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Suzuki Porphyrins: New Synthons for the Fabrication of Porphyrin-Containing Supramolecular Assemblies

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Palladium-catalyzed cross-coupling reactions that employ halogenated porphyrin templates and a wide range of organometallic moieties have provided synthetic entrée into new families of unusually elaborated porphyrin macrocyles.[1−3] General, economic syntheses of porphyryl organometallic reagents[4] would expand the scope of this methodology[5,6] and aid in the design of new classes of porphyrin-containing supramolecular assemblies and tetraazamacrocycles with unconventional peripheral substituents. Reported herein are the first examples of meso ring-metalated porphyrin species in which boronic esters are appended to a (porphinato)zinc(II) framework; we structurally characterize the archetypal members of this new class of macrocycle-derivatized porphyrins and briefly illustrate their utility in carbon−carbon bond-forming reactions.

Masuda recently described a series of reactions in which pinacolborane functions as a transmetalating reagent in Pd-catalyzed cross-coupling reactions, enabling the synthesis of a wide range of arylboronates from aryl halide precursors.[7] Application of this reaction to halogenated (porphinato)zinc(II) complexes such as (5-bromo-10,20-diphenylporphinato)zinc(II) and (5,15-dibromo-10,20-diphenylporphinato)zinc(II)[1] gives the corresponding [5-(4′,4′,5′,5′-tetramethyl[1′,3′,2′]dioxaborolan-2′-yl)-10,20-diphenylporphinato]zinc(II) (**I**) and [5,15-bis(4′,4′,5′,5′-tetramethyl[1′,3′,2′]dioxaborolan-2′-yl)-10,20-diphenylporphinato]zinc(II) (**II**) complexes in respective yields of 86 and 79%.[8] These compounds were structurally analyzed; the results of our single-crystal X-ray crystallographic studies of **I**·(benzene) and **II**·(pyridine) are shown in Figure 1.

In **II**·(pyridine), the metal−ligand bond lengths and the magnitude of the Zn atom displacement from the least-squares plane defined by the macrocycle's four $\mathrm{N_{pyrrolyl}}$ atoms (0.35 Å) typify that seen for other crystallographically characterized (porphinato)zinc(II)·(py) complexes.[1b] Interestingly, **II**'s axial pyridyl ligand lies in van der Waals contact with a second pyridyl ring (interplanar separation 3.46 Å); the plane defined by this pyridyl moiety lies parallel to that of the axial ligand. The noncoordinating pyridine is rotated 60° about its perpendicular C_1 axis with respect to the axial pyridyl moiety and vertically displaced 3.37 Å from the above-mentioned porphyrin plane; this positions the π system of each pyridine ring over the positively charged σ framework of the other, optimizing electronic interactions between the six-membered heteroaromatic rings.[9] Consistent with structural studies of borate ester derivatives of 1-naphthalene,[10] the steric interactions between the porphyrin β-hydrogens and the pinacolborane oxygen atoms enforce large dihedral angles (60.8 and 69.3°) between the planes defined by the two respective sets of pinacol ester O−B−O atoms and the four pyrrolyl nitrogens; the average O−(β-H) nonbonded contact distance is 2.65 Å,[11] lying just within the sum of their van der Waals radii (2.72 Å).[12]

In **I**·(benzene), the Zn atom is centered in the plane of the porphyrin ligand. The benzene molecule is positioned above the Zn atom in a π-donor configuration; the interplanar separation between the two aromatic ring systems is 3.10 Å, with the closest $\mathrm{Zn{-}C_{benzene}}$ distance being 3.16 Å. The orientation of the arene ring with respect to the porphyrin ligand is similar to that found in Scheidt's structure of the bis(toluene) solvate of (5,10,15,20-tetraphenylporphinato)zinc(II).[13] The dihedral angle between the planes defined by the O−B−O atoms of the *meso*-boronate group and the macrocyclic N atoms is 52.0° (O−(β-H) average nonbonded contact distance 2.53 Å); because a sterically unencumbered aromatic moiety functions as the axial ligand in **I**·(benzene), a more closely packed solid-state arrangement is possible and is thus the likely cause of reduction of the O−B−O plane-to-porphyrin plane dihedral angle with respect to those observed for **II**·(pyridine). The B−C [**I**, 1.575(5) Å; **II**, 1.565(5) Å] and B−O bond lengths [(**I**, 1.364(5) Å; **II**, 1.362(5) Å] for both complexes are similar to that previously reported for arylboronic acid esters.[10,14]

The utility of these air- and water-stable ring-metalated porphyrins is exemplified in reactions where **I** and **II** function as transmetalating reagents. An exemplary set of such Suzuki-type cross-couplings are presented in Scheme 1, which utilize a compound **I** synthon;[15] a number of principles are illustrated in these high-yield reactions: (i) Cross-coupling of **I** with N-(*tert*-butoxycarbonyl)-4-iodo-L-phenylalanine gives (5-[*N*-(*tert*-butoxycarbonyl)-L-phenylalanin-4′-yl]-10,20-diphenylporphinato)zinc(II) (**III**), corroborating the suitability of ring-metalated **I** with respect to coupling reactions involving nucleophile-sensitive substrates. (ii) The synthesis of 3,6-bis[10′,20′-diphenylporphinato(zinc)(II)-5′-yl]-9-*H*-carbazole (**IV**) demonstrates **I**'s value in the fabrication of porphyrin−spacer−porphyrin systems.[16] Such reactions can be exploited when a dihalogenated spacer moiety

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[4] Few examples of a ring-metalated porphyrins have been reported; these species include [2-(triphenylarsonium)-5,10,15,20-tetraphenylporphinato]zinc(II) perchlorate and 2,4-bis(chloromercuro)deuteroporphyrin IX dimethyl ester. See: (a) Shine, H. J.; Padilla, G. A.; Wu, S.-M. *J. Org. Chem.* **1979**, *44*, 4069−4075. (b) Minnetian, O. M.; Morris, I. K.; Snow, K. M.; Smith, K. M. *J. Org. Chem.* **1989**, *54*, 5567−5574.

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[8] Porphyrylboronates such as **I** and **II** can also be fabricated using synthetic approaches reported by Miyaura which utilize the pinacol ester of diboronic acid as a transmetalating reagent; see: Ishiyama, T.; Murata, M.; Miyaura, N. *J. Org. Chem.* **1995**, *60*, 7508−7510. At least for these halogenated porphyrinic substrates, this method afforded the porphyrylboronate products in slightly lower yield with respect to that obtained using the approach outlined in ref 7.

[9] (a) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525−5534. (b) Hunter, C. A. *Chem. Soc. Rev.* **1994**, 101−109.

[10] (a) de Rege, F. M. G.; Davis, W. M.; Buchwald, S. L. *Organometallics* **1995**, *14*, 4799−4807.

[11] Note that the O-β-H distance in a hypothetical structure in which the pinacolborane and porphyrin moieties are coplanar (porphyrin structure constant) is 2.14 Å.

[12] Pauling, L. *The Nature of the Chemical Bond and the Structure of Molecules and Crystals, an Introduction to Modern Structural Chemistry*, 3d ed.; Cornell University Press: Ithaca, NY, 1960.

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[15] Reaction conditions are similar to those developed for coupling reactions utilizing arylboronic acids (see ref 6); details are provided as Supporting Information.

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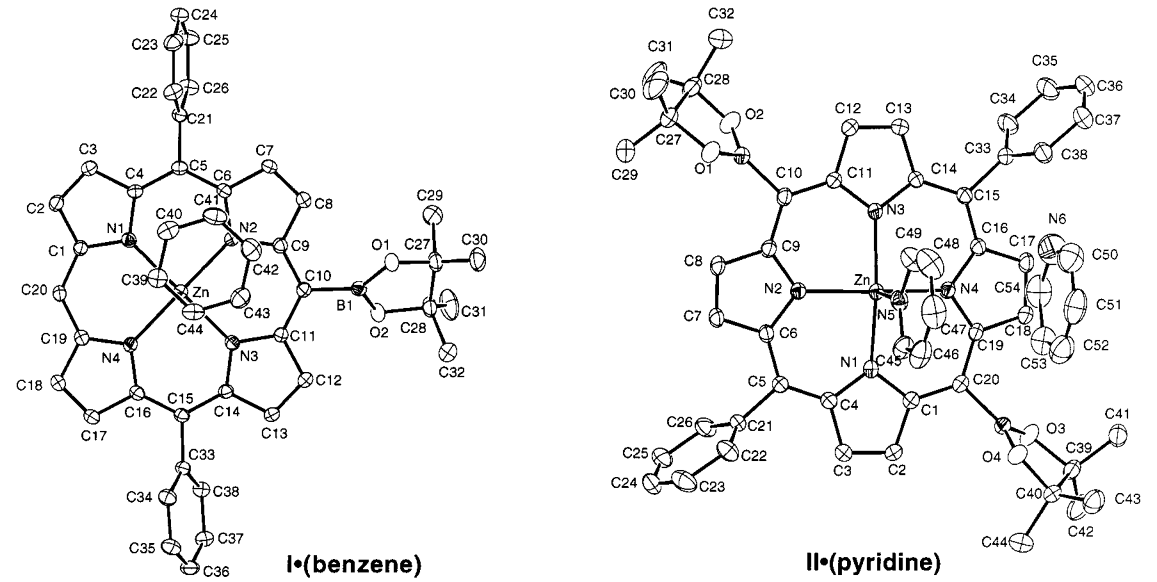
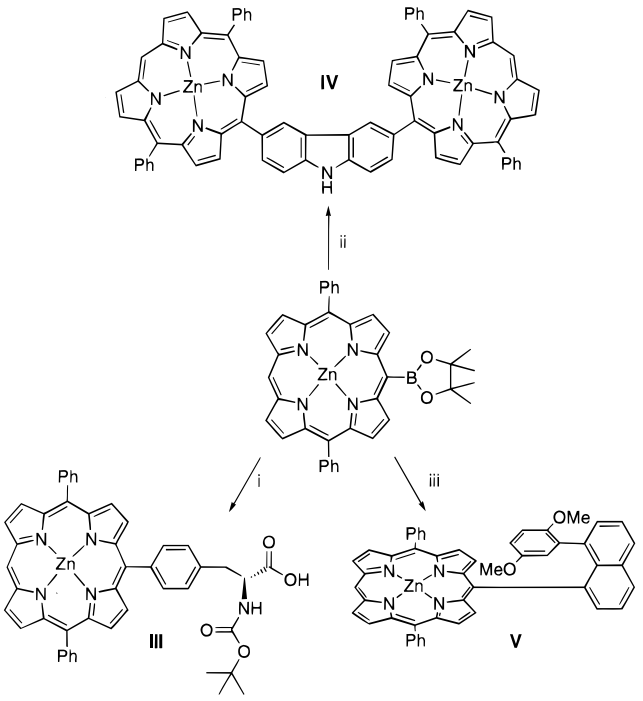


I•(benzene) **II•(pyridine)**

Figure 1. ORTEP views of (a) [5-(4′,4′,5′,5′-tetramethyl[1′,3′,2′]dioxaborolan-2′-yl)-10,20-diphenylporphinato]zinc(II)•(benzene) and (b) [5,15-bis-(4′,4′,5′,5′-tetramethyl[1′,3′,2′]dioxaborolan-2′-yl)-10,20-diphenylporphinato]zinc(II)•(pyridine) with thermal ellipsoids at 30% probability.

Scheme 1. Examples of Metal-Catalyzed Cross-Coupling Reactions Utilizing Porphyrylboronate Transmetalating Reagents[a]



[a] Reagents and conditions: Ba(OH)$_2$•8 H$_2$O (0.24 mmol), Pd(PPh$_3$)$_4$ (0.003 mmol), 50:1 DME/H$_2$O, 80 °C. (i) **I** (0.16 mmol), *N*-(*tert*-butoxycarbonyl)-4-iodo-L-phenylalanine (0.08 mmol); (ii) **I** (0.2 mmol), 3,6-dibromocarbazole (0.05 mmol); (iii) **I** (0.08 mmol), 1-(2′,5′-dimethoxyphenyl)-8-iodonaphthalene (0.08 mmol).

bears a functionality incompatible with direct formation of its corresponding bis(organometallic) derivative or when practical considerations warrant using porphyrylboronates as an expendable transmetalating species. Because **I** is available in two steps from (5,15-diphenylporphinato)zinc(II), carrying out carbon−carbon bond-forming reactions with excess **I** enables the most efficient use of mono- and dihalogenated organic substrates derived from multiple synthetic steps. (iii) The synthesis of [10-(8′-(2″,5″-dimethoxyphenyl)-1′-naphthyl)-5,15-diphenylporphinato]zinc(II) (**V**) from **I** and 1-(2′,5′-dimethoxyphenyl)-8-iodonaphthalene illustrates the efficacy of this porphyrylboronate in sterically congested cross-coupling reactions.[17] The close, sub van der Waals interplanar separation[18] between the cofacial aromatic entities of **V** is highlighted by the unusual local magnetic environment experienced by the C-4″ dimethoxyphenyl proton (δ = 2.42 ppm); this nucleus resonates 4.53 ppm upfield from that observed for the corresponding C-4′ proton of 1-(2′,5′-dimethoxyphenyl)-8-iodonaphthalene.

Ring-metalated porphyrylboronic acids and their corresponding esters expand the repertoire of reagents that can be utilized in metal-catalyzed coupling reactions that form new bonds at the porphyrin periphery. Given the established, rich chemistry of boronate, boronic acid, and borane derivatives of aromatic compounds,[19] porphyrylboronates should likely serve as versatile precursor molecules that enable facile introduction of carbon−heteroatom bonds directly at the macrocycle skeleton. Furthermore, diboronate-functionalized **II** and related multiply boronated porphyryl species constitute a new class of synthons for porphyrin-based conjugated materials that are formed via metal-catalyzed carbon−carbon bond-forming reactions[1−3] or hydroboration polymerization.[20]

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Supporting Information Available: Characterization data and detailed descriptions of the syntheses of compounds **I**−**V** along with tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for compounds **I**•(benzene) and **II**•(pyridine) (36 pages print/PDF). An X-ray crystallographic file, in CIF format, is available through the Internet only. See any current masthead page for ordering and Web access instructions.

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(17) While the underlying cause is unclear at present, similar cross-couplings involving (5-bromo-10,20-diphenylporphinato)zinc(II) with large excesses of organozinc and organoboronate derivatives of 1-(2′,5′-dimethoxyphenyl)-8-iodonaphthalene proceed at a fraction of the 74% yield observed for the stoichiometric coupling of **I** and 1-(2′, 5′-dimethoxyphenyl)-8-iodonaphthalene.

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