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Arylboration of 1-Arylalkenes by Cooperative Nickel/Copper Catalysis

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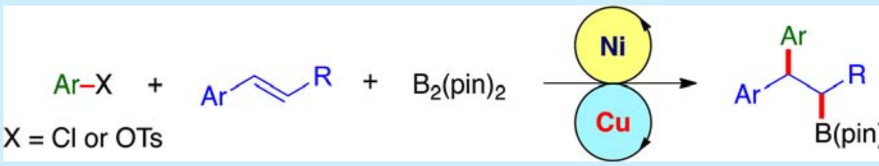
Supporting Information

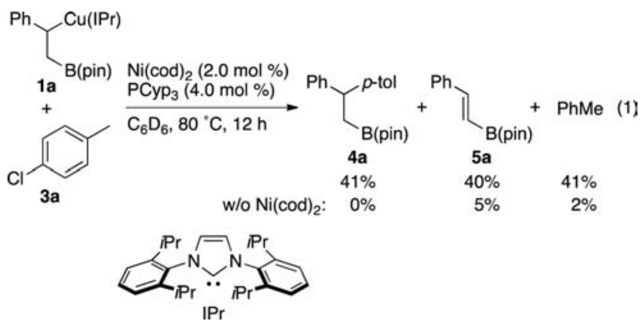


ABSTRACT: A method for the arylboration of 1-arylalkenes with bis(pinacolato)diboron and aryl chlorides or tosylates by cooperative Ni/Cu catalysis has been developed, which affords 2-boryl-1,1-diarylalkanes in high regio- and stereoselectivity. Under the applied conditions, this method is tolerant toward various functional groups, including silyl ether, alkoxycarbonyl, and aminocarbonyl moieties.

Alkylboranes are useful synthetic intermediates in organic synthesis, as the C−B bonds can be readily converted into C−C, C−O, or C−N bonds.[1] Conventionally, such C−B bonds are prepared via the hydroboration of alkenes[2] or the nucleophilic substitution of $B(OR)_3$ with organolithium or organomagnesium reagents.[3] Transition-metal-catalyzed carboborations[4] of alkenes represent another powerful tool for the preparation of alkylboranes, mostly on account of their high functional group tolerance and the readily available variety of alkenes.[5] To date, both the intra- and intermolecular carboborations of alkenes have been accomplished by catalytic methods based on a single metal. Recently, our group and that of Brown independently reported the intermolecular arylboration of alkenes with bis(pinacolato)diboron ($B_2(pin)_2$) and aryl halides by cooperative Pd/Cu catalysis.[6] However, the use of Pd catalysts is not cost-effective, and phenol-derived electrophiles, which are generally more readily available compared to aryl halides, are restricted to aryl triflates. Conversely, aryl tosylates, which are easier to access and handle than aryl triflates, cannot be used as substrates in such reactions. Herein, we report the arylboration of alkenes with aryl chlorides or tosylates and $B_2(pin)_2$ by cooperative Ni/Cu catalysis.[7,8]

To test the viability of a cooperative Ni/Cu catalysis, we initially examined the cross-coupling of alkylcopper **1a**,[9] which was prepared by a borylcupration of styrene (**2a**), with *p*-chlorotoluene (**3a**) (eq 1). Even though **4a** was gratifyingly obtained in 41% yield, alkenylboronate **5a** and toluene were also formed in 40% and 41% yield, respectively. In the absence of $Ni(cod)_2$, the formation of **4a** was not observed. These preliminary results encouraged us to investigate and develop cross-coupling reactions based further on cooperative Ni/Cu catalysis.

For that purpose, we carried out the arylboration of **2a** with **3a** and $B_2(pin)_2$ in the presence of $Ni(cod)_2$ (2.0 mol %), tricyclopentylphosphine ($PCyp_3$, 4.0 mol %), (IPr)CuCl (1.0 mol %), and LiO*t*Bu (1.5 mmol). The reaction proceeded



catalytically and furnished **4a** in 53% yield. Subsequently, we screened the reaction conditions with respect to various nickel and copper sources, phosphine ligands, and bases. As a result, we found that the arylboration of **2a** (1.0 mmol) with **3a** (1.0 mmol) and $B_2(pin)_2$ (1.0 mmol) afforded **4a** in 72% yield in the presence of $Ni(acac)_2$ (2.0 mol %), CuCl (1.0 mol %), $PCyp_3$ (6.0 mol %), and LiO*t*Bu (1.5 mmol), under concomitant formation of small amounts of **5a**, **6a**, and **7a** (entry 1, Table 1). The effects of varying the monodentate phosphine ligand are summarized in entries 2−6 (Table 1).[10] When PPh_3, P*n*Pr_3, and P*t*Bu_3 were employed, the formation of **4a** was not observed (entries 2, 3, and 6). The use of P*i*Pr_3 and PCy_3 resulted in the formation of **4a**, albeit in lower yield compared to using $PCyp_3$ (entries 4 and 5). Bidentate ligands such as 1,2-bis(diphenylphosphino)ethane (dppe) and 2,2′-bipyridine (bpy) did not promote the formation of **4a** (entries 7 and 8). Moreover, the presence of LiO*t*Bu was found to be crucial in order to obtain **4a** in good yield. Other bases such as LiOMe, NaO*t*Bu, or KO*t*Bu afforded **4a** in very low yield (entries 9−11). The arylboration of **2a** did not proceed in the absence of $Ni(acac)_2$, and without CuCl, the yield of **4a**

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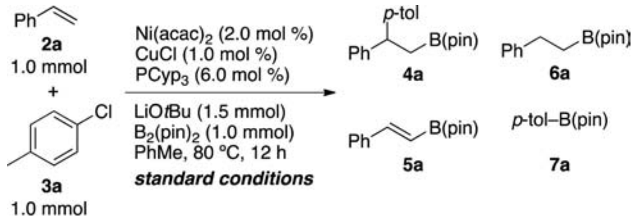
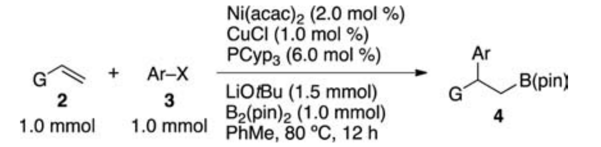
Table 1. Optimization of the Reaction Conditions for the Arylboration of 2a with 3a and $B_2(pin)_2$

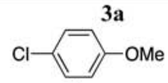
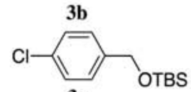
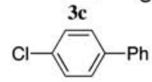
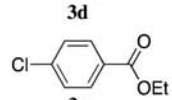
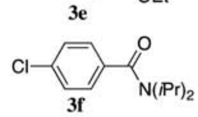
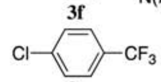
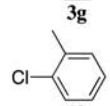
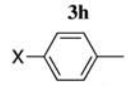
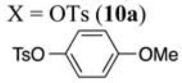
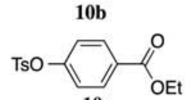
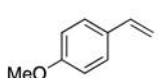
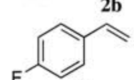
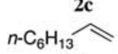


entry	variation from the standard conditions	yield 4a (%)[a]	yield 5a (%)[a]	yield 6a (%)[a]	yield 7a (%)[a]
1	none	72	3	1	1
2	PPh_3 instead of $PCyp_3$	<1	2	<1	<1
3	P^nPr_3 instead of $PCyp_3$	<1	2	24	<1
4	P^iPr_3 instead of $PCyp_3$	47	3	4	<1
5	PCy_3 instead of $PCyp_3$	56	3	2	5
6	P^tBu_3 instead of $PCyp_3$	<1	5	2	<1
7	dppe instead of $PCyp_3$	<1	3	15	<1
8	bpy instead of $PCyp_3$	<1	5	12	<1
9	LiOMe instead of LiO*t*Bu	5	9	2	<1
10	NaO*t*Bu instead of LiO*t*Bu	<1	5	12	<1
11	KO*t*Bu instead of LiO*t*Bu	<1	4	35	<1
12	without $Ni(acac)_2$	<1	<1	14	<1
13	without CuCl	11	5	<1	10

[a]The yield was estimated by GC, using $n\text{-}C_{13}H_{28}$ as an internal standard.

Table 2. Arylboration of 2 with 3 and $B_2(pin)_2$



entry	2	3	yield 4 (%)[a]
1	2a	3a	61 (4a)
2	2a	 3b	57 (4b)
3	2a	 3c	65 (4c)
4[b]	2a	 3d	70 (4d)
5	2a	 3e	67 (4e)
6	2a	 3f	62 (4f)
7	2a	 3g	65 (4g)
8[c]	2a	 3h	35 (4h)
			
9	2a	X = Br (8a)	70 (4a)[d]
10	2a	X = OTf (9a)	20 (4a)[d]
11[e]	2a	X = OTs (10a)	47 (4a)[d]
12[b,e]	2a	 10b	22 (4b)
13[b,e]	2a	 10c	55 (4e)
14	 2b	3a	62 (4i)
15	 2c	3a	62 (4j)
16	 2d	3a	< 1 (4k)

[a]Isolated yield. [b]Scale: 0.50 mmol. [c]Run at 100 °C using $Ni(acac)_2$ (5.0 mol %), CuCl (1.0 mol %), and $PCyp_3$ (12 mol %). [d]The yield was estimated by GC, using $n\text{-}C_{13}H_{28}$ as an internal standard. [e]Run at 100 °C using $NiCl_2(dme)$ (5.0 mol %), CuCl (5.0 mol %), and $PCyp_3$ (20 mol %).

decreased dramatically (entries 12 and 13). These results demonstrate that the cooperative Ni/Cu catalysis is indispensable for the present arylboration.

With optimized conditions in hand, we examined the substrate scope of this reaction (Table 2). Electron-donating and -withdrawing substituents at the *para*-position of the benzene ring of the aryl chlorides did not affect the yield, affording the corresponding products in moderate to good yield (entries 1−7), while the use of *o*-tolyl chloride (**3h**) resulted in a lower yield (entry 8). Under the identical conditions, *p*-tolyl bromide (**8a**) afforded **4a** in high yield (entry 9), whereas *p*-tolyl triflate (**9a**) reacted sluggishly (entry 10). Aryl tosylates gave the corresponding 1,1-diarylethanes albeit in modest yields (entries 11−13). Both electron-rich and -poor styrene derivatives were suitable substrates for the present reaction (entries 14 and 15). Various functional groups such as silyl ether, alkoxycarbonyl, aminocarbonyl, and trifluoromethyl moieties remained unaffected under the applied reaction conditions. The reaction of 1-octene (**2d**) proceeded sluggishly, most likely on account of the low reactivity of **2d** toward the borylcupration (entry 16).[11] The arylboration of (*E*)-1-phenyl-1-propene (**2e**) and (*Z*)-1-phenyl-1-propene (**2f**) proceeded to furnish *syn*-**4l** as a major diastereomer in both cases (eqs 2 and 3).[12]

A plausible reaction mechanism for the present reaction is outlined in Scheme 1. *In situ* generated LNi(0) (**11**) should oxidatively add across **3** to afford LNi(Ar)Cl (**12**) (step *a* in the Ni cycle). Transmetalation between **12** and alkylcopper **1**, which should be generated from the borylcupration of **2**, was followed by reductive elimination from **13** (steps *b* and *c* in the Ni cycle; eq 1). The catalytic cycle would be completed by the regeneration of borylcopper **14** from $B_2(pin)_2$ and LCuO*t*Bu **16**, which would have been obtained from **15** and LiO*t*Bu (steps *e* and *f* in the Cu cycle). The arylboration of (*E*)-1-phenyl-1-propene was stereospecific whereas that of the (*Z*)-isomer was not (eqs 2 and 3). The reason is not clear, but configurational isomerization of the alkylcopper intermediate derived from the (*Z*)-olefin may be responsible for this observation.[13]

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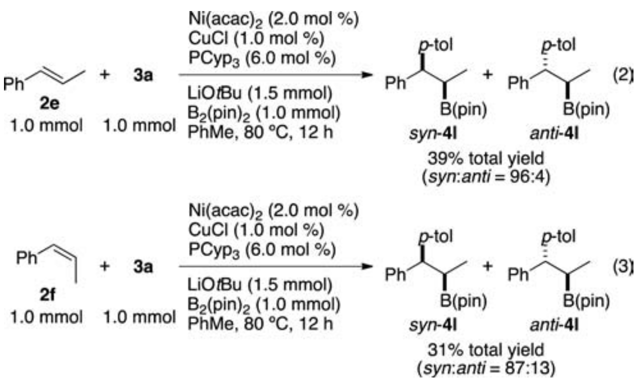
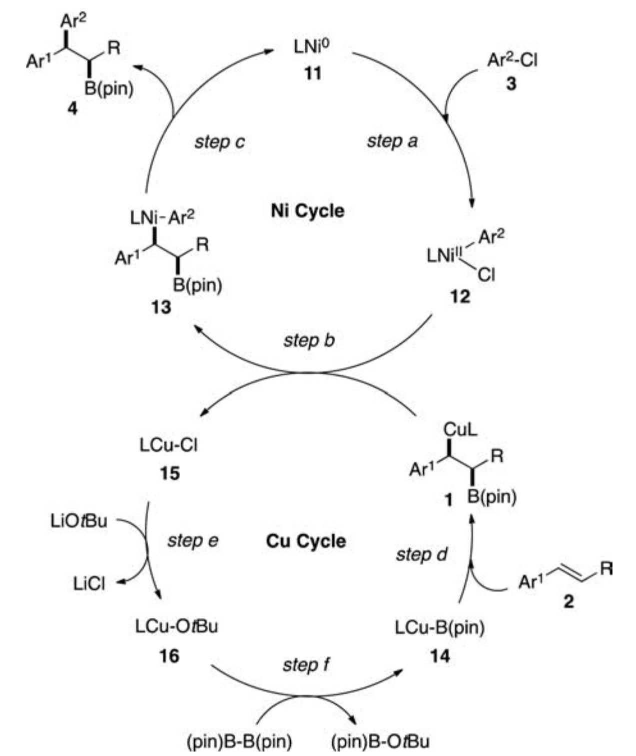


Scheme 1. A Plausible Mechanism for the Arylboration of 1-Arylalkenes by Cooperative Ni/Cu Catalysis



In conclusion, we have developed a method for the arylboration of alkenes with aryl chlorides or tosylates and $B_2(pin)_2$ by cooperative Ni/Cu catalysis. The reaction proceeds regio- and stereoselectively to afford 2-boryl-1,1-diarylalkanes, which represent potent intermediates for the generation of 1,1-diarylalkanes. This novel Ni/Cu catalysis should provide valuable insights for the development of advanced cooperative base metal catalysis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01675.

Detailed experimental procedures including spectroscopic and analytical data (PDF)

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Notes

The authors declare no competing financial interest.

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(10) When a mixture of pregenerated complexes $Ni(cod)_2/2PPh_3$ and $CuCl/2PCy_3$ or $Ni(cod)_2/2PCy_3$ and $CuCl/2PPh_3$ were used in the arylboration of **2a** with **3h** and $B_2(pin)_2$, the crossover of PPh_3 and PCy_3 on nickel and copper was observed. See the Supporting Information for details.

(11) The borylcupration of 1-hexene with (IPr)CuB(pin) proceeds sluggishly; see: Reference 9.

(12) For stereoselective arylborations, see: Reference 6c.

(13) For a reference of configurational isomerization of an alkylcopper, see: Morozova, V.; Moriya, K.; Mayer, P.; Knochel, P. *Chem. - Eur. J.* **2016**, *22*, 9962.

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