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Cross-Coupling

A General and Special Catalyst for Suzuki–Miyaura Coupling Processes

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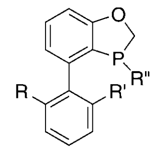
Since its discovery,[1] the Suzuki–Miyaura cross-coupling reaction has evolved into one of most powerful carbon–carbon bond-forming transformations and has shown increasing utility in synthetic organic chemistry.[2] Recent advances in novel catalyst development[3] have enabled this transformation to be applied with a broad substrate scope, a wide functional group tolerance, and low catalyst loadings. Palladium catalysts derived from electron-rich and sterically demanding ligands, such as trialkyl monophosphanes,[4] dialkyl aryl monophosphanes,[5] dialkyl biaryl monophosphanes,[6] *N*-heterocyclic carbenes,[7] and other ligands,[8] have been particularly effective. Despite these advances, limitations remain. For example, the Suzuki–Miyaura coupling of extremely hindered arylboronic acids, such as 2,4,6-triisopropylphenylboronic acid have been less explored. Few successful results have been reported for the preparation of tri-*ortho*-substituted biaryls from such extremely hindered boronic acids. The development of novel, efficient, and general catalysts for the Suzuki–Miyaura cross-coupling reaction to address these limitations and further expand the substrate scope has thus remained a very important area of research.

Ligand structure defines the steric and electronic properties of the palladium catalyst and thus plays a crucial role in the efficiency of the Suzuki–Miyaura cross-coupling reaction. The biaryl dialkyl monophosphane ligands developed by Buchwald and co-workers, such as SPhos, RuPhos, and Xphos have demonstrated a broad substrate scope in the Suzuki–Miyaura cross-coupling reaction.[3b,9] Although they all possess two cyclohexyl substituents at the phosphorus center, reports on variations of these substituents and their impact on reactivity are still limited.[10] The development of biaryl monophosphorus ligands that have a rigid framework to restrict the rotation of the phosphanyl group has rarely been explored.[11] Herein, we report a class of novel biaryl monophosphorus ligands **1a**–**d** whose structures feature a 2,3-dihydrobenzo[*d*][1,3]oxaphosphole framework (Figure 1). Unlike SPhos where the dicyclohexylphosphanyl group can freely rotate along the upper aryl ring and multiple conformers are present when coordinating with a metal center,[12] the structures of ligands **1a**–**d** completely block such rotation and establish a well-defined orientation of the phosphorus atom for metal coordination. We expected that these unique steric and electronic properties of **1a**–**d** would afford excellent reactivity and substrate scope for Suzuki–Miyaura couplings, and thus would be complementary to those known catalytic systems.[3–8]



1a: R = R' = H, R" = *t*Bu
1b: R = OMe, R' = H, R" = *t*Bu
1c: R = NMe$_2$, R' = H, R" = *t*Bu
1d: R = R' = OMe, R" = *t*Bu **(BI-DIME)**

Figure 1. Biaryl monophosphorus ligands.

The syntheses of **1a**–**d** were accomplished in two steps from aryl triflate **2**, which could be prepared on a kilogram scale from methyldichlorophosphine using our reported route.[13] The palladium-catalyzed Suzuki–Miyaura couplings of triflate **2** with various arylboronic acids provided **3a**–**d** in 75–91 % yield. Reduction of **3a**–**d** with PMHS/Ti(O*i*Pr)$_4$[14] afforded racemic ligands **1a**–**d** in excellent yields (Scheme 1).[15] It is noteworthy that ligands **1a**–**d** are accessible in kilogram quantities with this synthetic route, and they were found to be highly stable in open air. For example, ligand **1d** (**BI-DIME**) can be stored as a solid at room temperature in air for months without observing any oxidation side-products.

Ligands **1a**–**d** were applied in the palladium-catalyzed Suzuki–Miyaura coupling of sterically congested arylboronic acids. The cross-coupling between 2,4,6-triisopropylphenylboronic acid and 2-bromobiphenyl was chosen as the model system (Scheme 2). Besides ligands **1a**–**d**, various structurally diverse ligands were also examined for comparison. The reactions were carried out at 100 °C in toluene for 12 hours with [Pd$_2$(dba)$_3$] (0.5 mol %) as the catalyst precursor. Whereas low conversions (< 20 %) were generally observed

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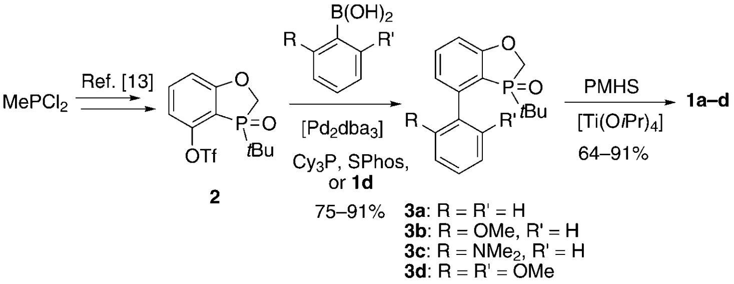
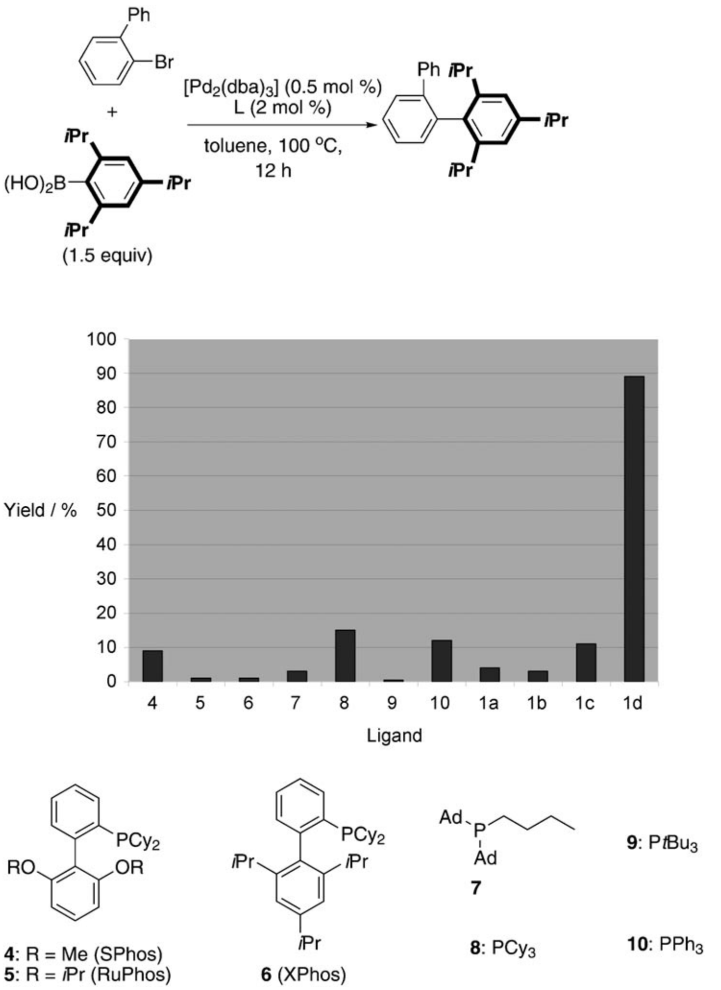


Scheme 1. Syntheses of monophosphorus ligands **1a–d** (for experimental details, see the Supporting Information). Tf = trifluoromethylsulfonate, dba = dibenzylideneacetone, Cy = cyclohexyl, SPhos = 2-dicylohexylphosphino-2′,6′-dimethoxybiphenyl, PMHS = polymethylhydrosiloxane.



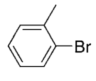
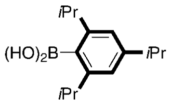
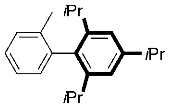
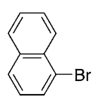
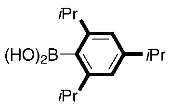
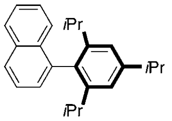
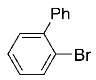
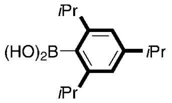
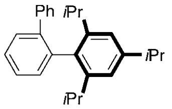
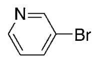
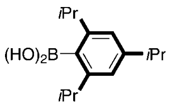
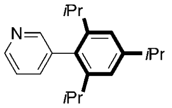
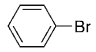
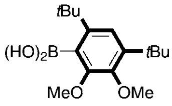
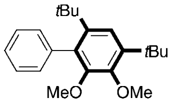
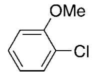
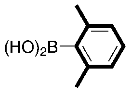
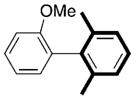
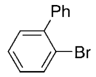
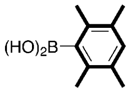
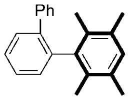
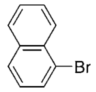
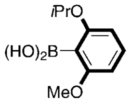
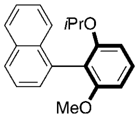
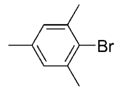
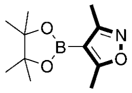
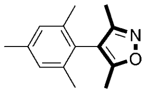
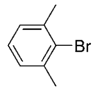
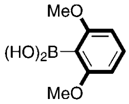
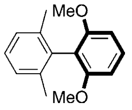
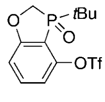
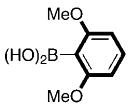
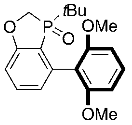
Scheme 2. Ligand screening for Suzuki–Miyaura coupling of 2,4,6-triisopropylphenylboronic acid and 2-bromobiphenyl. The reactions were heated at 100 °C in toluene (2 mL) for 12 h with 2-bromobiphenyl (1 mmol), 2,4,6-triisopropylphenyl boronic acid (1.5 mmol), and K_3PO_4 (3 mmol) in the presence of $[Pd_2dba_3]$ (0.5 mol %) and ligand (2 mol %). HPLC assay yields were averaged from two runs. Ad = adamantyl.

in this challenging cross-coupling reaction with ligands such as SPhos (**4**), RuPhos(**5**), XPhos (**6**), Ad_2PnBu (**7**), PPh_3 (**8**), Cy_3P (**9**), tBu_3P (**10**), and ligands **1a–c**, it is gratifying to report that ligand **1d** (**BI-DIME**) provided a rapid conversion and an excellent yield (89 %). To the best of our knowledge, this is the first high-yielding example for the preparation of a tri-*ortho*-substituted biaryl from 2,4,6-triisopropylphenylboronic acid using the Suzuki–Miyaura coupling reaction. Since both ligand **1d** and SPhos possess the same lower aryl ring, their dramatic difference in reactivity clearly demonstrates the influence of the steric and electronic properties of the upper ring on the reactivity. We hypothesized that the conformational rigidity and the relatively electron-poor nature of **1d** compared to SPhos facilitates the key transmetalation step of this reaction.[16] The high reactivity of ligand **1d** in contrast to ligands **1a–c** also indicated the importance of the two *ortho*-methoxy groups in the lower aryl ring, which is consistent with the observation by Buchwald's group.[6d]

The high effectiveness of ligand **1d** observed in the coupling of 2,4,6-triisopropylphenylboronic acid with 2-bromobiphenyl encouraged us to study the substrate scope in the Suzuki–Miyaura coupling of sterically congested di-*ortho*-substituted arylboronic acids. As illustrated in Table 1, ligand **1d** is capable of catalyzing the coupling of hindered arylboronic acids or esters to form tri-*ortho*-substituted or tetra-*ortho*-substituted biaryl products in excellent yields. A range of *ortho*-substituted aryl bromides were coupled with 2,4,6-triisopropylphenylboronic acid to afford the corresponding tri-*ortho*-substituted biaryl products in very high yields (Table 1, entries 1–3). 3-Pyridyl bromide was also successfully employed to provide the desired heterocyclic compound in 91 % yield (Table 1, entry 4). An extremely hindered arylboronic acid containing an *ortho-tert*-butyl substituent also gave the coupling product in good yield (Table 1, entry 5).[17] Various di-*ortho*-substituted arylboronic acids were coupled with *ortho*-substituted aryl chlorides or bromides to provide tri-*ortho*-substituted biaryl products in excellent yields (Table 1, entries 6–8). Two tetra-*ortho*-substituted biaryls were also prepared in high yields (Table 1, entry 9–10). Ligand **1d** was also required for the efficient cross-coupling of sterically hindered triflate **2** and 2,6-dimethoxyphenylboronic acid, and provided the desired coupling product **2d** in 91 % yield (Table 1, entry 11).[18]

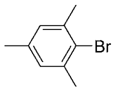
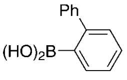
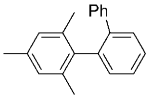
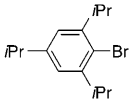
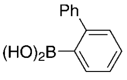
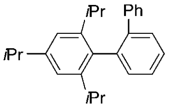
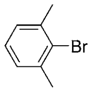
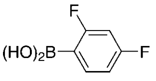
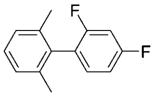
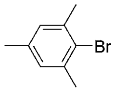
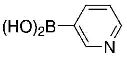
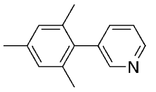
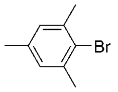
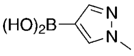
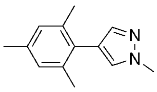
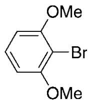
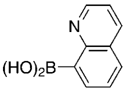
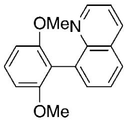
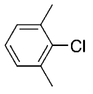
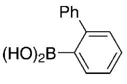
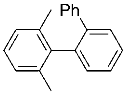
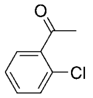
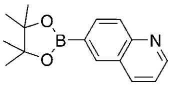
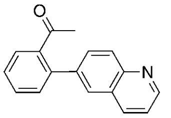
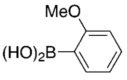
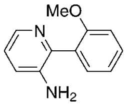
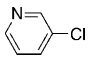
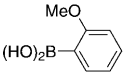
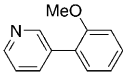
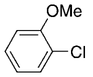
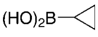
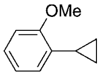
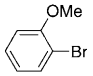
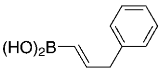
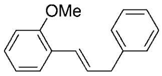
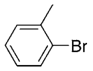
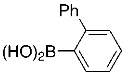
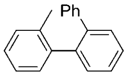
Besides its excellent reactivity for the coupling of sterically hindered arylboronic acids or esters, ligand **1d** is also applicable for the coupling of a broad range of challenging substrates, including sterically congested aryl halides, electron-withdrawing arylboronic acids, and compounds containing heteroaryl moieties. As shown in Table 2, an array of di-*ortho*-substituted aryl bromides or chlorides were coupled with various arylboronic acids to give their coupling products in excellent yields (Table 2, entries 1–6). Ligand **1d** provided a superior reaction rate over SPhos in a parallel study of the coupling of 2-bromo-1,3,5-trimethylbenzene with biphenyl-2-ylboronic acid (Table 2, entry 1).[19] Electron-poor arylbor-

Table 1: Sterically hindered Suzuki–Miyaura cross-couplings with di-*ortho*-substituted arylboronic acids or esters.[a]

Entry	Aryl halide	Boronic acid	Product	Pd [mol%]	Yield [%]
1				1	96
2				1	94
3				1	89
4				1	91[b]
5				2	80[c]
6				1	87
7				1	87[c]
8				1	89
9				1	89[b]
10				3	80[c]
11				1	91[d]

[a] Unless otherwise specified, the reactions were carried out at 100 °C in toluene (2 mL) for 24 h with aryl halide (1 mmol), arylboronic acid or ester (1.5 mmol), and K_3PO_4 (3 mmol) as the reagents in the presence of $[Pd_2dba_3]$ and ligand **1d** (Pd/**1d** = 1:2); yields are of the isolated product. [b] Water (1 mL) was added. [c] *m*-Xylene (2 mL) was employed as the solvent with a reaction temperature of 130 °C. [d] Dioxane (2 mL) as the solvent and KF (3 equiv) as the base were employed with a reaction temperature of 100 °C.

Table 2: Suzuki–Miyaura cross-couplings of sterically congested aryl bromides or chlorides, electron-poor arylboronic acids, heteroaryl-containing substrates, and at low catalyst loading with **1d** as the ligand.[a]

Entry	Aryl halide	Boronic acid	Product	Pd [mol%]	Yield [%]
1				0.2	95
2				1	95
3				0.5	74
4				0.5	95[b]
5				1	99[b]
6				1	99[b]
7				1	93
8				1	85[b]
9				0.5	85[b]
10				1	98[b]
11				0.5	99
12				0.5	99[c]
13				0.002	98

[a] Unless otherwise specified, the reactions were carried out at 100 °C in toluene (2 mL) for 24 h with aryl halide (1 mmol), arylboronic acid or ester (1.5 mmol), and K_3PO_4 (3 mmol) as the reagents in the presence of $[Pd_2dba_3]$ and ligand **1d** (Pd:**1d** = 1:2); yields are of isolated products. [b] 1-Butanol (2 mL) and water (1 mL) as the solvent. [c] $Pd(OAc)_2$ as the catalyst precursor with a reaction temperature of 40 °C.

onic acids, such as 2,4-difluorophenylboronic acid and 3-pyridineboronic acid, were well tolerated (Table 2, entries 3 and 4). Heteroaryl substrates with strong coordinating capabilities were also applicable (Table 2, entries 4–6). A variety of aryl chlorides could be employed (Table 2, entried 7–10) and a substrate containing a free amino group was successfully coupled under the reaction conditions (Table 2, entry 9). As well as arylboronic acids or esters, a cyclopropaneboronic acid and a vinylboronic acid were smoothly reacted with an aryl bromide or chloride to provide the desired coupling product in excellent yields (Table 2, entries 11–12). To further test the reactivity of ligand **1d**, the reaction of 1-bromo-2-methylbenzene and 2-biphenylboronic acid was carried out in the presence of 0.002 mol% of palladium and 0.004 mol% of **1d** to afford the di-*ortho*-substituted biaryl product in 98% yield (Table 2, entry 13).

A crystal structure of [PdCl$_2${(*S*)-**1d**}$_2$] revealed the influence of the rigid 2,3-dihydrobenzo[*d*][1,3]oxaphosphole upper aryl ring of the ligand (*S*)-**1d** on the conformation of the palladium complex (Figure 2).[20] Unlike in the structure of [PdCl$_2$(SPhos)$_2$],[6e] where the biaryl portion of the SPhos ligands are pointed away from the palladium center, the conformational rigidity of (*S*)-**1d** forces a close proximity of the biaryl moiety to the palladium center in [PdCl$_2${(*S*)-**1d**}$_2$]. This orientation could lead to a greater steric impact of the lower aryl ring on the metal complex. It is noteworthy that [PdCl$_2${(*S*)-**1d**}$_2$] can also be employed as a pre-catalyst for Suzuki–Miyaura coupling reactions.[21]

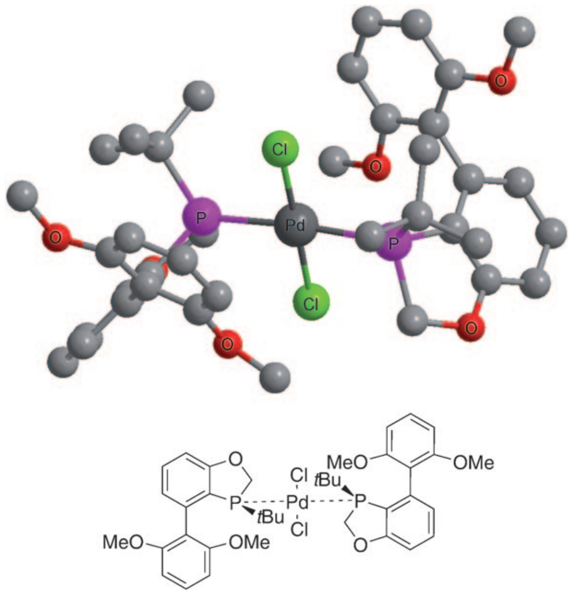


Figure 2. X-ray structure of [PdCl$_2${(*S*)-**1d**}$_2$]. The H atoms and THF solvent molecules are omitted for clarity.

In summary, we have developed a novel class of biaryl monophosphorus ligands **1a–d** for the Suzuki–Miyaura coupling reaction by incorporating a 2,3-dihydrobenzo[*d*][1,3]oxaphosphole framework. These biaryl ligands, which contain a well-defined orientation of the phosphorus center for metal coordination, have provided different steric and electronic properties in contrast to the biaryl ligands reported by Buchwald and co-workers, which have shown special applications for Suzuki–Miyaura coupling reactions. Besides a very broad substrate scope, which includes sterically congested aryl halides, electron-poor arylboronic acids, and substrates containing heteroaryl substituents, ligand **1d** has demonstrated its catalytic ability for the sterically congested Suzuki–Miyaura coupling reactions of extremely hindered arylboronic acids. This has resulted in the first high-yielding coupling reactions of 2,4,6-triisopropylphenyl boronic acid with *ortho*-substituted aryl bromides. Accessible in kilogram quantities and with great air-stability, ligand **1d** (**BI-DIME**) holds promise for practical applications in transition-metal-catalyzed cross-coupling reactions and progress towards this end is underway within the group.[22]

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Keywords: cross-coupling · monophosphanes · palladium · phosphorus ligands · Suzuki–Miyaura coupling

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[11] Restriction of the rotation of the phosphanyl group to fix the conformation of the ligand in its metal complex has appeared to be important for reactivity. Buchwald and co-workers have recently reported superior results for amination and amidation reactions with biaryl monophosphanes that contain an *ortho*-methyl or *ortho*-methoxy group on the upper aryl ring, which, to some extent, restricts the rotation of the phosphanyl groups. See: a) T. Ikawa, T. E. Barder, M. R. Biscoe, S. L. Buchwald, *J. Am. Chem. Soc.* **2007**, *129*, 13001; b) B. P. Fors, D. A. Watson, M. R. Biscoe, S. L. Buchwald, *J. Am. Chem. Soc.* **2008**, *130*, 13552; c) K. Dooleweerdt, B. P. Fors, S. L. Buchwald, *Org. Lett.* **2010**, *12*, 2350.

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[16] SPhos afforded an excellent yield in the cross-coupling reaction of 2-bromo-1,3,5-triisopropylbenzene and biphenyl-2-ylboronic acid, see Ref. [6e]. The low reactivity observed in cross-coupling between 2,4,6-triisopropylphenylboronic acid and 2-bromobiphenyl suggests that transmetalation rather than reductive elimination is the rate-determining step.

[17] There is only one high-yielding example of Suzuki–Miyaura coupling of arylboronic acid with an *ortho*-*tert*-butyl substituent: S. M. So, C. P. Lau, A. S. Chan, F. Y. Kwong, *J. Org. Chem.* **2008**, *73*, 7731.

[18] This procedure has been employed for the synthesis of ligand **1d** in kilogram quantities.

[19] See the Supporting Information for details.

[20] CCDC 773967 [PdCl$_2${(*S*)-**1d**}$_2$] contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[21] Both racemic **1d** and (*S*)-**1d** provide similar reaction rates for Suzuki–Miyaura couplings.

[22] The Supporting Information contains the experimental details, spectroscopic data, and NMR spectra of ligands **1a**–**d**, [PdCl$_2${(*S*)-**1d**}$_2$], and Suzuki–Miyaura coupling products.