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Platinum(0)-Catalyzed Diboration of Methylenecyclopropanes with Bis(pinacolato)diboron: A Selective Route to 2,4-Bis(boryl)-1-butenes

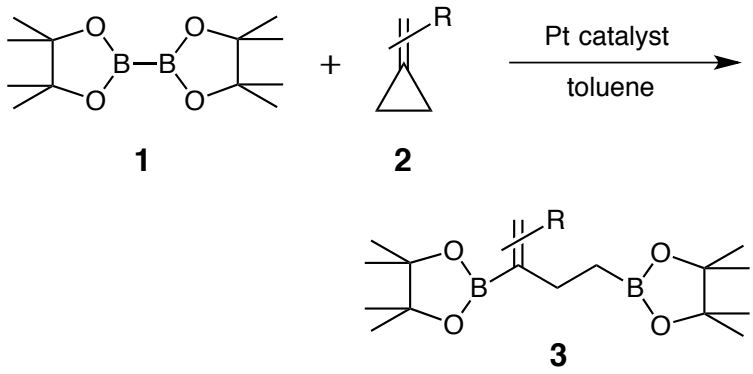
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Abstract: The platinum(0)-catalyzed diboration of methylenecyclo-propanes with bis(pinacolato)diboron [$(Me_4C_2O_2)B$-$B(O_2C_2Me_4)$] in toluene selectively provided the corresponding 2,4-bis(boryl)-1-butene and its analogs in good yields through the cleavage of the proximal bond of the cyclopropane ring.

Key words: diboron, platinum, methylenecyclopropane

The addition of the boron-boron bond to unsaturated hydrocarbons is an attractive and straightforward method to directly introduce two boryl groups into organic molecules. Although tetrakis(alkoxo)diborons are inert to ionic reactions, its oxidative addition to platinum(0) or rhodium(I) complexes allows the catalytic diboration of unsaturated hydrocarbons such as alkynes,[1] alkenes,[2] 1,3-dienes,[3] and allenes.[4] Since the reactions tolerate a wide variety of functional groups and proceed with highly regio- and stereoselective manner, the method provides an efficient and convenient route to bis(boryl)alkenes or -alkanes. The catalytic cycle involving an oxidative addition/ insertion/ reductive elimination sequence has been studied in detail.

The methylenecyclopropane and its derivatives are of interest as the substrate for the transition metal-catalyzed addition reactions due to their high and unique reactivities originating from its highly strained structure. The palladium-catalyzed reactions such as silylcyanation,[5] hydrocarbonation,[6] and hydroamination[7] give the products derived from the distal bond cleavage of the cyclopropane ring, whereas the proximal ring-opening products were reported in the palladium-catalyzed hydrostannation[8] and the rhodium-catalyzed hydrosilation.[9] Herein, we wish to describe the platinum-catalyzed addition reaction of bis(pinacolato)diboron (**1**) to methylenecyclopropanes (**2**) to afford the corresponding 2,4-bis(boryl)-1-butenes (**3**) through the proximal bond cleavage of cyclopropane ring (Eq. 1).



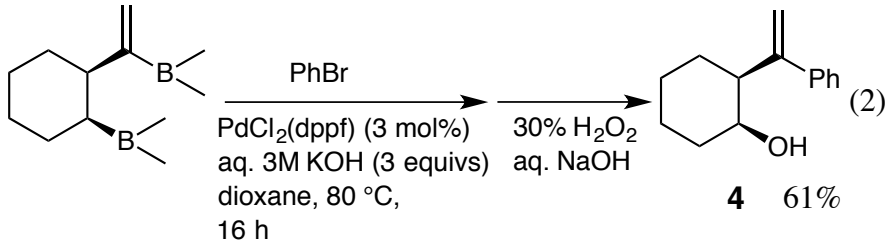
1 **2** **3** (1)

Representative results of the Pt-catalyzed diboration of **2** with **1** are summarized in Table 1. Methylenecyclopropene was initially chosen as a substrate and was allowed to react with **1** to optimize the reaction conditions. When methylenecyclopropane (1.1 mmol) was treated with **1** (1.0 mmol) in toluene at 80 °C for 5 h in the presence of 3 mol% of $Pt(PPh_3)_4$, the corresponding ring-opened diboration product **3** (R=H) was obtained in 75% yield, as a single isomer (run 1).[10] Similar reactions at 50 °C for 10 h in the presence of $Pt(dba)_2$/2P(*o*-tolyl)$_3$ or $Pt(dba)_2$/2P(cyclohexyl)$_3$ resulted in 62% and 68% yields respectively. The addition was further accelerated by platinum complex without a phosphine ligand. $Pt(dba)_2$ completed the addition within 3 h even at room temperature (run 1). Although the most of reaction was carried out in toluene, those reactions in DMF and dioxane resulted in similar yields and selectivity.

A variety of **2** bearing aryl and alkyl substituents at the three-membered ring or the double bond successfully participated in the $Pt(PPh_3)_4$-catalyzed reaction to provide the corresponding **3** with accompanying a less than 1% of unidentified by-product (runs 2-6). However, the increase of steric hindrance around the double bond significantly slowed down the reaction (runs 3 and 4). On the other hand, those reactions using $Pt(dba)_2$ resulted in relatively low yields due to the catalyst decomposition precipitating platinum metal and the formation of several by-products. The GC-Mass and ^{1}H NMR analyses indicated the formation of some by-products including a diboration product without ring-opening and the β-hydride elimination to provide a monoboration product.[2] A moderate regio- and stereoselectivity was observed in the diboration of **2** having an aryl and alkyl substituent. Thus, the substituent at the double bond exhibited a tendency to give *Z*-isomer, the stereoselectivity of which were slightly dependent on bulkiness of the substituent and ligand of the catalyst (runs 2 and 3). The ring substituent favored the formation of **3** having a substituent at the carbon adjacent to the double bond (C3), which derived from the ring cleavage at the less hindered proximal bond (runs 5 and 6).

The diboration of bicyclic **2** offered a stereochemical evidence for the cyclopropane ring-opening (runs 7-10). The C-C bond cleavage occurred with complete retention of configuration at the stereogenic center to provide *cis*-isomer as the sole product. The formation of *cis*-isomer was confirmed by its conversion into homoallylic alcohol **4**

via a cross-coupling/oxidation sequence. The presence of a doublet (J = 12.2 Hz) at 2.71 ppm was assignable to the allylic proton of *cis*-configuration (Eq. 2).



(2)

4 61%

The catalytic cycle may involve (a) oxidative addition of **1** to the platinum(0) complex producing a bis(boryl)platinum(II) intermediate (**5**), (b) regioselective insertion of **2** into the B-Pt bond to give a cyclopropylmethylplatinum(II) complex (**6**), (c) rearrangement to a homoallylplatinum(II) species (**7**), and finally (d) reductive elimination of **3** to regenerate a platinum(0) complex (Figure 1). The stoichiometric reaction between *cis*-$(Ph_3P)_2Pt(BO_2C_2Me_4)_2$[1b] and 2-phenylmethylene-cyclopropane at 50 °C for 3 h afforded a 64% yield of **3** with a regioselectivity same to the catalytic reaction, suggesting that the reaction is triggered by the oxidative addition of **1**. Another possible process starting from the oxidative addition of **2** to platinum(0) should be excluded because a stoichiometric reaction of **2** with $Pt(PPh_3)_4$ did not provide any evidences for oxidative addition.[11] Although both the rearrangement and the reductive elimination step are too rapid to observe the existence of **6** and **7**, the exclusive formation of *cis*-**3** in the reaction of bicyclic **2** (runs 7-10) suggested a four-centered cyclic transition state for the ring-opening rearrangement of **6**, which was proposed in the catalytic carbopalladation of **2**.[12]

References and Notes

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(10) A representative procedure for **3**: To a solution of $Pt(PPh_3)_4$ (0.03 mmol) and **1** (1.0 mmol) in toluene (6 ml) was added methylenecyclopropane[13] (1.1 mmol) under argon. The resulting solution was then stirred at 80 °C for 5 h in a sealed reaction tube. The reaction mixture was cooled to r.t. and submitted to a GC analysis. Kugelrohr distillation gave 2,4-bis(boryl)-1-butene: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, 2 H, *J* = 8.1 Hz), 1.16 (s, 12 H), 1.19 (s, 12 H), 2.20 (t, 2 H, *J* = 8.1 Hz), 5.54 (s, 1 H), 5.66 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.72, 24.82, 29.12, 82.83, 83.19, 127.57; ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.93, 34.11; HRMS, Found: *m/z*, 308.2321. Calcd for $C_{16}H_{30}O_4B_2$: M^+, 308.2330.
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Table 1. Pt-Catalyzed Diboration of **2** (Eq. 1)[a]

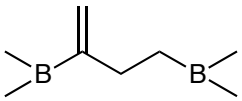
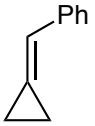
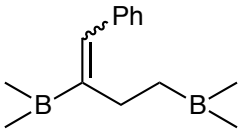
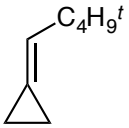
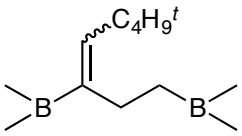
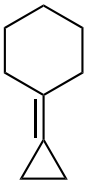
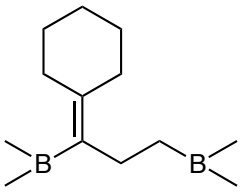
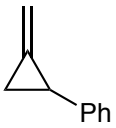
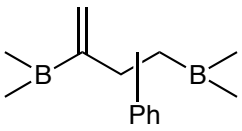
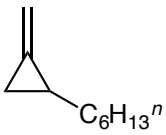
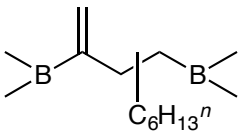
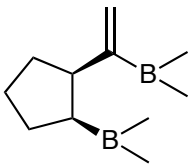
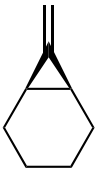
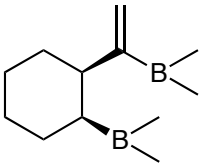
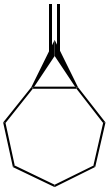
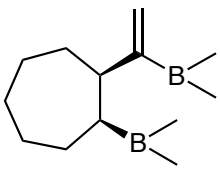
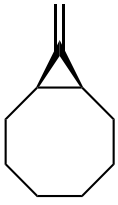
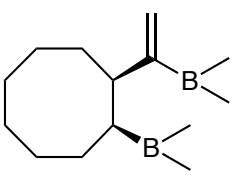
Run	**2**	Product (**3**)	Yield/%[b] (Time/h)	
			$Pt(PPh_3)_4$	$Pt(dba)_2$
1			75 (5)	71 (3)
2			66 (5) (68:32)[c]	60 (2) (92:8)[c]
3			60 (51) (75:25)[c]	15[d] (145) (74:26)[c]
4			57 (34)	36[d] (96)
5			72 (8) (63:37)[e]	54 (2) (57:43)[e]
6			60 (4) (61:39)[e]	54 (3) (79:21)[e]
7			60 (2)	32 (2)
8			60 (2)	45 (2)
9			69 (3)	52 (2)
10			75 (2)	68 (1)

Table 1 footnote

[a]The experimental procedure, see ref 10. $Pt(PPh_3)_4$-catalyzed reactions were conducted at 80 °C. $Pt(dba)_2$-catalyzed reactions were carried out at r.t.. [b]GLC yields based on **1**. [c]Ratios refer to *Z*:*E* ratios of **3**. [d]10 mol% of catalyst was used. [e]Ratios refer to 3-substituted **3**:4-substituted **3** ratios.

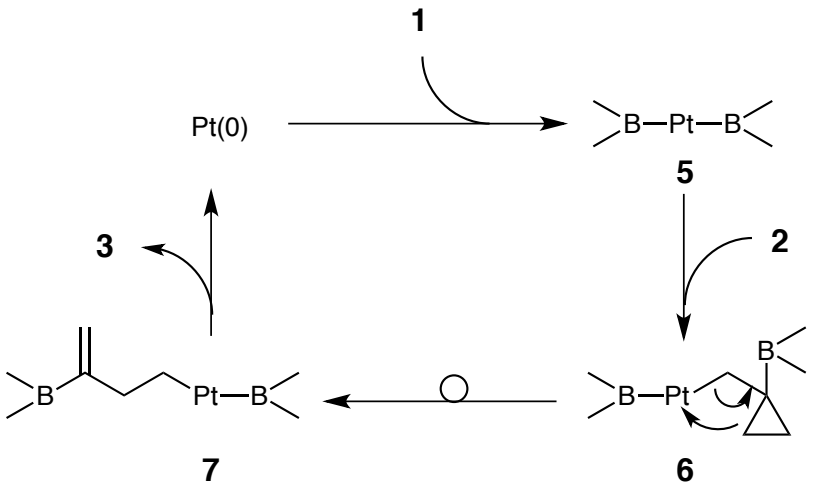


Figure 1. Proposed catalytic cycle