Platinum(0)-Catalyzed Diboration of Alkynes with **Tetrakis(alkoxo)diborons:** An Efficient and Convenient Approach to *cis*-Bis(boryl)alkenes

Tatsuo Ishiyama, Nobuo Matsuda, Miki Murata, Fumiyuki Ozawa,[†] Akira Suzuki,[‡] and Norio Miyaura*

Division of Molecular Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060, Japan

Received August 28, 1995[®]

Tetrakis(methoxo)- or bis(pinacolato)diboron $[(RO)_2BB(OR)_2; (RO)_2 = (MeO)_2$ (4a) and $Me_4C_2O_2$ (1)] added to both terminal and internal alkynes in the presence of a catalytic amount of $Pt(PPh_3)_4$ to provide stereodefined *cis*-bis(boryl)alkenes (3) in excellent yields. Because reagents and reaction conditions were sufficiently mild, the procedure was readily extended to various functionalized alkynes. Mechanistic study revealed that the oxidative addition of bis(pinacolato)diboron (1) to $Pt(PPh_3)_4$ generates cis- $Pt(BO_2C_2Me_4)_2(PPh_3)_2$ (5), whose structure was fully characterized by multinuclear NMR spectroscopies as well as single-crystal X-ray diffraction analysis. Complex 5 exhibited high reactivity for insertion to the alkyne giving **3** in high yields, thus implying that the oxidative addition of the B-Bbond to a Pt(0) complex is an initial step in the platinum(0)-catalyzed diboration of alkynes.

Introduction

The addition of diborons (X₂B-BX₂) to unsaturated hydrocarbons, first discovered by Schlesinger in 1954,¹ is an attractive and straightforward method to introduce two boryl units into organic molecules.² Although diboron tetrahalides (X = Cl, F) have been extensively used for this transformation, the synthetic use has been severely limited because of instability and availability of the reagents. Diboron tetrachloride synthesized by an electric discharge reduction of boron trichloride³ ignites in air and undergoes a partial decomposition into boron trichloride and colored solid materials at lower than room temperature.^{3b,4} Tetrakis(alkoxo)- and tetrakis(amido)diborons⁵ ($X = RO, R_2N$), which are readily available in large quantity by the Wurtz coupling of the corresponding haloboranes with sodium or potassium metal, are rather stable; however, the compounds are reported to be quite inert to alkenes and alkynes due

 (a) Massey, A. G.; Urch, D. S.; Holliday, A. K. J. Inorg. Nucl.
 (b) Massey, A. G.; Urch, D. S.; Holliday, A. K. J. Inorg. Nucl.
 (c) Chem. 1966, 28, 365–370. (b) Urry, G.; Wartik, T.; Moore, R. E.;
 (c) Schlesinger, H. I. J. Am. Chem. Soc. 1954, 76, 5293–5298. (c) Stock, A.; Brandt, A.; Fischer, H. Chem. Ber. 1925, 58, 643-657

(4) (a) Urry, G.; Wartik, T.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1952**, *74*, 5809. (b) Wartik, T.; Moore, R. E.; Schlesinger, H. I. *J. Am.* Chem. Soc. 1949, 71, 3265-3266.

to the low Lewis acidity of the boron centers conjugated with oxygen or nitrogen atoms and a high B-B bond energy.

Recently, considerable attention has been focused on the transition metal-catalyzed additions of metal reagents, including magnesium,⁶ aluminum.^{6e,f,7} silicon,^{6d,e,7d,8} zinc,^{6e,f,7d,9} germanium,¹⁰ and

[†] Present address: Faculty of Engineering, Osaka City University, Sumiyoshi-Ku Sugimoto, Japan

[‡] Present address: Kurashiki University of Science and Art, Kurashiki 712, Japan.

⁹ Abstract published in Advance ACS Abstracts, December 15, 1995. (1) Urry, G.; Kerrigan, J.; Parsons, T. D.; Schlesinger, H. I. J. Am. Chem. Soc. 1954, 76, 5299-5301.

⁽²⁾ For reviews, see: (a) Onak, T. Organoborane Chemistry; Academic Press: New York, 1975; pp 38–40. (b) Coyle, T. D.; Ritter, J. J. Advances in Organometallic Chemistry, Academic Press: New York, 1972; Vol. 10, pp 237–272. (c) Muetterties, E. L. The Chemistry of

^{(5) (}a) Nöth, H. Z. Naturforsch. 1984, 39b, 1463-1466. (b) Welch, C. N.; Shore, S. G. Inorg. Chem. 1968, 7, 225-230. (c) Brotherton, R. J.; McCloskey, A. L.; Boone, J. L.; Manasevit, H. M. J. Am. Chem. Soc. 1960, 82, 6245-6248. (d) Brotherton, R. J.; McCloskey, A. L.; Petterson, L. L.; Steinberg, H. J. Am. Chem. Soc. 1960, 82, 6242-6245.

⁽⁶⁾ Mg-C: (a) Houri, A. F.; Didiuk, M. T.; Xu, Z.; Horan, N. R.; Hoveyda, A. H. J. Am. Chem. Soc. 1993, 115, 6614-6624. (b) Knight, K. S.; Waymouth, R. M. J. Am. Chem. Soc. 1991, 113, 6268-6270. (c) Takahashi, T.; Seki, T.; Nitto, Y.; Saburi, M.; Rousset, C. J.; Negishi, Takahashi, T.; Seki, T.; Nitto, Y.; Saburi, M.; Rousset, C. J.; Negishi, E. J. Am. Chem. Soc. **1991**, *113*, 6266–6268. Mg–Si: (d) Okuda, Y.; Morizawa, Y.; Oshima, K.; Nozaki, H. Tetrahedron Lett. **1984**, *25*, 2483–2486. (e) Hayami, H.; Sato, M.; Kanemoto, S.; Morizawa, Y.; Oshima, K.; Nozaki, H. J. Am. Chem. Soc. **1983**, *105*, 4491–4492. Mg– Sn: (f) Matsubara, S.; Hibino, J.-I.; Morizawa, Y.; Oshima, K.; Nozaki, H. J. Organomet. Chem. **1985**, *285*, 163–172. (7) Al–C: (a) Zweifel, G.; Miller, J. A. Org. React. **1984**, *32*, 375– 517. (b) Negishi, E. Pure Appl. Chem. **1981**, *53*, 2333–2356. (c) Van Horn, D. E.; Negishi, E. J. Am. Chem. Soc. **1978**, *100*, 2252–2254. Al–Si: (d) Wakamatsu, K.; Nonaka, T.; Okuda, Y.; Tückmantel, W.; Oshima, K.; Utimoto, K.; Nozaki, H. Tetrahedron **1986**, *42* 4427–4436

Oshima, K.; Utimoto, K.; Nozaki, H. *Tetrahedron* **1986**, *42*, 4427–4436. Al–Sn: (e) Sharma, S.; Oehlschlager, A. C. *J. Org. Chem.* **1989**, *54*, 5064–5073. (f) Sharma, S.; Oehlschlager, A. C. *Tetrahedron Lett.* **1986**, 27, 6161-6164

⁽⁸⁾ Si-H: (a) Sakakura, T.; Lautenschlager, H.-J.; Tanaka, M. J. Chem. Soc., Chem. Commun. 1991, 40-41. (b) Hiyama, T.; Kasumoto, T. Comprehensive Organic Synthesis; Trost, B. M., Ed.; Pergamon: New York, 1991; Vol. 8, pp 763-792. (c) Ojima, I. The Chemistry of Organic Silicon Compounds; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; pp 1479-1526. Si-CN: (d) Chatani, N.; Hanafusa, T. J. Org. Chem. 1991. 56. 2166-2170. (a) Chotani N.; Takwasu, T. J. *Org. Chem.* **1991**, *56*, 2166–2170. (e) Chatani, N.; Takeyasu, T.; Horiuchi, N.; Hanafusa, T. J. Org. Chem. **1988**, *53*, 3539–3548. (f) Chatani, N.; Hanafusa, T. J. Org. Chem. **1987**, *52*, 4408–4409. Si–Si: (g) Ozawa, F.; Sugawara, M.; Hayashi, T. Organometallics 1994, 13, 3237-3243. (h) Murakami, M.; Suginome, M.; Fujimoto, K.; Nakamura, H.; Andersson, P. G.; Ito, Y. J. Am. Chem. Soc. 1993, 115, 6487-6498. (i) Ito, Y.; Suginome, M.; Murakami, M. J. Org. Chem. 1991, 56, 1948-1951. (j) Watanabe, H.; Kobayashi, M.; Higuchi, K.; Nagai, Y. J. Organomet. Chem. **1980**, *186*, 51–62. Si–Sin. (k) Murakami, M.; Amii, H.; Takizawa, N.; Ito, Y. Organometallics **1993**, *12*, 4223–4227. (l) Tsuji, Y.; Obora, Y. J. Am. Chem. Soc. **1991**, *113*, 9368–9369. (m) Mitchell, T. N.; Wickenkamp, R.; Amamria, A.; Dicke, R.; Schneider, U. J. Org. Chem. 1987, 52, 4868-4874. (n) Chenard, B. L.; Van Zyl, C. M. J. Org. Chem. 1986, 51, 3561-3566. Si-I: (o) Chatani, N.; Amishiro, N.; Morii, T.; Yamashita, T.; Murai, S. J. Org. Chem. 1995, *Soc.* **1991**, *113*, 7778–7780.

tin^{6f,7e,f,8k-n,9,10d,11} compounds, to unsaturated hydrocarbons. Although the corresponding reactions of boron compounds are not yet well developed, extensive studies have been done on the catalytic hydroboration of alkynes and alkenes with catecholborane or polyhedral boranes.¹² The mechanism is fundamentally different from an uncatalyzed process and was postulated to proceed through the catalytic cycle involving B-H bond activation by its oxidative addition to the low-valent transition-metal complexes, the migratory insertion of a C=C or C=C bond into the metal-hydride complexes, and the reductive elimination of a hydroboration product. Although the mechanism of the copper(I)- or cobalt(II)-catalyzed silylboration13 (B-Si) and stannylboration^{13,14} (B–Sn) of alkynes remains equivocal, the palladium(0)-catalyzed thioboration¹⁵ (B-S) of terminal alkynes and the palladium(0)-catalyzed Heck-type reaction of aryl- or vinylboranes¹⁶ (B-C) were also reported to proceed through an oxidative addition/ insertion sequence.

Recently, we have communicated a novel platinum(0)catalyzed addition reaction of the pinacol ester of diboron **1** to both terminal and internal alkynes to produce *cis*-bis(boryl)alkenes (**3**) (eq 1).¹⁷ In this paper,



we wish to report the scope of the reaction and evidence of the oxidative addition of the diboron to the platinum(0) complex by isolation of the adduct. The struc-

(11) Sn-H: (a) Zhang, H. X.; Guibé, F.; Balavoine, G. J. Org. Chem. **1990**, 55, 1857–1867. (b) Kikukawa, K.; Umekawa, H.; Wada, F.; Matsuda, T. Chem. Lett. **1988**, 881–884. Sn–Sn: (c) Mitchell, T. N.; Amamria, A.; Killing, H.; Rutschow, D. J. Organomet. Chem. **1986**, 304, 257–265. (d) Killing, H.; Mitchell, T. N. Organometallics, **1984**, 3, 1318–1320. (e) Mitchell, T. N.; Amamria, A.; Killing, H.; Rutschow, D. J. Organomet. Chem. **1983**, 241, C45-C47.

(12) (a) Gridnev, I. D.; Miyaura, N.; Suzuki, A. Organometallics
1993, 12, 589-592. (b) Burgess, K.; van der Donk, W. A.; Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. J. Am. Chem. Soc.
1992, 114, 9350-9359. (c) Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T. J. Am. Chem. Soc. 1992, 114, 8863-8869. (d) Evans, D. A.; Fu, G. C.; Anderson, B. A. J. Am. Chem. Soc. 1992, 114, 6679-6685. (e) Satoh, M.; Nomoto, Y.; Miyaura, N.; Suzuki, A. Tetrahedron Lett. 1989, 30, 3789-3792. (f) Hayashi, T.; Matsumoto, Y.; Ito, Y. J. Am. Chem. Soc. 1989, 111, 3426-3428. (g) Männig, D.; Nöth, H. Angew. Chem., Int. Ed. Engl. 1985, 24, 878-879. (h) Wilczynski, R.; Sneddon, L. G. J. Am. Chem. Soc. 1980, 102, 2857-2858. (i) For a recent review, see: Burgess, K.; Ohlmeyer, M. J. Chem. Rev. 1991, 91, 1179-1191. (13) Nozaki, K.; Wakamatsu, K.; Nonaka, T.; Tückmantel, W.;

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

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

(16) Cho, C. S.; Uemura, S. J. Organomet. Chem. 1994, 465, 85-92.

Table 1. Reaction Conditions for Diboration (Eq $1)^a$

entry	catalyst	solvent	temp/°C	yield/% ^b
1	none	DMF	80	0
2	Pt(PPh ₃) ₄	DMF	80	92
3	$Pt(CO)_2(PPh_3)_2$	DMF	80	94
4	PtCl ₂ (PPh ₃) ₂	DMF	80	0
5	$Pd(PPh_3)_4$	DMF	80	8
6	Pd(OAc) ₂ /15 t-BuN=C:	DMF	80	1
7	RhCl(PPh ₃) ₃	DMF	80	1
8	Ni(PPh ₃) ₄	DMF	80	0
9	CuCN	DMF	80	0
10	CoCl(PPh ₃) ₃	DMF	80	0
11	Pt(PPh ₃) ₄	DMF	50	76
12	Pt(PPh ₃) ₄	CH ₃ CN	50	68
13	Pt(PPh ₃) ₄	THF	50	58
14	Pt(PPh ₃) ₄	toluene	50	59
15	Pt(PPh ₃) ₄	hexane	50	80

^{*a*} All reactions were carried out for 24 h with use of diboron **1** (1.0 mmol), 1-octyne (1.1 mmol), catalyst (0.03 mmol), and solvent (6 mL). ^{*b*} GLC yields based on **1**.

ture and reactivity of the intermediate were fully characterized by NMR spectroscopies, single-crystal X-ray diffraction analysis, and its insertion reaction to alkynes, which would complement the related reactions of bis(catecholato)diboron, $C_6H_4O_2B-BO_2C_6H_4$, recently reported by Marder^{18,19} and Smith.²⁰

Results and Discussion

Reaction Conditions for Diboration. 1-Octyne (1.1 equiv) was initially chosen as a substrate and was allowed to react with 1 under various reaction conditions (Table 1). No detectable amount of addition product was observed without a catalyst (entry 1), but the reaction was efficiently catalyzed by platinum(0) complexes. The desired **3** ($R^1 = C_6 H_{13}$, $R^2 = H$) was produced in yields of 92% and 94% by heating the mixture at 80 °C in DMF for 24 h in the presence of a catalytic amount of Pt- $(PPh_3)_4$ or $Pt(CO)_2(PPh_3)_2$ (3 mol %) (entries 2 and 3). The formation of the *cis*-isomer with an isomeric purity over 99% was immediately established by the presence of one vinyl proton at 5.84 ppm and an NOE (5.7%) between the vinylic proton and allylic protons at 2.21 ppm in ¹H NMR. Among the catalysts we examined, only zerovalent platinum complexes exhibited excellent catalytic activity. The platinum(II) complexes such as PtCl₂(PPh₃)₂ (entry 4), Pd(PPh₃)₄ and Pd(OAc)₂ isocyanide complexes which have been used for silvl and stannyl metalation^{8g-n,11c-e} (entries 5 and 6), RhCl- $(PPh_3)_3$ used for catalytic hydroboration¹² (entry 7), and other metal complexes, e.g., Ni(PPh₃)₄, CuCN, and CoCl- $(PPh_3)_3$ (entries 8–10), were ineffective. The solvents did not play an important role, but a comparison of the reaction rates at 50 °C using Pt(PPh₃)₄ revealed that polar solvents accelerate the reaction (entries 11-14). However, the reaction in hexane resulted in an exceptionally high yield. Although Pt(PPh₃)₄ was used as a suspension in hexane, the reaction rate was apparently faster than the reactions in other solvents (entry 15).

The procedures could be applied for other (alkoxo)diboron derivatives. The addition of tetrakis(methoxo)-

⁽⁹⁾ Zn-Sn: Nonaka, T.; Okuda, Y.; Matsubara, S.; Oshima, K.;
Utimoto, K.; Nozaki, H. *J. Org. Chem.* **1986**, *51*, 4716–4718.
(10) Ge-H: (a) Ichinose, Y.; Oda, H.; Oshima, K.; Utimoto, K. *Bull.*

⁽¹⁰⁾ Ge-H: (a) Ichinose, Y.; Oda, H.; Oshima, K.; Utimoto, K. Bull. Chem. Soc. Jpn. 1987, 60, 3468-3470. (b) Corriu, R. J. P.; Moreau, J. J. E. J. Organomet. Chem. 1972, 40, 73-96. Ge-CN: (c) Chatani, N.; Horiuchi, N.; Hanafusa, T. J. Org. Chem. 1990, 55, 3393-3395. Ge-Sn: (d) Piers, E.; Skerlj, R. T. J. Chem. Soc., Chem. Commun. 1987, 1025-1026.

⁽¹⁷⁾ Preliminary communication of this work has appeared: Ishiyama, T.; Matsuda, N.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 11018–11019.

⁽¹⁸⁾ Baker, R. T.; Calabrese, J. C.; Westcott, S. A.; Nguyen, P.;
Marder, T. B. *J. Am. Chem. Soc.* **1993**, *115*, 4367–4368.
(19) Nguyen, P.; Lesley, G.; Taylor, N. J.; Marder, T. B.; Pickett, N.

⁽¹⁹⁾ Nguyen, P.; Lesley, G.; Taylor, N. J.; Marder, T. B.; Pickett, N. L.; Clegg, W.; Elsegood, M. R. J.; Norman, N. C. *Inorg. Chem.* **1994**, *33*, 4623–4624.

⁽²⁰⁾ Iverson, C. N.; Smith, M. R., III. J. Am. Chem. Soc. 1995, 117, 4403–4404.

Table 2. Diboration of A	lkynes with 1	(eq 1) ^a
--------------------------	---------------	---------------------

entry	alkyne	product 3	yield / % ^b
1	C ₈ H ₁₇ −C≡CH		86
2	C=CH	→ →B→ B<	78
3	C ₃ H ₇ −C≡C−C ₃ H ₇		86
4	Ph−C≡C−Ph	$\rightarrow B \xrightarrow{Ph} B \stackrel{Ph}{\leqslant} B \stackrel{Ph}{\leqslant}$	79
5	Ph−C≡CH	Ph→H →B→B<	79 ^c
6	$CH_2=CH(CH_2)_4-C\equiv CH$	CH ₂ =CH(CH ₂) ₄ H	85
7	CI-(CH ₂) ₃ −C≡CH	$\sim B^{CI-(CH_2)_3} H$	83
8	o↓(CH ₂)₄-C≡CH	o⊈ (CH ₂₎₄ H >B = B <	87
9	O CH ₃ O (CH ₂)₄−C≡CH		89
10	N≡C-(CH ₂) ₃ −C≡CH	N=C-(CH ₂) ₃ H	79
11	CH ₂) ₃ −C≡CH		77

^{*a*} All reactions were conducted in DMF (6 mL) at 80 °C for 24 h with use of 1 (1.0 mmol) and alkyne (1.1 mmol) in the presence of Pt(PPh₃)₄ (0.03 mmol).

^b Isolated yields based on 1. ^c The reaction was carried out at 120 °C.

diboron (**4a**) to 1-octyne (1.1 equiv) in DMF with $Pt(PPh_3)_4$ at 80 °C for 24 h gave an 89% yield of **3** ($R^1 = C_6H_{13}$, $R^2 = H$). For convenience of the analyses, the products were converted into the corresponding pinacol ester **3** (eq 2). On the other hand, the addition of tetrakis(dimethylamido)diboron was very slow even at 120 °C resulting in a 7% yield of **3** together with 86% of unreacted diboron.



Diboration of Representative Alkynes. In Table 2, the representative results of the diboration of various

alkynes with 1 in the presence of $Pt(PPh_3)_4$ are summarized. There were no large differences in the yields and the reaction rates between internal and terminal alkynes, and the additions to both types of alkynes were completed within 24 h at 80 °C to provide the corresponding **3** in a range of 78-86% yields (entries 1-4). The addition to phenylacetylene was very slow at 80 °C (less than 30%), but a 79% yield was achieved at 120 °C (entry 5). Alkynes which are especially good ligands for platinum(0) may inactivate the catalyst by their coordination to the metal, as discussed in the mechanistic section. The reaction was available with various functional groups. The carbon-carbon double bond, chloro, epoxy, ester, cyano, and ketone carbonyl groups remained intact during the diboration of the carboncarbon triple bonds (entries 6-11). However, the diboration of propargyl alcohol gave an inseparable mixture of **3** ($R^1 = H$, $R^2 = CH_2OH$) (~65%) and a unidentified byproduct. The diboration of dimethyl acetylenedicarboxylate smoothly proceeded at 120 °C, but the product was too labile to isolate. The addition to 5-bromo-1pentyne also failed, presumably due to the oxidative addition of the C-Br bond to the Pt(0) complex leading to an ineffective platinum(II) complex.²¹ Åll attempts at the diboration of alkenes with platinum complexes were unsuccessful.

Mechanism for Diboration. The reaction is catalyzed by platinum(0) complexes but not by divalent complexes. The addition proceeds through *syn* addition of the B–B bond to alkynes giving isomerically pure **3**. These results strongly suggested a mechanism involving the B–B bond activation by oxidative addition of **1** to the platinum(0) complex to form a bis(boryl)platinum-(II) intermediate, followed by alkyne insertion to the B–Pt bond and reductive elimination of **3**. A similar oxidative addition of B–H,²² Si–Si,^{8g,23} Sn–Sn,²⁴ and Si–Sn²⁵ compounds to low-valent transition-metal complexes has been extensively studied and postulated as a key step in the catalytic hydroboration¹² and additions of disilanes,^{8g–j} distannanes,^{11c–e} or silylstannanes^{8k–n} to alkenes and alkynes.

Monitoring of the reaction mixture of **1** (10 equiv) and $Pt(PPh_3)_4$ in toluene by multinuclear NMR spectroscopies revealed the formation of a new Pt(II) species. The low-temperature ³¹P NMR spectrum exhibited a singlet at 28.65 and its ¹⁹⁵Pt satellites at 35.61 and 21.73 ppm ($J_{Pt-P} = 1517$ Hz) which showed reasonable thermal stability for isolation and are characteristic of

(23) (a) Yamashita, H.; Kobayashi, T.-a.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **1990**, 1447–1450. (b) Eaborn, C.; Griffiths, R. W.; Pidcock, A. *J. Organomet. Chem.* **1982**, *225*, 331–341. (c) Glockling, F.; Houston, R. E. *J. Organomet. Chem.* **1973**, *50*, C31–C32. (d) Schmid, G.; Balk, H.-J. *Chem. Ber.* **1970**, *103*, 2240–2244.

(24) (a) Weichmann, H. J. Organomet. Chem. 1982, 238, C49-C52.
(b) Akhtar, M.; Clark, H. C. J. Organomet. Chem. 1970, 22, 233-240.
(25) Murakami, M.; Yoshida, T.; Kawanami, S.; Ito, Y. J. Am. Chem. Soc. 1995, 117, 6408-6409.

^{(21) (}a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 1988; pp 121–141. (b) Stille, J. K. *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1985; Vol. 2, pp 625–787.

<sup>Eds.; Wiley: New York, 1985; Vol. 2, pp 625-787.
(22) (a) Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. Can. J. Chem. 1993, 71, 930-936. (b) Westcott, S. A.; Taylor, N. J.; Marder, T. B.; Baker, R. T.; Jones, N. J.; Calabrese, J. C. J. Chem. Soc., Chem. Commun. 1991, 304-305. (c) Baker, R. T.; Ovenall, D. W.; Calabrese, J. C.; Westcott, S. A.; Taylor, N. J.; Williams, I. D.; Marder, T. B. J. Am. Chem. Soc. 1990, 112, 9399-9400. (d) Knorr, J. R.; Merola, J. S. Organometallics 1990, 9, 3008-3010. (e) Kono, H.; Ito, K.; Nagai, Y. Chem. Lett. 1975, 1095-1096. (f) Churchill, M. R.; Hackbarth, J. J.; Davison, A.; Traficante, D. D.; Wreford, S. S. J. Am. Chem. Soc. 1974, 96, 4041-4042.</sup>



Figure 1. Molecular structure of $Pt(BO_2C_2Me_4)_2(PPh_3)_2$ (5). Hydrogen atoms and the toluene molecule are omitted for clarity. Significant bond lengths (Å) and angles (deg): Pt-P(1) = 2.353(2), Pt-P(2) = 2.351(2), Pt-B(1) = 2.076(6),Pt-B(2) = 2.078(7), P(1)-Pt-P(2) = 102.65(5), B(1)-Pt-B(2) = 75.3(3), P(1)-Pt-B(1) = 92.9(2), P(2)-Pt-B(2) =89.0(2).

phosphines *cis*-coordinated to a platinum(II) center. (The J_{Pt-P} values of related bis(silyl)platinum derivatives are ca. 2800 Hz for the trans- and ca. 1500 Hz for the cis-complex.^{23a,26}) The reinvestigation of reaction conditions for oxidative addition of 1 to Pt(PPh₃)₄ (100: 1) was followed by ³¹P NMR spectroscopy in a variety of solvents and reaction temperatures. Interestingly, hexane was the best solvent of choice and most of the Pt(PPh₃)₄ was consumed even at room temperature within 24 h. A similar reaction in DMF or toluene proceeded more slowly with some unreacted Pt(PPh₃)₄ remaining which made the separation of the expected intermediate more difficult. Finally, a single crystal of 5 suitable for X-ray analysis was obtained in an 82% yield by treatment of Pt(PPh₃)₄ with 20 equiv of 1 in hexane at 80 °C for 2 h, followed by recrystallization from hexane/toluene (3:1) (eq 3).



The results of an X-ray diffraction analysis of **5** are shown in Figure 1 and Tables 3, and 4. The molecular structure of **5** consists of a distorted square-planar coordination geometry for the Pt atom containing two *cis* boryl and phosphine ligands where the significant bond angles are $\angle P(1)-Pt-P(2)$ (102.65(5)°) and $\angle B(1)-$ Pt-B(2) (75.3(3)°). The B-Pt bond lengths of 2.076(6) and 2.078(7) Å are closely similar to the Ir-B bond lengths (2.023–2.093 Å) in boryliridium complexes^{22b,c,e} and to the Pt-C bond distance (2.081 Å) in PtMeCl(PPh₂-Me)₂.²⁷ The characteristic feature of this crystal is a

 Table 3. Crystal Data and Details of the Structure

 Determination for Complex 5

	1
formula	$C_{48}H_{54}B_2P_2Pt \cdot 0.5C_7H_8$
fw	1019.68
habit	prismatic
temp, K	296
cryst system	triclinic
space group	<i>P</i> 1 (No. 2)
a, Å	13.245(3)
b, Å	15.761(2)
<i>c,</i> Å	13.032(2)
α, deg	92.48(1)
β , deg	112.49(2)
γ , deg	72.55(1)
V, Å ³	2390.0(8)
Ζ	2
$d_{ m calcd}$, g cm $^{-3}$	1.417
F(000)	1034
cryst size, mm	0.2 imes 0.2 imes 0.5
μ (Mo K α), cm ⁻¹	30.34
radiation	Mo K α ($\lambda = 0.710$ 69 Å)
diffractometer	Rigaku AFC5R
monochromator	graphite
data collcd	$+h,\pm k,\pm I$
scan type	$\omega - 2\theta$
scan range	$0.94 \pm 0.35 an heta$
2θ range, deg	5.0 - 50.0
scan speed, deg min ⁻¹	8, fixed
abs corr	empirical
min and max transm factors	0.698, 1.000
no. of reflcns collcd	8795
no. of unique reflcns	8400 ($R_{\rm int} = 0.062$)
no. of reflcns used	7447 ($I \ge 3\sigma(I)$)
no. of variables	518
R	0.032
$R_{ m w}$	0.037
GOF	2.81
max shift/error in final cycle	0.01
max and min peak, e ${ m \AA}^{-3}$	1.26, -1.35 (near Pt)

very narrow B-Pt-B bond angle and an almost parallel arrangement of two dioxaborolane rings. The perpendicular arrangement of two dioxaborolane ligands to the Pt(II) square plane may allow the $d_{\pi}-p_{\pi}$ back-bonding from the Pt to the B atom to develop the B-B interaction. Although the presence of a weak B–B interaction is not to be dismissed, the B-B distance of 2.538(7) Å indicates that the arrangement and the acute B-Pt-B angle are due to the steric requirement. During the course of our investigation, Iverson and Smith reported the X-ray structure of a very similar bis(boryl)platinum-(II) complex obtained by the oxidative addition of bis-(catecholato)diboron to Pt(PPh₃)₂(η^2 -CH₂=CH₂).²⁰ The observed bond angles and lengths, $\angle P(1) - Pt - P(2)$ $(107.4^{\circ}), \angle B(1) - Pt - B(2)$ (77.8°), and Pt-B (2.07 and 2.08 Å), are the same as that of 5, except the two dioxaborolane rings in 5 are slightly distorted to release the steric repulsion between the vicinal methyl groups in contrast to the almost planar structure of 1.5a

The isolated **5** exhibited high reactivity for the insertion of alkynes. Treatment of **5** with 1-octyne (1 equiv) in C_6D_6 at 50 °C for 6 h led to an 87% conversion of **5** to provide the corresponding **3** ($R^1 = C_6H_{13}$, $R^2 = H$) as the sole product (eq 4). Although the catalytic dibora-



tion of phenylacetylene proceeded slowly at 80 °C and

⁽²⁶⁾ Kobayashi, T.-a.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1988**, 1411–1414.

⁽²⁷⁾ Bennet, M. A.; Chee, H.; Robertson, G. B. *Inorg. Chem.* **1979**, *18*, 1061–1070.

 Table 4. Positional Parameters and Equivalent

 Isotropic Thermal Parameters (Å²) for Complex 5^a

	-			-
atom	X	у	Ζ	$B_{ m eq}{}^b$
Pt	0.03450(2)	0 23493(2)	0 13366(2)	2 369(5)
P(1)	0.00100(2)	0.2296(1)	-0.0557(1)	2.500(0) 2.57(3)
P(2)	-0.1529(1)	0.2200(1) 0.2651(1)	0.0001(1) 0.1271(1)	2.07(3)
$\mathbf{R}(1)$	0.1020(1)	0.2031(1) 0.2133(4)	0.1271(1)	2.40(3)
D(1) D(9)	0.2038(0)	0.2133(4) 0.2495(4)	0.1052(0) 0.2051(5)	2.0(1)
D(2)	0.0924(3)	0.2423(4)	0.3031(3)	2.8(1)
O(1)	0.2621(3)	0.2690(3)	0.1708(3)	4.0(1)
O(2)	0.2935(3)	0.1352(3)	0.2525(4)	4.5(1)
O(3)	0.1227(4)	0.3141(3)	0.3598(3)	4.1(1)
O(4)	0.1037(4)	0.1794(3)	0.3805(3)	4.2(1)
C(1)	0.4468(6)	0.2593(5)	0.1702(7)	6.2(2)
C(2)	0.3843(5)	0.2383(4)	0.2373(6)	4.4(2)
C(3)	0.4048(7)	0.2886(5)	0.3408(7)	6.6(2)
C(4)	0.4332(7)	0.0814(5)	0.1712(8)	7.1(2)
C(5)	0.4063(5)	0.1378(5)	0.2598(6)	4.7(2)
C(6)	0.4934(6)	0.0960(6)	0.3735(7)	7.6(2)
C(7)	0.0204(8)	0.3623(5)	0.4779(7)	7.2(3)
C(8)	0.1323(6)	0.3048(4)	0.4738(5)	4.2(2)
C(9)	0.2273(9)	0.3397(6)	0.5486(6)	8.0(3)
C(10)	0.0946(7)	0.1800(5)	0.5618(6)	5.8(2)
C(10)	0.0040(7) 0.1539(5)	0.1000(0) 0.2034(4)	0.0010(0) 0.4928(5)	38(2)
C(12)	0.1000(0) 0.9785(7)	0.1497(6)	0.45280(6)	6 9(2)
C(12)	0.2703(7)	0.1407(0)	0.0009(0)	0.0(2)
C(13)	0.1338(3) 0.1047(5)	0.1830(3)	-0.0908(4)	2.7(1)
C(14)	0.1647(5)	0.0951(4)	-0.1108(5)	3.0(2)
C(15)	0.2598(5)	0.0606(4)	-0.1438(5)	4.0(2)
C(16)	0.3242(5)	0.1147(4)	-0.1447(6)	4.3(2)
C(17)	0.2961(5)	0.2012(4)	-0.1181(6)	4.2(2)
C(18)	0.2023(5)	0.2346(4)	-0.0893(5)	3.6(1)
C(19)	-0.0506(5)	0.3423(4)	-0.1255(5)	2.8(1)
C(20)	-0.0923(5)	0.4123(4)	-0.0700(5)	3.7(2)
C(21)	-0.1320(6)	0.5001(4)	-0.1158(6)	4.7(2)
C(22)	-0.1291(6)	0.5184(4)	-0.2159(6)	4.7(2)
C(23)	-0.0885(6)	0.4503(5)	-0.2715(6)	4.7(2)
C(24)	-0.0485(5)	0.3622(4)	-0.2275(5)	3.9(2)
C(25)	-0.0851(5)	0.1651(4)	-0.1420(5)	2.9(1)
C(26)	-0.0960(5)	0.0957(4)	-0.0893(5)	3.3(1)
C(27)	-0.1551(6)	0.0394(4)	-0.1498(6)	4.3(2)
C(28)	-0.2052(6)	0.0509(5)	-0.2622(7)	5.0(2)
C(29)	-0.1982(7)	0.1208(6)	-0.3164(6)	5.9(2)
C(20)	-0.1376(6)	0.1200(0) 0.1772(5)	-0.2566(5)	47(2)
C(31)	-0.2205(5)	0.1772(0) 0.3821(4)	0.2000(0) 0.1451(4)	2.7(2)
C(31)	-0.1540(5)	0.3821(4) 0.4200(4)	0.1431(4) 0.1924(5)	2.3(1)
C(32)	-0.1349(3)	0.4350(4)	0.1034(3) 0.1047(g)	3.3(1)
C(33)	-0.2070(0)	0.5200(4)	0.1947(0)	4.0(2)
C(34)	-0.3232(0)	0.3367(4)	0.1709(0)	5.0(2)
C(35)	-0.3881(5)	0.5029(4)	0.1321(6)	4.6(2)
C(36)	-0.3396(5)	0.4152(4)	0.1193(5)	3.8(1)
C(37)	-0.1551(5)	0.1996(4)	0.2391(5)	3.1(1)
C(38)	-0.0887(5)	0.1106(4)	0.2592(5)	3.7(2)
C(39)	-0.0898(6)	0.0557(4)	0.3393(6)	4.5(2)
C(40)	-0.1562(6)	0.0894(5)	0.3994(6)	5.0(2)
C(41)	-0.2208(6)	0.1776(5)	0.3809(6)	5.1(2)
C(42)	-0.2209(5)	0.2328(4)	0.3011(5)	4.0(2)
C(43)	-0.2690(5)	0.2443(4)	0.0074(5)	3.1(1)
C(44)	-0.3179(5)	0.1792(4)	0.0113(6)	4.6(2)
C(45)	-0.4009(7)	0.1615(6)	-0.0810(8)	6.4(2)
C(46)	-0.4378(6)	0.2087(6)	-0.1788(7)	6.3(2)
C(47)	-0.3933(6)	0.2754(6)	-0.1880(6)	5.8(2)
C(48)	-0.3086(5)	0.2930(5)	-0.0937(6)	4.5(2)
C(49)	0.6118	0 4478	0.5635	20 4(7)*
C(50)	0.5787	0 4678	0 4499	21 7(7)*
C(51)	0.4669	0 5200	0 3863	19 8(R)*
C(52)	0.4003	0.3200	0.3003	92 (1)*
U(J2)	0.0000	0.4323	0.3943	23(1)

^{*a*} $B_{\text{eq}} = (8\pi^2/3)\sum_i\sum_j[U_{ij}(a_i^*a_j^*)(\mathbf{a}_i^*\mathbf{a}_j)] = (4/3)\sum_i\sum_j[\beta_{ij}(\mathbf{a}_i^*\mathbf{a}_j)]$. The *B* values with an asterisk are isotropic. The site occupation factor for C(52) is 0.5. The positional parameters for C(49), C(50), C(51), and C(52) were not refined.

gave a reasonable yield at 120 °C (entry 5 in Table 2), 5 smoothly added to phenylacetylene at 50 °C. The results suggest that, in the catalytic system, the coordination of phenylacetylene to the platinum(0) complex would retard the generation of a coordinatively unsaturated species active for oxidative addition. On the other hand, 5 did not provide addition products to alkenes such as 1-octene, thus limiting the present



Figure 2. Catalytic cycle for diboration.

reaction to alkynes, which is in contrast to the bis(boryl)rhodium(III) complex giving diboration products with styrenes.¹⁸

On the basis of these findings, we propose the catalytic cycle shown in Figure 2. The oxidative addition of diboron **1** to the platinum(0) complex produces **5**. The insertion of alkynes to the B–Pt bond to provide a vinylplatinum(II) species **6** is followed by the reductive elimination of **3**. The reductive elimination of **3** is too rapid to observe the existence of **6**, but its assumption can be consistent with numerous reports implying *cis* insertion from alkyne/platinum(II) complexes.²⁸

The addition of **1** to alkynes was not catalyzed by rhodium(I) or palladium(0) catalysts (entries 5-7 in Table 1); presumably, the oxidative addition step is very slow to develop the catalytic cycle due to the lower energy level of the d orbital.²⁹ In fact, the treatment of Pd(PPh₃)₄ with 10 equiv of **1** in toluene at 100 °C for 1 h provided no evidence of its oxidative addition. A similar low reactivity of **1** toward RhCl(PPh₃)₃ was also reported by Marder et al., although they found a high reactivity of **bis**(catecholato)diboron for the oxidative addition.¹⁹

Conclusion

We reported the first access to *cis*-bis(boryl)alkenes *via* the platinum(0)-catalyzed addition of tetrakis(alkoxo)diborons to alkynes. The reaction employs air-stable and accessible substrates and proceeds under mild conditions, tolerating a broad range of functionality and yielding stereodefined products in high isolated yields. The oxidative adduct intermediate **5** has been isolated and fully characterized by X-ray analyses and by observing its insertion reaction to alkynes. The observed catalytic cycle is very powerful and undergoes fundamentally common processes with a group 10 transition metal; therefore, the uses of this type of reaction will certainly be exploited in the future.

Experimental Section

All the experiments were carried out under nitrogen atmosphere. Solvents were purified by distillation from appropriate

^{(28) (}a) Alexander, J. J. *The Chemistry of the Metal-Carbon Bond*; Wiley: New York, 1985; Vol. 2, pp 339–400. (b) Otsuka, S.; Nakamura, A. *Advances in Organometallic Chemistry*; Academic, New York, 1976; Vol. 14, pp 245–283.

⁽²⁹⁾ Similar energy difference of the d orbital between Rh(I) and Ir(I) complexes affects on the rate of oxidative addition of molecular hydrogen: Dedieu, A.; Strich, A. *Inorg. Chem.* **1979**, *18*, 2940–2943.

drying reagents. IR spectra were taken on a Hitachi Perkin-Elmer Model 125 spectrometer. ¹H and ¹³C NMR spectra were recorded in CDCl₃ solutions by a JEOL EX-400 (400 or 100 MHz) using Me₄Si as an internal standard. ¹¹B and ³¹P NMR spectra were recorded with a Bruker MSL-400 (128 or 162 MHz) using BF₃·OEt₂ or H₃PO₄ as an external standard. Mass spectra were measured with a JEOL JMS-DX303 for the both low- and high-resolution analyses. GC analyses were performed on a Hitachi 263 equipped with a glass column (OV-17 on Uniport B, 2 m).

Diboron Reagents. Bis(pinacolato)diboron,^{5a} tetrakis-(methoxo)diboron,^{5c} and tetrakis(dimethylamido)diboron^{5d} were synthesized by reported procedures.

Catalysts and Ligands. Tetrakis(triphenylphosphine)platinum(0), tetrakis(triphenylphosphine)palladium(0), palladium(II) acetate, chlorotris(triphenylphosphine)rhodium(I), tetrakis(triphenylphosphine)nickel(0), copper(I) cyanide, and *tert*-butyl isocyanide are commercial products. Dicarbonylbis-(triphenylphosphine)platinum(0),³⁰ dichlorobis(triphenylphosphine)platinum(II),³¹ and chlorotris(triphenylphosphine)cobalt(I)³² were prepared by the reported procedures.

Alkynes. 1-Octyne, 1-decyne, cyclohexylethyne, 4-octyne, diphenylacetylene, phenylacetylene, 5-chloro-1-pentyne, and 5-cyano-1-pentyne are commercial products. 1-Octen-7-yne was prepared by the reaction between 6-iodo-1-hexene and sodium acetylide.³³ 7,8-Epoxy-7-methyl-1-octyne was obtained from 7-octyn-2-one by Corey's method.³⁴ The malonic ester synthesis³⁵ or the acetoacetic ester synthesis³⁶ gave methyl 6-heptynoate and 2-(4-pentynyl)cyclopentanone.

Reaction Conditions (Table 1). The conditions for the formation of 1,2-bis(boryl)-1-octene **3** ($R^1 = C_6H_{13}$, $R^2 = H$) were optimized by the following general procedure. The transition-metal catalyst (0.03 mmol) and pinacol ester of diboron **1** (254 mg, 1.0 mmol) were placed in a 25-mL flask equipped with a magnetic stirring bar, septum inlet, and a reflux condenser. The flask was flushed with nitrogen and then charged with solvent (6 mL) and 1-octyne (121 mg, 1.1 mmol). After being stirred for 24 h at the temperature indicated in Table 1, the reaction mixture was cooled to room temperature, diluted with benzene (30 mL), washed with cold water 5 times to remove DMF, and dried over magnesium sulfate. GLC yields are summarized in Table 1.

Addition of Tetrakis(methoxo)- or Tetrakis(dimethylamido)diboron (Eq 2). A mixture of Pt(PPh₃)₄ (37 mg, 0.03 mmol), tetrakis(methoxo)diboron (146 mg, 1.0 mmol), 1-octyne (121 mg, 1.1 mmol), and DMF (6 mL) was stirred at 80 °C. After being stirred for 24 h, the reaction mixture was treated with pinacol (472 mg, 4 mmol) at room temperature for 24 h to convert 1,2-bis(dimethoxyboryl)-1-octene into the corresponding pinacol ester. GLC analysis indicated the formation of **3** ($\mathbb{R}^1 = \mathbb{C}_6\mathbb{H}_{13}, \mathbb{R}^2 = \mathbb{H}$) in a yield of 89%. A similar reaction with tetrakis(dimethylamido)diboron (198 mg, 1.0 mmol) at 120 °C for 24 h gave **3** ($\mathbb{R}^1 = \mathbb{C}_6\mathbb{H}_{13}, \mathbb{R}^2 = \mathbb{H}$) (7%) and **1** (86%).

General Procedure for Diboration of Alkynes (Table 2). A 25-mL flask, equipped with a magnetic stirring bar, septum inlet, and a reflux condenser, was charged with Pt-(PPh₃)₄ (37 mg, 0.03 mmol) and **1** (254 mg, 1.0 mmol) and then flushed with nitrogen. DMF (6 mL) and alkyne (1.1 mmol)

(30) Beck, W.; Purucker, B. J. Organomet. Chem. 1976, 112, 361-368.

(31) Bailar, J. C.; Itatani, H. Inorg. Chem. 1965, 4, 1618-1620.

(32) Wakatsuki, Y.; Yamazaki, H. Inorg. Synth. **1989**, 26, 190–191. (33) Campbell, K. N.; Campbell, B. K. Organic Syntheses, Wiley:

(34) Corey, E. J.; Chaykovsky, M. Organic Syntheses, Wiley: New York, 1963; Collect. Vol. IV, pp 117–120.
 (34) Corey, E. J.; Chaykovsky, M. Organic Syntheses; Wiley: New York, 1973; Collect. Vol. V, pp 755–757.

(35) (a) Adams, R.; Kamm, R. M. *Organic Syntheses*; Wiley: New York, 1941; Collect. Vol. I, pp 250–251. (b) Vliet, E. B.; Marvel, C. S.; Hsueh, C. M. *Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. II, pp 416–417.

(36) (a) Marvel, C. S.; Hager, F. D. *Organic Syntheses*, Wiley: New York, 1941; Collect. Vol. I, pp 248–250. (b) Johnson, J. R.; Hager, F. D. *Organic Syntheses*, Wiley: New York, 1941; Collect. Vol. I, pp 351–353.

were successively added. After being stirred for 24 h at 80 °C, the reaction mixture was diluted with benzene (30 mL), repeatedly washed with cold water to remove DMF (5 times), and finally dried over anhydrous magnesium sulfate. Kugelrohr distillation (0.15 mmHg) gave the bis(boryl)alkene **3**.

The following compounds were prepared by the above general procedure.

(*E*)-1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-octene: $n_{\rm D}$ 1.4562; IR (film) 2980, 2940, 2860, 1620, 1400, 1380, 1340, 1300, 1220, 1140, 980, 850 cm⁻¹; ¹H NMR (CDCl₃) 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 vinylic proton at 5.84 ppm resulted in an 5.7% enhancement of the allylic methylene signal at 2.21 ppm]; ¹³C NMR (CDCl₃) δ 14.12, 22.59, 24.89, 24.93, 28.62, 29.13, 31.77, 39.92, 83.25, 83.61; ¹¹B NMR (CDCl₃) δ 30.24; MS (EI) m/e 41 (100), 55 (67), 69 (52), 83 (67), 95 (8), 109 (10), 153 (8), 179 (4), 223 (13), 237 (8), 264 (3), 306 (4), 349 (0.6), 364 (0.5, M⁺); exact mass calcd for C₂₀H₃₈O₄B₂ m/e 364.2957, found m/e 364.2932.

(*E*)-1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-decene: n_D 1.4622; IR (film) 2980, 2930, 2850, 1620, 1400, 1380, 1330, 1300, 1220, 1140, 970, 850 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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; ¹¹B NMR (CDCl₃) δ 30.26; MS (EI) m/e 41 (40), 55 (37), 69 (33), 84 (100), 101 (10), 153 (23), 165 (3), 207 (7), 237 (29), 251 (43), 292 (12), 334 (13), 377 (2), 392 (1, M⁺); exact mass calcd for C₂₂H₄₂O₄B₂ m/e 392.3269, found m/e 392.3271.

(*E*)-1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-cyclohexylethene: n_D 1.4800; IR (film) 2980, 2930, 2850, 1620, 1400, 1380, 1330, 1300, 1220, 1140, 980, 850 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) δ 24.91, 25.11, 26.28, 26.61, 32.30, 47.68, 83.25, 83.65; ¹¹B NMR (CDCl₃) δ 30.33; MS (EI) m/e 41 (57), 55 (48), 69 (46), 83 (100), 101 (11), 135 (19), 179 (31), 192 (80), 205 (5), 221 (32), 234 (11), 246 (3), 262 (4), 304 (17), 347 (2), 362 (2, M⁺); exact mass calcd for C₂₀H₃₆O₄B₂ m/e362.2800, found m/e 362.2811.

(Z)-4,5-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-octene: mp 35 °C; IR (Nujol) 2950, 2850, 1460, 1380, 1340, 1300, 1160, 1140 cm⁻¹; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) δ 14.61, 23.01, 24.95, 33.10, 83.29; ¹¹B NMR (CDCl₃) δ 30.72; MS (EI) *m*/*e* 41 (20), 55 (19), 69 (20), 84 (100), 95 (7), 125 (3), 139 (7), 180 (12), 207 (4), 223 (14), 264 (7), 306 (10), 349 (0.9), 364 (2, M⁺); exact mass calcd for C₂₀H₃₈O₄B₂ *m/e* 364.2956, found *m/e* 364.2997.

(Z)-1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-diphenylethene: mp 178 °C; IR (Nujol) 3050, 2920, 2850, 1460, 1380, 1300, 1140, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 1.32 (s, 24 H), 6.94 (d, 4 H, J = 6.8 Hz), 7.0–7.1 (m, 6 H); ¹³C NMR (CDCl₃) δ 24.89, 84.07, 125.79, 127.41, 129.32, 141.29; ¹¹B NMR (CDCl₃) δ 30.57; MS (EI) m/e 41 (18), 55 (12), 69 (21), 77 (9), 84 (100), 105 (5), 129 (8), 152 (3), 178 (73), 199 (5), 231 (2), 251 (2), 277 (19), 291 (13), 374 (3), 432 (5, M⁺); exact mass calcd for C₂₆H₃₄O₄B₂ m/e 432.2643, found m/e 432.2667.

(*E*)-1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenylethene: mp 68 °C; IR (Nujol) 3070, 2950, 2850, 1600, 1460, 1380, 1330, 1140, 970, 850, 760, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 1.31 (s, 12 H), 1.38 (s, 12 H), 6.29 (s, 1 H), 7.24 (t, 1 H, *J* = 7.3 Hz), 7.30 (t, 2 H, *J* = 7.3 Hz), 7.43 (d, 2 H, *J* = 6.8 Hz); ¹³C NMR (CDCl₃) δ 24.89, 25.09, 83.60, 84.14, 126.59, 127.62, 128.31, 143.05; ¹¹B NMR (CDCl₃) δ 29.97; MS (EI) *m/e* 41 (30), 55 (18), 69 (25), 84 (100), 97 (3), 105 (10), 131 (12), 157 (4), 175 (13), 199 (4), 215 (53), 273 (2), 298 (9), 356 (5, M⁺); exact mass calcd for C₂₀H₃₀O₄B₂ *m/e* 356.2331, found *m/e* 356.2337. (*E*)-1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,7-octadiene: $n_{\rm D}$ 1.4584; IR (film) 3000, 2950, 1620, 1400, 1380, 1340, 1310, 1220, 1140, 980, 860 cm⁻¹; ¹H NMR (CDCl₃) δ 1.26 (s, 12 H), 1.31 (s, 12 H), 1.3–1.5 (m, 4 H), 2.04 (dt, 2 H, J = 7.3 and 6.8 Hz), 2.22 (t, 2 H, J = 6.6 Hz), 4.91 (dd, 1 H, J= 10.3 and 2.0 Hz), 4.98 (dd, 1 H, J = 17.1 and 2.0 Hz), 5.79 (ddt, 1 H, J = 17.1, 10.3, and 6.8 Hz), 5.85 (s, 1 H); ¹³C NMR (CDCl₃) δ 24.87, 24.91, 28.11, 28.64, 33.67, 39.67, 83.25, 83.63, 114.23, 139.05; ¹¹B NMR (CDCl₃) δ 29.91; MS (EI) m/e 41 (37), 55 (34), 69 (36), 84 (100), 101 (13), 135 (11), 163 (10), 178 (11), 205 (7), 221 (39), 234 (7), 262 (4), 277 (3), 304 (9), 347 (2), 362 (0.1, M⁺); exact mass calcd for C₂₀H₃₆O₄B₂ m/e 362.2800, found m/e 362.2824.

(*E*)-1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-chloro-1-pentene: $n_{\rm D}$ 1.4613; IR (film) 3000, 2950, 1620, 1400, 1380, 1340, 1310, 1220, 1140, 980, 860 cm⁻¹; ¹H NMR (CDCl₃) δ 1.27 (s, 12 H), 1.31 (s, 12 H), 1.85–1.95 (m, 2 H), 2.36 (t, 2 H, J = 6.8 Hz), 3.52 (t, 2 H, J = 6.6 Hz), 5.92 (s, 1 H); ¹³C NMR (CDCl₃) δ 24.87, 24.91, 31.57, 36.63, 44.59, 83.41, 83.80; ¹¹B NMR (CDCl₃) δ 29.93; MS (EI) m/e 41 (71), 59 (45), 69 (43), 83 (100), 93 (8), 101 (12), 121 (6), 147 (7), 157 (16), 174 (5), 215 (74), 237 (6), 256 (31), 298 (11), 341 (2), 356 (0.3, M⁺); exact mass calcd for C₁₇H₃₁O₄B₂Cl m/e 356.2093.

(*E*)-1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-7,8-epoxy-7-methyl-1-octene: $n_{\rm D}$ 1.4618; IR (film) 3000, 2950, 1620, 1400, 1380, 1340, 1300, 1220, 1140, 980, 850 cm⁻¹; ¹H NMR (CDCl₃) δ 1.27 (s, 12 H), 1.29 (s, 3 H), 1.31 (s, 12 H), 1.3–1.7 (m, 6 H), 2.22 (t, 2 H, J = 6.8 Hz), 2.55 (d, 1 H, J = 4.9 Hz), 2.60 (d, 1 H, J = 4.9 Hz), 5.85 (s, 1 H); ¹³C NMR (CDCl₃) δ 20.92, 24.87, 24.91, 25.11, 28.64, 36.65, 39.70, 53.99, 57.02, 83.30, 83.65; MS (EI) m/e 41 (60), 55 (53), 69 (47), 83 (100), 101 (28), 121 (18), 137 (10), 149 (16), 177 (18), 192 (24), 234 (9), 264 (3), 276 (19), 292 (3), 334 (2), 392 (0.1, M⁺); exact mass calcd for C₂₁H₃₈O₅B₂ m/e 392.2905, found m/e 392.2890.

Methyl (*E***)-6,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-heptenoate:** $n_{\rm D}$ 1.4601; IR (film) 3000, 2950, 1740, 1620, 1400, 1380, 1330, 1310, 1220, 1140, 980, 850 cm⁻¹; ¹H NMR (CDCl₃) δ 1.26 (s, 12 H), 1.31 (s, 12 H), 1.40–1.50 (m, 2 H), 1.55–1.65 (m, 2 H), 2.23 (t, 2 H, J = 7.1 Hz), 2.29 (t, 2 H J = 7.6 Hz), 3.65 (s, 3 H), 5.86 (s, 1 H); ¹³C NMR (CDCl₃) δ 24.69, 24.87, 28.13, 34.02, 39.27, 51.41, 83.30, 83.67, 174.14; ¹¹B NMR (CDCl₃) δ 29.93; MS (EI) m/e 41 (28), 55 (25), 69 (21), 83 (49), 93 (15), 101 (5), 135 (4), 151 (8), 166 (8), 179 (4), 194 (100), 221 (5), 236 (15), 253 (3), 263 (14), 278 (11), 294 (15), 336 (3), 363 (0.8), 379 (0.8), 394 (0.1, M⁺); exact mass calcd for C₂₀H₃₆O₆B₂ m/e 394.2698, found m/e 394.2717.

(*E*)-5,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-hexenenitrile: $n_{\rm D}$ 1.4615; IR (film) 3000, 2950, 2250, 1620, 1400, 1380, 1340, 1320, 1220, 1140, 980, 850 cm⁻¹; ¹H NMR (CDCl₃) δ 1.28 (s, 12 H), 1.31 (s, 12 H), 1.75–1.85 (m, 2 H), 2.32 (t, 2 H, J = 7.3 Hz), 2.35 (t, 2 H, J = 7.3 Hz), 5.93 (s, 1 H); ¹³C NMR (CDCl₃) δ 16.50, 24.49, 24.87, 38.24, 83.54, 83.91, 119.79; ¹¹B NMR (CDCl₃) δ 30.05; MS (EI) m/e 41 (62), 55 (39), 69 (33), 83 (68), 93 (6), 122 (17), 148 (82), 166 (17), 188 (10), 206 (100), 232 (10), 247 (19), 289 (16), 319 (0.6), 332 (2), 347 (1, M⁺); exact mass calcd for C₁₈H₃₁O₄B₂N m/e 347.2439, found m/e 347.2437.

2-[(*E***)-4,5-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-4-pentenyl]cyclopentanone:** mp 54 °C; IR (Nujol) 3000, 2950, 1740, 1620, 1400, 1380, 1340, 1310, 1220, 1150, 980, 860 cm⁻¹; ¹H NMR (CDCl₃) δ 1.26 (s, 12 H), 1.30 (s, 12 H), 1.4–1.6 (m, 4 H), 1.7–1.8 (m, 2 H), 1.9–2.3 (m, 7 H), 5.85 (s, 1 H); ¹³C NMR (CDCl₃) δ 20.78, 24.87, 24.91, 26.74, 29.50, 29.59, 38.19, 39.76, 49.07, 83.30, 83.67, 221.41; ¹¹B NMR (CDCl₃) δ 30.02; MS (EI) *m*/e 41 (51), 55 (46), 69 (38), 83 (79), 93 (28), 101 (11), 133 (15), 162 (12), 176 (16), 204 (100), 221 (20), 246 (13), 263 (16), 288 (20), 321 (5), 346 (1), 389 (1), 404 (0.9, M⁺); exact mass calcd for C₂₂H₃₈O₅B₂ *m*/e 404.2905, found *m*/e 404.2880.

NMR Study for Oxidative Addition of 1 to $Pt(PPh_3)_4$. Pt(PPh_3)₄ (62 mg, 0.05 mmol), **1** (127 mg, 0.5 mmol), and toluene (4 mL) were sealed in a NMR tube. After being heated at 100 °C for 1 h, the solution was directly analyzed by ¹¹B and ³¹P NMR spectroscopies. The signals used for the identification are as follows: ¹¹B NMR (toluene) δ 46.0 (broad, two borons in **5**) and 29.9 (two boron in **1**); ³¹P NMR (toluene at -80 °C) δ -7.30 (br s, free Ph₃P), 10.68 (br s, unknown species), 25.34 (s, Pt(PPh₃)₄), 28.65, and its satellites at 35.61 and 21.73 ($J_{Pt-P} = 1517$ Hz) (two phosphines in **5**).

Synthesis of *cis*-Pt(BO₂C₂Me₄)₂(PPh₃)₂ (5) (Eq 3). A mixture of Pt(PPh₃)₄ (50 mg, 0.04 mmol) and 1 (203 mg, 0.8 mmol) in hexane (6 mL) was stirred at 80 °C for 2 h. To this suspension was added toluene (2 mL) at that temperature. The resulting homogeneous solution was cooled to room temperature over 1 day to give 82% yield of 5 as a colorless crystal: mp 145 °C (dec); ¹H NMR (C₆D₆) δ 1.02 (s, 24 H), 6.80–6.95 (m, 18 H), 7.55–7.65 (m, 12 H); ¹³C NMR (C₆D₆) δ 25.79, 81.22, 127.62, 129.04, 135.06, 136.87; ³¹P NMR (toluene at -55 °C) δ 27.79 and its satellites at 32.47 and 23.11 ($J_{Pt-P} = 1516$ Hz), ¹¹B NMR (toluene) δ 46.0.

X-ray Diffraction Study of 5. A colorless single crystal of approximate dimensions of $0.2 \times 0.2 \times 0.5$ mm was sealed in a glass capillary tube. Intensity data were collected on a Rigaku AFC5R four-circle diffractometer. Unit cell dimensions were obtained from a least-squares treatment of the setting angles of 25 reflections in the range $25.0 < 2\theta < 28.8^{\circ}$. The cell dimensions suggested a triclinic cell. Diffraction data were collected at 23 °C in the range 5.0 < 2θ < 50.0° using the ω - 2θ scan technique at a scan rate of 8° min⁻¹ in ω . Three standard reflections, monitored at every 150 reflection measurements, showed no significant variation in their intensities. The data was corrected for Lorentz and polarization effects and for absorption (empirical based on four azimuthal scans). Of the 8400 unique reflections measured, 7447 were classed as observed $(I > 3\sigma(I))$ and these were used for the solution and refinement of the structure. On the basis of a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P\overline{1}$ (No. 2). All calculations were performed with the TEXSAN Crystal Structure Analysis Package provided by Rigaku Corp., Tokyo, Japan. The scattering factors were taken from ref 37. All non-hydrogen atoms of the platinum complex were located by a heavy-atom Patterson method (PATTY) and subsequent Fourier syntheses (DIRDIF92). The difference map at this stage clearly showed four peaks $(2.0-1.4 \text{ e } \text{\AA}^{-3})$ around a center of symmetry, which best fit in with a toluene molecule used in recrystallization. The presence of toluene (0.5 equiv of the complex) in the crystal was also supported by ¹H NMR spectroscopy. With anisotropic thermal parameters for all non-hydrogen atoms of the platinum complex and isotropic thermal parameters for the toluene carbons, refinement converged at R = 0.038. At this stage, however, the structure of toluene was rather distorted. Therefore, an ideal model of toluene molecule was introduced in the most probable orientation and included in further least-squares calculations. The positions of toluene carbons were fixed, but the isotropic thermal parameters were refined. This model converged at R = 0.039. All hydrogen atoms of the platinum complex were successfully located by difference Fourier methods with electron densities in the range 0.706–0.403 e Å $^{-3}\!.$ The hydrogen atoms were placed at idealized positions (d(C-H) = 0.95 Å) using isotropic thermal parameters ($Biso = 1.2B_{bonded atom}$) and were included in the final cycles of calculation without refinement of their parameters. The function minimized in leastsquares was $\sum w(|F_0| - |F_c|)^2$ ($w = 1/[\sigma^2(F_0)]$). The final *R* index was 0.031 ($R_w = 0.037$, GOF = 2.11). $R = \sum ||F_0| - |F_c|| / \sum |F_0|$, and $R_{\rm w} = [\sum w(|F_0| - |F_c|)^2 / \sum w |F_0|^2]^{1/2}$. GOF = $[\sum w(|F_0| - |F_c|)^2 / \sum w |F_0|^2]^{1/2}$. $|F_{\rm c}|^{2/}(N_{\rm o}-N_{\rm p})]^{1/2}$, where $N_{\rm o}$ is the number of observed data and $N_{\rm p}$ is the number of parameters varied.

Reaction of 5 with Alkynes (Eq 4). 1-Octyne (0.015 mmol) was added to a solution of **5** (15 mg, 0.015 mmol) in

⁽³⁷⁾ Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974.

 C_6D_6 (0.5 mL) in a NMR tube. The mixture was heated at 50 °C for 6 h. ¹H NMR analysis indicated the presence of **5** (13%) and **3** (R¹ = C₆H₁₃, R² = H) (87%) in the solution. A similar reaction with phenylethyne (0.015 mmol) gave **3** (R¹ = Ph, R² = H) in a 74% yield.

Supporting Information Available: Figures showing ¹H NMR spectra for **3**, a figure showing an atom-numbering scheme, tables of crystal data, positional and equivalent isotropic thermal parameters for the non-hydrogen atoms,

positional parameters for the hydrogen atoms, anisotropic thermal parameters, and intramolecular distances and angles, text describing X-ray experimental details, and figures showing ¹H, ¹³C, ¹¹B, and ³¹P NMR spectra for **5** (27 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

OM950672B