Bis(pinacolato)diboron

Compiled by Xinyu Liu

Xinyu Liu was born in Shenyang, China in 1978. He studied chemistry in Kyoto University, Japan and received his B.E. in 2002. From April 2001 to May 2003, he was a research student in the group of Prof. Tamejiro Hiyama, Kyoto University, where he worked on the synthetic applications of stereoselectively generated CF3-substituted lithio-oxirane. In June 2003, he moved to ETH Zürich, Switzerland, and is currently working towards his Ph.D. degree under the supervision of Prof. Peter H. Seeberger.

Laboratorium für Organische Chemie, ETH Hönggerberg, Wolfgang-Pauli-Strasse 10, 8093 Zürich, Switzerland
E-mail: xliu@org.chem.ethz.ch

Introduction

Since Brown’s discovery of the hydroboration reaction, organoboron compounds have found wide application in organic synthesis.1 The synthesis of functional organoboranes has mostly relied on either the hydroboration of unsaturated hydrocarbons or the transmetalation between an organometallic precursor and an appropriate boron compound.

In 1993, Miyaura’s group reported the first platinum(0)-catalyzed vic-diboration of alkynes using bis(pinacolato) diboron (1).2 This group subsequently expanded the substrates to alkynes, 1,3-dienes, allenes, and α,β-unsaturated ketones.3 These reactions provide new alternatives to access the functional organoboron compounds and also popularized diboron 1 as a new boron source.

B2pin2 is used preferentially over other (alkoxo)diborons, because both the borylated products derived from it and itself can be handled in air and exhibit high stability towards hydrolysis, which facilitate reaction workup and purification.

Abstracts

(A) In the presence of a platinum(0) catalyst, 1 undergoes addition reaction to alkynes to give exclusive cis-diborylated alkenes.2,9 This reaction works very well on both terminal and internal alkynes. It also tolerates various functional groups in the side chain of R1 and R2, such as epoxy, cyano, and carbonyl groups. The key for this type of reaction is the oxidative addition of Pt(0) to B2pin2, forming a bis(boryl)platinum(II) complex.

(B) By modifying the platinum catalyst to Pt(dba)2, 1 undergoes cis-fashion addition to alkenes very smoothly.10 However, the substrate alkenes are limited to terminal alkenes and strained cyclic alkenes (cyclopentene and norbornene) under the given conditions.

(C) In the presence of a Pd catalyst, a direct cross-coupling reaction between 1 and aryl halides (including triflates) occurs.11 This reaction is now mostly referred to the Miyaura boration reaction in the literature. It has very broad functional group tolerance on the aromatic ring, hence has become a powerful method to construct aryl boronate for Suzuki–Miyaura coupling. It has been applied to the key diaryl synthesis in several natural product total syntheses.12
(D) By properly adjusting the palladium catalysts, bases, and solvents, a direct cross-coupling between 1 and alkenyl halides (including triflates) was achieved with the retention of the geometry of double bonds. This strategy allowed more diversified access to alkenyl boronates, in addition to the hydroboration reaction. By adopting this strategy, a one-pot synthesis of unsymmetrical 1,3-dienes was realized.

(E) Hartwig’s group achieved the catalytic terminal borylation of linear alkanes in the presence of a Rh catalyst under thermal conditions for the first time. The key intermediate was postulated as a rhodium mono(boryl) complex, which can activate the terminal C–H bond of a linear alkane. This reaction was applied to the functionalization of polyolefins in the melt by the same group.

(F) A mild protocol for catalytic borylation of arenes was developed using a Ir(I)/2,2'-bipyridine complex. The potential intermediate for this reaction was identified as an unusual iridium-tri(boryl) complex, which can activate the terminal C–H bond of a 1-haloalkene, to give idene type carbenoids, which are available from 1,1-dihaloalkenes and boronates, in addition to the hydroboration reaction. By adopting this strategy, a one-pot synthesis of unsymmetrical 1,3-dienes was realized.

(H) In contrast to the extensive use of Bpin₂ in transition-metal catalyzed reactions, Hiyama’s group disclosed that 1 reacts with alkylidene type carbeneoids, which are available from 1,1-dihaloalkanes and 1-haloalkenes, to give geni-diborylated alkenes. The reaction proceeds via the borate complex formation between 1 and 1-halo-1-lithio alkene, followed by stereospecific 1,2-migration of the boron substituents.

(I) Diboron 1 undergoes smooth reaction with the stereoselectively generated CF₃-substituted lithio-oxirane to afford β-CF₃ alkenylborane in excellent diastereoselectivity.

References


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