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Supplementary Material Available: Tables of crystal data and details of intensity collection, positional parameters, anisotropic thermal parameters, least-squares planes, and bond lengths and angles and the molecular structure of [{Li(2,4,6-^{t}Bu$_3$C$_6$H$_2$)}{LiP(H)(2,4,6-^{t}Bu$_3$C$_6$H$_2$)}]$_2$ with complete atom labeling (11 pages). Ordering information is given on any current masthead page.

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Palladium(0)-Catalyzed Hydroboration of 1-Buten-3-ynes: Preparation of Allenylboranes

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Summary: Reaction of 2-substituted 1-buten-3-ynes (CH_2=CR—C≡CH) with catecholborane in the presence of a palladium catalyst bearing a monodentate phosphine ligand such as PPh_3 or $PPh_2(C_6F_5)$ proceeded in a 1,4-fashion to give (3-substituted 1,2-butadienyl)-1,3,2-benzodioxaboroles (CH_3(R)C=C=CH($BO_2C_6H_4$)). Reaction of the allenylboranes with benzaldehyde gave the corresponding homopropargyl alcohols.

Recently, much attention has been paid to catalytic hydroboration of unsaturated compounds for its great potential in organic synthesis.[1-4] We have previously reported the asymmetric hydroboration of styrenes[2] and 1,3-dienes[3] catalyzed by rhodium–phosphine complexes, which proceeds with unusual regioselectivity and with high enantioselectivity. Here we report the palladium-catalyzed hydroboration of 1,3-enynes giving allenylboranes selectively and the effects of phosphine ligands on the selectivity in this reaction.

Suzuki and co-workers have briefly described[4] the formation of an allenylborane in the reaction of 2-methyl-1-buten-3-yne (**1a**) with catecholborane in the presence of $Pd(PPh_3)_4$. We examined the palladium-catalyzed hydroboration of **1a** (Scheme I), focusing our attention on the selectivity forming the allenylborane. Table I summarizes the results obtained for the reaction in the presence of several phosphine–palladium catalysts. Reaction

Scheme I

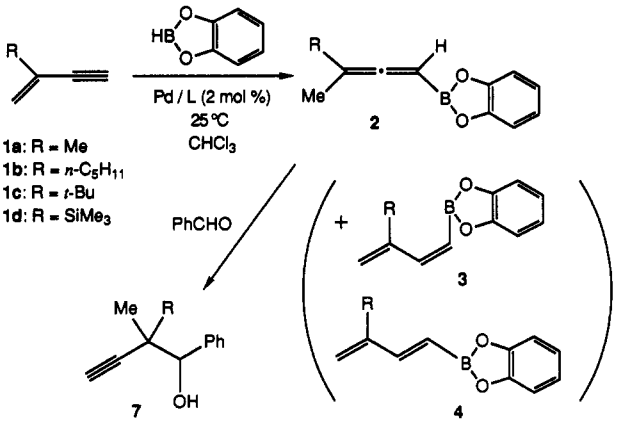

Table I. Hydroboration of 1-Buten-3-ynes 1 with Catecholborane Catalyzed by Palladium–Phosphine Complexes[a]

entry	substrate (R)	catalyst[b]	time (h)	yield[c] (%)	2/3/4[d]
1	**1a** (Me)	$Pd(PPh_3)_4$[e]	0.5	75	60/34/6
2	**1a** (Me)	[Pd]/5PPh_3	0.5	86	38/37/25
3	**1a** (Me)	[Pd]/4PPh_3	0.5	75	41/53/6
4	**1a** (Me)	[Pd]/2PPh_3	0.5	70	62/38/0
5	**1a** (Me)	[Pd]/1.5PPh_3	0.5	63	84/16/0
6	**1a** (Me)	[Pd]/1PPh_3	0.5	22	92/8/0
7	**1a** (Me)	[Pd]	5	0	
8	**1a** (Me)	[Pd]/dppe	2	39	0/0/100
9	**1a** (Me)	[Pd]/dppb	2	61	0/0/100
10	**1a** (Me)	[Pd]/dppf	0.5	89	0/0/100
11	**1a** (Me)	[Pd]/2$PPh_2(C_6F_5)$	0.5	73	83/17/0
12	**1b** (*n*-C_5H_{11})	[Pd]/2$PPh_2(C_6F_5)$	0.5	74	88/12/0
13	**1c** (*t*-Bu)	[Pd]/2$PPh_2(C_6F_5)$	2.5	89	83/4/13
14	**1d** ($SiMe_3$)	[Pd]/2$PPh_2(C_6F_5)$	0.5	46	*f*

[a] Carried out in chloroform at 25 °C with 1.2–1.5 equiv of catecholborane in the presence of 2 mol % of catalyst prepared from $Pd_2(dba)_3$·$CHCl_3$ and a phosphine ligand. [b] [Pd] = $^1/_2Pd_2(dba)_3$·$CHCl_3$. [c] Isolated yield by distillation. [d] Determined by ^{1}H NMR spectra. [e] 1 mol %. [f] The ratio was not determined.

of **1a** with 1.3 equiv of catecholborane in chloroform in the presence of 2 mol % of the palladium catalyst, generated in situ by mixing $Pd_2(dba)_3$·$CHCl_3$ and triphenylphosphine (5 equiv per Pd), was completed in 30 min at 25 °C. The products, which were isolated by bulb-to-bulb distillation in 86% yield, consisted of allenylborane **2a**, (*Z*)-dienylborane **3a**, and (*E*)-dienylborane **4a** in a ratio of 38:37:25 (entry 2). Allenylborane **2a** is the product formed by

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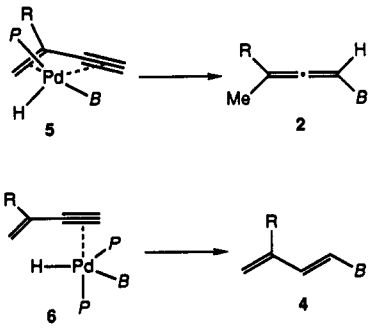
Scheme II



1,4-addition of catecholborane to 1,3-enyne **1a**, and dienylboranes **3a** and **4a** are those formed by 1,2-addition on the triple bond.

It was found that the product distribution in catalytic hydroboration of **1a** was dependent on the molar ratio of phosphine ligand to palladium as well as on the structure of phosphine ligand. Thus, the reaction of **1a** in the presence of 2 equiv of triphenylphosphine per palladium gave the hydroboration products in 70% yield, consisting of **2a**, **3a**, and **4a** in a ratio of 62:38:0 (entry 4), and that in the presence of 1 equiv of triphenylphosphine gave 22% yield of the products **2a** and **3a** in a ratio of 92:8 (entry 6). As the ratio of triphenylphosphine to palladium decreased, the total yield of the one-to-one hydroboration adducts, **2a**, **3a**, and **4a**, decreased while the selectivity forming **2a** increased (entries 2–6). No one-to-one adducts were produced in the absence of phosphine ligands (entry 7). The highest yield of allenylborane **2a** was obtained by the use of 1.5 equiv of triphenylphosphine per palladium (entry 5). The product distribution was also dependent on the phosphine ligands. Bidentate phosphine ligands, 1,2-bis(diphenylphosphino)ethane (dppe), 1,4-bis(diphenylphosphino)butane (dppb), and 1,1′-bis(diphenylphosphino)ferrocene (dppf), catalyzed the 1,2-addition to the triple bond in 1,3-enyne to give (*E*)-dienylborane **4a** exclusively (entries 8–10). The yield of the one-to-one adducts and the selectivity forming allenylborane **2a** were improved by the use of $PPh_2(C_6F_5)$. Allenylborane **2a** of 83% isomeric purity was isolated in 73% yield in the reaction with 2 equiv of $PPh_2(C_6F_5)$ per palladium (entry 11).

To summarize the results obtained above, 1,3-(*E*)-dienylborane **4** is formed in the presence of a chelating bis(phosphine) ligand or a large excess of monodentate phosphine ligand per palladium, while the use of a small amount (1–2 equiv per palladium) of a monodentate phosphine ligand gives allenylborane **2** preferentially. It is reasonable to propose that the coordination number of the phosphine ligand controls the selectivity forming allenylborane **2** or 1,3-(*E*)-dienylborane **4** (Scheme II). The key intermediate giving **2** is a palladium complex **5** bearing one molecule of a monodentate phosphine ligand and 1,3-enyne ligand in a bidentate coordination manner, which undergoes the 1,4-addition of the hydroborane.[5] The intermediate **6**, which is coordinated with two phosphorus atoms and can provide only one coordination site for the enyne, catalyzes the 1,2-addition on the triple bond to produce 1,3-(*E*)-dienylborane **4**.

Hydroboration of 1-buten-3-ynes **1b–d**, substituted with *n*-pentyl (**1b**), *tert*-butyl (**1c**), and trimethylsilyl (**1d**), with catecholborane in chloroform readily proceeded at 25 °C in the presence of 2 mol % of the $PPh_2(C_6F_5)$–Pd (P/Pd = 2/1) catalyst to give the corresponding allenylboranes **2b–d** with high selectivity (entries 12–14 in Table I). The 1,4-hydroboration forming allenylboranes was observed only for the reaction of the 1,3-enynes that are substituted at the 2-position. Enynes substituted at the 1-position, such as 1-phenyl-1-buten-3-yne, underwent selective 1,2-addition to the triple bond forming (*E*)-dienylboranes even with the $PPh_2(C_6F_5)$–Pd catalyst. Alkyl substitution at the 4-position inhibited the catalytic hydroboration.

Allenylboranes **2** were found to be useful as propargylating reagents for aldehydes.[4] Thus, a mixture of allenylborane **2a** and dienylborane **3a**, obtained by the catalytic hydroboration (entry 11 in Table I), was allowed to react with benzaldehyde in chloroform at −78 °C to give homopropargyl alcohol **7a** in 63% yield. The reaction of allenylborane **2b** with benzaldehyde gave a mixture of *syn*- and *anti*-homopropargyl alcohols **7b** (38%) in a ratio of 1:1.

Experimental Section

General Information. ^1H NMR spectra were measured with a JEOL JNM-EX-90 (90-MHz) or JNM-GX-270 (270-MHz) spectrometer. Catecholborane which is commercially available (Aldrich) was distilled under reduced pressure (bp 76–77 °C/100 mmHg) before use. Triphenylphosphine, dppe, dppb, dppf, and 2-methyl-1-buten-3-yne were obtained from commercial sources (Aldrich). $Pd_2(dba)_3{\cdot}CHCl_3$[6] and $PPh_2(C_6F_5)$[7] were prepared according to the reported procedures. Chloroform was dried by passing through aluminum oxide under nitrogen before use. Benzaldehyde was freshly distilled before use.

Preparation of 1,3-Enynes. 1,3-Enynes **1b–d** were prepared by palladium-catalyzed coupling[8] of (trimethylsilyl)acetylene with alkenyl triflates (for **1b**,**c**) or bromide (for **1d**) followed by desilylation.[9] A typical procedure is given for the preparation of 2-pentyl-1-buten-3-yne (**1b**). To a mixture of 29 mg (0.042 mmol) of $PdCl_2(PPh_3)_2$, 41 mg (0.22 mmol) of copper(I) iodide, and 9.88 g (40.1 mmol) of hept-1-en-2-yl trifluoromethanesulfonate[10] in 50 mL of diethylamine was added dropwise 3.97 g (40.4 mmol) of (trimethylsilyl)acetylene. The mixture was stirred at room temperature overnight and was extracted with pentane. The pentane extract was washed three times with water and once with brine, and dried over $MgSO_4$. Pentane was removed and the residue was distilled (bulb-to-bulb, bath temperature 120 °C/50 mmHg) to give 6.94 g (89% yield) of 2-pentyl-4-(trimethylsilyl)-1-buten-3-yne. To a solution of 9.2 g (158 mmol) of potassium fluoride and 314 mg (5.6 mmol) of potassium hydroxide in 65 mL of methanol was added dropwise 6.94 g (35.7 mmol) of the 2-pentyl-4-(trimethylsilyl)-1-buten-3-yne obtained above. The mixture was stirred for 1.5 h and was extracted with pentane after addition of water. The pentane layer was washed with brine, dried over $MgSO_4$, and carefully concentrated by evaporator. Bulb-to-bulb distillation of the residue gave 4.34 g (100% yield) of **1b**[11] as a colorless oil. **1b**: ^1H NMR ($CDCl_3$/TMS) δ 0.90 (t, J = 6.8 Hz, 3 H), 1.20–1.40 (m, 4 H), 1.54 (quint, J = 7.5 Hz, 2 H), 2.15 (t, J = 7.5 Hz, 2 H), 2.87 (s, 1 H), 5.29 (d, J = 1.3 Hz, 1 H), 5.41 (d, J = 1.3 Hz, 1 H). 2-*tert*-Butyl-1-buten-3-yne[11] (**1c**): ^1H NMR ($CDCl_3$/TMS) δ 1.14 (s, 9 H), 2.90 (s, 1 H), 5.30 (d, J = 1 Hz, 1 H), 5.38 (d, J = 1 Hz, 1 H). 2-(Trimethylsilyl)-1-buten-3-yne (**1d**): ^1H NMR ($CDCl_3$/TMS) δ −0.03 (s, 9 H), 3.18 (t, J = 1 Hz, 1 H), 5.78 (dd, J = 3 and 1 Hz, 1 H), 6.19 (dd, J = 3 and 1 Hz, 1 H).

General Procedure for the Palladium-Catalyzed Hydroboration of 1,3-Enynes with Catecholborane. All reactions

(5) The formation of allenylborane **2** is always accompanied by (*Z*)-dienylborane **3**. The latter is thought to be also formed via the intermediate **5**, though the mechanism for the formation remains to be clarified.

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(7) Dua, S. S.; Edmondson, R. C.; Gilman, H. *J. Organomet. Chem.* **1970**, *24*, 703.
(8) For example, see: Kende, A. S.; Smith, C. A. *J. Org. Chem.* **1988**, *53*, 2655.
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were carried out under a nitrogen atmosphere. Reaction conditions and results are summarized in Table I. Hydroboration of 2-methyl-1-buten-3-yne (**1a**) with catecholborane in the presence of palladium catalyst generated in situ by mixing $Pd_2(dba)_3$·$CHCl_3$ and $PPh_2(C_6F_5)$ is illustrative of the general methods for all catalytic reactions described in this study. A mixture of 8.3 mg (0.008 mmol) of $Pd_2(dba)_3$·$CHCl_3$ and 11 mg (0.03 mmol) of $PPh_2(C_6F_5)$ in 1 mL of chloroform was stirred at room temperature until the solution changed from red-purple due to $Pd_2(dba)_3$·$CHCl_3$ to yellow. To the catalyst solution was added successively at 25 °C 53 mg (0.80 mmol) of 2-methyl-1-buten-3-yne (**1a**) and 126 mg (1.0 mmol) of catecholborane, and the mixture was stirred at the same temperature for 30 min. Solvent was evaporated and the residue was distilled (bulb-to-bulb, bath temperature 100 °C/0.1 mmHg) to give 109 mg (73% yield) of the hydroboration product, which consisted of (3-methyl-1,2-butadienyl)-1,3,2-benzodioxaborole (**2a**) and {(*Z*)-3-methyl-1,3-butadienyl}-1,3,2-benzodioxaborole (**3a**) in a ratio of 83:17. The ratio was determined by the ^1H NMR spectrum. ^1H NMR ($CDCl_3$/TMS) data for the hydroboration products are as follows. (3-Methyl-1,2-butadienyl)-1,3,2-benzodioxaborole (**2a**): δ 1.79 (d, *J* = 3.4 Hz, 6 H), 5.18 (heptet, *J* = 3.4 Hz, 1 H), 7.01–7.13 (m, 2 H), 7.16–7.26 (m, 2 H). {(*Z*)-3-Methyl-1,3-butadienyl}-1,3,2-benzodioxaborole (**3a**): δ 1.97 (s, 3 H), 5.17 (s, 1 H), 5.20 (s, 1 H), 5.71 (d, *J* = 14.7 Hz, 1 H), 7.00 (d, *J* = 14.7 Hz, 1 H), 7.01–7.13 (m, 2 H), 7.16–7.26 (m, 2 H). {(*E*)-3-Methyl-1,3-butadienyl}-1,3,2-benzodioxaborole (**4a**): δ 1.94 (s, 3 H), 5.30 (s, 2 H), 5.87 (d, *J* = 18.1 Hz, 1 H), 7.01–7.13 (m, 2 H), 7.16–7.26 (m, 2 H), 7.46 (d, *J* = 18.1 Hz, 1 H). (3-Pentyl-1,2-butadienyl)-1,3,2-benzodioxaborole (**2b**): δ 0.88 (t, *J* = 7.2 Hz, 3 H), 1.20–1.60 (m, 6 H), 1.77 (d, *J* = 3.5 Hz, 3 H), 2.00–2.10 (m, 2 H), 5.23 (sextet, *J* = 3.5 Hz, 1 H), 7.00–7.12 (m, 2 H), 7.15–7.28 (m, 2 H). {(*Z*)-3-Pentyl-1,3-butadienyl}-1,3,2-benzodioxaborole (**3b**): δ 0.88 (t, *J* = 7.2 Hz, 3 H), 1.20–1.60 (m, 6 H), 2.28 (t, *J* = 5.7 Hz, 2 H), 5.08 (s, 1 H), 5.20 (s, 1 H), 5.71 (d, *J* = 14.7 Hz, 1 H), 6.96 (d, *J* = 14.7 Hz, 1 H), 7.00–7.12 (m, 2 H), 7.15–7.28 (m, 2 H). {(*E*)-3-Pentyl-1,3-butadienyl}-1,3,2-benzodioxaborole (**4b**): δ 0.88 (t, *J* = 7.2 Hz, 3 H), 1.20–1.60 (m, 6 H), 2.31 (t, *J* = 6.2 Hz, 2 H), 5.28 (s, 1 H), 5.32 (s, 1 H), 5.93 (d, *J* = 18.5 Hz, 1 H), 7.00–7.12 (m, 2 H), 7.15–7.28 (m, 2 H), 7.41 (d, *J* = 18.5 Hz, 1 H). (3-*tert*-Butyl-1,2-butadienyl)-1,3,2-benzodioxaborole (**2c**): δ 1.13 (s, 9 H), 1.78 (d, *J* = 3.3 Hz, 3 H), 5.22 (q, *J* = 3.3 Hz, 1 H), 7.01–7.13 (m, 2 H), 7.15–7.27 (m, 2 H). {(*Z*)-3-*tert*-Butyl-1,3-butadienyl}-1,3,2-benzodioxaborole (**3c**): δ 1.16 (s, 9 H), 4.93 (s, 1 H), 5.00 (s, 1 H), 5.74 (d, *J* = 14.1 Hz, 1 H), 7.00 (d, *J* = 14.1 Hz, 1 H), 7.01–7.13 (m, 2 H), 7.15–7.27 (m, 2 H). {(*E*)-3-*tert*-Butyl-1,3-butadienyl}-1,3,2-benzodioxaborole (**4c**): δ 1.16 (s, 9 H), 5.03 (s, 1 H), 5.35 (s, 1 H), 6.18 (d, *J* = 18.1 Hz, 1 H), 7.01–7.13 (m, 2 H), 7.15–7.27 (m, 2 H), 7.52 (d, *J* = 18.1 Hz, 1 H). {3-(Trimethylsilyl)-1,2-butadienyl}-1,3,2-benzodioxaborole (**2d**): δ 0.16 (s, 9 H), 1.79 (d, *J* = 3.3 Hz, 3 H), 4.81 (q, *J* = 3.3 Hz, 1 H), 7.01–7.12 (m, 2 H), 7.15–7.29 (m, 2 H). Analytical data for the products are as follows. Anal. Calcd for $C_{11}H_{11}BO_2$ [**2a** (a mixture of isomers, **2a**, **3a**, and **4a**)]: C, 71.03; H, 5.96. Found: C, 70.78; H, 5.90. Anal. Calcd for $C_{15}H_{19}BO_2$ [**2b** (a mixture of isomers, **2b**, **3b**, and **4b**)]: C, 74.41; H, 7.91. Found: C, 74.11; H, 7.95. For allenylboranes **2c** and **2d**, correct analyses could not be obtained due to the difficulty in purification.

Reaction of Allenylboranes with Benzaldehyde. The reaction mixture, which results from the catalytic hydroboration of **1a** (0.8 mmol) in chloroform described above and includes allenylborane **2a**, was used for the reaction with benzaldehyde without isolation of **2a**. The chloroform solution was cooled with a dry ice/acetone bath, and 119 mg (1.1 mmol) of benzaldehyde was added. The mixture was allowed to warm to room temperature under stirring. Water was added, and the mixture was extracted with ether. The organic layer was dried over $MgSO_4$ and was concentrated in vacuo. The residue was chromatographed on silica gel (hexane/ether = 10/1) to give 88 mg (0.51 mmol) of homopropargyl alcohol **7a** in 63% yield: ^1H NMR ($CDCl_3$/TMS) δ 1.10 (s, 3 H), 1.27 (s, 3 H), 2.24 (s, 1 H), 2.42 (bs, 1 H), 4.49 (s, 1 H), 7.2–7.5 (m, 5 H). Reaction of the chloroform solution containing allenylborane **2b**, which was obtained from 79 mg (0.64 mmol) of **1b**, with benzaldehyde in a similar manner gave 56 mg (0.24 mmol) of **7b** as a 1:1 mixture of syn and anti isomers in 38% yield: ^1H NMR ($CDCl_3$/TMS) for diastereomer A δ 0.87 (t, *J* = 7.1 Hz, 3 H), 1.1–1.7 (m, 8 H), 1.23 (s, 3 H), 2.25 (s, 1 H), 2.34 (d, *J* = 4.0 Hz, 1 H), 4.56 (d, *J* = 4.0 Hz, 1 H), 7.2–7.5 (m, 5 H); ^1H NMR ($CDCl_3$/TMS) for diastereomer B δ 0.90 (t, *J* = 7.1 Hz, 3 H), 1.04 (s, 3 H), 1.1–1.7 (m, 8 H), 2.29 (s, 1 H), 2.46 (d, *J* = 3.7 Hz, 1 H), 4.55 (d, *J* = 3.7 Hz, 1 H), 7.2–7.5 (m, 5 H). Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.21; H, 9.66.

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Supplementary Material Available: Figures of ^1H NMR spectra of hydroboration products **2a–d**, **3a–c**, and **4a–c** (5 pages). Ordering information is given on any current masthead page.

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A Homoleptic (Aryl isocyanide)iron(0) Dimer. X-ray Structure Determination of Nonakis(phenyl isocyanide)diiron

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Summary: Nonakis(phenyl isocyanide)diiron was prepared by sodium amalgam reduction of either *cis*- or *trans*-$[Fe_2(CNPh)_4]$. The new complex was characterized spectroscopically and by single-crystal X-ray analysis. Crystal data: monoclinic, space group $P2_1/n$, a = 12.692 (5) Å, b = 27.086 (8) Å, c = 15.735 (3) Å, β = 92.90 (2)°, V = 5402 (3) Å^3, Z = 4, R = 0.032.

Homoleptic metal isocyanide complexes form an important group of species that allow a comparison with their carbonyl analogs. Moreover, they offer the possibility of controlling the electronic and steric requirements of the complex by changing the substituents on the nitrogen atom of the isocyanide ligands. A few examples of homoleptic isocyanide metal(0) dimers are known,[1] but only for the alkyl isocyanide derivatives $[Fe_2(CNEt)_9]$[2] and $[Co_2(CNBu^t)_8]$[3] has an X-ray structural determination been

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