

# Electronic Supporting information for ‘*Strong agostic-type interactions in ruthenium benzylidene complexes containing 7-azaindole based scorpionate ligands*’

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## Reactivity of $[\text{RuCl}_2\{\text{=C(H)Ph}\}(\text{PCy}_3)_2]$ with $\text{K}[\text{Tai}]$ and $\text{Li}[\text{PhBai}]$

One equivalent of either  $\text{K}[\text{Tai}]$ <sup>S1</sup> or  $\text{Li}[\text{PhBai}]$ <sup>S2</sup> was added to THF solutions of  $[\text{RuCl}_2\{\text{=C(H)Ph}\}(\text{PCy}_3)_2]$ . The progress of the reactions was monitored by  $^{31}\text{P}\{^1\text{H}\}$  and  $^{11}\text{B}\{^1\text{H}\}$  NMR spectroscopy. The NMR spectra of these mixtures revealed no signs of significant reactivity at room temperature. At 80 °C however, a new signal was observed, in each case, in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra (42.2 ppm, in the case of **Tai** and 39.5 ppm, in the case of **PhBai**) along with the appearance and growth of a signal corresponding to free tricyclohexylphosphine. The NMR spectra showed incomplete conversion to the desired product however even after prolonged periods of heating or the addition of excess ligand. Furthermore after a number of hours, a number of new signals appeared in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra and for these reasons the target compounds were difficult to isolate. From one mixture involving **Tai**, it was possible to isolate single green crystals. The crystal structure revealed these single crystals to be co-crystals of two independent complexes; one being the target complex  $[\text{Ru}(\text{Tai})\text{Cl}\{\text{=C(H)Ph}\}(\text{PCy}_3)]$  (**4**) and the other  $[\text{Ru}(\text{Tai})\text{Cl}(\text{azaindole})(\text{PCy}_3)]$  (**4'**). Further details of this reaction and the molecular structure of **4'** are provided below.

**Synthesis and structural characterisation of co-crystals of **4** and [Ru{ $\kappa^3$ -*NNH*-HB(azaindoly)3}Cl(7-azaindole)(PCy3)] (**4'**)**

During the preparation of complex **4**, the formation of small quantities of another species, [Ru{ $\kappa^3$ -*NNH*-HB(azaindoly)3}Cl(7-azaindole)(PCy3)] (**4'**) was sometimes observed. On one occasion the single crystals were obtained of this mixture (see below). A crystal structure determination of these crystals revealed the co-crystallisation of both complexes **4** and **4'** (Figure S1). The synthesis of this mixture and selected data for **4'** are described below.

In the glove box a Schlenk tube was charged with 52.0 mg (0.063 mmol) of [RuCl<sub>2</sub>{=C(H)Ph}(PCy<sub>3</sub>)<sub>2</sub>] and 25.6 mg of K[**Tai**] (1 mol eq). The Schlenk flask was connected to a Schlenk line and THF (10 mL) was added with stirring at RT. The mixture was then heated at 80 °C in a thermostated oil bath for 1 h over which time it adopted a green/brown colouration. All volatiles were removed under reduced pressure and the residue extracted with pentane (4 × 15 mL) and filtered through Celite. The volume was reduced to approximately <sup>2</sup>/<sub>3</sub> and chilled at -80°C to yield a green precipitate overnight. The filtrate was left standing at RT to afford green crystals the asymmetric unit of which consists of **4** and **4'** in a 1:1 ratio. Data for **4'**: <sup>1</sup>H-NMR ( $\delta$  C<sub>7</sub>D<sub>8</sub>, 300 MHz): 13.16 (1H, broad s., *NH*); <sup>11</sup>B{<sup>1</sup>H}-NMR ( $\delta$  C<sub>7</sub>D<sub>8</sub>):-1.53 (broad s,  $\Delta v_{1/2}$  could not be determined due to overlap with the <sup>11</sup>B{<sup>1</sup>H} signal of **4**); <sup>11</sup>B-NMR ( $\delta$  C<sub>7</sub>D<sub>8</sub>):-1.53 (broad s,  $\Delta v_{1/2}$  could not be determined due to overlap with the <sup>11</sup>B signal (d) of **4**); <sup>31</sup>P{<sup>1</sup>H}-NMR ( $\delta$  C<sub>7</sub>D<sub>8</sub>): 38.02.

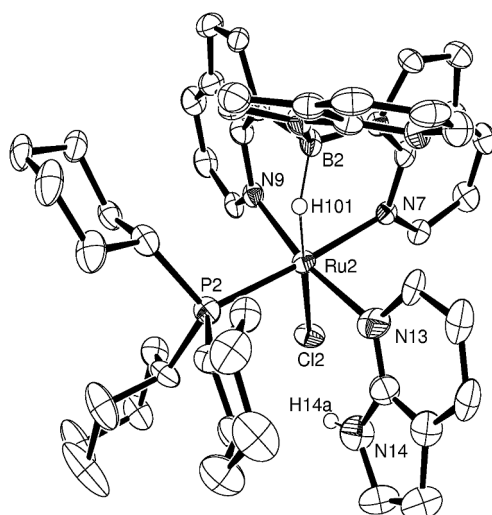


Figure S1 – Molecular structure of complex **4'** (complex **4** which co-crystallized with **4'** has been removed for clarity. Hydrogen atoms except for H101 and the indole N-H (H14a) have also been removed for clarity (thermal ellipsoids drawn at 50 % probability level).

Table S1 – Selected Bond distances and angles for complexes **4** and **4'** within the co-crystallized structure.

Bonding distance/ Angle	<b>4</b>	<b>4'</b>
Ru–P	2.3638(17)	2.368(2)
Ru–N	2.271(5)	2.202(8)
Ru–N ( <i>trans</i> to P)	2.157(5)	2.145(6)
Ru–N (free azaindole ring)	–	2.120(6)
Ru=C(H)Ph	1.885(7)	–
Ru–Cl	2.3890(16)	2.4383(16)
B–N ( <i>trans</i> to P)	1.507(9)	1.492(10)
B–N	1.532(9)	1.553(10)
B–N (uncoordinated)	1.528(9)	1.520(9)
N–B–N (coordinated)	111.6(5)	109.3(6)
N–Ru–N	82.5(2)	85.3(2)
P–Ru–N <sup>a</sup>	102.56(14)	93.35(16)
P–Ru–Cl	91.16(6)	89.92(15)
N( <i>trans</i> to P)–Ru–Cl	90.46(15)	88.74(14)
N–Ru–Cl	89.05(14)	89.92(15)
Ru–H–B	119(5)	115(5)

<sup>a</sup> where phosphine and azaindole groups are mutually *cis* transposed

Table S2 – Crystallographic Parameters for complexes **4**, **5** and **6** and co-crystals of **4** and **4'**.

Compound	<b>4</b>	<b>5</b>	<b>6</b>	Co-crystals of <b>4</b> and <b>4'</b>
Colour, habit	dichroic block	green plate	yellow block	green block
Size/mm	0.22×0.17×0.14	0.26×0.24×0.06	0.08×0.07×0.07	0.35×0.35×0.11
Empirical Formula	C <sub>46</sub> H <sub>55</sub> BClN <sub>6</sub> PRu	C <sub>45</sub> H <sub>55</sub> BClN <sub>4</sub> PRu	C <sub>42.50</sub> H <sub>51</sub> BClN <sub>6</sub> PRu	C <sub>92</sub> H <sub>110</sub> B <sub>2</sub> Cl <sub>2</sub> N <sub>14</sub> P <sub>2</sub> Ru <sub>2</sub>
M.W.	870.26	830.23	824.19	1768.54
Crystal system	triclinic	triclinic	orthorhombic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> -1
<i>a</i> /Å	12.6383(13)	11.1108(4)	17.0169(4)	14.0305(6)
<i>b</i> /Å	12.9075(13)	20.4596(8)	20.4376(5)	17.8271(7)
<i>c</i> /Å	13.6888(15)	20.6296(8)	21.4837(5)	21.7559(8)
$\alpha$ /°	83.130(7)	111.670(2)	90.00	66.035(2)
$\beta$ /°	83.887(7)	99.766(2)	90.00	71.542(3)
$\gamma$ /°	81.991(7)	102.853(2)	90.00	80.820(3)
<i>V</i> /Å <sup>3</sup>	2186.2(4)	4081.6(3)	7471.7(3)	4713.7(3)
<i>Z</i>	2	4	8	2
$\mu$ /mm <sup>-1</sup>	0.495	0.526	0.575	0.461
T/K	100	100	100	100
$\theta_{\min, \max}$	1.50, 30.90	3.42, 27.59	1.38, 27.52	1.07, 27.53
Completeness	0.977 to $\theta = 30.90^\circ$	0.978 to $\theta = 27.59^\circ$	0.999 to $\theta = 27.52^\circ$	0.993 to $\theta = 27.53^\circ$
Reflections: total/independent	74065/13505	60351/18505	65855/17180	82026/21604
<i>R</i> <sub>int</sub>	0.1098	0.0422	0.0732	0.1258
Final <i>R</i> <sub>1</sub> and <i>wR</i> <sub>2</sub>	0.0498, 0.1216	0.0386, 0.0941	0.0466, 0.1007	0.0839, 0.2526
Largest peak, hole/eÅ <sup>-3</sup>	1.441, -1.146	0.972, -0.746	0.951, -0.743	1.201, -1.610
$\rho_{\text{calc}}$ /g cm <sup>-3</sup>	1.322	1.351	1.465	1.246

### Crystallography Discussion

The ruthenium centers in the complexes presented in this paper have little distortion about the octahedral metal centers, the largest distortion from idealized geometry is found for the angles defined by C(H)Ph=Ru–Cl in both **4** and **5** [103.83(8)° for **4** and 105.59(8)°/104.40(8)° for two independent molecules in the structure of **5**]. This appears to originate from the steric clash of the benzylidene group and the chloride ligand. Focusing on the interaction of the borohydride interaction with the ruthenium center it can be seen that the

Ru(1)–H(1)–B(1) angles range between 128(3)° and 140.0(1)°. The ruthenium–hydride and boron–distances are discussed in detail and a comparison to literature examples is made in the following section.

The structural characterisation of the complexes reported herein allows a direct comparison of the Ru•••H–B metrics to be made, although it should be noted that the location of hydrogen atoms by X-ray crystallography cannot be determined precisely (Table S3). The ruthenium boron distances are therefore also provided for comparison. Closer inspection of the table reveals that complexes **4**, **4'**, **5**, **6** and **7**, which containing *trans* halide, have elongated B–H distances [*c.f.* 1.28(3) Å for **4**, 1.27(7) Å for **4'**, 1.25(4) Å and 1.27(4) Å for **5** and 1.291(34) Å for **7**]. With the exception of complex **4'**, these compounds have particularly short Ru•••H distances which are less than 0.1 Å of the sum of the covalent radii of these two atoms. The Ru•••H distances are comparable to complex **3**, [1.66(4) Å]. In **3** however, the B–H distance is 1.50(4) Å which is elongated even further and is 0.35 Å greater than the sum of the covalent radii of the two atoms. As a general trend, the complexes with the shortest ruthenium–boron distances do contain the highest upfield chemical shifts [*c.f.* 2.124(5) Å, –15.3 ppm (**3**); 2.445(4) Å, –15.9 ppm].

Table S3 – Comparison of metrical and <sup>1</sup>H NMR spectroscopic data for various ruthenium based scorpionate complexes.

Complex <sup>a</sup>	B-H distance	Ru•••H distance	Ru•••B distance <sup>b</sup>	Classification of interaction <sup>c</sup>	<sup>1</sup> H NMR B-H••Ru <sub>d</sub>	Reference
[Ru(Cp <sup>*</sup> )(κ <sup>2</sup> -NNH-Tai)]	1.301(7)	1.767(1)	2.786(6)	I	–	S3
[Ru(Cp <sup>*</sup> )(κ <sup>2</sup> -NH-Tai)(CO)]	1.131(9)	1.837(8)	2.918(9)	I	–	S3
[Ru(κ <sup>2</sup> -SSH-Bm)(C <sub>6</sub> Me <sub>6</sub> )Cl]	1.08(2)	1.81(2)	2.80(1)	I	–10.83 <sup>e</sup>	S4
[Ru(κ <sup>2</sup> -SSH-Bm)(Cp <sup>*</sup> )]	1.17(1)	1.81(2)	2.82(1)	I	–7.83 <sup>f</sup>	S4
[Ru(κ <sup>2</sup> -NNH-Bp <sup>*</sup> )H(COD)]	1.17(2)	2.06(2)	2.673(2)	II	–	S5
[Ru(κ <sup>2</sup> -NNH-Tp <sup>*</sup> )(Me)(COD)]	1.33(3)	1.77(3)	2.632(4)	I	1.47 <sup>h</sup>	S6
[Ru(κ <sup>2</sup> -NNH-Tp <sup>ipr-Bn</sup> )H(COD)]	1.25(4)	1.96(5)	2.706(6)	I	–	S7
[Ru(κ <sup>2</sup> -NH-Tp <sup>th</sup> )H(COD)(PMe <sub>3</sub> )]	1.14(5)	2.07(5)	2.848(6)	II	1.05 <sup>i</sup>	S8
[Ru(κ <sup>2</sup> -NH-Bp <sup>CF3</sup> )H(H <sub>2</sub> )(P <sup>t</sup> Pr <sub>3</sub> ) <sub>2</sub> ]	1.202(23)	1.840(25)	–	I	–2.90 <sup>i</sup>	S9
[Ru(κ <sup>2</sup> -NNH-Bp <sup>CF3</sup> )I( <sup>t</sup> BuNH <sub>2</sub> ) <sub>2</sub> ] (7)	1.291(34)	1.667(32)	2.445(4)	I	–15.90 <sup>i</sup>	S9
[Ru(κ <sup>2</sup> -NNH-Bp <sup>CF3</sup> )H(COD)( <sup>t</sup> BuNH <sub>2</sub> )]	1.19(3)	1.90(3)	2.810(4)	I	–	S9
[Ru(κ <sup>2</sup> -NNH-Bp <sup>CF3</sup> )H(PrNH <sub>2</sub> ) <sub>2</sub> (N <sub>2</sub> )]	1.17(4) / 1.25(5)	2.13(4) / 2.21(6)	2.783(6) / 2.761(6)	II	–	S9
[Ru(κ <sup>2</sup> -NNH-Bp <sup>CF3</sup> )(COC <sub>8</sub> H <sub>13</sub> )(CO) <sub>2</sub> ]	1.03(5)	2.11(5)	2.766(8)	II	–	S9
[Ru(κ <sup>2</sup> -NNH-Bp <sup>CF3</sup> )H(COD)]	1.18(3)	1.97(3)	2.672(5)	I	–4.7 <sup>g</sup>	S10

[Ru( $\kappa^3$ -SSH-Tm)H(PPh <sub>3</sub> )(CO)]	1.29(5)	1.75(4)	2.829(5)	I	-3.87 <sup>i</sup>	<b>S11</b>
[Ru( $\kappa^3$ -SSH-Tm)H(PPh <sub>3</sub> )(CO)] <sup>k</sup>	1.19(4)	1.84(4)	2.839(5)	I	-3.87 <sup>i</sup>	<b>S11</b>
[Ru( $\kappa^3$ -SSH-Bm)H(PPh <sub>3</sub> ) <sub>2</sub> ]	1.20(2)	1.77(2)	2.774(3)	I	-5.7 <sup>i</sup>	<b>S12</b>
[Ru( $\kappa^3$ -SSH-Tm)H(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>l</sup>	1.20(7)	1.90(7)	2.931(8)	I	-3.89 <sup>e</sup>	<b>S13</b>
[Ru( $\kappa^3$ -SSH-Tm)Cl(dmsO) <sub>2</sub> ]	1.14(6)	1.84(6)	2.817(6)	I	-9.02 <sup>i</sup>	<b>S14</b>
[Ru( $\kappa^3$ -NNH-Tai)Cl{C(H)Ph}{(PCy <sub>3</sub> )}] ( <b>4</b> )	1.28(3)	1.63(3)	2.673(3)	I	-14.30 <sup>g</sup>	this work
[Ru( $\kappa^3$ -NNH-Tai)Cl{7-azaindole}{(PCy <sub>3</sub> )}] ( <b>4</b> ) <sup>m</sup>	1.27(7)	1.92(7)	2.71(1)	I	-	<sup>n</sup>
[Ru( $\kappa^3$ -NNH- <sup>Ph</sup> Bai)Cl{C(H)Ph}{(PCy <sub>3</sub> )}] ( <b>5</b> ) <sup>n</sup>	1.25(4)/ 1.27(4)	1.64(4) / 1.68(4)	2.694(4) / 2.675(4)	I	-14.20 <sup>g</sup>	this work
[Ru( $\kappa^3$ -NNH-Tai)Cl{PCy <sub>2</sub> ( $\eta^2$ -C <sub>6</sub> H <sub>9</sub> )}] ( <b>6</b> )	1.43(4) / 1.14(4)	1.54(4) / 1.83(4)	2.769(4) / 2.766(4)	I	-9.01 <sup>f</sup>	this work
Ru{ $\kappa^4$ -HBSS- <sup>Ph</sup> CH <sub>2</sub> Bm}(Cl)(PCy <sub>3</sub> ) <sup>o</sup>	1.50(4)	1.66(4)	2.124(5)	I	-15.3 <sup>j</sup>	<b>S15</b>

<sup>a</sup> **Tp**, **Tp**<sup>iPr</sup>, **Tp**<sup>iPr-Br</sup>, **Tp**<sup>n</sup>, **Bp** and **Tm** represent the various abbreviations utilized for the scorpionate ligands – see references **S16** for further details, <sup>b</sup> The metal–boron distance has been provided where available, <sup>c</sup> classification of Ru••H–B interactions as defined by Spicer and Reglinski – see reference **S17**, <sup>d</sup> The chemical shift of the B–H•Ru proton has been provided where available, <sup>e</sup> in CD<sub>2</sub>Cl<sub>2</sub>, <sup>f</sup> - C<sub>6</sub>D<sub>6</sub>, <sup>g</sup> - C<sub>7</sub>D<sub>8</sub>, <sup>h</sup> - (CD<sub>3</sub>)<sub>2</sub>CO, <sup>i</sup> - CDCl<sub>3</sub>, <sup>j</sup> - (CD<sub>3</sub>)<sub>2</sub>NC(O)D, <sup>k</sup> - a second structure containing a CH<sub>2</sub>Cl<sub>2</sub> solvate, <sup>l</sup> isomer where PPh<sub>3</sub> are *trans* to the sulfur donors, <sup>m</sup> Details for this structure can be found herein, <sup>n</sup> - Two independent molecules within the same structure, <sup>o</sup> - CH<sub>2</sub>Ph<sup>h</sup>**Bm** – see scheme 2 in manuscript.

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