*Inorg. Chem.* **2009**, *48*, 795−797

Inorganic Chemistry

Communication

# Double Cleavage of sp$^2$ C−H and sp$^3$ C−H Bonds on One Metal Center: DMF-Appended Cyclometalated Platinum(II) and -(IV) Porphyrins

**Shigeru Yamaguchi, Hiroshi Shinokubo,[†,*] and Atsuhiro Osuka***

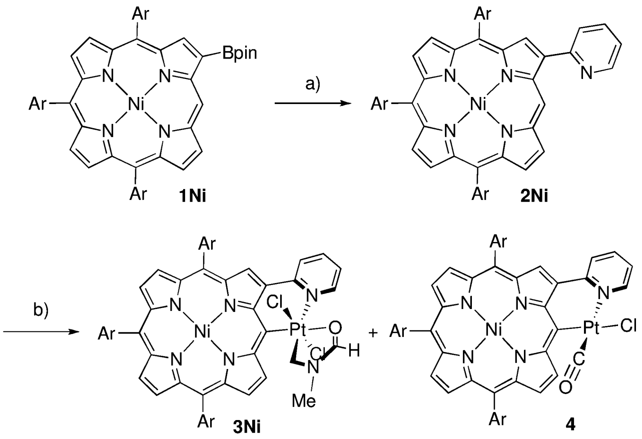
*Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-Ku, Kyoto 606-8502, Japan*

Received October 8, 2008

DMF-appended cyclometalated platinum(II) and -(IV) porphyrins were synthesized via the double cleavage of sp$^2$ C−H and sp$^3$ C−H bonds on one platinum center.

Porphyrins generally accommodate a variety of metals in the central cavity, and the research on peripherally metalated porphyrins is a relatively new area.[1] In particular, porphyrins with a peripheral carbon−transition metal (M−C) $\sigma$ bond are still rare.[2−4] The pioneering work of such porphyrins was reported by Arnold et al., who synthesized $\eta^1$-*meso*-palladium or platinum porphyrins by the oxidative addition of Pt$^0$ or Pd$^0$ species to *meso*-haloporphyrins.[2a] Recently, we have introduced cyclometalation strategy to access these types of porphyrins by use of coordinating substituents such as pyridyl groups.[3] Matano and co-workers reported the $\beta$-M−C $\sigma$-bond-linked dimers of *meso*-phosphanylporphyrins (M = Pd$^{II}$ or Pt$^{II}$).[4] Metallacycles on benzene rings have been extensively investigated in terms of their reactivity, catalytic activity, and photophysical property.[5] However, the chemistry of peripherally cyclometalated porphyrins is still in their infancy. Here we report the serendipitous isolation of novel porphyrin metallacycles constituted by $\beta$-(2-pyridyl)porphyrins and *N*,*N*-dimethylformamide (DMF) via the double cleavage of sp$^3$ C−H and sp$^2$ C−H bonds on one platinum center. *The transition-metal complex resulting from a double-cleavage event of sp$^2$ C−H and sp$^3$ C−H bonds on one metal center is unprecedented, despite recent enthusiastic efforts to develop a C−H bond functionalization strategy.*[6,7]

**Scheme 1.** Isolation of DMF-Appended Platinum(IV) Porphyrin **3Ni**[a]



[a] Reagents and conditions: (a) 2-iodopyridine, Pd$_2$(dba)$_3$, PPh$_3$, Cs$_2$CO$_3$, CsF, toluene/DMF/H$_2$O, 100 °C; (b) K$_2$PtCl$_4$, toluene/DMF, 100 °C. Ar = 3,5-di-*tert*-butylphenyl, Bpin = 3,3,4,4-tetramethyl-2,5-dioxaboranyl.

The synthesis of DMF-appended platinum(IV) porphyrin **3Ni** is shown in Scheme 1. $\beta$-(2-Pyridyl)porphyrin **2Ni** was prepared by the Suzuki−Miyaura cross-coupling reaction of $\beta$-borylated porphyrin **1Ni**[8] with 2-iodopyridine. The reaction

---

[*] To whom correspondence should be addressed. E-mail: hshino@apchem.nagoya-u.ac.jp (H.S.), osuka@kuchem.kyoto-u.ac.jp (A.O.). Fax: +81-52-789-5113 (H.S.), +81-75-753-3970 (A.O.).

[†] Present address: Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan.

(1) Klein Gebank, R. J. M.; Suijkerbuijk, B. M. J. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 7396.

(2) (a) Arnold, D. P.; Sakata, Y.; Sugiura, K.; Worthington, E. I. *Chem. Commun.* **1998**, 2331. (b) Hartnell, R. D.; Arnold, D. P. *Organometallics* **2004**, *23*, 391. (c) Hartnell, R. D.; Arnold, D. P. *Eur. J. Inorg. Chem.* **2004**, 1262. (d) Hodgson, M. J.; Healy, P. C.; Williams, M. L.; Arnold, D. P. *J. Chem. Soc., Dalton Trans.* **2002**, 4497. (e) Arnold, D. P.; Healy, P. C.; Hodgson, M. J.; Williams, M. L. *J. Organomet. Chem.* **2000**, *607*, 41. (f) Atefi, F.; Arnold, D. P. *J. Porphyrins Phthalocyanines* **2008**, *12*, 801.

(3) (a) Yamaguchi, S.; Katoh, T.; Shinokubo, H.; Osuka, A. *J. Am. Chem. Soc.* **2007**, *129*, 6392. (b) Yamaguchi, S.; Katoh, T.; Shinokubo, H.; Osuka, A. *J. Am. Chem. Soc.* **2008**, *130*, 14440.

(4) Matano, Y.; Matsumoto, K.; Nakano, Y.; Uno, H.; Sakaki, S.; Imahori, H. *J. Am. Chem. Soc.* **2008**, *130*, 4588.

(5) (a) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750. (b) Dupont, J.; Consorti, C. S.; Spencer, J. *Chem. Rev.* **2005**, *105*, 2527. (c) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759. (d) Singleton, J. T. *Tetrahedron* **2003**, *59*, 1837.

(6) (a) Stuart, D. R.; Fagnou, K. *Science* **2007**, *316*, 1172. (b) Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2007**, *129*, 11904. (c) Xia, J.-B.; You, S.-L. *Organometallics* **2007**, *26*, 4869. (d) Dwight, T. A.; Rue, N. R.; Charyk, R.; Josselyn, R.; DeBoef, B. *Org. Lett.* **2007**, *9*, 3137. (e) Li, R.; Jiang, L.; Lu, W. *Organometallics* **2006**, *25*, 5973.

(7) sp$^2$ C−H and sp$^3$ C−H dehydrogenated cross-coupling reaction has been reported. In the literature, the authors suggest that the coupling occurs via the Friedel−Crafts-type reaction mechanism. (a) Li, Z.; Li, C.-H. *J. Am. Chem. Soc.* **2005**, *127*, 6968. For related reactions, see: (b) Li, Z.; Li, C.-H. *J. Am. Chem. Soc.* **2005**, *127*, 3672. (c) Li, Z.; Li, C.-H. *J. Am. Chem. Soc.* **2004**, *126*, 11810. (d) Murahashi, S.-I.; Komiya, N.; Terai, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 6931.

(8) Hata, H.; Shinokubo, H.; Osuka, A. *J. Am. Chem. Soc.* **2005**, *127*, 8264.

10.1021/ic8019149 CCC: $40.75

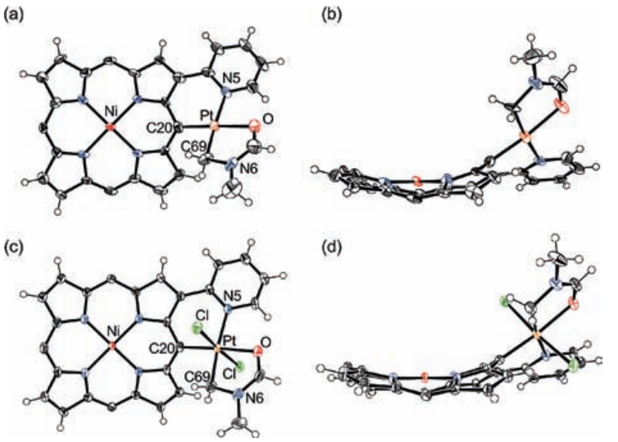


**Figure 1.** X-ray crystal structure of DMF-appended platinum porphyrins: (a) top view of **5Ni**; (b) side view of **5Ni**; (c) top view of **3Ni**; (d) side view of **3Ni**. The thermal ellipsoids are scaled to 50% probability level. *meso*-Aryl substituents are omitted for clarity.

of ligand **2Ni** with $K_2PtCl_4$ at 100 °C for 24 h in a toluene/DMF solution afforded **3Ni** in 8% yield as an air- and moisture-stable green solid after separation by silica gel column chromatography.[9,10] The parent mass ion peak was observed at *m*/*z* 1345.4783 (calcd for $(C_{70}H_{80}N_6NiOPtCl_2)^+$ = *m*/*z*1345.4762 $[(M)^+]$) in its high-resolution electrospray ionization time-of-flight (HR ESI-TOF) mass spectrum. In the $^1H$ NMR spectrum, no meso proton was observed, suggesting metalation at the meso position. The peak due to the C*H*O proton is observed as a singlet at 7.85 ppm, which has a correlation in the CH-hetero COSY with the peak observed at 168.0 ppm in the $^{13}C$ NMR spectrum. The signal due to the methyl protons of the DMF group is observed as a singlet at 3.07 ppm. The methylene protons of the DMF group attached to the Pt atom are not observed at room temperature but appear as mutually coupled doublet peaks at 5.49 and 3.59 ppm at −50 °C because of different circumstances of the two protons. Finally, X-ray diffraction analysis unambiguously elucidated the structure bearing $sp^2$ C−Pt and $sp^3$ C−Pt bonds in a cis configuration with an octahedral $Pt^{IV}$ center (Figure 1c,d).

From the reaction mixture, a CO complex **4** was also isolated in 29% yield (Scheme 1). The CO complex **4** was characterized by IR [$\nu(CO) = 2103\ cm^{-1}$], mass (HR-ESI: observed = *m*/*z* 1266.4635 (calcd for $(C_{68}H_{75}N_5NiPtOCl)$ = *m*/*z* 1266.4655 $[(M + H)^+]$), $^1H$ NMR and X-ray diffraction analyses.[11] To prevent the generation of CO, which is probably caused by the decomposition of DMF by acid generated from the C−H bond cleavage, the reaction was carried out in the presence of NaOAc as a proton scavenger. The reaction proceeded via simultaneous C−H bond double cleavage to provide DMF-appended platinum(II) porphyrin **5Ni** instead of **3Ni** in 64% yield as an air- and moisture-stable green solid (Scheme 2). The parent mass ion peak was observed at *m*/*z* 1274.5446 (calcd for $(C_{70}H_{80}N_6NiOPt)^+$ = *m*/*z* 1274.5396 $[(M)^+]$) in its HR ESI-TOF mass spectrum. In the $^1H$ NMR spectrum, no signal due to a meso proton was observed. Doublet peaks at 4.17 and 2.84 ppm and a singlet peak at 2.99 ppm are assigned as methylene and methyl protons of the DMF group. In the $^{13}C$ NMR spectrum, a peak due to the carbonyl carbon of the DMF group appeared at 168.8 ppm, which has a correlation in the CH-hetero COSY spectrum with the C*H*O signal ($\delta = 8.13$) in the $^1H$ NMR spectrum.

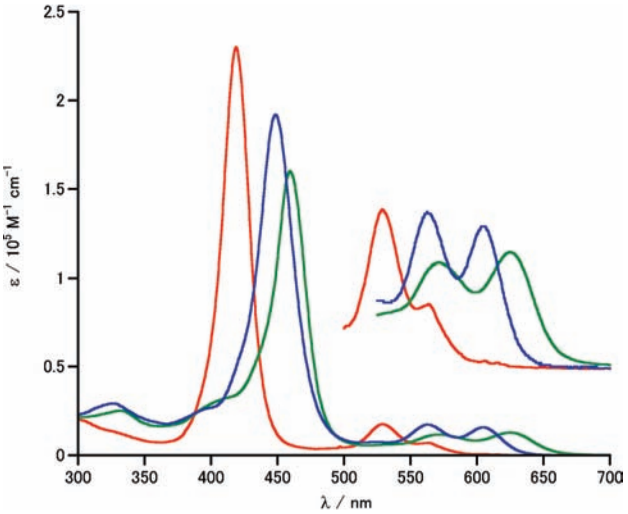
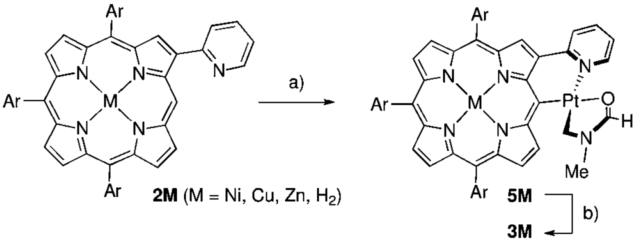


**Figure 2.** UV−vis absorption spectra of **2Ni** (red), **3Ni** (blue), and **5Ni** (green) in $CH_2Cl_2$.

**Scheme 2.** Synthesis of DMF-Appended Platinum(II) Porphyrin **5M** and the Oxidation Reaction of **5M**[a]



[a] Reagents and conditions: (a) $K_2PtCl_4$, NaOAc, toluene/DMF, 100 °C; (b) $FeCl_3\cdot 6H_2O$, $CH_2Cl_2$/MeOH, rt. Ar = 3,5-di-*tert*-butylphenyl.

This procedure works nicely for the synthesis of **5M** (M = Zn, Cu, $H_2$). **$2H_2$** was synthesized from **$1H_2$** as a similar procedure of the synthesis of **2Ni**. **2Zn** and **2Cu** were obtained by metalation of **$2H_2$** with the corresponding metal salts. C−H bond double cleavages between **2M** (M = Zn, Cu, $H_2$) and DMF also occurred smoothly to provide **5M** (M = Zn, Cu, $H_2$) in 49%, 39%, and 45% yield, respectively. The divalent platinum centers of **5M** are susceptible to oxidation reaction: treatment of **5Ni** with an excess amount of $FeCl_3\cdot 6H_2O$ in a $CH_2Cl_2$/MeOH solution provided platinum(IV) complex **3Ni** in 73% yield. **3M** (M = Cu, Zn, $H_2$) was also synthesized by the same procedure in 30%, 36%,

---

[9] The $Pt^{II}$ atom was oxidized to $Pt^{IV}$ probably by air in the course of the reaction. The reaction under an inert atmosphere did not afford **4Ni**. For an oxidant-promoted C−H bond activation reaction, see: Newman, C. P.; Casey-Green, K.; Clarkson, G. J.; Cave, G. W. V.; Errington, W.; Rourke, J. P. *Dalton Trans.* **2007**, 3170.

[10] The reaction of **1Ni** with a platinum(IV) salt in toluene/AcOH provided a platinum(IV)-bridged cofacial diporphyrin. See ref 3b. However, none of such diporphyrins was detected in the reaction in toluene/DMF.

[11] Crystallographic data for **4**: $C_{68}H_{74}ClN_5NiOPt\cdot 3CCl_4$, $M_w = 1728.00$, triclinic, space group $P\bar{1}$ (No. 2), $a = 11.841(5)$ Å, $b = 16.521(5)$ Å, $c = 19.620(5)$ Å, $\alpha = 99.387(5)°$, $\beta = 103.850(5)°$, $\gamma = 93.508(5)°$, $V = 3656(2)$ Å$^3$, $Z = 2$, $D_{calc} = 1.569$ Mg/cm$^3$, $R = 0.0807$ [$I > 2.0\sigma(I)$], $R_w = 0.2353$ (all data), GOF = 1.006 [$I > 2.0\sigma(I)$].

**Table 1.** Selected Bond Lengths (Å) of **3Ni**, **3H$_2$**, **5Ni**, and **5Zn**

| | 3Ni | 3H$_2$ | 5Ni | 5Zn |
|---|---|---|---|---|
| C20−Pt | 2.021(4) | 2.028(3) | 1.960(4) | 1.988(5) |
| C69−Pt | 2.017(5) | 2.042(4) | 2.019(4) | 2.032(6) |
| N5−Pt | 2.116(4) | 2.124(3) | 2.084(4) | 2.074(4) |
| O−Pt | 2.138(3) | 2.141(3) | 2.129(3) | 2.134(4) |

and 53% yield, respectively. **3M** or **5M** (M = Zn, H$_2$) displayed similar spectral features in the $^1$H NMR as **3Ni** or **5Ni**.

The crystal structures of **3Ni**, **3Zn**, **5Ni**, and **5H$_2$** were determined by X-ray diffraction analyses (Figure 1 and the Supporting Information).[12] In all of the complexes, the DMF group is out of the plane of the porphyrin core because of the repulsion between methylene protons of DMF and $\beta$ protons of the porphyrin. Because of the repulsion, the Pt atom is also out of the plane. Thus, deviations of the *meso*-C attached to the Pt atom are slightly large. Displacements of the *meso*-C from the plane of 24 atoms are 0.784 Å for **3Ni**, 0.403 Å for **3H$_2$**, 0.852 Å for **5Ni**, and 0.395 Å for **5Zn**. The mean plane deviations of porphyrins from the 4N plane are 0.386 Å for **3Ni**, 0.158 Å for **3H$_2$**, 0.333 Å for **5Ni**, and 0.180 Å for **5Zn**. In **3Ni** and **5Ni**, the macrocycle takes a ruffled conformation, as is often seen in nickel porphyrins. The pyridyl groups are rather coplanar (ca. 1−11°) to the adjacent pyrrole units in the porphyrin core. The coordination mode of the platinum centers of **5M** is square planar and that of **3M** is octahedral. The bond lengths around the Pt atom are listed in Table 1. Although C69−Pt bond lengths of **3M** and **5M** are almost the same, C20−Pt bond lengths of **3M** are slightly longer than those of **5M**. This fact indicates repulsion between the Cl ion and $\pi$ orbitals of the ligand.

The UV−vis absorption spectra of **2Ni**, **3Ni**, and **5Ni** in CH$_2$Cl$_2$ are shown in Figure 2. The spectrum of **5Ni** exhibits a substantial red shift as compared to that of **2Ni** ($\Delta\lambda = 64$ nm for the Q bands), which is mainly due to expansion of conjugation by the forced coplanarity of the pyridyl group and the porphyrin core. Although the absorption spectrum of **3Ni** also exhibits a red shift as compared to that of **2Ni**, the spectrum is substantially more blue-shifted than that of **5Ni** ($\Delta\lambda = 20$ nm for the Q bands). The same tendency is also observed between **3M** and **5M** (M = Cu, Zn, H$_2$; see the Supporting Information). The result can be accounted for by the difference in the electron density between Pt$^{II}$ and Pt$^{IV}$ atoms. The electron-rich Pt$^{II}$ atom raises the highest occupied molecular orbital (HOMO) energy of the porphyrin macrocycles to a higher level than the less electron-rich Pt$^{IV}$ atom, while the energy levels of $\pi^*$ orbitals are similar. Thus, the optical energy gaps of **5M** are narrower than those of **3M**. In fact, the difference of the lowest unoccupied molecular orbital energy between **3Ni** and **5Ni** obtained by density functional theory calculations is smaller (0.25 eV) than that of the HOMO energy (0.39 eV) (see the Supporting Information).

In conclusion, the synthesis of DMF-appended cyclometalated platinum(II) and -(IV) porphyrins was achieved. This is the first example of double cleavage of sp$^2$ C−H and sp$^3$ C−H bonds on one metal center. The synthesis of other types of peripherally cyclometalated porphyrins toward reaction catalysts or functional materials is currently underway in our laboratory.

**Acknowledgment.** This work was supported by Grant-in-Aid for Scientific Research on Priority Areas (No. 20037034, "Chemistry of Concerto Catalysis") from MEXT, Japan. S.Y. appreciates the JSPS Research Fellowships for Young Scientists.

**Supporting Information Available:** General procedures, spectral data for compounds, absorption spectra, and CIF files for the X-ray analysis of **3Ni**, **3H**, **4**, **5Ni**, and **5Zn**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC8019149

---

(12) Crystallographic data for **3Ni**: $C_{70}H_{80}Cl_2N_6NiOPt\cdot 3C_6H_5Cl$, $M_w = 1683.75$, triclinic, space group $P\bar{1}$ (No. 2), $a = 14.277(4)$ Å, $b = 16.450(5)$ Å, $c = 17.619(4)$ Å, $\alpha = 89.353(12)°$, $\beta = 78.992(11)°$, $\gamma = 85.740(12)°$, $V = 4051(2)$ Å$^3$, $Z = 2$, $D_{calc} = 1.380$ Mg/cm$^3$, $T = 90$ K, $R = 0.0521$ [$I > 2.0\sigma(I)$], $R_w = 0.1396$ (all data), GOF = 1.047 [$I > 2.0\sigma(I)$]. Crystallographic data for **3H$_2$**: $C_{70}H_{82}Cl_2N_6OPt\cdot 4C_6H_5Cl$, $M_w = 1739.61$, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.117(5)$ Å, $b = 16.014(5)$ Å, $c = 31.276(5)$ Å, $\alpha = 78.593(5)°$, $\beta = 89.631(5)°$, $\gamma = 74.974(5)°$, $V = 4318(5)$ Å$^3$, $Z = 2$, $D_{calc} = 1.338$ Mg/cm$^3$, $R = 0.0465$ [$I > 2.0\sigma(I)$], $R_w = 0.1335$ (all data), GOF = 1.147 [$I > 2.0\sigma(I)$]. Crystallographic data for **5Ni**: $C_{70}H_{80}N_6NiOPt\cdot 1.5C_4H_8O_2$, $M_w = 1407.36$, triclinic, space group $P\bar{1}$ (No. 2), $a = 11.816(5)$ Å, $b = 17.236(5)$ Å, $c = 19.442(5)$ Å, $\alpha = 115.141(5)°$, $\beta = 100.801(5)°$, $\gamma = 93.685(5)°$, $V = 3475(2)$ Å$^3$, $Z = 2$, $D_{calc} = 1.345$ Mg/cm$^3$, $R = 0.0453$ [$I > 2.0\sigma(I)$], $R_w = 0.1094$ (all data), GOF = 1.027 [$I > 2.0\sigma(I)$]. Crystallographic data for **5Zn**: $C_{73}H_{87}N_6O_2PtZn\cdot C_3H_8O\cdot 2CHCl_3$, $M_w = 1639.78$, triclinic, space group $P\bar{1}$ (No. 2), $a = 11.446(4)$ Å, $b = 14.031(4)$ Å, $c = 25.134(6)$ Å, $\alpha = 82.391(9)°$, $\beta = 81.968(11)°$, $\gamma = 78.623(12)°$, $V = 3895(2)$ Å$^3$, $Z = 2$, $D_{calc} = 1.398$ Mg/cm$^3$, $R = 0.0544$ [$I > 2.0\sigma(I)$], $R_w = 0.1505$ (all data), GOF = 1.048 [$I > 2.0\sigma(I)$].