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Synthesis of Tri- and Tetrasubstituted Alkenyl Boronates from Alkynes

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Javier Carreras was nominated to be part of this collection by EurJOC Board Member José González

The synthesis of organoboron compounds have attracted the attention of the synthetic community. In particular, molecules with C(sp²)-B bonds enable the transformation to new C—C or C-heteroatom bonds by well-established methodologies. Alkenyl boronates have the possibility for further conversion of the boron moiety or functionalization of the double bond. This review gives an overview on the recent methodologies for the selective preparation of the challenging highly substituted alkenyl boronates from alkynes.

1. Introduction

Boronic acids and their derivatives[1] are very useful intermediates in synthetic organic chemistry, particularly in highly important C—C bond-forming reactions such as the Suzuki-Miyaura cross coupling[2] and the Petasis boron-Mannich reaction.[3] Transformations of the boryl motif of organoboronates into a range of functional groups are also well known, including protodeboronation, oxidation, amination and the Chan-Lam coupling, many of which have been developed stereospecifically from enantioenriched secondary and tertiary boronic esters.[4] In addition to those processes, the family of alkenyl boronates are key precursors in cycloaddition reactions (cyclopropanation, epoxidation, aziridination, [2 + 2], [3 + 2] and [4 + 2]) for the preparation of cycloalkylboronates and boryl-substituted saturated heterocycles.[5] Other useful transition metal-catalyzed transformations from alkenyl boronates include the Wacker oxidation, which led to α-borylated ketones,[6] the C(sp²)—H alkenylation of aromatic rings and the C(sp³)—H vinylation of cyclopropanes.[7]

The classical synthesis of alkenyl boronates from organo-lithium compounds or Grignard reagents and trialkylborates is an efficient and scalable method but can suffer from selectivity issues and lacks functional group compatibility.[1,2b] To over-come these problems, a variety of methods have been developed for the selective synthesis of alkenyl boronates.[8]

Despite the excellent reviews on alkenyl boronates and some of their synthetic methods, the synthesis of more complex tri- and tetrasubstituted alkenyl boronates has not been specifically covered. In this review, we will focus on the synthesis of tri- and tetrasubstituted alkenyl boronates by hydroboration, carboboration or elementoboration of alkynes. Other strategies to produce tri- or tetrasubstituted alkenylboronates, which use allenes, alkenes (dehydrogenative[9] or defluorinative[10] borylation), aldehydes/ketones (Boron-Wittig olefination[11]) as starting materials or the isomerization of alkenyl boronates,[12] will not be covered. All transformations involving polyboronates will be omitted since this topic has been conveniently reviewed.[13]

2. Hydroboration of Internal Alkynes

Since the discovery of the hydroboration reaction by Nobel laureate H. C. Brown,[14] the hydroboration of alkynes with di(alkoxy)boranes and bis(boronates)[15] has become a well-established methodology for the obtention of alkenyl boronates.

In particular, the hydroboration of internal alkynes, which is the addition of a boryl group and a hydrogen atom to a disubstituted triple carbon-carbon bond, is arguably one of the most studied strategies for the synthesis of trisubstituted alkenyl boronates. This approach was already studied by Brown *et al.* by heating alkynes with catecholborane.[16] The problematic regiocontrol was partially overcome when Knochel *et al.* introduced pinacolborane (HBpin) as a new hydroboration reagent,[17] which also offered other advantages, such as milder reaction conditions and higher stability of the resulting alkenyl boronates.

Since then, the hydroboration of alkynes has been extensively studied under metal and metal-free catalysis. Nevertheless, in contrast to the huge development of metal-catalyzed hydroboration of terminal alkynes, a comparatively small number of reports have been devoted to the hydroboration of

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internal alkynes. Typically, only a few examples of internal alkynes, if any, can be found in the scope of hydroboration protocols optimized for terminal alkynes, probably due to their inferior reactivity and the regioselectivity issues that arise from the hydroboration of unsymmetrical internal alkynes.

Two types of reagents have been employed as the source of the boron moiety, bis(alkoxy)boranes [H—B(OR)$_2$] and bis(boronates) B$_2$(OR)$_4$, and in many cases a complementary regioselectivity was found when unsymmetrical alkynes were hydroborated. This section will cover the *syn-* and *anti-*hydroboration of internal alkynes with bis(alkoxy)boranes and with bis(boronates). In all cases, trisubstituted alkenyl boronates are obtained.

2.1. *syn-*Hydroboration with di(alkoxy)boranes [HB(OR)$_2$]

The hydroboration of internal alkynes typically takes place in a *syn* fashion, i.e., the hydrogen atom and the boryl motif end up attached at the same side of the double bond of the resulting (*Z*)-alkenyl boronates. In metal-catalyzed transformations, a general mechanism involving hydrometallation of the alkyne by a M—H species, followed by boryl demetallation, is typically considered.

One of the first studies of metal-catalyzed hydroboration of internal alkynes was reported by Suzuki, Miyaura et al.[18] In this report, methylthioalkynes were reacted with catecholborane (HBcat) in the presence of a catalytic amount of NiCl$_2$(dppe), and the β-thio vinylboronates were obtained regio- and stereoselectively (Scheme 1).

Since that report, numerous examples of *syn-*hydroboration of internal alkynes have been reported in which pinacolborane
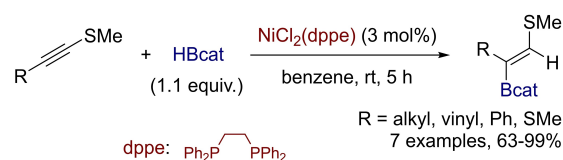
Scheme 1. Nickel-catalyzed hydroboration of internal alkynyl thioethers.

(HBpin) was employed as the borylating species. In particular, the hydroboration of alkyl aryl acetylenes has been extensively studied in terms of regioselectivity, since the boryl group can be attached to the α or the β position relative to the aryl substituent (Scheme 2). Tsuji et al. reported a catalyst system formed by CuCl, bisphosphine ligand MeAr-Xan and NaO*t*-Bu, which afforded preferentially the α-aryl vinylboronates.[19] The copper-hydride species generated *in situ* from pinacolborane and the copper-alkoxide complex is responsible for the hydrocupration of the alkyne, which is followed by boryldemetallation with pinacolborane. Similarly, a copper complex with an *N*-heterocyclic carbene as ligand[20] and an iron complex also afforded α-aryl vinylboronates.[21] Other catalyst systems based on Cu,[22] Fe[23] and Mg[24] provided similar α-selectivity. In contrast, a cobalt-based catalyst system with Xantphos as ligand provided preferentially the isomeric β-aryl vinylboronates (Scheme 2).[25] Mechanistically, in this case the initial borylmetallation of the alkyne is believed to be followed by a reductive elimination to generate the alkenyl boronate. Other catalyst systems based on Co,[26] Sc,[27] Zn,[28] Ir,[29] Li,[30] boranes[31] and tropylium ion[32] also provided β-selectivity.

The hydroboration of symmetrical diaryl or dialkyl acetylenes has not been, in general, systematically studied with

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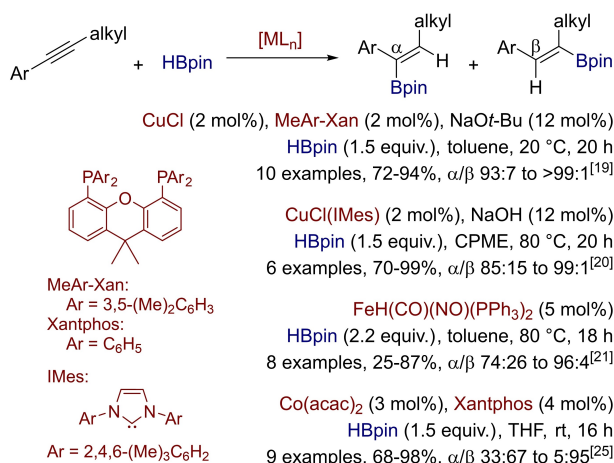
Antonio Valero (1998) studied Chemistry in Valencia, where he also received his Master's degree in Organic Chemistry in 2020, working on functionalised silica nanoparticle with Dr. Costero and Dr. Parra. Currently, he is PhD candidate at the Universidad de Alcalá supervised by Dr. Carreras and Dr. Sucunza. He is interested in the application of novel boron and fluorinated structures in medicinal chemistry.

Ruben Manzano graduated in Chemistry from the Universidad de Valladolid (Spain) and obtained his PhD degree (2010) under the supervision of Profs. Pedrosa and Andres. During his postdoctoral studies in the groups of Prof. Hashmi (Heidelberg, Germany), Prof. Martin (ICIQ, Spain), Prof. Dixon (Oxford, UK) and Prof. Vicario (UPV-EHU, Spain) he focused on metal- and organocatalyzed methodologies. He is currently assistant professor at the Universidad de Alcalá and his current interests are the development of enantioselective organo- and dual catalyzed transformations.

Javier Carreras graduated in Chemistry at the Universidad de La Rioja (Spain) and obtained his PhD under the supervision of Profs. Avenoza and Busto (2010). After postdoctoral appointments working on metal-catalyzed transformations at the Max Planck Institut fur Kohlenforschung with Prof. Alcarazo, ICIQ with Prof. Echavarren and Universidad de Huelva with Prof. Pérez he moved in 2018 to Universidad de Alcalá as assistant professor. In recent years, he has focused on the preparation of organoboron and organofluorine compounds.

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Scheme 2. Hydroboration of alkyl aryl acetylenes with pinacolborane.

pinacolborane as the borylating agent, but some examples indicate that the reaction can be performed successfully under a variety of catalyst systems (see for example references 21–24, 26–31, 33, 34, 35, 36). In contrast, the hydroboration of unsymmetrical diaryl or dialkyl acetylenes has been scarcely explored due to the more challenging selectivity issues. For unsymmetrical diaryl acetylenes, electronic differences between both aryl substitutents do not lead to high selectivities, and only in the case of having a sterically hindered 2,6-disubstituted aromatic ring, the regioselectivity is synthetically useful.[22,23a,25,26a–b,31c] In the case of unsymmetrical dialkyl acetylenes, the difference in size of both substituents typically determines the regioselectivity, and high selectivity is obtained when a bulky *tert*-butyl or *iso*-propyl group is present.[21,24,25,30a,36,37]

The hydroboration of internal aryl silyl acetylenes has also been explored under different transition metal catalyst systems. The copper catalyst systems described in Scheme 2[19,20] led to the same regiocontrol as that observed for alkyl aryl alkynes, and β-silyl vinylboronates were obtained. In contrast, a cobalt(I)-hydride complex provided the isomeric α-silyl vinyl-boronates (Scheme 3a).[26a] Similarly, alkyl silyl acetylenes were converted to α-silyl vinylboronates by treatment with a combination of trimethylaluminium and pinacolborane (Scheme 3b).[38]
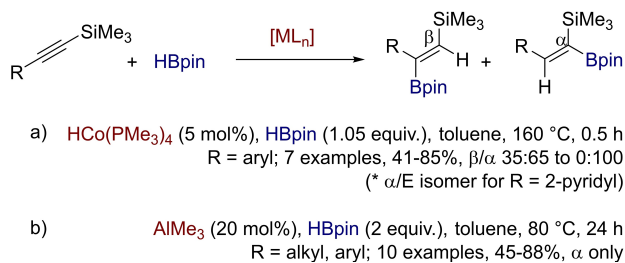
Interestingly, *gem*-hydroboration was observed when a ruthenium catalyst system[39] was applied to internal alkyl silyl acetylenes (Scheme 4), and the isolated silyl vinylboronates are isomers of those previously obtained under copper or cobalt catalysis. The analogous germanyl alkynes also worked well with this protocol.
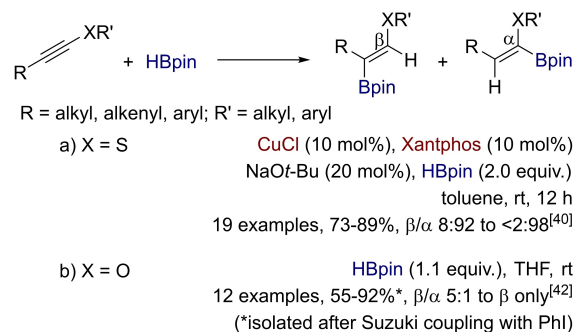
Internal alkynes with other heteroatoms, such as oxygen or sulfur, directy attached to the triple bond have also been studied. In contrast to the early report on thioalkynes by Suzuki, Miyaura *et al.*,[18] where β-thio vinylboronates were obtained selectively (Scheme 1), a recent study based on a copper/bisphosphine catalyst system has allowed the obtention of the regioisomeric α-thio vinylboronates from similar substrates (Scheme 5).[40] Thio vinylboronates are synthetically useful intermediates which can be further transformed by cross-coupling reactions on the Bpin moiety and by substitution of the SR group by Grignard reagents, for example. Remarkably, the hydroboration of ynol ethers was found to take place in the absence of any catalyst system,[41] and treatment of the alkyne with HBpin led to the regioselective formation of air-sensitive β-oxy vinylboronates, which were intercepted in a subsequent Suzuki-Miyaura coupling reaction with aryl halides.[42]

The *syn*-hydroboration of internal alkynoic acid derivatives with pinacolborane has been studied under copper catalysis,[19,43] and α-borylated alkenoates were typically isolated in short times with high regio- and stereoselectivity by using a combination of Stryker's reagent and triphenylphosphine (Scheme 6).
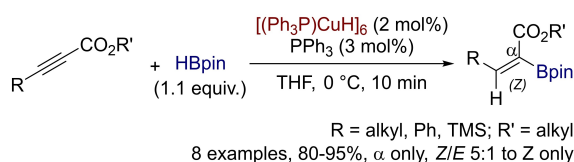
The selective hydroboration of internal propargylic alcohol or amine derivatives has been studied under transition metal catalysis. Rueping *et al.* found that the use of a manganese complex as precatalyst and NaBHEt$_3$ as activator promoted the hydroboration of TBDMS-protected propargylic alcohols and dibenzyl propargylic amines. The boryl moiety was exclusively
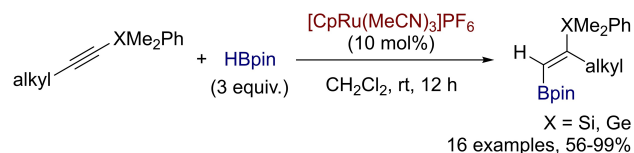
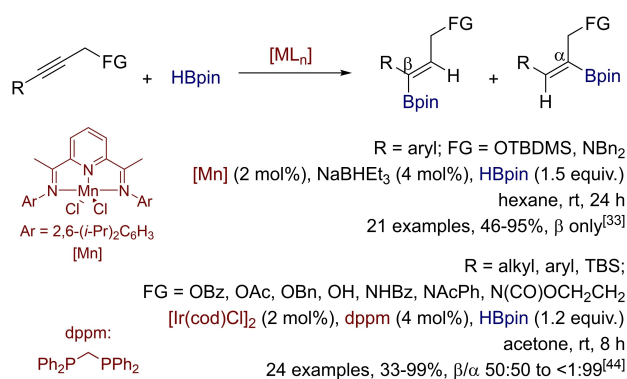**Scheme 4.** Ruthenium-catalyzed *gem*-hydroboration of internal silylalkynes with pinacolborane.

Scheme 3. Hydroboration of internal silylalkynes with pinacolborane.

Scheme 5. Hydroboration of internal alkynyl (thio)ethers with pinacolborane.

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Scheme 6. Copper-catalyzed hydroboration of internal alkynoates with pinacolborane.

attached to the furthest position with respect to the functional group (Scheme 7, top).[33] Complementarily, the copper catalyst system reported by Tsuji et al.[19] was found to provide the regioselective α-borylation for some propargylic alcohol and amine derivatives. Analogously, the use of an iridium complex as catalyst for the hydroboration of similar substrates allowed in many cases the regioselective formation of the α-functionalized vinylboronates (Scheme 7, bottom).[44]

The hydroboration of 1,3-diynes has been investigated under cobalt catalysis and alkynyl vinylboronates were isolated

Scheme 7. Hydroboration of internal propargylic alcohols and amines with pinacol borane.
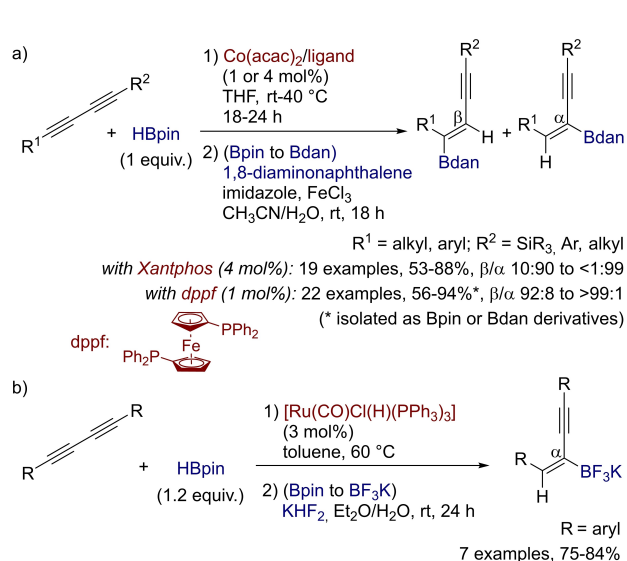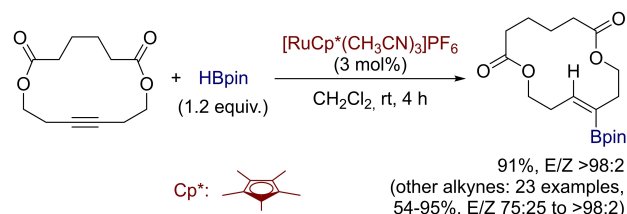

Scheme 8. Hydroboration of 1,3-diynes.

(Scheme 8).[45,46] Interestingly, a change of ligand from Xantphos to dppf led to a reversal of regioselectivity (Scheme 8a), as demonstrated by Ge et al.[45] A ruthenium catalyst system afforded similar regioselectivity to that observed for the cobalt/Xantphos system (Scheme 8b).[46] Symmetrical 1,4-diaryl-1,3-diynes were tolerated as substrates, whereas dialkyl diynes provided mixtures with bis-adducts and other mono-adducts under the same conditions. In many cases, the enynyl pinacolboronates were transformed into 1,8-diaminonaphthalene boronates (Bdan) or trifluoroborate salts due to instability issues on silica in air.
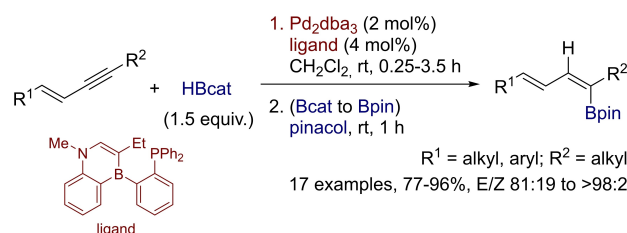
2.2. anti-Hydroboration with di(alkoxy)boranes [HB(OR)$_2$]

Some exceptions to the usual syn-addition mode of hydroboration with HB(OR)$_2$ have been reported in which a formal anti-hydroboration of internal alkynes takes place, i.e., the boryl fragment and the H atom are attached to different sides of the double bond of the vinylboronate. The first example documented in the context of tri- and tetrasubstituted vinylboronates was reported by Fürstner et al., in which a variety of internal alkynes, including medium-sized cycles and macrocycles, were treated with HBpin and a ruthenium complex as catalyst (Scheme 9).[47] The E-configured alkenyl boronates arising from anti-addition were selectively formed, and the mechanism was studied computationally.[48]

The anti-hydroboration of 1,3-enynes was achieved with catecholborane and a palladium/azaborine phosphine catalyst system, followed by treatment with excess of pinacol to isolate the Bpin derivatives (Scheme 10).[49] The E-configured dienylboronates were obtained selectively, in accordance with the mechanism proposed based on computational calculations.[50]

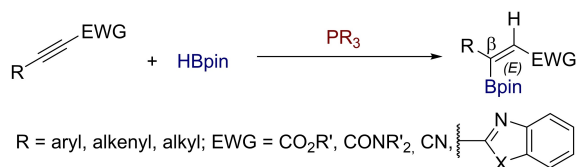In 2018, three independent reports on the phosphine-catalyzed anti-hydroboration of alkynoic acid derivatives were

Scheme 9. Ruthenium-catalyzed anti-hydroboration of internal alkynes.

Scheme 10. Palladium-catalyzed anti-hydroboration of 1,3-enynes.

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disclosed (Scheme 11).[51] The protocol by Sawamura, Ohmiya *et al.* involved the use of PMe_3 or PBu_3 to promote the *anti*-hydroboration of alkynoates, alkynamides and 2-alkynylazoles.[51a] Similar metal-free protocols based on PBu_3 were reported for the *anti*-hydroboration of alkynoates and alkynamides by Vilotijevic *et al.*[51b] and Santos *et al.*[51c] In most cases, the *E*-configured olefin was formed with high selectivity or exclusively. It is worth noting that similar selectivity was found under cobalt catalysis.[26a] Very recently, Santos *et al.* reported the phosphine-catalyzed *anti*-hydroboration of propio-nitriles with HBpin, and (*E*)-borylated acrylonitriles were selectively isolated.[51d]

A protocol for the *anti*-hydroboration of NH-propiolamides was later reported by Santos *et al.*, where a combination of n-BuLi and pinacolborane afforded primary and secondary (*E*)-β-borylacrylamides with complete selectivity (Scheme 12).[52] Inter-
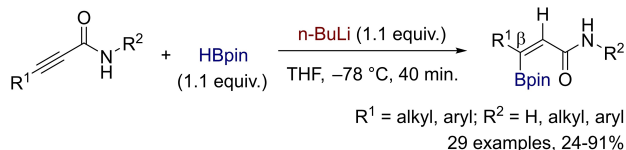
estingly, X-ray studies confirmed the internal coordination between carbonyl oxygen and boron of the *E*-configured products.

The *anti*-hydroboration of propargylic alcohol derivatives was achieved under ruthenium catalysis,[53] and the formation of vinylboronates with the boryl group attached to the distal position (β) relative to the functional group was favored (Scheme 13).

2.3. *syn*-Hydroboration with bis(boronates) $B_2(OR)_4$

The hydroboration of internal alkynes with bis(boronates) is dominated by copper catalysis and bis(pinacolboronate), and follows a *syn*-addition mode, with few exceptions. The generally accepted mechanism involves an initial boryl metallation of the alkyne by a M–[B] species, followed by protonation. The typical reaction conditions involve the use of a copper source/ligand or a preformed copper complex, a metal alkoxide, methanol as the proton source and bis(pinacolboronate).

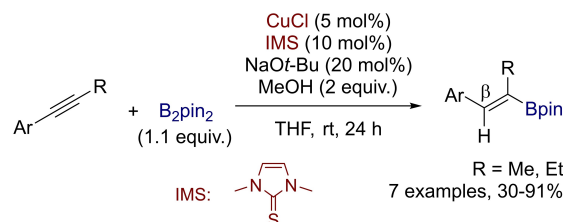One of the first reports of *syn*-hydroboration of internal alkynes with $B_2(OR)_4$ was disclosed by Yun, Son et al.[54] Alkyl aryl acetylenes were studied, and it was observed that prop-1-yn-1-ylarenes (R=Me) were successfully hydroborated by means of a catalyst system formed by CuCl/IMS, NaO*t*-Bu and MeOH (Scheme 14), and β-aryl vinylboronates were isolated. However, slightly larger but-1-yn-1-ylbenzene (R=Et) led to a decreased yield, and very bulky (3,3-dimethylbut-1-yn-1-yl)benzene (R=*t*-Bu) prevented the transformation. It is remark-able that the regioselectivity observed was opposite to that found for the hydroboration of aryl alkyl alkynes with HBpin and similar copper catalyst systems, where α-aryl vinylboro-nates were the major product (Scheme 2).[19,20]

Other copper-based catalyst systems with phosphines or N-heterocyclic carbenes as ligands provided similar regioselectiv-ity for the hydroboration of alkyl aryl acetylenes, and β-aryl vinylboronates were selectively formed (Scheme 15a).[55,20] Nota-bly, the catalyst system formed by $CuCl/P(o\text{-tolyl})_3$ was com-petent for the hydroboration of internal *t*-butyl acetylenes, but the isolated products resulted from an *anti*-addition mode (Scheme 15b).[55a] An iron-based hydroboration protocol was also applied to alkyl aryl acetylenes and in this case β-aryl vinylboronates were typically isolated as the major product (Scheme 15c).[21] This protocol was also useful for symmetrical diaryl and dialkyl acetylenes.

Scheme 11. Phosphine-catalyzed *anti*-hydroboration of alkynoic acid deriva-tives.

Scheme 12. Butyllithium-catalyzed *anti*-hydroboration of internal propiola-mides.

Scheme 13. Ruthenium-catalyzed *anti*-hydroboration of propargylic alcohol derivatives.

Scheme 14. Hydroboration of alkyl aryl acetylenes with bis(pinacolboronate).

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Scheme 15

a)

CuCl (5 mol%), P(o-tolyl)$_3$ (6 mol%), NaOt-Bu (20 mol%)
B$_2$pin$_2$ (1.1 equiv.), MeOH (2 equiv.), THF, rt, 4–24 h
13 examples, 82–93%, α/β 20:80 to β only[55a]

CuCl(IMes) (0.04–2 mol%), NaOH (5 mol%)
B$_2$pin$_2$ (1.1 equiv.), MeOH (2 equiv.), CPME, rt, 16 h
9 examples, 70–98%, α/β 20:80 to >98:2[55b]

Cu(OTf)$_2$ (2.5 mol%), rac-SIPHOS (3 mol%), Cs$_2$CO$_3$ (10 mol%)
B$_2$pin$_2$ (1.5 equiv.), H$_2$O, rt, 12 h
15 examples, 75–95%, β isomer[55c]

rac-SIPHOS:

b)

CuCl (5 mol%)
P(o-tolyl)$_3$ (6 mol%)
NaOt-Bu (20 mol%)
MeOH (2 equiv.)
B$_2$pin$_2$ (1.1 equiv.)
THF, rt–50 °C, 20–24 h
R = alkyl, aryl: 5 examples, 37–92%[55a]

c)

FeH(CO)(NO)(PPh$_3$)$_2$ (0.5 mol%)
NaOMe (5 mol%)
B$_2$pin$_2$ (1.5 equiv.)
THF/MeOH 80 °C, 9 h

R^1 = aryl, R^2 = alkyl: 9 examples, 45–90%, α/β 59:41 to 4:96[21]
R^1 = R^2 = alkyl, aryl: 10 examples, 44–94%, Z/E 97:3 to 99:1[21]

Scheme 15. Hydroboration of alkyl aryl acetylenes with bis(pinacolboronate).

The B$_2$pin$_2$-hydroboration of 1,3-enynes was studied by Ito et al. with a copper alkoxide/ligand/methanol catalyst system (Scheme 16a).[56] An increase of the steric hindrance around the alkene fragment shifted the site-selectivity of the hydroboration from the alkene to the alkyne, and the best results were obtained with trisubstituted alkenes. The hydroboration of 1,3-enynes with a hydroxy or p-toluenesulfonamide group was also successfully developed (Scheme 16b).[57] Interestingly, when the acetylene was capped with an aryl group the β-aryl vinylboronate was isolated selectively.
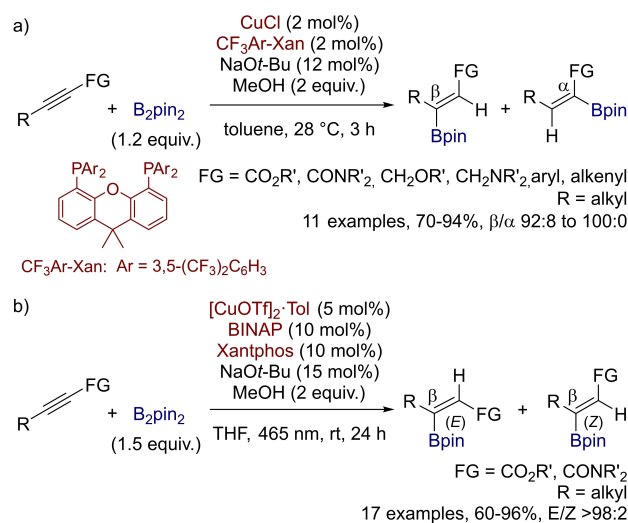
Scheme 16

a)

Cu(Ot-Bu) (5 mol%)
PPh$_3$ or Xantphos (5 mol%)
MeOH (2 equiv.)
B$_2$pin$_2$ (1.1–2 equiv.)
THF, rt, 1.5–17 h

R^1, R^2, R^3 = H or Me (trisubst.); R^4 = alkyl
7 examples, 58%–quant.

b)

CuCl (10 mol%)
PCy$_3$ (10 mol%)
NaOt-Bu (15 mol%)
B$_2$pin$_2$ (1–2 equiv.)
toluene, rt, 14 h

X = O; R = alkyl, aryl; n = 1–3
12 examples, 70–96%
X = NTs, NBn; R = alkyl, aryl; n = 1
10 examples, 53–93%
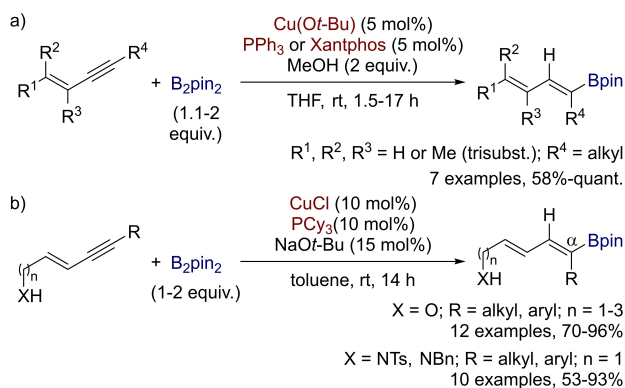
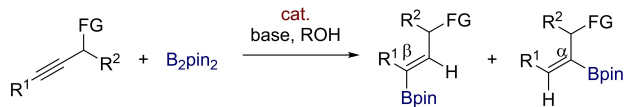**Scheme 16.** Hydroboration of 1,3-enynes with bis(pinacolboronate).

The influence of functional groups in the vicinity of the triple bond of internal alkynes was also studied for the hydroboration with bis(boronates) under copper catalysis. Tsuji et al. reported a catalyst system formed by CuCl/phosphine/NaOt-Bu for the B$_2$pin$_2$-hydroboration of propargylic esters, amides, protected alcohols and amines (Scheme 17a), which invariably afforded the products with the boryl group at the β position with respect to the functional group.[19] Very recently, Mauleón, Gómez Arrayás et al. reported a dual catalyst system based on copper and two phosphines for the anti-hydroboration of densely-functionalized propiolates and propiolamides via β-selective hydroboration and photoinduced Z to E isomerization of the obtained trisubstituted alkenylboronates (Scheme 17b).[58]

Carretero, Gómez Arrayás et al. reported a typical catalyst system formed by CuCl/PCy$_3$/NaOt-Bu and methanol as the proton source which tolerated thioethers, alcohols, ethers and amines, and the boryl group was also attached to the β position of the propargylic function (Scheme 18a),[59] similarly to Tsuji's system (Scheme 17a).[19] A Cu/NHC catalyst system was disclosed by McQuade et al. which was very successful for the hydroboration of free propargylic alcohols, and allowed the selective obtention of β-borylated allylic alcohols after treatment with triethanolamine to hydrolyze the borate intermediate (Scheme 18b).[60] Notably, a reversal in the selectivity was found with that catalyst system when 4-nitrophenyl ether derivatives of propargylic alcohols were used as substrates, and the α isomers were isolated selectively. A protocol based on lithium hydroxide in an ionic liquid medium promoted the hydroboration of propargylic alcohols to yield selectively the α isomers of vinylboronates (Scheme 18c).[61]
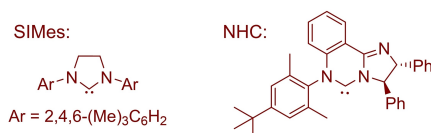
The B$_2$pin$_2$-hydroboration of internal alkynyl silanes was carried out under a copper-based catalyst system, and the β-silyl vinylboronates were selectively isolated. It was found that aryl silyl acetylenes required bisphosphine Xantphos as ligand, whereas N-heterocyclic carbene SIMes was the optimal ligand

Scheme 17

a)

CuCl (2 mol%)
CF$_3$Ar-Xan (2 mol%)
NaOt-Bu (12 mol%)
MeOH (2 equiv.)
B$_2$pin$_2$ (1.2 equiv.)
toluene, 28 °C, 3 h

FG = CO$_2$R', CONR'$_2$, CH$_2$OR', CH$_2$NR'$_2$, aryl, alkenyl
R = alkyl
11 examples, 70–94%, β/α 92:8 to 100:0

CF$_3$Ar-Xan: Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$

b)

[CuOTf]$_2$·Tol (5 mol%)
BINAP (10 mol%)
Xantphos (10 mol%)
NaOt-Bu (15 mol%)
MeOH (2 equiv.)
B$_2$pin$_2$ (1.5 equiv.)
THF, 465 nm, rt, 24 h

FG = CO$_2$R', CONR'$_2$
R = alkyl
17 examples, 60–96%, E/Z >98:2

Scheme 17. Copper-catalyzed hydroboration of unsymmetrical internal alkynes with bis(pinacolboronate).

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Scheme 18. Hydroboration of unsymmetrical alkynes with bis(pinacolboronate).

a) FG = SR, SO$_2$R, OH, OR, NR$_2$, CH$_2$OR; R^1 = alkyl, R^2 = H; Me, Ph
CuCl (10 mol%), PCy$_3$ (12 mol%), NaOt-Bu (15 mol%)
B$_2$pin$_2$ (1.1 equiv.), MeOH (2 equiv.), toluene, rt, 1-5 h
21 examples, 53-89%, β/α = 84:16 to >98:2

b) FG = OH; R^1 = alkyl, Ph; R^2 = H, alkyl, Ph
(SIMes)CuCl (1 mol%), NaOt-Bu (0.3 equiv.), MeOH (2 equiv.)
B$_2$pin$_2$ (1.2 equiv.), Et$_2$O, 0 °C, 0.5 h
7 examples, 90->95%, β/α = 87:13 to >98:2

FG = O(4-NO$_2$C$_6$H$_4$); R^1 = alkyl, Ph; R^2 = H, alkyl, Ph
(NHC)CuCl (1 mol%), NaOt-Bu (0.3 equiv.), MeOH (2 equiv.)
B$_2$pin$_2$ (1.2 equiv.), Et$_2$O, 0 °C, 0.5 h
8 examples, 27-89%, β/α = 16:84 to <2:98

c) FG = OH; R^1 = alkyl, Ar, alkenyl; R^2 = alkyl, alkenyl
LiOH·H$_2$O (1 equiv.), B$_2$pin$_2$ (1.1 equiv.), [bmim]OAc, 50 °C, 4 h
11 examples, 56-90%, α isomer

SIMes:
Ar$-$N$\frown$N$-$Ar
Ar = 2,4,6-(Me)$_3$C$_6$H$_2$

NHC:

Scheme 20. Copper-catalyzed hydroboration of internal thio- and selenoalkynes with bis(pinacolboronate).

Y = SEt, SPh; R = alkyl, alkenyl, aryl
CuCl (10 mol%), DPEphos (10 mol%), NaOt-Bu (15 mol%),
B$_2$pin$_2$ (1.1 equiv.), MeOH, 35 °C, 12 h
19 examples, 45-91%, β/α = 92:8 to >98:2[40]

DPEphos:
PPh$_2$ PPh$_2$

Y = SR', SeR', R = alkyl, aryl
IPrCuCl (10 mol%), NaOt-Bu (15 mol%), Na$_2$SO$_4$ (6 equiv.)
B$_2$pin$_2$ (1.2 equiv.), MeOH (2 equiv.), toluene, rt, 0.5 h
22 examples, 20-85%, β isomer[63a]

IPr:
Ar$-$N$\frown$N$-$Ar
Ar = 2,6-(iPr)$_2$C$_6$H$_3$

Y = SeR'; R = alkyl, alkenyl, aryl
CuCl (20 mol%), NaOH (2 equiv.),
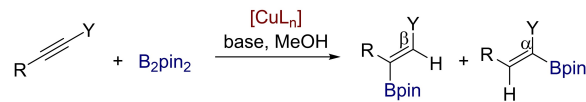B$_2$pin$_2$ (1.5 equiv.), MeOH, rt, 20 h
23 examples, 35-98%, β isomer[63b]

for alkyl silyl acetylenes (Scheme 19).[62] Remarkably, a subtle change in the conditions for the B$_2$pin$_2$-hydroboration of TMS-phenylacetylene [(IMes)CuCl, NaOH] led to the opposite selectivity, and the α-silyl vinylboronate was selectively formed.[20] It is also worth mentioning that HBpin-based copper-catalyzed hydroborations of alkynylsilanes produced β-silyl vinylboronates,[19,20] whereas the α-silyl vinylboronates were produced by HBpin-based cobalt- or aluminium-catalyzed hydroboration (Scheme 3).[26a,38]

Internal thioalkynes were also successfully hydroborated under copper catalysis in the presence of a base and methanol, and the β-thio vinylboronates were selectively obtained (Scheme 20).[40,63a] This is a complementary approach to that reported with HBpin and a similar copper catalyst system, where α-thio vinylboronates were isolated (Scheme 5).[40] Analogous selenoalkynes afforded exclusively the β isomer of the vinylboronates (Scheme 20).[63a] Even a ligand free protocol based solely on CuCl, NaOH and methanol was efficient for the

hydroboration of internal selenoalkynes to afford β-seleno vinylboronates.[63b]

A very interesting example of complementary catalyst systems has been reported for the hydroboration of alkynamides with bis(boronates) under copper catalysis (Scheme 21).[64] When a bisphosphine like Xantphos was used as ligand in the hydroboration of N-alkynyloxazolidinones, the α isomer of the corresponding vinylboronates was obtained exclusively.[64a] Similarly, monophosphine LB-Phos was optimal for the hydroboration of N-alkynylsulfonamides and the α isomer was also obtained exclusively. However, when P(2-furyl)$_3$ was employed under the appropriate conditions for both oxazolidinone and sulfonamide derivatives, a complete reversal of regioselectivity was observed, and the β isomer of the vinylboronates were isolated selectively.[64b]

CuCl (5 mol%)
ligand (6 mol%)
NaOt-Bu (20 mol%)
MeOH (2 equiv.)
THF, rt or 50 °C
3-24 h

with *SIMes*: R = alkyl, 6 examples, 71-86%, β isomer
with *Xantphos*: R = alkenyl, aryl, 8 examples, 65-93%, β/α = 1.2:1 to >99:1

Scheme 19. Hydroboration of alkynylsilanes with bis(pinacolboronate).
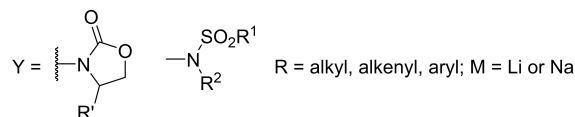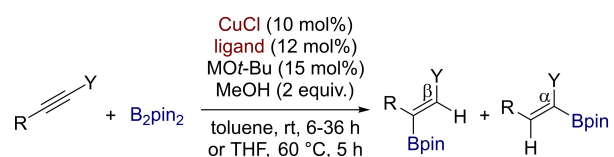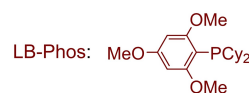
CuCl (10 mol%)
ligand (12 mol%)
MOt-Bu (15 mol%)
MeOH (2 equiv.)
toluene, rt, 6-36 h
or THF, 60 °C, 5 h

Y =

R = alkyl, alkenyl, aryl; M = Li or Na

with *Xantphos* or *LB-Phos*: 14 examples, 66-100%, α isomer[64a]
with *P(2-furyl)$_3$*: 20 examples, 41-97%, β isomer[64b]

LB-Phos: MeO$-$$\bigcirc$$-PCy_2$ (OMe, OMe)

Scheme 21. Copper-catalyzed hydroboration of ynamides with bis(pinacolboronate).

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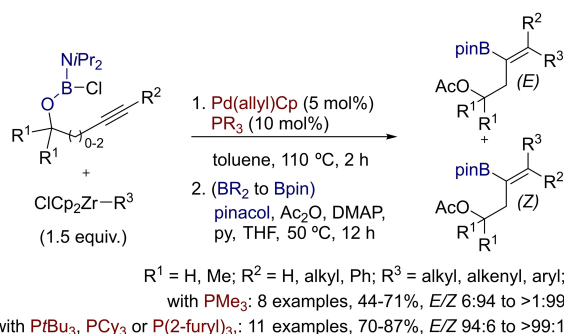
3. Carboboration of Alkynes

Carboboration reaction has become one of the main methodologies developed in the last years to obtain polysubstituted alkenyl boronates. New carbon-boron and carbon-carbon bonds are formed using alkynes as starting materials. This section has been organized by the catalyst employed, as most of the methodologies follow a *syn* addition of the reagents.
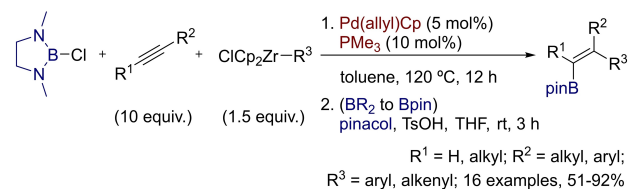
3.1. Metal-catalyzed carboboration

Pioneering work was developed by Suginome group in 2003,[65] by reacting cyano(amino)boryl homopropargyl ethers in the presence of nickel or palladium catalyst, getting the *syn*-cyanoboration of the alkyne (Scheme 22). Further studies led to optimize the intermolecular version of this reaction.[66] This boron moiety can be converted into standard pinacol boronate or employed in Suzuki-Miyaura coupling, among other transformations.
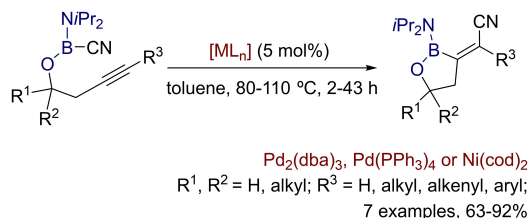
Scheme 22. Intramolecular cyanoboration of alkynes.

Scheme 23. Palladium-catalyzed carboboration of chloro(amino)boranes derivatives with organozirconium reagents.

Scheme 24. Palladium-catalyzed carboboration of alkynes with chloro(amino)borane derivatives and organozirconium reagents.

Subsequently, the same group developed two-component reactions between chloro(amino)boranes tethered to alkynes and alkynylstannanes,[67a] organozirconium reagents[67b] or olefins.[67c] The phosphine employed in the case of zirconium species controls the stereoselectivity.[67c] PMe₃ favored *syn*-carboboration, meanwhile bulkier phosphines induced *anti*-selectivity (Scheme 23).
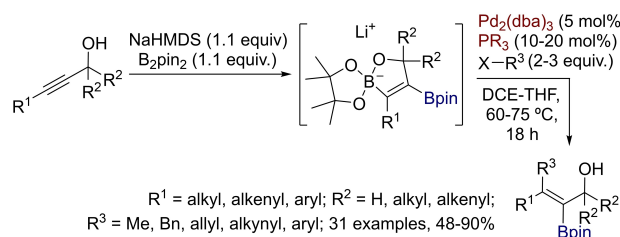
In 2008, Suginome *et al.* developed the intermolecular reaction of terminal and internal alkynes with diaminochloroboranes and organozirconium reagents (Scheme 24).[68] Palladium complexes were employed as catalyst, and the insertion of the alkyne into the B–Pd bond and further transmetallation with zirconium compounds led to a *syn*-carboboration. Treatment with pinacol gave the pinacol boronate products in high yields and stereoselectivity directed by the sterically hindrance.

Other authors have developed in the last years carboboration reactions catalyzed by palladium complexes. Fürstner optimized in 2019 the *anti*-carboboration of propargyl alcohols,[69a] by diboration of the alkyne and subsequent chemoselective Suzuki-Miyaura cross-coupling (Scheme 25). The base used in the first step was crucial for the outcome of the reaction (see Scheme 43, ref. 106). By adding an acid chloride and using a Pd/Cu co-catalyst system, a furyl boronate ester can be obtained.[69b]
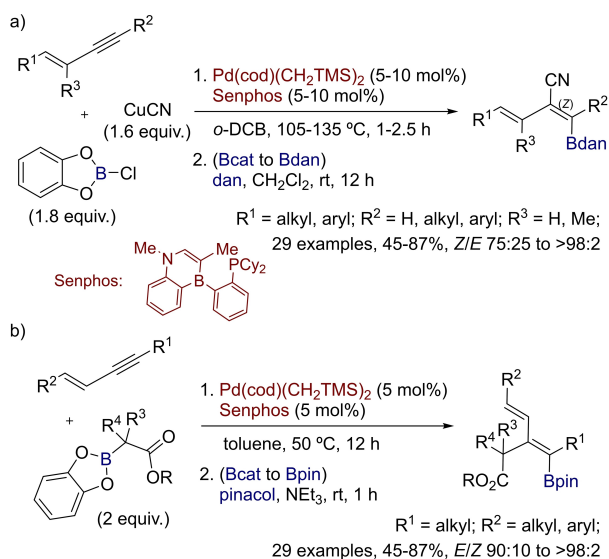
Recently, the *anti*-cyanoboration of enynes was developed by Liu group[70] using a 1,4-azaborine phosphine-based ligand (Senphos) to enhance the *anti*-stereoselectivity (Scheme 26a). The same group have recently developed the selective carboboration of 1,3-enynes with a C-boron enolate.[71] A cooperative activation of the enyne by Pd-catalyst and boron reagent led to regio- and diastereoselective tetrasubstituted alkenyl boronates in a *syn*-carboboration (Scheme 26b).

In the last few years, several authors have explored palladium-catalyzed fluoroalkylboration three component reactions, getting *anti*-selectivity (Scheme 27).[72] A radical mechanism has been proposed, obtaining a *trans*-vinyl iodide as intermediate that is borylated *in situ*. Chadalaj group performed a cross-coupling reaction of the pinacol boronate in a one-pot fashion by controlling the reaction temperature.[72c]

Despite the development of the carboboration reaction with palladium and scarce examples with nickel[73a] and iron,[73b] the most employed metal complexes are based on copper.[74,8b] The β-borylalkenylcopper species, formed by *syn*-addition of borylcopper to the alkyne, is the key catalytic intermediate. The first examples were developed by Yamashita/Nozaki with

Scheme 25. Palladium-catalyzed *anti*-carboboration of propargyl alcohols.
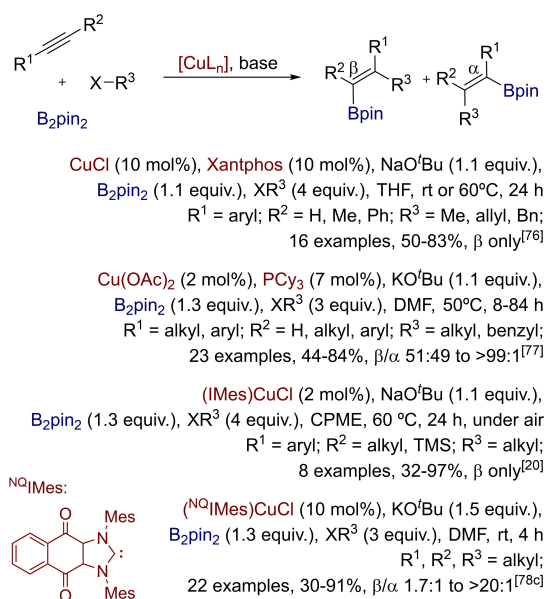
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a)

Scheme 26. Palladium-catalyzed *anti*-cyanoboration and *syn*-carboboration of enynes.
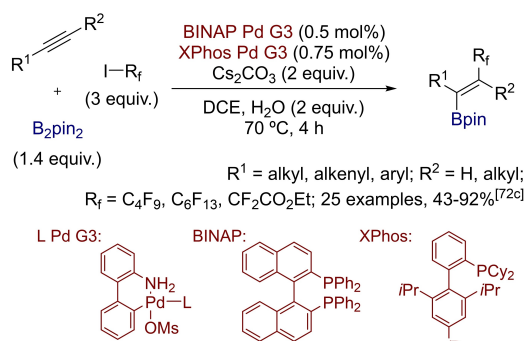
Scheme 27. Palladium-catalyzed *anti*-fluoroalkylboration of alkynes.

Scheme 28. Copper-catalyzed *syn*-carboboration of alkynes.

ligand, Kanai *et al.* prepared trialkylsubstituted alkenyl boronates from good to excellent regio- and stereoselectivity.[78c]

Allyl and alkynyl derivatives have also been employed in this type of reactions as electrophiles. Zhong studied the carboboration of alkynes with allyl phosphates to get 1,4-dienes.[79a] The selectivity was defined by the substitution pattern of the reagents. Fañanas-Mastral group prepared dendralenes by *syn*-addition of 1,4-dibromo-2-butenes to alkynes after dehydrobromination (Scheme 29a).[79b] Later, Yun[80a] and Gong/Fu[80b] have used bromoalkynes to obtain,
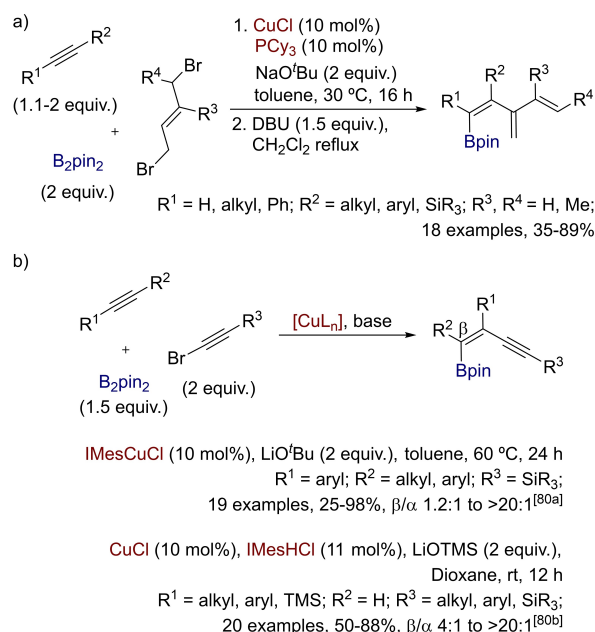
stoichiometric borylcyanocuprates.[75] In the following years, various catalytic conditions were optimized based on phosphine and carbene ligands. Firstly, Tortosa *et al.* used Xantphos as ancillary ligand in combination with CuCl for the *syn*-carboboration of aryl-substituted alkynes (Scheme 28).[76] MeI was selected as electrophile (also allylBr and BnBr) as methyl branched alkenes are common motifs in biologically active compounds. Next, Yoshida demonstrated that Cu(OAc)₂–PCy₃ complex is also active for the reaction of terminal and internal alkynes using alkyl and benzyl bromides as electrophiles.[77] Unsymmetrical diaryl and terminal alkyl alkynes gave regioisomer ratios close to 1:1. In 2014, Cazin explored (IMes)CuCl as catalyst in the preparation of tetra-substituted alkenyl boronates (Scheme 28).[20] No inert atmosphere was necessary and a low catalyst loading gave excellent reactivity for *syn*-carboboration. In contrast to the previous reports, α-boryl derivative was the major product. Guanidine-linked NHC-[78a] and cyclodextrin-encapsulated NHC-copper complexes[78b] have also been employed on the methylboration of alkynes. By increasing the π-acceptor properties of the NHC

a)

b)

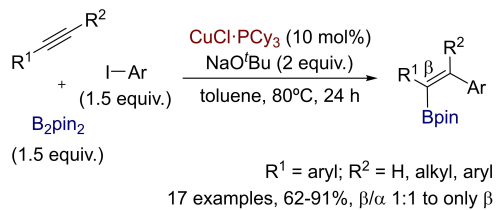**Scheme 29.** Copper-catalyzed carboboration of alkynes.

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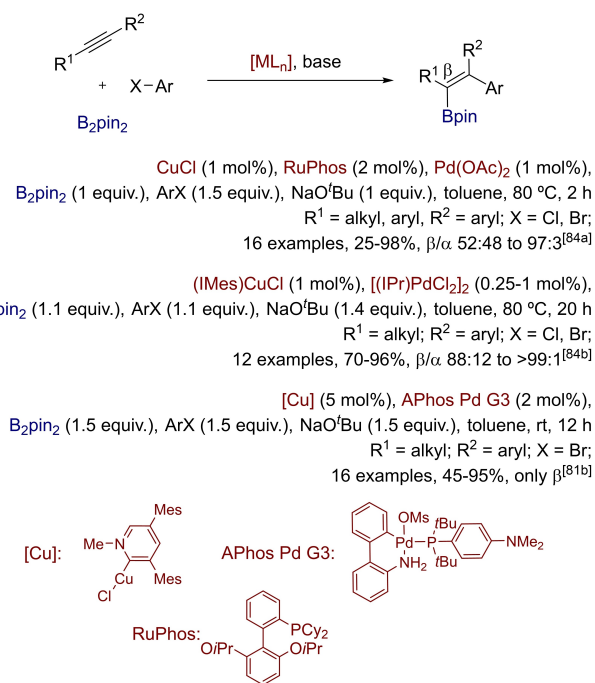European Chemical Societies Publishing

after *syn*-carboboration, enynylboronates as products (Scheme 29b), using respectively internal or terminal alkynes.

Scheme 30. Copper-catalyzed arylboration of alkynes.
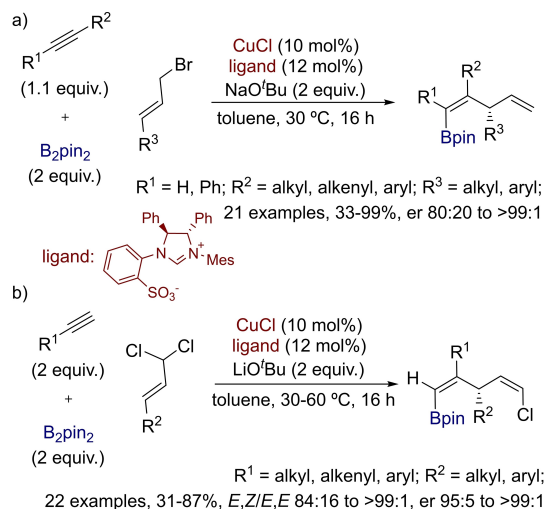
Scheme 31. Asymmetric allylboration of alkynes.

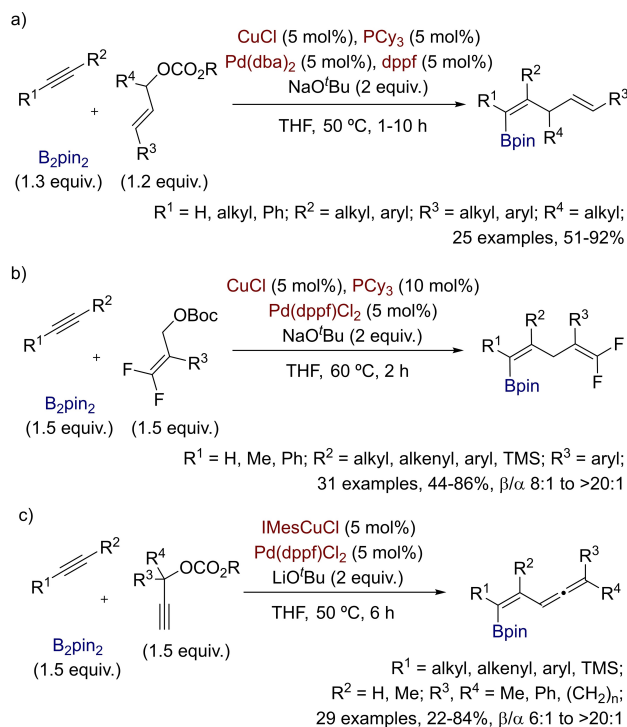**Scheme 32.** Metal-catalyzed arylboration of alkynes.

In the previous examples, aryl halides have not been employed as reagents. After the development of copper-catalyzed Suzuki-Miyaura-type cross-coupling, Brown group presented in 2014 the *syn*-carboboration of alkynes by using aryl iodides and CuCl·PCy3 as catalyst (Scheme 30).[81a]

Recently Fañanás-Mastral *et al.* optimized the enantioselective allylboration of alkynes using a different chiral NHC ligand and substituted allyl bromides as electrophiles (Scheme 31a).[82] The products, 1,4-dienes, are interesting building blocks to prepare asymmetric cyclopropanes, heterocycles or polysubstituted dienes. The same group has developed the reaction with allylic *gem*-dichlorides getting chiral trisubstituted *E*-alkenyl boronates with a *Z*-alkenyl chloride fragment (Scheme 31b).[83]

In the last years, a synergic bimetallic catalysis of copper and palladium complexes has emerged as an alternative system for the carboboration reactions, in all cases with *syn*-selectivity. Once the β-borylalkenylcopper intermediate has been formed, transmetallation occurs and organopalladium reactivity is exploited. This alternative has been applied to arylboration of internal alkynes by Semba/Nakao[84a] and Cazin[84b] with aryl chlorides or bromides, and Brown, expanding this method to heteroaryl bromides[81b] (Scheme 32).

Allylboration of alkynes has been another reaction that has lately utilized this bimetallic strategy. Fañanás-Mastral[85a,b] and Gong/Fu[85c] have prepared functionalized 1,4-dienes, in the latter case difluorinated (Scheme 33a,b). Borylallenylation of alkynes has also facilitated the preparation of functionalized boryl-substituted ene-allenes (Scheme 33c).[86]
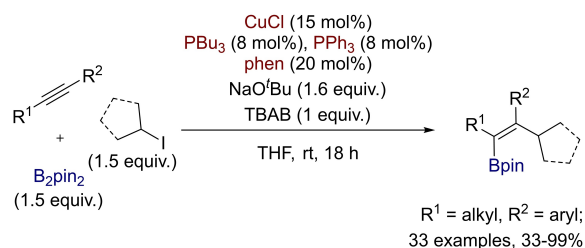
In contrast to synergistic Cu/Pd catalysis, Mauleón/Gomez Arrayás recently developed the carboboration of alkynes with
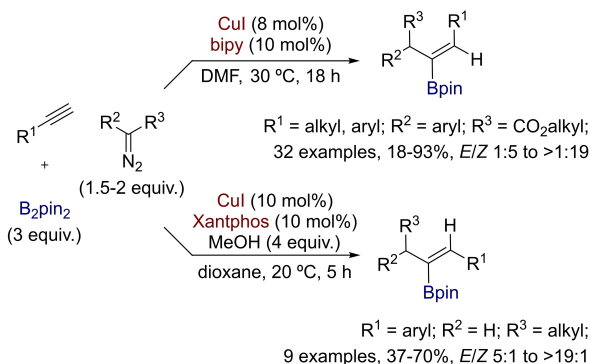

Scheme 33. Metal-catalyzed allylboration and allenylboration of alkynes.

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poorly reactive secondary alkyl halides with multiligand copper catalysis (Scheme 34).[87] After the addition of Cu–B bond to the alkyne, enabled by the phosphine ligand, phenanthroline facilitated a radical mechanism to form the new carbon-carbon bond with the alkyl halide. The authors accomplished a deep mechanistic study to fully understand this unprecedented catalytic system.
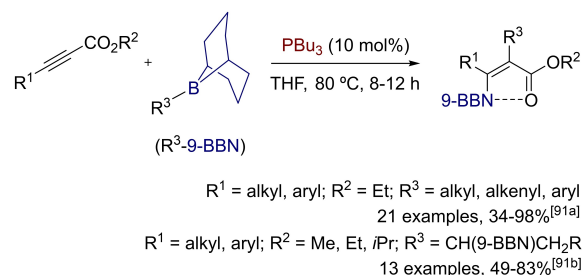
All the previous methods described on this section involve 1,2-carboboration reactions. Nevertheless, 1,1-carboboration has also been developed, initially with trialkylboranes by Wrackmeyer[88] or very electrophilic boranes $RB(C_6F_5)_2$ by Erker et al.[89] Recently, a three-component reaction of terminal alkynes, diazo compounds, and B_2pin_2 reported by Sun group introduced the two new substituents on the terminal carbon (Scheme 35).[90] Copper complexes play a dual role, coupling the alkyne and the diazo compound and performing the borylation of the allene intermediate. When diazo acetates were used, Z-alkenes were the major products, but the E-isomer was predominant with alkyl diazo compounds (formed in situ from the corresponding hydrazone).
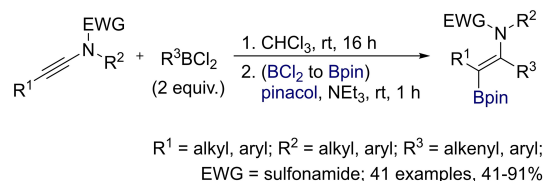
3.2. Organocatalyzed carboboration

Besides the organometallic methodologies for carboboration reactions, some examples of organocatalyzed procedures have been reported. Although with a borane group (9-BBN: 9-borabicyclo[3.3.1]nonane) and not a boronate, firstly Ohmiya/Sawamura discovered the anti-carboboration of alkynoates with alkyl-, alkenyl- and aryl-9-BBN reagents (Scheme 36).[91] The coordination of the boron atom to an allenoate intermediate delivered a complete stereoselectivity. The same group developed the reaction with 1,1-diborylalkane compounds, introducing a second 9-BBN moiety at allylic position.[91b]

In this metal-free context, the syn-carboboration of ynamides has been recently reported by Yamaguchi/Studer.[92] Highly electrophilic aryl- or alkenyldichloroboranes reacted smoothly in a regio- and stereoselective manner to obtain tetrasubstituted alkenyl boronates (Scheme 37).

3.3. Borylative cyclization (formation of C–B and C–C bonds)

In several studies the carboboration reaction originates an intramolecular cyclization to form a carbo- or heterocycle.[93] Early studies by Tanaka et al. focused on the palladium-catalyzed cyclization of diynes with borylstannane derivatives (Scheme 38).[94] Cyclic structures that contain external alkenyl boronates and alkenyl stannanes were obtained in good yields.

Different substrates have been employed in palladium-catalyzed borylative cyclizations. In 2010, Morberg group explored the cyclization of 1,6-enynes making use of silaboranes as boron source to get five-membered ring derivatives in high yields (Scheme 39a).[95] More recently, the same group have used a similar strategy to obtain chromane derivatives from 1,7-enynes.[96] Bäckvall achieved the borylative cyclization of

Scheme 34. Copper-catalyzed syn-carboboration of alkynes.

Scheme 35. Copper-catalyzed 1,1-carboboration of terminal alkynes.

Scheme 36. Phosphine-catalyzed carboboration.

Scheme 37. Metal-free carboboration of ynamides.
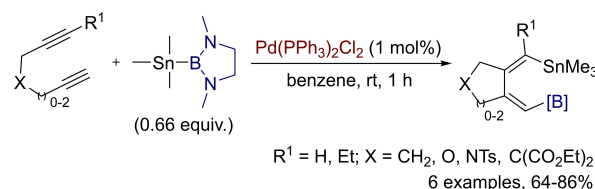
Scheme 38. Palladium-catalyzed borylative cyclization of diynes.

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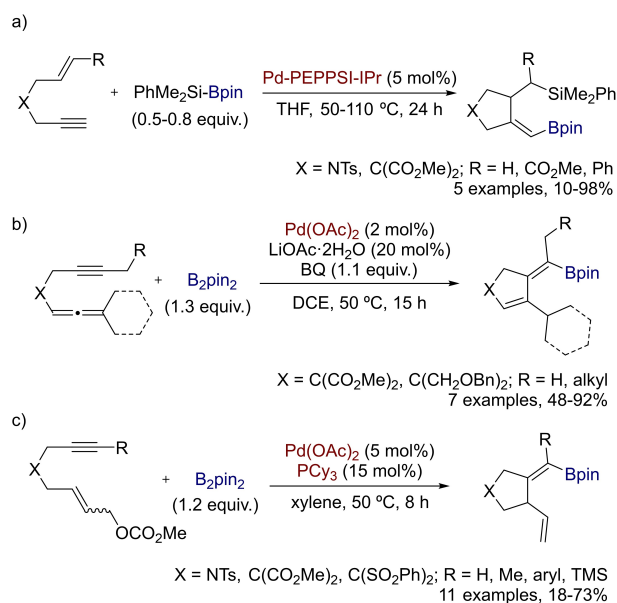
Scheme 39. Palladium-catalyzed borylative cyclization of 1,6-enynes and allenynes.

Scheme 40. Metal-catalyzed borylative cyclization.

Scheme 41. Asymmetric synthesis of hydrobenzofurane.

allenynes[97] and Cárdenas used 1,6-enynes containing an allylic carbonate group.[98] Besides the external alkenyl boronate, additional unsaturated bonds are present in the final products in both cases (Scheme 39b,c).

Other metal complexes have been used in the formation of five-membered ring (hetero)cycles that include a tri- or tetrasubstituted exocyclic alkenyl boronate. The borylative cyclization of 1,6-enynes has been explored with several catalysts. Widenhoefer performed this reaction with a chiral rhodium catalyst.[99] However, catechol boronate group was directly oxidized or arylated. Later, Lu optimized the Co-catalyzed cyclization of 1,6-enynes with HBpin to get pyrrolidines or tetrahydrofuran derivatives[100a] (Scheme 40a) and Zhu group applied this reactivity to 1,6-diynes.[100b] 1,6-Enynes could also be cyclized by a nickel catalyst to get a diboronate system, as reported by Buñuel/Cárdenas using B₂pin₂[101a] or the corresponding hydroborylative cyclization with HBpin[101b] (Scheme 40b,c).

Copper complexes have also been applied for cyclization-borylation of 1,6-enynes. A first example, in an asymmetric version, was developed by Tian/Lin with cyclohexadienone substrates with a pending propargylic ether (Scheme 41).[102] The hydrobenzofuran derivatives obtained could be converted to bridged and tricyclic ring structures.

Next, Carretero et al. developed the synthesis of substituted pyrrolidines by carboboration of β,β-disubstituted acrylates attached to an internal alkyne in a copper-catalyzed reaction (Scheme 42a).[103] They also studied the role of the alkoxide additive, commonly used in Cu-catalyzed carboboration of alkynes. Other type of substrates that have been cyclized are alkynes with an alkyl halide chain. Ito et al. synthesized cyclic compounds including a silicon atom[104] (Scheme 42b) and, Wang/Zhao optimized the borylative cyclization starting from
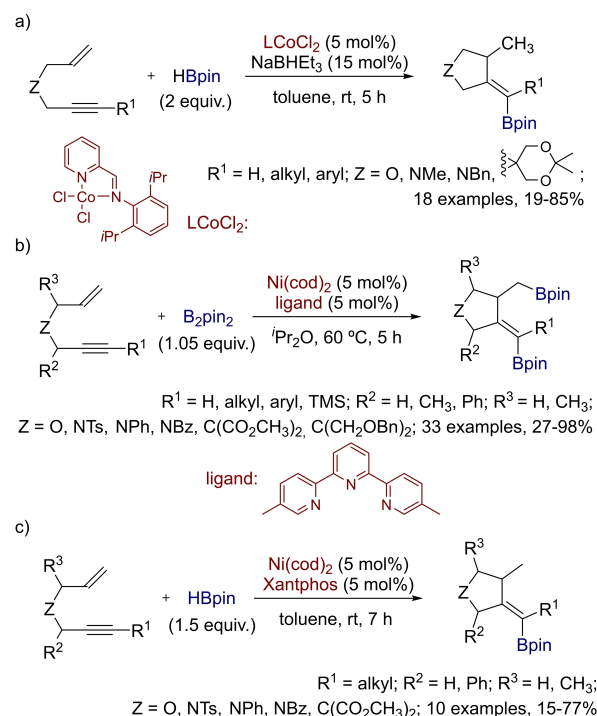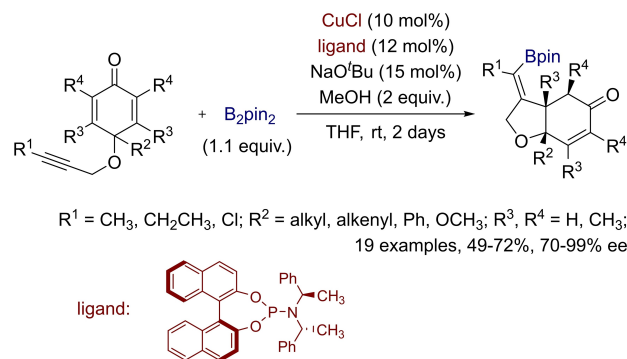
acetylenic iodides (Scheme 42c), in a phosphine-free process under a proposed radical mechanism.[105]

A boron atom can also be included in the heterocycle formed. Hou group synthesized oxaborolone heterocycles by a three component reaction of an alkyne, B₂pin₂ and CO₂ in a borylcupration/carboxylation cascade (Scheme 43a).[106a] Next, Csákÿ achieved the transition metal-free carboboration of propargylic alcohols with alkenyl boronic acids to form oxaboroles.[106b] Later, Hirano and Uchiyama group increased the scope to alkynyl boronates by adding a strong base (Scheme 43b).[106c] In both cases the coordination of the alcohol to the boron atom established the reactivity and the boron group behaved similarly to a boronic acid.

The intramolecular carboboration has been achieved with simple BCl₃ by Ingleson et al.[107a] employing a variety of

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a)

R^1 = alkyl; R^2, R^3 = alkyl, aryl;
EWG = CO_2R, CN, Weinreb amide; 15 examples, 60-98%

b)

R^1 = alkyl, aryl; 10 examples, 42-98%

c)

R^1 = aryl; 18 examples, 41-70%
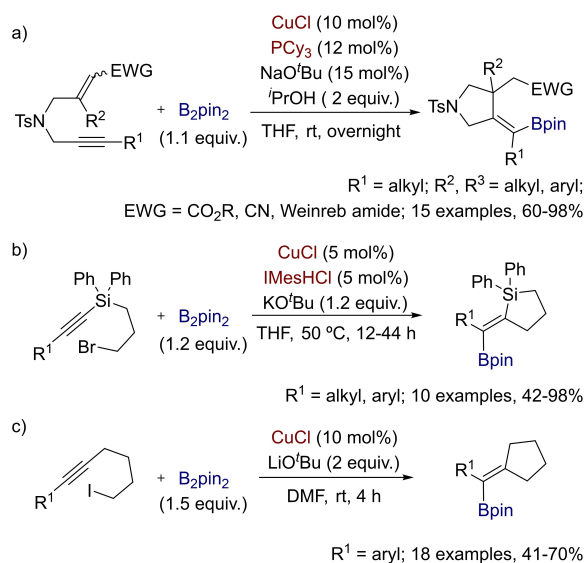
Scheme 42. Copper-catalyzed borylative cyclization.

a)

R^1 = H, alkyl, aryl; R^2 = alkyl, aryl;
10 examples, 64-94%[106a]

b)

R^4-$B(OH)_2$ (2 equiv.), tartaric acid (1 equiv.), CH_2Cl_2, 60 °C, 2 h
R^1 = HetAr; R^2, R^3 = H, Me; R^4 = alkenyl;
13 examples, 50-77%[106b]

1. ^nBuLi (1 equiv), THF, -78 °C to rt, 30 min
2. R^4—≡—Bpin (1.5 equiv.), 90 °C, 16 h
R^1 = aryl, C_4F_9, $CO_2{}^tBu$; R^2, R^3 = alkyl, alkenyl, aryl;
R^4 = alkyl, aryl, TBS; 37 examples, 15-86%[106c]
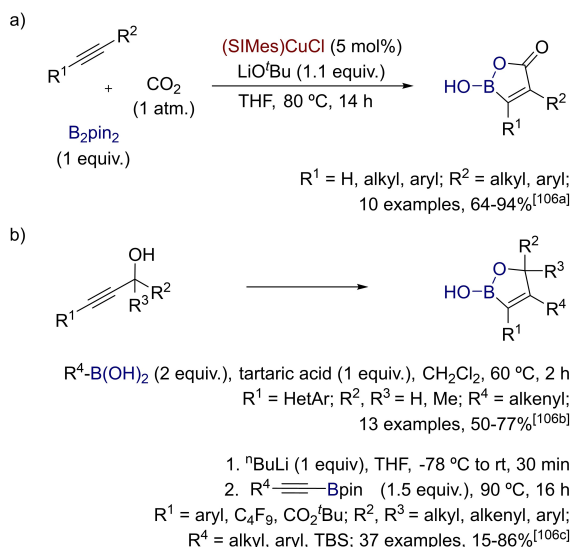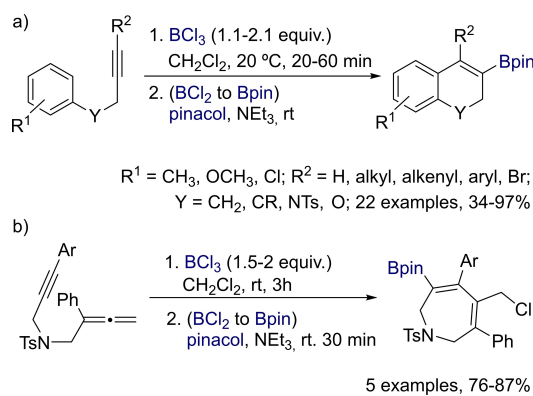
Scheme 43. Oxaborolone and oxaboroles synthesis by carboboration.

substituted alkynes, with an aromatic ring or another alkyne as internal nucleophile (Scheme 44a). This methodology allowed the formation of polycyclic structures with a boronate group for further functionalization. Recently, under similar conditions, Kong/Yang have developed the borylative cyclization of 1,6-allenynes to get 3,5-dihydroazepine derivatives (Scheme 44b).[108] The substituent in the allene controlled the cyclization to the five- or seven-membered ring.

4. Elementoboration of Alkynes

In a similar manner to carboboration, a heteroatom can be included together with the boronate group in the alkyne. In

a)

R^1 = CH_3, OCH_3, Cl; R^2 = H, alkyl, alkenyl, aryl, Br;
Y = CH_2, CR, NTs, O; 22 examples, 34-97%

b)

5 examples, 76-87%

Scheme 44. Metal-free borylative cyclization.

contrast to the hydroboration of alkynyl derivatives, this process allows the preparation of tetrasubstituted alkenyl boronates.
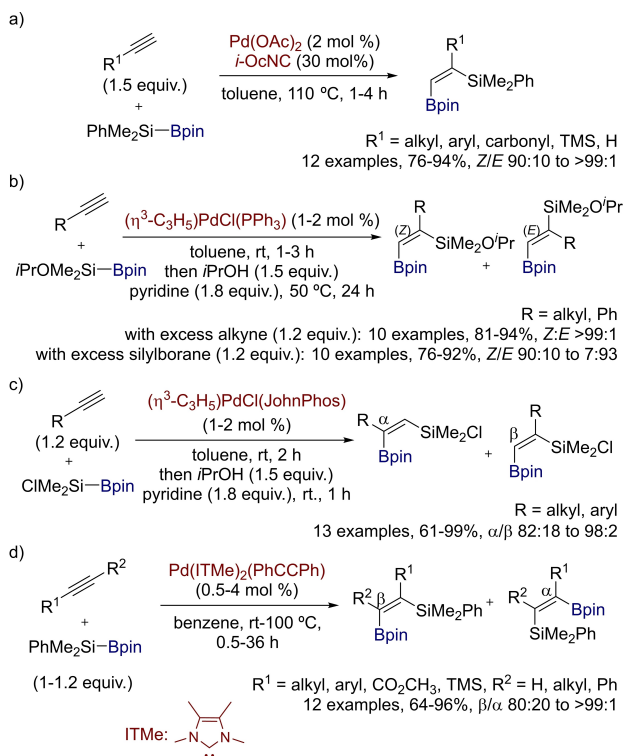
4.1. Silaboration

Silylboranes reagents have become attractive precursors to introduce simultaneously a silicon and a boryl groups, which can be used for further transformations. The latest developments on the chemistry of silylboranes and silylboronates have been recently summarized.[109]

Suginome/Ito were pioneers on this reaction, employing platinum and palladium complexes.[110] A palladium(0)-isonitrile catalyst led to the *syn*-addition of the silylboronate reagent (Scheme 45a), with an oxidative addition of the B—Si bond to palladium as initial step, and the β-boryl adduct was selectively obtained. Ohmura and Suginome developed under palladium-catalyzed conditions the *syn*- and *anti*-silaboration of terminal alkynes, and controlled the selectivity just by changing the stoichiometry of both reagents (Scheme 45b).[111] Next, the same group was able to switch the regioselectivity to the α-boryl products (*syn*-addition) by using electron-rich and sterically demanding phosphines (Scheme 45c).[112] In 2016, Spencer/Navarro performed the *syn*-silaboration of terminal and internal alkynes with NHC—Pd complexes (Scheme 45d).[113]

In 2014, Stratakis and co-workers reported that gold nanoparticles supported on titania (Au/TiO_2) catalyzed the *syn*-addition of silylboranes to terminal alkynes, leading to the α-boryl regioisomer (Scheme 46a).[114] The regioselectivity has been attributed to steric factors of the gold nanoparticles. Supported platinum nanoparticles also catalyzed this reaction at high temperatures (160 °C).[115] Stratakis group also disclosed the three-component *syn*-silaboration using bis(pinacolboronate) and disilanes (Scheme 46b).[116]

Activation of silylboranes by palladium or gold catalysts involved oxidative addition of the Si—B bond to the metal. Uchiyama and co-workers disclosed the Zn-catalyzed *syn*-silaboration of terminal alkynes by generation of silylzinc species and further borylation of the intermediate alkenyl zinc
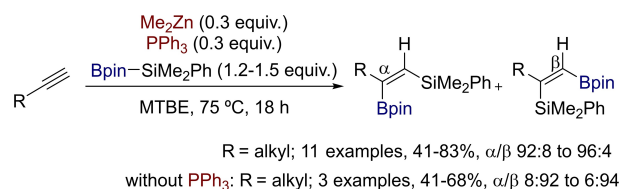
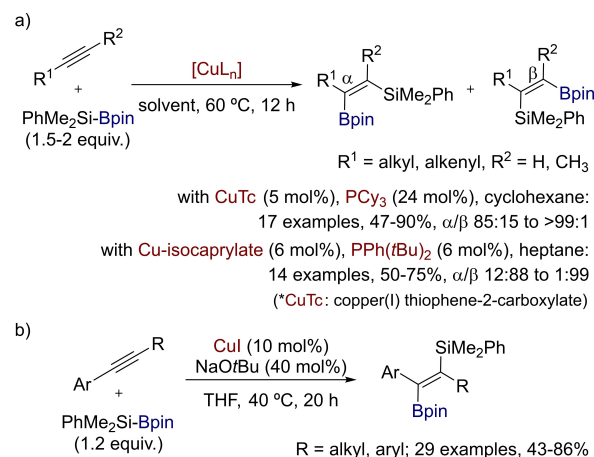**Scheme 45.** Palladium-catalyzed silaboration.
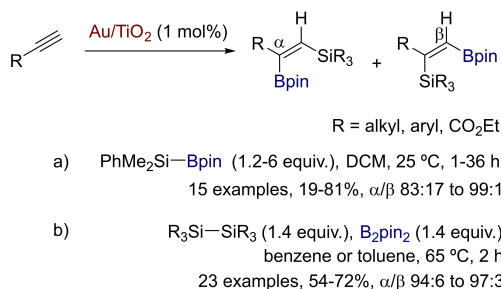
Scheme 46. Nanogold-catalyzed *syn*-silaboration of terminal alkynes.

derivatives (Scheme 47).[117] The authors noticed that removing the ligand led to an opposite 2,1-silaboration.

Copper complexes have also facilitated the *syn*-silaboration of terminal alkynes. Fu/Xu could selectively obtain the α or β regioisomer by tuning the copper catalysts and phosphine ligands (Scheme 48a).[118] Recently, the *anti*-silaboration of sym-

Scheme 47. Zinc-catalyzed silaboration of alkynes.

Scheme 48. Copper-catalyzed silaboration of alkynes.

metrical and unsymmetrical internal alkynes has been reported by Moniwa/Shintani (Scheme 48b).[119a] An isomerization of the intermediate alkenylcuprate was proposed to explain the unusual stereoselectivity. A simple combination of CuI and NaO*t*Bu under mild conditions led to the products in moderate to excellent yields. Simultaneously, Ohmura/Suginome developed the *anti*-silaboration by using a CuCl/CyJohnPhos catalytic system and showed a stereoselectivity switch depending on the solvent.[119b]

Metal-free procedures have also been developed for silaboration reactions. Propargylamides and esters have been studied by Sawamura and Ohmiya group[120] and Santos *et al.*[121] respectively (Scheme 49a,b). In both cases, β-boryl-α-silyl products were obtained with *anti*-selectivity. Mechanistically different, alkynoates proceed via phosphine addition to form a zwitterionic allenolate intermediate, whereas propargylamides are deprotonated and coordinate to the silylborane. For this
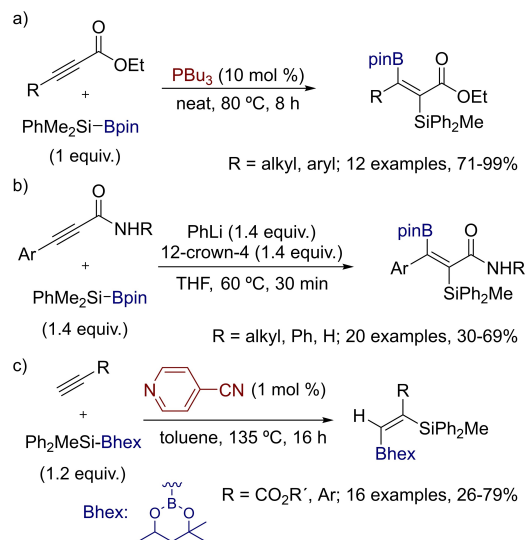
Scheme 49. Silaboration of propagilamides and esters.

reason, no reaction occurred with tertiary amides. Later, Suginome *et al.* investigated the *syn*-silaboration of terminal alkynes (alkynoates and acetylenes) using pyridine-based catalysts (Scheme 49c).[122] The authors suggested 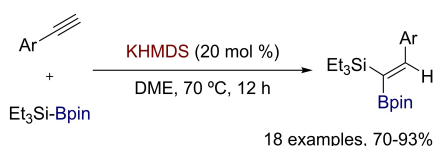a radical mechanism, in which the Si—B bond is activated by the pyridine catalyst. In the screening of the catalyst, the authors discovered ICy carbene catalyzed the 1,1-silaboration as a *Z:E* mixture for ethyl propiolate.

The 1,1-silaboration of terminal acetylenes has been optimized by Martin group (Scheme 50).[123] Catalytic KHMDS (potassium bis(trimethylsilyl)amide) led to *Z*-products in excellent yields from aromatic alkynes. Remarkably, ethyl propiolate gave *E/Z* 3:1 mixtures.
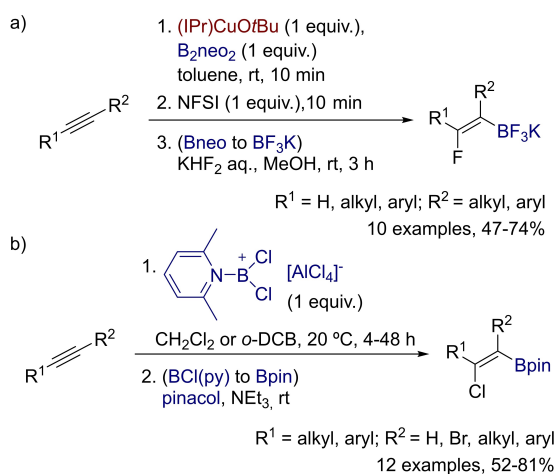
4.2. Haloboration

The haloboration of alkynes is a useful tool to achieve alkenes with a nucleophilic and an electrophilic position. A recent review reported the latest developments, mechanistic studies and the utility in synthetic chemistry of this reaction.[124]

Sadighi and co-workers investigated the borofluorination of alkynes by using copper complexes. By employing a sterically demanding ligand IDipp, the *syn*-1,2-haloboration products were formed, which were stabilized by conversion into the corresponding potassium trifluoroborate salts (Scheme 51a). For terminal alkynes, the α-borylated products were obtained.[125] Metal-free protocols have been reported for this reaction in the past few years. In 2013, Ingleson and co-workers achieved the haloboration of internal and terminal alkynes to produce tri-

and tetra-substituted alkenyl boronates by using dichloroborenium cations (Scheme 51b).[126] Five years later, Erker and co-workers employed $B(C_6F_5)_2$ to perform the *syn*-1,2-haloboration followed by an oligomerization reaction.[127]

The 1,2-haloboration and 1,1-haloboration reactions between BX_3 with internal alkynes, followed by intramolecular cyclisation have been applied to form B-doped PAHs (polycyclic aromatic hydrocarbons) or BN-PAHs, which have promising applications in material science (Scheme 52).[128]

4.3. Thioboration

The first thioboration of terminal alkynes with phenylthio or alkylthio derivatives of 9-BBN catalyzed by palladium(0) was described by Suzuki and Miyaura in 1993,[129] in a direct thioboration-coupling sequence to get 1-alkenyl sulfides. More recently, Wang and co-workers achieved a metal-free photocatalyzed radical methodology for the *anti*-trifluoromethylthiolation-borylation of internal and terminal alkynes (Scheme 53).[130]

4.4. Borylstannation

The borylstannation of alkynes allowed the formation of alkenyl boronates with new C—B and C—Sn bonds, that could be successively transformed into C—C bonds by Stille and Suzuki couplings. In 1996 Tanaka and co-workers described the first borylstannation by catalytic $Pd(PPh_3)_4$ (Scheme 54a).[131] *Syn*-

Scheme 50. Base promoted 1,1-silaboration of terminal alkynes.

Scheme 51. *syn*-Haloboration of alkynes.
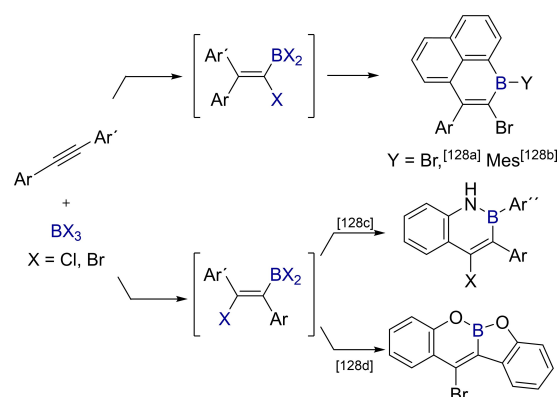
Scheme 52. Haloborations applied to prepare boracycles.
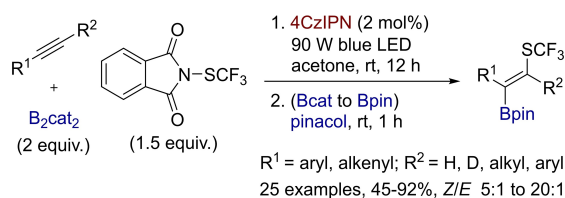
Scheme 53. *anti*-Trifluoromethylthioboration of terminal and internal alkynes.

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a)

R^1 = alkyl, aryl, CO_2CH_3; R^2 = H, alkyl, aryl, CO_2CH_3
5 examples, 73-86%, β/α 85:15 to 99:1

b)

R^1 = alkyl, aryl, TMS; R^2 = H, alkyl, aryl
19 examples, 36-86%, β/α 52:48 to 99:1

R^1 = alkyl, aryl, TMS; R^2 = H
12 examples, 66-87%, β/α 6:94 to >1:99

c)

R^1 = alkyl, aryl; R^2 = Me, Bu
13 examples, 55-92%, anti/syn >93:7
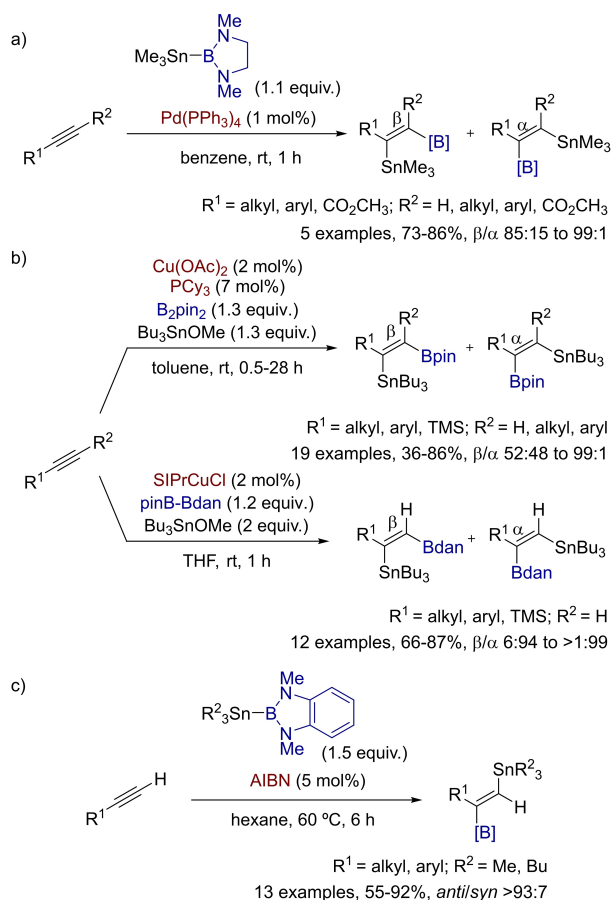
Scheme 54. Borylstannation of alkynes.

a)

R^1 = H, Cl, OMe, CO_2Et; R^2 = alkyl, aryl
11 examples, 31-86%

b)

R^1 = alkyl, aryl; R^2 = Ms, Ts; R^3 = H, Cl, X = C, N
9 examples, 51-79%

c)

X = O; R^1 = alkyl, aryl; R^2 = Br, I, CN, CO_2Me, C≡CH
[B] = B(MIDA), BF_3K, 10 examples, 23-79%
X = NSO$_2$R; R^1 = alkyl, alkenyl, aryl; R^2 = Br, CF_3, CN, CO_2Me
[B] = Bpin, 10 examples, 55-80%

Scheme 55. Metal-catalyzed borylative cyclization.

benzofuran and indole derivatives (Scheme 55c).[136] Initial formation of O-Bcat or RSO$_2$N-Bcat intermediates and further treatment with the metallic complex led to the alkoxy- or aminoboration. Similar conditions gave access to borylated isoxazoles, dihydrofurans and isochromenes,[137] or borylated pyrazoles by copper-catalysis.[138]

Metal free procedures have been recently developed to get borylated heterocycles. On one hand, Blum group have employed the 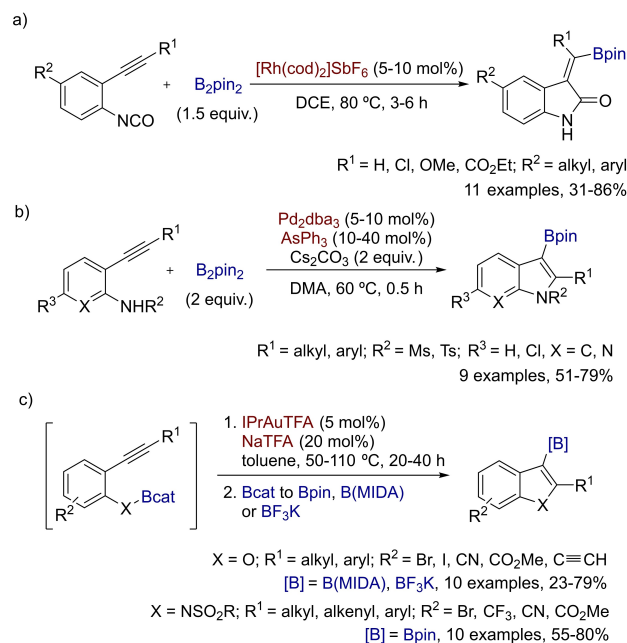highly electrophilic ClBcat reagent for the formation of borylated benzothiophenes (Scheme 56a),[139] thiophenes,[140] isocoumarins[141] and 2-pyrones[141] by thioboration and oxyboration. The mechanism involved the activation of the alkyne by the boron reagent, without previous formation of O—B or S—B bonds. On the other hand, Ingleson

addition was obtained with high levels of regioselectivity of the boron group at the β position. The oxidative addition of B—Sn bond to palladium was the initial step. Later, Yoshida detailed a three-component coupling reaction catalyzed by copper, using bisboronates and tributyltin methoxide (Scheme 54b).[132] By changing the catalyst and boron source α or β regioisomers could be selectively obtained. Very recently, Nishimoto, Yasuda et al. have achieved the anti-borylstannation by a radical mechanism (Scheme 54c).[133]

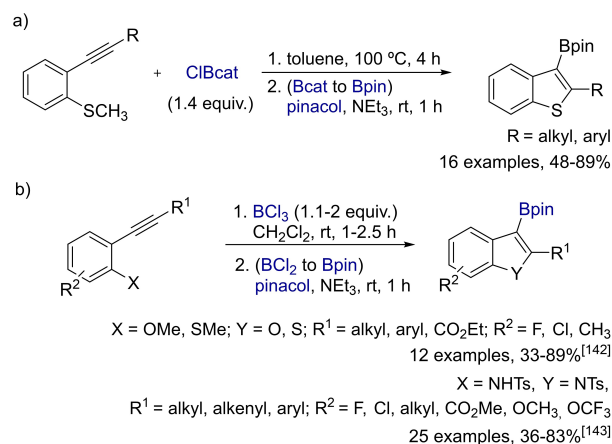### 4.5. Borylative cyclization (formation of C–B and C–X bonds)

Numerous research groups have applied elementoboration reactions to get heterocycles that contain a boronate group, forming the carbon-boron and carbon-heteroatom bonds in a single step. Initial efforts were made by Murakami et al. in a rhodium-catalyzed cyclization of 2-alkynylaryl isocyanates with B_2pin_2, to get borylated 3-alkylideneoxindoles in a stereoselective manner (Scheme 55a).[134] By changing the aromatic derivative and metal catalyst, 2- and 3-borylated indoles were efficiently prepared by Harrity (Scheme 55b) and Chatani groups.[135] Later, Blum at al. have established a gold-catalyzed intramolecular addition of B—X σ bonds to alkynes to get

a)

R = alkyl, aryl
16 examples, 48-89%

b)

X = OMe, SMe; Y = O, S; R^1 = alkyl, aryl, CO_2Et; R^2 = F, Cl, CH_3
12 examples, 33-89%[142]
X = NHTs, Y = NTs,
R^1 = alkyl, alkenyl, aryl; R^2 = F, Cl, alkyl, CO_2Me, OCH$_3$, OCF$_3$
25 examples, 36-83%[143]

Scheme 56. Metal-free borylative cyclization.

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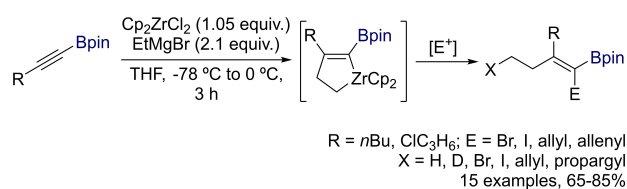**Chemistry Europe**
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and Han/Yuan/Shi used BCl_3 as boron source for the borylative cyclization of anisoles,[141] thioanisoles[142] and tosylanilines (Scheme 56b).[143]
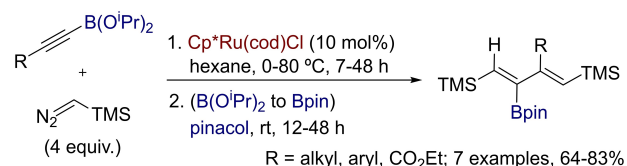
5. Other Methods

Besides the main methodologies described in the previous sections, other methods efficiently enable the preparation of polysubstituted alkenyl boronates.

Alkynyl boronates are suitable sources to get highly functionalized alkenyl boronates. Srebnik group formed α-borylzirconacyclopentenes from the corresponding alkynes, and subsequent reaction with electrophiles led to versatile tetrasubstituted alkenyl boronates in good yields (Scheme 57).[144] Complete regio- and stereoselectiviy was observed on the formation of the initial metallacycle.

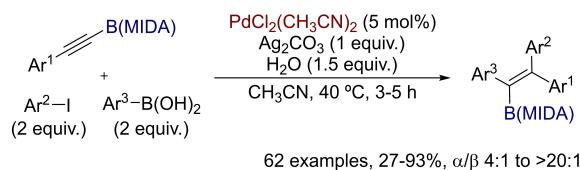Later, Shirakawa et al. developed conditions for the ruthenium catalyzed double addition of trimethylsilyldiazomethane to alkynyl boronates, leading to 1,3-butadienes (Scheme 58). Alkyl or ethoxycarbonyl substituents required higher temperatures than aryl derivatives.[145]

Suginome group developed the addition of alkynyl boronates to alkynes catalyzed by nickel complexes (Scheme 59).[146] The reaction proceeded with good yields, regio- and stereoselectivity, and is a complementary strategy to the copper-catalyzed carboboration of alkynes (Scheme 29b).[80]

MIDA protected alkynyl boronates have been employed by Glorius and Wang groups in a palladium-catalyzed three-component coupling with aryl iodides and aryl boronic acids (Scheme 60).[147] Excellent regioselectivity was controlled by the BMIDA group, and the alkenyl (MIDA)boronates are precursors of tetrasubstituted olefins.

Fürstner et al. developed the anti-hydrostannation of alkynyl boronates protected as anthranilamido derivatives (Scheme 61).[148] The [Cp*RuCl]₄ catalyst led to gem-dimetalated olefins, useful building blocks to get a variety of trisubstituted alkenes. This methodology complemented borylstannation reactions described in section 4.4.

Scheme 57. Formation and reactivity of α-borylzirconacyclopentenes.

Scheme 58. Addition of trimethylsilyldiazomethane to alkynyl boronates.
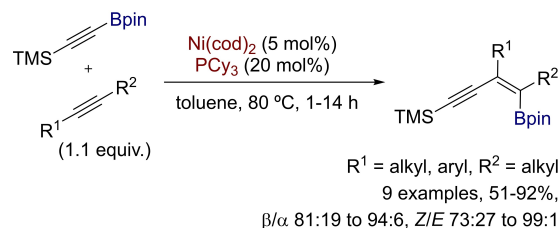
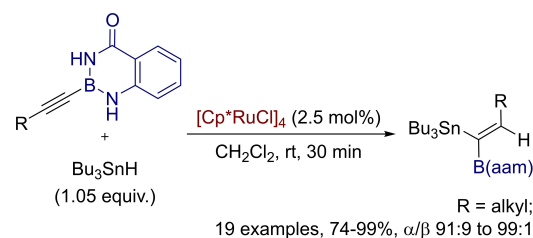**Scheme 59.** Nickel-catalyzed addition of alkynyl boronates to alkynes.

Scheme 60. Palladium-catalyzed synthesis of alkenyl (MIDA)boronates.

Scheme 61. Ruthenium-catalyzed anti-hydrostannation of alkynyl boronates.
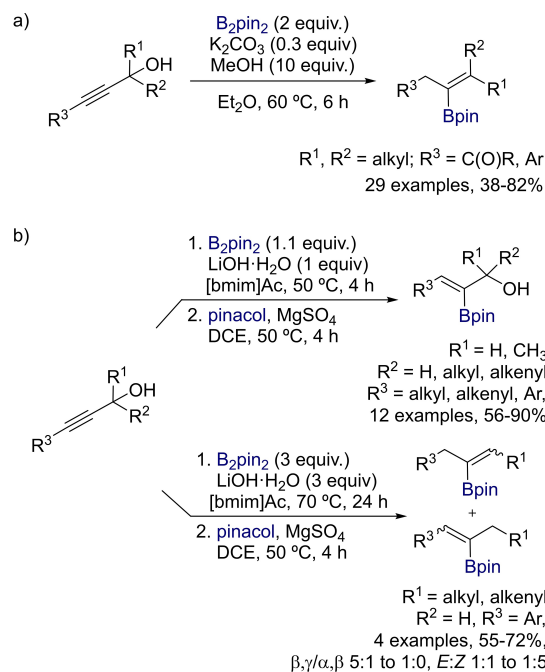
Scheme 62. Borylation reactions of propynols.

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Another recent strategy has been the cascade borylation/ B–O elimination of propynols, which employs a catalytic base and B₂pin₂. Song *et al.* optimized the preparation of tetrasubstituted alkenyl boronates under metal-free conditions (Scheme 62a).[149] In a similar diborylation/protodeboronation strategy,[150] Liu/Xie groups observed that the use of B₂pin₂ in stoichiometric amount in an ionic liquid as solvent did not lead to water elimination, and the allylic alcohol derivatives were obtained. However, an excess of the reagent and base led to mixture of alkenylboronates after B–O elimination (Scheme 62b).[151]

6. Summary and Outlook

In the last decades, the development of new methods for the preparation of tri- and tetrasubstituted alkenyl boronates from alkynes have been of great interest for the synthetic community, as valuable intermediates for the preparation of polysubstituted olefins or cyclic derivatives among others.

Most of the methodologies relied on metal-catalysis to overcome the reactivity, regio- and stereoselectivity difficulties. Although palladium and mainly copper catalysts have dominated the field, nickel, cobalt or iron have emerged last years as first-row transition metal alternatives. In general, mild conditions are required, so functional group tolerance is usually not a problem. In an effort to reduce the dependance on transition metals, methods based on boron trihalides and derivatives continue under development, as well as metal-free catalytic procedures. In addition, early examples of contemporary photoredox catalysis start to appear for the borylation of alkynes. We believe these procedures will be further explored in the next years.

A wide spectrum of substitution patterns for tri- and tetrasubstituted alkenylboronates has been effectively achieved by different methodologies starting from electronically or sterically biased alkynes. Nevertheless, unsymmetrically substituted dialkyl or diaryl alkynes remain highly challenging substrates in terms of regio- and stereoselectivity for hydroboration reactions. Further studies are required for this type of substrates. Carboboration and elementoboration reactions have been comparatively less studied than hydroboration, but many protocols allow the synthesis of trisubstituted alkenyl boronates. The controlled introduction of three alkyl or aryl groups in the synthesis of tetrasubstituted alkenyl boronates by these approaches has also been documented.

Despite the advances on the synthesis of these families of compounds, the applications in organic synthesis and material science are still under progress. We hope that the current contribution will facilitate the synthetic chemist the preparation and application of these versatile olefins and inspire further research on the topic.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: alkenyl boronates · alkynes · metal catalysis · metal-free · synthetic methods

[1] *Boronic Acids: Preparation and Applications in Organic Synthesis, Medicine and Materials*, 2nd ed. (Ed.: D. G. Hall), Wiley-VCH, **2011**.
[2] a) N. Miyaura, in *Cross-Coupling Reactions: A Practical Guide* (Ed.: N. Miyaura), Springer, Berlin, Heidelberg, **2002**, pp. 11–59; b) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457–2483.
[3] a) N. R. Candeias, F. Montalbano, P. M. S. D. Cal, P. M. P. Gois, *Chem. Rev.* **2010**, *110*, 6169–6193; b) P. Wu, M. Givskov, T. E. Nielsen, *Chem. Rev.* **2019**, *119*, 11245–11290.
[4] C. Sandford, V. K. Aggarwal, *Chem. Commun.* **2017**, *53*, 5481–5494.
[5] O. O. Grygorenko, V. S. Moskvina, O. V. Hryshchuk, A. V. Tymtsunik, *Synthesis* **2020**, *52*, 2761–2780.
[6] V. B. Corless, A. Holownia, H. Foy, R. Mendoza-Sanchez, S. Adachi, T. Dudding, A. K. Yudin, *Org. Lett.* **2018**, *20*, 5300–5303.
[7] a) J.-J. Li, C.-G. Wang, J.-F. Yu, P. Wang, J.-Q. Yu, *Org. Lett.* **2020**, *22*, 4692–4696; b) L. Hu, P.-X. Shen, Q. Shao, K. Hong, J. X. Qiao, J.-Q. Yu, *Angew. Chem. Int. Ed.* **2019**, *58*, 2134–2138; *Angew. Chem.* **2019**, *131*, 2156–2160.
[8] a) J. Carreras, A. Caballero, P. J. Pérez, *Chem. Asian J.* **2019**, *14*, 329–343; b) S. Alam, R. Karim, A. Khan, A. K. Pal, A. Maruani, *Eur. J. Org. Chem.* **2021**, 6115–6160.
[9] S. Li, X. Cui, Y. Wang, L. Wu, *Synlett* **2021**, *32*, 102–108.
[10] J. Zhang, S. Geng, Z. Feng, *Chem. Commun.* **2021**, *57*, 11922–11934.
[11] A. B. Cuenca, E. Fernández, *Chem. Soc. Rev.* **2021**, *50*, 72–86.
[12] a) J. J. Molloy, M. Schäfer, M. Wienhold, T. Morack, C. G. Daniliuc, R. Gilmour, *Science* **2020**, *369*, 302–306; b) T. Brégent, J. Bouillon, T. Poisson, *Chem. Eur. J.* **2021**, *27*, 13966–13970; c) S. Xu, P. Geng, Y. Li, G. Liu, L. Zhang, Y. Guo, Z. Huang, *ACS Catal.* **2021**, *11*, 10138–10147; d) L. Segura, I. Massad, M. Ogasawara, I. Marek, *Org. Lett.* **2021**, *23*, 9194–9198 and references cited therein.
[13] a) J. Royes, A. B. Cuenca, E. Fernández, *Eur. J. Org. Chem.* **2018**, 2728–2739; see also: b) X. Wang, Y. Wang, W. Huang, C. Xia, L. Wu, *ACS Catal.* **2021**, *11*, 1–18.
[14] a) H. C. Brown, B. C. S. Rao, *J. Am. Chem. Soc.* **1959**, *81*, 6423–6428; b) H. C. Brown, B. C. S. Rao, *J. Am. Chem. Soc.* **1959**, *81*, 6428–6434.
[15] a) J. Chen, J. Guo, Z. Lu, *Chin. J. Chem.* **2018**, *36*, 1075–1109; b) H. Yoshida, *ACS Catal.* **2016**, *6*, 1799–1811; c) K. Semba, T. Fujihara, J. Terao, Y. Tsuji, *Tetrahedron* **2015**, *71*, 2183–2197; d) S. Rej, A. Das, T. K. Panda, *Adv. Synth. Catal.* **2021**, *363*, 4818–4840.
[16] a) H. C. Brown, S. K. Gupta, *J. Am. Chem. Soc.* **1975**, *97*, 5249–5255; b) H. C. Brown, S. K. Gupta, *J. Am. Chem. Soc.* **1972**, *94*, 4370–4371.
[17] C. E. Tucker, J. Davidson, P. Knochel, *J. Org. Chem.* **1992**, *57*, 3482–3485.
[18] I. D. Gridnev, N. Miyaura, A. Suzuki, *Organometallics* **1993**, *12*, 589–592.
[19] K. Semba, T. Fujihara, J. Terao, Y. Tsuji, *Chem. Eur. J.* **2012**, *18*, 4179–4184.
[20] Y. D. Bidal, F. Lazreg, C. S. J. Cazin, *ACS Catal.* **2014**, *4*, 1564–1569.
[21] F. Rami, F. Bächtle, B. Plietker, *Catal. Sci. Technol.* **2020**, *10*, 1492–1497.
[22] J. W. Hall, D. M. L. Unson, P. Brunel, L. R. Collins, M. K. Cybulski, M. F. Mahon, M. K. Whittlesey, *Organometallics* **2018**, *37*, 3102–3110.

[23] a) M. Espinal-Viguri, C. R. Woof, R. L. Webster, *Chem. Eur. J.* **2016**, *22*, 11605–11608; b) A. Singh, S. Shafiei-Haghighi, C. R. Smith, D. K. Unruh, M. Findlater, *Asian J. Org. Chem.* **2020**, *9*, 416–420.

[24] M. Magre, B. Maity, A. Falconnet, L. Cavallo, M. Rueping, *Angew. Chem. Int. Ed.* **2019**, *58*, 7025–7029; *Angew. Chem.* **2019**, *131*, 7099–7103.

[25] M. J. González, F. Bauer, B. Breit, *Org. Lett.* **2021**, *23*, 8199–8203.

[26] a) L. Ferrand, Y. Lyu, A. Rivera-Hernández, B. J. Fallon, M. Amatore, C. Aubert, M. Petit, *Synthesis* **2017**, *49*, 3895–3904; b) G. Zhang, S. Li, J. Wu, H. Zeng, Z. Mo, K. Davis, S. Zheng, *Org. Chem. Front.* **2019**, *6*, 3228–3233; c) C. K. Blasius, V. Vasilenko, R. Matveeva, H. Wadepohl, L. H. Gade, *Angew. Chem. Int. Ed.* **2020**, *59*, 23010–23014; *Angew. Chem.* **2020**, *132*, 23210–23214.

[27] S. Mandal, P. K. Verma, K. Geetharani, *Chem. Commun.* **2018**, *54*, 13690–13693.

[28] S. Mandal, S. Mandal, K. Geetharani, *Chem. Asian J.* **2019**, *14*, 4553–4556.

[29] N. Iwadate, M. Suginome, *Org. Lett.* **2009**, *11*, 1899–1902.

[30] a) Z.-C. Wang, M. Wang, J. Gao, S.-L. Shi, Y. Xu, *Org. Chem. Front.* **2019**, *6*, 2949–2953; b) M. K. Bisai, S. Yadav, T. Das, K. Vanka, S. S. Sen, *Chem. Commun.* **2019**, *55*, 11711–11714; c) J. Liu, C. Wu, T. Hu, W. Yang, Y. Xie, Y. Shi, Q. Liu, Y. Shao, F. Zhang, *J. Org. Chem.* **2022**, *87*, 3442–3452.

[31] a) M. Fleige, J. Möbus, T. vom Stein, F. Glorius, D. W. Stephan, *Chem. Commun.* **2016**, *52*, 10830–10833; b) J. R. Lawson, L. C. Wilkins, R. L. Melen, *Chem. Eur. J.* **2017**, *23*, 10997–11000; c) N. W. J. Ang, C. S. Buettner, S. Docherty, A. Bismuto, J. R. Carney, J. H. Docherty, M. J. Cowley, S. P. Thomas, *Synthesis* **2018**, *50*, 803–808; d) J. L. Carden, L. J. Gierlichs, D. F. Wass, D. L. Browne, R. L. Melen, *Chem. Commun.* **2019**, *55*, 318–321; e) A. Bismuto, M. J. Cowley, S. P. Thomas, *Adv. Synth. Catal.* **2021**, *363*, 2382–2385.

[32] N. N. H. Ton, B. K. Mai, T. V. Nguyen, *J. Org. Chem.* **2021**, *86*, 9117–9133.

[33] A. Brzozowska, V. Zubar, R.-C. Ganardi, M. Rueping, *Org. Lett.* **2020**, *22*, 3765–3769.

[34] H. E. Ho, N. Asao, Y. Yamamoto, T. Jin, *Org. Lett.* **2014**, *16*, 4670–4673.

[35] J. Szyling, A. Franczyk, K. Stefanowska, J. Walkowiak, *Adv. Synth. Catal.* **2018**, *360*, 2966–2974.

[36] S. Pereira, M. Srebnik, *Organometallics* **1995**, *14*, 3127–3128.

[37] A. Bismuto, S. P. Thomas, M. J. Cowley, *Angew. Chem. Int. Ed.* **2016**, *55*, 15356–15359; *Angew. Chem.* **2016**, *128*, 15582–15585.

[38] F. Li, X. Bai, Y. Cai, H. Li, S.-Q. Zhang, F.-H. Liu, X. Hong, Y. Xu, S.-L. Shi, *Org. Process Res. Dev.* **2019**, *23*, 1703–1708.

[39] Q. Feng, H. Wu, X. Li, L. Song, L. W. Chung, Y.-D. Wu, J. Sun, *J. Am. Chem. Soc.* **2020**, *142*, 13867–13877.

[40] G. Zhu, W. Kong, H. Feng, Z. Qian, *J. Org. Chem.* **2014**, *79*, 1786–1795.

[41] M. Satoh, N. Miyaura, A. Suzuki, *Synthesis* **1987**, 373–377.

[42] W. Cui, M. Mao, Z. He, G. Zhu, *J. Org. Chem.* **2013**, *78*, 9815–9821.

[43] B. H. Lipshutz, Ž. V. Bošković, D. H. Aue, *Angew. Chem. Int. Ed.* **2008**, *47*, 10183–10186; *Angew. Chem.* **2008**, *120*, 10337–10340.

[44] H. Ding, W. Gao, T. Yu, Z. Wang, F. Gou, S. Ding, *J. Org. Chem.* **2022**, *87*, 1526–1536.

[45] H. L. Sang, C. Wu, G. G. D. Phua, S. Ge, *ACS Catal.* **2019**, *9*, 10109–10114.

[46] T. Sokolnicki, J. Szyling, A. Franczyk, J. Walkowiak, *Adv. Synth. Catal.* **2020**, *362*, 177–183.

[47] B. Sundararaju, A. Fürstner, *Angew. Chem. Int. Ed.* **2013**, *52*, 14050–14054; *Angew. Chem.* **2013**, *125*, 14300–14304.

[48] L.-J. Song, T. Wang, X. Zhang, L. W. Chung, Y.-D. Wu, *ACS Catal.* **2017**, *7*, 1361–1368.

[49] S. Xu, Y. Zhang, B. Li, S.-Y. Liu, *J. Am. Chem. Soc.* **2016**, *138*, 14566–14569.

[50] Y. Yang, J. Jiang, H. Yu, J. Shi, *Chem. Eur. J.* **2018**, *24*, 178–186.

[51] a) K. Nagao, A. Yamazaki, H. Ohmiya, M. Sawamura, *Org. Lett.* **2018**, *20*, 1861–1865; b) Y. Zi, F. Schömberg, F. Seifert, H. Görls, I. Vilotijevic, *Org. Biomol. Chem.* **2018**, *16*, 6341–6349; c) R. Fritzemeier, A. Gates, X. Guo, Z. Lin, W. L. Santos, *J. Org. Chem.* **2018**, *83*, 10436–10444; d) J. Bowen, C. Slebodnick, W. L. Santos, *Chem. Commun.* **2022**, *58*, 5984–5987.

[52] R. J. Grams, R. G. Fritzemeier, C. Slebodnick, W. L. Santos, *Org. Lett.* **2019**, *21*, 6795–6799.

[53] L. E. Longobardi, A. Fürstner, *Chem. Eur. J.* **2019**, *25*, 10063–10068.

[54] H. R. Kim, I. G. Jung, K. Yoo, K. Jang, E. S. Lee, J. Yun, S. U. Son, *Chem. Commun.* **2010**, *46*, 758–760.

[55] a) H. R. Kim, J. Yun, *Chem. Commun.* **2011**, *47*, 2943–2945; b) Q.-Q. Xuan, Y.-H. Wei, Q.-L. Song, *Chin. Chem. Lett.* **2017**, *28*, 1163–1166; c) J. Zhao, Z. Niu, H. Fu, Y. Li, *Chem. Commun.* **2014**, *50*, 2058–2060; d) M. Zhong, Y. Gagné, T. O. Hope, X. Pannecoucke, M. Frenette, P. Jubault, T. Poisson, *Angew. Chem. Int. Ed.* **2021**, *60*, 14498–14503.

[56] Y. Sasaki, Y. Horita, C. Zhong, M. Sawamura, H. Ito, *Angew. Chem. Int. Ed.* **2011**, *50*, 2778–2782; *Angew. Chem.* **2011**, *123*, 2830–2834.

[57] H.-D. Xu, H. Wu, H. Jiang, P. Chen, M.-H. Shen, *Tetrahedron Lett.* **2016**, *57*, 2915–2918.

[58] J. Corpas, M. Gomez-Mendoza, J. Ramírez-Cárdenas, V. A. de la Peña O'Shea, P. Mauleón, R. Gómez Arrayás, J. C. Carretero, *J. Am. Chem. Soc.* **2022**, *144*, 13006–13017.

[59] A. L. Moure, R. Gómez Arrayás, D. J. Cárdenas, I. Alonso, J. C. Carretero, *J. Am. Chem. Soc.* **2012**, *134*, 7219–7222.

[60] J. K. Park, B. A. Ondrusek, D. T. McQuade, *Org. Lett.* **2012**, *14*, 4790–4793.

[61] S. Bhavanarushi, Y. Xu, I. Khan, Z. Luo, B. Liu, J. Xie, *Org. Chem. Front.* **2019**, *6*, 1895–1899.

[62] Y. M. Chae, J. S. Bae, J. H. Moon, J. Y. Lee, J. Yun, *Adv. Synth. Catal.* **2014**, *356*, 843–849.

[63] a) I. M. de Oliveira, H. A. Esteves, M. P. Darbem, A. Sartorelli, T. C. Correra, A. F. Rodrigues-Oliveira, D. C. Pimenta, J. Zukerman-Schpector, F. Manarin, H. A. Stefani, *ChemCatChem* **2020**, *12*, 3545–3552; b) L. L. Baldassari, K. S. Santos, C. P. Ebersol, D. S. Lüdtke, A. V. Moro, *Catal. Sci. Technol.* **2020**, *10*, 7476–7480.

[64] a) G. He, S. Chen, Q. Wang, H. Huang, Q. Zhang, D. Zhang, R. Zhang, H. Zhu, *Org. Biomol. Chem.* **2014**, *12*, 5945–5953; b) Y. Bai, F. Zhang, J. Shen, F. Luo, G. Zhu, *Asian J. Org. Chem.* **2015**, *4*, 626–629.

[65] M. Suginome, A. Yamamoto, M. Murakami, *J. Am. Chem. Soc.* **2003**, *125*, 6358–6359.

[66] M. Suginome, A. Yamamoto, M. Murakami, *Angew. Chem. Int. Ed.* **2005**, *44*, 2380–2382; *Angew. Chem.* **2005**, *117*, 2432–2434.

[67] a) A. Yamamoto, M. Suginome, *J. Am. Chem. Soc.* **2005**, *127*, 15706–15707; b) M. Daini, A. Yamamoto, M. Suginome, *J. Am. Chem. Soc.* **2008**, *130*, 2918–2919; c) K. Nakada, M. Daini, M. Suginome, *Chem. Lett.* **2013**, *42*, 538–540.

[68] M. Daini, M. Suginome, *Chem. Commun.* **2008**, 5224–5226.

[69] a) H. Jin, A. Fürstner, *Org. Lett.* **2019**, *21*, 3446–3450; b) H. Jin, A. Fürstner, *Angew. Chem. Int. Ed.* **2020**, *59*, 13618–13622; *Angew. Chem.* **2020**, *132*, 13720–13724.

[70] Y. Zhang, B. Li, S.-Y. Liu, *Angew. Chem. Int. Ed.* **2020**, *59*, 15928–15932; *Angew. Chem.* **2020**, *132*, 16062–16066.

[71] Z. Wang, J. Wu, W. Lamine, B. Li, J.-M. Sotiropoulos, A. Chrostowska, K. Miqueu, S.-Y. Liu, *Angew. Chem. Int. Ed.* **2021**, *60*, 21231–21236.

[72] a) S. Wang, J. Zhang, L. Kong, Z. Tan, Y. Bai, G. Zhu, *Org. Lett.* **2018**, *20*, 5631–5635; b) W.-H. Guo, H.-Y. Zhao, Z.-J. Luo, S. Zhang, X. Zhang, *ACS Catal.* **2019**, *9*, 38–43; c) S. Domański, B. Gatlik, W. Chaładaj, *Org. Lett.* **2019**, *21*, 5021–5025.

[73] a) S. Mannathan, M. Jeganmohan, C.-H. Cheng, *Angew. Chem. Int. Ed.* **2009**, *48*, 2192–2195; *Angew. Chem.* **2009**, *121*, 2226–2229; b) N. Nakagawa, T. Hatakeyama, M. Nakamura, *Chem. Eur. J.* **2015**, *21*, 4257–4261.

[74] A. Whyte, A. Torelli, B. Mirabi, A. Zhang, M. Lautens, *ACS Catal.* **2020**, *10*, 11578–11622.

[75] a) Y. Okuno, M. Yamashita, K. Nozaki, *Angew. Chem. Int. Ed.* **2011**, *50*, 920–923; *Angew. Chem.* **2011**, *123*, 950–953; b) Y. Okuno, M. Yamashita, K. Nozaki, *Eur. J. Org. Chem.* **2011**, *2011*, 3951–3958.

[76] R. Alfaro, A. Parra, J. Alemán, J. L. García Ruano, M. Tortosa, *J. Am. Chem. Soc.* **2012**, *134*, 15165–15168.

[77] H. Yoshida, I. Kageyuki, K. Takaki, *Org. Lett.* **2013**, *15*, 952–955.

[78] a) C.-C. Tai, M.-S. Yu, Y.-L. Chen, W.-H. Chuang, T.-H. Lin, G. P. A. Yap, T.-G. Ong, *Chem. Commun.* **2014**, *50*, 4344–4346; b) Z. Wen, Y. Zhang, S. Roland, M. Sollogoub, Y. Shimizu, M. Kanai, *Eur. J. Org. Chem.* **2019**, 2682–2687; c) T. Itoh, Y. Shimizu, M. Kanai, *J. Am. Chem. Soc.* **2016**, *138*, 7528–7531.

[79] a) H.-Y. Bin, X. Wei, J. Zi, Y.-J. Zuo, T.-C. Wang, C.-M. Zhong, *ACS Catal.* **2015**, *5*, 6670–6679; b) E. Rivera-Chao, M. Fañanás-Mastral, *Angew. Chem. Int. Ed.* **2018**, *57*, 9945–9949; *Angew. Chem.* **2018**, *130*, 10093–10097.

[80] a) J. T. Han, J. Yun, *Org. Lett.* **2018**, *20*, 2104–2107; b) K. Li, S.-H. Yu, K.-F. Zhuo, X. Lu, B. Xiao, T.-J. Gong, Y. Fu, *Adv. Synth. Catal.* **2019**, *361*, 3937–3942.

[81] a) Y. Zhou, W. You, K. B. Smith, M. K. Brown, *Angew. Chem. Int. Ed.* **2014**, *53*, 3475–3479; *Angew. Chem.* **2014**, *126*, 3543–3547; b) Y. Huang, A. M. Bergmann, M. K. Brown, *Org. Biomol. Chem.* **2019**, *17*, 5913–5915.

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[82] E. Rivera-Chao, M. Mitxelena, J. A. Varela, M. Fañanás-Mastral, *Angew. Chem. Int. Ed.* **2019**, *58*, 18230–18234; *Angew. Chem.* **2019**, *131*, 18398–18402.

[83] A. Chaves-Pouso, A. M. Álvarez-Constantino, M. Fañanás-Mastral, *Angew. Chem. Int. Ed.* **2022**, DOI 10.1002/anie.202117696.

[84] a) K. Semba, M. Yoshizawa, Y. Ohtagaki, Y. Nakao, *Bull. Chem. Soc. Jpn.* **2017**, *90*, 1340–1343; b) M. Lesieur, Y. D. Bidal, F. Lazreg, F. Nahra, C. S. J. Cazin, *ChemCatChem* **2015**, *7*, 2108–2112.

[85] a) J. Mateos, E. Rivera-Chao, M. Fañanás-Mastral, *ACS Catal.* **2017**, *7*, 5340–5344; b) J. Mateos, N. Fuentes-Vara, L. Fra, E. Rivera-Chao, N. Vázquez-Galiñanes, A. Chaves-Pouso, M. Fañanás-Mastral, *Organometallics* **2020**, *39*, 740–745; c) K.-F. Zhuo, W.-Y. Xu, T.-J. Gong, Y. Fu, *Chem. Commun.* **2020**, *56*, 2340–2343.

[86] S.-H. Yu, T.-J. Gong, Y. Fu, *Org. Lett.* **2020**, *22*, 2941–2945.

[87] S.-H. Kim-Lee, P. Mauleón, R. Gómez Arrayás, J. C. Carretero, *Chem* **2021**, *7*, 2212–2226.

[88] B. Wrackmeyer, E. Khan, *Eur. J. Inorg. Chem.* **2016**, *2016*, 300–312 and references cited therein.

[89] K. Škoch, C. Pauly, C. G. Daniliuc, K. Bergander, G. Kehr, G. Erker, *Dalton Trans.* **2019**, *48*, 4837–4845 and references cited therein.

[90] Z. Li, J. Sun, *Org. Lett.* **2021**, *23*, 3706–3711.

[91] a) K. Nagao, H. Ohmiya, M. Sawamura, *J. Am. Chem. Soc.* **2014**, *136*, 10605–10608; b) A. Yamazaki, K. Nagao, T. Iwai, H. Ohmiya, M. Sawamura, *Angew. Chem. Int. Ed.* **2018**, *57*, 3196–3199; *Angew. Chem.* **2018**, *130*, 3250–3253.

[92] a) C. You, M. Sakai, C. G. Daniliuc, K. Bergander, S. Yamaguchi, A. Studer, *Angew. Chem. Int. Ed.* **2021**, *60*, 21697–21701; see also:; b) J. R. Lawson, V. Fasano, J. Cid, I. Vitorica-Yrezabal, M. J. Ingleson, *Dalton Trans.* **2016**, *45*, 6060–6070.

[93] E. Buñuel, D. J. Cárdenas, *Eur. J. Org. Chem.* **2016**, 5446–5464.

[94] a) S. Onozawa, Y. Hatanaka, N. Choi, M. Tanaka, *Organometallics* **1997**, *16*, 5389–5391; see also: b) R. R. Singidi, A. M. Kutney, J. C. Gallucci, T. V. RajanBabu, *J. Am. Chem. Soc.* **2010**, *132*, 13078–13087.

[95] M. Gerdin, S. K. Nadakudity, C. Worch, C. Moberg, *Adv. Synth. Catal.* **2010**, *352*, 2559–2570.

[96] Y.-C. Xiao, C. Moberg, *Org. Lett.* **2016**, *18*, 308–311.

[97] Y. Deng, T. Bartholomeyzik, J.-E. Bäckvall, *Angew. Chem. Int. Ed.* **2013**, *52*, 6283–6287; *Angew. Chem.* **2013**, *125*, 6403–6407.

[98] A. Martos-Redruejo, R. López-Durán, E. Buñuel, D. J. Cárdenas, *Chem. Commun.* **2014**, *50*, 10094–10097.

[99] R. E. Kinder, R. A. Widenhoefer, *Org. Lett.* **2006**, *8*, 1967–1969.

[100] a) T. Xi, Z. Lu, *ACS Catal.* **2017**, *7*, 1181–1185; b) Q. Huang, M.-Y. Hu, S.-F. Zhu, *Org. Lett.* **2019**, *21*, 7883–7887.

[101] a) N. Cabrera-Lobera, M. T. Quirós, W. W. Brennessel, M. L. Neidig, E. Buñuel, D. J. Cárdenas, *Org. Lett.* **2019**, *21*, 6552–6556; b) N. Cabrera-Lobera, M. T. Quirós, E. Buñuel, D. J. Cárdenas, *Catal. Sci. Technol.* **2019**, *9*, 1021–1029; see also: c) N. Cabrera-Lobera, M. T. Quirós, E. Buñuel, D. J. Cárdenas, *Chem. Eur. J.* **2019**, *25*, 14512–14516.

[102] P. Liu, Y. Fukui, P. Tian, Z.-T. He, C.-Y. Sun, N.-Y. Wu, G.-Q. Lin, *J. Am. Chem. Soc.* **2013**, *135*, 11700–11703.

[103] S.-H. Kim-Lee, I. Alonso, P. Mauleón, R. G. Arrayás, J. C. Carretero, *ACS Catal.* **2018**, *8*, 8993–9005.

[104] K. Kubota, H. Iwamoto, E. Yamamoto, H. Ito, *Org. Lett.* **2015**, *17*, 620–623.

[105] S. Zhou, F. Yuan, M. Guo, G. Wang, X. Tang, W. Zhao, *Org. Lett.* **2018**, *20*, 6710–6714.

[106] a) L. Zhang, J. Cheng, B. Carry, Z. Hou, *J. Am. Chem. Soc.* **2012**, *134*, 14314–14317; b) S. Roscales, A. G. Csákÿ, *Org. Lett.* **2015**, *17*, 1605–1608; c) M. Nogami, K. Hirano, M. Kanai, C. Wang, T. Saito, K. Miyamoto, A. Muranaka, M. Uchiyama, *J. Am. Chem. Soc.* **2017**, *139*, 12358–12361.

[107] a) A. J. Warner, J. R. Lawson, V. Fasano, M. J. Ingleson, *Angew. Chem. Int. Ed.* **2015**, *54*, 11245–11249; *Angew. Chem.* **2015**, *127*, 11397–11401; see also:; b) D. L. Crossley, R. J. Kahan, S. Endres, A. J. Warner, R. A. Smith, J. Cid, J. J. Dunsford, J. E. Jones, I. Vitorica-Yrezabal, M. J. Ingleson, *Chem. Sci.* **2017**, *8*, 7969–7977.

[108] C.-H. Yang, X. Sun, C. Niu, Z. Zhang, M. Liu, F. Zheng, L. Jiang, X. Kong, Z. Yang, *Org. Lett.* **2021**, *23*, 8050–8055.

[109] a) J.-J. Feng, W. Mao, L. Zhang, M. Oestreich, *Chem. Soc. Rev.* **2021**, *50*, 2010–2073; see also:; b) M. B. Ansell, O. Navarro, J. Spencer, *Coord. Chem. Rev.* **2017**, *336*, 54–77.

[110] a) M. Suginome, T. Matsuda, H. Nakamura, Y. Ito, *Tetrahedron* **1999**, *55*, 8787–8800; see also: b) M. Suginome, H. Nakamura, Y. Ito, *Chem. Commun.* **1996**, 2777–2778.

[111] T. Ohmura, K. Oshima, M. Suginome, *Chem. Commun.* **2008**, 1416–1418.

[112] T. Ohmura, K. Oshima, H. Taniguchi, M. Suginome, *J. Am. Chem. Soc.* **2010**, *132*, 12194–12196.

[113] M. B. Ansell, J. Spencer, O. Navarro, *ACS Catal.* **2016**, *6*, 2192–2196.

[114] C. Gryparis, M. Stratakis, *Org. Lett.* **2014**, *16*, 1430–1433.

[115] A. Khan, A. M. Asiri, S. A. Kosa, H. Garcia, A. Grirrane, *J. Catal.* **2015**, *329*, 401–412.

[116] M. Kidonakis, M. Stratakis, *Eur. J. Org. Chem.* **2017**, *2017*, 4265–4271.

[117] Y. Nagashima, D. Yukimori, C. Wang, M. Uchiyama, *Angew. Chem. Int. Ed.* **2018**, *57*, 8053–8057; *Angew. Chem.* **2018**, *130*, 8185–8189.

[118] M. Zhao, C.-C. Shan, Z.-L. Wang, C. Yang, Y. Fu, Y.-H. Xu, *Org. Lett.* **2019**, *21*, 6016–6020.

[119] a) H. Moniwa, R. Shintani, *Chem. Eur. J.* **2021**, *27*, 7512–7515; b) T. Ohmura, Y. Takaoka, M. Suginome, *Chem. Commun.* **2021**, *57*, 4670–4673.

[120] K. Nagao, H. Ohmiya, M. Sawamura, *Org. Lett.* **2015**, *17*, 1304–1307.

[121] R. Fritzemeier, W. L. Santos, *Chem. Eur. J.* **2017**, *23*, 15534–15537.

[122] Y. Morimasa, K. Kabasawa, T. Ohmura, M. Suginome, *Asian J. Org. Chem.* **2019**, *8*, 1092–1096.

[123] Y. Gu, Y. Duan, Y. Shen, R. Martin, *Angew. Chem. Int. Ed.* **2020**, *59*, 2061–2065; *Angew. Chem.* **2020**, *132*, 2077–2081.

[124] a) S. Kirschner, K. Yuan, M. J. Ingleson, *New J. Chem.* **2021**, *45*, 14855–14868; see also:; b) C. Wang, M. Uchiyama, *Eur. J. Org. Chem.* **2012**, 6548–6554.

[125] A. J. Jordan, P. K. Thompson, J. P. Sadighi, *Org. Lett.* **2018**, *20*, 5242–5246.

[126] J. R. Lawson, E. R. Clark, I. A. Cade, S. A. Solomon, M. J. Ingleson, *Angew. Chem. Int. Ed.* **2013**, *52*, 7518–7522; *Angew. Chem.* **2013**, *125*, 7666–7670.

[127] A. Ueno, J. Li, C. G. Daniliuc, G. Kehr, G. Erker, *Chem. Eur. J.* **2018**, *24*, 10044–10048.

[128] a) K. Yuan, R. J. Kahan, C. Si, A. Williams, S. Kirschner, M. Uzelac, E. Zysman-Colman, M. J. Ingleson, *Chem. Sci.* **2020**, *11*, 3258–3267; b) R. J. Kahan, D. L. Crossley, J. Cid, J. E. Radcliffe, M. J. Ingleson, *Angew. Chem. Int. Ed.* **2018**, *130*, 8216–8220; c) F.-D. Zhuang, J.-M. Han, S. Tang, J.-H. Yang, Q.-R. Chen, J.-Y. Wang, J. Pei, *Organometallics* **2017**, *36*, 2479–2482; d) Y. Uchikawa, K. Tazoe, S. Tanaka, X. Feng, T. Matsumoto, J. Tanaka, T. Yamato, *Can. J. Chem.* **2012**, *90*, 441–449.

[129] T. Ishiyama, K. Nishijima, N. Miyaura, A. Suzuki, *J. Am. Chem. Soc.* **1993**, *115*, 7219–7225.

[130] Q. Zhang, X. Li, W. Zhang, Y. Wang, Y. Pan, *Org. Lett.* **2021**, *23*, 5410–5414.

[131] a) S. Onozawa, Y. Hatanaka, T. Sakakura, S. Shimada, M. Tanaka, *Organometallics* **1996**, *15*, 5450–5452; see also:; b) R. R. Singidi, T. V. RajanBabu, *Org. Lett.* **2010**, *12*, 2622–2625.

[132] a) Y. Takemoto, H. Yoshida, K. Takaki, *Chem. Eur. J.* **2012**, *18*, 14841–14844; b) H. Yoshida, Y. Takemoto, K. Takaki, *Chem. Commun.* **2015**, *51*, 6297–6300; see also: H. Yoshida, M. Kimura, I. Osaka, K. Takaki, *Organometallics* **2017**, *36*, 1345–1351.

[133] K. Suzuki, N. Sugihara, Y. Nishimoto, M. Yasuda, *Angew. Chem. Int. Ed.* **2022**, *61*, E202201883.

[134] T. Miura, Y. Takahashi, M. Murakami, *Org. Lett.* **2008**, *10*, 1743–1745.

[135] a) J. Huang, S. J. F. Macdonald, J. P. A. Harrity, *Chem. Commun.* **2009**, *46*, 8770–8772; b) M. Tobisu, H. Fujihara, K. Koh, N. Chatani, *J. Org. Chem.* **2010**, *75*, 4841–4847.

[136] a) J. J. Hirner, D. J. Faizi, S. A. Blum, *J. Am. Chem. Soc.* **2014**, *136*, 4740–4745; b) E. Chong, S. A. Blum, *J. Am. Chem. Soc.* **2015**, *137*, 10144–10147.

[137] a) K. N. Tu, J. J. Hirner, S. A. Blum, *Org. Lett.* **2016**, *18*, 480–483; b) K. N. Tu, C. Gao, S. A. Blum, *J. Org. Chem.* **2018**, *83*, 11204–11217.

[138] K. N. Tu, S. Kim, S. A. Blum, *Org. Lett.* **2019**, *21*, 1283–1286.

[139] D. J. Faizi, A. J. Davis, F. B. Meany, S. A. Blum, *Angew. Chem. Int. Ed.* **2016**, *55*, 14286–14290; *Angew. Chem.* **2016**, *128*, 14498–14502.

[140] H. Bel Abed, S. A. Blum, *Org. Lett.* **2018**, *20*, 6673–6677.

[141] D. J. Faizi, A. Issaian, A. J. Davis, S. A. Blum, *J. Am. Chem. Soc.* **2016**, *138*, 2126–2129.

[142] A. J. Warner, A. Churn, J. S. McGough, M. J. Ingleson, *Angew. Chem. Int. Ed.* **2017**, *56*, 354–358; *Angew. Chem.* **2017**, *129*, 360–364.

[143] J. Lv, B. Zhao, L. Liu, Y. Han, Y. Yuan, Z. Shi, *Adv. Synth. Catal.* **2018**, *360*, 4054–4059.

[144] S. Ben-Valid, A. A. A. Quntar, M. Srebnik, *J. Org. Chem.* **2005**, *70*, 3554–3559.

[145] R. Morita, E. Shirakawa, T. Tsuchimoto, Y. Kawakami, *Org. Biomol. Chem.* **2005**, *3*, 1263–1268.

[146] M. Suginome, M. Shirakura, A. Yamamoto, *J. Am. Chem. Soc.* **2006**, *128*, 14438–14439.

[147] E. E. Lin, J.-Q. Wu, F. Schäfers, X.-X. Su, K.-F. Wang, J.-L. Li, Y. Chen, X. Zhao, H. Ti, Q. Li, T.-M. Ou, F. Glorius, H. Wang, *Commun. Chem.* **2019**, *2*, 1–9.

[148] R. Melot, T. J. Saiegh, A. Fürstner, *Chem. Eur. J.* **2021**, *27*, 17002–17011.

[149] a) Z. Kuang, H. Chen, J. Yan, K. Yang, Y. Lan, Q. Song, *Org. Lett.* **2018**, *20*, 5153–5157; see also: b) H. Chen, T. Zhang, C. Shan, S. Liu, Q. Song, R. Bai, Y. Lan, *Org. Lett.* **2019**, *21*, 4924–4928.

[150] Z. Kuang, K. Yang, Y. Zhou, Q. Song, *Chem. Commun.* **2020**, *56*, 6469–6479.

[151] S. Bhavanarushi, Y. Xu, I. Khan, Z. Luo, B. Liu, J. Xie, *Org. Chem. Front.* **2019**, *6*, 1895–1899.