

SYNLETT Spotlight 426

Bis(pinacolato)diboron

Compiled by Rémy Hemelaere

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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Introduction

Bis(pinacolato)diboron (B_2pin_2 , Figure 1, CAS: 73183-34-3) is an air-stable, odourless, colorless powder that is commercially available. Being a major tool for the introduction of boron atoms into organic compounds, it is widely known as a good reagent to prepare substrates for the Suzuki–Miyaura reaction.

An extensive scope of reactions, including C–H activation of $C(sp^2)$ –H and $C(sp^3)$ –H bonds,¹ borylation of α,β -unsaturated derivatives and substitutions of allylic carbonates, have been recently described in the literature. Over

the past few years, extensive efforts have been devoted to the borylation of dienes, allenes,² alkenes,³ and alkynes. More recently, B_2pin_2 found application in the borylation of aldehydes and imines opening new ways of research.

Borylated products, obtained from these new strategies, could successfully be used in oxidation, allylation or coupling reactions.

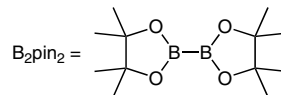
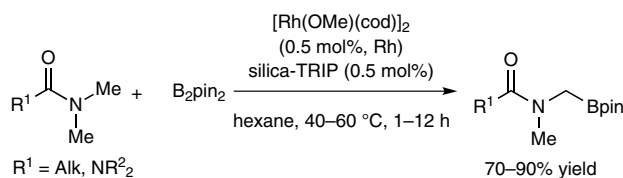


Figure 1

Abstracts

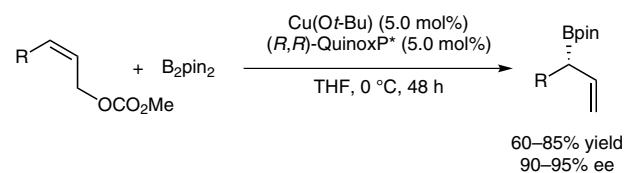
(A) $C(sp^3)$ –H Activation

Very recently, Sawamura et al. reported a rhodium-catalyzed $C(sp^3)$ –H borylation of amides and urea derivatives at the position adjacent to nitrogen with a silica-supported triarylphosphine ligand (silica-TRIP).⁴ The reaction was carried out under mild conditions with good to excellent yield. Compounds obtained with this method can undergo Suzuki–Miyaura coupling.



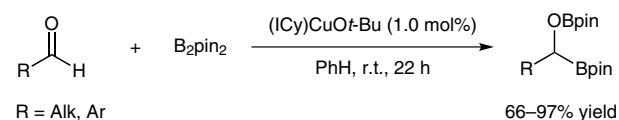
(B) Allylic Substitution

Under mild conditions, allylic carbonates can be borylated by treatment with bis(pinacolato)diboron in the presence of a copper catalyst to give the corresponding allyl boronates.⁵ Using a chiral ligand, excellent enantioselectivities were obtained.⁶



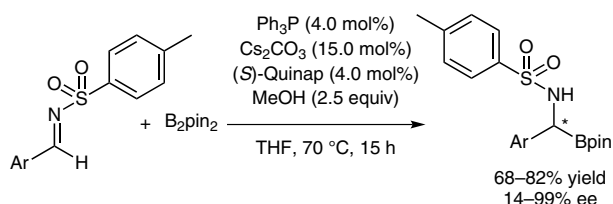
(C) Borylation of Aldehydes

Treatment of aldehydes with B_2pin_2 , in the presence of a copper catalyst, led to the formation of diboration products as stable compounds in the solid state. A mechanistic study was performed confirming the insertion of the carbonyl group into the copper–boron bond. A selective hydrolysis of the B–O bond during chromatographic purification can provide the corresponding α -hydroxyboronates.⁷

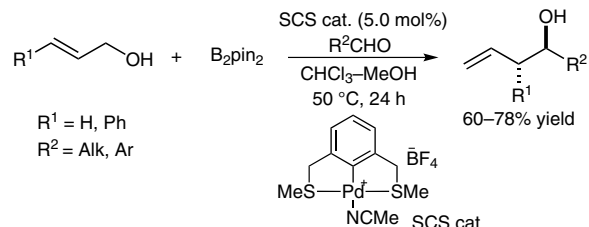


(D) *Borylation of Imines*

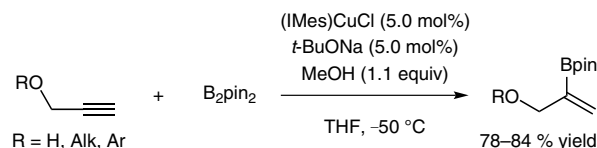
Ellman et al. reported that the (ICy)CuOt-Bu-B₂pin₂ system can promote asymmetric borylation of chiral *N*-*tert*-butanesulfinyl aldimines.⁸ More recently, Fernandez and co-workers described the enantioselective synthesis of α -amino boronate esters via an addition of B₂pin₂ to *N*-tosyl aldimines without transition-metal complexes.⁹

(E) *Borylation of Allylic Alcohols*

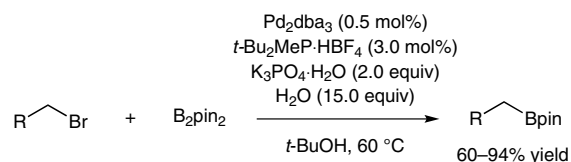
Szabó and co-workers described the borylation of allylic alcohols using a SCS palladium pincer complex catalyst. Depending on the solvent system, a regioselective formation of linear or branched allyl boronates is possible. Using an aldehyde, allylic alcohols were obtained via a one-pot borylation–allylation process.¹⁰

(F) *Borylation of Alkynes*

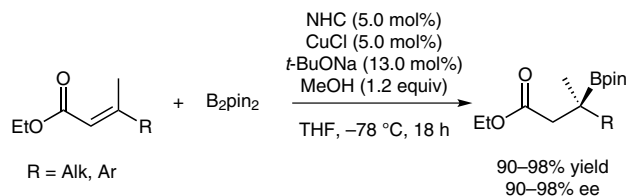
Catalytic systems used for the introduction of boron atoms into alkynes have been improved over the past ten years in order to obtain better regioselectivity. Hoveyda et al. developed a highly selective method to synthesize internal vinylboronates from terminal alkynes by using *N*-heterocyclic carbene (NHC) complexes of copper(I).¹¹ Excellent regioselectivities were observed with a high level of functional group tolerance.

(G) *Borylation of Primary Alkyl Halides*

Starting from primary alkyl bromides, Biscoe et al. reported the synthesis of alkylboronates, catalyzed by complexes of palladium. Diverse functional groups were tolerated on the starting material, such as nitrile, alcohol, ester and amide. Moderate to good yields were obtained with complete selectivity over secondary bromides.¹²

(H) *Addition to α,β -Unsaturated Carbonyl Compounds*

Over the past eight years, research has focused on β -borylation of α,β -unsaturated esters,¹³ amides,¹⁴ and ketones.¹⁵ These processes are efficiently catalyzed by *N*-heterocyclic carbene (NHC) complexes of copper(I). Hoveyda's group applied this strategy to trisubstituted alkenes of acyclic α,β -unsaturated esters. With a chiral NHC–copper complex, they developed an enantioselective pathway to boron-substituted quaternary carbons.



References

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