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Rhodium(I) catalysed diboration of (*E*)-styrylboronate esters: molecular structures of (*E*)-*p*-MeO–C_6H_4–CH=CH–B(1,2-$O_2C_6H_4$) and *p*-MeO–C_6H_4–$CH_2C\{B(1,2\text{-}O_2C_6H_4)\}_3$

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Abstract

Diboration of the styrylboronate esters (*E*)-*p*-R–C_6H_4–CH=CH–Bcat (**1**) (R = H, (**1a**) MeO (**1b**); cat = 1,2-$O_2C_6H_4$), with B_2cat_2 in the presence of a variety of rhodium phosphine catalysts gives predominantly either *p*-R–C_6H_4–$CH_2C(Bcat)_3$ (**2**), which contains three boronate ester groups on one carbon atom, or its isomer *p*-R–C_6H_4–CH(Bcat)$CH(Bcat)_2$ (**3**). The formation of **2** apparently involves regiospecific insertion of the vinylboronates into a Rh–B bond followed by β-hydride elimination, another regiospecific insertion of the 2,2-vinyl bis(boronate) into the remaining Rh–B bond followed by C–H reductive elimination leading to 2,2-diboration and a 2,1-hydrogen shift. Wilkinson's catalyst (**7**) gives the highest yields of 2 with 75 and 71% yields from **1a** and **1b**, respectively, while $[Rh(COE)_2(\mu\text{-}Cl)]_2$ (**10**) with two equivalents of P(*o*-tol)$_3$ gave **3** in highest yield with 50 and 49% from **1a** and **1b**, respectively. The crystal structure of (*E*)-*p*-MeO–C_6H_4–CH=CH–Bcat shows the molecule to be essentially planar, with the phenyl ring twisted slightly out of the plane. The tris(boronate) *p*-MeO–C_6H_4–$CH_2C(Bcat)_3$ crystallises with two independent molecules in the unit cell, which differ in the rotational orientation of the phenyl ring in relation to the catecholate groups; the latter are arranged in a propeller-like fashion. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Boron; Diboration; Rhodium; Vinylboronate ester; Diborane (**4**); tris(Boronate) ester

1. Introduction

Transition metal catalysed diboration [1,2] of unsaturated organic compounds is a new tool in the arsenal of synthetic chemists. Platinum-catalysed alkyne diboration is now a well understood [3–10] process which involves a mono-phosphine [5,6,10] complex as the active species. The reactions provide the *syn*-addition product exclusively and new high-efficiency catalysts have been reported [10]. In contrast, the 1,2-addition [11–15] of diborane compounds B_2cat_2 or B_2pin_2 (cat = 1,2-$O_2C_6H_4$; pin = $OCMe_2CMe_2O$) to alkenes remains a challenge, with clean reactions being observed for terminal and strained internal alkenes only using phosphine-free Pt-catalyst precursors [12,13], and for the unstrained internal alkenes *cis*- and *trans*-stilbene and *trans*-β-methylstyrene using an in situ prepared zwitterionic rhodium complex [16] [Rh(dppm)(η^6-catB-cat)]. The difficulty with alkene diborations arises from competing β-hydride elimination and reductive elimination processes which can occur subsequent to alkene insertion into an M–$B(OR)_2$ bond. The β-hydride elimination leads to accompanying dehydrogenative borylation [17–27] and hydroboration [28–30] processes. For example, we have observed [1,11] up to nine products arising from the metal-catalysed addition of B_2cat_2 to 4-vinylanisole, with yields of up to ca. 25% of the unusual tris(boronate) ester 4-MeO–$C_6H_4CH_2C(Bcat)_3$ (2,2,2-TBE). Compounds such as (2,2,2-TBE), containing three or even four boronate groups on a single carbon atom [31–33], are relatively rare but are very interesting due to their documented

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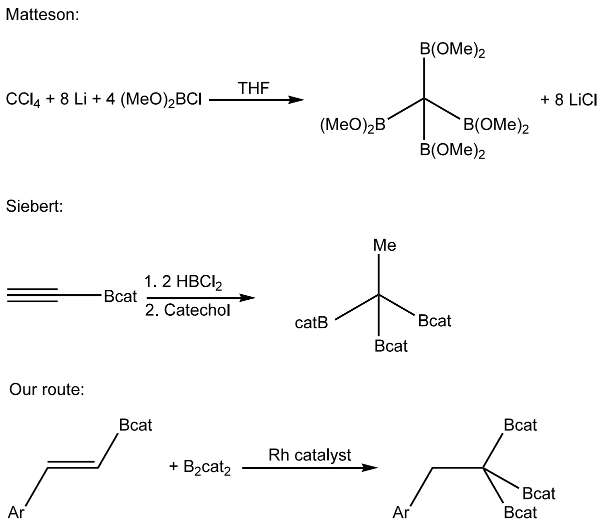
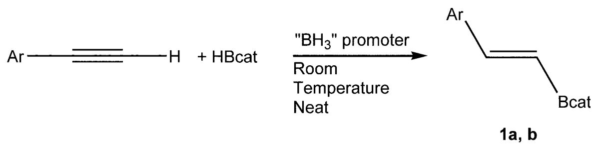
reactivity arising from the stabilisation of a carbanion centre by the α-boronate ester moieties. Previous routes to these compounds, developed [31–33] by Matteson and co-workers, required reactions of $RCCl_3$ with $ClB(OR')_2$ and lithium metal (Scheme 1), and these could prove difficult to control. More recently, Siebert et al. reported [34] the syntheses of tris(boronate) esters via hydroboration of alkynylboronates using $HBCl_2$ (Scheme 1). We report herein a catalytic route to the tris(boronate)esters in good yield under mild conditions and in a single step from readily accessible vinylboronates (VBEs).

2. Results and discussion

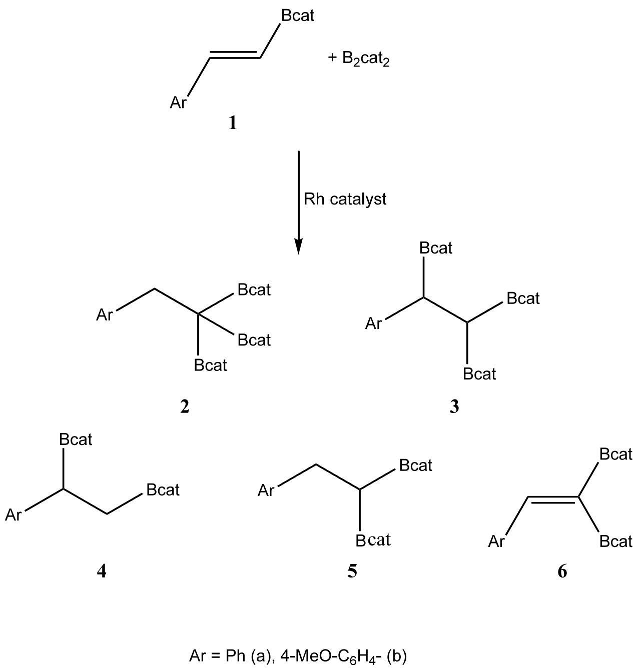
The styrylboronate esters (VBEs) were prepared in high yields via conventional hydroboration [35,6] of the corresponding ethynylbenzenes with HBcat, Eq. (1). While this reaction would typically [35,36] require a temperature of ca. 80 °C, the use of HBcat containing a small amount of 'BH_3' impurity, resulting from the redistribution [37–39] of HBcat to B_2cat_3 and BH_3, allowed the reaction to proceed rapidly at ambient temperature in the absence of solvent [40–43]. Compounds **1a** and **1b** were subsequently reacted with B_2cat_2 in the presence of 1 mol% catalyst and heated to 58 °C for 12 h using THF as solvent. The products obtained are shown in Scheme 2, and product distributions, determined by high-field ^1H-NMR spectroscopy, are given Table 1. In general, there is a similarity in the product distributions resulting from the diboration of either **1a** or **1b**. The catalyst precursor $[Rh(PPh_3)_3Cl]$ (**7**), gave the highest yield of **2**, 75 and 71% for **1a** and **1b**, respectively, with the reactions essentially going to completion. Yields of **3**, **4** and **5** were between 5 and 15%. The use of **7** in the presence of ten equivalents of PPh_3 again gave predominantly **2**, but proved slightly less selective than **7** alone, giving 62 and 70% yields with **1a** and **1b**, respectively. The zwitterionic catalysts $[Rh(dppb)(\eta^6\text{-catBcat})]$ (**8**) and $[Rh(dppm)(\eta^6\text{-catBcat})]$ (**9**), formed as shown in Eq. (2), also yielded **2** predominantly (63 and 67% for **8**, 66 and 74% for **9**, for **1a** and **1b**, respectively). Reactions with **8** were 87–94% complete in 12 h but reaction with **9** only achieved 67–79% completion in this time. The 74% yield of **2b** using **9**, however, was the highest obtained for this substrate.



Scheme 1. Published routes to tetra and tris boronate esters.



Equation (1). 'BH_3' promoted hydroboration of ethynylarenes.



Scheme 2. Products resulting from the diboration of **1**.

The use of $[Rh(COE)_2(\mu\text{-Cl})]_2$ (**10**) in the presence of two equivalents of $P(o\text{-tol})_3$, one equivalent per Rh as shown in Eq. (3), gave the highest yields of **3** of 50 and 49% for **1a** and **1b**, respectively, with completions of at least 96%.

The use of four equivalents of $P(o\text{-tol})_3$ (two equivalents per Rh) gave very similar product distributions and hence it would appear that only one $P(o\text{-tol})_3$ binds to Rh. This was confirmed by the reaction of $[Rh(COE)_2(\mu\text{-Cl})]_2$ with one equivalent $P(o\text{-tol})_3$ per Rh which gave rise to one doublet at δ 50.7 (J_{P-Rh} = 190 Hz) in the $^{31}P\{^1H\}$-NMR spectrum; addition of two equivalents per Rh resulted in the same doublet and also a singlet at δ −28.7 due to free $P(o\text{-tol})_3$. Using **10** in

Table 1

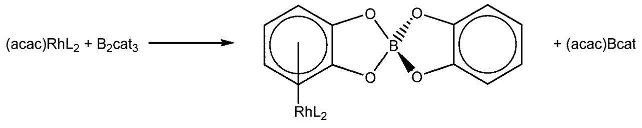
Product distributions for the diboration of **1a** and **1b** with different rhodium catalysts

Catalyst	Substrate	$ArCH_2C(Bcat)_3$ (**2**)	$ArCH(Bcat)CH(Bcat)_2$ (**3**)	$ArCH(Bcat)CH_2(Bcat)$ (**4**)	$ArCH_2CH(Bcat)_2$ (**5**)	$ArCH=C(Bcat)_2$ (**6**)	Completion [a]
$[Rh(PPh_3)_3Cl]$ (**7**)	**1a**	75	9	6	5	4	91
	1b	71	15	7	6	1	96
$[Rh(PPh_3)_3Cl]$ (**7**)$+10PPh_3$	**1a**	62	13	10	9	7	93
	1b	70	17	2	3	7	91
$[Rh(dppb)(\eta^6\text{-catBcat})]$ (**8**) [b]	**1a**	63	6	14	10	7	87
	1b	67	5	15	8	5	94
$[Rh(dppm)(\eta^6\text{-catBcat})]$ (**9**) [b]	**1a**	66	17	5	5	8	79
	1b	74	15	Trace	3	8	67
$[Rh(COE)_2(\mu\text{-Cl})]_2$ (**10**)	**1a**	3	50	0	32	15	96
$+2P(o\text{-tol})_3$	**1b**	11	49	0	35	5	99
$[Rh(COE)_2(\mu\text{-Cl})]_2$ (**10**)	**1a**	1	47	0	31	21	98
$+4P(o\text{-tol})_3$	**1b**	8	48	0	33	11	98
$[Rh(COE)_2(\mu\text{-Cl})]_2$ (**10**)	**1a**	49	7	8	23	14	77
$+2PPh_2(o\text{-tol})$	**1b**	47	7	9	22	16	76
$[Rh(COE)_2(\mu\text{-Cl})]_2$ (**10**)	**1a**	30	45	5	15	4	84
$+2PCy_3$	**1b**	38	37	4	16	6	87
$[Rh(dppb)(\eta^6\text{-catBcat})]$ (**8**)	**1a**	70	6	11	7	6	100
+excess B_2cat_2 [c]	**1b**	73	8	11	6	2	100
$[Rh(COE)_2(\mu\text{-Cl})]_2$ (**10**)	**1a**	3	53	0	35	9	98
$+4P(o\text{-tol})_3$+excess B_2cat_2 [c]	**1b**	7	51	0	36	7	100

[a] Completion was calculated as the percentage of boron-containing products relative to the sum of products plus any unreacted (**1**).

[b] Generated in situ as shown in Eq. (2).

[c] A threefold excess of B_2cat_2 relative to **1** was used.



8a - L_2 = dppb
9a - L_2 = dppm
8 - L_2 = dppb
9 - L_2 = dppm

Equation (2). Formation of [$RhL_2(\eta^6$-catBcat)].

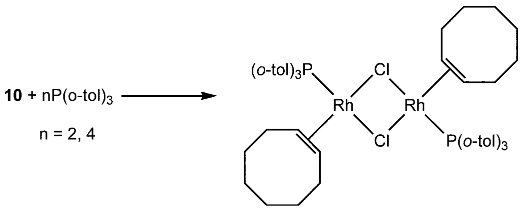
combination with two equivalents of the less bulky phosphines PPh_2(*o*-tol) or PCy_3 (i.e. P:Rh = 1:1), gave yields of **3** which were lower than those found for P(*o*-tol)$_3$. Thus, PPh_2(*o*-tol) gave mainly **2** (~ 50%), whereas PCy_3 gave a nearly even split in distributions of both **2** and **3**. It is clear, therefore, that cone angle, and possibly basicity, of the phosphine are important factors in the product distributions obtained.

Commercially available [$Pt(COD)Cl_2$], which has been shown to diborate alkenes,[15] failed to diborate **1a** and **1b** but considerable reaction with the THF solvent was observed. Repeating the reaction in benzene showed no diboration to have taken place.

Two reactions were conducted using a threefold excess of B_2cat_2, relative to **1**, with catalyst **8**, which had given predominantly **2**, and catalyst **10**+4P(*o*-tol)$_3$, which had given predominantly **3**. In both cases, the product distributions were similar to those obtained in reactions employing one equivalent of B_2cat_2. In the former case, a small increase in the yield of **2** was observed whereas in the latter case, the yield of **3** was slightly increased. In both cases the reactions went to completion indicating some rate dependence on B_2cat_2 concentration.

A plausible schematic catalytic cycle is shown in Scheme 3. In this, oxidative addition of B_2cat_2 to the Rh centre forms an unsaturated bis-boryl complex, of which [$RhCl(Bcat)_2(PPh_3)_2$] is representative [44,45]. Coordination of **1** is followed by insertion of the alkene linkage into a Rh–B bond. Reductive elimination of the B–C bond yields **3**. Alternatively, β-hydride elimination gives **6**, and an [Rh(H)(Bcat)] species. Subsequent addition of HBcat, via this complex, to **1** gives **4** or **5**, and addition to **6** yields **2**.

As discussed previously [18,46] the regiochemistry of compound **2** is consistent with insertion of the styryl C=C unit into a Rh–B bond, in such a fashion as to give an η^3-benzyl intermediate. The presence of two Bcat groups on the terminal carbon of the η^3-benzyl intermediate enhances the rate of β-hydride elimination leading to **6**. This then reinserts into the Rh–B bond of the [Rh(H)(Bcat)] intermediate with the same regiochemistry to give a 2,2,2-trisboronate-η^3-benzyl complex, with no remaining β-hydrogen, and hence C–H reductive elimination leads to **2**. Thus, the overall catalytic process involves both diboration and a 1,2-hydrogen shift. The high yield of **2** in particular is a result of the tendency of alkyl–Rh complexes with β-boryl groups to undergo rapid β-hydride elimination. If **6** were to insert into the Rh–B bond of a [$Rh(Bcat)_2$] intermediate, this would lead to a tetra(boronate) product which we have not yet identified, vide infra.



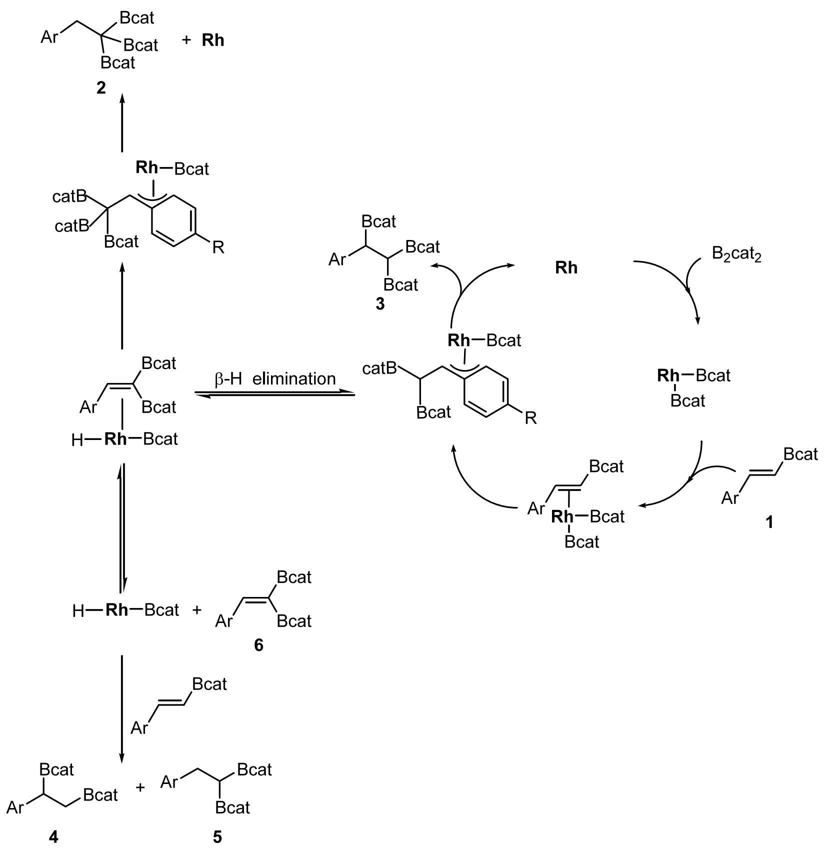
Equation (3). Reaction of [$Rh(COE)_2(\mu$-$Cl)]_2$ with P(*o*-tol)$_3$.

It is clear from Table 1 that the presence of bulkier phosphines in the catalyst precursor produces significantly larger quantities of **5** in relation to **4** and, with P(*o*-tol)$_3$, no **4** is produced at all. This phosphine also provides the highest yield of **3**. Thus, with the bulkiest phosphine, our results suggest that insertion of C=C(Bcat) into the Rh–B bond in a [$Rh(Bcat)_2$] intermediate may take place with either of the two possible regiochemistries. If it inserts as discussed above to give the η^3-benzyl intermediate, β-hydride elimination again gives **6**+[Rh(H)(Bcat)] whereas reductive elimination would give **3**. However, if it inserts the other way around giving [Rh(Bcat)(CH(Bcat)CH(Bcat)Ar)], which should be favoured on steric grounds, reductive elimination of the B–C bond yielding **3** is rapid compared with β-hydride elimination. Likewise, insertion of VBE into the Rh–H bond of any [Rh(H)(Bcat)] present would likely lead to [$Rh(Bcat)(CH(Bcat)CH_2Ar)$], again on steric grounds, giving **5** after B–C reductive elimination.

The significance of the experiments conducted in the presence of excess B_2cat_2 is as follows. If the mechanism involved a Rh(I) mono-boryl [Rh(Bcat)] species which inserts C=C(Bcat) to give e.g. [$Rh^I(CHArCH(Bcat)_2)$], we could envisage reaction of this species with B_2cat_2 to give [$Rh^{III}(Bcat)_2(CHArCH(Bcat)_2)$] which would yield **3** by reductive elimination regenerating [Rh^I(Bcat)]. This would compete with β-hydride elimination to give [Rh^I(H)]+**6**. One would have expected this partitioning to be dependent strongly on the concentration of B_2cat_2. In fact, we see a small rise in the formation of **2** with catalyst **8** for which **2** already predominated, and a rise in formation of **3** with catalyst (**10**+4P(*o*-tol)$_3$) for which **3** already predominated. Thus, our results do not support a Rh(I) boryl pathway to be operating here.

Clearly, the reaction is rather complex and a detailed mechanistic interpretation is not yet possible although some of the basic features have been identified.

As discussed above, products **2** and **3** result from the diboration of **1** by B_2cat_2. The formation of **6** generates HBcat, which reacts with **1** to give **4** and **5**. The fact that the total amount of **4** and **5** is always greater than the amount of **6**, however, indicates that there is either an excess of hydrogen or a deficiency of boron in the



Scheme 3. Plausible schematic catalytic cycle for the diboration of **1**.

observed product mixture. One possibility is that small amounts of highly boronated organic species are present, such as ArCH(Bcat)C(Bcat)$_3$ (**11**) or ArC(Bcat)= C(Bcat)$_2$ (**12**), which result from the diboration and dehydrogenative borylation of **6** respectively. Both would be virtually undetectable by NMR spectroscopy in the complex product mixtures, for Ar = Ph, and very difficult to assign unambiguously for Ar = MeOC$_6$H$_4$. Thus **11** would give only a weak singlet in the region δ 3-4, probably obscured by **2**, and an MeO singlet for **11b**. Complex **12a** would contain only aromatic hydrogens and **12b** an additional MeO singlet. Both **11** and **12** would also be undetectable by GC/MS under conditions we typically employ. It is also possible that some B$_2$cat$_3$ is being formed as a decomposition product. Although rigorous techniques are employed to avoid the presence of any water, the possibility of small amounts of surface –OH on glass vessels cannot be ignored as a source of H in these small scale reactions. Additionally, there is evidence for the formation of THF-oligomers in reactions using [Rh(COE)$_2$(μ-Cl)]$_2$/*n*PR$_3$ catalyst precursors, and it is possible that these could be partially boronated in some way.

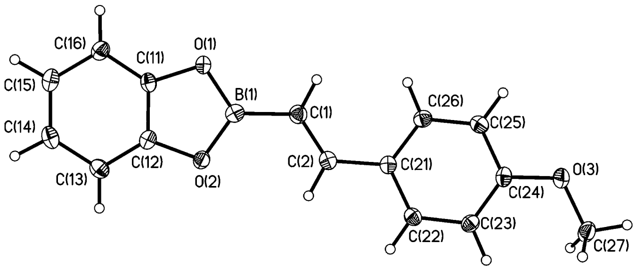


Fig. 1. Molecular structure of **1b**. Ellipsoids shown at 50% probability for non-H atoms, with H atoms shown as circles of arbitrary radius.

The molecular structures of **1b** and **2b** are shown in Figs. 1 and 2, respectively, and important bond lengths and angles are listed in Table 2. In the solid state, **1b** is essentially planar with a slight twist (ca. 10°) of the phenyl ring out of the plane of the molecule. This twist is due presumably to a packing effect, resulting from an intermolecular π-interaction between catecholate and adjacent phenyl groups in an asymmetric manner. The sum of the angles around the boron atom is 360.0(1)°. Bond lengths and angles are comparable to the literature values for **1a** [47]. Compound **2b** crystallises in space group P$\bar{1}$ with two unique molecules in the crystallographic asymmetric unit. The two molecules differ predominantly in the rotational orientation of the MeOC$_6$H$_4$ moiety with respect to the catecholate groups; the latter are arranged in a propeller-like fashion. Bond lengths are comparable to analogous values in CH$_3$C(Bcat)$_3$ [34], which crystallises with three THF solvent molecules in the unit cell.

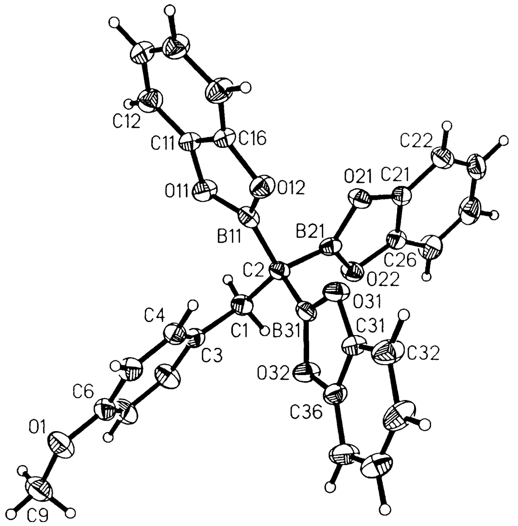


Fig. 2. Molecular structure of one of the two independent molecules in the asymmetric unit of **2b**. Ellipsoids shown at 50% probability for non-H atoms, with H atoms shown as circles of arbitrary radius.

Table 2
Selected bond lengths (Å) and bond angles (°) for **1b** and **2b**

	1b	**2b**	
		Molecule A	Molecule B [a]
Bond lengths (Å)			
C(1)–C(2)	1.340(2)	1.557(5)	1.549(4)
C(1)–B(1)	1.532(2)		
B(1)–O(1)	1.3954(19)		
B(1)–O(2)	1.3937(19)		
C(11)–O(1)	1.3848(17)		
C(2)–C(21)	1.470(2)		
B(11)–C(2)		1.557(5)	1.561(5)
B(21)–C(2)		1.577(5)	1.572(5)
B(31)–C(2)		1.561(5)	1.565(5)
B(11)–O(11)		1.390(5)	1.393(5)
B(11)–O(12)		1.380(5)	1.388(5)
B(21)–O(21)		1.385(4)	1.378(4)
B(21)–O(22)		1.376(4)	1.391(5)
B(31)–O(31)		1.380(5)	1.386(4)
B(31)–O(32)		1.381(4)	1.374(4)
Bond angles (°)			
O(1)–B(1)–O(2)	111.32(13)		
O(1)–B(1)–C(1)	123.98(14)		
O(2)–B(1)–C(1)	124.70(14)		
O(11)–B(11)–O(12)		110.6(3)	110.4(3)
O(21)–B(21)–O(22)		111.2(3)	111.8(3)
O(31)–B(31)–O(32)		111.2(3)	110.3(3)
B(11)–C(2)–B(21)		106.0(3)	103.9(3)
B(11)–C(2)–B(31)		112.8(3)	111.2(3)
B(21)–C(2)–B(31)		103.9(3)	103.8(3)
C(1)–C(2)–B(11)		112.5(3)	113.1(3)
C(1)–C(2)–B(21)		110.3(3)	110.3(3)
C(1)–C(2)–B(31)		110.9(3)	113.6(3)

[a] Compound **2b** contains two independent molecules in the asymmetric unit. Equivalent atoms in molecule B are primed.

3. Conclusion

The catalysed diboration of styrylboronate esters provides a novel route to **2** and **3** under mild conditions using readily available boron reagents, with selectivity between the two isomeric products depending on the catalyst used. Whilst **3** represents 1,2-addition of the two borons to the C=C double bond, formation of **2** involves a 1,2-hydrogen shift and addition of both borons to a single carbon centre.

4. Experimental

All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques or an Innovative Technology, Inc. System 1 glove box. Glassware was oven dried before transfer into the glove box. THF was dried over sodium/benzophenone and $CDCl_3$ was dried over calcium hydride; both were distilled under nitrogen. B_2cat_2 was prepared by established procedures (see, for example, Refs. [48–50]) and checked for purity by NMR spectroscopy and GC/MS techniques. The catalyst precursors $[Rh(PPh_3)_3Cl]$ [51,52], $[Rh(COE)_2(\mu\text{-}Cl)]_2$ [53], [Rh(dppb)(acac)] [54] and [Rh(dppm)(acac)] [16,54] were prepared using published procedures and checked for purity by NMR spectroscopy. Phosphines were purchased from Aldrich or Strem and were checked for purity by ^1H- and $^{31}P\{^1H\}$-NMR spectroscopy before use. ^1H-NMR experiments were performed on Varian Inova 500 and Varian C 500 spectrometers and were referenced to residual protio-solvent resonances. $^{31}P\{^1H\}$-NMR experiments were performed on either Varian Unity 200 or a Varian VXR-400 instruments and were referenced to external 85% H_3PO_4. $^{11}B\{^1H\}$-NMR experiments were performed on a Bruker AC200 instrument and were referenced to external $BF_3 \cdot OEt_2$. Coupling constants are reported in Hertz (Hz).

4.1. Synthesis of (*E*)-*p*-R–C_6H_4–CH=CH–Bcat

The compounds phenyl acetylene or 4-methoxyphenylethyne (0.0196 mol) and HBcat containing 'BH_3' impurity (2.35g, 0.0196 mol) in a round-bottom flask were stirred at ambient temperature for 1 h, after which an orange solid resulted. Successive recrystallisations from Et_2O + hexane (50:50) at −30 °C gave pure **1** as a white solid (~83% yield). For spectroscopic data see Refs. [21,44,47].

4.2. General procedure for the catalysed diboration of styrylboronate esters

A solution of B_2cat_2 (54 mg, 0.23 mmol), styrylboronate ester (0.23 mmol) and catalyst precursor (0.0023 mmol Rh) in THF (1.5 ml) was heated to 58 °C under N_2 in a ca. 10 ml tube sealed with a Young's tap. After 12 h, the solution was allowed to cool to room temperature and the solvent removed in vacuo. The crude reaction mixture was then dissolved in $CDCl_3$ and analysed by high field ^{1}H-NMR spectroscopy.

4.2.1. Selected NMR data ($CDCl_3$) and elemental analyses for boron containing products (see also Refs. [21] and [44])

2a: δ 3.83 (s, 2H, $CH_2C(Bcat)_3$), 7.02–7.41 (ov. m, 17H, catecholate+phenyl H); $^{11}B\{^1H\}$ δ 35.3; $^{13}C\{^1H\}$ δ 33.6, 112.7, 122.9, 126.4, 128.7, 128.9, 141.4, 148.4. The $C(Bcat)_3$ resonance was not observed due to severe quadrupolar broadening. Anal. Calc. $C_{26}H_{19}B_3O_6$: C, 67.91; H, 4.16. Found: C, 68.09; H, 4.37%.

2b [21]: δ 3.67 (s, 3H, OCH_3), 3.83 (s, 2H, $CH_2C(Bcat)_3$), 6.66 (m, 2H, p-C_6H_4), 7.05-7.10 (ov. m. 8H, catecholate+p-C_6H_4), 7.25 (m, 6H, catecholate H); $^{11}B\{^1H\}$ δ 37.2; $^{13}C\{^1H\}$ 32.9, 55.2, 112.7, 113.9, 122.9, 129.8, 133.6, 148.4, 158.4. The $C(Bcat)_3$ resonance was not observed due to severe quadrupolar broadening.

3a: δ 2.75 (d, $J_{H-H}=11.7$, 1H, $CH(Bcat)_2$), 3.69 (d, $J_{H-H}=11.7$, 1H, CHBcat).

3b: δ 2.68 (d, $J_{H-H}=11.5$, 1H, $CH(Bcat)_2$), 3.69–3.74 (ov. m, 4H, CHBcat+OCH_3), 6.78 (m, 2H, p-C_6H_4), 7.01 (m, 2H, catecholate H), 7.14 (m, 2H, catecholate H), 7.33 (m, 2H, p-C_6H_4); $^{11}B\{^1H\}$ δ 23.8; $^{13}C\{^1H\}$ 13.6, 27.0, 55.2, 112.5, 112.6, 114.4, 122.7, 122.8, 129.0, 129.3, 140.0, 148.3, 158.1.

4a: δ 1.93 (second-order dd, 1H, CH_2Bcat), 2.19 (second-order dd, 1H, CH_2Bcat), 3.36 (second-order dd, 1H, $CH(Bcat)_2$, 7.00–7.08 (m, 4H, catecholate H), 7.13–7.20 (m, 4H, catecholate H), 7.27–7.41 (m, 5H, phenyl H); $^{11}B\{^1H\}$ δ 36.8. Anal. Calc. $C_{20}H_{16}B_2O_4$: C, 70.25; H, 4.72. Found: C, 70.12; H, 4.70%.

4b [21,44]: δ 1.88 (second-order dd, 1H, CH_2Bcat), 2.12 (second-order dd, 1H, CH_2Bcat), 3.28 (second order dd, 1H, CHBcat), 3.76 (s, 3H, OCH_3), 6.85 (m, 2H, p-C_6H_4), 7.00–7.18 (ov. m, 8H, catecholate H), 7.33 (m, 2H, p-C_6H_4); $^{11}B\{^1H\}$ δ 37.1.

5a: δ 2.12 (t, $J_{H-H}=7.8$, 1H, $CH(Bcat)_2$), 3.69 (d, $J_{H-H}=7.8$, 2H, CH_2).

5b: δ 2.12 (t, $J_{H-H}=7.8$, 1H, $CH(Bcat)_2$), 3.66 (d, $J_{H-H}=7.8$, 2H, CH_2).

6a [55] and **6b**: δ 8.40 (s, 1H, $CH{=}C(Bcat)_2$).

4.3. Crystallography

A colourless crystal of **1b** dimensions 0.30 × 0.15 × 0.05 mm was used for the single crystal structure determination. Data were collected using graphite monochromated Mo–K_α radiation ($\lambda = 0.71073$) on a Bruker SMART-CCD 1K detector diffractometer equipped with a Cryostream N_2 flow cooling device [56]. Series of narrow ω-scans (0.3°) were performed at several ϕ-settings in such a way as to cover a sphere of data to a maximum resolution of 0.77 Å. Cell parameters were determined and refined using the SMART software [57] from the centroid values of 5356 reflections with 2θ values between 5 and 55°. Raw frame data were integrated using the SAINT program [58]. The structure was solved using Direct Methods and refined by full-matrix least squares on F^2 using SHELXTL [59]. The reflection intensities were corrected for absorption and other effects by the multi-scan method [60] based on multiple scans of identical and Laue equivalent reflections, $T_{max}=0.995$, $T_{min}=0.973$. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters (adps). Hydrogen atoms were located from difference Fourier maps and their coordinates and isotropic adps refined.

Table 3
Crystal data and processing parameters for **1b** and **2b**

	1b	**2b**
Empirical formula	$C_{15}H_{13}BO_3$	$C_{27}H_{21}B_3O_7$
Formula weight	252.1	489.9
Temperature (K)	105(2)	180
Diffractometer	Bruker SMART-CCD 1K	Siemens $R3m/v$
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	6.8374(8)	9.607(3)
b (Å)	24.170(3)	13.307(5)
c (Å)	7.4719(8)	20.485(7)
α (°)	90	99.34(3)
β (°)	94.102(2)	90.65(3)
γ (°)	90	94.06(3)
V (Å^3)	1231.2(2)	2383.1(14)
D_{calc} (Mg m^{-3})	1.360	1.365
Z	4	4
μ (Mo–K_α) (mm^{-1})	0.093	0.096
$F(000)$	528	1016
θ Range for data collected (°)	1.69–27.49	2.0–22.5
Reflections collected	12831	6284
Independent reflections	2822	6284
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares using 4099 data for which $F > 6.0\sigma(F)$
Goodness-of-fit on F^2	1.066	1.92 [a]
Final R indices	$R_1 = 0.0425$ [b], $wR_2 = 0.0906$ [b]	$R_1 = 0.0371$ [c], $wR_2 = 0.0369$ [c]
R indices (all data)	$R_1 = 0.0577$, $wR_2 = 0.0971$	$R_1 = 0.0563$, $wR_2 = 0.0382$
Largest difference peak and hole (e Å^{-3})	0.268 and −0.241	0.21 and −0.17

[a] $GoF = [\Sigma_w(|F_o|-|F_c|)^2/(NO-NV)]^{1/2}$.
[b] $[I > 2\sigma(I)]$.
[c] $[F > 6\sigma(F)]$.

Data for **2b** were collected from a colourless prism of dimensions 0.29 × 0.20 × 0.44 mm mounted on a glass fibre, using ω scans with variable scan rates (2.93–29.3°

$\min^{-1}$). From a total of 6284 reflections, 4099 with $F > 6.0\sigma(F)$ were used in the structure solution and refinement [61]. Data were collected for Lorentz and polarisation effects, and for absorption (face indexed numerical method). The structure was solved by direct methods and Fourier techniques and refined by full matrix least squares. Hydrogen atoms were located in difference maps and refined anisotropcially (riding model). An empirical weighting scheme $w^{-1} = \sigma^2(F)$ was employed. Scattering factors and anomalous dispersion coefficients were taken from Ref. [62]. Crystal data and processing parameters for the two structures are given in Table 3.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 172402 and 172548. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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