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1,1-Carboboration of 1-Alkynes: A Conceptual Alternative to the Hydroboration Reaction

Chao Chen, Tanja Voss, Roland Fröhlich, Gerald Kehr, and Gerhard Erker*

Organisch-Chemisches Institut, Westfälische Wilhelms-Universität, Corrensstrasse 40,
48149 Münster, Germany

erker@uni-muenster.de

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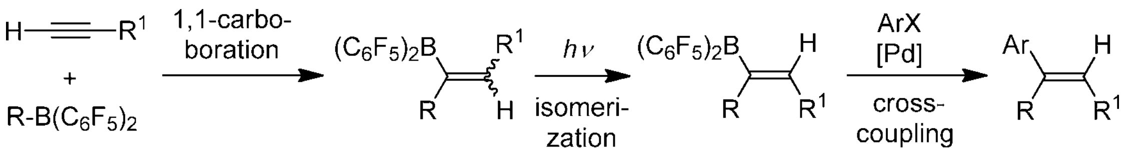
ABSTRACT



Strongly electrophilic boranes R-B(C_6F_5)$_2$ react readily with a variety of 1-alkynes by means of a 1,1-carboboration reaction to yield alkenylborane products, which can subsequently be used as reagents in metal catalyzed cross-coupling reactions.

The 1,1-carboboration of alkynes previously had been a rather specific reaction leading to boryl-functionalized alkenes.[1] Formally it might be regarded as an insertion reaction of the vinylidene isomer of the acetylene into a boron−carbon bond of the borane reagent.[2] However, mechanistically it proceeds by means of an abstraction/rearrangement sequence.[3] So far it required the presence of particular substituents at the alkyne, mostly main group or transition metal derived, that served as good 1,2-migrating groups in this scheme.[1,3] We had quite recently found that 1,1-carboboration reactions of simple 1-alkynes can easily be performed with the strongly electrophilic R-B(C_6F_5)$_2$ reagents,[4] which are readily available.[5] In this account we will report on some significant progress including utilization of the resulting 1,1-carboboration products in cross-coupling reactions.

In a typical example, we mixed the terminal alkyne 5-phenyl-1-pentyne (**1a**) with B(C_6F_5)$_3$ (**2a**)[6] in CD_2Cl_2. Inspection by NMR spectroscopy (^{1}H, ^{13}C, ^{19}F, ^{11}B) revealed that the 1,1-carboboration reaction was complete within minutes to give a close to quantitative conversion to a ca. 1:1.2 mixture of the isomeric products *E*-**3a** and *Z*-**3a** (for details see the Supporting Information). Subsequent photolysis (HPK 125, Pyrex filter, 15 min, rt) resulted in a >95% conversion of the *E*-**3a** to the *Z*-**3a** isomer (see Scheme 1). We then performed this reaction on a preparative scale. In an one-pot procedure the thermally induced 1,1-carboboration reaction of the 1-alkyne **1a** with the borane **2a** was carried out in pentane at ambient conditions. Subsequent photolysis

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(1) Wrackmeyer, B. *Coord. Chem. Rev.* **1995**, *145*, 125–156.

(2) In a formal sense this reaction is remotely related to the reverse of the Fritsch−Buttenberg−Wiechell reaction. Review: Tykwinski, R. R. *Chem. Commun.* **2010**, *46*, 3235–3249.

(3) Review: (a) Wrackmeyer, B. *Heteroat. Chem.* **2006**, *17*, 188–208, and references cited therein. See also selected examples: (b) Wrackmeyer, B.; Horchler, K.; Boese, R. *Angew. Chem.* **1989**, *101*, 1563–1565. (c) Wrackmeyer, B.; Horchler, K.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1500–1502. (d) Wrackmeyer, B.; Kehr, G.; Boese, R. *Angew. Chem.* **1991**, *103*, 1374–1376. (e) Wrackmeyer, B.; Kehr, G.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1370–1372. (f) Wrackmeyer, B.; Kehr, G.; Sebald, A.; Kümmerlen, J. *Chem. Ber.* **1992**, *125*, 1597–1603. (g) Wrackmeyer, B.; Kundler, S.; Milius, W.; Boese, R. *Chem. Ber.* **1994**, *127*, 333–342. (h) Wrackmeyer, B.; Kenner-Hofmann, B. H.; Milius, W.; Thoma, P.; Tok, O. L.; Herberhold, M. *Eur. J. Inorg. Chem.* **2006**, 101–108.

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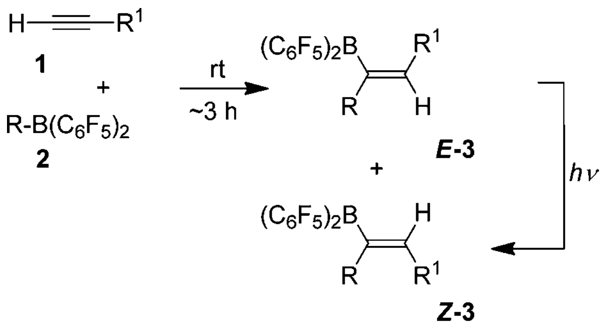
(5) For their preparation, see the Supporting Information. See also: Spence, R. E. v. H.; Piers, W. E.; Sun, Y.; Parvez, M.; MacGillivray, L. R.; Zaworotko, M. J. *Organometallics* **1998**, *17*, 2459–2469.

(6) (a) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245–250. (b) Wang, C.; Erker, G.; Kehr, G.; Wedeking, K.; Fröhlich, R. *Organometallics* **2005**, *24*, 4760–4773.

10.1021/ol102544x

Scheme 1

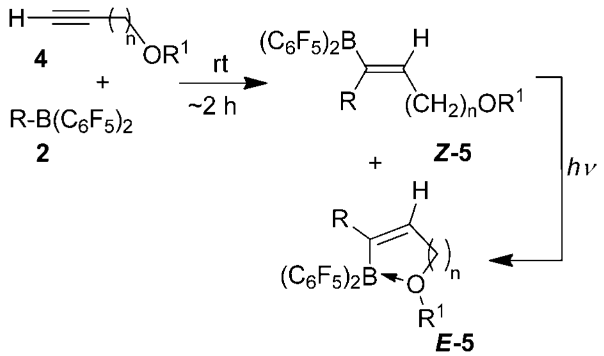


2	R	1	R^1	3	E/Z	$\xrightarrow{h\nu}$ %Z[a]
a	C_6F_5	**a**	$(CH_2)_3Ph$	**a**	1:1.2	63
a	C_6F_5	**b**	$(CH_2)_4Cl$	**b**	1:1.9	83
a	C_6F_5	**c**	^tBu	**c**	[b]	84
b	CH_3	**d**	Pr	**d**	1:1.6	69
c	$(CH_2)_2Ph$	**d**	Pr	**e**	1:1.4	69

[a] Isolated yield. [b] Not determined.

(3 h) followed by workup eventually gave the pure *Z*-**3a** product in 63% yield. Similarly, the products *Z*-**3b** and *Z*-**3c** were obtained in good yield starting from **1b** and **1c**, respectively. The X-ray crystal structure analysis of *Z*-**3c** clearly shows the substituent pattern at the double bond originating from the 1,1-carboboration reaction after subsequent irradiation.

Scheme 2



2	R	4	n	R^1	5	Z/E	$\xrightarrow{h\nu}$ %E[a]
a	C_6F_5	**a**	1	$CH_2C{\equiv}CH$	**a**	1:1.8	62
a	C_6F_5	**b**	1	CH_3	**b**	1:2.8	49
a	C_6F_5	**c**	1	TMS	**c**	1:1.5	73
a	C_6F_5	**d**	2	TMS	**d**	1:1.0	56
b	CH_3	**d**	2	TMS	**e**	1:1.2[b]	58

[a] Isolated yield. [b] 75 °C for 5 h.

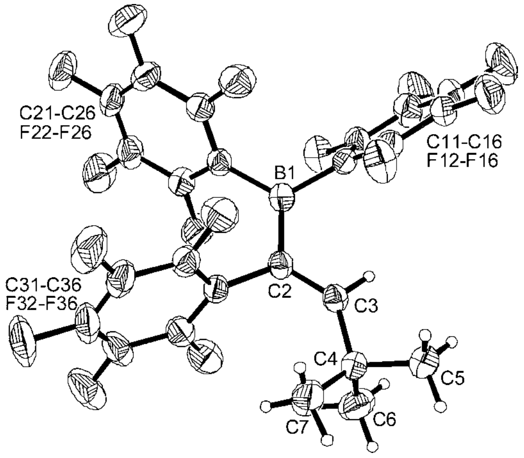


Figure 1. Molecular structure of *Z*-**3c**.

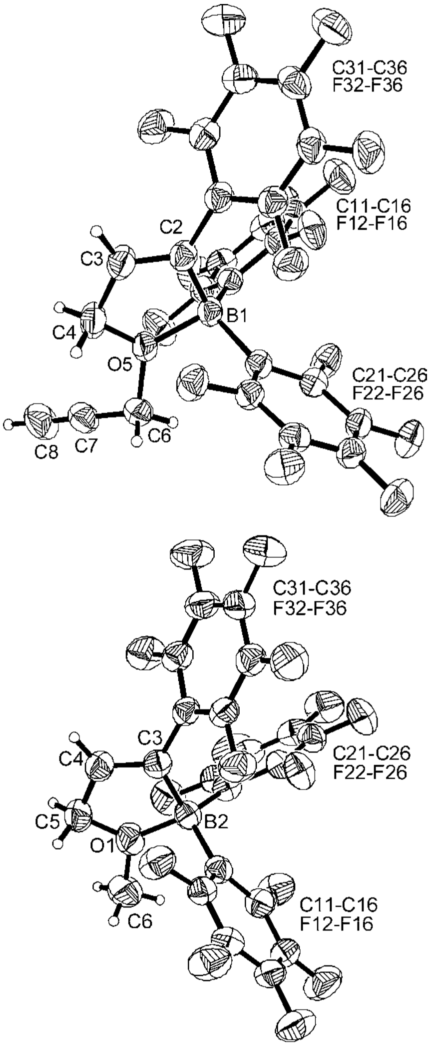
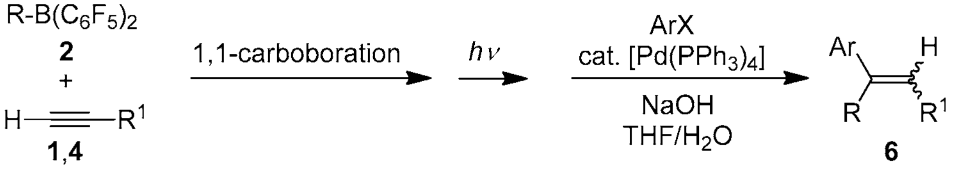
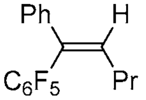
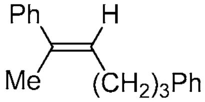
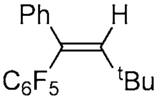
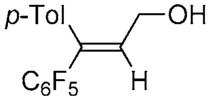
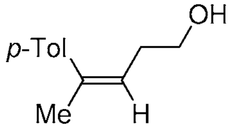
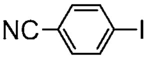
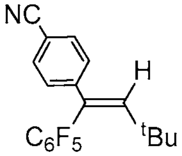


Figure 2. Molecular structures of the 1,1-carboboration products *E*-**5a** (top) and *E*-**5b** (bottom).

Scheme 3



2	R	alkyne	Ar-X	method[a]	product		yield
a	C_6F_5	$H-\equiv-Pr$ (**1d**)	Ph-I	**A**		***Z*-6a**[b]	86%
b	Me	$H-\equiv-(CH_2)_3Ph$ (**1a**)	Ph-I	**B**		***E*-6b**	76%
a	C_6F_5	$H-\equiv-{}^tBu$ (**1c**)	Ph-I	**A**		***Z*-6c**	64%
a	C_6F_5	$H-\equiv-CH_2OTMS$ (**4c**)	*p*-Tol-I	**A**		***E*-6d**[c]	90%
b	Me	$H-\equiv-(CH_2)_2OTMS$ (**4d**)	*p*-Tol-I	**A**		***Z*-6e**[c]	73%
a	C_6F_5	$H-\equiv-{}^tBu$ (**1c**)		**A**		***Z*-6f**	74%

[a] **A**: starting from the isolated alkenylboranes *Z*-**3** or *E*-**5**, respectively. **B**: one-pot procedure. [b] For the respective alkenylborane see ref 4a. [c] Trimethylsilyl groups were removed during workup.

The 1,1-carboboration reaction of 1-alkynes is chemoselective with regard to the substituents employed at the borane. We treated 1-pentyne with the reagent $H_3C-B(C_6F_5)_2$ (**2b**) under similar conditions and found that exclusively the methyl substituent was transferred from boron to carbon in the course of the 1,1-carboboration reaction to give a mixture of the *Z*-**3d** and *E*-**3d** isomers. Subsequent photolysis again gave the pure *Z*-**3d** product (69% isolated, see Scheme 1). Similarly, we obtained the product *Z*-**3e** selectively from the 1,1-carboboration/photochemical isomerization sequence, in which only the 2-phenylethyl substituent had migrated.

Since we could selectively prepare substituted alkenyl boranes (*Z*-**3**) with a *Z*-configuration by this facile 1,1-carboboration/photolysis sequence, we searched for an *E*-selective alternative. This was found by employing 1-alkyne substrates bearing alkoxyalkyl or trimethylsiloxyalkyl substituents. A typical example is the reaction of bis-propargyl ether (**4a**) with $B(C_6F_5)_3$ (**2a**). The 1,1-carboboration reaction took place readily at room temperature selectively with one alkynyl moiety to generate a ca. 1:1.8 mixture of the products *Z*-**5a** and *E*-**5a**. Subsequent photolysis again resulted in a fast and efficient isomerization of the carbon−carbon double bond of the product, but in this case the photostationary equilibrium lay on the side of the *E*-**5a** isomer (>95%, see Scheme 2). We isolated this crystalline product in 62% yield and characterized it by X-ray diffraction (see Figure 2). The X-ray crystal structure analysis confirmed the formation of **5a** by the 1,1-carboboration sequence and revealed stabilization of the borane product by internal oxygen to boron coordination (B1−O5 1.617(2) Å). This structural feature of compound *E*-**5a** is retained in solution (e.g., ^{11}B NMR, δ 9.1; ^{19}F NMR, $\Delta\delta_{m,p}[B(C_6F_5)_2] = 8.5$).[7]

The 1,1-carboboration/photolysis sequence of the $-OCH_3$ or -OTMS functionalized 1-alkynes **4b**−**d** proceeds analogously. In each case we eventually isolated the respective *E*-alkenylborane product in good yield (see Scheme 2). Compound **5b** was also characterized by X-ray diffraction

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(7) (a) Piers, W. E. *Adv. Organomet. Chem.* **2005**, *52*, 1–76. (b) Beringhelli, T.; Donghi, D.; Maggioni, D.; D'Alfonso, G. *Coord. Chem. Rev.* **2008**, *252*, 2292–2313, and references cited therein.

(see Figure 2). The crystal structure analysis confirmed the *E*-configuration of the C═C double bond in **5b** and shows the internal stabilization of the borane by internal oxygen to boron coordination. The oxygen−boron bond in **5b** (B2−O1 1.595(3) Å) is shorter than in **5a**.

The alkenylboranes **3** and **5** are interesting products in themselves as functionalized strong boron Lewis acids. They have now also been employed as reactive reagents in Pd-catalyzed cross-coupling reactions. For this purpose the isolated alkenylborane products were used (method **A**, Scheme 3), but it was also possible to alternatively employ these reagents generated in situ without additional workup in an one-pot procedure (method **B**). The reaction starting from 5-phenyl-1-pentyne (**1a**) is a typical example. Selective 1,1-carboboration with $CH_3B(C_6F_5)_2$ took place at room temperature; this was followed by photolysis and then $Pd(PPh_3)_4$ (10 mol %) catalyzed coupling with phenyl iodide (see Scheme 3)[8] to selectively give the product *E*-**6b**, which was isolated in a yield of 76%. The -OTMS functionalized alkynes reacted similarly, only in these cases the corresponding alcohols (*E*-**6d**, *Z*-**6e**, see Scheme 3) were isolated in 90 or 73% yield, respectively. The *p*-cyanophenyl substituted alkene *Z*-**6f** was obtained in good yield from the Pd-catalyzed cross-coupling reaction of *Z*-**3c** with *p*-iodobenzonitrile.[9]

The new 1,1-carboboration reaction of simple 1-alkynes makes *Z*-substituted reactive alkenylboranes readily available. In principle, such products could also be prepared by a hydroboration route of the corresponding alkyne backbones with Pier's borane $HB(C_6F_5)_2$.[10−12] Of course, our procedure shows a different pattern of forming the essential new bonds and, thus, provides a useful alternative to the hydroboration reaction,[13] especially in cases (e.g., **3d**, **3e**) where the latter might encounter regioselectivity problems. This new sequence makes the 1,1-carboboration reaction of 1-alkynes an interesting and useful methodological addition to the synthetic repertoire of organo-boron reagent chemistry.

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Supporting Information Available: Experimental procedures and spectroscopic data for all new compounds **3**, **5** and **6**. CIF files for compounds *Z*-**3c**, *E*-**5a** and *E*-**5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) See for a comparison: (a) Ishiyama, T.; Mori, M.; Suzuki, A.; Miyaura, N. *J. Organomet. Chem.* **1996**, *525*, 225–231. (b) Alacid, E.; Nájera, C. *J. Org. Chem.* **2009**, *74*, 2321–2337.

(10) (a) Parks, D. J.; Spence, R. E. v H.; Piers, W. E. *Angew. Chem.* **1995**, *107*, 895–897. (b) Parks, D. J.; Spence, R. E. v H.; Piers, W. E. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 809–810. (c) Parks, D. J.; Piers, W. E.; Yap, G. P. A. *Organometallics* **1998**, *17*, 5492–5503.

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