Introduction

Bis(pinacolato)diboron (B₂pin₂, 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(sp³)–H and C(sp³)–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, B₂pin₂ 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(sp³)–H Activation

Very recently, Sawamura et al. reported a rhodium-catalyzed C(sp³)–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 B₂pin₂ 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
Over the past eight years, research has focused on copper complexes, they developed an enantioselective pathway to the synthesis of alkylboronates, catalyzed by complexes of palladium. Di-tertiary boronates is possible. Using an aldehyde, allylic alcohols were obtained via a one-pot borylation–allylation process. Starting from primary alkyl bromides, Biscoe et al. reported the synthesis of α,β-unsaturated esters, amides, 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 68–82% yield at 14–99% ee.

References