Inorganica Chimica Acta 365 (2011) 408–413

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

$[Cp^*IrCl_2]_2$ catalyzed hydroborations of alkenes using a bulky dioxaborocine

Nicole M. Hunter [a], Christopher M. Vogels [a], Andreas Decken [b], Andrew Bell [c,*], Stephen A. Westcott [a,*]

[a] Department of Chemistry and Biochemistry, Mount Allison University, Sackville, NB, Canada E4L 1G8
[b] Department of Chemistry, University of New Brunswick, Fredericton, NB, Canada E3B 5A3
[c] Promerus LLC, 9921 Brecksville Road, Brecksville, OH 44141-3289, USA

ARTICLE INFO

Article history:
Received 18 July 2010
Accepted 28 September 2010
Available online 4 November 2010

Keywords:
Borylation
Catalysis
Dioxaborocine
Hydroboration
Iridium

ABSTRACT

4,8-Di-*tert*-butyl-2,10-dimethyl-12*H*-dibenzo[*d*,*g*][1,3,2]dioxaborocine (**1**) has been prepared in high yield by the addition of $H_3B{\cdot}SMe_2$ to 6,6′-methylene(2-*tert*-butyl-4-methylphenol). Dioxaborocine **1** is a relatively stable solid that reacts with a variety of aliphatic alkenes in the presence of catalytic amounts of $[Cp^*IrCl_2]_2$ to give the terminal hydroboration products. Analogous reactions with vinylarenes, however, afford the corresponding alkenylboronate esters along with equal amounts of the hydrogenation products. Boron products have been characterized by a number of physical and analytical methods, including single-crystal X-ray diffraction studies.

1. Introduction

The discovery that certain transition metal complexes catalyze the addition of catecholborane (HBcat, cat = 1,2-$O_2C_6H_4$) or pinacolborane (HBpin, 1,2-$O_2C_2Me_4$) to unsaturated substrates has become an important strategy in organic synthesis [1–8]. Products obtained using a transition metal catalyzed hydroboration can have regio-, chemo-, or stereoselectivities complementary, or more remarkably, opposite to those from products obtained via the uncatalyzed route. For instance, Männig and Nöth demonstrated that addition of catecholborane to 5-hexen-2-one proceeded readily at room temperature to give the expected borate, where addition of the borane has occurred at the more reactive ketone functionality [9]. However, selective addition of HBcat to the less reactive alkene group was achieved if the reaction was carried out at lower temperatures in the presence of a rhodium catalyst, e.g. $RhCl(PPh_3)_3$. Since this remarkable discovery, a considerable amount of research has focussed on investigating the mechanism and scope of catalyzed hydroboration reactions [6,10–13]. Much less studied, however, is the use of alternate borane sources [14–18]. Indeed, pinacolborane, (4,4,5,5-tetramethyl-1,3,2-dioxaborolane or HBpin) is occasionally used as a replacement for HBcat as the resulting organoborane products are stable to air and chromatography. Unfortunately, these reactions can suffer from poor selectivities or competing pathways (i.e. hydrogenation and/or dehydrogenative borylations) to give several organoboronate ester products. As such, we have investigated the use of bulky 4,8-di-*tert*-butyl-2,10-dimethyl-12*H*-dibenzo[*d*,*g*][1,3,2]dioxaborocine (**1**, HBdd, where dd = 6,6′-methylenebis(2-*tert*-butyl-4-methylphenolato)) for its use in the catalyzed hydroboration of alkenes.

Compound **1** (Fig. 1) was prepared by modification of a known procedure in 90% yield by the addition of 6,6′-methylene(2-*tert*-butyl-4-methylphenol) to a solution of $H_3B{\cdot}SMe_2$ in toluene heated at reflux for 18 h and characterized by multinuclear NMR spectroscopy [14]. Compound **1** is a white solid that can be kept indefinitely at room temperature under a nitrogen atmosphere. A broad peak in the ^{11}B NMR spectrum at δ 21 ppm and a broad singlet at 4.57 ppm in the ^1H NMR data are consistent with chemical shifts found in other bulky diorganyloxyboranes.

Although the synthesis and structure of **1** have been reported in an elegant study by Nöth and co-workers [14], its potential to act as a hydroboration agent has not yet been investigated. We therefore decided to examine its reactivity with a number of unsaturated substrates and report our findings herein.

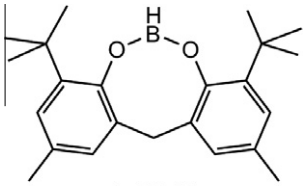
2. Experimental

2.1. General

Reagents and solvents were purchased from Aldrich Chemicals and used as received with the exception of **1** which was synthesized by modification of a known method [14]. NMR spectra were recorded on a JEOL JNM-GSX270 FT NMR (^1H 270 MHz; ^{11}B 87 MHz; ^{13}C 68 MHz; ^{19}F 254 MHz) spectrometer. Chemical shifts (δ) are reported in ppm [relative to residual solvent peaks (^1H and ^{13}C) or external $BF_3{\cdot}OEt_2$ (^{11}B) and CF_3CO_2H (^{19}F)] and coupling constants (J) in Hz. Multiplicities are reported as singlet (s), doublet

* Corresponding authors.
E-mail address: swestcott@mta.ca (S.A. Westcott).

0020-1693/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2010.09.051



1, HBdd

Fig. 1. 4,8-Di-*tert*-butyl-2,10-dimethyl-12*H*-dibenzo[*d*,*g*][1,3,2]dioxaborocine (**1**).

(d), triplet (t), quartet (q), quintet (quint), multiplet (m), broad (br), and overlapping (ov). A CEM Discover microwave reactor was employed for all microwave reactions and the reaction temperature was monitored by an internal IR pyrometer. Reactions were performed under an atmosphere of dinitrogen.

*2.2. Synthesis of 4,8-di-tert-butyl-2,10-dimethyl-6-octyl-12H-dibenzo[d,g][1,3,2]dioxaborocine (**2**)*

Compound **1** (284 mg, 0.81 mmol) in toluene (2 mL) was added to a toluene (3 mL) solution of 1-octene (100 mg, 0.89 mmol) and $[Cp^*IrCl_2]_2$ (13 mg, 0.016 mmol). The reaction was allowed to proceed for 18 h then passed through a small plug of alumina to remove the catalyst and impurities. Removal of solvent under vacuum afforded **2** as a colorless oil. Yield: 0.25 g (67%). ^{1}H NMR (C_6D_6): ∂ 7.00 (s, 2H, Ar), 6.99 (s, 2H, Ar), 4.21 (d, *J* = 13.6 Hz, 1H, bridging-C*H*H), 3.51 (d, *J* = 13.6 Hz, 1H, bridging-CH*H*), 2.33 (s, 6H, CH_3), 1.79 (m, 2H, octyl), 1.52–1.29 (ov m, 30H, octyl & *t*-butyl), 1.00 (t, *J* = 8.1 Hz, 3H, octyl-CH_3); ^{11}B NMR (C_6D_6): ∂ 28 (br); ^{13}C{^{1}H} NMR (C_6D_6): ∂ 148.8, 139.4, 131.8, 131.1, 127.9, 126.3, 35.4, 34.9, 33.0, 32.3, 30.1, 29.9, 29.7, 25.1, 23.1, 21.3, 17.6 (br, *C*B), 14.5. *Anal.* Calc. for $C_{31}H_{47}BO_2$ (462.59): C, 80.48; H, 10.26. Found: C, 80.00; H, 10.74%.

*2.3. Synthesis of 6-(2-(bicyclo[2.2.1]heptan-2-yl)ethyl)-4,8-di-tert-butyl-2,10-dimethyl-12H-dibenzo[d,g][1,3,2]dioxaborocine (**3**)*

Compound **1** (930 mg, 2.65 mmol) in toluene (5 mL) was added to a toluene (3 mL) solution of 2-norbornene (250 mg, 2.66 mmol) and $[Cp^*IrCl_2]_2$ (40 mg, 0.050 mmol). The reaction was allowed to proceed for 18 h, at which point the solvent was removed under vacuum and the resulting solid was dissolved in a minimum amount of hot THF. The solution was stored at −30 °C and the resulting precipitate was collected by suction filtration to afford **3** as an off-white solid. Yield: 0.98 g (83%); mp 174–176 °C. ^{1}H NMR (C_6D_6): ∂ 6.90 (s, 2H, Ar), 6.76 (s, 2H, Ar), 4.05 (d, *J* = 13.9 Hz, 1H, bridging-C*H*H), 3.23 (d, *J* = 13.9 Hz, 1H, bridging-CH*H*), 2.79 (br s, 1H), 2.33 (br s, 1H), 2.00 (s, 6H, CH_3), 1.60 (m, 2H), 1.46–1.26 (ov m, 25H, norbornyl & *t*-butyl); ^{11}B (C_6D_6): ∂ 29 (br); ^{13}C{^{1}H} (C_6D_6): ∂ 149.1, 138.9, 131.4, 130.9, 127.6, 126.1, 39.4, 38.7, 37.2, 35.3, 34.6, 33.7, 32.6, 31.4 (br, *C*B), 29.8, 29.4, 20.7. *Anal.* Calc. for $C_{30}H_{41}BO_2{\cdot}C_4H_8O_2$ (516.64): C, 79.04; H, 9.58. Found: C, 79.30; H, 9.56%.

2.4. The $[Cp^*IrCl_2]_2$ catalyzed addition of 4,8-di-tert-butyl-2,10-dimethyl-12H-dibenzo[d,g][1,3,2]dioxaborocine to 4-allylanisole

To a stirred toluene (2 mL) solution of 4-allylanisole (140 mg, 0.94 mmol) and $[Cp^*IrCl_2]_2$ (10 mg, 0.013 mmol) was added a toluene (3 mL) solution of **1** (164 mg, 0.47 mmol). The reaction was allowed to proceed for 18 h at which point solvent was removed under vacuum to afford an orange oil. Selected spectroscopic NMR data (in $CDCl_3$): ^{1}H ∂ 7.33 (d, *J* = 8.9 Hz, Ar), 7.20–6.75 (ov m, Ar), 6.52 (m), 6.43 (d of q, *J* = 16.1, 1.7 Hz), 6.17 (d of q, *J* = 16.1, 6.7 Hz), 4.24 (d, *J* = 13.6 Hz), 4.14 (d, *J* = 13.6 Hz), 3.86 (s, OCH_3), 3.85 (s, OCH_3), 3.84 (s, OCH_3), 3.47 (d, *J* = 13.6 Hz), 2.80 (t, *J* = 7.4 Hz), 2.52 (t, *J* = 7.9 Hz, CH_2CH_2CH_2B, **4**), 2.41 (m), 2.30 (s), 2.08 (m), 1.93 (d of d, *J* = 6.7 Hz, 1.7 Hz), 1.70 (m), 1.58 (quint, *J* = 7.9 Hz, CH$_2$CH_2CH$_2$B, **4**), 1.43 (s), 1.42 (s), 0.92 (t, *J* = 7.9 Hz, CH$_2$CH$_2$CH_2B, **4**); ^{11}B ∂ 27 (br).

*2.5. Synthesis of (E)-4,8-di-tert-butyl-6-(4-methoxystyryl)-2,10-dimethyl-12H-dibenzo[d,g][1,3,2]dioxaborocine (**5**)*

Compound **1** (250 mg, 0.71 mmol) in toluene (5 mL) was added to a toluene (5 mL) solution of 4-methoxystyrene (192 mg, 1.43 mmol) and $[Cp^*IrCl_2]_2$ (11 mg, 0.014 mmol). The reaction was allowed to proceed for 18 h, at which point solvent was removed under vacuum and the residual oily solid was dissolved in a THF:hexane (1 mL:5 mL) mixture and stored at −30 °C. The resulting precipitate was collected by suction filtration to afford **5** as an off-white solid. Yield: 0.27 g (79%); mp 218–220 °C. ^{1}H NMR (C_6D_6): ∂ 8.02 (d, *J* = 18.0 Hz, 1H, C*H* = CHB), 7.45 (d, *J* = 8.6 Hz, 2H, Ar), 6.98 (s, 2H, Ar), 6.82 (s, 2H, Ar), 6.72 (d, *J* = 8.6 Hz, 2H, Ar), 6.67 (d, *J* = 18.0 Hz, 1H, CH=*CH*B), 4.28 (d, *J* = 13.6 Hz, 1H, C*H*H), 3.25 (s, 3H, OCH_3), 3.24 (d, *J* = 13.6 Hz, 1H, CH*H*), 2.07 (s, 6H, CH_3), 1.51 (s, 18H, *t*-butyl); ^{11}B (C_6D_6): ∂ 23 (br); ^{13}C{^{1}H} (C_6D_6): ∂ 160.9, 150.7, 149.0, 139.2, 131.6, 131.4, 130.6, 129.0, 127.8, 126.2, 119.3 (br, *C*B), 114.2, 54.5, 35.1, 34.7, 29.9, 20.8. *Anal.* Calc. for $C_{32}H_{39}BO_3{\cdot}C_4H_8O_2$ (554.64): C, 77.95; H, 8.56. Found: C, 78.48; H, 8.90%.

*2.6. Synthesis of (E)-4,8-di-tert-butyl-6-(4-fluorostyryl)-2,10-dimethyl-12H-dibenzo[d,g][1,3,2]dioxaborocine (**6**)*

Compound **1** (250 mg, 0.71 mmol) in toluene (5 mL) was added to a toluene (5 mL) solution of 4-fluorostyrene (174 mg, 1.42 mmol) and $[Cp^*IrCl_2]_2$ (11 mg, 0.014 mmol). The reaction was allowed to proceed for 18 h, at which point the solvent was removed under vacuum and the resulting colorless oil was dissolved in a THF:hexane (2 mL:10 mL) mixture and stored at −30 °C. The resulting white precipitate was collected by suction filtration to afford compound **6** as a white solid. Yield: 0.29 g (87%); mp 200–203 °C. ^{1}H NMR (C_6D_6): ∂ 7.83 (d, *J* = 18.1 Hz, 1H, C*H*=CHB), 7.22 (d of d, J_{HH} = 8.7 Hz, J_{HF} = 5.7 Hz, 2H, Ar), 6.97 (d, *J* = 2.0 Hz, 2H, Ar), 6.81 (d, *J* = 2.0 Hz, 2H, Ar), 6.74 (ov d of d, *J* = 8.7 Hz, 2H, Ar), 6.57 (d, *J* = 18.1 Hz, 1H, CH=*CH*B), 4.24 (d, *J* = 13.6 Hz, 1H, C*H*H), 3.24 (d, *J* = 13.6 Hz, 1H, CH*H*), 2.07 (s, 6H, CH_3), 1.49 (s, 18H, *t*-butyl); ^{11}B (C_6D_6): ∂ 22 (br); ^{13}C{^{1}H} (C_6D_6): ∂ 163.4 (d, J_{CF} = 245.2 Hz, *C*F), 149.4, 148.8, 139.2, 133.9 (d, J_{CF} = 3.1 Hz, Ar), 131.8, 131.5, 129.2 (d, J_{CF} = 8.2 Hz, Ar), 127.7, 126.2, 121.9 (br, *C*B), 115.6 (d, J_{CF} = 21.5 Hz, Ar), 35.0, 34.6, 29.9, 20.8; ^{19}F{^{1}H} (C_6D_6): ∂−112. *Anal.* Calc. for $C_{31}H_{36}BFO_2{\cdot}0.5\ C_4H_8O_2$ (506.54): C, 78.24; H, 7.98. Found: C, 78.12; H, 7.91%.

*2.7. Synthesis of (E)-4,8-di-tert-butyl-2,10-dimethyl-6-(2,4,6-trimethylstyryl)-12H-dibenzo[d,g][1,3,2]dioxaborocine (**7**)*

Compound **1** (250 mg, 0.71 mmol) in toluene (5 mL) was added to a toluene (5 mL) solution of 2,4,6-trimethylstyrene (208 mg, 1.42 mmol) and $[Cp^*IrCl_2]_2$ (11 mg, 0.014 mmol). The reaction was allowed to proceed for 18 h, at which point the solvent was removed under vacuum and the resulting colorless oil was dissolved in hot hexane (5 mL) and stored at −30 °C. The resulting white precipitate was collected by suction filtration to afford compound **7** as a white solid. Yield: 0.27 g (77%); mp 159–162 °C. ^{1}H NMR (C_6D_6): ∂ 8.10 (d, *J* = 18.5 Hz, 1H, C*H*=CHB), 6.95 (s, 2H, Ar), 6.82 (s, 2H, Ar), 6.81 (s, 2H, Ar), 6.34 (d, *J* = 18.5 Hz, 1H, CH = C*H*B), 4.30 (d, *J* = 13.6 Hz, 1H, C*H*H), 3.22 (d, *J* = 13.6 Hz, 1H, CH*H*), 2.42 (s, 6H, CH_3), 2.17 (s, 3H, CH_3), 2.06 (s, 6H, CH_3), 1.47 (s, 18H, *t*-butyl); ^{11}B (C_6D_6): ∂ 24 (br); ^{13}C{^{1}H} ($CDCl_3$): ∂ 149.2, 148.4, 139.5,

136.9, 136.0, 135.6, 131.8, 131.2, 128.9, 128 (br, *C*B), 127.7, 126.1, 35.1, 34.7, 29.9, 21.1, 21.0 (2C). *Anal.* Calc. for $C_{34}H_{43}BO_2{\cdot}C_6H_{14}$ (580.78): C, 82.72; H, 9.91. Found: C, 82.36; H, 10.10%.

2.8. Synthesis of (E)-4,8-di-tert-butyl-2,10-dimethyl-6-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)styryl)-12H-dibenzo[d,g][1,3,2]-dioxaborocine (**8**)

To a THF (10 mL) solution of 4-vinylphenylboronic acid (300 mg, 2.03 mmol) and pinacol (240 mg, 2.03 mmol) was added activated molecular sieves (2 g, 5 Å). The mixture was allowed to stand at RT for 3 days at which point the sieves were removed by suction filtration. To the resulting clear solution was added a THF (5 mL) solution of **1** (355 mg, 1.01 mmol) and $[Cp^*IrCl_2]_2$ (40 mg, 0.05 mmol). The reaction was allowed to proceed for 20 h, at which point the solvent was removed under vacuum and the resulting colorless oil was dissolved in hot hexane (5 mL) and stored at −30 °C. The resulting white precipitate was collected by suction filtration to afford compound **8** as a white solid. Yield: 0.40 g (68%); mp 248–250 °C. ^{1}H NMR (C_6D_6): ∂ 8.17 (d, *J* = 7.9 Hz, 2H, Ar), 7.95 (d, *J* = 18.1 Hz, 1H, C*H*=CHB), 7.55 (d, *J* = 7.9 Hz, 2H, Ar), 6.95 (s, 2H, Ar), 6.80 (s, 2H, Ar), 6.78 (d, *J* = 18.1 Hz, 1H, CH=C*H*B), 4.22 (d, *J* = 13.6 Hz, 1H, C*H*H), 3.22 (d, *J* = 13.6 Hz, 1H, CH*H*), 2.06 (s, 6H, CH_3), 1.46 (s, 18H, *t*-butyl), 1.12 (s, 12H, Bpin); ^{11}B (C_6D_6): ∂ 30 (br) & 23 (br); ^{13}C{^{1}H} (C_6D_6): ∂ 150.8, 148.8, 140.4, 139.3, 135.6, 131.7, 131.4, 130.4 (br, *C*-B), 127.7, 127.0, 126.2, 123.3 (br, *C*-B), 83.6, 35.1, 34.6, 29.9, 24.7, 20.8. *Anal.* Calc. for $C_{37}H_{48}B_2O_4$ (578.47): C, 76.82; H, 8.38. Found: C, 77.05; H, 8.28%.

2.9. Crystallography

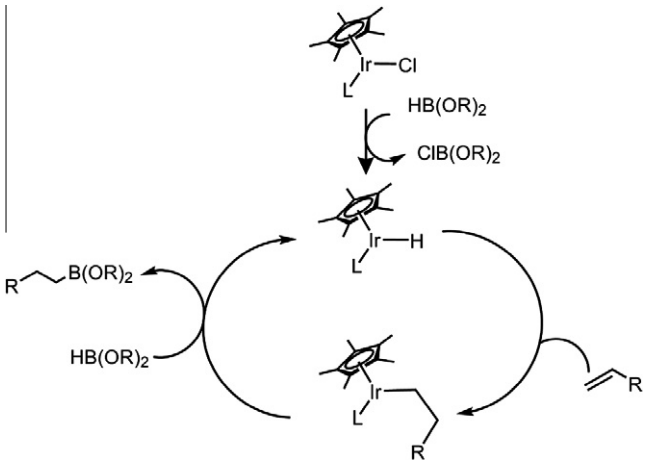
Crystals of **3** were grown from a saturated toluene solution at −30 °C and crystals of **5** were grown by slow evaporation of a C_6D_6 solution at RT. Single crystals were coated with Paratone-N oil, mounted using a polyimide MicroMount and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and θ scans with a scan width of 0.3° and 20 s (**3**) or 10 s (**5**) exposure times. The detector distance was 5 cm. The data were reduced (SAINT) [19] and corrected for absorption (SADABS) [20]. The structures were solved by direct methods and refined by full-matrix least squares on F^2 (SHELXTL) [21]. Part of the molecule for **3** was disordered over two sites and the occupancies determined using an isotropic model as 0.85 (O(2), C(24) > C(30)) and 0.15 (O(2′), C(24′) > C(30′)) and fixed in subsequent refinement cycles. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms for **3** were included in calculated positions and refined using a riding model while the hydrogen atoms for **5** were found in Fourier difference maps and refined using isotropic displacement parameters.

3. Results and discussion

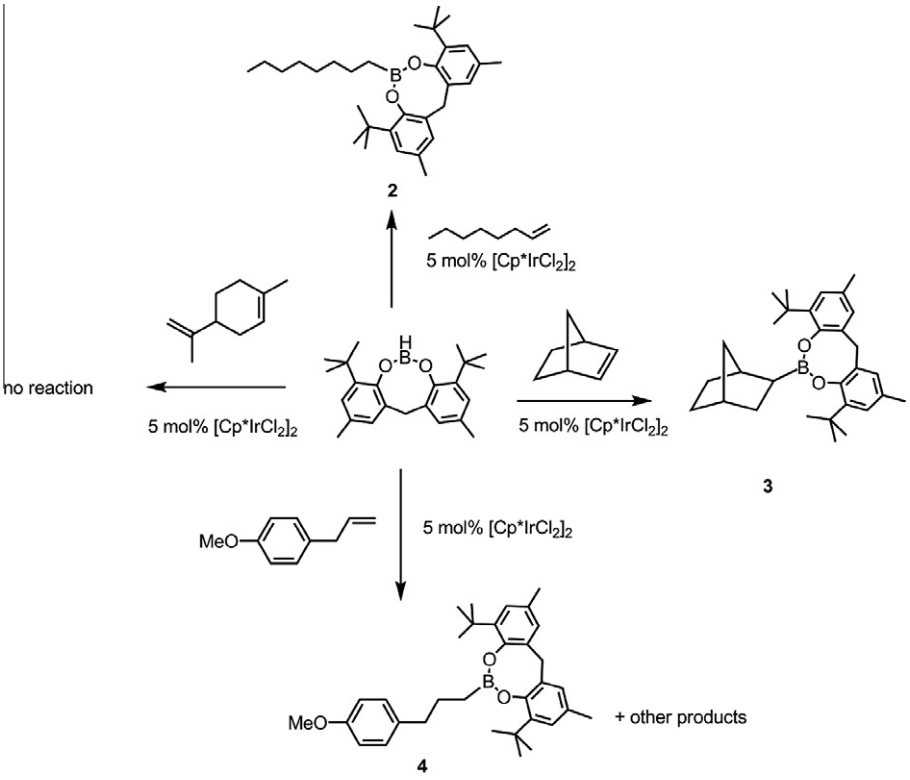
As with other diorganyloxyboranes, no significant reaction was observed with **1** and 1-octene at room temperature. Addition of the B-H bond did occur at elevated temperatures but competing degradation of the borane made these reactions synthetically unattractive. With rhodium complexes being the most commonly used in catalyzed hydroborations, we decided to initiate our studies using 5 mol% $RhCl(PPh_3)_3$. Unlike other diorganyloxyboranes, however, no reaction was observed with **1** and 1-octene using this catalyst precursor. We then decided to examine reactions using dimeric $[Cp^*IrCl_2]_2$ as a catalyst precursor, as we have previously found this to be remarkably active and selective for the hydroboration of a wide range of alkenes using HBcat [22]. Reactions with HBcat are specific in the formation of the terminal hydroboration products and have been postulated to proceed via metathesis of the Ir–Cl bond with the borane B–H to give a iridium hydride species. Coordination and regioselective insertion of the alkene into the Ir–H bond, followed by a metathesis step with the borane gives the linear product and regenerates the active Ir–H catalyst (Scheme 1).

We have found that **1** (HBdd) adds to 1-octene and 2-norbornene using 5 mol% $[Cp^*IrCl_2]_2$ to give the expected terminal addition products $CH_3(CH_2)_7$Bdd (**2**) and norbornylBdd (**3**), respectively, with excellent selectivity (Scheme 2). Although the corresponding hydrogenation products are frequently observed in catalyzed hydroborations [1,2], reactions using HBdd and the iridium catalyst precursor only gave minor amounts (<2%) of the undesired saturated products. Compounds **2** and **3** have been characterized by a number of analytical methods including a single crystal X-ray diffraction study for **3** (Fig. 2, Table 1), confirming that the H–B bond of **1** has added to the alkene group in an exo fashion [23]. The boron oxygen bond distances of B(1)–O(1) 1.361(2) and B(1)–O(2) 1.361(4) Å are similar to those reported previously for **1** [14] and the B(1)–C(24) bond distance of 1.599(3) Å is within the range reported for other diorganyloxyboranes [24–29]. More significantly, the C(24)–C(29) bond length of 1.559(3) Å is typical for a single bond. Attempts to affect the hydroboration of limonene [30] using **1** and $[Cp^*IrCl_2]_2$ proved unsuccessful, even when reactions were carried out at elevated temperatures using a microwave reactor [18], and additions appear to be remarkably selective for unhindered aliphatic alkenes.

Conversely, reactions of **1** with 4-allylanisole 4-$MeOC_6H_4CH_2$-$CH{=}CH_2$ were found to proceed at room temperature to give the expected terminal hydroboration product 4-$MeOC_6H_4CH_2CH_2$-CH_2Bdd (**4**) along with considerable amounts of hydrogenation product 4-$MeOC_6H_4CH_2CH_2CH_3$ and other unidentified boron-containing products. As metal catalyzed hydroborations of allylbenzene ($C_6H_5CH_2CH{=}CH_2$) are known to give complicated product distributions arising from a competing isomerization reaction, where the borane can add to the resulting transient isomer $C_6H_5CH{=}CHCH_3$ [31], it is possible that a similar mechanism is occurring with reactions of **1** and 4-allylanisole. To gain further insight into the nature of products formed during these reactions, we therefore investigated reactions of vinylarenes using HBdd and $[Cp^*IrCl_2]_2$ as a catalyst precursor. Considerable recent interest has focussed on the hydroboration [32–38] and subsequent transformation [39] of these important substrates. While reactions of 4-vinylanisole (4-$MeOC_6H_4CH{=}CH_2$) with HBcat and HBpin using a catalytic amount of $[Cp^*IrCl_2]_2$ proceed to give the terminal hyd-



Scheme 1. A possible mechanism for the $[Cp^*IrCl_2]_2$ catalyzed hydroboration of alkenes.



Scheme 2. Addition of **1** to various aliphatic alkenes.

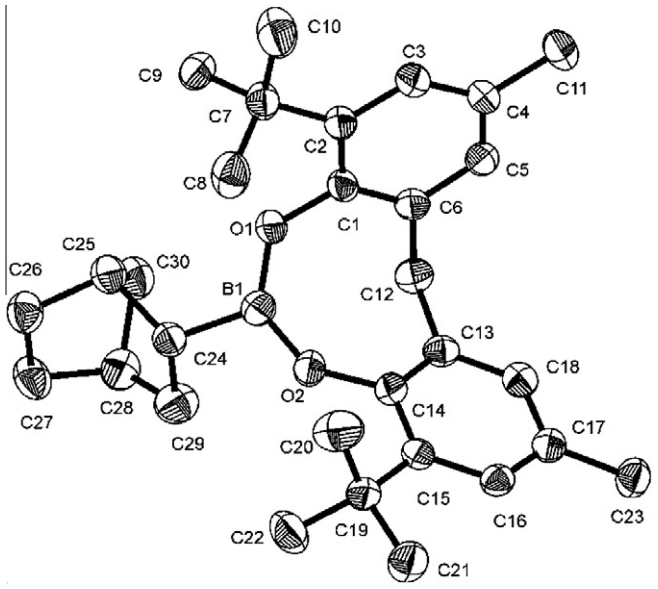


Fig. 2. Molecular structure of **3** with atom labeling scheme. Thermal ellipsoids are drawn at the 50% probability level with hydrogen atoms omitted for clarity. Selected bond distances (Å): B(1)–O(1) 1.361(2), B(1)–O(2) 1.361(4), B(1)–C(24) 1.599(3), C(24)–C(29) 1.559(3), C(24)–C(25) 1.587(3); selected bond angles (°): O(1)–B(1)–O(2) 128.20(19), O(1)–B(1)–C(24) 117.62(17), O(2)–B(1)–C(24) 113.81(18), B(1)–O(1)–C(1) 128.06(15), B(1)–O(2)–C(14) 139.2(3), C(29)-C(24)–C(25) 103.0(2).

roboration products 4-$MeOC_6H_4CH_2CH_2Bcat$ [40] and 4-$MeOC_6H_4$-CH_2CH_2Bpin, respectively, reactions with HBdd gave the unusual *trans*-4-$MeOC_6H_4CH$=CHBdd (**5**) as the only new boron-containing product. Also observed in these reactions are equimolar amounts of saturated product 4-$MeOC_6H_4CH_2CH_3$ [41].

Compound **5** has been characterized by a number of methods, including ^{1}H NMR spectroscopy which shows two doublets at δ 8.02 and 7.45 ppm with J_{H-H} = 18.0 Hz for the two *trans* alkene protons. Also consistent with this structure are two sp^2 carbon peaks for the alkene at δ 150.7 and 119.3 ppm in the ^{13}C NMR spectrum, along with a broad peak at δ 23 ppm in the ^{11}B NMR spectrum. To confirm the formation of **5**, we have carried out a single crystal X-ray diffraction study and the molecular structure of the alkenylboronate ester is shown in Fig. 3. The short C(8)–C(9) distance of 1.3335(18) Å illustrates that the alkene has not been reduced, as compared to the C(5)–C(8) single bond length of 1.4671(17) Å. Bond distances and angles for the boron atom are typical of related organoboronate esters [28,42].

The formation of alkenylboronate ester **5** in these reactions is of particular interest as it appears to suggest that hydroborations of vinylarenes using **1** are proceeding by a different mechanism to the one outlined in Scheme 1. Indeed, products from this 'addition reaction' presumably arise from an alternate dehydrogenative borylation pathway, which is generally believed to occur via initial oxidative addition of the borane to the metal center to give a hydrido boryl metal intermediate, followed by coordination of the alkene and subsequent insertion into the M–B bond [43–46]. This is followed by a selective β-hydride elimination to give the *trans*-alkenylboronate ester along with formation of one equivalent of dihydrogen (Scheme 3).

The formation of alkenylboronate esters in these reactions is of significant importance as these compounds have found considerable utility in organic synthesis [47–51]. We therefore decided to look at reactions with other vinylarenes and found that **1** reacts with 4-FC_6H_4CH=CH_2, 2,4,6-$Me_3C_6H_2CH$=CH_2, and 4-$BpinC_6H_4$ CH=CH_2 in the presence of a catalytic amount of $[Cp^*IrCl_2]_2$ to give *trans*-4-FC_6H_4CH=CHBdd (**6**), *trans*-2,4,6-$Me_3C_6H_2CH$=CHBdd (**7**), and *trans*-4-$BpinC_6H_4CH$=CHBdd (**8**), respectively, as the only new boron-containing products. Unfortunately, hydrogenation was also significant in these reactions and one equivalent of the

Table 1
Crystallographic data collection parameters.

Complex	**3**	**5**
Formula	$C_{30}H_{41}BO_2$	$C_{32}H_{39}BO_3$
Formula weight	444.44	482.44
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	*P*2(1)/*c*
a (Å)	18.4499(17)	13.6818(12)
b (Å)	14.6402(17)	15.4771(14)
c (Å)	19.446(2)	13.4015(12)
α (°)	90	90
β (°)	97.897(2)	96.521(1)
γ (°)	90	90
V (Å^3)	5202.8(10)	914.1(12)
Z	8	4
ρ_{calc} (mg m^{-3})	1.135	1.137
Crystal size (mm^3)	0.55 × 0.45 × 0.40	0.60 × 0.55 × 0.38
Temperature (K)	173(1)	173(1)
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
μ (mm^{-1})	0.068	0.070
Total reflections	17614	19294
Total unique reflections	5812	6332
Number of variables	330	481
Theta range (°)	1.78–27.50	1.50–27.50
Largest difference peak/hole (e Å^{-3})	0.677/−0.359	0.276/−0.135
S Goodness-of-fit (GOF) on F^2	1.039	1.031
R_1[a] ($I > 2\sigma(I)$)	0.0590	0.0394
wR_2[b] (all data)	0.1769	0.1139

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^4])^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0496 \times P)^2 + (0.8563 \times P)]$ (**3**) and $1/[\sigma^2(F_o^2) + (0.0804 \times P)^2 + (6.5500 \times P)]$ (**5**), where $P = (\max(F_o^2, 0) + 2 \times F_c^2)/3$.

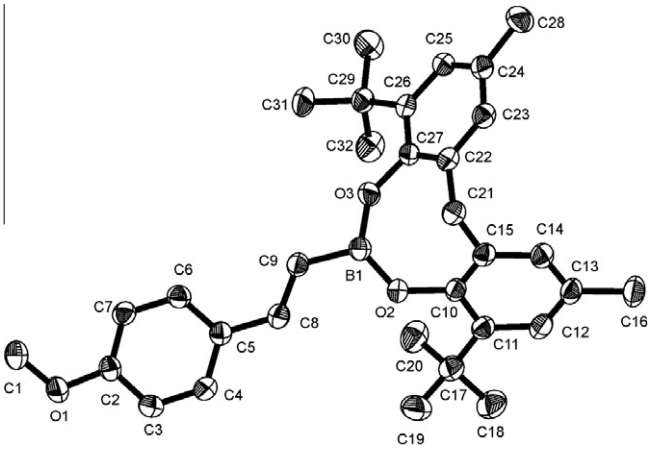
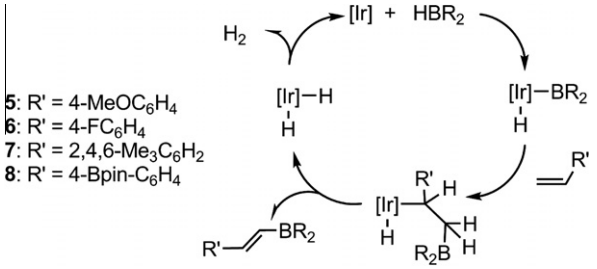


Fig. 3. Molecular structure of **5** with atom labeling scheme. Thermal ellipsoids are drawn at the 50% probability level with hydrogen atoms omitted for clarity. Selected bond distances (Å): B(1)–O(2) 1.3632(16), B(1)–O(3) 1.3660(17), B(1)–C(9) 1.5521(19), C(8)–C(9) 1.3335(18), C(5)–C(8) 1.4671(17); selected bond angles(°): O(2)–B(1)-O(3) 128.72(12), O(2)–B(1)–C(9) 116.82(11), O(3)–B(1)-C(9) 114.38(11), C(2)–O(1)–C(1) 117.09(11), B(1)–O(2)–C(10) 130.59(10), B(1)–O(3)–C(27) 140.35(10), C(9)–C(8)–C(5) 127.25(12), C(8)–C(9)–B(1) 125.05(12).

starting alkene was sacrificed to give the corresponding saturated ethyl styrene derivatives. Attempts to catalyze the hydroboration of **1** to bulkier vinylarenes, such as α- and β-methylstyrene, once again proved unsuccessful, even under microwave conditions. In light of these results, we thought that 'hydroboration' products **2**–**4** could be arising from an initial dehydrogenative borylation step followed by hydrogenation of the corresponding alkenylboronate esters. This hypothetical hydrogenation step would have to be kinetically faster than a competing hydrogenation of the starting alkene as only minor amounts of 'hydrogenation' product were observed in these initial reactions. However, no such alkenylboronate esters were observed by ^{1}H NMR spectroscopy, even when reactions were conducted at low temperature. Further studies in this area will focus on expanding the scope and utility of reactions using 4,8-di-*tert*-butyl-2,10-dimethyl-12*H*-dibenzo[*d*,*g*][1,3,2]dioxaborocine (**1**), the results of which will be published in due course.



Scheme 3. Catalyzed hydroboration of vinylarenes using **1** and 5 mol% $[Cp^*IrCl_2]_2$.

4. Conclusions

We have found that 4,8-di-*tert*-butyl-2,10-dimethyl-12*H*-dibenzo[*d*,*g*][1,3,2]dioxaborocine (**1**) fails to add to alkenes at room temperature or in the presence of a catalytic amount of $RhCl(PPh_3)_3$. However, the iridium complex $[Cp^*IrCl_2]_2$ can be used as a precatalyst with aliphatic alkenes to give selective formation of the corresponding terminal hydroboration products. Analogous reactions with vinylarenes afforded alkenylboronate esters along with equal amounts of the hydrogenation products. Unlike most catalyzed hydroborations using the iridium precatalyst $[Cp^*IrCl_2]_2$, these reactions are unique in that they appear to be proceeding via a competing dehydrogenative pathway. Boron products have been characterized by a number of physical and analytical methods, including single- crystal X-ray diffraction studies. We will continue to expand the use of **1** in hydroboration reactions as well as investigating its potential as a bulky borane counterpart in Frustrated Lewis Pair chemistry [52], and will report our findings in due course.

Acknowledgments

Thanks are gratefully extended to the Canada Research Chairs Programme, Canadian Foundation for Innovation-Atlantic Innovation Fund, Natural Science and Engineering Research Council of Canada, and Mount Allison University for financial support. Roger Smith and Dan Shrubnel Durant are thanked for their expert technical assistance.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.09.051.

References

[1] C.M. Crudden, D. Edwards, Eur. J. Org. Chem. (2003) 4695.
[2] C.M. Vogels, S.A. Westcott, Curr. Org. Chem. 9 (2005) 687.
[3] P.J. Guiry, M. McCarthy, P.M. Lacey, C.P. Saunders, S. Kelly, D.J. Connolly, Curr. Org. Chem. 4 (2000) 821.
[4] T. Riehm, G. De Paoli, H. Wadepohl, L. De Cola, L.H. Gade, Chem. Commun. (2008) 5348.
[5] K. Endo, M. Hirokami, K. Takeuchi, T. Shibata, Synlett (2008) 3231.
[6] V. Lillo, J.A. Mata, A.M. Segarra, E. Peris, E. Fernández, Chem. Commun. (2007) 2184.
[7] S. Werle, T. Fey, J.M. Neudörfl, H.-G. Schmalz, Org. Lett. 9 (2007) 3555.
[8] S. Chakraborty, J. Zhang, J.A. Krause, H. Guan, J. Am. Chem. Soc. 132 (2010) 8872.

[9] D. Männig, H. Nöth, Angew. Chem., Int. Ed. Engl. 24 (1985) 878.
[10] A.-M. Carroll, T.P. O'Sullivan, P.J. Guiry, Adv. Synth. Catal. 347 (2005) 609.
[11] V. Lillo, E. Fernández, A.M. Segarra, Tetrahedron: Asymmetry 18 (2007) 911.
[12] S.M. Smith, N.C. Thacker, J.M. Takacs, J. Am. Chem. Soc. 130 (2008) 3734.
[13] P. Patel, C.-T. Chang, N. Kang, G.-J. Lee, W.S. Powell, J. Rokach, Tetrahedron Lett. 48 (2007) 5289.
[14] A. Lang, H. Nöth, M. Thomann-Albach, Chem. Ber. Recl. 130 (1997) 363.
[15] N. PraveenGanesh, S. d'Hondt, P.Y. Chavant, J. Org. Chem. 72 (2007) 4510.
[16] S. Pereira, M. Srebnik, Organometallics 14 (1995) 3127.
[17] N. Iwadate, M. Suginome, Org. Lett. 11 (2009) 1899.
[18] S.W. Hadebe, R.S. Robinson, Tetrahedron Lett. 47 (2006) 1299.
[19] SAINT 7.23A, Bruker AXS, Inc., Madison, WI, USA, 2006.
[20] G.M. Sheldrick, SADABS 2004, Bruker AXS, Inc., Madison, WI, USA, 2004.
[21] G.M. Sheldrick, SHELXTL 6.14, Bruker AXS, Inc., Madison, WI, USA, 2000.
[22] J.D. Webb, D.J. Harrison, D.W. Norman, J.M. Blacquiere, C.M. Vogels, A. Decken, C.G. Bates, D. Venkataraman, R.T. Baker, S.A. Westcott, J. Mol. Catal. A: Chem. 275 (2007) 91.
[23] H.C. Brown, S.K. Gupta, J. Am. Chem. Soc. 97 (1975) 5249.
[24] C.M. Vogels, A. Decken, S.A. Westcott, Tetrahedron Lett. 47 (2006) 2419.
[25] M.J.G. Lesley, W. Clegg, T.B. Marder, N.C. Norman, A.G. Orpen, A.J. Scott, J. Starbuck, Acta Crystallogr., Sect. C 55 (1999) 1272.
[26] W. Clegg, A.J. Scott, F.E.S. Souza, T.B. Marder, Acta Crystallogr., Sect. C 55 (1999) 1885.
[27] S. Hawkswood, D.W. Stephan, Dalton Trans. (2005) 2182.
[28] R.B. Coapes, F.E.S. Souza, M.A. Fox, A.S. Batsanov, A.E. Goeta, D.S. Yufit, M.A. Leech, J.A.K. Howard, A.J. Scott, W. Clegg, T.B. Marder, J. Chem. Soc., Dalton Trans. (2001) 1201.
[29] A. Goswami, C.-J. Maier, H. Pritzkow, W. Siebert, Eur. J. Inorg. Chem. (2004) 2635.
[30] S.P. Thomas, V.K. Aggarwal, Angew. Chem., Int. Ed. 48 (2009) 1896.
[31] M.G. Hamilton, C.E. Hughes, A.M. Irving, C.M. Vogels, S.A. Westcott, J. Organomet. Chem. 680 (2003) 143.
[32] C.J. Lata, C.M. Crudden, J. Am. Chem. Soc. 132 (2010) 131.
[33] S.M. Smith, J.M. Takacs, J. Am. Chem. Soc. 132 (2010) 1740.
[34] D. Imao, B.W. Glasspoole, V.S. Laberge, C.M. Crudden, J. Am. Chem. Soc. 131 (2009) 5024.
[35] M.J. Geier, C.M. Vogels, A. Decken, S.A. Westcott, J. Organomet. Chem. 694 (2009) 3154.
[36] A. Black, J.M. Brown, C. Pichon, Chem. Commun. (2005) 5284.
[37] D. Noh, H. Chea, J. Ju, J. Yun, Angew. Chem., Int. Ed. 48 (2009) 6062.
[38] A. Caballero, S. Sabo-Etienne, Organometallics 26 (2007) 1191.
[39] A. Ros, V.K. Aggarwal, Angew. Chem., Int. Ed. 48 (2009) 6289.
[40] S.A. Westcott, T.B. Marder, R.T. Baker, J.C. Calabrese, Can. J. Chem. 71 (1993) 930.
[41] S.J. Roseblade, A. Pfaltz, Comp. Rend. Chim. 10 (2007) 178.
[42] C.B. Fritschi, S.M. Wernitz, C.V. Vogels, M.P. Shaver, A. Decken, A. Bell, S.A. Westcott, Eur. J. Inorg. Chem. (2008) 779.
[43] M. Murata, K. Kawakita, T. Asana, S. Watanabe, Y. Masuda, Bull. Chem. Soc. Jpn. 75 (2002) 825.
[44] A. Kondoh, T.F. Jamison, Chem. Commun. (2010) 907.
[45] I.A.I. Mkhalid, R.B. Coapes, S.N. Edes, D.N. Coventry, F.E.S. Souza, R.Ll. Thomas, J.J. Hall, S.-W. Bi, Z. Lin, T.B. Marder, Dalton Trans. (2008) 1055.
[46] S.J. Geier, E.E. Chapman, D.I. McIsaac, C.M. Vogels, A. Decken, S.A. Westcott, Inorg. Chem. Commun. 9 (2006) 788.
[47] C. Morrill, R.H. Grubbs, J. Org. Chem. 68 (2003) 6031.
[48] T.E. Pennington, C. Kardiman, C.A. Hutton, Tetrahedron Lett. 45 (2004) 6657.
[49] R.E. Shade, A.M. Hyde, J.-C. Olsen, C.A. Merlic, J. Am. Chem. Soc. 132 (2010) 1202.
[50] K. Endo, M. Hirokami, T. Shibata, J. Org. Chem. 75 (2010) 3469.
[51] E. Negishi, G. Wang, H. Rao, Z. Xu, J. Org. Chem. 75 (2010) 3151.
[52] D.W. Stephan, Dalton Trans. (2009) 3129.