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Preliminary communication

Synthesis of organometallic hydrotris(pyrazol-1-yl)boratoruthenium(II) complexes

Anthony F. Hill
Department of Chemistry, University of Warwick, Coventry CV4 7AL (U.K.)

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Abstract

The reactions of K[HB(pz)$_3$] (pz = pyrazol-1-yl) with the coordinatively unsaturated σ-vinyl complexes [Ru(CR=CHR)Cl(CO)(PPh$_3$)$_2$] (R = H, Me, C$_6$H$_5$) proceed with loss of a chloride and a phosphine ligand to provide the compounds [Ru(CR=CHR)(CO)(PPh$_3$){HB(pz)$_3$}] in high yield. Similar treatment of the complex [Ru(C$_6$H$_4$Me-4)Cl(CO)(PPh$_3$)$_2$] leads to the related σ-aryl derivative [Ru(C$_6$H$_4$Me-4)(CO)(PPh$_3$){HB(pz)$_3$}] whilst the complex [RuClH(CO)(PPh$_3$)$_3$] treated successively with diphenylbutadiyne and K[HB(pz)$_3$] provides the unusual derivative [Ru{C(C≡CPh)=CHPh}(CO)(PPh$_3$){HB(pz)$_3$}].

The rapid expansion in research into the coordination chemistry of poly(pyrazol-1-yl)borates has focussed on the first row transition metals and Group 6 [1]. The chemistry of hydrotris(pyrazol-1-yl)borato complexes of the second and third transition series and in particular that of Group 8 [2–6] remains underdeveloped, though for no obvious reason. This report describes a facile and high yielding entry into organometallic hydrotris(pyrazol-1-yl)boratoruthenium chemistry.

The 16-electron σ-*Z*-vinyl complexes [Ru(CR=CHR)Cl(CO)(PPh$_3$)$_2$] (R = H, Me, C$_6$H$_5$) are readily obtained in high yield via the insertion of the appropriate disubstituted alkyne into the ruthenium hydride bond of [RuClH(CO)(PPh$_3$)$_3$] [7]. Treating bright red solutions (dichloromethane or tetrahydrofuran) of these complexes with K[HB(pz)$_3$] results in slow decolourisation and formation of the colourless 6-coordinate compounds [Ru(CR=CHR)(CO)(PPh$_3$){HB(pz)$_3$}] [R = H (**1**), Me (**2**), C$_6$H$_5$ (**3**)]. Addition of hexane completes precipitation of potassium chloride and the products are obtained in high yield by concentrating the solvent mixture under reduced pressure. Because the syntheses of the vinylruthenium precursors are high yielding and produce no major side products which react with K[HB(pz)$_3$] it is also possible to prepare the complexes **1**–**3** in "one pot" starting from the hydridoruthenium complex [RuClH(CO)(PPh$_3$)$_3$] and the appropriate alkyne.

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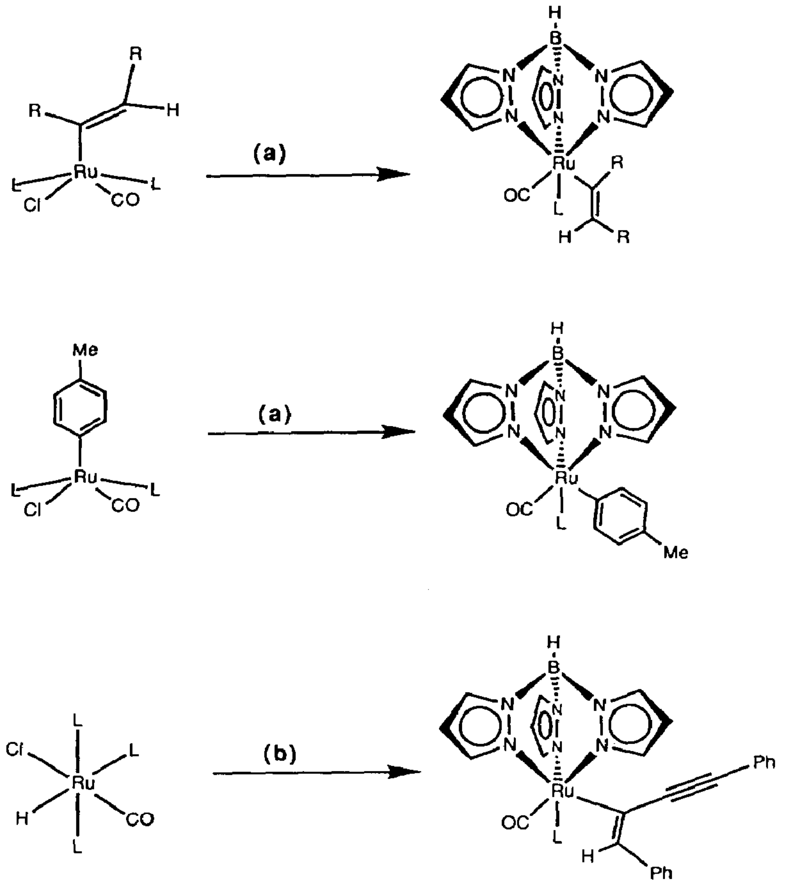
Table 1

Spectroscopic data; [Ru] = $\mathrm{Ru(CO)(PPh_3)\{HB(pz)_3\}}$

Compound	Infrared [a] ($\mathrm{cm^{-1}}$)		NMR [b] ^{1}H (δ)
	ν(CO)	ν(BH)	
[Ru]($\mathrm{CH{=}CH_2}$) (**1**)	1927vs	2500s	5.44, 5.52 [m×2, 3H, $\mathrm{C}H\mathrm{C}H_2$], 6.05, 6.24, 6.73, 6.80 [m×4, 3H, $\mathrm{C_3}H_3\mathrm{N_2}$], 7.21, 7.57, 7.68, 7.84 [m×4, 21H, $\mathrm{C_6}H_5$ and $\mathrm{C_3}H_3\mathrm{N_2}$]
[Ru](CMe=CHMe) (**2**)	1921vs	2458w	1.58 [s, 3H, $\mathrm{RuCC}H_3$], 1.64 [d, 3H, $\mathrm{{=}CHC}H_3$, J(HH) 7 Hz], 4.92 [q, 1H, $\mathrm{C}H\mathrm{CH_3}$, J(HH) 7 Hz], 5.89, 6.15, 6.79, 6.86 [m×4, 3H, $\mathrm{C_3}H_3\mathrm{N_2}$], 7.25, 7.66 [m×2, $\mathrm{C_6}H_4$ and $\mathrm{C_3}H_3\mathrm{N_2}$].
[Ru](CPh=CHPh) (**3**)	1940vs	2450w	5.35 [s(br), 1H, $\mathrm{C}H\mathrm{Ph}$], 5.66, 5.83, 6.03, 6.15, 6.22, 7.02, 7.26, 7.55, 7.65, 7.96, 8.04 [m×11, 34H, $\mathrm{C_6}H_5$ and $\mathrm{C_3}H_3\mathrm{N_2}$]
[Ru]($\mathrm{C_6H_4Me}$-4) (**4**)	1941vs	2462w	2.26 [s, 3H, $\mathrm{C}H_3$], 5.90, 5.94, 6.04 [m×3, 3H, $\mathrm{C_3}H_3\mathrm{N_2}$] 6.59, 6.90, 7.18, 7.39, 7.63, 7.68, 7.79 [m×6, 25H, $\mathrm{C_6}H_5$ and $\mathrm{C_3}H_3\mathrm{N_2}$]

[a] Data were obtained from Nujol mulls between KBr discs in the range 4000–400 $\mathrm{cm^{-1}}$. [b] From saturated solutions of the complex in $\mathrm{CDCl_3}$ at ambient temperature, chemical shifts (δ) in ppm relative to internal $\mathrm{Me_4Si}$ (δ 0.00). All complexes gave satisfactory elemental microanalyses (C, H, and N).



Scheme 1. Hydrotris(pyrazol-1-yl)boratoruthenium(II) complexes (a) + K[HB(pz)]$_3$, −KCl, −PPh$_3$; (b) PhC≡CC≡CPh, + K[HB(pz)$_3$], −KCl, −2 PPh$_3$. L = PPh$_3$; R = H, Me, C_6H_5.

The pale yellow or white complexes show one CO-associated infrared absorbance [e.g., **1**: 1927 cm^{-1} (Nujol)] in addition to bands typical of phosphine and hydrotris(pyrazol-1-yl)borate ligands (Table 1). The borohydride moiety is particularly evident, with a band being observed in the region 2450–2500 cm^{-1}. The molecular composition was confirmed by FAB-EI mass spectrometry (nitrobenzyl alcohol) with peaks being observed in all cases for the molecular ions in addition to those for sequential loss of the vinyl, carbonyl, borate and phosphine ligands.

The class of compounds **1**–**3** was extended to include σ-aryl derivatives by employing the corresponding complex [Ru(C_6H_4Me-4)Cl(CO)(PPh$_3$)$_2$] [8]. Treating the latter with K[HB(pz)$_3$] provided [Ru(C_6H_4Me-4)(CO)(PPh$_3$){HB(pz)$_3$}] (**4**) as colourless air-stable crystals. Spectroscopic data (Table 1) indicate that the compound **4** is analogous to **1**–**3**.

The molecular geometry of this class of compounds was confirmed by a crystal structure determination of the unusual *Z*-α-(phenylethynyl)-β-styryl derivative obtained by treating the hydrido complex [RuClH(CO)(PPh$_3$)$_3$] successively with diphenylbutadiyne and the salt K[HB(pz)$_3$] [9].

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