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ALKYNYLBORANES IN THE SUZUKI-MIYAURA COUPLING

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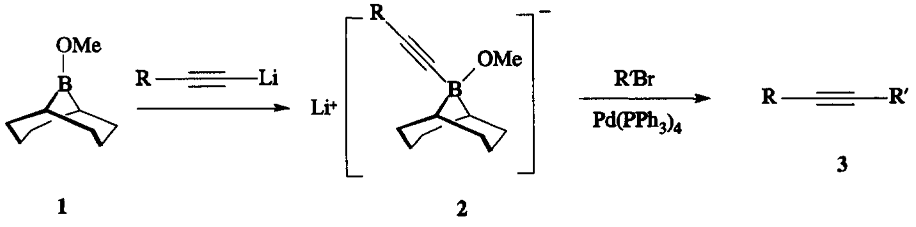
Abstract: *The addition of B-methoxy-9-borabicyclo[3.3.1]nonane (**1**) to alkynyllithium reagents gives stable complexes (**2**) which undergo efficient Suzuki-Miyaura coupling to produce a variety of alkynyl derivatives (**3**).*

Alkynylboranes have long been known to be useful synthetic intermediates.[4] Compared to alkylboranes, they are stronger Lewis acids and are easily hydrolyzed. These features have led to numerous synthetic applications for these intermediates which include 1,4-addition to enones[5] and 1,2-addition to aldehydes,[6] the latter process having been recently developed into an enantioselective synthesis of propargylic alcohols.[7] Diels-Alder cycloadditions[8] have also been reported for these derivatives, and their borate complexes are readily converted to diynes with molecular iodine.[9] However, despite numerous potentially useful applications, they have not been employed in the Suzuki-Miyaura coupling[10] possibly due to their known instability to the aqueous basic conditions normally employed for this process.[4] It occurred to us that the intermediate leading to their normal preparation (*i.e.* **2**) may serve as the ideal combining partner for the coupling procedure, thereby simplifying the overall conversion by avoiding the necessity to isolate the alkynylborane (*e.g.* **4**), compounds which are easily oxidized by atmospheric oxygen and are generally quite difficult to handle. In this Letter, we report the Suzuki-Miyaura coupling methoxy(alkynyl)borate complexes (**2**) to aryl and vinyl bromides to efficiently produce arylacetylenes and stereodefined enynes (**3**), respectively (Table 1).[11]



The complexes **2** (^{11}B NMR δ -6.7) were prepared as reported[12] from the addition of **1** to alkynyllithiums in THF at -78 °C. They are thermally stable at the reflux temperatures where their Pd-catalyzed cross coupling to both aromatic and olefinic substrates is best carried out. Moreover, complete retention of the double bond geometry is observed in the enyne products (*i.e.* **3g,f**).

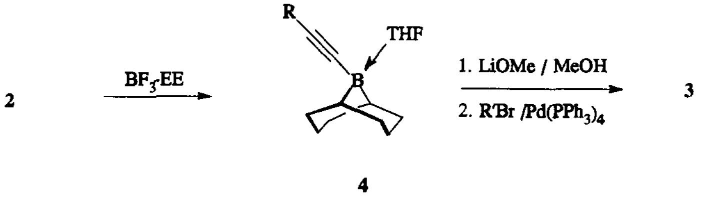
Several of these borate complexes **2** were converted to their alkynyl-9-BBN-THF complexes

Table 1. Arylacetylenes and Enynes from **1**.

entry	R	R'	Product	% Yield[a]
1	*n*-Bu	C_6H_5	**3a**	60(92)
2	$SiMe_3$	C_6H_5	**3b**	64
3	Ph	C_6H_5	**3c**	94
4	*n*-Bu	*p*-$MeOC_6H_5$	**3d**	62(68)
5	$SiMe_3$	$CH_2=CC_6H_5$	**3e**	88
6	*t*-Bu	*cis*-CH=CH-*t*-Bu	**3f**	56
7	$SiMe_3$	*trans*-CH=CH-*n*-Bu	**3g**	55

[a] Isolated yields of analytically pure material (GC yields).

(**4**) with BF_3-EE.[12] The alkynylborane (R = Bu) was dissolved in THF and solid LiOMe (1 equiv) was added resulting in a slurry in which no **2** was observable by ^{11}B NMR after several hours. However, with the addition of MeOH, **2** does form (albeit incompletely) and this mixture was submitted to the Suzuki-Miyaura process with PhBr resulting in a 36% yield of **3a** after 72 h at reflux temperature. Thus, the simple use of **2**, generated from the alkynyllithium and **1** rather than from **4**, not only saves steps, but also, gives superior results for this coupling process.



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3. Graduate Student supported by U.S. Department of Education Graduate Fellowship (P200A902093).
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11. Representative procedure: To a well-stirred solution of trimethylsilylacetylene (0.575 g, 5.85 mmol) in THF (10 mL) at -78 °C was added *n*-BuLi (2.60 mL (2.13 M in hexanes), 5.5 mmol). After 30 min, **1** (0.845 g, 5.56 mmol) was added, and after 2 h, this solution was transferred to a second consisting of $Pd[PPh_3]_4$ (0.195 g, 0.169 mmol) and PhBr (0.766 g, 4.88 mmol) in THF (5 mL). The reaction mixture was heated at reflux for 18 h (monitored by GC), allowed to cool to room temperature and pentane (50 mL) was added. The organic phase was washed with water (20 X 100 mL) and filtered through alumina. Concentration, followed by Kugelrohr distillation gave 0.547 g (64%, bp 67.5 °C at 3 Torr lit.[13] bp 87.5 °C at 9 Torr) of **3b**.
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