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ALKYNYLBORINATES IN ORGANOBORANE CONVERSIONS

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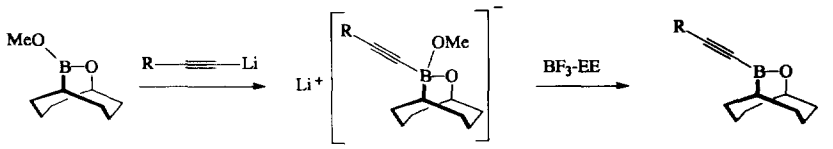
Abstract *10-Methoxy-9-oxa-10-bora[3.3.2]decane (**1**), easily prepared from the oxidation of B-MeO-9-BBN with trimethylamine N-oxide (TMANO), is readily converted to alkynylborinate complexes (**2**) with its reaction with representative lithium acetylides. These complexes serve as efficient alkynylating agents in the Suzuki-Miyaura coupling and their demethoxylation furnishes stable alkynylboranes (**3**) which also provide a convenient new entry to cis-vinylboranes (**5**).*

Alkynylboranes have proven value in chemical synthesis.[4] Recent applications demonstrate their utility in enantioselective additions to aldehydes,[5] as acetylene equivalents in Diels-Alder cycloadditions,[6] as effective precursors to *cis*-vinylboronates,[7] and as alkynylating agents through the Suzuki-Miyaura coupling.[8] These intermediates are normally prepared either through the acid-mediated (BF_3-EE, HCl) demethoxylation of their lithium "ate" complexes[9] or, alternatively, through the transmetallation of alkynyltins with bromoboranes.[5,6] Both methods can be used for the preparation of dialkyl derivatives, but difficulties are encountered with the isolation of the alkynylborane product in pure form due to THF complexation in the first case, and with the separation of the organotin by-product in the second. Unlike their dialkyl counterparts, alkynylboronates (*i.e.* RC≡CB(OR')$_2$), with lowered boron Lewis acidities, are isolable free of coordinated solvents.[9b] It occurred to us that alkynylborinates (*i.e.* RC≡CBR''(OR')) may be efficiently isolable in pure uncomplexed form, while still retaining much of the desirable Lewis acid character of the dialkyl derivatives. In this Letter, we wish to report a convenient entry to alkynylborinates (*i.e.* **3**), highly versatile alkynylborane reagents which possess remarkable oxidative and thermal stabilities.



1 2 3

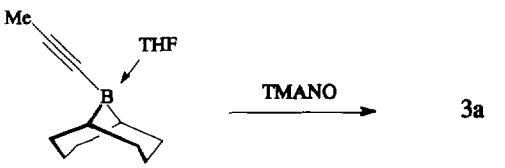
The boronic ester **1** is readily prepared from *B*-MeO-9-BBN through its selective oxidation with anhydrous trimethylamine *N*-oxide (TMANO) (85%, $CHCl_3$, 0 °C), a process which is general for *B*-substituted 9-BBN derivatives.[10] The stable 9-oxa-10-borabicyclo[3.3.2]decane (OBBD) ring system allows the alkynylation and demethoxylation of **1** to proceed cleanly. Free of coordinated THF, the isolation of **3** is a simple operation compared to their 9-BBN counterparts.[9a]

Table 1. Alkynylborinates from **1**.

R	product	% yield[a]
Me	**3a**	71
Et	**3b**	89
Bu	**3c**	86
t-Bu	**3d**	96(86)
TMS	**3e**	81

[a] Isolated yields of pure **3** (yield after recrystallization from pentane).

The process was examined with representative 1-alkynes which were smoothly converted *via* a one-pot procedure to **3** in high yields and chemical purities in all of the systems studied (Table 1).[11] For comparison purposes, *B*-1-propynyl-9-BBN-THF complex (**4**, 69%) was prepared following the method of Brown and Sinclair[9a] and this was oxidized cleanly to **3a** (TMANO, $CHCl_3$, 0 °C, 99%). These borinic esters (**3**) can be handled for brief periods of time in the open atmosphere. Longer times (8 h) do result in the hydrolysis of the alkynyl moiety, but **3** is definitely easier to handle than its unoxidized counterpart (*i.e.* **4**). Moreover, the preparation of **3** through **1** is a much simpler overall operation than through **4**.



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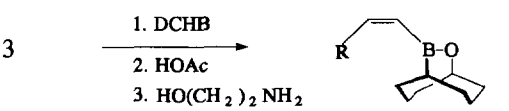
The synthesis of *cis*-vinylboranes normally involves the hydroboration/reductive rearrangement of 1-halo-1-alkynes,[12] the addition of *Z*-alkenyllithiums to borate esters,[13] or through the hydrogenation or hydrozirconation of alkynylboronates.[7] Having developed a simple non-oxidative hydroboration/protonolysis protocol for *cis*-vinylsilanes,[14] we felt that **3** would be an ideal precursor to **5** in light of our recent discovery that *trans*-*B*-vinyl-OBBD derivatives are very stable to either further oxidation or to protonolysis with HOAc.[15] While the hydroboration of **3** with 9-BBN-H gives a mixture of mono and dihydroboration products, dicyclohexylborane (DCHB) adds to **3** giving the 1:1 *gem*-diboryl adduct cleanly (^{11}B NMR δ 46 and 80).[16] This is selectively protiodeborylated with HOAc at 0 °C producing the corresponding vinylboranes **5** [R = Me (92%), Bu (75%) , *t*-Bu (83%)].



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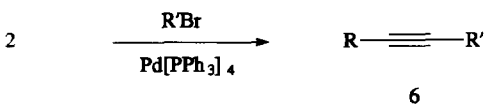
To further demonstrate the value of **1** in alkynylations, **2** (^{11}B NMR δ 0.5) was prepared from the addition of **1** to various alkynyllithiums. This complex was submitted to Suzuki-Miyaura conditions[17] to effect their efficient cross coupling to a variety of aryl and vinyl bromides. Both

Table 2. Suzuki-Miyaura couplings with alkynylborate complexes **2**.

R	R'	Product	% yield[a]
Me	C_6H_5	**6a**	88(64)
TMS	*cis*-CH=CH-*n*-Bu	**6b**	83
TMS	*trans*-CH=CH-*n*-Bu	**6c**	59(55)
TMS	*p*-$CH_3OC_6H_4$	**6d**	62

[a] Isolated yields of analytically pure material (Yields employing *B*-MeO-9-BBN rather than **1**).

arylacetylenes and stereodefined enynes **6** are obtained in yields which match or exceed those obtained in the 9-BBN process (Table 2). [8,18]



In summary, alkynylborinates (**3**) have been prepared for the first time which has led to a new route to *cis*-vinylboranes (**5**). Their methoxy complexes (**2**) not only serve as a convenience source of **3**, but also function as highly efficient partners in the Suzuki-Miyaura coupling to provide acetylenes and stereodefined enynes.

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2. Graduate Student supported by Patricia Robert Harris Graduate Fellowship (P094B0116-94).

3. Graduate Student supported by U.S. Department of Education Graduate Fellowship (P200A902093).

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11. Representative procedure for the preparation of **3** (All operations were conducted under a N_2 atmosphere): To THF (10 mL) at -78 °C was added 1-butyne (0.283 g, 5.25 mmol (5% excess)), followed by the dropwise addition of *n*-BuLi

in hexane (2.3 mL (2.13 M), 5.0 mmol). After 15-30 min of stirring to ensure complete generation of the anion, **1** (0.84 g, 5.0 mmol) was added dropwise and stirred for 2 h at -78 °C. BF_3-EE (0.74 g, 5.0 mmol) was added, and after 15 min, a white slurry formed (not for all of the examples examined). The mixture was rapidly warmed to *ca.* 0 °C to dissolve the white precipitate after which it was further allowed to warm to 25 °C and the volatiles were removed *in vacuo*. The residue was washed with pentane (3 X 10 mL). The combined washings were slowly cooled to -78 °C to crystallize the product. Decantation and drying afforded 0.854 g (89%) of **3b**: ^{1}H NMR ($CDCl_3$) δ 1.12 (t, J = 7.2 Hz, 3H), 1.38 (m, 6H), 1.54-1.85 (m, 7H), 2.25 (q, J = 7.2 Hz, 2H), 4.55 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.2, 13.3, 21.9, 25.4, 26.5, 31.2, 74.1, 85.0, 107.7; ^{11}B NMR ($CDCl_3$) δ 38.8; IR (TF) 2190 cm^{-1}; MS *m/z* (rel intensity) 190 (M^+, 1.4), 110 (48), 82 (57), 67 (100).

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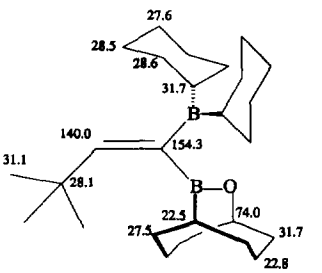
16. Into a pre-dried centrifuge tube containing cyclohexene (30 mmol, 2.46 g) in ether (10 mL) was added, at 0 °C, BH_3.SMe_2 (1.50 mL (10 M), 15 mmol). After stirring for 3 h at 0 °C and 1 h at 25 °C, the white slurry was centrifuged. The solid dimer was washed with dry ether (3 X 20 mL) and dried under a stream of nitrogen. Fresh dry ether (10 mL) was added followed by the addition of **3a** (1.76 g, 10 mmol) in ether (10 mL). After 1 h at 25 °C, the mixture was protonolyzed with AcOH (15 mmol, 0.650 g) and ethanolamine (30 mmol, 1.220 g) was added. The solution was filtered through silica (eluted with pentane), concentrated to give 1.635 g (92%, 62 °C/0.05 Torr) of *cis*-vinylborane (**5**, R = Me). ^{1}H NMR ($CDCl_3$) δ 1.44 (m, 4H), 1.84 (m, 4H), 1.91 (dd, J = 6.9, 1.5 Hz, 3H), 4.60 (m, 1H), 5.52 (dq, J = 13.8, 1.5 Hz, 1H), 6.27 (qd, J = 13.8, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 17.7, 22.1, 25.6, 31.6, 72.9, 130.8, 144.0; ^{11}B NMR ($CDCl_3$) δ 45.3; IR (TF) 1620, 735 cm^{-1}. For R = *t*-Bu, the complete ^{13}C NMR assignments for the 1,1-diboryl intermediate are given with its structure illustrated on the right.



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18. Representative procedure for the cross coupling: To a well-stirred solution of trimethylsilylacetylene (0.516 g, 5.25 mmol) in THF (10 mL) at -78 °C was added *n*-BuLi in hexanes (2.3 mL (2.13 M), 5.0 mmol). After stirring the mixture for 30 min at -78 °C, **1** (0.84 g, 5.0 mmol) was added. After 2 h, this solution was transferred to a another flask equipped with a reflux condenser and containing $Pd[PPh_3]_4$ (0.100 g, 0.086 mmol), *p*-$MeOC_6H_4Br$ (0.874 g, 4.55 mmol) in THF (5 mL). After 12 h at reflux temperature, pentane (50 mL) was added and organic phase was washed with water (10 X 100 mL) and filtered through alumina. Concentration, followed by distillation gave 0.579 g (62%) of **6d**:[19] ^{1}H NMR ($CDCl_3$) δ 0.70 (s, 9H), 3.60 (s, 3H), 6.81 (d, J = 8.7 Hz, 2H), 7.42 (d, J = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 0.0, 55.1, 92.3, 105.2, 115.2, 113.7, 133.3, 159.7; IR (TF) 2960, 2160, 1610, 1250 cm^{-1}; MS *m/z* (rel intensity) 204 (M^+, 29), 146 (11), 115 (5), 105 (6), 95 (6), 77 (5), 59 (6).

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