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Reactions of Cyanoboranes with a Palladium−PMe_3 Complex: Mechanism for the Catalytic Cyanoboration of Alkynes

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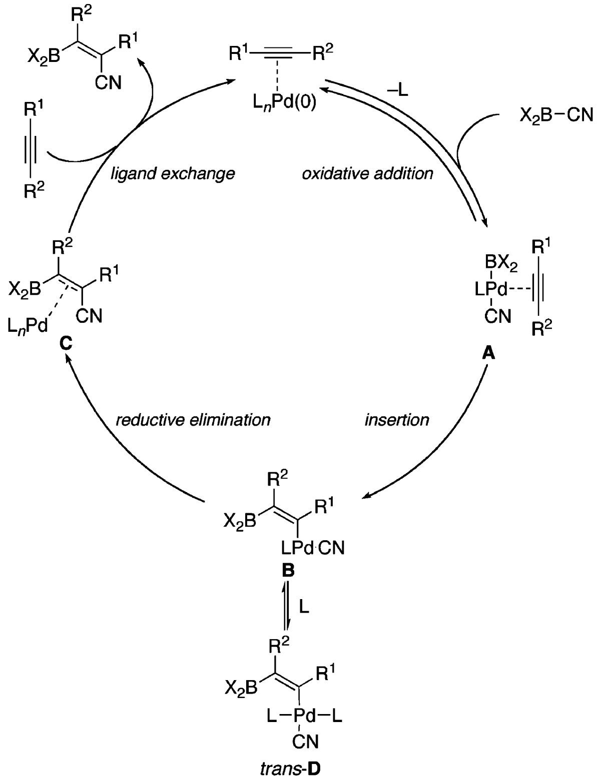
Summary: Reversible oxidative addition of the B−CN bond to palladium was observed in a reaction of a ^{13}C-labeled cyanoborane, having an N,N′-dimethyl-o-phenylenediamido ligand on the boron atom, with a palladium−PMe_3 complex, which was generated from (π-cyclopentadienyl)(π-allyl)palladium(II) with 2 equiv of PMe_3. The same borylbis(trimethylphosphine)-palladium(II) cyanide complex was formed in the reaction of borylbis(trimethylphosphine)palladium(II) chloride with trimethylsilyl cyanide. Reaction of the palladium−PMe_3 complex with a cyanoborane bearing a tethered carbon−carbon triple bond gave a (2-borylalkenyl)palladium(II) cyanide complex, whose structure was determined by a single-crystal X-ray analysis, via insertion of the C−C triple bond into the B−Pd bond of a transiently formed borylpalladium(II) cyanide complex. The (2-borylalkenyl)palladium(II) cyanide complex underwent reductive elimination at 60 °C. Significant retardation of the reductive elimination step by addition of 2 equiv of trimethylphosphine was observed.

Increasing attention has been paid to the transition-metal-catalyzed syntheses of organoboranes with growing demands for the development of efficient access to synthetically useful organoboron compounds.[1] Until recently, catalytic reactions such as hydroboration,[2] diboration,[3] stannaboration,[4] and silaboration[5] have been developed and utilized for organic synthesis. It seems to be critically important to get insight into the mechanisms of the catalytic reactions not only for improvement of the efficiency of the reaction but also for further exploration of new catalytic processes.[6]

We recently found new catalytic reactions that involve possible activation of the boron−cyanide bond of cyanoboranes.[7−9] The cyanoboration was catalyzed by palladium or nickel catalysts, leading to the addition of the boryl and cyano groups onto carbon−carbon triple bonds in a *cis*-fashion. The proposed mechanism involves a catalytic cycle consisting of oxidative addition, migratory insertion, and reductive elimination steps, which is commonly accepted for many transition metal-catalyzed addition reactions (Scheme 1).[9] Our interest was then focused on the validity of the proposed mechanism and on the further mechanistic details. Herein, we report the results of stoichiometric reactions of cyanoboranes with palladium complexes, which are closely related to the mechanism of the catalytic cyanoboration.

Scheme 1. Possible Mechanism for the Catalytic Cyanoboration of Alkynes



Cyanoboranes **1a−1d**, shown in Chart 1, were reacted in C_6D_6 at room temperature with an equimolar amount of a

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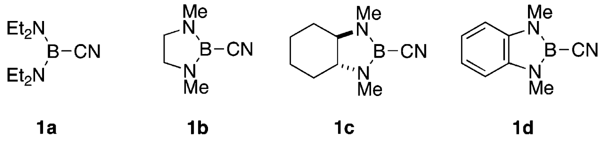
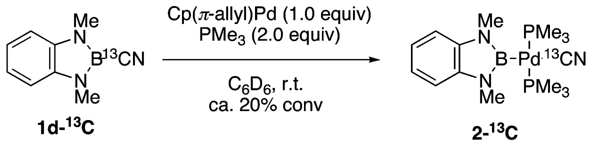
Chart 1. Structures of Cyanoboranes Used in the Reaction with a Palladium−PMe$_3$ Complex



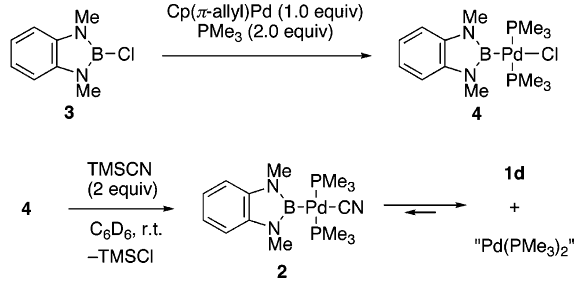
Scheme 2. Reaction of ^{13}C-Labeled Cyanoborane 1d-^{13}C with a “(PMe$_3$)$_2$Pd(0)” Complex Leading to Oxidative Addition



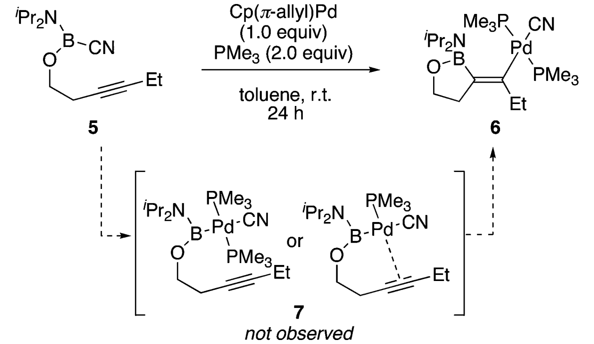
palladium complex “Pd(PMe$_3$)$_2$” generated from 2 equiv of trimethylphosphine with (π-cyclopentadienyl)(π-allyl)palladium(II).[10] ^{1}H NMR measurements suggested that an appreciable change was observed only in the reaction of **1d**, while no reactions took place for cyanoboranes **1a**−**1c**. We then carried out a reaction of cyanoborane **1d**-^{13}C, whose cyano carbon was labeled with ^{13}C (Scheme 2). The cyanoborane **1d**-^{13}C was prepared by reaction of the corresponding chloroborane with TMS-^{13}CN.[11] The ^{11}B NMR spectrum showed a doublet at 15.9 ppm (J_{B-C} = 108 Hz), while the corresponding coupled signal was observed at 119.7 ppm (J_{B-C} = 100−110 Hz) as a broad quartet in the ^{13}C NMR spectrum.[12] On reacting **1d**-^{13}C with “Pd(PMe$_3$)$_2$”, gradual conversion of **1d**-^{13}C into a new palladium complex was observed until ca. 20% conversion. The new palladium species showed characteristic signals at 145.8 ppm (br t, J_{C-P} = ca. 14−17 Hz) in the ^{13}C NMR spectrum, −16.4 ppm (d, J_{C-P} = 16.1 Hz) in the ^{31}P NMR spectrum, and 40.3 ppm (br s)[13] in the ^{11}B NMR spectrum. The lack of B−C coupling and the presence of a reasonable P−C coupling pattern for the newly formed complex may suggest that the *trans*-borylpalladium(II) cyanide complex **2** was formed in ca. 20% yield in the reaction mixture.

To obtain further evidence for the formation of the borylpalladium(II) cyanide species **2**, the generation of **2** was attempted independently via a different reaction pathway. The borylpalladium(II) chloride complex **4** was prepared via oxidative addition of the B−Cl bond of **3** to “Pd(PMe$_3$)$_2$” according to the reported procedure (Scheme 3).[13] The chloropalladium complex **4** was then reacted with trimethylsilyl cyanide at room temperature. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. We observed the formation of the borylcyanopalladium complex **2** at the early stage of the reaction. The concentration of **2** then decreased at a rate similar to that for the formation of cyanoborane **1d**. Finally, **2** and **1d** existed in a ratio of 1:13, which was a little smaller than that for the direct reaction of **1d** with “Pd(PMe$_3$)$_2$”. These results clearly indicate that the oxidative addition of the B−CN bond to palladium(0) takes place in a reversible manner.

Scheme 3. Generation of Borylpalladium Cyanide by Treatment of the Corresponding Borylpalladium Chloride with Trimethylsilyl Cyanide



Scheme 4. Reaction of Cyanoborane 5 with “(PMe$_3$)$_2$Pd(0)” Leading to the Formation of (2-Borylalkenyl)palladium Cyanide 6



The successful observation of the oxidative addition step prompted us to examine the subsequent steps by stoichiometric reactions. To validate the alkyne insertion step, the reaction of 4-octyne with an equilibrating mixture of **2** and **1d** (ca. 1:4) was attempted. However, the reaction afforded no desired products or intermediates, but gave a complex mixture of unidentifiable products. We then examined the reaction of cyanoborane **5** bearing a tethered alkynyl group. Stoichimetric reaction of **5** with “Pd(PMe$_3$)$_2$” at room temperature led to the direct formation of alkenylpalladium(II) cyanide complex **6** in high yield (Scheme 4). Presumed formation of borylcyanopalladium(II) intermediate **7**, which corresponds to **2**, was not observed by ^{1}H NMR measurements.

The structure of **6** was determined by a single-crystal X-ray analysis (Figure 2). The square planar palladium complex was formed via insertion of the triple bond into the boron−palladium bond in a *cis*-fashion. The angle between the square plane of palladium and the C=C plane is ca. 75° to avoid steric repulsion with the diisopropylamino group, of which the C−N−C plane

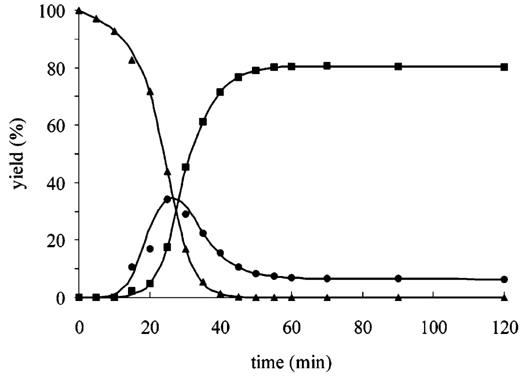


Figure 1. Changes of the concentrations of **4** (▲), **2** (●), and **1d** (■) in the reaction of **4** with 2 molar equiv of TMSCN at room temperature in C$_6$D$_6$.

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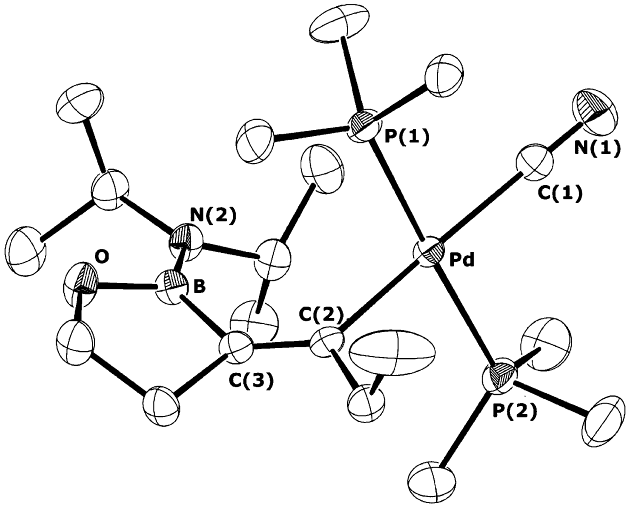
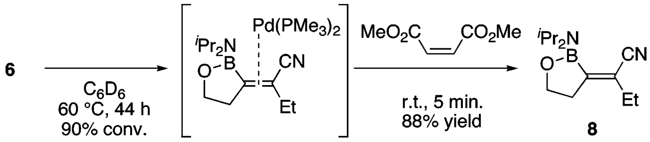


Figure 2. X-ray crystal structure of **6**. Selected bond lengths (Å) and angles (deg) are as follows: Pd−P(1) = 2.3103(6), Pd−P(2) = 2.3098(7), Pd−C(1) = 2.052(3), Pd−C(2) = 2.056(2), C(1)−N(1) = 1.134(4), C(2)−C(3) = 1.340(3), B−C(3) = 1.579(4), B−N(2) = 1.408(3), B−O = 1.390(3); P(1)−Pd−C(1) = 87.94(7), P(2)−Pd−C(1) = 90.47(8), P(1)−Pd−C(2) = 91.34(7), P(2)−Pd−C(2) = 90.10(7), Pd−C(1)−N(1) = 175.8(2), Pd−C(2)−C(3) = 126.9(2), C(2)−C(3)−B = 134.3(2), C(3)−B−O = 108.1(2).

Scheme 5. Reductive Elimination of the Carbon−Cyanide Bond from 6



is almost coplanar with the O−B−C plane in the five-membered ring.

Although stable at room temperature, the palladium complex **6** underwent reductive elimination gradually at 60 °C (Scheme 5). After 44 h at 60 °C, 90% of the starting palladium complex **6** was consumed, forming unidentifiable palladium complexes, in which the reductive elimination product presumably coordinated to palladium, along with a small amount of freed cyanoboration product **8**. Addition of 2 equiv of dimethyl maleate to the reaction mixture forced the complete liberation of the olefinic ligand from palladium, leading to the high-yield formation of **8** (88% yield based on the conversion of **6**). The reductive elimination was completed within 30 min at 110 °C in toluene-d_8. At this temperature, the effect of additives on the rate of the reductive elimination was examined (Table 1). In the presence of 2 equiv of 1,2-diphenylethyne ($t_{1/2}$ = 20 min) or cyanoborane **1d** ($t_{1/2}$ = 9 min), the reactions were only slightly retarded in comparison with the reaction in the absence of the additives ($t_{1/2}$ = 5 min). In contrast, considerable retardation was observed in the reaction in the presence of 2 equiv of trimethylphosphine ($t_{1/2}$ = 260 min). These results suggest that the dissociation of a phosphine ligand from **1d** is essential for the reductive elimination step, which may be the actual rate-determining step in the catalytic cycle (Scheme 1).

Table 1. Half-life for the Reductive Elimination of Complex 6 at 110 °C in Toluene-d_8 [a]

entry	additive (2 equiv)	half-life $t_{1/2}$ (min)
1	none	5
2	**1d**	9
3	PhC≡CPh	20
4	PMe_3	260

[a] The reactions were monitored by ^{1}H NMR.

It was demonstrated that the (2-borylalkenyl)palladium cyanide complex **6** served as an effective catalyst for the intramolecular cyanoboration of **5** (eq 1). This result clearly shows that complex **6** is actually involved in the catalytic process.

$$\mathbf{5} \xrightarrow[\text{toluene, 80 °C , 94\% (NMR)}]{\mathbf{6}\text{ (3 mol\%)}} \mathbf{8} \qquad (1)$$

The observations well support the reaction mechanism that we have proposed in our previous reports. In addition, we now point out a few mechanistic aspects of the cyanoboration reaction. One is the reversibility of oxidative addition of the B−CN bond to palladium, where the reverse reaction is more favorable. The other is the sluggishness of the reductive elimination step. The fact that the presence of two or more equivalents of phosphine inhibits the product formation from **1d** suggests that the reductive elimination takes place through a monophosphine Pd(II) species in the catalytic reaction.[14] These findings may be useful information for further development of new catalytic processes using boron compounds.[15]

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Supporting Information Available: Experimental procedures, details of the X-ray analysis of **6**, and spectral data for the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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