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The ligand properties of 2-vinyl-1,2-azaboratabenzene

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This paper is dedicated to Professor Christoph Elschenbroich on the occasion of his 70th birthday and in honor of his many contributions to organometallic chemistry.

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ABSTRACT

Lithium 2-vinyl-1,2-azaboratabenzene **1b** has been prepared by a multistep synthesis from 2,2-dibutyl-2,5-dihydro-1-trimethylsilyl-1*H*-1,2-azastannole **6**. The reaction of **1b** with one equivalent of $[Cp^*RuCl]_4$ gave the very labile sandwich compound **11**. However, the reaction of **1b** with 2 equiv. of $[Cp^*RuCl]_4$ afforded the stable diruthenium complex **12.** The X-ray structure of **12** shows that the first Cp^*Ru moiety is π-bound to the 1,2-azaboratabenzene ring while the second is bound to Cl and to the nitrogen and the pendant B-vinyl of the 1,2-azaboratabenzene group.

1. Introduction

1,2-Azaboratabenzene **1** [1,2] is an anionic 6-π electron aromatic ligand which is closely related to boratabenzene **2** and pyridine **3**. Boratabenzene has a rich π-coordination chemistry which has been explored extensively by the work of Herberich et al. [3,4] and others [4–6]. In contrast pyridine forms few π-coordinated complexes with metals [7]. Rather pyridines usually form complexes in which the nitrogen atom is bound to a metal in an η^1-manner [8]. Of course pyridines are well known in organic chemistry as bases/nucleophiles [9]. Indeed electron-rich pyridines such as 4-(dimethylamino)pyridine (DMAP) are widely used as nucleophilic catalysts [9].

We have been interested in exploring the coordination chemistry of **1** [1,2]. It was felt that 1,2-azaboratabenzenes might form metal π-complexes **4**, which would retain their N-basicity/nucleophilicity. Indeed, it was our hope that complexes **4** might have an adjustable basicity/nucleophilicity which would be tunable by the judicious choice of metals and ancillary ligands. In prior work we reported that **1a** could be converted to Ru(II) complex **5**, which is much less basic than **1a** [1]. Although pK_a of **5** is nearly identical to that of DMAP, it is a much poorer nucleophilic catalyst. Since the nucleophilicity of pyridines is markedly effected by α substitution [10], we speculate that this decrease of nucleophilicity was a consequence of steric hindrance by the large phenyl group α to the nitrogen.

We now wish to report on the synthesis of 2-vinylazaboratabenzene **10** and its conversion to Ru(II) complexes **11** and **12**. The 2-vinyl substituent was chosen because the smaller size of vinyl (A = 1.5) relative to phenyl (A = 3.0) [11] might be expected to increase the nucleophilicity of **11** relative to **5**. In addition the combination of the vinyl substituent and the adjacent nitrogen might be expected to form a chelating ligand which might resemble 2-vinylpyridine [12] (Scheme 1).

2. Results and discussion

The synthesis of lithium 2-vinyl-1,2-azaboratabenzene **1b** [1] was achieved using the same general route which had been used to prepare **1a.** It is unfortunate that this synthesis involves introduction of the B-pendant substituent at the first step which makes changing substituents laborious. However, **1b** was prepared in an efficient manner as illustrated in Scheme 2.

The boron–tin exchange reaction of 2,2-dibutyl-2,5-dihydro-1-trimethylsilyl-1,2-azastannole **6** [13] with the highly labile but readily available vinylboron dichloride [14] gave a 77% conversion to 2,5-dihydro-1-trimethylsilyl-2-vinyl-1*H*-1,2-azaborole **7**. Deprotonation of **7** with LDA afforded a 72% yield of the lithium 1,2-azaborolide **8**, which can be isolated as a white solid.

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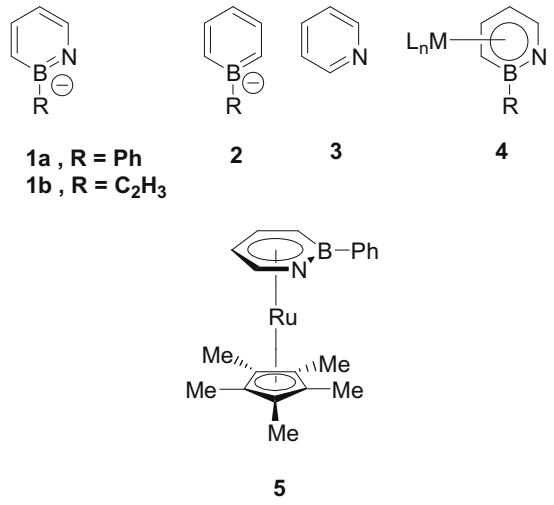
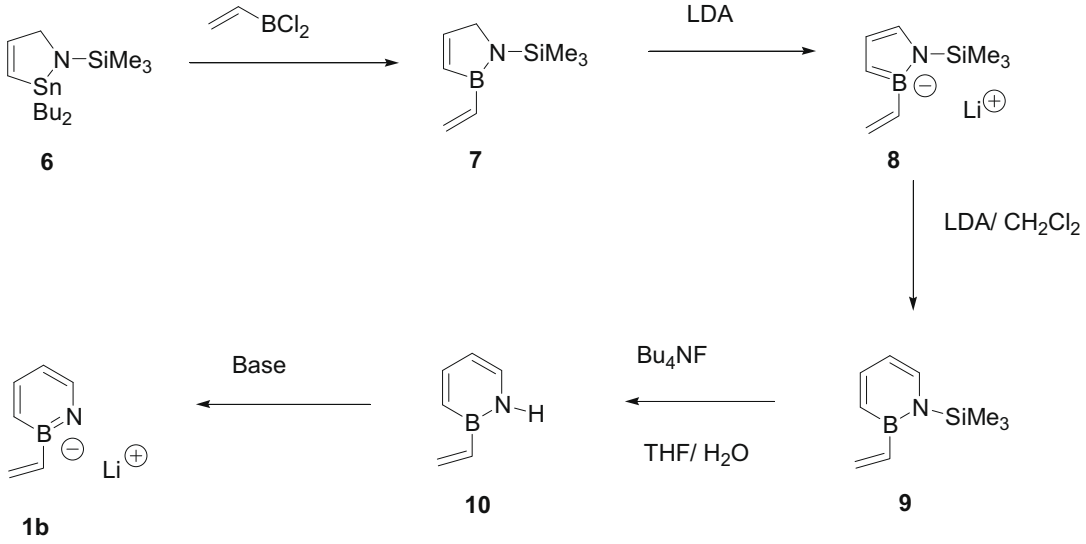


Scheme 1. Structures **1**–**5**.

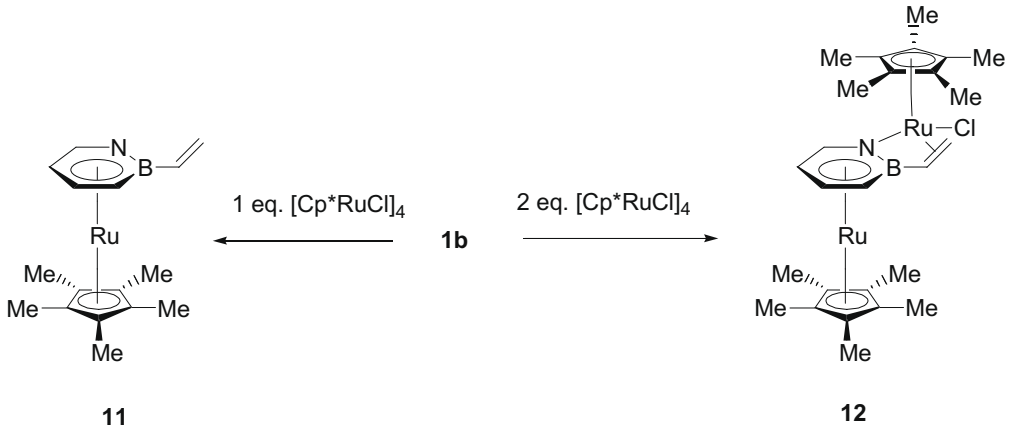
Treatment of **8** with LDA/CH_2Cl_2 in ether [15] gave the ring expanded product **9** as a yellow oil in 34% yield. Desilylation of **9** with Bu_4NF in THF/water gave the desired 1,2-dihydro-2-vinyl-1,2-azaborine **10** as colorless oil in 70% yield. Compound **10** is isoelectronic with styrene. Deprotonation of **10** with LDA in ether gave the desired lithium 2-vinyl-1,2-azaboratabenzene **1b** which could be isolated as a white powder in 63% yield (Scheme 3).

The reaction of **1b** with 1 equiv. of $[Cp^*RuCl]_4$ [16], where $Cp^* = \eta^5$-$CpMe_5$, gave a crude product which was a sand colored powder. This product was unexpectedly labile and manipulation of it led to its destruction with the formation of unidentified products. In spite of its great lability the ^1H NMR spectrum of the crude product in DMSO-d_6 is first-order and can be readily assigned by inspection. The signals for the four protons of the coordinated 1,2-azaboratabenzene ring have very similar chemical shift values and coupling constants to those of complex **5**. In place of the phenyl signals of **5** there are now low field signals for an uncoordinated vinyl group. The ^{11}B and ^{13}C NMR spectra and high resolution mass spectra are similarly consistent with the assignment this product as the expected complex **11.**

The lability of **11** prevented us from exploring its use as a nucleophilic catalyst. Prior work had shown that **5** was an effective catalyst for the acylation of benzyl alcohol by phenylethylketene. Nucleophilic pyridine catalysts are well known to be strongly influenced by steric hindrance at the α-position [10]. Thus it is reasonable to assume that **11** is more nucleophilic than **5.** This (presumed) nucleophilicity may be a factor in the lability of **11**.



Scheme 2. Synthesis of lithium 2-vinyl-1,2-azaboratabenzene **1b**.



Scheme 3. Syntheses of complexes **11** and **12**.

As described below the juxtaposition of the vinyl group and the nucleophilic nitrogen provide a site for further reaction with metals.

The reaction of **1b** with two equivalents of $[Cp^*RuCl]_4$ in THF gave diruthenium complex **12** as a red crystalline product in 85% yield. Unlike complex **11** this product was easy to handle. Like **11** the ^1H NMR spectrum of **12** is first-order and readily assigned by inspection. Apart from the presence of signals for a second η^5-Cp^* group, the major change in the spectrum relative to **11** is the shift of the vinyl signals to higher field and the marked reduction in the vinyl vicinal coupling constants. Both changes are consistent with π-coordination of the vinyl group [17,18]. Other spectroscopic characterization is also consistent with the formulation of this product as **12.** This assignment was confirmed by obtaining a crystal structure which is illustrated in Fig. 1. Selected bond distances of **12** are listed in Table 1.

The molecular structure of **12** shows that the Ru(1) is sandwiched between an η^5-Cp^* and the η^6-1,2-azaboratabenzene group in the same manner as had been observed for **5**. The 1,2-azaboratabenzene ring is completely planar (±0.018(1) Å). The Ru(2), which is η^5-bound to the second Cp^*, is also bound to a chloride and to the nitrogen and η^2 to the B-pendant vinyl group of the 1,2-azaboratabenzene ring. The plane of vinyl group [B(1)C(5)C(6)] is inclined by 45.2(1)° to that of the 1,2-azaboratabenzene ring so that it is oriented *exo* with respect to Ru(2). Since the distances, Ru(2)–C(5) = 2.232(2) Å and Ru(2)–C(6) = 2.231(2) Å), are identical, there is no asymmetry in binding to the olefin. Overall the binding of the vinyl-1,2-azaboratabenzene unit to Ru(2) is very similar to that recently found for the ruthenium coordination to a 2-vinylpyridine group in the complex $RuCl_2(2\text{-}CH_2 = CHC_5H_3N)(PPh_3)_2$ [12c] and other complexes [12].

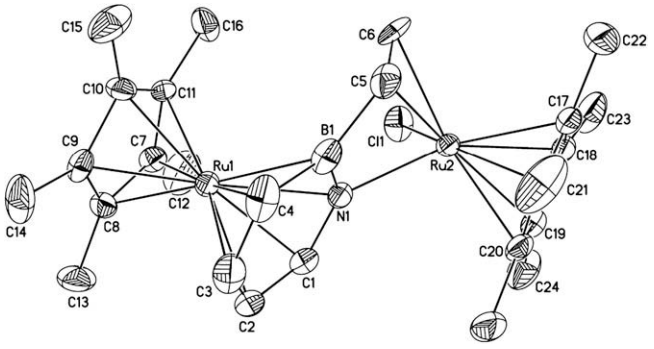


Fig. 1. Solid-state structure of **12** (ORTEP). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 1
Selected bond distances (Å) for **12**.

Bond	12
N(1)–C(1)	1.371(2)
C(1)–C(2)	1.443(3)
C(2)–C(3)	1.406(3)
C(3)–C(4)	1.390(3)
C(4)–B(1)	1.519(3)
B(1)–N(1)	1.435(3)
B(1)–C(5)	1.575(3)
C(5)–C(6)	1.438(3)
$C(Cp^*)$–$C(Cp^*)$	1.425(5)–1.475(5)
Ru(1)–N(1)	2.283(2)
Ru(1)–C(1)	2.203(3)
Ru(1)–C(2)	2.170(2)
Ru(1)–C(3)	2.196(2)
Ru(1)–C(4)	2.258(2)
Ru(1)–B(1)	2.353(2)
Ru(1)–$C(Cp^*)$	2.141(5)–2.182(4)
Ru(2)–Cl(1)	2.446(1)
Ru(2)–C(5)	2.232(2)
Ru(2)–C(6)	2.231(2)
Ru(2)–N(1)	2.107(2)
Ru(2)–$C(Cp^*)$	2.161(1)–2.215(2)

3. Conclusion

The new ligand 2-vinyl-1,2-azaboratabenzene **1b** has been prepared by a multistep synthesis. The reaction of **1b** with 1 equiv. of $[Cp^*RuCl]_4$ afforded the very labile sandwich complex **11.** The unforgiving lability of **11** has prevented us from measuring the nucleophilicity of its ring nitrogen atom. Since the corresponding complex of 2-phenyl-1,2-azaboratabenzene is quite tractable, the lability of **11** is due to the presence of the pendant B-vinyl group. The combination of the B-vinyl group and the nucleophilic ring nitrogen provides **11** with an additional coordination site for metals. Thus reaction of **1b** with 2 equiv. of $[Cp^*RuCl]_4$ affords a good yield of **12** which has been structurally characterized.

4. Experimental

4.1. General

^1H, ^{13}C and ^{11}B NMR spectra were recorded on Varian Inova 400 or 500 MHz FT NMR spectrometers. The solvents used were chloroform-d_1 ($CDCl_3$), benzene-d_6 (C_6D_6), dimethyl sulfoxide-d_6 (DMSO-d_6), tetrahydrofuran-d_8 (THF-d_8), or dichloromethane-d_2 (CD_2Cl_2) as indicated. Chemical shifts are reported in parts per million (δ). Proton and carbon chemical shifts are relative to respective solvent internal standards shown below: $CDCl_3$ δ 7.27(^1H), 77.23(^{13}C); C_6D_6 δ 7.16(^1H), 128.39(^{13}C); CD_2Cl_2 δ 5.32(^1H), 54.00(^{13}C); DMSO-d_6 δ 2.50(^1H), 39.51(^{13}C); THF-d_8 δ 3.58(^1H), 67.57(^{13}C). Boron chemical shifts are relative to the external reference (δ 0.00): BF_3/Et_2O. The coupling constants (J) are reported in hertz. The following abbreviations are used to describe peak patterns: br = broad, s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. Data are presented as follows: chemical shift (multiplicity, coupling constants, integrated intensity, and assignment). All ^{13}C and ^{11}B spectra were determined with complete proton decoupling. Mass spectra were recorded on a VG-250S spectrometer or a Finnigan Trace.

GC/MS spectrometer with 70 eV electron impact. High-resolution mass spectra were recorded on a VG-250S spectrometer with an electron-impact at 70 eV. Elemental analyses were conducted on a Perkin–Elmer 240 CHN analyzer by the Analytical Service Department of the Chemistry Department at the University of Michigan, Ann Arbor.

Solvents were freshly distilled prior to use. THF and diethyl ether were distilled from sodium and benzophenone ketyl under N_2. Pentane, hexanes and toluene were distilled from sodium metal under N_2. Dichloromethane was distilled from CaH_2 under N_2. 2,2-Dibutyl-2,5-dihydro-trimethylsilyl-1*H*-1,2-azastannole (**6**) and chloro(pentamethylcyclopentadienyl) ruthenium (II) tetramer were prepared according to the literature procedures. All other reagents were purchased from commercial vendors, and were used as received or distilled if necessary. All reactions were conducted under an inert atmosphere of nitrogen or argon unless otherwise specified.

4.2. 2,5-Dihydro-2-vinyl-1-trimethylsilyl-1H-1,2-azaborole (7)

A solution of 2,2-dibutyl-2,5-dihydro-trimethylsilyl-1*H*-1,2-azastannole (**6**) [13] (62.1 g, 0.17 mol) in 50 mL of pentane was

gradually added at −78 °C to a solution of vinylboron dichloride (0.19 mol) which had been prepared in situ from vinyltributyltin and BCl_3 [14]. After stirring at −78 °C for 20 min, the reaction mixture was allowed to warm to room temperature and then stirred for 12 h. Once the solvent had been removed, the residue was vacuum distilled to give the product as a colorless liquid (21.9 g, 77%), b.p. 37–42 °C at 0.05 Torr. ^{1}H NMR (500 MHz, C_6D_6): δ 0.15 (s, 9H, $SiMe_3$); 3.59 (t, J = 1.6 Hz, 2H, C(5)H); 6.08 (dd, J = 13.2, 4.2 Hz, 1H, (Vinyl)H); 6.22 (dd, J = 19.5, 4.2 Hz, 1H, (Vinyl)H); 6.66 (m, 2H, (Vinyl)H and C(3)H); 7.06 (d, J = 7.8 Hz, 1H, C(4)H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 1.25; 60.0; 135.2; 153.2. Signal for C_3 and $C_{(Vinyl\ CH)}$, not observed. ^{11}B NMR (160.4 MHz, $CDCl_3$): δ 43.3. HRMS (EI, m/z): calcd for $C_8H_{16}{}^{11}BNSi$ (M^+), 165.1145; found, 165.1151.

4.3. 2,3-Dihydro-1-trimethylsilyl-2-vinyl-1H-1,2-azaborol-3-yllithium (8)

A solution of **7** (21.94 g, 0.13 mol) in 50 mL of diethyl ether was slowly added to a solution of LDA (16.65 g, 0.16 mol) in 125 mL of diethyl ether at −78 °C. The mixture was stirred at −78 °C for 2 h and allowed to warm to room temperature for 10 h. After removal of the solvent under reduced pressure, the residue was washed with 3 × 20 mL of pentane and then dried under vacuum, leaving lithium salt **8** as a white solid (16.41 g, 72%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.16 (s, 9H, $SiMe_3$); 4.38 (d, J = 4.6 Hz, 1H, C(3)H); 4.92 (dd, J = 13.2, 5.5 Hz, 1H, (Vinyl)H); 5.11 (dd, J = 19.0, 5.5 Hz, 1H, (Vinyl)H); 5.64 (t, J = 2.1 Hz, 1H, C(5)H); 5.74 (dd, J = 4.6, 2.1 Hz, 1H, C(4)H); 6.47 (dd, J = 19.0, 13.2 Hz, 1H, (Vinyl)H). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 2.50; 93.8 (br), 110.3, 114.6, 117.3, 144.0 (br). ^{11}B NMR (160.4 MHz, DMSO-d_6): δ 28.2.

4.4. 1,2-Dihydro-1-trimethylsilyl-2-phenyl-1,2-azaborine (9)

A solution of LDA (3.84 g, 35.8 mmol) in 50 mL of diethyl ether was added gradually to a suspension of **8** (6.25 g, 36.5 mmol) in 25 mL of CH_2Cl_2 at −78 °C. The mixture was stirred at −78 °C for 2 h and allowed to warm to room temperature for 10 h. Once the solvent was removed under reduced pressure, the residue was extracted with 3 × 20 mL of pentane. After filtration and removal of the solvent, the dark red oily residue was vacuum distilled to give the product **9** as a pale yellow oil (2.15 g, 34%), b.p. 30–35 °C at 0.05 Torr. ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.43 (s, 9H, $SiMe_3$); 5.88 (dd, J = 13.7, 4.0 Hz, 1H, (Vinyl)H); 6.02 (dd, J = 19.3, 4.0 Hz, 1H, (Vinyl)H); 6.34 (t, J = 6.5 Hz, 1H, C(5)H); 6.68 (dd, J = 19.3, 13.7 Hz, 1H, (Vinyl)H); 6.86 (d, J = 11.1 Hz, 1H, C(3)H); 7.36 (d, J = 6.5 Hz, 1H, C(6)H); 7.55 (dd, J = 11.1, 6.5 Hz, 1H, C(4)H). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 1.5, 111.7, 127.8 (br), 130.2, 137.4, 140.0 (br), 143.6. ^{11}B NMR (160.4 MHz, DMSO-d_6): δ 36.1. HRMS (EI, m/z): calcd for $C_9H_{16}{}^{11}BNSi$ (M^+), 177.1145; found, 177.1137.

4.5. 1,2-Dihydro-2-vinyl-1,2-azaborine (10)

A 1.0 M solution of Bu_4NF (14.4 mL, 14.4 mmol) in THF was added slowly to a solution of **9** (2.14 g, 12.1 mmol) in 15 mL of THF at 0 °C. The mixture was stirred at 0 °C for 4 h and allowed to warm to room temperature for 10 h. After reducing the volume of THF to 10 mL in vacuo, 60 mL of ice water was added and the mixture was extracted with 3 × 25 mL of pentane. The combined pentane extracts were washed with 2 × 20 mL of H_2O and dried over anhydrous Na_2SO_4. After filtration and removal of the solvent, the residue was vacuum distilled to give the product **10** as a colorless oil (887 mg, 70%), b.p. 50–55 °C at 2.25 Torr. ^{1}H NMR (500 MHz, DMSO-d_6): δ 5.80 (dd, J = 13.4, 3.9 Hz, 1H, (Vinyl)H), 6.02 (dd, J = 19.8, 3.9 Hz, 1H, (Vinyl)H), 6.27 (t, J = 6.4 Hz, 1H, C(5)H); 6.38 (dd, J = 19.8, 13.4 Hz, 1H, (Vinyl)H); 6.79 (d, J = 11.0 Hz, 1H, C(3)H); 7.36(t, J = 7.0 Hz, 1H, C(6)H); 7.57 (dd, J = 11.0, 6.4 Hz, 1H, C(4)H), 10.22 (br, 1H, NH). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 110.2, 126.6 (br), 129.4, 134.9, 138.2 (br), 143.8. ^{11}B NMR (160.4 MHz, DMSO-d_6): δ 32.1. HRMS (EI, m/z): calcd for $C_6H_8{}^{11}BN$ (M^+), 105.0750; found, 105.0749.

4.6. 1,2-Dihydro-2-vinyl-1,2-azaborine-1-yllithium (1b)

A solution of **10** (266 mg, 2.5 mmol) in 10 mL of diethyl ether was added gradually to a solution of LDA (285 mg, 2.7 mmol) in 10 mL of diethyl ether at −78 °C. The mixture was stirred at −78 °C for 1 h and allowed to warm to room temperature for 10 h. After removal of the volatiles in vacuo, the residue was washed with 3 × 10 mL of hexanes and dried in vacuo to give the product as a white powder (176 mg, 63%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 5.37 (dd, J = 13.1, 5.2 Hz, 1H, (Vinyl)H); 5.66 (dd, J = 19.7, 5.2 Hz, 1H, (Vinyl)H); 5.89 (t, J = 6.1 Hz, 1H, C(5)H); 6.19 (d, J = 10.5 Hz, 1H, C(3)H); 6.61 (dd, J = 19.7, 13.1 Hz, 1H, (Vinyl)H); 7.11 (dd, J = 10.5, 6.1 Hz, 1H, C(4)H); 7.97(d, J = 4.0 Hz, 1H, C(6)H). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 109.6, 120.2 (br), 120.8, 138.4, 150.0, 151.0 (br). ^{11}B NMR (160.4 MHz, DMSO-d_6): δ 34.3.

4.7. [η^6-1,2-Dihydro-2-vinyl-1,2-azaborine-1-yl][pentamethylcyclopentadienyl] ruthenium(II) (11)

A solution of **1b** (183 mg, 1.65 mmol) in 5 mL of THF was added all at once to a suspension of $[Cp^*RuCl]_4$ (449 mg, 0.413 mmol) in 10 mL of THF at 0 °C. The mixture was stirred at 0 °C for 15 min and allowed to warm to room temperature for 2 h. The solvent was removed in vacuo, and the residue was washed with 3 × 5 mL of pentane. After filtration and removal of the solvent, the crude product mixed with LiCl was obtained as a sand color powder (120 mg). Since attempted purification lead to destruction of the sample, a pure sample of the product cannot be obtained. However, satisfactory spectra were obtained from the crude prod-

Table 2
Crystallographic data for compound **12**.

	Compound **12**
Formula	$C_{26}H_{37}BClNRu_2$
F_w	611.97
Colour/habit	Orange/plates
Crystal dimensions (mm)	0.28 × 0.28 × 0.12
Crystal system	Orthorhombic
Space group	*Pna*2(1)
a (Å)	21.245(3)
b (Å)	8.653(1)
c (Å)	13.849(2)
V (Å^3)	2545.9(7)
Z	4
T (K)	123(2)
D_{calc} (g cm^{-3})	1.597
μ (mm^{-1})	1.305
$F(000)$	1240
θ Range (°)	1.92–28.30
Index ranges (h, k, l)	±28, ±11, ±18
Number of reflections collected	46592
Number of independent reflections/R_{int}	6332/0.0395
Number of observed reflections [$I_o > 2\sigma(I_o)$]	5978
Number of data/restraints/parameters	6332/1/375
R_1/wR_2 [$I_o > 2\sigma(I_o)$][a]	0.0195/0.0462
R_1/wR_2 (all data)[a]	0.0223/0.0470
Goodness-on-fit (on F^2)[a]	1.099
Largest difference in peak and hole (e Å^{-3})	0.482 and −0.485

[a] $R_1 = \sum(||F_o| - |F_c||)$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)]\}^{1/2}$; GOF = $\{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$.

uct. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.79 (s, 15H, Cp*Me); 4.22 (d, J = 8.1 Hz, 1H, C(3)H); 5.15 (dd, J = 5.4, 2.9 Hz, 1H, C(5)H); 5.25 (dd, J = 8.1, 5.4 Hz, 1H, C(4)H); 5.64 (dd, J = 12.9, 4.6 Hz, 1H, (Vinyl)H); 5.79 (dd, J = 19.5, 4.6 Hz, 1H, (Vinyl)H); 6.22 (m, 2H, C(6)H and (Vinyl)H). ^{13}C NMR (125.7 MHz, DMSO-d_6): δ 10.6, 77.5 (br), 81.5, 89.7, 93.8, 106.3, 126.1, 141.8 (br). ^{11}B NMR (160.4 MHz, DMSO-d_6): δ 14.8. HRMS (EI, m/z): calcd for $C_{16}H_{22}{}^{11}BN^{102}Ru$, 341.0889; found, 341.0888.

4.8. Preparation of **12**

A solution of **1b** (110 mg, 1.0 mmol) in 8 mL of THF was slowly added to a suspension of $[Cp^*RuCl]_4$ (536 mg, 0.493 mmol) in 20 mL of THF at 25 °C. The mixture was stirred at 25 °C for 2 h. The solvent was removed in vacuo, and the residue was washed with 3 × 10 mL of hexanes. After filtration and removal of the solvent, the residue was extracted with 2 × 7 mL CH_2Cl_2. Removal of the solvent in vacuo yielded the product as a red powder (516 mg, 85%). ^{1}H NMR (500 MHz, THF-d_8): δ 1.35 (s, 15H, Cp*Me); 1.90 (s, 15H, Cp*Me); 2.70 (dd, J = 12.7, 10.7 Hz, 1H, (Vinyl)H); 3.30 (d, J = 12.7 Hz, 1H, (Vinyl)H); 3.38 (d, J = 10.7 Hz, 1H, (Vinyl)H); 3.89 (d, J = 8.1 Hz, 1H, C(3)H); 4.91 (dd, J = 5.6, 3.2 Hz, 1H, C(5)H); 4.99 (dd, J = 8.1, 5.6 Hz, 1H, C(4)H); 6.19 (d, J = 3.2 Hz, 1H, C(6)H). ^{13}C NMR (125.7 MHz, CD_2Cl_2): δ 9.3, 12.0, 60.4 (br), 63.8, 76.3 (br), 81.1, 86.4, 91.8, 93.7, 106.5. ^{11}B NMR (160.4 MHz, THF-d_8): δ 18.7. Anal. Calcd for $C_{26}H_{37}BClNRu_2$: C, 51.03; H, 6.09; N, 2.29. Found: C, 50.91; H, 6.02; N, 2.09.

4.9. X-ray crystallography

Details of the data collection and refinement are summarized in Table 2.

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Appendix A. Supplementary material

CCDC 689554 contains the supplementary crystallographic data for **12**. 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.2008.10.043.

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