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

Bis(pinacolato)diboron

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Introduction

Bis(pinacolato)diboron (B\textsubscript{2}pin\textsubscript{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\textsuperscript{3})–H and C(sp\textsuperscript{3})–H bonds\textsuperscript{1}, borylation of \(\alpha,\beta\)-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, allennes\textsuperscript{2}, alkenes\textsuperscript{3}, and alkynes. More recently, B\textsubscript{2}pin\textsubscript{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\textsuperscript{3})–H Activation

Very recently, Sawamura et al. reported a rhodium-catalyzed C(sp\textsuperscript{3})–H borylation of amides and urea derivatives at the position adjacent to nitrogen with a silica-supported triarylphosphine ligand (silica-TRIP).\textsuperscript{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.\textsuperscript{5} Using a chiral ligand, excellent enantioselectivities were obtained.\textsuperscript{6}

(C) Borylation of Aldehydes

Treatment of aldehydes with B\textsubscript{2}pin\textsubscript{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 \(\alpha\)-hydroxyboronates.\textsuperscript{7}

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Over the past eight years, research has focused on boron-substituted quaternary carbons. Using a copper complex, they developed an enantioselective pathway to the α-amino boronate esters via an addition of B₂pin₂ to N-aryl aldehydes with complete selectivity over secondary bromides. Ellman et al. reported that the (Cy)CuCl₂ added to alkenes of acyclic α,β-unsaturated esters, aldehydes, 13 amides, 14 and ketones. These processes are efficiently catalyzed by N-heterocyclic carbene (NHC) complexes of copper(I). Hoveyda’s group applied this strategy to trisubstituted 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). Excellent regioselectivities were observed with a high level of functional group tolerance.

**References**