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Metal catalysed hydroboration of vinyl sulfides, sulfoxides, sulfones, and sulfonates

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Abstract

The hydroboration of phenyl vinyl sulfide with catecholborane (HBcat) and pinacolborane (HBpin) has been examined with a number of rhodium complexes, all of which proceed with excellent regiocontrol in favour of the branched product $PhSCH(B(OR)_2)CH_3$. The corresponding linear product can be obtained exclusively in reactions employing $[Cp^*IrCl_2]_2$ and HBcat. Catalysed hydroborations of (*E*)-2-(*p*-toluenethio)styrene with HBcat using Rh(acac)(dppp) gave predominant formation of one product while reactions using HBpin afforded several products arising from a competing C–S bond cleavage (acac = acetylacetonato, dppp = 1,3-bis(diphenylphosphino)propane). Although reactions of phenyl vinyl sulfoxide were complicated by a competing deoxygenation reaction, hydroborations of phenyl vinyl sulfone using HBcat once again gave regioselective formation of either the branched or linear products, depending on the choice of catalyst used to effect this transformation. Catalysed hydroborations of phenyl vinyl sulfonate were less chemo- and regioselective, yielding hydrogenation and diboration products in addition to the two hydroboration product isomers.

Keywords: Boronate esters; Catalysis; Hydroboration; Regioselectivity; Vinyl sulfides

1. Introduction

The hydroboration of alkenes and alkynes, which constitutes the addition of a B–H bond across a carbon–carbon multiple bond, is a remarkably important reaction in organic synthesis [1]. Although simple boron hydride reagents such as borane ($H_3B{\cdot}X$, where X is a Lewis base) and 9-borabicyclo [3.3.1] nonane react readily with alkenes at room temperature, hydroborations with catecholborane (HBcat, cat = 1,2-$O_2C_6H_4$) generally require elevated temperatures. The discovery that transition metals can be used to catalyse the addition of HBcat to substrates has become an important and well-established technique in organic synthesis [2–6]. These reactions can have regio-, chemo-, and stereoselectivities that are complementary, or more remarkably, opposite to those obtained *via* the uncatalysed variant. For example, hydroboration of vinyl arenes ($ArCH{=}CH_2$) with HBcat give selectively either the expected linear boronate ester products ($ArCH_2CH_2Bcat$) or the branched boronate ester products ($ArCH(Bcat)CH_3$), depending upon the choice of catalyst used in these reactions (Scheme 1) [3]. While many transition metals can be used to catalyse these reactions, rhodium complexes are the most common and synthetically useful. A plausible mechanism for these reactions involves initial oxidative addition of HBcat [7] followed by coordination of the alkene to the metal centre, with subsequent insertion of the alkene into either the Rh–H [8] or the Rh–B bond [9], and reductive

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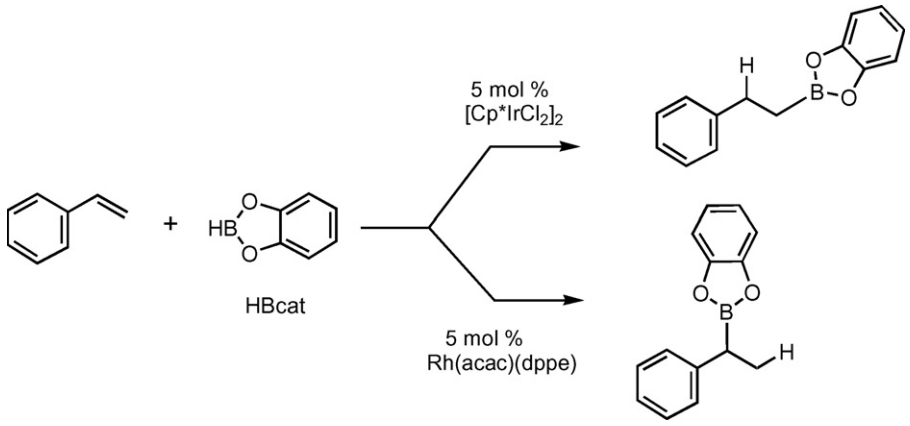


Scheme 1. The hydroboration of styrene with HBcat.

elimination to yield the desired product [10]. The branched boronate ester product is believed to arise when the metal centre can best stabilise a benzylic intermediate during the catalytic cycle.

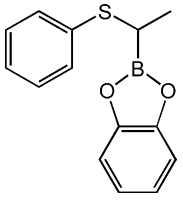
Although a considerable amount of research has focused on the catalysed hydroboration of simple unsaturated hydrocarbon systems, much less is known about analogous reactions with heteroatom-containing substrates [3,11–17]. For instance, catalysed hydroborations of pyrrolidinyl amides with HBcat gave, after oxidation, *syn* 1,3-hydroxy amides with high levels of regio- and stereochemical control. The remarkable selectivities observed in these reactions are believed to arise from a directing effect of the amide moiety [18]. In a similar study, Dai and co-workers found that rhodium catalysed hydroborations of allyl sulfones gave the branched boronate ester, where the directing effect of the sulfone oxygen is believed to be responsible for the regiocontrol in these reactions [17]. As part of our ongoing investigation into generating biologically active boron compounds [19], we have examined the catalysed hydroboration of vinyl sulfides, sulfoxides, sulfones, and sulfonates in an effort to expand the scope of these reactions and to see what effect different oxidation states of sulfur had on product selectivities. A preliminary account of this work has been published [16].

2. Experimental

Reagents and solvents used were purchased from Aldrich Chemicals and HBcat was distilled prior to use. NMR spectra were recorded on a JEOL JNM-GSX270 FT spectrometer. ^{1}H NMR chemical shifts are reported in ppm and referenced to residual solvent protons in deuterated solvent at 270 MHz. ^{13}C NMR chemical shifts are referenced to solvent carbon resonances as internal standards at 68 MHz and are reported in ppm. ^{11}B NMR chemical shifts are reported in ppm and are referenced to $BF_3{\cdot}OEt_2$ as an external standard at 87 MHz. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad (br), and overlapping (ov). All reactions were performed under an atmosphere of dinitrogen. GC/MS analyses were conducted using a Varian Saturn 2000 GC/MS/MS coupled to a CP-3800 GC. The GC was equipped with both the 1177 injection port with a CP-8410 liquid autoinjector connected to an SPB-1 (Supelco) fused silica column (30 m × 0.25 mm i.d. × 0.25 μm) and the 1079 solid injector chromatoprobe, attached to a 50 cm transfer line. The GC/MS spectrometer is controlled by the Saturn Workstation software, Version 5.51.

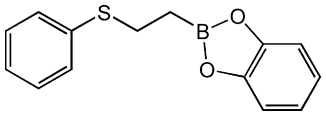
2.1. Preparation of *1a*

A solution of HBcat (22 mg, 0.18 mmol) in C_6D_6 (0.5 mL) was added dropwise to a mixture of phenyl vinyl sulfide (20 mg, 0.15 mmol) and $RhCl(PPh_3)_3$ (7 mg, 0.010 mmol) in C_6D_6 (0.5 mL). The reaction was allowed to stand for 24 h at room temperature at which point NMR spectroscopic data were collected. ^{1}H NMR δ 1.38 (d, J = 7.2 Hz, 3H, CH_3), 2.93 (q, J = 7.2 Hz, 1H, CHB), 6.70 (m, 2H, Ar), 6.89–6.97 (ov m, 5H, Ar), 7.30 (m, 2H, Ar); ^{13}C{^{1}H} NMR δ 16.6, 24.1 (br, CB), 112.7, 122.9, 126.9, 129.0, 131.6, 135.6, 148.3; ^{11}B NMR δ 33.5 (br).



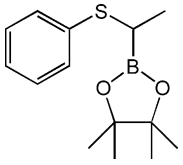
2.2. Preparation of *2a*

A solution of HBcat (60 mg, 0.50 mmol) in C_6D_6 (0.5 mL) was added dropwise to a mixture of phenyl vinyl sulfide (62 mg, 0.46 mmol) and $[Cp^*IrCl_2]_2$ (9 mg, 0.010 mmol) in C_6D_6 (0.5 mL). The reaction was allowed to stand for 24 h at room temperature at which point NMR spectroscopic data were collected. ^{1}H NMR δ 1.41 (t, J = 7.9 Hz, 2H, CH_2B), 2.94 (t, J = 7.9 Hz, 2H, CH_2), 6.80 (m, 2H, Ar), 6.90–7.05 (ov m, 5H, Ar), 7.25 (m, 2H, Ar); ^{13}C{^{1}H} NMR δ 11.6 (br, CB), 28.6, 112.4, 122.7, 126.0, 129.0, 129.7, 134.2, 148.5; ^{11}B NMR δ 34.2 (br).



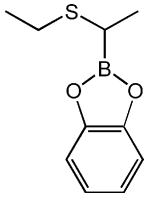
2.3. Preparation of **1b**

A solution of HBpin (34 mg, 0.26 mmol) in C_6D_6 (0.5 mL) was added dropwise to a mixture of phenyl vinyl sulfide (30 mg, 0.22 mmol) and $RhCl(PPh_3)_3$ (9 mg, 0.010 mmol) in C_6D_6 (0.5 mL). After 24 h at room temperature the solvent was removed under reduced pressure. The residue was purified using an alumina filter with hexane as the eluent. Yield: 40 mg (70%), clear oil. ^{1}H NMR δ 0.94 (s, 12H, pin), 1.41 (d, $J = 7.2$ Hz, 3H, CH_3), 2.85 (q, $J = 7.2$ Hz, 1H, CHB), 6.85–7.03 (ov m, 3H, Ar), 7.40 (m, 2H, Ar); $^{13}C\{^1H\}$ NMR δ 16.7, 24.1 (br, CB), 24.5, 83.6, 125.8, 128.8, 130.2, 133.5; ^{11}B NMR δ 32.2 (br).



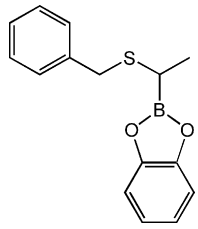
2.4. General procedure for the hydroboration of ethyl vinyl sulfide

A solution of HBcat (37 mg, 0.31 mmol) in C_6D_6 (0.5 mL) was added dropwise to a mixture of ethyl vinyl sulfide (25 mg, 0.28 mmol) and $RhCl(PPh_3)_3$ (5 mg, 0.006 mmol) in C_6D_6 (0.5 mL). The reaction was allowed to stand for 24 h at room temperature at which point NMR spectroscopic data were collected. ^{1}H NMR δ 1.03 (t, $J = 7.4$ Hz, 3H, CH_2CH_3), 1.41 (d, $J = 7.4$ Hz, 3H, CH(Bcat)CH_3), 2.40–2.46 (ov m, 3H, CH_2CH_3 and CH(Bcat)CH_3), 6.75–6.85 (second order m, 2H, Bcat), 6.95–7.05 (second order m, 2H, Bcat); $^{13}C\{^1H\}$ NMR δ 14.5, 16.1, 19.9 (br, CB), 25.4, 112.5, 122.8, 148.3; ^{11}B NMR δ 33.4 (br).



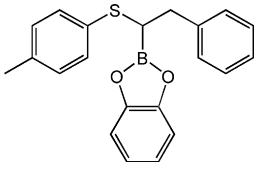
2.5. General procedure for the hydroboration of benzyl vinyl sulfide

A solution of HBcat (22 mg, 0.18 mmol) in C_6D_6 (0.5 mL) was added dropwise to a mixture of benzyl vinyl sulfide (25 mg, 0.17 mmol) and $RhCl(PPh_3)_3$ (3 mg, 0.003 mmol) in C_6D_6 (0.5 mL). The reaction was allowed to stand for 24 h at room temperature at which point NMR spectroscopic data were collected. ^{1}H NMR δ 1.34 (d, $J = 7.7$ Hz, 3H, CH(Bcat)CH_3), 2.38 (q, $J = 7.7$ Hz, 1H, CH(Bcat)CH_3), 3.62 (d, $J = 16.8$ Hz, 2H, CH_2S), 6.70–7.25 (ov m, 9H, Ar and Bcat); $^{13}C\{^1H\}$ NMR δ 15.7, 18.9 (br, CB), 35.7, 112.5, 114.0, 122.7, 126.9, 128.4, 129.1, 138.4; ^{11}B NMR δ 32.9 (br).



2.6. Preparation of **3**

$RhCl(PPh_3)_3$ (0.040 g, 0.040 mmol) in toluene (1 mL) was added to (*E*)-2-(*p*-toluenethio)styrene (200 mg, 0.88 mmol) in toluene (3 mL). Catecholborane (160 mg, 1.33 mmol) in toluene (1 mL) was then added dropwise and the reaction was allowed to stand for 24 h at room temperature. Removal of solvent under vacuum afforded an oily residue which was dissolved in hexane (3 mL) and stored at −30°C. Compound **3** was isolated as a white solid after two recrystallizations from hexane; yield: 150 mg (49%). NMR spectroscopic data (in C_6D_6): ^{1}H NMR δ 1.98 (s, 3H, CH_3), 3.20–3.42 (ov m, 3H, CH_2 and CHB), 6.68–6.72 (second order m, 2H, cat), 6.77 (d, $J = 7.9$ Hz, 2H, Ar), 6.91–6.95 (second order m, 2H, cat), 6.97–7.05 (ov m, 3H, Ar), 7.10 (m, 2H, Ar), 7.35 (d, $J = 7.9$ Hz, 2H, Ar); $^{13}C\{^1H\}$ NMR δ 20.8, 32.9 (br, CB), 37.9, 112.5, 122.8, 126.6, 128.6, 128.9, 129.8, 131.5, 133.1, 137.5, 140.0, 148.3; ^{11}B NMR δ 33.4 (br).

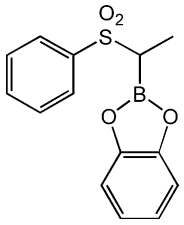


2.7. General procedure for the hydroboration of phenyl vinyl sulfoxide

In a typical reaction, HBcat or HBpin (0.30 mmol) was dissolved in C_6D_6 (0.5 mL) and added dropwise to a mixture of phenyl vinyl sulfoxide (20 mg, 0.13 mmol) and catalyst (0.010 mmol) in C_6D_6 (0.5 mL). The reaction mixtures were allowed to stand for 24 h at room temperature at which point NMR spectroscopic data were collected.

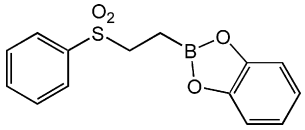
2.8. Preparation of **8a**

1,1′-Bis(diphenylphosphino)ferrocene (4 mg, 0.007 mmol) was dissolved in C_6D_6 (0.25 mL) and added to $Rh(acac)(coe)_2$ (3 mg, 0.007 mmol) in C_6D_6 (0.25 mL). This mixture was added to a solution of phenyl vinyl sulfone (20 mg, 0.12 mmol) and HBcat (22 mg, 0.18 mmol) in C_6D_6 (0.5 mL). The reaction mixture was allowed to stand for 24 h at room temperature at which point NMR spectroscopic data were collected. ^{1}H NMR δ 1.24 (d, $J = 7.4$ Hz, 3H, CH_3), 3.12 (q, $J = 7.4$ Hz, 1H, CHB), 6.69 (m, 2H, Ar), 6.79–6.93 (ov m, 5H, Ar), 7.72 (m, 2H, Ar); $^{13}C\{^1H\}$ NMR δ 10.8, 49.1 (br, CB), 112.9, 123.3, 128.7, 128.8, 133.1, 139.8, 148.1; ^{11}B NMR δ 31.4 (br).



2.9. Preparation of **9a**

A solution of HBcat (36 mg, 0.30 mmol) in C_6D_6 (0.5 mL) was added dropwise to a mixture of phenyl vinyl sulfone (20 mg, 0.12 mmol) and $[Cp^*IrCl_2]_2$ (5 mg, 0.006 mmol) in C_6D_6 (0.5 mL). The reaction mixture was allowed to stand for 24 h at room temperature at which point NMR spectroscopic data were collected. ^{1}H NMR δ 1.26 (t, J = 7.2 Hz, 2H, CH_2B), 2.88 (t, J = 7.2 Hz, 2H, CH_2), 6.66–6.96 (ov m, 7H, Ar), 7.72 (m, 2H, Ar); ^{13}C{^{1}H} NMR δ 4.6 (br, CB), 51.5, 112.4, 122.8, 128.4, 128.9, 133.0, 139.4, 148.3; ^{11}B NMR δ 34.8 (br).

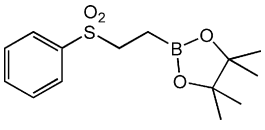


2.10. General procedure for the hydroboration of phenyl vinyl sulfone

A solution of HBcat or HBpin (0.18 mmol) in C_6D_6 (0.5 mL) was added dropwise to a mixture of phenyl vinyl sulfone (30 mg, 0.18 mmol) and catalyst (3 mg, 0.003 mmol) in C_6D_6 (0.5 mL). The reaction was allowed to stand for 24 h at room temperature at which point NMR spectroscopic data were collected. Selected NMR data for $PhSO_2CH_2CH(Bcat)_2$, **10a**: ^{1}H δ 2.34 (t, J = 8 Hz, 1H), 3.74 (d, J = 8 Hz, 2H). $PhSO_2CH_2CH(Bpin)_2$, **10b**: ^{1}H δ 1.47 (t, J = 7.8 Hz, 1H), 3.55 (d, J = 7.8 Hz, 2H). $PhSO_2CH_2CH_3$, **11**: ^{1}H δ 0.91 (t, J = 7.3 Hz, 3H), 2.63 (q, J = 7.3 Hz, 2H).

2.11. Preparation of **9b**

1,4-Bis(diphenylphosphino)butane (4 mg, 0.007 mmol) was dissolved in C_6D_6 (0.25 mL) and added to $Rh(acac)(coe)_2$ (3 mg, 0.007 mmol) in C_6D_6 (0.25 mL). This mixture was added to a solution of phenyl vinyl sulfone (20 mg, 0.12 mmol) and HBpin (23 mg, 0.18 mmol) in C_6D_6 (0.5 mL). The reaction mixture was allowed to stand for 24 h at room temperature at which point NMR spectroscopic data were collected. ^{1}H NMR δ 0.94 (s, 12H, pin), 1.14 (t, J = 7.2 Hz, 2H, CH_2B), 3.02 (t, J = 7.2 Hz, 2H, CH_2), 6.82–7.12 (ov m, 3H, Ar), 7.73 (m, 2H, Ar); ^{13}C{^{1}H} NMR δ 5.0 (br, CB), 24.6, 52.1, 83.4, 128.3, 128.8, 132.7, 139.8; ^{11}B NMR δ 33.4 (br).



2.12. General procedure for the hydroboration of phenyl vinyl sulfonate

In a typical reaction, HBcat or HBpin (0.18 mmol) in C_6D_6 (0.5 mL) was added dropwise to a mixture of phenyl vinyl sulfonate (20 mg, 0.11 mmol) and catalyst (0.01 mmol) in C_6D_6 (0.5 mL). The reaction mixtures were allowed to stand for 24 h at room temperature at which point NMR spectroscopic data were collected. Selected NMR data for $PhOSO_2CH(Bcat)CH_3$, **12a**: ^{1}H δ 1.62 (d, J = 7.3 Hz, 3H), 3.32 (q, J = 7.3 Hz, 1H); ^{13}C 11.3, 43.8 ppm (br, CB); ^{11}B 30.9 ppm. $PhOSO_2CH_2CH_2(Bcat)$, **13a**: ^{1}H δ 1.64 (m, 2H), 3.11 (m, 2H); ^{13}C 5.0 (br, CB), 45.7 ppm; ^{11}B 33.2 ppm. $PhOSO_2CH_2CH_2(Bpin)$, **13b**: 1.26 (t, J = 7.8 Hz, 2H), 3.01 (t, J = 7.8 Hz, 2H). $PhOSO_2CH_2CH(Bcat)_2$, **14a**: ^{1}H δ 2.58 (t, J = 8 Hz, 1H), 3.85 (d, J = 8 Hz, 2H). $PhOSO_2CH_2CH(Bpin)_2$, **14b**: 3.59 (d, J = 7.9 Hz, 2H). $PhOSO_2CH_2CH_3$, **15**: ^{1}H δ 1.04 (t, J = 7.3 Hz, 3H), 2.61 (q, J = 7.3 Hz, 2H); ^{13}C 7.8, 44.5 ppm.

2.13. X-ray diffraction studies

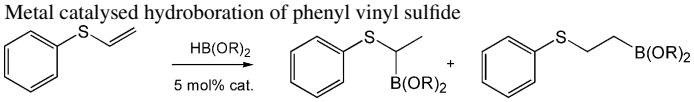
Crystals of **9a** were grown from a saturated C_6D_6 solution at 20 °C. Single crystals were coated with Paratone-N oil, mounted using a glass fibre and frozen in the cold stream of the goniometer. A hemisphere of data were collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and θ scans with a scan width of 0.3° and exposure time of 30 s. The detector distance was 5 cm. The data were reduced [20] and corrected for absorption [21]. The structures were solved by direct methods and refined by full-matrix least squares on F^2 [22]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in Fourier difference maps and refined isotropically (CCDC 642558).

3. Results and discussion

3.1. Vinyl sulfides

Boronate esters have proven to be remarkably useful intermediates in organic synthesis, particularly as substrates for metal catalysed carbon–carbon bond formation using the Suzuki-Miyaura coupling reaction [23]. Compounds containing boronate esters, or boronic acids, have also found a number of molecular recognition applications such as amine and sugar sensors [24,25], saccharide transport [26,27], and as enzyme inhibitors [28]. For instance, several research groups have shown that α-aminoboron compounds are particularly selective enzyme inhibitors for serine proteases [29–31], and related work has shown that α-phosphonylboronate esters also exhibit significant bioactivity [32]. Although some excellent chemistry has been developed for the preparation of compounds containing both a Lewis basic site and a Lewis acidic boronate ester group [33,34], we have investigated the metal catalysed hydroboration of vinyl heteroatom derivatives as a direct route to these compounds. In this report, we have examined the hydroboration of sulfur derivatives, owing to the wealth of bioactivity associated with these compounds [35].

Table 1
Metal catalysed hydroboration of phenyl vinyl sulfide



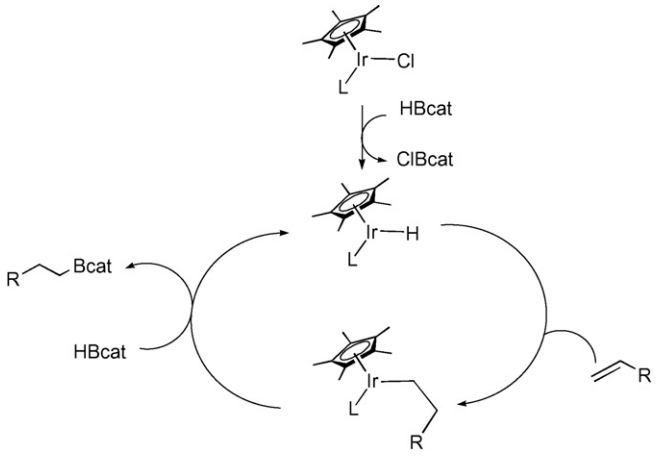
1 2

Entry	Catalyst precursor	Borane	1[a]	2[a]
1	$RhCl(PPh_3)_3$	HBcat	>98	–
2	$[RhCl(coe)_2]_2/2PPh_3$	HBcat	>98	–
3	$Rh(acac)(coe)_2$/dppp	HBcat	>98	–
4	$Rh(acac)(coe)_2$/dppb	HBcat	>98	–
5	$[Rh(cod)(dppp)]BF_4$[b]	HBcat	>98	–
6	$[Cp^*IrCl_2]_2$	HBcat	–	>98
7	$RhCl(PPh_3)_3$	HBpin	>98	–
8	$[RhCl(coe)_2]_2/2PPh_3$	HBpin	>98	–
9	$Rh(acac)(coe)_2$/dppb	HBpin	>98	–
10	$[Cp^*IrCl_2]_2$	HBpin	–	–

[a] All reactions were conducted in C_6D_6 at RT and product ratios were determined by ^1H NMR spectroscopy and confirmed by GC/MS. Complete conversion of starting materials was observed.
[b] Reactions conducted in THF.

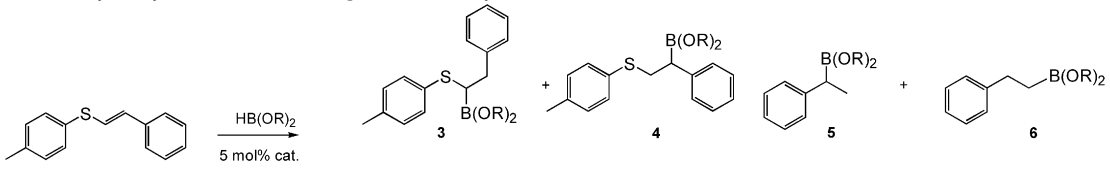
We have found that a number of rhodium complexes (Table 1, entries 1–5) could be used in the hydroboration of $PhSCH{=}CH_2$ with HBcat to give *exclusive* formation of the unexpected branched product $PhSCH(Bcat)CH_3$ (**1a**). These results are particularly intriguing as this predominant regioselectivity has only been observed in hydroborations of vinyl arenes [36–42] and fluoroalkenes [43]. Like the fluorinated examples, the directing effect of the sulfur heteroatom is presumably responsible for this present selectivity. Of singular interest are reactions using the catalyst system $[RhCl(coe)_2]_2/2PPh_3$ (coe = *cis*-cyclooctene) which gave the branched product selectively (entry 2), as analogous hydroborations of vinyl arenes using this catalyst are known to give predominant formation of the corresponding linear boronate ester products [44]. It is also interesting to note that reactions with pinacolborane (HBpin; pin = 1,2-$O_2C_2Me_4$) and a rhodium catalyst (entries 7–9) also gave selective formation of the branched product $PhSCH(Bpin)CH_3$ (**1b**). An interesting paper by Crudden et al. has shown that cyclooctadiene rhodium complexes can be used in the hydroboration of vinyl arenes with HBpin to give branched products [37]. Reactions of vinyl arenes with iridium catalysts and HBpin, however, give predominantly the corresponding linear products [45]. Unlike the Bcat derivatives, pinacol boronate ester compounds are of considerable interest owing to their inherent air and moisture stability [46,47]. Selective formation of the linear boronate ester product $PhSCH_2CH_2Bcat$ (**2a**) was only obtained in reactions using the iridium catalyst precursor $[Cp^*IrCl_2]_2$ ($Cp^* = \eta^5$-C_5Me_5, entry 6). While this isomer also slowly formed at low conversions by heating HBcat and phenyl vinyl sulfide at 80 °C, extensive nucleophilic degradation of the borane was observed as the reaction proceeded [48,49]. Previous studies using this Ir(III) complex have shown that hydroborations with HBcat always proceed with great selectivity to give linear boronate ester products [50]. It is possible that these reactions may proceed *via* a mechanism unlike those associated with hydroborations using a rhodium catalyst. A plausible mechanism for these iridium catalysed reactions is shown in Scheme 2 and is similar to one reported for the lanthanum catalysed hydroboration of alkenes, which also gives linear products selectively [51]. Reactions of HBpin using $[Cp^*IrCl_2]_2$, however, gave products arising from competing cleavage of the C–S bond (entry 10). The cleavage of C–S bonds by late metals is an important step in the catalytic hydrodesulfurization reaction [52].

Other primary vinyl sulfides were also investigated ($PhCH_2SCH{=}CH_2$ and $CH_3CH_2SCH{=}CH_2$) in the rhodium catalysed hydroboration with HBcat, and these examples also gave selective formation of the corresponding branched products. These results prompted us to investigate the catalysed hydroboration of substituted vinyl sulfide derivatives, prepared by coupling vinyl iodides and thiols using a well-defined copper(I) catalyst [53]. Hydroborations of (*E*)-2-(*p*-toluenethio)styrene with HBcat using either



Scheme 2. A possible alternate mechanism for the $[Cp^*IrCl_2]_2$ catalysed hydroboration of alkenes.

Table 2
Metal catalysed hydroboration of (*E*)-2-(*p*-toluenethio)styrene



Entry	Catalyst precursor	Borane	3[a]	4[a]	5[a]	6[a]
1	$Rh(acac)(coe)_2$/dppp	HBcat	90	–	10	–
2	$RhCl(PPh_3)_3$	HBcat	90[b]	–	10	–
3	$[Cp^*IrCl_2]_2$	HBcat	45	35	–	20
4	$RhCl(PPh_3)_3$	HBpin	–	–	80	20
5	$Rh(acac)(coe)_2$/dppp	HBpin	–	–	50	50
6	$[Cp^*IrCl_2]_2$	HBpin	–	–	60	40

[a] All reactions were conducted in C_6D_6 at RT and product ratios were determined by ^1H NMR spectroscopy and confirmed by GC/MS. Complete conversion of starting materials was observed.
[b] Compound **3** was isolated in 49% yield.

a catalytic amount of $RhCl(PPh_3)_3$ (Table 2, entry 2) or $Rh(acac)(coe)_2$/dppp (acac = acetylacetonato; dppp = 1,3-bis(diphenylphosphino)propane) [44] gave significant amounts (*ca*. 90% by ^1H NMR spectroscopy) of product **3** (entry 1). Unequivocal assignment of **3** was accomplished through the interpretation of ^1H, ^{13}C, 135°DEPT, gHMQC, and gHMBC NMR spectra [54]. The key long-range correlation that shows the regiochemistry is the CH_2 carbon at δ 37.9 ppm with the aryl hydrogens of the phenyl group at δ 6.97–7.05 ppm. Once again, however, all reactions with HBpin (entries 4–6) were complicated by a competing C–S bond cleavage and gave products arising from hydroboration of the liberated styrene. Similar reactivities were observed for other 1,2-disubstituted vinyl sulfides (*trans*-PhSCH=CHC(O)OEt and *trans*-PhSCH=CH^{i}Pr).

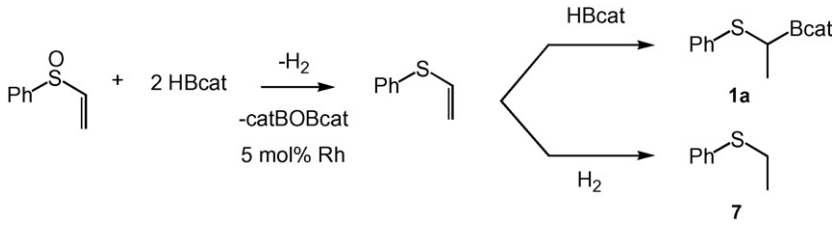
3.2. Phenyl vinyl sulfoxide

The rhodium catalysed addition of HBcat and HBpin to phenyl vinyl sulfoxide lead to several products (Scheme 3) arising from a competing deoxygenation reaction [55]. For instance, the addition of HBcat proceeded to give catBOBcat, dihydrogen, and phenyl vinyl sulfide, the latter of which reacted with either excess HBcat to give **1a** or dihydrogen to give $PhSCH_2CH_3$ (**7**). Although this deoxygenation reaction proceeds with the addition of a catalyst, reactions can take days depending on the sulfoxide [56]. The reduction of sulfoxides to the corresponding sulfides is an important reaction that has found considerable utility in organic synthesis [57] and biochemistry [58]. A proposed mechanism for these catalysed deoxygenations involves initial oxidative addition of HBcat to the metal centre, followed by insertion of the basic oxygen (arising from the polar S–O bond, as opposed to the more covalent S–O bonds in sulfones) into the rhodium boron bond. Reductive extrusion would afford the transient catBOH species, which would react with another equivalent of HBcat to give dihydrogen and catBOBcat [55]. Unfortunately, all attempts to circumvent this pathway proved unsuccessful.

3.3. Phenyl vinyl sulfone

We then decided to examine the catalysed hydroboration of phenyl vinyl sulfone, where the oxygen atoms are considerably less basic than those in related sulfoxides [59]. Interestingly, addition of HBcat to phenyl vinyl sulfone at 80 °C slowly affords the branched isomer **8a** indicating that the sulfone group is capable of functioning as a directing group in the uncatalysed reaction. A number of rhodium and iridium complexes were investigated as potential catalysts and the results are illustrated in Table 3. Although deoxygenation was not a problem in these reactions, generation of diborated products **10** and hydrogenation product **11** complicated product distributions. Compound **10** presumably arises from initial formation of the vinyl boronate esters $PhSO_2CH{=}CHB(OR)_2$ followed by subsequent addition of either HBcat or HBpin. Vinyl boronate esters are frequently observed as products in catalysed 'hydroboration' reactions [60–64], and are believed to form by a competing dehydrogenative borylation reaction. This reaction is believed to involve the insertion of the alkene into the Rh–B bond, and not the Rh–H bond, followed by a β-hydride elimination step to give the corresponding vinyl boronate ester and dihydrogen. In a previous study, high yields of vinyl boronate esters were formed in the catalysed addition of HBpin to vinyl arenes using a number of rhodium and ruthenium cyclooctadiene complexes [60]. We were able to generate the branched isomer $PhSO_2CH(Bcat)CH_3$ (**8a**) with selectivity of up to 98% in reactions using Rh(acac)(dppf) (dppf = 1,2-bis(diphenylphosphino)ferrocene) (entry 1). Unlike reactions with the vinyl sulfide, other rhodium catalysts gave a mixture of products, demonstrating that the sulfone group is a much less effective directing group. Conversely, using the iridium catalyst $[Cp^*IrCl_2]_2$ with HBcat (entry 8), the linear isomer **9a** could once again be generated as the only new boron containing product.

We have found that reactions of phenyl vinyl sulfone with HBpin also gave a considerable amount of dehydrogenative borylation derived products (Table 3, entries 9–11). While the



Scheme 3. Metal catalysed addition of HBcat to phenyl vinyl sulfoxide.

linear boronate ester **9** could arise from a simple hydroboration reaction, it is also plausible that formation of this compound arises from a catalysed hydrogenation of the transient vinyl boronate ester $PhSO_2CH{=}CHBpin$. Indeed, in reactions using a deficiency of borane, this vinyl boronate ester is observed initially by ^1H NMR spectroscopy. Catalysed hydrogenations of related bis vinyl boronate esters have also been reported [64]. Formation of **11** arises from a simple hydrogenation of the starting phenyl vinyl sulfone.

The molecular structure of **9a** is shown in Fig. 1 and confirms the formation of this isomer. Crystallographic data are provided in Table 4 and selected bond distances and angles are given in Table 5. Although this molecule contains both a Lewis acidic (Bcat) and Lewis basic site (oxygen atoms of SO_2), no appreciable intramolecular or intermolecular interactions exist in the solid state. The boron atom lies in a trigonal environment where the sum of the angles around boron is 359.9(2)Å. The B–O distances of B(10)–O(11) 1.386(2) and B(10)–O(18) 1.390(2) are similar to those reported in related structures [65–67].

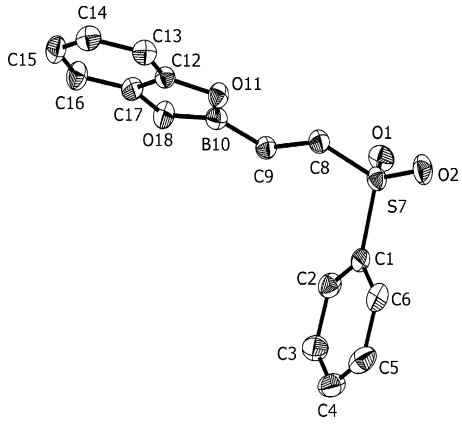
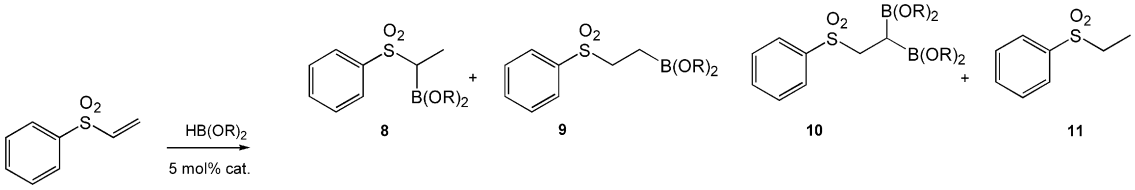


Fig. 1. The molecular structure of **9a** showing the atomic labeling scheme and 30% probability displacement ellipsoids with hydrogen atoms omitted for clarity.

3.4. Phenyl vinyl sulfonate

Uncatalysed reaction of HBcat with phenyl vinyl sulfonate at 80 °C afforded multiple products derived from borane degradation and cleavage of the sulfonate group [68]. Unfortunately, catalysed hydroborations of phenyl vinyl sulfonate at 20 °C also gave a mixture of products regardless of the borane or metal complex used to facilitate this reaction. For example, hydroboration of phenyl vinyl sulfonate using HBcat and Wilkinson's catalyst (Table 6, entry 6) gave only 42% of the branched isomer **12** and 29% of the corresponding linear product **13**. Up to

Table 3
Metal catalysed hydroboration of phenyl vinyl sulfone



Entry	Catalyst precursor	Borane	8[a]	9[a]	10[a]	11[a]
1	$Rh(acac)(coe)_2$/dppf	HBcat	98	2	–	–
2	$Rh(acac)(coe)_2$/dppb	HBcat	95	5	–	–
3	$RhCl(PPh_3)_3$	HBcat	80	10	5	5
4	$[Rh(cod)(dppp)]BF_4$[b]	HBcat	75	25		
5	$Rh(acac)(coe)_2$/dppp	HBcat	70	20	5	5
6	$Rh(acac)(coe)_2$/dppe	HBcat	60	15	5	20
7	$[RhCl(coe)_2]_2$/$2PPh_3$	HBcat	20	55	5	20
8	$[Cp^*IrCl_2]_2$	HBcat	–	>98	–	–
9	$RhCl(PPh_3)_3$	HBpin	–	25	30	45
10	$[Cp^*IrCl_2]_2$	HBpin	–	25	–	75[c]
11	$Rh(acac)(coe)_2$/dppb	HBpin	–	90	–	10

[a] All reactions were conducted in C_6D_6 at RT and product ratios were determined by ^1H NMR spectroscopy and confirmed by GC/MS. Complete conversion of starting materials was observed.
[b] Reactions conducted in THF.
[c] Five equivalents of HBpin were used.

Table 4
Crystallographic data collection parameters for **9a**

Formula	$C_{14}H_{13}BO_4S$
fw	288.11
Crystal system	Monoclinic
Space group	*P*2(1)/*c*
a (Å)	6.2886(7)
b (Å)	9.5719(10)
c (Å)	22.378(2)
β (°)	91.223(2)
V (Å^3)	1346.7(2)
Z	4
ρ_{calcd} (mg m^{-3})	1.421
Crystal size (mm^3)	1.00 × 0.10 × 0.10
Temperature (K)	198(1)
Radiation	Mo Kα (λ = 0.71073)
μ (mm^{-1})	0.249
Total reflections	8938
Total unique reflections	3012
No. of variables	233
R_{int}	0.0235
Theta range (°)	1.82–27.50
Largest difference peak/hole (e Å^{-3})	0.421/−0.343
S (GoF) on F^2	1.074
R_1[a] ($I > 2\sigma(I)$)	0.0354
wR_2[b] (all data)	0.0941

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.

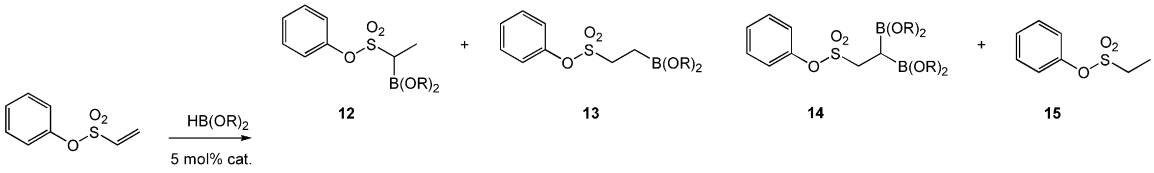
[b] $wR_2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum[wF_o^4])^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0428P)^2 + (0.4406P)]$, where $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

Table 5
Selected bond lengths (Å) and angles (°) for **9a**

Bond lengths	
S(7)–O(2)	1.4408(13)
S(7)–O(1)	1.4438(12)
S(7)–C(8)	1.7781(17)
C(8)–C(9)	1.523(2)
C(1)–S(7)	1.7687(17)
C(9)–B(10)	1.557(2)
B(10)–O(11)	1.386(2)
B(10)–O(18)	1.390(2)
O(11)–C(12)	1.3872(19)
C(17)–O(18)	1.3879(19)
Bond angles	
C(6)–C(1)–S(7)	119.16(14)
C(2)–C(1)–S(7)	119.73(13)
O(2)–S(7)–O(1)	118.58(8)
O(2)–S(7)–C(1)	107.93(8)
O(1)–S(7)–C(1)	108.17(7)
O(2)–S(7)–C(8)	107.46(8)
O(1)–S(7)–C(8)	108.98(8)
C(1)–S(7)–C(8)	104.90(8)
C(9)–C(8)–S(7)	114.59(11)
O(11)–B(10)–O(18)	111.63(15)
O(11)–B(10)–C(9)	124.33(16)
O(18)–B(10)–C(9)	123.97(15)
B(10)–O(11)–C(12)	104.90(13)
C(17)–O(18)–B(10)	105.02(12)

84% of the branched product could be generated (entries 1 and 2), however, along with a considerable amount of **13**, hydrogenation product **15**, and minor amounts of diborated product **14**. Interestingly, the iridium catalyst [Cp*IrCl$_2$]$_2$ (entry 3) also gave 60% of the branched isomer in reactions using HBcat. It is unclear at this time why the branched isomer was favoured in this reaction, as hydroborations using this catalyst precursor always appear to favour linear products. Attempts to catalyse this reaction using this iridium complex and HBpin gave a complicated product distribution arising from competing degradation reactions. Excess borane had to be used (up to 5 equivalents) in all of these reactions to effect complete reduction of the double bond, as considerable degradation of the starting borane was always observed. Further work is therefore needed to understand the poor selectivities observed in these reactions, the results of which will be published in due course.

Table 6
Metal catalysed hydroboration of phenyl vinyl sulfonate



Entry	Catalyst precursor	Borane	12[a]	13[a]	14[a]	15[a]
1	Rh(acac)(coe)$_2$/dppb	HBcat	84	7	2	7
2	[Rh(cod)(dppp)]BF$_4$[b]	HBcat	80	5	–	15
3	[Cp*IrCl$_2$]$_2$	HBcat	60	30	–	10
4	Rh(acac)(coe)$_2$/dppf	HBcat	59	11	7	23
5	Rh(acac)(coe)$_2$/dppp	HBcat	55	20	5	20
6	RhCl(PPh$_3$)$_3$	HBcat	42	29	4	25
7	Rh(acac)(coe)$_2$/dppe	HBcat	35	30	–	35
8	[RhCl(coe)$_2$]$_2$/2PPh$_3$	HBcat	15	55	5	25
9	RhCl(PPh$_3$)$_3$	HBpin	–	40	15	45

[a] All reactions were conducted in C_6D_6 at RT and product ratios were determined by ^{1}H NMR spectroscopy and confirmed by GC/MS. Complete conversion of starting materials was observed.

[b] Reactions conducted in THF.

4. Conclusions

We have investigated the catalysed hydroboration of vinyl sulfides and found that reactions using rhodium complexes proceed with excellent regiocontrol in favour of the unexpected branched product. The directing effect of the sulfur atom is believed to be responsible for these observed selectivities. The iridium(III) catalyst precursor $[Cp^*IrCl_2]_2$ could be used effectively with HBcat to reverse this selectively and generate the corresponding linear boronate ester product. Although, 1,2-disubstituted vinyl sulfides gave products arising from a competing C–S bond cleavage in reactions using HBpin, analogous reactions with HBcat gave up to 90% of one isomer, where the boron has added α to the sulfur atom. Hydroborations of phenyl vinyl sulfoxide gave products derived from an initial deoxygenation to give phenyl vinyl sulfide and catBOBcat. Catalysed hydroborations of phenyl vinyl sulfone with HBcat generated the corresponding branched product with high selectivity using Rh(acac)(dppf). Reactions of phenyl vinyl sulfonate suffered from moderate selectivities, borane degradation, and in some cases, cleavage of the sulfonate group. Of these systems, it appears that the sulfide group is the best at directing these catalysed hydroborations to give the corresponding branched products.

Acknowledgements

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