Platinum(0)-Catalyzed Diboration of Alkynylboronates and Alkynylphosphonates with Bis(pinacolato)diborane(4): Molecular Structures of $[((Me_4C_2O_2)B)(C_6H_5)C{=}C(P(O)(OC_2H_5)_2)(B(O_2C_2Me_4))]$ and $[((Me_4C_2O_2)B)(C_4H_9)C{=}C(B(O_2C_2Me_4))_2]$

Hijazi Abu Ali,[†] Abed El Aziz Al Quntar,[†] Israel Goldberg,[‡] and Morris Srebnik*,[†]

Department of Medicinal Chemistry and Natural Products, School of Pharmacy, Hebrew University in Jerusalem, Jerusalem, Israel, and School of Chemistry, Tel-Aviv University, Ramat-Aviv 69987, Tel-Aviv, Israel

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The platinum(0)-catalyzed diboration addition reaction of bis(pinacolato)diborane(4) [$(Me_4C_2O_2)BB(O_2C_2Me_4)$, **1**] with various 1-alkynylphosphonates and 1-alkynylboronates **3a**−**d** gave the desired novel *cis*-1,2-diboronated vinylphosphonate and trisboronated alkene products **5a**, **5b** and **5c**, **5d** respectively, in high yields. No detectable amount of the desired trisboronated alkene products **5c** and **5d** were isolated when the alkynylboronate was immediately added to a toluene solution of the catalyst and bis(pinacolato)diborane(4) followed by stirring overnight at 80 °C. Under these conditions, *cis*-1,2-diboronated alkenes **6c** and **6d** were obtained in 100% conversion yields. Only after changing the reaction conditions were **5c** and **5d** obtained in high yields. The structure and configuration of the new compounds have been fully characterized by ^{1}H, ^{13}C, ^{31}P, and ^{11}B NMR, GCMS, elemental analysis, and single-crystal X-ray structure determination. The structure of **5d** was found to be fully isomorphous to that of **5c**, with the C_6H_5 ring located in place (and similarly disordered about the 2-fold symmetry axis) of the C_4H_9 residue; therefore the results of the diffraction analysis, crystal data, and details of the structure determination of **5d** are not included.

Introduction

Derivatives of diborane(4) are an important class of compounds in boron chemistry. Diborane(4) itself, B_2H_4, is stable only when complexed by Lewis base ligands such as amines or phosphines. Although the tetrahalides, B_2X_4 (X = F, Cl, Br, I), have a reasonably well-established chemistry, they suffer from low thermal stability (with the exception of B_2F_4) and preparative difficulties. Tetraorganodiborane compounds, B_2R_4, are stable only when substituted with sterically demanding R groups such as *t*-Bu, CH_2-*t*-Bu, and mesityl. The most stable derivatives are those in which good π-donor groups are present such as amido (NR_2) or alkoxy (OR).[1,2] More recently, as part of the interest in the oxidative addition chemistry of the B−B bond and metal-catalyzed diborations of alkenes[3] and alkynes,[4] syntheses of stable, crystalline bispinacolato and bis(catecholato)diborane(4) derivatives have been reported.[5,6]

The development of new strategies in organic syntheses with a minimum of chemical steps is becoming more and more important for the efficient assembly of complex molecular structures.[7]

So the combination of multiple reactions in a single operation represents a particularly efficient approach. Among different strategies,[8] geminated organobismetallic derivatives (1,1-bisanions) are becoming more and more useful. During the past decades considerable efforts have been made to find new routes for the preparation of geminated sp^2 organobismetallic derivatives and for their selective reactions with several electrophiles.[9] The addition of tetrakis(alkoxy)diborane(4) derivatives to unsaturated hydrocarbons is an attractive and straightforward method to introduce two boryl units or more into organic molecules.[4a,10,11] In

[†] Hebrew University in Jerusalem.
[‡] Tel-Aviv University.

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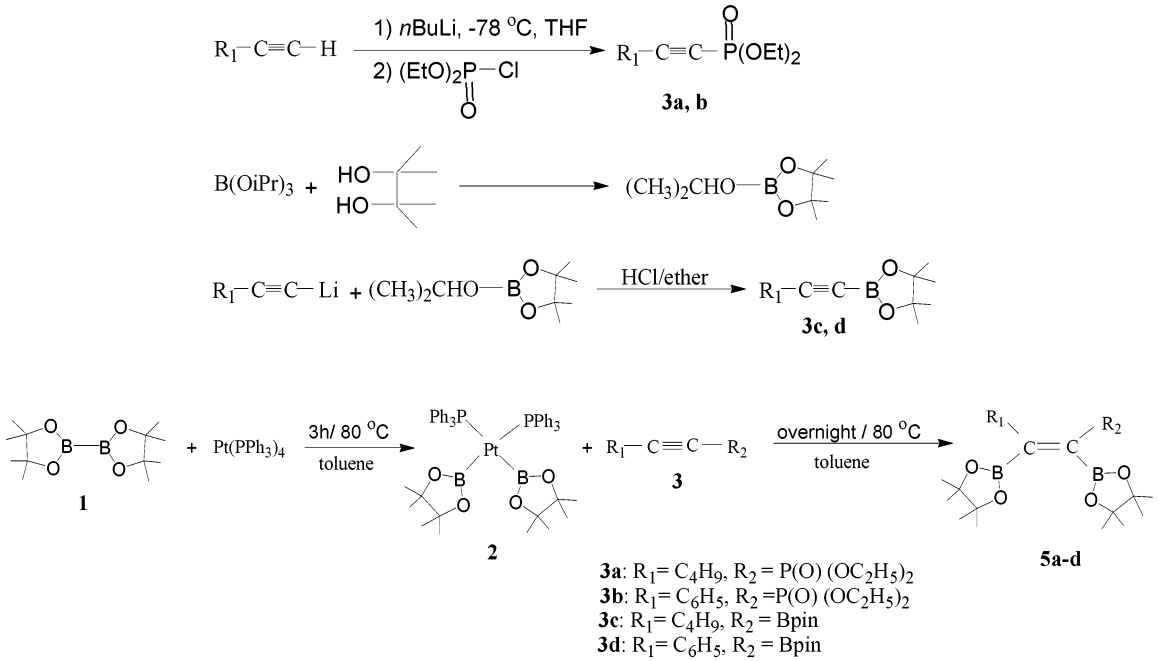
Scheme 1. Synthesis of 3a−d and 5a−d



1993, Ishiyama et al. reported the first synthesis of isomerically pure *cis*-1,2-bis(boryl)alkenes via the platinum(0)-catalyzed addition of tetrakis(alkoxy)diborane(4) compounds to alkynes.[12a,b] Organoboron compounds are among the most useful reagents in organic synthesis since the carbon−boron bond can be cleaved in different ways.[11] The combination of the chemistry of 1,1-bismetallic and 1,2-bismetallic compounds should open a way to many interesting synthetic transformations. One particularly useful common example is the Suzuki−Miyaura palladium-catalyzed cross-coupling reaction between aryl boronates or vinyl boronates for carbon−carbon bond formation.[12c] This encouraged us to search for new approaches for the synthesis of novel trisboronated double-bond compounds and bisboronated vinyl phosphonates through diboration of 1-alkynylboronates and 1-alkynylphosphonates as described in Scheme 1.

The first 1-alkynylphosphonate was described in 1957,[12d] and the syntheses forming the basis of modern 1-alkynylphosphonates chemistry were elaborated in the 1960s. On the other hand, the chemistry of 1-alkynylboronates has been relatively little explored, apparently due to the lack of suitable synthetic methodology for the synthesis of these compounds.[13] The breakthrough came in 1983, when H. C. Brown reported a general synthesis of 1-alkynyldiisopropoxyboranes in high yield.[14] Later on, this strategy was used for the preparation of large-scale 1-alkynylboronic ester compounds.[15] While it is known that diboron tetrahalides B_2X_4 add across unsaturated substrates in the absence of a catalyst,[16] the tetrakis(alkoxy)diborane(4) compounds fail to add to alkenes or alkynes under conventional reaction conditions.[17,18] Thus, a metal catalyst is required to cleave the B−B bond, generally via oxidative addition, to form the intermediate metal bis(boryl) complex **2**, as described in detail in the proposed mechanism in Figure 1. Platinum complexes lead to different selectivities[19a] or enable processes that are not possible with other transition metal homogeneous catalysts. It is worth highlighting that platinum complexes have two key advantages as tools to investigate reaction mechanisms: ^{195}Pt is an NMR active isotope, and consequently NMR spectroscopy is a powerful and useful tool for characterization. Second, many species that are transient intermediates for other metals were isolated and fully characterized for similar platinum complexes.[4a]

Results and Discussion

The diboration reaction of bis(pinacolato)diborane(4), **1**, with diethyl 1-hexynylphosphonate, **3a**, diethyl phenylethynyl phosphonate, **3b**, 1-hexynylpinacolatoborane, **3c**, and phenylethynylpinacolatoborane, **3d**, in the presence of a catalytic amount of $Pt(PPh_3)_4$ (3 mol %) in toluene at 80 °C overnight gave the desired novel *cis*-

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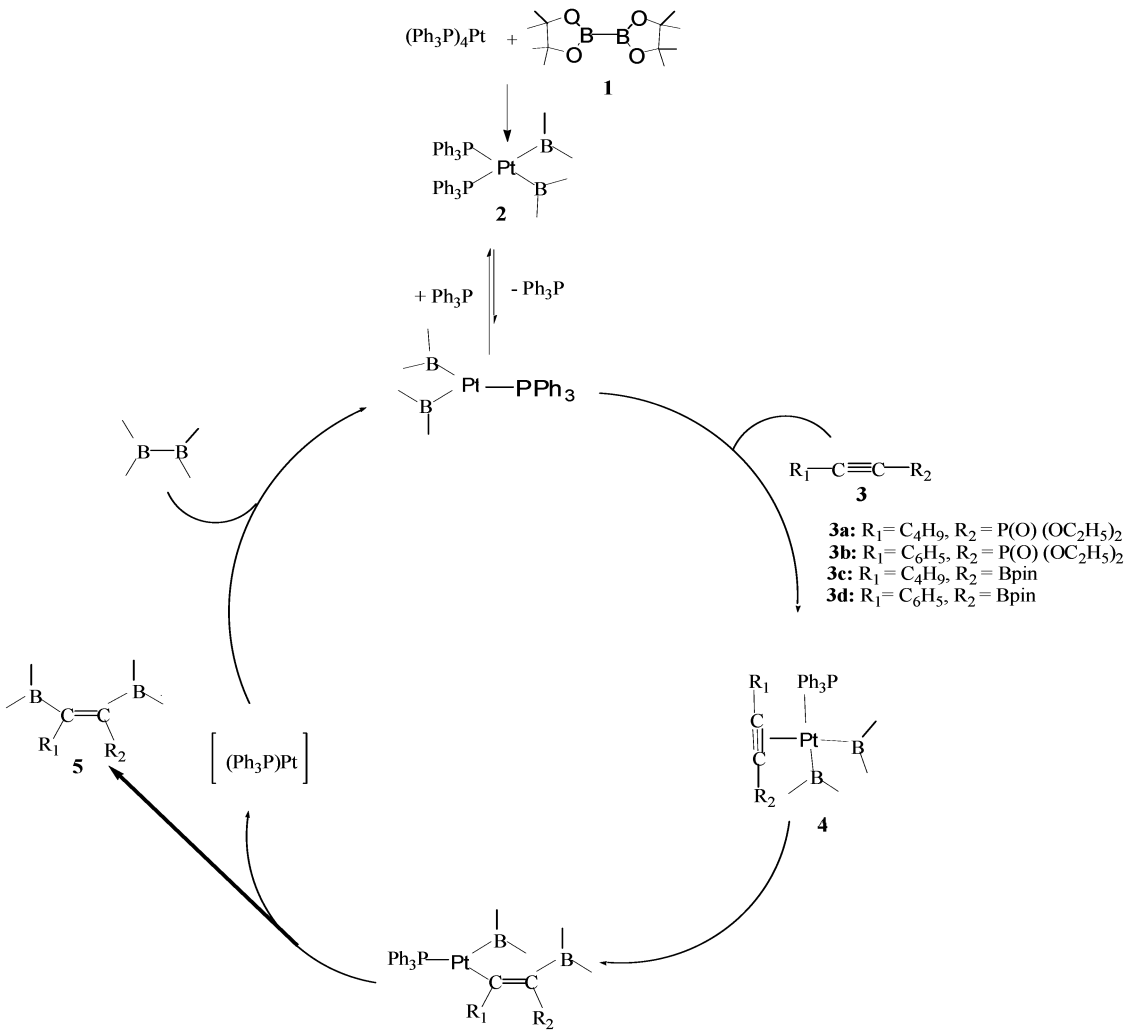


Figure 1. Suggested catalytic cycle for the di- and triboration reactions.

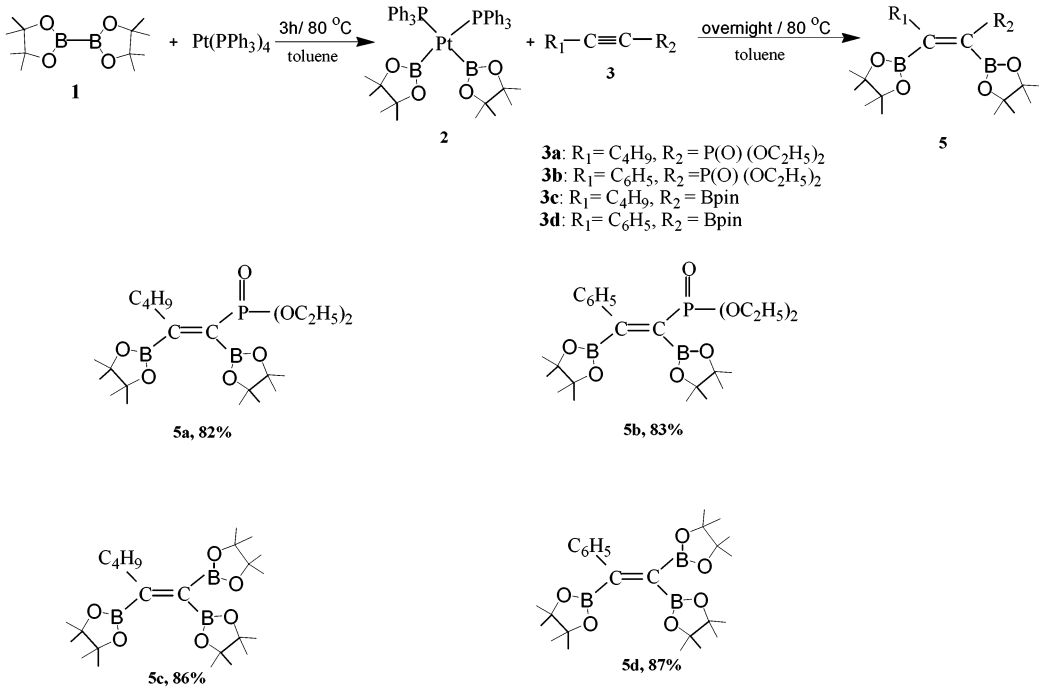
1,2-diboronated vinylphosphonate and trisboronated alkene addition products **5a**, **5b**, **5c**, and **5d**, respectively, in high yields (Scheme 2).

In general no detectable amount of addition product was observed without catalyst, but the reaction was efficiently catalyzed by $Pt(PPh_3)_4$. It is worth highlighting a very important finding that no detectable amount of the desired trisboronated alkene products **5c** and **5d** were indicated when the alkynylboronate was added directly to the reaction mixture of the catalyst and bis(pinacolato)diborane(4) in dry toluene and stirred overnight at 80 °C, but the *cis*-1,2-diboronated alkenes **6c** and **6d** were obtained in 100% conversion yields. This may be due to the cleavage of the labile C−B bond, first leading to nonboronated alkyne, the latter eventually being diboronated to give *cis*-1,2-diboronated alkenes **6c** and **6d** (Scheme 3).

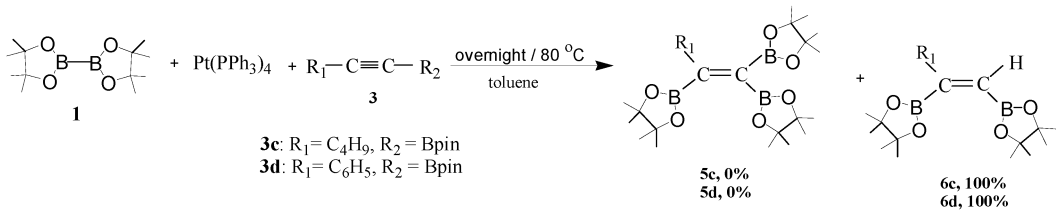
The apparent hydrodeboronation followed by deboronation when the B−B and Pt compounds are not preequilibrated may be due to either water or other such protic impurities since it is known that 1-alkynylboronates are very susceptible to cleavage by water. However, we have repeated this reaction on numerous occasions under anhydrous conditions and the results were always duplicated. Preequilibrium is necessary, otherwise the products of diboration of the alkyne are obtained. The same solvent was used in the preequilibration procedure. Preequilibration of $Pt(PPh_3)_4$ + excess B−B would lead to $(PPh_3)_2Pt(B)_2$. If adventitious water were present, $(PPh_3)_2Pt(B)_2$ would react with H_2O to give $(PPh_3)_2PtH_2$ + B−O−B. $(PPh_3)_2PtH_2$ would lose H_2 and with excess B−B give more $(PPh_3)_2Pt(B)_2$, which, using PPh_3 and B−B, is in equilibrium with $(PPh_3)_3Pt$ or $(PPh_3)_4Pt$ + B−B, by the way, as well as with the $(PPh_3)Pt(B)_2$ species. So, in effect, Pt can catalyze the hydrolysis of the B−B bond. There is no other source of H, and the preequilibration step just serves to dry the system before the 1-alkynylboronate is added.[19b]

The desired products **5a**, **5b**, **5c**, and **5d** were produced in 100% conversion yields and an isolated yields of 82%, 83%, 86%, and 87%, respectively, only after we changed the reaction conditions as follows: the catalyst and bis(pinacolato)diborane(4) in toluene were allowed to react for 3 h at 80 °C and then the 1-alkynylboronate dissolved in toluene was added, and the whole mixture was stirred overnight at 80 °C (Scheme 2). The reaction initially requires a Pt(0) complex, which we believe generates the active Pt(II) catalytic species. The reaction is apparently similar to other reactions catalyzed by transition metals involving oxidative addition of B−H,[20] Si−Si,[21] Sn−Sn,[22] and Si−Sn[23] compounds to low-valent transiton metal complexes, the key step in the catalytic diboration,[24] hydroboration,[25] and addition of disi-

Scheme 2. Synthesis of Novel Trisboronated Double-Bond Compounds and Bisboronatedvinyl Phosphonates



Scheme 3. Diboration of 1-Alkynylboronate If All the Reactants Were Immediately Added Together



lanes,[26] distannanes,[27] or silylstannanes[28] to alkenes[28e] and alkynes.[12b]

Extensive work have been done on the catalytic diboration addition to alkynes and alkenes.[3,4,12a,24,29]

Figure 1 illustrates a more detailed description of the suggested catalytic cycle in the present reaction and similar catalytic diboration of alkynes.[4c,19a] The mechanism may involve (a) rapid B−B bond activation by oxidative addition of **1** to the platinum(0) complex to form a bis(boryl) platinum(II) intermediate **2**; (b) the dissociation of a phosphine ligand and association of the alkyne to give the intermediate **4**, as it has been shown that the addition of PPh_3 or the presence of a more strongly bound bidentate phosphine ligand inhibits the reaction;[24] (c) the probably rapid reductive elimination of the diboronated alkene product to give **5** and complete the reaction; and (d) the role of the phosphine in the later stages of the proposed catalytic cycle is not clear. Either the phosphine can add to the metal center in the final reductive elimination step or the mono(phosphine)

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species may add another 1 equiv of diborane and continue the catalytic cycle.

The structure of bis(pinacolato)diborane(4) platinum(II) intermediate **2** was confirmed by Ishiyama et al.,[4a] who obtained a single crystal of **2** suitable for X-ray analysis in an 82% yield by treatment of $Pt(PPh_3)_4$ with 20 equiv of **1** in hexane at 80 °C for 2 h, followed by recrystallization from hexane/toluene. Lesley et al.[24] also determined various molecular structures of bis(boryl)diborane(4) platinum(II) intermediates, and they also show by means of ^1H and ^{31}P NMR studies that a mono(phosphine) species has not been detected, although they do indicate the presence of bis(phosphine) complex **2** through the course of the reaction. This may indicate that **2** is the catalyst resting state and that alkyne addition or insertion into the B−Pt bond may be rate determining (vide infra).

The structure and configuration of the new compounds have been fully characterized by ^1H, ^{13}C, ^{31}P, and ^{11}B NMR, GC/MS, elemental analysis, and single-crystal X-ray structure determination. The compounds are all thermally and air stable in their solid state as well as in solution. An important finding worth mentioning is that the vinylphosphonate products **5a** and **5b** were not stable to silica gel column chromatography since they decomposed to pinacol and unidentified products. These two compounds were purified by multiple pentane extraction and recrystallization, as cited in detail in the Experimental Section. The solubility of the compounds in common organic solvents ranges from quite good (alkanes) to excellent (chloronated solvents, ethers, and aromatic solvents). The solubility of the triboronated compounds **5c** and **5d** in alkanes is lower than the diboronated similar alkenes, which in turn are lower than the monoboronated derivatives.[30] In the ^1H NMR spectra ($CDCl_3$) of compounds **5a** and **5b** the pinacolato methyl resonances are observed as two singlets at 1.26 ppm (s, 12H) and 1.31 ppm (s, 12H) for **5a** and at 1.23 ppm (s, 12H) and 1.36 ppm (s, 12H) for **5b** as expected. From this work and similar previous reports[24] the downfield shifts at 1.31 and 1.36 ppm might be assigned for the methyl pinacolato boryl groups located *trans* to the phosphorus moiety, respectively. The pinacolato methyl resonances are observed as three singlets for the triboronated compounds **5c** and **5d** and are found at 1.23 (s, 12H), 1.24 (s, 12H), and 1.28 ppm (s, 12H) for **5c** and at 1.08 (s, 12H), 1.27 (s, 12H), and 1.30 ppm (s, 12H) for **5d**. The downfield shifts at 1.28 and 1.30 ppm for **5c** and **5d**, respectively, could be assigned for the methyl pinacolato boryl groups located on C(16), where an *n*-Bu or phenyl group is attached (see Figure 3). The pronounced upfield shift at 1.08 ppm for **5d** might be assigned to the boryl group *cis* to the phenyl group. The assignment of the ^{13}C NMR spectra ($CDCl_3$) is straightforward except for the C−C carbon atoms due to the quadrupole effect of the closely attached boron atoms. In the ^1H and ^{13}C NMR spectra the coupling constants are consistent with the assignments (see Experimental Section). In the ^{31}P NMR

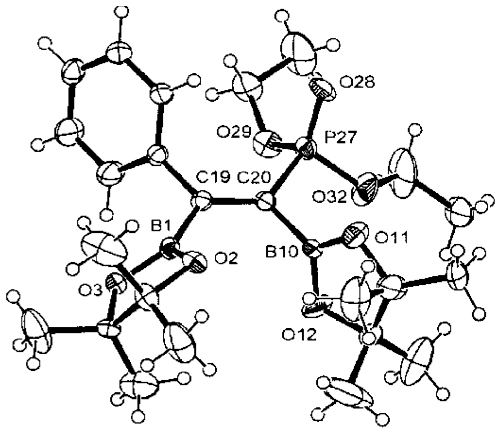

Figure 2. Perspective view of the molecular structure of **5b**. For clarity, only the major conformation is shown. Ellipsoids represent thermal displacement parameters at the 40% probability level. Their relatively large amplitudes reflect on the structural disorder even at low temperature. Selected bond distances (Å) and angles and torsion angles (deg): B(1)−O(2) = 1.387(7), B(1)−O(3) = 1.397(7), B(1)−C(19) = 1.583(6), B(10)−O(11) 1.350(6), B(1)−O(12) = 1.344(6), B(10)−C(20) = 1.578(6), C(19)−C(20) = 1.351(5), C(20)−P(27) = 1.796(4), P(27)−O(28) = 1.468(3), P(27)−O(29) = 1.574(4), P(27)−O(32) = 1.584(3); C(19)−C(20)−B(10) = 124.1(4), C(19)−C(20)−P(27) = 123.4(4), B(10)−C(20)−P(27) = 112.5(3), O(11)−B(10)−C(20) = 124.1(4), O(2)−B(1)−C(19) = 123.1(4); B(1)−C(19)−C(20)−B(10) = 3.0(6), B(1)−C(19)−C(20)−P(27) = 178.5(3).

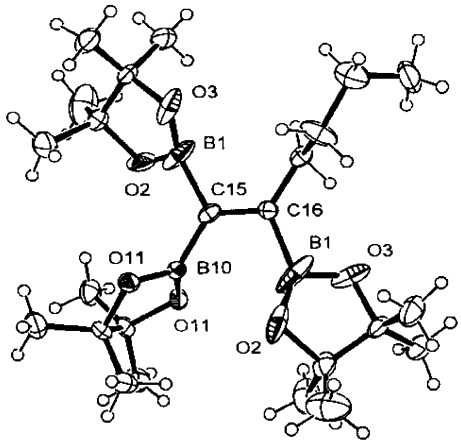

Figure 3. Perspective view of the molecular structure of **5c**. Ellipsoids represent thermal displacement parameters at the 40% probability level. The molecules are located in the crystal on, and are orientationally disordered about, a 2-fold symmetry axis ($1 - x$, $1 - y$, z), which passes diagonally through B(10), center of C(15)═C(16) and the alkyl residue. This rotation axis relates atoms shown with the same labels. The elongated ellipsoids of B(1), O(2), and O(3) indicate additional unresolved disorder in the molecular plane of this fragment. Selected bond distances (Å) and angles and torsion angles (deg): B(1)−O(2) = 1.356(7), B(1)−O(3) = 1.346(6), B(10)−O(11) = 1.371(3), B(1)−C(15) = 1.590(6), B(10)−C(15) = 1.578(6), C(15)−C(16) = 1.353(7); O(3)−B(1)−C(16) = 108.8(5), C(16)−C(15)−B(10) = 150.8(5), O(2)−B(1)−C(15) = 102.2(5), O(2)−B(1)−C(16) = 138.4(4); B(1)−C(15)−C(16)−B(10) = 10.6(6), B(1)−C(15)−C(16)−B(1) = 167.6(3).

spectra ($CDCl_3$) of compounds **5a** and **5b** the resonances are observed at 19.65 and 18.47 ppm, showing shifts of 24.77 and 23.59 downfield, respectively, compared to the 1-alkynylphosphonate starting materials. Only broad

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Table 1. Crystal Data and Structure Refinement for 5b and 5c

	5b	5c
formula	$C_{24}H_{39}B_2O_7P$	$C_{24}H_{45}B_3O_6$
fw	492.14	462.03
habit	prisms	prisms
color	colorless	colorless
temp, K	110(2)	110(2)
radiation	Mo Kα	Mo Kα
cryst size, mm	0.35 × 0.20 × 0.10	0.15 × 0.15 × 0.10
cryst syst	orthorhombic	orthorhombic
space group	$P2_12_12_1$	*Aba*2
a, Å	10.2840(2)	12.4210(5)
b, Å	11.9170(2)	12.6030(7)
c, Å	21.7700(5)	17.9240(6)
α, deg	90.00	90.00
β, deg	90.00	90.00
γ, deg	90.00	90.00
V, Å^3	2668.0(8)	2806(4)
Z	4	4
d_{calcd}, g cm^{-3}	1.225	1.094
F(000)	1056	1008
μ, mm^{-1}	0.143	0.074
2*θ* range, deg	3.90−55.8	7.26−55.74
no. of unique reflns	3572	3107
restraints	0	1
hkl limits	0,13/0,15/0,28	−16,16/−16,16/−22,22
no. of variables	404	184
no. of reflns with [$I>2\sigma(I)$]	2653	2129
final *R* indices[a] [$I>2\sigma((I)$]		
R1	0.058	0.062
wR2	0.141	0.111
$\|\Delta\rho\|$, e Å^{-3}	≤0.478	≤0.003
GOF	0.998	1.081

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

singlets for **5a**, **5b**, **5c**, and **5d** were observed in the ^{11}B NMR spectra due to the broad nature of the ^{11}B NMR resonances and are comparable with those found in the literature for similar boronic acid ester derivatives.[24,30] Mass spectra for **5a** and **5b** show molecular ion $(M - 2C_2H_5)^+$ peaks, respectively, at *m*/*e* values of 414 and 434 mass units, while **5c** shows a molecular ion $(M - CH_3)^+$ peak at an *m*/*e* value of 447 mass units and **5d** shows a molecular ion $(M - 4CH_3)^+$ peak at an *m*/*e* value of 422 mass units. The most abundant ion was different from one compound to another, but a prominent fragment at $(M - 100)^+$ was pronounced.

Crystallography. The molecular structures of **5b** and **5c** were determined by single-crystal X-ray diffraction. The results of the diffraction analysis, crystal data, and details of the structure determination are shown in Figures 2 and 3, and the data are summarized in Table 1. The two pinacol rings and one of the O-ethyl residues in **5b** reveal severe conformational disorder in the loosely packed crystal even at the low temperature. They were represented in the crystallographic refinement by a two-site model with correspondingly constrained occupancies. In the crystal of **5c**, the molecules are positioned on, and disordered about, symmetry axes of 2-fold rotation (parallel to *c*). The symmetry axis crosses the central C═C bond, one of the pinacol rings, and the aliphatic residue aligned *trans* to it. The rotational disorder also persists when the crystal structure was assigned lower monoclinic or triclinic symmetry, indicating that it is a genuine phenomenon (due to an approximate square shape of the molecule) not artificially imposed by the choice of the higher orthorhombic mm2-type space symmetry. The structure of **5d** was found to be fully isomorphous to that of **5c**, with the C_6H_5 ring located in place (and similarly disordered about the 2-fold symmetry axis) of the C_4H_9 residue; therefore the results of the diffraction analysis, crystal data, and details of the structure determination of **5d** are not included.

Experimental Section

General Comments. All reactions were carried out under a nitrogen atmosphere using vacuum line and glovebox techniques. Solvents were purified by distillation from appropriate drying agents under a nitrogen atmosphere. Starting materials were purchased from commercial suppliers and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution with a Varian Unity spectrometer (300 or 75 MHz) using Me_4Si as an internal standard. ^{11}B NMR spectra were also recorded in $CDCl_3$ solution with a Varian Unity spectrometer (96 MHz) using $BF_3{\cdot}OEt_2$ as an external standard. ^{31}P NMR spectra were recorded in $CDCl_3$ solution with a Varian Unity spectrometer (121 MHz) using 85% H_3PO_4 as an external standard. GC/MS analyses were performed on an HP GC/MS instrument (Model GCD PLUS), with an EI detector and 30 m methyl silicone column.

Diboron Reagent. Bis(pinacolato)diborane(4) was prepared from tetrakis(pyrrolidino)diborane(4) by Wurtz coupling of bis(pyrrolidino)bromoborane and then obtained by solvolysis of tetrakis(pyrrolidino)diborane(4) with 2 equiv of pinacol in benzene solution at room temperature.[1]

1-Alkynylboronates. Borylation reaction of pinacol with triisopropylborate gave 2-isopropyloxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.[31] This borate ester reacted with 1-alkynyllithium to produce, after treatment with anhydrous hydrogen chloride, the corresponding 1-alkynylpinacolatoborane.

General Procedure for the Preparation of 1-Alkynylboronates. *n*-BuLi (31.3 mL, 1.6 M solution in hexane, 50 mmol) was added slowly to a stirred solution of 1-alkyne (50.1 mmol) dissolved in diethyl ether (50 mL) at −78 °C. Using a douple-ended needle the whole mixture was then slowly added to 2-isopropyloxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9.3 g, 50 mmol) in diethyl ether (50 mL) at −78 °C. The reaction was maintained at the same temperature for 2 h, and then the mixture was stirred overnight at room temperature. Anhydrous hydrogen chloride (20 mL, 3 M solution in ether, 60 mmol) was then added at −50 °C to the reaction mixture, and the solution was allowed to warm to room temperature. The mixture was filtered under a nitrogen atmosphere to remove the undesired solids. The volatiles were removed from the clear solution under vacuum, and the residue was distilled under vacuum to give the product as a pure oily liquid.

1-Alkynylphosphonates. 1-Alkynylphosphonates were prepared from the corresponding alkynes and diethylchlorophosphonate according to literature procedure as follows: Alkynes were metalated with *n*-BuLi in THF solution at low temperature, and the resultant lithium acetylides were treated with diethylchlorophosphonate at the same temperature. This procedure minimizes side reactions and provides high and reproducible yields of diethyl 1-alkynyl phosphonates.[32]

General Procedure for Diboration of Alkynylboronates and Alkynylphosphonates with Bis(pinacolato)-diborane(4). A dry nitrogen flushed 50 mL flask equipped with a magnetic stirring bar was charged with $Pt(PPh_3)_4$ (74.7 mg, 0.06 mmol) and bis(pinacolato)diborane(4) (508 mg, 2 mmol); 15 mL of toluene was then added to the mixture. After the mixture was stirred for 3 h at 80 °C the alkyne (1.9 mmol) dissolved in 10 mL of toluene was then added. The mixture

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was stirred overnight at 80 °C, and the toluene was removed under vacuum. The residue was extracted with pentane, which was then washed twice with water and dried over anhydrous sodium sulfate. The solvent was then removed under vacuum, and the residue was dissolved in hot pentane and filtered to remove any undissolved impurites. The vinylboronates were purified by silica gel column chromatography with 10% ether/petroleum ether as eluent to give the product as colorless crystals. Vinylphosphonate diborane derivatives were purified by pentane extraction and recrystallization since they are not stable to silica gel column chromatography. The solid products were crystallized from hot pentane.

[((Me$_4$C$_2$O$_2$)B)(C$_4$H$_9$)C=C(P(O)(OC$_2$H$_5$)$_2$)(B(O$_2$C$_2$-Me$_4$))], 5a: 82% (0.73 g) yield; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, 3H, CH_3, $^3J_{H-H}$ = 6.9 Hz), 1.27 (t, 6H, CH_3, $^3J_{H-H}$ = 7.1 Hz), 1.26 (s, 12H, CH_3), 1.31 (s, 12H, CH_3), 1.36 (m, 4H, CH_2), 2.66 (t, 2H, CH_2, $^3J_{H-H}$ = 6.0 Hz), 4.06 (m, 4H, OCH_2); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 13.98 (CH_3), 16.36 (d, CH_3, $^3J_{P-C}$ = 6.2 Hz), 23.05 (CH_2), 24.71 (CCH_3), 25.01 (CCH_3), 31.65 (d, CH_2, $^4J_{P-C}$ = 2.9 Hz), 35.48 (d, CH_2, $^3J_{P-C}$ = 16.6 Hz), 61.22 (d, OCH_2, $^3J_{P-C}$ = 5.9 Hz), 83.96 (CCH$_3$), 84.25 (CCH$_3$) ($C-C$B cannot be detected); ^{11}B NMR ($CDCl_3$) δ 30.22; ^{31}P NMR ($CDCl_3$) δ 19.65; MS (EI) *m*/*z* (%) 414 (M^+ − 58, 100), 399 (6.9), 384 (23.1), 372 (13.1), 330 (11.1), 315 (7.0), 264 (13.1), 245 (12.3), 233 (27.1), 218 (9.0), 204 (47.1), 199 (17.7), 187 (31.2), 179 (11.4), 157 (15.9), 151 (13.3), 127 (12.6), 101 (23.8), 83 (89.6), 69 (4.0), 58 (14.1), 57 (32.1), 45 (13.1), 29 (29.9). Anal. Calcd for $C_{22}H_{43}B_2O_7P$: C, 55.96; H, 9.18; P, 6.56. Found: C, 55.84; H, 8.99; P, 6.46.

[((Me$_4$C$_2$O$_2$)B)(C$_6$H$_5$)C=C(P(O)(OC$_2$H$_5$)$_2$)(B(O$_2$C$_2$-Me$_4$))], 5b: 83% (0.78 g) yield, mp 128 °C; ^{1}H NMR ($CDCl_3$) δ 1.05 (t, 6H, CH_3, $^3J_{H-H}$ = 7.2 Hz), 1.23 (s, 12H, CH_3), 1.36 (s, 12H, CH_3), 3.74 (m, 4H, OCH_2), 7.28 (m, 5H, Ph); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 16.36 (d, CH_3, $^3J_{P-C}$ = 6.5 Hz), 24.68 (CCH_3), 24.94 (CCH_3), 61.14 (d, OCH_2, $^3J_{P-C}$ = 6.2 Hz), 84.40 (CCH$_3$), 84.50 (CCH$_3$), 127.10 (para CH), 127.35 (ortho or meta CH), 127.47 (ortho or meta CH), 141.65 (ipso, $^3J_{P-C}$ = 16.5 Hz), ($C-C$B cannot be detected); ^{11}B NMR ($CDCl_3$) δ 29.76; ^{31}P NMR ($CDCl_3$) δ 18.47; MS (EI) *m*/*z* (%) 434 (M^+ − 58, 2.5), 415 (3.7), 292 (5.6), 282 (14.7), 263 (12.2), 254 (4.8), 237 (30.6), 209 (12.9), 193 (14.6), 157 (14.1), 143 (15.4), 129 (100), 127 (10.1), 101 (47.9), 91 (16.8), 84 (32.6), 83 (64.7), 77 (10.8), 69 (27.4), 58 (15.1), 29 (26.4). Anal. Calcd for $C_{24}H_{39}B_2O_7P$: C, 58.57; H, 7.99; P, 6.29. Found: C, 57.98; H, 7.95; P, 6.23.

[((Me$_4$C$_2$O$_2$)B)(C$_4$H$_9$)C=C(B(O$_2$C$_2$Me$_4$))$_2$], 5c: 86% (0.75 g) yield, mp 230 °C; ^{1}H NMR ($CDCl_3$) δ 0.86 (t, 3H, CH_3, $^3J_{H-H}$ = 7.2 Hz), 1.23 (s, 12H, CH_3), 1.24 (s, 12H, CH_3), 1.28 (s, 12H, CH_3), 1.35 (m, 4H, CH_2), 2.36 (t, 2H, CH_2, $^3J_{H-H}$ = 7.6 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 14.06 (CH_3), 22.82 (CH_2), 24.73 (CCH_3), 24.76 (CCH_3), 24.90 (CCH_3), 32.74 (CH_2), 37.44 (CH_2), 82.82 (CCH$_3$), 83.08 (CCH$_3$), 83.64 (CCH$_3$) ($C=C$B cannot be detected); ^{11}B NMR ($CDCl_3$) δ 30.75. MS (EI) *m*/*z* (%) 447 (M^+ − 15, 0.4), 404 (1.2), 362 (1.4), 279 (7.0), 278 (4.1), 262 (0.8), 254 (0.4), 221 (9.9), 209 (0.8), 178 (1.6), 162 (0.6), 154 (0.6), 129 (1.0), 101 (7.9), 84 (100), 69 (16.6), 57 (8.3), 43 (9.3), 28 (29.4). Anal. Calcd for $C_{24}H_{45}B_3O_6$: C, 62.39; H, 9.82. Found: C, 61.95; H, 9.72.

[((Me$_4$C$_2$O$_2$)B)(C$_6$H$_5$)C=C(B(O$_2$C$_2$Me$_4$))$_2$], 5d: 87% (0.80 g) yield, mp 251 °C; ^{1}H NMR ($CDCl_3$) δ 1.08 (s, 12H, CH_3), 1.27(s, 12H, CH_3), 1.30 (s, 12H, CH_3), 7.22 (m, 5H, Ph); ^{13}C-{^{1}H} NMR ($CDCl_3$) δ 24.45 (CCH_3), 24.79 (CCH_3), 24.89 (CCH_3), 83.13 (CCH$_3$), 83.40 (CCH$_3$), 83.82 (CCH$_3$), 126.64 (para CH), 127.60 (ortho or meta CH), 127.68 (ortho or meta CH), 145.20 (ipso) ($C-C$B cannot be detected); ^{11}B NMR ($CDCl_3$) δ 30.58. MS (EI) *m*/*z* (%): 422 (M^+-60, 0.1), 382 (0.7), 325 (0.2), 299 (3.6), 282 (0.2), 254 (0.2), 239 (1.1), 229 (2.2), 154 (0.5), 143 (0.8), 129 (3.0), 127 (0.3), 101 (4.7), 84 (100), 77 (0.4), 69 (11.8), 55 (7.5), 42 (1.1). Anal. Calcd for $C_{26}H_{41}B_3O_6$: C, 64.78; H, 8.57. Found: C, 64.14; H, 8.49.

X-ray Crystallographic Study. Colorless single crystals of **5b** and **5c** suitable for X-ray diffraction analysis were obtained from a saturated pentane solution at ca. −20 °C. The X-ray diffraction measurements were carried out at ca. 110 K on a Nonius KappaCCD diffractometer, using Mo Kα (λ = 0.7107 Å) radiation and 1.0° ϕ scans. The intensity data were integrated and scaled by the programs DENZO-SMN and Scalepack.[33] The analyzed crystals were coated with a layer of hydrocarbon oil (in order to avoid deterioration) and mounted on a glass fiber. The structures were solved by direct methods (SIR-92 and SIR-97)[34] and refined by full-matrix least-squares based on F^2 for all reflections (SHELXL-97).[35] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles and were included in the refinement with isotropic displacement parameters using a riding model. The two crystal structures suffer from a considerable rotational and/or conformational disorder, which affected the precision of the crystallographic determination. The crystal and experimental data are summarized in Table 1.

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Supporting Information Available: Tables of atomic positional and thermal displacement parameters, bond distances, bond angles, and torsion angles, together with details of data collection and structure solution and refinement as a CIF file for compounds **5b** and **5c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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