Preparation of (Z)-1-Alkenyl Dioxaborolanes by Hydrolysis of Boryl Zirconocene 1,1-Dimetalloalkenes

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Due to syn addition of borane reagents to carbon–carbon double bonds, (Z)-1-alkenyl boranes cannot be obtained directly by hydroboration. Several alternative methods have been developed. These include reduction of 1-halo-1-alkenyl boranes with either LiEt$_3$BH[1] or *tert*-butyllithium,[2] hydrogenation of 1-alkynyl boranes,[3] and photoisomerization of (E)-tri-(1-alkenyl) boranes.[4] These methods all involve some incompatibility with various function groups. We have recently been exploring the preparation of boron zirconocene 1,1-dimetalloalkanes. Since hydrozirconation is tolerant of many functional groups and, as part of our program exploring the chemistry of boryl zirconocene 1,1-dimetallics,[5] we were interested in examining the hydrozirconation of 1-alkynyl boronates. The latter are readily available by reaction of 1-lithioalkynes and either 2-methoxy or 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.[6,7] Indeed, hydrozirconation of the 1-alkynyl dioxaborolanes with 1.2 equiv of HZrCp$_2$Cl in either THF or 1,4-dioxane proceeded readily by *syn* addition to give essentially pure boryl zirconocene *E*-1,1-dimetallics **2** (eq 1). It is interesting to note that in all cases examined to date, zirconium is placed on the same carbon as boron. The reason for this is not clear at the present.
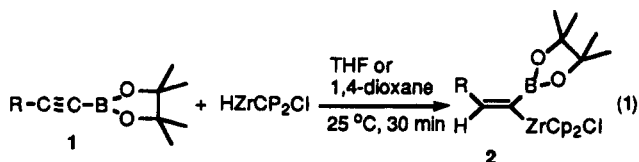
Compounds **2** are stable under an inert atmosphere. Some of these compounds are solids and we recently obtained the first crystal structure of a representative boryl zirconocene 1,1-dimetalloalkene.[8] These 1,1-dimetalloalkenes now have the advantage of having two metals[9] of different reactivities attached to the same carbon, thus enabling selective reactions with various

electrophiles.[10] This is distinctly different from other 1,1-dimetalloalkenes which in essence act as ketene transfer reagents.[11]

As an example of selective reactivity we examined the hydrolysis of the boryl zirconocene 1,1-dimetalloalkenes. The carbon–zirconium bond is more reactive than the carbon–boron bond toward various electrophiles[5] and we thus expected hydrolysis to occur preferentially with cleavage of the former bond. Since hydrolysis of alkenyl zirconocenes is known to proceed with retention of configuration,[12] a direct utility of our 1,1-dimetalloalkenes would be the preparation of (Z)-1,1-alkenyl boronates (eq 2).
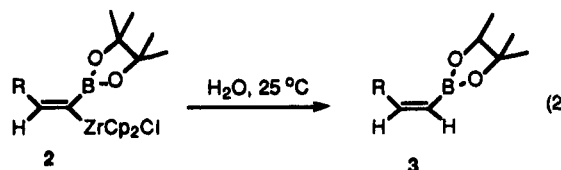
Though the 1,1-dimetalloalkenes can be isolated, in the present case, however, it is not necessary. The desired (Z)-1-alkenyl boronates can be obtained in a one-pot procedure by hydrozirconation followed by hydrolysis with excess H$_2$O.

The (Z)-1-alkenyl dioxaborolanes are obtained in excellent yield as isomerically pure compounds. The J_{ab} coupling constants are consistent with (Z)-1–alkenyl boranes[13] and are generally about 3–5 Hz smaller than the *E*-diastereomers. The reaction sequence is operationally simple and is compatible with various functional groups as indicated in Table 1. Thus we have determined that the reaction is compatible with halides, acetals, silanes, and silyloxy protecting groups.

Experimental Section

Glassware, syringes and needles were oven dried at 120 °C, assembled while hot and dried under a flow of Ar. All reactions were done under a positive pressure of Ar.[15] THF was distilled from sodium ketyl and used immediately. ^{1}H-NMR spectra were obtained at 400 MHz and ^{13}C-NMR were obtained at 100 MHz both relative to TMS. Mass spectra were obtained on a GC/MS fitted with a 25 m methylsilicone column.

General Procedure for the Preparation of (Z)-1-Alkenylboronates. To a stirred suspension of Cp$_2$ZrCl(H)[14] (0.74 mmol, 0.191 g) in dry THF at 25 °C under an atmosphere of argon was added 1.2 mL of a 0.5 M solution of 2-(3,3-dimethyl-1-butynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.60 mmol) in THF. The reaction was stirred for an additional 30 min until

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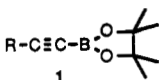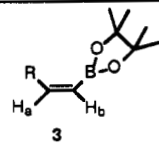
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Table 1. (Z)-1-Alkenyl Dioxaborolanes from 1-Alkynyl Boronates by Hydrozirconation/Hydrolysis

$$R-C{\equiv}C-B{<}^{O}_{O}{\diagdown}\qquad\qquad {}^{R}_{H_a}{>}{=}{<}^{B{<}^{O}_{O}}_{H_b}$$

	R	Yield[a]	Bp °C / mm Hg	Yield[b]	B^{11} (ppm)	J_{ab}(Hz)
a	n-Bu	87	71-72 / 1.25	95	29.48	13.51
b	t-Bu	89	78-79 / 5	93	30.30	15.01
c	ClCH$_2$CH$_2$CH$_2$	81	126-128 / 3.75	94	29.33	13.46
d	Cyclopentyl	86	66-68 / 0.2	90	29.44	13.46
e	PhCH$_2$CH$_2$	80	c	90[d]	29.46	13.55
f	Ph	85	68-70 / 0.01	86[d]	30.30	14.93
g	Me$_3$Si	83	108-109[e]	88	28.96	18.92
h	CH$_3$CH$_2$CH (CH$_3$)	85	75-77 / 0.2	93	29.52	13.47
i	(EtO)$_2$CH	72	c	89[f]	29.08	13.79
j	t-Bu(Me)$_2$SiO(CH$_2$)$_3$	71	c	92	29.45	13.46

[a] Isolated yields. [b] Yields calculated by ^{1}H-NMR using benzene as an internal standard. All compounds gave ^{1}H-NMR, ^{13}C-NMR and MS spectra consistent with their structures. [c] Volatiles were removed under reduced pressure and the compound used directly in the hydrozirconation step. [d] Yields calculated by gas chromatography using dodecane as an internal standard. [e] The product was isolated by crystallization from hexanes. The value in the table is the melting point. [f] Integration of the ^{1}H-NMR indicates partial decompostition of the acetal under conditions of the reaction.

it turned clear and became green-yellow in color. Addition of excess H$_2$O led to the discharge of the color and the appearance of a precipitate. After stirring for an additional 30 min, the THF was evaporated and the reaction mixture was extracted with hexanes (3 × 10 mL). Evaporation of the solvent afforded the essentially pure (Z)-alkenyl boronates as colorless oils. The yields are given in Table 1.

3a: ^{1}H-NMR (CDCl$_3$) δ 6.41 (m, 1 H), 5.30 (d, 1 H), 2.37 (m, 2 H), 1.32 (m, 2H), 1.27 (m, 2H), 1.24 (s, 12 H), 0.87 (t, 3 H); ^{13}C-NMR (CDCl$_3$) δ 152.5, 118.2, 83.6, 44.4, 32.5, 29.6, 24.9, 22.5; MS (EI) °C (relative intensity) 210 (M$^+$, 16.7), 195 (43.5), 182 (10.9), 168 (23.5), 153 (61.8), 140 (13.5), 124 (66.2), 111 (79.0), 110 (100), 109 (45.9), 101 (85.3), 95 (46.7), 85 (67.3), 84 (62.6), 83 (86.7), 82 (69.9), 81 (44.6), 69 (97.0), 68 (71.7), 67 (66.7), 59 (57.3), 56 (19.1), 55 (94.4), 53 (17.9).

3b: ^{1}H-NMR (CDCl$_3$) δ 6.23 (d, 1 H, J = 15.01 Hz), 5.15 (d, 1 H, J = 15.01 Hz), 1.25 (s, 12 H), 1.07 (s, 9 H); ^{13}C-NMR (CDCl$_3$) δ 159.7, 121.4, 83.3, 35.2, 29.9, 24.8; MS (EI) °C (relative intensity) 210 (M$^+$, 11.8), 195 (18.8), 153 (61.8), 137 (43.6), 111 (39.1), 110, (43.6), 109 (38.2), 101 (70.0), 95 (47.3), 85 (30.9), 84 (100), 83 (47.3), 69 (75.3), 55 (34.5).

3c: ^{1}H-NMR (CDCl$_3$) δ 6.37 (m, 1 H), 5.38 (d, 1 H), 3.51 (t, 2 H), 2.52 (m, 2 H), 1.84 (m, 2 H), 1.23 (s, 12 H); ^{13}C-NMR (CDCl$_3$) δ 152.5, 119.8, 83.0, 44.4, 32.5, 29.6, 24.9; MS (EI) °C (relative intensity) 230 (M$^+$, 11.7), 215 (45.7), 195 (13.3), 182 (10.9), 162 (11.9), 153 (65.5), 144 (53.7), 130 (22.9), 111 (26.5), 110 (9.1), 109 (27.3), 101 (58.3), 95 (35.5), 85 (56.0), 84 (62.6), 83 (33.7), 82 (33.2), 81 (21.4), 69 (76.5), 68 (64.6), 67 (90.1), 59 (100), 55 (49.0), 53 (23.4).

3d: ^{1}H-NMR (CDCl$_3$) δ 6.28 (dd, 1 H), 5.20 (d, 1 H), 3.14 (m, 1 H), 1.78 (m, 2 H), 1.49 (m, 4 H), 1.24 (s, 12 H); ^{13}C-NMR (CDCl$_3$) δ 160.0, 117.7 , 82.6, 42.4, 33.7, 25.6, 24.7; MS (EI) °C

(relative intensity) 222 (M$^+$, 3.75), 207 (5.19), 178 (3.58), 165 (32.4), 153 (5.44), 136 (9.39), 123 (8.54), 122 (23.0), 121 (17.0), 101 (30.3), 95 (14.3), 94 (26.6), 93 (10.3), 85 (25.3), 84 (100), 83 (86.716.2), 82 (2.61), 81 (18.5), 69 (16.0), 68 (8.73), 67 (17.2), 66 (10.9), 59 (11.2), 55 (21.8), 53 (8.31).

3e: ^{1}H-NMR (CDCl$_3$) δ 7.28 (m, 5 H), 6.55 (m, 1 H), 5.44 (d, 1 H), 2.78 (m, 1 H), 1.31 (s 12 H); ^{13}C-NMR (CDCl$_3$) δ 153.9, 142.0, 128.6, 128.3, 125.8, 118.5, 82.9, 36.1, 34.0, 24.9; MS (EI) °C (relative intensity) 258 (M$^+$, 1.53), 243 (3.16), 215 (1.04), 201 (2.26), 174 (10.9), 158 (42.0), 157 (16.9), 143 (4.66), 131 (9.25), 130 (47.6), 129 (12.9), 128 (6.40), 117 (8.00), 105 (4.85), 104 (4.71), 101 (9.77), 92 (8.36), 91 (100), 85 (26.1), 84 (30.8), 83 (7.60), 81 (5.05), 69 (5.23), 68 (5.28), 67 (3.13), 59 (6.13), 57 (4.26), 55 (8.76), 51 (2.42).

3f: ^{1}H-NMR (CDCl$_3$) δ 7.53 (d, 2 H), 7.27 (m, 4 H), 5.60 (d, 1 H), 1.29 (s, 12 H); ^{13}C-NMR (CDCl$_3$) δ 148.1, 138.4, 128.6, 128.0, 127.9, 118.9, 83.5, 24.8; MS (EI) °C (relative intensity) 230 (M$^+$, 49.1), 215 (26.2), 145 (42.6), 144 (79.0), 131 (58.6), 130 (97.5), 129 (100), 114 (48.9), 105 (53.9), 104 (23.7), 103 (24.0), 77 (23.5).

3g: ^{1}H-NMR (CDCl$_3$) δ 6.90 (d, 1 H), 6.43 (d, 1H), 1.29 (s, 12 H), 0.2 (s, 9 H); ^{13}C-NMR (CDCl$_3$) δ 158.0, 138.8, 83.3, 24.9, 0.2; MS (EI) °C (relative intensity) 212 (8.02), 211 (49.4), 210 (13.2), 169 (35.8), 141 (5.35), 129 (50.1), 128 (14.6), 127 (20.7), 113 (17.2), 112 (6.89), 111 (36.4), 110 (12.3), 85 (16.0), 84 (26.6), 83 (100), 75 (12.5), 73 (22.9), 69 (20.6), 67 (6.62), 59 (14.2), 58 (4.99), 57 (7.45), 55 (28.15), 53 (4.98).

3h: ^{1}H-NMR (CDCl$_3$) δ 6.08 (dd, 1 H), 5.23 (d, 1 H), 2.75 (m, 1 H), 1.29 (m, 2 H), 1.21 (s, 12 H), 0.91 (d, 3 H), 0.79 (t, 3 H); ^{13}C-NMR (CDCl$_3$) δ 160.7, 118.2, 82.7, 37.7, 30.0, 24.9, 20.9, 11.8; MS (EI) °C (relative intensity) 210 (M$^+$, 4.15), 195 (12.6), 181 (4.10), 166 (4.04), 154 (4.81), 153 (49.0), 152 (15.9), 137 (6.17), 125 (4.08), 124 (13.6), 123 (5.05), 111 (20.2), 110 (47.8), 109

(31.0), 101 (43.2), 95 (20.6), 85 (29.9), 84 (100), 83 (38.3), 82 (19.5), 81 (12.0), 69 (39.4), 68 (6.82), 67 (12.45), 59 (12.4), 57 (16.2), 55 (32.7), 53 (9.33), 52 (1.46).

3i: ^{1}H-NMR (CDCl$_3$) δ 6.27 (m, 1 H), 5.53 (d, 1 H), 5.40 (d, 1 H), 3.54 (m, 4 H), 1.21 (s, 12 H), 1.17 (t, 6 H). Integration indicates partial decomposition and therefore the reaction does not completely tolerate acetals. MS (EI) °C (relative intensity) 227 (11.0), 211 (38.8), 210 (9.28), 127 (20.1), 126 (23.2), 112 (8.18), 111 (35.1), 110 (12.4), 103 (34.5), 98 (24.0), 84 (14.3), 83 (100), 82 (16.3), 75 (24.4), 59 (7.89), 57 (9.25), 55 (19.0).

3j: ^{1}H-NMR (CDCl$_3$) δ 6.38 (m, 1 H), 5.29 (d, 1 H), 3.58 (t, 2 H), 2.39 (m, 2 H), 1.57 (m, 2 H), 1.25 (s, 12 H), 0.88 (s, 9 H), 0.01 (s, 6 H); ^{13}C-NMR (CDCl$_3$) δ 154.6, 119.1 , 82.8, 63.0, 32.8, 28.9, 26.0, 24.8, 18.4, −5.3; MS (EI) °C (relative intensity) 269 (2.99), 211 (6.21), 210 (1.83), 171 (4.83), 170 (13.8), 169 (100), 168 (26.7), 151 (11.6), 128 (5.13), 127 (37.9), 126 (1.76), 111 (3.06), 110 (1.94), 109 (10.2), 101 (7.26), 95 (3.74), 85 (3.12), 84 (1.74), 83 (7.84), 75 (25.9), 73 (18.8), 67 (8.45), 61 (7.12), 59 (9.27), 57 (5.35), 55 (5.75), 53 (1.17).

Supplementary Material Available: ^{1}H-NMR and ^{13}C-NMR of compounds **3a**−**j** (19 pages). This material is available in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.