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Regiodivergent copper catalyzed borocyanation of 1,3-dienes

Tao Jia,[a],[b] Qiong He,[a] Rebecca E. Ruscoe,[a] Alexander P. Pulis,[a] and David J. Procter*[a]

Abstract: Copper catalyzed multifunctionalization of unsaturated carbon-carbon bonds is a powerful tool for the generation of complex molecules. We report a regiodivergent process that allows a switch between 1,4-borocupration and 4,1-borocupration of 1,3-dienes upon a simple change in ligand. The subsequently generated allyl coppers are trapped in an electrophilic cyanation to selectively generate densely functionalized and synthetically versatile 1,2- or 4,3- borocyanation products.

Catalytic multi-functionalization reactions enable the expedient synthesis of complex molecules from simple starting materials. In particular, catalytic methods that selectively generate different complex molecules from the same material input via a simple change in reagents (e.g. ligand) facilitate efficient access to chemical space.[1]

Copper catalyzed[2] multi-functionalization of unsaturated carbon-carbon bonds is a low cost strategy for chemical synthesis that operates under mild conditions. For example, the copper catalyzed borylative[3] functionalization of alkenes,[4] alkynes,[5] allenes,[6] 1,3-enynes,[7] 1,3-diynes,[8] and 1,3-dienes,[9, 10, 11] generates an array of complex molecules that are amenable to further elaboration. In the case of the later, 1,3-dienes undergo borocupration to generate allyl organocopper intermediates. This in situ, catalytic generation and use of allyl metal species circumvents many problems associated with the preparation of stoichiometric allyl metals. As such, allyl coppers generated from 1,3-dienes (and other unsaturated carbon frameworks)[12] react with electrophilic coupling partners under mild conditions, with excellent functional group tolerance, leading to densely functionalized and versatile products.[9,10] For example, copper catalyzed borylative processes of 1,3-dienes exist where the allyl copper is protonated,[9a,b] quenched with imines[9c] or Michael acceptors,[9d] or utilized in palladium catalyzed arylation.[9e,f]

Unfortunately, non-symmetrically substituted 1,3-dienes present acute challenges in terms of regiocontrol: borocupration can occur at different positions – 4,3-, 4,1-, 1,2- and 1,4-borocupration[13] – which is further complicated by the possibilty of S_E and S_E' (alpha and gamma)[12] reaction modes of the generated allyl copper (Scheme 1). Crucially, if regioselectivity during borocupration could be controlled by a simple change in ligand, then different products would be accessible from the same simple starting materials.[14] However, previous element-cupration of 2-substituted 1,3-dienes predictably occurred at the vinyl portion of the diene (in a 4,1-fashion), where in the case of

borocupration, 4-boryl substituted products are observed.[9a,c-e, 10a,b] Notably, only Brown has reported a switch in 4,1- and 1,2-selectivity in a boroarylation of 2-alkyl substituted 1,3-dienes in a Cu/Pd cooperatively catalyzed process upon the addition of 2 equivalents of DMAP.[15] Thus, processes involving 1,4-element cupration of 1,3-dienes remain a significant challenge and a regiodivergent element-cupration of 1,3-dienes using a single metal catalyst has not previously been reported.

Herein, we disclose that a simple switch in commercially available phosphine ligand results in a regiodivergent borocupration of 2-substituted 1,3-dienes. The catalytically generated allyl coppers undergo regioselective trapping with the readily available electrophilic cyanating agents, N-cyano sulfonamides,[16] resulting in versatile borocyanated[17] products of 1,3-dienes. The bidentate phosphine XantPhos allows for overall 4,1-borocupration, resulting in 4,3-borocyanation products. Upon a simple switch in ligand, to the monodentate tricyclohexyl phosphine, unprecedented 1,4-borocupration was achieved and allowed the generation of 1,2-borocyanated products. The process is general and both product families are rich in synthetic potential.
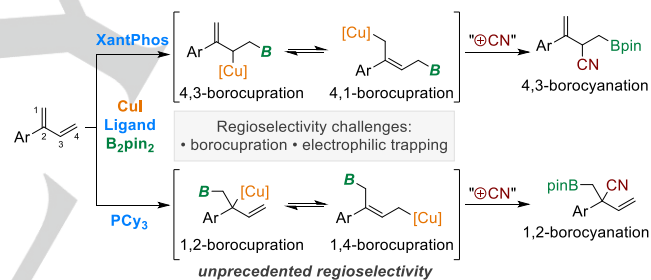
Scheme 1. Copper catalyzed, regiodivergent borocyanation of 2-substituted 1,3-dienes.

Table 1. Optimization.[a]

Entry	Conditions	Yield (%)	3a:4a
1	CuI, **XantPhos**, 2a	51	1:>20
2	CuI, **XantPhos**, 2b	66	1:>20
3	CuBr·SMe₂, **XantPhos**, 2b	78	1:>20
4	CuBr·SMe₂, **XantPhos**, 2b, B₂pin₂ (2 eq.)	87	1:>20
5	CuBr·SMe₂, **XantPhos**, 2c, B₂pin₂ (2 eq.)	56	1:>20
6	CuI, **PCy₃**, 2a	75	3.2:1
7	CuI, **PCy₃**, 2c	59	5.5:1
8	CuBr·SMe₂, **PCy₃**, 2c, B₂pin₂ (2 eq.)	80	7:1
9	CuBr·SMe₂, **PCy₃**, 2c, B₂pin₂ (2 eq.), 0 °C	90	10:1
10	CuBr·SMe₂, **PCy₃**, 2b, B₂pin₂ (2 eq.)	78	3.9:1

[a] Yield and regioselectivity determined by ¹H-NMR analysis of crude reaction mixtures.

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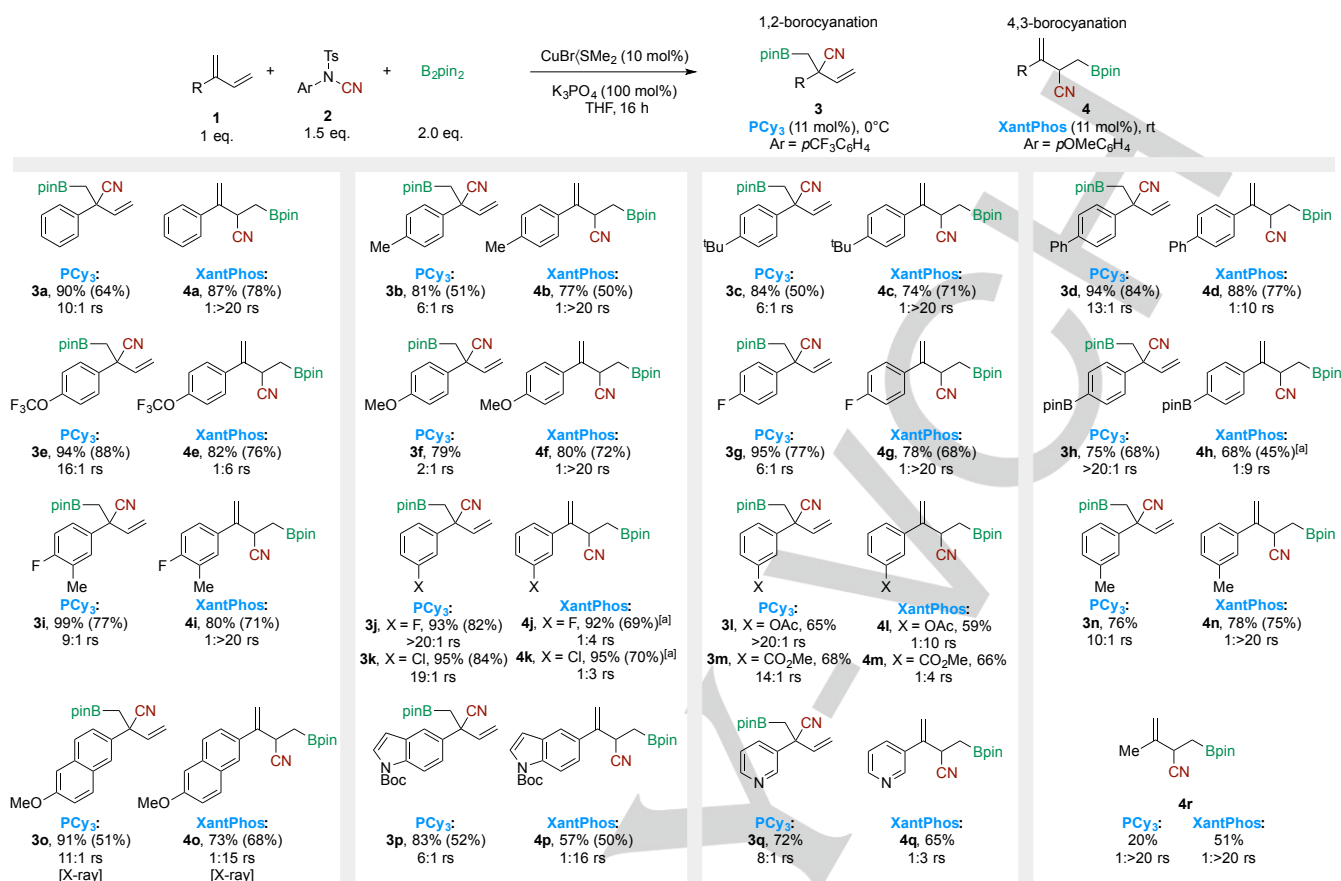
Scheme 2. Substrate scope. Yields and regioselectivity determined by ^{1}H-NMR analysis of crude reaction mixtures. Isolated yield of major regioisomer in parentheses. Regioselectivity, (rs) = **3**:**4**. [a] Isolated yield of regioisomeric mixture in parentheses.

N-Cyano sulfonamides **2** are the cyanating agent of choice as they are bench stable, crystalline solids that are readily prepared from sulfonyl chlorides and aryl ureas.[16] We therefore began by investigating the copper catalyzed multicomponent coupling of diene **1a**, B$_2$pin$_2$ and *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (NCTS, **2a**) by varying the ligand for copper (Table 1).[18] In our initial survey, we found that NHC ligands performed poorly, giving low yields and regioselectivities. However, using CuI, we found that, in general, bidentate phosphine ligands gave 4,3-borocyanated products **4** as the major component, and monodentate phosphines resulted in 1,2-borocyanation (**3**).[18] Formation of **3a** and **4a**, and the absence of other borocyanation products (e.g. 1,4- and 4,1-borocyanation) indicated excellent regioselectivity in trapping of the allyl coppers generated in situ.

The optimal ligand for 4,3-borocyanation was found to be XantPhos with excellent regioselectivity observed (>20:1) (Table 1, entries 1-5). Changing the cyanating agent from NCTS (**2a**) to the *para*-methoxy derivative **2b**, and fine tuning the copper source, led to an improved yield (87%) of **4a**.

Having established conditions for 4,3-borocyanation, we turned our attention to 1,2-borocyanation, which generates quaternary nitriles **3a** and relies on the more challenging 1,4-

borocupration mode (Table 1, entries 6-10). PCy$_3$ was found to be the best performing ligand for 1,2-borocyanation, yet in employing NCTS (**2a**) the regioselectivity at 3.2:1 was unsatisfactory (entry 6). Moving to the *para*-trifluoromethyl derivative of NCTS (**2c**), using CuBr·SMe$_2$ and operating at 0 °C, led to **3a** in 90% yield and 10:1 regioselectivity (entries 7-9).

Crucially, the choice of ligand dictates the regiochemical course of the reaction. Under XantPhos conditions, the cyanating agent had no discernable effect on the regiochemical outcome (Table 1, entires 4 vs 5). In the case of the PCy$_3$ protocol, the cyanating agent did allow for an increase in regioselectivity (Table 1, entries 8 vs 10), but it is clear that the choice of ligand is the dominant factor governing regiocontrol.

The scope of the regiodivergent borocyanation was investigated with various 2-substituted 1,3-dienes under both 1,2-borocyanation (PCy$_3$) and 4,3-borocyanation (XantPhos) conditions (Scheme 2). The reaction tolerated a range of substitutents and reactive functional groups in various positions (*ortho*, *meta*, and *para*) on the aryl ring of 2-aryl buta-1,3-dienes, such as alkyl, aryl, methoxy, trifluoromethoxy, ester, boro, chloro and fluoro, and the expected products were generally obtained in good yield and importantly, with high regioselectivity for both borocyanation modes. Napthyl, indoyl and pyridyl, bearing a

basic nitrogen atom, in the 2-position of the 1,3-diene, were also compatible with the borocyanation protocols.

In the case of 2-alkyl 1,3-dienes, such as isoprene, regiodivergency was not achieved, but the 4,3-cyanoboration product **4r** was formed in >20:1 regioselectively and moderate yield under the XantPhos conditions.

Other diborane reagents were employed in the borocyanation, however, the process was less efficient in terms of regioselectivity and/or yield.[18]

Based on these observations and literature precedent, we propose the following catalytic cycle and working models for selectivity in the regiodivergent borocyanation of 1,3-dienes (Scheme 3). The key copper boryl complex **5** is formed from B_2pin_2, phosphine-copper complex and K_3PO_4. In the case of the monodentate phosphine protocol, the tetrahedral[19] Cu(I) boryl intermediate **6** is formed where the diene, in the s-cis conformation,[20,21] is able to coordinate in a η^4 fashion.[22] The nucleophilic boron is then delivered to the terminal styrenyl carbon, akin to borocupration of styrenes,[23] and therefore 1,4-borocupration results generating allyl copper **7**.

With only one vacant coordination site in copper boryl complexes ligated to bidentate phosphines (*cf*. **8**),[19] the diene may coordinate in a η^2 fashion. Evidently, the more electron rich vinyl alkene of the diene coordinates, allowing 4,3-borocupration to occur. Allyl copper **9** is likely to rapidly isomerize to the more stable 4,1-borocuprated intermediate **10**.
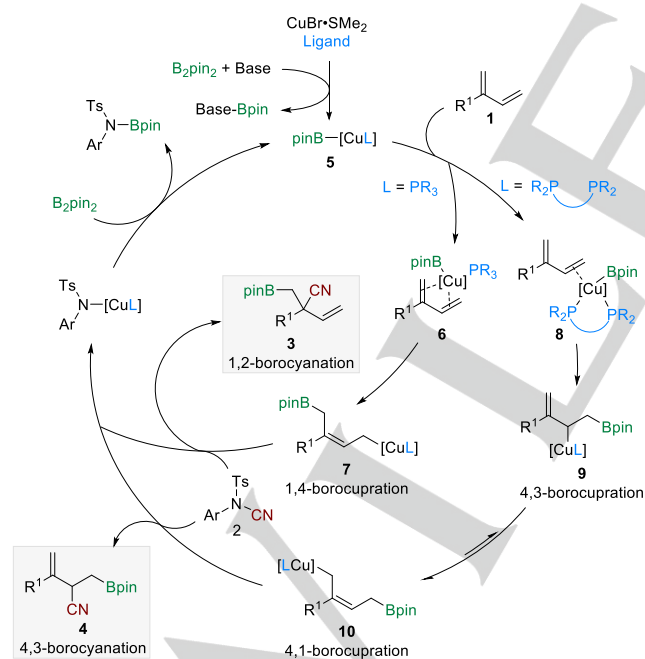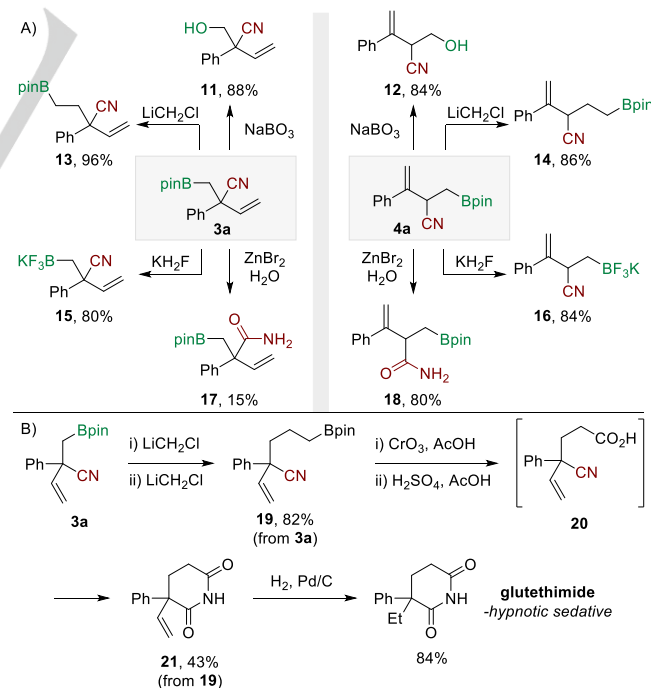
2 occurs, which arises from an addition elimination type process proceeding via a 6 membered transition state structure.[17e]

The lower regioselectivity observed in the case of the 1,3-diene bearing the electron rich aryl group (*p*OMe, formation of **3f**) under PCy_3 conditions might be explained on the basis of slower borylation of the styrenyl alkene (1,4-borocupration), akin to the observed slower rates in the borocupration of electron rich styrenes,[24] thus allowing borylation at the vinyl moiety (4,3-borocupration) to compete. On similar grounds, the reduced regioselectivity observed for some substrates bearing electron poor aryl groups (*cf*. formation of **4j** and **4k**) under XantPhos conditions may be attributed to faster borylation of the more electrophilic styrenyl alkene (1,2-borocupration).

In the case of 2-alkyl substituted 1,3-dienes, where the electronic bias in 2-aryl 1,3-dienes is absent (cf. **4r**), the formation of 4,3-borocyanation products under both XantPhos and PCy_3 conditions is due to faster borocupration of the less hindered and less electron rich vinyl portion of the diene.[25]

Further investigation into the complex and subtle interplay between ligands, substrate, electrophilic partners, and counter ions and their impact on regiodivergency is ongoing.

To demonstrate the versatility of products generated in the regiodivergent borocyanation of 1,3-dienes, we selectively oxidized (**11**, **12**), homologated[26] (**13**, **14**) and formed trifluoroborate salts[27] (**15**, **16**) from the boronic ester moiety of both 1,2- and 4,3-borocyanation products (Scheme 4A). In addition, the nitrile group was converted into the corresponding amide (**17**, **18**).

Scheme 3. Proposed mechanism.

Scheme 4. Manipulations of borocyanation products.

Having selectively formed either allyl coppers **7** or **10**, highly regioselective electrophilic cyanation with *N*-cyano sulfonamides

We then demonstrated further utility by sequentially elaborating each functional group in **3a**, the product of the PCy₃ method, enroute to the hypnotic sedative glutethimide[28] (Scheme 4B). Thus, boronic ester **3a** was homologated twice,[26] oxidized to the carboxylic acid, cyclized, and finally hydrogenated to give the target glutethimide.

In conclusion, we have discovered a simple strategy for the regiodivergent multi-functionalization of 1,3-dienes and applied it to a borocyanation process that delivers high value products. In utilizing the bidentate ligand XantPhos, 2-substiuted 1,3-dienes underwent copper catalyzed 4,1-borocupration. Upon switching to the monodentate phosphine, PCy₃, unprecedented 1,4-borocupration occurred. The catalytically generated allyl copper intermediates in both processes were successfully trapped with excellent regioselectivity using the readily available cyanating agents, *N*-cyano sulfonamides, to produce densely functionalized and versatile 4,3- or 1,2-borocyanated products. We envisage that this ligand controlled regiodivergent strategy may be applied in other copper catalyzed processes involving dienes.

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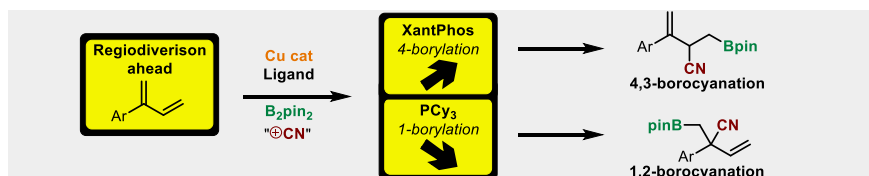
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Regiodivergent copper catalyzed borocyanation of 1,3-dienes

Copper catalyzed multifunctionalization of unsatururated carbon-carbon bonds is a powerful tool for the generation of complex molecules. We report a regiodivergent process that allows a switch between 1,4-borocupration and 4,1-borocupration of 1,3-dienes upon a simple change in ligand. The subsequently generated allyl coppers are trapped in an electrophilic cyanation to selectively generate densely functionalized and synthetically versatile 1,2- or 4,3- borocyanation products.