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Polyazolyl chelate chemistry

IV *. Dihydrobis(benzotriazolyl)borato complexes of ruthenium(II)

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Abstract

The reactions of the salt K[$H_2B(bta)_2$] (bta = benzotriazol-1-yl) with the compounds [RuClR(CO)(PPh_3)$_n$] ($n = 3$, R = H; $n = 2$, R = C_6H_4Me-4, CH=CHC_6H_4Me-4, CH=CHC_4H_9, C(C≡CPh)=CHPh) give high yields of the chelate complexes [RuR(CO)(PPh_3)$_2${η^2-$H_2B(bta)_2$}]. The hydrido complex can also be made by similar treatment of the salt [RuH(NCMe)$_2$(CO)(PPh_3)$_2$]BF_4, and gives the chloro-derivative [RuCl(CO)(PPh_3)$_2${η^2-$H_2B(bta)_2$}] upon treatment with *N*-chlorosuccinimide.

Introduction

The chemistry of poly(pyrazolyl)borate chelates has grown immensely owing to the ability of these ligands to support metals in a wide range of electronic configurations, oxidation states and coordination numbers [2]. The bis(pyrazol-1-yl)borates are particularly intriguing in that, notwithstanding their superficial similarity to 1,3-diketonates, situations have been observed in which the remaining boron substituents can coordinate in an agostic manner to the metal centre [2]. Recently Lalor [3] and Shiu [4] independently described the syntheses of a range of chelates notionally related to Trofimenko's pyrazolylborates based on the benzotriazole heterocycle (Scheme 1).

Of special interest to us is the chelate chemistry of the dihydrobis (benzotriazolyl)borates, since the question of increased hapticity via agostic coordination might once again arise. We have described the reactions of σ-aryl and σ-vinyl complexes of ruthenium(II) with salts of the hydrotris(pyrazolyl)borate anion, which give the pseudo-octahedral complexes [RuR(CO)(PPh_3){HB(pz)$_3$}] (R = CH=CH_2, CPh=CHPh, CMe=CHMe, C_6H_4Me-4, pz = pyrazol-1-yl) in which the

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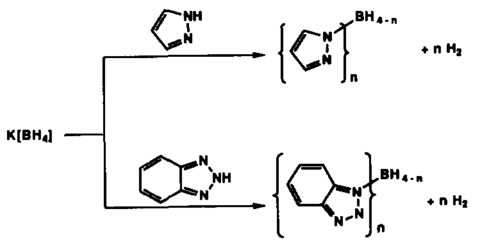
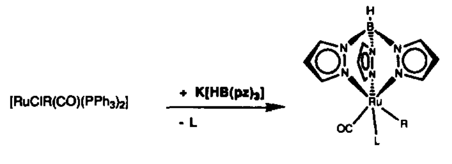
* For Part III see Ref. 1.



Scheme 1. Synthesis of poly(pyrazolyl)borates and poly(benzotriazolyl)borates (Refs. 2–4).



Scheme 2. Hydrotris(pyrazol-1-yl)boratoruthenium(II) complexes R = C_6H_4Me, C(C≡CPh)=CHPh; L = PPh_3.

$HB(pz)_3$ ligand is bound in the expected trihapto facial manner [1,5] (Scheme 2).

We report here a study of the related reactions involving the dihydrobis(benzotriazolyl)borate anion with a range of ruthenium (II) complexes, which lead to the dihapto complexes $[RuR(CO)(PPh_3)_2\{H_2B(bta)_2\}]$ (R = H, Cl, Br, I, C_6H_4Me-4, $CH{=}CHC_6H_4Me$-4, and C(C≡CPh)=CHPh). A preliminary report of aspects of this work has appeared [6].

Results and discussion

σ-Organyl complexes

The complexes $[RuRCl(CO)(PPh_3)_2]$ (R = C_6H_4Me-4 [7], $CH{=}CHC_6H_4Me$-4 [8*], C(C≡CPh)=CHPh [9]) are convenient starting materials for a range of ligand addition and insertion reactions by virtue of their high stability coupled with their coordinative unsaturation and halide lability [1,5,10–18]. Treating a suspension of $[Ru(C_6H_4Me\text{-}4)Cl(CO)(PPh_3)_2]$ in dichloromethane with the salt $K[H_2B(bta)_2]$ results in dissolution of the organometallic, decolourisation, and precipitation of KCl. A pale yellow complex of composition $[Ru(C_6H_4Me\text{-}4)(CO)(PPh_3)_2\{H_2B(bta)_2\}]$ (**1**) may be isolated from the supernatant solution in high yield (Scheme 3). We had initially expected the formation of a monophosphine complex $[Ru(C_6H_4\text{-}Me\text{-}4)(CO)(PPh_3)\{H_2B(bta)_2\}]$ with a trihapto bis(benzotriazolyl)borato ligand but the FAB mass spectrum of the product clearly shows a molecular ion in addition to peaks attributable to the loss of toluene, borate and carbonyl ligands and the fragments $[Ru(PPh_3)_2]^+$ (625) and $[Ru(C_7H_8)(PPh_3)]^+$ (455). Despite the clear case of migratory insertion processes in many ligand addition reactions of the complexes $[RuRCl(CO)(PPh_3)_2]$ [7,10,11], and the implication of such pathways in the isomerisation of the derived adducts [18], the infrared spectrum of $[Ru(C_6H_4Me\text{-}4)(CO)(PPh_3)_2\{H_2B(bta)_2\}]$ shows only one peak for a single termi-

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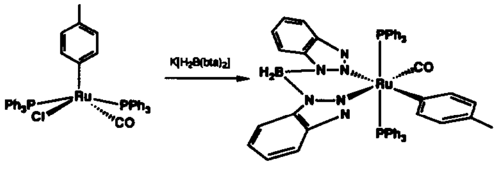
* Reference number with asterisk indicates a note in the list of references.



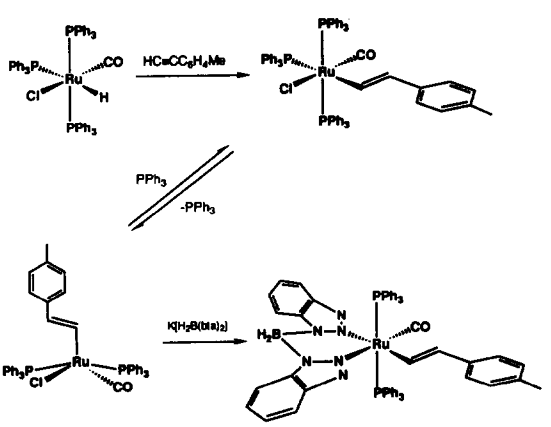
Scheme 3. Synthesis of [Ru(C_6H_4Me)(CO)(PPh_3)$_2${H_2B(bta)$_2$}].

nal carbonyl ligand even when the solution spectrum (CH_2Cl_2) is recorded under an atmosphere of CO. Migratory insertion, which would lead to a toluyl complex [Ru{C(O)C_6H_4Me-4}(CO)(PPh_3)$_2${H_2B(bta)$_2$}], appears not to occur readily in this system, reflecting the behaviour of the tris(pyrazolyl)borato complex [Ru(C_6H_4-Me-4)(CO){HB(pz)$_3$}] but in contrast to that of the parent complex [Ru(C_6H_4Me-4)Cl(CO)(PPh_3)$_2$], which undergoes addition of carbon monoxide to produce a tautomeric mixture of the complexes [Ru(C_6H_4Me-4)Cl(CO)$_2$(PPh_3)$_2$] and [Ru-{η^2-C(O)C_6H_4Me-4}Cl(CO)(PPh_3)$_2$] [7,18]. The infrared spectrum of **1** also shows a structured absorbance in the region 2390–2460 cm^{-1} which may be assigned to ν(BH_2) activity.

The ^{1}H NMR spectrum of the complex [Ru(C_6H_4Me-4)(CO)(PPh_3)$_2${H_2B (bta)$_2$}], while characteristic, is unremarkable other than in respect of the appearance of a broad resonance centred at *ca.* δ 3.6 ppm (half-height-width *ca.* 50 Hz). The broadness of this peak prevents the discernment of any AB-quartet fine-structure that might indicate a static non-planar RuN_4BH_2 metallacycle. However, the appearance of a singlet resonance in the ^{31}P NMR spectrum indicates that for a *trans* arrangement of the two phosphines, a fluxional metallacycle inversion process must operate to render the phosphine environments chemically equivalent. The alternative, and sterically less favoured, geometric isomer involving the mutually *cis* coordination of the two phosphines *trans* to the chelate might seem likely in view of the observed absence of migratory insertion of carbonyl and σ-tolyl ligands, but the ^{13}C NMR data for the related complex [Ru{C(C≡CPh)=CHPh} (CO)(PPh_3)$_2${H_2B(bta)$_2$}] (*vide supra*) shows twin resonances for each of the benzotriazolyl carbons, indicating chemically distinct environments. Furthermore, the virtual triplicity for the resonances of the phosphine phenyl substituents is indicative of mutually *trans* coordination.

The 4-methyl-*trans*-β-styryl complex [Ru(CH=CHC_6H_4Me-4)Cl(CO)(PPh_3)$_2$] was obtained by reaction of Vaska's ruthenium complex [RuClH(CO)(PPh_3)$_3$] [19*] with 4-ethynyltoluene by a procedure described by Santos and her colleagues for the corresponding phenyl-substituted complex [Ru(CH=CHPh)Cl(CO)(PPh_3)$_2$] [8] (Scheme 4). This red complex is formed as a mixture with the coordinatively saturated tris(phosphine) complex [Ru(CH=CHC_6H_4Me-4)Cl(CO)(PPh_3)$_3$], but the latter can be converted to the desired bis(phosphine) complex by crystallisation from a mixture of chloroform and ethanol or by ultrasonic trituration with diethyl ether.

Reaction of either the tris- or bis-(phosphine) complex with K[H_2B(bta)$_2$] gives the derivative [Ru(CH=CHC_6H_4Me-4)(CO)(PPh_3)$_2${H_2B(bta)$_2$}] (**2**) in high yield as the only organometallic product. Similar treatment of [Ru(CH=CH^nC_4H_9)-Cl(CO)(PPh_3)$_2$] gives [Ru(CH=CHC_4H_9)(CO)(PPh_3)$_2${H_2B(bta)$_2$}] (**3**).



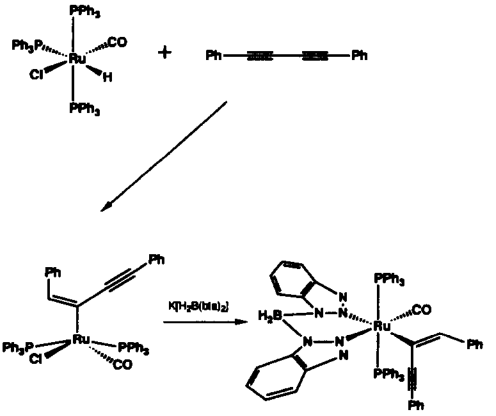
Scheme 4. Synthesis of [Ru(CH=CHC$_6$H$_4$Me)(CO)(PPh$_3$)$_2${H$_2$B(bta)$_2$}].

Reaction of [RuClH(CO)(PPh$_3$)$_3$] with diphenylbutadiyne leads to the α-phenylethynyl-*trans*-β-styryl complex [Ru{σ-C(C≡CPh)=CHPh}Cl(CO)(PPh$_3$)$_2$], which reacts with K[H$_2$B(bta)$_2$] to give [Ru{σ-C(C≡CPh)=CHPh}(CO)(PPh$_3$)$_2${H$_2$B(bta)$_2$}] (**3**) (Scheme 5).

Spectroscopic data for the σ-vinyl derivatives **2**–**4** are similar to those for the σ-tolyl complex; in particular each species gives rise to one singlet resonance in the ^{31}P NMR spectrum, a broad resonance at δ 3.6 ppm in the ^{1}H NMR spectrum, and a structured absorption centred at *ca.* 2440 cm^{-1} in the infrared spectrum. Characteristic spectroscopic data for the complexes **1**–**3** are listed in Tables 1–4.

Hydride and halide complexes

The complex [RuClH(CO)(PPh$_3$)$_3$] may be usefully viewed as synthetically equivalent to the metal ligand fragment "[RuH(CO)(PPh$_3$)$_2$]$^+$" by virtue of the lability of the phosphine and halide ligands. Thus reaction of [RuClH(CO)(PPh$_3$)$_3$] with K[H$_2$B(bta)$_2$] in dichloromethane gives the hydrido complex [RuH(CO)(PPh$_3$)$_2${H$_2$B(bta)$_2$}] in high yield (Scheme 6). The reaction proceeds cleanly for



Scheme 5. Synthesis of [Ru{C(C≡CPh)=CHPh}(CO)(PPh$_3$)$_2${H$_2$B(bta)$_2$}].

Table 1

Infrared data for the complexes: [**Ru**] = Ru(CO)(PPh_3)$_2${H_2B(bta)$_2$}

Compound	Infrared [a] (cm^{-1})		
	ν(CO)	ν(BH)	other
[**Ru**](C_6H_4Me-4) (**1**)	1955vs	2420w	1295w, 1271w, 1245w, 1214w, 1152m, 1131 m, 1070s, 865w, 842w, 800m
[**Ru**](CH=CHC_6H_4Me-4) (**2**)	1958vs	2438w	1297w, 1263w, 1188w, 1158m, 1148m, 1134m, 1077m, 851w
[**Ru**](CH=CHC_4H_9) (**3**)	1952vs	2436w	1298w, 1274w, 1243w, 1160m, 1149m, 1139m, 1109m, 1075m, 850w
[**Ru**]{C(C≡CPh)=CHPh} (**4**)	1975vs	2440	2157m (ν(C≡C)), 1583m, 1295w, 1272w, 1242w, 1155m, 1145m, 1131m, 1105w, 1075m, 910w, 870w
[**Ru**]H (**5**)	1939vs	2427w	1292w, 1270w, 1242w, 1212w, 1160m, 1138m, 1108m, 1077s, 930w, 918w, 878w, 848w
[**Ru**]Cl (**6**)	1991vs 1974m 1967m [b]	2417w	1300w, 1270w, 1262m, 1160m, 1150m, 1139m, 1109m, 1079m, 910w, 870w, 320w (ν(RuCl))

[a] Data were obtained for Nujol mulls between KBr discs in the range 4000–400 cm^{-1}, infrared data characteristic of triphenylphosphine ligands not listed. [b] Solid-state splitting, ν(CO) (CH_2Cl_2) 1989 cm^{-1}.

Table 2

FAB Mass spectroscopic data [a] for the new complexes: [**Ru**] = Ru(CO)(PPh_3)$_2${H_2B(bta)$_2$}

Compound	M_{max} (Intensity (%)) [Assignment]
[**Ru**](C_6H_4Me-4) (**1**)	994 (2.3)$[M]^+$, 903 (1.9) $[M - C_7H_7]$, 807 (13.6) $[M - HPPh_2]^+$, 745 (9.3) $[M - H_2B(bta)_2]^+$, 716 (3.3) $[Ru(C_7H_7)(PPh_3)_2]^+$, 625 (6.8) $[Ru(PPh_3)_2]^+$, 584 (9.9) $[?]^+$, 545 (12.0) $[M - HPPH_2 - PPh_3]^+$, 455 $[Ru(C_7H_8)(PPh_3)]^+$, 363 (30.8) $[RuPPh_3]^+$, 263 (32.0) $[HPPh_3]^+$
[**Ru**](CH=CHC_6H_4Me-4) (**2**)	1019 (3.3) $[M]^+$, 902 (1.7) $[M - C_6H_9]^+$, 770 (1.1) $[M - H_2B(bta)_2]^+$, 741 (1.0) $[Ru(C_9H_9)(PPh_3)_2]^+$, 625 (6.9) $[Ru(PPh_3)_2]^+$, 571 (2.0) $[M - HPPh_2 - PPh_3]^+$, 480 (16.4) $[Ru(C_9H_9)(PPh_3)]^+$, 363 (44.0) $[RuPPh_3]^+$
[**Ru**](CH=CHC_4H_9) (**3**)	985 (0.2) $[M]^+$, 902 (0.2) $[M - C_6H_{11}]^+$, 736 (0.2) $[M - H_2B(bta)_2]^+$, 708 (0.2) $[Ru(C_6H_{11})(PPh_3)_2]^+$, 625 (1.3) $[Ru(PPh_3)_2]^+$, 537 (0.8) $[Ru(C_6H_{11})(PPh_3)]^+$, 363 (7.0) $[RuPPh_3]^+$
[**Ru**]{C(C≡CPh)=CHPh} (**4**)	1106 (1.6) $[M]^+$, 919 (7.2) $[?]^+$, 857 (6.7) $[M - H_2B(bta)_2]^+$, 826 (0.8) $[M - H_2B(bta)_2 - CO]$, 716 (31.3) $[?]^+$, 583 (14.4) $[?]^+$, 489 (9.9) $[?]^+$, 363 (21.6) $[RuPPh_3]^+$, 262 (36.8) $[HPPh_3]^+$
[**Ru**]H (**5**)	903 (52.5) $[M - H]^+$, 655 (44.4) $[M - H_2B(bta)_2]^+$, 625 (18.9) $[Ru(PPh_3)_2]^+$, 547 (20.0) $[?]^+$, 363 (50.8) $[RuPPh_3]^+$, 263 (100) $[HPPh_3]^+$
[**Ru**]Cl (**6**)	938 (0.2) $[M]^+$, 690 (1.8) $[M - H_2B(bta)_2]^+$, 626 (0.3)$[Ru(PPh_3)_2]^+$

[a] Data collected from solutions of the complexes in nitrobenzyl alcohol. Isotope patterns consistent with formulation of $[M]^+$.

Table 3

$^{31}P\{^1H\}$ and ^1H NMR data for the complexes [a]: **[Ru]** = $Ru(CO)(PPh_3)_2\{H_2B(bta)_2\}$

Compound	$^{31}P\{^1H\}$ [b]	^1H (δ) [c]
[Ru](C_6H_4Me-4) (**1**)	28.5	2.32 [s, 3H, $C_6H_4CH_3$], *ca.* 3.7 [s(v.br.), 2H, BH_2], 6.55, 6.65, 6.91, 7.11, 7.29, 7.49, 7.68, 7.92 [m × 8, 42H, PC_6H_5, $C_6H_4CH_3$ and $C_6H_4N_3$]
[Ru]($CH{=}CHC_6H_4Me$-4) (**2**)	29.4	2.35 [2, 3H, $C_6H_3CH_3$], *ca.* 3.55 [s(v.br), 2H, BH_2], 5.78 [d, 1 H, $RuCH{=}CH$, J (HH) 17.1], 6.63–6.86 [m, 46H, PC_6H_5, CC_6H_4Me and $C_6H_4N_3$], 8.86 [dt, 1H, $P_2RuCH{=}CH$, J (HH) 17.1, J (PH) 23.0]
[Ru]($CH{=}CHC_4H_9$) (**3**)	29.0	0.84 [t, 3H, CH_3, J (HH) 7.0], 1.00–1.27 [m, 4H, $CH_2CH_2CH_3$] 1.97 [m, 2H, $CHCH_2CH_2$], 3.50 [s(v.br), 2H, BH_2], 4.83 [dt, 1H J (allyl) 6.43, J (vinyl) 16.1 $RuCH{=}CHCH_2$], 6.89–7.75 [m, 39 H, $RuCH{=}CH$, PC_6H_5 and $C_6H_4N_3$]
[Ru]{$C(C{\equiv}CPh){=}CHPh$} (**4**)	28.1	*ca.* 3.7 [s(v.br.), 2H, BH_2], 6.87, 7.06, 7.19, 7.31, 7.57, 7.67, 7.83 [m × 7, 47H, PC_6H_5, CC_6H_5, $C_6H_4N_3$ and CHC_6H_5]
[Ru]H (**5**)	45.0	−8.6 [t, 1H, J(PH) 20.8], *ca.* 3.7 [s(v.br.), 2H, BH_2], 7.03, 7.29,7.68, 7.81 [m × 4, 38H, PC_6H_5 and $C_6H_4N_3$]
[Ru]Cl (**6**)	23.1	3.6 [s(v.br), 2H, BH_2], 6.83–7.86 [m, 42H, PC_6H_5 and $C_6H_4N_3$]

[a] From saturated solutions of the complex in $CDCl_3$ at ambient temperature. Chemical shifts are given in ppm, coupling constants in Hz. [b] Relative to external H_3PO_4 (δ 0.00). [c] Relative to internal $SiMe_4$ (δ 0.00).

the preparation of small amounts (0.1–0.5 mmol) of the complex but for larger quantities the precipitation of a sparingly soluble intermediate inhibits completion of the reaction and necessitates the use of impractically large quantities of solvent. It is therefore more convenient for large scale preparations to use the bis(acetonitrile) salt $[RuH(NCMe)_2(CO)(PPh_3)_2]BF_4$ [20] which upon treatment with $K[H_2B(bta)_2]$ gives the desired complex **5**.

The coordination geometry of the hydrido derivative $[RuH(CO)(PPh_3)_2\{H_2B(bta)_2\}]$ (**5**) can be derived from the ^1H and ^{31}P NMR data: The hydride resonance appears as a triplet at δ 11.48 ppm (J(PH) 21 Hz), indicating chemically equivalent phosphorus environments, and this is confirmed by the appearance of a single resonance in the ^{31}P NMR at δ 45.0 ppm.

It is appropriate to speculate on the nature of the intermediate formed in the synthesis of **5**. Two plausible species are shown in Scheme 7, both of which might be expected to show limited solubility. The first involves the coordination of a triphenylphosphine ligand that is ultimately lost upon ring closure of the chelate. The alternative ionic possibility, which is perhaps the more likely, involves the monodentate coordination of the dihydrobis(benzotriazolyl)borate in place of one of the phosphines in the precursor. The loss of potassium chloride from this species then allows metallacyclisation to **5**. Either alternative involves monodentate coordination through a benzotriazole ring, and a precedent for this type of coordination was provided recently by the isolation of benzotriazole [21] and 2,1,3-benzothiadiazole [22] complexes of the $[RuClH(CO)(PPh_3)_2]$ fragment. The type of monodentate coordination which we propose here is possibly significant in

Table 4

$^{13}C\{^1H\}$ NMR data for the complexes [a]: [**Ru**] = $Ru(CO)(PPh_3)_2\{H_2B(bta)_2\}$

Compound	$^{13}C\{^1H\}$ (δ)
[**Ru**](C_6H_4Me-4) (1)	206.3 [t, J(PC) 14.5, RuCO], 147.9 [t, J(PC) 11.6, $C^1(C_6H_4Me)$], 146.4, 145.9 [$C_6H_4N_3$], 145.6, 143.1 [br, $C^{2,3,5,6}(C_6H_4Me)$], 138.7, 138.0 [$C_6H_4N_3$], 134.0 [t, J(PC) 5.1, $C^{2,6}(PC_6H_5)$], 132.3 [t, J(PC) 21, $C^4(PC_6H_5)$] 130.4 [$C^4(C_6H_4Me)$], 128.8 [$C^4(PC_6H_5)$], 126.9 [t, J(PC) 4.6, $C^{3,5}(PC_6H_5)$], 126.5, 124.9, 123.3, 122.7, 118.4, 117.0, 113.1, 112.2 [$C_6H_4N_3$], 20.7 [CH_3]
[**Ru**](CH=CHC_6H_4Me-4) (2)	206.4 [t, J(PC) 15.2, RuCO], 156.0 [t(br), Ru*C*H=CH], 146.3 145.4 [$C^{2,2'}(C_6H_4N_3)$, 139.2, 138.6 [$C^{1,1'}(C_6H_4N_3)$], 133.8 [vt, J(PC) 5.0, $C^{2,6}(PC_6H_5)$], 132.1 [vt, J(PC) 21.2, $C^1(PC_6H_5)$], 128.8 [$C^4(PC_6H_5)$], 127.0 [vt, J(PC) 4.4, $C^{3,5}(PC_6H_5)$], 126.0, 125.1, 123.3, 122.7, 118.2, 117.2, 112.8, 112.4 [$C_6H_4N_3$], 130.4 [$C^4(C_6H_4Me)$], 138.1, 137.2 [br, $C^{2,3,5,6}(C_6H_4Me)$], 21.2 [CH_3]
[**Ru**](CH=CHC_4H_9) (3)	206.6 [t, J(PC) 15.0, RuCO], 146.4, 145.5 [$C^{2,2'}(C_6H_4N_3)$], 145.2 t, J(PC) 12.8, Ru*C*H=CH], 140.3 [s(br), RuCH=*C*H], 138.7, 138.1 [$C^{1,1'}(C_6H_4N_3)$], 133.9 [vt, J(PC) 5.2, $C^{2,6}(PC_6H_5)$], 132.7 [vt, J(PC) 21.1, $C^1(PC_6H_5)$], 128.8 [$C^4(PC_6H_5)$], 126.8 [vt, J(PC) 4.3, $C^{3,5}(PC_6H_5)$], 126.0, 124.9, 123.2, 122.6, 118.0, 117.2 [$C_6H_4N_3$], 39.0 [s, $CH_2C_3H_7$], 31.8 [$CH_2C_2H_5$], 22.6 [CH_2CH_3, 14.1 [CH_3]
[**Ru**]{C(C≡CPh)=CHPh} (4)	205.2 [t, J(PC) 14.5, RuCO], 146.5, 146.2 [$C^{2,2'}(C_6H_4N_3)$], 140.1 [$C^{1,1'}(C_6H_5)$], 138.5, 138.3 ($C_6H_4N_3$), 133.9 [s(br), $C^{2,6}(PC_6H_5)$], 131.9 [t, J(PC) 21.2, $C^1(PC_6H_5)$], 129.0 [s, $C^4(PC_6H_5)$], 127.1 [t, J(PC) 4.8, $C^{3,5}(PC_6H_5)$], 127.7, 127.5, 127.3, 126.3, 126.2, 125.9, 125.4 [$C_6H_4N_3$], 124.6, 123.2 [C_6H_5 and CHC_6H_5], 118.0, 117.3 [$C_6H_4N_3$], 103.0, 101.0 [C≡C]
[**Ru**]H (5)	204.9 [t, J(PC) 15.2, RuCO], 146.2, 145.9 [$C^{2,2'}(C_6H_4N_3)$], 138.1[$C^{1,1'}(C_6H_4N_3)$] 133.6 [vt, J(PC) 6.0, $C^{2,6}(PC_6H_5)$], 129.0 [s, $C^4(PC_6H_5)$], 127.3 [vt, J(PC) 4.8, $C^{3,5}(PC_6H_5)$], 125.5, 125.1, 122.7, 117.6, 117.3, 112.4 [$C_6H_4N_3$]
[**Ru**]Cl (6)	203.2 [t, J(PC) 13.8, RuCO], 146.4, 146.0 [$C^{2,2'}(C_6H_4N_3)$], 138.7, 138.4 [$C^{1,1'}(C_6H_4N_3)$], 133.9 [vt, J(PC) 5.2, $C^{2,6}(PC_6H_5)$], 131.2 vt, J(PC) 22.0, $C^1(C_6H_5)$], 129.3 [s, $C^4(PC_6H_5)$], 127.2 [vt, J(PC) 4.4, $C^{3,5}(PC_6H_5)$], 126.4, 125.4, 123.4, 123.2, 118.8, 116.5, 112.5, 111.8 [$C_6H_4N_3$]

[a] From saturated solutions of the complex in $CDCl_3$ at ambient temperature. Chemical shifts are given relative to internal $CDCl_3$ (δ 77.0 ppm), coupling constants in Hz.

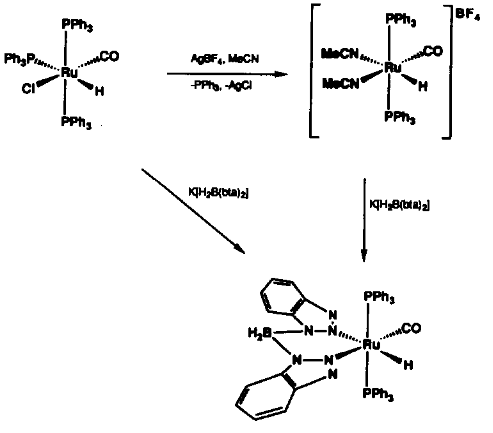
the large number of reactions of poly(pyrazolyl)borates with transition metal halides that lead to cleavage of the borate chelate and isolation of pyrazole complexes [2].

The hydride complex **5** is a convenient precursor for the synthesis of the chloride derivative via the smooth reaction with *N*-chlorosuccinimide: Thus treatment of a suspension of **5** in ether with *N*-chlorosuccinimide gives succinimide and the chloride complex $[RuCl(CO)(PPh_3)_2\{H_2B(bta)_2\}]$ (**6**) in good yield. This electrophilic chlorination of the metal hydride complex can be extended to the synthesis of the other halides (except fluoride) from *N*-halogenosuccinimides, and provides a clean alternative to the more common haloform route (Scheme 8).

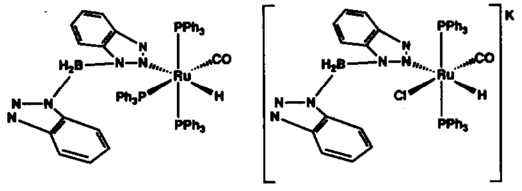
Experimental

General procedures

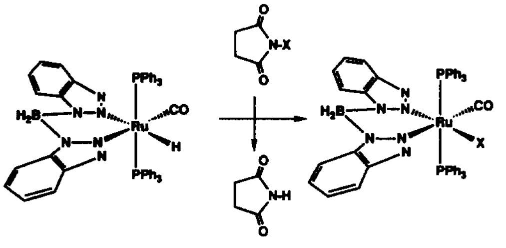
All distillations and manipulations were carried out under pre-purified nitrogen by conventional Schlenk-tube techniques. Dichloromethane was dried over and distilled from calcium hydride and purged with nitrogen prior to use. The compounds $[RuRCl(CO)(PPh_3)_2]$ ($R = C_6H_4Me$-4 [18], $CH{=}CHC_6H_4Me$-4 [8] and $C(C{\equiv}CPh){=}CHPh$ [9]), $[RuClH(CO)(PPh_3)_3]$ [19] and $[RuH(NCMe)_2(CO)(PPh_3)_2]BF_4$ [20], and $K[H_2B(bta)_2]$ [3] have been described elsewhere. ^1H, ^{31}P and ^{13}C-$\{^1H\}$ NMR spectra were recorded on either a Bruker WH-400 or Perkin-Elmer R34 NMR spectrometer. (The assistance of O.W. Howarth and the University of Warwick NMR service is gratefully acknowledged.) FT-Infrared data were re-



Scheme 6. Synthesis of $[RuH(CO)(PPh_3)_2\{H_2B(bta)_2\}]$.



Scheme 7. Possible intermediates in the synthesis of complex 4.



Scheme 8. Synthesis of $[RuX(CO)(PPh_3)_2\{H_2B(bta)_2\}]$ (X = Cl, Br, I).

corded on a Perkin–Elmer 1720-X instrument. FAB Mass spectra were obtained from nitrobenzyl alcohol solutions with a Kratos MS80 mass spectrometer. Light petroleum refers to the fraction of b.p. 40–60°C. Spectroscopic data for the new complexes are listed in Tables 1–4.

Syntheses

$[Ru(C_6H_4Me\text{-}4)(CO)(PPh_3)_2\{H_2B(bta)_2\}]$ (1). To a suspension of $[Ru(C_6H_4Me\text{-}4)Cl(CO)(PPh_3)_2]$ (0.50 g, 0.64 mmol) in dichloromethane (50 cm^3) was added solid $K[H_2B(bta)_2]$ (0.20 g, 0.69 mmol). The mixture was stirred until the original red colour had completely disappeared and the complex had completely dissolved. Light petroleum (50 cm^3) was added to the suspension to complete the precipitation of KCl and the mixture filtered through Celite. The volume of the filtrate was reduced *in vacuo*, resulting in the formation of white crystals of $[Ru(C_6H_4Me\text{-}4)(CO)(PPh_3)_2\{H_2B(bta)_2\}]$, which were filtered off and washed with light petroleum (2 × 20 cm^3). The product could be recrystallised from dichloromethane/petroleum at −30°C as a dichloromethane hemisolvate (as indicated by ^1H NMR spectroscopy). Yield: 0.45 g (70%). M.p.: 208–210°C. Anal. Found: C, 65.43; H, 4.62; N, 9.08. $C_{56}H_{47}BN_6OP_2Ru \cdot 0.5CH_2Cl_2$ calc.: C, 65.48; H, 4.67; N, 8.11%.

$[Ru(CH{=}CHC_6H_4Me\text{-}4)(CO)(PPh_3)_2\{H_2B(bta)_2\}]$ (2), $[Ru(CH{=}CHC_4H_9)(CO)(PPh_3)_2\{H_2B(bta)_2\}]$ (3) and $[Ru\{C(C{\equiv}CPh){=}CHPh\}(CO)(PPh_3)_2\{H_2B(bta)_2\}]$ (4). Compounds **2–4** were prepared analogously from the compounds $[Ru(CH{=}CHC_6H_4Me\text{-}4)Cl(CO)(PPh_3)_2]$, $[Ru(CH{=}CHC_4H_9)Cl(CO)(PPh_3)_2]$ and $[Ru\{C(C{\equiv}CPh){=}CHPh\}Cl(CO)(PPh_3)_2]$: (**2**) Yield: 0.51 g (83%). M.p. 202–204°C. (**3**) Yield: 0.55 g (86%). M.p. 214–216°C. (**4**) Yield: 0.51 g (83%). M.p. 200–202°C, Anal. Found: C, 67.62; H, 4.57; N, 7.70. $C_{65}H_{57}BN_6OP_2Ru \cdot 0.5CH_2Cl_2$ calc.: C, 68.50; H, 4.56; N, 7.32%.

$[RuH(CO)(PPh_3)_2\{H_2B(bta)_2\}]$ (5). (a) A suspension of $[RuClH(CO)(PPh_3)_3]$ (0.50 g, 0.53 mmol) in dichloromethane (50 cm^3) was treated with a slight excess of solid $K[H_2B(bta)_2]$ (0.16 g, 0.55 mmol) and the mixture was stirred for 24 h, after which the hydride had dissolved. Light petroleum (50 cm^3) was added to the suspension to complete the precipitation of KCl and the mixture filtered through diatomaceous earth. The volume of the filtrate was reduced *in vacuo*, resulting in the formation of white crystals of $[RuH(CO)(PPh_3)_2\{H_2B(bta)_2\}]$ (**5**), which were filtered off and washed with light petroleum (2 × 20 cm^3). The product could be recrystallised from dichloromethane/petroleum at −30°C. Yield: 0.30 g (61%). M.p. 223–225°C. Anal. Found: C, 64.90; H, 4.53; N, 9.27. $C_{49}H_{41}N_6OBP_2Ru$ calc.: C, 65.12; H, 4.57; N, 9.30%.

(b) To a solution of $[RuH(NCMe)_2(CO)(PPh_3)_2]BF_4$ (0.25 g, 0.30 mmol) in dichloromethane (50 cm^3) was added solid $K[H_2B(bta)_2]$ (0.10 g, 0.35 mmol) and the mixture was stirred for 24 h. Light petroleum (50 cm^3) was added to the suspension to complete the precipitation of KCl, and the mixture filtered through diatomaceous earth. The volume was reduced *in vacuo*, resulting in formation of white crystals of $[RuH(CO)(PPh_3)_2\{H_2B(bta)_2\}]$ (**4**), which were filtered off and washed with light petroleum (2 × 20 cm^3). The product could be recrystallised from dichloromethane/petroleum at −30°C. Yield: 0.25 g (91%). M.p.: 223–224°C.

$[RuCl(CO)(PPh_3)_2\{H_2B(bta)_2\}]$ (6). To a suspension of $[RuH(CO)(PPh_3)_2\{H_2B(bta)_2\}]$ (**5**) (0.18 g, 0.20 mmol) in diethyl ether (20 cm^3) was added *N*-chloro-

succinimide (0.045 g, 0.25 mmol) and the mixture was stirred for 2 h. The yellow precipitate was filtered off and washed twice with diethyl ether (2×20 cm^{-3}) to remove succinimide. The residue was recrystallised from a mixture of dichloromethane and ethanol. Yield 0.16 g (88%).

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