Platinum(0)-Catalyzed Diboration of Alkynes[1]

Tatsuo Ishiyama, Nobuo Matsuda, Norio Miyaura,* and
Akira Suzuki*

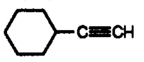
Department of Applied Chemistry
Faculty of Engineering
Hokkaido University, Sapporo 060, Japan

Received August 12, 1993

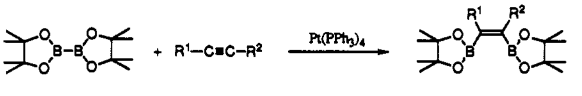
Recently, much attention has been focused on the addition reactions of the metal–metal bonds to alkynes or alkenes as a simple method for the direct synthesis of polymetallic organic compounds. The additions of bimetallic reagents such as the silicon–metal[2] and the tin–metal[3] compounds to the C–C unsaturated bonds have been extensively studied; however, there are few reports concerning the metal–boron compounds. For instance, there are only two known addition reactions of the Si–B (silylboration) and the Sn–B compounds (stannylboration) to alkynes.[4] Perhaps prejudice due to the fact that the boron compounds have a relatively high bond energy has precluded investigation in this area. We have recently reported that the additions of catecholborane to alkenes and alkynes are catalyzed by the Pd(0), Rh(I), or Ni(0) complexes[5–7] and that the thioboration of alkynes with 9-organothio-9-BBN derivatives is induced by using catalytic amounts of the Pd(0) complex.[8] As a part of this program on the catalytic addition reactions of boron compounds, we report here the first example of the *syn*-selective addition of tetraalkoxydiboron **1** to alkynes **2**. The reaction was efficiently catalyzed by the platinum(0) complex (eq 1).

Although the additions of diboron tetrahalides $X_2B–BX_2$ (X = Cl, F) to alkenes and alkynes were already reported by Schlesinger in 1959,[9] their ester or amide analogues are completely inactive toward diboration.[10] Since the pinacol ester derivative **1** is thermally stable and can be easily handled in air, the reaction should allow the synthesis of a wide range of stereodefined bis(boryl)alkenes and their additional synthetic applications.

Table I. Diboration of Alkynes (eq 1)[a]

alkyne (2)	product (3)	yield[b] (%)
$C_6H_{13}C{\equiv}CH$	**3a**	82
$C_8H_{17}C{\equiv}CH$	**3b**	86
	**3c**	78
$C_3H_7C{\equiv}CC_3H_7$	**3d**	86
$PhC{\equiv}CPh$	**3e**	79

[a] All reactions were carried out in DMF at 80 °C for 24 h using **1** (1 equiv), **2** (1.1 equiv), and $Pt(PPh_3)_4$ (3 mol %). [b] Isolated yields based on **1**.



(1)

1 **2** **3a-e**

The preliminary results for the addition of **1** to 1-octyne indicated that only the platinum complexes such as $Pt(PPh_3)_4$ exhibited excellent catalytic activity. $Pd(PPh_3)_4$ and $Pd(OAc)_2$–isocyanide complexes, which have been best catalysts for the silyl- and stannylmetalation,[2,3] and other metal complexes, e.g., $NiCl_2$(dppe)–DIBAL, $RhCl(PPh_3)_3$, and $CoCl(PPh_3)_3$, were ineffective. The solvents did not play an important role in the reaction, but a comparison of the reaction rates at 50 °C revealed that the addition was apparently accelerated in polar solvents: e.g., DMF > CH_3CN > THF > toluene.

The representative results are summarized in Table I.[11,12] There are no large differences in the yields and the reaction rates between internal and terminal alkynes. The additions to alkynes in DMF with $Pt(PPh_3)_4$ were completed within 24 h at 80 °C to provide **3a–e** in a range of 78–86% yields. The *cis*-diboration of alkynes with an isomeric purity of over 99% was unambiguously established by the presence of NOE between the vinylic proton and allylic protons in ^1H NMR. On the other hand, the addition to phenylethyne was very slow and was not completed under similar conditions (<30%). All attempts to induce reaction with alkenes were unsuccessful.

---

(1) This work was presented at the 8th International Meeting on Boron Chemistry, Knoxville, TN, July 11–15, 1993.

(2) (a) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9263–9264. (b) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *Ibid.* **1975**, *97*, 931–932. (c) Watanabe, H.; Kobayashi, M.; Higuchi, K.; Nagai, Y. *J. Organomet. Chem.* **1980**, *186*, 51–62. (d) Hayami, H.; Sato, M.; Kanemoto, S.; Morizawa, Y.; Oshima, K.; Nozaki, H. *J. Am. Chem. Soc.* **1983**, *105*, 4491–4492. (e) Okuda, Y.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, *25*, 2483–2486. (f) Wakamatsu, K.; Nonaka, T.; Okuda, Y.; Tuckmantel, W.; Oshima, K.; Utimoto, K.; Nozaki, H. *Tetrahedron* **1986**, *42*, 4427–4436. (g) Chenard, B. L.; Van Zyl, C. M. *J. Org. Chem.* **1986**, *51*, 3561–3566. (h) Mitchell, T. N.; Wickenkamp, R.; Amamria, A.; Dicke, R.; Schneider, U. *J. Org. Chem.* **1987**, *52*, 4868–4874. (i) Ito, Y.; Suginome, M.; Murakami, M. *J. Org. Chem.* **1991**, *56*, 1948–1951. (j) Murakami, M.; Andersson, P. G.; Suginome, M.; Ito, Y. *J. Am. Chem. Soc.* **1991**, *113*, 3987–3988. (k) Tsuji, Y.; Obora, Y. *J. Am. Chem. Soc.* **1991**, *113*, 9368–9369. (l) Ishikawa, M.; Nishimura, Y.; Sakamoto, H.; Ono, T.; Ohshita, J. *Organometallics* **1992**, *11*, 483–484. (m) Tsuji, Y.; Lago, R. M.; Tomohiro, S.; Tsuneishi, H. *Ibid.* **1992**, *11*, 2353–2355. (n) Finckh, W.; Tang, B.-Z.; Lough, A.; Manners, I. *Ibid.* **1992**, *11*, 2904–2911.

(3) (a) Mitchell, T. N.; Amamria, A.; Killing, H.; Rutschow, D. *J. Organomet. Chem.* **1983**, *241*, C45–C47. (b) Killing, H.; Mitchell, T. N. *Organometallics* **1984**, *3*, 1318–1320. (c) Matsubara, S.; Hibino, J.-I.; Morizawa, Y.; Oshima, K.; Nozaki, H. *J. Organomet. Chem.* **1985**, *285*, 163–172. (d) Mitchell, T. N.; Amamria, A.; Killing, H.; Rutschow, D. *J. Organomet. Chem.* **1986**, *304*, 257–265. (e) Nonaka, T.; Okuda, Y.; Matsubara, S.; Oshima, K.; Utimoto, K.; Nozaki, H. *J. Org. Chem.* **1986**, *51*, 4716–4718. (f) Sharma, S.; Oehlschlager, A. C. *Tetrahedron Lett.* **1986**, *27*, 6161–6164. (g) Piers, E.; Skerlj, R. T. *J. Chem. Soc., Chem. Commun.* **1987**, 1025–1026. (h) Sharma, S.; Oehlschlager, A. C. *J. Org. Chem.* **1989**, *54*, 5064–5073.

(4) (a) Nozaki, K.; Wakamatsu, K.; Nonaka, T.; Tuckmantel, W.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1986**, *27*, 2007–2010. (b) Sharma, S.; Oehlschlager, A. C. *Tetrahedron Lett.* **1988**, *29*, 261–264.

(5) Satoh, M.; Nomoto, Y.; Miyaura, N.; Suzuki, A. *Tetrahedron Lett.* **1989**, *30*, 3789–3792.

(6) Satoh, M.; Miyaura, N.; Suzuki, A. *Tetrahedron Lett.* **1990**, *31*, 231–234.

(7) Gridnev, I. D.; Miyaura, N.; Suzuki, A. *Organometallics* **1993**, *12*, 589–592.

(8) Ishiyama, T.; Nishijima, K.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 7219–7225.

(9) Ceron, P.; Finch, A.; Frey, J.; Kerrigan, J.; Parsons, T.; Urry, G.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1959**, *81*, 6368–6371.

(10) (a) Muetterties, E. L. *The Chemistry of Boron and its Compounds*; Wiley: New York, 1967; pp 398–399. (b) Onak, T. *Organoborane Chemistry*; Academic Press: New York, 1975; pp 38–40.

(11) Nōth, H. *Z. Naturforsch.* **1984**, *39b*, 1463–1466.

(12) A typical procedure is as follows: the flask was charged with $Pt(PPh_3)_4$ (38 mg, 0.03 mmol) and **1**[11] (1.0 mmol) and flushed with nitrogen. DMF (6 mL) and alkyne (1.1 mmol) were added successively. After being stirred for 24 h at 80 °C, the reaction mixture was diluted with benzene (ca. 30 mL), repeatedly washed with cold water to remove DMF (5×), and finally dried over $MgSO_4$. Kugelrohr distillation (0.15 mmHg) gave the bis(boryl)alkene. **3a**: ^1H NMR ($CDCl_3$) δ 0.87 (t, 3 H, $J = 6.8$ Hz), 1.26 (s, 12 H), 1.31 (s, 12 H), 1.2–1.3 (m, 6 H), 1.35–1.45 (m, 2 H), 2.21 (t, 2 H, $J = 7.1$ Hz), 5.84 (s, 1 H) [The irradiation of the vinyl proton at 5.84 ppm resulted in an 5.7% enhancement of the allylic methylene signal at 2.21 ppm]; ^{13}C NMR ($CDCl_3$) δ 14.12, 22.59, 24.89, 24.93, 28.62, 29.13, 31.77, 39.92, 83.25, 83.61; ^{11}B NMR ($CDCl_3$) δ 30.24; exact mass calcd for $C_{20}H_{38}O_4B_2$ 364.2957, found 364.2932. **3b**: ^1H NMR ($CDCl_3$) δ 0.87 (t, 3 H, $J = 6.8$ Hz), 1.26 (s, 12 H), 1.31 (s, 12 H), 1.2–1.3 (m, 10 H), 1.35–1.45 (m, 2 H), 2.21 (t, 2 H, $J = 7.1$ Hz), 5.84 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.12, 22.72, 24.89, 24.93, 28.64, 29.21, 29.45, 29.48, 31.93, 39.92, 83.25, 83.61; ^{11}B NMR ($CDCl_3$) δ 30.26; exact mass calcd for $C_{22}H_{42}O_4B_2$ 392.3269, found 392.3271. **3c**: ^1H NMR ($CDCl_3$) δ 1.1–1.3 (m, 5 H), 1.26 (s, 12 H), 1.33 (s, 12 H), 1.60–1.65 (m, 1 H), 1.70–1.75 (m, 4 H), 2.05–2.15 (m, 1 H), 5.80 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 24.91, 25.11, 26.28, 26.61, 32.30, 47.68, 83.25, 83.65; ^{11}B NMR ($CDCl_3$) δ 30.33; exact mass calcd for $C_{20}H_{36}O_4B_2$ 362.2800, found 362.2811. **3d**: ^1H NMR ($CDCl_3$) δ 0.91 (t, 6 H, $J = 7.3$ Hz), 1.28 (s, 24 H), 1.3–1.4 (m, 4 H), 2.17 (t, 4 H, $J = 8.1$ Hz); ^{13}C NMR ($CDCl_3$) δ 14.61, 23.01, 24.95, 33.10, 83.29; ^{11}B NMR ($CDCl_3$) δ 30.72; exact mass calcd for $C_{20}H_{38}O_4B_2$ 364.2956, found 364.2977. **3e**: ^1H NMR ($CDCl_3$) δ 1.32 (s, 24 H), 6.94 (d, 4 H, $J = 6.8$ Hz), 7.0–7.1 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 24.89, 84.07, 125.79, 127.41, 129.32, 141.29; ^{11}B NMR ($CDCl_3$) δ 30.57; exact mass calcd for $C_{26}H_{34}O_4B_2$ 432.2643, found 432.2667.

0002-7863/93/1515-11018$04.00/0

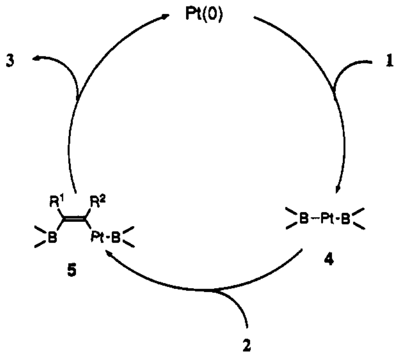
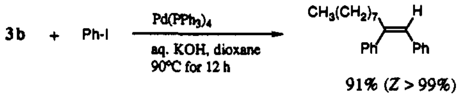


Figure 1. Catalytic cycle of diboration.

To confirm the structure of the diboration adducts and their potential ability for use in the boron cross-coupling reaction,[13] **3b** was allowed to react with iodobenzene (2.4 equiv) at 90 °C in dioxane in the presence of 3 mol % Pd(PPh_3)$_4$ and aqueous 3 M KOH (6 equiv) (eq 2). The reaction provided (*Z*)-1,2-diphenyl-1-decene as the sole product whose stereochemistry was consistent with that of **3b**.



(2)

A proposed catalytic cycle for the diboration of alkynes, which involves the oxidative addition of the B–B bond to the platinum(0) complex, the stereospecific insertion of alkyne to the B–Pt bond, and finally the reductive elimination of the bis(boryl)alkene, is outlined in Figure 1.

Very recently, Baker, Marder, and co-workers succeeded in isolating the novel bis(boryl) complex RhCl(Bcat)$_2$(PPh_3)$_2$ by dehydrogenative coupling of two catecholboranes with RhCl(PPh_3)$_3$.[14] Alkene insertion into the Rh–B bond and its reductive elimination were investigated in connection with the mechanism of the catalytic hydroboration. Although the formation of a similar bis(boryl) complex by oxidative addition of diborons to the transition-metal complexes has not been previously reported, the related mechanism for the catalytic addition of disilanes[15] to alkenes or alkynes strongly suggests the generation of a X_2B–Pt(II)–BX_2 species (**4**). In fact, the formation of an oxidative adduct was observed in the NMR analysis of the reaction mixture of Pt(PPh_3)$_4$ and **1** (10 equiv) in toluene at room temperature for 12 h or at 100 °C for 1 h. The ^{31}P NMR spectrum[16] exhibited a singlet at 28.65 and its ^{195}Pt satellites at 35.61 and 21.73 ppm (J_{Pt-P} = 1517 Hz), which are characteristic of phosphines *cis*-coordinated to platinum(II).[17] The generation of a new signal at 21.50 ppm besides that for the starting **1** (29.94 ppm) in the ^{11}B NMR spectrum also supports the formation of an oxidative adduct. The following two steps, the insertion of alkynes to the B–Pt bond and the reductive elimination of bis(boryl)alkenes from the vinyl–Pt(II)–BX_2 complexes **5**, may proceed through a process similar to that of the diboration of 4-methoxystyrene[14] and the disilylation of alkenes and alkynes.[2,15]

In summary, the catalytic addition reaction of the ester derivative of diboron **1** to alkynes provides a new access to isomerically pure *cis*-1,2-bis(boryl)alkenes **3** which can be easily isolated in a pure form. Because of the simple experimental procedure using a catalytic amount of platinum complex, we anticipate additional synthetic applications of our method to other metal–boron compounds. The synthetic applications of the bis(boryl)alkenes thus obtained and isolation of the oxidative adduct intermediate **4** are being actively investigated.

Acknowledgment. We wish to thank Professor F. Ozawa, Catalysis Research Center of Hokkaido University, for the measurement of the low-temperature ^{31}P NMR spectra of the oxidative adduct and for his helpful discussions and suggestions as to the structure.

Supplementary Material Available: Copies of the ^{1}H NMR spectra of **3a–e** and the ^{31}P NMR spectrum of the oxidative adduct intermediate (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS. Ordering information is given on any current masthead page.

---

[13] (a) Miyaura, N.; Yamada, K.; Suginome, H.; Suzuki, A. *J. Am. Chem. Soc.* **1985**, *107*, 972–980. (b) Miyaura, N.; Ishiyama, T.; Sasaki, H.; Ishikawa, M.; Sato, M.; Suzuki, A. *Ibid.* **1989**, *111*, 314–321. (c) Oh-e, T.; Miyaura, N.; Suzuki, A. *J. Org. Chem.* **1993**, *58*, 2201–2208. (d) Suzuki, A. *Pure Appl. Chem.* **1985**, *57*, 1749–1958; (e) **1991**, *63*, 419–422.

[14] Baker, R. T.; Calabrese, J. C.; Westcott, S. A.; Nguyen, P.; Marder, T. B. *J. Am. Chem. Soc.* **1993**, *115*, 4367–4368.

[15] (a) Schmid, G.; Balk, H.-J. *Chem. Ber.* **1970**, *103*, 2240–2244. (b) Glockling, F.; Houston, R. E. *J. Organomet. Chem.* **1973**, *50*, C31–C32. (c) Eaborn, C.; Griffiths, R. W.; Pidcock, A. *J. Organomet. Chem.* **1982**, *225*, 331–341. (d) Yamashita, H.; Kobayashi, T.-a.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **1990**, 1447–1450. (e) Pan, Y.; Mague, J. T.; Fink, M. J. *Organometallics* **1992**, *11*, 3495–3497.

[16] ^{31}P NMR (109.25 MHz; toluene at –80 °C) δ –7.30 (br s, free Ph_3P), 10.68 (br s, unknown species), 25.34 (s, (Ph_3P)$_4$Pt), 28.65 and its satellites at 35.61 and 21.73 (J_{Pt-P} = 1517 Hz). The resonance of phosphines coordinated to platinum(II) at 28.65 and its satellites gives rather broad signals even at low temperature, apparently due to the long-range coupling with boron atoms.

[17] Judging from the coupling constants of related bis(silyl)platinum analogs (ca. 2800 Hz for *trans*- and ca. 1500 Hz for *cis*-complex),[15] the resulting low value can be assigned to the *cis*-[(Me_2CO)$_2$B]$_2$Pt(II)(PPh_3)$_2$ complex.