Platinum(0)-catalysed diboration of alka-1,3-dienes with bis(pinacolato)diboron

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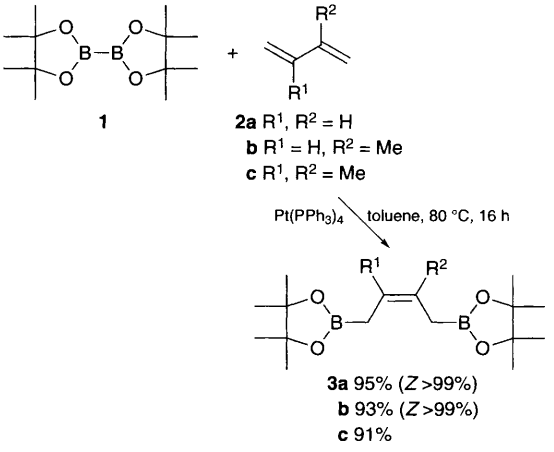
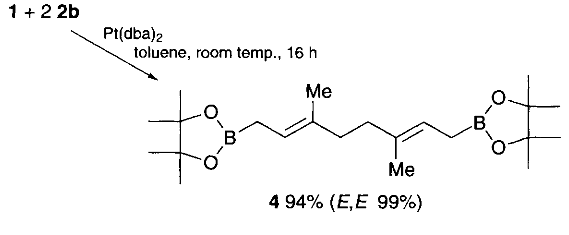
Bis(pinacolato)diboron 1 is selectively added to 1,3-dienes in the presence of an platinum(0) catalyst.

Addition of hydrogen–metal or metal–metal bonds to 1,3-dienes using transition metal-catalysed protocols has attracted considerable attention as a powerful route to prepare synthetically useful allylic metal reagents. Hydrosilanes,[1] disilanes,[2] digermanes[3] or silylstannanes[4] smoothly add 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–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)-catalysed 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 catalysed by the platinum(0) complex.[7] The rhodium(I)- or gold(I)-catalysed diboration of alkenes with bis(catecholato)diboron has been reported by Baker and Marder.[8] The mechanism, which involves B–B bond activation by its oxidative addition to low-valent transition metal complexes,[7,9] is similar to that for the related disilylation,[2] distannylation[10] and silylstannylation reactions.[11] Thus, the results prompted us to develop a novel route to bis(allyl)boronates **3** and **4** *via* the addition of diboron **1** to 1,3-dienes [eqns. (1) and (2)].



(1)



(2)

When isoprene **2b** (1.5 equiv.) was allowed to react with **1** (1.0 equiv.) at 80 °C for 16 h in the presence of 3 mol% of $Pt(PPh_3)_4$ in DMF, the 1 : 1 adduct **3b** was obtained in 57% yield as the sole product. The use of toluene in place of DMF accelerated the addition rate improving the yield to 93% [eqn. (1)]. ^1H NMR spectra exhibited a doublet at δ 1.59 ($=CHCH_2$) and a singlet at δ 1.65 ($=CMeCH_2$) indicating the formation of 1,4-addition product as a single isomer. The identity of the (*Z*)-conformation, with an isomeric purity of over 99%, was immediately established by the presence of one vinylic proton at δ 5.23 and an NOE (5.0%) between the vinylic proton and the methyl protons at δ 1.73.

Similar reactions of **1** with buta-1,3-diene and 2,3-dimethylbuta-1,3-diene stereoselectively provided **3a** and **3c** in 95 and 91% yields, respectively.† The addition product to butadiene **3a** was rather unstable, partially decomposing during the distillation; however, rapid trap-to-trap distillation within a short period allowed the isolation of almost pure compound.

Interestingly, changing the catalyst resulted in dimerization of the diene during the addition of the diboron. The addition of **1** to isoprene (1.5 equiv.) 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 catalyst. Although the reaction with a phosphine-based platinum catalyst was very slow at room temperature, $Pt(dba)_2$ exhibited high catalytic activity, readily reacting even at room temperature to yield **4**‡ and **3b** in 57 and *ca.* 6% yields respectively. Finally, a 94% yield was regio- and stereo-selectively achieved when using 3 equiv. of isoprene at room temperature [eqn. (2)]. The four methylene protons adjacent to the borons exhibited one doublet at δ 1.59 (*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 δ 2.06 revealed the (*E*,*E*)-configuration.

Like other related reactions catalysed by transition metals, especially the catalytic additions of disilanes and silylstannanes to 1,3-dienes,[2,4] the present 1,4-diboration shown in eqn. (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 π-allyl(boryl)platinum(II) intermediate **6**, and finally (*c*) the reductive elimination to give **3** (Fig. 1). It was anticipated that the *anti*-**6** might isomerize to the thermally more stable *syn*-**6**,[12]

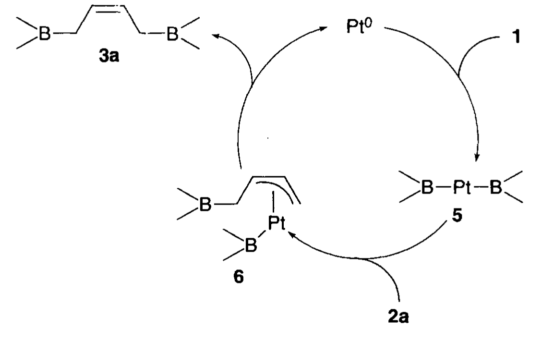


Fig. 1

but the reductive elimination (**6** to **3**) appears to be faster than the *syn–anti* isomerization.

However, the mechanism for the dimerization–diboration reaction shown in eqn. (2) remains controversial. Tsuji has recently proposed a sequence of dimerization of dienes within a palladium coordination sphere followed by addition of disilane for the mechanism of the palladium(0)-catalysed reaction of disilanes with 1,3-dienes,[13] but another possible process proceeding through the insertion of diene into the B–Pt or C–Pt bond in **6** cannot be disregarded because the present reaction competitively afforded a mixture of 1 : 1 and 1 : 2 adducts when using less than 2 equiv. of isoprene. Such dimerization *via* a stepwise insertion process can be easily catalysed by a platinum complex without phosphine ligands because the generation of a coordinatively unsaturated platinum(II) species allows further coordination of a diene to **6**.

Footnotes

† A representative procedure for **3**: To Pt(PPh$_3$)$_4$ (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 16 h in a sealed reaction tube. Concentration of the reaction mixture and Kugelrohr distillation gave **3b** in 93% yield: bp 110 °C/0.1 mmHg (oven temperature); ^{1}H NMR (400 MHz, CDCl$_3$) 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) and 5.23 (dt, 1 H, *J* 1.2, 7.4 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 24.71, 24.77, 25.67, 82.97, 117.68 and 132.11; ^{11}B NMR (128 MHz, CDCl$_3$ δ 33.12.

‡ *Synthesis* of **4**: A mixture of Pt(dba)$_2$ (0.03 mmol), diboron **1** (1.0 mmol) and isoprene (3.0 mmol) in toluene (6 ml) was stirred at room temp. for 16 h in a sealed reaction tube. GC analysis revealed the formation of **4** in 94%: ^{1}H 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) and 5.24 (t, 2 H, *J* 7.2 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 15.91, 24.74, 38.75, 83.01, 118.20 and 135.52; ^{11}B NMR (128 MHz, CDCl$_3$) δ 33.28.

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