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VIP **Borylation**

Palladium-Catalyzed Borylation of Sterically Demanding Aryl Halides with a Silica-Supported Compact Phosphane Ligand**

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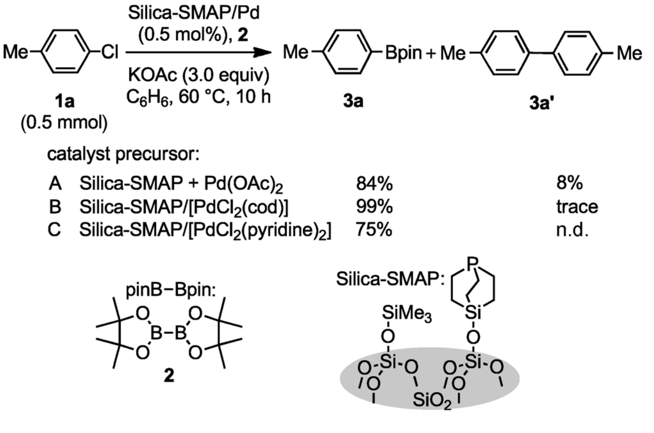
Arylboronic acid derivatives are versatile intermediates in organic synthesis because of their broad availability, air stability, and ease of handling.[1] Among the routes to arylboronic acid derivatives, the conventional methods that use aryllithium or Grignard reagents have a problem with functional-group compatibility. More recently, functional-group-tolerating approaches such as the transition-metal-catalyzed borylation of aryl halides[2,3] and the direct C–H borylation[4] of arenes have been introduced, and both are complementarily applicable to the preparation of a wide range of arylboronates. Specifically for the borylation of aryl halides, aryl chlorides are the most desirable substrates because of their low cost and broad availability; however, they are less reactive than the corresponding bromides, iodides, and triflates. Accordingly, only a few catalyst systems are effective for reactions of unactivated aryl chlorides.[2f,h–m] A common feature of effective systems is the use of electron-rich and sterically demanding phosphane ligands in combination with a palladium source. The most efficient catalyst systems reported to date are those based on (dicyclohexylphosphino)biphenyl-type ligands such as SPhos and XPhos, which were originally described by Buchwald and co-workers.[2i,j] The use of these catalysts allowed for the borylation of sterically or electronically challenging aryl chlorides such as 1-chloro-2,6-dimethylbenzene (2 mol% Pd/SPhos, RT, 86%) and 4-chloroanisole (0.1 mol% Pd/XPhos, 110°C, 94%).[2i]

Buchwald and co-workers described that the efficacy of biphenyl-type ligands for the borylation is attributed at least in part to their sterically demanding nature, which promotes the formation of a highly reactive 1:1 Pd^0/P complex over less reactive 1:2 Pd^0/P species.[2i,5] On the other hand, we have developed Silica-SMAP, which is a silica-supported "compact" phosphane ligand.[6,7] Because of its immobilized nature, this ligand forms 1:1 metal/P complexes exclusively with a range of transition-metal species, despite its extreme compactness.[7a,b] We demonstrated that the surface-bound 1:1 metal/P complexes afford highly active catalysts for the hydrosilylation and the hydrogenation of ketones (with Rh),[7a–c] and the directed *ortho* borylation of functionalized arenes (with Ir).[7d–f] In particular, these reactions showed remarkable tolerance toward the reactions of sterically demanding substrates. Accordingly, we envisioned that, despite its compactness, the supported phosphane would be useful in creating a highly active catalytic environment for the palladium-catalyzed borylation of sterically or electronically challenging aryl halides.[5i,8,9] Furthermore, this utility means that the steric demand of a ligand would not be essential for the high catalytic activity in the palladium-catalyzed borylation of aryl chlorides, as has been proved by the experiments described below.

The reaction of 4-chlorotoluene (**1a**, 0.5 mmol) with bis(pinacolato)diboron (**2**, 0.5 mmol) in the presence of $Pd(OAc)_2$ (0.5 mol%), Silica-SMAP (0.5 mol%), and KOAc (3 equiv) in benzene at 60°C for 10 h gave the desired arylboronate **3a** in 84% yield, but the reaction also formed a significant amount of biaryl compound **3a′** (8% yield), which likely resulted from a Suzuki–Miyaura coupling between the arylboronate product **3a** and aryl chloride **1a** (Scheme 1, catalyst precursor A).[10] The undesired biaryl formation was almost completely inhibited by using the Silica-SMAP/Pd system that was prepared in advance (from Silica-SMAP and $[PdCl_2(cod)]$, P/Pd = 1:1, catalyst precursor B), instead of the in situ generated complex (catalyst precursor A); **3a** was thus produced in an excellent yield (Scheme 1). Furthermore, another preformed complex Silica-SMAP/$[PdCl_2(pyridine)_2]$ afforded exclusively the borylation product **3a**, albeit in a lower conversion (Scheme 1, catalyst precursor C). It should



catalyst precursor:

		3a	3a'
A	Silica-SMAP + $Pd(OAc)_2$	84%	8%
B	Silica-SMAP/$[PdCl_2(cod)]$	99%	trace
C	Silica-SMAP/$[PdCl_2(pyridine)_2]$	75%	n.d.

Scheme 1. Borylation of 4-chlorotoluene (**1a**) catalyzed by Silica-SMAP/Pd systems. 1.0 equiv of **2** were used with catalyst precursors A and C, and 1.1 equiv of **2** was used with catalyst precursor B.

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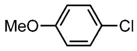
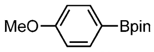
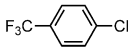
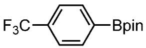
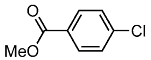
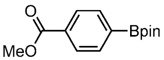
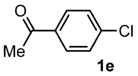
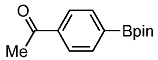
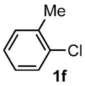
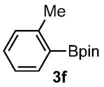
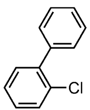
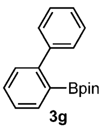
be noted that the corresponding homogeneous catalyst systems based on Ph-SMAP[6] and Pd(OAc)$_2$ (0.5 mol% Pd, Pd/P = 1:1 or 1:2) resulted in no reaction under conditions that were otherwise the same, thus indicating that the immobilization of the phosphane ligand is crucial for the borylation activity.[11]

In heterogeneous systems, the catalysts were easily separated from the products by filtration through Celite. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis indicated that the Pd leaching was below the detection limit (0.02% of the loaded Pd). Unfortunately, however, our attempts to reuse the immobilized catalysts were unsuccessful.

The effect of the substituent on aryl chlorides is shown in Table 1. The Silica-SMAP/Pd systems were also effective for the reaction of 4-chloroanisole (**1b**), which is an electronically deactivated substrate. While the in situ generated Silica-SMAP/Pd(OAc)$_2$ system (catalyst precursor A) afforded arylboronate **3b** and biaryl **3b′** in 80% and 10% yield, respectively, the reaction with the preformed Silica-SMAP/Pd system (catalyst precursor B) resulted in an excellent yield of the arylboronate **3b** (96%) with the formation of only a trace of **3b′** (2%; Table 1, entries 1 and 2). Similarly, the reaction of 4-(trifluoromethyl)chlorobenzene **1c**, which is a weakly activated substrate, afforded a mixture of **3c** (86%) and **3c′** (7%) with catalyst precursor A, while boronate **3c** was obtained quantitatively with catalyst precursor B (Table 1, entries 3 and 4).

Strongly electron-withdrawing substituents such as methoxycarbonyl (**1d**) or acetyl (**1e**) groups at the *para* position caused marked rate enhancement; the reactions were completed within 2 h (monitored by GC) to afford boronates **3d** and **3e** in quantitative yields (Table 1, entries 5 and 6). Notably, in both cases, no biaryl was formed even with the in situ generated Silica-SMAP/Pd(OAc)$_2$ system (catalyst precursor A). This result seems to be due to lower reactivities (nucleophilicities) of the arylboronate products **3d** and **3e** toward the subsequent Suzuki–Miyaura coupling.

Table 1: Silica-SMAP/Pd-catalyzed borylation reaction.[a]

Entry	Aryl chloride **1**	Arylboronate **3**	Cat. prec.[b]	Yield [%][c]
1[d]	 **1b**	 **3b**	A	80 (55)
2[d,e]			B	96 (82)
3[d]	 **1c**	 **3c**	A	86
4[e]			B	99 (89)
5	 **1d**	 **3d**	A	99 (75)
6	 **1e**	 **3e**	A	98 (80)
7	 **1f**	 **3f**	A	96 (78)
8	 **1g**	 **3g**	A	98 (74)

[a] Conditions: **1** (0.5 mmol), **2** (0.5 mmol), Silica-SMAP/Pd (0.5 mol%), KOAc (3 equiv), benzene (1.0 mL) at 60°C for 10 h. All reactions proceeded with full conversion. [b] See Scheme 1. [c] Yield (based on **1**) determined by ^{1}H NMR spectroscopy. The yield of the isolated product is given in parentheses. [d] Biaryl **3′** was detected in the crude mixture: 10% (entry 1), 2% (entry 2), 7% (entry 3). [e] 0.55 mmol of **2** was used.

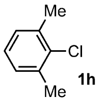
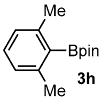
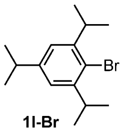
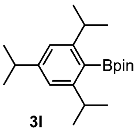
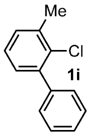
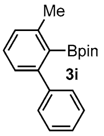
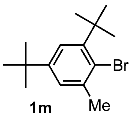
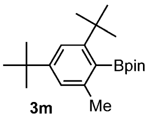
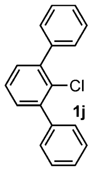
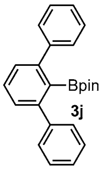
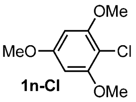
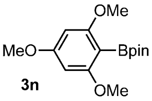
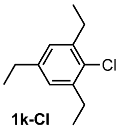
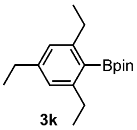
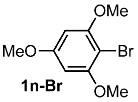
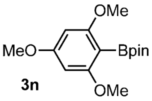
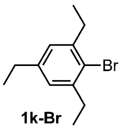
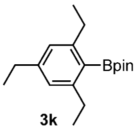
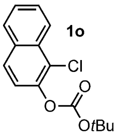
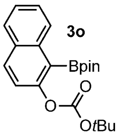
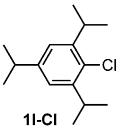
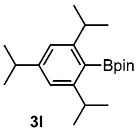
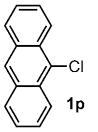
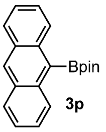
Sterically challenging *ortho*-substituted aryl chlorides such as 2-chlorotoluene (**1f**) and 2-chloro-1,1′-biphenyl (**1g**) were also suitable substrates, and their reactions produced the corresponding arylboronates quantitatively without the formation of homocoupling products, even under conditions A (Table 1, entries 7 and 8). The steric hindrance of the *ortho* substituents seems to prevent the overreaction of the arylboronates **3f** and **3g**.

Table 2 shows the excellent applicability of the Silica-SMAP/Pd catalyst systems for the borylation of even more challenging 2,6-disubstituted aryl halides, which furnished highly hindered arylboronates **3h**–**p**. These molecular transformations have not been described to date, except for the conversion of **1h** to **3h** (Table 2, entry 1).[2i,12] Specifically, the reactions of 2,6-dimethyl- (**1h**), 2-methyl-6-phenyl- (**1i**), and 2,6-diphenylchlorobenzenes (**1j**) with the use of catalyst precursor A proceeded in the temperature range 60–90°C to afford the corresponding 2,6-disubstituted arylboronates **3h**–**j** in excellent yields (Table 2, entries 1–3). Notably, 2,4,6-triethyl- (**1k**-Cl and **1k**-Br),[13] 2,4,6-triisopropyl- (**1l**-Cl and **1l**-Br), and 2,4-*tert*-butyl-6-methyl-substituted (**1m**-Br) aryl halides also underwent an efficient borylation, despite the extremely crowded and electronically inactivated nature of the substrates (Table 2, entries 4–8).[14] Furthermore, the electronically even more deactivated 2,4,6-trisubstituted aryl chloride **1n**-Cl underwent the borylation when catalyst precursor C was used, while the use of catalyst presursor A resulted in a lower substrate conversion (Table 2, entries 9 and 10). The corresponding bromide **1n**-Br also served as a suitable substrate (catalyst precursor A, Table 2, entry 11). The borylation of chloronaphthalene derivative **1o** with a bulky oxygen-based functional group (-OCO$_2t$Bu) at the *ortho* position proceeded more efficiently with catalyst precursor C rather than with catalyst presursor A (Table 2, entries 12 and 13). The anthracenyl chloride **1p** underwent efficient borylation at a relatively low temperature (60°C) with catalyst precursor A (Table 2, entry 14).

While Buchwald and co-workers described reaction conditions in which sterically demanding biphenyl-based phosphane ligands such as XPhos and SPhos were useful for the borylation of 2,6-dimethylchlorobenzene (**1h**),[2i] this transformation did not occur at all when these ligands were used in place of Silica-SMAP under the reaction conditions described for Table 2, entry 1 (0.5 mol% Pd(OAc)$_2$, Pd/P = 1:1 or 1:2).[11] It should be noted, however, that the use of XPhos (Pd/P = 1:2) in place of Silica-SMAP resulted in a quantitative conversion in the borylation of the sterically less demanding 2,4,6-trimethoxychlorobenzene (**1n**-Cl). On the other hand, the use of SPhos under the same conditions resulted in only 7% conversion.

In summary, a silica-supported "compact" phosphane, Silica-SMAP, was successfully used for the palladium-cata-

Table 2: Borylation of 2,6-disubstituted aryl halides.[a]

Entry	Aryl halide **1**	Arylboronate **3**	Cat. prec.[b]	*T* [°C]	Conv. [%]	Yield [%][c]	Entry	Aryl halide **1**	Arylboronate **3**	Cat. prec.[b]	*T* [°C]	Conv. [%]	Yield [%][c]
1[d]	 **1h**	 **3h**	A	60	90	90 (82)	7	 **1l-Br**	 **3l**	A	110	100	93 (89)[e]
2	 **1i**	 **3i**	A	80	100	85 (84)[e]	8	 **1m**	 **3m**	A	110	100	83 (88)[e]
3	 **1j**	 **3j**	A	90	90	80 (80)[e]	9[g] 10[g]	 **1n-Cl**	 **3n**	A C	100 100	55 97	45[e] 88 (81)[e]
4	 **1k-Cl**	 **3k**	A	90	100	91 (77)[e]	11[g]	 **1n-Br**	 **3n**	A	100	96	86 (80)[e]
5	 **1k-Br**	 **3k**	A	80	82	76 (73)[e]	12[g] 13[g]	 **1o**	 **3o**	A C	100 100	67 100	66 99 (88)
6[f]	 **1l-Cl**	 **3l**	A	110	76	64 (64)[e]	14[d]	 **1p**	 **3p**	A	60	95	87 (92)[e]

[a] Conditions: **1** (0.5 mmol), **2** (0.5 mmol), Silica-SMAP/Pd (0.5 mol%), KOAc (3 equiv), toluene (1.0 mL) for 16 h. [b] See Scheme 1. [c] Yield (based on **1**) determined by ^{1}H NMR spectroscopy. The yield of the isolated product is given in parentheses. [d] Benzene was used as the solvent. [e] The protonated arene was detected in the crude mixture: 15% (entry 2), 10% (entry 3), 9% (entry 4), 6% (entry 5), 12% (entry 6), 7% (entry 7), 17% (entry 8), 10% (entry 9), 9% (entry 10), 10% (entry 11), 8% (entry 14). [f] 1.5 equiv of **2** were used. [g] 1,4-Dioxane was used as the solvent.

lyzed borylation of aryl chlorides or bromides with bis(pinacolato)diboron. The Silica-SMAP/Pd systems significantly expanded the substrate scope of the borylation toward sterically and electronically challenging aryl halides. As for the borylation of moderately challenging substrates such as 2,6-dimethylchlorobenzene, the efficacy of the immobilized catalyst systems with the "compact" phosphane is comparable or exceeds that of homogeneous palladium systems with biphenyl-based "bulky" phosphane ligands such as XPhos and SPhos. Furthermore, borylation reactions of several sterically more challenging substrates represented by 2,4,6-triethyl- and 2,4,6-triisopropylchlorobenzenes have been demonstrated for the first time. Accordingly, it is concluded that the steric demand of a ligand is not essential for high catalytic activity in the palladium-catalyzed borylation of unactivated aryl chlorides if a monodentate ligand is immobilized on a solid support, so that only one ligand participates in the coordination to the metal center.[8,9] Investigations on the effects of the steric and electronic natures of immobilized phosphane ligands toward aryl halide activation by palladium and related catalysis are ongoing.

Experimental Section

Typical procedure for the borylation reaction (catalyst precursor A): In a glove box, Silica-SMAP (0.069 mmol g^{-1}, 36.0 mg, 0.0025 mmol, 0.5 mol%), **2** (127.0 mg, 0.50 mmol), KOAc (149.0 mg, 1.5 mmol), and anhydrous, degassed benzene (0.72 mL) were placed in a 10 mL glass tube containing a magnetic stirring bar. Then, a solution of Pd(OAc)$_2$ (0.56 mg, 0.0025 mmol, 0.5 mol%) in benzene (0.28 mL) and **1a** (61.1 mg, 0.48 mmol) were added. The tube was sealed with a screw cap and removed from the glove box. The mixture was stirred at 60°C for 10 h, then filtered through a Celite pad. The solvent was removed under reduced pressure. An internal standard (1,1,2,2-tetrachloroethane) was added to the residue. The yield of the product (84%) was determined by ^{1}H NMR spectroscopy. The crude material was then purified by column chromatography on silica gel (EtOAc/hexane = 1:9) to give arylboronate **3a** (75.3 mg, 0.35 mmol) in 72% yield.

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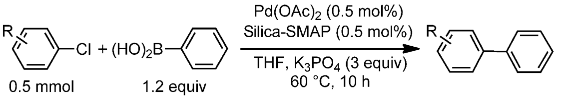
[10] The Silica-SMAP/Pd system is also useful for the Suzuki–Miyaura cross-coupling reaction of unactivated aryl halides.



R = *p*-Me; 85% conv. 82% yield (NMR)
R = *o*-Me; 79% conv. 74% yield (NMR)

[11] See the Supporting Information for details of ligand effects. The lower activity of the homogeneous catalysts with soluble phosphane ligands such as Ph-SMAP should be due to the formation of multi-phosphane-coordinated, catalytically inactive palladium complexes.

[12] Arylboronates **3l** and **3p** have been synthesized through the Pd-catalyzed borylation of the corresponding bromides, see Ref. [2h] and a) W. Tang, S. Keshipeddy, Y. Zhang, X. Wei, J. Savoie, N. D. Patel, N. K. Yee, C. H. Senanayake, *Org. Lett.* **2011**, *13*, 1366–1369. Arylboronate **3n** has been obtained in a low yield through the nano-Fe_2O_3-catalyzed borylation of 1,3,5-trimethoxybenzene. See b) G. Yan, Y. Jiang, C. Kuang, S. Wang, H. Liu, Y. Zhang, J. Wang, *Chem. Commun.* **2010**, *46*, 3170–3172. Arylboronates **3i**–**k**,**m**,**o** were not described previously.

[13] The increase of the reaction temperature did not improve the yield. The reason for the lower reactivity of **1k**-Br relative to **1k**-Cl is unclear.

[14] The reaction of 2,4-di-*tert*-butyl-6-methyl-substituted chlorobenzene (**1m**-Cl) has not been examined because this substrate was difficult to prepare.