

## Platinum(II) and Platinum(IV) Porphyrin Pincer Complexes: Synthesis, Structures, and Reactivity

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Summary: Pt(II) and Pt(IV) porphyrin pincer complexes were synthesized and characterized. Their structures and electronic properties were influenced by the valence state of platinum at the outer coordination site. The considerable distortion in the porphyrin core of the Pt(II) complex was relieved in the Pt(IV)complex, due to the change of the coordination geometry of platinum. Oxidation of the phenylplatinum(II) pincer complex with iodine induced a facile carbon–carbon bond formation reaction at the meso position via reductive elimination.

Since the first report of pincer type complexes in the late 1970s, these complexes have attracted considerable attention, owing to the intriguing properties imparted by the pincer ligands.<sup>1</sup> Usually such ligands comprise a central anionic aryl ring bearing two supporting coordinating groups at the ortho positions. Various arenes have been employed for the anionic ring in pincer type complexes. Although porphyrins have been extensively investigated aromatic macrocycles, due to their promising properties as functional materials, there had been no example of pincer complexes bearing porphyrins as anionic aromatic backbones until our recent reports.<sup>2-4</sup> We have reported the synthesis and structural elucidation of these types of pincer complexes with a square-planar Pd(II) as an outer metal.<sup>2,3</sup> Porphyrins are certainly known to be conformationally flexible and quite susceptible to peripheral conjugation. Hence, it is intriguing how the structure and properties of porphyrin pincer complexes are altered by the coordination geometry and the valence state of the metal at the outer coordination site. In this context, we have explored the synthesis and reactivity of porphyrin

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pincer complexes bearing a Pt center, which takes a stable octahedral tetravalent state in contrast to a Pd center. Here we disclose the synthesis, structure, and reactivity of Pt(II) and Pt(IV) porphyrin pincer complexes.

## **Results and Discussion**

Scheme 1 depicts the synthesis of Pt(II) and Pt(IV) porphyrin pincer complexes. The pincer ligand 1 was prepared according to our reported procedure.<sup>2</sup> The reaction of **1** with K<sub>2</sub>PtCl<sub>4</sub> in a toluene/DMF solution proceeded smoothly to provide the Pt(II) porphyrin pincer complex 2 in 96% yield as a green solid. Upon treatment of 2 with CuCl<sub>2</sub> in a CH<sub>2</sub>Cl<sub>2</sub>/MeOH solution, 2 was readily oxidized to afford Pt(IV) porphyrin pincer complex 3 in 48% yield. None of the proton signals assignable to the meso protons of 2 and 3 were observed in the <sup>1</sup>H NMR spectra, clearly indicating metalation at the meso positions. X-ray diffraction analyses unambiguously elucidated the structures of 2 (Figure 1a,b) and 3 (Figure 1c,d). The macrocycles of 2 and 3 assume distorted structures (the saddle-type conformation) induced by the outer metalation, similarly to Pd porphyrin pincer complexes. However, the degree of distortion is substantially larger in 2 than in 3. The mean plane deviations of 2 and 3 from the 4N plane are 0.41 and 0.25 Å, respectively. This change is a result of the different coordination geometries of the outer metal, which are square planar for 2 and octahedral for 3, respectively. The notable difference in the coordination geometries is bond lengths of the Cmeso-Pt bonds, 1.957 Å for 2 and 2.206 Å for 3, presumably due to the absence of  $\pi$ back-donation of the d orbital of platinum to the macrocycle in 3 (Table S1, Supporting Information).

Then, replacement of the chlorine atom in 2 with another ligand was examined to reveal the influence of an ancillary ligand on the property of the complex. The exchange of the chloride ligand of 2 with 10 equiv of phenylmagnesium bromide provided the novel porphyrin pincer complex 4 in 76% yield (Scheme 2). The X-ray crystal structure is shown in Figure 1e,f. The macrocycle takes a saddle conformation, and the mean plane deviation of 4 from the 4N plane is 0.39 A. In general, the trans influence of a phenyl group is stronger than that of chloride. Thus, the Cmeso-Pt bond in 4 is elongated (2.028 Å) in comparison to that of 2. With 4 in hand, we then attempted to synthesize Pt(IV) porphyrin pincer complexes via oxidation of 4. Upon treatment of 4 with iodine, the vivid color change of green for 4 to red was observed on the TLC analysis (Scheme 2). On the basis of ESI-TOF mass and <sup>1</sup>H NMR analyses, the product was

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Scheme 1. Synthesis of Pt(II) and Pt(IV) Porphyrin Pincer Complexes<sup>*a*</sup>



<sup>*a*</sup>Reagents and conditions: (a)  $K_2PtCl_4$ , toluene/DMF, 100 °C; (b) CuCl<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH, room temperature.



**Figure 1.** X-ray crystal structures of Pt porphyrin pincer complexes and *meso*-phenyl  $\beta$ -dipyridyl porphyrin: (a) top view of **2**; (b) side view of **2**; (c) top view of **3**; (d) side view of **3**; (e) top view of **4**; (f) side view of **4**; (g) top view of **5**; (h) side view of **5**. The thermal ellipsoids are scaled to the 50% probability level. *meso*-Aryl substituents and hydrogen atoms are omitted for clarity.

assigned to be the *meso*-phenyl-substituted porphyrin **5**, the structure of which was confirmed by X-ray diffraction analysis (Figure 1g,h). At this stage, we propose that reductive elimination from the possible diiodophenylplatinum(IV) intermediate **A** would afford the coupling product **5** and PtI<sub>2</sub>.

Scheme 2. Ligand Exchange Reaction and Reductive Elimination Reaction of the Pt Porphyrin Pincer Complexes<sup>*a*</sup>



<sup>*a*</sup> Reagents and conditions: (a) PhMgBr, THF, room temperature; (b) I<sub>2</sub>, THF, room temperature.



Figure 2. UV-vis absorption spectra of 1 (purple), 2 (red), 3 (green), 4 (blue), and 5 (black) in  $CH_2Cl_2$ .

In the case of the diaminobenzene-based NCN Pt pincer complexes, analogous *cis*-dihalophenylplatinum(IV) complexes are known to be stable.<sup>5</sup> Thus, the unique structure and electronic state of porphyrin pincer complexes might be a reason for this facile reductive elimination reaction.

The valence state of the outer platinum center influences the absorption and electrochemical properties of the complexes. The difference in electronic states of the Pt porphyrin pincer complexes 2-4 is apparent in the UV-vis absorption spectra (Figure 2). The Soret and Q bands of these complexes exhibit red shifts relative to those of 1 and 5. The degrees of the red shifts are different, depending on the valence states of the Pt centers. The Q bands of complexes 2 and 4 appear at wavelengths longer than that of 3. DFT calculations indicate that the HOMO-LUMO gaps of 2 and 4 are smaller than that of 3, mainly due to the HOMO energies of 2 and 4 being substantially higher than that of 3 (Figure 3). This situation can be explained by destabilization of the HOMOs of 2 and 4 because of the electron-rich Pt(II) center. The cyclic voltammograms of 1-4 were measured, and the potentials are given in Table 1. Irreversible oxidation waves for 1 and 4 and

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Figure 3. Energy diagrams and pictorial representations of HOMOs and LUMOs for 2–4, calculated at the B3LYP/LANL2DZ level.

Table 1. Oxidation and Reduction Potentials of 1–4 in CH<sub>2</sub>Cl<sub>2</sub> (in V vs Ferrocene/Ferrocenium Ion Pair)<sup>*a*</sup>

complex	$E_{\rm ox1}$	$E_{\rm ox2}$	$E_{\rm red1}$	$E_{\rm red2}$
1	$0.59^{b}$		-1.64	
23	0.38	0.87	-1.63 $-1.27^{b}$	-1.66
4	$0.32^{b}$		-1.69	

<sup>*a*</sup> These values were measured by cyclic voltammetry using a platinum working electrode, a platinum-wire counter electrode, and an Ag/AgClO<sub>4</sub> reference electrode. The measurements were carried out in  $CH_2Cl_2$  solutions containing 0.10 M Bu<sub>4</sub>NPF<sub>6</sub> as a supporting electrolyte. <sup>*b*</sup> Irreversible waves.

reversible oxidation waves for 2 and 3 were observed. The first oxidation potentials of 2 (0.38 V) and 4 (0.32 V) are substantially lower than that of 1 (0.59 V) because of backdonation of Pt(II) to the macrocycle. In sharp contrast, complex 3 exhibits the first oxidation potential at 0.61 V. The higher oxidation potential of 3 is probably accounted for by the electronically positive metal center of the high oxidation state. This trend again matches well with the theoretical calculations. Reversible reduction waves were observed for 1, 2, and 4, which are at almost the same potentials (-1.64 V for 1, -1.63 V for 2, and -1.69 V for 4). In the case of 3, however, an irreversible reduction wave is frequently observed in Pt(IV) complexes, which can be assigned as a reduction process of the Pt(IV) center to a Pt(II) center.<sup>6</sup>

## Conclusion

In conclusion, the synthesis of the Pt(II) and Pt(IV) porphyrin pincer complexes has been achieved. The structures of the complexes have been revealed by X-ray diffraction analyses. Importantly, the valence state of the outer Pt center has a significant influence on the structure of porphyrinic macrocycles and electrochemistry of the complexes. Oxidation of the phenylplatinum(II) complex induced

carbon-carbon bond formation via reductive elimination. Further investigation of porphyrin pincer complexes bearing a variety of outer transition metals is currently underway in our laboratory.

## **Experimental Section**

General Considerations. <sup>1</sup>H NMR spectra were recorded on a Varian INOVA-500 (500 MHz) spectrometer, and chemical shifts were reported as the  $\delta$  scale in ppm relative to CHCl<sub>3</sub> as internal reference for <sup>1</sup>H NMR ( $\delta$  7.260 ppm). UV/vis absorption spectra were recorded on a Shimadzu UV-2550 spectrometer. Mass spectra were recorded on a Bruker microTOF instrument using the positive mode ESI-TOF method for acetonitrile solutions. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

**Compound 2.** A toluene/DMF solution (5 mL/5 mL) of 1 (109) mg, 0.1 mmol) and K<sub>2</sub>PtCl<sub>4</sub> (209 mg, 0.5 mmol) was stirred for 15 h at 105 °C under an N2 atmosphere. The resulting mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with water, extracted with CH<sub>2</sub>Cl<sub>2</sub>, and dried through Na<sub>2</sub>SO<sub>4</sub>. Removal of solvents in vacuo, followed by recrystallization from CH2Cl2/CH3CN, afforded **2** in 96% yield (126 mg, 95.5  $\mu$ mol) as a green solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.98 (d, J = 6.3 Hz, 2H, Py), 8.88 (s, 2H,  $\beta$ ),  $8.54 (d, J = 4.8 Hz, 2H, \beta), 8.49 (d, J = 4.8 Hz, 2H, \beta), 7.97 (d, J = 4$ J = 4.8 Hz, 2H,  $\beta$ ), 7.93 (d, J = 1.1 Hz, 4H, Ar-o), 7.82 (m, 4H, Py and Ar-o), 7.77 (d, J = 4.3 Hz, 1H, Py), 7.69 (t, J = 1.1 Hz, 1H, Ar), 7.11 (t, J = 4.4 Hz, 2H, Py), 1,53 (s, 36H, t-Bu), and 1.48 (s, 18H, *t*-Bu). UV/vis (CH<sub>2</sub>Cl<sub>2</sub>;  $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)): 406 (38 000), 478 (120 000), 576 (14 000), 628 (8000). HR-MS (ESI-MS): m/z 1279.5177, calcd for  $(C_{72}H_{77}N_6NiPt)^+$  $1279.5212 (M - Cl)^+$ 

**Compound 3.** Compound **2** (90.8 mg, 69  $\mu$ mol) and CuCl<sub>2</sub>·2H<sub>2</sub>O (118 mg, 0.69 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub>/ MeOH and stirred at room temperature for 19 h. The mixture was washed with water, extracted with CH<sub>2</sub>Cl<sub>2</sub>, and dried through Na<sub>2</sub>SO<sub>4</sub>. Solvents were removed in vacuo. The mixture was passed through a short silica column (AcOEt and hexane as an eluent). Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN provided **3** (46.6 mg, 33.6  $\mu$ mol) as a green solid in 49% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  10.16 (d, J = 5.4 Hz, 2H, Py), 9.06 (s, 2H,  $\beta$ ), 8.60 (d, J = 5.1 Hz, 2H,  $\beta$ ), 8.55 (d, J = 4.8 Hz, 1H,  $\beta$ ), 8.06 (d, J = 6.5 Hz, 2H, Py), 7.93 (m, 2H, Py and Ar-o), 7.83 (d, J = 1.9 Hz, 4H, Ar-o), 7.79 (t, J = 1.7 Hz, 2H, Ar-p), 7.71 (t, J = 1.7 Hz, Ar-p),

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7.23 (t, J = 6.8 Hz, 2H, Py), 1.53 (s, 36H, *t*-Bu), and 1.48 (s, 18H, *t*-Bu). UV/vis (CH<sub>2</sub>Cl<sub>2</sub>;  $\lambda_{max}$ , nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)): 363 (34 000), 387 (37 000), 467 (160 000), 571 (16 000), 615 (12 000). HR-MS (ESI-MS): m/z 1349.4589, calcd for (C<sub>72</sub>H<sub>77</sub>N<sub>6</sub>NiPtCl<sub>2</sub>)<sup>+</sup> 1349.4577 (M - Cl)<sup>+</sup>.

Compound 4. Under an N<sub>2</sub> atmosphere, to a THF solution (4 mL) of 2 (105 mg, 80  $\mu$ mol) was added a THF solution of phenylmagnesium bromide (0.58 M, 0.69 mL) at room temperature and the mixture was stirred at room temperature for 1.5 h. The reaction was quenched by aqueous NH<sub>4</sub>Cl, and the organic layer was dried through Na<sub>2</sub>SO<sub>4</sub>. After removal of solvents in vacuo, the mixture was separated by column chromatography on silica (AcOEt/hexane as an eluent). Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/ CH<sub>3</sub>CN afforded 4 (82.2 mg, 60.6 µmol) in 76% yield as a green solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.93 (s, 2H,  $\beta$ ), 8.65 (d, J = 6.1 Hz, 2H, Py), 8.53 (d, J = 5.0 Hz, 2H,  $\beta$ ), 8.48 (d, J =5.0 Hz, 2H,  $\beta$ ), 8.00 (d, J = 7.2 Hz, 2H, Py), 7.95 (d, J = 1.6 Hz, 1H, Ar-*o*), 7.83 (d, *J* = 1.9 Hz, 4H, Ar-*o*), 7.76 (t, *J* = 1.9 Hz, 2H, Ar-o, 7.72 (t, J = 6.6 Hz, 2H, Py), 7.68 (t, J = 1.9 Hz, 2H, Ar-p), 7.52 (d, J = 6.4 Hz, 2H, Ph-o), 7.21 (t, J = 7.4 Hz, 2H, Ph-*m*), 7.05 (t, J = 7.1 Hz, 1H, Ph-*p*), 6.64 (t, J = 5.6 Hz, 2H, Py), 1.54 (s, 36H, *tert*-butyl), and 1.47 (s, 18H, *tert*-butyl) ppm; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$  [M<sup>-1</sup> cm<sup>-1</sup>]) = 371 (42000), 413 (50000), 482 (140000), 577 (18000), and 630 (9000) nm; HR-MS (ESI-MS): m/z = 1356.5648, calcd for (C<sub>78</sub>H<sub>82</sub>N<sub>6</sub>-NiPt)<sup>+</sup> = 1356.5605 (*M* - *Cl*)<sup>+</sup>.

Compound 5. To a CH<sub>2</sub>Cl<sub>2</sub> solution (1 mL) of 4 (27.5 mg, 20  $\mu$ mol) was added iodine (22.2 mg, 87  $\mu$ mol) in THF (1 mL) via syringe. The mixture was stirred at room temperature for 12 h under an N<sub>2</sub> atmosphere. The mixture was washed with water, extracted with CH<sub>2</sub>Cl<sub>2</sub>, and dried through Na<sub>2</sub>SO<sub>4</sub>. The solvents were removed in vacuo. Short column chromatography on silica (AcOEt/hexane as an eluent), followed by recrystallization from  $CH_2Cl_2/CH_3CN$ , provided 5 (19.4 mg, 17  $\mu$ mol) as a red solid in 84% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.84 (s, 2H,  $\beta$ ), 8.71 (d, J = 5.0Hz, 2H,  $\beta$ ), 8.69 (d, J = 4.9 Hz, 2H,  $\beta$ ), 8.38 (d, J = 4.5 Hz, 2H, Py), 7.89 (m, 6H, Ar-o), 7.70 (t, J = 1.5 Hz, 1H, Ar-p), 7.67 (t, J = 1.5 Hz, 2H, Ar-p), 7.53 (d, J = 6.0 Hz, 2H, Py), 7.10 (t, J =7.5 Hz, 2H, Py), 6.82 (t, J = 5.5 Hz, 2H, Py), 6.75-6.60 (m, Ph), 1.49 (s, 18H, *tert*-butyl), and 1.47 (s, 36H, *tert*-butyl). UV/vis (CH<sub>2</sub>Cl<sub>2</sub>;  $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>)) 306 (18 000), 431 (160 000), 542 (13000). HR-MS (ESI-MS): m/z 1161.6028, calcd for  $(C_{78}H_{83}N_6Ni)^+$  1161.6027  $(M + H)^+$ 

X-ray Crystallographic Analyses. Single crystals of 2–5 suitable for X-ray diffraction analyses were grown by vapor diffusion of CH<sub>3</sub>CN into a 1,2-dichloroethane solution of 2, of CH<sub>3</sub>CN into a CHCl<sub>3</sub> solution of 3, of CH<sub>3</sub>CN into a CHCl<sub>3</sub> solution of 4, and of CH<sub>3</sub>CN into a chlorobenzene solution of 5. The diffraction data were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). An empirical absorption correction was applied by using SADABS. The structure was solved by

direct methods and refined by full-matrix least squares on  $F^2$  using SHELXTL. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic data: for **2**,  $C_{74}H_{77}Cl_3N_6NiPt$ ,  $M_w = 1410.57$ , orthorhombic, space group *Pbca* (No. 61), a = 19.056(3) Å, b = 13.8732(19) Å, c = 49.033(7) Å, V = 12963(3) Å<sup>3</sup>, Z = 8,  $D_{calcd} = 1.446$  Mg/cm<sup>3</sup>, T = 90 K, R = 0.0929 ( $I > 2.0\sigma(I)$ ),  $R_w = 0.2128$  (all data), GOF = 1.125 ( $I > 2.0\sigma(I)$ ); for **3**,  $C_{73}H_{78}Cl_6N_6NiPt$ ,  $M_w = 1505.91$ , monoclinic, space group C2/c (No. 15), a = 42.745(5) Å, b = 14.683(5) Å, c = 27.725(5) Å,  $\beta = 125.799(5)^\circ$ , V = 14113(6) Å<sup>3</sup>, Z = 8,  $D_{calcd} = 1.418$  Mg/cm<sup>3</sup>, T = 153 K, R = 0.0519 ( $I > 2.0\sigma(I)$ ),  $R_w = 0.1491$  (all data), GOF = 1.032 ( $I > 2.0\sigma(I)$ ); for **4**,  $C_{73}H_{78}Cl_6N_6NiPt$ ,  $M_w = 155.14$ , triclinic, space group  $P\overline{1}$  (No. 2), a = 15.130(5) Å, b = 17.343(5) Å, c = 17.879(5) Å,  $\beta = 103.735(5)^\circ$ , V = 4502(2) Å<sup>3</sup>, Z = 2,  $D_{calcd} = 1.418$  Mg/cm<sup>3</sup>, T = 153 K, R = 0.0786 ( $I > 2.0\sigma(I)$ ); for **5**,  $C_{90}H_{92}Cl_2N_6Ni$ ,  $M_w = 1387.31$ , monoclinic, space group  $P2_1/r$  (No. 24), a = 12.014(5) Å, b = 33.877(5) Å, c = 18.949(5) Å,  $\beta = 101.791(5)^\circ$ , V = 7549(4) Å<sup>3</sup>, Z = 4,  $D_{calcd} = 1.221$  Mg/ cm<sup>3</sup>, T = 153 K, R = 0.0595 ( $I > 2.0\sigma(I)$ ),  $R_w = 0.1792$  (all data), GOF = 1.042 ( $I > 2.0\sigma(I)$ ).

**Theoretical Calculations.** All calculations were carried out using the Gaussian 03 program.<sup>7</sup> Initial geometries of the model compounds for **2**–**4** were obtained from their X-ray structures, but all 3,5-di-*tert*-butylphenyl substituents were replaced with hydrogen. Optimizations were performed with Becke's three-parameter hybrid exchange functional and the Lee–Yang–Parr correlation functional (B3LYP),<sup>8</sup> employing a basis set consisting of LANL2DZ. Optimized geometries appear to be in agreement with the crystal structures. The molecular orbital diagrams were calculated at the B3LYP/ LANL2DZ level.

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**Supporting Information Available:** Figures giving spectral data for 2–5 and cyclic voltammograms for 1–4, a table giving bond lengths and angles for 2–4, and CIF files giving crystallographic data for 2–5. This material is available free of charge via the Internet at http://pubs.acs.org.

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