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The transition metal catalyzed hydroboration of enamines

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ABSTRACT

The addition of catecholborane (HBcat, cat = 1,2-$O_2C_6H_4$) to 9-vinylcarbazole can give either the branched or linear hydroboration product depending upon the judicious choice of metal catalyst used in these reactions. Analogous reactions with pinacolborane (HBpin, pin = 1,2-$O_2C_2Me_4$) and HBBzpin (Bzpin = 1,2-$O_2C_2Ph_4$) using catalytic amounts (5 mol%) of either Rh(acac)(dppb) or $[Cp^*IrCl_2]_2$ gave the linear hydroboration product selectively. Hydroborations of 1-pyrrolidino-1-cyclopentene and 1-pyrrolidino-1-cyclohexene were complicated by a competing dehydrogenative borylation pathway. The branched isomer was not observed to any significant extent in these reactions, suggesting that the directing effect of the nitrogen atom is negligible. Although catalyzed additions of HBcat to 1-vinyl-2-pyrrolidinone gave complicated product distributions arising from competing reactions, addition of HBpin effectively generated the corresponding linear hydroboration product in good yields.

1. Introduction

The discovery that transition metals can be used to catalyze the addition of catecholborane (HBcat, cat = 1,2-$O_2C_6H_4$) or pinacolborane (HBpin, 1,2-$O_2C_2Me_4$) to substrates has become an important and well-established technique in organic synthesis [1–10]. 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 example, hydroborations of vinyl arenes ($ArCH{=}CH_2$) with HBcat proceed to give selectively either the expected primary boronate ester ($ArCH_2CH_2Bcat$) or the secondary boronate ester ($ArCH(Bcat)CH_3$), depending upon the choice of catalyst used to affect this transformation [11–21].

Although a considerable amount of research has focussed on the catalyzed hydroboration of simple unsaturated hydrocarbon systems, much less is known about analogous reactions with heteroatom-containing substrates [22–28]. For instance, catalyzed hydroborations of pyrrolidinyl amides with HBcat gave, after oxidation, *syn* 1,3-hydroxy amides with high levels of regio- and stereochemical control [22]. The remarkable selectivities observed in these reactions are believed to arise from a directing effect of the amide moiety. Likewise, Takacs and co-workers [29,30] have shown in an elegant study that acyclic β,γ-unsaturated amides also undergo regio- and enantioselective rhodium-catalyzed hydroboration with HBpin to give β-hydroxycarbonyl derivatives upon oxidative work-up (Scheme 1).

We have also reported that rhodium-catalyzed hydroboration of phenyl vinyl sulfide ($PhSCH{=}CH_2$) and phenyl vinyl sulfone ($PhSO_2CH{=}CH_2$) with HBcat gave the unusual branched addition products, $PhSCH(Bcat)CH_3$ and $PhSO_2CH(Bcat)CH_3$, respectively [31]. The directing effect of the sulfur atom (sulfides) and the oxygen atoms (sulfones) is once again presumably responsible for these unusual selectivities. Hydroborations of diphenylvinylphosphine ($Ph_2PCH{=}CH_2$) with HBcat give either the branched product $Ph_2PCH(Bcat)CH_3$ [32] or the linear species $Ph_2PCH_2CH_2(Bcat)$ [33], depending on the choice of the metal catalyst. These results, along with our interest in expanding the scope of metal catalyzed hydroborations, prompted us to investigate the analogous reactions with enamines, the results of which are presented herein.

2. Results and discussion

Enamines have a prominent role as intermediates in organic synthesis [34–37], and reduction of these compounds provides a valuable synthetic methodology to trisubstituted amines [38]. A series of phenethylamines, important substructures in biologically relevant molecules such as dopamine, amphetamine, and adrenaline, have recently been prepared by the hydroboration of enamines using 9-BBN [39]. Although the amine-directed uncatalyzed hydroboration using $H_3B{\cdot}THF$ is known [40,41], to the best of our knowledge, the metal catalyzed hydroboration of enamines has not yet been reported. While a number of different transition metals are known to catalyze hydroborations, reactions employing rhodium complexes are the most common. In this study, we have found that addition of HBcat to commercially available 9-vinylcarbazole using 5 mol% of $RhCl(PPh_3)_3$ (Table 1, entry 5) led to a

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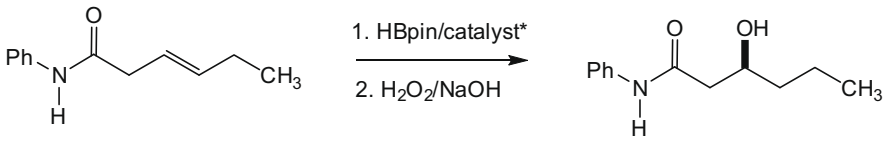


Scheme 1. Catalyzed hydroboration of β,γ-unsaturated amides.

Table 1
Metal catalyzed hydroboration of 9-vinylcarbazole.[a]

Entry	Catalyst[b]	Borane	1	2	3	4	5
1	Rh(acac)(dppb)	HBcat	97	2	0	1	0
2	Rh(acac)(dppp)	HBcat	68	23	0	8	1
3	$RhH(PPh_3)_4$	HBcat	55	15	15	10	5
4	Rh(acac)(dppm)	HBcat	47	32	0	12	9
5	$RhCl(PPh_3)_3$	HBcat	35	10	25	20	10
6	Rh(acac)(dppe)	HBcat	35	63	0	1	1
7	$Rh(acac)(coe)_2$	HBcat	1	28	20	13	38
8	$[RhCl(coe)_2]_2/2PPh_3$	HBcat	0	100	0	0	0
9	$[Cp^*IrCl_2]_2$	HBcat	0	100	0	0	0
10	$RhCl(PPh_3)_3$	HBpin	0	40	30	10	20
11	Rh(acac)(dppb)	HBpin	0	100	0	0	0
12	$[Cp^*IrCl_2]_2$	HBpin	0	100	0	0	0
13	Rh(acac)(dppb)	HBBzpin	0	100	0	0	0
14	$[Cp^*IrCl_2]_2$	HBBzpin	0	100	0	0	0

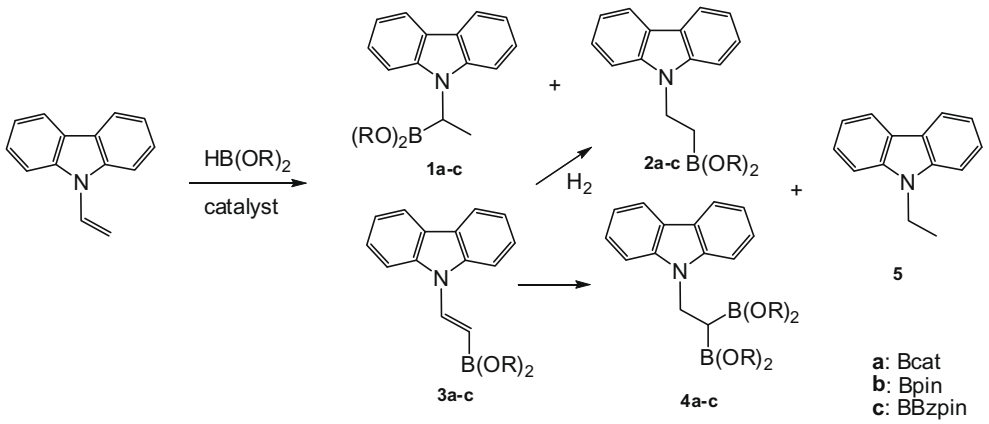
[a] Reactions were carried out with excess borane (up to 1.3 equivalents) to ensure 100% conversion of 9-vinylcarbazole and product ratios were determined using multinuclear NMR spectroscopy and confirmed by GC/MS.

[b] acac = acetylacetonato, dppb = 1,4-bis(diphenylphosphino)butane, dppm = 1,1-bis(diphenylphosphino)methane, dppe = 1,2-bis(diphenylphosphino)ethane, coe = *cis*-cyclooctene, $Cp^* = C_5Me_5$.

complicated mixture of boron-containing products (Scheme 2). Although products **1a** and **2a** are derived from traditional hydroboration pathways, where the directing effect of the aromatic group or the enamine nitrogen atom may be responsible for the formation of the branched product **1a**, a competing dehydrogenative borylation pathway [42–48] is likely responsible for the other boron-containing products. Dehydrogenative borylation products are believed to arise from initial oxidative addition of the borane to the metal center, followed by coordination and insertion of the alkene into the Rh–B bond, with a subsequent and selective β-hydride elimination to give the corresponding *trans*-vinyl boronate ester (**3a**), along with concomitant formation of dihydrogen. A second addition of HBcat to the activated alkene **3a** would give the diboron compound **4a** whereas hydrogenation of **3a** is an alternate route to 'hydroboration' product **2a**. A considerable amount of hydrogenated starting material **5** is also observed in these reactions.

A number of different metal complexes were examined for their ability to catalyze this reaction and, remarkably, we have found that Rh(acac)(dppb) (acac = acetylacetonato; dppb = 1,4-bis(diphenylphosphino)butane, entry 1) gave predominant formation (97%) of the branched product **1a**. It is interesting to note that reactions using other diphosphines proceeded with much lower selectivity than those reactions using the dppb precatalyst. Conversely, the linear product **2a** was the sole product in reactions using $[RhCl(coe)_2]_2/2PPh_3$ (coe = *cis*-cyclooctene, entry 8) or $[Cp^*IrCl_2]_2$ (entry 9). Compound **2a** has also been characterized by a single crystal X-ray diffraction study, the molecular structure of which is shown in Fig. 1a. Details of the data collection, structure solution and refinement are presented in Table 2. The B–O bond distances of B(1)–O(2) 1.387(5) Å and B(1)–O(1) 1.393(5) Å are typical for those seen in other Bcat structures [49–51] and no appreciable intermolecular interaction is observed between the Lewis basic nitrogen and the empty orbital of boron. Related 9*H*-carbazol-9-yl boron compounds have been used to prepare phenanthroline derivatives for phosphorescent organic light-emitting devices [52].

Pinacolborane is often used as a replacement for HBcat in catalyzed reactions as the resulting organoborane products are stable to air and water and are generally purified by chromatography [53–55]. As such we have also examined reactions with HBpin. While reactions using 5 mol% of $RhCl(PPh_3)_3$ led to the formation of several products (Table 1, entry 10), those employing Rh(acac)-(dppb) (entry 11) gave selective formation of the linear product **2b**. This result demonstrates the sensitive nature of these reactions as a complete reversal in regioselectivity is observed by simply varying the borane, as reactions using this catalyst system and HBcat gave the branched product. The linear Bpin product could also be obtained cleanly in reactions using $[Cp^*IrCl_2]_2$ (entry 12) as the catalyst precursor. Likewise, hydroborations using the bulky HBBzpin (Bzpin = 1,2-$O_2C_2Ph_4$) and either catalytic amounts of Rh(acac)(dppb) or $[Cp^*IrCl_2]_2$ gave the corresponding linear product **2c** with excellent selectivity (entries 13 and 14). Compound **2c** was also characterized by a single crystal X-ray diffraction study (Fig. 1b), and bond distances and angles are similar to **2a** and those reported for other benzopinacol derivatives [53].



Scheme 2. Catalyzed hydroboration of 9-vinylcarbazole.

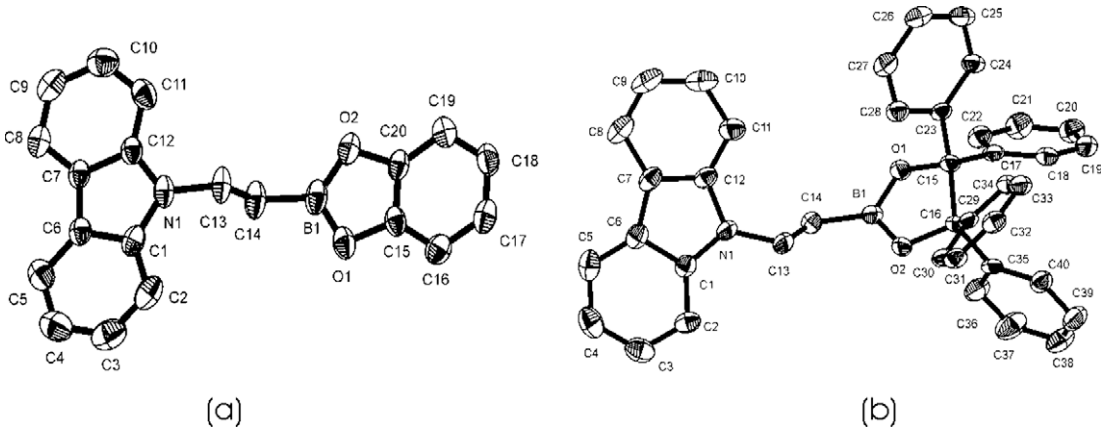
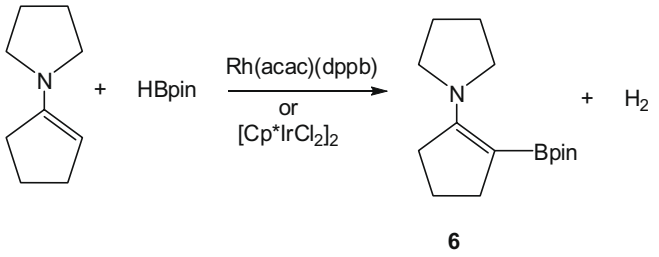


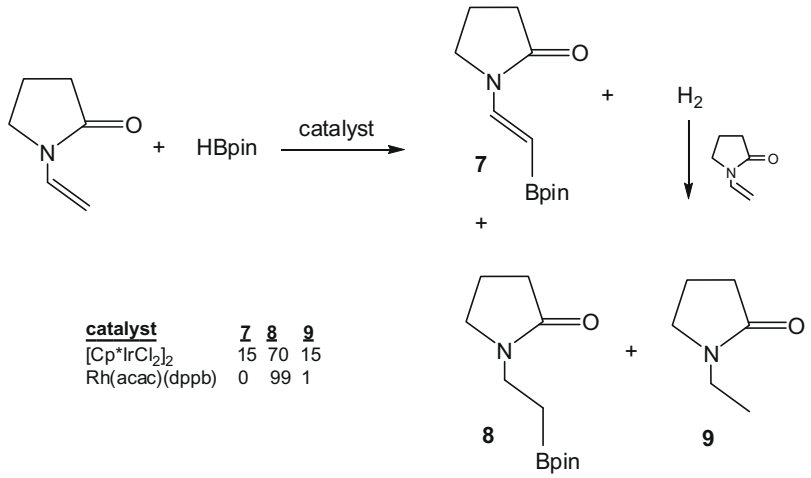
Fig. 1. Molecular structure of (a) **2a** and (b) **2c** with atom labelling scheme. Thermal ellipsoids are drawn at the 50% probability level with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles for **2a** (°): C(14)–B(1) 1.554(4), B(1)–O(2) 1.387(5), B(1)–O(1) 1.393(5), O(1)–C(15) 1.392(3), O(2)–C(20) 1.394(3); O(2)–B(1)–O(1) 111.0(2), O(2)–B(1)–C(14) 125.5(4), O(1)–B(1)–C(14) 123.2(3); selected bond distances (Å) and angles for **2c** (°): B(1)–O(2) 1.363(3), B(1)–O(1) 1.371(3), B(1)–C(14) 1.557(3), N(1)–C(1) 1.380(3), N(1)–C(12) 1.385(3), N(1)–C(13) 1.455(3); O(2)–B(1)–O(1) 112.85(18), O(2)–B(1)–C(14) 123.82(18), O(1)–B(1)–C(14) 122.99(18).

Upon successful and regioselective hydroboration of 9-vinylcarbazole, we then investigated the metal catalyzed B–H addition of boranes to 1-pyrrolidino-1-cyclopentene and 1-pyrrolidino-1-cyclohexene. Unfortunately, attempts to catalyze the addition of HBcat to 1-pyrrolidino-1-cyclopentene led to a number of different products, regardless of the choice of metal complex. The branched isomer was not observed to any significant extent in these reactions, suggesting the directing effect of the nitrogen atom is negligible. Reactions with HBpin using either Rh(acac)(dppb) or $[Cp^*IrCl_2]_2$ gave what appears to be the corresponding alkenylboronate ester **6** (Scheme 3) as the major boron containing product in solution (up to 80% by NMR spectroscopy). While no 'hydroboration' products were observed in this reaction, compound **6** presumably arises from a dehydrogenative borylation pathway where the liberated dihydrogen does not add to the newly formed tetrasubstituted alkene. The ^{13}C NMR data for **6** shows a broad peak at δ 89.9 ppm corresponding to the vinylic B–C bond. Likewise, the quaternary carbon peak for this species is observed at δ 160.1 ppm. Contrary to other boronate ester derivatives of Bpin, attempts to isolate **6** using chromatography resulted in cleavage of the B–C bond and gave the starting enamine and B_2pin_3, along with a number of yet unidentified compounds. Reactions with HBBzpin were sluggish and gave a mixture of products that could not be isolated further. Catalytic addition of boranes to the six-membered ring enamine 1-pyrrolidino-1-cyclohexene all gave complicated product distributions, even with reactions employing HBpin.



Scheme 3. The HBpin catalyzed hydroboration of 1-pyrrolidino-1-cyclopentene.

The hydroboration of 1-vinyl-2-pyrrolidinone was also undertaken as related boroproline derivatives are active catalysts in the asymmetric aldol reaction [56]. In this study, we have found that competing reduction of the amide carbonyl group and the alkene functionality was observed for uncatalyzed reactions with HBcat. Conversely, reactions using a transition metal gave a wide range of products derived from addition of the borane to the alkene, where product distributions were once again complicated by a competing dehydrogenative borylation pathway. For instance,



Scheme 4. Catalyzed hydroboration of 1-vinyl-2-pyrrolidone using HBpin.

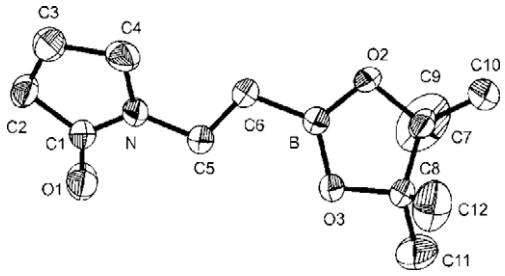


Fig. 2. Molecular structure of **8** with atom labelling scheme. Thermal ellipsoids are drawn at the 50% probability level with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): B–O(2) 1.359(3), B–O(3) 1.378(5), B–C(6) 1.567(3), N–C(1) 1.344(3), N–C(4) 1.452(3), N–C(5) 1.459(3), C(1)–O(1) 1.227(3), C(5)–C(6) 1.520(3); O(2)–B–O(3) 114.7(2), O(2)–B–C(6) 122.1(2), O(3)–B–C(6)123.1(2).

reactions using HBpin and a catalytic amount of $[Cp^*IrCl_2]_2$ afforded the corresponding alkenylboronate ester **7**, along with 'hydroboration' product **8** and minor amounts of hydrogenation product **9** (Scheme 4). This observation is somewhat unusual as reactions using this iridium species are known to give selective formation of the linear hydroboration product, where the alkenylboronate esters are not normally observed [3,25]. Monitoring this reaction by ^{1}H NMR spectroscopy showed that compound **7** formed initially but was not converted over time to hydroboration product **8** as both products remained upon complete conversion of the starting material.

We were able to control both the chemoselectivity and the regioselectivity of this reaction using Rh(acac)(dppb) to form exclusively the linear hydroboration product **8**. A resonance at 173 ppm in the ^{13}C NMR spectra and a strong band at 1671 cm^{-1} in the FT-IR indicate that the carbonyl functionality is still present. A peak at 32 ppm in the ^{11}B NMR spectrum indicates that the boron atom exists in a three coordinate environment in solution [57]. The linear hydroboration product was confirmed by a single crystal X-ray diffraction study, Fig. 2. Reactions with HBBzpin gave the corresponding linear product along with a significant amount (up to 40%) of hydrogenation product **9** and degradation of the borane.

In summary, hydroborations of 9-vinylcarbazole can be controlled to give selective formation of either of the branched or linear product where the selectivity appears to arise from the aromatic nature of this substrate. Indeed, no directing effect was observed in reactions of either 1-pyrrolidino-1-cyclopentene or 1-pyrrolidino-1-cyclohexene and products derived from a competing dehydrogenative borylation pathway seem to dominate these substrates. Hydroborations of the unsaturated amide 1-vinyl-2-pyrrolidinone also gave several products but reactions using HBpin and catalytic amounts of Rh(acac)(dppb) gave selective formation of the linear hydroboration product, which could be isolated in good yield. Further studies in this area are currently underway and will be reported in due course.

3. Experimental

3.1. General

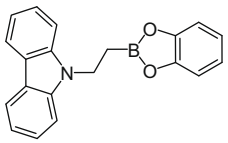
Reagents and solvents were purchased from Aldrich Chemicals and used as received with the exception of catecholborane which was distilled prior to use and 4,4,5,5-tetraphenyl-1,3,2-dioxaborolane (HBBzpin) which was synthesized by a known method [53]. NMR spectra were recorded on a JEOL JNM-GSX270 FT NMR (^{1}H 270 MHz; ^{11}B 87 MHz; ^{13}C 68 MHz) spectrometer. Chemical shifts (δ) are reported in ppm [relative to residual solvent peaks (^{1}H and ^{13}C) or external $BF_3{\cdot}OEt_2$ (^{11}B)] and coupling constants (J) in Hz. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), multiplet (m), broad (br), and overlapping (ov). Infrared spectra were obtained using a Mattson Genesis II FT-IR spectrometer and are reported in cm^{-1}. Melting points were determined using a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Guelph Chemical Laboratories (Guelph, ON). Reactions were performed under an atmosphere of dinitrogen.

3.2. General procedure for the catalyzed hydroboration of 9-vinylcarbazole

The appropriate borane (0.28 mmol) in THF (0.5 mL) was added to a stirred mixture of 9-vinylcarbazole (0.05 g, 0.26 mmol) and the desired catalyst (5 mol%) in THF (0.5 mL) and the reaction was allowed to proceed for 18 h. Upon removal of solvent under vacuum, the reaction was analyzed by NMR spectroscopy. Selected ^{1}H NMR data (in C_6D_6): **1a**: δ 4.37 (q, J = 7.7 Hz, C*H*(Bcat)CH$_3$), 1.47 (d, J = 7.7 Hz, CH(Bcat)C*H*$_3$); **2a**: δ 4.13 (app t, J = 8.2 Hz, C*H*$_2$CH$_2$(Bcat)), 1.39 (app t, J = 8.2 Hz, CH$_2$C*H*$_2$(Bcat)); **3a**: δ 8.17 (d, J = 16.6 Hz, C*H*=CH(Bcat)), 5.93 (d, J = 16.6 Hz, CH=C*H*(Bcat)); **4a**: δ 4.75 (d, J = 7.7 Hz, C*H*$_2$CH(Bcat)$_2$), 2.47 (t, J = 7.7 Hz, CH$_2$C*H*(Bcat)$_2$); **5**: δ 3.68 (q, J = 7.2 Hz, C*H*$_2$CH$_3$), 0.88 (t, J = 7.2 Hz, CH$_2$C*H*$_3$). **2b**: δ 4.21 (t, J = 7.9 Hz, C*H*$_2$CH$_2$(Bpin)), 1.35 (t, J = 7.9 Hz, CH$_2$C*H*$_2$(Bpin)); **3b**: δ 8.16 (d, J = 16.6 Hz, C*H*=CH(Bpin)), 5.99 (d, J = 16.6 Hz, CH=C*H*(Bpin)); **4b**: δ 4.70 (d, J = 8.7 Hz, C*H*$_2$CH(Bpin)$_2$), 2.09 (t, J = 8.7 Hz, CH$_2$C*H*(Bpin)$_2$). **2c**: δ 4.30 (t, J = 7.5 Hz, C*H*$_2$CH$_2$(BBzpin)), 1.73 (t, J = 7.5 Hz, CH$_2$C*H*$_2$(BBzpin)).

3.3. Preparation of 9-(2-(benzo[d][1,3,2]dioxaborol-2-yl)ethyl)-9H-carbazole (*2a*)

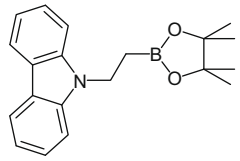
A THF (1 mL) solution of HBcat (0.39 g, 3.25 mmol) was added dropwise to a stirred THF (6 mL) solution of 9-vinylcarbazole (0.60 g, 3.10 mmol) and $[Cp^*IrCl_2]_2$ (25 mg, 0.03 mmol). The reaction was allowed to proceed for 18 h, at which point solvent was removed under vacuum to afford an orange oil. The oil was dissolved in hot hexane (5 mL) and a small amount of solid was removed by filtration. Upon storing the solution at −30 °C, **2a** precipitated as a white solid and was collected by suction filtration. Yield: 0.85 g (88%). NMR spectroscopic data (in C_6D_6): ^{1}H NMR δ: 8.04 (d, J = 7.7 Hz, 2H, Ar), 7.39 (d d d, J = 8.2, 7.7, 1.2 Hz, 2H, Ar), 7.22 (d d d, J = 8.2, 7.7, 1.2 Hz, 2H, Ar), 7.14 (d, J = 8.2 Hz, 2H, Ar), 7.00 (second order m, 2H, catechol), 6.80 (second order m, 2H, catechol), 4.13 (app t, J = 8.2 Hz, 2H, C*H*$_2$CH$_2$(Bcat)), 1.39 (app t, J = 8.2 Hz, 2H, CH$_2$C*H*$_2$(Bcat)); ^{11}B NMR δ: 34 (br); ^{13}C{^{1}H} NMR δ: 148.3, 140.0, 125.7, 123.5, 122.8, 120.6, 119.1, 112.4, 108.7, 37.8, 11.0 (br, *C*–B).



3.4. Preparation of 9-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-9H-carbazole (*2b*)

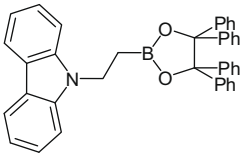
A THF (1 mL) solution of HBpin (0.35 g, 2.73 mmol) was added dropwise to a stirred THF (5 mL) solution of 9-vinylcarbazole (0.52 g, 2.69 mmol) and Rh(acac)(dppb) (19 mg, 0.03 mmol). The reaction was allowed to proceed for 18 h, at which point solvent was removed under vacuum to afford an orange oil. The oil was

dissolved in hot hexane (5 mL) and passed through a small plug of alumina. The solution was stored at −30 °C and **2b** precipitated as a white solid and was collected by suction filtration. Yield: 0.65 g (75%); mp = 107–110 °C. NMR spectroscopic data (in C_6D_6): ^{1}H NMR δ: 8.03 (d, J = 7.7 Hz, 2H, Ar), 7.38–7.15 (ov m, 6H, Ar), 4.21 (t, J = 7.7 Hz, 2H, CH_2CH_2(Bpin)), 1.35 (t, J = 7.7 Hz, 2H, CH_2CH_2-(Bpin)), 0.90 (s, 12H, pinacol); ^{11}B NMR δ: 32 (br); ^{13}C{^{1}H} NMR δ: 140.3, 125.5, 123.3, 120.4, 118.8, 109.2, 83.1, 38.6, 24.5, 11.8 (br, *C*–B). IR (nujol): 3051, 2994, 2921, 1597, 1485, 1386, 1348, 1324, 1271, 1237, 1143, 1061, 965, 846, 748, 722. Anal. Calc. for $C_{20}H_{24}BNO_2$ (321.26): C, 74.77; H, 7.55; N, 4.36. Found: C, 75.03; H, 7.29; N 4.29%.



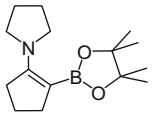
3.5. Preparation of 9-(2-(4,4,5,5-tetraphenyl-1,3,2-dioxaborolan-2-yl)ethyl)-9H-carbazole (**2c**)

A toluene (5 mL) solution of HBBzpin (0.54 g, 1.44 mmol) was added dropwise to a stirred toluene (5 mL) solution of 9-vinylcarbazole (0.25 g, 1.29 mmol) and Rh(acac)(dppb) (16 mg, 0.026 mmol). The reaction was allowed to proceed for 48 h, at which point hexane (5 mL) was added and the mixture was stored at −30 °C. **2c** precipitated as an off-white solid and was collected by suction filtration. Yield: 0.46 g (63%); mp = 165–168 °C. NMR spectroscopic data (in $CDCl_3$): ^{1}H NMR δ: 8.15 (d, J = 8.2 Hz, 2H, Ar), 7.58 (d, J = 8.2 Hz, 2H, Ar), 7.47 (t, J = 8.2 Hz, 2H, Ar), 7.27 (t, J = 8.2 Hz, 2H, Ar), 7.09–7.07 (br ov m, 20H, Ar), 4.74 (t, J = 7.4 Hz, 2H, CH_2CH_2(BBzpin)), 1.97 (t, J = 7.4 Hz, 2H, CH_2CH_2(BBzpin)); ^{11}B NMR δ: 33 (br); ^{13}C{^{1}H} NMR δ: 142.4, 140.1, 128.6, 127.4, 127.2, 125.8, 123.2, 120.5, 118.9, 109.2, 96.4, 38.6, 12.0 (br, *C*–B). IR (nujol): 2922, 2879, 1627, 1597, 1485, 1446, 1427, 1402, 1327, 1273, 1238, 1200, 1182, 1122, 1011, 976, 955, 854, 825, 754, 725, 702, 660, 617. Anal. Calc. for $C_{40}H_{32}BNO_2$ (569.54): C, 84.35; H, 5.67; N, 2.46. Found: C, 84.49; H, 6.03; N, 2.68%.



3.6. Preparation of 1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopent-1-enyl)pyrrolidine (**6**)

To a stirred toluene (2 mL) solution of 1-pyrrolidino-1-cyclopentene (200 mg, 1.46 mmol) and $[Cp^*IrCl_2]_2$ (23 mg, 0.029 mmol) was added a toluene (3 mL) solution of HBpin (206 mg, 1.61 mmol). The reaction was allowed to proceed for 18 h, at which point solvent was removed under vacuum and the resulting orange–brown oil was analyzed by multinuclear NMR spectroscopy in C_6D_6. ^{1}H NMR δ: 3.29 (second order m, 4H), 3.07 (t, J = 7.2 Hz, 2H), 2.39 (t, J = 7.2 Hz, 2H), 1.83 (quint, J = 7.2 Hz, 2H, $CH_2CH_2CH_2$), 1.45 (second order m, 4H), 1.17 (s, 12H, pinacol), 1.00 (s, B_2pin_3, minor impurity); ^{11}B NMR δ: 29 (br), 21 (s, B_2pin_3, minor impurity); ^{13}C{^{1}H} NMR δ: 160.1, 89.9 (br, *C*–B), 82.6 (B_2pin_3, minor impurity), 81.5, 50.5, 37.1, 36.5, 25.6, 24.7, 24.3 (B_2pin_3, minor impurity), 23.8.

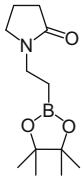


3.7. $[Cp^*IrCl_2]_2$ catalyzed addition of pinacolborane to 1-vinyl-2-pyrrolidinone

A C_6D_6 (0.5 mL) solution of HBpin (63 mg, 0.49 mmol) was added to a stirred mixture of 1-vinyl-2-pyrrolidinone (50 mg, 0.45 mmol) and $[Cp^*IrCl_2]_2$ (7 mg, 0.009 mmol) in C_6D_6 (0.5 mL). The reaction was allowed to proceed for 18 h then analyzed by multinuclear NMR spectroscopy. Selected ^{1}H NMR spectroscopic data (in C_6D_6): **7**: δ 8.22 (d, J = 16.8 Hz, C*H*=CH(Bpin)), 4.61 (d, J = 16.8 Hz, CH=C*H*(Bpin)); **8**: δ 3.50 (t, J = 7.7 Hz, 2H, CH_2CH_2 (Bpin)); **9**: δ 3.10 (q, J = 6.9 Hz, CH_2CH_3), 0.77 (t, J = 6.9 Hz, CH_2CH_3).

3.8. Preparation of 1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)pyrrolidin-2-one (**8**)

A THF (2 mL) solution of HBpin (0.63 g, 4.92 mmol) was added dropwise to a stirred THF (7 mL) solution of 1-vinyl-2-pyrrolidinone (0.50 g, 4.50 mmol) and Rh(acac)(dppb) (30 mg, 0.048 mmol). The reaction was allowed to proceed for 18 h, at which point solvent was removed under vacuum to afford an orange oil. The oil was dissolved in hot hexane (5 mL) and passed through a small plug of alumina. The solution was then stored at −30 °C and compound **8** precipitated as a white solid and was collected by suction filtration. Yield: 0.89 g (83%), mp = 66–68 °C. NMR spectroscopic data (in C_6D_6): ^{1}H NMR δ: 3.50 (t, J = 7.7 Hz, 2H, CH_2CH_2(Bpin)), 2.71 (t, J = 7.4 Hz, 2H), 1.98 (t, J = 7.4 Hz, 2H), 1.25 (quint, J = 7.4 Hz, 2H, $CH_2CH_2CH_2$), 1.11−0.99 (ov, 14H, CH_2CH_2(Bpin) and pinacol); ^{11}B NMR δ: 32 (br); ^{13}C{^{1}H} NMR δ: 172.8 (*C*=O), 82.9, 45.6, 38.2, 30.7, 24.7, 17.7, 10.4 (br, *C*–B). IR (nujol): 2976, 2926, 1671 (C=O), 1498, 1473, 1406, 1381, 1333, 1282, 1142, 968, 887, 849, 746, 669. Anal. Calc. for $C_{12}H_{22}BNO_3$ (239.16): C, 60.26; H, 9.29; N, 5.86. Found: C, 59.95; H, 9.47; N, 5.68%.



3.9. X-ray crystallography

Crystals of **2a**, **2c** and **8** were grown from saturated diethyl ether, cyclohexane and hexane solutions, respectively, at RT. Single crystals were coated with Paratone-N oil, mounted using an amide melt 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 times of 10 s (**2a**) and 30 s (**2c**, **8**). The detector distances were 5 cm. The data were reduced (SAINT) [58] and corrected for absorption (SADABS) [59]. The structures were solved by direct methods and refined by full-matrix least squares on F^2 (SHELXTL) [60]. The oxygen atoms of the Bpin group in **8** were disordered and the site occupancy determined using an isotropic model as 0.85 (O(2)), 0.15 (O(2′)), 0.64 (O(3)), and 0.18 (O(3′)–O(3″)) and

Table 2
Crystallographic data collection parameters for **2a**, **2c** and **8**.

Complex	**2a**	**2c**	**8**
Chemical formula	$C_{20}H_{16}BNO_2$	$C_{40}H_{32}BNO_2$	$C_{12}H_{22}BNO_3$
Formula mass	313.15	569.48	239.12
Crystal dimensions (mm^3)	0.45 × 0.40 × 0.15	0.50 × 0.25 × 0.20	0.40 × 0.23 × 0.17
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2(1)$	$P\bar{1}$	$P2(1)/c$
Z	2	2	4
a (Å)	10.448(5)	10.825(4)	6.250(2)
b (Å)	7.453(3)	12.332(4)	15.346(6)
c (Å)	10.475(5)	13.494(6)	14.319(5)
α (0)	90	103.407(6)	90
β (°)	94.493(7)	112.565(4)	101.032(5)
γ (°)	90	104.276(5)	90
Volume ($Å^3$)	813.1(6)	1501.0(10)	1348.0(8)
D_{calcd} (mg m^{-3})	1.279	1.260	1.178
T (K)	173(1)	173(1)	173(1)
Radiation (Å)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
μ (mm^{-1})	0.081	0.076	0.082
Total reflections collected	5582	9839	8981
Total unique reflections	1955	6428	3010
Number of variables	218	525	167
θ (°)	1.96–27.49	1.76–27.50	1.96–27.50
Goodness of fit (GOF) on F^2	1.101	1.027	1.033
R_1[a] [$I > 2\sigma(I)$]	0.0311	0.0670	0.0619
wR_2[b] (all data)	0.0763	0.1969	0.1782
Largest difference in peak and hole (Å)	0.138 and −0.118	0.538 and −0.454	0.362 and −0.304

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

[b] $wR_2 = (\sum[w(F_o^2 - F_c^2)^2]/[F_o^4])^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0375 * P)^2 + (0.036 * P)]$ (**2a**), $w = 1/[\sigma^2(F_o^2) + (0.1281 * P)^2 + (0.2316 * P)]$ (**2c**) and $w = 1/[\sigma^2(F_o^2) + (0.0659 * P)^2 + (0.8851 * P)]$ (**8**), where $P = (\max(F_o^2,0) + 2 * F_c^2)/3$.

fixed in subsequent refinement cycles. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were included in calculated positions and refined using a riding model.

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Appendix A. Supplementary material

CCDC 723348, 723372 and 723373 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.05.016.

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