Regio- and Stereospecific Preparation of β-(Alkylthio)alkenyl-1,3,2-benzodioxaboroles by Nickel-Catalyzed Hydroboration of Thioacetylenes with Catecholborane

Ilya D. Gridnev, Norio Miyaura,* and Akira Suzuki*

Department of Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060, Japan

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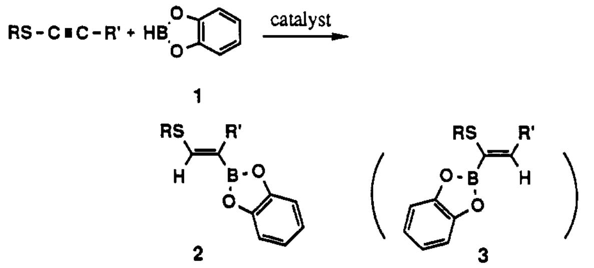
Summary: Hydroboration of 1-(alkylthio)-1-alkynes with catecholborane 1 in the presence of 3 mol % of $NiCl_2$(dppe) or $NiCl_2$(dppp) proceeds regio- and stereospecifically, giving excellent yields of [(E)-1-(alkylthio)-1-alken-2-yl]-1,3,2-benzodioxaboroles 2 under mild conditions.

Although the hydroboration of acetylenes has been intensively studied for years,[1] reports on this subject are still appearing.[1e] Conventional hydroboration methods do not provide access to functionalized vinylic boron compounds because hydroboration of disubstituted acetylenes is usually not regiospecific. Recently, it was found that catalytic hydroborations of alkenes and alkynes with catecholborane can proceed under very mild conditions with the use of Pd, Rh, or Ir catalysts.[2] It was also observed that catalysis can direct the course of the addition of borane to different regioselectivity than the uncatalyzed reaction.[3] In connection with our recent work on the synthetic application of vinylic boron compounds using palladium catalysts,[4] we have studied the synthesis of (thioalkenyl)boronates 2 via the catalytic hydroboration of thioacetylenes with catecholborane 1 (eq 1). Such (thioalkenyl)boronates have several advantages in terms of their practical use for boron cross-coupling reactions with organic halides, since vinylic sulfides are synthetically equivalent to carbonyls and can be stereospecifically converted to alkenes by nickel-catalyzed coupling reactions with Grignard reagents.[5]



(1)

Results and Discussion

Arase and his co-workers have recently shown that the hydroboration of thioacetylenes with several dialkylboranes gives high yields of vinylborane intermediates with strong preference for the addition of the boron atom at the carbon adjacent to the alkylthio group.[6] Although our preliminary results also indicate that such an addition of a boron atom occurs preferentially at the carbon α to sulfur, the regioselectivity of addition is highly dependent upon substituents on the thioacetylenes and dialkylboranes employed, and complete control of regioselectivity is generally difficult. However, we have found that the catalytic hydroboration of thioacetylenes with catecholborane in the presence of Ni, Pd, or Rh catalysts allows a complete reversal of the regiochemical preference. Representative results are summarized in Table I.

It is interesting to note that rhodium catalysts, which have been most commonly applied for the catalytic hydroboration of alkenes and alkynes,[2] result only in low regioselectivity for thioacetylenes (entries 4-9). Better results are obtained with palladium complexes (entries 1-3). In the presence of $Pd(PPh_3)_4$ (entry 1) or $PdCl_2$(dppf) (entry 3), the reactions give almost quantitative yields of 2 after overnight reaction. However, the best catalysts proved to be bidentate phosphine complexes of nickel such as $NiCl_2$(dppe) (entry 11) and $NiCl_2$(dppp) (entry 12) which give 2 quantitatively and regioselectively within 5 h at room temperature. It is reasonable to assume that the coordination number of the phosphine ligand controls both the yields and selectivities of the reactions because better results are always produced by using the bidentate ligands or four equiv of triphenylphosphine per nickel or palladium. In contrast, the uncatalyzed reaction at 80 °C for 5 h provides only a 1:1 mixture of 2 and 3 in less than 20% yield (entry 14).

The representative results of the hydroboration of thioacetylenes with catecholborane in the presence of 3 mol % of $NiCl_2$(dppe) are summarized in Table II.

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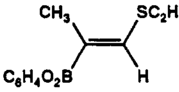
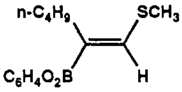
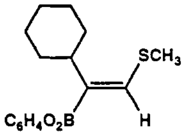
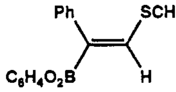
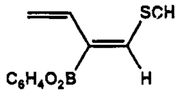
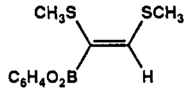
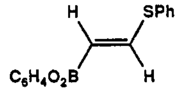
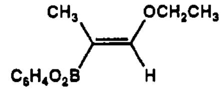
Table I. Effect of Catalysts on Hydroboration of 1-(Ethylthio)-1-propyne with Catecholborane (Eq 1)[a]

entry	catalyst	% yield[b]	ratio **2**:**3**
1	Pd(PPh$_3$)$_4$	54	98:2
2	PdCl$_2$(PPh$_3$)$_2$	29	66:34
3	PdCl$_2$(dppf)[c]	69	96:4
4	RhCl(PPh$_3$)$_3$	40	58:42
5	RhCp(PPh$_3$)$_2$	12	91:9
6	[RhCl(C$_2$H$_4$)$_2$]$_2$	23	90:10
7	[Rh(COD)(PPh$_3$)$_2$]$_2$PF$_6$[d]	45	74:26
8	HRh(CO)(PPh$_3$)$_2$	46	59:41
9	Rh$_4$(CO)$_{12}$	19	66:34
10	NiCl$_2$(PPh$_3$)$_2$	19	52:48
11	NiCl$_2$(dppe)[e]	100	>99:1
12	NiCl$_2$(dppp)[f]	97	98:2
13	NiCl$_2$(dppf)[c]	58	94:6
14	none[g]	20	50:50

[a] Reactions were conducted in benzene at room temperature for 5 h with 3 mol % of catalyst, catecholborane (1.1 mmol), and 1-(ethylthio)-1-propyne (1 mmol). [b] GLC yields. [c] 1,1′-Bis(diphenylphosphino)ferrocene. [d] COD is 1,5-cyclooctadiene. [e] 1,2-Bis(diphenylphosphino)ethane. [f] 1,4-Bis(diphenylphosphino)propane. [g] The reaction was carried out for 5 h at 80 °C.

Table II. Nickel-Catalyzed Hydroboration of Thioalkynes (Eq 1)[a]

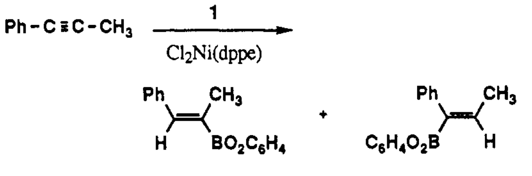
entry	alkyne	product **2**[b]	% yield[c]
1	$CH_3-\equiv-SC_2H_5$		99
2	$n\text{-}C_4H_9-\equiv-SCH_3$		93
3			92
4	$Ph-\equiv-SCH_3$		95
5			63
6	$CH_3S-\equiv-SCH_3$		78
7	$H-\equiv-SPh$		93[d]
8	$CH_3-\equiv-OCH_2CH_3$		98

[a] All reactions were carried out in benzene at room temperature for 5 h by using 3 mol % of NiCl$_2$(dppe), alkynes (1 equiv), and catecholborane (1.1 equiv), unless otherwise noted. [b] All products are catecholborane derivatives. [c] Isolated yields by distillation. [d] NiCl$_2$(dppp) (3 mol %) was used as a catalyst. A lower yield (ca. 30%) was obtained by NiCl$_2$(dppe) catalyst.

Hydroboration of all thioacetylenes studied (entries 1–7) provides the vinylboronates with the boryl group in the β position relative to the sulfur atom regioselectively. Even bulky substituents such as cyclohexyl do not change the regioselectivity, though uncatalyzed hydroboration of thioacetylenes is likely to be more sensitive to steric hindrance than to electronic effects.[6] We reported previously that palladium-catalyzed hydroboration of 2-methyl-1-buten-3-yne produces the allenic boronate[2e] via 1,4-addition of borane; whereas, the conjugated thio enyne yields the corresponding dienylboronate as a sole product (entry 5). On the other hand, the same reaction catalyzed by NiCl$_2$(dppe) is significantly less effective for (phenylthio)ethyne, resulting in only 30% of the product under similar conditions. Hydroboration of such terminal thioacetylenes can be well catalyzed by nickel(II) chloride with the 1,3-bis(diphenylphosphino)phosphine (dppp) ligand (entry 7).

Uncatalyzed hydroboration of oxyacetylenes[7] gives vinylboronates with the boron atom located at the β position relative to the oxygen, which is opposite to that of the uncatalyzed hydroboration[6] of thioacetylenes. This difference can be best explained by the opposite electrostatic charge distribution in oxy- and thioacetylenes.[8] However, the present Ni-catalyzed reaction strongly prefers the addition of boron at the β-carbon both in oxy- and thioacetylenes (entry 8).

To examine the scope of palladium- or nickel-catalyzed hydroboration of acetylenes, we have studied the catalytic hydroboration of 1-octyne and 1-phenyl-1-propyne. The Rh(PPh$_3$)$_3$Cl-catalyzed hydroboration of 1-octyne with catecholborane at room temperature for 2 h gives a 16:84 mixture of octenylboronate favoring the terminal boron compound. In contrast, the same reaction catalyzed by Pd(PPh$_3$)$_4$ is significantly more selective, resulting in a regioselectivity of 4:96 which is better than that of the uncatalyzed reaction (7:93). Although the NiCl$_2$(dppe)-catalyzed reaction of 1-phenyl-1-propyne leads to a regioselectivity similar to that of the uncatalyzed reaction (eq 2), the catalytic effect of nickel is very distinct: catecholborane in the absence of catalyst yields 86% of a mixture of **7** and **8** in a ratio of 73:27 after 4 h at 70 °C. Thus, the present procedure affords a general route to the vinylic boronates by hydroboration of alkynes with catecholborane. However, these nickel and palladium catalysts are less effective than rhodium catalysts for the hydroboration of alkenes.



7 66% **8** 32% (2)

The extremely high efficiency of nickel complexes having bidentate ligands over that of the monodentate complexes is unlikely to correspond to the substitution of a strongly chelated diphosphine ligand with alkynes which is generally speculated to be the coordination step in the mechanism of hydrosilylation[9] and hydroboration[2a,g] of

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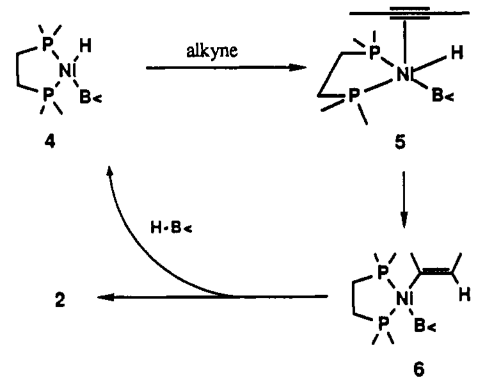
Scheme I. Proposed Mechanism for Catalytic Hydroboration



alkenes catalyzed by monophosphine transition-metal complexes. Most probably, the coordination and insertion of alkyne may proceed through a saturated five-coordinated Ni(II) complex **5** without elimination of a phosphine ligand, as shown in Scheme I. Such a five-coordinated intermediate can be best stabilized by electron-rich nickel rather than palladium or rhodium.[10]

A complete opposite addition of tin at the α position relative to the sulfur was reported in the related palladium-catalyzed hydrostannylation of thioacetylenes.[11] The mechanisms of both reactions remain to be established, but quite different mechanisms such as alkyne insertion into palladium–tin rather than palladium–hydride bonds[12] or radical addition[13] of stannanes to alkynes induced by a palladium(0) complex are often proposed to account for the unusual regioselectivity of the catalytic hydrostannylation.

In conclusion, we have shown the first example of a Ni- or Pd-catalyzed hydroboration reaction and the practical use of catalyzed hydroboration for alkynes. The reaction of thioacetylenes with catecholborane in the presence of catalytic amounts of $NiCl_2$(dppe) proceeds regio- and stereospecifically, giving excellent yields of (β-thioalkyl)vinylboronates. The reaction is synthetically complementary to the catalytic hydrostannylation of thioacetylenes providing (α-thioalkyl)vinylstannanes.[11] The synthetic applications of the (β-thioalkyl)vinylboranes thus obtained are being actively investigated.

Experimental Section

All the reactions were run under an atmosphere of nitrogen. Thioacetylenes were prepared from corresponding sodium acetylenides and methyl thiocyanate.[14] Bidentate phosphine nickel complexes were obtained according to the known procedures.[15]

^{1}H NMR and ^{13}C NMR spectra were measured on a JEOL XL-400 spectrometer (400 MHz) using TMS as an internal standard. GLC analysis was performed on a Hitachi 263 instrument using 10% silicon OV-17 on Uniport B. GLC yields were determined by using pentadecane as an internal standard. High-resolution electron-impact mass-spectra were taken by a JEOL JMS HX-100 spectrometer with 10000 resolution. Specimens for analysis were prepared by distillation with Kugelrohr (Shibata GTO-250R).

Hydroboration of Thioacetylenes. Typical Procedure. The general procedure for the hydroboration of thioacetylenes is illustrated by the hydroboration of 1-(methylthio)-1-hexyne. A dry 50-mL flask equipped with a septum inlet, reflux condenser, and magnetic stirring bar was flushed with nitrogen and charged with 48 mg (0.09 mmol) of $NiCl_2$(dppe), 10 mL of dry benzene, 0.36 mL (3.3 mmol) of freshly distilled catecholborane (1,3,2-benzodioxaborole), and 0.42 mL (3 mmol) of 1-(methylthio)-1-hexyne. The reaction mixture was stirred at room temperature overnight, and then 0.3 mL of MeOH[16] was added to decompose the excess of catecholborane. Solvent was removed in vacuo and the residue was distilled by Shibata GTO-250R Kugelrohr to give 0.69 g (93%) of [(*Z*)-1-(methylthio)-1-hexen-2-yl]-1,3,2-benzodioxaborole, bp 150 °C (0.02 mmHg) (oven temperature of (Kugelrohr): ^{1}H NMR ($CDCl_3$) δ 0.94 (t, 3 H, CH_3), 1.40 (m, 2 H, CH_2), 1.52 (m, 2 H, CH_2), 2.38 (t, 2 H, CH_2), 2.43 (s, 3 H, CH_3), 7.05 and 7.18 (AA′BB′ system, 4 H, C_6H_4), 7.33 (s, 1 H, CH=); ^{13}C NMR ($CDCl_3$) δ 14.03 (CH_3), 17.14 (CH_3S), 22.82, 30.40, 30.79 (3 CH_2), 112.20, 122.42, 148.45 (C_6H_4), 148.24 (=CH—S); exact mass calcd for $C_{13}H_{17}O_2BS$ 248.1042, found, 248.1069.

[(*Z*)-1-(Ethylthio)-1-propen-2-yl]-1,3,2-benzodioxaborole: bp 150 °C (0.04 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.39 (t, 3 H, CH_3), 1.94 (d, 3 H, CH_3, J = 1.3 Hz), 2.87 (q, 2 H, CH_2), 7.05 and 7.20 (m, 4 H, C_6H_4), 7.40 (q, 1 H, CH=, J = 1.3 Hz); ^{13}C NMR ($CDCl_3$) δ 15.36 (CH_3), 15.88 (CH_3), 28.07 (CH_2S), 112.20, 122.44, 148.46 (C_6H_4), 146.74 (=CH—S); exact mass calcd for $C_{11}H_{13}O_2BS$ 220.0730, found 220.0718. Anal. Calcd for $C_{11}H_{13}O_2BS$: C, 60.03; H, 5.95. Found: C, 59.95; H, 5.77.

[(*Z*)-1-Cyclohexyl-2-(methylthio)ethenyl]-1,3,2-benzodioxaborole: bp 165 °C (0.05 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.34 (m, 4 H, C_6H_{11}), 1.68 (m, 7 H, C_6H_{11}), 2.44 (s, 3 H, CH_3), 7.05 and 7.20 (AA′BB′ system, 4 H, C_6H_4), 7.27 (s, 1 H, CH=); ^{13}C NMR ($CDCl_3$) δ 17.32 (CH_3S), 26.04, 26.76, 31.29 (5 CH_2), 41.92 (CH), 112.18, 122.38, 148.28 (C_6H_4), 147.26 (=CH—S); exact mass calcd for $C_{15}H_{19}O_2BS$ 274.1199, found 274.1182. Anal. Calcd for $C_{15}H_{19}O_2BS$: C, 65.72; H, 6.99. Found: C, 65.54; H, 7.06.

[(*Z*)-1-(Methylthio)-1,3-butadien-2-yl]-1,3,2-benzodioxaborole: bp 135 °C (0.03 mmHg); ^{1}H NMR ($CDCl_3$) δ 2.46 (s, 3 H, CH_3), 5.37 (ddd, 1 H, J = 1.9, 1.9, and 11.2 Hz), 5.94 (dd, 1 H, J = 1.9 and 17.1 Hz), 6.67 (dd, 1 H, J = 11.2 and 17.1 Hz), 7.06 (m, 2 H, C_6H_4), 7.21 (m, 2 H, C_6H_4), 7.41 (s, 1 H, CH=); ^{13}C NMR ($CDCl_3$) 17.78 (CH_3S), 112.27 (C_6H_4), 118.07 (=CH_2), 122.55 (C_6H_4), 132.94 (=CH), 148.10 (C_6H_4), 150.22 (=CHS); exact mass calcd for $C_{11}H_{11}O_2BS$ 218.0573, found 218.0597.

[(*Z*)-1-Phenyl-2-(methylthio)ethenyl]-1,3,2-benzodioxaborole: bp 185 °C (0.05 mmHg); ^{1}H NMR ($CDCl_3$) δ 2.37 (s, 3 H, CH_3), 7.09 and 7.27 (AA′BB′ system, 4 H, C_6H_4), 7.18 (m, 5 H, C_6H_5), 7.34 (s, 1 H, CH=); ^{13}C NMR ($CDCl_3$) δ 18.81 (CH_3S), 112.49, 122.88, 148.24 (C_6H_4), 122.81, 127.23, 128.44, 133.94 (C_6H_5), 147.55 (=CH—S); exact mass calcd for $C_{15}H_{13}O_2BS$ 268.0730, found 268.0728.

[(*E*)-2-(Phenylthio)ethenyl]-1,3,2-benzodioxaborole: bp 160 °C (0.03 mmHg); ^{1}H NMR ($CDCl_3$) δ 5.73 (d, 1 H, CH=, J = 17.6 Hz), 7.01 and 7.13 (AA′BB′ system, 4 H, C_6H_4), 7.33 and 7.47 (m, 5 H, C_6H_5), 7.75 (d, 1 H, CH=, J = 17.6 Hz); ^{13}C NMR ($CDCl_3$) δ 110.90 (broad s, =CH—B), 112.18, 122.49, 148.12 (C_6H_4), 128.60, 129.43, 131.44, 132.75 (C_6H_5), 151.88 (=CH—S); exact mass calcd for $C_{14}H_{11}O_2BS$ 254.0553, found 254.0548.

[(*Z*)-1,2-Bis(methylthio)ethenyl]-1,3,2-benzodioxaborole: bp 170 °C (0.05 mmHg); ^{1}H NMR ($CDCl_3$) δ 2.49 (s, 6 H, 2CH_3), 7.06 and 7.21 (AA′BB′ system, 4 H, C_6H_4), 7.66 (s, 1 H, CH=); ^{13}C NMR ($CDCl_3$) δ 16.95, 17.47 (2 CH_3S), 112.34, 122.68, 148.10 (C_6H_4), 153.20 (=CH—S); exact mass calcd for $C_{11}H_{11}O_2BS_2$ 238.0296, found 238.0322.

[(*Z*)-2-Ethoxy-1-propen-2-yl]-1,3,2-benzodioxaborole: bp 140 °C (0.03 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.33 (t, 3 H, CH_3), 1.79

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[15] Van Hecke, G. R.; Horrocks, W. W. *Inorg. Chem.* **1966**, *5*, 1968–1974.

[16] Isolation of **2** should be carried out without delay because the treatment with methanol often causes the protodeboronation to give the corresponding vinylic sulfide.

(d, 3 H, CH_3, J = 1.3 Hz), 4.02 (q, 2 H, CH_2), 6.9–7.3 (m, 5 H, C_6H_4 and CH=); exact mass calcd for $C_{11}H_{13}O_3B$ 204.0958, found 204.0930. The compound was directly compared with an authentic sample[17] we prepared previously.

All these compounds are rather sensitive to air and moisture. For oils or low melting solids, correct elemental analyses could not be obtained; however, spectroscopically pure compounds can be readily obtained by repeated Kugelrohr distillation.

Supplementary Material Available: Figures of ^1H NMR (400 MHz) spectra of β-(alkylthio)alkenyl-1,3,2-benzodioxaboroles in Table II (7 pages). Ordering information is given on any current masthead page.

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[17] Satoh, M.; Miyaura, N.; Suzuki, A. *Synthesis* 1987, 373–377.

Additions and Corrections

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Raymond N. Vrtis, Simon G. Bott, and Stephen J. Lippard*: Linear CO-Bridged Dinuclear Tantalum Siloxycarbyne Complexes.

Page 270. The unit cell parameters for [$(dmpe)_2(CO)TaCOZrCp^*{}_2Cl$] (4) should be changed to a = 9.687 (2) Å, b = 12.288 (2) Å, c = 17.851 (2) Å, α = 80.46 (1)°, β = 89.33 (1)°, γ = 78.46 (1)°, and V = 2053 (1) Å^3. This cell was used for solving and refining the structure, whereas the one reported is an equivalent, more conventional choice. Bond distances, angles, positional parameters, and discussion contained within the paper are unaffected by this substitution. In Table V, the phosphorus atoms numbered as P(1), P(2), P(3), and P(4) should be changed to P(3), P(4), P(2), and P(1), respectively.

Supplementary Material Available: Tables of anisotropic thermal parameters for the non-hydrogen atoms and positional and isotropic thermal parameters for the hydrogen atoms of 4 (6 pages); a table of observed and calculated structure factors (40 pages). Ordering information is given on any current masthead page.