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Platinum(0)-Catalysed Diboration of Alka-1,3-dienes with Bis(pinacolato)diboron

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Abstract: The addition of bis(pinacolato)diboron (1) to 1,3-dienes was achieved in the presence of platinum(0) catalyst. The addition of the diboron to 1,3-butadiene or isoprene with Pt(PPh₃)₄ regio- and stereoselectively produced (Z)-1,4-bis(boryl)-2-butenes (3a and 3b) at 80 °C in toluene. On the other hand, the Pt(dba)₂-catalyzed reaction of the diboron with isoprene (3 equivs) at room temperature exclusively produced (E,E)-1,8-bis(boryl)-3,6-dimethyl-2,6-octadiene (4) resulting from a formal dimerization \rightarrow 1,8-diboration process.

The addition of the hydrogen-metal or the metal-metal bonds to 1,3-dienes using the transition-metal-catalyzed protocol has attracted considerable attention as a powerful route to prepare synthetically useful allylic metal reagents. Hydrosilanes,¹ disilanes,² digermanes,³ or silylstannanes⁴ smoothly adds to the dienes in the presence of a variety of transition-metal catalysts to produce the corresponding 1:1 adduct (metal reagent : diene) having one or two allylic metal units. Careful tuning of both the catalysts and the reaction conditions allows the formal dimerization \rightarrow 1,8-addition reaction leading to the 1:2 adduct.^{1,2,5} Although the corresponding reaction of boron derivatives has not yet been well studied, the palladium(0)-catalyzed 1,4-hydroboration of conjugated dienes with catecholborane stereoselectively gave (Z)-allylic boronates.⁶

Recently, we have found that the addition of bis(pinacolato)diboron (1) to alkynes to give cis-bis(boryl)alkenes is effectively catalyzed by platinum(0) complex.⁷ The rhodium(I)- or gold(I)-catalyzed diboration of alkenes with bis(catecholato)diboron has been also reported by Baker and Marder.⁸ The mechanism, which involves the B-B bond activation by its oxidative addition to low-valent transition-metal complexes,^{7,9} is closely similar to that for the related disilylation,² distannylation,¹⁰ and silylstannylation¹¹ reactions. Thus, the results prompted us to develop a novel route

to bis-allylboronates (3 and 4) via the addition of diboron (1) to 1,3-dienes (eqs. 1 and 2).

When isoprene (2b) (1.5 equiv) was allowed to react with 1 (1.0 equiv) at 80 °C for 4 h in the presence of 3 mol% of Pt(PPh₃)₄ in DMF, the 1:1 adduct (3b) was obtained in a yield of 57% as the sole product. The use of toluene in place of DMF accelerated the addition rate improving the yield to 78% (eq 1). ¹H NMR spectra exhibited a doublet at 1.59 ppm (=CHCH₂) and a singlet at 1.65 ppm (=CMeCH₂) indicating the formation of 1,4-addition product as a single isomer. The (*Z*)-conformation with an isomeric purity over 99% was immediately established by the presence of one vinylic proton at 5.23 ppm and an NOE (5.0%) between the vinylic proton and the methyl protons at 1.73 ppm.

Similar reaction with 1,3-butadiene gave a 1,4-addition product (3a), a GC analysis revealing the formation of a single compound with high yield, but the isolation was somewhat troublesome. The product was rather unstable partially decomposing during the distillation, presumably due to the decomposition catalyzed by the platinum residue. However, the quick trap-to-trap distillation within 5 min allowed the isolation of almost pure 3a in a 89% yield.

insert Eq 1

Quite interestingly, the change of the catalyst resulted in dimerization of diene during the addition of the diboron. The addition of 1 to isoprene (1.5 equivs) at 80 °C in toluene afforded a 1:2 adduct (4) (37%) together with a 1:1 adduct (3b) (ca. 20%) when using Pt(dba)₂ as a catalyst. Although the reaction with a phosphine-based platinum catalyst was very slow at room temperature, Pt(dba)₂ exhibited high catalytic activity readily undergoing even at room temperature to yield 57% of 4 and ca. 6% of 3b. Finally, a 94% yield was regio- and stereoselectively achieved when using 3 equivs of isoprene at room temperature (eq 2). The four methylene protons adjacent to the borons exhibited one doublet at 1.59 ppm (*J* = 6.1 Hz) indicating the symmetrical structure derived from the head-to-head dimerization. An NOE (7.0%) between the vinylic protons and internal allylic methylene protons at 2.06 ppm revealed the (*E,E*) configuration.

insert Eq 2

Like other related reactions catalyzed by transition-metals, especially the catalytic additions of disilanes and silylstannanes to 1,3-dienes,^{2,4} the present 1,4-diboration shown in eq 1 may involve (a) the oxidative addition of the B-B bond to the platinum(0) complex giving bis(boryl)platinum(II) complex (5), (b) the insertion of a diene to the B-Pt bond to form p-allyl(boryl)platinum(II) intermediate (6), and finally (c) the reductive elimination to give 3 (Figure 1). It was anticipated that the syn-6 readily isomerizes to the thermally more stable anti-6,¹² but the reductive elimination (6 to 3), which has been often regarded as the rate determining step, can be reasonably faster than that of syn-anti isomerization. However, the mechanism for the dimerization-diboration reaction shown in eq 2 remains controversial. Tsuji has recently proposed a sequence of dimerization of dienes within a palladium coordination sphere followed by addition of a disilane for the mechanism of the palladium(0)-catalyzed addition of disilanes to 1,3-dienes,¹³ but another quite possible process proceeding through the insertion of diene to the B-Pt or the C-Pt bond in 6 can not be disregarded because the present reaction competitively afforded a mixture of 1:1 and 1:2 adducts when using less than two equivalents of isoprene. Such dimerization via the stepwise insertion process can be well catalyzed by a platinum complex without phosphine ligand because the generation of a coordinatively unsaturated platinum(II) species allows the coordination of a diene to 6.

insert Figure 1

In conclusion, we communicated the first example of the conjugated addition of tetrakis(alkoxy)diboron to 1,3-dienes, which was efficiently catalyzed by platinum(0) complex to regio- and stereoselectively provide synthetically useful allylic boron compounds. Details of the mechanism, the reaction scope including the diboration of other dienes such as allenes, and the synthetic application are under current investigation.

Footnotes

The synthesis of 3b: To Pt(PPh₃)₄ (0.03 mmol) and 1 (1.0 mmol) were successively added toluene (6 ml) and isoprene (1.5 mmol), and the resulting solution was then stirred at 80 °C for 4 h in a sealed reaction tube. The Kugelrohr distillation gave a 78% yield of 3: ¹H NMR (400 MHz, CDCl₃) δ 1.23 (s, 12 H), 1.24 (s, 12 H), 1.59 (d, 2 H, J = 7.3 Hz),

1.65 (s, 2 H), 1.73 (d, 3 H, $J = 1.2$ Hz), 5.23 (dt, 1 H, $J = 1.2, 7.4$ Hz) [the irradiation of the vinylic proton at 5.23 ppm resulted in an 5.0% enhancement of the allylic methyl signal at 1.73 ppm]; ^{13}C NMR (100 MHz, CDCl_3) δ 24.71, 24.77, 25.67, 82.97, 117.68, 132.11; ^{11}B NMR (128 MHz, CDCl_3) δ 33.12; MS (EI) m/e 41 (24), 59 (18), 69 (19), 84 (100), 95 (20), 108 (7), 129 (6), 165 (8), 179 (7), 194 (5), 207 (8), 222 (4), 265 (4), 307 (0.7), 322 (0.7, M⁺); exact mass calcd for $\text{C}_{17}\text{H}_{32}\text{O}_4\text{B}_2$ m/e 322.2487, found m/e 322.2498.

A similar reaction with 1,3-butadiene at 80 °C for 16 h gave a 89% yield of 3a:

The synthesis of 4: A mixture of $\text{Pt}(\text{dba})_2$ (0.03 mmol), diboron 1 (1.0 mmol), and isoprene (3.0 mmol) in toluene (6 ml) was stirred at room temperature for 16 h in a sealed reaction tube. GC analysis revealed the formation of 4 in 94%: ^1H NMR (400 MHz, CDCl_3) δ 1.24 (s, 24 H), 1.58 (s, 6 H), 1.59 (d, 4 H, $J = 6.1$ Hz), 2.06 (s, 4 H), 5.24 (t, 2 H, $J = 7.2$ Hz) [the irradiation of the vinylic protons at 5.24 ppm resulted in an 7.0% enhancement of the internal allylic methylene signal at 2.06 ppm]; ^{13}C NMR (100 MHz, CDCl_3) δ 15.91, 24.74, 38.75, 83.01, 118.20, 135.52; ^{11}B NMR (128 MHz, CDCl_3) δ 33.28; MS (EI) m/e 41 (22), 55 (26), 69 (21), 83 (100), 95 (23), 101 (32), 121 (10), 149 (11), 195 (25), 208 (5), 235 (11), 249 (23), 275 (6), 290 (11), 307 (2), 375 (2), 390 (4, M⁺); exact mass calcd for $\text{C}_{22}\text{H}_{40}\text{B}_2\text{O}_4$ m/e 390.3113, found m/e 390.3133.

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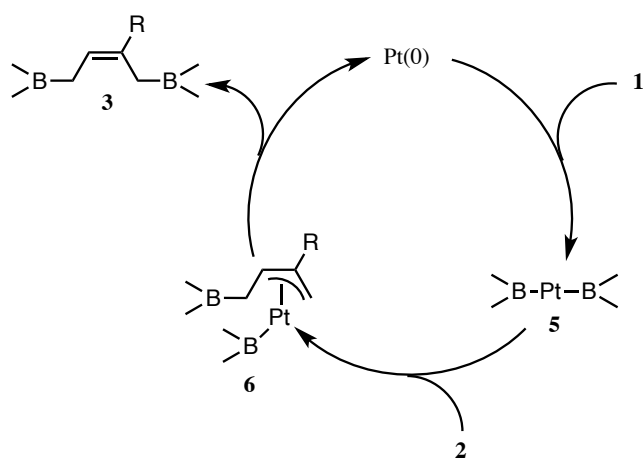
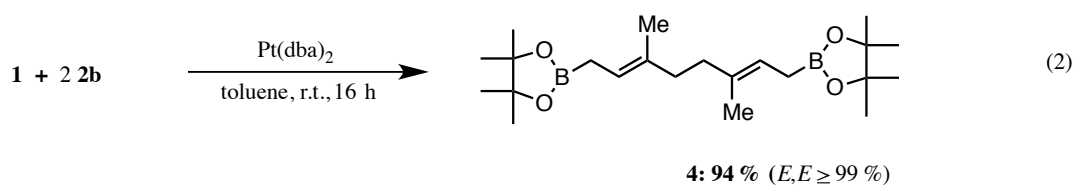
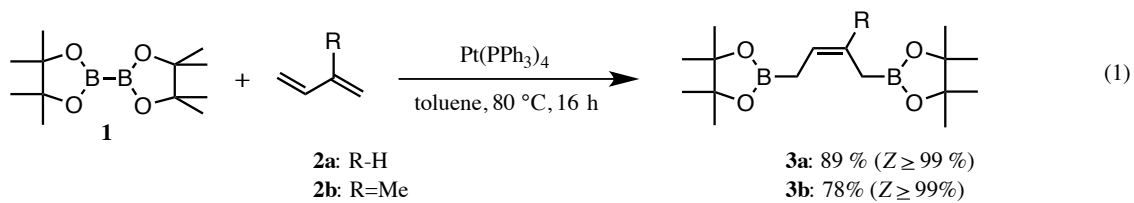


Figure 1