

Strong agostic-type interactions in ruthenium benzyldiene complexes containing 7-azaindole based scorpionate ligands

TSOUREAS, Nikolaos, NUNN, Joshua, BEVIS, Thomas, HADDOW, Mairi F., HAMILTON, Alex and OWEN, Gareth R.

Available from Sheffield Hallam University Research Archive (SHURA) at:

<https://shura.shu.ac.uk/9925/>

This document is the Published Version [VoR]

Citation:

TSOUREAS, Nikolaos, NUNN, Joshua, BEVIS, Thomas, HADDOW, Mairi F., HAMILTON, Alex and OWEN, Gareth R. (2011). Strong agostic-type interactions in ruthenium benzyldiene complexes containing 7-azaindole based scorpionate ligands. Dalton Transactions, 40 (4), 951-958. [Article]

Copyright and re-use policy

See <http://shura.shu.ac.uk/information.html>

Cite this: *Dalton Trans.*, 2011, **40**, 951

www.rsc.org/dalton

PAPER

Strong agostic-type interactions in ruthenium benzylidene complexes containing 7-azaindole based scorpionate ligands†

Nikolaos Tsoureas, Joshua Nunn, Thomas Bevis, Mairi F. Haddow, Alex Hamilton and Gareth R. Owen*‡

Received 1st September 2010, Accepted 5th November 2010

DOI: 10.1039/c0dt01148g

The complexes $[\text{Ru}(\text{Tai})\text{Cl}\{\text{C}(\text{H})\text{Ph}\}(\text{PCy}_3)]$ (**4**) and $[\text{Ru}(\text{PhBai})\text{Cl}\{\text{C}(\text{H})\text{Ph}\}(\text{PCy}_3)]$ (**5**) [where **Tai** = $\text{HB}(7\text{-azaindoly})_3$ and $\text{PhBai} = \text{Ph}(\text{H})\text{B}(7\text{-azaindoly})_2$] have been prepared and structurally characterised. The borohydride unit is located in the coordination site *trans* to the chloride ligand in both complexes. The degree of interaction between the borohydride group and the metal centre was found to be significantly large in both cases. Thermolysis reactions involving complex **4** led to a dehydrogenation reaction forming $[\text{Ru}(\text{Tai})\text{Cl}\{\text{PCy}_2(\eta^2\text{-C}_6\text{H}_9)\}]$ (**6**) where the benzylidene group acts as a hydrogen acceptor.

Introduction

The introduction of new generation of ‘flexible scorpionate ligands’,§ has added a new dimension to the field of scorpionate based chemistry. The first examples were developed by Reglinski,¹ providing a rapid expansion and diverse reactivity within the coordination and organometallic chemistry in compounds of this type.² The implications of such flexibility were realized by the isolation of metallaboratrane complexes;³ the first complexes to authenticate metal-to-borane dative interactions.^{4,5} Since their discovery in 1999, metallaboratrane complexes have attracted considerable attention.^{6–12} Until recently, the majority of examples have been focused on soft donor atom scaffolds such as sulfur,^{8,9,11} and phosphines¹² (Fig. 1). Over the past few years we have reported a number of examples involving nitrogen based donors.¹⁰ During

these investigations, we have been interested in exploring transition metal-borane complexes as potential ‘hydride stores’ via a process involving transfer of hydride between metal and boron centres.^{10b,13} Such compounds could have a number of applications in catalysis and in hydrogen storage technologies.

We have carried out a number of investigations on the relatively new ligand **Tai**¹⁴ [**Tai** = $\text{HB}(7\text{-azaindoly})_3$], a flexible analogue of Trofimenko’s ubiquitous ligand, **Tp** [**Tp** = hydrotris(pyrazolyl)borate].¹⁵ To date, little investigation has been carried out on **Tai**.^{14,16,17} In one example, Kuwata and Ikariya have reported the interconversion between two coordination modes of **Tai** ($\kappa^3\text{-NNH}$ and $\kappa^2\text{-NH}$) by addition and removal of carbon monoxide (Scheme 1).¹⁶

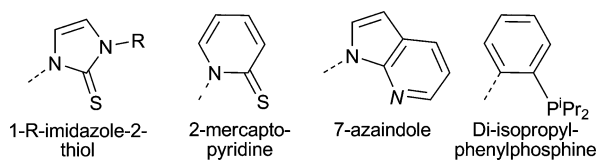
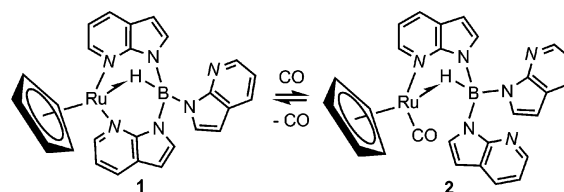


Fig. 1 Sulfur, nitrogen and phosphine based scaffolds.



Scheme 1 Interconversion between the $\kappa^3\text{-NNH}$ and $\kappa^2\text{-NH}$ coordination modes of **Tai**.

We set out to explore the hydride migration properties of this novel flexible scorpionate ligand and have reported a series of group 9 transition metal complexes containing both **Tai** and **PhBai** [$\text{PhBai} = \text{Ph}(\text{H})\text{B}(7\text{-azaindoly})_2$].^{10b,18} Such complexes revealed $\kappa^3\text{-NNH}$ coordination modes in all cases for those complexes where the B–H bond is present. The degree of interaction of the borohydride group and the metal centre can vary in strength and involve three-centre-two-electron $\text{M} \cdots \text{H} \cdots \text{B}$ interactions. In an attempt to further understand the specific conditions required for hydride migration between the boron and metal centres, we began to investigate a series of ruthenium compounds containing the **Tai** and **PhBai** ligands. During the course of these investigations

The School of Chemistry, University of Bristol, Cantock's Close, Bristol, UK, BS8 1TS. E-mail: gareth.owen@bristol.ac.uk; Fax: 44 (0)117 929 0509; Tel: 44 (0)117 928 7652

† Electronic supplementary information (ESI) available: Details outlining our attempts to synthesise **4** and **5**, additional crystallographic details and a discussion regarding other scorpionate complexes containing $\text{Ru} \cdots \text{H} \cdots \text{B}$ interactions. CCDC reference numbers 791419–791422. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01148g

‡ Royal Society Dorothy Hodgkin Research Fellow.

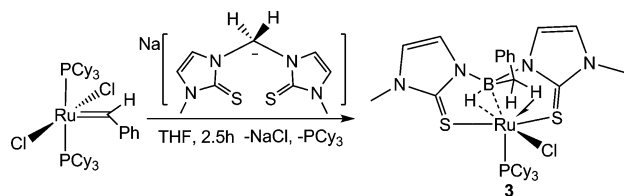
§ We use the term ‘flexible scorpionate’ to represent those ligands which contain two atoms between the boron centre and the donor atom. This additional atom providing access to transition metal-boron interactions.

we obtained evidence for strong ruthenium-hydride character within the borohydride interaction with the ruthenium centre, providing insight into the processes involved in hydride migration (*i.e.* from borohydride to metal-hydride). Herein, we wish to report details from these investigations including i) the synthesis and characterisation of a number of novel ruthenium complexes containing the 7-azaindole based ligands **Tai** and **^{Ph}Bai** and ii) the observation of unusually large upfield chemical shifts for the *BH* resonances in the ¹H NMR spectra, indicating a very strong agostic-type interaction between the B–H moiety and the ruthenium centre.

Results and discussion

Synthesis of ruthenium benzylidene complexes **4** and **5**

We have recently reported a ‘scorpionate sting’ on Grubbs’ first generation catalyst involving its reaction with the flexible scorpionate ligand dihydrobis(methimidazolyl)borate (**Bm**) (Scheme 2).¹³ In this reaction a transfer of a hydride from boron occurred resulting in an unusual rearrangement and transfer of the former benzylidene fragment to the boron centre (Scheme 2). Isolation and characterisation of the resulting species **3** revealed a compound where the newly formed borohydride species was ‘frozen’ at an intermediate point of transfer between the boron and ruthenium centres.



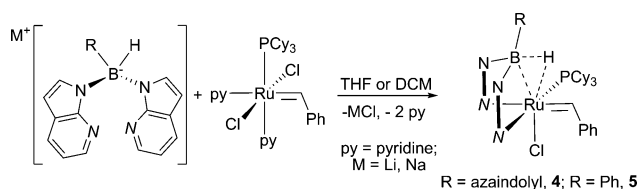
Scheme 2 Reaction of Na[**Bm**] with Grubbs’ first generation catalyst to form **3**.

In order to explore the reactivity of the ‘flexible scorpionates’ with Grubbs’ based compounds further, we set out to investigate their reactivity with **Tai** and **^{Ph}Bai**. These nitrogen based scorpionates might show a similar reactivity to that found in the case of **Tp**.¹⁹ The reactions were initially attempted using [RuCl₂{=C(H)Ph}(PCy₃)₂] as the precursor (see ESI for details). Reactions involving this starting material showed incomplete conversions to the desired products, leading to decomposition after prolonged periods of heating. From one mixture involving **Tai**, it was possible to isolate green crystals. The structure revealed these single crystals to be co-crystals of two independent complexes; one being the target complex [Ru(**Tai**)Cl{=C(H)Ph}(PCy₃)] (**4**) and the other [Ru(**Tai**)Cl(azaindole)(PCy₃)] (**4'**). Further details of this reaction together with the crystal structure of **4'** are provided in the ESI. In view of the low reactivity of [RuCl₂{=C(H)Ph}(PCy₃)₂] with these ligands, an alternative precursor [RuCl₂{=C(H)Ph}(PCy₃)(pyridine)₂]²⁰ was employed (Scheme 3). In this case, the reactions proceeded at room temperature and the ³¹P{¹H} and ¹¹B{¹H} NMR spectra indicated that the reactions were complete within three hours. The expected products, [Ru(**Tai**)Cl{=C(H)Ph}(PCy₃)] (**4**) and [Ru(**^{Ph}Bai**)Cl{=C(H)Ph}(PCy₃)] (**5**) were obtained as green solids in moderate yields.

Table 1 ¹¹B{¹H} NMR and infrared spectroscopic data for scorpionate complexes of 7-azaindole based ligands

Complex	¹¹ B{ ¹ H} (ppm)	¹ J _{B-H} (Hz)	B–H...Ru ^f (cm ⁻¹)
[Ru(Tai)Cl{=C(H)Ph}(PCy ₃)] (4)	−0.8 ^a	49	1929
[Ru(Tai)Cl{PCy ₂ (η ² -C ₆ H ₆)}] (6)	−0.3 ^b	54	^d
[Rh(COD)(κ ³ - <i>NNH</i> - Tai)] ^g	−2.2 ^b	78	2106
[Rh(NBD)(κ ³ - <i>NNH</i> - Tai)] ^h	−1.6 ^a , −1.5 ^c	78	2015
[Ir(COD)(κ ³ - <i>NNH</i> - Tai)] ^g	2.1 ^b	59	2102
[Ru(^{Ph}Bai)Cl{=C(H)Ph}(PCy ₃)] (5)	−1.1 ^a	unresolved ^e	1922
[Rh(COD)(κ ³ - <i>NNH</i> - ^{Ph}Bai)] ^h	−4.6 ^b	unresolved ^e	2117
[Rh(NBD)(κ ³ - <i>NNH</i> - ^{Ph}Bai)] ^h	−3.5 ^b	unresolved ^e	2022
[Ir(COD)(κ ³ - <i>NNH</i> - ^{Ph}Bai)] ^h	−0.3 ^b	unresolved ^e	2004

^a C₇D₈, ^b C₆D₆, ^c CD₂Cl₂, ^d not determined, ^e the B–H coupling constant was unresolved due to the broadness of the signal, ^f powder film, ^g reference 10b, ^h reference 18; COD = 1,5-cyclooctadiene, NBD = norbornadiene.



Scheme 3 Reaction of K[**Tai**] and Li[**^{Ph}Bai**] with [RuCl₂{=C(H)Ph}(PCy₃)(pyridine)₂] (N–N represents 7-azaindolyl units).

The new complexes were fully characterised by spectroscopic and analytical methods. The ¹¹B{¹H} NMR spectra revealed single peaks at −0.8 ppm [h.h.w. 58 Hz] and −1.1 ppm [h.h.w. 246 Hz] in C₇D₈ for **4** and **5** respectively. In the corresponding ¹¹B NMR experiments, the signal appeared as a doublet in the case of **4** (¹J_{BH} = 49 Hz) as a result of coupling to the adjacent hydrogen atom. As found in all other cases involving **^{Ph}Bai**, the boron signal for complex **5** was too broad to resolve coupling to the adjacent hydrogen [h.h.w. 274 Hz]. The ¹H and ¹³C{¹H} NMR data for **4** were consistent with the formation of [Ru{κ³-*NNH*-HB(azaindolyl)₃}Cl{=C(H)Ph}(PCy₃)]. The presence of the benzylidene group was confirmed by a characteristic signal at 19.3 ppm (d, ³J_{PH} = 9.3 Hz) in the ¹H NMR spectrum and a signal at 320.3 ppm in a ¹³C{¹H} NMR experiment.¶ The NMR spectra of **4** is consistent with a static coordination of the ligand with three different chemical environments of the azaindolyl rings. The ¹H and ¹³C{¹H} NMR data for **5** were also consistent with the formation of [Ru{κ³-*NNH*-Ph(H)B(azaindolyl)₂}Cl{=C(H)Ph}(PCy₃)]. Of particular note was the Ru...H–B resonances for both complex **4** and **5** which were located as doublet signals at −14.30 ppm (²J_{PH} = 13.8 Hz) for **4** and −14.20 ppm (²J_{PH} = 13.3 Hz) for **5** in the ¹H{¹¹B} NMR spectra. The unusually large upfield chemical shifts are suggestive of a considerable interaction of this group with the ruthenium centres. The formation of complexes **4** and **5** was also supported by IR spectroscopy which showed characteristic bands corresponding to the ruthenium-borohydride stretching frequencies. In the solid state, bands at 1929 cm⁻¹ (ν_{Ru...H-B}) and 1922 cm⁻¹ (ν_{Ru...H-B}) were observed for **4** and **5** respectively (Table 1). These are lower than those found in the previously reported group nine complexes^{10b,18} and are comparable to ruthenium–hydride stretching frequencies.²¹

¶ This signal was located indirectly by a gc2hsqsc correlation experiment.

Table 2 Selected bond distances (Å) and angles (°) for complexes **4**, **5** and **6**

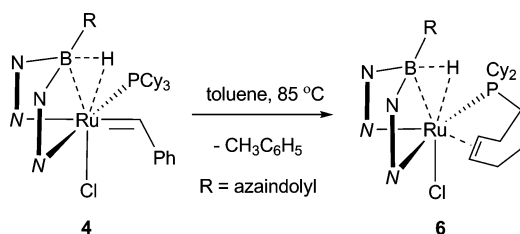
Bonding distance/Angle	4	5^a	6^{a,b}
Ru(1)–N(2)	2.263(2)	2.234(2)/2.245(2)	2.154(3)/2.156(3)
Ru(1)–N(4)	2.160(2)	2.185(2)/2.163(2)	2.154(3)/2.149(3)
Ru(1)–P(1)	2.3732(7)	2.3640(7)/2.3675(7)	2.2981(12)/2.2975(11)
Ru(1) = C(H)Ph	1.902(2)	1.885(3)/1.888(3)	—
Ru(1)–Cl(1)	2.4031(6)	2.4128(6)/2.3951(6)	2.4312(12)/2.4251(12)
Ru(1)– η^2 -C=C ^c	—	—	2.210(4)/2.224(4)
Ru(1)– η^2 -C=C ^c	—	—	2.209(4)/2.234(4)
B(1)–N(1)	1.527(4)	1.539(4)/1.535(4)	1.515(6)/1.506(6)
B(1)–N(3)	1.518(4)	1.528(4)/1.541(4)	1.527(6)/1.526(6)
B(1)–N(5)/B(1)–C ₆ H ₅	1.527(3)	1.606(4)/1.605(4)	1.509(6)/1.510(6)
B(1)–H(1)	1.28(3)	1.25(4)/1.27(4)	1.43(4)/1.14(4)
Ru(1)–H(1)	1.63(3)	1.64(4)/1.68(4)	1.54(4)/1.83(4)
Ru(1)–B(1)	2.673(3)	2.694(4)/2.675(4)	2.769(4)/2.766(4)
N(3)–B(1)–N(1)	114.7(13)	111.7(2)/112.0(2)	111.9(4)/112.3(4)
N(4)–Ru(1)–N(2)	81.11(8)	82.84(8)/80.82(8)	91.69(14)/92.87(14)
P–Ru(1)–N(2) ^d	102.26(5)	103.18(6)/102.51(6)	93.87(10)/93.60(10)
Ru(1)–H(1)–B(1)	134(2)	136(2)/130(2)	138(3)/136(3)

^a Two independent molecules in the same structure, ^b one molecule of toluene solvent of crystallisation, ^c the two ruthenium-carbon distances for each independent molecule are provided in the table, ^d where phosphine and azaindole groups are mutually *cis* transposed.

Reactivity of complexes **4** and **5**

It was of interest to explore the potential activities of complexes **4** and **5** within olefin metathesis. Accordingly, following Grubbs' standard system for evaluating olefin metathesis catalysts,²² these complexes were tested for ring closing metathesis of diethyl diallyl malonate. Unfortunately, neither of these complexes showed any signs of activity under reflux in DCM, even after prolonged periods of time or heating up to 65 °C (Young's NMR tube). This is perhaps unsurprising in view of the chemical environment of the borohydride moiety (*vide infra*). Octahedral complexes such as [RuCl(Tp){=C(H)Ph}(PCy₃)] have previously been found to be inactive compounds since they do not allow access to the 14-valence electron active species.^{19,23,24}

A toluene-d₈ solution of complex **4** was heated up to 85 °C over a period of 48 h after which time the ³¹P{¹H}, ¹¹B{¹H} and ¹H NMR spectra revealed complete consumption of the starting material (Scheme 4). The ³¹P{¹H} NMR spectrum showed one major signal at 57.1 ppm. A small crop of yellow crystals was obtained from this mixture by slow diffusion of pentane into the solution. The isolated crystalline material (**6**) was analyzed by X-ray crystallography (see below for details) and by NMR spectroscopy. The ¹¹B{¹H} NMR spectrum of **6** revealed a single peak at –0.3 ppm [h.h.w. 53 Hz]. The signal appeared as a doublet (¹J_{BH} = 54 Hz) in the corresponding ¹¹B NMR experiment confirming the presence of the BH group in complex **6**.



Scheme 4 Thermolysis reaction of **4** leading to the formation of one equivalent of toluene.

The ¹H NMR spectrum was notable for the absence of the benzyldiene proton in the expected region of the spectrum. The corresponding phenyl protons were also absent from the spectrum suggesting that this functional group had been lost from the complex. Additionally, a BH resonance was located as a broad signal at –9.01 ppm. This signal resolved into a broad doublet (d, ²J_{PH} = 3.5 Hz) in the ¹H{¹¹B} NMR spectrum indicating coupling to the phosphine ligand. The small coupling constant suggests that the phosphine and BH group were mutually *cis* disposed. Finally, the signals corresponding to the PCy₃ group integrated for a total of 31 protons rather than the expected 33 protons. Two of these signals were observed at 3.49 ppm and 4.05 ppm, which is typical for coordinated alkene protons.²⁵ The molecular structure of complex **6**, shown below, confirms the dehydrogenation of the cyclohexyl group and loss of the benzyldiene group (Scheme 4).

Leung has recently reported a similar reactivity where the benzyldiene fragment from the complex is lost as toluene *via* the transfer of two hydrogen atoms from a tricyclohexylphosphine ligand to the metal centre.²⁵ The dehydrogenation of PCy₃ and related ligands has previously been observed in many examples.²⁶ The majority of other examples involving PCy₃ require the presence of a hydrogen acceptor such as CH₂=CH^tBu. In complex **6**, it appears that the benzyldiene group acts as a hydrogen scavenger although it is unclear whether the B–H group is involved in the transformation of complex **4** to **6**.

X-ray crystallography

Single crystals were obtained for each of the complexes **4**, **5** and **6** and the molecular structures are provided in Fig. 2, 3 and 4, respectively. A further structure, consisting of co-crystals of **4** and a side product [Ru{κ³-NNH-HB(azaindoly)₃}Cl{κ¹-N-azaindole}(PCy₃)] (**4'**) was also obtained and is presented in the ESI. Selected bond lengths and angles for complexes **4**, **5** and **6** are presented in Table 2.

All complexes adopt octahedral geometries at the ruthenium centres and feature the ligands **Tai** or **^{Ph}Bai** with a κ³-NNH coordination mode. This coordination motif consists of two

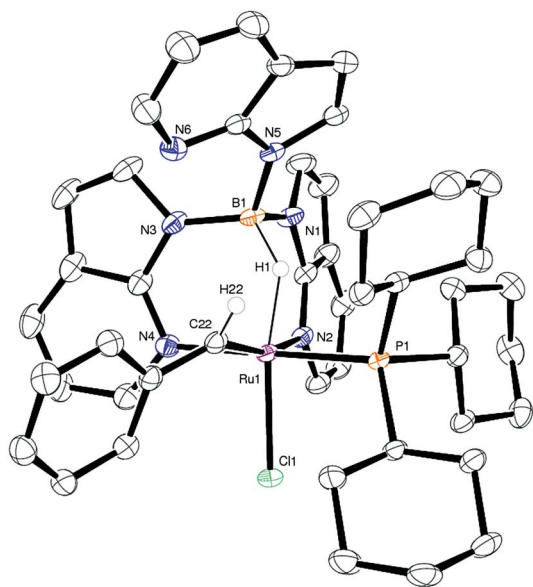


Fig. 2 Molecular structure of $[\text{Ru}\{\kappa^3\text{-NNH-HB(azaindoly)}_3\}\text{Cl}\{\text{PCy}_2\text{-C(H)Ph}\}]\text{(4)}$. Hydrogen atoms with the exception of H1 and H22 have been omitted for clarity (thermal ellipsoids drawn at 50% probability level).

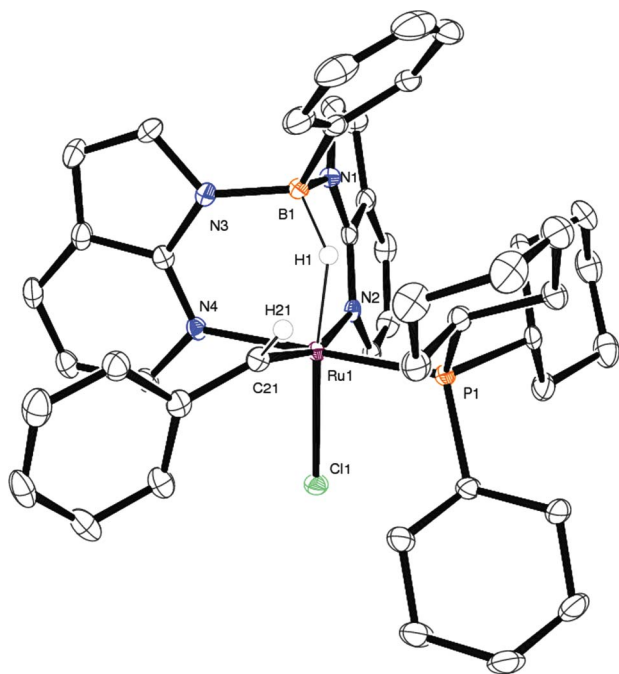


Fig. 3 Molecular structure of $[\text{Ru}\{\kappa^3\text{-NNH-Ph(H)B(azaindoly)}_3\}\text{Cl}\{\text{PCy}_2\text{-C(H)Ph}\}]\text{(5)}$. Hydrogen atoms with the exception of H1 and H21 have been omitted for clarity (thermal ellipsoids drawn at 50% probability level).

azaindoly moieties coordinating through the nitrogen atom of the pyridine heterocycles and a B–H interaction at an apical site on the ruthenium centre. A similar coordination motif (*i.e.* $\kappa^3\text{-NNH}$) has also been reported by Kuwata and Ikariya in the molecular structure of $[\text{Ru}(\text{Cp}^*)\{\kappa^3\text{-NNH-HB(azaindoly)}_3\}]$.¹⁶ Complexes **4** and **5** are further coordinated by a chloride ligand, which is located *trans* to the B–H group, in addition to a tricyclohexylphosphine

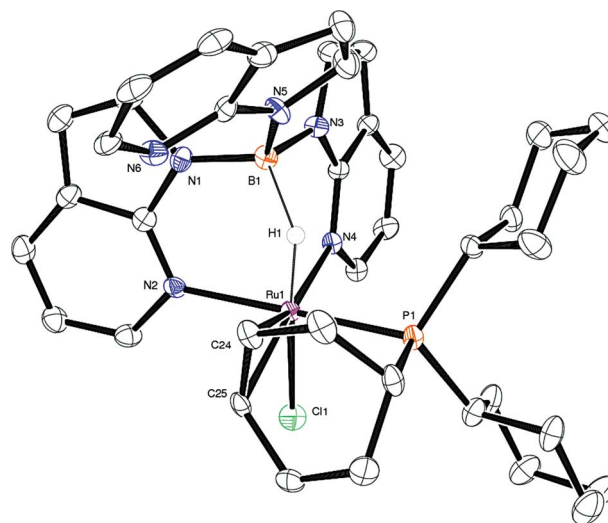


Fig. 4 Molecular structure of $[\text{Ru}\{\kappa^3\text{-NNH-HB(azaindoly)}_3\}\text{Cl}\{\text{PCy}_2\text{-(}\eta^2\text{-C}_6\text{H}_9\text{)}\}]\text{(6)}$. The solvent molecule and hydrogen atoms with the exception of H1 have been omitted for clarity (thermal ellipsoids drawn at 50% probability level).

ligand and a benzylidene group (which are located *cis* relative to each other and *cis* to the chloride ligand). The structure for complex **5** consists of two independent molecules in the unit cell. Finally, complex **6** is also further coordinated by a chloride ligand, which is located *trans* to the B–H group, in addition to a tricyclohexylphosphine ligand where two hydrogen atoms have been eliminated from one of the cyclohexyl groups. The new ligand, $\text{P(Cy)}_2(\text{C}_6\text{H}_9)$ coordinates with a $\kappa^1\text{-P-}\eta^2\text{-C}\equiv\text{C}$ coordination mode.

The nature of the boron–hydrogen \cdots ruthenium interaction

The nature of the boron–hydrogen \cdots transition metal interactions within scorpionate complexes has been studied for some time.^{2,15} Some examples have shown reactivity of the B–H bond within the original rigid type scorpionates (such as **Tp** and its derivatives). For example, the insertion of fragments such as acyl, iminoacyl, thioacyl, alkoxide and cumulene into the B–H bond of dihydrobis(pyrazolyl)borate complexes.²⁷ However, recent investigations have revealed significant differences between the rigid scorpionates compared to the new generation flexible scorpionates. This is exemplified in the large number of recent reports highlighting the activation of this bond to form new metal–borane (metallaboratrane type) complexes^{8–11} as well as other activation products.^{13,28}

There are over 21 structurally characterised ruthenium complexes which contain either the original type or new generation flexible scorpionate ligands with $\kappa^3\text{-NNH}$ or $\kappa^3\text{-SSH}$ coordination modes reported in the chemical literature to date (further details are provided in Table S3 of the ESI). The proton chemical shifts of the $\text{Ru}\cdots\text{H-B}$ group, in complexes of the type $\{\text{Ru}\cdots\text{H-BN}_n\}$ (where $n = 2$ or 3) span a wide range (1.47 to -18 ppm). It has previously been noted that the high field shielding effects on terminal transition metal hydrides are highly dependent on the coordination environment at the metal centre and the ligand *trans* to the hydride has an influence on its chemical shift.²¹ The two

complexes with the highest recorded $\text{Ru} \cdots \text{H}-\text{B}$ upfield shifts, $[\text{Ru}(\kappa^3\text{-NNH-Bp}^{\text{CF}_3})\text{Cl}(\text{tBuNH}_2)_2]$ **(7)**, (−15.9 ppm) and $[\text{Ru}(\kappa^3\text{-NNH-Bp}^{\text{CF}_3})\text{I}(\text{tBuNH}_2)_2]$ **(8)**, (−18 ppm)²⁹ however appeared to be isolated cases since all other complexes were reported to be downfield of −11 ppm.³⁰ The complexes which contain halides in the *trans* position relative to this group appear to possess chemical shifts outside the range of the other structurally characterised $\text{Ru} \cdots \text{H}-\text{B}$ compounds. In our previously reported complex **3** (Scheme 2), where the hydride was located at an intermediate point between the boron and ruthenium centres the $\text{Ru} \cdots \text{H}-\text{B}$ signal was found at −15.3 ppm.¹³ The complexes which are *trans* to strong sigma donors such as hydride or methyl have chemical shifts which generally fall within the range from 1.47 ppm to −5.7 ppm (Table S3). The chemical shift of the $\text{Ru} \cdots \text{H}-\text{B}$ group is clearly dependent on the ligand in the *trans* site and the hydrogen atom has greater ruthenium–hydride character (*i.e.* $\text{Ru}-\text{H} \cdots \text{B}$) when *trans* to a halide. This is supported by the significantly low frequency bands found in the infrared spectra of both complexes **4** and **5** (see Table 1).

The J_{BH} coupling constants can be determined by boron-coupled (^{11}B) NMR experiments and can provide further information regarding the strength of the $\text{Ru} \cdots \text{H}-\text{B}$ interaction. In some cases, where the multiplicity is resolved, a ^1H NMR experiment can also provide this constant.^{30,31} Unfortunately this information is limited within the chemical literature due, in part, to the broad unresolved signals typically observed within the ^{11}B NMR spectra of compounds of this type. As indicated in Table 1, all of the ^{11}B NMR spectra for the complexes involving **PhBai** are too broad to resolve this coupling constant. On the other hand, the signals for the complexes containing **Tai** are sharp enough to resolve the J_{BH} coupling constants. It was seen that the coupling constant is significantly lower in complexes **4** (49 Hz) and **6** (54 Hz) than the previously reported rhodium complexes, $[\text{Rh}(\text{COD})(\kappa^3\text{-NNH-Tai})]$ and $[\text{Rh}(\text{NBD})(\kappa^3\text{-NNH-Tai})]$ ^{10b,18} (78 Hz) (Table 1). These data provide further evidence to a significant weakening of the B–H bond in the cases where the BH group is situated *trans* to a halide ligand. A possible explanation for this is the π -donation effect of the halide which pushes electron density into the antibonding orbital (σ^*) of the B–H bond.

The flexible scorpionates such as **Tai** and **Tm** show a general preference for $\kappa^3\text{-NNH}$ and $\kappa^3\text{-SSH}$ coordination modes over their respective $\kappa^3\text{-NNN}$ and $\kappa^3\text{-SSS}$ coordination modes on the basis that two six-membered rings are formed instead of three-eight membered rings (Fig. 5). There are limited examples of the $\kappa^3\text{-NNN}$ coordination mode¹⁴ for **Tai**, however this is perhaps a consequence of the limited exploration of this ligand to date. On the other hand, there are a number of examples of the $\kappa^3\text{-SSS}$ coordination for the sulfur based flexible scorpionate **Tm** and its derivatives,² although only two examples involving a ruthenium metal centre.³² The ring size formed upon chelation is only one

factor in determining the mode of coordination.^{2,33,34} Additionally, the strength of the transition metal $\cdots \text{H}-\text{B}$ interaction can be particularly strong and play an important role in some cases. As previously described, Kuwata and Ikariya had shown the loss of an azaindole ring from the coordination sphere in preference to loss of the borohydride interaction (Scheme 1).¹⁶

Concluding remarks

In summary, a number of ruthenium complexes have been prepared based on the flexible scorpionate ligands **Tai** and **PhBai**. A comparison has been made to the original nitrogen based scorpionate ligands based on pyrazole rings in addition to the sulfur ligands based on 1-methyl-imidazole-2-thione and their derivatives. It was found that in the majority of cases the flexible type ligands adopt $\kappa^3\text{-NNH}$ or $\kappa^3\text{-SSH}$ coordination modes within ruthenium complexes and exhibit strong $\text{Ru} \cdots \text{H}-\text{B}$ interactions. In complexes where the B–H group is situated in a position *trans* to a halide ligand, the $\text{Ru} \cdots \text{H}-\text{B}$ motif exhibits strong ruthenium–hydride character as determined by IR and NMR spectroscopy. The $\text{Ru} \cdots \text{H}-\text{B}$ interaction within these complexes provides highly stable octahedral complexes which, in the case of the benzylidene examples, limits their activity in the olefin metathesis reaction investigated.

Experimental

General considerations

All manipulations were performed in a Braun glovebox with an O_2 and H_2O atmosphere of below 5 ppm or by using standard Schlenk techniques. $[\text{RuCl}_2(\text{py})_2\text{PCy}_3\{=\text{C}(\text{H})\text{Ph}\}]$ ²⁰ was prepared according to literature procedures. Grubbs' 1st generation catalyst was purchased from Aldrich and was used as received. Solvents (toluene, THF, DCM) were dried using a Grubbs' alumina system, and were kept in flame-dried Young's ampoules under N_2 over molecular sieves (4 Å). Dry n-pentane (<0.05 ppm H_2O) was purchased from Fluka and was kept in a flame-dried Young's ampoule under N_2 over molecular sieves (4 Å). Deuterated toluene and C_6D_6 was degassed by three freeze-thaw cycles, dried by refluxing over Na or Na/benzophenone respectively for 12 h, vacuum distilled and kept in a flame-dried Young's ampoule over 4 Å molecular sieves under N_2 . Deuterated DCM was degassed by three freeze-thaw cycles, dried by refluxing over CaH_2 for 12 h, vacuum distilled and kept in a Young's ampoule over 4 Å molecular sieves under N_2 . ^1H -NMR, $^{11}\text{B}\{^1\text{H}\}$ -NMR, ^{11}B -NMR and $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra were recorded on a JEOL ECP300 spectrometer operating at 300 MHz (^1H). $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra and correlation experiments were recorded on a Varian VNMR S500 operating at 500 MHz (^1H). The spectra were referenced internally, to the residual protic solvent (^1H) or the signals of the solvent (^{13}C). $^{11}\text{B}\{^1\text{H}\}$ -NMR and ^{11}B -NMR spectra were referenced externally relative to $\text{BF}_3 \cdot \text{OEt}_2$. $^{31}\text{P}\{^1\text{H}\}$ -NMR were referenced externally relative to 85% H_3PO_4 in D_2O . Mass spectra were recorded on a VG Analytic Quattro in ESI⁺ mode. Elemental analyses were performed at the microanalytical laboratory of the School of Chemistry at the University of Bristol. Infrared spectra were recorded on a Perkin–Elmer Spectrum 100 FTIR spectrometer (solid state, neat) from 4000 cm^{-1} to 650 cm^{-1} .

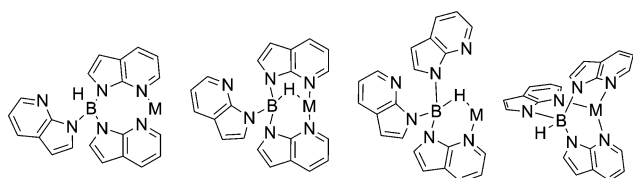


Fig. 5 $\kappa^2\text{-NN}$, $\kappa^3\text{-NNH}$, $\kappa^2\text{-NH}$ and $\kappa^3\text{-NNN}$ coordination modes of **Tai**.

[Ru{ κ^3 -*NNH*-HB(azaindoly)l₃}Cl(=CHPh)(PCy₃)] (4). In the glovebox 100 mg (0.14 mmol) [RuCl₂(=CHPh)(PCy₃)(pyridine)₂] and 56.3 mg (1 mol eq) K[Tai]¹⁶ were charged in a Schlenk tube. This was connected to a Schlenk line and THF (approximately 15 mL) was added at room temperature to give a deep green solution. This was stirred at room temperature for approximately 3 h upon which time it adopted a brown-green hue. The volatiles were removed under vacuum and the residue was extracted with n-pentane (3 × 20 mL) and filtered through a glass-microfibre cannula. Volatiles were removed to approximately half, upon which time a yellow-brown precipitate started forming. Evaporation was stopped and the Schlenk was placed under N₂ and gently warmed until a homogeneous solution had formed. This was placed in the freezer (−30 °C) to give **4** as an olive-green microcrystalline solid, which was isolated by filtration, washed with 2 × 3 mL n-pentane and dried under vacuum. Yield: 42 mg (34%).

¹H-NMR (δ C₇D₈, 300 MHz): −14.30 (1H, broad s, BH), 0.72 (6H, broad m, Cy), 1.02 (6H, broad m, Cy), 1.25 (3H, m, Cy), 1.42 (8H, broad d, Cy), 1.50 (4H, broad s, Cy), 1.72 (2H, broad d, Cy), 1.84 (2H, broad s, Cy), 1.98 (2H, broad m, Cy), 5.84 (1H, d, ³J_{HH} = 3.67 Hz), 6.17 (1H, d, ³J_{HH} = 3.67 Hz), 6.37 (1H, dd, ⁴J_{HH} = 1.83 Hz, ³J_{HH} = 7.33 Hz), 6.66 (1H, d, ³J_{HH} = 3.67 Hz), 6.77 (1H, d, ³J_{HH} = 2.75 Hz), 6.83 (2H, m), 6.96 (1H, d, ³J_{HH} = 4.58 Hz), 7.02 (1H, broad s), 7.06 (1H, m), 7.16 (1H, d, ³J_{HH} = 2.75 Hz), 7.36 (1H, dd, ⁴J_{HH} = 1.83 Hz, ³J_{HH} = 7.33 Hz), 7.76 (2H, m), 8.39 (1H, dd, ⁴J_{HH} = 1.33 Hz, ³J_{HH} = 4.58 Hz), 8.65 (2H, d, ³J_{HH} = 7.33 Hz), 9.67 (2H, ddd, ⁴J_{HH} = 1.83 Hz, ³J_{HH} = 5.50 Hz, ³J_{HH} = 7.33 Hz), 19.3 (1H, d, ³J_{PH} = 9.26 Hz, [Ru] = C(H)Ph); ¹H{¹¹B} (δ C₇D₈, 300 MHz): −14.3 (d, ²J_{PH} = 13.8 Hz); ¹³C{¹H}-NMR (δ C₇D₈, 125.71 MHz): 26.77 (s, CH₂ of Cy), 27.71 (d, J_{PC} = 8.80 Hz, CH₂ of Cy), 27.91 (d, J_{PC} = 9.78 Hz, CH₂ of Cy), 29.08 (s, CH₂ of Cy), 29.8 (CH₂ of Cy), 36.52 (d, ²J_{PC} = 19.6 Hz, CH of Cy), 102.68, 103.02, 103.49, 114.68, 115.33, 116.52, 122.11, 122.37, 122.55, 124.33, 128.03, 128.46, 128.71 (appears in the DEPT-135), 129.62, 130.33, 130.44, 130.59, 132.31, 140.88, 142.33, 142.81, 153.53, 154.50, 155.19 (aromatics), 320.3 (detected indirectly by a gc2hsqcse experiment, [Ru] = C(H)Ph) (the *ipso* carbon in [Ru] = C(H)C₆H₅ could not be located); ³¹P{¹H}-NMR (δ C₇D₈): 42.2 (s, [Ru]PCy₃); ¹¹B{¹H}-NMR (δ C₇D₈): −0.82 (s, Δv_{1/2} = 57.6 Hz); ¹¹B-NMR (δ C₇D₈): −0.82 (d, ¹J_{BH} = 49.4 Hz); MS (ESI)⁺: Low resolution: 871.3 [M+H]⁺, 835.3 [M-Cl]⁺, 744.3 [M-Cl-benzylidene]⁺; High resolution: Calcd for [C₄₆H₅₅BClN₆PRu+H]⁺: 871.3106; Found: 871.3124; Elem. Anal.: Found: C 63.87; H 7.26; N 9.04 Calcd for C₄₆H₅₅BClN₆PRu.0.5 pentane: C 64.27; H 6.78; N 9.23; IR (neat): 1929.3 cm^{−1} (ν_{RuH-B}).

[Ru{ κ^3 -*NNH*-Ph(H)B(azaindoly)l₂}Cl(=CHPh)(PCy₃)] (5). In the glovebox 100 mg (0.14 mmol) [RuCl₂(=CHPh)(PCy₃)(pyridine)₂] and 57.4 mg (1 mol eq) [Li(THF)]^{10b} were charged in a Schlenk tube. This was connected to a Schlenk line and DCM (approx. 15 mL) was added at RT to give a green solution. This was stirred for 3 h or until the solution adopted a brown-green colouration, upon which time complete conversion of the starting materials was evidenced by ³¹P{¹H} and ¹¹B{¹H}-NMR spectroscopy. Volatiles were removed under reduced pressure and the yellow-brown residue was extracted with n-pentane (3 × 10 mL) and filtered through a microfiber cannula to give a brown-green filtrate. This was reduced to approximately 1/3 of volume upon which time it was stored at −30 °C overnight

to give an orange microcrystalline precipitate. This was separated from the mother-liquor by filtration and the brown-green filtrate was further reduced to almost half, and placed in a 5 °C for 36 h, upon which time dark olive-green crystals were formed. These were isolated from the supernatant by filtration, washed twice with 2 mL of n-pentane and dried in vacuum overnight to give **5** as the pentane solvate. Yield: 52 mg (40%).

¹H-NMR (δ C₇D₈, 500 MHz): −14.20 (1H, broad s, BH), 0.78 (m, 3H, Cy), 0.95 (2H, m, Cy), 1.05 (6H, m, Cy), 1.19 (m, 2H Cy), 1.36 (3H, m, Cy), 1.47 (6H, m, Cy), 1.6 (3H, broad d, Cy), 1.81 (6H, m, Cy), 2.05 (2H, m, Cy), 5.91 (1H, d, ³J_{HH} = 3.50 Hz), 6.21 (1H, d, ³J_{HH} = 3.11 Hz), 6.40 (1H, ddd, ⁴J_{HH} = 1.17 Hz, ³J_{HH} = 4.45 Hz, ³J_{HH} = 5.62 Hz), 6.82 (1H, dd, ³J_{HH} = 5.45 Hz, ³J_{HH} = 7.79 Hz), 6.85 (1H, dd, ⁴J_{HH} = 1.17 Hz, ³J_{HH} = 7.79 Hz), 6.90 (1H, broad d), 6.92 (1H, broad d), 7.05 (1H, m), 7.04 (1H, t, ³J_{HH} = 7.04 Hz), 7.21 (1H, d, ³J_{HH} = 3.50 Hz), 7.38 (1H, dd, ⁴J_{HH} = 1.56 Hz, ³J_{HH} = 7.79 Hz), 7.41 (1H, m), 7.48 (2H, m), 8.10 (2H, dd, ⁴J_{HH} = 1.56 Hz, ³J_{HH} = 8.18 Hz), 8.45 (2H, d, ³J_{HH} = 5.45 Hz), 9.67 (1H, dd, ⁴J_{HH} = 1.56 Hz, ³J_{HH} = 5.45 Hz), 9.79 (1H, ddd, ⁴J_{HH} = 1.56 Hz, ⁴J_{HH} = 2.34 Hz, ³J_{HH} = 4.19 Hz), 18.72 (1H, dd, ⁴J_{HH} = 1.56 Hz, ⁴J_{PH} = 8.57 Hz, [Ru] = C(H)Ph); ¹H{¹¹B} (δ C₇D₈, 300 MHz): −14.2 (1H, d, ²J_{PH} = 13.3 Hz); ¹³C{¹H}-NMR (δ C₇D₈, 75.42 MHz): 26.81 (CH₂ of Cy), 27.81 (d, J_{PC} = 6.45 Hz, CH₂ of Cy), 27.87 (d, J_{PC} = 7.40 Hz, CH₂ of Cy), 29.09 (CH₂ of Cy), 29.55 (CH₂ of Cy), 36.32 (d, ²J_{PC} = 20.3 Hz, CH of Cy), 102.86, 103.22, 114.73, 115.04, 122.21, 122.86, 125.37, 128.03, 128.21, 128.70, 128.74, 129.13, 129.48, 130.59, 130.80, 134.69, 140.80, 141.93, 154.27, 155.56, 156.61, 319.00 (broad d, ²J_{PC} = 18.4 Hz, [Ru] = C(H)Ph), (the quaternary aromatic carbon of *ipso* β-C could not be located); ³¹P{¹H}-NMR (δ C₇D₈): 39.5 (s, [Ru]PCy₃); ¹¹B{¹H}-NMR (δ C₇D₈): −1.09 (broad s, Δv_{1/2} = 245.7 Hz); ¹¹B-NMR (δ C₇D₈): −1.09 (broad s, Δv_{1/2} = 273.5 Hz); MS (ESI)⁺: 515.1 [M-Cl-PCy₃]⁺, 704.28 [M-Cl-benzylidene]⁺, 795.3 [M-Cl]⁺, 837.3 [M-Cl+CH₃CN]⁺; Elem. Anal.: Found: C 66.91; H 7.45; N 6.48 Calcd for C₄₅H₅₅BClN₄PRu.pentane: C 66.55; H 7.48; N 6.21; IR (neat): 1922 cm^{−1} (ν_{RuH-B}). NOTE: The compound is air sensitive in the solid state. Nevertheless its solution in d⁸-toluene seems to be stable enough provided it is kept at −30 °C for longer periods of time.

Thermolysis of [Ru{ κ^3 -*NNH*-HB(azaindoly)l₃}Cl(=CHPh)(PCy₃)] A Young's NMR tube was charged with 25 mg (0.029 mmol) of complex **4** and toluene (0.7 mL). The tube was placed in a thermostated oil bath and monitored by ¹H, ³¹P{¹H}, ¹¹B{¹H}-NMR spectroscopy. It was heated at 55 °C (14 h), 65 °C (2 h), 75 °C (12 h), and finally 85 °C (12 h) until no starting material was detected by ³¹P{¹H}, ¹¹B{¹H}-NMR spectroscopy and the benzylidene proton could not be detected in the ¹H-NMR spectrum. The reaction upon completion adopted a yellow-orange colouration. Due to the complexity of the reaction mixture, pentane was slowly diffused into the d⁸-toluene solution to yield overnight a small crop of yellow needles of **6**, which were isolated from the mother-liquor carefully by means of a syringe and washed with 1 ml of n-pentane and dried in vacuum.

¹H-NMR (δ C₆D₆, 500 MHz): −9.01 (1H, broad s, BH), 0.01 (1H, broad s, Cy), 0.43 (2H, broad s), 0.56 (1H, broad s), 0.64 (3H, broad s), 1.07 (4H, m), 1.24 (2H, broad s), 1.39 (2H, m), 1.49 (2H, m), 1.58 (1H, broad s), 1.66 (1H, broad s), 1.81 (4H, broad s), 1.89 (1H, m), 1.97 (2H, m), 2.24 (2H, m), 2.56 (1H, broad s), 3.49 (1H, broad s, CH=CH), 4.05 (1H, broad s, CH=CH), 6.33

(2H, m), 6.38 (1H, dd, $^3J_{\text{HH}} = 6.15$ Hz, $^3J_{\text{HH}} = 7.42$ Hz), 6.69 (1H, d, $^3J_{\text{HH}} = 3.39$ Hz), 6.81 (1H, m), 7.05 (1H, dd, $^3J_{\text{HH}} = 7.63$ Hz, $^4J_{\text{HH}} = 1.27$ Hz), 7.23 (1H, broad s), 7.26 (1H, dd, $^3J_{\text{HH}} = 7.63$ Hz, $^4J_{\text{HH}} = 1.27$ Hz), 7.32 (1H, broad s), 7.51 (1H, broad s), 7.74 (1H, dd, $^3J_{\text{HH}} = 7.85$ Hz, $^4J_{\text{HH}} = 1.70$ Hz), 7.81 (1H, broad s), 8.28 (1H, broad d, $^3J_{\text{HH}} = 4.24$ Hz), 9.56 (1H, broad d, $^3J_{\text{HH}} = 5.30$ Hz), 9.78 (1H, broad s); $^1\text{H}\{^{11}\text{B}\}$ (δ C_6D_6 , 300 MHz): -9.0 (broad d, $^2J_{\text{PH}} = 3.5$ Hz) $^{11}\text{B}\{^1\text{H}\}$ -NMR (δ C_6D_6): -0.33 (s, $\Delta\nu_{1/2} = 52.7$ Hz); ^{11}B -NMR (δ C_6D_6): -0.33 (d, $^1J_{\text{BH}} = 54.1$ Hz); $^{31}\text{P}\{^1\text{H}\}$ -NMR (δ C_6D_6): 57.1; $^{13}\text{C}\{^1\text{H}\}$ -NMR data could not be collected as the compound decomposes at room temperature. Elemental analysis and accurate mass spectra could not be obtained due to the low yield of the reaction and the thermal instability of the compound.

Crystallography

Single crystals of **4** and **5** were obtained by slow evaporation of a saturated toluene solution of **4** or by cooling a pentane solution of **5** at 5°C overnight. A summary of the crystallographic data collection parameters and refinement details for **4**, **5** and **6** are presented in the ESI (Table S2). Anisotropic parameters, bond lengths and (torsion) angles for these structures are available from the cif files (see ESI). All data were collected at 100 K on a Bruker Apex II diffractometer with a Mo-K α (wavelength 0.71073 Å) radiation source and an Oxford Cryosystems Cryostream low temperature device. Collections of all data were performed using a CCD area detector from a single crystals mounted on a glass fibre. Intensities were integrated³⁵ from several series of exposures measuring 0.5° in ω or ϕ . Absorption corrections were based on equivalent reflections using SADABS,³⁶ and structures were refined against all F_o^2 data. All hydrogen atoms were refined using a riding model using SHELX,³⁷ except for those attached to boron, which were found in the difference map and their positions allowed to refine freely with thermal parameters limited to 1.2 times that of the boron atom.

Acknowledgements

G.R.O. gratefully acknowledges the award of a Royal Society Dorothy Hodgkin Research Fellowship from the Royal Society. The authors would like to thank the Leverhulme Trust (N. T.) and EPSRC (J. N. and A. H.) for funding and Johnson Matthey for the loan of the ruthenium salts.

Notes and References

- 1 M. Garner, J. Reglinski, I. Cassidy, M. D. Spicer and A. R. Kennedy, *Chem. Commun.*, 1996, 1975.
- 2 M. D. Spicer and J. Reglinski, *Eur. J. Inorg. Chem.*, 2009, 1553.
- 3 A. F. Hill, G. R. Owen, A. J. P. White and D. J. Williams, *Angew. Chem., Int. Ed.*, 1999, **38**, 2759.
- 4 (a) Previous examples of Z-class coordination (some of which were latterly disproved). D. F. Shriver, *J. Am. Chem. Soc.*, 1963, **85**, 3509; (b) G. W. Parshall, *J. Am. Chem. Soc.*, 1964, **86**, 361; (c) M. P. Johnson and D. F. Shriver, *J. Am. Chem. Soc.*, 1966, **88**, 301; (d) H. Braunschweig and T. Wagner, *Chem. Ber.*, 1994, **127**, 1613; (e) H. Braunschweig and T. Wagner, *Z. Naturforsch. B.*, 1996, **51**, 1618; (f) H. Braunschweig and C. Kollann, *Z. Naturforsch. B.*, 1999, **54**, 839; (g) J. M. Burlitch, M. E. Leonowicz, R. B. Peterson and R. E. Hughes, *Inorg. Chem.*, 1979, **18**, 1097; (h) K. S. Cook, W. E. Piers and R. McDonald, *Organometallics*, 1999, **18**, 1575; (i) K. S. Cook, W. E. Piers and R. McDonald, *Organometallics*, 2001, **20**, 3927; (j) K. S. Cook, W. E. Piers and R. McDonald, *J. Am. Chem. Soc.*, 2002, **124**, 5411.
- 5 (a) R. B. King, *Adv. Chem.*, 1967, **62**, 203; (b) M. L. H. Green, *J. Organomet. Chem.*, 1995, **500**, 127.
- 6 (a) I. Krummenacher Kuzu, F. Armbruster and F. Breher, *Dalton Trans.*, 2008, 5836; (b) F.-G. Fontaine, J. Boudreau and M.-H. Thibault, *Eur. J. Inorg. Chem.*, 2008, 5439; (c) G. R. Owen, *Transition Met. Chem.*, 2010, **35**, 221; (d) H. Braunschweig, R. D. Dewhurst and A. Schneider, *Chem. Rev.*, 2010, **110**, 3924; (e) H. Braunschweig, C. Kollann and D. Rais, *Angew. Chem., Int. Ed.*, 2006, **45**, 5254; (f) J. I. Van Der Vult, *Angew. Chem. Int. Ed.*, 2010, **49**, 252.
- 7 (a) A. F. Hill, *Organometallics*, 2006, **25**, 4741; (b) G. Parkin, *Organometallics*, 2006, **25**, 4744.
- 8 (a) M. R. St.-J. Foreman, A. F. Hill, G. R. Owen, A. J. P. White and D. J. Williams, *Organometallics*, 2003, **22**, 4446; (b) M. R. St.-J. Foreman, A. F. Hill, A. J. P. White and D. J. Williams, *Organometallics*, 2004, **23**, 913; (c) I. R. Crossley and A. F. Hill, *Organometallics*, 2004, **23**, 5656; (d) I. R. Crossley, M. R. St.-J. Foreman, A. F. Hill, A. J. P. White and D. J. Williams, *Chem. Commun.*, 2005, 221; (e) I. R. Crossley, A. F. Hill and A. C. Willis, *Organometallics*, 2005, **24**, 1062; (f) I. R. Crossley, A. F. Hill, E. R. Humphrey and A. C. Willis, *Organometallics*, 2005, **24**, 4083; (g) I. R. Crossley, A. F. Hill and A. C. Willis, *Organometallics*, 2006, **25**, 289; (h) I. R. Crossley, A. F. Hill and A. C. Willis, *Organometallics*, 2007, **26**, 3891; (i) I. R. Crossley, A. F. Hill and A. C. Willis, *Dalton Trans.*, 2008, 201; (j) I. R. Crossley, A. F. Hill and A. C. Willis, *Organometallics*, 2008, **27**, 312; (k) I. R. Crossley, M. R. St.-J. Foreman, A. F. Hill, G. R. Owen, A. J. P. White, D. J. Williams and A. C. Willis, *Organometallics*, 2008, **27**, 381; (l) I. R. Crossley, A. F. Hill and A. C. Willis, *Organometallics*, 2010, **29**, 326.
- 9 (a) V. K. Landry, J. G. Melnick, D. Bucella, K. Pang, J. C. Ulichny and G. Parkin, *Inorg. Chem.*, 2006, **45**, 2588; (b) K. Pang, S. M. Quan and G. Parkin, *Chem. Commun.*, 2006, 5015; (c) D. J. Mihalick, J. L. White, J. M. Tanski, L. N. Zakharov, G. P. A. Yap, C. D. Incarvito, A. L. Rheingold and D. Rabinovich, *Dalton Trans.*, 2004, 1626; (d) R. J. Blagg, J. P. H. Charmant, N. G. Connelly, M. F. Haddow and A. G. Orpen, *Chem. Commun.*, 2006, 2350; (e) J. S. Figueroa, J. G. Melnick and G. Parkin, *Inorg. Chem.*, 2006, **45**, 7056; (f) R. J. Blagg, C. J. Adams, J. P. H. Charmant, N. G. Connelly, M. F. Haddow, A. Hamilton, J. Knight, A. G. Orpen and B. M. Ridgway, *Dalton Trans.*, 2009, (40), 8724; (g) M. J. López-Gómez, N. G. Connelly, M. F. Haddow, A. Hamilton and A. G. Orpen, *Dalton Trans.*, 2010, **39**, 5221; (h) X. Zhao, E. Otten, D. Song and D. W. Stephan, *Chem.-Eur. J.*, 2010, **16**, 2040.
- 10 (a) N. Tsoureas, M. F. Haddow, A. Hamilton and G. R. Owen, *Chem. Commun.*, 2009, 2538; (b) N. Tsoureas, T. Bevis, C. P. Butts, A. Hamilton and G. R. Owen, *Organometallics*, 2009, **28**, 5222; (c) N. Tsoureas, Y.-Y. Kuo, M. F. Haddow and G. R. Owen, *Chem. Commun.*, 2011, **47**, C0CC02245D.
- 11 (a) G. R. Owen, P. H. Gould, J. P. H. Charmant, A. Hamilton and S. Saithong, *Dalton Trans.*, 2010, **39**, 392; (b) G. R. Owen, P. H. Gould, A. Hamilton and N. Tsoureas, *Dalton Trans.*, 2010, **39**, 49.
- 12 (a) S. Bontemps, H. Gornitzka, G. Bouhadir, K. Miqueu and D. Bourissou, *Angew. Chem., Int. Ed.*, 2006, **45**, 1611; (b) S. Bontemps, G. Bouhadir, K. Miqueu and D. Bourissou, *J. Am. Chem. Soc.*, 2006, **128**, 12056; (c) M. Sircoglou, S. Bontemps, M. Mercy, N. Saffon, M. Takahashi, G. Bouhadir, L. Maron and D. Bourissou, *Angew. Chem., Int. Ed.*, 2007, **46**, 8583; (d) M. Sircoglou, S. Bontemps, G. Bouhadir, N. Saffon, K. Miqueu, W. Gu, M. Mercy, C.-H. Chen, B. M. Foxman, L. Maron, O. V. Ozerov and D. Bourissou, *J. Am. Chem. Soc.*, 2008, **130**, 16729; (e) S. Bontemps, G. Bouhadir, W. Gu, M. Mercy, C.-H. Chen, B. M. Foxman, L. Maron, O. V. Ozerov and D. Bourissou, *Angew. Chem., Int. Ed.*, 2008, **47**, 1481; (f) S. Bontemps, M. Sircoglou, G. Bouhadir, H. Puschmann, J. A. K. Howard, P. W. Dyer, K. Miqueu and D. Bourissou, *Chem.-Eur. J.*, 2008, **14**, 731; (g) M. Sircoglou, S. Bontemps, M. Mercy, K. Miqueu, S. Ladeira, N. Saffon, L. Maron, G. Bouhadir and D. Bourissou, *Inorg. Chem.*, 2010, **49**, 3983.
- 13 G. C. Rudolf, A. Hamilton, A. G. Orpen and G. R. Owen, *Chem. Commun.*, 2009, 553.
- 14 D. Song, W. L. Jia, G. Wu and S. Wang, *Dalton Trans.*, 2005, 433.
- 15 (a) S. Trofimenko in *Scorpionates: The Coordination of Poly(pyrazolyl)borate Ligands*, Imperial College Press, London, 1999; (b) S. Trofimenko, *Chem. Rev.*, 1993, **93**, 943; (c) S. Trofimenko, *Polyhedron*, 2004, **23**, 197; (d) C. Pettinari in *Scorpionates II: Chelating Borate Ligands*, Imperial College Press, London, 2008.
- 16 T. Saito, S. Kuwata and T. Ikariya, *Chem. Lett.*, 2006, **35**, 1224.
- 17 The coordination chemistry of a ligand closely related to Tai has also been reported by J. Wagler and A. F. Hill, *Organometallics*, 2008, **27**, 2350.

- 18 G. R. Owen, N. Tsoareas, A. Hamilton and A. G. Orpen, *Dalton Trans.*, 2008, 6039.
- 19 (a) M. S. Sanford, L. M. Henling and R. H. Grubbs, *Organometallics*, 1998, **17**, 5384; (b) M. S. Sanford, J. A. Love and R. H. Grubbs, *Organometallics*, 2001, **20**, 5314; (c) K. J. Harlow, A. F. Hill and J. D. E. T. Wilton-Ely, *J. Chem. Soc., Dalton Trans.*, 1999, 285.
- 20 T. M. Trnka, E. L. Dias, M. W. Day and R. H. Grubbs, *ARKIVOC*, 2002, **13**, 28.
- 21 (a) X. Wang and L. Andrews, *J. Phys. Chem. A*, 2009, **113**, 551; (b) L. L. Lohr and W. N. Lipscomb, *Inorg. Chem.*, 1964, **3**, 22; (c) R. G. Pearson, *Chem. Rev.*, 1985, **85**, 41; (d) G. S. McGrady and G. Guilera, *Chem. Soc. Rev.*, 2003, **32**, 383.
- 22 T. Ritter, A. Hejl, A. G. Wenzel, T. W. Funk and R. H. Grubbs, *Organometallics*, 2006, **25**, 5740.
- 23 J. Patel, W. R. Jackson and A. K. Serelis, *Inorg. Chim. Acta*, 2004, **357**, 2374.
- 24 M. S. Sanford, M. Ulman and R. H. Grubbs, *J. Am. Chem. Soc.*, 2001, **123**, 749.
- 25 W.-M. Cheung, W.-H. Chiu, Z.-Y. Yi, Q.-F. Zhang, I. D. Williams and W.-H. Leung, *Organometallics*, 2010, **29**, 1981.
- 26 (a) B. Alcaide, P. Almendros and A. Luna, *Chem. Rev.*, 2009, **109**, 3817; (b) A. F. Borowski, S. Sabo-Etienne, M. L. Christ, B. Donnadiu and B. Chaudret, *Organometallics*, 1996, **15**, 1427; (c) T. Arliguie, B. Chaudret, G. Chung and F. Dahan, *Organometallics*, 1991, **10**, 2973; (d) T. Arliguie, B. Chaudret, F. A. Jalon, A. Otero, J. A. Lopez and F. J. Lahoz, *Organometallics*, 1991, **10**, 1888; (e) S. Moret, R. Dallanegra, A. B. Chaplin, T. M. Douglas, R. M. Hiney and A. S. Weller, *Inorg. Chim. Acta*, 2010, **363**, 574; (f) T. M. Douglas and A. S. Weller, *New J. Chem.*, 2008, **32**, 966; (g) T. M. Douglas, S. K. Brayshaw, R. Dallanegra, G. Kociok-Köhn, S. A. Macgregor, G. L. Moxham, A. S. Weller, T. Wondimagegn and P. Vadivelu, *Chem.-Eur. J.*, 2008, **14**, 1004; (h) P. D. Bolton, M. Grellier, N. Vautravers, L. Vendier and S. Sabo-Etienne, *Organometallics*, 2008, **27**, 5088; (i) T. M. Douglas, E. Molinos, S. K. Brayshaw and A. S. Weller, *Organometallics*, 2007, **26**, 463; (j) M. Grellier, L. Vendier and S. Sabo-Etienne, *Angew. Chem., Int. Ed.*, 2007, **46**, 2613; (k) T. M. Douglas, J. Le Nôtre, S. K. Brayshaw, C. G. Frost and A. S. Weller, *Chem. Commun.*, 2006, 3408; (l) E. Solari, S. Gauthier, R. Scopelliti and K. Severin, *Organometallics*, 2009, **28**, 4519.
- 27 (a) A. Pizzano, L. Sánchez, E. Gutiérrez, A. Monge and E. Carmona, *Organometallics*, 1995, **14**, 14; (b) A. F. Hill and J. M. Malget, *J. Chem. Soc., Dalton Trans.*, 1997, 2003; (c) P. Ghosh and G. Parkin, *Chem. Commun.*, 1998, 413; (d) P. Ghosh and G. Parkin, *J. Chem. Soc., Dalton Trans.*, 1998, 2281; (e) S. Yeston and R. G. Bergman, *Organometallics*, 2000, **19**, 2947; (f) D. J. Cook and A. F. Hill, *Organometallics*, 2003, **22**, 3502; (g) M. J. Page, B. A. M. Messerle and J. Wagler, *Organometallics*, 2009, **28**, 6145; (h) R. J. Abernethy, A. F. Hill, M. K. Smith and A. C. Willis, *Organometallics*, 2009, **28**, 6152.
- 28 I. R. Crossley, A. F. Hill and A. C. Willis, *Organometallics*, 2007, **26**, 3891.
- 29 V. Rodriguez, I. Atheaux, B. Donnadiu, S. Sabo-Etienne and B. Chaudret, *Organometallics*, 2000, **19**, 2916.
- 30 S. L. Kuan, W. K. Leong, L. Y. Goh and R. D. Webster, *J. Organomet. Chem.*, 2006, **691**, 907.
- 31 R. J. Abernethy, Hill, A. F. Tshabang, N. Willis, D. Rowan and A. C. Young, *Organometallics*, 2009, **28**, 488.
- 32 L. A. Graham, A. R. Fout, K. R. Kuehne, J. L. White, B. Mookherji, F. M. Marks, G. P. A. Yap, L. N. Zakharov, A. L. Rheingold and D. Rabinovich, *Dalton Trans.*, 2005, 171.
- 33 H. M. Alvarez, J. M. Tanski and D. Rabinovich, *Polyhedron*, 2004, **23**, 395.
- 34 (a) P. J. Bailey, D. J. Lorono-Gonzales, C. McCormack, S. Parsons and M. Price, *Inorg. Chim. Acta*, 2003, **354**, 61; (b) P. J. Bailey, A. Dawson, C. McCormack, S. A. Moggach, I. D. H. Oswald, S. Parsons, D. W. H. Rankin and A. Turner, *Inorg. Chem.*, 2005, **44**, 8884.
- 35 Bruker-AXS SAINT V7.60A.
- 36 G. M. Sheldrick, *SADABS V2008/1-2*, University of Göttingen, Germany.
- 37 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112.