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Synthesis and Genuine Catalytic Activities of Porphyrin-based PCP Pincer Complexes

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Supporting Information Placeholder

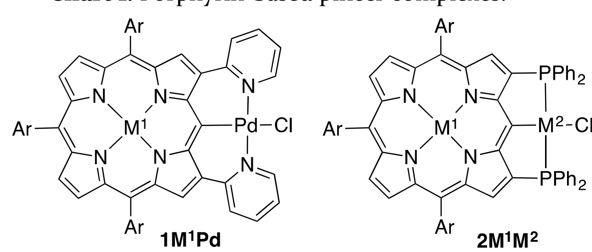
ABSTRACT: 2,18-Bis(diphenylphosphino)porphyrins undergo peripheral cyclometalation with group 10 transition metal salts to afford the corresponding porphyrin-based PCP pincer complexes. The porphyrinic plane and the PCP-pincer unit are apparently coplanar with small strain. The genuine catalytic activities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

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.[1,2,3] They are not only structurally novel but also intriguing to investigate electronic interplay between the inner metal and the outer metal.[2b,e,h,3a,b] In addition, peripherally cyclometalated motifs can serve as linkers in multiporphyrinic assemblies of interest,[2c,h–j,3c,e,] and potent chromophores for luminescent and nonlinear optical mateials.

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.[3h,5,6] We reported the synthesis of porphyrin-based NCN-pincer palladium complexes **1M¹Pd** as the first porphyrin-based pincer complexes[3a,7] (Chart 1, Ar = 3,5-tBu$_2$C$_6$H$_3$ throughout the manuscript). Intriguingly, their catalytic activities in the Heck reaction depended on the inner metal M^1. This activity/inner metal relationship seemed to display the electronic interaction between the inner and outer metals.[8] However, 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.[9] In other words, **1M¹Pd** would be structurally labile under the reaction conditions to result in irreversible dissociation of the porphyrinic C–Pd σ bond. Thus, there are no distinct reports on the genuine catalytic activity of peripherally metalated porphyrins[10] or on electronic interplay between the inner metal and the outer metal in catalysis.[6]

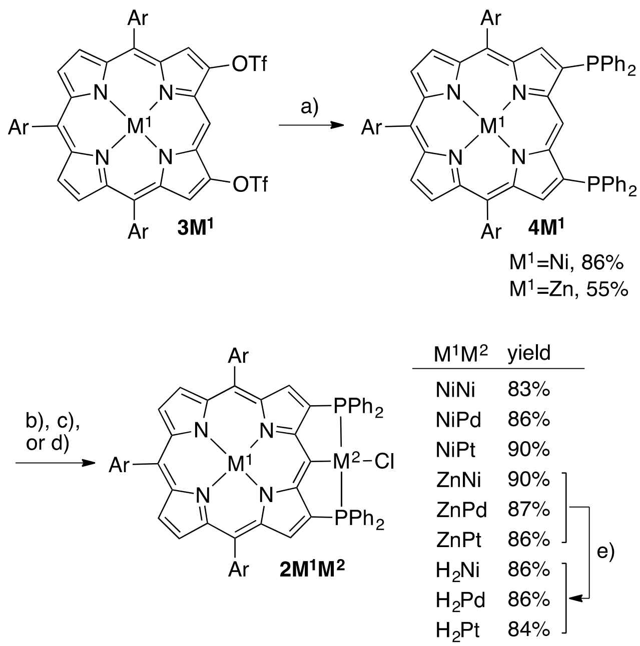
The structures of the NCN pincer complexes **1M¹Pd** are significantly distorted due to the fused six-membered rings with long C–Pd and N–Pd bonds as well as the rigid square planar geometry of the palladium center.[4a] In pursuit of peripherally metalated porphyrins that are catalytically active without considerable decomposition, we have now developed porphyrin-based PCP-pincer complexes **2M¹M²**. The PCP pincer unit of **2M¹M²** 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 ampler possibilities of **2M¹M²** as catalysts but not merely a metal source.

Chart 1. Porphyrin-based pincer complexes.



The synthesis of pincer ligand **4M¹** (M^1 = Ni and Zn) was achieved through palladium-catalyzed phosphination[11] of porphyrinyl ditriflate **3M¹** (Scheme 1). We were anxious about possible oxidation of the trivalent phosphines to phosphine oxides in air. Indeed, **4Zn** is sensitive to air and was gradually oxidized in solution to lead to a decreased yield of **4Zn**. However, **4Ni** is stable in air and can be handled without special care, and its structure has been confirmed by X-ray diffraction analysis (SI). Porphyrin **4Ni** exhibits a Soret band at 427 nm that is red-shifted by 18 nm from the parent Ni(II) porphyrin as an influence of *β,β*-diphosphination. The following cyclometalation with soluble group 10 metal salts proceeded smoothly in the presence of sodium acetate as a base. Bimetallic pincer complexes **2M¹M²** were isolated as stable solids by recrystallization in good yields. Freebase porphyrin pincer complexes **2H₂M²** were obtained by selective removal of the inner zinc of **2ZnM²** under acidic conditions, which underscores the robustness of the PCP-pincer structure.

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_2PtCl_4, 1.1 equiv. NaOAc, toluene/DMF, 100 °C, 10 h; e) TFA/CH_2Cl_2, 20 °C, 10 min.

The structures of **2NiM²** were unambiguously determined by X-ray crystallographic analysis (Figure 1 for **2NiPd** and Figure SXX in SI for **2NiNi** and **2NiPt**). The porphyrinic plane and the PCP-pincer unit are obviously flat together and, especially for **2NiPd**, constitute an almost perfect plane, which is in sharp contrast to the previous NCN-pincer complexes that take highly distorted structures.[3a] The porphyrinic C–P bonds are directed inward to the outer metal due to strong coordination with P1-C1-C2 and P2-C5-C4 angles of 114.25° for both in **2NiPd**. The length of the C3–Pd bond is 2.014 Å, which is apparently longer than that of our previous NCN-pincer palladium complex[3a] (1.977 Å) and is similar to that of the closely related anthracene-based PCP-pincer palladium complex[12] (2.010 Å).

Electronic perturbations induced by the outer metals were investigated through UV/vis absorption spectroscopy (Figure 2). Compared to parent bidentate ligand **4Ni**, palladium and platinum pincer complexes **2NiPd** and **2NiPt** exhibit similar yet enhanced and red-shifted Soret bands, which would be ascribable to their more rigid conformations. In contrast, homobimetallic nickel complex **2NiNi** displays a broad and largely split Soret band at 397 and 458 nm and the most red-shifted Q-band. Since **2NiM²** are structurally similar to other porphyrin pincer complexes Figure SXX in SI), the unique absorption of **2NiNi** is attributable to rather strong interaction between the outer nickel d orbitals and the porphyrinic π orbitals.

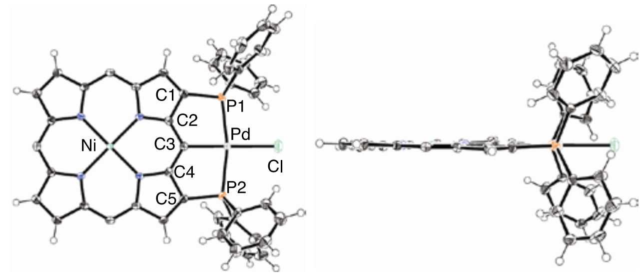


Figure 1. ORTEP Drawings of **2NiPd**. Thermal ellipsoids represent 50% probability. The *meso*-aryl groups are omitted for clarity.

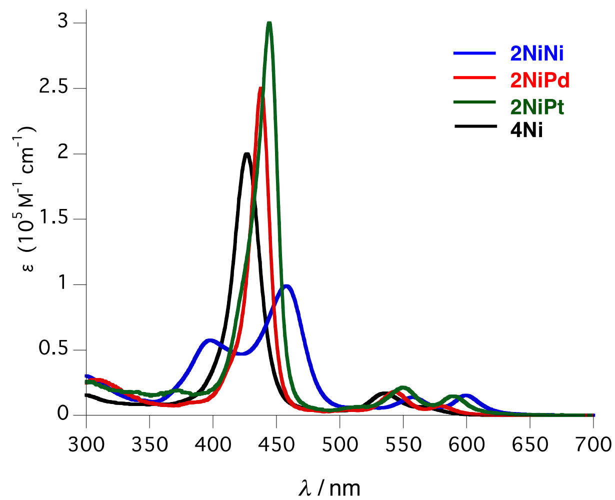
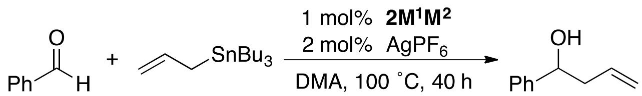


Figure 2. UV/vis absorption spectra of **2NiNi**, **2NiPd**, **2NiPt**, and **4Ni** in dichloromethane.

Pincer complexes are well known to show a wide spectrum of catalytic activity.[7] Seeking after the catalytic activity of porphyrin-based pincer complexes that sustain their pincer structures during catalytic cycles, we firstly selected catalytic allylation of benzaldehyde with allyltributyltin[13] as a model reaction. Different from the Heck reaction, the allylation is known to proceed with keeping the valence of the transition metal during the catalytic cycle and without significant decomposition of the catalyst.[14] Therefore, we considered that the allylation is an ideal reaction to investigate the genuine catalytic activity of porphyrin-based pincer complexes.

The allylation indeed occurred in the presence of **2M¹M²** (Table 1). Additions of $AgPF_6$ are essential to generate catalytically active cationic pincer complexes by removal of the chloride on M². The allylation that was catalyzed by **2NiNi** or **2H₂Ni** did not go to completion due to decomposition of the catalysts during the reaction. With these two exceptions, the other **2M¹M²** were robust enough to complete the allylation and exhibited very similar catalytic activities regardless of the inner and outer metals. It is worth noting that the pincer catalysts **2M¹M²** could be recovered after the reactions. For example, we recovered 72% of **2NiPd** after work-up with brine followed by silica gel column purification and recrystallization. The recyclability indicates that the PCP-pincer complexes served as catalysts with their framework intact under the reaction conditions.

Table 1. Allylation of Benzaldehyde with Allyltin Catalyzed by **2M¹M²**



2M¹M²	Yield	**2M¹M²**	Yield	**2M¹M²**	Yield
2NiNi	68%	**2ZnNi**	90%	**2H₂Ni**	70%
2NiPd	95%	**2ZnPd**	97%	**2H₂Pd**	94%
2NiPt	95%	**2ZnPt**	88%	**2H₂Pt**	93%

We have also found that peripheral palladium complexes **2M¹Pd** catalyze 1,4-reduction of chalcone in 1-butanol through transfer hydrogenation.[15] Interestingly, the catalytic activities have proved to depend on the inner metals. Notably, **2ZnPd** showed the highest catalytic activity not only among three **2M¹Pd** complexes (Figure 3) but also among all the pincer complexes reported so far.[15] The reduction did not take place in the presence of $PdCl_2(PPh_3)_2$, $Pd_2(dba)_3$, or $Pd(OAc)_2$ instead of **2M¹Pd**, which indicates that not palladium colloids but the pincer complexes do have the catalytic activity.

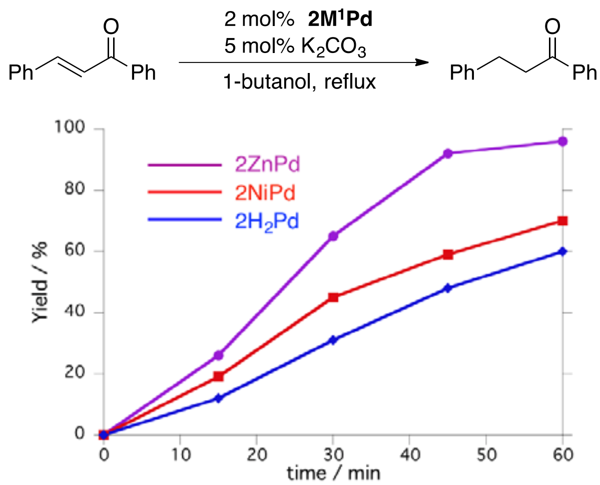


Figure 3. Effect of inner metals on 1,4-reduction catalyzed by **2M¹Pd**.

In conclusion, we have synthesized a family of new peripherally metalated porphyrins, 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 **2M¹M²** were investigated in allylation of benzaldehyde with allylstannane and in 1,4-reduction of chalcone. In the latter catalytic reaction, apparent electronic interplay of **2M¹Pd** in catalysis was observed for the first time. Development of new peripherally metalated porphyrin catalysts is under way by taking advantage of the electronic effect of inner metals.

Supporting Information Available

Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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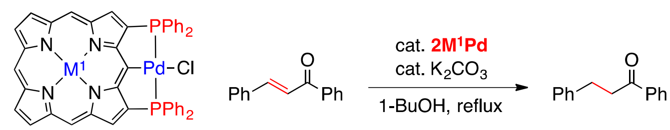

2M^{1}Pd

M^1 = Zn, Ni, H_2

electronic interplay of the inner and outer metals