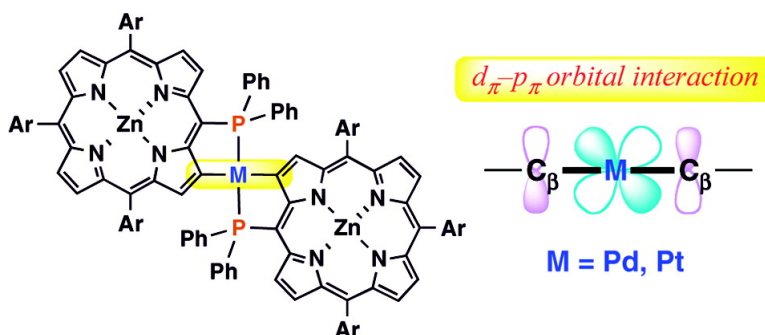


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Regioselective β -Metalation of *meso*-Phosphanylporphyrins. Structure and Optical Properties of Porphyrin Dimers Linked by Peripherally Fused Phosphametallacycles

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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 platinoporphyryns, which were prepared by oxidative addition of the corresponding zerovalent metals to C–Br bonds of *meso*-bromoporphyryns.² Recently, Osuka, Shinokubo, and co-workers synthesized the pincer-type *meso*- η^1 -palladioporphyryns 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 platinoporphyryns, which are formed by regioselective metalation at the β carbon of *meso*-phosphanylporphyryns.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_π – d_π orbital interaction.

The Pd-catalyzed C–P cross-coupling reaction of *meso*-iodoporphyryns **1a,b**^{1c,e} with diphenylphosphane in MeCN–THF produced the corresponding *meso*-phosphanylporphyryns **2a,b** as air-sensitive substances (Scheme 1). For instance, **2a** was oxidized rapidly in air to *meso*-phosphorylporphyryn **3a**.⁷ Due to difficulty of isolating **2a,b** at this stage, the crude reaction mixtures were subsequently treated with elemental sulfur, affording *meso*-thiophosphorylporphyryns **4a,b** as air-stable solids in 87–92% yields based on **1a,b**. Desulfurization of **4a,b** with excess P(NMe₂)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 PtCl₂(cod) (cod = 1,5-cyclooctadiene) in the presence of Et₃N gave

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

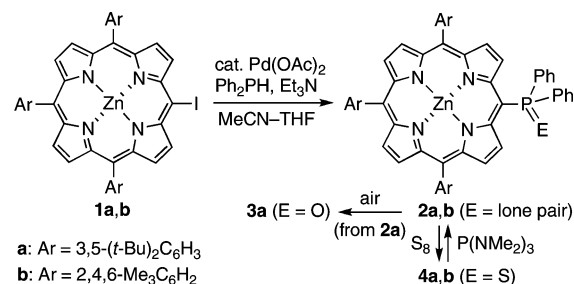


Table 1. Complexation of **2a,b** with Pd(II) and Pt(II) Salts

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 ₂ Cl ₂	1/0.5	7a (62%)

^a Isolated yield based on **2a,b**. ^b Et₃N was added.

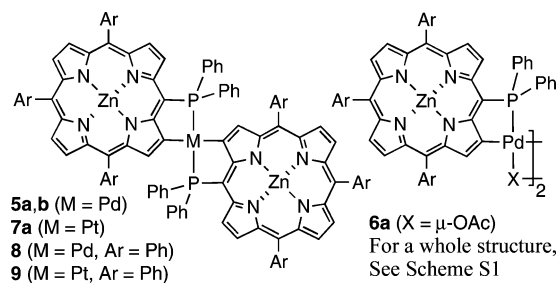


Figure 1. Structures of β - η^1 -palladio- and platinoporphyryns **5–9**.

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 ³¹P 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 ³¹P–¹⁹⁵Pt 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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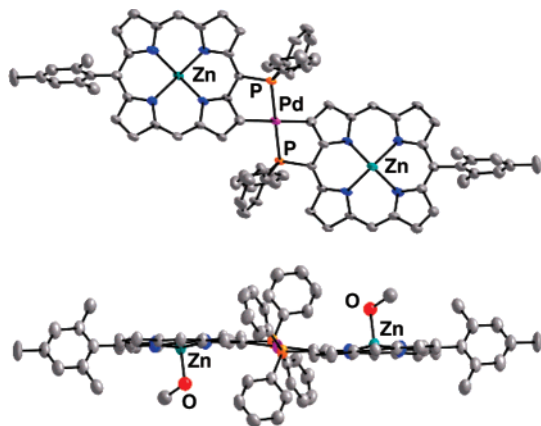


Figure 2. Top view (upper) and side view (lower) of **5b**. Hydrogen atoms, 10,20-*meso*-aryl groups, solvents, and MeOH (top view) are omitted for clarity: Pd–C $_{\beta}$, 2.046(4) Å; Pd–P, 2.2904(14) Å; C $_{\beta}$ –Pd–P, 81.84(11) $^{\circ}$ and 98.16(11) $^{\circ}$; Pd–P–C $_{meso}$, 104.85(13) $^{\circ}$.

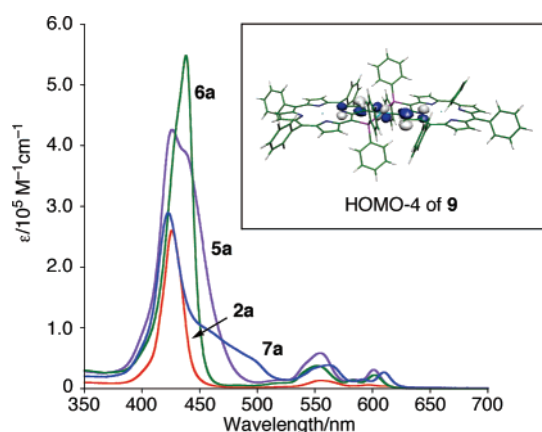


Figure 3. UV-vis absorption spectra of **2a** (red), **5a** (purple), **6a** (green), and **7a** (blue) in toluene. The inset shows HOMO-4 of **9**.

Information), the Pd center in the phosphapalladacycles adopts a distorted square planar geometry ($\Sigma_{C-Pd-P} = 360^{\circ}$) 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 ($\lambda_{max} = 426$ 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 ($\Delta E_{ox} = 0.06$ 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.

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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 $_2$ Cl $_2$) of **2a**, **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 $_8$ O $_4$ P $_2$ PdZn $_2$, PI , $a = 11.030(5)$ Å, $b = 16.207(8)$ Å, $c = 16.613(8)$ Å, $\alpha = 97.695(8)^{\circ}$, $\beta = 91.885(8)^{\circ}$, $\gamma = 98.247(9)^{\circ}$, $V = 2909(2)$ 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 $_2$ Cl $_2$ with 0.1 M n Bu $_4$ 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**.

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