Rhodium catalysed dehydrogenative borylation of alkenes: Vinylboronates *via* C–H activation†

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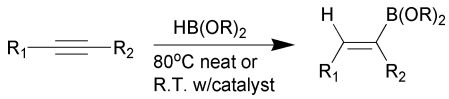
We present herein a high yield, highly selective catalytic synthesis of vinylboronate esters (VBEs), including 1,1-disubstituted VBEs, from alkenes without significant hydrogenation or hydroboration, using the simple catalyst precursor, *trans*-[RhCl(CO)(PPh_3)$_2$] (**1**), and the diboron reagents B_2pin_2 (**2a**, pin = pinacolato = $OCMe_2CMe_2O$) or B_2neop_2 (**2b**, neop = neopentylglycolato = $OCH_2CMe_2CH_2O$), or the monoboron reagent HBpin, all of which are commercially available. The reactions were conducted at 80 °C using conventional heating, or in a microwave reactor at 150 °C.

Introduction

Vinylboronate esters (VBEs) are useful synthetic intermediates in many reactions, including C–C bond formation *via* Pd-catalysed Suzuki–Miyaura cross-coupling.[1] VBEs are also important for homologation to prepare chiral allylboronates,[2] in Diels–Alder reactions,[3] in multicomponent chiral amine synthesis,[4] in the preparation of chiral cyclopropanones,[5] and in Heck reactions.[6] They can be prepared by uncatalysed[7] or metal catalysed[8] hydroboration of alkynes, eqn (1). Recently, VBEs have been synthesised by Pd-catalysed cross-coupling of alkenyl halides or triflates with B_2pin_2,[9] eqn (2), by reaction of 1-halo-1-lithioalkenes and HBpin at −110 °C,[10] eqn (3), by Pt-catalysed 1,2-diboration of alkynes,[11] eqn (4), by Pd-catalysed diboration of methylenecyclopropanes,[12] eqn (5) and by Pd-catalysed borylsilylation or borylstannylation of 1,2-dienes,[13] eqn (6). Other interesting procedures for the formation of VBEs include Miyaura's unusual *trans*-hydroboration of alkynes,[14] presumably taking place *via* a vinylidene intermediate, eqn (7), the Ru-catalysed olefin cross-metathesis of vinyl boronates and alkenes,[15] eqn (8), catalytic boryl group transfer from a VBE to an alkene,[16] eqn (9), and the enyne cross metathesis reaction between alkynylboronates and terminal alkenes,[17] eqn (10). An exciting alternative is the catalytic dehydrogenative borylation of alkenes,[8a,18] eqn (11), a C–H bond functionalisation process which would allow the direct synthesis of 1,1-disubstituted VBEs that cannot be made *via* the hydroboration of alkynes. However, conditions must be found wherein the H_2 produced is *not* consumed *via* hydrogenation of half of the alkene substrate. In 1992, Brown *et al.*[18a,c] showed that reaction of 4-vinyl anisole (VA) with *N*-isopropyl oxazaborolidine in the presence of an [(η^2-alkene)$_2$RhCl]$_2$ complex gave the *trans*-VBE and ethyl anisole in a 1 : 1 ratio. Several reports followed using Rh,[8a,18a–c,g,h,j] Ti,[18d,f] Ru,[18e,j,l] Pd[18i] and Pt[18i] catalysts and $(RO)_2BH$ reagents, but only in one case[18b] was the VBE produced in the absence of significant hydrogenation, and a 1,1-disubstituted alkene was employed. The main problem is that most catalysts used in these reactions are efficient hydrogenation and/or hydroboration catalysts. Thus, in order to overcome competing hydrogenation and/or hydroboration of the alkene substrate, catalyst systems must be capable of carrying out the dehydrogenative borylation reaction, but must show little or no catalytic activity in alkene hydrogenations or hydroborations under the conditions employed. We present herein a high yield, highly selective catalytic synthesis of VBEs, including 1,1-disubstituted VBEs, from alkenes without significant hydrogenation or hydroboration using the simple catalyst precursor, *trans*-[RhCl(CO)(PPh_3)$_2$] (**1**), and the diboron reagents B_2pin_2 (**2a**) or B_2neop_2 (**2b**), or the monoboron reagent HBpin, all of which are commercially available. Preliminary results of this study have been communicated.[18k]



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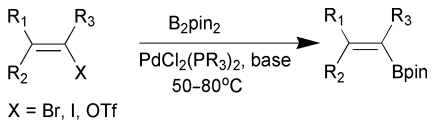

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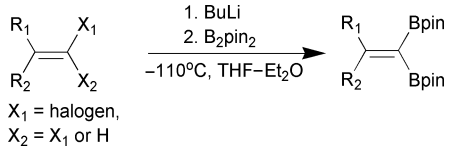

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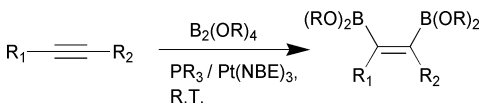

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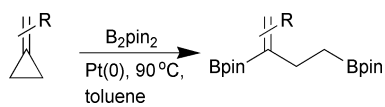

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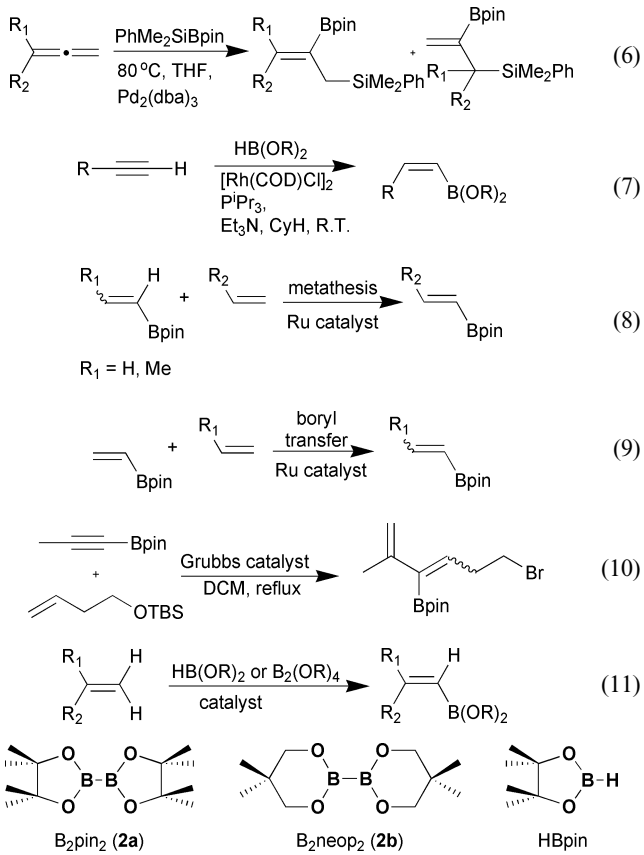
† This paper is dedicated to Prof. Ken Wade, FRS, on the occasion of his 75th birthday, in recognition of his numerous contributions to boron (and other!) chemistry.



Results and discussion

In the course of our studies on alkene diboration,[19] we examined the reaction of 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, vinylbis(boronate) esters (VBBEs). In contrast, the reaction in CH_3CN was clean, but the rate was much slower than that in toluene, for example. We therefore examined the reaction in 3 : 1 toluene–acetonitrile (3 : 1 T–A) which proved an excellent compromise between selectivity and rate. In our preliminary study,[18k] the yields and selectivities were determined by *in situ* GC-MS which, for truly quantitative analysis, requires a knowledge of the response factors for the starting materials and products, which in turn, requires their isolation and calibration against standards. However, as some of the compounds or isomers were only produced in very small quantities, this was not possible in all cases. We relied on our previous experience in which related reaction mixtures had been studied by a combination of *in situ* NMR spectroscopy and GC-MS, which showed that isomeric hydroboration products have quite similar response factors. In order to improve the accuracy of our measurements in the current study, we re-examined all of the previous reactions, and carried out all new reactions, in deuterated solvents in order to obtain both *in situ* GC-MS and NMR spectra of the crude reaction mixtures, using long enough relaxation times to insure accurate integrations. To this end, we chose to examine these reactions in 3 : 1 C_6D_6–CD_3CN (3 : 1 d_6–d_3). For completeness, we also examined the reactions in protio benzene–acetonitrile (3 : 1) and compared these results to those which were obtained from the reactions in toluene–acetonitrile (3 : 1 T–A), and we found no difference between toluene and benzene as solvents. The results presented herein are those obtained *via in situ* NMR spectroscopy. In general, this data is, as expected, quite similar to that obtained by GC-MS, with the notable exception that hydroboration products appear to have somewhat larger MS response factors than expected, such that amounts of these were slightly overestimated in the preliminary studies.

Dehydrogenative borylations using conventional heating

Firstly, we examined the mono substituted alkenes, styrene and 4-vinylanisole (VA). The reaction of styrene with 0.67 equiv. of **2a** and 3 mol% of **1** in 2 ml of (3 : 1 d_6–d_3) at 80 °C gave 100% conversion in 5 days by NMR spectroscopy (Table 1, entry 1) with 86% selectivity for *trans*-VBE (*i.e.* (*E*)-VBE) and 11 and 3% selectivity for the 2,2-vinylbis(boronate) ester (VBBE) and hydroboration, respectively. On the other hand, the conversion by GC-MS was 100% with 66% selectivity for VBE, 19 and 4% selectivity for two hydroboration isomers and 11% selectivity for VBBE. Thus, as noted above, the hydroboration products appear to have a higher response factor than the VBE or VBBE in the GC-MS. It is also worth noting that the (*E*)-VBE isomer is produced in all of the dehydrogenative borylations of the styrene derivatives.

The reaction of VA with 0.67 equiv. of **2a** and 3 mol% of **1** gave 99% conversion during 2 days by NMR spectroscopy with 93% selectivity for VBE and 7% hydroboration. It appears, from ^{1}H NMR spectroscopy, that small amounts of both terminal and internal hydroboration isomers are produced, with the internal one predominating (Table 1, entry 2). As only 0.67 equiv. of **2a** was used, it is evident that both boron atoms of **2a** are being incorporated into the product. As will be shown below from studies with disubstituted alkenes, it is likely that most of the hydroboration byproduct arises after the diboron reagent is consumed, at which point HBpin becomes the boron source.

In an investigation of **2b** as a source of boron, VA was reacted with 0.67 equiv. of **2b** and 3 mol% of **1**, giving 44% conversion over 2 days and 65% over 4 days by NMR spectroscopy with complete selectivity for VBE (Table 1, entries 3 and 4). When the concentration of **2b** was increased to 1 equiv. under the above conditions, after 2 days NMR spectroscopy showed 100% conversion and excellent selectivity for the VBE (Table 1, entry 5), although small amounts of what appears to be the 2,2-vinylbis(boronate) ester (VBBE), *vide infra*, are also formed. Thus, **2b** is also an effective reagent for the diboration of alkenes, and indeed, is somewhat more reactive than **2a** with this substrate. Interestingly, reaction of VA with 2 equiv. of **2a** and 5 mol% of **1** (Table 1, entry 6) gave 93% selectivity for VBBE and 7% VBE by NMR spectroscopy. Thus, both hydrogens of the $=CH_2$ group can be replaced by Bpin in a single catalytic reaction.

The reaction of 1-octene with 0.67 equiv. of **1a** and 3 mol% catalyst (Table 1, entry 7) gave 100% conversion with 67% selectivity for a mixture of VBBEs with 33% mono-dehydrogenative borylation product (VBE) produced. The GC-MS showed 100% conversion with 66% selectivity for VBBEs, of which 60% is the $C_6H_{13}CH{=}C(Bpin)_2$ isomer, with 34% of a mixture of VBEs produced. This distribution of products likely results from the

Table 1 Product distribution and conversion for the dehydrogenative borylation of alkenes with B_2pin_2, B_2neop_2 and HBpin *via* conventional heating[a]

Entry	Substrate	Boron reagent	Hydroboration (%)	Total VBE[b] (major isomer) (%)	Total VBBE[c] %	Time/days	Solvent[d]	Conversion (%)
1	Styrene	B_2pin_2	3	86	11	5	3 : 1 B–A	100
2	4-Vinyl anisole	B_2pin_2	7	93		2	3 : 1 B–A	99
3	4-Vinyl anisole	B_2neop_2		100		2	3 : 1 B–A	44
4	4-Vinyl anisole	B_2neop_2		100		4	3 : 1 B–A	65
5	4-Vinyl anisole[e]	B_2neop_2		*ca.* 90	*ca.* 10	2	3 : 1 B–A	100
6	4-Vinyl anisole[f]	B_2pin_2		7	93	4	3 : 1 B–A	100
7	Octene	B_2pin_2		33	67	3	3 : 1 B–A	100
8	Indene	B_2pin_2		100		6	3 : 1 B–A	19
9	α-Methyl styrene	B_2pin_2		100		4	3 : 1 B–A	90
10	α-Methyl styrene	B_2pin_2	4	96		2	B	54
11	α-Methyl styrene	B_2pin_2		100		6	A	52
12	α-Methyl styrene[g]	B_2pin_2	3	97		2	3 : 1 B–A	86
13	α-Methyl styrene	HBpin	5	95		2	3 : 1 B–A	55
14	α-Methyl styrene	B_2neop_2		100		2	3 : 1 B–A	42
15	α-Methyl styrene	B_2neop_2		100		4	3 : 1 B–A	53
16	α-Methyl styrene[e]	B_2neop_2		100		2	3 : 1 B–A	96
17	α-Methyl styrene[e]	B_2neop_2		100		3	3 : 1 B–A	100
18	1,1-Diphenylethylene	B_2pin_2		100		4	3 : 1 B–A	67
19	1,1-Diphenylethylene	B_2pin_2	6	94		1	B	71
20	1,1-Diphenylethylene	B_2pin_2		100		4	A	48
21	1,1-Diphenylethylene[h]	B_2pin_2		100		3	3 : 1 B–A	70
22	1,1-Diphenylethylene[g]	B_2pin_2		100		3	3 : 1 B–A	100
23	1,1-Diphenylethylene	HBpin	10	90		2	3 : 1 B–A	44
24	1,1-Diphenylethylene	B_2neop_2		100		2	3 : 1 B–A	29
25	Methylene cyclopentane	B_2pin_2		100 (91)		3	3 : 1 B–A	96
26	Methylene cyclohexane	B_2pin_2		100		5	3 : 1 B–A	81
27	Methylene cyclohexane[g]	B_2pin_2		100		5	3 : 1 B–A	96

[a] For detailed reaction conditions, see the Experimental section. Reactions were carried out in deuterated solvents. Conversion and product distributions were determined by *in situ* ^{1}H-NMR spectroscopy (see text). [b] VBE = vinylboronate ester. [c] VBBE = vinylbis(boronate) ester. [d] B = benzene-d_6, A = acetonitrile-d_3. [e] 1 equiv. of B_2neop_2 used. [f] 2 equiv. of B_2pin_2 and 5 mol% of catalyst used. [g] 1 equiv. of B_2pin_2 used. [h] 5 mol% of catalyst used.

isomerisation of the double bond along the hydrocarbon chain during the reaction. As such, the catalytic dehydrogenative borylation reaction appears best suited for systems which cannot undergo facile double bond isomerisation.

The 1,2-disubstituted alkene, indene, and the 1,1,2-trisubstituted alkenes 2-methyl-2-butene and 3,4,4-trimethyl-2-pentene were also examined under the above conditions. Indene showed lower reactivity than the mono-substituted alkenes giving 100% selectivity for VBE but with only 19% conversion by NMR spectroscopy after 6 days (Table 1, entry 8). NMR spectroscopy unambiguously identified the VBE as the 2-Bpin isomer (see the Experimental section), which requires further comment from a mechanistic point of view, *vide infra*. No reaction at all was observed with either 2-methyl-2-butene or 3,4,4-trimethyl-2-pentene. Consequently, this system appears to be generally unsuitable for dehydrogenative borylation of 1,1,2-trisubstituted alkenes.

In contrast, 1,1-disubstiuted alkenes such as α-methylstyrene and 1,1-diphenylethylene show higher activity than indene and 1,1,2-trisubstituted alkenes. The reaction of 0.67 equiv. of **2a** with α-methylstyrene in the presence of 3 mol% of **1** gave, by NMR spectroscopy, 100% of the (E)–VBE (Table 1, entry 9) with 90% conversion in 4 days. Under the same reaction conditions, 1,1-diphenylethylene proved less reactive than α-methylstyrene, most likely due to increased steric bulk, giving 67% conversion in 4 days, with 100% selectivity for VBE as determined by both techniques (GC-MS and ^{1}H NMR spectroscopy), and only traces of hydroboration (Table 1, entry 18).

Investigation of solvent effects on the reactions of 1,1-diphenylethylene and α-methylstyrene showed that the reaction in neat C_6D_6 was faster than in neat CD_3CN. For 1,1-diphenylethylene in C_6D_6, 71% conversion was observed in 1 day, with 94% VBE and 6% of the hydroboration side product (Table 1, entry 19). On the other hand, the reaction in CD_3CN was very clean, giving 100% selectivity for VBE, but only 48% conversion over 4 days, as indicated by both NMR and GC-MS (Table 1, entry 20). In addition, α-methylstyrene gave 54% conversion in 2 days when C_6D_6 was used, with 94% VBE and 6% of the hydroboration byproduct (Table 1, entry 9). The reaction in CD_3CN gave only 52% conversion in 6 days with 100% VBE (Table 1 and 2, entry 10). Why the reaction of 1,1-diphenylethylene in C_6D_6 is more efficient than that of α-methylstyrene is not clear.

The substrate 1,1-diphenylethylene was reacted with 1 equiv. of **2a** in the presence of 3 mol% of **1** and (3 : 1 d_6–d_3) to examine the effect of providing a stoichiometric quantity of the diboron reagent, **2a**, and to see whether or not the reaction went to completion. After 3 days, 100% conversion to the VBE was observed (Table 1, entry 22). Similarly, using 1 equiv. of **2a**, 86% conversion of α-methylstyrene was observed within 2 days (Table 1, entry 12); surprisingly, a small amount (3%) of hydroboration was found under these conditions. Thus, whereas conversions greater than 67% can be achieved for α-methylstyrene with prolonged heating, using 0.67 equiv. of **2a**, the reaction is clearly more efficient when a stoichiometric quantity of the diboron reagent is used. For 1,1-diphenylethylene, conversions of greater than *ca.* 70% were only observed when 1 equiv. of **2a** was used, indicating that only

Table 2 Product distribution and conversion for the dehydrogenative borylation of alkenes with B_2pin_2, B_2neop_2 and HBpin *via* microwave heating[a]

Entry	Substrate	Boron reagent	Hydroboration (%)	VBE[b] (%)	VBBE[c] (%)	Solvent[d]	Conversion (%)
1	Styrene[e]	B_2pin_2		90	10	3 : 1 B–A	100
2	4-Vinyl anisole	B_2pin_2		100		3 : 1 B–A	77
3	4-Vinyl anisole[f,g]	B_2pin_2		100		3 : 1 B–A	100
4	4-Vinyl anisole[g,h,i]	B_2pin_2		87	13	3 : 1 B–A	100
5	Octene[f]	B_2pin_2		35	65	3 : 1 B–A	100
6	Indene	B_2pin_2		100		3 : 1 B–A	5
7	α-Methyl styrene	B_2pin_2		100		3 : 1 B–A	55
8	α-Methyl styrene[g,h]	B_2pin_2		100		3 : 1 B–A	65
9	1,1-Diphenylethylene	B_2pin_2		100		3 : 1 B–A	50
10	1,1-Diphenylethylene	B_2pin_2	5	95		B	48
11	1,1-Diphenylethylene	B_2pin_2		100		A	44
12	1,1-Diphenylethylene[i]	B_2pin_2		100		3 : 1 B–A	62
13	1,1-Diphenylethylene[j]	B_2pin_2		100		3 : 1 B–A	83
14	1,1-Diphenylethylene	HBpin		100		3 : 1 B–A	39
15	1,1-Diphenylethylene	B_2neop_2		100		3 : 1 B–A	29

[a] For detailed reaction conditions, see the Experimental section. Reactions were carried out in deuterated solvents. Conversion and product distributions were determined by *in situ* ^{1}H-NMR spectroscopy (see text). [b] VBE = vinylboronate ester. [c] VBBE = vinylbis(boronate) ester. [d] B = benzene-d_6, A = acetonitrile-d_3. [e] 180 °C used. [f] 10 min heating. [g] 2 equiv. of B_2pin_2 used. [h] 30 min heating. [i] 5 mol% of catalyst used. [j] 1 equiv. of B_2pin_2 used.

one of the two available borons is being incorporated with this substrate.

To investigate HBpin as a source of boron, both of the alkenes 1,1-diphenylethylene and α-methylstyrene were reacted with 1.34 equiv. of HBpin in place of **2a** under the above conditions. All reactions gave VBE with modest amounts of hydroboration. The reaction of 1,1-diphenylethylene gave 44% conversion over 2 days with 90% selectivity for VBE and 10% for hydroboration (Table 1, entry 23) whereas α-methylstyrene gave 55% conversion by NMR spectroscopy during 2 days with 95% selectivity for VBE and 5% for hydroboration (Table 1, entry 13). These experiments indicate that HBpin can indeed be used in these reactions with fairly limited hydroboration taking place, although the amount of this competing reaction is greater than when the diboron reagents are employed. Hydrogenation was not significant in any case. The above results, when taken together, also indicate that whilst HBpin is indeed formed from **2a** after initial dehydrogenative borylation takes place, high initial concentrations of this reagent do lead to some hydroboration. Also, if formed from 1,1-diphenylethylene dehydrogenative borylation using **2a**, HBpin is not effective, presumably due to catalyst and/or HBpin decomposition during the prolonged heating periods. In addition, the reaction of 1,1-diphenylethylene was examined with 5 mol% of catalyst and 0.67 equiv. of B_2pin_2, (Table 1, entry 21), which gave 70% conversion during 3 days with 100% selectivity for VBE. While the reaction proceeds somewhat faster with the higher catalyst loading, no significant effect on total conversion was observed for this system, so the key factor is increasing the amount of B_2pin_2 to 1 equiv.

Diboron compound **2b** was then investigated as a source of boron with the substrates 1,1-diphenylethylene and α-methylstyrene. The reaction of 1,1-diphenylethylene with 0.67 equiv. of **2b** gave 29% conversion during 2 days by both GC-MS, ^{1}H NMR spectroscopy, with 100% selectivity for VBE (Table 1, entry 24). Reaction with α-methylstyrene gave 42% conversion during 2 days with 100% selectivity for VBE (Table 1, entry 14). This shows that **2b** has a lower reactivity than **2a** in this reaction.

When the reaction of α-methylstyrene with **2b** was carried out under the above conditions but with an extended reaction time (4 days), the conversion was only increased to 53%. However, increasing the concentration of **2b** to 1 equiv. instead of 0.67 equiv. gave 96% conversion of α-methylstyrene with 100% selectivity for VBE within 2 days, and 100% conversion after 3 days (Table 1, entries 16 and 17). Thus, in no case was the second boron incorporated when **2b** was employed, presumably a result of the fact that HBneop is much less thermally stable than HBpin.

Methylene cyclopentane and methylene cyclohexane were examined as 1,1-disubstituted alkenes which do not contain aromatic substituents. The borylation of methylene cyclopentane was achieved during 3 days with 0.67 equiv. of **2a** giving 96% conversion with 91% selectivity for the parent VBE and 9% constituting isomeric VBE (Table 1, entry 25). The GC-MS showed the same result, and that the VBE consist of 3 isomers, the parent constituting 92% of the total VBEs. Two other isomeric VBEs (5% and 3%) presumably result from double bond isomerisation into the ring, but their small quantities precluded detailed analysis by NMR spectroscopy, as the aliphatic protons resonances are overlapped. Finally, methylene cyclohexene was reacted with 0.67 and 1 equiv. of **2a** giving 86 and 96% conversions, respectively, in 5 days with complete selectivity for a single VBE (Table 1, entries 26 and 27).

Dehydrogenative borylations using microwave heating

The thermal reactions discussed above were re-examined using microwave heating in the presence of 3 mol% of **1** with 0.67 equiv. of **2a** in a mixture of deuterated solvents (3 : 1 d_6–d_3) under a variety of conditions. Selectivities and conversions were measured by *in situ* ^{1}H NMR spectroscopy, and these can be compared with those obtained from conventional thermal reactions. It should be noted that the reactions of styrene, 1-octene, indene and 1,1-diphenylethylene were carried out in a CEM microwave reactor at 150 W maximum microwave power and 150 °C, unless otherwise stated. Reactions of 4-vinylanisole and α-methylstyrene were carried out in a Biotage Personal Chemistry Optimizer microwave reactor with a maximum input power 300 W to reach the required temperature of 150 °C. Once the required temperature

is reached, monitored internally by an infrared sensor, the reactor automatically adjusts the microwave input power to maintain the setpoint temperature.

The reaction of styrene (Table 2, entry 1) with 0.67 equiv. of **2a** and 3 mol% of **1** was carried out at a higher temperature, 180 °C, than the other microwave reactions. The conversion was 100%, with 90% selectivity for VBE and 10% for VBBE after only 1 hour. Reaction of VA at 150 °C gave 77% conversion after 1 hour, with 100% selectivity for VBE (Table 2, entry, 2). The reaction was re-examined with 2 equiv. of **2a** to attempt to improve the selectivity for VBBE; 100% conversion occurred within only 10 minutes, giving 100% selectivity for VBE (Table 2, entry 3). Increasing the reaction time to either 30 or 60 minutes, using 5 mol% of **1**, gave 13% VBBE and 87% VBE, with 100% conversion (Table 2, entry 4).

The reaction of 1-octene with 0.67 equiv. of **2a** (150 W) at 150 °C for 10 minutes gave 100% conversion, with 35% VBE and 65% VBBE (Table 2, entry 5). Indene gave only 5% conversion during 1 hour, but with 100% selectivity for VBE (Table 2, entry 6).

The reaction of α-methylstyrene was examined at 150 °C with 0.67 equiv. of **2a** in the presence of 3 mol% of **1**. After 1 hour, the reaction gave 100% selectivity for VBE with 55% conversion (Table 2, entry 7). Using 2 equiv. of **2a**, increased the conversion slightly to 65% after 30 minutes with 100% selectivity for VBE (Table 2, entry 8). Similar conversions and selectivities were observed when the reaction time was extended to 60 minutes. The reaction of 1,1-diphenylethylene was examined with 0.67 equiv. of **2a** in the presence of 3 mol% of **1** at 150 °C for 1 hour. The conversion was 50% with 100% selectivity for VBE (Table 2, entry 9). Increasing the concentration of catalyst to 5 mol%, with 0.67 equiv. of **2a** only increased the conversion to 62% (Table 2, entry 12). Using 1 equiv. of **2a** with 3 mol% of **1**, however, gave 83% conversion with 100% selectivity for VBE (Table 2, entry 13). To investigate the solvent effect on the dehydrogenative borylation of 1,1-diphenylethylene under microwave heating, the reaction was carried out in neat C_6D_6 and neat CD_3CN at 150 °C for 1 hour. The reaction in neat C_6D_6 gave 95% selectivity for VBE with 5% hydroboration and 48% conversion (Table 2, entry 10), whereas CD_3CN gave 44% conversion with 100% selectivity for VBE (Table 2, entry 11). Using 1.34 equiv. of HBpin in place of B_2pin_2 resulted in only 39% conversion after 1 hour, but with 100% selectivity for VBE (Table 2, entry 14), whereas using 0.67 equiv. of **2b** gave 29% conversion after 1 hour with 100% selectivity for VBE (Table 2, entry 15).

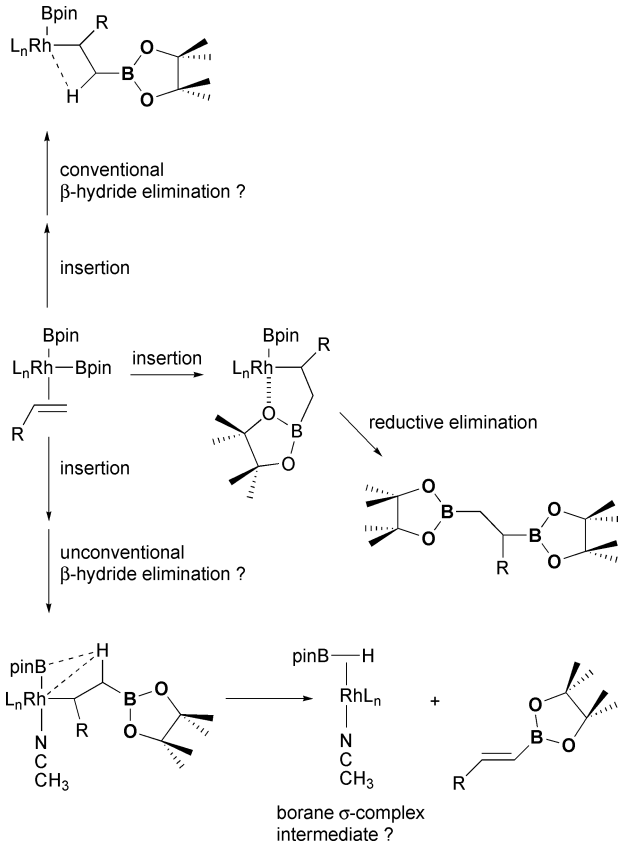
Comparison between thermal and microwave reactions

The conversions of styrene by thermal or microwave heating were similar, although the reaction time under microwave irradiation at 180 °C, compared with the thermal reaction at 80 °C, was reduced from 5 days to 1 hour. VA was converted completely to its VBE in only 10 minutes using 2 equiv. of **2a** at 150 °C. Even with 2 equiv. of **2a**, larger amounts of catalyst, and heating for 1 hour, relatively little progression to the VBBE was observed. The reaction of 1-octene with 0.67 equiv. of **2a** gave the same conversion (100%) and the same selectivities for VBE and VBBE by both thermal and microwave heating, but the reaction time was reduced from 3 days at 80 °C to only 10 minutes at 150 °C. Indene showed even lower conversion at 150 °C than at 80 °C.

With 0.67 equiv. of **2a**, 1,1-diphenylethylene gave 67% conversion after 3 days at 80 °C and 50% conversion by the microwave reaction after 1 hour with the same selectivity for VBE. Moreover, increasing the amount of **2a** to 1 equiv. in the microwave reaction gave 83% conversion after only 1 hour. Similar and relatively low conversion but excellent selectivity was observed in the reaction of 1,1-diphenylethylene with **2b** by either heating technique, but the higher temperature of the microwave reactions again allowed the reaction times to be reduced from days to 1 hour. For α-methylstyrene, we were only able to achieve 65% conversion in the microwave reaction when the amount of **2a** was increased to 2 equiv.

Preliminary theoretical studies of and comments on some possible reaction mechanisms

Given the presence of the strong π-acceptor CO ligand and the relatively weak PPh_3 donor ligand, it is extremely unlikely that the C–H activation process involves a direct oxidative addition of the vinylic-C–H bond of the substrate, and we are not aware of any such C–H oxidative additions involving **1**. With this in mind, a more likely scenario involves formation of a Rh–boryl complex followed by insertion of alkene into the Rh–B bond and subsequent β-hydride elimination giving the VBE product and a rhodium hydride. Indeed, the results of such a process were observed[20] in the stoichiometric reaction of VA with $[RhCl(Bcat)_2(PPh_3)_2]$, which also led to the diborated alkene *via* competing reductive elimination following the initial alkene insertion process. In addition, the $[RhClH(Bcat)(PPh_3)_2]$ formed *via* β-hydride elimination led to hydroborated products. As neither significant amounts of hydroboration nor any diboration products were observed in the current study, a related mechanism would require that β-hydride elimination be much faster than B–C reductive elimination and that subsequent insertion of alkene into the resulting $[RhClH(Bpin)(PPh_3)(CO)]$ would take place only into the Rh–B bond leading again to rapid β-hydride elimination rather than C–H reductive elimination (giving hydroboration), and would still fail to explain the influence of acetonitrile on greatly improving selectivity to VBE. For a host of reasons, this type of mechanism thus seems unlikely. If acetonitrile were to coordinate to the 'vacant' site in a putative alkene insertion product of the form $[RhClH(CHRCH_2Bpin)(PPh_3)(CO)]$, this would inhibit coordination of a Bpin oxygen atom at this site (Scheme 1), which has been predicted theoretically to enhance reductive elimination in a similar system, due to ring strain.[21] However, this would also block the site required for β-hydride elimination. We therefore considered the possibility (Scheme 1) of an unconventional β-hydride elimination pathway which could potentially occur in a coordinatively-saturated complex, involving direct B–H bond formation *via* β-hydride transfer to the electron-deficient *cis*-boryl ligand on an acetonitrile-coordinated boryl–alkyl Rh intermediate (1) in Fig. 1. We investigated this possibility with the aid of DFT calculations at the B3LYP level. Indeed, we were able to locate a transition state for the direct B–H bond formation (see **TSA** in Fig. 1). However, the corresponding reaction free energy barrier (43.30 kcal mol^{-1}) is extremely high, suggesting that the reaction path (path **A** in Fig. 1) is unlikely. Alternatively, we found that a two-step reaction pathway (path **B** in Fig. 1), which involves β-hydride elimination giving a Rh(III) intermediate (**INTB**) followed



Scheme 1 Some possible reaction pathways.

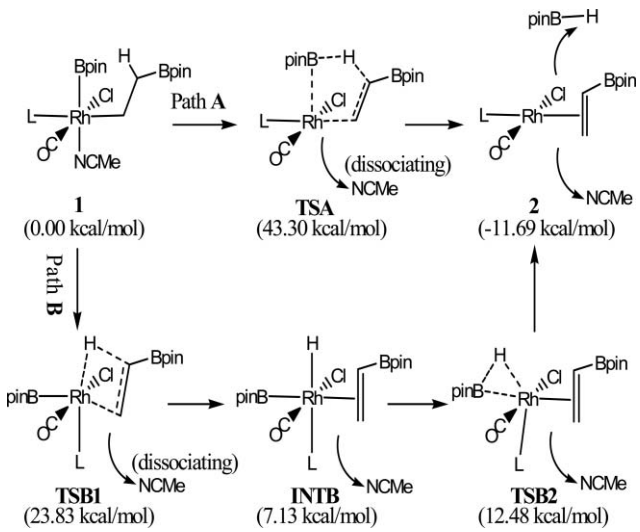


Fig. 1 Computed energies for some possible intermediates and transition states for conventional and unconventional β-hydride elimination pathways.

by reductive elimination leading to the B–H bond formation, has a much lower barrier. The β-hydride elimination step is the rate-determining step and requires a free energy barrier of 23.83 kcal mol^{-1}. In the calculations of **TSA** and **TSB1**, the coordinated acetonitrile was found to be dissociating. This phenomenon is understandable because the conversion from **I** to **II** or **I** to **INTB** in the related β-hydride elimination steps involves an increase of the electron count by two around the metal centre. The ligand dissociation is necessary in order to maintain an acceptable electron count, *i.e.* 18 electrons or 16 electrons depending on the structure considered. Therefore, in the determination of the transition state structures, we considered the acetonitrile as a separate entity.

As pointed out above, a process such as that in path **B** seems unlikely to account for the lack of any diboration products, the overall selectivities observed or the unusual solvent effects. Thus, the overall mechanism of the current reaction remains unclear. However, the fact that **TSA** was located at all is interesting in its own right, and suggests the possibility that diverse and unconventional mechanism may operate in appropriate circumstances. A direct B–C bond formation path, considered as a σ-bond metathesis path, was found to be feasible, for example, in alkane borylations mediated by Cp-containing Fe and W boryl complexes.[22] The results here suggest that different coordination environments and metal centres have significant influences in the selection of favourable reaction pathways, and that a variety of mechanisms are worth investigating, even if they involve unusual steps.

It remains to address the fact that only (*E*)-VBEs are formed in these reactions. We believe that this is a result of the fact that, following alkene insertion into a Rh–B bond (which no doubt is a *syn*-addition process), either of the two diastereotopic β-hydrogens could be transferred to the Rh. As this β-hydride elimination process also requires a *syn*-disposition of the hydride and Rh groups, rotation around the C–C bond is required (Fig. 2). The least hindered rotamer, illustrated for the α-methylstyrene case, would thus lead to the observed (*E*)-product. Clearly this would be even more prevalent in styrene and VA, in which the α-Me group is replaced by an even smaller H atom. The case of indene requires additional discussion. In this case, *syn*-addition of Rh–B across the double bond leads to a ring system in which the Rh and β-H groups are mutually *trans*. If both occupy pseudo axial positions, an *anti* disposition would make β-hydride elimination impossible. However, a conformation in which the two groups are pseudo-equatorial would bring them much closer together, although the Rh–C–C–H group could not attain complete planarity. As a result, β-hydride elimination might be expected to be quite slow, consistent with the observed low conversions for this substrate. Finally, it is worth pointing out that the insertion of alkenes into M–B bonds can be a reversible process, as β-boryl elimination can also have a relatively small barrier.[23]

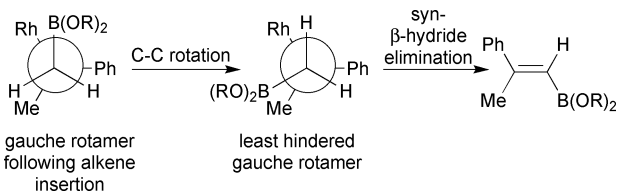


Fig. 2 Conformation leading to (*E*)-VBE.

Conclusions

Mono and 1,1-disubstituted alkenes can be converted into VBEs in high yield and with excellent selectivity *via* dehydrogenative borylation of C–H bonds using the simple catalyst, **1**, and commercially available diboron reagents, **2a** and **2b**, which give better selectivities than HBpin.

In situ ^{1}H NMR spectroscopy, which was used to determine the conversions of the reactions, was slightly more accurate than GC-MS due to the fact that the NMR technique does not depend on a response factor for each compound; however, it is difficult to estimate, by ^{1}H NMR, the side products such as those arising from hydroboration and hydrogenation if they are present in very small quantities. To improve the accuracy of the GC-MS method, it is necessary to obtain response factors for the starting materials and every product; however, this is not always practical, especially when many different substrates are employed, as it would entail isolation of every possible product and isomer. What is clear, however, is that, in this study, closely related isomeric products have very similar response factors, and that hydroboration products have somewhat larger response factors than VBEs, which in turn have larger response factors than the hydrocarbons. In any event, the differences are not very large, and for this chemistry, GC-MS, even without predetermined response factors, provides reasonable quality data which can be considered as at least semi-quantitative.

Microwave heating is a useful technique to reduce the time of the reaction from days to minutes. Noting that the temperatures used in the two types of reactions were 80 and 150 °C, and that, as a rule of thumb, one may expect an approximate doubling of reaction rates with every 10 °C increase in temperature, we might expect rate increases of *ca.* $2^7 = 128$ in the microwave reactions. Thus, 60 minutes at 150 °C is roughly comparable to 5 days at 80 °C. With this in mind, we can suggest that there is nothing unusual about the microwave results to imply any special effect rather than the ability to heat the sample to 150 °C safely and rapidly, well above the solvent boiling points in a sealed system, allowing for convenient, rapid reactions. As these are carried out in sealed tubes, the higher temperature results in a much higher pressure which could inhibit reactions which produce gaseous products such as H_2. Obviously, care needs to be taken to calculate the maximum potential pressure to avoid explosions, although the reactor monitors pressure *in situ* and shuts off the heating when a preselected maximum (safe) pressure is reached. In addition, the reactor is designed to withstand explosion of the thick-walled, glass reaction tubes, although this was not encountered.

It can be seen that the selectivities were fairly similar but the overall conversions were often significantly higher in the thermal reactions compared to the microwave ones. We attribute the somewhat lower conversions obtained with less reactive substrates to significant catalyst decomposition after 1 hour at the higher temperatures employed in the microwave reactions, whereas the more reactive substrates, such as VA, allowed complete conversion within 10 minutes during which time catalyst decomposition is apparently not significant.

Finally, the detailed mechanism of the reaction remains unknown, although with the CO-containing catalyst system employed, it most likely involves insertion of the alkene into a Rh–B bond, followed by β-hydride elimination, as opposed to direct C–H bond oxidative addition. In view of the preliminary calculational results, we feel that the reaction mechanism involved in the dehydrogenative borylation reactions is more complicated and probably very different from that which we initially thought. The role of CH_3CN in greatly enhancing the selectivity towards VBE with styrene substrates remains unclear. Further experimental studies as well as theoretical studies of various possible reaction pathways are required to elucidate the mechanism and to develop higher activity catalyst systems capable of carrying out the reactions at lower temperatures and with reduced reaction times. In addition, it can be envisaged that more stable catalyst systems would allow for higher conversions with very short reaction times at the high temperatures employed in the microwave reactions. The excellent selectivity of the reactions, especially with 1,1-disubstituted substrates, makes this technology suitable for applications involving the conversion of hydrocarbons into high-value added species *via* dehydrogenative borylation/Suzuki–Miyaura cross-coupling sequences, and such studies are in progress in our laboratory.

Experimental

All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques or in an Innovative Technology, Inc. System 1 glove box. Glassware was oven dried before transfer into the glove box. Toluene was dried and deoxygenated by passage through columns of activated alumina and BASF-R311 catalyst under Ar pressure using a locally modified version of the Innovative Technology, Inc. SPS-400 solvent purification system.[24] The solvents CH_3CN, CD_3CN, C_6D_6 and $CDCl_3$ were dried over calcium hydride, and 1,4-dioxane, THF and C_7D_8 were dried over sodium–benzophenone; all were distilled under nitrogen. Alkenes were purchased from Aldrich Chemical Company, Lancaster Synthesis or Avocado Research Chemicals, and were checked for purity by NMR and GC-MS techniques and distilled from calcium hydride under nitrogen. The boron reagents B_2pin_2[25] and B_2neop_2[25b,26] were generously donated by Frontier Scientific Inc., NetChem Inc. and AllyChem Co. Ltd. and were checked for purity by NMR and GC-MS techniques. HBpin was purified as in ref. 27. The catalyst precursor $[Rh(CO)(Cl)(PPh_3)_2]$ was prepared using published procedures[28] and checked for purity by NMR spectroscopy. NMR spectra were recorded at 25 °C on Varian Inova 500 (^{1}H, $^{13}C\{^1H\}$, HSQC, NOESY), Bruker Avance (^{1}H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$), Varian Mercury 400 (^{1}H, $^{13}C\{^1H\}$), Varian Unity 300 (^{11}B and $^{11}B\{^1H\}$) and Bruker AC200 ($^{11}B\{^1H\}$) instruments. Proton and carbon spectra were referenced to external $SiMe_4$ *via* residual protons in the deuterated solvents or solvent resonances, respectively. ^{11}B chemical shifts were referenced to external $BF_3{\cdot}OEt_3$. Elemental analyses were conducted in the Department of Chemistry at the University of Durham using an Exeter Analytical Inc. CE-440 Elemental Analyzer. GC-MS analyses were performed on a Hewlett-Packard 5890 Series II gas chromatograph equipped with a 5971A mass selective detector and a 7673 autosampler. A fused silica capillary column (10 or 12 m cross-linked 5% phenylmethylsilicone) was used, and the oven temperature was ramped from 50 to 280 °C at a rate of 20 °C min^{-1}. UHP grade helium was used as the carrier gas. The screw-cap autosampler vials used were supplied by Thermoquest Inc. and were fitted with teflon/silicone/teflon septa and 0.2 ml micro inserts. Microwave reactions were carried out in a CEM Corporation or a Biotage Personal Chemistry Optimizer microwave reactor, in the latter case, using an automated sample changer. The reactions were carried in thick-walled, glass reaction-tubes with septum seals, specifically designed to withstand the pressures generated.

Typical catalytic reaction conditions

Conventional heating. All reactions were carried out in deuterated solvents and were prepared in a nitrogen-filled glove box (Innovative Technology, Inc.). To a solution of *trans*-[Rh(Cl)(CO)(PPh_3)$_2$] (3 mol% unless otherwise indicated) in 1 ml of solvent was added a mixture of boron reagent (0.4 mmol total boron unless otherwise indicated) and alkene (0.3 mmol) 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 and then heated to 80 °C. The reaction was monitored by either GC-MS or a combination of GC–MS and ^{1}H NMR spectroscopy. In the latter case, an aliquot of the solution was removed by syringe under nitrogen and was then diluted with additional dry, O_2-free C_6D_6 in an NMR tube.

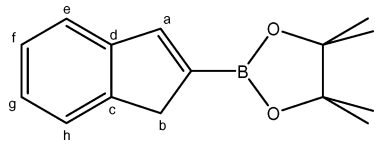
Microwave heating. In a nitrogen-filled glove box, a mixture of boron reagent (0.4 mmol total boron unless otherwise indicated) and alkene (0.3 mmol) in 1 ml of deuterated solvent was added to a solution of *trans*-[Rh(Cl)(CO)(PPh_3)$_2$] (3 mol% unless otherwise indicated) in 1 ml of solvent (2 ml total solvent volume). The mixture was shaken vigorously to ensure complete mixing, transferred to a microwave reactor tube (5 ml) which was then crimp sealed and heated in the microwave reactor at 150 or 300 W, unless otherwise stated, and 150 °C for 60 min. Reactions of styrene, 1-octene, indene and 1,1-diphenylethylene were carried out in the CEM microwave reactor (150 W) at 150 °C, unless otherwise stated. Reactions of 4-vinylanisole and α-methylstyrene were carried out in a Biotage Personal Chemistry Optimizer reactor, (300 W) at 150 °C. Pressure and temperature were monitored automatically, *in situ*, to assure that safe limits were maintained. The crude reaction solutions were examined by either NMR spectroscopy or a combination of NMR spectroscopy and GC–MS.

(*E*)-(Ph)CH=CH(Bpin). ^{1}H NMR (500 MHz, C_6D_6): δ 1.12 (s, 12H, Bpin), 6.44 (d, ^3J(H,H) = 18 Hz, 1H, =C*H*Bpin), 7.00 (m, 3H, C_6H_5), 7.24 (m, 2H, C_6H_5), 7.75 (d, ^3J(H,H) = 18 Hz, 1H, ArC*H*=); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): 24.8 (s, $BO_2C_2(CH_3)_4$), 83.3 (s, $BO_2C_2(CH_3)_4$), 116.9 (s, br, =*C*HBpin) 127.4, 128.8, 129.0, 137.9 (s, C_6H_5), 150.4 (s, Ar*C*H=); ^{11}B{^{1}H} NMR (96 MHz, C_6D_6): 30.4 (s, br); MS (EI) *m*/*z* (rel. int.): 230 (10) [M$^+$], 215 (7) [M$^+$-Me], 120 (100).

(*E*)-(4-MeO–C_6H_4)CH=CH(Bpin). ^{1}H NMR (500 MHz, C_6D_6): δ 1.14 (s, 12H, Bpin), 3.23 (s, 3H, CH_3O), 6.34 (d, ^3J(H,H) = 18 Hz, 1H, =C*H*Bpin), 6.62 (m, 2H, C_6H_4), 7.28 (d, 2H, C_6H_4), 7.76 (d, ^3J(H,H) = 18 Hz, 1H, ArC*H*=); ^{13}C{^{1}H} (126 MHz, C_6D_6): δ 24.8 (s, $BO_2C_2(CH_3)_4$), 54.6 (s, *C*H$_3$O), 83.0 (s, $BO_2C_2(CH_3)_4$), 114.2 (s, br, =*C*HBpin), 116.0 (s, C_6H_4), 128.7 (s, C_6H_4), 130.8 (s, C_6H_4), 145.1 (s, Ar*C*H=), 160.7 (s, C_6H_4); ^{11}B{^{1}H} NMR (64 MHz, C_6D_6) 30.9 (s, br); MS (EI): *m*/*z* (rel. int.): 260 (100) [M$^+$], 245 (16) [M$^+$-Me].

4-MeO–C_6H_4CH=C(Bpin)$_2$. ^{1}H NMR (500 MHz, C_6D_6): δ 1.24 (s, 24H, Bpin), 3.31 (s, 3H, CH_3O), 6.70 (d, ^3J(H,H) = 8 Hz, 2H, *o*-C_6H_4), 7.49 (d, ^3J(H,H) = 8 Hz, 2H, *m*-C_6H_4), 7.98 (s, 1H, ArC*H*=); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 24.8 (s, $BO_2C_2(CH_3)_4$), 54.6 (s, *C*H$_3$O), 83.4 (s, $BO_2C_2(CH_3)_4$), 127.2, 128.8, 129.3, 137.8 (s, C_6H_4), 145.1 (s, Ar*C*H=), the resonance for the carbon attached to boron was not observed; ^{11}B{^{1}H} NMR (128.4 MHz, C_6D_6): δ 30.25 (s, br); MS (EI): *m*/*z* (rel. int.): 386 (2) [M$^+$], 371 (0.2) [M$^+$-Me], 84 (100) [Me_2C=CMe_2]$^+$. The NOESY NMR spectrum shows a correlation between the *ortho* CH on the arene ring and the CH= of the alkene.

$CH_3(CH_2)_5CH$=C(Bpin)$_2$. ^{1}H NMR (400 MHz, C_6D_6): δ 0.76 (t, $^3J_{H\text{-}H}$ = 6.95, 3H, CH_3), 0.89–1.13 (m, 32H, (Bpin)$_2$ +(CH_2)$_4$), 2.25 (q, $^3J_{H\text{-}H}$ = 7.32, 2H, =CHCH_2(CH$_2$)$_4$), 6.62 (m, 1H, C*H*=C(Bpin)$_2$); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 14.0 (s, *C*H$_3$), 22.7 (s, CH$_3$*C*H$_2$(CH)$_4$), 24.6 (s, $C_3H_6CH_2CH_3$), 24.7, 24.8 (s, $BO_2C_2(CH_3)_4$), 29.4 (s, $C_3H_6CH_2CH_3$), 31.6 (s, $C_3H_6CH_2CH_3$), 32.8 (s, *C*H$_2$CH=C(Bpin)$_2$), 83.0 (s, $BO_2C_2(CH_3)_4$), 163.7 (s, CH$_2$*C*H=C(Bpin), the resonance for the carbon attached to boron was not observed; ^{11}B{^{1}H} NMR (128.4 MHz, C_6D_6): δ 28.3 (s, br); MS (EI): *m*/*z* (rel. int.): 364 (0.31) [M$^+$], 349 (2) [M$^+$-Me], 84 (100).



Inden-2-yl(Bpin). ^{1}H NMR (400 MHz, C_6D_6): δ 1.26 (s, 12H, Bpin), 3.28 (s, 2H, b), 7.14–7.42 (m, 4H, e, f, g, h), 8.14 (s, 1H, a);^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 22.7 (s, $BO_2C_2(CH_3)_4$), 38.9 (s, b), 83.3 (s, $BO_2C_2(CH_3)_4$), 124.6, 125.8, 126.1, 126.3 (s, e, f, g, h) 134.2, 134.8 (s, c, d), 149.4 (s, a); the resonance for the carbon attached to boron was not observed ^{11}B{^{1}H} NMR (128.4 MHz, C_6D_6): δ 28.3 (s, br); MS (EI): *m*/*z* (rel. int.): 242 (4) [M$^+$], 227 (2) [M$^+$-Me], 142 (100).

(*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, *C*H$_3$PhC=), 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, 128.0, 128.2, 143.8, 157.8 (MePh*C*=); ^{11}B{^{1}H} NMR (96 MHz, $CDCl_3$) δ 29.0 (s, br); anal. 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 (21) [M$^+$], 229 (8) [M$^+$-Me], 105 (100). The NOESY NMR spectrum shows correlations consistent with this molecular geometry.

Ph_2C=CH(Bpin). ^{1}H NMR (400 MHz, C_6D_6): δ 1.04 (s, 12H, Bpin), 6.01 (s, 1H, =C*H*Bpin), 7.06–7.8 (m, 10H, Ph$_2$); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 24.5 (s, $BO_2C_2(CH_3)_4$), 83.1 (s, $BO_2C_2(CH_3)_4$), 128.2, 128.3, 130.1 143.2 (s, C_6H_4), 160.3 (s, Ph_2C=), the resonance for the carbon attached to boron was not observed; ^{11}B{^{1}H} NMR (128.4 MHz, C_6D_6): δ 30.25 (s, br); MS (EI): *m*/*z* (rel. int.): 306 (21) [M$^+$], 291 (3) [M$^+$-Me], 190 (100).

C_6H_{10}=CH(Bpin). ^{1}H NMR (500 MHz, C_6D_6): δ 1.24 (s, 12H, Bpin), 1.35 (m, 2H, CH_2), 1.43 (m, 2H, CH_2), 1.51 (m, 2H, CH_2), 2.10 (t, $^3J_{H\text{-}H}$ = 6 Hz, 2H, CH_2), 2.68 (t, $^3J_{H\text{-}H}$ = 6 Hz, 2H, CH_2), 5.29 (s, 1H, =C*H*Bpin); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 25 (s, $BO_2C_2(CH_3)_4$), 26.8 (s, *C*H$_2$), 28.9 (s, *C*H$_2$), 29.1 (s, *C*H$_2$), 33.5 (s, *C*H$_2$), 40.5 (s, *C*H$_2$), 83 (s, $BO_2C_2(CH_3)_4$), 112 (s, br, =*C*HBpin), 167.19 (s, *C*=CHBpin); ^{11}B{^{1}H} NMR (128.4 MHz, C_6D_6): δ 30.2 (s, br); MS (EI): *m*/*z* (rel. int.): 222 (1) [M$^+$], 207 (0.006) [M$^+$-Me], 55 (100).

C_5H_8=CH(Bpin). ^{1}H NMR (500 MHz, C_6D_6): δ 1.09 (s, 12H, Bpin), 1.41 (m, 2H, CH_2), 1.51 (m, 2H, CH_2), 2.24

(t, $^3J_{H-H}$ = 7.32 Hz, 2H, CH_2), 2.69 (t, $^3J_{H-H}$ = 7.32 Hz, 2H,CH_2), 5.58 (s, 1H, =C*H*Bpin); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 25.14 (s, $BO_2C_2(CH_3)_4$), 26.34 (s, *C*H$_2$), 27.34 (s, *C*H$_2$), 33.87 (s, *C*H$_2$), 37.39 (s, *C*H$_2$), 82.64 (s, $BO_2C_2(CH_3)_4$), 110 (s, br, =*C*HBpin), 171.67 (s, *C*=CHBpin); ^{11}B{^{1}H} NMR (128.4 MHz, C_6D_6): δ 30.18 (s, br); MS (EI): *m*/*z* (rel. int.): 207 (6) [M$^+$], 192 (8) [M$^+$-Me], 55 (100).

(*E*)-(MeOC$_6$H$_4$)CH=CH(Bneop). ^{1}H NMR (500 MHz, C_6D_6): δ 0.63 (s, 6H, Bneop-CH_3), 3.23 (s, 4H, Bneop-CH_2), 3.40 (s, 3H, CH_3O), 6.41 (d, $^3J_{H-H}$ = 18 Hz, 1H, =C*H*Bneop), 7.01 (m, 2H, C$_6H_4$), 7.37 (m, 2H, C$_6H_4$), 7.79 (d, $^3J_{H-H}$ = 18 Hz, 1H, ArC*H*=); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): 21.5 (s, Bneop-*C*H$_3$), 30.1 (s, Bneop-*C*(CH$_3$)$_2$), 70.6 (s, Bneop-*C*H$_2$), 71.9 (s, *C*H$_3$O), 115.9 (s, *C*$_6$H$_4$), 119.0 (s, br, =*C*HBneop), 128.8, 131.3 (s, *C*$_6$H$_4$), 147.6 (s, Ar*C*H=), 160.5 (s, *C*$_6$H$_4$); ^{11}B{^{1}H} NMR (96 MHz, C_6D_6): δ 27.1 (s, br); MS (EI) *m*/*z* (rel. int.): 256 (100) [M$^+$], 231 (3) [M$^+$-Me].

(*E*)-PhC(Me)=CH(Bneop). ^{1}H NMR (500 MHz, C_6D_6): δ 0.60 (s, 6H, neop-CH_3), 2.50 (d, $^3J_{H-H}$ = 1 Hz, 3H, CH_3PhC=), 3.38 (s, 4H, Bneop-CH_2), 6.06 (q, $^3J_{H-H}$ = 1 Hz, 1H, =C*H*Bneop), 7.14 (m, 2H, C$_6H_5$), 7.31 (m, 3H, C$_6H_5$); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 21.8 (s, *C*H$_3$PhC=), 21.9 (s, neop-*C*H$_3$), 31.6 (s, neop-*C*(CH$_3$)$_2$), 72.1 (s, neop-*C*H$_2$), 119.8 (s, br, =*C*HBpin), 126.5, 128.1, 128.5, 143.5 (*C*$_6$H$_5$), 155.4 (s, MePh*C*=); ^{11}B{^{1}H} NMR (96 MHz, C_6D_6): δ 26.7 (s, br); MS (EI) *m*/*z* (rel. int.): 230 (100) [M$^+$], 215 (3) [M$^+$-Me]. The NOESY NMR spectrum shows correlations consistent with this molecular geometry.

Ph$_2$C=CH(Bneop). ^{1}H NMR (500 MHz, C_6D_6): δ 0.58 (s, 6H, neop-CH_3), 3.21 (s, 4H, neop-CH_2), 6.24 (s, 1H, =C*H*Bneop), 7.11 (m, 4H, Ph), 7.27 (m, 6H, Ph); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): 21.5 (s, neop-*C*H$_3$), 31.4 (s, neop-*C*Me$_2$), 71.7 (s, neop-*C*H$_2$), 123.0 (s, br, =*C*HBneop), 127.9, 128.1, 128.4, 130.1, (s, Ph) 158.2 (s, Ph$_2$*C*=); ^{11}B{^{1}H} NMR (96 MHz, C_6D_6): 26.7 (s, br); MS (EI) *m*/*z* (rel. int.): 292 (100) [M$^+$], 277 (3) [M$^+$-Me].

Theoretical studies

Density functional theory calculations at the Becke3LYP (B3LYP) level have been performed to optimise all of the model species in which the phosphine ligands were modeled with PH_3. Frequency calculations at the same level of theory have also been performed to identify all stationary points as minima (zero imaginary frequencies) or transition states (one imaginary frequency). In the B3LYP calculations, the Lan2DZ[29] basis set was used to describe Rh, P and Cl, whereas the 6–31G basis set[30] was used for C, B, O and H atoms. Polarisation functions were added for P (ζ_d = 0.34) and Cl (ζ_d = 0.514).[31] All calculations were performed using the Gaussian 98 package.[32]

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References

1 (*a*) N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 49; (*b*) A. Suzuki, *J. Organomet. Chem.*, 1999, **576**, 147.
2 R. W. Hoffmann and B. Landman, *Chem. Ber.*, 1986, **119**, 2013.
3 (*a*) P.-Y. Reynard, Y. Six and J.-Y. Lallemand, *Tetrahedron Lett.*, 1997, **38**, 6589; (*b*) A. Zhang, Y. Kan and B. Jiang, *Tetrahedron*, 2001, **57**, 2305.
4 (*a*) R. A. Batey, D. B. MacKay and V. Santhakumar, *J. Am. Chem. Soc.*, 1999, **121**, 5075; (*b*) N. A. Petasis and S. Boral, *Tetrahedron Lett.*, 2001, **42**, 539.
5 J. E. A. Luithle and J. Pietruszka, *Liebigs Ann.*, 1997, 2297.
6 N. Hénaff and A. Whiting, *Tetrahedron*, 2000, **56**, 5193.
7 (*a*) H. C. Brown and S. K. Gupta, *J. Am. Chem. Soc.*, 1975, **97**, 5249; (*b*) C. F. Lane and G. W. Kabalka, *Tetrahedron*, 1976, **32**, 981.
8 (*a*) K. Burgess, W. A. van der Donk, S. A. Westcott, T. B. Marder, R. T. Baker and J. C. Calabrese, *J. Am. Chem. Soc.*, 1992, **114**, 9350; (*b*) K. Burgess and M. J. Ohlmeyer, *Chem. Rev.*, 1991, **91**, 1179; (*c*) S. Pereira and M. Srebnik, *Organometallics*, 1995, **14**, 3127; (*d*) X. He and J. F. Hartwig, *J. Am. Chem. Soc.*, 1996, **118**, 1696; (*e*) I. Beletskaya and A. Pelter, *Tetrahedron*, 1997, **53**, 4957; (*f*) T. Ohmura, Y. Yamamoto and N. Miyaura, *J. Am. Chem. Soc.*, 2000, **122**, 4990.
9 (*a*) K. Takahashi, J. Takagi, T. Ishiyama and N. Miyaura, *Chem. Lett.*, 2000, 126; (*b*) T. Ishiyama and N. Miyaura, *J. Organomet. Chem.*, 2000, **611**, 392.
10 T. Hata, H. Kitagawa, H. Masai, T. Kurahashi, M. Shimizu and T. Hiyama, *Angew. Chem.*, 2001, **113**, 812, (*Angew. Chem., Int. Ed.*, 2001, **40**, 790).
11 (*a*) T. Ishiyama, N. Matsuda, N. Miyaura and A. Suzuki, *J. Am. Chem. Soc.*, 1993, **115**, 11018; (*b*) T. Ishiyama, N. Matsuda, M. Murata, F. Onazawa, A. Suzuki and N. Miyaura, *Organometallics*, 1996, **15**, 713; (*c*) G. Lesley, P. Nguyen, N. J. Taylor, T. B. Marder, A. J. Scott, W. Clegg and N. C. Norman, *Organometallics*, 1996, **15**, 5137; (*d*) C. N. Iverson and M. R. Smith, III, *Organometallics*, 1996, **15**, 5155; (*e*) R. Ll. Thomas, F. E. S. Souza and T. B. Marder, *J. Chem. Soc., Dalton Trans.*, 2001, 1650.
12 T. Ishiyama, S. Momato and N. Miyaura, *SYNLETT*, 1999, **11**, 1790.
13 S.-Y. Onozawa, Y. Hatanaka and M. Tanaka, *Chem. Commun.*, 1999, 1863.
14 T. Ohmura, Y. Yamamoto and N. Miyaura, *J. Am. Chem. Soc.*, 2000, **122**, 4990.
15 (*a*) H. E. Blackwell, D. J. O'Leary, A. K. Chatterjee, R. A. Washenfelder, D. A. Bussmann and R. H. Grubbs, *J. Am. Chem. Soc.*, 2000, **122**, 58; (*b*) C. Morrill and R. H. Grubbs, *J. Org. Chem.*, 2003, **68**, 6031; (*c*) C. Morrill, T. W. Funk and R. H. Grubbs, *Tetrahedron Lett.*, 2004, **45**, 7733.
16 (*a*) B. Marciniec, M. Jankowska and C. Pietraszuk, *Chem. Commun.*, 2005, 663; (*b*) K. C. Lam, Z. Lin and T. B. Marder, *Organometallics*, 2007, **26**, 3149.
17 M. Kim and D. Lee, *Org. Lett.*, 2005, **7**, 1865.
18 (*a*) J. M. Brown and G. C. Lloyd-Jones, *J. Chem. Soc., Chem. Commun.*, 1992, 710; (*b*) S. A. Westcott, T. B. Marder and R. T. Baker, *Organometallics*, 1993, **12**, 975; (*c*) J. M. Brown and G. C. Lloyd-Jones, *J. Am. Chem. Soc.*, 1994, **116**, 866; (*d*) D. H. Motry and M. R. Smith, III, *J. Am. Chem. Soc.*, 1995, **117**, 6615; (*e*) R. T. Baker, J. C. Calabrese, S. A. Westcott and T. B. Marder, *J. Am. Chem. Soc.*, 1995, **117**, 8777; (*f*) D. H. Motry, A. G. Brazil and M. R. Smith, III, *J. Am. Chem. Soc.*, 1997, **119**, 2743; (*g*) M. Murata, S. Watanabe and Y. Masuda, *Tetrahedron Lett.*, 1999, **40**, 2585; (*h*) C. M. Vogels, P. G. Hayes, M. P. Shaver and S. A. Westcott, *Chem. Commun.*, 2000, 51; (*i*) D. E. Kadlecek, P. J. Carroll and L. G. Sneddon, *J. Am. Chem. Soc.*, 2000, **122**, 10868; (*j*) M. Murata, K. Kawakita, T. Asana, S. Watanabe and Y. Masuda, *Bull.*

Chem. Soc. Jpn., 2002, **75**, 825; (*k*) R. B. Coapes, F. E. S. Souza, R. Ll. Thomas, J. J. Hall and T. B. Marder, *Chem. Commun.*, 2003, 614; (*l*) A. Caballero and S. Sabo-Etienne, *Organometallics*, 2007, **26**, 1191.

19 (*a*) R. T. Baker, P. Nguyen, T. B. Marder and S. A. Westcott, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1336, (*Angew. Chem.*, 1995, **107**, 1451); (*b*) T. B. Marder, N. C. Norman and C. R. Rice, *Tetrahedron Lett.*, 1998, **39**, 155; (*c*) C. Y. Dai, E. G. Robins, A. J. Scott, W. Clegg, D. S. Yufit, J. A. K. Howard and T. B. Marder, *Chem. Commun.*, 1998, 1983; (*d*) P. Nguyen, R. B. Coapes, A. D. Woodward, N. J. Taylor, J. M. Burke, J. A. K. Howard and T. B. Marder, *J. Organomet. Chem.*, 2002, **652**, 77; (*e*) for other examples of catalysed alkene diboration, see: C. N. Iverson and M. R. Smith, III, *Organometallics*, 1997, **16**, 2757; (*f*) T. Ishiyama, M. Yamamoto and N. Miyaura, *Chem. Commun.*, 1997, 689; (*g*) J. B. Morgan, S. P. Miller and J. P. Morken, *J. Am. Chem. Soc.*, 2003, **125**, 8702; (*h*) S. P. Miller, J. B. Morgan, F. J. Nepveux and J. P. Morken, *Org. Lett.*, 2004, **6**, 131; (*i*) D. M. Kalendra, R. A. Dueñes and J. P. Morken, J. P., *SYNLETT*, 2005, 1749; (*j*) S. Trudeau, J. B. Morgan, M. Shrestha and J. P. Morken, *J. Org. Chem.*, 2005, **70**, 9538; (*k*) J. Ramírez, R. Corberán, M. Sanau, E. Peris and E. Fernández, *Chem. Commun.*, 2005, 3056; (*l*) J. Ramírez, A. M. Segarra and E. Fernández, *Tetrahedron: Asymmetry*, 2005, **16**, 1289; (*m*) R. Corberán, J. Ramírez, M. Poyatos, E. Peris and E. Fernández, *Tetrahedron: Asymmetry*, 2006, **17**, 1759; (*n*) V. Lillo, J. Mata, J. Ramírez, E. Peris and E. Fernández, *Organometallics*, 2006, **25**, 5829; (*o*) V. Lillo, M. R. Fructos, J. Ramírez, A. A. C. Braga, F. Maseras, M. Mar Díaz-Requejo, P. J. Peréz and E. Fernández, *Chem.–Eur. J.*, 2007, **13**, 2614; (*p*) for reviews, see: T. B. Marder and N. C. Norman, *Top. Catal.*, 1998, **5**, 63; (*q*) T. Ishiyama and N. Miyaura, *J. Synth. Org. Chem., Jpn.*, 1999, **57**, 503; (*r*) T. Ishiyama and N. Miyaura, *J. Organomet. Chem.*, 2000, **611**, 392; (*s*) V. M. Dembitsky, H. Abu, Ali and M. Srebnik, *Appl. Organomet. Chem.*, 2003, **17**, 327; (*t*) T. Ishiyama and N. Miyaura, *Chem. Rec.*, 2004, **3**, 271.

20 R. T. Baker, J. C. Calabrese, S. A. Westcott, P. Nguyen and T. B. Marder, *J. Am. Chem. Soc.*, 1993, **115**, 4367.

21 C. Widauer, H. Grützmacher and T. Ziegler, *Organometallics*, 2000, **19**, 2097.

22 C. E. Webster, Y. Fan, M. B. Hall, D. Kunz and J. F. Hartwig, *J. Am. Chem. Soc.*, 2003, **125**, 858.

23 (*a*) K. C. Lam, Z. Y. Lin and T. B. Marder, *Organometallics*, 2007, **26**, 3149; (*b*) B. Marcinec, M. Jankowska and C. Pietraszuk, *Chem. Commun.*, 2005, 663; (*c*) N. Miyaura and A. Suzuki, *J. Organomet. Chem.*, 1981, **213**, C53; (*d*) K. Nilsson and A. Hallberg, *Acta Chem. Scand.*, 1987, **38**, 569.

24 A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timers, *Organometallics*, 1996, **15**, 1518.

25 (*a*) D. Manning and H. Nöth, *J. Chem. Soc., Dalton Trans.*, 1985, 1689; (*b*) F. J. Lawlor, N. C. Norman, N. L. Pickett, E. G. Robins, P. Nguyen, G. Lesley, T. B. Marder, J. A. Ashmore and J. C. Green, *Inorg. Chem.*, 1998, **37**, 5282; (*c*) T. Ishiyama, M. Murata, T.-A. Ahiko and N. Miyaura, *Org. Synth.*, 1999, **77**, 176.

26 (*a*) P. Nguyen, G. Lesley, N. J. Taylor, T. B. Marder, N. L. Pickett, W. Clegg, M. R. J. Elsegood and N. C. Norman, *Inorg. Chem.*, 1994, **33**, 4623; (*b*) W. Clegg, M. M. J. Elsegood, F. J. Lawlor, N. C. Norman, N. L. Pickett, E. G. Robins, A. J. Scott, P. Nguyen, N. J. Taylor and T. B. Marder, *Inorg. Chem.*, 1998, **37**, 5289.

27 S. Shimada, A. S. Batsanov, J. A. K. Howard and T. B. Marder, *Angew. Chem., Int. Ed.*, 2001, **40**, 2168, (*Angew. Chem.*, 2001, **113**, 2226).

28 (*a*) D. Evans, J. A. Osborn and G. Wilkinson, *Inorg. Synth.*, 1966, **8**, 215; (*b*) J. A. McLeverty and G. Wilkinson, *Inorg. Synth.*, 1968, **11**, 99.

29 (*a*) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270; (*b*) W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284; (*c*) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.

30 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.

31 S. Huzinaga, *Gaussian Basis Sets for Molecular Calculations*, Elsevier Science Pub. Co., Amsterdam, 1984.

32 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, *GAUSSIAN 98 (Revision A.9)*, Gaussian, Inc., Pittsburgh, PA, 1998.

