

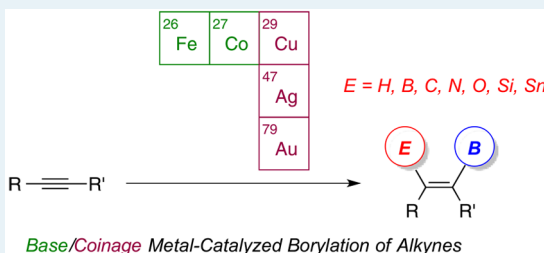
Borylation of Alkynes under Base/Coinage Metal Catalysis: Some Recent Developments

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ABSTRACT: Alkenylboranes have been vital reagents in modern synthetic organic chemistry, whose carbon–boron bond is transformable into a carbon–carbon bond stereoretentively to give such invaluable multisubstituted alkenes as natural products, biologically active molecules, and functional materials. Introduction of a boryl moiety across a carbon–carbon triple bond of alkynes (borylation of alkynes) is one of the most direct and potent methods for synthesizing alkenylboranes, and this field has thus far experienced remarkable progress mainly with group 10 transition metal catalysts (Ni, Pd, Pt), which enables highly functionalized alkenylboranes to be constructed stereoselectively. On the other hand, much attention has recently been focused on the appealing catalysis of base (Fe, Co) and coinage (Cu, Ag, Au) metals toward the borylation of alkynes, which is summarized in this perspective.

KEYWORDS: alkenylborane synthesis, alkynes, base metal catalysis, boron, coinage metal catalysis, regioselectivity, stereoselectivity



1. INTRODUCTION

Organoboron compounds play a pivotal role in modern synthetic organic chemistry, being utilized as essential carbon nucleophiles for introduction of functional groups and a carbon–carbon bond-forming process such as Suzuki–Miyaura coupling and Petasis reaction.¹ Their characteristics are superior to those of other organometallics and include bench stability and easy-to-handle properties arising from the inertness toward oxygen and moisture, low toxicity, moderate reactivities suitable for chemoselective transformations, high functional group compatibility, and so on. Of particular interest are alkenylboron compounds, whose versatility has been demonstrated by stereodefined construction of valuable multisubstituted alkenes² including natural products, biologically active molecules, and functional materials. Although various alkenylboron compounds are conventionally available by metal exchange reactions between organometallics of high nucleophilicity (organolithium, Grignard reagents) and boron electrophiles, as well as such uncatalyzed borylation reactions of alkynes as hydroboration³ and haloboration,⁴ the search for new synthetic approaches to alkenylboron compounds, being hardly accessible by the conventional methods, with controlled regio- and stereochemistry, has been a challenging issue in chemical synthesis.

In this context, much effort have been devoted to developing borylation of alkynes under transition metal catalysis, which allows highly functionalized alkenylboron compounds to be synthesized stereoselectively in a straightforward manner, and this field has hitherto made exciting progress mainly with group 10 metal catalysts (Ni, Pd, Pt).⁵ Recently, the catalytic borylation of alkynes has taken a new turn, and copper catalysis has especially been the mainstay of the remarkable expansion of the field.⁶ This perspective aims to summarize the

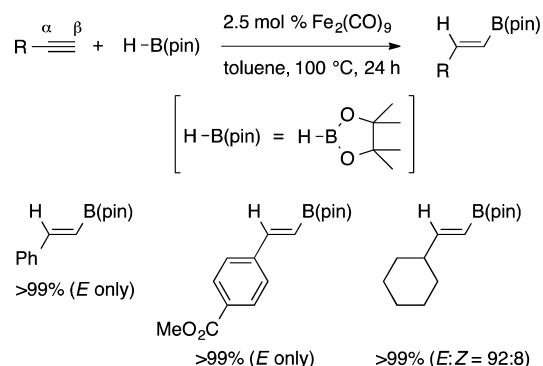
recent developments in the copper-catalyzed borylation of alkynes, focusing mainly on those involving a borylcopper species as a key intermediate. Some appealing catalysis toward the borylation based on base (Fe, Co) or coinage (Ag, Au) metals is also included in this paper. Because this perspective especially focuses on new aspects of the catalytic borylation of alkynes, the well-known nickel catalyst has not been included as a base metal catalyst.

2. Fe CATALYSIS

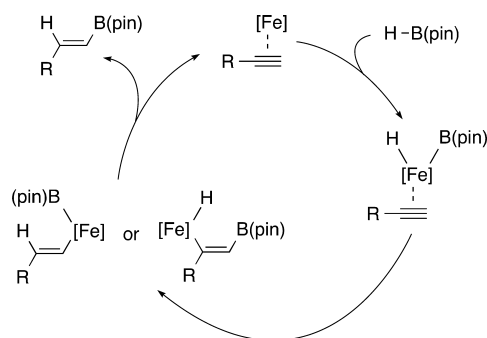
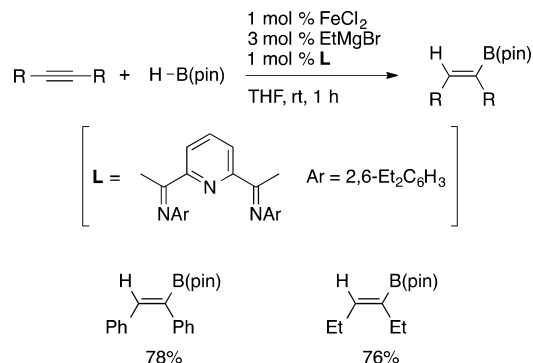
2.1. Hydroboration. In view of natural abundance, low cost, and low toxicity, iron should be of significant advantage as a practical catalyst in the borylation, and Enthaler has first proved the potential iron catalysis by the reaction of alkynes with pinacolborane, giving alkenylboranes through hydroboration (Scheme 1).⁷ Aromatic and aliphatic terminal alkynes smoothly underwent the *syn*-hydroboration with high β -selectivity in the presence of diiron nonacarbonyl ($Fe_2(CO)_9$) to provide (*E*)-*anti*-Markovnikov adducts, whereas the reaction of such unsymmetrical internal alkynes as 1-phenyl-1-hexyne and trimethyl(phenylethynyl)silane resulted in the formation of a mixture of four possible isomers. A proposed reaction pathway for the hydroboration includes oxidative addition of pinacolborane, insertion of an alkyne into the resulting $[Fe]-H$ and/or $[Fe]-B$ bond, and reductive elimination (Scheme 2). A low-valent iron species generated *in situ* from $FeCl_2$, a bis(imino)pyridine ligand and $EtMgBr$ was also found to efficiently catalyze the *syn*-hydroboration of symmetrical internal alkynes (Scheme 3).^{8,9}

Received: December 30, 2015

Revised: February 2, 2016

Scheme 1. $\text{Fe}_2(\text{CO})_9$ -Catalyzed Hydroboration

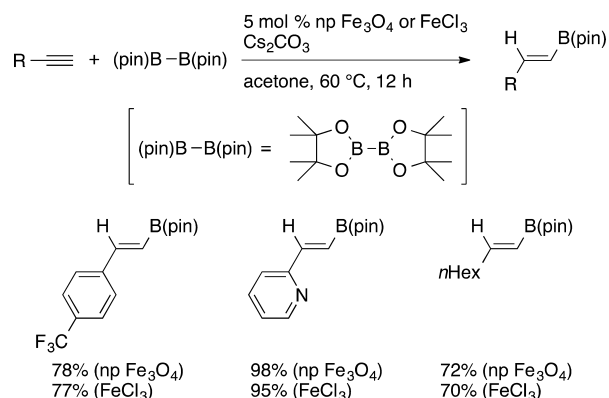
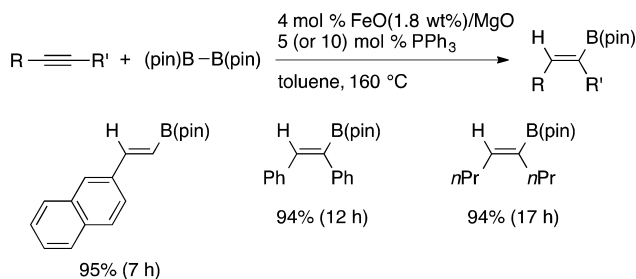
Scheme 2. Proposed Catalytic Cycle

Scheme 3. FeCl_2 -Bis(imino)pyridine-Catalyzed Hydroboration

Treatment of bis(pinacolato)diboron, alkynes, and Cs_2CO_3 in the presence of magnetic nanoferrites (np Fe_3O_4) or FeCl_3 led to formal hydroboration in a *syn*-selective manner (Scheme 4).¹⁰ The regioselectivity was high regardless of terminal alkynes employed, and linear (*E*)-alkenylboranes were produced with high β -selectivity. Although a detailed reaction pathway was unclear, the introduced proton in the products was found to come from residual water in the reaction medium. A similar reaction was promoted also by use of triphenylphosphine and iron oxide nanoparticles supported on magnesia (FeO/MgO) (Scheme 5).¹¹ The authors proposed that the reaction may be commenced by formation of a $[\text{FeO}]\text{-B}$ species derived from PPh_3 -activated diboron. Subsequent insertion of an alkyne followed by protonation with residual water affords the product.¹²

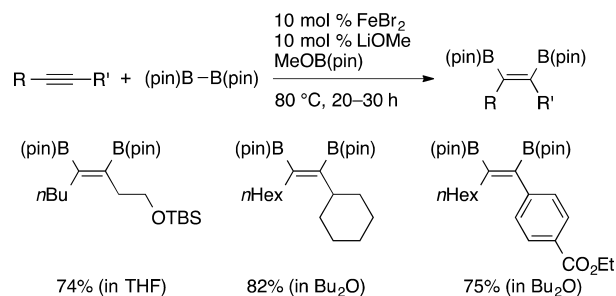
2.2. Diboration. The versatility of iron catalysis in the borylation was further expanded by Nakamura: FeBr_2 in combination with LiOMe turned out to be an efficacious

Scheme 4. Fe-Catalyzed Formal Hydroboration

Scheme 5. FeO/MgO -Catalyzed Formal Hydroboration

catalyst for *syn*-diboration of internal alkynes, affording *vic*-diborylalkenes in good yield (Scheme 6).¹³ Addition of

Scheme 6. Fe-Catalyzed Diboration

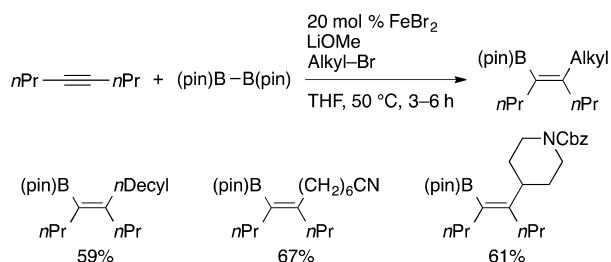


$\text{MeOB}(\text{pin})$, which served as a boron electrophile trapping an alkenyliron intermediate (*vide infra*), was essential for the diboration to proceed with high efficiency.

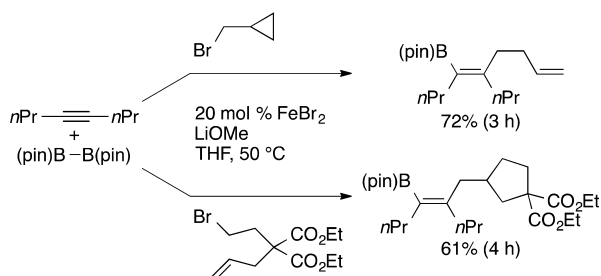
2.3. Carboboration. The use of alkyl bromides instead of $\text{MeOB}(\text{pin})$ in the reaction of bis(pinacolato)diboron and internal alkynes with the above iron catalyst system resulted in the stereoselective carboboration, where carbon–boron and carbon–carbon bonds were constructed simultaneously (Scheme 7).¹³ The iron-catalyzed carboboration with (cyclopropyl)methyl bromide furnished solely a ring-opened product, and furthermore cyclization accompanied the reaction using diethyl 2-allyl-2-(2-bromoethyl)malonate (Scheme 8). These results strongly indicate the intermediacy of alkyl radical species from the alkyl bromides in the carboboration.

The diboration and carboboration are triggered by σ -bond metathesis between a methoxyiron(II) and a diboron (Scheme 9). The resulting boryliron(II) species is then added across an alkyne to give an β -borylalkenyliron species, which is finally convertible into the diboration or carboboration product

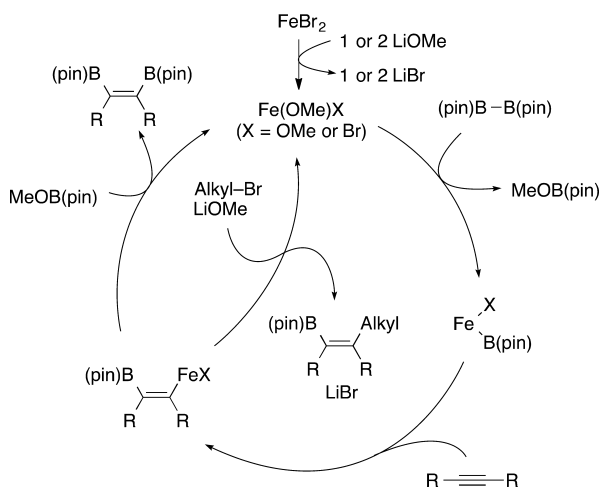
Scheme 7. Fe-Catalyzed Carboboration



Scheme 8. Radical Probe Experiments



Scheme 9. Proposed Catalytic Cycles

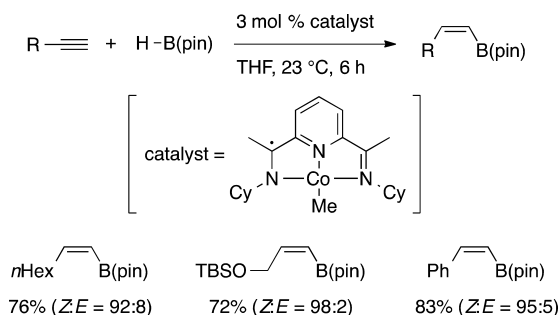


through capture with MeOB(pin) or an alkyl bromide. The energy profile of the reaction was shown by DFT calculations.

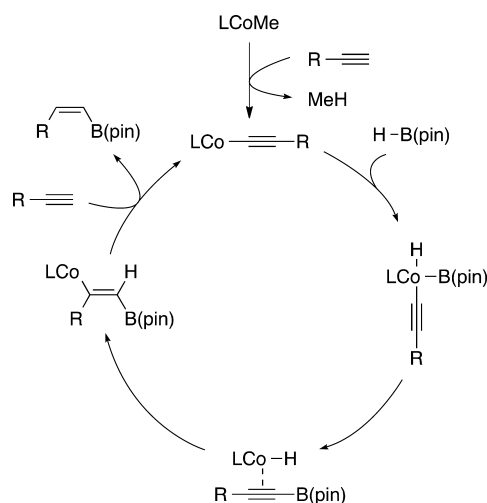
3. Co CATALYSIS

3.1. Hydroboration. Chirik has recently reported regio- and stereoselective hydroboration of terminal alkynes with pinacolborane catalyzed by a methylcobalt complex coordinated by a bis(imino)pyridine ligand having a cyclohexyl substituent on both imine nitrogens (Scheme 10).^{14,15} In marked contrast to the iron-catalyzed hydroboration (see 2.1), the reaction of aliphatic or aromatic terminal alkynes provided linear (*Z*)-alkenylboranes with high yield and selectivity. The reaction is proposed to proceed through the formation of a cobalt acetylide with liberation of methane (Scheme 11). Subsequent oxidative addition of pinacolborane, followed by reductive elimination affords an alkenylborane and a cobalt hydride. *syn*-Hydrocobaltation of the alkenylborane then takes place to give an alkenylcobalt species, which is finally transformed into an (*Z*)-alkenylborane via protonation by an alkyne.

Scheme 10. Co-Catalyzed Hydroboration



Scheme 11. Proposed Catalytic Cycle

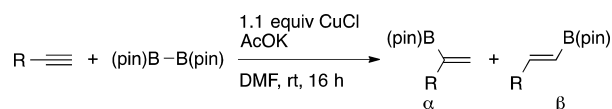


3.2. Diboration. Diboration of a diarylalkyne with bis(catecholato)diboron was reported to proceed with *syn*-selectivity in the presence of a catalytic amount of Co-(PMe₃)₄.¹⁶ Unfortunately, the yield of the diboration product was not described.

4. Cu CATALYSIS

4.1. Hydroboration. A pioneering work on the copper-mediated borylation of alkynes was reported by Miyaura, who developed formal hydroboration using bis(pinacolato)diboron and a stoichiometric amount of a copper salt.^{17,18} The reaction of 1-decyne or TBS-protected propargyl alcohol took place with α -selectivity, while linear (*E*)-alkenylboranes were preferentially formed with *t*-butylacetylene and phenylacetylene (Scheme 12). The catalytic use of a copper complex in hydroboration of this type was first realized by Yun in the

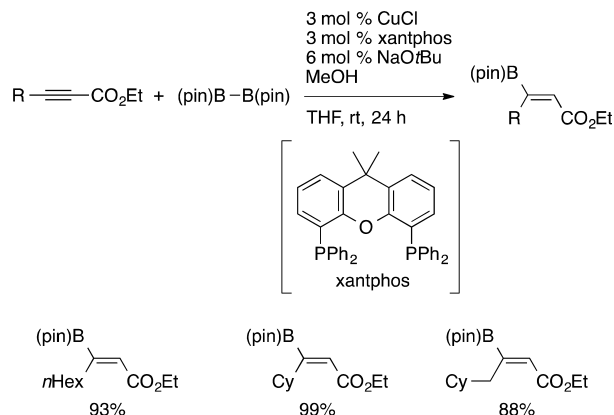
Scheme 12. Cu-Mediated Formal Hydroboration



R	additive	yield (%)	α : β
nOct	LiCl	90	91:9
TBSOCH ₂	PtBu ₃	62	91:9
tBu	PPr ₃	54	9:91
Ph	PBu ₃	56	1:99

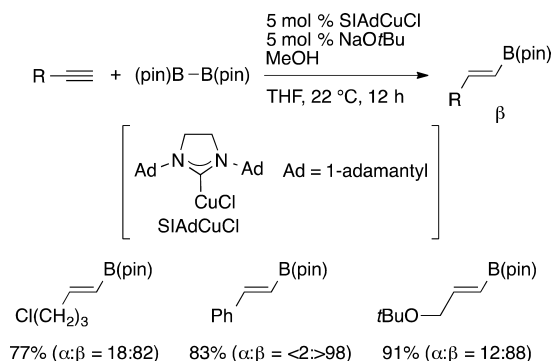
reaction of ynoates: a boryl moiety was installed into a β -position regio- and stereoselectively by employing MeOH as a proton source in the presence of xantphos ligand (Scheme 13),¹⁹ and the copper-catalyzed formal hydroboration made dramatic progress thereafter.

Scheme 13. Cu-Catalyzed Formal Hydroboration of Ynoates



Aliphatic, aryl, and propargyl-functionalized terminal alkynes were also found to undergo the formal hydroboration under similar reaction conditions, and β -selectivity was usually observed to afford linear (*E*)-alkenylboranes with *syn*-stereoselectivity (Scheme 14).^{19a,20} Hoveyda^{20a} and Carretero²¹

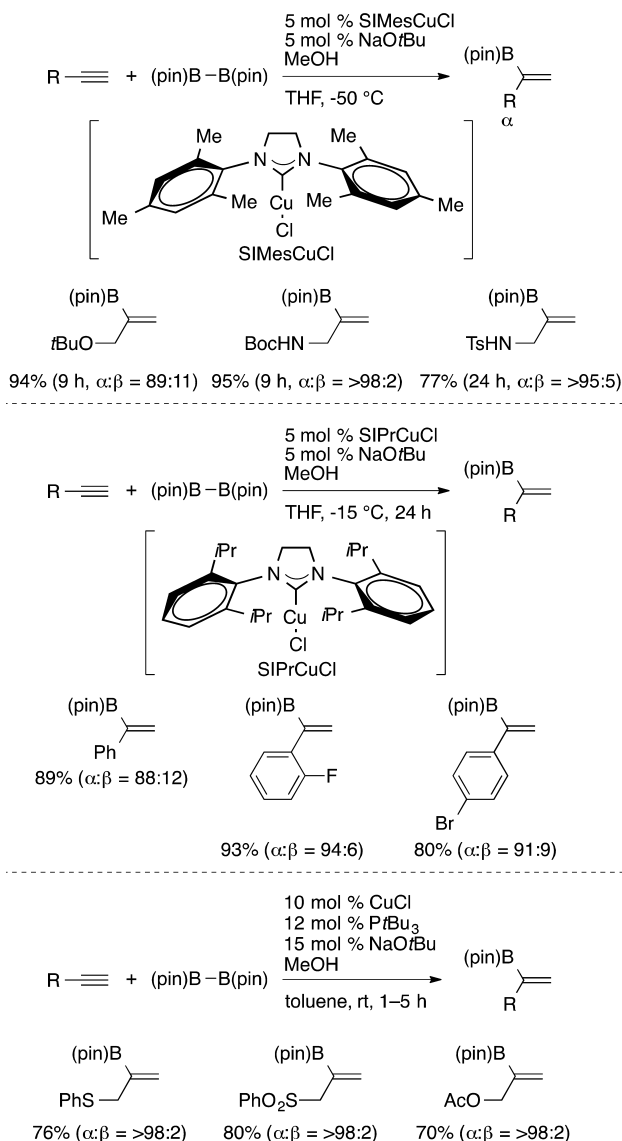
Scheme 14. Cu-Catalyzed β -Selective Formal Hydroboration of Terminal Alkynes



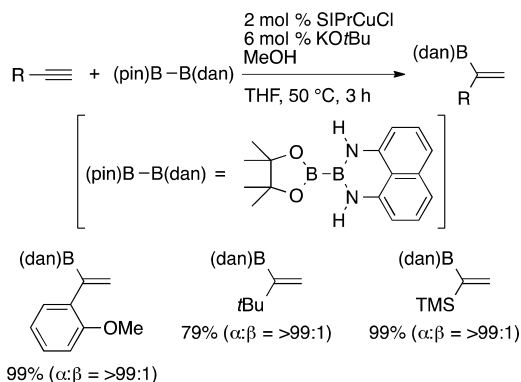
independently demonstrated that the use of such a bulky ligand as SIMes, SIPr, or PtBu_3 enabled α -selective installation of a boryl moiety to occur to provide branched alkenylboranes; however, the substrate scope was limited to propargyl-functionalized alkynes, electron-deficient and -neutral aryl alkynes (Scheme 15). On the other hand, Yoshida developed the general α -selective hydroboration, in which branched alkenylboranes were accessible with excellent regioselectivity, regardless of the electronic and steric characters of terminal alkynes employed (Scheme 16).²² The use of a masked diboron [(pin)B-B(dan)] was the key for the successful transformation.

The above reaction system was also applicable to internal alkynes to give *syn*-hydroboration products.²³ Alkyl(aryl)-alkynes generally accepted the boryl-addition at a β -position of the aryl substituent,^{20b-c,24} whereas inverse regioselectivity was exceptionally observed with aryl(*t*-butyl)alkynes probably owing to steric repulsion between *t*Bu and B(pin) in the

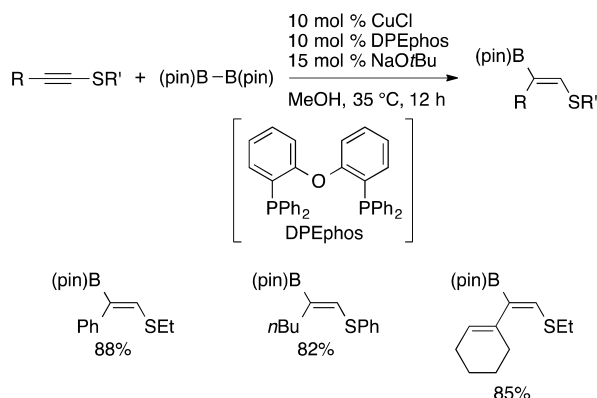
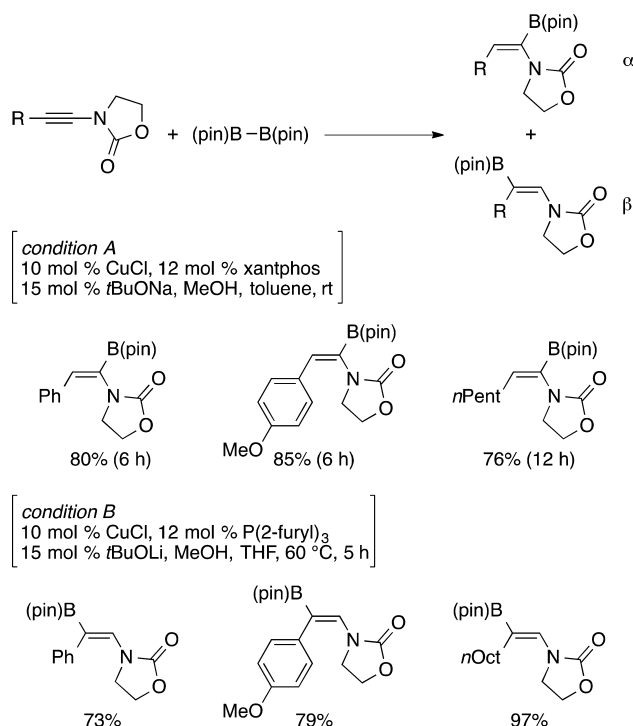
Scheme 15. Cu-Catalyzed α -Selective Formal Hydroboration of Terminal Alkynes



Scheme 16. Cu-Catalyzed α -Selective Formal Hydroboration of Terminal Alkynes with a Masked Diboron



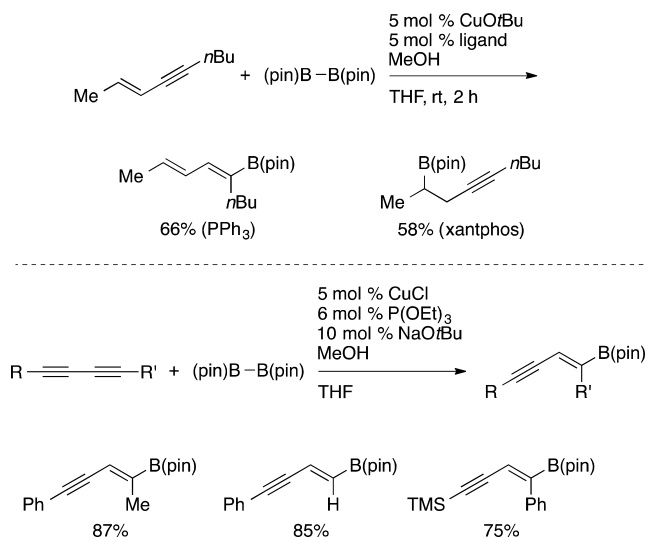
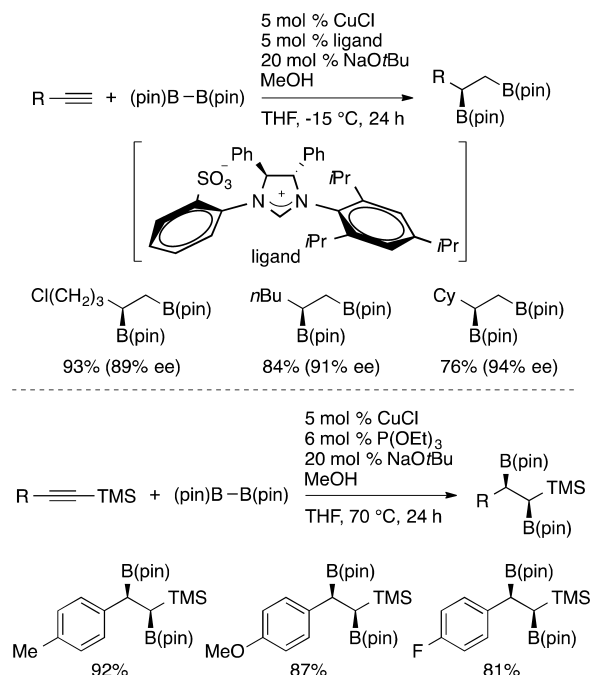
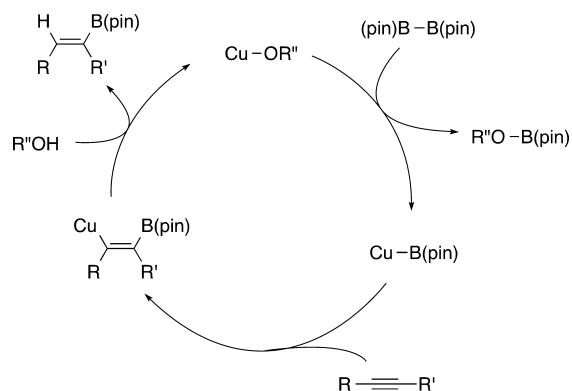
borylcupration step (Scheme 17).^{24b-d} The reaction of alkyl(aryl)alkynes with a masked diboron furnished B(dan)-substituted products with the normal regioselectivity in the

Scheme 21. Cu-Catalyzed Formal Hydroboration of Thioalkynes**Scheme 22. Cu-Catalyzed Formal Hydroboration of Ynamides**

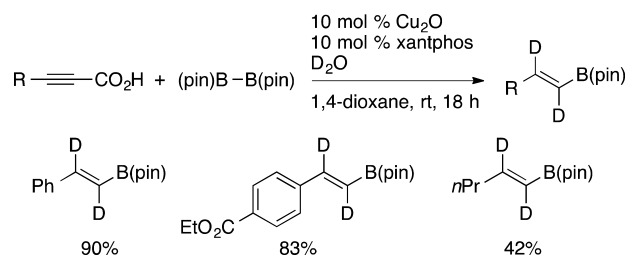
The formal hydroboration is commenced by σ -bond metathesis between a diboron and Cu-OR'' as described in Scheme 25. The resulting borylcopper is then added across an alkyne to give a boryl-substituted alkenylcopper, which is protonated with an alcohol, providing an alkenylborane.³⁴

Recently Song developed a unique formal deuterioboration using alkynyl carboxylic acids, where (*E*)-1,2-dideuterioborylstyrene derivatives were formed by treating with bis-(pinacolato)diboron and D₂O in the presence of a xantphos-Cu₂O catalyst (Scheme 26).³⁵ The authors proposed a pathway, which included borylcupration of an alkynylcopper species arising from decarboxylation of an alkynyl carboxylic acid (Scheme 27).

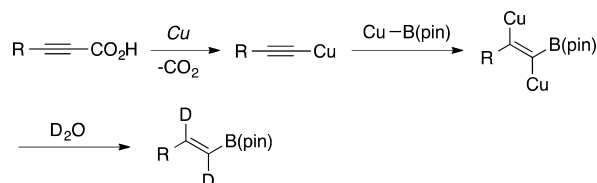
Lipshutz and Aue reported that direct addition of a H-B bond of pinacolborane across internal alkynoates occurred facily under the copper catalysis to provide α -boryl- α,β -unsaturated esters regio- and stereoselectively (Scheme 28),³⁶ being in marked contrast to the regiochemistry observed in the

Scheme 23. Cu-Catalyzed Formal Hydroboration of Conjugated Enynes and Diynes**Scheme 24. Cu-Catalyzed Formal Dual Hydroboration****Scheme 25. Proposed Catalytic Cycle**

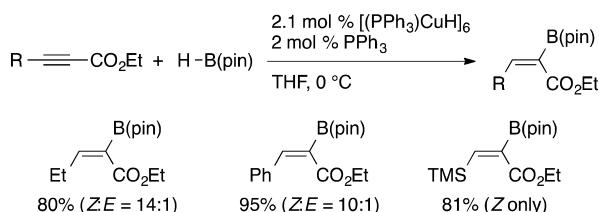
Scheme 26. Cu-Catalyzed Formal Dideuterioboration



Scheme 27. Proposed Pathway

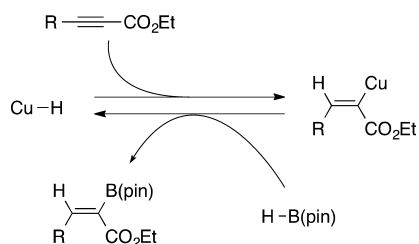


Scheme 28. Cu-Catalyzed Hydroboration of Ynoates



formal hydroboration with bis(pinacolato)diboron (see Scheme 13). The opposite regioselectivity should be ascribable to a reaction pathway including a copper hydride as a key intermediate as depicted in Scheme 29. Tsuji developed the

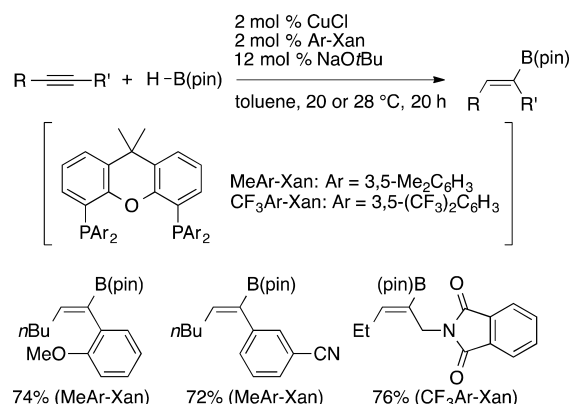
Scheme 29. Proposed Catalytic Cycle



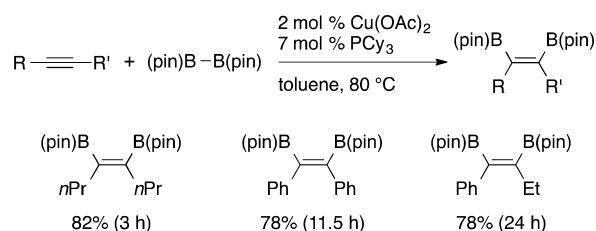
regio-complementary approach to disubstituted alkenylboranes from alkyl(aryl)alkynes or propargyl-functionalized internal alkynes by the copper-catalyzed reaction with pinacolborane (Scheme 30 vs Schemes 17 and 19).^{37,38}

4.2. Diboration. After the preliminary results on copper-catalyzed diboration of phenylacetylene or diphenylacetylene with bis(catecholato)diboron (detailed reaction conditions and yields were not given),³⁹ Yoshida disclosed the general *syn*-diboration with bis(pinacolato)diboron using $\text{Cu}(\text{OAc})_2\text{-PCy}_3$ catalyst,⁴⁰ being equally effective as the established platinum catalytic system.⁴¹ The reaction was applicable to a variety of internal alkynes bearing dialkyl-, diaryl- or alkyl(aryl) substituents to provide *vic*-diborylalkenes in high yield (Scheme 31), and furthermore 1,4-dimethoxy-2-butyne was converted into a tetraborated product, in which the MeO groups were also replaced by B(pin) groups (Scheme 32). This result was completely different from that obtained with the platinum catalyst, which afforded the diboration product.

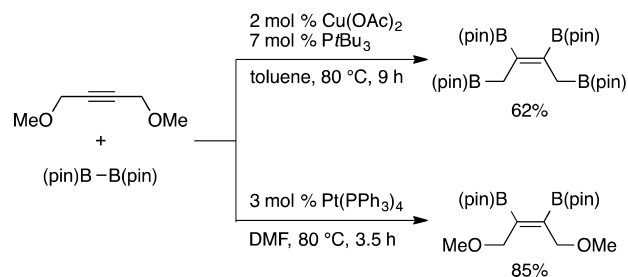
Scheme 30. Cu-Catalyzed Hydroboration of Internal Alkynes



Scheme 31. Cu-Catalyzed Diboration



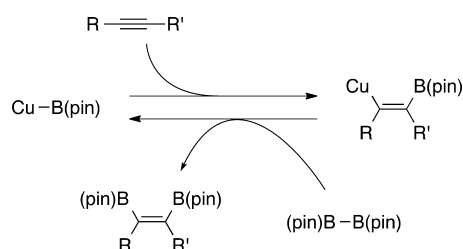
Scheme 32. Cu-Catalyzed Tetraboration



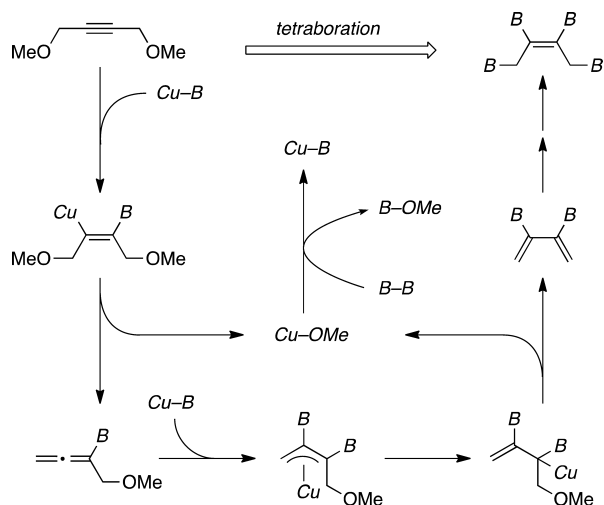
As was the case with the hydroboration, the reaction proceeds through the boryl-substituted alkenylcopper intermediate, which finally reacts with a diboron to give a product with regenerating the borylcopper species (Scheme 33). On the other hand, the tetraboration involves the formation of a boryllallene and 2,3-diboryl-1,3-butadiene as key intermediates via β -oxygen elimination (Scheme 34).

4.3. Carboboration. Tortosa⁴² and Yoshida⁴³ independently expanded the copper-catalyzed borylation into the carboboration by employing alkyl and benzyl halides (Schemes 35 and 36). Treatment of terminal aryl alkynes or propargyl ethers with bis(pinacolato)diboron and carbon electrophiles in the presence of xantphos or PCy₃ as the optimal ligand resulted

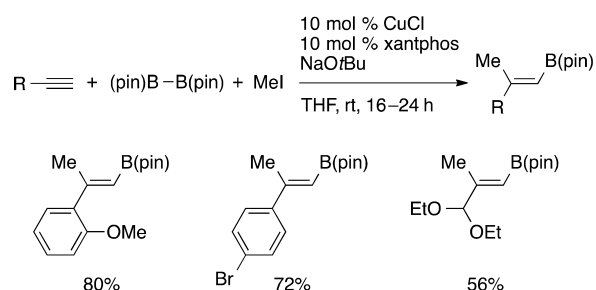
Scheme 33. Proposed Catalytic Cycle for Diboration



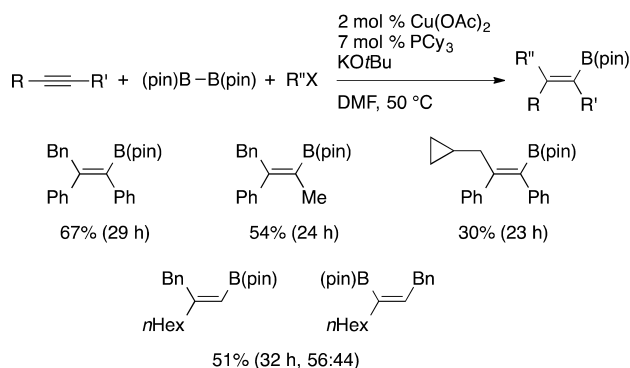
Scheme 34. Proposed Catalytic Cycle for Tetraboration



Scheme 35. Cu-Catalyzed Carboboration with Methyl Iodide



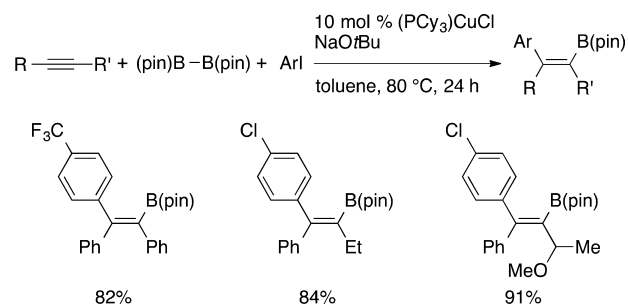
Scheme 36. Cu-Catalyzed Carboboration with Benzyl/Cyclopropylmethyl Halide



in the regioselective formation of the carboboration products, whose boryl moieties were installed into the terminal carbons, with exclusive *syn* stereoselectivity. High regioselectivity was also observed with alkyl(aryl)alkynes, whereas the reaction of terminal aliphatic alkynes afforded a mixture of regioisomers, and moreover the result that the reaction with cyclopropylmethyl bromide took place without ring-opening should rule out a radical pathway in the carboboration. A similar alkylboration was reported to proceed with an NHC-CuCl catalyst.^{20e,24e}

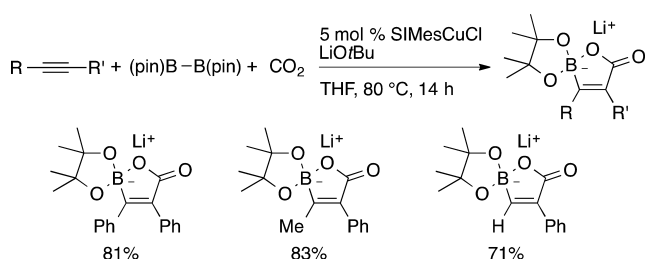
Arylboration of alkynes by use of aryl iodides as carbon electrophiles was reported by Brown (Scheme 37).⁴⁴ The optimal ligand for the transformation was determined to be PCy₃, and various internal alkynes were smoothly converted into trisubstituted alkenylboranes, although the reaction of

Scheme 37. Cu-Catalyzed Carboboration with Aryl Iodides



terminal alkynes led to low yields of the desired products. The regioselectivity of the reaction with alkyl(aryl)alkynes was similar to that observed in the alkylboration.

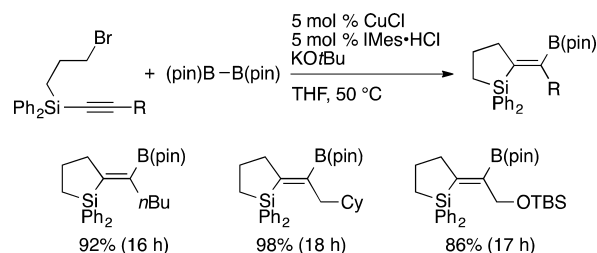
Carbon dioxide was found to act as an effective electrophile in the presence of an NHC-CuCl catalyst (SImesCuCl), leading to boracarboxylation (Scheme 38).⁴⁵ As were the cases

Scheme 38. Cu-Catalyzed Carboboration with CO₂

with the above carboborations, a boron moiety was attached regioselectively to a β -position of a phenyl substituent of 1-phenyl-1-propyne or phenylacetylene, affording boralactones with *syn*-stereoselectivity.

Silylalkynes having an alkyl bromide moiety⁴⁶ and propargyl ethers having a cyclohexadienone unit⁴⁷ could also be coupled with bis(pinacolato)diboron under the copper catalysis, providing borylative cyclization products through the intramolecular carboboration (Schemes 39 and 40). The regiocon-

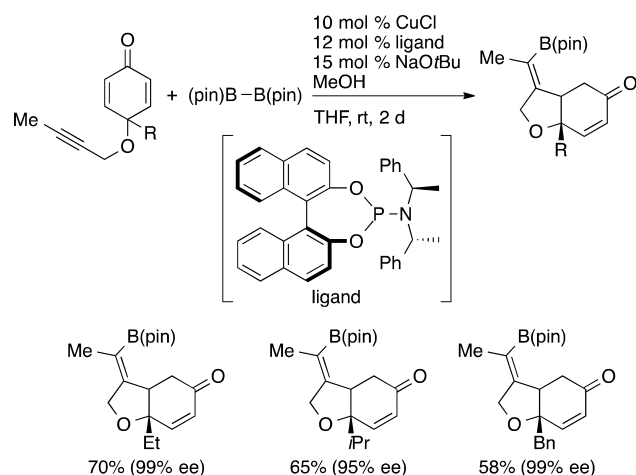
Scheme 39. Cu-Catalyzed Intramolecular Carboboration with Alkylbromides



trol of the borylcupration, which was essential for the intramolecular capture with the carbon electrophile, was achieved by the silyl substituent or the propargylic C-O bond. High enantioselectivity was also observed in the latter reaction by employing a binaphthol-based phosphoramidite ligand.

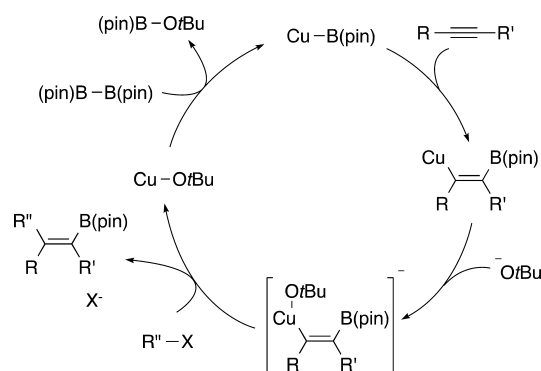
Formation of the boryl-substituted alkenylcopper intermediate should also trigger the carboboration (Scheme 41). Then an alkenylcuprate species is proposed to be generated via action

Scheme 40. Cu-Catalyzed Intramolecular Carboboration with Enones



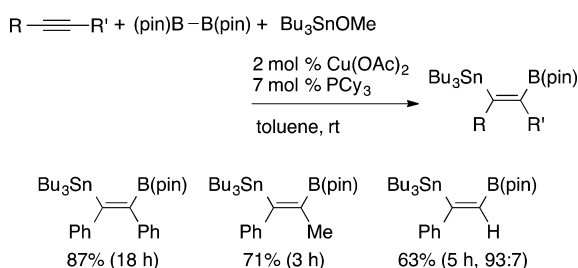
with a base, and its capture with a carbon electrophile finally provides the product.

Scheme 41. Proposed Catalytic Cycle



4.4. Stannylation. Yoshida demonstrated that *syn*-stannylation efficaciously occurred to give *vic*-boryl-(stannyl)alkenes in the reaction with bis(pinacolato)diboron by using a stannyl alkoxide as an electrophile (Scheme 42).⁴⁸

Scheme 42. Cu-Catalyzed Stannylation

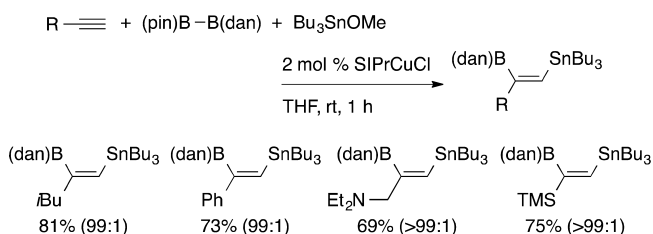


Exclusive formation of single regioisomers, whose boron moiety was attached to β -position of an aryl substituent, was observed with alkyl(aryl)alkynes, and terminal alkynes accepted the boryl-addition preferentially at the terminal carbons.

Yoshida also reported that the use of a masked diboron [(pin)B-B(dan)] as a boron source in the borylstannylation of terminal alkynes completely inverted the regioselectivity.⁴⁹ By employing an NHC-CuCl catalyst with a bulky ligand

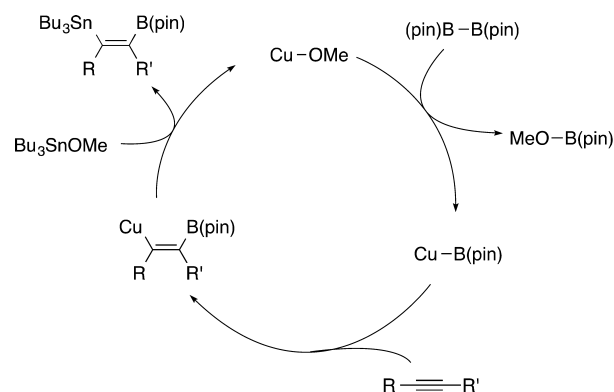
(SIPrCuCl), aliphatic, aryl, propargyl-functionalized, or silyl terminal alkynes were readily convertible into the *syn*-borylstannylation products, bearing the boryl moiety at the internal carbons, with high regioselectivity, irrespective of the electronic characters of the alkynes (Scheme 43). As depicted in section 4.1, the B(dan) moiety was solely installed in the product, and a borylstannylation product having the B(pin) moiety was not formed at all.

Scheme 43. Cu-Catalyzed Stannylation with a Masked Diboron



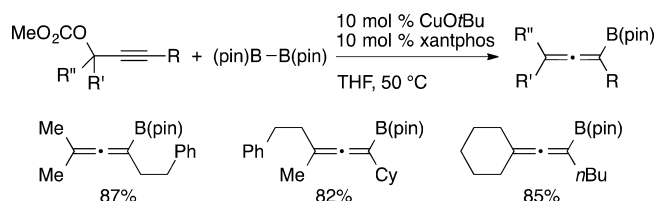
A plausible catalytic cycle for the borylstannylation also includes the formation of the boryl-substituted alkenylcopper intermediate, which is transformed into the product upon reaction with a stannyl alkoxide (Scheme 44).

Scheme 44. Proposed Catalytic Cycle



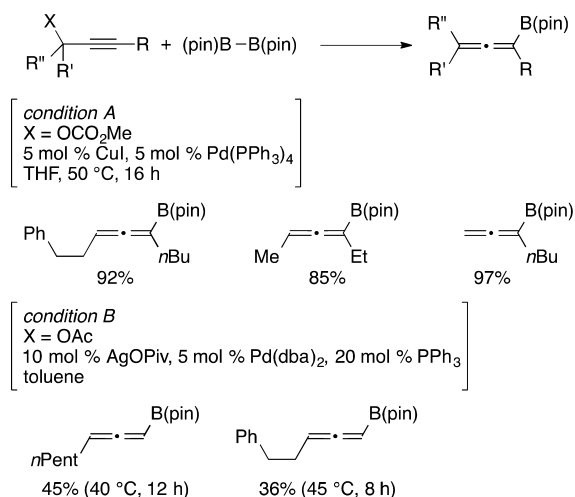
4.5. Boryl Substitution. Ito and Sawamura developed the direct synthesis of multisubstituted allenylboranes from propargyl carbonates by the copper-catalyzed boryl substitution with bis(pinacolato)diboron (Scheme 45).⁵⁰ Xantphos was the

Scheme 45. Cu-Catalyzed Boryl Substitution



ligand of choice, and allenylboranes of structural diversity were facily accessible through formal S_N2' substitution. No S_N2 -type product was detected in the reaction mixture. Substrate scope of the substitution was further expanded by using bimetallic catalysis (Pd/Cu or Pd/Ag) (Scheme 46).⁵¹

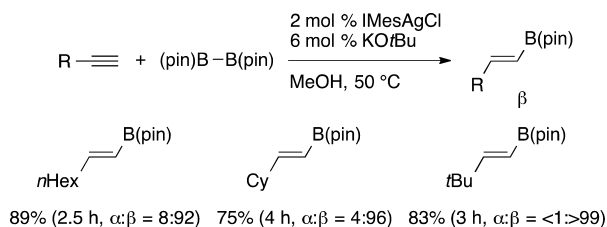
Scheme 46. Pd/Cu or Pd/Ag-Catalyzed Boryl Substitution



5. Ag CATALYSIS

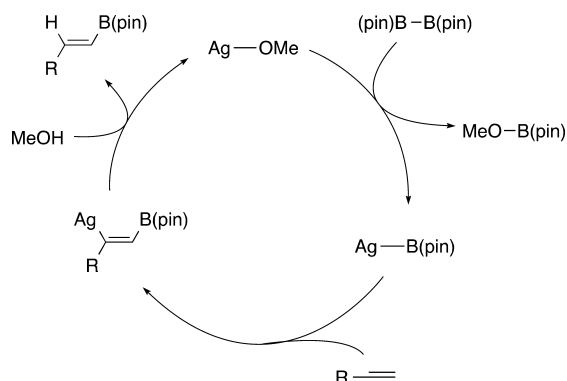
5.1. Hydroboration. In marked contrast to the great progress in the copper-catalyzed borylation of alkynes as depicted above, the catalytic use of silver for synthesizing alkenylboranes remained totally unexplored until Yoshida developed the NHC(IMes)–AgCl-catalyzed formal hydroboration (Scheme 47).⁵² Various substituted aliphatic

Scheme 47. Ag-Catalyzed Formal Hydroboration



terminal alkynes and a conjugated enyne were facilely transformed into linear (*E*)-alkenylboranes with high regio- and stereoselectivity by treating with bis(pinacolato)diboron and MeOH. As was the case with the copper-catalyzed formal hydroboration, the reaction may proceed through *syn*-addition of a borylsilver(I) species across an alkyne (borylarylation) (Scheme 48).

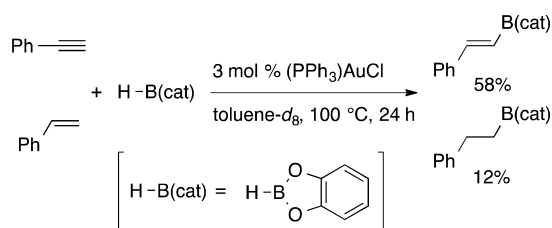
Scheme 48. Proposed Catalytic Cycle



6. Au CATALYSIS

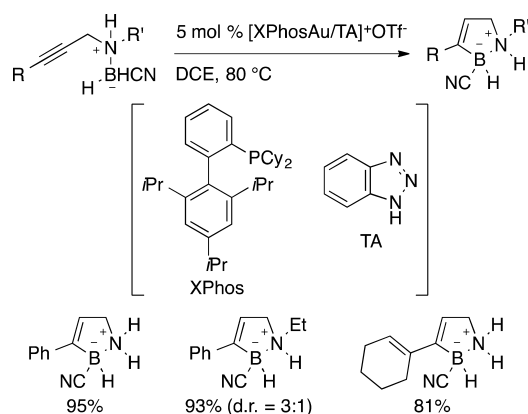
6.1. Hydroboration. A gold complex [(Ph₃P)AuCl] was also found to promote the hydroboration: phenylacetylene was preferentially hydroborated to give (*E*)-β-borylstyrene in the presence of styrene, although the chemoselectivity was modest (Scheme 49).⁵³

Scheme 49. Au-Catalyzed Hydroboration



Lewis acid–base adducts of cyanoborane and propargyl amines smoothly underwent intramolecular hydroboration (Scheme 50).⁵⁴ A cationic triazole-modified gold complex

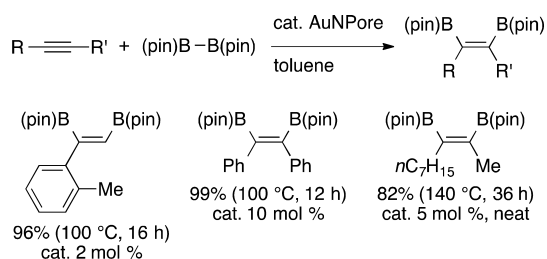
Scheme 50. Au-Catalyzed Intramolecular Hydroboration



(TA–Au) bearing XPhos as an additional ligand was the catalyst of choice, and a variety of five-membered amine boranes were accessible in high yield.

6.2. Diboration. Jin developed the diboration of alkynes catalyzed by nanoporous gold (AuNPore) (Scheme 51).^{55,56} A

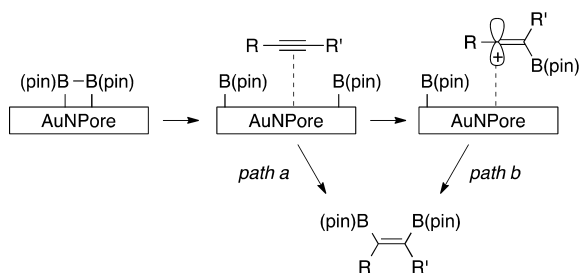
Scheme 51. Au-Catalyzed Diboration



variety of terminal and internal alkynes were applicable to the diboration to afford *syn-vic*-diborylalkenes stereoselectively; however, *anti*-adducts also formed as byproducts in some cases. Based on the result that the reaction using two diborons gave crossover diboration products, the authors ruled out a reaction pathway which included oxidative addition of a diboron to Au(0). Instead, a B–B bond may be cleaved on

the surface of AuNPore to give $[\text{Au}-\text{B}(\text{pin})]$ species (Scheme 52). Then an alkyne interacts with two $[\text{Au}-\text{B}(\text{pin})]$ species

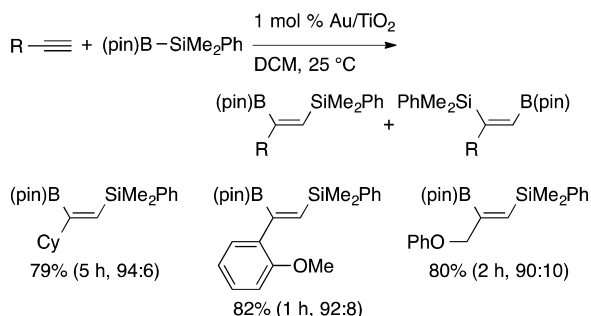
Scheme 52. Proposed Catalytic Cycle



either through a simultaneous path (*path a*) or through a stepwise path (*path b*) to finally provide the diboration product.

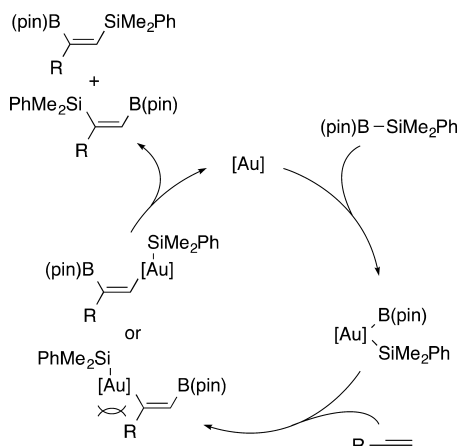
6.3. Silylboration. Supported gold nanoparticles (Au/TiO_2) turned out to catalyze facilely *syn*-selective silylboration of alkynes, giving *vic*-boryl(silyl)alkenes (Scheme 53).⁵⁷ The

Scheme 53. Au-Catalyzed Silylboration



striking feature of the gold-catalyzed silylboration is regioselectivity with terminal alkynes, being opposite to that observed with Pd or Pt catalysts.^{58,59} The regioselective silylboration was applicable to aliphatic, aromatic, and propargyl-functionalized terminal alkynes to lead to the preferential installation of the boryl moiety into the internal carbon. As described in Scheme 54, oxidative addition of a silylboration and insertion of an alkyne into $[\text{Au}]-\text{B}(\text{pin})$ are proposed to be key steps of the silylboration. The observed regioselectivity may be attributable

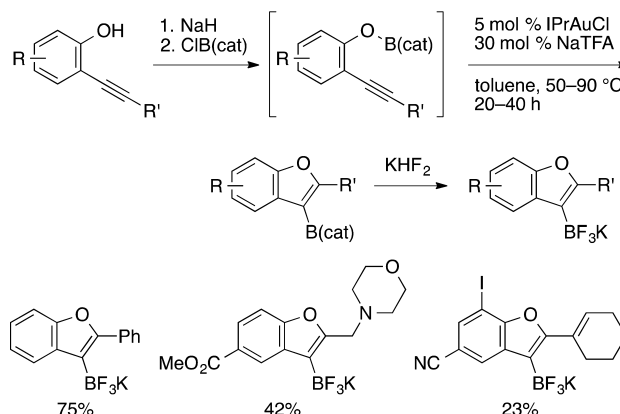
Scheme 54. Proposed Catalytic Cycle



to steric repulsion between $[\text{Au}]$ and a substituent of an alkyne in the insertion step.

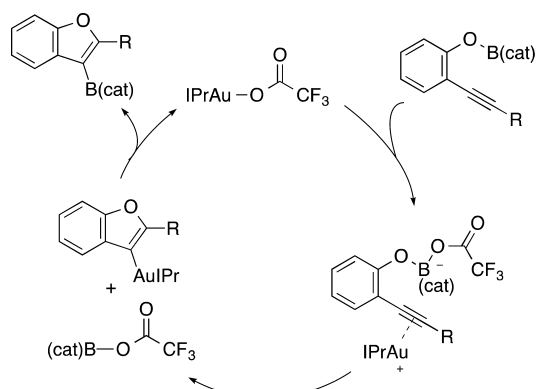
6.4. Alkoxyboration. Blum reported the first alkoxyboration, in which a boron-oxygen bond was added across a carbon-carbon triple bond intramolecularly (Scheme 55).⁶⁰

Scheme 55. Au-Catalyzed Alkoxyboration



Thus, treatment of boronic esters generated *in situ* from 2-alkynylphenols and *B*-chlorocatecholborane with $\text{IPrAuCl}/\text{NaTFA}$ catalyst provided variously substituted 3-borylbenzofuran derivatives through *anti*-B-O bond addition, being hardly available by the established benzofuran synthesis/catalytic borylation reactions. The alkoxyboration was proposed to commence with formation of a nucleophilic borate derived from a boronic ester and *in situ*-generated IPrAuTFA (Scheme 56). The resulting cationic gold then binds to an alkyne moiety,

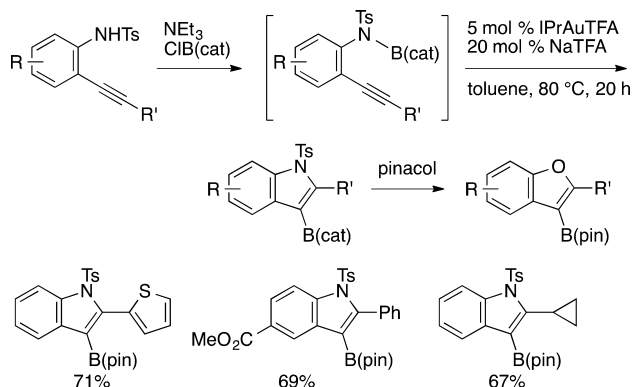
Scheme 56. Proposed Catalytic Cycle



increasing its electrophilicity. Nucleophilic attack on the gold-activated alkyne by a phenolic oxygen provides an organogold and a boron trifluoroacetate, which finally undergo gold-to-boron transmetalation to give a product with regeneration of IPrAuTFA .

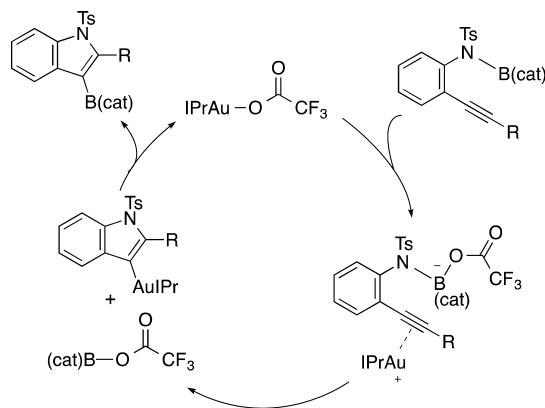
6.5. Aminoboration. Intramolecular aminoboration of alkynes has been found to take place also under the gold catalysis.⁶¹ When aminoboronic esters, derived from 2-alkynylaniline derivatives and *B*-chlorocatecholborane, was treated with IPrAuTFA catalyst, 3-borylated indoles of structural diversity were efficiently produced via *anti* B-N bond addition process (Scheme 57). The aminoboration proceeds through a pathway similar to that of the above alkoxyboration: formation of a nucleophilic borate, whose

Scheme 57. Au-Catalyzed Aminoboration



alkyne moiety is activated by a cationic gold, should trigger the reaction (Scheme 58). Subsequent intramolecular nucleophilic

Scheme 58. A Proposed Catalytic Cycle



attack by a nitrogen, followed by transmetalation between the resulting organogold and boron trifluoroacetate leads to the formation of the borylindoles.

7. CONCLUSION

We have been experiencing the “mushroom growth” of the catalytic borylation of alkynes especially with a borylcopper species, which give us convenient and potent methods for synthesizing stereodefined alkenylboranes of high synthetic significance. Because the common intermediate of the borylation is a boryl-substituted alkenylcopper(I) species of high nucleophilicity, the reaction modes and the borylated products obtained thereby can facilely be diversified by treating with a suitable third component (electrophile). Although the range of the borylation with Fe, Co, Ag, or Au catalyst remains still narrower at present as compared with that with the Cu catalyst, this field is likely to grow in the near future with their promising catalysis toward borylation.

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Notes

The authors declare no competing financial interest.

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