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Synthesis and Catalytic Activities of Porphyrin-Based PCP Pincer Complexes**

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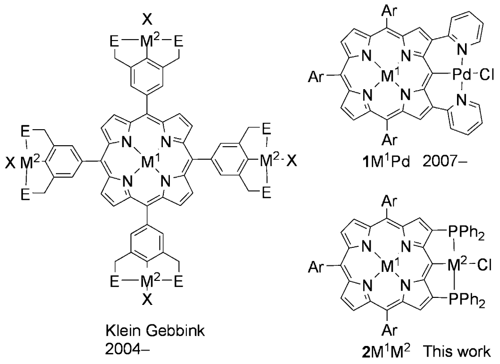
***Abstract:** 2,18-Bis(diphenylphosphino)porphyrins undergo peripheral cyclometalation with group 10 transition-metal salts to afford the corresponding porphyrin-based PCP pincer complexes. The porphyrinic plane and the PCP-pincer unit are apparently coplanar, with small strain. The catalytic activities of the porphyrin-based pincer complexes at the periphery were investigated in the allylation of benzaldehyde with allylstannane and in the 1,4-reduction of chalcone to discover the electronic interplay between the inner metal and the outer metal in catalysis.*



Whereas a porphyrin scaffold usually accommodates a metal in its inner cavity to alter its electronic and structural properties, porphyrins bearing a porphyrinic carbon–transition metal σ bond on the periphery have been emerging as a new class of porphyrin complexes.[1–3] They are not only structurally novel but also intriguing to investigate because of the electronic interplay between the inner metal and the outer metal.[2b,e,h,3a,b]

Many conventional porphyrin/transition metal complexes show important catalytic activities such as oxygenation.[4] In contrast, the catalytic activities of peripherally metalated porphyrins remain unexplored.[1] Among peripherally metalated porphyrins, porphyrin-based pincer complexes have been attracting attention because of the chemical stabilities, physicochemical properties, and catalytic activities of pincer structures.[5]

In pioneering work, Klein Gebbink et al. synthesized porphyrins which have meso aryl substituents bearing a pincer unit (E = coordinating heteroatom, Ar = 3,5-tBu$_2$C$_6$H$_3$ throughout the manuscript).[6] After their interesting reports about the indirectly peripherally metalated porphyrin pincer complexes, we reported the synthesis of the NCN pincer palladium complexes **1**M^{1}Pd as the first porphyrin-based pincer complexes wherein the palladium is directly attached to a porphyrinic carbon atom.[3a] Both groups found that the catalytic activities of the pincer complexes in the Heck reaction depend on the inner metal, and thus implies electronic interplay between the inner metalloporphyrin core and the outer palladium pincer units.[7]

Despite the observations that imply inner and outer electronic interplay, the mechanism of the Heck reaction catalyzed by a pincer palladium complex has been under intense debate. Many researchers suggested that pincer palladium complexes are most likely to act simply as precursors of highly active palladium(0) colloids at higher temperatures in the Heck reaction.[8] In other words, **1**M^{1}Pd would be structurally labile under the reaction conditions and result in irreversible dissociation of the porphyrinic C–Pd σ bond. Thus, there are no distinct reports on the catalytic activity of porphyrin-based pincer complexes with regard to electronic interplay between the inner metal and the outer metal.[9,10]

The structures of the NCN pincer complexes **1**M^{1}Pd are significantly distorted because of the fused six-membered rings with long C–Pd and N–Pd bonds, as well as the rigid square-planar geometry of the palladium center.[3a] In pursuit of peripherally metalated porphyrins that are catalytically active without considerable decomposition, we have now developed the porphyrin-based PCP pincer complexes **2**M^{1}M^2. The PCP pincer unit of **2**M^{1}M^2 consists of two fused five-membered rings and is hence expected to take a less biased conformation. As phosphines represent the most popular ligands for transition-metal catalysts, we envisioned more possibilities for **2**M^{1}M^2 to serve as catalysts, but not as merely a metal source.

The synthesis of the pincer ligand **4**M^1 (M^1 = Ni and Zn) was achieved through palladium-catalyzed phosphination[11] of the porphyrinyl ditriflate **3**M^1 (Scheme 1). We were anxious about possible oxidation of the trivalent phosphines to phosphine oxides in air. Indeed, **4**Zn is sensitive to air and was gradually oxidized in solution, thus leading to a decreased

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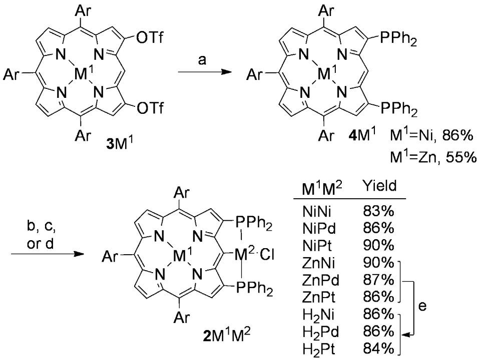


3M^{1} **4M^{1}** **2M^{1}M^{2}**

M^{1}M^{2}	Yield
NiNi	83%
NiPd	86%
NiPt	90%
ZnNi	90%
ZnPd	87%
ZnPt	86%
H$_2$Ni	86%
H$_2$Pd	86%
H$_2$Pt	84%

Scheme 1. Synthesis of porphyrin-based PCP pincer complexes. a) 5 equiv HPPh$_2$, 20 mol% Pd(OAc)$_2$, 20 mol% dppb, 10 equiv NEt$_3$, DMF, 90 °C, 12 h; b) 1.1 equiv [NiCl$_2$(PPh$_3$)$_2$], 1.1 equiv NaOAc, toluene, 110 °C, 24 h; c) 1.1 equiv [PdCl$_2$(MeCN)$_2$], 1.1 equiv NaOAc, toluene, 80 °C, 3 h; d) 1.1 equiv K$_2$PtCl$_4$, 1.1 equiv NaOAc, toluene/DMF, 100 °C, 10 h; e) TFA/CH$_2$Cl$_2$, 20 °C, 10 min.

yield of **4**Zn. However, **4**Ni is stable in air and can be handled without special care, and its structure has been confirmed by X-ray diffraction analysis (see Figure S36). The porphyrin **4**Ni exhibits a Soret band at $\lambda = 427$ nm, which is red-shifted by 18 nm from the parent β-unsubstituted Ni^{II} porphyrin because of the influence of β,β-diphosphination (see Figure S33). The following cyclometalation with soluble group 10 metal salts proceeded smoothly in the presence of sodium acetate as a base. The bimetallic pincer complexes **2**M^{1}M^{2} were isolated as stable solids in good yields by recrystallization. Freebase porphyrin pincer complexes (**2**H$_2$M^{2}) were obtained by selective removal of the inner zinc of **2**ZnM^{2} under acidic conditions, which underscores the robustness of the PCP pincer structure.

The structures of **2**NiM^{2} were unambiguously determined by X-ray crystallographic analysis (Figure 1 for **2**NiPd, Figures S37 and S39 for **2**NiNi and **2**NiPt, respectively). The porphyrinic plane and the PCP pincer unit are flat and, especially for **2**NiPd, constitute an almost perfect plane, which is in sharp contrast to the previous NCN pincer complexes having highly distorted structures.[3a] The porphyrinic C–P bonds are directed inward to the outer metal because of strong coordination, with P1-C1-C2 and P2-C5-C4 angles of 114.24(14)° for both in **2**NiPd. The length of the C3–Pd bond is 2.014(3) Å, which is apparently longer than that of our previous NCN pincer palladium complex[3a] [1.977(7) Å] and is similar to that of the closely related anthracene-based PCP pincer palladium complex[12] [2.010(5) Å].

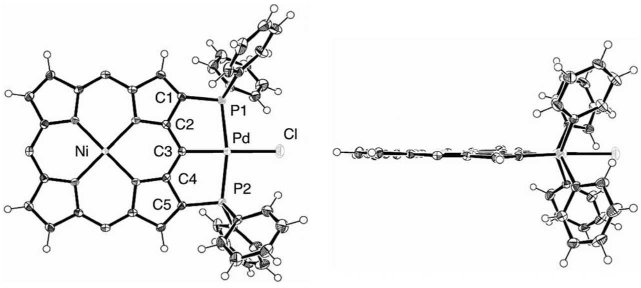


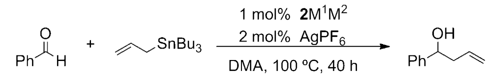
Figure 1. ORTEP drawings of **2**NiPd. Thermal ellipsoids represent 50% probability. The meso aryl groups are omitted for clarity.

Electronic perturbations induced by the outer metals were investigated through UV/Vis absorption spectroscopy (Figure S33). Compared to the parent bidentate ligand **4**Ni, palladium (**2**NiPd) and platinum (**2**NiPt) pincer complexes exhibit similar yet enhanced and red-shifted Soret bands, which could be ascribed to their more rigid conformations. In contrast, the homobimetallic nickel complex **2**NiNi displays a broad and largely split Soret band at $\lambda = 397$ and 458 nm and the most red-shifted Q-band. Since **2**NiM^{2} are structurally similar (see Figures S37–S39 in the Supporting Information), the unique absorption of **2**NiNi is attributable to a rather strong interaction between the outer nickel d orbitals and the porphyrinic π orbitals.[13]

Pincer complexes are known to have a wide spectrum of catalytic activity.[5] In exploring the catalytic activity of porphyrin-based pincer complexes which sustain their pincer structures during catalytic cycles, we firstly selected catalytic allylation of benzaldehyde with allyltributyltin[14] as a model reaction. Unlike the Heck reaction, the allylation is known to proceed by maintaining the valence of the transition metal during the catalytic cycle and without significant decomposition of the catalyst.[14b,15] Therefore, we considered that the allylation an ideal reaction to investigate the genuine catalytic activity of porphyrin-based pincer complexes.

The allylation indeed occurred in the presence of **2**M^{1}M^{2} (Table 1). Additions of AgPF$_6$ are essential for generating catalytically active cationic pincer complexes by removal of the chloride on M^{2}. The allylation that was catalyzed by **2**NiNi or **2**H$_2$Ni did not go to completion because of decomposition of the catalysts during the reaction. With these two exceptions, the other **2**M^{1}M^{2} catalysts were robust enough to complete the allylation and exhibited very similar catalytic activities regardless of the inner and outer metals.

Table 1: Allylation of benzaldehyde with allyltin catalyzed by **2**M^{1}M^{2}.



2M^{1}M^{2}	Yield [%][a]	**2**M^{1}M^{2}	Yield [%][a]	**2**M^{1}M^{2}	Yield [%][a]
2NiNi	68	**2**ZnNi	90	**2**H$_2$Ni	70
2NiPd	95	**2**ZnPd	97	**2**H$_2$Pd	94
2NiPt	95	**2**ZnPt	88	**2**H$_2$Pt	93

[a] Yields are those of isolated products.

According to Szabó's report,[14b] the allylation should begin with the formation of the cationic pincer complex by means of AgPF$_6$ (see Scheme S1). The catalytic cycle of the allylation consists of a) transmetalation between allyltributyltin and the cationic pincer complex to form the corresponding η^{1}-allyl M^{2} complex and Bu$_3$SnPF$_6$, b) allylation of the aldehyde with the η^{1}-allyl M^{2} complex through a six-membered cyclic transition state to form the corresponding group 10 metal homoallyloxide, and c) alkoxide exchange with Bu$_3$SnPF$_6$ to form tributyltin homoallyloxide and to regenerate the initial cationic pincer complex. The similar behavior of **2**M^{1}M^{2} in the catalytic activities regardless of the inner and outer metals implies that the inner and outer metals

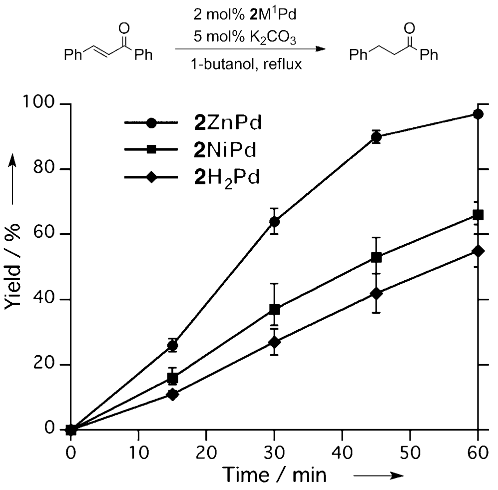


Figure 2. Effect of inner metals on 1,4-reduction catalyzed by **2**M^1Pd. Each reaction was performed three times under the same reaction conditions. The top and bottom of each error bar indicate the highest and lowest yields, respectively. The line plots were made with the average yields of the three runs.

have only little influence in the rate-limiting step[16] of the three steps.

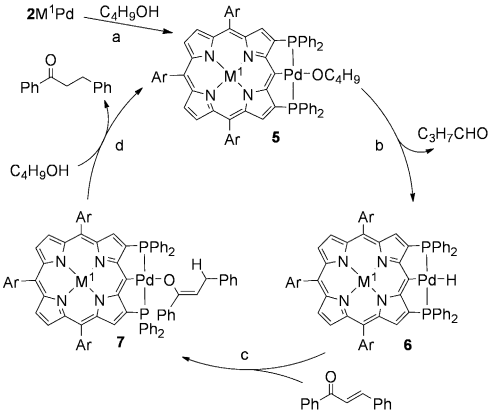
We have also found that the palladium complexes **2**M^1Pd catalyze 1,4-reduction of chalcone in 1-butanol through transfer hydrogenation.[17] Interestingly, the catalytic activities depend on the inner metals. Notably, **2**ZnPd showed the highest catalytic activity among the three **2**M^1Pd complexes (Figure 2) as well as all of the pincer complexes reported so far.[17] Notably, the presence of elemental mercury had no influence on the 1,4-reduction. In addition, the reduction did not take place when either $[PdCl_2(PPh_3)_2]$, $[Pd_2(dba)_3]$, or $Pd(OAc)_2$ was used instead of **2**M^1Pd. These experimental results indicate that the pincer complexes, and not palladium colloids, have catalytic activity.

To reveal the origin of the interesting electronic interplay between the inner metal and the outer palladium in the 1,4-reduction, we looked to the electronic nature of the palladium pincer complexes for clues. We measured the oxidation potentials of the complexes by cyclic voltammetry (see Table 2 and Figure S41). It is clear that **2**ZnPd is much more readily oxidized than **2**NiPd and **2**H_2Pd and that the oxidation potentials of **2**NiPd and of **2**H_2Pd are similar. This trend (**2**ZnPd > **2**NiPd ≈ **2**H_2Pd) parallels the catalytic activities of the three outer palladium complexes (Figure 2). The electron-rich nature of **2**ZnPd or the ligand **4**Zn would be mainly responsible for its highest catalytic activity.

Table 2: Oxidation potentials of **2**M^1Pd.[a]

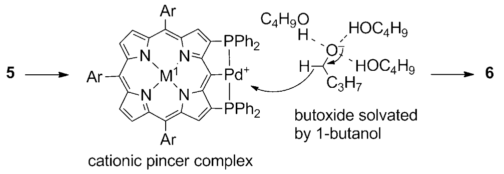
2M^1Pd	$E^{1/2}_{ox1}$ [V]	$E^{1/2}_{ox2}$ [V]
2ZnPd	0.26	0.73
2NiPd	0.51	0.91
2H_2Pd	0.41	1.01

[a] Potentials vs ferrocene/ferrocenium cation. In CH_2Cl_2. Scan rate, 0.2 $V s^{-1}$. Working electrode: Pt. Counter electrode: Pt wire. Supporting electrolyte: 0.1 M Bu_4NPF_6.



Scheme 2. Plausible mechanism of 1,4-reduction according to the report of Szabó et al.

As shown in Scheme 2, the reaction mechanism of the 1,4-reduction would comprise a) formation of the palladium butoxide **5** from **2**M^1Pd, b) generation of the palladium hydride **6** with concomitant elimination of butanal, c) 1,4-reduction to form the palladium enolate **7**, and d) protonation of **7** with 1-butanol to complete the catalytic cycle. It is not easy to identify the rate-limiting step in our system because the rate of each step depends on reaction conditions. Alternatively, to discuss the electronic interplay between the inner metal and the outer palladium, the most closely related and reliable information may come from the thoughtful mechanistic analysis, by Goldberg and co-workers, on the behaviors of PCP pincer palladium alkoxide complexes.[17b] According to Goldberg's report, the generation of a palladium hydride pincer complex from the corresponding palladium alkoxide complex should be slow and proceed through an alcohol-promoted dissociative β-hydride abstraction mechanism[18] (Scheme 3). The dissociative mechanism involves the formation of the cationic pincer complex. We assume that the electron-rich nature of **2**ZnPd or **4**Zn would facilitate the solvation-assisted formation of the cationic complex through stabilizing the cation, which leads to the highest activity of **2**ZnPd.



Scheme 3. Formation of palladium hydride through alcohol-promoted dissociative β-hydride abstraction.

In conclusion, we have synthesized a family of new peripherally metalated porphyrins, that is, porphyrin-based PCP pincer complexes bearing a meso carbon–metal σ bond. The complexes take rather unbiased and flat geometry. The legitimate catalytic activities of **2**M^1M^2 were investigated in the allylation of benzaldehyde with allylstannane and in the 1,4-reduction of chalcone. In the latter catalytic reaction, the apparent electronic interplay within **2**M^1Pd in the catalysis was observed for the first time. Development of new peripherally metalated porphyrin catalysts, by taking advantage of the electronic effect of inner metals, is under way.

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