J. Am. Chem. Soc. **2001,** *123,* 761−762

Unusual Diboration of Allenes Catalyzed by Palladium Complexes and Organic Iodides: A New Efficient Route to Biboronic Compounds

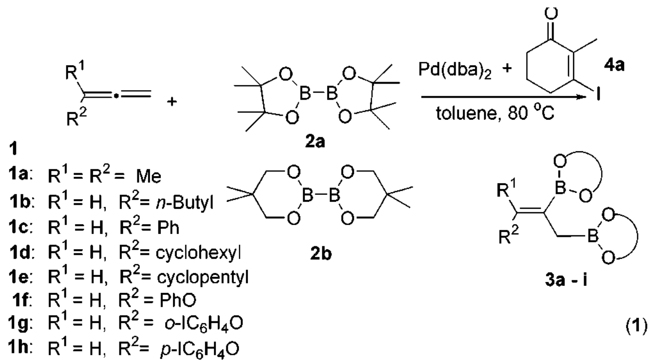
Feng-Yu Yang and Chien-Hong Cheng*

Department of Chemistry, Tsing Hua University
Hsinchu, Taiwan 300

Received September 8, 2000

Transition metal-catalyzed addition of a diboron to unsaturated carbon−carbon bonds[1,2] has provided an efficient and convenient route for the preparation of biboronic compounds that are versatile intermediates for organic synthesis.[3] While Pt complexes readily catalyze this type of addition reaction,[1] the Pd analogues, which are the best catalysts for silyl-[4] and stannylmetalation,[5] are not active in the diboration of alkynes or alkenes. The reactivity difference between Pd and Pt complexes lies in the ability of oxidative addition of a B−B bond to these metal(0) species.[6] Stable oxidative adducts of diboron compounds to Pt species were reported, but no similar Pd products have been observed.[7] Theoretical calculation also indicates that oxidative addition products of diboron compounds to Pd are generally not stable.[6] In this paper, we wish to report the first example of the Pd-catalyzed diboration of allenes using an aryl or alkenyl iodide as the cocatalyst. A new catalytic pathway other than one involving the oxidative addition of diboron to Pd(0) species operates in this new Pd-catalyzed reaction.

In an effort to achieve the three-component assembling reaction[8] of 1,1-dimethylallene (**1a**), alkenyl iodide **4a**, and diboron **2a**, we observed the diboration of **1a** to give product **3a** bearing both vinylic and allylic boron moieties (eq 1). The result is intriguing in view of the fact that Pd complexes generally do not catalyze diboration of alkenes or alkynes.[6] Further studies show that the diboration can be achieved with a catalytic amount of Pd complex and **4a**. Thus, treatment of **1a** and **2a** in the presence of 5 mol % of Pd(dba)$_2$ and 5 mol % of **4a** at 80 °C in toluene for 4 h gave diboration product **3a** in 92% isolated yield. No diboration occurs in the absence of either Pd complexes or the alkenyl iodide. The catalytic reaction is completely regioselective with one boryl group adding to the middle carbon and the other to the nonsubstituted terminal carbon of the allene moiety. No other regioisomer was detected by ^{1}H NMR spectroscopy.



In addition to Pd(dba)$_2$, several phosphine-free Pd complexes Pd(OAc)$_2$, PdCl$_2$(CH$_3$CN)$_2$, and PdCl$_2$(PhCN)$_2$ also show high catalytic activity for the diboration giving **3a** in 96−97% yields. [PdCl(allyl)]$_2$ is less active affording **3a** in 79% yield. The catalytic reaction is remarkably sensitive to the amount of phosphine used. Addition of 1 equiv of PPh$_3$ to the Pd(dba)$_2$ system reduced the yield to 73% and 2 equiv or more of PPh$_3$ completely inhibits the diboration reaction.

To unravel the nature of the present diboration reaction, we explore the possibility of using other organic halides as cocatalysts in reaction 1. Both vinyl iodide (*Z*-ICHCHCOOEt, 99% of **3a**) and aryl iodides (*p*-iodoanisole, 91%; *p*-iodoacetophenone, 93%) were effective cocatalysts for this diboration. However, *p*-bromoacetophenone is less reactive giving **3a** in only 5% yield. Interestingly, I$_2$ is also an effective cocatalyst producing **3a** in 94% yield. The selection of solvent is crucial for achieving high yield of product **3a**. Toluene appears to be the best among the solvents used giving product **3a** in quantitative yield. THF, CH$_3$CN, and DMF are less effective affording **3a** in 52, 77, and 64% yields, respectively.

The observation that an aryl, alkenyl iodide, or I$_2$ was required to initiate the present catalytic reaction is interesting and vital to the understanding of the catalytic mechanism. A reasonable common product from the Pd-catalyzed reaction of allene **1a**, RI (R = aryl, alkenyl), and **2a** is iodo(pinacolato)boron **6** generated from the Pd-mediated three-component assembling of organiciodide, allene, and diboron **2a** (eq 2). **6** likely starts the catalytic diboration by oxidative addition to Pd(0). The adduct then reacts

---

(1) For the Pt-catalyzed diboration reaction see: (a) Ishiyama, T.; Matsuda, N.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 11018−11019. (b) Ishiyama, T.; Yamamoto, M.; Miyaura, N. *Chem. Commun.* **1997**, 689−690. (c) Ishiyama, T.; Kitano, T.; Miyaura, N. *Tetrahedron Lett.* **1998**, *39*, 2357−2360. (d) Iverson, C. N.; Smith, M. R., III *Organometallics* **1997**, *16*, 2757−2759. (e) Ishiyama, T.; Yamamoto, M.; Miyaura, N. *Chem. Commun.* **1996**, 2073−2074. (f) Iverson, C. N.; Smith, M. R., III *J. Am. Chem. Soc.* **1995**, *117*, 4403−4404. (g) Mann, G.; John, K. D.; Baker, R. T. *Org. Lett.* **2000**, *2*, 2105−2108. (h) Ishiyama, T.; Matsuda, N.; Murata, M.; Ozawa, F.; Suzuki, A.; Miyaura, N. *Organometallics* **1996**, *15*, 713−720. (i) Marder, T. B.; Norman, N.; Rice, C. R. *Tetrahedron Lett.* **1998**, *39*, 155−158. (j) Clegg, T. M.; Johann, T. R. F.; Marder, T. B.; Norman, N. C.; Orpen, A. G.; Peakman, T. M.; Quayle, M. J.; Rice, C. R.; Scott, A. J. *J. Chem. Soc., Dalton Trans.* **1998**, 1431−1438. (k) Anderson, K. M.; Lesley, M. J. G.; Norman, N. C.; Orpen, A. G.; Starbuck, J. *Chem. Commun.* **1999**, 1053−1055. (l) Marder, T. B.; Norman, N. C. *Top. Catal.* **1998**, *5*, 63−73. (m) Lawson, Y. G.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R. *J. Chem. Soc., Chem. Commun.* **1997**, 2051−2052. (n) Maderna, A.; Pritzkow, H.; Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1501−1502. (o) Lesley, G.; Nguyen, P.; Taylor, N. J.; Marder, T. B.; Scott, A. J.; Clegg, W.; Norman, N. C. *Organometallics* **1996**, *15*, 5137−5154. (p) Iverson, C. N.; Smith, M. R., III *Organometallics* **1996**, *15*, 5155−5165.

(2) For Rh- or Au-catalyzed diboration reactions see: (a) Baker, R. T.; Nguyen, P.; Marder, T. B.; Westcott, S. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1336−1338. (b) Cameron, T. M.; Baker, R. T.; Westcott, S. A. *Chem. Commun.* **1998**, 2395−2396. (c) Dai, C.; Robins, E. G.; Scott, A. J.; Clegg, W.; Yufit, D. S.; Howard, J. A. K.; Marder, T. B. *Chem. Commun.* **1998**, 1983−1984.

(3) (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457−2483. (b) Trost, B. M.; Spagnol, M. D. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2083−2096. (c) Brown, H. C.; Singaram, B. *Pure Appl. Chem.* **1987**, *59*, 897−894. (d) Pelter, A.; Smith, K.; Brown, H. C. *Brorane Reagents*; Academic Press: New York, 1988.

(4) (a) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1975**, *97*, 931−932. (b) Tamao, K.; Hayashi, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *114*, C19−C21. (c) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* **1975**, *86*, C27−C30. (d) Ozawa, F.; Sugawara, M.; Hayashi, T. *Organometallics* **1994**, *13*, 3237−3234. (e) Onozawa, S. Y.; Hatanaka, Y.; Tanaka, M. *Chem. Commun.* **1999**, 1863−1864.

(5) (a) Mitchell, T. N.; Amamria, A.; Killing, H.; Rutschow, D. *J. Organomet. Chem.* **1983**, *241*, C45−C47. (b) Piers, E.; Skerlj, R. T. *J. Chem. Soc., Chem. Commun.* **1986**, 626−627. (c) Mitchell, T. N.; Wickenkamp, R.; Amamria, A.; Dicke, R.; Schneider, U. *J. Org. Chem.* **1987**, *52*, 4868−4874.

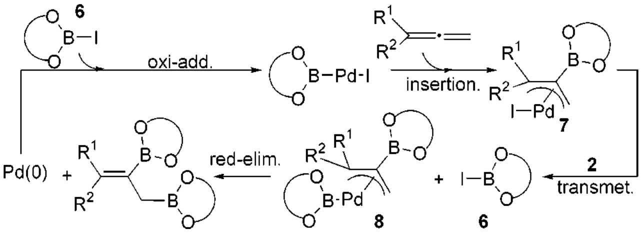
(6) (a) Cui, Q.; Musaev, D. G.; Morokuma, K. *Organometallics* **1998**, *17*, 1383−1392. (b) Cui, Q.; Musaev, D. G.; Morokuma, K. *Organometallics* **1998**, *17*, 742−751. (c) Cui, Q.; Musaev, D. G.; Morokuma, K. *Organometallics* **1997**, *16*, 1355−1364.

(7) Irvine, G. J.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper, W. R.; Whittell, C. R.; Wright, L. J. *Chem. Rev.* **1998**, *98*, 2685−2722.

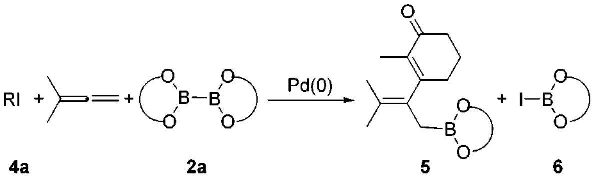
(8) (a) Wu, M. Y.; Yang, F. Y.; Cheng, C. H. *J. Org. Chem.* **1999**, *64*, 2471−2474. (b) Yang, F. Y.; Wu, M. Y.; Cheng, C. H. *Tetrahedron Lett.* **1999**, *40*, 6055−6058. (c) Yang, F. Y.; Wu, M. Y.; Cheng, C. H. *J. Am. Chem. Soc.* **2000**, *122*, 7122−7123.

10.1021/ja005589g CCC: $20.00

Scheme 1

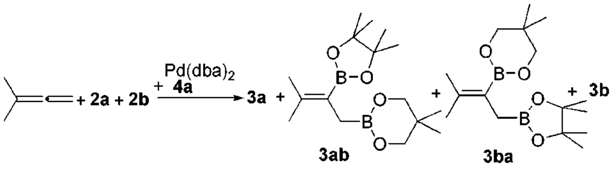


with allene to give a Pd-allyl species **7** with the boryl attached to the central carbon of the π-allyl group. Transmetalation of **7** with the diboron reagent gives **6** and intermediate **8**. Reductive elimination of **8** yields the final biboronic compound and regenerates Pd(0) (Scheme 1). Evidence for the formation of three-component coupling products **5** was observed in GC-MS in ~3% yields from the reaction of **1a**, **2a**, and **4a** in the presence of Pd(dba)$_2$.



(2)

The proposed mechanism gains strong support from the following cross-addition experiment. Treatment of **2a** (0.250 mmol) and **2b** (0.250 mmol) with dimethylallene (1.00 mmol) in 5 mol % of Pd(dba)$_2$ and **4a** gave four diboration products **3a**, **3ab**, **3ba**, and **3b** (eq 3). GC-MS and ^{1}H NMR analyses of the product mixture show that the ratio **3a**/(**3ab** + **3ba**)/**3b** is 24:52:23. The ratio is close to the statistic value of 1/2/1 expected based on the present mechanism assuming the same reactivity of **2a** and **2b**. It should be noted that if diboration occurs via oxidative addition of diborons **2a** and **2b** to Pd(0) species, only products **3a** and **3b** will be observed.



(3)

Monosubstituted allenes RCH=C=CH$_2$ (**1b**–**h**, eq 1) also undergo diboration with **2a** to give the corresponding biboronic products in good to excellent yields (Table 1). These reactions are highly regio- and stereoselective. In all cases, only the biboronic products with one boryl group adding to the middle carbon and the other to the nonsubstituted terminal carbon of the allene moiety were observed. The stereochemistry of these biboronic products is little affected by the substituent R on allenes. Each reaction gave the corresponding *Z* isomer of the biboronic product as the major species with a *E/Z* ratio falling in the narrow range 5/95 to 7/93. The observed stereoselectivity may be rationalized based on face-selective coordination of allenes to the Pd center. For a monosubstituted allene, the terminal double bond is selectively π-bound to the Pd moiety at the face opposite to the substituents R favorably to avoid steric congestion (Scheme 2).[8c] This face selection determines the stereoselectivity of diboration and eventually results in the formation of *Z*-form products. The stereochemistry of these biboronic products **3** was determined by using typical ^{1}H NMR NOE technique.

Scheme 2

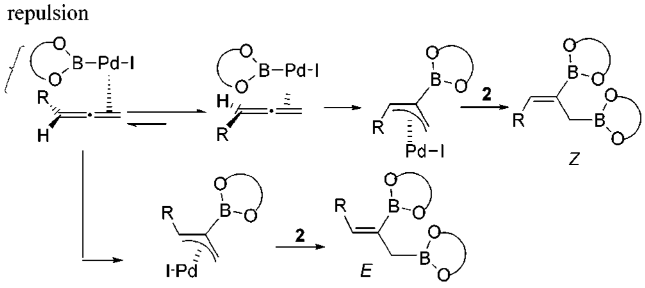
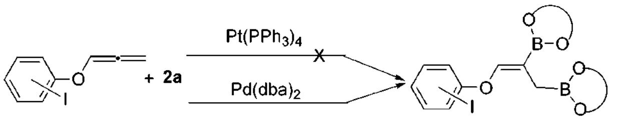


Table 1. Palladium-Catalyzed Diboration of Diboron **2** and Allenes[a]

entry	allenes	diboron	product	*E/Z*	yield (%)[b,c]
1	**1a**	**2a**	**3a**		93
2	**1a**	**2b**	**3b**		85
3	**1b**	**2a**	**3c**	6/94	88
4	**1c**	**2a**	**3d**	5/95	87
5	**1d**	**2a**	**3e**	6/94	85
6	**1e**	**2a**	**3f**	5/95	86
7	**1f**	**2a**	**3g**	6/94	86
8	**1g**	**2a**	**3h**	5/95	76 (90)
9	**1g**	**2a**	**3h**	5/95	– (80)[d]
10	**1h**	**2a**	**3i**	7/93	52 (77)
11	**1h**	**2a**	**3i**	7/93	– (64)[d]

[a] Reaction procedure: To a 25-mL sidearm flask were added **4a** (0.025 mmol, 5 mol %), Pd(dba)$_2$ (0.025 mmol, 5 mol %), and diboron **2** (0.500 mmol). The system was evacuated and purged with nitrogen three times. Toluene (1.5 mL) and allene **1** (1.00 mmol) were added to the system and the reaction mixture was stirred at 80 °C for 4 h. [b] Isolated yield. [c] Yields determined by the ^{1}H NMR integration method using mesitylene as an internal standard are shown in parentheses. [d] Yields obtained in the absence of **4a**.

Comparison of the catalytic activity of Pd(dba)$_2$ and Pt(PPh$_3$)$_4$ on the diboration of iodophenoxylallenes explains the fundamental difference of these two catalyst systems. As shown in Table 1, the diboration of iodophenoxylallenes IC$_6$H$_4$OCHCCH$_2$ (**1g**–**h**, eq 1) by **2a** in the presence of Pd(dba)$_2$ and **4a** proceeds smoothly to afford the diboration products in good yields (entries 8 and 10). Interestingly, these palladium-catalyzed reactions go on even without **4a** (entries 9 and 11), presumably initiated by the iodo group on the allene substrate. In contrast, the same diboration does not occur with Pt(PPh$_3$)$_4$ as the catalyst (eq 4). It should be noted that in the absence of iodo source, Pt(PPh$_3$)$_4$ is an efficient catalyst,[1c] but Pd(dba)$_2$ is ineffective for the diboration of allenes by **2a**.



(4)

In summary, we have demonstrated that phosphine-free Pd complexes together with alkenyl or aryl iodides were very efficient catalysts for 1,2-diboration of allenes. This reaction is completely regioselective and highly stereoselective. Monosubstituted allenes afford diboration products with mainly *Z* stereochemistry. This Pd-catalyzed reaction proceeds via a previously unknown mechanism involving the oxidative addition of an I–B bond to the palladium center instead of the oxidative addition of a B–B bond to metal. Studies on the application of this new catalytic mechanism to the addition of B–B, Si–Si, Sn–Sn, or Si–B bonds to unsaturated organic systems are underway.

Acknowledgment. We thank the National Science Council of the Republic of China for support of this research.

Supporting Information Available: Preparation details, characterization data, NOE experimental data of **3c**–**i**, and cross-addition experimental data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA005589G