Borylation

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A Facile Route to Aryl Boronates: Room-Temperature, Copper-Catalyzed Borylation of Aryl Halides with Alkoxy Diboron Reagents**

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Aryl boronic acid derivatives, especially aryl boronate esters of diols, are of great importance in organic synthesis, in particular as substrates for the Suzuki–Miyaura cross-coupling.[1a,b] Classically, they are prepared by the treatment of trialkyl borates with magnesium or lithium alkyl reagents, followed by hydrolysis or transesterification with the diol of interest. However, this method is restricted to substrates free of reactive functional groups: additional costly protection/deprotection steps may be required.[1] Alternative routes to aryl boronates have been developed, including palladium-catalyzed cross-coupling reactions of alkoxy diboron[2] or alkoxy borane[3] reagents with aryl halides, the related nickel-catalyzed[4] borylation of aryl halides with alkoxy borane reagents, and the selective iridium-catalyzed C–H-borylation[5] of aromatic substrates. The copper-catalyzed coupling of aryl iodides (but not aryl bromides) with pinacolborane (HBpin, pin = $OCMe_2CMe_2O$) in the presence of copper(I) iodide and sodium hydride at room temperature was also reported recently by Zhu and Ma.[6] Furthermore, copper(I) boryl complexes are of interest in their own right, as intermediates in the borylation of α,β-unsaturated carbonyl compounds,[7,8a,9] the diboration of alkenes[10,8b,c,11] and aldehydes,[8d,12] and the reduction of CO_2 to CO.[8e,13] However, thus far only two copper(I) boryl complexes have been isolated and characterized in detail.[13,14]

In the course of our studies of copper-catalyzed borylation reactions,[8] we investigated the reaction of a copper(I) boryl complex with various substrates, in particular with aryl halides (Figure 1). Treatment of the known and well-characterized[13] boryl complex [(*i*PrNHC)CuBpin] (**2a**; *i*PrNHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), prepared in situ from [(*i*PrNHC)CuO*t*Bu] (**1a**) and B_2pin_2, with $4\text{-}MeC_6H_4I$ led to the formation of $4\text{-}MeC_6H_4Bpin$ (**4a**), as shown by in situ NMR spectroscopy (Figure 1; see Figure S1 in the Supporting Information for ¹H NMR spectroscopic data).

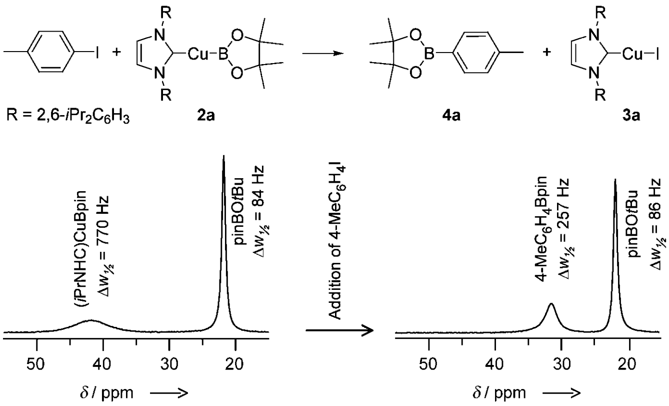
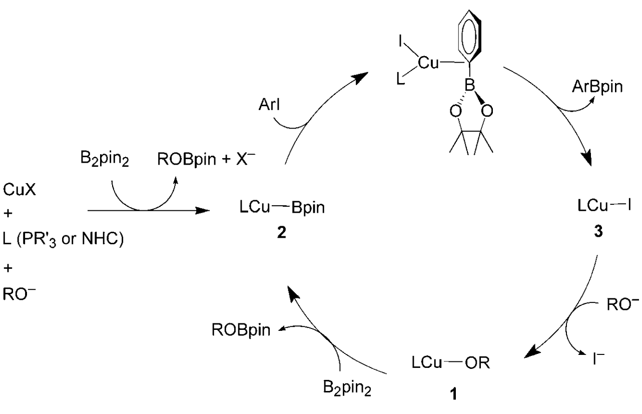


Figure 1. Formation of **4a**, as monitored by in situ $^{11}B\{^1H\}$ NMR spectroscopy (128 MHz, C_6D_6, room temperature). Left-hand spectrum: formation of **2a** from **1a** and B_2pin_2; right-hand spectrum: subsequent reaction with $4\text{-}MeC_6H_4I$ to form **4a** and **3a**.

On the basis of this observation, and assisted by DFT calculations,[15] we envisaged a catalytic cycle for a potentially very useful, copper-catalyzed borylation of aryl halides (Scheme 1, L = *i*PrNHC). All steps of the outlined catalytic cycle, aside from the C–B bond-formation step, can be assumed to proceed smoothly, as they, or closely related stoichiometric reactions, have been reported previously to



Scheme 1. A possible, simple catalytic cycle for the copper-catalyzed borylation of aryl halides.

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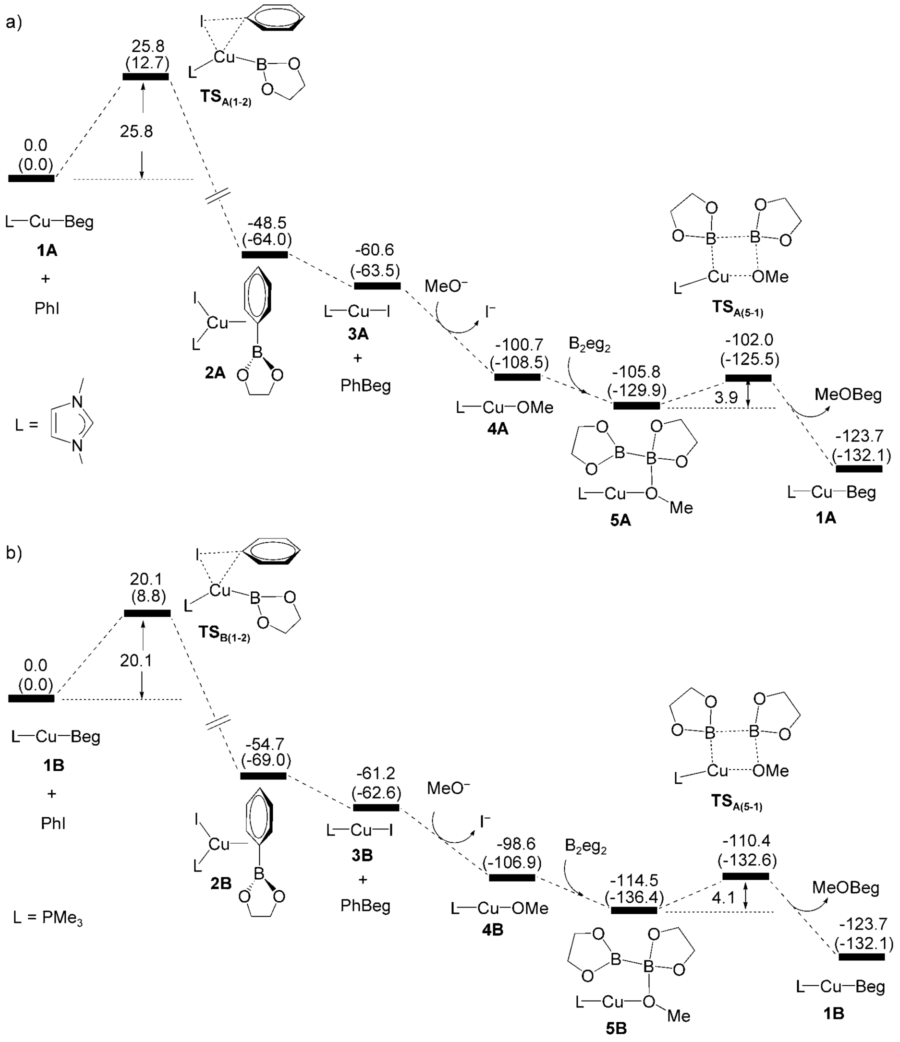


Figure 2. Energy profiles calculated for the copper-catalyzed borylation of PhI with the model ligand a) Me_2NHC or b) Me_3P on the basis of the catalytic cycle proposed in Scheme 1. Relative free energies and electronic energies (in parentheses) are given in kcal mol^{-1}. Beg (eg = OCH_2CH_2O) was used to model Bpin.

proceed readily.[8a,13,16] Our DFT calculations[15] show that the C—B bond-formation step is indeed favorable, and could proceed through σ-bond metathesis, with an activation barrier of $\Delta E^{\neq} = 12.7$ kcal mol^{-1}, $\Delta G^{\neq} = 25.8$ kcal mol^{-1} for PhI (Figure 2a).

Indeed, when the reaction was performed in the manner outlined with [(*i*PrNHC)CuO*t*Bu] (**1a**; 10 mol%) as the catalyst precursor in THF at ambient temperature, 4-MeC_6H_4Bpin was formed, but only with moderate conversion (18% after 5 h, 55% after 17 h). According to our theoretical studies, phosphanyl copper boryl complexes, suspected to be the catalytically active species in the well-established borylation of α,β-unsaturated carbonyl compounds, are closely related to N-heterocyclic carbene (NHC) copper boryl complexes (Figure 2).[8a] In fact, our computed activation energy for the C—B bond-formation step is lower with L = PMe_3 than with L = Me_2NHC. We therefore used [(*n*Bu_3P)CuO*t*Bu] (**1b**; 10 mol%) as the catalyst precursor and observed complete borylation of 4-MeC_6H_4I within 5 h at ambient temperature. The process can be simplified significantly through the in situ formation of the phosphanyl copper alkoxide complex formed from CuX, the phosphine, and KO*t*Bu.

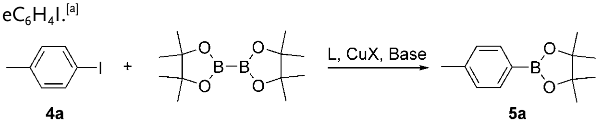
We screened a range of reaction conditions, phosphine ligands, copper sources, bases, and solvents to determine the scope and limitations of this reaction. The reactions were typically carried out for 17 h to overcome mixing problems associated with the in situ formation of the copper phosphine complex and the formation of a sparingly soluble B_2pin_2/KO*t*Bu adduct,[17] even though catalytic conversion may be complete much earlier in some cases.

Initially, we screened a variety of copper sources. Copper powder and copper(II) sulphate (anhydrous) did not show significant catalytic activity, nor did the reaction proceed in the absence of a copper source (the nature of a possible uncatalyzed background reaction will be addressed elsewhere[17]). In contrast, all copper(I) sources employed, aside from copper(I) oxide, promoted high conversion (Table 1, entries 1–4). Hence, comparatively inexpensive and air-stable CuI was used in subsequent studies.

Next, the influence of the ligand was studied by using three different phosphines (Table 1, entries 4–6) together with CuI. All reactions in the presence of a phosphine ligand were essentially complete after 17 h or less. In the presence of nitrogen ligands, pyridine, and 4,4′-dimethyl-2,2′-bipyridine, no significant conversion was observed (Table 1, entries 7 and 8). The need for a suitable ligand was demonstrated by the low conversion observed in the absence of a ligand (Table 1, entry 9).

When KO*t*Bu was omitted from the reaction mixture, no significant amount of the aryl boronate was formed (Table 1, entry 10). The replacement of KO*t*Bu with less basic KOAc (in THF or DMF) or K_2CO_3 (in DMF) resulted in no conversion, either under standard conditions or under microwave irradiation at 60 °C (Table 1, entries 11–13). An increase in the reaction temperature to 60 °C, or microwave irradiation at 60 °C, resulted in a drastically increased reaction rate (Table 1, entries 14 and 15). With microwave irradiation, 4-MeC_6H_4Bpin (**5a**) was formed in 90% yield in only 5 min. A reaction performed under microwave irradiation at 60 °C without the addition of CuI showed no significant conversion after 20 min; thus, any uncatalyzed reaction is minimal, even under microwave irradiation.

Table 1: Screening of reaction conditions for the borylation of 4-MeC_6H_4I.[a]



Entry	CuX (mol %)	L (mol %)	Base	t [h]	Conv. [%][b] (yield [%])
1	CuCl (10)	nBu$_3$P (13)	KOtBu	17	100
2	CuOAc (10)	nBu$_3$P (13)	KOtBu	17	100
3	Cu_2O (10)	nBu$_3$P (13)	KOtBu	17	trace
4	CuI (10)	nBu$_3$P (13)	KOtBu	24	100 (92)
5	CuI (10)	Ph_3P (13)	KOtBu	17	91
6	CuI (10)	dtbpe[c] (13)	KOtBu	17	100
7	CuI (10)	pyridine (13)	KOtBu	17	0
8	CuI (10)	Me$_2$bipy[c] (13)	KOtBu	17	0
9	CuI (10)	none	KOtBu	22	12
10	CuI (10)	nBu$_3$P (13)	none	5	0
11	CuI (10)	nBu$_3$P (13)	KOAc	17	trace
12[d,e]	CuI (10)	nBu$_3$P (13)	KOAc	0.3	trace
13[d,e]	CuI (10)	nBu$_3$P (13)	K_2CO_3	0.3	trace
14[d]	CuI (10)	nBu$_3$P (13)	KOtBu	0.08	93 (90)
15[f]	CuI (10)	nBu$_3$P (13)	KOtBu	0.5	100
16	CuI (3)	nBu$_3$P (3)	KOtBu	24	75
17[f]	CuI (3)	nBu$_3$P (3)	KOtBu	2.5	100
18[g]	CuCl (10)	nBu$_3$P (13)	KOtBu	22	64
19[h]	CuI (10)	nBu$_3$P (13)	KOtBu	22	50
20[i]	CuI (10)	nBu$_3$P (13)	KOtBu	22	0
21[j]	CuI (10)	nBu$_3$P (13)	KOtBu	22	100
22[e]	CuI (10)	nBu$_3$P (13)	KOtBu	22	100

[a] Reaction conditions, unless otherwise stated: 4-MeC_6H_4I (459 μmol, 1 equiv), base (1.5 equiv), B_2pin_2 (1.5 equiv), THF, room temperature. [b] The conversion was determined by GC-MS of a diluted and filtered aliquot of the reaction mixture from the ratio of the peak areas for 4-MeC_6H_4I and the aryl boronate. The yield of the isolated product is given in parentheses. [c] dtbpe = tBu$_2$PCH$_2$CH$_2$PtBu$_2$, Me$_2$bipy = 4,4′-dimethyl-2,2′-bipyridine. [d] The reaction was performed at 60 °C under microwave irradiation. [e] The reaction was performed in *N*,*N*-dimethylformamide (DMF). [f] The reaction was performed at 60 °C. [g] The reaction was performed in toluene. [h] The reaction was performed in MeCN. [i] The reaction was performed in MeOH. [j] The reaction was performed in methyl *tert*-butyl ether (MTBE).

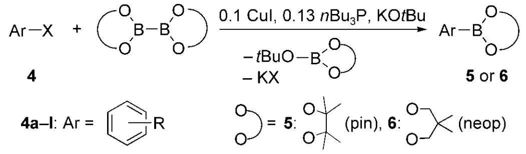
With a reduced catalyst loading of 3 mol % (Table 1, entry 16), the reaction was not complete after 17 h at room temperature; it required approximately 48 h to reach completion. However, when the reaction with a catalyst loading of 3 mol % was performed at 60 °C, complete conversion was observed after 2.5 h (Table 1, entry 17).

We tested the compatibility of the borylation reaction with a range of solvents, from the aromatic hydrocarbon toluene to polar solvents, such as THF, MTBE, MeCN, and DMF (Table 1, entries 18–22). The limited solubility of KOtBu or the initially formed B_2pin_2/KOtBu adduct[17] may account for the only moderate conversion in toluene and MeCN (Table 1, entries 18 and 19). The lack of conversion in MeOH (Table 1, entry 20) is not yet well understood.

We screened different aryl halides and alkoxy diboron reagents in the copper-catalyzed borylation reaction. In these experiments, the aryl halide was treated with the diboron reagent (1.5 equiv) in the presence of KOtBu (1.5 equiv) as the base, CuI (0.1 equiv), and nBu$_3$P (0.13 equiv) as the ligand in THF at room temperature (Table 2).

Aryl halides with different steric and electronic properties as well as different halogen substituents were investigated. A wide range of aryl iodides were converted into the corresponding ArBpin compounds in satisfactory to excellent yields (Table 2, entries 1–8 and 15); furthermore, aryl and heteroaryl bromides were borylated in good yields (Table 2, entries 9–14). In fact, the yield of the isolated product appears to be largely independent of the nature of the halide (compare entries 1 and 9, 5 and 12 in Table 2). This observation is especially remarkable, as aryl bromides were not suitable substrates in the copper-catalyzed borylation procedure of Zhu and Ma.[6] Sterically encumbered, *ortho*-substituted phenyl derivatives were also borylated in moderate to good yields (Table 2, entries 4, 10, 11, 15, and 17).

Table 2: Screening of aryl halides and diboron reagents for the copper-catalyzed borylation reaction.[a]



Entry	Diboron reagent	ArX	Conv. [%] (ArH [%])	Product (yield [%][b])
1	B_2pin_2	**4a** (4-MeC_6H_4I)	100 (–)[c]	**5a** (92)
2	B_2pin_2	**4b** (4-$MeOC_6H_4I$)	> 97 (< 3)	**5b** (91)
3	B_2pin_2	**4c** (4-$MeO_2CC_6H_4I$)	100[d] (0)	**5c** (77)[d]
4	B_2pin_2	**4d** (2-$MeOC_6H_4I$)	100[e] (–)[c]	**5d** (74)[e,f]
5	B_2pin_2	**4e** (4-$CF_3C_6H_4I$)	100 (–)[c]	**5e** (69)
6[g]	B_2pin_2	**4f** (1,4-$I_2C_6H_4$)	78[h] (–)[c]	**5f** (70)[f,h]
7[i]	B_2pin_2	**4f** (1,4-$I_2C_6H_4$)	81[j] (–)[c]	**5g** (76)[j]
8[g]	B_2pin_2	**4g** (4-BrC_6H_4I)	89 (6)[k]	**5h** (73)[f,k]
9	B_2pin_2	**4h** (4-MeC_6H_4Br)	100 (–)[c]	**5a** (83)
10	B_2pin_2	**4i** (2-MeC_6H_4Br)	100 (–)[c]	**5i** (91)
11	B_2pin_2	**4j** (2,4,6-$Me_3C_6H_2Br$)	90 (10)	**5j** (69)
12	B_2pin_2	**4k** (4-$CF_3C_6H_4Br$)	100 (–)[c]	**5l** (65)
13	B_2pin_2	**4l** (4-$Me_2NC_6H_4Br$)	88 (12)	**5l** (69)
14	B_2pin_2	**4m** (2-bromothiophene)	100[l] (–)[c]	**5m** (83)[f]
15	B_2pin_2	**4n** (1-iodonaphthalene)	> 97 (< 3)	**5n** (74)
16	B_2neop_2	**4a** (4-MeC_6H_4I)	93 (–)[c]	**6a** (91)[f]
17	B_2neop_2	**4j** (2,4,6-$Me_3C_6H_2Br$)	91 (7)	**6b** (60)[f]
18	B_2neop_2	**4b** (4-$MeOC_6H_4I$)	100 (0)	**6c** (83)
19	B_2neop_2	**4l** (4-$Me_2NC_6H_4Br$)	57 (16)	**6d** (48)[f]

[a] Reaction conditions: aryl halide (typically 459 μmol, 1 equiv), diboron reagent (1.5 equiv), CuI (10 mol %), nBu$_3$P (13 mol %), KOtBu (1.5 equiv), THF, room temperature. [b] Yield after chromatographic workup. [c] ArH peak was not separated from the solvent peak. [d] Total borylation yield. A mixture of the methyl (45 %) and *tert*-butyl esters (32 %) was isolated. The reaction mixture contained the methyl and *tert*-butyl esters in a 58:42 ratio (GC-MS). [e] Total borylation yield. The product underwent partial hydrolysis during chromatographic workup. [f] The compound was characterized by single-crystal X-ray diffraction.[15,18] [g] B_2pin_2: 1 equivalent. [h] C_6H_5Bpin (13 %) and $C_6H_4(Bpin)_2$ (9 %) were also detected by GC-MS. A mixture of 4-IC_6H_4Bpin (70 %) and 1,4-$(Bpin)_2C_6H_4$ (7 %) was isolated. [i] B_2pin_2: 3 equivalents. [j] Compound **5g** is 1,4-$(Bpin)_2C_6H_4$. C_6H_5Bpin (19 %) was also detected by GC-MS. [k] Compound **5h** is 4-BrC_6H_4Bpin, ArH is C_6H_5Br. [l] The reaction mixture contained a trace amount of bithiophene (GC-MS).

The reaction is faster for iodides. With 1 equivalent of B_2pin_2/KO*t*Bu, 4-bromophenyl iodide (**4g**) was borylated to give the 4-bromophenyl boronate **5h** exclusively (Table 2, entry 8). 1,4-Diiodobenzene (**4f**) also underwent predominant monoborylation if only 1 equivalent of the borylating reagent was used (Table 2, entry 6). The 1,4-diborylated product **5g** was isolated in 76% yield when **4f** was treated with 3 equivalents of B_2pin_2/KO*t*Bu (Table 2, entry 7).

Not only does the reaction show wide scope with respect to the aryl halide substrate, but B_2neop_2 (neop = $OCH_2CMe_2CH_2O$) can be substituted for B_2pin_2 (Table 2, entries 16–19) to give the corresponding ArBneop compounds in similar yields to those observed with B_2pin_2.

The procedure is also applicable to the borylation of benzyl and allyl halides,[9b,19] as exemplified by the borylation of benzyl and allyl chloride. $PhCH_2Bpin$ (**7a**) was isolated in 61% yield; GC-MS showed that **7a**, $PhCH_2O$*t*Bu, and $(PhCH_2)_2$ were present in the reaction mixture in a 73:2:25 ratio. However, when allyl chloride was used, $CH_2{=}CHCH_2Bpin$ (**7b**) was isolated in only 9% yield, probably as a result of decomposition during the workup.[15] Complete consumption of the allyl chloride and the formation of $CH_2{=}CHCH_2Bpin$ (**7b**) accompanied by an as yet unidentified side product was observed by ^1H NMR spectroscopy of the reaction mixture (see Figure S2 in the Supporting Information).

Although the reaction shows broad scope, there are some substrate restrictions. Aryl chlorides are not readily converted,[15] and certain functional groups are not well tolerated. For example, a substrate containing a methyl ester group underwent partial transesterification with the O*t*Bu$^-$ nucleophile (Table 2, entry 3). The reason for the failure of the reaction with other functional groups is less clear. When hydroxy- or cyano-substituted arenes were used, the aryl boronate was detected in only small amounts by GC-MS, and was not readily isolated. Aryl halides containing a nitro or aldehyde moiety reacted under the conditions employed, but none of the products could be identified by GC-MS.

In some cases, the formation of the hydrodehalogenation product, ArH, was observed (Table 2, entries 2, 8, 11, 13, 15, 17, and 19). Hydrodehalogenation during coupling reactions of aryl halides with boron reagents has been reported previously for palladium- and nickel-catalyzed reactions with $(RO)_2BH$,[3,4] but, to the best of our knowledge, not for coupling reactions involving alkoxy diboron reagents[2,20] or copper catalysts.[6] The addition of H_2O or D_2O (20 mol%) to the reaction mixture did not result in an increased amount of, or deuterium incorporation into, the hydrodehalogenation product, so adventitious moisture can be ruled out as the cause of this undesired side reaction. Moreover, the borylation of **4l** in [D_8]THF led to selective deuteration at the *para* position of the resulting *N*,*N*-dimethylaniline (70% deuteration by ^1H NMR spectroscopy).[15] Present research is directed towards a closer understanding of this pathway. Such an understanding appears to be necessary for detailed mechanistic insight into the borylation reaction.

The excellent applicability of the borylation procedure to synthetic chemistry is illustrated by a series of findings. The reaction can be performed successfully in nitrogen-flushed glassware with commercial, reagent-grade KO*t*Bu in dry THF. Even brief exposure of the reaction mixture to air did not influence the outcome greatly. However, when the reaction was performed in air, low conversion and low reproducibility were observed. Catalyst degradation is not a problem, as complete conversion was observed with 10 mol% of the catalyst within 17 h upon recharging an already completed borylation reaction with the substrates (4-MeC_6H_4I, B_2pin_2, and KO*t*Bu); recharging four additional times resulted in 82% overall yield of the isolated product.[15]

Mechanistic studies on the borylation reaction catalyzed by the copper phosphine complex are ongoing. However, we can put forward a preliminary proposal based on our experimental observations and calculations to date: As discussed above for the *i*PrNHC ligand, the crucial C–B bond-formation step, proceeds, according to our calculations (Figure 2b, L = Me_3P), through a σ-bond-metathesis step with a small activation barrier ($\Delta E^{\neq} = 8.8\ \text{kcal mol}^{-1}$, $\Delta G^{\neq} = 20.1\ \text{kcal mol}^{-1}$). We therefore propose a catalytic cycle according to Scheme 1 (L = Me_3P). However, the individual steps for the L = phosphine case are not yet supported by other reported studies, as well as they are for an NHC ligand. Phosphanyl copper alkoxy complexes are not unprecedented,[21] and phosphanyl copper boryl complexes are widely accepted intermediates in the borylation of α,β-unsaturated carbonyl compounds, although no such complex has yet been isolated.[7–9] However, this simple cycle does not explain the occurrence of hydrodehalogenation, nor does it take into account the possible formation of aggregated[22] phosphanyl copper species. Moreover, it has to be considered that copper nanoparticles might be the actual catalyst.[15]

In summary, we have developed a simple catalytic process for the borylation of aryl halides, including electron-rich and sterically hindered bromides, under mild conditions (ambient temperature) in the presence of an inexpensive metal (Cu) and ligand (*n*Bu_3P) in a solvent with a modest boiling point (THF). The process thus represents a cost-effective alternative to the widely employed palladium-based ArX/B coupling reactions developed by Miyaura and co-workers[2] or Masuda and co-workers.[3a,b] The large-scale (e.g. 100 kg) commercial production of the diboron reagents B_2pin_2 and B_2neop_2 and consequent price reduction make such a process very attractive.

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