Diboration of Alkenes with Bis(pinacolato)diboron Catalysed by Platinum(0) Complex

Tatsuo Ishiyama, Masafumi Yamamoto, and Norio Miyaura*
Division of Molecular Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060, Japan

Abstract: Bis(pinacolato)diboron (1) added to alkenes (2), such as 1-decene, styrene, and cyclopentene, in the presence of a catalytic amount of Pt(dba)2 at 50。C in toluene to provide the corresponding bis(boryl)alkanes (3) in 76-86% yields.

Increasing attention has been focused on the transition metal-catalysed addition of boron-heteroatom reagents such as thioboranes,1 stannylboranes,2 and silylboranes3 to unsaturated hydrocarbons as a powerful tool for preparing functionalized organoboron compounds. We have recently found that the addition reaction of bis(pinacolato)diboron (1) to both terminal and internal alkynes is effectively catalysed by platinum(0) complexes to provide a new access to isomerically pure cis-bis(boryl)alkenes.4,5 Following our preliminary communication had appeared, a similar reaction of alkenes with bis(catecholato)diboron was reported by Baker, Marder, Westcott, and their co-workers using Rhodium(I) or Gold(I) catalyst.6 However, the practical use of the method is severely limited due to the low catalytic activity of the complexes or the formation of side products arising from b-hydride elimination. In the course of our study directed toward the catalytic diboration of unsaturated compounds, we attempted to apply the platinum(0) catalyst system for the diboration of alkene (2) with 1 and found that the addition was efficiently proceeded in the presence of a phosphine-free platinum(0) catalyst, Pt(dba)2, to give the corresponding bis(boryl)alkanes (3) in high yields.

Our initial studies were carried out using Pt(PPh3)4 catalyst which worked well for the alkyne diboration of 1;4,5 however, this catalyst exhibited no catalytic activities for the reaction of 2. Most recently , we have reported the platinum(0)-catalysed addition

of 1 to 1,3-alkadienes.7 The reaction with Pt(PPh3)4 catalyst proceeded by a 1,4-manner to give (Z)-1,4-bis(boryl)-2-butenes and that with Pt(dba)2 catalyst proceeded through a formal dimerization ≀ 1,8-addition process to produce (E,E)-1,8-bis(boryl)-2,6-octadienes. It is also worth noting that Pt(dba)2 showed high catalytic activity rather than Pt(PPh3)4; the Pt(PPh3)4-catalysed reaction required high temperature (80 。C), whereas the Pt(dba)2-catalysed reaction completed even at room temperature. The results prompted us to examine the alkene diboration using Pt(dba)2 catalyst (Scheme 1).

insert Scheme 1

The representative results are summarized in Table 1. The diboration of monosubstituted alkenes proceeded smoothly with Pt(dba)2 catalyst. When 1-decene 2a (1.5 equiv) was allowed to react with 1 (1.0 equiv) in toluene at 50 。C in the presence of 3 mol% of Pt(dba)2, the addition was completed within 1 h to afford the desired 1,2-bis(boryl)decane 3a in 82% yield. Similar reaction with vinylarenes, such as styrene 2b (1.5 equiv) and 4-methoxystyrene 2c (3.0 equiv), also provided the corresponding diborated products 3b and 3c in yields of 86% and 76%, respectively. Although Baker et al. have already shown the catalytic addition of bis(catecholato)diboron to 2c, the rhodium(I)-catalysed reaction only gave 10-44% yields of 1,2-bis(boronate) ester and the gold(I)-catalyzed reaction required 8 mol% of catalyst.6 In the case of the reaction with disubstituted alkenes, the yields of 3 was markedly affected by the substituents on 2. Cyclopentene 2d (1.5 equiv) and norbornene 2e (3.0 equiv) successfully underwent the reaction to produce the bis(boryl)alkanes 3d and 3e in 85% yield while all attempts at the reaction with 4-octene, stilbene, cyclohexene, and 2-methylpropene were failed, indicating that the reactivity difference between these may be attributed to both the steric hindrance and the internal strain energy of 2. The cis addition of 1 to 2 was immediately established by 1H NMR spectra of 3e, which exhibited only one methyl singlet at 1.24 ppm. Since electrophilic addition to 2e generally proceed by attack of the exo face, syn-exo-2,3-bicyclo[2.2.1]heptane is the most likely product.

insert Table 1

Although we have not yet conducted mechanistic studies, the present diboration of alkenes may proceed through the catalytic cycle as similar to the reaction with alkynes4,5,8,9 and 1,3-alkadienes,7 which involves (a) the oxidative addition of 1 to the platinum(0) complex giving bis(boryl)platinum(II) intermediate (4), (b) the insertion of 2 into the boron-platinum bond to form alkyl(boryl)platinum(II) species (5), and (c) the reductive elimination of 3 (Fig. 1). A similar mechanism was also proposed for the palladium-catalysed addition of thioboranes1 and stannylboranes2 to alkynes.

insert Fig. 1

Recently, Baker9 and Smith10 independently reported that phosphine dissoiciation from 4 is a critical step in the alkyne diboration with phosphine-based platinum(0) catalyst. Thus, the high catalytic activity of Pt(dba)2 over Pt(PPh3)4 observed in the present reaction may be reasonably explained by a facile exchange between dibenzylideneacetone ligand and 2, which enhance the rate of the insertion step.

In summary, we demonstrated that the phosphine-free platinum(0) complex, Pt(dba)2, effectively catalyzed the diboration of simple alkenes. Further investigation are in progress in an attempt to extend the reaction scope, to clarify the reaction mechanism, and to apply the method for organic synthesis.

Footnotes

A representative procedure for 3: The flask was charged with Pt(dba)2 (0.03 mmol) and 1 (1.0 mmol) and flushed with nitrogen. Toluene (6 ml) and 2 (1.5-3.0 mmol) were successively added, and the resulting solution was then stirred at 50 。C for 1 h. Concentration of the reaction mixture and Kugelrohr distillation gave the bis(boryl)alkanes: 3a: 1H NMR (400 MHz, CDCl3) d 0.79 (dd, 1 H, J 6.0, 15.6 Hz), 0.87 (t, 3 H, J 6.8 Hz), 0.87 (dd, 1 H, J 9.5, 15.6 Hz), 1.0-1.5 (m, 15 H), 1.22 (s, 12 H) and 1.23 (s, 12 H); 13C NMR (100 MHz, CDCl3) d 14.10, 22.69, 24.73, 24.77, 24.83, 24.90, 28.86, 29.28, 29.56, 29.86, 31.91, 33.83, 82.71 and 82.78; 11B NMR (128 MHz, CDCl3) d 34.14; exact mass calcd for C22H4404B2 m/e 394.3426, found m/e 394.3405. 3b: 1H NMR (400 MHz, CDCl3) d 1.11 (dd, 1 H, J 5.7, 16.0 Hz), 1.17 (s, 6 H), 1.19 (s, 6 H), 1.20 (s, 12 H), 1.38 (dd,

1 H, J 11.0, 15.9 Hz), 2.52 (dd, 1 H, J 5.6, 11.0 Hz), 7.07-7.13 (m, 1 H) and 7.22 (d, 4 H, J 4.4 Hz); 13C NMR (100 MHz, CDCl3) d 24.46, 24.65, 24.68, 24.95, 83.01, 83.18, 124.87, 127.89, 128.12 and 145.38; 11B NMR (128 MHz, CDCl3) d 33.62; exact mass calcd for C20H3204B2 m/e 358.2487, found m/e 358.2533. 3c: 1H NMR (400 MHz, CDCl3) d 1.08 (dd, 1 H, J 5.9, 15.9 Hz), 1.18 (s, 6 H), 1.19 (s, 6 H), 1.20 (s, 12 H), 1.33 (dd, 1 H, J 11.0, 15.9 Hz), 2.46 (dd, 1 H, J 5.7, 10.9 Hz), 3.76 (s, 3 H), 6.78 (dt, 2 H, J 2.6, 8.8 Hz) and 7.14 (dt, 2 H, J 2.4, 8.3 Hz); 13C NMR (100 MHz, CDCl3) d 24.45, 24.63, 24.65, 24.91, 55.13, 82.94, 83.08, 113.56, 128.69, 137.43 and 157.08; 11B NMR (128 MHz, CDCl3) d 33.53; exact mass calcd for C21H3405B2 m/e 388.2593, found m/e 388.2569. 3d: 1H NMR (400 MHz, CDCl3) d 1.23 (s, 12 H), 1.24 (s, 12 H), 1.35-1.45 (m, 2 H), 1.45-1.55 (m, 1 H), 1.55-1.65 (m, 3 H) and 1.65-1.75 (m, 2 H); 13C NMR (100 MHz, CDCl3) d 24.71, 24.82, 25.61, 28.58 and 82.72; 11B NMR (128 MHz, CDCl3) d 34.04; exact mass calcd for C17H3204B2 m/e 322.2487, found m/e 322.2462. 3e: 1H NMR (400 MHz, CDCl3) d 1.11 (s, 2 H), 1.13 (d, 1 H, J 9.5 Hz), 1.24 (s, 24 H), 1.25-1.30 (m, 2 H), 1.45 (d, 1 H, J 9.03 Hz), 1.52 (d, 2 H, J 7.3 Hz) and 2.27 (s, 2 H); 13C NMR (100 MHz, CDCl3) d 24.71, 24.82, 32.01, 37.91, 39.21 and 82.77; 11B NMR (128 MHz, CDCl3) d 33.58; exact mass calcd for C19H3404B2 m/e 348.2643, found m/e 348.2666.

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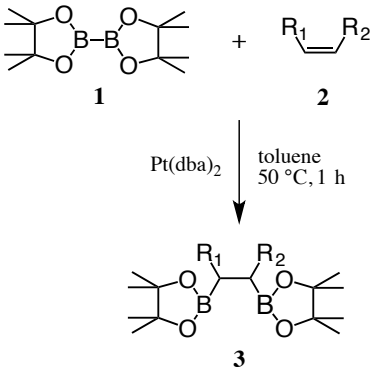
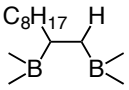
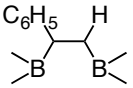
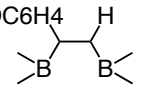
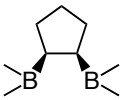
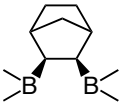


Scheme 1

Table 1 $Pt(dba)_2$-catalysed addition of **1** to **2**[a]

Alkene	Product	Yield (%)[b]
1-Decene		82
2a	**3a**	
Styrene		86
2b	**3b**	
4-Methoxystyrene		76[c]
2c	**3c**	
Cyclopentene		85
2d	**3d**	
Norbornene		85[c]
2e	**3e**	

a All reactions were carried out at 50 °C for 1 h with use of Pt(dba)$_2$ (0.03 mmol), **1** (1.0 equiv), **2** (1.5 equiv), and toluene (6ml). [b] Isolated yields based on **1**. [c] 3.0 equiv of **2** was used.

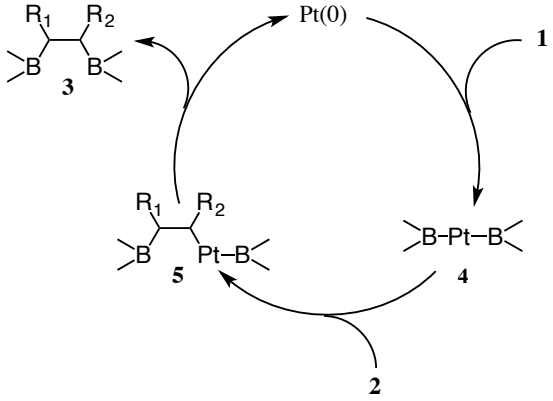


Fig. 1