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# Synthesis and characterisation of a series of ruthenium scorpionate complexes with B–H · · · M agostic interactions. Crystal structure of [RuH(κ²-*N*,*BH* $Tp^{Tn}$)($PMe_3$)(cod)] ($Tp^{Tn}$ = hydrotris[3-(2-thienyl)pyrazol-1-yl]borate) † ‡

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A series of monohydrides of $Ru^{II}$ of formula RuH($Tp^R$)(cod) **1**–**3** have been synthesized from the reaction of [RuH($NH_2NMe_2$)$_3$(cod)]$BPh_4$ with the corresponding $Tp^R$ ligand {hydrotris(7-methylindazol-2-yl)borate, $Tp^{Bo,7Me}$, **1**; hydrotris[3-(2-thienyl)pyrazol-1-yl]borate, $Tp^{Tn}$, **2**; tris[3-(2,4-dimethoxyphenyl)pyrazol-1-yl]hydroborate, $Tp^{(2,4(OMe)_2Ph)}$, **3**}. In these compounds the Tp ligand is κ³ *N*,*N*′,*BH* coordinated with a B–H · · · Ru agostic interaction. Reactions of **1** and **2** with two-electron donor ligands, L = $PMe_3$, $PMe_2Ph$ and CN-*t*-Bu, led to the formation of complexes of formula RuH($Tp^R$)(L)(cod) ($Tp^R$ = $Tp^{Bo,7Me}$, L = $PMe_3$ **4**, $PMe_2Ph$ **5** or CN-*t*-Bu **6**; $Tp^R$ = $Tp^{Tn}$, L = $PMe_3$ **7**, $PMe_2Ph$ **8** or CN-*t*-Bu, **9**). In this new series the incoming ligands replace one of the coordinated pyrazole rings instead of the stated B–H · · · Ru interaction which remains and consequently the $Tp^R$ ligands are κ² *N*,*BH* coordinated. The molecular structure of **7** was determined by an X-ray diffraction study. The ruthenium atom has a distorted octahedral environment with the ligand $Tp^{Tn}$ coordinated through only one pyrazole ring and an agostic B–H group. The two hydrides are in a mutually *trans* disposition with an angle of 166°. The Ru · · · H distance is 2.07(5) and Ru–$H_{terminal}$ 1.33(5) Å. The molecular structure of the model complex [RuH(κ²-*N*,*BH*-Tp)($PH_3$)($H_2C{=}CH_2$)$_2$] has been optimised with the aid of *ab initio* calculations in order to compare the structural parameters with those of the experimentally determined structure.

## Introduction

Transition metal complexation of σ-X–H interactions has a key role in the chemical reactions of these bonds. In contrast with C–H and H–H σ bonds coordinated to metal centres, largely exemplified, scarce examples have been found for BH σ interactions and the majority of these examples are restricted to coordination of the $BH_4^-$ group.

Hydridotris(pyrazol-1-yl)borato ligands ($Tp^x$) [$Tp^x$ refers to a generic hydridotris(pyrazol-1-yl)borate ligand] have received considerable attention in coordination chemistry.[1] Tris-pyrazolylborates of ruthenium have recently been reviewed.[2] Although few examples of a κ³ hapticity consisting in the coordination of two pyrazoles accompanied by a B–H · · · M interaction have been described,[3,4] κ³ *N*,*N*′,*N*″ coordination is the strongly preferred bonding mode in mononuclear complexes. Very recently a κ² *N*,*BH* coordination has been reported in rhodium complexes.[5,6] A κ¹ *N* and κ⁰ situation have also been reported in nickel[7] and rhodium[6] chemistry respectively. In the literature there are few precedents describing a RuX(cod) (X = H or Me; cod = 1,5-cyclooctadiene) fragment coordinated either to $Tp^x$,[4,8] or to dihydridobis(pyrazol-1-yl)borate[9] ligands that exhibit B–H agostic interactions with the metallic centre. We have been interested in studying the competitive coordination ability of the pyrazole and B–H functional groups in the $Tp^R$ ligands depicted in Chart 1.[10] The three ligands may be classified as scorpionates of second generation, of which $Tp^{Tn}$

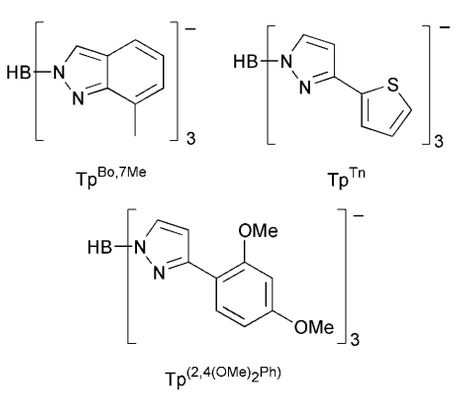



**Chart 1**

† Dedicated to Professor Elguero on the occasion of his 60th birthday as a recognition of his contributions to Chemistry and an expression of gratitude.

‡ Electronic supplementary information (ESI) available: unit cell contents of complex **7**. See http://www.rsc.org/suppdata/dt/b0/b008986i/

**Table 1** Selected spectroscopic data for complexes **1**–**9** [a]

| Complex | $\nu$(BH) | $\nu$(RuH) | $\delta$(Ru*H*)/$J$ [b] | $\delta$($^{11}B$H)/$J_{BH}$ [b] | $\delta$($^{31}$P) [b] |
|---|---|---|---|---|---|
| **1** RuHTp$^{Bo,7Me}$(cod) | 2150 | 2032 | −6.18(br s) | −0.62(d)/83.5 | — |
| **4** RuHTp$^{Bo,7Me}$($PMe_3$)(cod) | 2144 | 2022 | −9.72(dd)/$J_{HP}$ = 14.9, $J_{HH}$ = 9.2 | 3.31(d)/80.1 | −0.77 |
| **5** RuHTp$^{Bo,7Me}$($PMe_2Ph$)(cod) | 2137 | 1999 | −9.86(br s)/$J_{HH}$ = 10.0 | 3.51(d)/83.0 | 11.37 |
| **6** RuHTp$^{Bo,7Me}$(CN-*t*-Bu)(cod) | [c] | 2009 | −8.72(br d)/$J_{HH}$ = 13.4 | 3.26(d)/80.7 | — |
| **2** RuHTp$^{Tn}$(cod) | 2132 | 2001 | −6.94(br s) | −2.56(d)/86.0 | — |
| **7** RuHTp$^{Tn}$($PMe_3$)(cod) | 2118 | 1929 | −9.32(dd)/$J_{HP}$ = 10.0, $J_{HH}$ = 13.5 | 1.05(d)/81.1 | −0.48 |
| **8** RuHTp$^{Tn}$($PMe_2Ph$)(cod) | 2137 | 1953 | −9.58(dd)/$J_{HP}$ = 13.9, $J_{HH}$ = 12.1 | 0.85(d)/81.0 | 13.10 |
| **9** RuHTp$^{Tn}$(CN-*t*-Bu)(cod) | [c] | 1994<br>1955 | −8.42(br d)/$J_{HH}$ = 14.2 | 0.63(d)/77.6 | — |
| **3** RuHTp$^{(2,4(OMe)_2Ph)}$(cod) | 2012 | 1900 | −7.56(br s) | 5.38(d)/78.8 | — |

$\nu$(CN): 2140 (**6**); 2133 (**9**) cm$^{-1}$. [a] $\nu$ in cm$^{-1}$, $J$ in Hz. [b] Solvent: benzene-$d_6$. [c] Obscured by $\nu$(CN).

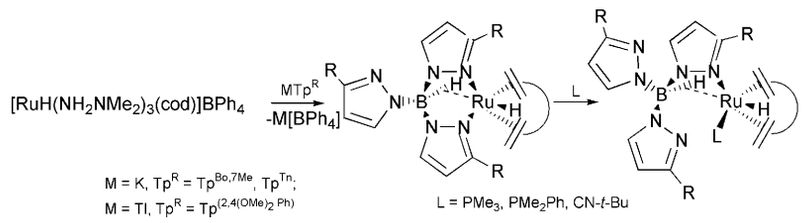



**Chart 2**

could be considered as unhindered and the other two as sterically demanding (Tp$^{Bo,7Me}$ and Tp$^{(2,4(OMe)_2Ph)}$).

## Results and discussion

Reactions of [RuH($NH_2NMe_2$)$_3$(cod)]$BPh_4$ with potassium (Tp$^{Bo,7Me}$, Tp$^{Tn}$) or thallium (Tp$^{(2,4(OMe)_2Ph)}$) salts of the corresponding scorpionates in refluxing acetone yielded complexes of general formula RuHTp$^R$(cod) (Tp$^R$ = Tp$^{Bo,7Me}$, **1**; Tp$^{Tn}$, **2**; or Tp$^{(2,4(OMe)_2Ph)}$, **3**), as represented in Chart 2.

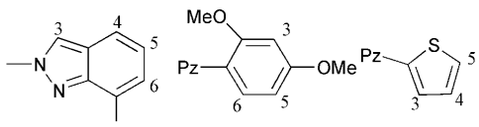
IR, $^1$H and $^{13}$C NMR information is compiled in Tables 1–4. The $^1$H NMR spectra (benzene-$d_6$ solution) of complexes **1**–**3** showed the corresponding resonances of the Tp$^R$ ligands with a 2:1 distribution of the pyrazole rings. The number of proton (6) and carbon (4) resonances of the cod ligand reflected the low local symmetry of this group ($C_s$) in the complexes. A broad singlet was observed for the hydride ligand between $\delta$ −6 and −8. This resonance became sharper when the $^{11}$B band was irradiated, suggesting the possible existence of an agostic B–H interaction resulting in a small coupling constant between this terminal hydride and the boron atom. The $\nu$(RuH) band in the IR spectra between 1900 and 2032 cm$^{-1}$ supported the existence of terminal Ru–H bonds. In the IR spectra $\nu$(BH) bands at about 2000–2150 cm$^{-1}$ were observed, lower than that of the "free" ligands (*ca.* 2420 cm$^{-1}$), indicating the existence of a B–H···Ru interaction in this series of compounds.[11] In accordance with these observations the $^{11}$B NMR spectra exhibited a broad doublet for each complex ($\delta$ −2.56 to 5.38) with a $^1J_{B\text{-}H}$ coupling constant of 78–86 Hz. The decrease in the value of this coupling constant with respect to that of the "free" ligands (*ca.* 105 Hz) is indicative of elongation of the B–H bond. In accordance with all these data we propose a κ$^3$ *N*,*N*′,*BH* coordination of the Tp$^R$ ligands for **1**–**3**. The observation of broadening (coupling) in the RuH resonance suggests a mutually *trans* arrangement of the RuH and agostic BH groups which has been confirmed by the NOE observed between the terminal hydride and only one olefinic signal of the cod. The $^1$H NMR spectra of compounds **1**–**3** were unchanged between 283 and 323 K in benzene-$d_6$, a fact indicating that the κ$^2$ *N*,*N*′,*BH* coordination is retained even at high temperature and that other coordination modes for the Tp$^R$ ligand such as κ$^2$ *N*,*N*′ or κ$^2$ *N*,*N*′,*N*″ do not participate. This fact is in contrast with other RuH(Tp$^R$)(cod) complexes[12] where the B–H agostic interaction, although present in the solid state, is not observed in solution.

The proposed B–H···Ru interaction implies a consequent pseudo-equatorial disposition of the bulky uncoordinated pz$^R$ ring in the boat conformation of the κ$^2$-Tp$^R$ ligand, a situation that can be considered as unfavourable from a steric point of view considering the high hindrance of the pyrazole substituents.[13]

In order to evaluate the possible replacement of the B–H agostic interaction by two electron-donor ligands, we envisaged the reactions of complexes **1** and **2** with $PMe_3$, $PMe_2Ph$ and CN-*t*-Bu. These reactions gave quantitative yields of compounds of formula RuHTp$^R$(L)(cod) [Tp$^R$ = Tp$^{Bo,7Me}$, L = $PMe_3$ **4**, $PMe_2Ph$ **5** or CN-*t*-Bu **6**; Tp$^R$ = Tp$^{Tn}$, L = $PMe_3$ **7**, $PMe_2Ph$ **8** or CN-*t*-Bu **9**] as depicted in Chart 2. With $PPh_3$ no reaction was observed at r.t. and intractable mixtures were obtained upon prolonged heating. Complexes **4**–**9** exhibit comparable spectroscopic characteristics in their IR and NMR spectra. The $\nu$(CN) band[14] for **6** and **9** appeared at around 2100 cm$^{-1}$. A general 1:1:1 distribution of the pyrazole resonances was observed in the $^1$H and $^{13}$C NMR spectra (Tables 2 and 4). A totally asymmetric environment was also deduced for the cod (Tables 3 and 4). The Ru–H group appeared at high field between $\delta$ −9.32 and −9.86 for the phosphine derivatives, whereas for the isocyanide compounds it was observed at $\delta$ −8.42 (**9**) or −8.72 (**6**), a reasonable deshielding if the back bonding of the isocyanide ligand is considered. The $^2J_{HP}$ coupling constants (10–14.9 Hz) were typical for a mutually *cis* arrangement of the phosphines and the Ru–H bond.

Several spectroscopic data showed unambiguously that, unexpectedly, the B–H···Ru interactions were maintained in complexes **4**–**9**. First of all, in addition to other coupling constants, the hydride resonances were coupled with the proton of the B–H groups and $J_{HH}$ coupling constants could be observed (9.2–14.2 Hz, see Table 1). The existence of this coupling constant was supported by the fact that the Ru–H resonance was unaffected when two different magnetic fields were used (300 and 200 MHz). The possibility of a chemical coupling between the Ru–H group and a cod or Tp$^R$ proton could be excluded since in the $^1$H–$^1$H COSY experiments no correlation with these groups could be observed. Although the corresponding resonance of the B–H group was not observed in the $^1$H NMR spectra for the whole set of adducts, the existence of such a

**Table 2** $^{1}$H NMR data for Tp$^{R}$ ligands in complexes **1**–**9**[a]




| Complex | Pyrazole H$^3$ | Bo, 7Me[b] Me | H$^4$ | H$^5$ | H$^6$ |
|---|---|---|---|---|---|
| **1**[c] | 8.52 (2H) | 2.78 (3H) | 7.47 d (2H, $J$ = 8.4) | 6.85 d ($J$ = 8.4) | 7.05 dt (2H, $J$ = 6.7, 1.1) |
| | 8.95 | 3.12 (6H) | 7.73 d ($J$ = 8.4) | 6.88 d (2H, $J$ = 8.4) | 7.16 dt ($J$ = 6.7, 1.1) |
| **4**[d] | 7.54, 7.60, 7.97 | 2.50, 2.81, 2.91 | 7.27 d ($J$ = 8.2) 7.41 m, 7.45 m | 6.80–7.10 m (6H) | |
| **5**[d] | 7.62, 7.74, 8.26 | 2.52, 2.85, 3.05 | 6.80–7.55 m (9H) | | |
| **6**[d] | 7.85, 8.00, 8.04 | 2.70, 2.76, 3.04 | 6.78 d ($J$ = 8.1), 6.76 d ($J$ = 6.9), 6.89 d ($J$ = 6.7), 7.00 m (3H), 7.23 d ($J$ = 8.3), 7.49 m (2H) | | |

| | Pyrazole H$^4$ | Pyrazole H$^5$ | 2-Thienyl (Tn) H$^3$ | H$^4$ | H$^5$ |
|---|---|---|---|---|---|
| **2**[c] | 6.40 d (2H, $J_{45}$ = 2.4) | 7.82 d (2H) | 7.54 dd ($J_{34}$ = 3.4) | 7.14 dd ($J_{45}$ = 5.1) | 7.42 dd ($J_{35}$ = 1.1) |
| | 6.83 d (1H, $J_{45}$ = 2.4) | 8.22 d | 7.82 dd (2H, $J_{34}$ = 3.6) | 7.22 dd (2H, $J_{45}$ = 5.1) | 7.68 dd (2H, $J_{35}$ = 1.3) |
| **7**[d] | 6.18 d ($J_{45}$ = 2.6) | 7.18 d | 7.21 m, 7.39 m (2H), 6.74–6.92 m (6H) | | |
| | 6.48 d ($J_{45}$ = 2.4) | 7.81 d | | | |
| | 6.52 d ($J_{45}$ = 2.1) | 7.27 d | | | |
| **8**[d] | 6.18 d ($J_{45}$ = 2.6) | 7.16 d | 6.73 d ($J$ = 2.3), 6.78 dd ($J$ = 5.0, 3.8), 6.81 d ($J$ = 1.9), 6.92 m (2H), 7.20 m (2H), | | |
| | 6.46 d ($J_{45}$ = 2.1) | 7.24 d | 7.37 m (2H) | | |
| | 6.47 d ($J_{45}$ = 1.9) | 7.89 d | | | |
| **9**[d] | 6.04 d ($J_{45}$ = 2.5) | 6.79 d (2H) | 6.43 d ($J$ = 2.1), 6.73 d (2H, $J$ = 2.1), 7.24 d (2H, $J$ = 2.1), 7.36 d (2H, $J$ = 2.7), 7.55 d | | |
| | 6.48 d ($J_{45}$ = 2.1) | 7.40 d | ($J$ = 2.7), 7.59 d ($J$ = 2.1) | | |
| | 6.49 d ($J_{45}$ = 2.0) | | | | |

| | Pyrazole H$^4$ | Pyrazole H$^5$ | 2,4(OMe)$_2$Ph |
|---|---|---|---|
| **3**[d] | 6.42 d (2H, $J_{45}$ = 2.3) | 8.10 d | Ph: 6.40 (d, 2H, $J_{56}$ = 2.2, H$^5$); 6.5–6.6 (m, 2H, H$^5$ + H$^6$); 6.77 (dd, 2H, $J_{36}$ = 8.5, H$^6$); |
| | 7.40 d ($J_{45}$ = 2.3) | 8.14 d (2H) | 8.40 (d, 2H, H$^3$); 8.67 (d, H$^3$) |
| | | | OMe: 3.16 (6H), 3.34 (6H), 3.36 (3H), 3.39 (3H) |

[a] See inset for atom numbering schemes; $J$ in Hz. Data are singlets if not specified, d = doublet, m = multiplet, t = triplet. Some signals were assigned by means of NOE and COSY experiments. [b] Benzo ring of indazole. [c] Solvent: acetone-$d_6$. [d] Solvent: benzene-$d_6$.

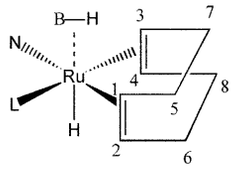
signal, obscured by the cod resonances, was shown by INDOR (internuclear double resonance) experiments. For instance, for complex **5**, when these experiments were made for each 0.1 ppm in the region from $\delta$ 0 to 4, the hydride signal was affected when the irradiation was made at $\delta$ 1.05. To the best of our knowledge this coupling constant has not previously been observed for other B–H···Ru–H arrangements and supports a mutually *trans* disposition of these functional groups in our complexes. In addition the IR $\nu$(BH) bands appeared at low wavenumbers (2118–2144 cm$^{-1}$) and the $^{11}$B NMR spectra showed broad signals with low $J_{BH}$ constants (77.6–83.0 Hz). According to these spectroscopic data, the ligands (L) have replaced one of the coordinated pz rings in **1** and **2** instead of breaking the B–H···Ru interaction. Although a stepwise pyrazole displacement of Tp$^{R}$ coordinated ligands is well established,[5,6] this behaviour, where a σ-donor ligand replaces another σ-donor centre and does not affect an apparently weaker B–H agostic interaction, is scarcely represented.[8]

In order to confirm the structural characteristics of this family of compounds, the molecular structure of **7** has been determined by an X-ray study. Selected bond distances and angles are compiled in Table 5. The corresponding ORTEP representation is shown in Fig. 1. The ruthenium atom has a distorted octahedral environment with the ligand Tp$^{Tn}$ coordinated through one pyrazole ring and an agostic B–H group. The two hydrides are in a mutually *trans* disposition with an angle of 166°. The most peculiar feature of the crystal structure is the presence of two uncoordinated pyrazolyl rings. The Ru···Hb distance of 2.07(5) Å compares well with those published for similar interactions[3,9] being slightly long for **7**. According with this relatively long distance the B1–Hb bond of **7** is the shortest of the structures compared. These data suggest that in **7** the agostic interaction is weaker than in the rest of the structures. Probably as a consequence the Ru–Ha distance of 1.33(5) Å is shorter than corresponding distances in comparable systems[3,9] because of a combination of the high electron donor character of the terminal hydride and the existence of a weakly interacting group in *trans* position. In the Tp$^{Tn}$ ligand the two non-coordinated pyrazolyl groups and the corresponding thienyl rings are contained practically in the same plane with dihedral angles of 8.0(1) and 3.7(2)°. The dihedral angle of the coordinated pyrazole and the adjacent thienyl ring is 20.2(2)°. In order to compare the structural parameters of **7** with those of an optimised model we have made theoretical calculations on the basis of this experimental structure.

### Theoretical calculations on [RuH(κ$^2$-*N*,*BH*-Tp)(PH$_3$)-(H$_2$C=CH$_2$)$_2$]

The geometry of complex **7** has been also investigated theoretically by means of *ab initio* calculations at the DFT level. Owing to the high number of atoms, and with the aim of speeding up the calculations, the analysis was undertaken using the model [RuH(κ$^2$-*N*,*BH*-Tp)(PH$_3$)(H$_2$C=CH$_2$)$_2$] in

**Table 3** Selected $^1$H NMR data for complexes **1**–**9** [a]




| | Cod | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Olefinic | | | | Alkylic | | | | |
| Complex | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | Other ligands |
| **1** [b] | | 3.43 m (2H), 3.80 m (2H) | | | | 2.58 m (4H), 2.83 m (4H) | | | — |
| **4** [c] | 3.45 m | 2.71 m | 3.33 m | 4.31 pt ($J$ = 7.5) | 2.13 m<br>3.52 m | 1.77 m<br>2.01 m | 1.05 m<br>1.42 m | 1.40 m<br>2.26 m | $PMe_3$: 0.68 d ($J$ = 8.8) |
| **5** [c] | 3.17 m | 2.64 m | 3.35 m | 4.38 pt ($J$ = 7.3) | 2.10 m<br>3.60 m | 1.95 m<br>2.23 m | 0.81 m<br>1.29 m | 1.43 m<br>1.62 m | P$Me_2$Ph: 1.06 d, 1.12 d ($J$ = 8.9) |
| **6** [c] | 3.87 pt ($J$ = 6.8) | 3.20 m | 5.42 m | 4.44 pt ($J$ = 7.5) | 1.05 m<br>2.04 m | 1.94 m<br>2.04 m | 1.35 m<br>2.33 m | 1.54 m<br>2.35 m | CN-*t*-Bu: 0.32 |
| **2** [b] | | 3.32 m (2H), 3.38 m (2H) | | | | 1.83 m (4H), 2.27 m (2H), 2.62 m (2H) | | | |
| **7** [c] | 3.42 m | 2.82 m | 3.70 m | 4.40 pt ($J$ = 8.2) | 2.24 m<br>3.42 m | 1.47 m<br>1.86 m | 1.23 m<br>1.86 m | 2.50 m<br>2.06 m | $PMe_3$: 0.88 d ($J$ = 9.0) |
| **8** [c] | 3.29 pt ($J$ = 6.5) | 2.53 m | 3.49 m | 4.43 pt ($J$ = 7.3) | 1.13 m, 1.24 m, 1.56 m, 1.81 m, 1.93 m, 2.15 m, 2.40 m, 3.44 m | | | | P$Me_2$Ph: 1.22 d, 1.26 d ($J$ = 8.8) |
| **9** [c] | 3.76 pt ($J$ = 6.8) | 3.25 m | 5.33 q ($J$ = 14.0, 7.8) | 4.49 pt ($J$ = 7.5) | 1.40 m, 1.52 m, 1.90 m (2H), 2.18 m, 2.33 m (2H), 2.58 m | | | | CN-*t*-Bu: 0.32 |
| **3** [c] | | 3.15 m (2H), 3.35 m (2H) | | | | 1.46 m (4H), 1.93 m (2H), 2.20 m (2H) | | | — |

[a] See inset for numbering scheme. Data are singlets if not specified. q = quadruplet, pt = pseudotriplet, m = multiplet. The cod signals were assigned by means of NOE and COSY experiments. [b] Solvent: acetone-$d_6$. [c] Solvent: benzene-$d_6$.

**Table 4** Main $^{13}$C-{$^1$H} NMR data for complexes **1**–**9** [a]

| | cod | | $Tp^R$ | | | | |
|---|---|---|---|---|---|---|---|
| Complex | Olefinic | Alkylic | Me | Bo, Pz | | | Other ligands |
| **1** [b] | 72.7, 74.2 | 31.8, 33.0 | 17.8 | 119.7, 120.9, 122.8, 129.2, 130.0 | | | — |
| **4** [c] | 68.8, 69.0, 89.3 d ($J$ = 14.1), 92.2 d ($J$ = 10.7) | 25.9, 30.0, 35.0, 35.9 | 17.7, 18.2, 18.7 | 118.7, 119.0, 120.6, 121.4, 121.8, 121.9, 122.1, 122.6, 124.2, 124.8, 127.2, 127.5, 125.1, 128.5, 128.6, 130.3, 149.1, 151.8, 152.6 | | | $PMe_3$: 17.5 d ($J$ = 27.7) |
| **5** [c] | 68.6, 69.5, 90.0 d ($J$ = 14.6), 93.1 d ($J$ = 10.1) | 26.0, 29.5, 35.9, 34.8 d ($J$ = 5.5) | 17.7, 18.0, 18.7 | 118.7, 119.0, 120.7, 121.5, 121.8, 121.9, 124.8, 128.9, 129.7, 128.8, 128.9, 129.7, 129.8, 130.9 | | | P$Me_2$Ph: 14.7 d ($J$ = 23.7), 16.6 d ($J$ = 28.2) |
| **6** [c] | 68.7, 69.8, 94.1, 96.2 | 26.6, 30.7, 35.3, 35.5 | 18.1, 18.2, 19.4 | 118.8, 119.4, 121.1, 121.9, 122.0, 122.1, 124.9, 125.1, 128.7, 128.8, 129.4, 131.2 | | | CN-*t*-*Bu*: 30.3 |
| | | | Pyrazole | | | | |
| | | | $C^4$ | $C^3$ | $C^5$ | 2-Thienyl | |
| **2** [b] | 72.6, 73.7 | 31.0, 32.5 | 103.9, 106.3 | 149.5<br>150.4 | 134.9<br>137.0 | 122.1, 122.2, 124.4, 125.1, 127.6, 127.7 | — |
| **7** [c] | 69.2, 67.6, 89.0 d ($J$ = 14.1), 91.2 d ($J$ = 9.6) | 30.1, 35.2, 35.6 | 102.4, 103.2, 106.7 | 148.6<br>149.3<br>153.5 | 135.9<br>134.3<br>134.1 | 123.2, 123.5, 124.0, 125.7, 126.6, 136.1, 139.1, 139.2 | P$Me_3$: 17.4 d ($J$ = 27.2) |
| **8** [c] | 70.0, 70.3, 90.2 d ($J$ = 14.2), 92.6 d ($J$ = 9.7) | 26.4, 30.1, 36.0, 35.5 d ($J$ = 6.0) | 102.8, 103.8, 107.5 | [d] | 134.4<br>136.8 (2C) | 123.7, 124.1, 124.5, 126.4, 127.4, 127.7, 128.3, 129.3, 130.3, 130.4, 134.4, 136.8 | P$Me_2$Ph: 14.8 d ($J$ = 23.5), 17.0 d ($J$ = 28.4) |
| **9** [c] | 69.1, 69.7, 93.7, 95.3 | 26.7, 31.8, 34.8, 34.9 | 103.2, 103.3, 107.1 | [d] | [d] | 123.6, 124.2, 124.3, 126.3, 127.1, 127.7, 127.9, 128.8 | CN-*t*-*Bu*: 30.6 |
| | | | | | | 2,4(OMe)$_2$Ph | |
| **3** [c] | 71.2, 71.7 | 30.76, 32.63 | 98.9, 99.5 | 150.5<br>151.6 | 132.7<br>133.5 | OMe: 55.1, 55.0, 54.9, 54.8<br>CH: 104.3, 105.2, 107.2, 107.8<br>$C_{quat}$: 158.1, 158.5, 158.9, 160.8, 160.9, 161.6 | — |

[a] Singlets if not specified. Coupled resonances are always doublets by $J_{HP}$ coupling. Bo = Benzo ring of indazole. [b] Solvent : acetone-$d_6$. [c] Solvent : benzene-$d_6$. [d] Not distinguished.

which the cod ligand was replaced by two ethylene ligands and the $PMe_3$ ligand by $PH_3$.

The final optimised geometry of the model complex is depicted in Fig. 2, while an overlay of the optimised structure and the experimental one is shown in Fig. 3. Selected calculated structural parameters are reported in Table 5. For the sake of

**Table 5** Selected bond distances (Å) and bond angles (°) calculated for the model complex [RuH(κ²-*N*,*BH*-Tp)($PH_3$)($H_2C{=}CH_2$)$_2$] and experimental data for **7**[a]

| | calc. | exptl. | | calc. | exptl. |
|---|---|---|---|---|---|
| Ru(1)–Ha | 1.393 | 1.33(5) | N(21)–Ru(1)–C(2) | 158.54 | 157.24(1) |
| Ru(1)–Hb | 1.969 | 2.07(5) | N(21)–Ru(1)–C(1) | 164.40 | 164.15(1) |
| Ru(1)–N(21) | 2.097 | 2.119(4) | C(2)–Ru(1)–C(1) | 36.04 | 36.9(2) |
| Ru(1)–C(1) | 2.240 | 2.204(5) | N(21)–Ru(1)–C(6) | 87.09 | 89.33(17) |
| Ru(1)–C(2) | 2.240 | 2.184(5) | C(2)–Ru(1)–C(6) | 102.72 | 94.49(19) |
| Ru(1)–C(5) | 2.249 | 2.278(5) | C(1)–Ru(1)–C(6) | 86.81 | 79.64(19) |
| Ru(1)–C(6) | 2.274 | 2.237(5) | N(21)–Ru(1)–C(5) | 89.72 | 90.78(16) |
| Ru(1)–P(1) | 2.360 | 2.3276(1) | C(2)–Ru(1)–C(5) | 87.39 | 79.75(19) |
| B(1)–Hb | 1.167 | 1.14(5) | C(1)–Ru(1)–C(5) | 93.15 | 86.79(18) |
| B(1)–N(22) | 1.554 | 1.519(7) | C(6)–Ru(1)–C(5) | 36.20 | 35.41(18) |
| B(1)–N(31) | 1.531 | 1.515(7) | N(21)–Ru(1)–P(1) | 89.68 | 90.84(11) |
| B(1)–N(41) | 1.532 | 1.522(7) | C(2)–Ru(1)–P(1) | 89.49 | 95.76(14) |
| N(21)–N(22) | 1.383 | 1.383(5) | C(1)–Ru(1)–P(1) | 89.96 | 93.83(14) |
| N(31)–N(32) | 1.395 | 1.369(5) | C(6)–Ru(1)–P(1) | 153.88 | 152.82(1) |
| N(41)–N(42) | 1.397 | 1.360(5) | C(5)–Ru(1)–P(1) | 169.89 | 171.64(1) |
| N(21)–C(23) | 1.325 | 1.345(6) | Ha–Ru(1)–Hb | 167.28 | 166 |
| N(22)–C(21) | 1.369 | 1.347(6) | Ru(1)–Hb–B(1) | 125.90 | 123 |
| N(31)–C(31) | 1.380 | 1.350(6) | C(2)–C(1)–Ru(1) | 71.95 | 70.8(3) |
| N(32)–C(33) | 1.355 | 1.329(6) | C(1)–C(2)–Ru(1) | 72.00 | 72.3(3) |
| N(41)–C(41) | 1.378 | 1.348(7) | C(6)–C(5)–Ru(1) | 70.92 | 70.7(3) |
| N(42)–C(43) | 1.356 | 1.354(6) | C(5)–C(6)–Ru(1) | 72.88 | 73.9(3) |

[a] Numbering scheme as in Fig. 1.

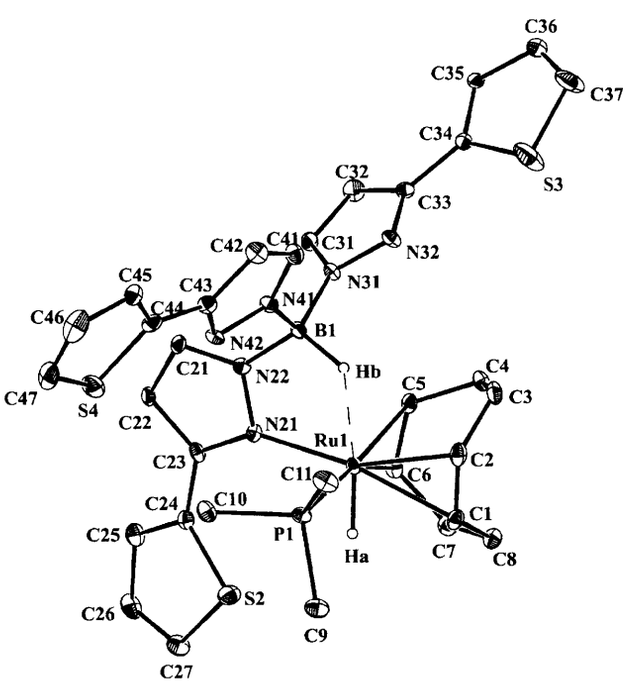



**Fig. 1** An ORTEP[15] drawing of complex **7**. Thermal ellipsoids are drawn at the 30% probability level.

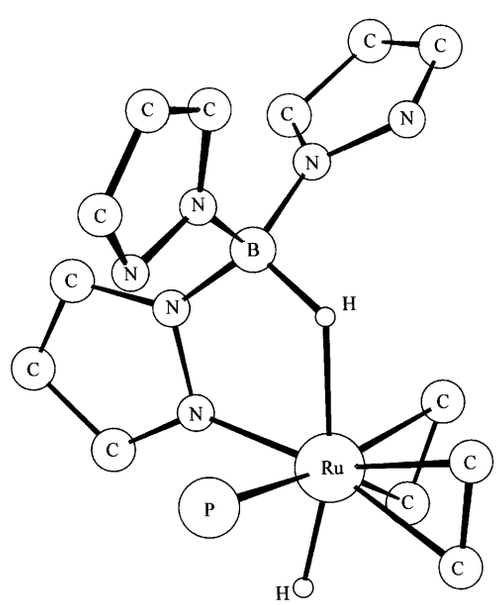



**Fig. 2** Optimised geometry of the model complex [RuH(κ²-*N*,*BH*-Tp)($PH_3$)($H_2C{=}CH_2$)$_2$] (hydrogens not shown).

comparison, the experimental data are also included in the Table. In general, and taking into account that the model is simplified and surely less hindered, one can observe quite a satisfactory agreement between the model and the experimental values of the geometrical parameters. Bond distances agree within 0.06 Å, while the largest deviation of bond angles appears to be about 8°. The more pronounced discrepancies appeared as expected in bond angles describing the relative position of the two ethylene ligands in the calculated model compared to the two C=C bonds of the cod ligand in the actual complex.

Examination of the calculated Ru–H overlap population reveals the weak coordination of B(μ-H)Ru type. Thus the Ru–Hb overlap population is only 0.140 compared to 0.288 for the normal ruthenium hydride bond Ru–Ha. Finally both the long Ru–B distance (calc. 2.900 Å, exptl. 2.849 Å) and the negative Ru–B overlap population calculated exclude any Ru–B interaction.

## Conclusion

We have described a series of $Tp^R$ monohydride derivatives of ruthenium(II) where the $Tp^R$ ligand is κ³ *N*,*N*,*BH* or κ² *N*,*BH* coordinated. The agostic B–H···Ru interaction that exists both in the solid state and in solution is, in all these compounds, *trans* to the hydride ligand coordinated to the metallic centre. This agostic bond is maintained after reactions with phosphine and isocyanide ligands in which one of the coordinated pyrazole rings is replaced. This fact reflects the remarkable stability of this type of coordination of the $Tp^R$ ligand when compared with other possibilities.

**Table 6** Crystal data and structure refinement for complex **7**

| | |
|---|---|
| Empirical formula | $C_{32}H_{38}BN_6PRuS_3$ |
| Formula weight | 745.71 |
| $T$/K | 180 |
| $\lambda$/Å | 0.71069 |
| Crystal system, space group | Triclinic, $P\bar{1}$ |
| $a$/Å | 10.682(5) |
| $b$/Å | 11.427(5) |
| $c$/Å | 14.375(5) |
| $\alpha$/° | 97.020(5) |
| $\beta$/° | 105.600(5) |
| $\gamma$/° | 94.070(5) |
| $V$/Å$^3$ | 1667.4(12) |
| $Z$ | 2 |
| $\mu$/cm$^{-1}$ | 7.39 |
| Reflections collected/unique | 8005/8005 [$R$(int) = 0.0000] |
| Data/restraints/parameters | 8005/0/423 |
| Final $R1$, $wR2$ indices [$I > 2\sigma(I)$] | 0.0487, 0.1069 |
| (all data) | 0.0883, 0.1503 |

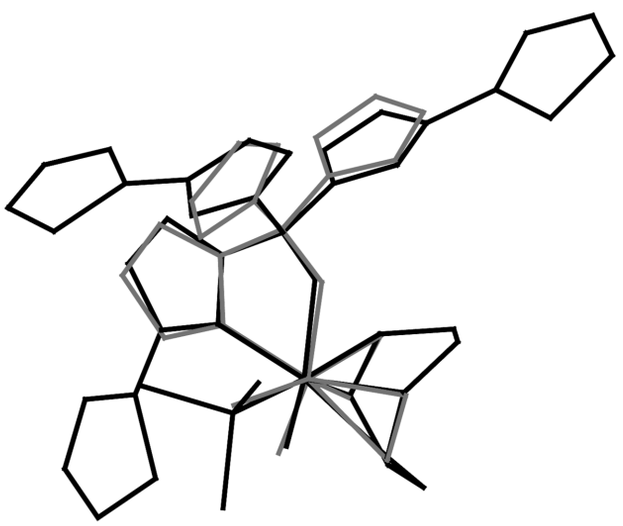


**Fig. 3** Overlay of the optimised structure of the model complex [RuH(κ$^2$-*N*,*BH*-Tp)($PH_3$)($H_2C{=}CH_2$)$_2$] (grey) and the structure of the experimental complex **7** (black) (hydrogens not shown).

## Experimental

### General comments

All manipulations were carried out under an atmosphere of dry oxygen-free nitrogen using standard Schlenk techniques. Solvents were distilled from appropriate drying agents and degassed before use. Elemental analyses were performed with a Perkin-Elmer 2400 microanalyser. IR spectra were recorded in Nujol mulls with a Perkin-Elmer PE 883 IR spectrometer. $^1$H, $^{13}$C, $^{11}$B and $^{31}$P NMR spectra were obtained on a Varian UNITY 300 or a Varian GEMINY 200 spectrometer. Chemical shifts ($\delta$) are given relative to TMS ($^1$H, $^{13}$C), $BF_3{\cdot}OEt_2$ ($^{11}$B) or 85% $H_3PO_4$ ($^{31}$P). COSY spectra: standard pulse sequence with an acquisition time of 0.214 s, pulse width 10 ms, relaxation delay 1 s, number of scans 16, number of increments 512. The NOE difference spectra were recorded with the following acquisition parameters: spectral width 5000 Hz, acquisition time 3.27 s, pulse width 18 μs, relaxation delay 4 s, irradiation power 5–10 dB, number of scans 240. The INDOR experiments in a $\delta$ 0 to 4 window were recorded under standard conditions. The starting material [RuH($NH_2NMe_2$)$_3$(cod)]$BPh_4$ [16] and $Tp^R$ ligands [17] were prepared according to literature methods. $PMe_3$, $PMe_2Ph$, $PPh_3$ and CN-*t*-Bu were used as purchased from Aldrich.

### X-Ray crystallography

A yellow crystal was mounted in a glass capillary. Intensity data were collected on a NONIUS-MACH3 diffractometer equipped with graphite monochromated Mo-Kα radiation using an $\omega$–$2\theta$ scan technique to a maximum value of 56°. Data were corrected in the usual fashion for Lorentz and polarisation effects; an empirical absorption correction was not necessary. The structure was solved using direct methods (SIR 92).[18] Refinement on $F^2$ was carried out by full-matrix least-squares techniques (SHELXL 97).[19] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in calculated positions except for Ha and Hb which were located in the Fourier-difference map and refined isotropically. See Table 6 for crystal data and structure refinement details.

CCDC reference number 153203.

See http://www.rsc.org/suppdata/dt/b0/b008986i/ for crystallographic data in CIF or other electronic format.

### Computational details

The electronic structure and geometry of a model of complex **7** was computed within density functional theory using gradient corrected functionals, at the Becke 3LYP computational level.[20,21] The effective core potential (ECP) approximation of Hay and Wadt [22–24] was used. For the Ru atom, the outermost core orbitals 4s and 4p were not replaced by the ECP but were treated explicitly. The basis set used was of valence double-ζ quality.[25] Full geometry optimisation was carried out with no symmetry constraints. All of the calculations were performed using the GAUSSIAN 98 package.[26]

### Synthesis of compounds

**RuHTp$^{Bo,7Me}$(cod) 1.** To a solution of [RuH($NH_2NMe_2$)$_3$-(cod)]$BPh_4$ (200 mg, 0.282 mmol) in 20 mL of acetone $KTp^{Bo,7Me}$ (125.2 mg, 0.282 mmol) was added. The yellow suspension was refluxed and stirred for 2.5 h. The resulting yellow solid obtained after evaporation to dryness was extracted with toluene (2 × 15 mL), obtaining a yellow solution which was evaporated under vacuum to obtain a yellow powder of the product. The solid was crystallised by slow evaporation of an acetone solution and yellow-orange crystals were obtained. Yield 81%. Calc. for $C_{32}H_{35}BN_6Ru$: C, 62.32; H, 5.73; N, 13.63. Found: C, 61.91; H, 5.61; N, 13.23%.

**RuHTp$^{Tn}$(cod) 2.** This compound was prepared in a way similar to that for **1** using [RuH($NH_2NMe_2$)$_3$(cod)]$BPh_4$ (200 mg, 0.282 mmol) and $KTp^{Tn}$ (140.4 mg, 0.282 mmol). Yield: 94%. Calc. for $C_{29}H_{29}BN_6RuS_3$: C, 51.86; H, 4.51; N, 12.52. Found: C, 52.27; H, 4.44; N, 12.64%.

**RuHTp$^{(2,4(OMe)_2Ph)}$(cod) 3.** This compound was prepared in a way similar to that for **1** using [RuH($NH_2NMe_2$)$_3$(cod)]$BPh_4$ (200 mg, 0.282 mmol) and $KTp^{(2,4(OMe)_2Ph)}$ (233 mg, 0.282 mmol). Yield: 72%. It was not possible to get crystals and good elemental analysis of this product due to its high solubility in all the solvents assayed.

**RuHTp$^{Bo,7Me}$($PMe_3$)(cod) 4.** To a solution of complex **1** (100 mg, 0.162 mmol) in 10 mL of toluene were added 1.5 equivalents of $PMe_3$ (244 μL, 1 M solution in toluene). The yellow solution was stirred at room temperature for 16 h. A brown solid was obtained after evaporation to dryness, crystallised from THF–pentane and colourless crystals were obtained. Yield: 74%. Calc. for $C_{35}H_{44}BN_6PRu$: C, 60.67; H, 6.41; N, 12.15. Found: C, 60.13; H, 5.92; N, 11.89%.

**RuHTp$^{Bo,7Me}$($PMe_2Ph$)(cod) 5.** The reaction was performed in an NMR tube. To a solution of complex **1** (19.1 mg, 0.031 mmol) in 0.5 mL of benzene-$d_6$ was added one equivalent of $PMe_2Ph$ (4.4 μL, 0.031 mmol). The benzene-$d_6$ solution was poured into a tube (1 × 5 cm) which was placed into a Schlenk vessel containing pentane (20 mL) and pale yellow crystals were obtained. Yield: 78%. Calc. for $C_{40}H_{46}BN_6PRu$: C, 63.64; H, 6.15; N, 11.14. Found: C, 63.35; H, 5.89; N, 10.89%.

**RuHTp$^{Bo,7Me}$(CN-*t*-Bu)(cod) 6.** This compound was prepared in a way similar to that for **5**, using **1** (16.3 mg, 0.0265 mmol) and CN-*t*-Bu (3.0 μL, 0.0265 mmol). Yield: 79%. It was not possible to get crystals and good elemental analysis of this product due to its high solubility in all the solvents assayed.

**RuHTp$^{Tn}$(PMe$_3$)(cod) 7.** This compound was prepared in a way similar to that for **5**, using **2** (100 mg, 0.149 mmol) and 1.5 equivalents of $PMe_3$ (224 μL, 1 M solution in toluene). The brown solution was stirred at room temperature for 1 h. A brown solid was obtained after evaporation to dryness, crystallised from acetone–pentane and colourless crystals suitable for an X-ray study were obtained. Yield: 67%. Calc. for $C_{32}H_{38}BN_6PRuS_3$: C, 51.47; H, 5.13; N, 11.26. Found: C, 51.02; H, 4.97; N, 10.87%.

**RuHTp$^{Tn}$(PMe$_2$Ph)(cod) 8.** This compound was prepared in a similar way to that for **5**, using **2** (17.4 mg, 0.026 mmol) and $PMe_2Ph$ (3.7 μL, 0.026 mmol). Yield: 75%. Calc. for $C_{37}H_{40}BN_6PRuS_3$: C, 54.94; H, 4.99; N, 10.40. Found: C, 54.52; H, 4.89; N, 9.97%.

**RuHTp$^{Tn}$(CN-*t*-Bu)(cod) 9.** The compound was prepared in a similar way to that for **5**, using **2** (19.5 mg, 0.029 mmol) and CN-*t*-Bu (3.3 μL, 0.029 mmol). Yield: 74%. It was not possible to get crystals and good elemental analysis of this product due to its high solubility in all the solvents assayed.

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