Facile Boron Migration during Hydrozirconation of Alkenylboronates

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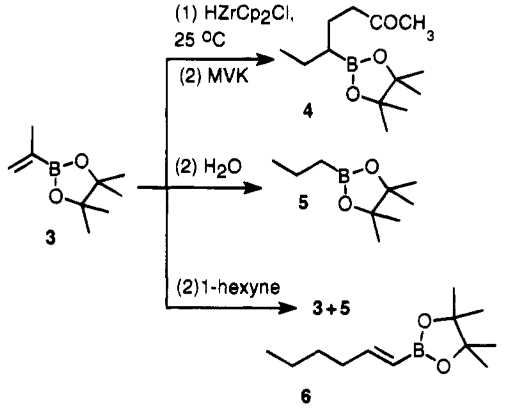
Hydrozirconation of alkenes is known to place zirconium on the least hindered carbon of a chain by a process involving dehydrozirconation/hydrozirconation.[1] This isomerization is rapid at 25 °C. Some exceptions exist, and these are primarily thought to be due to the directing effect of lone pairs on a heteroatom substituted on the carbon skeleton.[2] In contrast, thermal isomerization of trialkylboranes is less facile and generally occurs in the range 100–150 °C.[3] Very sterically hindered R_3B may rearrange at 25 °C.[4] This communication presents some unusual chemistry involving boron migrations that result from the juxtaposition of boron and zirconium in the same molecule.

We have demonstrated that 1-hexenyl- and 1-hexynylboronates exclusively yield terminal *gem*-borazirconocene alkyl and alkenyl compounds, respectively.[5] To investigate the propensity of the zirconium and boron atoms to become attached to the same terminal carbon, we decided to study the hydrozirconation of several alkenylboronates. As a method of characterizing the regioselectivity of hydrozirconation of alkenylboronates, we have found that conjugate addition of borazirconocene alkanes to methyl vinyl ketone (MVK) is useful.[6] Thus when **3** was hydrozirconated and added to MVK we were surprised to observe the formation of **4** exclusively. Clearly, migration of boron had occurred. Quenching hydrozirconated **3** with H_2O gave linear boronate **5**. To test whether boron migration had occurred by a dehydroboration process to give a "BH species", we added 1 equiv of 1-hexyne to **3** 5 min after hydrozirconation. Indeed, we observed the formation of pinacol 1-hexenylboronate **6**. Results are summarized in Scheme 1.

Scheme 1



Similarly, **8**, and a mixture of **10** and **11**, gave **9** and **12**, respectively, the products of boron migration to the terminal carbon as indicated by the MVK adducts (Table 1). Trapping experiments with 1-hexyne are summarized in Table 2. The fact that even **6** eliminated a "BH species" 5 min after hydrozirconation is noteworthy. However, addition of 1-hexyne or 1-octyne to alkenylboronates **3**, **6**, **8**, **10**, and **11**, 24 h after hydrozirconation showed no formation of hydroborated alkyne, with the exception of **1** (Table 2).

Hydroboration of alkynes with pinacolborane is slow at 25 °C and requires 2 equiv of reagent and heating to go to completion.[7] Hydroboration of alkenes is even more sluggish. We prepared pinacolborane and reacted it with 1-hexyne in CH_2Cl_2 in the absence and in the presence of $HZrCp_2Cl$ (7 mol %). Hydroboration with pinacolborane was considerably faster in the presence of $HZrCp_2Cl$.[8] Therefore, it is highly unlikely that free pinacolborane is the active hydroborating species in our system. Rather it is most likely associated with the presumed alkenylzirconocenes present in equilibrium, possibly as π-complexes.[1a,2b,4,9] Solution ^{1}H NMR and ^{13}C NMR spectra of the borazirconocene derived from **1** indicate multiple species in solution, favoring the *gem*-borazirconocene.[10a] That these species are in equilibrium was demonstrated by variable temperature ^{1}H NMR studies.[10b] Thus, alkenylboronate systems, such as **3**, **8**, and **11**, exhibit boron migration during hydrozirconation, until boron reaches the end carbon of the alkyl chain after which no "BH species" can be detected upon addition of an alkyne. Furthermore, since we have established that terminal *gem*-borazirconocenes are stable compounds[5] and do not liberate "BH" after equilibrating for 24 h, hydrozirconation in the early stages (within 5 min) of 1-alkenyl boronates such as **6** and **10**, apparently occurs on C2 of the vinylic system to give 1,2-borazirconocenes.[11]

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(1) (a) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1971,** *27,* 373. (b) Schwartz, J.; Labinger, J. A.; *Angew. Chem., Int. Ed. Engl.* **1976,** *15,* 333. (c) Labinger, J. A. In *Comprehensive Organic Synthesis;* Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 8, p 667.

(2) (a) Buchwald, S. L. LaMaire, S. J. *Tetrahedron Lett.* **1987,** *28,* 295. (b) Annby, U.; Karlsson, S.; Gronowitz, S.; Hallberg, A.; Alvhäll, J.; Svenson, R. *Acta Chem. Scand.* **1993,** *47,* 425.

(3) (a) Brown, H. C.; Subba Rao, B. C. *J. Am. Chem. Soc.* **1959,** *81,* 6434. (b) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1960,** *82,* 1504.

(4) Field, L. D.; Gallagher, S. P. *Tetrahedron Lett.* **1985,** *26,* 6125.

(5) (a) Zheng, B.; Srebnik, M. *Tetrahedron Lett.* **1993,** *34.* 4133. Skrzypczak-Jankun, E.; Cheesman, B.; Zheng, B.; Lemert, R. M.; Asthana, S.; Srebnik, M. *J. Chem. Soc., Chem. Commun.* **1994,** 127. (c) Deloux, L; Skrzypczak-Jankun, E.; Cheesman, B. V.; Sabat, M; Srebnik, M. *J. Am. Chem. Soc.* **1994,** *116,* 10302. (d) Zheng, B.; Srebnik, M. *J. Org. Chem.* **1995,** *60,* 486.

(6) (a) Pereira, S.; Srebnik, M. *Tetrahedron Lett.* **1995,** *36,* 1805. (b) For conjugate addition of alkylzirconocene chlorides, see: Wipf, P. Xu, W.; Smitrovich, J. H.; Lehmann, R.; Venanzi, L. M. *Tetrahedron* **1994,** *50,* 1935.

(7) (a) Tucker, C. E.; Davidson, J.; Knochel, P. *J. Org. Chem.* **1992,** *57,* 3482. (b) Another hindered dialkoxyborane, 4,4,6-trimethyl-1,3,2-dioxaborinane, hydroborates alkynes and alkenes only above 100 °C: Woods, W. G.; Strong, P. L. *J. Am. Chem. Soc.* **1966,** *88,* 4667. (c) Fish, R. H. *J. Org. Chem.* **1973,** *38,* 158.

(8) For catalysis involving catecholborane and transition metals, see: (a) Männig, D.; Nöth, H. *Angew. Chem. Int. Ed.. Engl.* **1985,** *24,* 878. (b) Burgess, K.; Ohlmeyer, M. J. *Chem. Rev.* **1991,** *91,* 1179.

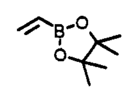
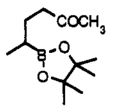
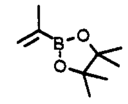
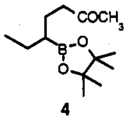
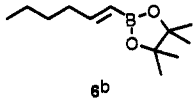
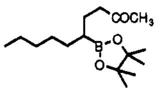
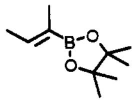
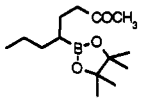
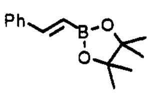
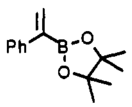
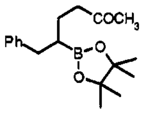
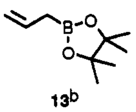
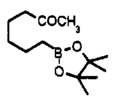
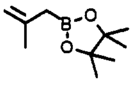
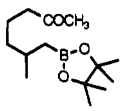
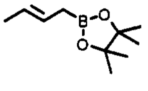
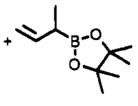
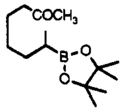
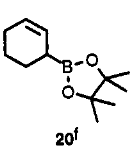
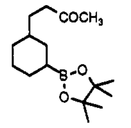
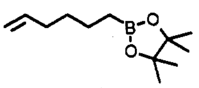
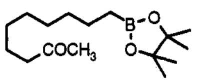
(9) (a) Dasgupta, S.; Datta, M. K.; Datta, R. *Tetrahedron Lett.* **1978,** 1309. (b) Dewar, M. J. S.; McKee, M. L. *Inorg. Chem.* **1978,** *17,* 1075.

(10) (a) *gem*-Borazirconocene derived from **1.** CD_2Cl_2 δ 6.47 (s, 5 H), 6.35 (s, 5 H), 2.01 (q, 1 H, J = 6.4 Hz), 1.32 (d, 3 H), J= 6.4 Hz). (b) ^{1}H NMR studies of hydrozirconated 1 show an increase of the *gem*-borazirconocene when the temperature is lowered. The original spectrum is obtained upon warming up. (c) Hydrozirconated **13**: CD_2Cl_2 δ 6.18 (s, 10 H), 1.58 (m, 2 H), 1.2 (s, 12 H), 1.03 (m, 2 H), 0.66 (t, 2 H, J = 6.9 Hz).

(11) Hydrozirconation of various vinylic systems is complex and leads to different solution chemistry and regioselectivity in reaction with electrophiles: (a) Vinyl phosphines and phosphine oxides though existing as the 1,2-species in solution react to give 1,1-products: Zablocka, M.; Igau, A.; Marjoral, J.-P.; Pietrusiewicz, K. M. *Organometallics* **1994,** *12,* 603. (b) Vinyltrimethylsilane: Jordan, R. F. *Adv. Organomet. Chem.* **1991,** *32,* 325. (c) Hydrozirconation of $Cp(PMe_3)_2RhCH{=}CH_2$: Lemke, F. R.; Bullock, R. M. *Organometallics* **1992,** *11,* 4261. Lemke, F. R.; Szalda, D. J.; Bullock, R. M. *J. Am. Chem. Soc.* **1991,** *113,* 8466. (d) Vinyl oxazolines are hydrogenated with $HZrCp_2Cl$: ref 2b.

0022-3263/95/1960-4316$09.00/0

Table 1. Reaction of Borazirconocenes with MVK

Boronate	Adduct with MVK[a]	Yield %
 1[b]	 2	93
 3[c]	 4	87
 6[b]	 7	93
 8[c]	 9	86
 +  10[c,d] 11[c,d]	 12	91
 13[b]	 14	87
 15[b]	 16	83
 +  17[b,e] 18[b,e]	 19	82
 20[f]	 21[g]	67
 22[b]	 23	81

[a] Obtained by conjugate addition in the presence of 10 mol% $CuBr\cdot SMe_2$ of the hydrozirconated boronate. [b] Prepared according to: Washburn, R.M.; Billig, F.A.; Bloom, M; Albright, M.; Levens, E. in *Borax to Boranes;* Martin, D.L., Ed; *Adv. Chem. Ser.* No. 32; American Chemical Society: Washington, D.C.: 1961; p 208. However the mixed pinacol isopropyl borate was used: Wallace, R.H.; Zong, K.K. *Tetrahedron Lett.* **1992,** *33,* 6941, and the reaction worked up with anhydrous HCl. [c] Prepared according to: Brown, H.C.; Campbell, J.B., Jr. *J. Org. Chem.* **1980,** *45,* 389. [d] 85:15 mixture of **10** and **11**. [e] 1:1 Mixture of **17** and **18.** [f] Prepared according to: Brown, H.C.; Bhat, K.S. *J. Am. Chem. Soc.* **1986,** *108,* 293. [g] Relative stereochemistry was not determined.

This is followed by loss of "BH". An ensuing series of "ZrH" and "BH" additions and losses proceeds until the stable terminal *gem*-borazirconocenes are obtained. Boron elimination is especially facile in the styrene system **10 and 11.** Within 5 min, approximately 60% of boron is lost (Table 2)!

Table 2. Quenching the Hydrozirconated Alkenyl Boronates with 1-Hexyne

		distribution of boronates, %[a]		
boronate	time[b]	starting alkenyl boronate	hydrogenated alkenyl boronate[c]	**6**
1	5 min	37.4	33.7	28.9
	24 h	7.2	86.3	6.5
3	5 min	39.7	39.2	21.1
	24 h	7.5	92.5	0
6	5 min	91.8	5.8	2.4[d]
	24 h	4.0	96.0	0
8	24 h[e]	17.2	82.8	0
10 + 11	5 min	41.3	0	58.7
	24 h	10.3	89.7	0
13	5 min	55.3	44.7	0
	24 h	5.3	94.7	0
15	5 min	51.3	48.7	0
	24 h	6.7	93.3	0
17 + 18	5 min	77.3	22.7	
	24 h	13.5	86.5	0
20	5 min	92.5	7.5	0[d]
	24 h	21.8	78.2	0[d]
22	5 min	52.1	47.9	0[d]
	24 h	5.3	94.7	0[d]

[a] 1-Hexyne was added 5 min or 24 h after hydrozirconation and then quenched with H_2O and analyzed GCMS. [b] Time at which 1-hexyne was added to the reaction mixture after hydrozirconation. [c] Indicative of the amount of hydrozirconation that has taken place. [d] 1-Octyne was used. [e] Hydrozirconation is too slow to be determined after 5 min.

The forgoing implies that 1,2-borazirconocene alkanes are unstable and rearrange to terminal *gem*-borazirconocene alkanes. As a corollary, hydrozirconation of allylic boronates must occur on C3 of the allylic system to give 1,3-borazirconocenes since no "BH species" is detected at any stage during hydrozirconation. Indeed, ^1H NMR of the hydrozirconated product of **13** indicates the presence of only the 1,3-borazirconocene.[10c] No hydroborated alkyne is produced by adding alkyne either 5 min or 24 h after hydrozirconation. Similarly, no hydroborated alkyne is detected during the hydrozirconation of a 1:1 mixture of allylic boronates **17** and **18** that gives only **19.**[12] For ω-alkenylboronates, such as **22,** hydrozirconation occurs to give 1,ω-borazirconocenes, confirmed by the MVK addition adduct **23.** The yields of the MVK adducts are generally excellent (Table 1).

The exact mechanism and series of events in this very facile migration observed during the hydrozirconation of 1-alkenylboronates is at present still unknown. $HZrCp_2Cl$ apparently catalyzes hydroboration, and it appears to catalyze isomerization of 1-alkenylboronates.[13] Ongoing studies will hopefully elucidate the process and provide useful synthetic applications.

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Supporting Information Available: General experimental procedures (7 pages).

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(12) Presumably, hydrozirconation preferentially occurs on the less hindered terminal double bond in **18** which equilibrates with its isomer **17** by a fast borotropic shift: Kramer, G. W.; Brown, H. C. *J. Organomet. Chem.* **1977,** *132,* 9.

(13) Pereira, S.; Srebnik, M. The results of this study will be published elsewhere.