Porphyrinoids

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A *meso*-Spiro[Cyclopentadiene-Isoporphyrin] from a Phenylethynyl Porphyrin Platinum(II) Pincer Complex**

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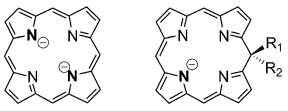
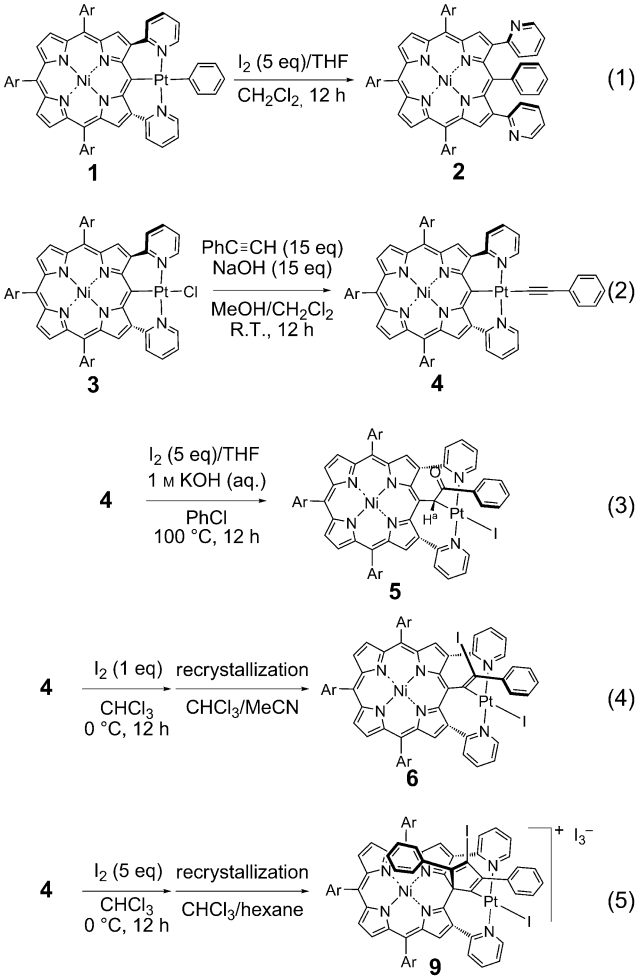
Pincer-type organometallic complexes have received much attention as non-linear optical (NLO) materials, light emitting dyes, and highly active and stable catalysts in a number of organic transformations.[1] The tridentate ligand strongly binds a metal to prevent ligand dissociation, thus achieving high thermal stability. We have explored porphyrin pincer complexes bearing palladium or platinum metal bound to the tridentate ligand consisting of a porphyrin *meso* carbon and two 2-pyridyl groups substituted at the adjacent β positions.[2–4] These porphyrin pincer complexes exhibit catalytic reactivity in Heck reactions,[2a,b] redox-responsive pivotal conformational switching,[4a] and large two-photon absorption cross-sections.[2c] Porphyrin pincer complexes may serve as precursors for peripheral functionalization of porphyrin, but such a possibility has been scarcely tested to date. As a rare case, we have reported that the oxidation of the phenylplatinum(II) pincer complex **1** with iodine induced a facile *meso*-phenylation by reductive elimination (Scheme 1, (1)).[5] Herein, we report quite different chemical behaviors of (phenylethynyl)platinum(II) pincer complex **4** upon treatment with iodine. Interestingly, in this case, reductive elimination occurs to allow a carbon–carbon bond formation but without liberation of platinum(II) metal, which is left tightly bound by the two 2-pyridyl groups. Furthermore, a *meso*-spiro[cyclopentadiene-isoporphyrin] was formed unexpectedly as a doubly phenylethynylated product. Isoporphyrins are porphyrin tautomers that carry an interrupted





Scheme 1. Synthesis and transformations of porphyrin pincer complexes **1**–**6**, **9**. Ar = 3,5-di-*tert*-butylphenyl.

macrocyclic conjugation owing to the presence of an sp^3-hybridized *meso* carbon. The existence of this tautomer was first suggested by Woodward in 1961,[6] whose prediction was first confirmed by Dolphin et al. by their synthesis.[7] Isoporphyrins have been considered to be key intermediates in the heme oxidation catalyzed by heme oxygenase,[8] but synthetic investigations of isoporphyrins have been rather limited.[9]

Pincer complex **3** was prepared according to our reported procedure,[5] and was converted into phenylethynyl pincer complex **4** by a ligand-exchange reaction (Scheme 2). This complex was sensitive to hydrolytic cleavage on a silica gel column and was thus isolated by recrystallization from a mixture of CH_2Cl_2 and methanol in 72% yield

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(Scheme 1, (2)). The high-resolution electrospray ionization time-of-flight (HR-ESI-TOF) mass and ^{1}H NMR spectra of **4** are consistent with the structure, which has been confirmed by X-ray diffraction analysis (Figure 1 a).[10] The porphyrin ring of **4** is distorted to a saddle shape owing to the peripheral metalation, which is similar to the porphyrin palladium(II) pincer complexes.[2a]

To induce the reductive elimination of **4**, oxidation of the Pt^{II} center was attempted by treatment with iodine. Initially, complex **4** was reacted with iodine under the reaction conditions used for the *meso*-phenylation of **1**.[5] Aqueous work up produced a complicated mixture from which a product was isolated in a trace amount. Fortunately, good-quality crystals were obtained, allowing the structural determination by X-ray diffraction analysis as *meso*-phenacylated porphyrin **5**. In this complex, the platinum(II) ion is bound to the α position of the phenacyl group, the two nitrogen atoms of the 2-pyridyl groups, and iodide to give a square-planar coordination (Figure 1 b).[10] Consistent with the structure, the parent ion peak of **5** was observed at $m/z = 1524.4638$ (calcd for $C_{80}H_{83}N_6ONiPtI = 1524.4697$ $[M]^+$) in the HR-ESI-TOF mass spectrum, and the ^{1}H NMR spectrum of **5** at −60 °C exhibits a singlet signal at 6.44 ppm for H^a, a set of three signals for the phenyl group, and sets of non-equivalent signals for both the porphyrinic β protons and pyridyl protons (Supporting Information). On the basis of the consideration that **5** should be a hydrolyzed product, we attempted to improve the yield of **5** by the addition of water or hydroxide ion. After extensive optimization, the complex **5** was obtained in 39 % yield by refluxing a mixture of **4** in chlorobenzene and THF in the presence of I_2 and aqueous KOH at 100 °C for 12 h (Scheme 1, (3)).

In a next step, we examined the reaction of **4** with I_2 under rigorously anhydrous conditions. Treatment of **4** with I_2 in anhydrous $CHCl_3$ at 0 °C for 12 h furnished *meso*-alkenylated porphyrin **6** in 48 % yield after recrystallization from acetonitrile (Scheme 1, (4)). The parent ion peak of **6** was observed at $m/z = 1634.3634$ (calcd for $C_{80}H_{82}N_6NiPtI_2 = 1634.3715$ $[M]^+$) in the HR-ESI-TOF mass spectrum, indicating an addition of I_2. The ^{1}H NMR spectrum of **6** now exhibits higher symmetry: a set of porphyrin signals were observed at 8.69–8.61 ppm and the phenyl protons at 7.18–6.46 ppm. The X-ray diffraction analysis revealed the structure of **6** to be a *meso*-alkenyl porphyrin (Figure 1 c).[10] Compound **6** is sensitive to water and could be easily hydrolyzed by aqueous KOH to afford **5** quantitatively.

The formation of **5** and **6** can be understood in terms of iodination of **4** to form Pt^{IV} pincer porphyrin **7**[11] and subsequent reductive elimination to yield *meso*-ethynyl porphyrin **8** (Scheme 2). The acetylene moiety in **8** is activated by the interaction with the captured Pt^{II} ion, so that nucleophilic attack on the ethynyl group in **8** by hydroxide or iodide ion is facilitated to form **5** or **6** (Scheme 2).

Furthermore, during the analysis of the reaction of **4** with I_2 under anhydrous conditions, we noticed the formation of a very polar byproduct in addition to **6**, which was characterized as *meso*-spiro[cyclopentadiene-isoporphyrin] **9**. This unique product was obtained in 22 % yield (on the basis of the

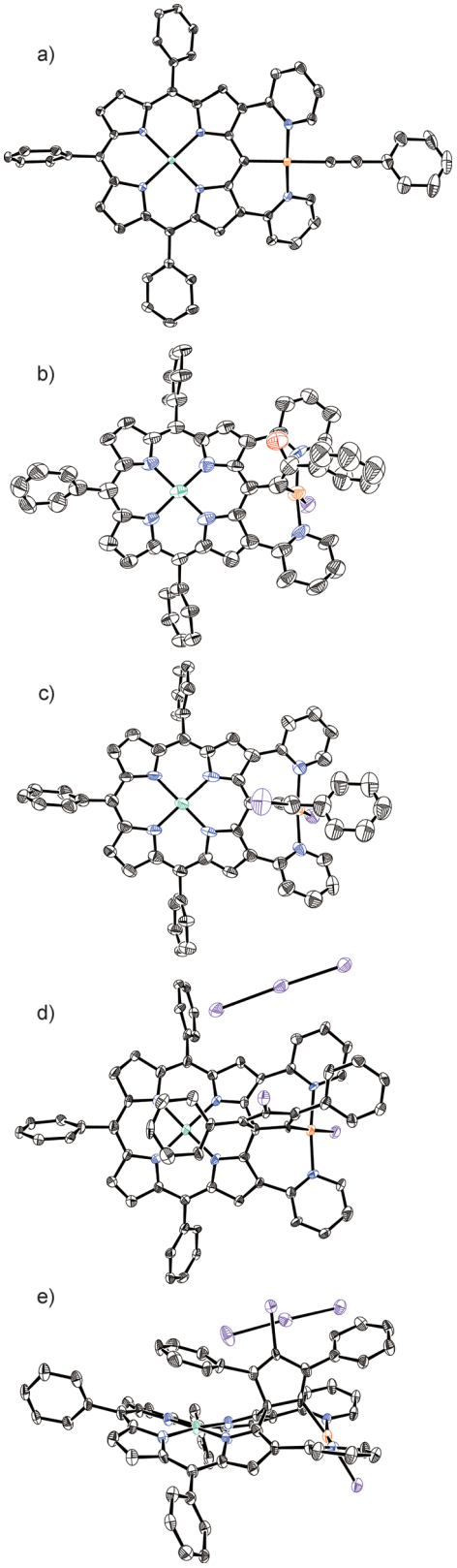
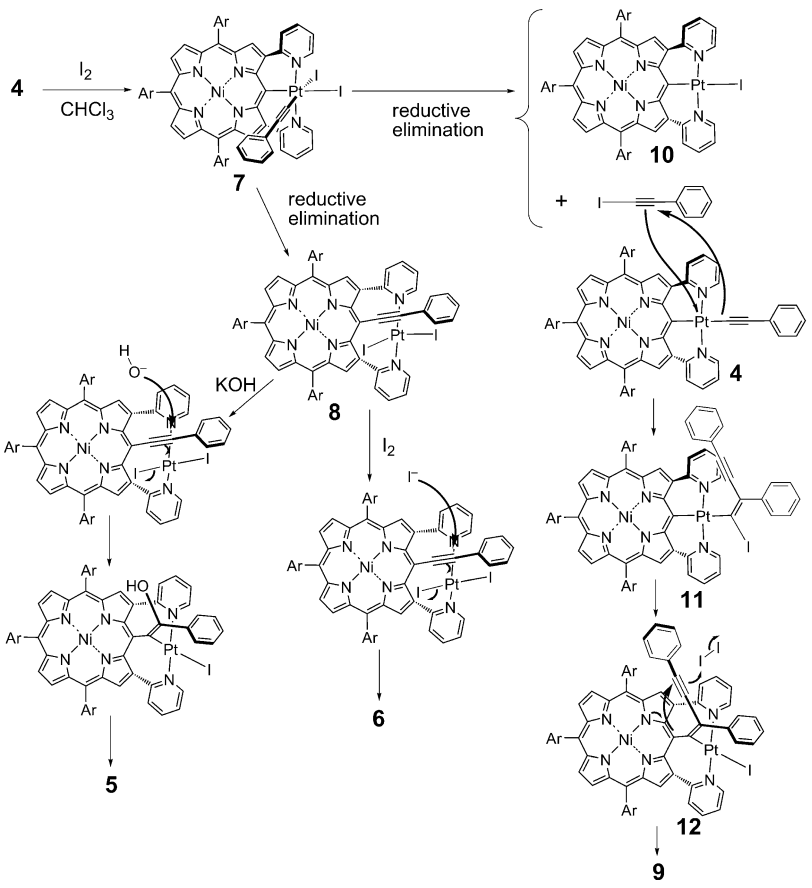


Figure 1. X-ray crystal structures of a) **4**, b) **5**, c) **6**, and d, e) **9**. Ni green, Pt yellow, N blue, O red, I purple. *tert*-Butyl groups, hydrogen atoms, disordered parts, and solvent molecules are omitted for clarity. Ellipsoids are set at 50 % (**4**) and 30 % probability (**5**, **6**, and **9**).



Scheme 2. Plausible mechanisms for the formation of **5**, **6**, and **9**.

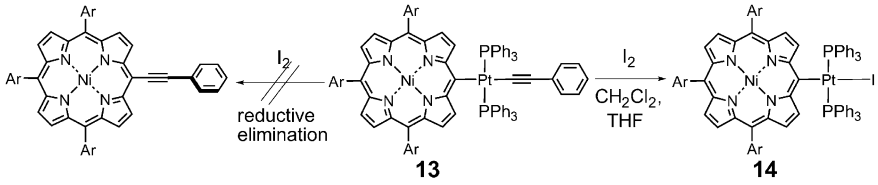
amount of **4**) and 44% yield (on the basis of the phenylethynyl moiety) under the conditions shown in Scheme 1, (5). The parent ion peak of **9** was observed at $m/z = 1735.4126$ (calcd for $C_{88}H_{87}N_6NiPtI_2 = 1735.4106$ $[M-I_3]^+$) in its HR-ESI-TOF mass spectrum, thus indicating the presence of an additional phenylethynyl unit. The ^{1}H NMR spectrum of **9** exhibited less-deshielded signals for the porphyrinic β protons, thus indicating a loss of a diatropic ring current. Single crystals of **9** suitable for X-ray diffraction analysis were grown by slow vapor diffusion of methanol into its chloroform solution. The X-ray diffraction study revealed a newly formed cyclopentadiene moiety that is connected at the *meso* position in a spiro manner with a dihedral angle of 73.2° relative to the porphyrin mean plane, thus disrupting a porphyrin conjugated aromatic circuit to form an isoporphyrin skeleton (Figure 1 d,e).[10] The diamagnetic character of **9** indicates a low-spin Ni^{II} ion in the isoporphyrin ligand. As an isoporphyrin is a monoanionic ligand, I_3^- is found as a counterion to balance the charge for the resulting Ni^{II} isoporphyrin cation. It is worth noting that **9** is the first example of nickel(II) isoporphyrin.[9l]

A plausible reaction mechanism for the formation of **9** is shown in Scheme 2, which involves the reductive elimination of **7** to afford pincer complex iodide **10** and iodoethynylbenzene. Subsequent insertion of iodoethynylbenzene to **4** to form 1,3-enynylated pincer complex **11**, which is converted into **9** via I_2-assisted intramolecular cyclization.[12] To confirm this mechanism, the reaction of **4** with iodine in the presence of 5 equiv iodoethynylbenzene was attempted, which indeed led to the formation of **9** in 68% yield.

As a separate test reaction, we examined the reaction of *meso*-[phenylethynylbis(triphenylphosphino)platinum(II)] porphyrin **13**[13] with iodine (Scheme 3). Interestingly, this reaction did not produce the reductive elimination product but instead afforded iodinated Pt^{II} complex **14** in 85% yield, suggesting that the unique reactivity of the complex **4** arises from the tightly bound pincer structure.

The UV/Vis absorption spectra of **4**–**6** and **9** are shown in Figure 2. The complexes **5** and **6** exhibit broader Soret bands and red-shifted Q bands relative to those of **4**. The cationic isoporphyrin **9** displays a significantly red-shifted Q band reaching to infrared region up to 1200 nm, which is characteristic of isoporphyrins but much more red-shifted than those of other isoporphyrin metal complexes (typically around 800–900 nm).[9]

In summary, the oxidation of phenylethynyl Pt^{II} pincer complex **4** with iodine led



Scheme 3. Formation of **14** from the reaction of **13** with iodine.

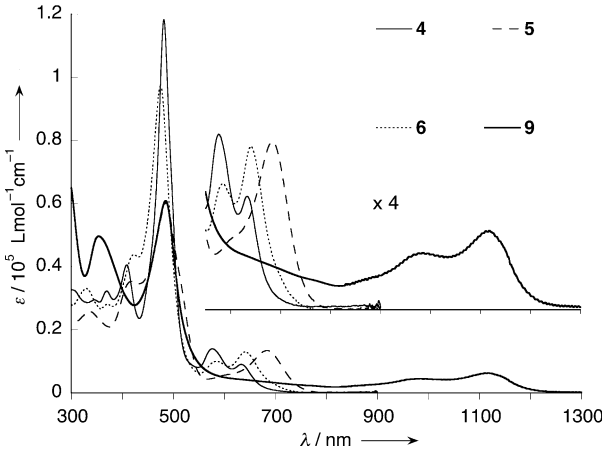


Figure 2. UV/Vis absorption spectra of **4**–**6** and **9** in CH_2Cl_2.

to formal reductive elimination, but without the liberation of Pt^{II}, which was caught by the 2-pyridyl pincer substituents. Importantly, the remaining Pt^{II} ion activates the ethynyl moiety by π coordination to assist the facile formations of **5** and **6**. We also found the reaction conditions under which *meso*-spiro[cyclopentadiene-isoporphyrin] **9** was formed in good yield by an additional coordination–insertion of iodoethynylbenzene to **4** followed by I_2-assisted intramolecular cyclization. Further exploration of unique reactions of porphyrin pincer complexes for porphyrin peripheral modifications is actively in progress in our laboratories.

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[10] Crystal data for **4**: $C_{80}H_{82}N_6NiPt\cdot5\,CHCl_3$, $M_r = 1973.12$, triclinic, space group $P\bar{1}$ (no. 2), $a = 14.5824(12)$, $b = 17.7665(15)$, $c = 17.7761(15)$ Å, $\alpha = 91.675(2)$, $\beta = 102.2010(10)$, $\gamma = 98.3630(10)°$, $V = 4444.9(6)$ Å^3, $Z = 2$, $T = 90(2)$ K, $D_{calcd} = 1.474\,g\,cm^{-3}$, $R_1 = 0.0503$ ($I > 2\sigma(I)$), $R_w = 0.1384$ (all data), GOF = 1.055; **5**: $C_{80}H_{83}N_6ONiPtI$, $M_r = 1525.22$, monoclinic, space group $P2/n$ (no. 13), $a = 13.0267(4)$, $b = 21.2118(7)$, $c = 35.4248(11)$ Å, $\beta = 97.8789(12)°$, $V = 9696.2(5)$ Å^3, $Z = 4$, $T = 93(2)$ K, $D_{calcd} = 1.045\,g\,cm^{-3}$, $R_1 = 0.0858$ ($I > 2\sigma(I)$), $R_w = 0.2397$ (all data), GOF = 0.833; **6**: $C_{80}H_{82}N_6NiPtI_2$, $M_r = 1635.12$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.7306(2)$, $b = 14.8418(4)$, $c = 26.9882(5)$ Å, $\alpha = 99.1516(10)$, $\beta = 98.6274(14)$, $\gamma = 111.7004(9)°$, $V = 4197.00(15)$ Å^3, $Z = 2$, $T = 93(2)$ K, $D_{calcd} = 1.294\,g\,cm^{-3}$, $R_1 = 0.0969$ ($I > 2\sigma(I)$), $R_w = 0.2611$ (all data), GOF = 1.007; **9**: $C_{88}H_{87}N_6Ni_1Pt_1I_5\cdot2.73\,CHCl_3\cdot0.27\,I_2$, $M_r = 2511.35$, triclinic, space group $P\bar{1}$ (no. 2), $a = 15.2725(3)$, $b = 17.3994(3)$, $c = 19.6955(4)$ Å, $\alpha = 88.3329(7)$, $\beta = 69.6501(7)$, $\gamma = 74.1108(7)°$, $V = 4706.89(16)$ Å^3, $Z = 2$, $T = 93(2)$ K, $D_{calcd} = 1.772\,g\,cm^{-3}$, $R_1 = 0.0973$ ($I > 2\sigma(I)$), $R_w = 0.2465$ (all data), GOF = 1.027. The contributions to the scattering arising from the presence of the disordered solvents in the crystals of **5** and **6** were removed by use of the utility SQUEEZE in the PLATON software package.[14] CCDC 857634 (**4**), 857635 (**5**), 857636 (**6**), and 857637 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[12] An alternative route involving the initial coordination-insertion of iodoethynylbenzene between the porphyrin–Pt^{II} bond followed by reductive elimination also provides **12**. However, this route may be considered energetically unfavorable because of the rigid structure of the porphyrin pincer part.

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