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Nickel-Catalyzed Addition of Organoboronates to 1,2-Dienes and the Corresponding Three-Component Reaction with an Alkyne

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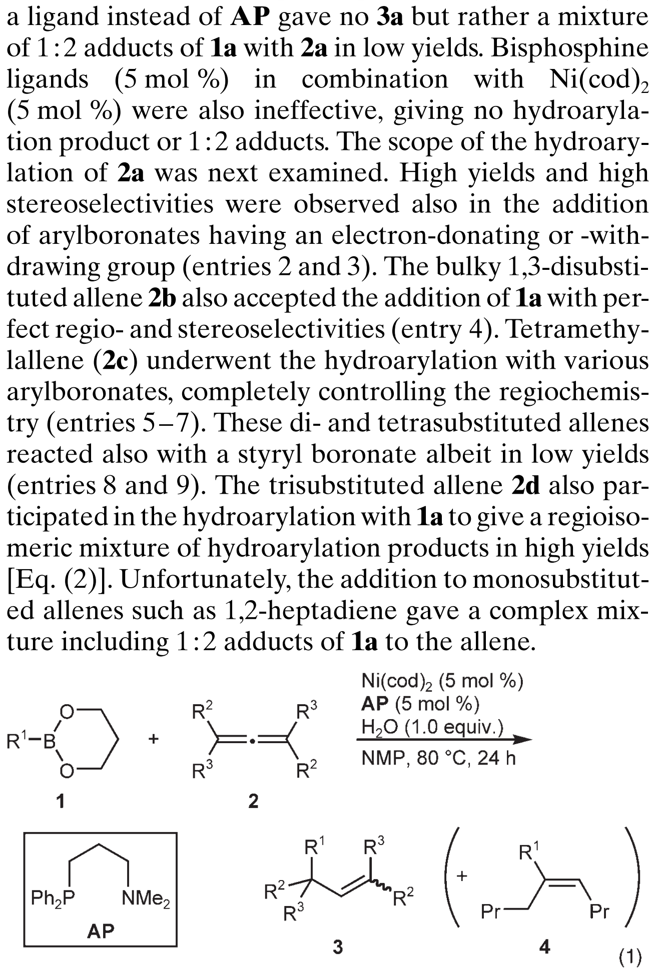
Abstract: A Ni(cod)$_2$–aminophosphine complex catalyzed the addition of aryl- and alkenylboronates to 1,2-dienes to give the hydroarylation and hydroalkenylation products of the 1,2-dienes, whereas the hydroarylation products of a 1,2-diene and an alkyne were obtained with a Ni(cod)$_2$–PPh$_3$ catalyst.

Keywords: alkynes; allenes; arylboronates; hydroalkenylation; hydroarylation; nickel

The transition metal-catalyzed addition of organoboron compounds to carbon–carbon unsaturated bonds has recently attracted much attention due mainly to the high chemoselectivity and low toxicity of organoboron compounds. In particular, rhodium catalysts have established their place since the pioneering report on the conjugate addition of arylboronic acids to enones by Miyaura and co-workers in 1997,[1] which was followed by reports on the addition to other Michael acceptors,[1c, d] alkenes[2] and alkynes.[3] We reported in 2001 the nickel-catalyzed hydroarylation of alkynes with arylboron compounds as the first example of the group 10 metal-catalyzed addition of organoboron compounds to carbon–carbon unsaturated bonds.[4] The nickel catalysis was further applied to the addition of aryl- and alkenylboronates to 1,3-dienes[5] and aldehydes.[6] On the other hand, the palladium-catalyzed addition of organoboron compounds to alkynes[7] or 1,2-dienes[8,9] was reported by Oh as well as Ma in 2003, although the addition to 1,2-dienes is applicable mainly to heteroatom-containing 1,2-dienes and relatively electron-rich organoboron compounds. Here we report the nickel-catalyzed addition of organoboronates to di-, tri- and tetrasubstituted allenes as well as the hydroarylation of 1,2-dienes and alkynes through a three-component reaction.[10–12]

We first investigated suitable conditions for the nickel-catalyzed addition of 2-(p-tolyl)-1,3,2-dioxaborinane (**1a**) to 4,5-nonadiene (**2a**). Thus, treatment of **1a** and **2a** with Ni(cod)$_2$ (5 mol %), 1-dimethylamino-3-(diphenylphosphino)propane (**AP**: 5 mol %) and H$_2$O (1.0 equiv.) in NMP at 80 °C for 24 h gave 6-(p-tolyl)-4-nonene (**3a**) in 82% yield with a high stereoselectivity (E:Z=91:9), whereas a regioisomer, (Z)-5-(p-tolyl)-4-nonene (**4a**), was generated only in 1% yield [Eq. (1) and entry 1 of Table 1]. The use of triphenylphosphine (10 mol %) as a ligand instead of **AP** gave no **3a** but rather a mixture of 1:2 adducts of **1a** with **2a** in low yields. Bisphosphine ligands (5 mol %) in combination with Ni(cod)$_2$ (5 mol %) were also ineffective, giving no hydroarylation product or 1:2 adducts. The scope of the hydroarylation of **2a** was next examined. High yields and high stereoselectivities were observed also in the addition of arylboronates having an electron-donating or -withdrawing group (entries 2 and 3). The bulky 1,3-disubstituted allene **2b** also accepted the addition of **1a** with perfect regio- and stereoselectivities (entry 4). Tetramethylallene (**2c**) underwent the hydroarylation with various arylboronates, completely controlling the regiochemistry (entries 5–7). These di- and tetrasubstituted allenes reacted also with a styryl boronate albeit in low yields (entries 8 and 9). The trisubstituted allene **2d** also participated in the hydroarylation with **1a** to give a regioisomeric mixture of hydroarylation products in high yields [Eq. (2)]. Unfortunately, the addition to monosubstituted allenes such as 1,2-heptadiene gave a complex mixture including 1:2 adducts of **1a** to the allene.



(1)

Table 1. Nickel-catalyzed addition of organoboronates to 1,2-dienes.[a]

Entry	R^1	R^2	R^3	Yield [%][b]	E:Z[c]	Product
1	4-Me-C_6H_4 (**1a**)	Pr	H (**2a**)	82	91:9[d]	**3a**
2	4-MeO-C_6H_4 (**1b**)	Pr	H (**2a**)	77	92:8[e]	**3b**
3	4-Ac-C_6H_4 (**1c**)	Pr	H (**2a**)	85	93:7	**3c**
4	4-Me-C_6H_4 (**1a**)	*i*-Pr	H (**2b**)	83	>99:1	**3d**
5	4-Me-C_6H_4 (**1a**)	Me	Me (**2c**)	94	–	**3e**
6	4-MeO-C_6H_4 (**1b**)	Me	Me (**2c**)	79	–	**3f**
7	4-Ac-C_6H_4 (**1c**)	Me	Me (**2c**)	84	–	**3g**
8	styryl (**1d**)	Pr	H (**2a**)	42	>99:1	**3h**
9	styryl (**1d**)	Me	Me (**2c**)	37	–	**3i**

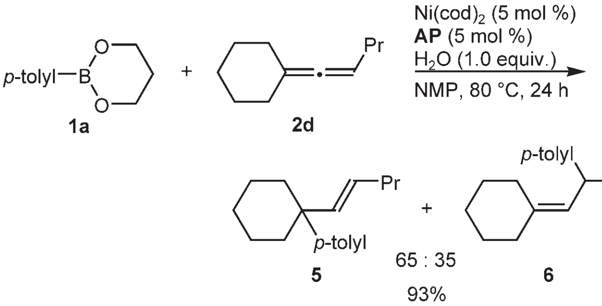
[a] The reaction was carried out in NMP (0.45 mL) at 80 °C for 24 h using an organoboronate (0.30 mmol) and a 1,2-diene (0.90 mmol) in the presence of Ni(cod)$_2$ (15 μmol), 1-dimethylamino-3-(diphenylphosphino)propane (**AP**: 15 μmol) and H_2O (0.30 mmol).

[b] Isolated yield based on the arylboronate.

[c] Determined by ^{1}H NMR.

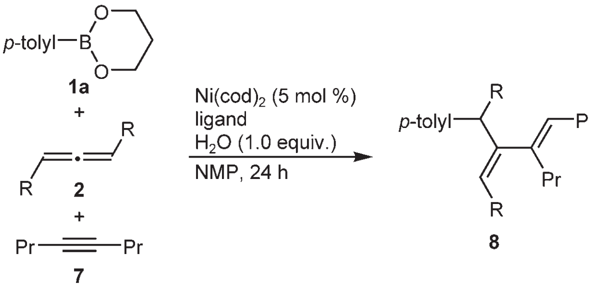
[d] (*Z*)-5-(*p*-Tolyl)-4-nonene (**4a**) was also produced in 1% yield.

[e] (*Z*)-5-(4-Methoxyphenyl)-4-nonene (**4b**) was also produced in 2% yield.



(2)

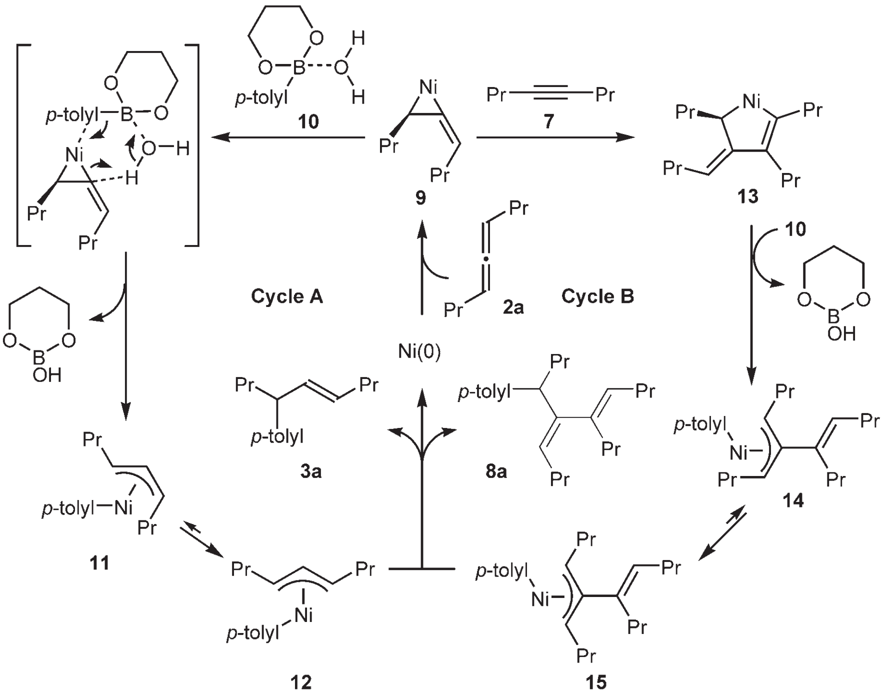
The present catalyst system was found to be applicable also to the three-component reaction between an arylboronate, a 1,2-diene and an alkyne. Treatment of *p*-tolylboronate **1a**, 4,5-nonadiene (**2a**) and 4-octyne (**7**) with Ni(cod)$_2$ (5 mol %), **AP** (5 mol %) and H_2O (1.0 equiv.) in NMP at 80 °C for 24 h gave a three-component reaction product, (4*E*,6*Z*)-5-propyl-6-[1-(*p*-tolyl)but-1-yl]-4,6-decadiene (**8a**), in 54% yield in addition to 10% yield of **3a** [Eq. (3)]. Use of triphenylphosphine as a ligand instead of **AP** slightly increased the yield of **8a**. 2,6-Dimethyl-3,4-heptadiene (**2b**) also underwent the three-component reaction with **1a** and alkyne **7**.



(3)

R	**1** : **2** : **7**	ligand	temp.	**8**	**3**
Pr	1 : 3 : 6	**AP** (5 mol %)	80 °C	54%	10%
Pr	1 : 3 : 6	PPh_3 (10 mol %)	80 °C	60%	5%
i-Pr	1 : 2 : 6	PPh_3 (10 mol %)	60 °C	48%	17%

In the present nickel-catalyzed reaction of arylboronates with the aid of H_2O, aryl groups add to a terminal sp^2-carbon atom of allenes, in contrast to which arylboronic acids attack the central allene carbon in the presence of a palladium catalyst and acetic acid as reported by Oh or Ma.[8,9] The difference in regioselectivities should imply that these reactions proceed through different catalytic cycles. Ma and co-workers have recently clarified the mechanism of the palladium-catalyzed hydroarylation using ESI-FT-MS analysis, where the catalytic cycle includes oxidative addition of acetic acid to a palladium(0) complex.[9b] On the other hand, H_2O in the addition to organoboronates seem not to undergo oxidative addition to a nickel(0) complex in our reaction conditions.[5] Thus, based on the mechanism of the nickel-catalyzed addition of organoboronates to 1,3-dienes,[5] a nickel(0) complex may first react with 1,2-dienes and/or alkynes. Possible catalytic cycles exemplified by the reaction of 2-(*p*-tolyl)-1,3,2-dioxaborinane (**1a**), 4,5-nonadiene (**2a**) and 4-octyne (**7**) are shown in Scheme 1. In the addition to **2a** (Cycle A), oxidative cyclization of **2a** to a nickel(0) complex gives nickelacyclopropane **9**, which reacts with the **1a**–H_2O complex **10**, making bonds with the *p*-tolyl group and a proton of **10** at Ni and the C(sp^2) of nickelacycle **9**, respectively. The resulting *anti*-π-allylnickel complex **11** isomerizes to the thermodynamically more stable *syn*-isomer **12**, which undergoes reductive elimination to give (*E*)-**3a** as the main product and regenerate the nickel(0) complex. In contrast, in the presence of 4-octyne (**7**), nickelacyclopropane **9** accepts insertion of **7** to give nickelacyclopentene **13** (Cycle B).[13] Complex **10** reacts with **13**, cleaving the Ni–C(sp^2) bond to give π-allylnickel complex **14**. After isomerization from the *anti*- to the *syn*-π-allylnickel complex **15**, reductive elimination gives **8a** and the nickel(0) complex.



Scheme 1. Proposed catalytic cycles A and B.

In conclusion, we have disclosed that nickel(0) complexes are effective catalysts for the addition of organoboron compounds to 1,2-dienes, where hydroarylation and hydroalkenylation products of 1,2-dienes in addition to the corresponding three-component reaction product with an alkyne are obtained. Further studies on details of the reaction mechanism as well as application of the reaction to other substrates are in progress.

Experimental Section

General Remarks

All manipulations of oxygen- and moisture-sensitive materials were conducted with standard Schlenk techniques under a nitrogen atmosphere. Column chromatography was performed using silica gel 60N purchased from Kanto Chemicals. Nuclear magnetic resonance spectra were taken on a Varian Gemini 2000 (^{1}H, 300 MHz; ^{13}C, 75 MHz) spectrometer using tetramethylsilane (^{1}H and ^{13}C) as an internal standard. High-resolution mass spectra were obtained with a Bruker Bio APEX 70e spectrometer. Unless otherwise noted, reagents were commercially available and used without further purification. Anhydrous NMP was purchased from Kanto Chemicals. Bis(1,5-cyclooctadiene)nickel was purchased from Kanto Chemicals or Strem and recrystallized from toluene/1,5-cyclooctadiene (50:1). Organoboronic acids were purchased from Aldrich Chemical Co. 4-Octyne was purchased from Kanto Chemicals and fractionally distilled. Grignard reagents were purchased from Kanto Chemicals. CuBr was washed with methanol prior to use. Diethyl ether and THF were distilled from sodium/benzophenone ketyl just prior to use. 1,2-Dienes, 4-octyne and NMP were degassed through four freeze-thaw cycles just before use.

Nickel-Catalyzed Hydroarylation and hydroalkenylation of 1,2-Dienes with Organoboronates; General Procedure

To a mixture of an organoboronate (0.30 mmol), a 1,2-diene (0.90 mmol) and 1-(dimethylamino)-3-(diphenylphosphino)-propane (8.1 mg, 30 μmol) were added successively an NMP (0.45 mL) solution of Ni(cod)$_2$ (4.1 mg, 15 μmol) and water (5.4 mg, 0.30 mmol). After the mixture had been stirred at 80 °C for 24 h, the resulting mixture was treated with saturated NaHCO$_3$ aqueous solution and extracted with diethyl ether (10 mL × 3). The combined organic layer was washed with brine (10 mL), and then dried over anhydrous magnesium sulfate. Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane–ethyl acetate) gave the corresponding products. The results are summarized in Table 1.

Nickel-Catalyzed Tandem Hydroarylation of 1,2-Dienes and 4-Octyne with 2-(*p*-Tolyl)-1,3,2-dioxaborinane; General Procedure

To a mixture of 2-(*p*-tolyl)-1,3,2-dioxaborinane (52.8 mg, 0.300 mmol), a 1,2-diene (0.60 or 0.90 mmol), 4-octyne (0.26 mL, 1.8 mmol) and PPh$_3$ (7.9 mg, 30 μmol) were added an NMP (0.45 mL) solution of Ni(cod)$_2$ (4.1 mg, 15 μmol) and water (5.4 mg, 0.30 mmol), successively. After the mixture had been stirred at 80 or 60 °C for 24 h, the resulting mixture was treated with saturated $NaHCO_3$ aqueous solution and extracted with diethyl ether (10 mL × 3). The combined organic layer was washed with brine (10 mL), and then dried over anhydrous magnesium sulfate. Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane–ethyl acetate) gave the corresponding products. The results are summarized in Eq. (3).

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[12] For a recent review on 1,2-dienes, see: N. Krause, S. Hashmi, *Modern Allene Chemistry*, John Wiley & Sons, Weinheim, **2004**.

[13] As formation of nickelacyclopentene **13** should require more coordination sites than nickelacyclopropane **9**, monodentate PPh_3 is more effective than bidentate aminophosphine **AP** in the three-component reaction.