Borylation Hot Paper

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Catalytic Borylation using an Air-Stable Zinc Boryl Reagent: Systematic Access to Elusive Acylboranes

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Abstract: *The use of borylzinc reagents in palladium-catalyzed borylation chemistry is described (i.e. a boron analogue of the Negishi coupling), including a one-pot bench-top protocol using an air- and moisture-stable bis(boryl)zinc reagent. The steric/electronic properties of the boryl fragment employed enable a systematic method for accessing acylboranes, a rare class of organoboron species with great potential in chemical synthesis. The reactions proceed under mild conditions, use inexpensive commercial sources of palladium, and demonstrate a remarkable functional-group tolerance.*

Organoboron compounds are highly versatile reagents for transition-metal-catalyzed cross-coupling reactions, and are recognized as one of the most powerful tools in synthetic organic/medicinal chemistry.[1] Boronic acids/esters and related derivatives represent the most widely used class of such compounds, with diboron(4) esters, $B_2(OR)_4$, typically being employed to access such species by borylation of C–halogen (and even C–H) bonds.[1] Aminoboranes have been used as alternative sources of the boron component,[2] and more recently a silylborane has also been exploited in the metal free borylation of C–halogen bonds (halogen = Br, I).[3] Transient masked boryl anions are frequently postulated as key intermediates in these transformations,[4] and a few examples of anionic sp^2–sp^3 tetraalkoxy diboron compounds have been successfully isolated and proved to be catalytically relevant.[5] However, well-defined mononuclear formally anionic boryl systems, such as $[(thf)_2Li\{B(NDippCH)_2\}]$,[6] have not been widely employed, despite their strong nucleophilicity, in part because of their sensitivity to moisture and air, and the availability of competing reaction pathways stemming from potent reducing properties.[7]

We hypothesized that less-polar borylzinc species would offer better control of reactivity, and that palladium-catalyzed borylation chemistry (in effect a boron version of the Negishi C–C coupling reaction), might constitute a practical methodology for C–B bond formation. In practice, such chemistry proves not only to be feasible (using an air-stable borylzinc reagent), but also to be remarkably versatile and functional-group tolerant. Moreover, it can be extended beyond aryl C–B bonds, to offer facile access to a library of hitherto difficult-to-access three-coordinate acylboranes.

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We initially tested three borylzinc compounds, by using the palladium-catalyzed borylation of bromobenzene as a benchmark reaction (Figure 1). Compound **1** and the backbone-saturated version of **2** were previously reported by Nozaki and Yamashita,[7c] while **3** was synthesized herein, and its molecular structure confirmed by NMR spectroscopy and X-ray crystallography (see the Supporting Information). Both **2** and **3** showed comparable catalytic performance, while the bis(boryl) system **1** was less reactive under identical reaction conditions, presumably reflecting kinetic stabilization resulting from the increased steric encumbrance at zinc.[8]

We next optimized the borylation of bromobenzene (catalyst, solvent, added base) by using **3** as the borylating reagent (see Table S1 in the Supporting Information). In the absence of a palladium catalyst borylation did not take place, in contrast to the chemistry displayed by its related lithium analogue.[7a] The inexpensive commercially available $[Pd(PPh_3)_2Cl_2]$ catalyst outperformed the more sophisticated PEPPSI or $[Pd(dppf)Cl_2]$ systems (dppf = 1,1′-bis(diphenylphosphino)ferrocene), while the related P(*o*-Tol)$_3$ complex

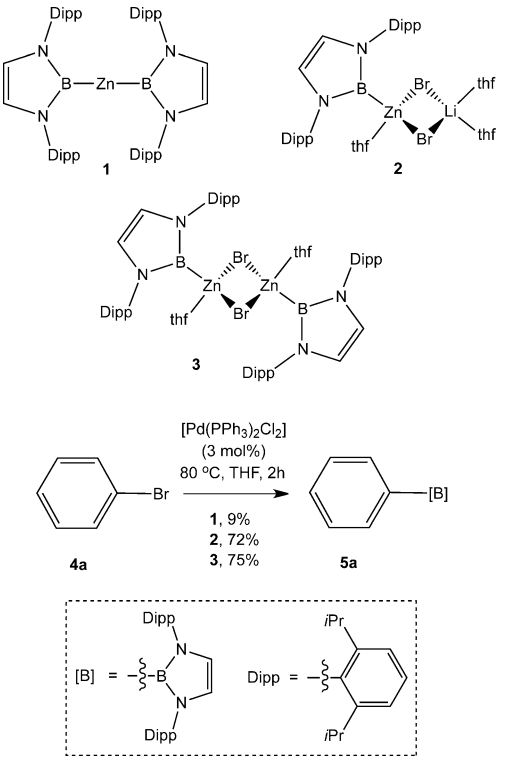


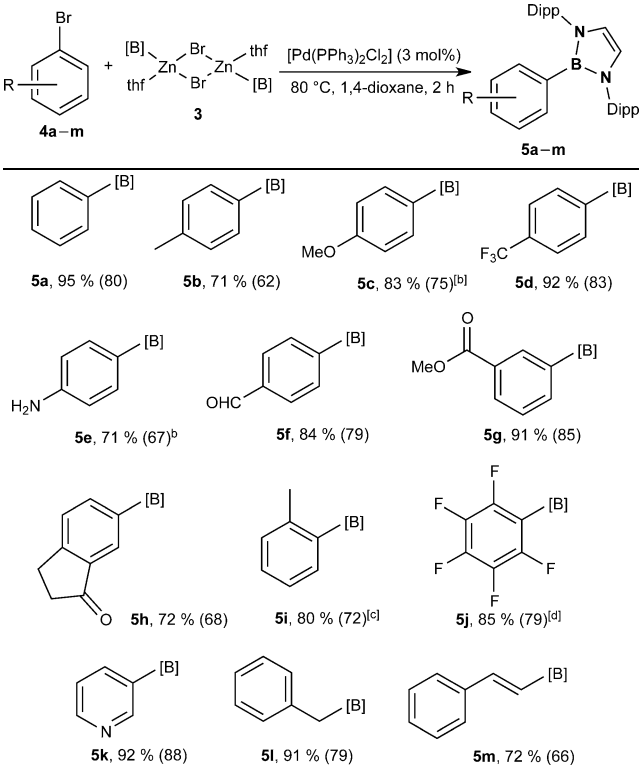
Figure 1. Borylzinc compounds employed in this work and their application in bromobenzene borylation chemistry.

exhibited poor activity, with rapid decomposition and formation of palladium black. Simpler forms of palladium also gave poorer results with the formation of significant quantities of the hydroborane $HB(NDippCH)_2$ (**6**). From the perspective of solvent, polar ethereal media are found to be most suitable, with best results obtained using 1,4-dioxane (95% conversion).

At variance with previous borylation strategies employing diboron(4) reagents, the addition of a base either had no effect (K_2CO_3) or was significantly deleterious (KOAc or Et_3N). Presumably, while the added base plays a key role in the formation of sp^2–sp^3 activated diboron species in typical Miyaura borylations,[4] it is not needed in this case since borylzinc complexes have sufficient nucleophilic character to perform the C–B coupling. Base-free conditions could be advantageous in accessing borylated products containing base-sensitive functional groups, a feature which is in common with the related Negishi C–C coupling reaction using alkylzinc reagents.

The substrate scope under optimized reaction conditions was then examined (Table 1). Both electron-rich and electron-deficient aryl bromides were successfully borylated, although those containing strongly electron-donating groups (**4c** and **4e**) required an additional equivalent of PCy_3 to prevent catalyst decomposition to palladium black (yields of around 20 to 30% were obtained in the absence of additional phosphine). Harsher reaction conditions (90°C, 36 h) were needed for the hindered *ortho*-substituted **4i**, as expected considering the steric bulk of the boryl reagent. Importantly, this new method is effective in the presence of a range of reactive functional groups, including ethers, anilines, aldehydes, ketones, and esters, the majority of which are incompatible with boryllithium reagents. In addition, heterocyclic 3-bromopyridine (**4k**) was also successfully coupled using **3**, and the borylation of related benzyl (**4l**) and vinyl (**4m**) bromides could be effected with good yields/selectivity.

Table 1: Substrate scope for the borylation of aryl and related bromides using the $[Pd(PPh_3)_2Cl_2]$/**3** system.[a]

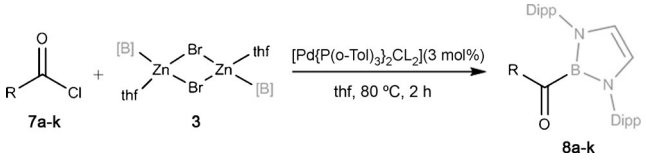


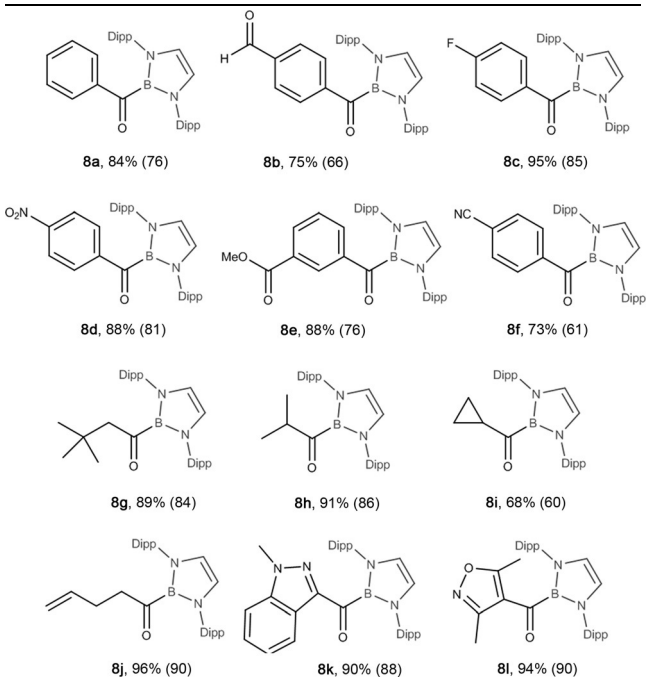
[a] Reaction conditions: **3** (0.022 mmol), **4a–m** (0.040 mmol) and $[Pd(PPh_3)_2Cl_2]$ (3 mol%), 1,4-dioxane (0.5 mL), 80°C, 2 h. Yields calculated by ^1H NMR spectroscopy using an internal standard. Yields of isolated products given within parentheses. [b] One additional equiv of PCy_3. [c] 90°C, 36 h. [d] 24 h.

With the utility of borylzinc reagents in the borylation of organic electrophiles established, we targeted systematic access to acylboranes, a rare class of boron compounds, the synthesis of which by catalytic C–B coupling reactions has largely been unsuccessful.[9] Although they have been proposed as intermediates in several transformations (e.g. the carbonylation of organoboranes),[10] it was noted in 2005 that "no verified examples of acylboron derivatives have ever been isolated" and it was not until 2007 that the first example (**8a**; for structure see Table 2) was obtained from the reactions of either boryllithium or borylmagnesium reagents with benzoyl chloride[7a,11] or benzaldehyde,[11] respectively. The boron-containing heterocycle apparently confers reduced lability on the acyl borane **8a** because of the π donation from the α-nitrogen atoms and steric shrouding from the pendant Dipp groups. However, yields obtained using highly polar Li/Mg boryls are moderate (57% and 18–34%, respectively),[7a,11] and as a general synthetic method this strategy suffers from the lack of functional-group tolerance of these s-block boryl reagents. Examples of Lewis base stabilized acyl boranes have more recently been reported.[12] Molander et al. synthesized the first example of an acyltrifluoroborate,[13] while the groups of Bode[14] and Yudin[15] have designed elegant, although lengthy, stoichiometric strategies to access acyl boronates. However, here too a significant limitation arises from functional-group intolerance because of the necessity to use aggressive reagents such as *n*BuLi.

In marked contrast, **2** and **3** proved to be excellent reagents for the synthesis of acyl boranes through their palladium-catalyzed reactions with acyl chlorides in a single step and with extraordinary functional-group tolerance (Table 2). Better results were obtained using $[Pd\{P(o\text{-}Tol)_3\}_2Cl_2]$ rather than $[Pd(PPh_3)_2Cl_2]$. The latter was shown shown to promote minor formation (5 to 15%) of the corresponding aryl borane because of a combination of decarbonylation and phosphorus/palladium aryl group exchange. These processes appear to be minimized with the bulkier *ortho*-tolyl phosphine.[16] Remarkably, halo, nitrile, ester, and nitro functionalities, and even the pendant aldehyde function in **8b**, remained untouched during borylation. In addition, the reaction proceeds equally well for aliphatic acyl chlorides, and even the reactive cyclopropanecarbonyl chloride (**7i**) was successfully borylated. In similar fashion, compounds **8k**/**8l** could be synthesized in high yields. These two systems feature heterocyclic cores of biological and pharmacological relevance,[17] and feature in oxacilin antibiotic derivatives[18] and in the serotonin receptor antagonist granisetron.[19]

Table 2: Substrate scope for the borylation of acyl chlorides (**7**) using [Pd{P(*o*-Tol)$_3$}$_2$Cl$_2$]/**3** system.[a]





[a] Reaction conditions: **3** (0.022 mmol), **7** (0.040 mmol), [Pd{P(*o*-Tol)$_3$}$_2$Cl$_2$] (3 mol%), THF (0.5 mL), 80 °C, 2 h. Yields were calculated by ^{1}H NMR spectroscopy using an internal standard. Yields of isolated products are given within parentheses.

Compounds **8a–k** were isolated/purified using preparative TLC glass plates (PTLC). In each case a distinctive ^{11}B-{^{1}H} NMR signal was measured in the $\delta = 19$–21 ppm range. Infrared bands in the range 1610–1640 cm^{-1} were observed for the acyl group, consistent with that reported for **8a** (1618 cm^{-1}).[11] The structures of **8h** and **8k** were further determined by X-ray diffraction studies (Figure 2). As with **8a**,[11] the C–O bond lengths [**8h**: 1.229(3) Å; **8k**: 1.234(4) Å] are slightly longer than those found in related ketones, presumably because of the strong σ-donor character of the boryl substituent. Other metrical parameters are comparable to those of **8a**.[11]

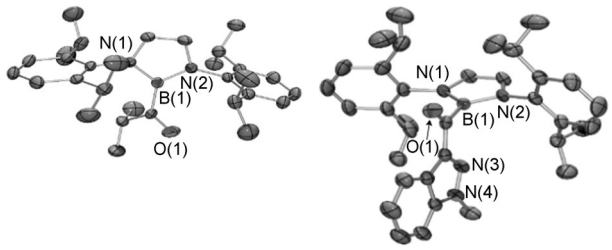
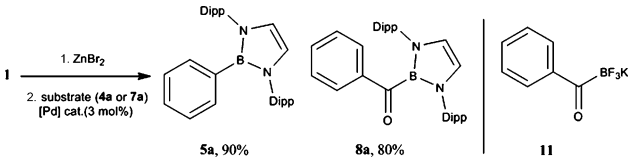


Figure 2. Molecular structures of **8h** and **8k** determined by crystallographically (thermal ellipsoids at 50% probability; H atoms omitted for clarity).[25]

From an ease-of-synthesis perspective the stability of the borylzinc compounds **1**–**3** towards air and moisture is of prime importance. Borylation reactions and subsequent C–X (X = C, N, O) cross-coupling processes have become ubiquitous in synthetic chemistry, in part due to the high stability to air and moisture of arylboronic acids and esters. Analysis of **1**–**3**, however, shows that the most active systems, namely **2** and **3**, possess half-lives in air (in the solid state) of only about 12 hours (see Figure S1). In contrast, the least active complex, **1**, is found to be stable in the solid state in air, showing no sign of decomposition over at least one month (see the Supporting Information). Crucially, we were able to show that the addition of one equivalent of $ZnBr_2$ to **1** in THF generates **3** in situ, which is competent for the synthesis of aryl-/acylboranes under our standard reaction conditions (Scheme 1).[20] Thus, bromobenzene (**4a**) and benzoylchloride



Scheme 1. Left: Convenient one-pot/two-step borylation protocol using the air- and moisture-stable **1**. Right: The acyltrifluoroborate **11**.

(**7a**) were converted into the phenylborane **5a** and benzoylborane **8a**, respectively, in yields essentially identical to those obtained using isolated samples of **3**. A simple one-pot procedure for the synthesis of acyl boranes is therefore feasible using materials which can be manipulated easily under bench-top conditions.

The versatility of acylborane synthesis described above relies, at least in part, on the kinetic inertness imposed by the bulky heterocyclic boryl substituent in **8**. To explore its usefulness in further synthetic applications, however, we have also explored onward conversion into more labile functionalities. As a representative example, the reaction of **8a** with [Bu$_4$N]F·4H$_2$O in tetrahydrofuran affords the corresponding acyltrifluoroboronate **11** in 93% spectroscopic yield (Scheme 1). The utility of **11** for the synthesis of amides,[14b,f] MIDA acylboronates (MIDA = *N*-methyliminodiacetyl)[14d] and monofluoroacylboronates[14e] has already been reported by Bode and co-workers. More comprehensive reactivity studies on **8** are ongoing and will be reported in due course.

Preliminary experiments also provide insight into mechanistic aspects of C–B bond formation. Carbon disulfide and phosphine quenching experiments suggest that a homogeneous palladium species is the active catalyst (see the Supporting Information).[21] This finding is in agreement with the fact that simple and heterogeneous forms of palladium (see Table S1), as well as palladium black generated in situ, are barely active. Nevertheless, the role of palladium nanoparticles cannot be completely ruled out at this stage. A radical pathway related to that previously proposed in zinc-catalyzed borylation reactions seems unlikely,[22] since little

cyclopropane ring opening and no cyclization reactions were observed in the synthesis of **8i** and **8j**, respectively. In the classically accepted Miyaura-type C–B coupling mechanism, $[Pd(PPh_3)_2(Ph)Br]$ (**9**) and $[Pd(PPh_3)_2\{C(O)Ph\}Cl]$ (**10**) are catalytic intermediates. Thus, isolated samples of **9** and **10** were investigated in stoichiometric reactions with **3** in $[D_8]$THF, revealing that 1) the reaction of **9** with **3** results in formation of the phenylborane **5a** in 89% yield; and 2) that the reaction of **10** with **3** does indeed yield **8a**, although contaminated with a higher proportion of the decarbonylation product **5a** than is observed under catalytic conditions. Whether the latter observation speaks to a different mechanistic pathway involving alternative (but precedented) steps such as generation of a palladium boryl species prior to C–halogen oxidative addition,[23] or direct attack of the boryl nucleophile at the carbonyl carbon atom of the Pd{C(O)Ar} function,[24] is currently being explored by both experimental and computational approaches.

In summary, nucleophilic borylzinc reagents prove to be efficient and versatile boron sources for the palladium-catalyzed borylation of aryl, vinyl, and benzylic bromides. Moreover, the kinetic inertness and thermodynamic stability of the heterocyclic boryl fragment employed has allowed us to develop the first systematic method for the preparation of acylboranes, whose potential utility for accessing acyltrifluoroboronates has also been demonstrated. Catalytic reactions proceed under mild reaction conditions by using simple and affordable palladium precatalysts, and exhibit remarkable functional-group tolerance. Furthermore, a robust and convenient one-pot/two-step procedure has been devised to enable this chemistry to be carried out using air-stable borylzinc reagents on the bench top.

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[25] CCDC 1410127 (**8h**) and 1410128 (**8k**)contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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