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Nickel-catalysed addition of organoboronates to 1,3-dienes†

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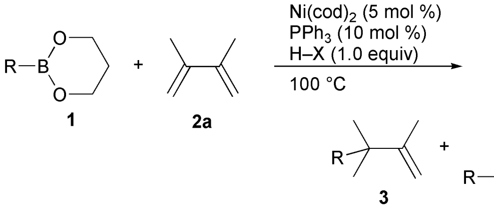
Aryl- and alkenylboronates were found to add to 1,3-dienes in the presence of a catalytic amount of bis(1,5-cyclooctadiene)nickel, where a proton source in combination with a solvent considerably controls the regioselectivity.

Conjugated dienes are one of the best partners of late transition metal complexes, which effectively catalyse polymerization, oligomerization including cyclization and co-cyclization with other unsaturated compounds.[1] Although the reactions with organometallic compounds are also widely known, most of them utilize the addition of a metal–metal or metal–hydrogen bond and those accompanied by carbon–carbon bond formation are extremely rare except for a few carbometalation reactions using allylmagnesium reagents[2] or acylstannanes.[3,4] The scarcity should mainly owe to the deficiency of appropriate methods of activating carbon–metal bonds with transition metals to react with 1,3-dienes. We have disclosed that carbon–boron bonds of arylboron compounds were activated by nickel complexes,[5] which catalysed the hydroarylation and dimerization–hydroarylation of alkynes.[6] Here we report the nickel-catalysed hydroarylation and -alkenylation[7] of 1,3-dienes, where the regioselectivity concerning the addition of the organic group of organoboron compounds can be controlled considerably with the choice of the reaction conditions.

First we investigated suitable conditions for the hydroarylation of 1,3-dienes using 2-(*p*-tolyl)-1,3,2-dioxaborinane (**1a**, R = *p*-tolyl) and 2,3-dimethyl-1,3-butadiene (**2a**) and found that the tolyl group of **1a** added to **2a** in the presence of 5 mol% of Ni(cod)$_2$, 10 mol% of triphenylphosphine and 1 equiv. of BuOH in 1,4-dioxane to give a 74 : 26 ratio of internal adduct **3a** of the *p*-tolyl group to **2a** and terminal adduct **4a** in 82% yield in addition to 3% yield of another terminal adduct, 2,3-dimethyl-4-(*p*-tolyl)-1-butene (**4′a**) (eqn. (1) and entry 1 of Table 1).‡ Use of a nickel(II) complex like (Ph$_3$P)$_2$NiBr$_2$,



(1)

cond.	solvent	H–X	time
A	1,4-dioxane	H–OBu	2 h
B	1,4-dioxane	H–NHPh	2 h
C	NMP	H–OH	2 h
D	NMP	H–NH(CH$_2$)$_2$NMe$_2$	24 h

Table 1 Nickel-catalysed addition of organoboron compounds to 2,3-dimethyl-1,3-butadiene[a]

Entry	R	Conditions[b]	Yield (%)[c]	**3** : **4**[d]	Products
1	4-tolyl	A	82[e]	74:26	**3a**, **4a**, **4′a**
2		B	93	84:16	**3a**, **4a**
3		C	97	35:65	**3a**, **4a**
4		D	78	18:82	**3a**, **4a**
5	4-MeO-C$_6$H$_4$	A	82	72:28	**3b**, **4b**
6		B	85	83:17	**3b**, **4b**
7		C	88	37:63	**3b**, **4b**
8		D	80	21:79	**3b**, **4b**
9	4-CF$_3$-C$_6$H$_4$	A	81	67:33	**3c**, **4c**
10		B	84	56:44	**3c**, **4c**
11		C	74	18:82	**3c**, **4c**
12		D	35	7:93	**3c**, **4c**
13	3-NH$_2$-C$_6$H$_4$	A	86	86:14	**3d**, **4d**
14		C	87	48:52	**3d**, **4d**
15	2-naphthyl	A	94	82:18	**3e**, **4e**
16		B	94	83:17	**3e**, **4e**
17		C	80	42:58	**3e**, **4e**
18		D	86	13:87	**3e**, **4e**
19	3-thienyl	A	74	52:48	**3f**, **4f**
20		C	78	27:73	**3f**, **4f**
21	1-octen-1-yl	A	68	83:17	**3g**, **4g**
22		C	79	36:64	**3g**, **4g**
23	styryl	A[f]	87	84:16	**3h**, **4h**
24		C[g]	82	42:58	**3h**, **4h**

[a] The reaction was carried out in a solvent (0.45 mL) at 100 °C using a 2-(aryl or alkenyl)-1,3,2-dioxaborinane (**1**, 0.30 mmol), 2,3-dimethyl-1,3-butadiene (**2a**, 0.90 mmol), an additive (0.30 mmol), Ni(cod)$_2$ (15 μmol) and PPh$_3$ (30 μmol). [b] Conditions A: solvent = 1,4-dioxane, additive = BuOH, 2 h; B: solvent = 1,4-dioxane, additive = PhNH$_2$, 2 h; C: solvent = NMP, additive = H$_2$O, 2 h; D: solvent = NMP, additive = Me$_2$N(CH$_2$)$_2$NH$_2$, 24 h. [c] Isolated yield based on the boronate. [d] Determined by GC. [e] Another terminal adduct, 2,3-dimethyl-4-(*p*-tolyl)-1-butene (**4′a**), was also obtained in 3% yield. [f] Time = 9 h. [g] Time = 6 h.

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† Electronic supplementary information (ESI) available: ^{1}H NMR spectra and MS data. See http://www.rsc.org/suppdata/cc/b2/b207185a/

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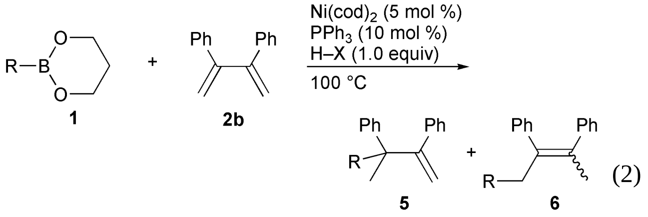
$Ni(acac)_2/Ph_3P$ (1 : 2) or $Ni(OAc)_2/Ph_3P$ (1 : 2) as a catalyst precursor was totally ineffective. The reaction did not take place in the absence of a proton donor. Aniline as a proton donor was effective to improve the yields and the selectivity for internal adduct **3a** (Table 1, entry 2), whereas the reaction using NMP as a solvent in combination with water or *N*,*N*-dimethylethylenediamine as an additive proceeded in a reversed regioselectivity to give **4a** as the major product (entries 3 and 4 of Table 1). Use of a more acidic proton donor like acetic acid and phenol or a simple aliphatic amine such as butylamine was much less effective.

The scope of the addition reaction was next examined using these four sets of conditions as summarized in entries 5–24 of Table 1. The regioselectivities with conditions A–D observed in the reaction of **1a** with **2a** were conserved, on the whole, also in the reaction with phenylboronates having an electron-donating (entries 5–8), electron-withdrawing (entries 9–12) or protic (entries 13 and 14) substituent. A naphthylboronate (entries 15–18), a heteroarylboronate (entries 19 and 20) and alkenylboronates (entries 21–24) also underwent the addition reaction.

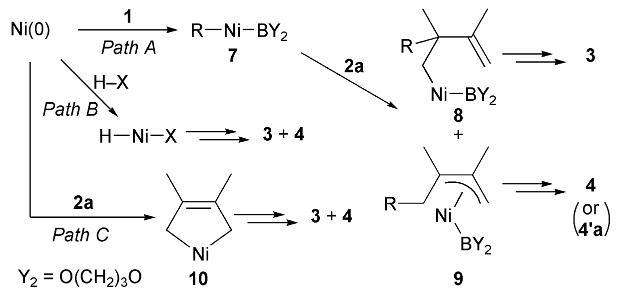
Besides **2a**, 2,3-diphenyl-1,3-butadiene (**2b**) accepts the addition of organoboronates [eqn. (2)]. Under both conditions A and C, the addition proceeded regioselectively to give 1,4-addition products **6** predominantly, though a small amount of the (*E*)-isomer was produced in some cases. Under similar conditions, the reaction of less substituted 1,3-dienes such as 1,3-butadiene and isoprene unfortunately gave complex mixtures including the dimerization–hydroarylation products of the 1,3-dienes.



(2)

R	cond.	solvent	H–X	time	yield	**5**:(*Z*)-**6**:(*E*)-**6**
p-tolyl	A	1,4-dioxane	H–OBu	2 h	60%	0:93:7
p-tolyl	C	NMP	H–OH	2 h	77%	0:100:0
styryl	C	NMP	H–OH	12 h	67%	6:92:2

Although the reaction mechanism is not clear at present, the fact that nickel(II) complexes did not catalyse the reaction should imply that a nickel(0) complex is an active catalyst, which reacts first with an organoboronate (*Path A* in Scheme 1), a proton source (*Path B*) or a 1,3-diene (*Path C*). *Path A*, a similar mechanism to that we proposed in the nickel-catalysed hydroarylation of alkynes,[6] seems to be less probable because internal adduct **3** has to be produced through insertion of **2a** to the carbon–nickel bond of oxidative adduct **7** in an unfavorable regioselective manner giving alkylnickel complex **8**, which cannot take stabilization by π-coordination found in π-allylnickel **9** leading to **4**. The probability of *Path B* must rely on the reactivity of H–X with nickel(0) complexes, H–N bonds in conditions B and D being unlikely to add oxidatively to nickel(0) complexes. Consequently, it seems to be more plausible that a nickel(0) catalyst first reacts with a 1,3-diene (*Path C*), the resulting complex, *e.g.*, nickelacyclopentene **10**,[8] accepting the addition of an organoboronate, though we do not have any evidence to solve the mechanistic details, including the role of proton sources.



Scheme 1

In conclusion, we have demonstrated that organoboronates activated by a nickel catalyst in combination with a stoichiometric amount of a proton source added to 1,3-dienes. Further studies on details of the reaction mechanism, as well as application of the activation method of carbon–boron bonds to development of new reactions, are in progress.

Notes and references

‡ *General procedure for the nickel-catalysed addition of organoboronates to 1,3-dienes*: An additive (0.30 mmol) was added to a solution (0.45 mL) of an organoboronate (0.30 mmol), a 1,3-diene (0.90 mmol), $Ni(cod)_2$ (4.1 mg, 15 μmol) and triphenylphosphine (7.9 mg, 30 μmol). After the mixture was stirred at 100 °C for 2 or 24 h, the resulting solution was treated with saturated $NaHCO_3$ aqueous solution (3 mL) and extracted with ether (5 mL × 3). The combined organic layer was washed with brine (10 mL) and dried over anhydrous magnesium sulfate. Bulb-to-bulb distillation or evaporation of the solvent followed by purification with silica gel chromatography (hexane–ethyl acetate) gave **3** and **4** (**5** and **6**).

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