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Synthesis and characterisation of ruthenium(II) arene complexes containing κ^3- and κ^2-poly(pyrazolyl)borates and methanes†

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Treatment of a fresh acetonitrile solution of $[\{Ru(\eta^6\text{-arene})Cl_2\}_2]$ with poly(pyrazolyl)borates and methanes such as $[HXR_3]^{n-}$ [X = B, R = pyrazolyl (pz); X = C, R = 3,5-dimethylpyrazolyl (dmpz)] resulted in formation of novel ruthenium compounds of the following type $[Ru(\eta^6\text{-arene})\{\kappa^2\text{-}HXR_3\}Cl]^{n+}$ (X = B, *n* = 0, R = pz, arene = *p*-xylene **2**, mesitylene **3** or hexamethylbenzene **6**; X = C, *n* = 1, R = pz **7**, dmpz **8**, arene = benzene; R = dmpz, arene = *p*-xylene **9**). Syntheses of the mixed-sandwich complexes of the type $[Ru(\eta^6\text{-arene})\{\kappa^3\text{-}HB(pz)_3\}][PF_6]$ (arene = *p*-xylene **1a**, mesitylene **4** or hexamethylbenzene **5a**) are also reported from aged solutions. The hapticity change of the tridentate ligand from κ^2 to κ^3 can be affected by either warming the bis-chelated compounds in a polar solvent such as MeCN or by treatment with methanolic $[NH_4][PF_6]$. Crystal structures of $[Ru(\eta^6\text{-}C_6Me_6)\{\kappa^2\text{-}HB(pz)_3\}Cl]$ and $[Ru(\eta^6\text{-}C_6H_6)\{\kappa^2\text{-}HC(dmpz)_3\}Cl][PF_6]$ have been determined.

Although the co-ordination chemistry of the poly(pyrazolyl)-borate ligand class has been extensively explored for most of the transition elements,[1–3] ruthenium hitherto has received scant attention. In order to redress this imbalance several recent publications have explored the chemistry of ruthenium derivatives with respect to ligand-exchange reactions,[4,5] C–H activation in presence of co-ordinated molecular dihydrogen,[6] redox and spectral properties of a variety of bipyridyl derivatives[7] and charge-transfer reactions.[8,9] Attempts to extend the range of ruthenium poly(pyrazolyl)borates and methanes available has recently led us to synthesize a number of arene derivatives. In addition to the expected mixed-sandwich complexes incorporating the tridentate nitrogen-donor ligands with a κ^3 co-ordination mode, half-sandwich complexes consisting of bis-chelated ligands can be isolated. These are some of the first examples of ruthenium complexes containing κ^2-co-ordinated poly(pyrazolyl)borates and methanes to be isolated. The preparation and characterisation of these complexes is the subject of this report.

Experimental

Instrumental

Infrared spectra were recorded on a Nicolet-205 spectrometer between 4000 and 400 cm^{-1} as KBr discs, NMR spectra on a Varian VXR400 or Bruker 300 spectrometer and referenced internally against the respective deuteriated solvents [$(CD_3)_2CO$, δ 2.04; $(CD_3)_2SO$, δ 2.49; $CDCl_3$]. Microanalyses were carried out by the departmental service at University College London. Fast atom bombardment (FAB) mass spectra (assignments based on the ^{102}Ru isotope) were recorded by the University of London Intercollegiate Research Service (ULIRS) at the London School of Pharmacy. All manipulations were carried out under nitrogen with degassed laboratory-grade solvents using conventional Schlenk-line techniques.

Starting materials

Ruthenium trichloride hydrate was obtained on loan from Johnson Matthey plc and purified before use by repeated dissolution in water and boiling to dryness. The appropriate dichloride dimer $[\{Ru(\eta^6\text{-arene})Cl_2\}_2]$,[10,11] potassium tris(3,5-dimethylpyrazolyl)hydridoborate $K[HB(dmpz)_3]$,[12] tris(pyrazolyl)methane and tris(3,5-dimethylpyrazolyl)methane[13] were synthesized by published methods. Sodium hydridotris(pyrazolyl)borate $Na[HB(pz)_3]$ and all other reagents were obtained from the usual commercial sources (Aldrich).

Preparations

$[Ru(\eta^6\text{-}p\text{-}Me_2C_6H_4)\{\kappa^3\text{-}HB(pz)_3\}][PF_6]$ 1a. The compound $[\{Ru(\eta^6\text{-}p\text{-}Me_2C_6H_4)Cl_2\}_2]$ (0.148 g, 0.266 mmol) was dissolved in acetonitrile (30 cm^3). After 2 h the solution was filtered through Celite to remove any undissolved material. The $Na[HB(pz)_3]$ (0.129 g, 0.547 mmol) was added and the mixture stirred for 3 h during which time precipitation of NaCl occurred. The mixture was filtered through Celite and the filtrate evaporated to dryness. Although most of the residue underwent dissolution in methanol (10 cm^3) some of it remained undissolved and was identified as compound **2**. Treatment of the extracts with methanolic $[NH_4][PF_6]$ led to precipitation of **1a** as a yellow solid which was filtered off, washed with cold methanol (10 cm^3) and air dried. Yield: 0.209 g, 0.370 mmol, 35% (Found: C, 36.19; H, 3.44; N, 15.04. Calc. for $C_{17}H_{20}BF_6N_6PRu$: C, 36.13; H, 3.56; N, 14.87%). Mass spectrum: *m*/*z* 421, $[M - PF_6]^+$. Infrared: ν(BH), 2523; ν(PF_6), 835 cm^{-1}.

$[Ru(\eta^6\text{-}p\text{-}Me_2C_6H_4)\{\kappa^2\text{-}HB(pz)_3\}Cl]$ 2 and $[Ru(\eta^6\text{-}p\text{-}Me_2C_6H_4)\{\kappa^3\text{-}HB(pz)_3\}]Cl$ 1b. (*a*) The compound $[\{Ru(\eta^6\text{-}p\text{-}Me_2C_6H_4)Cl_2\}_2]$ (0.0651 g, 0.117 mmol) was dissolved in acetonitrile (30 cm^3). After 20 min the solution was filtered through Celite and evaporated to dryness. The residue was extracted into CH_2Cl_2 and was treated with $Na[HB(pz)_3]$ (0.0647 g, 0.274 mmol). The mixture was stirred for 2 h, filtered through Celite, and reduced in volume. Addition of diethyl ether resulted in precipitation of an orange product. This was redissolved into acetone and reprecipitated with diethyl ether to yield compound **2** as an orange-yellow powder. The powder was washed with acetone–diethyl ether (1:5) and air dried. The major component of the filtrate was **1b**, as identified by NMR spectroscopy. Yield for **2**: 0.032 g, 0.0702 mmol, 30% (Found: C, 44.71; H, 4.32; N, 18.61. Calc. for $C_{17}H_{20}BClN_6Ru$: C, 44.81; H, 4.42; N, 18.44%). Mass spectrum: *m*/*z* 456, M^+; 421, $[M - Cl]^+$. Infrared: ν(BH), 2449 cm^{-1}.

† This paper is dedicated to the memory of Professor Sir Geoffrey Wilkinson FRS who was an inspiration to generations of postgraduate students.

(*b*) Treatment of compound **2** (0.0721 g, 0.158 mmol) with methanolic $[NH_4][PF_6]$ (1 g, excess) followed by concentration of the solution and cooling led to precipitation of **1a**. Yield: 0.0632 g, 0.112 mmol, 70.7%.

$[Ru(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)\{\kappa^2\text{-}HB(pz)_3\}Cl]$ 3 and $[Ru(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)\{\kappa^3\text{-}HB(pz)_3\}][PF_6]$ 4. The compound $[\{Ru(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)Cl_2\}_2]$ (0.3163 g, 0.541 mmol) was dissolved in acetonitrile (55 cm^3) and stirred (2.5 h), then filtered through Celite. The salt $Na[HB(pz)_3]$ (0.261 g, 1.11 mmol) was added and the mixture stirred (5 h) at room temperature, filtered through Celite, and the filtrate evaporated to dryness. The residue was redissolved in methanol (10 cm^3) and treated with methanolic $[NH_4][PF_6]$ (excess) leading to precipitation of compound **4** as a yellow solid, which was filtered off, washed with cold methanol (10 cm^3) and air dried. After extraction of the residue a small quantity of undissolved solid was left behind which was identified as **3**. Yield for **3**: 0.064 g, 0.136 mmol, 13% (Found: C, 45.85; H, 4.66; N, 17.76. Calc. for $C_{18}H_{22}BClN_6Ru$: C, 46.03; H, 4.72; N, 17.89%). Mass spectrum: *m*/*z* 470, M^+; 435, $[M - Cl]^+$. Infrared: ν(BH), 2425 cm^{-1}. Yield for **4**: 0.333 g, 0.575 mmol, 53% (Found: C, 36.89; H, 3.67; N, 14.36. Calc. for $C_{18}H_{22}BF_6N_6PRu$: C, 37.82; H, 3.82; N, 14.51%). Mass spectrum: *m*/*z* 435, $[M - PF_6]^+$. Infrared: ν(BH), 2489; ν(PF_6), 850 cm^{-1}.

$[Ru(\eta^6\text{-}C_6Me_6)\{\kappa^3\text{-}HB(pz)_3\}][PF_6]$ 5a and $[Ru(\eta^6\text{-}C_6Me_6)\{\kappa^3\text{-}HB(pz)_3\}]Cl$ 5b. The compound $[\{Ru(\eta^6\text{-}C_6Me_6)Cl_2\}_2]$ (0.107 g, 0.160 mmol) was dissolved in acetonitrile (30 cm^3) at 45 °C and stirred (25 min), filtered through Celite, and treated with $Na[HB(pz)_3]$ (0.089 g, 0.377 mmol). The mixture was stirred for 4 h at room temperature, filtered through Celite, and the filtrate evaporated to dryness. The residue was redissolved in methanol (10 cm^3) and treated with methanolic $[NH_4][PF_6]$ (excess). A yellow compound identified as **5a** was precipitated, filtered off, washed with cold methanol (10 cm^3) and $CHCl_3$ (40 cm^3) and air dried. The filtrate derived from the $CHCl_3$ washings comprised mainly compound **5b**. Yield for **5a**·MeCN: 0.132 g, 0.213 mmol, 66% (Found: C, 42.49; H, 4.86; N, 14.51. Calc. for $C_{23}H_{31}BF_6N_7PRu$: C, 41.71; H, 4.72; N, 14.80%). Mass spectrum: *m*/*z* 477, $[M - PF_6]^+$. Infrared: ν(BH), 2495; ν(PF_6), 841 cm^{-1}. Yield for **5b**: 0.0249 g, 0.0487 mmol, 15.2%. Mass spectrum: *m*/*z* 477, $[M - Cl]^+$. Infrared: ν(CH), 3149, 2981; ν(BH), 2529 cm^{-1}.

$[Ru(\eta^6\text{-}C_6Me_6)\{\kappa^2\text{-}HB(pz)_3\}Cl]$ 6. The compound $[\{Ru(\eta^6\text{-}C_6Me_6)Cl_2\}_2]$ (0.118 g, 0.176 mmol) was dissolved in acetonitrile (30 cm^3) and stirred at 45 °C (20 min), filtered through Celite, and evaporated to dryness. The residue was extracted into CH_2Cl_2 and treated with $Na[HB(pz)_3]$ (0.088 g, 0.373 mmol). The mixture was stirred (6 h), filtered through Celite, and reduced in volume. Addition of diethyl ether resulted in precipitation of an orange-yellow product which was filtered off, washed with cold CH_2Cl_2–Et_2O (1 : 5, 10 cm^3) and air dried. Yield: 0.124 g, 0.242 mmol, 69% (Found: C, 49.06; H, 5.32; N, 16.58. Calc. for $C_{21}H_{28}BClN_6Ru$: C, 49.28; H, 5.51; N, 16.42%). Mass spectrum: *m*/*z* 477, $[M - Cl]^+$. Infrared: ν(BH), 2441 cm^{-1}.

$[Ru(\eta^6\text{-}C_6H_6)\{\kappa^2\text{-}HC(pz)_3\}Cl][PF_6]$ 7. The compound $[\{Ru(\eta^6\text{-}C_6H_6)Cl_2\}_2]$ (0.237 g, 0.474 mmol) was dissolved in acetonitrile (40 cm^3), stirred (30 min) and subsequently treated with $HC(pz)_3$ (0.203 g, 0.947 mmol). After stirring the mixture (3 h) the solution was filtered through Celite and evaporated to dryness. The residue was redissolved in methanol (10 cm^3) and treated with methanolic $[NH_4][PF_6]$ (excess). A yellow compound was precipitated, which was filtered off, washed with cold methanol (10 cm^3) and air dried. Yield: 0.192 g, 0.34 mmol, 35% (Found: C, 32.33; H, 2.65; N, 13.98. Calc. for $C_{16}H_{16}ClF_6N_6PRu$: C, 33.49; H, 2.81; N, 14.65%). Mass spectrum: *m*/*z* 429, $[M - PF_6]^+$; 394, $[M - PF_6 - Cl]^+$. Infrared: ν(PF_6), 838 cm^{-1}.

$[Ru(\eta^6\text{-}C_6H_6)\{\kappa^2\text{-}HC(dmpz)_3\}Cl][PF_6]\cdot Me_2CO$ 8. The compound $[\{Ru(\eta^6\text{-}C_6H_6)Cl_2\}_2]$ (0.329 g, 0.658 mmol) was dissolved in acetonitrile (60 cm^3), stirred (2 h), filtered through Celite and the filtrate treated with $HC(dmpz)_3$ (0.404 g, 0.135 mmol) and then stirred (3 h). The solution was filtered through Celite then evaporated to dryness. The residue was redissolved in methanol (10 cm^3) and treated with methanolic $[NH_4][PF_6]$ (excess). A yellow compound was precipitated, filtered off, washed with cold methanol (10 cm^3) and $CHCl_3$ (40 cm^3) and air dried. Yield: 0.432 g, 0.603 mmol, 46% (Found: C, 41.77; H, 4.56; N, 12.00. Calc. for $C_{25}H_{34}ClF_6N_6OPRu$: C, 41.93; H, 4.79; N, 11.74%). Mass spectrum: *m*/*z* 513, $[M - PF_6]^+$; 478, $[M - PF_6 - Cl]^+$. Infrared: ν(PF_6), 845 cm^{-1}.

$[Ru(\eta^6\text{-}p\text{-}Me_2C_6H_4)\{\kappa^2\text{-}HC(dmpz)_3\}Cl][PF_6]$ 9. The compound $[\{Ru(\eta^6\text{-}p\text{-}Me_2C_6H_4)Cl_2\}_2]$ (0.099 g, 0.178 mmol) was dissolved in acetonitrile (30 cm^3) and stirred (2 h), then filtered through Celite; $HC(dmpz)_3$ (0.107 g, 0.358 mmol) was added to the filtrate which was stirred (4 h). The mixture was filtered through Celite and evaporated to dryness. The residue was dissolved into methanol (10 cm^3) and treated with methanolic $[NH_4][PF_6]$ which led to precipitation of compound **9** as an orange solid which was filtered off, washed with cold methanol (10 cm^3), and air dried. Yield: 0.096 g, 0.140 mmol, 39% (Found: C, 41.98; H, 4.69; N, 12.06. Calc. for $C_{24}H_{32}ClF_6N_6PRu$: C, 42.02; H, 4.70; N, 12.25%). Mass spectrum: *m*/*z* 541, $[M - PF_6]^+$; 506, $[M - PF_6 - Cl]^+$. Infrared: ν(PF_6), 842 cm^{-1}.

Crystallography

Crystal data. $[Ru(\eta^6\text{-}C_6Me_6)\{\kappa^2\text{-}HB(pz)_3\}Cl]\cdot CHCl_3$ **6**. $C_{22}H_{29}BCl_4N_6Ru$, $M = 631.19$, monoclinic, space group $P2_1/n$, $a = 11.884(3)$, $b = 15.525(4)$, $c = 15.583(3)$ Å, $U = 2688.9(12)$ $Å^3$ (by least-squares refinement of diffractometer angles for 26 centred reflections in the range $12.48 < 2\theta < 24.48°$), $\lambda = 0.710\ 73$ Å, $Z = 4$, $F(000) = 1280$, $D_c = 1.559$ g cm^{-3}, μ(Mo-Kα) = 10.04 cm^{-1}.

$[Ru(\eta^6\text{-}C_6H_6)\{\kappa^2\text{-}HC(dmpz)_3\}Cl][PF_6]\cdot Me_2CO$ **8**. $C_{25}H_{34}ClF_6N_6OPRu$, $M = 716.07$, monoclinic, space group $P2_1/n$, $a = 10.687(2)$, $b = 10.773(6)$, $c = 28.214(6)$ Å, $U = 3233.7(11)$ $Å^3$ (by least-squares refinement of diffractometer angles for 25 centred reflections in the range $16.98 < 2\theta < 26.79°$), $\lambda = 0.710\ 73$ Å, $Z = 4$, $F(000) = 1456$, $D_c = 1.471$ g cm^{-3}, μ(Mo-Kα) = 6.80 cm^{-1}.

Data collection and processing. The ω–2θ technique was used to measure 4759 (4516 unique) for compound **6** and 5967 reflections (5649 unique) for **8** in the range of $5 \leqslant 2\theta \leqslant 50°$ using an automated four-circle diffractometer (Nicolet R3mV) equipped with Mo-Kα radiation operating at 293 K. Three standard reflections (remeasured every 97 scans) showed no significant loss in intensity during the data collection. The data were corrected for Lorentz-polarisation effects and for absorption, based on additional azimuthal scan data. The analysis made use of 4511, **6**, and 5647, **8**, data.

Structure analysis and refinement. The structures were solved by Patterson methods and developed by using alternating cycles of full-matrix least-squares refinement and Fourier-difference synthesis. The non-hydrogen atoms were refined anisotropically while hydrogens were placed in idealised positions (C–H 0.96 Å) and assigned a common isotropic thermal parameter ($U = 0.08$ $Å^2$). In the final stages of the refinement the presence of a chloroform, **6**, and acetone, **8**, molecules in the asymmetric unit were observed. These refined routinely with no apparent disorder. The final cycle of the refinement included 308, **6**, and 370, **8**, parameters for 4511, **6** and 5647, **8**, variables, and did not shift any parameter by more than 0.001 times its standard

Table 1 Proton NMR data (in $CDCl_3$) for ruthenium(II) arene complexes containing bis- and tris-chelated poly(pyrazolyl)borate/methane ligands

	Pyrazolyl borate (δ, *J*/Hz)			
Complex	3-	4-	5-Position	Other signals
1a $[Ru(\eta^6\text{-}p\text{-}Me_2C_6H_4)\{\kappa^3\text{-}HB(pz)_3\}][PF_6]$[a]	8.54 (d, 3 H, *J* = 2.0)	6.43 (dd, 3 H)	7.87 (d, 3 H, *J* = 2.40)	6.31 (s, 4 H, *p*-$Me_2C_6H_4$), 2.49 (s, 6 H, *p*-$Me_2C_6H_4$)
1b $[Ru(\eta^6\text{-}p\text{-}Me_2C_6H_4)\{\kappa^3\text{-}HB(pz)_3\}]Cl$	8.42 (d, 3 H, *J* = 2.0)	6.33 (dd, 3 H)	7.54 (d, 3 H, *J* = 2.8)	6.20 (s, 4 H, *p*-$Me_2C_6H_4$), 2.41 (s, 6 H, *p*-$Me_2C_6H_4$)
2 $[Ru(\eta^6\text{-}p\text{-}Me_2C_6H_4)\{\kappa^2\text{-}HB(pz)_3\}Cl]$	7.74 (d, 2 H, *J* = 2.1), 7.79 (d, 1 H, *J* = 2.0)	6.21 (dd, 2 H), 6.38 (dd, 1 H)	6.99 (d, 2 H, *J* = 2.5), 7.72 (d, 1 H, *J* = 2.2)	5.45 (s, 4 H, *p*-$Me_2C_6H_4$), 2.07 (s, 6 H, *p*-$Me_2C_6H_4$)
3 $[Ru(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)\{\kappa^2\text{-}HB(pz)_3\}Cl]$[a]	7.90 (d, 2 H), 7.47 (d, 1 H)	6.43 (dd, 2 H), 6.25 (dd, 1 H)	7.85 (d, 2 H), 6.94 (d, 1 H)	4.45 (s, 3 H, $C_6H_3Me_3$), 1.82 (s, 9 H, $C_6H_3Me_3$)
	7.82[b] (d, 2 H), 7.62 (d, 1 H)	6.43 (dd, 2 H), 6.27 (dd, 1 H)	7.82[b] (d, 2 H), 6.92 (d, 1 H)	4.21 (s, 3 H, $C_6H_3Me_3$), 1.84 (s, 9 H, $C_6H_3Me_3$)
4 $[Ru(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)\{\kappa^3\text{-}HB(pz)_3\}][PF_6]$[a]	8.60 (d, 3 H, *J* = 2.40)	6.46 (dd, 3 H)	7.88 (d, 3 H, *J* = 2.80)	6.55 (s, 3 H, $C_6H_3Me_3$), 2.39 (s, 9 H, $C_6H_3Me_3$)
5a $[Ru(\eta^6\text{-}C_6Me_6)\{\kappa^3\text{-}HB(pz)_3\}][PF_6]$[c]	7.61 (d, 3 H)	6.29 (dd, 3 H)	6.84 (d, 3 H)	1.96 (s, 18 H)
5b $[Ru(\eta^6\text{-}C_6Me_6)\{\kappa^3\text{-}HB(pz)_3\}]Cl$[a]	8.33 (d, 3 H, *J* = 2.4)	6.44 (dd, 3 H)	7.84 (d, 3 H, *J* = 2.4)	2.43 (s, 18 H)
6 $[Ru(\eta^6\text{-}C_6Me_6)\{\kappa^2\text{-}HB(pz)_3\}Cl]$	7.81 (dd, 1 H, *J* = 1.5), 7.60 (dd, 2 H, *J* = 2.1)	6.41 (dd, 1 H), 6.22 (dd, 2 H)	7.70 (d, 1 H, *J* = 2.1), 6.98 (d, 2 H, *J* = 2.4)	2.06 (s, 18 H)
7 $[Ru(\eta^6\text{-}C_6H_6)\{\kappa^2\text{-}HC(pz)_3\}Cl][PF_6]$[a]	8.59 (d, 2 H, *J* = 1.5), 7.74 (d, 1 H, *J* = 3.0)	6.87 (dd, 2 H), 6.60 (dd, 1 H)	8.51 (d, 2 H, *J* = 2.2), 7.25 (d, 1 H, *J* = 2.6)	9.09 (s, 6 H, C_6H_6), 5.79 [s, 1 H, *H*C$(pz)_3$]
8 $[Ru(\eta^6\text{-}C_6H_6)\{\kappa^2\text{-}HC(dmpz)_3\}Cl][PF_6]$[a]	2.70 (s, 6 H), 2.15 (s, 3 H)	6.46 (s, 2 H), 6.17 (s, 1 H)	2.69 (s, 6 H), 1.73 (s, 3 H)	5.78 (s, 6 H, C_6H_6), 8.35 [s, 1 H, *H*C$(dmpz)_3$]
9 $[Ru(\eta^6\text{-}p\text{-}Me_2C_6H_4)\{\kappa^2\text{-}HC(dmpz)_3\}Cl][PF_6]$[a]	2.64 (s, 6 H), 2.14 (s, 3 H)	6.28 (s, 2 H), 6.10 (s, 1 H)	2.48 (s, 6 H), 1.70 (s, 3 H)	7.58 [s, 1 H, *H*C$(dmpz)_3$], 5.38 (s, 4 H, $C_6H_4Me_2$), 1.90 (s, 6 H, $C_6H_4Me_2$)

[a] In $(CD_3)_2CO$. [b] Signals overlapping. [c] In $(CD_3)_2SO$.

deviation. The final *R* values were 0.0575, **6**, and 0.0556, **8** [for data with $I > 2\sigma(I)$, based on *F*] and 0.0951, **6**, and 0.0813, **8** (for all unique reflections, based on F^2), and the final Fourier-difference map was featureless with no peaks greater than 0.68, **6**, and 0.48 e $Å^{-3}$, **8**. Structure solution used the SHELXL 93 program package[14] on a personal computer.

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Results and Discussion

The first reported synthesis of the ruthenium(II) (arene)-poly(pyrazolyl)borate complexes dates back to the work done by Ferguson[15,16] and Lalor[17] in the mid-seventies. It is carried out by directly treating an acetonitrile solution of $[\{Ru(\eta^6\text{-arene})Cl_2\}_2]$ with $Na[B(pz)_4]$ under refluxing conditions for 5 min. Subsequent attempts to extend the synthesis by McCleverty and co-workers[18] to second-generation poly(pyrazolyl)borates, namely $[HB(dmpz)_3]^-$ resulted in the fragmentation of the tripodal ligand. The latter result was attributed to the unfavourable intramolecular interactions between the methyl substituents on the pyrazolyl ligands and the benzene hydrogen atoms. Since the synthesis of $[Ru(\eta^6\text{-}C_6H_6)\{HB(dmpz)_3\}]^+$ had not been attempted under less vigorous conditions, reinvestigation of the reactivity under moderate conditions was warranted. Successful isolation of the compound in question has been discussed in a previous report.[19] During attempts to synthesize a range of ruthenium(II) (arene)poly(pyrazolyl)borate and methane complexes it was realised that the reaction temperature and the extent of dissolution of the precursor dimer, $[\{Ru(\eta^6\text{-arene})Cl_2\}_2]$, have an important role to play in directing the nature of the isolated products.

Treatment of $[\{Ru(\eta^6\text{-}p\text{-}Me_2C_6H_4)Cl_2\}_2]$ (which has been stirred in acetonitrile for 2 h) with $Na[HB(pz)_3]$ for 3 h followed by work-up with methanolic $[NH_4][PF_6]$ leads to isolation of $[Ru(\eta^6\text{-}p\text{-}Me_2C_6H_4)\{\kappa^3\text{-}HB(pz)_3\}][PF_6]$ in 35% yield. The infrared spectrum exhibits a ν(BH) absorption at 2523 cm^{-1}, about 80 cm^{-1} higher than that found for the free borate. The ^1H NMR spectrum consists of five signals, with the three of lowest field due to the κ^3-co-ordinated $[HB(pz)_3]^-$ ligand, δ 8.54 (H^3), 7.87 (H^5) and 6.43 (H^4). The remaining two signals in the spectrum are due to the η^6-co-ordinated *p*-xylene ligand (δ 6.31 and 2.49). The pyrazolyl signals have undergone an average downfield shift of +0.61 ppm with respect to the free borate environment. The largest of these shifts is observed for H^3, +0.94 ppm, consistent with the proton in the 3 position being structurally *endo* to 'the arene ruthenium' fragment and hence most likely to experience the greatest change in chemical environment.

If prior to reaction with $Na[HB(pz)_3]$ the compound $[\{Ru(\eta^6\text{-}p\text{-}Me_2C_6H_4)Cl_2\}_2]$ is stirred in acetonitrile for only 20 min, work-up leads to isolation of a new compound which exhibits eight signals in the ^1H NMR spectrum. Two of the signals are due to the arene and the remaining six arise from the pyrazolyl groups. It is reasonable to assume that only a single complex containing a tripodal ligand $[HB(pz)_3]^-$ co-ordinated in a κ^2 mode had been isolated. To investigate this reaction further $[\{Ru(\eta^6\text{-}p\text{-}Me_2C_6H_4)Cl_2\}_2]$ was dissolved in acetonitrile for 20 min, then the solvent mixture was filtered through Celite and evaporated to dryness. After extraction with CH_2Cl_2 and treatment with a stoichiometric amount of $Na[HB(pz)_3]$ the reaction mixture was left to stir at room temperature for 2 h. Filtration of the reaction mixture followed by treatment with diethyl ether led to precipitation of an orange-yellow product which was identified as $[Ru(\eta^6\text{-}p\text{-}Me_2C_6H_4)\{\kappa^2\text{-}HB(pz)_3\}Cl]$ **2**. The major component in the filtrate at this stage was identified by ^1H NMR spectroscopy as $[Ru(\eta^6\text{-}p\text{-}Me_2C_6H_4)\{\kappa^3\text{-}HB(pz)_3\}]Cl$ **1b**, in which the chloride resides outside the first co-ordination sphere.

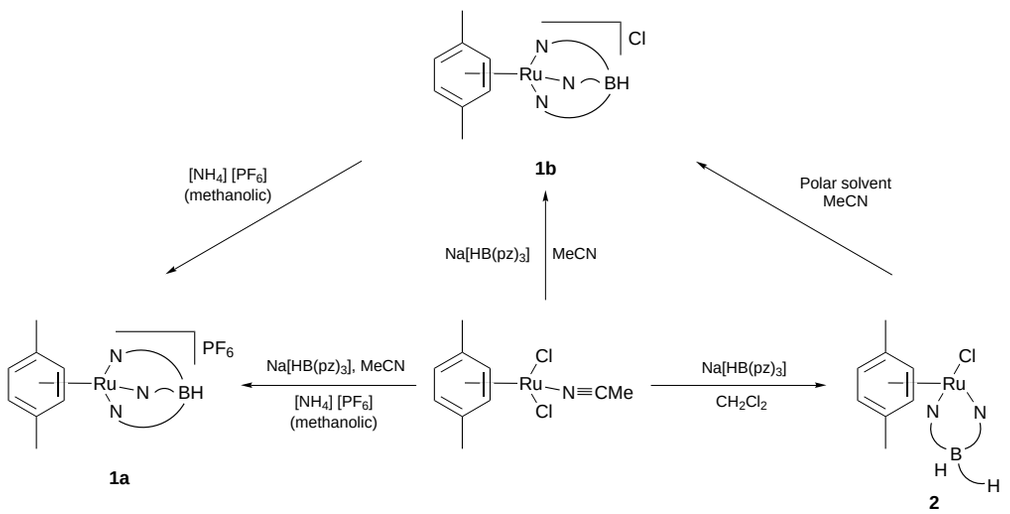
The infrared spectra of both compounds **1b** and **2** are consistent with the presence of the arene and the $[HB(pz)_3]^-$ ligands. It is however surprising to find that the band for the ν(BH) stretch in **2** appears at 2449 cm^{-1}, only 9 cm^{-1} higher than the corresponding absorption of the free borate. This contrasts with the large shift observed for related mixed-sandwich complexes (*ca.* 90 cm^{-1}).[19]

The differences in the co-ordination modes adopted by the potentially tridentate ligands in compounds **1b** and **2** become more obvious from close inspection of the ^1H NMR spectra (see Table 1). The pyrazolyl signals are sharp at room temperature

Table 2 Carbon-13 NMR data (in $CDCl_3$) on ruthenium(II) arene complexes containing bis- and tris-chelated poly(pyrazolyl)borate/methane ligands

	Pyrazolyl borate (δ)			
Complex	3-	4-	5-Position	Other signals
1a*	146.00	107.82	136.86	100.96, 87.90, 18.42 (Me)
1b	145.04	107.26	135.41	99.20, 87.48, 18.71 (Me)
2	144.70, 141.81	106.46, 105.48	135.84, 135.74	96.82, 86.26, 18.06 (Me)
3	146.30, 140.14	107.42, 105.10	139.48, 131.20	92.31, 74.70, 19.06 (Me)
4*	145.92	108.09	136.96	93.74, 93.17, 17.83 (Me)
5b*	144.64	107.98	136.95	96.43, 17.17 (Me)
6	143.90, 141.50	106.10, 105.40	133.50, 135.60	93.70, 15.80 (Me)
8*	159.53, 16.70 (Me)	111.52, 110.87	148.38, 11.75 (Me)	86.73 (C_6H_6), 75.36 [H*C*(dmpz)$_3$]
	150.65, 13.49 (Me)		142.52, 10.54 (Me)	
9*	158.83, 16.75 (Me)	111.81, 110.92	146.43, 11.83 (Me)	99.51, 84.92, 73.86 [H*C*(dmpz)$_3$], 18.13 (Me)
	151.52, 13.45 (Me)		142.24, 10.05 (Me)	

* In $(CD_3)_2CO$.



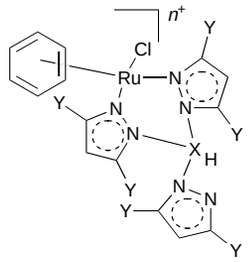
Scheme 1 Reaction pathways from [{Ru(η^6-*p*-$Me_2C_6H_4$)Cl_2(MeCN)] to **1a**, **1b** and **2**

and remain so irrespective of whether the temperature is raised or lowered. The absence of broadening and coalescence of these resonances is in accord with the hydridotris(pyrazolyl)borate ligand being stereochemically rigid and not being involved in a process requiring trigonal-twist rotation of the $[HB(pz)_3]^-$ ligand around the ruthenium–boron axis, as has been noted previously with related compounds.[20–23] The appearance of the H^4 signal for all of the pyrazolyl groups as a pseudo-triplet rather than as a doublet of a doublet can be rationalised by considering the small differences in the coupling of H^4 to H^3 and H^5. Although the initial assignment of resonances to H^3 and H^5 is somewhat ambiguous, inspection of the literature[24] reveals that while, for the ligand $[H_2B(pz)_2]^-$, the H^5 resonates relatively more downfield than H^3, the reverse is generally true for the ligand $[HB(pz)_3]^-$. The assignments of the pyrazolyl signals in the ^{1}H and ^{13}C NMR spectra (Tables 1 and 2) for all of the isolated complexes have been made on this basis.

The fact that the spectrum of compound **2** contains two sets of pyrazolyl signals (relative intensity 1:2) as opposed to the single set exhibited for **1a** and **1b** is in accord with the presence of two inequivalent pyrazolyl environments in **2**. The singly degenerate signals appear at lower fields (^{1}H NMR: δ 7.79, 7.72 and 6.38) compared with the remaining signals (δ 7.74, 6.99 and 6.21). In fact the chemical shifts of the signals of the unique pyrazolyl groups are comparable with those observed for the related complex [Ru{κ^2-$HB(pz)_3$}$_2$(thf)$_2$] (thf = tetrahydrofuran) which was solely characterised by NMR spectroscopy.[25] Interestingly though in the ^{13}C NMR spectra the signals for the unique pyrazolyl group [δ 141.81 (C^3), 135.74 (C^5) and 105.48 (C^4)] appear at relatively higher fields to the doubly degenerate signals [δ 144.70 (C^3), 135.84 (C^5) and 106.46 (C^4)].

Neither compound **1b** nor **2** requires a large anion for isolation indicating a chloride must be present to balance the charge. That chloride could either be directly bound to ruthenium(II) or reside in the outer co-ordination sphere, as a component of a tight ion pair, with a solvent molecule occupying the vacant site. The former situation is more likely for **2**. Not only is this substantiated by the microanalytical data but also it seems reasonable in that if the sixth co-ordination site on the ruthenium(II) centre is occupied by a solvent molecule this molecule would be labile and there would be a tendency for the $[HB(pz)_3]^-$ ligand to undergo a rapid hapticity change from κ^2 to κ^3, resulting in tris chelation and only one set of NMR signals. Only the presence of a co-ordinated chloride will prevent this hapticity change. If compound **2** is left in acetonitrile for prolonged periods or treated with methanolic $[NH_4][PF_6]$, complexes **1b** and **1a** respectively can be isolated. Similarly compound **1b** can be converted into **1a** by treatment of the latter with $[NH_4][PF_6]$. These conversions are illustrated in Scheme 1.

The observation that two products can be isolated after reaction for different times is readily understood. When an [{Ru(η^6-arene)Cl_2}$_2$] compound is placed in a strongly co-ordinating solvent, such as MeCN, the monomeric 1:1 adduct [Ru(η^6-arene)Cl_2(MeCN)] is formed virtually instantaneously. In the polar solvent the rate at which the chloride ligands are replaced is significant and 1:2, [Ru(η^6-arene)Cl(MeCN)$_2$]$^+$, and 1:3, [Ru(η^6-arene)(MeCN)$_3$]$^{2+}$, adducts are formed rapidly and sequentially (^{1}H NMR evidence). Clearly with short reaction times the metal complex is being removed from solution before both chlorides can be replaced by solvent. This is confirmed by the reactions which we have carried out in CH_2Cl_2. In these reactions the Na[$HB(pz)_3$] is being treated with what is pre-



	X	Y	arene	*n*
2	B	H	*p*-$Me_2C_6H_4$	0
3	B	H	1,3,5-$Me_3C_6H_3$	0
6	B	H	C_6Me_6	0
7	C	H	C_6H_6	1
8	C	Me	C_6H_6	1
9	C	Me	*p*-$Me_2C_6H_4$	1

dominantly [Ru(η^6-arene)Cl(MeCN)$_2$]Cl, in a solvent which will not promote Ru–Cl bond cleavage, and hence gives good yields of the complex with the κ^2-co-ordinated tripodal ligand.

The isolation of both the bis- and tris-chelated compounds is not restricted to the *p*-xylene derivative. Complexes incorporating bulkier arenes, such as mesitylene and hexamethylbenzene, can also be synthesized by analogous procedures. As observed for the *p*-xylene derivatives the mesitylene and the hexamethylbenzene complexes [Ru(η^6-1,3,5-$Me_3C_6H_3$){κ^2-HB(pz)$_3$}Cl] **3** and [Ru(η^6-C_6Me_6){κ^2-HB(pz)$_3$}Cl] **6** exhibit two sets of pyrazolyl signals in integral ratio of 1:2. The microanalytical data of all of these complexes are consistent with the proposed formulations.

Inspection of the NMR data for the *p*-xylene derivatives (Table 1) reveals that the protons of the pyrazolyl groups in the tris-chelated complexes **1a** and **1b** resonate at lower field than those of the metallated pyrazolyl groups in **2**. While a similar pattern is manifest for the mesitylene derivatives in the case of the hexamethylbenzene complexes no such characteristic pattern of chemical shifts is observed.

Attempts were also made so synthesize bis-chelated complexes incorporating the second-generation poly(pyrazolyl)borate ligand [HB(dmpz)$_3$]$^-$, but were unsuccessful due to extensive decomposition. Unexpectedly though it is possible to synthesize analogous bis-chelated derivatives with the neutral tripodal ligands HC(pz)$_3$ and HC(dmpz)$_3$. Treatment of the complex [{Ru{η^6-C_6H_6)Cl$_2$}$_2$], pre-stirred in MeCN for 30 min, with HC(pz)$_3$ or HC(dmpz)$_3$ followed by work-up with methanolic [NH_4][PF_6] results in the isolation of [Ru(η^6-C_6H_6){κ^2-HC(pz)$_3$}Cl][PF_6] **7** and [Ru(η^6-C_6H_6){κ^2-HC(dmpz)$_3$}Cl][PF_6] **8**, respectively. This synthesis can be extended to compounds in which both the arene and the tripodal ligand carry bulky substituents, *e.g.* [Ru(η^6-*p*-$Me_2C_6H_4$){κ^2-HC(dmpz)$_3$}Cl][PF_6] **9**. The appearance of two sets of signals for the pyrazolyl groups, with 1:2 integral ratio, in the ^{1}H NMR spectra is consistent with the presence of two distinct pyrazolyl environments. Additionally for all of the compounds containing the carbon-centred tridentate ligands, the appearance of the signals for the unique pyrazolyl group at higher fields is consistent with it being unco-ordinated. This pattern is repeated in the ^{13}C NMR spectrum for **8** [unique pz 150.65 (C^3), 13.49 (Me^3), 142.52 (C^5), 10.54 (Me^5) and 110.87 (C^4); doubly degenerate signals 159.53 (C^3), 16.70 (Me^3), 148.38 (C^5), 11.75 (Me^5) and 111.52 (C^4)] but is in fact reversed in the ^{13}C NMR spectrum of the sterically congested **9** [unique pz 151.52 (C^3), 13.45 (Me^3), 142.24 (C^5), 10.05 (Me^5) and 110.92 (C^4); doubly degenerate signals 158.83 (C^3), 16.75 (Me^3), 146.43 (C^5), 11.83 (Me^5) and 111.81 (C^4)]. It is surprising to find that the bis-chelated derivatives of the neutral carbon-centred tripodal ligands can be readily isolated in moderate yields (*e.g.* the dimethylated ligand derivative **8**, 46%), as attempts to synthesize hydridotris(3,5-dimethylpyrazolyl)borate derivatives led to extensive decomposition and negligible

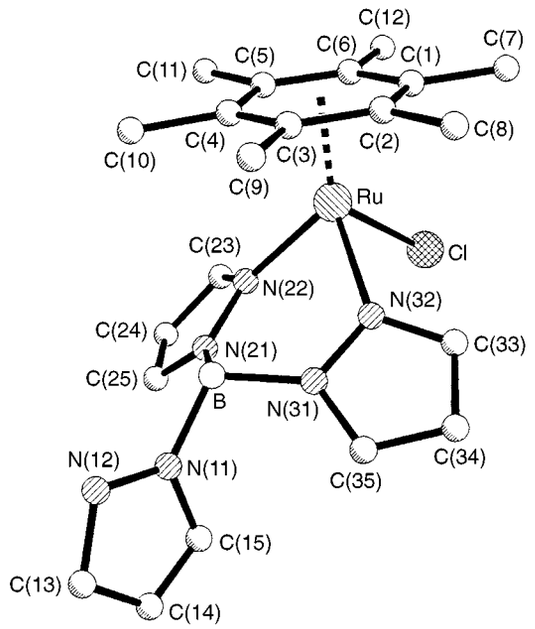


Fig. 1 Crystal structure of [Ru(η^6-C_6Me_6){κ^2-HB(pz)$_3$}Cl] **6** showing the atomic numbering scheme

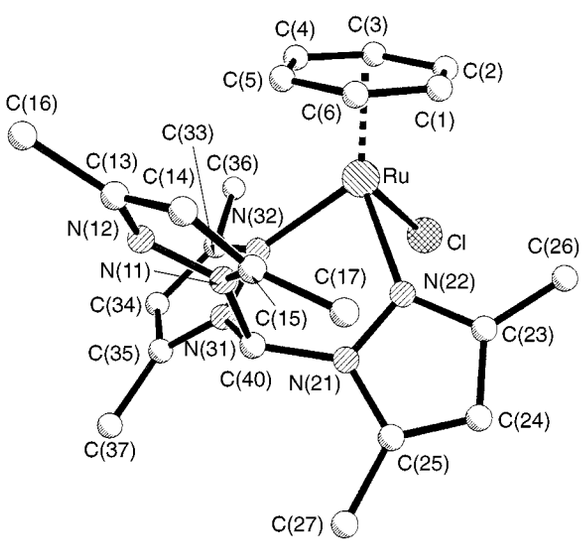


Fig. 2 Crystal structure of the cation in [Ru(η^6-C_6H_6){κ^2-HC(dmpz)$_3$}Cl][PF_6] **8** showing the atomic numbering scheme

yields of the target compounds (*e.g.* 22% reported for [Ru(η^6-C_6H_6){κ^3-HB(dmpz)$_3$}][PF_6][19]) even under mild conditions. While we have not investigated κ^2 to κ^3 conversion for the neutral tripodal ligands, HC(pz)$_3$ and HC(dmpz)$_3$, there is no reason to suppose that the reaction would not occur. Indeed we recently reported on the synthesis of a number of [Ru(η^6-arene){κ^3-HC(pz)$_3$}]$^{2+}$ complexes using methods analogous to those described herein.[19] The observation that the carbon-centred ligand system is robust presents an excellent opportunity further to exploit this area of mixed-sandwich ruthenium(II) arene chemistry.

The conversion of the κ^2- into the κ^3-co-ordinated ligand is apparently irreversible as, in our hands, the reaction of solutions of a number of compounds containing the κ^3-hydridotris(pyrazolyl)borate ligand with an excess of [NBu_4]Cl or carbon monoxide yield only unreacted starting materials.

The formulation of **6** and **8** as bis-chelated complexes was unequivocally confirmed by carrying out crystal structure determinations. Whereas crystals of **6** suitable for crystallography were grown by the vapour-diffusion method with $CHCl_3$–Et_2O as the solvent medium, crystals of **8** were obtained from Me_2CO–Et_2O. The molecular structures of the complexes

Table 3 Geometric parameters (bond lengths in Å, angles in °) for complexes **6** and **8**

	$[Ru(\eta^6\text{-}C_6Me_6)\{\kappa^2\text{-}HB(pz)_3\}Cl]\cdot CHCl_3$ **6**	$[Ru(\eta^6\text{-}C_6H_6)\{\kappa^2\text{-}HC(dmpz)_3\}Cl][PF_6]\cdot Me_2CO$ **8**
Ru–C(1)	2.204(6)	2.207(7)
Ru–C(2)	2.195(6)	2.201(6)
Ru–C(3)	2.190(6)	2.210(6)
Ru–C(4)	2.186(6)	2.218(6)
Ru–C(5)	2.207(6)	2.207(7)
Ru–C(6)	2.197(7)	2.183(7)
Ru–Cl	2.397(2)	2.415(2)
Ru–N(22)	2.081(5)	2.149(4)
Ru–N(32)	2.083(5)	2.140(4)
N(22)–Ru–N(32)	84.8(2)	84.9(2)
Cl–Ru–N(22)	86.0(2)	84.9(1)
Cl–Ru–N(32)	85.3(2)	85.5(1)
N(11)–X–N(21)	109.5(6)	112.0(4)
N(11)–X–N(31)	109.9(6)	110.0(4)
N(21)–X–N(31)	107.5(5)	112.4(4)

X = B for **6** and C(40) for **8**.

are shown in Figs. 1 and 2. Selected bond angles and lengths are presented in Table 3.

Both compounds **6** and **8** exist as half-sandwich complexes with, if one assumes the arene occupies three facial sites, a distorted octahedral geometry at the ruthenium centre. The ruthenium atom is π bonded to the arene ligand with an average Ru–C distance of 2.197(6) **6** and 2.204(7) **8**, and a separation between the arene plane and the ruthenium atom of 1.68 **6** and 1.71 Å **8**, very similar to that observed in many related arene-ruthenium complexes. The distance between the ruthenium atom and the chloride ligand is 2.397(2) Å for complex **6** which is significantly shorter than that found in **8**, 2.415(2) Å. In addition to being bonded to the arene and the chloride ligand the ruthenium atom is also directly co-ordinated to two endocyclic nitrogen atoms [N(22) and N(32)] of the pyrazolyl groups, with an average distance of 2.082(5) **6** and 2.144(4) Å **8**. It is notable that all three metal–ligand distances are shorter for **6**, most likely as a consequence of the electrostatic attraction between the two components, a feature clearly absent in **8**. It should also be noted that the metal–nitrogen distances in the bis-chelated derivatives are shorter than those in related tris-chelated compounds, such as $[Ru(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)\{\kappa^3\text{-}HB(pz)_3\}][PF_6]$, 2.113(4) Å,[19] and $[Ru(\eta^5\text{-}C_5H_5)\{\kappa^3\text{-}HB(pz)_3\}]$, 2.128(3) Å.[26]

The bite angles of the chelating ligands are 84.8(2) **6** and 84.9(2)° **8**, not very different from those reported for the tris-chelated complexes, $[Ru(\eta^6\text{-}C_6H_6)\{\kappa^3\text{-}B(pz)_4\}][PF_6]$,[15,16] 84.2°, and $[Ru(\eta^5\text{-}C_5H_5)\{\kappa^3\text{-}B(pz)_4\}]$,[26] 83.8°. In complex **6** the overall geometry at the boron atom is tetrahedral (average N–B–N angle of 109.0°) with the smallest of these angles being subtended by the endocyclic nitrogens of the pyrazolyl groups N(31)–B–N(21) 107.5(5)°. In the case of **8** the average N–C–N angle is somewhat larger, at around 111.5°.

The most notable difference between the two structures is the relative positions of the unco-ordinated pyrazolyl groups with respect to the molecular framework. Examination of Figs. 1 and 2 clearly shows that while in compound **6** the unco-ordinated 'leg' of the tripodal ligand is placed far from the arenemetal fragment the corresponding substituent in **8** is in relatively close proximity to the ruthenium and the arene. Indeed hydrogen atoms on the benzene make short contacts of 2.65 and 2.70 Å with atoms N(12) and C(15) of the uncomplexed pyrazolyl ring. It is interesting to speculate as to whether these interactions could result in a stabilisation of the complex, as to achieve this orientation the pyrazolyl group must rotate about the C–N bond destroying the C_3 symmetry of the free pyrazolylborate. It is notable that in **6** the pyrazolylborate ligand has retained its approximate C_3 symmetry. However, in the absence of other evidence it is equally likely that the orientation is a consequence of subtle crystal-packing effects.

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