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Bis(pinacolato)diboron
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Introduction
Bis(pinacolato)diboron (B$_2$pin$_2$, 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$^3$)–H and C(sp$^3$)–H bonds, 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, alkenes, and alkynes. More recently, B$_2$pin$_2$ 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.

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).

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

(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. Using a chiral ligand, excellent enantioselectivities were obtained.

(C) Borylation of Aldehydes

Treatment of aldehydes with B$_2$pin$_2$, 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.

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(D) Borylation of Imines
Ellman et al. reported that the (ICy)CuO–Bu–B2pin2 system can promote asymmetric borylation of chiral N-tert-butanesulphonyl aldimines.10 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 allylborationates, 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 esters of copper(I). 11 Excellent regioselectivities were observed with a high level of functional group tolerance.

References