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Rhodium catalysed dehydrogenative borylation of vinylarenes and 1,1-disubstituted alkenes without sacrificial hydrogenation—a route to 1,1-disubstituted vinylboronates

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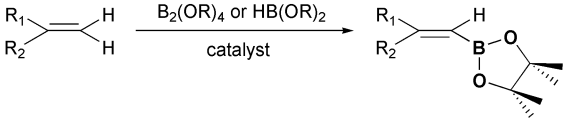
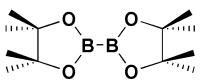
The complex *trans*-[Rh(Cl)(CO)(PPh$_3$)$_2$] (1) is an efficient catalyst precursor for the dehydrogenative borylation of alkenes without consumption of half the alkene substrate by hydrogenation, giving useful vinylboronate esters including 1,1-disubstituted derviatives that cannot be made by alkyne hydroboration.

Vinylboronate esters (VBEs) are useful synthetic intermediates in many reactions, including C–C bond formation *via* Pd-catalysed Suzuki-Miyaura cross-coupling.[1] They can be prepared by uncatalysed[2] or metal catalysed[3] hydroboration of alkynes. Recently, VBE's have been synthesised from alkenyl halides *via* catalysed[4] or stoichiometric reactions,[5] the latter requiring lithiation at −110 °C. An exciting alternative is the catalytic dehydrogenative borylation of alkenes[3a,6] eqn. (1),

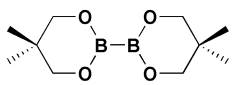


(1)

which would allow the direct synthesis of 1,1-disubstituted VBEs that cannot be made by hydroboration of alkynes. However, conditions must be found wherein the H_2 produced is **not** consumed *via* hydrogenation of half of the alkene substrate, a problem which has plagued this approach from the earliest reports. We present herein a novel, high yield, highly selective catalytic synthesis of VBEs, including 1,1-disubstituted VBEs, directly from alkenes **without** significant hydrogenation or hydroboration using the catalyst precursor *trans*-[RhCl(CO)(PPh$_3$)$_2$] (**1**) and the diboron reagents B_2pin_2 or B_2neop_2 (pin = $OCMe_2CMe_2O$; neop = $OCH_2CMe_2CH_2O$), all of which are commercially available.



B_2pin_2



B_2neop_2

In the course of our studies on alkene diboration,[7] we examined the reaction of 4-vinylanisole (VA) with B_2pin_2 catalysed by **1** in a variety of solvents. Toluene, THF and 1,4-dioxane all gave complicated mixtures containing dehydrogenative borylation, diboration, hydroboration and hydrogenation products and, in some cases, vinyl-bis(boronate) esters (VBBEs). In contrast, reaction in CH_3CN was clean giving 93% VBE but the rate was much slower than that in *e.g.* toluene. We therefore examined the reaction using 3 mol% of **1** and 0.67 equiv. (a slight excess) of B_2pin_2 in 3:1 toluene:acetonitrile (3:1 T:A) which proved an excellent compromise between selectivity and rate, giving 88% selectivity towards VBE, with 12% hydroboration and 100% conversion in 2 days (Table 1, Entry 1). Importantly, the stoichiometry demonstrates the potential to use both boron atoms of the diboron reagent. Reaction with B_2neop_2 was less selective (Entry 2). Reaction of VA with 2 equiv. of B_2pin_2 in the presence of 5 mol% of **1** in 3:1 T:A (Entry 3) gave 85% selectivity for VBBE,†

Table 1 Product distribution for the dehydrogenative borylation of alkenes with B_2pin_2 and B_2neop_2[a]

Entry	Substrate	Boron reagent	Hydroboration (hydrogenation) (%	BBE[b] (%)	Total VBE (Maj. isomer) (%)	Total VBBE (Maj. isomer) (%)	Time/ days	Solvent[c]	Conversion (%)
1	4-Vinyl anisole	B_2pin_2	12 (trace)		88		2	3:1 T:A	100
2	4-Vinyl anisole	B_2neop_2	5 (22)		73		1	3:1 T:A	62
3	4-Vinyl anisole[d]	B_2pin_2	1		14	85 (83)	5	3:1 T:A	100
4	α-Methyl styrene	B_2pin_2	1		99 (97)		4	3:1 T:A	68
5	α-Methyl styrene	B_2pin_2	9	4	87 (74)		2	T	72
6	α-Methyl styrene	B_2pin_2	trace		100 (98)		6	A	70
7	α-Methyl styrene[e]	B_2pin_2			100 (97)		3	3:1 T:A	90
8	α-Methyl styrene[f]	B_2pin_2			100 (98)		2	3:1 T:A	100
9	α-Methyl styrene	B_2neop_2	9		91 + trace		1	3:1 T:A	49
10	1,1-Diphenylethylene	B_2pin_2	2		98		4	3:1 T:A	48
11	1,1-Diphenylethylene[f]	B_2pin_2	1		99		3	3:1 T:A	100
12	Methylene cyclopentane	B_2pin_2			100 (92, 4, 4) [3 isomers]		3	3:1 T:A	100[g]
13	Methylene cyclohexane	B_2pin_2	8		92		5	3:1 T:A	80[g]

[a] Typical reaction conditions: in a nitrogen-filled glove box, a mixture of boron reagent (0.4 mmol total boron) and alkene (0.3 mmol) in 1 ml of solvent was added to a solution of *trans*-[Rh(Cl)(CO)(PPh$_3$)$_2$] (3 mol%) in 1 ml of solvent (2 ml total solvent volume). The mixture was shaken vigorously to ensure complete mixing, transferred to ampoules sealed with a Teflon Young's tap, removed from the glove box, and then heated to 80 °C. The reaction was monitored by either GC-MS or a combination of GC-MS and NMR spectroscopy. [b] BBE = saturated bis(boronate)ester. [c] T = toluene, A = acetonitrile. [d] 2 equiv. of B_2pin_2 and 5 mol% of catalyst used. [e] 5 mol% of catalyst used. [f] 1 equiv. of B_2pin_2 used. [g] Conversion determined by ^{1}H NMR spectroscopy.

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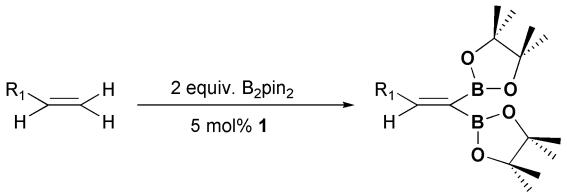
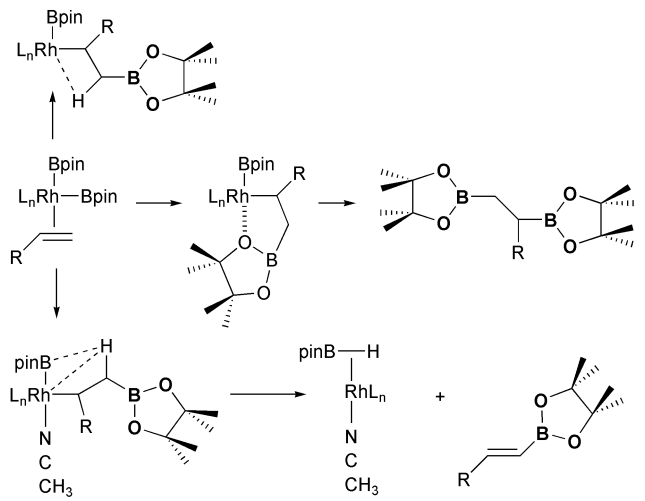
4-$MeOC_6H_4CH=C(Bpin)_2$. Thus, both H's of the $=CH_2$ group were replaced by Bpin in a single catalytic reaction [eqn. (2)].



(2)

Whilst 1,1,2-trisubstituted alkenes proved unreactive, reaction of 0.67 equiv. of B_2pin_2 with α-methylstyrene, a 1,1-disubstituted alkene, in the presence of 3 mol% of **1** in 3 : 1 T:A at 80 °C gave 97% (*E*)-Ph(Me)C=CH(Bpin)† 2% (*Z*)-Ph(Me)C=CH(Bpin) and 1% Ph(Me)(H)C–CH_2Bpin (Entry 4) with 68% conversion. Selectivity was lower using toluene alone (Entry 5) but the reaction was faster; the opposite was true using neat acetonitrile (Entry 6). Conversion was increased to 90% using 5 mol% of **1** in 3 : 1 T : A, and to 100% using 3 mol% **1** with 1 equiv. of B_2pin_2, with excellent selectivity in both cases (Entries 7,8). Again, B_2neop_2 was less selective and with this substrate also less reactive (Entry 9). With 0.67 equiv. of B_2pin_2, 1,1-diphenylethylene was less reactive than α-methylstyrene, most likely due to increased steric bulk, but highly selective, giving 98% VBE (Entry 10); again, using 1 equiv. of B_2pin_2 increased conversion to 100% giving 99% VBE (Entry 11). Interestingly, methylenecyclopentane gave 92% VBE + 4% each of two isomeric derivatives (Entry 12), whereas methylenecyclohexane gave 92% VBE (Entry 13), demonstrating that 1,1-disubstituted alkenes other than styrene derivatives are suitable substrates for the reaction.

Whilst the detailed mechanism of the reaction is not yet known, the following points are worth considering. The simplest pathway (Scheme 1) would involve B–B oxidative addition, and then alkene insertion into Rh–B followed by β-hydride elimination. Interestingly, the boryl ligand migrates preferentially to the least substituted carbon centre with all substrates we have examined. Reductive elimination processes, which can compete with β-hydride elimination, and lead to saturated diboration or hydroboration products, are effectively inhibited when acetonitrile is present. Reductive elimination may be aided by ring strain induced by coordination of a boryl oxygen atom to Rh in the β-borylalkyl intermediate[8] (see Scheme 1). The presence of strongly coordinating acetonitrile may inhibit this chelation, making β-hydride elimination faster than reductive elimination. Finally, the possibility of a β-hydride elimination pathway involving direct B–H bond formation to a *cis*-boryl ligand on Rh (Scheme 1) would provide an alternative to a planar agostic Rh–C–C–H intermediate typically expected for β-H elimination, and would lead to an H–Bpin σ-complex.[9]



Scheme 1 Some mechanistic possibilities for the dehydrogenative borylation reaction.

In conclusion, with appropriate choice of solvent, monosubstituted and 1,1-disubstituted alkenes can be converted directly into useful vinylboronates or even vinyl bis(boronate) esters in high yield and with excellent selectivity *via* catalytic borylation of C–H bonds employing commercially available catalyst and diboron reagents.

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Notes and references

† Selected characterisation data: **4-MeO-C_6H_4CH=C(Bpin)$_2$:** ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.24 (s, 24H, $(Bpin)_2$), 3.79 (s, 3H, CH_3O), 6.81 (m, 2H, C_6H_4), 7.43 (m, 2H, C_6H_4), 7.64 (s, 1H, ArC*H*=); ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$): 30.7 (s, br); MS (EI): *m/z* (rel. int.): 386 (33) [M$^+$], 371 (3) [M$^+$ − Me]. The NOESY NMR spectrum shows a correlation between *ortho* CH on arene ring and CH= of alkene. **(*E*)-PhC(Me)=CH(Bpin)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.3 (s, 12H; Bpin), 2.41 (d, ^3J(H,H) = 1 Hz, 3H, CH_3PhC=), 5.77 (q, ^3J(H,H) = 1 Hz, 1H; =CHBpin), 7.31 (m, 2H, C_6H_5), 7.48 (m, 3H C_6H_5); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 20.1 (s, CH_3PhC =), 24.8 (s, $BO_2C_2(CH_3)_4$), 82.9 (s, $BO_2C_2(CH_3)_4$), 115.5 (s, br, =*C*HBpin), 125.8 (s, C_6H_5), 128.0 (s, C_6H_5), 128.2 (s, C_6H_5), 143.8 (s, C_6H_5), 157.8 (MePh*C*=); ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$) δ 29.0 (s, br); Elemental analysis calcd. (%) for $C_{15}H_{21}O_2B$: C 73.79, H 8.67; found C 73.21, H 8.67; MS (EI): *m/z* (rel. int.): 244 (89) [M$^+$], 229 (24) [M$^+$ − Me]. The NOESY NMR spectrum shows correlations consistent with this molecular geometry.

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