SYNTHESES WITH ORGANOBORANES. X. MONOHYDROBORATION OF CONJUGATED ENYNES WITH CATECHOLBORANE CATALYZED BY NICKEL(II) CHLORIDE COMPLEXES WITH DIPHOSPHINES

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Dedicated to Dr Stanislav Heřmánek on the occasion of his 70th birthday.

The monohydroboration of representative conjugated enynes – but-1-en-3-yne (**1**), 2-methylbut-1-en-3-yne (**2**), pent-3-en-1-yne (**3**), hex-1-en-3-yne (**4**), 2-methyl-4-phenylbut-1-en-3-yne (**5**), 4-methyl-1-phenylpent-3-en-1-yne (**6**) and 1-ethynylcyclohex-1-ene (**7**), with catecholborane in the presence of the nickel(II) chloride complex with 1,2-bis(diphenylphosphino)ethane gave the corresponding 1,3-dien-1-yl organoboranes in 54–87% yield. High regioselectivity of the addition leading to the boron atom at the 4-position of the 1-en-3-yne system was observed for **1**, **2**, **3**, **6** and **7**.

Key words: Catalytic hydroboration; 1,3-Dien-1-yl organoboranes; 1-En-3-ynes; Catecholborane; Boronates; Alkynes; Nickel.

Catalytic hydroboration is a new methodology complementary to the uncatalyzed reaction[2]. These processes often show different reactivities, regio- and stereoselectivities. Catecholborane in the presence of rhodium, iridium, ruthenium and palladium complexes is the reagent most often used, although other substituted boranes have also been applied[3]. Considering the costs, catalysts derived from other transition metals are highly desirable. Recently, we discovered the catalytic activity of nickel(II) chloride and cobalt(II) chloride complexes with 1,2-bis(diphenylphosphino)ethane (dppe) and 1,3-bis(diphenylphosphino)propane (dppp) in the monohydroboration of conjugated dienes[4]. Extending our studies to other conjugated systems, we turned to the catalyzed hydroboration of conjugated enynes as a potential route to 1,3-dien-1-yl organoboranes. Hayashi and coworkers[5] described the reaction of 2-substituted but-1-en-3-ynes with catecholborane in the presence of palladium(0) complexes with monodentate and bidentate phosphine ligands – triphenylphosphine, dppe, dppb and dppf.

The formation of 1,2- and 1,4-addition products, depending on the ligand structure and the molar ratio of palladium to ligand, was observed. Here, the monohydroboration of representative conjugated enynes – but-1-en-3-yne (**1**), 2-methylbut-1-en-3-yne (**2**), pent-3-en-1-yne (**3**), hex-1-en-3-yne (**4**), 2-methyl-4-phenylbut-1-en-3-yne (**5**), 4-methyl-1-phenylpent-3-en-1-yne (**6**) and 1-ethynylcyclohex-1-ene (**7**), with catecholborane in the presence of nickel(II) chloride complex with dppe is described.

EXPERIMENTAL

^{1}H, ^{13}C and ^{11}B NMR spectra were recorded on Varian Gemini 200 and Varian Inova 500 spectrometers. High resolution mass spectra were recorded on a AMD 604 instrument. All glassware was dried for several hours in an oven at 120 °C, assembled hot and cooled in an argon atmosphere. Catecholborane was prepared according to the literature procedure[6], stirred with a small amount of hex-1-ene for 3 h, and distilled. The enynes **1**–**7** (ref.[7]), $NiCl_2(PPh_3)_2$ (ref.[8]), $NiCl_2$(dppe) (ref.[9]), $NiCl_2$(dppp) (ref.[8]), $CoCl_2$(dppe) (ref.[9]) and $CoCl_2$(dppp) (ref.[10]), were prepared according to the literature. The enyne **3** was an *E/Z* mixture 43 : 57. $NiCl_2(PPh_3)_2$ was also obtained from a commercial source (Aldrich). Tetrahydrofuran was distilled from sodium benzophenone ketyl prior to use. Melting points are uncorrected.

(*E*)-2-(3-Methylbuta-1,3-dien-1-yl)benzo[1,3,2]dioxaborole (**2a**). General Procedure for the Monohydroboration of 1,3-Enynes

Catecholborane (3.00 g, 25 mmol) was added to a mixture of $NiCl_2$(dppe) (0.132 g, 0.25 mmol), 2-methylbut-1-en-3-yne (2.00 g, 30 mmol) and tetrahydrofuran (20 ml) at room temperature under argon atmosphere. The mixture was stirred at room temperature and monitored by ^{11}B NMR analysis. After 8 h the catecholborane signal at δ 28.0 ppm disappeared. The solvent was removed and **2a** was isolated by distillation, 2.75 g (59%), b.p. 91–93 °C/0.2 mm Hg. ^{1}H NMR ($CDCl_3$): 1.95 s, 3 H (CH_3); 5.35 s, 2 H (H-4); 5.90 d, 1 H, *J*(1,2) = 18.2 (H-1); 7.11 m, 2 H (H-Ar); 7.25 m, 2 H (H-Ar); 7.49 d, 1 H, *J*(1,2) = 18.2 (H-2). ^{13}C NMR ($CDCl_3$): 17.58 q, 112.36 d, 121.82 t, 122.62 d, 142.92 s, 148.39 s, 154.73 d. HR MS, for $C_{11}H_{11}O_2{}^{11}B$ calculated: 186.08521; found: 186.08670. For $C_{11}H_{11}O_2B$ (186.0) calculated: 71.03% C, 5.96% H; found: 70.83% C, 5.87% H.

(E)-2-(Buta-1,3-dien-1-yl)benzo[1,3,2]dioxaborole (**1a**). ^{1}H NMR ($CDCl_3$): 5.42 d, 1 H, *J*(3,4a) = 10.2 (H-4a); 5.54 d, 1 H, *J*(3,4b) = 17.6 (H-4b); 5.92 d, *J*(1,2) = 17.6 (H-1); 6.55 dt, *J*(3,4a) = 10.2, *J*(3,4b) = 17.6 (H-3); 7.11 m, 2 H (H-Ar); 7.25 m, 2 H (H-Ar); 7.37 dd, 1 H *J*(2,3) = 10.3, *J*(1,2) = 17.8 (H-2). ^{13}C NMR ($CDCl_3$): 112.39 d, 122.69 d, 122.76 t, 138.58 d, 148.40 s, 152.53 d.

(1E,3E/Z)-2-(Penta-1,3-dien-1-yl)benzo[1,3,2]dioxaborole (**3a**/**3b**) *isolated as an E/Z mixture 43 : 57*. HR MS, for $C_{11}H_{11}O_2{}^{11}B$ calculated: 186.08521; found: 186.08613. For $C_{11}H_{11}O_2B$ (186.0) calculated: 71.03% C, 5.96% H; found: 70.73 % C, 5.83% H.

(1*E*,3*E*)-isomer **3a**: ^{1}H NMR (500 MHz, $CDCl_3$): 1.88 d, 3 H, *J*(4,5) = 7.0 (H-5); 5.77 d, 1 H, *J*(1,2) = 17.5 (H-1); 6.09 dq, 1 H, *J*(3,4) = 16.2, *J*(4,5) = 7.0 (H-4); 6.24–6.33 m, 1 H (H-3); 7.10 m, 2 H (H-Ar); 7.25 m, 2 H (H-Ar); 7.37 dd, 1 H, *J*(1,2) = 17.5, *J*(2,3) = 10.5 (H-2).

^{13}C NMR ($CDCl_3$), a mixture of **3a** and **3b**: 13.37 q, 17.82 q, 111.82 d, 111.87 d, 122.08 d, 122.15 d, 130.93 d, 132.16 d, 133.31 d, 135.76 d, 146.36 d, 147.97 s, 152.21 d.

(1*E*,3*E*)-isomer **3b**: ^{1}H NMR ($CDCl_3$): 1.95 d, 3 H, *J*(4,5) = 7.4 (H-5); 5.85 dq, 1 H, *J*(3,4) = 10.5, *J*(4,5) = 7.4 (H-4); 5.89 d, 1 H, *J*(1,2) = 18.0 (H-1); 6.24–6.33 m, 1 H (H-3); 7.10 m, 2 H (H-Ar); 7.25 m, 2 H (H-Ar); 7.76 dd, 1 H, *J*(1,2) = 17.5, *J*(2,3) = 10.5 (H-2).

(Z)-2-(Hexa-1,3-dien-4-yl)benzo[1,3,2]dioxaborole (**4a**) *and (Z)-2-(Hexa-1,3-dien-3-yl)benzo-[1,3,2]dioxaborole* (**4b**) *isolated as a* **4a**/**4b** *mixture 66 : 34*. For $C_{12}H_{13}O_2B$ (200.0) calculated: 72.05% C, 6.55% H; found: 72.32% C, 6.79% H.

Compound **4a**: ^{1}H NMR (500 MHz, $CDCl_3$): 1.19 t, 3 H *J*(5,6) = 7.6 (H-6); 2.56 q, 2 H, *J*(5,6) = 7.6 (H-5); 5.45 d 1 H, *J*(1a,2) = 10.0 (H-1a); 5.57 d, 1 H, *J*(1b,2) = 16.7 (H-1b); 6.82–6.94 m, 1 H (H-2); 7.12 m, 2 H (H-Ar); 7.21 d, 1 H, *J*(3,4) = 11.3 (H-3); 7.28 m, 2 H (H-Ar). ^{13}C NMR ($CDCl_3$): 14.94 q, 21.94 t, 112.37 d, 122.21 t, 122.60 d, 132.29 d, 144.67 d, 148.60 s.

Compound **4b**: ^{1}H NMR (500 MHz, $CDCl_3$): 1.17 t, 3 H, *J*(5,6) = 7.5 (H-6); 2.46 quintet, 2 H, *J*(5,6) = 7.6 (H-5); 5.40 d, 1 H, *J*(1a,2) = 11 (H-1a); 6.00 d, 1 H, *J*(1b,2) = 18.0 (H-1b); 6.82–6.94 m, 2 H (H-2, H-4); 7.12 m, 2 H (H-Ar); 7.28 m, 2 H (H-Ar). ^{13}C NMR ($CDCl_3$): 13.36 q, 22. 39 t, 112.37 d, 118.23 t, 122.60 d, 132.76 d, 148.60 s, 153.13 d.

(Z)-2-(4-Methyl-1-phenylpenta-1,3-dien-1-yl)benzo[1,3,2] dioxaborole (**6a**). ^{1}H NMR ($CDCl_3$): 1.95 s, 3 H (CH_3); 2.17 s, 3 H (CH_3); 6.43 d, 1 H, *J*(2,3) = 11.4 (H-3); 7.16–7.21 m, 2 H (H-Ar) 7.35–7.39 m, 2 H (H-Ar); 7.56–7.60 m, 5H (H-Ar) 7.93 d, 1 H, *J*(2,3) = 11.4 (H-2). ^{13}C NMR ($CDCl_3$): 18.85 q, 26.67 q, 112.43 d, 122.59 d, 123.05 d, 126.67d, 128.23 d, 129.64 d, 139.39 s, 142.42 d, 144.03 s, 148.77 s.

(E)-2-[2-(Cyclohex-1-en-1-yl)ethenyl]benzo[1,3,2]dioxaborole (**7a**). ^{1}H NMR ($CDCl_3$): 1.64–1.74 m, 4 H (CH_2); 2.22–2.27 m, 4 H (CH_2); 5.75 d, 1 H, *J*(1,20) = 18.4 (H-1); 6.12 m, 1 H (H-4); 7.07 m, 2 H (H-Ar); 7.23 m, 2 H (H-Ar); 7.40 d, 1 H, *J*(1,2) = 18.4 (H-2). ^{13}C NMR ($CDCl_3$): 22.12 t, 22.17 t, 23.66 t, 26.18 t, 112.15 d, 122.38 d, 136.20 d, 137.18 s, 148.40 s, 155.67 d. For $C_{14}H_{15}O_2B$ (226.1) calculated: 74.38% C, 6.69% H; found: 74.50%C, 6.62% H.

1-Methyl-4-oxo-2-*exo*-phenyl-3-oxabicyclo[3.3.1]non-7-ene-6-*endo*-carboxylic acid (**8**)

A solution of **2a** (2.98 g, 16 mmol) and maleic anhydride (1.57 g, 16 mmol) in toluene (20 ml) was kept at 80 °C for 3 h. After cooling to 0 °C, freshly distilled benzaldehyde (1.70 g, 16 mmol) was added. The mixture, which solidified, was allowed to reach room temperature and then it was warmed to 80 °C. Water (1.5 ml) was added and the mixture was kept at 80 °C for 0.5 h. Toluene was removed under vacuum, the solid was washed with diethyl ether (20 ml) and crystallized from acetonitrile (25 ml) to give **8**, 3.12 g (71%), m.p. 240–242 °C (ref.[11] gives m.p. 242–243 °C).

RESULTS AND DISCUSSION

Nickel(II) chloride and cobalt(II) chloride complexes with triphenylphosphine, dppe and dppp were used as catalysts. The stability of 1 M catecholborane solution in tetrahydrofuran in the presence of 1 mole % of these complexes was monitored by ^{11}B NMR. For all the complexes, the catecholborane signal at δ 28.0 ppm remained the major signal after 24 h at room temperature. No signal at δ 1.0 ppm corresponding to borane–tetrahydrofuran,

a possible disproportionation product, was observed. A signal at δ 18.8 ppm integrating for 10–12% of the total area of the signals was present after 6 h and was not further increasing at a longer time. Its chemical shift corresponds to a borate ester. The hydroboration of 2-methylbut-1-en-3-yne (**2**) with catecholborane in the presence of the complexes shown in Table I was monitored by ^{11}B NMR.

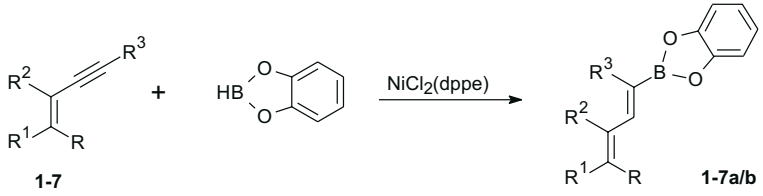
As follows from the data presented in Table I, only two types of products were formed. In addition to a signal at δ 31–32 ppm corresponding to the hydroboration product, a signal at δ 18–20 ppm corresponding to a borate ester was observed. Nickel(II) chloride in the presence of various amounts of triphenylphosphine showed low activity. Similarly, the commercial

TABLE I
Hydroboration products of 2-methylbut-1-en-3-yne with catecholborane (molar ratio 1 : 1) in the presence of $NiCl_2$ or $CoCl_2$ complexes with phosphines at room temperature in tetrahydrofuran

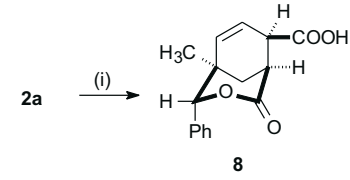
Catalyst[a]	Time h	^{11}B NMR δ, ppm (content, %)[b]		
		unreacted catecholborane	hydroboration product	other products
$NiCl_2/PPh_3$ 1 : 1	10	26.60 (56.0)	32.09 (27.1)	20.15 (16.9)
$NiCl_2/PPh_3$ 1 : 2	10	26.35 (52.5)	31.96 (27.1)	19.82 (20.4)
$NiCl_2/PPh_3$ 1 : 4	10	25.46 (49.5)	30.92 (23.9)	19.06 (26.6)
$NiCl_2(PPh_3)_2$	8	26.25 (52.6)	31.94 (21.6)	19.63 (25.8)
$NiCl_2$(dppe)	8		31.81 (88.2)	18.59 (11.8)
$NiCl_2$(dppp)	8		31.16 (84.8)	18.15 (15.2)
$CoCl_2$(dppe)	8	26.19 (77.3)	30.65 (15.2)	19.52 (7.5)
$CoCl_2$(dppp)	8	26.31 (43.5)	31.87 (34.5)	19.63 (22.0)

[a] 1 mole %; [b] calculated from the signal area.

$NiCl_2(PPh_3)_2$ complex was of low activity. In the presence of these compounds, only 24–27% of the hydroboration product was formed after 24 h. In contrast, the hydroboration reaction in the presence of nickel(II) chloride complexes with dppe or dppp was complete in 8 h, the ^{11}B NMR spectrum indicating 88.2 or 84.8% of the hydroboration products, respectively. The activity of the corresponding cobalt(II) chloride complexes was much lower. Consequently, the most active $NiCl_2$(dppe) was selected for further experiments. Thus, the hydroboration of representative acyclic and cyclic conjugated enynes **1**–**7** at the molar ratio 1 : 1, in the presence of 1 mole % $NiCl_2$(dppe), was carried out at room temperature in tetrahydrofuran (Scheme 1), monitoring the reaction by ^{11}B NMR. The organoborane products were isolated by distillation and analyzed by ^1H and ^{13}C NMR. The results are presented in Table II.



	R	R^1	R^2	R^3
1	H	H	H	H
2	H	H	CH_3	H
3	CH_3,H		H	H
4	H	H	H	CH_2CH_3
5	H	H	CH_3	Ph
6	CH_3	CH_3	H	Ph
7	H	-$(CH_2)_4$-		H



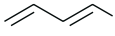
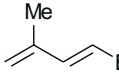
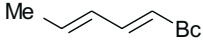
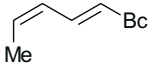
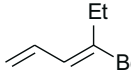
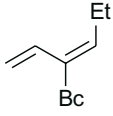
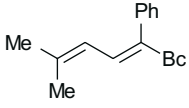
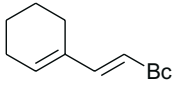
(i) 1. maleic acid anhydride, 2. benzaldehyde

SCHEME 1

The monohydroboration of but-1-en-3-yne (**1**) was complete in 10 h. The product readily isolated by distillation is of limited stability becoming a glassy solid in a few hours at room temperature. A moderate 53% yield is most probably due to partial oligomerization of the product during distillation. The ^1H and ^{13}C NMR spectra of the freshly distilled product indicate (*E*)-2-(buta-1,3-dien-1-yl)benzo[1,3,2]dioxaborole (**1a**). It is interesting to note that the reactivity of **1a** in the Diels–Alder reaction with tetracyanoethylene was lower compared with buta-1,3-diene. The diene reacted

TABLE II

Hydroboration products of conjugated 1-en-3-ynes with catecholborane (molar ratio 1 : 1) in the presence of $NiCl_2$(dppe) at room temperature in tetrahydrofuran

Enyne	Time h	Hydroboration products					
		structure[a]		content[b,c] %	b.p. °C/mmHg	^{11}B NMR δ, ppm	yield[d] %
1	10		(**1a**)	>95	78–80/1.0	33.26	54
2	8		(**2a**)	>95	91–93/0.2	31.49	59
3[e]	8		(**3a**)	43	88–90/0.1	33.96	79
			(**3b**)	57			
4	8		(**4a**)	66	81–82/0.02	31.31	78
			(**4b**)	34			
5	24			*f*			
6	24		(**6a**)	>95	*g*	31.49	
7	8		(**7a**)	>95	136–138/0.07	31.79	87

a Bc =  ; *b* by ^{1}H NMR; *c* in $CDCl_3$; *d* isolated; *e* the starting enyne **3** was an *E/Z* mixture 43 : 57; *f* not isolated, only 30% of catecholborane reacted; *g* not distilled.

in 1 h at room temperature in tetrahydrofuran as reported earlier[12], whereas no reaction with **1a** under the same conditions was observed by ^{11}B NMR.

The monohydroboration of 2-methylbut-1-en-3-yne (**2**) was complete in 8 h. The product **2a** formed with high regioselectivity was isolated by distillation in 59.1% yield. It was more stable compared to **1a** and readily reacted with maleic anhydride to give the corresponding Diels–Alder adduct, further transformed into the addition product **8** on reaction with benzaldehyde[11]. In contrast to the palladium catalyzed hydroboration of 2-substituted 1-en-3-ynes leading to 1,2- and 1,4-addition products depending on the reaction conditions, no 1,4-addition was observed in the presence of nickel(II) chloride complexes used in this study. Similarly, the enynes **3** and **7** having a terminal triple bond were hydroborated with high regioselectivity to place the boron atom at the terminal position. Clearly, the substitution pattern of the double bond has no effect on the course of addition to the terminal triple bond in **1**–**3** and **7**.

The enyne **4** reacted in 8 h to give a mixture of **4a** and **4b** in 78.4% yield. In contrast to the palladium-catalyzed hydroboration[5], alkyl substitution at the 4-position of the enyne system does not inhibit the addition. However, the phenyl substituent at the 4-position has a rate-retarding effect. Both phenyl substituted enynes **5** and **6** reacted much slower compared with the alkyl substituted **4**. The reaction with **5** was very sluggish and after 24 h only 30% of catecholborane was consumed. The enyne **6** reacted completely in the same time indicating that the substitution pattern of the double bond influences the reactivity of the phenyl substituted triple bond. The addition to **6** is regioselective affording **6a** with the boron atom placed at the phenyl substituted carbon atom.

In conclusion, the monohydroboration of conjugated 1-en-3-ynes **1**–**4**, **6** and **7** with catecholborane, in the presence of nickel(II) chloride complex with dppe proceeds under mild conditions to give the corresponding 1,3-dien-1-yl organoboronates in 53–87% yields. Mild reaction conditions enable the synthesis of labile products, *e.g.*, the buta-1,3-dien-1-yl catecholborane derivative **1a**, not readily available by other methods. The 1,2-addition products were obtained exclusively, regardless of the substitution pattern of the enyne system. High regioselectivity of the addition to enynes with terminal triple bonds is observed, whereas for internal triple bonds, the direction of addition and reactivity depend, on the substituents of the enyne system.

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