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COMMUNICATIONS

Published on Web 03/18/2008

Regioselective β-Metalation of *meso*-Phosphanylporphyrins. Structure and Optical Properties of Porphyrin Dimers Linked by Peripherally Fused Phosphametallacycles

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Peripherally metalated porphyrins bearing a carbon−metal σ-bond play a crucial role in transition-metal-catalyzed functionalization of porphyrin rings.[1] This class of compounds should also provide valuable information on electronic communication between the porphyrin π-system and the metal d orbitals attached at the periphery. Arnold and co-workers investigated the structures and fundamental properties of *meso*-η^1-palladio- and platinioporphyrins, which were prepared by oxidative addition of the corresponding zerovalent metals to C−Br bonds of *meso*-bromoporphyrins.[2] Recently, Osuka, Shinokubo, and co-workers synthesized the pincer-type *meso*-η^1-palladioporphyrins via *meso*-C−H activation directed by two neighboring 2-pyridyl groups.[3] However, the number of structurally characterized examples, especially those containing a β-C−M bond,[4,5] is still limited. Here we report the first examples of β-η^1-palladio- and platinioporphyrins, which are formed by regioselective metalation at the β carbon of *meso*-phosphanylporphyrins.[6] Most importantly, the coplanar porphyrin dimers linked by peripherally fused phosphametallacycles have been found to exhibit characteristic optical and electrochemical properties derived from the $p_\pi-d_\pi$ orbital interaction.

The Pd-catalyzed C−P cross-coupling reaction of *meso*-iodoporphyrins **1a**,**b**[1c,e] with diphenylphosphane in MeCN−THF produced the corresponding *meso*-phosphanylporphyrins **2a**,**b** as air-sensitive substances (Scheme 1). For instance, **2a** was oxidized rapidly in air to *meso*-phosphorylporphyrin **3a**.[7] Due to difficulty of isolating **2a**,**b** at this stage, the crude reaction mixtures were subsequently treated with elemental sulfur, affording *meso*-thiophosphorylporphyrins **4a**,**b** as air-stable solids in 87−92% yields based on **1a**,**b**. Desulfurization of **4a**,**b** with excess $P(NMe_2)_3$ in refluxing toluene reproduced **2a**,**b** quantitatively. Remarkably, this two-step protocol enabled us to isolate pure **2a**,**b** in 90−95% isolated yields (based on **4a**,**b**) by simple reprecipitation under inert atmosphere.[8]

Treatment of **2a**,**b** with palladium(II) and platinum(II) salts yielded novel classes of porphyrin dimers **5**−**7**, which contain two phosphametallacycle linkages as depicted in Figure 1 and Scheme S1 (Supporting Information). The complexation of **2a** with 0.5 equiv of $Pd(OAc)_2$ in toluene afforded Pd-mononuclear complex **5a** and bis-μ-acetato-bridged Pd-dinuclear complex **6a** in 55% and 23% yield, respectively (Table 1, entry 1). When **2a** was slowly added to a toluene solution of 1 equiv of $Pd(OAc)_2$, **6a** was formed predominantly in 73% yield (entry 2). By contrast, **2b** reacted with 0.5 equiv of $Pd(OAc)_2$ to produce Pd-mononuclear complex **5b** exclusively (entry 3). The complexation of **2a** with 0.5 equiv of $PtCl_2(cod)$ (cod = 1,5-cyclooctadiene) in the presence of Et_3N gave

Scheme 1. Synthesis and Reactions of *meso*-Phosphanylporphyrins

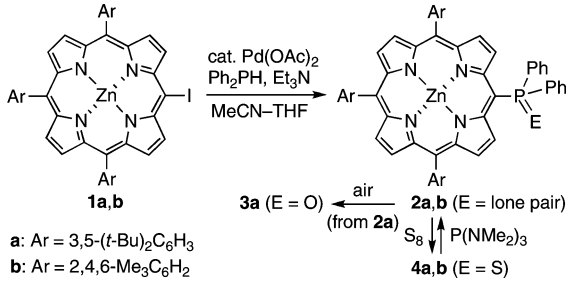

Table 1. Complexation of **2a**,**b** with Pd(II) and Pt(II) Salts

entry	**2**	MX_2·L/solvent	**2**/MX_2	product (yield[a])
1	**2a**	$Pd(OAc)_2$/toluene	1/0.5	**5a** (55%), **6a** (23%)
2	**2a**	$Pd(OAc)_2$/toluene	1/1	**5a** (trace), **6a** (73%)
3	**2b**	$Pd(OAc)_2$/toluene	1/0.5	**5b** (70%)
4[b]	**2a**	$PtCl_2(cod)/CH_2Cl_2$	1/0.5	**7a** (62%)

[a] Isolated yield based on **2a**,**b**. [b] Et_3N was added.

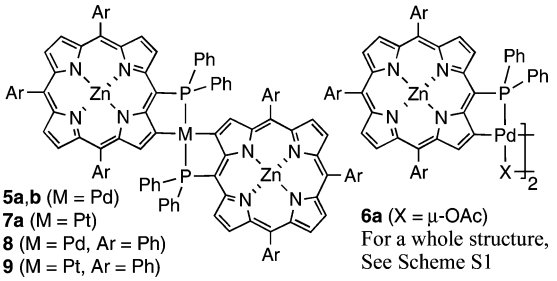

Figure 1. Structures of β-η^1-palladio- and platinioporphyrins **5**−**9**.

Pt-mononuclear complex **7a** in 62% yield (entry 4). All the products were fully characterized by MS and NMR spectroscopies. In the MS spectra, intense molecular ion peaks were detected. The ^{31}P NMR spectra displayed single peaks at δ 46.7−51.1,[8] indicating that two phosphorus atoms coordinate to the palladium or platinum center equivalently. The $^{31}P-^{195}Pt$ coupling constant of 2834 Hz observed for **7a** suggests that the two phosphine ligands are coordinated in a trans geometry. The appearance of seven kinds of peripheral β protons (each 2H) in the ^1H NMR spectra of **5**−**7** reveals that one of the β-H atoms of the porphyrin ring is replaced by the Pd(II) or Pt(II) salt through the complexation (Figures S24−S27, Supporting Information). It is likely that the *meso*-phosphanyl group directs the P-ligated metal center to activate the neighboring β-C−H bond regioselectively.

The structure of **5b** was unambiguously elucidated by X-ray crystallography.[9] As shown in Figures 2 and S1 (Supporting

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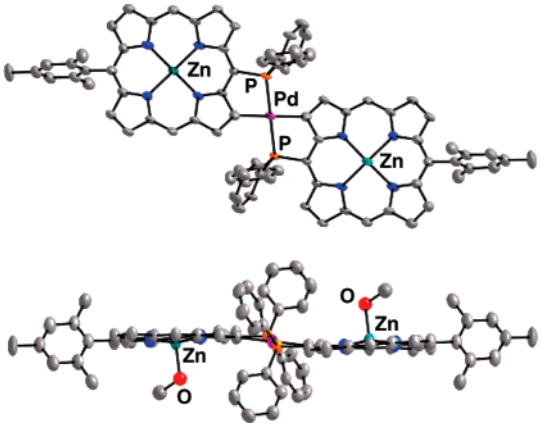

Figure 2. Top view (upper) and side view (lower) of **5b**. Hydrogen atoms, 10,20-*meso*-aryl groups, solvents, and MeOH (top view) are omitted for clarity: Pd−C_β, 2.046(4) Å; Pd−P, 2.2904(14) Å; C_β−Pd−P, 81.84(11)° and 98.16(11)°; Pd−P−C_{meso}, 104.85(13)°.

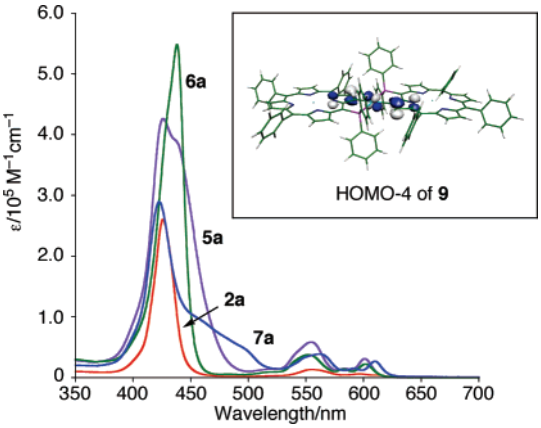

Figure 3. UV−vis absorption spectra of **2a** (red), **5a** (purple), **6a** (green), and **7a** (blue) in toluene. The inset shows HOMO-4 of **9**.

Information), the Pd center in the phosphapalladacycles adopts a distorted square planar geometry ($\Sigma_{C-Pd-P} = 360°$) with C_i symmetry. As a consequence, two porphyrin rings are almost on the same plane with a Zn−Zn distance of 12.1 Å.[10] The Pd−C bond length [2.046(4) Å] of **5b** is comparable to the reported value [2.05(2) Å] of Arnold's *meso*-η^1-palladioporphyrin[2a] and longer than those [1.969(6)−1.977(7) Å] of Osuka's pincer-type *meso*-η^1-palladioporphyrins.[3]

The UV−vis absorption spectra of phosphanylporphyrin **2a** and the Pd-dinuclear complex **6a** displayed relatively narrow Soret bands at λ_{max} 426 and 438 nm, respectively (Figures 3 and S2, Supporting Information). In sharp contrast, the Pd- and Pt-mononuclear complexes **5a** and **7a** showed rather broad absorptions at the Soret-band regions (λ_{max} = 426 and 422 nm). To gain a deep insight into the character of these transitions, we performed time-dependent density functional theory (TD-DFT) calculations of their model complexes **8** and **9** and 5,10,15,20-tetraphenylporphyrinatozinc(II) (TPPZn) (Figures S3−S14 and Tables S1−S4, Supporting Information). Notably, the excitations from HOMO-4 largely contribute to Soret bands of **8** and **9**, which are split or broadened as compared to that calculated for TPPZn, although the calculated excitation energies are somewhat larger than the observed values.[11] As visualized in Figures S5−S8 (Supporting Information) and 3 (inset), the HOMO-4 in **8** and **9** involves antibonding character between the pyrrolic p_π orbitals and the metal d_π orbital, which implies possible electronic communication between the coplanar porphyrin π systems through the peripheral β-C−M bonds. Indeed, cyclic voltammograms of **5a** and **7a** displayed appreciably broadened or split cathodic and anodic waves for their electrochemical oxidation processes (Figure S19, Supporting Information),[12] suggesting that the π-radical cations delocalize over the metal-linked two porphyrin rings. The relatively large splitting potential (ΔE_{ox} = 0.06 V) observed for **7a** indicates that the delocalization between the Pt-linked porphyrin π systems occurs more efficiently than that between the Pd-linked π systems.

In summary, we have successfully applied the phosphane-directed regioselective β-C−H activation by Pd(II) and Pt(II) salts to the synthesis of new classes of porphyrin dimers linked by the peripherally fused phosphametallacycles. The present results demonstrate that the p_π−d_π orbital interaction at the peripheral β-carbon−metal bond potentially affects the optical and electrochemical properties of the metal-linked coplanar porphyrin π systems.

Acknowledgment. This work was partially supported by Grants-in-Aid (No. 17350018 and No. 461) from the Ministry of Education, Culture, Sports, Science and Technology of Japan. We thank Dr. Motoo Shiro for X-ray crystallography.

Supporting Information Available: Experimental details, CIF file for **5b**, and DFT computational results. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) δ_P (162 MHz; $CDCl_3$ or CD_2Cl_2) of **2a**, **2b**, **5a**, **5b**, **6a**, and **7a** are −5.4, −6.0, 51.1, 48.6, 50.5, and 46.7 (^1J_P−Pt = 2834 Hz), respectively.

(9) $C_{140}H_{134}N_8O_4P_2PdZn_2$, *P*1, a = 11.030(5) Å, b = 16.207(8) Å, c = 16.613-(8) Å, α = 97.695(8)°, b = 91.885(8)°, γ = 98.247(9)°, V = 2909(2) Å^3, Z = 1, D_c = 1.308 g cm^{-3}, 13199 obsd, 764 variables, R_w = 0.1690, R = 0.0691 (I>2.00$\sigma(I)$), GOF = 1.064. Although the quality of crystallographic data is not at the publishable level, a similar planar structure of **7a** was confirmed by X-ray diffraction analysis.

(10) The zinc atom is deviated from the 24-atom mean plane (0.32 Å) due to the coordination by the methanol-oxygen.

(11) The calculated wavelengths of Soret bands are red-shifted when solvation effects are incorporated. In a Zn analog of **8**, the splitting of Soret band becomes much smaller, indicating that the p_π−d_π orbital interaction between porphyrin and bridging Pd atom is important to lead to a broad Soret band of **8**. For details, see the Supporting Information.

(12) E_{ox} and E_{red} (vs Fc/Fc$^+$; in CH_2Cl_2 with 0.1 M nBu$_4$N$^+$PF$_6^-$; Ag/Ag$^+$ [0.01 M $AgNO_3$ (MeCN)]): +0.35/+0.60 V and −1.82 V for **5a**; +0.42/+0.67 V and −1.71 V for **6a**; +0.31/+0.37/+0.57 V and −1.83 V for **7a**.

JA710542E