CH_2Cl_2$/hexane 15/8, v/v)) and **3** also as a reddish orange solid (0.35 g, 0.42 mmol, 52.7%, $R_f = 0.69$ ($CH_2Cl_2$/hexane 15/8, v/v)). $^1H$ NMR($CDCl_3$) of **2**: $\delta$ 8.79–8.73 (m, 6H, pyrrole-$\beta$H), 8.67 (d, $^3J = 5.19$ Hz, 2H, pyrrole-$\beta$H), 8.39 (d, $^3J = 8.24$ Hz, 2H, ArH), 8.22 (d, $^3J = 8.54$ Hz, 2H, ArH), 8.16–8.12 (m, 6H, *o*-PhH), 7.78–7.68 (m, 9H, m, *p*-PhH), 4.09 (s, 3H, –$COOCH_3$). Anal. Calcd. for $C_{46}H_{30}O_2N_4Pt$: C, 63.81; H, 3.49; N, 6.47. Found: C, 62.38; H, 3.31; N, 6.54%. FAB–MS of **2**: *m/z* 866.3 ($[M + H]^+$). $^1H$ NMR ($CDCl_3$) of **3**: $\delta$ (ppm) = 8.82–8.74 (m, 6H, pyrrole-$\beta$H), 8.62 (d, $^3J = 5.19$ Hz, 2H, pyrrole-$\beta$H), 8.27 (d, $^3J = 8.24$ Hz, 2H, ArH), 8.16–8.12 (m, 6H, *o*-PhH), 8.03 (d, $^3J = 8.54$ Hz, 2H, ArH), 7.80–7.71 (m, 9H, m, *p*-PhH). Anal. Calcd. for $C_{45}H_{27}N_5Pt$: C, 64.90; H, 3.27; N, 8.41. Found: C, 64.86; H, 3.20; N, 8.51%. FAB–MS of **3**: *m/z* 833.3 ($[M + H]^+$).

7 **1** (1.43 g, 2.13 mmol), sodium acetate (3.76 g, 45.9 mmol), and $K_2[PtCl_4]$ (2.34 g, 5.64 mmol) were dissolved in $CH_3COOH$ (80 mL) and chlorobenzene (100 mL). The mixture was stirred at 150–160 °C for 96 h under $N_2$. The solvent was removed by vacuum distillation and the crude product was purified by silica gel column chromatography eluted with $CH_2Cl_2$/hexane (15/8, v/v). An orange band was separated and precipitated from $CH_2Cl_2$/methanol to afford **2** as a reddish orange solid (1.76 g, 2.03 mmol, 95.4%, $R_f = 0.67$ ($CH_2Cl_2$/hexane 15/8, v/v)).

8 A violet crystal of **3** was mounted on a glass fiber and cooled in a stream of cold $N_2$ gas. The reflections were collected on Rigaku/MSC Mercury CCD X-ray diffractometer, with graphite-monochromated Mo K$\alpha$ radiation, controlled by the Crystal Clear program (Rigaku). The structure was solved by direct methods (SIR92). Crystal data for **3**: $C_{45}H_{27}N_5Pt$, $M_r = 832.83$, tetragonal, $a = 15.4029(10)$ Å, $c = 13.8930(11)$ Å, $V = 3296.1(4)$ Å$^3$, $T = 173$ K, space group *I*-42d(#122), $Z = 4$, $\mu$(Mo K$\alpha$) = 42.83 cm$^{-1}$, 12773 reflections measured, 1047 unique ($R_{int} = 0.050$) which were used in all calculations. Final $R_1 = 0.025$ with $I > 2.00\,\sigma(I)$, $R = 0.034$, $wR(F^2) = 0.062$ for all 1047 data, and GOF = 0.93. Details of the crystallographic data (excluding structure factor) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-215090. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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