Synthesis and Nuclear Magnetic Resonance Studies of Halogeno and Hydrido Tris(pyrazol-1-yl)borato Ruthenium(II) Complexes

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The reaction of polymeric $[\{RuCl_2(cod)\}_n]$ (cod = cycloocta-1,5-diene) with potassium tris(pyrazol-1-yl)borate, $KHB(pz)_3$, in refluxing tetrahydrofuran leads to $[Ru\{HB(pz)_3\}Cl(cod)]$ **1**, and the pyrazole-containing $[RuCl_2(Hpz)_2(cod)]$ **2** which arises from thermolysis of pyrazolylborate. Reaction of $[RuCl_2(tht)_4]$ (tht = tetrahydrothiophene) with the same salt at room temperature affords a mixture of $[Ru\{HB(pz)_3\}Cl(tht)_2]$ **3** and $[Ru\{HB(pz)_3\}_2(tht)_2]$ **4**, which have been efficiently isolated. The product ratio of this process greatly depends on the reaction conditions. The compound $[Ru\{HB(pz)_3\}_2]$ **5** forms by transformation of **4** in chloroform solution, a reaction which is slow but complete in one week. The compound $[RuClH(bpzm)(cod)]$ [bpzm = bis(pyrazol-1-yl)methane] reacts with $KHB(pz)_3$ to give $[Ru\{HB(pz)_3\}H(cod)]$ as the only ruthenium product. Nuclear Overhauser enhancement (NOE) measurements have been used as a valuable method for the assignment of the H^3 and H^5 resonances of the pyrazolyl groups. Heteronuclear $^1H-^{13}C$ correlation (COSY) experiments have been recorded to determine the assignment of the C^3 and C^5 carbons of the pz groups.

Poly(pyrazol-1-yl)borates are important ligands in co-ordination chemistry and in recent years a significant number of complexes with most metals of the Periodic Table have been prepared.[1] This widespread applicability is partly attributable to the similarity in co-ordination and electronic properties of tridentate $RB(pz)_3^-$ (pz = pyrazol-1-yl) with the cyclopentadienyl ligand. Several classes of poly(pyrazol-1-yl)borato ruthenium complexes have been prepared,[2–9] for instance, the ruthenocene analogue $[Ru\{HB(pz)_3\}_2]$ and related complexes,[8] mixed-sandwich ruthenium–cyclopentadienyl–tris(pyrazol-1-yl)borato complexes[4a,c] as well as species containing a single $HB(pz)_3^-$ moiety have been described, although some of these have not been completely characterized. Consequent to our investigation into ruthenium complexes with N-donor ligands, we reported[10] the preparation of several ruthenium(II) complexes with isosteric poly(pyrazol-1-yl)methane ligands. We subsequently became interested in the behaviour of some of these products and the more conventional precursors $[\{RuCl_2(cod)\}_n]$ (cod = cycloocta-1,5-diene) and $[RuCl_2(tht)_4]$ (tht = tetrahydrothiophene) towards $HB(pz)_3^-$, with a view to synthesizing tris(pyrazol-1-yl)borato ruthenium derivatives. This paper focuses on the preparation and structural details of some chloro- and hydrido-tris(pyrazol-1-yl)borato ruthenium complexes.

Results and Discussion

Synthetic and Spectroscopic Studies.—Reaction of the polymeric derivative $[\{RuCl_2(cod)\}_n]$ with 1 equivalent of $KHB(pz)_3$ in refluxing tetrahydrofuran (thf) [equation (1)]

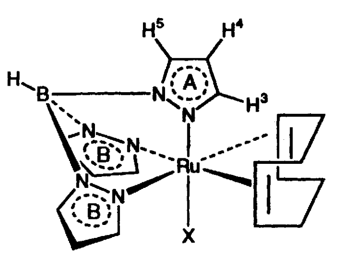
$$\tfrac{1}{n}[\{RuCl_2(cod)\}_n] + KHB(pz)_3 \xrightarrow[-KCl]{\text{thf, heat}} \underset{\mathbf{1}}{[Ru\{HB(pz)_3\}Cl(cod)]} + \underset{\mathbf{2}}{[RuCl_2(cod)(Hpz)]} \qquad (1)$$

gives compounds **1** and **2** in a 2 : 1 molar ratio as measured from ^1H NMR integration. Both compounds can be separated as orange materials by crystallization and have been structurally identified by ^1H and ^{13}C NMR spectroscopy. Compound **1** has been previously synthesized *via* another route, but was not fully characterized.[4b]

When this reaction is carried out with an excess of $KHB(pz)_3$ (> 1.5 equivalents), **1** is obtained as the only product. We propose that **2** is formed from a pyrolytic degradation of an unidentified pyrazole-containing polymeric material, generated and observed at the initial stages of the reaction.

The direct formation of **2**, by reaction of the starting material with pyrazole, can be ruled out since pyrazole was not observed when a solution of pure $KHB(pz)_3$ in thf was heated at reflux, and because the reaction of $[\{RuCl_2(cod)\}_n]$ with 2 equivalents of pyrazole gave only very low yields of **2**. Unfortunately, the proposed polymeric product could not be isolated from the insoluble starting materials in order to demonstrate our proposal. Bond breaking of pyrazolylborate ligands to give pyrazole has been observed previously in ruthenium chemistry.[11]

The IR spectra of **1** and **2** show the different absorption characteristics of their respective pyrazole fragments. Complex **1** shows the ν(B–H) vibration at 2502 cm^{-1} whereas **2** does not show such a band but instead a typical ν(N–H) vibration at 3254 cm^{-1}. The ^1H and ^{13}C NMR spectra of **1** exhibited two distinct sets of pyrazol-1-yl resonances indicating the existence of two types of pyrazol-1-yl rings in a 2 : 1 ratio (see Experimental section). The H^3 and H^5 proton resonances appear as doublets due to coupling with H^4, while the H^4 signal is found as a pseudo-triplet due to the similar $^3J(H^4H^5)$ and $^3J(H^3H^4)$ values. This behaviour is in accordance with the coupling constant criterion for pyrazoles where $^3J(H^4H^5) > {}^3J(H^3H^4)$.[12] The poorly defined resonance of the BH group appears in the ^1H NMR spectrum as a broad signal in the region δ 1–7 as a consequence of the electric quadrupole moments of the boron isotopes. This behaviour is seen for all the isolated complexes (see below). Although irradiation of the BH_x moiety in nuclear Overhauser enhancement (NOE) experiments[13] was not possible in these poly(pyrazol-1-yl)borato complexes due to the very broad signal, enhancement



X
1 Cl
6 H

Fig. 1 Proposed structures for complexes 1 and 6

was observed in the H^3 resonance upon irradiation of the cod signals, which served in assigning the H^5 and H^3 resonances. Selective irradiation of certain ancillary ligand signals in order to observe the enhancement of some pyrazolic protons and so assign the H^3 and H^5 signals in poly(pyrazol-1-yl)borato metal derivatives has previously been successfully employed.[14] The assigment for the ^{13}C NMR resonances was made based on $^1H-^{13}C$ heteronuclear correlation spectroscopy (COSY) which establishes that $^1J(CH^5) > {}^1J(CH^3)$, in accordance with the observation for free pyrazoles.[14a,15]

These results indicate a non-fluxional $HB(pz)_3$ ligand co-ordinated in an octahedral environment for 1 (Fig. 1).

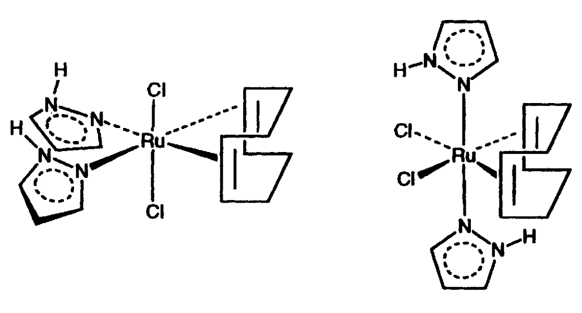
In addition, the ^1H NMR spectrum shows the signals of the cod ligand to be compatible with its expected C_s symmetry within the molecule:[16] two broad signals for the olefinic protons and four signals for the aliphatic protons are observed, while the ^{13}C NMR spectrum shows two resonances for the olefinic and two for the aliphatic carbons (see Experimental section).

The ^1H and ^{13}C NMR spectra of 2 show broad signals corresponding to only one set of pyrazole resonances (see Experimental section), implying the equivalence of the two pyrazole ligands. The H^3 and H^5 signals were inferred from NOE experiments by observing an enhancement of the signal corresponding to H^3, on irradiating the olefinic signal of the cod ligand. In the ^{13}C NMR spectrum the assignment for the C^5 and C^3 signals was based on a $^1H-^{13}C$ heteronuclear COSY experiment. In this case, $^1J(CH^3) > {}^1J(CH^5)$, which is contrary to previous observations. The ^1H and ^{13}C NMR spectra also show the resonances of a cod group with C_{2v} symmetry (see Experimental section). Two different *trans* octahedral structures (**a** and **b**) can be proposed on the basis of these results (Fig. 2).

The reaction of $[RuCl_2(tht)_4]$ with $KHB(pz)_3$ in dichloromethane affords a mixture of ruthenium complexes according to equation (2).

$$[RuCl_2(tht)_4] + KHB(pz)_3 \longrightarrow \underset{3}{[Ru\{HB(pz)_3\}Cl(tht)_2]} + \underset{4}{[Ru\{HB(pz)_3\}_2(tht)_2]} \quad (2)$$

The ratio of these two products is very dependent on the reaction conditions. When the process is carried out with 1 equivalent of $KHB(pz)_3$ in dichloromethane at room temperature, 3 and 4 are obtained in similar amounts, together with the ruthenium starting material. However, if 2 equivalents of $KHB(pz)_3$ are used under similar reaction conditions, 3 and 4 are obtained in a 3 : 1 ratio. Compound 4 slowly transforms into $[Ru\{HB(pz)_3\}_2]$ 5 in $CDCl_3$, this taking one week for completion as monitored by ^1H NMR spectroscopy. Although synthetic procedures for different cyclopentadienyl ruthenocene derivatives are well known, analogous complexes with the $HB(pz)_3^-$ ligand have only recently been prepared[8] and synthetic and spectroscopic data published for $[Ru\{HB(pz)_3\}_2]$ 5 are scarce. The complex is a white solid, quite soluble in non-polar solvents such as hexane and very soluble in diethyl ether. It crystallizes from polar solvents such as chloroform retaining some molecules of solvent. The composition of 5 was confirmed by FAB mass spectrometry, the mass spectrum showing the molecular ion as the major peak (*m*/*z* 528) and one other minor peak corresponding to the loss of one pyrazolyl fragment (*m*/*z* 460).



a b

Fig. 2 Proposed structure for complex 2

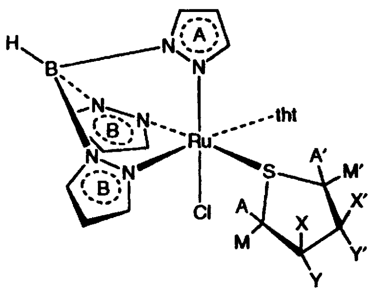


Fig. 3 Proposed structure for complex 3

In spite of tht being considered as a good leaving group, examples exist where tht ligands remain co-ordinated to ruthenium centres in the presence of similar nitrogen donor ligands. Thus, $[Ru(\eta^5\text{-}C_5Me_5)Cl_2(tht)_2]PF_6$[17] does not react with pyrazolylmethane derivatives. In contrast, cyclopentadienyl is capable of totally substituting the ligands in $[RuCl_2(tht)_4]$ to afford ruthenocene.[18] Differing behaviour of $HB(pz)_3^-$ and $C_5H_5^-$ has also been recently observed in nickel chemistry.[19]

The three complexes 3, 4 and 5 can be isolated separately owing to their different solubilities (see Experimental section).

The IR spectra of 3 and 4 show the expected ν(B–H) vibrations at 2488 and 2434 cm^{-1} respectively.

The ^1H and ^{13}C NMR spectra of 3 indicate that one of the pyrazolyl rings differs from the other two (see Experimental section); this is in accord with non-rotation of the $HB(pz)_3^-$ ligand around the Ru–B–H axis, and a static octahedral structure is proposed (Fig. 3).

The assignment of the H^3 and H^5 proton signals was again facilitated by NOE experiments with H^3 of the pyrazolyl undergoing a NOE effect from the protons of the tht ligand. In the ^{13}C NMR the C^3 and C^5 resonances were assigned by $^1H-^{13}C$ heteronuclear COSY experiments. Finally, the methylenes of the tht group show three broad signals in the ^1H NMR spectrum in agreement with the non-equivalence of these protons in a C_s environment, appearing as a non-resolved AA'MM'XX'YY' system.

The low-field ^1H NMR spectrum of 4 shows nine signals in the aromatic region, six doublets of doublets $[^3J(H^3H^4), {}^3J(H^4H^5), {}^3J(H^3H^5)]$, and three pseudo-triplets which correspond to three different types of pyrazole rings, indicating that each $HB(pz)_3^-$ group acts as a bidentate ligand with two pyrazole groups co-ordinated to the ruthenium centre and the third remaining unco-ordinated (see Experimental section).

Assuming an octahedral geometry, the observed NMR data suggest the structure depicted in Fig. 4.

Proton homonuclear COSY experiments, complemented with conventional double-resonance techniques were used to assign the signals of each ring. The H^3 proton signals of the two co-ordinated pyrazole rings were confirmed by NOE experiments, since the selective irradiation of the tht α resonances enhanced the H^3 signals of those pyrazole rings.

In the ^{13}C NMR spectrum nine resonances are found for the $HB(pz)_3^-$ ligands and two for the tht groups. In order unambiguously to assign the signals in the pyrazole region, a heteronuclear COSY experiment was performed (see Experimental section).

The ^1H and ^{13}C NMR spectra of **5** are very simple because they show only three signals corresponding to the pyrazole rings (see Experimental section). The lack of ancillary ligands precluded the use of NOE experiments in the assignment of the H^3 resonances. However, a ^1H–^{13}C heteronuclear COSY experiment showed the consistency of the coupling constant method and so the signal with the larger constant in the ^1H NMR spectrum correlated with that of the larger ^1J value in the ^{13}C NMR spectrum (C^5) and so this criterion was employed for the assignment.

Finally, *trans*-[RuHCl(bpzm)(cod)] [bpzm = bis(pyrazol-1-yl)methane] reacts with 1 equivalent of $KHB(pz)_3$ in acetone at room temperature according to equation (3). We have already reported this synthesis in a preliminary communication.[20] In contrast, the analogous *trans*-[$RuCl_2$(bpzm)(cod)], under similar conditions, is unreactive. The *trans* effect of the hydride group probably promotes the chloride displacement. We have previously observed the facile substitution of the bis(pyrazol-1-yl)methane group in similar ruthenium(II) derivatives, by N- and P-donor ligands.[10]

$$[\mathrm{RuHCl(bzpm)(cod)}] + \mathrm{KHB(pz)_3} \longrightarrow \underset{\mathbf{6}}{[\mathrm{Ru\{HB(pz)_3\}H(cod)}]} + \mathrm{bpzm} \quad (3)$$

Compound **6**, which is soluble in toluene, diethyl ether and polar solvents, is obtained as a yellow product, after subliming the unco-ordinated bpzm from the crude mixture. Compound **6** and related complexes constitute excellent precursors to polyhydrido ruthenium products. For instance, the reaction of complexes containing substituted tris(pyrazol-yl)borate with H_2 afforded stable hydrido bis(dihydrogen) derivatives.[20] Work aimed at studying the behaviour of these complexes is in progress.[21]

The IR spectrum of **6** shows the ν(Ru–H) and ν(B–H) vibrations at 2015 and 2456 cm^{-1} respectively. The ^1H and ^{13}C NMR spectra show the expected resonances for two distinct sets of pyrazole rings. In addition the signals of the hydride ligand (^1H NMR) and those corresponding to a cod ligand, bonded in a C_s symmetry mode are present (see Experimental section). The data are in agreement with an octahedral environment as depicted in Fig. 1. Once again the enhancement of the signals corresponding to the H^3 pyrazole protons, on irradiation of the olefinic hydrogens, allowed the assignment of those signals in the ^1H NMR spectrum. A ^1H–^{13}C heteronuclear COSY experiment permitted the assignment of the C^3 and C^5 carbons. The results are in accordance with the aforementioned coupling constant criterion, $^1J(HC^5) > {}^1J(HC^3)$.

Conclusion

In this paper we have reported some new ways to prepare tris(pyrazol-1-yl)borato ruthenium derivatives starting from typical complexes such as [{$RuCl_2$(cod)}$_n$] or some other less employed complexes such as [$RuCl_2(tht)_4$] and [RuClH(bpzm)(cod)]. The complexes can be obtained in good yields in larger scale reaction work and some of these may be interesting potential starting materials in tris(pyrazol-yl)borato ruthenium chemistry, especially complex [Ru{$HB(pz)_3$}H(cod)] **6** the significance of which in the synthesis of polydihydrogen derivatives of ruthenium has been demonstrated.[20,21]

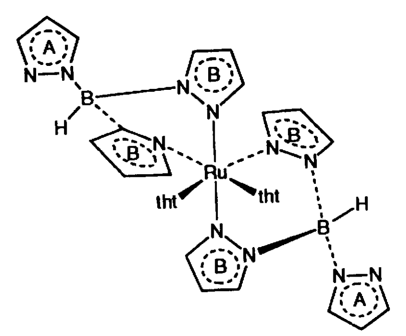


Fig. 4 Proposed structure for complex **4**

Experimental

All reactions were performed using standard Schlenk-tube techniques in an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use. Potassium tris(pyrazol-1-yl)borate[22] and the ruthenium compounds [{$RuCl_2$(cod)}$_n$][23] and [RuHCl(cod)(bpzm)][10] were prepared as previously reported. The compound [$RuCl_2(tht)_4$] was prepared by a different method to the one previously reported in the literature.[24] Microanalyses were performed with a Perkin-Elmer 2400 CHN instrument. Infrared spectra were obtained in the region 4000–200 cm^{-1} using a Perkin-Elmer 883 spectrophotometer. Proton (300 MHz) and ^{13}C (75 MHz) NMR and NOE difference spectra were recorded at room temperature (19 °C) on a Unity Varian FT300 spectrometer and were referenced to the deuteriated solvents. NOE difference spectra were recorded with the following acquisition parameters: spectral width 5000 Hz, acquisition time 3.27 s, pulse width (90°), relaxation delay 4 s, irradiation power 5–10 L, number of scans 120. Two-dimensional NMR spectra were acquired using standard Varian FT sofware, and processed using an IPC-Sun computer. FAB mass spectrometry was carried out using a VG Autospec instrument (3-nitrobenzyl alcohol matrix).

Preparations.—[Ru{$HB(pz)_3$}Cl(cod)] **1**. The salt $KHB(pz)_3$ (810 mg, 3.21 mmol) was added to a thf (80 cm^3) suspension of [{$RuCl_2$(cod)}$_n$] (300 mg, 1.07 mmol). The mixture was heated at reflux for 5 h and the resulting solution was filtered and evaporated to dryness. The residue was extracted with toluene (50 cm^3). Compound **1** was obtained as a microcrystalline orange solid from dichloromethane–hexane. Yield 426 mg (87%) (Found: C, 44.60; H, 4.85; N, 17.90. $C_{17}H_{22}BClN_6Ru$ requires C, 44.60; H, 4.80; N, 18.35%). IR (KBr, cm^{-1}): 2502 ν(B–H). NMR($CDCl_3$, reference $SiMe_4$): ^1H, δ 8.11 [d, 1 H, $^3J(H^3H^4) = 2.1$, $H_A{}^3$], 7.77 [d, 1 H, $^3J(H^4H^5) = 2.4$, $H_A{}^5$], 7.63 [d, 2 H, $^3J(H^4H^5) = 2.4$, $H_B{}^5$], 7.55 [d, 2 H, $^3J(H^3H^4) = 2.1$, $H_B{}^3$], 6.30 (pseudo t, 1 H, $H_A{}^4$), 6.19 (pseudo t, 2 H, $H_B{}^4$), 4.89 (m, 2 H, olefinic H of cod), 4.01 (m, 2 H, olefinic H of cod), 2.92 (m, 2 H, H^{exo} of cod), 2.64 (m, 2 H, H^{exo} of cod), 2.40 (d, 2 H, $J_{gem} = 8.6$, H^{endo} of cod) and 2.23 (d, 2 H, $J_{gem} = 7.8$ Hz, H^{endo} of cod); ^{13}C, δ 144.92 ($^1J = 180.22$, $C_A{}^3$), 141.64 ($^1J = 187.8$, $C_B{}^3$), 137.43 ($^1J = 183.56$, $C_A{}^5$), 134.76 ($^1J = 191.32$, $C_B{}^5$), 106.15 ($^1J = 179.83$, $C_A{}^4$), 106.07 ($^1J = 179.83$, $C_B{}^4$), 94.40 ($^1J = 159.10$, sp^2 C of cod), 86.94 ($^1J = 157.10$ sp^2 C of cod), 30.3 ($^1J = 130.2$, sp^3 C of cod), 29.67 ($^1J = 130.2$ Hz, sp^3 C of cod).

[$RuCl_2$(cod)$(Hpz)_2$] **2**. The salt $KHB(pz)_3$ (180 mg, 0.71 mmol) was added to a thf (30 cm^3) suspension of [{$RuCl_2$(cod)}$_n$] (200 mg, 0.71 mmol) and the mixture was heated at reflux for 5 h. The resulting orange solution was filtered and evaporated to dryness. Complex **2** was obtained as an orange microcrystalline solid by crystallization from dichloromethane–hexane. Yield 88.3 mg (30%) (Found: C, 40.40; H, 4.55; N, 13.90. $C_{14}H_{20}Cl_2N_4Ru$ requires C, 40.40; H, 4.80; N, 13.45%. IR (KBr, cm^{-1}): 3254 ν(N–H). NMR($CDCl_3$, reference $SiMe_4$): ^1H, δ 12.39 (br s, 2 H, NH); 8.29 (br s, 2 H, H^3), 7.48 (br s, 2 H, H^5), 6.31 (br s, 2 H, H^4), 4.20 (br s, 4 H, olefinic H of cod), 2.70 (m, 4 H, H^{exo} of cod), 2.07 (d, 4 H, $J_{gem} = 8$, H^{endo} of cod); ^{13}C, δ 140.56 ($^1J = 191.4$, C^3), 128.77 ($^1J = 181.3$, C^5), 106.00 ($^1J = 179.8$, C^4), 90.07 ($^1J = 157.1$, sp^2 C of cod) and 29.75 ($^1J = 126.4$ Hz, sp^3 of cod).

$[Ru\{HB(pz)_3\}Cl(tht)_2]$ **3** *and* $[Ru\{HB(pz)_3\}_2(tht)_2]\cdot 0.5Et_2O$ **4**. The salt $KHB(Pz)_3$ (240 mg, 0.95 mmol) was added to a dichloromethane solution (30 cm^3) of $[RuCl_2(tht)_4]$ (250 mg, 0.48 mmol). The solution was stirred for 12 h. A yellow solution was obtained which was filtered and evaporated to dryness. The residue was dissolved in diethyl ether which after cooling to −18 °C allowed the isolation of **4** as a yellowish solid. Yield 60 mg (18%). Compound **3** was obtained from the diethyl ether solution of the previous reaction after filtration and evaporation to dryness. Yield 143 mg (57%).

For **3** (Found: C, 38.80; H, 5.05; N, 15.30. $C_{17}H_{26}BClN_6RuS_2$ requires C, 38.85; H, 5.00; N, 16.00%). IR (KBr, cm^{-1}): 2488 ν(B–H). NMR ($CDCl_3$, reference $SiMe_4$): ^1H, δ 7.83 [d, 2 H, $^3J(H^3H^5) = 1.65$, $H_B{}^3$], 7.73 [d, 1 H, $^3J(H^5H^4) = 2.5$, $H_A{}^5$], 7.66 [d, 2 H, $^3J(H^5H^4) = 2.4$, $H_B{}^5$], 7.49 [d, 1 H, $^3J(H^3H^4) = 1.7$, $H_A{}^3$], 6.19 (pseudo t, 2 H, $H_B{}^4$), 6.17 (pseudo t, 1 H, $H_A{}^4$), 3.03 (br s, 4 H, tht), 2.54 (br s, 4 H, tht) and 1.99 (br s, 8 H, tht); ^{13}C, δ 144.01 ($^1J = 184.3$, $C_A{}^3$), 143.55 ($^1J = 186.4$, $C_B{}^3$), 136.18 ($^1J = 188.4$, $C_A{}^5$), 135.15 ($^1J = 186.3$, $C_B{}^5$), 105.84 ($^1J = 176.84$, $C_A{}^4$), 105.68 ($^1J = 175.4$, $C_B{}^4$), 34.37 ($^1J = 144.3$, α-H of tht) and 30.05 ($^1J = 131.65$ Hz, β-H of tht).

For **4** (Found: C, 45.05; H, 5.30; N, 22.25. $C_{28}H_{41}B_2N_{12}O_{0.5}RuS_2$ requires C, 45.35; H, 5.55; N, 22.70%). IR (KBr, cm^{-1}): 2434 ν(B–H). NMR ($CDCl_3$, reference $SiMe_4$): ^1H, δ 7.89 [dd, 1 H, $^3J(H^3H^4) = 1.95$, $H_B{}^{3'}$], 7.82 [dd, 1 H, $^3J(H^3H^4) = 1.5$, $H_A{}^3$], 7.69 [dd, 1 H, $^3J(H^5H^4) = 2.25$, $H_A{}^5$], 6.95 [dd, 1 H, $^3J(H^5H^4) = 2.4$, $H_B{}^{5'}$], 6.90 [dd, 1 H, $^3J(H^5H^4) = 2.55$, $H_B{}^{5''}$], 6.84 [dd, 1 H, $^3J(H^3H^4) = 1.95$ Hz, $H_B{}^{3''}$], 6.28 (m, 2 H, $H_A{}^{4,4'}$ and $H_B{}^{4,4'}$], 6.07 (pseudo t, 1 H, $H_B{}^{4''}$), 2.28 (m, 4 H, α-H of tht), 2.16 (br s, 4 H, α-H of tht) and 1.61 (m, 8 H, β-H of tht); ^{13}C, δ 144.32 ($^1J = 183.53$, $C_B{}^{3,3''}$), 142.13 ($^1J = 180.53$, $C_A{}^{3'}$), 137.80 ($^1J = 183.75$, $C_A{}^5$), 136.57 ($^1J = 188.77$, $C_B{}^{5'}$), 135.12 ($^1J = 187.05$, $C_B{}^{5''}$), 105.73 ($^1J = 175.72$, $C_A{}^4$ or $C_B{}^{4'}$), 105.15 ($^1J = 175.72$, $C_B{}^{4''}$), 104.16 ($^1J = 174.30$, $C_A{}^4$ or $C_B{}^{4'}$), 35.42 ($^1J = 144.22$, α-H of tht) and 29.56 ($^1J = 131.62$ Hz, β-H of tht).

$[Ru\{HB(pz)_3\}_2]\cdot CDCl_3$ **5**. The compound $[Ru\{HB(pz)_3\}_2(tht)_2]$ (60 mg, 0.085 mmol) was dissolved in $CDCl_3$ (0.5 cm^3) and **5** formed in this solution after a week in quantitative yield. This transformation can be monitored by ^1H NMR spectroscopy. White crystalline **5** (43.45 mg) was isolated by partial evaporation of this solution. Yield 97% (Found: C 36.45; H, 3.40; N, 26.40. $C_{19}H_{20}DB_2Cl_3N_{12}Ru$ requires C, 35.30; H, 3.40; N, 26.40%). We were not successful in obtaining a good elemental analysis for this complex, even though the spectra indicated the product to be pure. NMR ($CDCl_3$, reference $SiMe_4$): ^1H, δ 7.82 [d, 6 H, $^3J(H^4H^5) = 2.5$, H^5], 6.83 [d, 6 H, $^3J(H^3H^4) = 1.4$ Hz, H^3] and 6.13 (pseudo t, 6 H, H^4); ^{13}C, δ 143.1 (C^3), 134.88 (C^5) and 105.32 (C^4).

$[Ru\{HB(pz)_3\}H(cod)]$ **6**. The salt $KHB(pz)_3$ (64 mg, 0.25 mmol) was added to an acetone solution (20 cm^3) of [RuHCl(bpzm)(cod)] (100 mg, 0.25 mmol). The solution was stirred for 12 h and the green solution obtained was filtered and evaporated to dryness. Compound **6** was obtained after subliming the displaced bis(pyrazol-1-yl)methane (10^{-4} mbar, *ca.* 10^{-7} Pa 100 °C). Yield 83 mg (83%) (Found: C, 48.60; H, 5.40; N, 19.25. $C_{17}H_{23}BN_6Ru$ requires C, 48.25; H, 5.50; N, 19.85%). IR (KBr, cm^{-1}): 2456 ν(B–H) and 2015 ν(Ru–H). NMR [$(CD_3)_2CO$, reference $SiMe_4$]: ^1H, δ 8.50 [d, 1 H, $^3J(H^3H^4) = 1.9$, $H_A{}^3$], 7.87 [d, 1 H, $^3J(H^5H^4) = 2.2$, $H_A{}^5$], 7.68 [d, 2 H, $^3J(H^5H^4) = 2.4$, $H_B{}^5$], 7.53 [d, 2 H, $^3J(H^3H^4) = 2.0$ Hz, $H_B{}^3$], 6.43 (pseudo t, 1 H, $H_A{}^4$), 6.27 (pseudo t, 2 H, $H_B{}^4$), 3.73 (br s, 2 H, olefinic H of cod), 2.73 (br s, 4 H, olefinic H of cod and H^{exo} of cod), 2.46 (m, 2 H, H^{exo} of cod), 1.89 (br s, 4 H, H^{endo} of cod) and −4.58 (s, 1 H, RuH); ^{13}C, δ 142.13 ($^1J = 183.75$, $C_A{}^3$), 140.63 ($^1J = 184.5$, $C_B{}^3$), 134.99 ($^1J = 186.0$, $C_A{}^5$), 134.33 ($^1J = 183.0$, $C_B{}^5$), 105.19 ($^1J = 175.5$, $C_A{}^4$), 104.63 ($^1J = 176.25$, $C_B{}^4$), 70.41 ($^1J = 152.25$, sp^2 C of cod), 66.32 ($^1J = 150.75$ sp^2 C of cod), 32.28 ($^1J = 125.62$ sp^3 C of cod) and 28.74 ($^1J = 124.5$ Hz sp^3 C of cod).

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