Cross-Coupling

Preparation and Synthetic Applications of [2.2]Paracyclophane Trifluoroborates: An Efficient and Convenient Route to Nucleophilic [2.2]Paracyclophane Cross-Coupling Building Blocks

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Abstract: We report the synthesis of [2.2]paracyclophane (PCP) trifluoroborate building blocks that can be used for the incorporation of the PCP moiety into a wide range of (hetero)aryl chlorides, bromides and triflates by a Pd(II)/RuPhos mediated Suzuki–Miyaura cross-coupling reaction. The PCP trifluoroborate species are bench stable with extended shelf life and easily accessible on a multigram scale by a two-step synthesis from commercially available PCP. They can be handled conveniently without special precautions, thus overcoming many of the limitations of other PCP cross-coupling reagents. Additionally, a high yielding regioselective monolithiation/borylation protocol for the synthesis of pseudo-*para* and pseudo-*ortho* PCP halotrifluoroborates and their subsequent Suzuki–Miyaura cross-coupling are described.

Introduction

The intriguing shape of [2.2]paracyclophane has fascinated researchers for over 70 years. It has been the subject of countless studies concerning its slightly off-aromatic character caused by the nonplanar geometry of the two co-facially stacked benzene rings. This has been described by Cram et al. as "bent and battered".[1]

Besides this fundamental curiosity, PCP has received increasing attention for its wide applications as a planar chiral ligands in asymmetric synthesis,[2] purely carbon and hydrogen based optical materials,[3] molecular junctions[4] and as a rigid backbone in light-emitting diode TADF emitters.[5]

In the last couple of years, transition-metal mediated cross-coupling reactions have dramatically changed the face of modern paracyclophane chemistry.[6] However, a common struggle in PCPs' synthetic transformation is the often unexpected and non-analogue reactivity when compared to the seemingly similar benzene or *p*-xylene chemistry. This disparity in chemical reactivity is most pronounced in cross-couplings and related reactions. Although cross-coupling reactions are among the most common methods to forge new carbon–carbon and carbon–heteroatom bonds, the unique electronic properties and geometric shape of the PCP make cross-coupling chemistry cumbersome,[7] sometimes surprising products are obtained,[8] or no conversion is observed altogether.

In cumulated work spanning decades, chemists succeeded in making most known cross-coupling reactions available for the functionalization of PCP.[9]

Our group has recently reported on efficient synthesis of carbon–carbon bond formation employing palladium-catalyzed reactions in combination with different PCP-based nucleophiles, for instance, PCP derivatives of magnesium (Kumada–Corriu), tin (Stille–Migita) and zinc (Negishi) (Scheme 1).[10] An exploration of [2.2]paracyclophane boronic acids in Suzuki–Miyaura cross-coupling has been examined.[11] However, PCP borates and their synthetic applications in carbon–carbon bond formation have not been reported to be successful so far (Scheme 1).

X = Mg, Zn, Sn, Hal   Y = B, Mg, Zn, Sn, Hal
no B
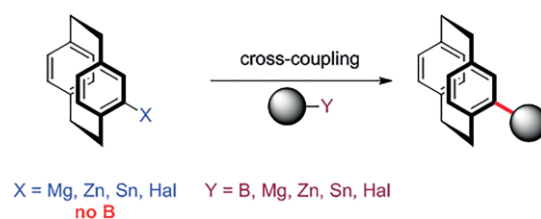
Scheme 1. Stable and cross-coupling active PCP borates have not been reported until very recently.[12]

Results and Discussion

Free PCP boronic acids suffer from prompt decomposition, while the corresponding boronic esters are inactive under catalytic reaction conditions.[11] To overcome this hurdle, very re-

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cently, we reported on the missing puzzle piece in the form of trifluoroborate **2**. This nucleophilic Suzuki–Miyaura cross-coupling building block is easily accessible in two steps from the PCP parent compound in high yield and gram scale batches (Scheme 2).[12]
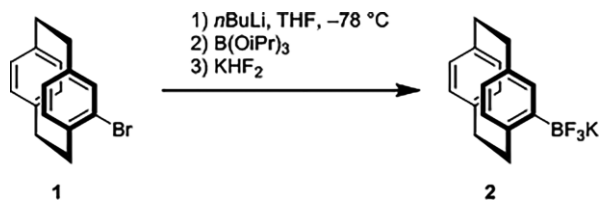
Scheme 2. Synthesis of PCP trifluoroborate **2**.

We reported on a cross-coupling protocol with the new PCP trifluoroborate to efficiently access pyridine and pyrimidine substituted PCPs.[12] The substrate scope was limited to 6-membered *N*-heterocycles. Various attempts to increase the reactivity of the catalyst system by use of common promoter-ligands like SPhos and XPhos were met with failure (even diminishing yields). RuPhos has been reported as the ligand of choice for the cross-coupling of alkyltrifluoroborates,[13] which in face of PCP's bulky, electron-rich and bent – thus less aromatic – character seemed like a possible solution to this challenge. Indeed, in stark contrast to the other phosphane ligands we have tested, the use of RuPhos not only gave better yields (Table 1) but showed great potential when applied to previously unreacting aryl halides.

Table 1. Effect of different phosphane ligands to promote the cross-coupling of bromopyridine.

Entry	Catalyst/ligand [mol-%]	Yield [%]
1	5/– ligand-free	37
2	5/15 SPhos	25
3	5/15 XPhos	35
4	5/15 RuPhos	**42**

After careful optimization of the reaction parameters including palladium source/ligand (Pd(OAc)$_2$/RuPhos), temperature (80 °C) and solvent effects (toluene/water), we subsequently studied the diverse substrate scope of [2.2]paracyclophane trifluoroborates in Suzuki–Miyaura cross-coupling reaction. The

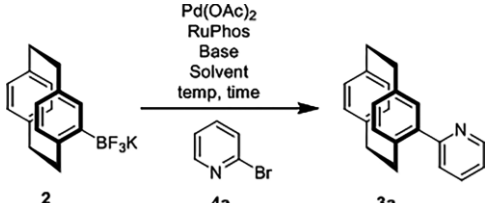Table 2. Substrate scope of the Suzuki–Miyaura cross-coupling protocol.

Entry	Halide	Product	Yield (%)[a]
1	**4a**	**3a**	42
2	**4b**	**3b**	92
3	X = Cl **4c-Cl**, Br **4c-Br**, OTf **4c-OTf**	**3c**	Cl 69, Br 81, OTf 79
4	**4d**	**3d**	87
5	**4e**	**3e**	74
6	**4f**	**3f**	89
7	**4g**	**3g**	91
8	**4h**	**3h**	86
9	**4i**	**3i**	23
10	**4j**	**3j**	88
11	**4k**	**3k**	90
12	**4l**	**3l**	78
13	**4m**	**3m**	34
14	**4n**	**3n**	87
15	**4o**	**3o**	25
16	**4p**	**3p**	51
17	**4q**	**3q**	-

[a] Isolated yields.

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results are shown in Table 2. The protocol tolerates a wide range of functional groups like nitriles, esters, ethers, hydroxides, alkynes, ketones, nitroarenes and amines. The PCP can be coupled efficiently regardless of the steric and electronic effects of the coupling substrates. Even though electron withdrawing groups (entries 2–6) consistently lead to better results, electron rich derivatives (entries 7–10) were obtained in high yields as well. The successful coupling of sterically very demanding mesitylene (entry 15), thiophene (entry 14) and benzylic nitrile (entry 16) derivatives emphasize the versatility of this approach. The substrate scope not only comprises bromides but also triflates and less reactive chlorides which were converted in good yields (entry 3). However, sp^3-hybridized cyclohexyl bromide **4q** did not give the desired product (entry 17). Aromatic amines proved to be challenging substrates and lead to a significantly reduced yield of 23 % (entry 9).

The substrate scope shows good to excellent yields for a wide range of electrophiles. Optimization to improve reaction conditions for the synthesis of the sluggishly reacting **4a** was conducted as shown in Table 3. The combination of sodium carbonate as base and a mixture of toluene and water (1:1) provided **3a** in excellent yields of up to 82 %. Further increasing the water content of the solvent mixture (entries 14–15) did not lead to improved results. The yield obtained in this way is almost a twofold improvement when compared to our earlier reports employing the Stille cross-coupling protocol.[10,12] However, the newly optimized reaction conditions did not improve yields for entries 2–17 in Table 2. The cross-coupling of bromopyridines seems to generally require different conditions, as already was shown by the substrate scope of our previous report.[12]

Inspired by the work on iterative cross-coupling methodology developed by Burke et al.,[14] we then set out to synthesize PCP halotrifluoroborates. The required monolithiation of dibromo PCPs exploits the following finding: The two-fold metal-halogen exchange of pseudo-*ortho* and pseudo-*para* dibromo[2.2]paracyclophane (**5** and **7**) has been described as tedious and requires *tert*-butyllithium or large excess of *n*-butyllithium in THF.[15] Thus, the synthesis of unexplored halotrifluoroborates containing a bromide substituent for further transformation was achieved in good yield for the pseudo-*para* and pseudo-*ortho* derivatives **6** and **8** (Scheme 3). These PCP halotrifluoroborates can be utilized to produce a wide range of diverse PCP molecular architectures.
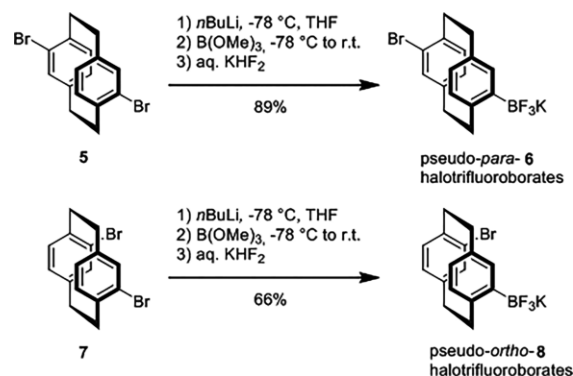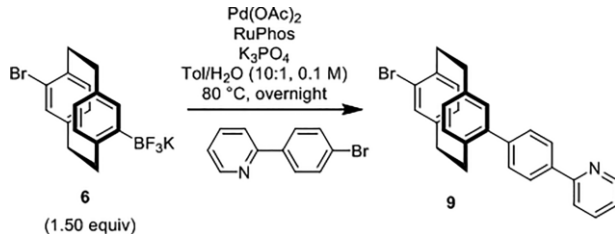

Scheme 3. Synthesis of the pseudo-*para* and pseudo-*ortho* halotrifluoroborate salts **6** and **8**.

A subsequent Suzuki–Miyaura cross-coupling reaction was carried out employing halotrifluoroborate **6** with 2-(4-bromophenyl)pyridine leading to the desired product **9**. However, the product was obtained in a poor yield of 20–30 %. This drastic change in reactivity apparently imparted by just one remote bromide substituent has been reported before.[16]

Optimization of the reaction conditions lead to satisfying yields of 50 % for **9** (Table 4). Interestingly, increasing the equivalents of the trifluoroborate salt had the adverse effect of lower-

Table 3. Optimization study for the synthesis of **3**.

Entry	Base	Temp (°C)	Solvent[a]	Yield [%][b]
1	K$_3$PO$_4$	80	Tol/H$_2$O 10:1	39
2	K$_3$PO$_4$	80	Tol/H$_2$O 3:1	41
3	K$_3$PO$_4$	80	Tol/H$_2$O 1:1	48
4	K$_2$CO$_3$	80	Tol/H$_2$O 1:1	63
5	KOH	80	Tol/H$_2$O 1:1	58
6	Cs$_2$CO$_3$	80	Tol/H$_2$O 1:1	61
7	Na$_2$CO$_3$	80	Tol/H$_2$O 1:1	71 (73)[c]
8	Na$_2$CO$_3$	60	Tol/H$_2$O 1:1	56 (60)[c]
9	Na$_2$CO$_3$	100	Tol/H$_2$O 1:1	42
10[d]	Na$_2$CO$_3$	80	Tol/H$_2$O 1:1	57
11[f]	Na$_2$CO$_3$	80	Tol/H$_2$O 1:1	66
12[e]	Na$_2$CO$_3$	80	Tol/H$_2$O 1:1	**73**
13[g]	Na$_2$CO$_3$	80	Tol/H$_2$O 1:1	48
14	Na$_2$CO$_3$	80	Tol/H$_2$O 1:2	70
15	Na$_2$CO$_3$	80	Tol/H$_2$O 1:5	71

[a] 0.1 M, 10 mol-% catalyst load. [b] Yield determined by NMR, 1,3,5-Trimethoxybenzene as standard. [c] After 3 days. [d] 0.2 M. [e] 5 mol-% catalyst load. [f] 2 mol-% catalyst load. [g] 1 mol-% catalyst load.

Table 4. Optimization study for the synthesis of **9**.

Entry	Deviation from standard	Yield [%][a]
1	none	22
2	1.00 equiv. **6**	35
3	3.00 equiv. **6**	18
4	Tol/H$_2$O 10:1 0.2 M	50
5	Tol/H$_2$O 1:1 0.2 M	50
6	Tol/H$_2$O 1:1 0.6 M	37
7	Na$_2$CO$_3$, 0.2 M	16
8	K$_2$CO$_3$, 0.2 M	43
9	Cs$_2$CO$_3$, 0.2 M	44

[a] NMR yields, 1,3,5-trimethoxybenzene as standard.

ing the yield, while equimolar amounts led to an increase in yield (entry 2 and 3). Concentration of the reagents in the organic phase seem to be the most important aspect where 0.2 M seems to be the sweet spot as more and less concentrated conditions both led to lower yields (entry 1 and 6). We have also examined the Suzuki–Miyaura cross-coupling reaction employing halotrifluoroborate **8** based on the pseudo-*ortho* regioisomer. While NMR analysis confirm the coupling product, however our efforts using the standard optimized protocol were disappointing as we were not able yet to improve/isolate the resulting coupling product in sufficient purity. One possible explanation might be the high steric repulsion.

Conclusions

We have successfully prepared and characterized PCP trifluoroborate building blocks that are a convenient starting point for the incorporation of the PCP core by palladium-catalyzed Suzuki–Miyaura cross-coupling into a wide range of (hetero)aryl bromides, chlorides and triflates. These [2.2]paracyclophane trifluoroborates can be easily prepared on a multi-gram-scale by a two-step synthesis from commercially available PCP. The nucleophilic species are bench-stable without special precautions/degradation for months comparing to their boronic acid/boronate esters and other counterparts which overcome many of the limitations and can find widespread use as alternative to boronic acids in PCP-based cross-coupling reactions. The reaction is generally high-yielding and tolerates most functional groups. Selective monolithiation/borylation/Suzuki–Miyaura coupling offers entry into dissymmetric PCPs by exclusive cross-coupling of the trifluoroborate moiety described herein and subsequent functionalization of the remaining bromide substituent. Research efforts towards the development of dissymmetric metal-based bitopic ligand systems based on the corresponding PCP-hetero(aryl) products are currently underway in our laboratories.

Experimental Section

Synthesis of potassium 4-trifluoroborate[2.2]paracyclophane (2).

In a round bottom-flask under argon, 4-bromo[2.2]paracyclophane (5.02 g, 17.5 mmol, 1.00 equiv.) was dissolved in 250 mL anhydrous THF. The solution was cooled to −78 °C and *n*BuLi (7.70 mL, 2.5 M, 19.3 mmol, 1.10 equiv.) was added dropwise by syringe. After one hour, the yellow solution was quenched with trimethylborate (6.1 mL, 26.2 mmol, 1.50 equiv.). The now colorless solution was allowed to slowly warm to room temperature. The next day, aqueous potassium hydrogen difluoride (23.3 mL, 4.5 M, 105 mmol, 6.00 equiv.) was added by syringe and the mixture was stirred vigorously for 3 hours. After removal of the solvents under reduced pressure, the white residue was triturated with acetone (2 × room temperature, 2 × boiling, 50 mL each) and the acetone removed under reduced pressure subsequently. The white residue was washed with dichloromethane and diethyl ether (100 mL each) and dried in high vacuum to yield a powdery white crystalline solid (4.79 g, 87 %).

^{1}H NMR (400 MHz, [D$_6$]Acetone) δ [ppm] = 6.76 (dd, J = 7.8, 1.5 Hz, 1H), 6.69 (s, 1H), 6.43 (d, J = 1.7 Hz, 2H), 6.30 (dd, J = 7.8, 1.5 Hz,

1H), 6.17 (d, J = 1.7 Hz, 2H), 3.67 (ddd, J = 12.5, 10.5, 2.5 Hz, 1H), 3.15–3.00 (m, 3H), 2.93–2.70 (m, 4H). – ^{13}C NMR (101 MHz, [D$_6$]-Acetone) δ [ppm] = 144.1 (C$_{quat.}$), 141.1 (C$_{quat.}$), 139.6 (C$_{quat.}$), 137.4 (C$_{quat.}$), 137.1 (C$_{quat.}$), 134.7 (+, C$_{Ar}$H), 134.7 (+, C$_{Ar}$H), 133.7 (+, C$_{Ar}$H), 133.6 (+, C$_{Ar}$H), 132.8 (+, C$_{Ar}$H), 132.6 (+, C$_{Ar}$H), 131.2 (+, C$_{Ar}$H), 36.51 (−, CH$_2$), 36.41 (−, CH$_2$), 36.33 (−, CH$_2$), 36.16 (−, CH$_2$). ^{11}B NMR (128 MHz, [D$_6$]Acetone) δ [ppm] −15.2 (d, J = 59.2 Hz). – ^{19}F NMR (376 MHz, [D$_6$]Acetone) δ [ppm] −143.23 (m). IR (ATR) $\tilde{v}$ = = 3569 (w), 3378 (w), 2925 (w), 2851 (w), 1894 (vw), 1589 (w), 1552 (vw), 1500 (vw), 1478 (vw), 1436 (vw), 1410 (w), 1330 (w), 1231 (w), 1186 (vw), 1149 (w), 1107 (w), 938 (w), 901 (w), 834 (w), 793 (w), 736 (w), 719 (w), 643 (w), 615 (vw), 590 (vw), 511 (w), 482 (vw). HRMS (FAB) (C$_{16}$H$_{15}$^{11}B$_1$F$_3$K$_1$) calcd. 314.0856, found 314.0854.

Synthesis of potassium 4-bromo-16-trifluoroborate[2.2]para-cyclophane (6).

A flame-dried 1 L Schlenk flask was charged with 4,16-dibromo[2.2.]paracyclophane (3.00 g, 8.20 mmol, 1.00 equiv.) and dry THF (900 mL). The reaction mixture was stirred at room temperature until the starting material was completely dissolved and then was cooled to −78 °C and *n*BuLi (3.61 mL, 9.01 mmol, 1.10 equiv.) was added dropwise via syringe. The solution became orange in color and faded to a pale yellow. This step was allowed to proceed for 30 minutes. Then dry trimethyl borate (2.08 mL, 9.01 mmol, 1.10 equiv.) was added all at once. The mixture was stirred for 30 minutes and warmed slowly to room temperature. The next day, sat. aqueous potassium hydrogen fluoride (10.9 mL, 49.2 mmol, 6 equiv.) was added and the mixture stirred for 1 h. The solvents were removed under reduced pressure. The residue was triturated with hot acetone (4 × 100 mL). After removal of the solvent, the residue was washed thoroughly with diethyl ether and dichloromethane and dried under reduced pressure to yield the pure product as a white solid.

Yield 2.55 g, 79 %. ^{1}H NMR (500 MHz, [D]Chloroform) δ [ppm] = 6.87 (dd, J = 7.6, 1.7 Hz, 1H), 6.80 (dd, J = 7.5, 2.1 Hz, 1H), 6.71 (d, J = 2.1 Hz, 1H), 6.50 (d, J = 1.7 Hz, 1H), 6.33 (d, J = 7.7 Hz, 1H), 6.15 (d, J = 7.6 Hz, 1H), 3.70 (dd, J = 10.7, 8.8 Hz, 1H), 3.32 (ddd, J = 13.1, 10.3, 2.8 Hz, 1H), 3.14–3.03 (m, 2H), 2.95–2.73 (m, 5H). – ^{13}C NMR (101 MHz, CDCl$_3$) δ [ppm] = 143.9, 143.8, 138.9, 137.7, 137.7, 136.9, 136.9, 136.0, 133.7, 132.8, 126.8, 126.5, 36.0, 35.9, 35.3, 34.7. ^{11}B NMR (128 MHz, [D$_6$]Acetone) δ [ppm] −14.9. ^{19}F NMR (376 MHz, [D$_6$]Acetone) δ [ppm] −143.1. HRMS (C$_{16}$H$_{14}$BBrF$_3$K) calcd. 391.9961, found 391.9963.

Synthesis of potassium 4-bromo-12-trifluoroborate[2.2]para-cyclophane (8).

A flame-dried 1 L Schlenk flask was charged with 4,16-dibromo[2.2.]paracyclophane (3.00 g, 8.20 mmol, 1.00 equiv.) and dry THF (300 mL). The reaction mixture was stirred at room temperature until the starting material was completely dissolved and then was cooled to −78 °C and *n*BuLi (3.61 mL, 9.01 mmol, 1.10 equiv.) was added dropwise via syringe. The solution became orange in color and faded to a pale yellow. This step was allowed to proceed for 30 minutes. Then dry trimethyl borate (2.08 mL, 9.01 mmol, 1.10 equiv.) was added all at once. The mixture was stirred for 30 minutes and warmed slowly to room temperature. The next day, sat. aqueous potassium hydrogen fluoride (10.9 mL, 49.2 mmol, 6 equiv.) was added and the mixture stirred for 1 h. The solvents were removed under reduced pressure. The residue was triturated with hot acetone (4 × 100 mL). After removal of the solvent, the residue was washed thoroughly with diethyl ether and dichloromethane and dried under reduced pressure to yield the pure product as a white solid.

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Yield 2.13 g, 66 %. ^{1}H NMR (500 MHz, [D]Chloroform) δ [ppm] = 7.29 (d, J = 2.1 Hz, 1H), 6.83 (d, J = 1.6 Hz, 1H), 6.54 (dd, J = 7.7, 1.6 Hz, 1H), 6.47 (d, J = 7.7 Hz, 1H), 6.31 (d, J = 7.6 Hz, 1H), 6.23 (dd, J = 7.6, 2.1 Hz, 1H), 3.67 (ddd, J = 12.1, 10.4, 1.8 Hz, 1H), 3.38–3.29 (m, 1H), 3.11–2.94 (m, 2H), 2.92–2.83 (m, 2H), 2.82–2.67 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ [ppm] = 144.0, 143.5, 139.2, 138.2, 138.2, 138.1, 138.1, 136.8, 135.2, 133.3, 133.3, 133.3, 131.8, 131.5, 127.6, 36.7, 36.6, 35.1, 33.8. ^{11}B NMR (128 MHz, [D$_6$]Acetone) δ [ppm] –15.0. ^{19}F NMR (376 MHz, [D$_6$]Acetone) δ [ppm] –144.0. HRMS (C$_{16}$H$_{14}$BBrF$_3$K) calcd. 391.9961, found 391.9962.

General cross-coupling procedure for the synthesis of (3a–q).

In a vial fitted with a magnetic stirring bar, potassium 4-trifluoroborate[2.2]paracyclophane (1.50 equiv.), potassium phosphate (4.00 equiv.), palladium acetate (0.05 equiv.), RuPhos (0.15 equiv.) and the respective halide (1.00 equiv., if solid) were placed. The vial was capped, evacuated and backfilled with argon three times. After addition of the solvent (toluene/water, 10:1, 0.1 M), the respective halide (1.00 equiv., if liquid) was added via syringe. The vial was put into a vial heating block and heated to 80 °C for 24 hours. The reaction was cooled to ambient temperature and quenched with sat. aq. ammonium chloride. After separation of the phases, the aqueous phase was extracted with dichloromethane (3 × 15 mL). The organic phases were dried with sodium sulfate and the solvent was removed under reduced pressure. The crude product was purified via column chromatography (silica, pentane/ethyl acetate).

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