

SYNTHESIS OF BINUCLEAR HYDROXO- AND ALKOXO-BRIDGED ARENE COMPLEXES OF RUTHENIUM(II) AND OSMIUM(II)

T. ARTHUR, D.R. ROBERTSON, D.A. TOCHER and T.A. STEPHENSON *

Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ (Great Britain)

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Summary

Reactions of aqueous solutions of $[\{M(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2]$ ($M = \text{Ru, Os}$) with an excess of either NaOH or Na_2CO_3 followed by addition of NaBPh_4 gave as the major product $[\eta\text{-C}_6\text{H}_6(\text{OH})M(\text{OH})_2M(\text{H}_2\text{O})(\eta\text{-C}_6\text{H}_6)]\text{BPh}_4$ together with some $[(\eta\text{-C}_6\text{H}_6)M(\text{OH})_3M(\eta\text{-C}_6\text{H}_6)]\text{BPh}_4$. Recrystallisation from acetone then gave pure samples of $[\text{M}_2(\eta\text{-C}_6\text{H}_6)_2(\text{OH})_3]\text{BPh}_4\text{Me}_2\text{CO}$. Reaction of other $[\{\text{Ru}(\eta\text{-arene})\text{Cl}_2\}_2]$ with NaOH or Na_2CO_3 gave only the $[\text{Ru}_2(\eta\text{-arene})_2(\text{OH})_3]^+$ cations (arene = $p\text{-MeC}_6\text{H}_4\text{CHMe}_2$, $\text{C}_6\text{H}_3\text{Me}_3$, C_6Me_6). Similarly, treatment of $[\{M(\eta\text{-arene})\text{Cl}_2\}_2]$ with NaOR/ROH and NaBPh_4 gave the triple alkoxo-bridged complexes $[\text{M}_2(\eta\text{-arene})_2(\text{OR})_3]\text{BPh}_4$ ($M = \text{Ru, R} = \text{Me, Et, Ph}$; arene = C_6H_6 ; $M = \text{Ru, R} = \text{Me}$, arene = $\text{C}_6\text{H}_3\text{Me}_3$, C_6Me_6 ; $M = \text{Os, R} = \text{Me}$; arene = C_6H_6). These compounds can also be synthesised by reaction of $[\text{Ru}_2(\eta\text{-C}_6\text{H}_6)_2(\text{OH})_3]\text{BPh}_4 \cdot \text{Me}_2\text{CO}$ with ROH ($\text{R} = \text{Me, Et}$).

As an extension of our studies on the synthesis of compounds containing $-\text{RuX}_3\text{Ru}-$ bridging units ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$) [1] we present in this paper the full results [2] of our attempts to prepare and characterise binuclear η -arene-ruthenium(II) complexes containing hydroxo and alkoxo bridging ligands.

Results and discussion

a) Synthesis of binuclear hydroxo-bridged complexes

Maitlis and Kang [3] have previously shown that reaction of $[\{\text{Rh}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_2\}_2]$ with aqueous sodium hydroxide gave the triple hydroxo-bridged complex $[\text{Rh}_2(\eta\text{-C}_5\text{Me}_5)_2(\text{OH})_3]\text{Cl} \cdot 4 \text{H}_2\text{O}$ which was also isolated as its tetraphenylborate salt by addition of a methanolic solution of NaBPh_4 to a methanolic solution of the chloride salt. The reactions of the isoelectronic $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2]$ (I) compound with aqueous NaOH has also been investigated by Zelonka and Baird [4], but was reported to give unstable compounds whose formation

and decomposition could only be followed by ^1H NMR spectroscopy. Thus, "addition of NaOH to D_2O solutions of I gave new species with ^1H NMR signals at δ 5.43 and 5.58 ppm which readily decomposed as suggested by the appearance of the resonance of free benzene".

However, we have found that reaction of an aqueous solution of I with an excess of NaOH gave, on warming, a yellow solution from which a yellow solid (II) could be precipitated by addition of NaBPh_4 . The mull IR spectrum of II contained two $\nu(\text{OH})$ stretching vibrations at 3615 and 3520 cm^{-1} with a shoulder at 3530 cm^{-1} (cf. $[\{\text{Pd}(\text{OH})(\text{PPh}_3)_2\}_2](\text{BF}_4)_2$, $\nu(\text{OH})$ 3590 cm^{-1} [5]; $[\text{Rh}_2(\eta\text{-C}_5\text{Me}_5)_2(\text{OH})_3]\text{BPh}_4$, $\nu(\text{OH})$ 3600 cm^{-1} [3]). On recrystallisation from acetone, the IR spectrum of the product showed only one $\nu(\text{OH})$ band at 3530 cm^{-1} and good evidence for acetone of solvation ($\nu(\text{CO})$ 1695 cm^{-1}). The ^1H NMR spectrum at 298 K of the initial solid II in either $(\text{CD}_3)_2\text{CO}$ or CD_3NO_2 contained a strong resonance at δ 5.33 ppm and a weak one at δ 5.56 ppm (relative intensity ca. 6 : 1) attributable to $\eta\text{-C}_6\text{H}_6$ ligands (cf Zelonka and Baird's observation [4]). In addition to BPh_4^- resonances (δ 6.9–7.70 ppm) there was a broad weak resonance at δ 2.60 ppm which probably arises from the hydroxo protons*. In support of this conclusion, loss of this latter signal occurred on standing, probably because of facile H/D exchange with the solvent (cf. similar observations for $[\{\text{M}(\text{OH})(\text{PR}_3)_2\}_2](\text{BF}_4)_2$ ($\text{M} = \text{Pd}, \text{Pt}$) [5] and $[\text{Rh}_2(\eta\text{-C}_5\text{Me}_5)_2(\text{OH})_3]\text{BPh}_4$ [3]). The $^{13}\text{C}\text{-}\{^1\text{H}\}$ NMR spectrum of II in CD_3NO_2 also showed two $\eta\text{-C}_6\text{H}_6$ resonances at δ 77.8 (strong) and 79.4 (weak) ppm. The product recrystallised from acetone showed one $\eta\text{-C}_6\text{H}_6$ resonance at δ 5.56 ppm when its ^1H NMR spectrum was run in CD_3NO_2 at 298 K, and one $^{13}\text{C}\text{-}\{^1\text{H}\}$ NMR resonance at δ 79.4 ppm.

The same solid II was precipitated if an aqueous solution of $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{-Cl}_2\}_2]$ was treated with an excess of Na_2CO_3 and then NaBPh_4 added to the solution. By using D_2O rather than H_2O , this method afforded a good synthetic route to the corresponding deuterioxo product. This deuterated material provided further evidence for the assignment of the IR bands in II at ca 3600 cm^{-1} to $\nu(\text{OH})$ vibrations since these were absent in the former, being replaced by bands at 2595 and 2670 cm^{-1} which could be attributed to $\nu(\text{OD})$ stretching vibrations (cf. $[\{\text{Pt}(\text{OD})(\text{PPh}_3)_2\}_2](\text{BF}_4)_2$ ($\nu(\text{OD})$ 2650 cm^{-1}) [5], $[\text{Rh}_2(\eta\text{-C}_5\text{Me}_5)_2(\text{OD})_3]\text{BPh}_4$ ($\nu(\text{OD})$ 2450 cm^{-1}) [3]).

Furthermore, on leaving II in $(\text{CD}_3)_2\text{CO}$, precipitation of some yellow solid slowly occurred and the IR spectrum of this solid showed bands at 2600 cm^{-1} ($\nu(\text{OD})$), 3530 cm^{-1} ($\nu(\text{OH})$) and solvent $(\text{CD}_3)_2\text{CO}$ ($\nu(\text{CO})$ 1695 cm^{-1}). The ^1H NMR spectrum of the material in CD_3NO_2 contained one strong $\eta\text{-C}_6\text{H}_6$ resonance at δ 5.56 ppm.

Thus, all this evidence clearly indicates that reaction of $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2]$ with an excess of either aqueous NaOH or Na_2CO_3 gives two cationic products which can be isolated by addition of NaBPh_4 . Furthermore the major product

* This assignment is supported by similar assignments in related complexes e.g. $[\{\text{Pt}(\text{OH})(\text{PEt}_3)_2\}_2](\text{BF}_4)_2$ ($\delta(\text{OH})$ 2.85 ppm) and $[\{\text{Pd}(\text{OH})(\text{PPh}_3)_2\}_2](\text{BF}_4)_2$ ($\delta(\text{OH})$ 2.00 ppm) [5]. However, earlier studies also revealed that the chemical shift of the hydroxo protons can vary considerably from compound to compound e.g. $[\text{Rh}_2(\eta\text{-C}_5\text{Me}_5)_2(\text{OH})_3]\text{BPh}_4$ ($\delta(\text{OH})$ 4.95 ppm), $\text{Fe}_2(\text{CO})_6\text{-P}(\rho\text{-C}_6\text{H}_4\text{Me}_2)_2\text{OH}$ ($\delta(\text{OH})$ -2.86 ppm) [6] and $[\text{Ru}_2(\text{PMe}_2\text{Ph})_6(\text{OH})_3]\text{BPh}_4$ ($\delta(\text{OH})$ -2.10 ppm) [7].

TABLE 1

ANALYTICAL AND CONDUCTIVITY DATA FOR SOME BINUCLEAR HYDROXO- AND ALKOXO-BRIDGED RUTHENIUM (II) AND OSMIUM (II) COMPLEXES

Compound	Analyses (%) ^a		Λ_m^b
	C	H	
[C ₆ H ₆ (OH)Ru(OH) ₂ Ru(H ₂ O)C ₆ H ₆]BPh ₄ ^c	56.5 (57.9)	4.9 (5.0)	61.0
[C ₆ H ₆ Ru(OH) ₃ RuC ₆ H ₆]BPh ₄ · Me ₂ CO	59.7 (59.5)	5.2 (5.2)	55.0
[C ₆ H ₆ (OD)Ru(OD) ₂ Ru(D ₂ O)C ₆ H ₆]BPh ₄	58.6 (57.5)	3.9 (4.2)	
[C ₆ H ₆ (OH)Ru(OH) ₂ Ru(H ₂ O)C ₆ H ₆]Cl · 2H ₂ O ^c	28.6 (28.8)	4.4 (4.2)	168.0 ^d
[C ₆ H ₆ (OH)Ru(OH) ₂ Ru(H ₂ O)C ₆ H ₆]Br · 3H ₂ O ^c	26.0 (25.7)	4.7 (4.1)	
[C ₆ H ₆ (OH)Os(OH) ₂ Os(H ₂ O)C ₆ H ₆]BPh ₄ ^c	47.9 (46.9)	3.9 (4.0)	83.0
[(C ₆ H ₃ Me ₃)Ru(OH) ₃ Ru(C ₆ H ₃ Me ₃)]BPh ₄	61.2 (62.0)	5.8 (5.8)	55.0
[(C ₆ H ₃ Me ₃)Ru(OH) ₃ Ru(C ₆ H ₃ Me ₃)]Cl · 3H ₂ O	37.2 (37.1)	5.3 (5.2)	100.0 ^d
[(MeC ₆ H ₄ CHMe ₂)Ru(OH) ₃ Ru(MeC ₆ H ₄ CHMe ₂)]BPh ₄	63.1 (62.9)	6.3 (6.1)	70.0
[C ₆ Me ₆ Ru(OH) ₃ RuC ₆ Me ₆]Cl · 4H ₂ O	41.1 (42.1)	6.5 (6.9)	50.0 ^e
[C ₆ H ₆ Ru(OMe) ₃ RuC ₆ H ₆]BPh ₄	60.5 (60.8)	5.3 (5.3)	68.0
[C ₆ H ₆ Ru(OMe) ₃ RuC ₆ H ₆]PF ₆	30.3 (30.2)	3.6 (3.5)	54.0
[C ₆ H ₆ Ru(OEt) ₃ RuC ₆ H ₆]BPh ₄	61.9 (62.1)	5.8 (5.8)	50.0
[C ₆ H ₆ Ru(OEt) ₃ RuC ₆ H ₆]PF ₆	33.7 (33.9)	4.2 (4.2)	
[C ₆ H ₆ Ru(OPh) ₃ RuC ₆ H ₆]BPh ₄	67.6 (67.8)	5.2 (5.0)	52.0 ^e
[C ₆ H ₆ Os(OMe) ₃ OsC ₆ H ₆]BPh ₄	48.1 (49.3)	4.8 (4.3)	54.0 ^e
[C ₆ Me ₆ Ru(OMe) ₃ RuC ₆ Me ₆]BPh ₄	65.4 (65.2)	7.3 (7.0)	54.0
[C ₆ H ₃ Me ₃ Ru(OMe) ₃ RuC ₆ H ₃ Me ₃]BPh ₄	63.3 (63.2)	6.2 (6.3)	55.0

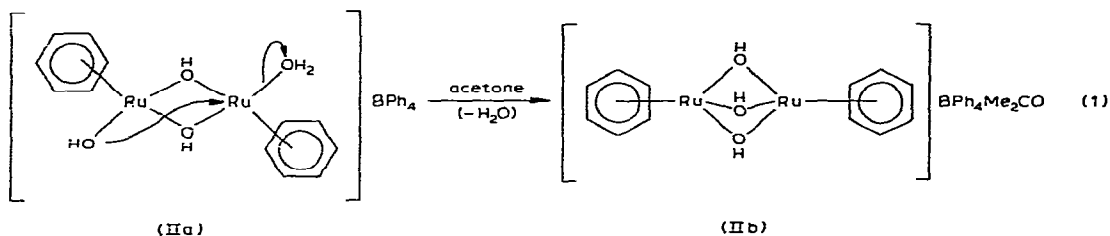
^a Calculated figures in parenthesis. ^b Molar conductivities (S cm² mol⁻¹) measured in CH₃NO₂ (unless stated) at 10⁻³ mol dm⁻³ concentration. ^c IR and ¹H NMR evidence indicate these samples contain small amounts of the appropriate triple hydroxo bridged complex [(arene)M(OH)₃M(arene)]BPh₄. ^d Measured in water. ^e Not very soluble, measured at 5 × 10⁻⁴ mol dm⁻³ concentration.

IIa [characterised by two $\nu(\text{OH})$ vibrations at 3615, 3520 cm⁻¹ and one $\eta\text{-C}_6\text{H}_6$ resonance at δ 5.33 ppm (¹H), δ 77.8 ppm (¹³C)] is converted irreversibly and completely, by recrystallisation from acetone, into the minor product IIb [characterised by one $\nu(\text{OH})$ vibration at 3530 cm⁻¹ and one $\eta\text{-C}_6\text{H}_6$ resonance at δ 5.56 ppm (¹H) and δ 79.4 ppm (¹³C)].

On the basis of its NMR and IR spectra, together with analytical and conductivity data (Table 1), compound IIb is formulated as the triple hydroxo-bridged complex [Ru₂($\eta\text{-C}_6\text{H}_6$)₂(OH)₃]BPh₄Me₂CO. Further support for this proposal comes from preliminary X-ray structural analysis studies [8] on the corresponding [Ru₂($\eta\text{-C}_6\text{H}_3\text{Me}_3$)₂(OH)₃]Cl 3 H₂O (see below).

The nature of compound IIa is less clear-cut. Both analytical data (Table 1) and integration of the ¹H NMR spectrum (in which IIa is the major species) suggested two benzene rings per BPh₄⁻ and conductivity measurements in CH₃NO₂ over a concentration range gave a linear $\Lambda_0 - \Lambda_e$ vs $C_e^{1/2}$ plots of slope 214 which is characteristic of that expected for a 1 : 1 electrolyte [9]. Therefore, in the absence of any X-ray structural data, we tentatively suggest that IIa should be formulated as the di-hydroxo-bridged cation [($\eta\text{-C}_6\text{H}_6$)(OH)Ru(OH)₂Ru(H₂O)($\eta\text{-C}_6\text{H}_6$)]BPh₄. This structure is consistent with both the observed IR spectrum (more than one $\nu(\text{OH})$) and the facile irreversible rearrangement of IIa to IIb (eq. 1) on recrystallisation from acetone.

Similar double-bridged binuclear intermediates have been proposed elsewhere in reactions leading to complexes such as [Ru₂($\eta\text{-C}_6\text{H}_6$)₂Cl₃]PF₆ [10], [Ru₂(OH)₃(PR₃)₆]BPh₄ [7] and [Ru₂Cl₃(PR₃)₆]Cl [11]. The observation of



only one $\eta\text{-C}_6\text{H}_6$ resonance for IIa can be rationalised on the basis of either fast intramolecular rearrangement processes involving terminal and bridging hydroxo (or aqua) groups and/or facile proton transfer between coordinated hydroxo and aqua groups.

Similarly, reaction of $[\{\text{Os}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2]$ with an excess of aqueous NaOH followed by addition of NaBPh_4 gave a product whose IR spectrum contained two $\nu(\text{OH})$ bands at 3580, 3530 cm^{-1} and whose ^1H NMR spectrum in CD_3NO_2 showed a strong $\eta\text{-C}_6\text{H}_6$ resonance at δ 5.97 ppm. This was formulated as $[(\eta\text{-C}_6\text{H}_6)(\text{OH})\text{Os}(\text{OH})_2\text{Os}(\text{H}_2\text{O})(\eta\text{-C}_6\text{H}_6)]\text{BPh}_4$. A small amount of $[\text{Os}_2(\eta\text{-C}_6\text{H}_6)_2(\text{OH})_3]\text{BPh}_4$ [$\nu(\text{OH})$, 3495 cm^{-1} ; ^1H NMR in CD_3NO_2 : δ 6.08 ppm ($\eta\text{-C}_6\text{H}_6$)] was also present.

In contrast, reaction of $[\{\text{Ru}(\eta\text{-C}_6\text{H}_3\text{Me}_3)\text{Cl}_2\}_2]$ with an aqueous solution of NaOH, followed by addition of NaBPh_4 yielded a yellow solid shown by elemental analysis and conductance measurements (Table 1), IR spectrum ($\nu(\text{OH})$ 3600 cm^{-1}) and ^1H NMR spectrum in CD_3NO_2 (Table 2) to contain only the triple hydroxo-bridged complex $[\text{Ru}_2(\eta\text{-C}_6\text{H}_3\text{Me}_3)_2(\text{OH})_3]\text{BPh}_4$. As for the corresponding $\eta\text{-C}_6\text{H}_6$ complexes, facile H/D exchange of the hydroxo protons occurred in deuterated solvents, although unlike the $[\text{Rh}_2(\eta\text{-C}_5\text{Me}_5)_2(\text{OH})_3]^+$ cation [3] no exchange of the methyl protons was observed.

If the solvent was removed under vacuo from the $[\{\text{Ru}(\eta\text{-C}_6\text{H}_3\text{Me}_3)\text{Cl}_2\}_2]/\text{NaOH}$ reaction mixture before addition of NaBPh_4 , a crystalline yellow solid which analysed for $[\text{Ru}_2(\eta\text{-C}_6\text{H}_3\text{Me}_3)_2(\text{OH})_3]\text{Cl} \cdot 3\text{H}_2\text{O}$ was deposited*. Although strong broad water bands centred at ca. 3300 cm^{-1} obscured any $\nu(\text{OH})$ bands in the IR spectrum of this compound, a preliminary X-ray structural analysis [8] has confirmed the presence of the $-\text{Ru}(\text{OH})_3\text{Ru}-$ bridging unit.

Likewise, reaction of $[\{\text{Ru}(\eta\text{-C}_6\text{Me}_6)\text{Cl}_2\}_2]$ with an excess of NaOH in water gave a product formulated as $[\text{Ru}_2(\eta\text{-C}_6\text{Me}_6)_2(\text{OH})_3]\text{Cl} \cdot 4\text{H}_2\text{O}$ (one $\eta\text{-C}_6\text{Me}_6$ resonance in its ^1H NMR spectrum at δ 2.05 ppm)** and $[\{\text{Ru}(\eta\text{-}i\text{-C}_6\text{H}_4\text{CHMe}_2)\text{Cl}_2\}_2]$ on treatment with an excess of NaOH or Na_2CO_3 in water followed by addition of NaBPh_4 gave a pure sample of $[\text{Ru}_2(\eta\text{-}i\text{-C}_6\text{H}_4\text{CHMe}_2)_2(\text{OH})_3]\text{BPh}_4$ ($\nu(\text{OH})$ 3550 cm^{-1}) (see Table 1 and 2 and ^{13}C - ^1H) NMR spectrum in Experimental section). Thus it appears that the greater the degree of

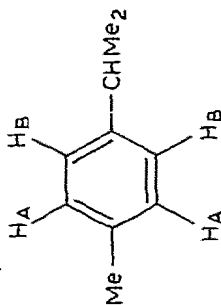
* A solid can also be isolated from the $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2]/\text{NaOH}(\text{aq})$ reaction mixture by slow evaporation of the solvent. Initially this was claimed to be $[\text{Ru}_2(\eta\text{-C}_6\text{H}_6)_3(\text{OH})_3]\text{Cl} \cdot 3\text{H}_2\text{O}$ [2]. However, if this material is redissolved in water and treated with NaBPh_4 , the product precipitated has the same IR and ^1H NMR spectra as that found for product II, i.e. it is a mixture of the cations $[\text{C}_6\text{H}_6(\text{OH})\text{Ru}(\text{OH})_2\text{Ru}(\text{H}_2\text{O})\text{C}_6\text{H}_6]^+$ and $[\text{Ru}_2(\eta\text{-C}_6\text{H}_6)_2(\text{OH})_3]^+$.

** $[\text{Ru}_2(\eta\text{-C}_6\text{Me}_6)_2(\text{OH})_3]\text{Y}$ ($\text{Y} = \text{Cl}^-, \text{PF}_6^-$) has been recently reported to be an active homogeneous catalyst for the disproportionation of acetaldehyde to acetic acid and ethanol but its method of synthesis has not been published [12].

TABLE 2 HYDROGEN-1 NMR DATA FOR SOME BINUCLEAR HYDROXO AND ALKOXO COMPLEXES AT 298 K

Compound	Solvent	δ ppm ^{a,b}	OH ⁻ /OR ⁻
[C ₆ H ₆ (OH)Ru(OH) ₂ Ru(H ₂ O) ₂ C ₆ H ₆]BPh ₄ ^c	CD ₃ NO ₂	5.33 (s)	2.60 (s)
[C ₆ H ₆ Ru(OH) ₃ Ru(C ₆ H ₆)BPh ₄ · Me ₂ CO	CD ₃ NO ₂	5.56 (s)	2.60 (s)
[C ₆ H ₆ (OD)Ru(OD) ₂ Ru(D ₂ O) ₂ C ₆ H ₆]BPh ₄ ^c	(CD ₃) ₂ CO	5.33 (s)	e
[C ₆ H ₆ (OH)Ru(OH) ₂ Ru(H ₂ O) ₂ C ₆ H ₆]Cl · 2H ₂ O ^{c,d}	D ₂ O	5.88 (s)	e
[C ₆ H ₆ (OH)Ru(OH) ₂ Ru(H ₂ O) ₂ C ₆ H ₆]Br · 3H ₂ O ^{c,d}	D ₂ O	5.85 (s)	e
[C ₆ H ₆ (OH)Os(OH) ₂ Os(H ₂ O) ₂ C ₆ H ₆]BPh ₄ ^c	(CD ₃) ₂ CO	5.93 (s)	e
[C ₆ H ₃ Me ₃ Ru(OH) ₃ Ru(C ₆ H ₃ Me ₃)BPh ₄	CD ₃ NO ₂	4.09 (s) (H); 2.04 (s) Me	2.32 (s)
[C ₆ H ₃ Me ₃ Ru(OH) ₃ Ru(C ₆ H ₃ Me ₃)Cl · 3H ₂ O ^d	(CD ₃) ₂ CO	5.32 (s) H; 2.55 (s) Me	e
[(MeC ₆ H ₄ CHMe ₂)Ru(OH) ₃ Ru(MeC ₆ H ₄ CHMe ₂)]- BPh ₄ ^f	D ₂ O	4.76 (Δ H _A H _B 30 Hz, J 6.0 Hz)	1.65 (s)
	CDCl ₃	2.49 (sp CHMe ₂) 1.90 (s, CH ₃)	
		1.18 (d, CH ₃ of CHMe ₂ , J 7.0 Hz)	
[C ₆ Me ₆]Ru(O ⁻) ₃ Ru(C ₆ Me ₆)Cl · 4H ₂ O	CD ₃ NO ₂	2.05 (s)	e
[C ₆ H ₆ Ru(OMe) ₃ Ru(C ₆ H ₆)BPh ₄	(CD ₃) ₂ CO	5.48 (s)	4.42 (s)
[C ₆ H ₆ Ru(C ₆ H ₆) ₂ PF ₆	(CD ₃) ₂ CO	5.86 (s)	4.68 (s)
[C ₆ H ₆ Ru(OEt) ₃ Ru(C ₆ H ₆)BPh ₄	(CD ₃) ₂ SO	5.43 (s)	4.50 (q) 1.35 (t)
			(³ J(CH ₂ CH ₃) 7.0 Hz)
[C ₆ H ₆ Ru(OEt) ₃ Ru(C ₆ H ₆)PF ₆	(CD ₃) ₂ CO	5.50 (s)	4.33 (q) 1.58 (t)
			(³ J(CH ₂ CH ₃) 7.0 Hz)
[C ₆ H ₆ Ru(OPh) ₃ Ru(C ₆ H ₆)BPh ₄	CD ₃ NO ₂	5.12 (s)	6.95 (m) ^g
[C ₆ H ₆ Os(OMe) ₃ OsC ₆ H ₆]BPh ₄	(CD ₃) ₂ CO	6.15 (s)	4.63 (s)
[C ₆ Me ₆ Ru(OMe) ₃ Ru(C ₆ Me ₆)BPh ₄	CDCl ₃	1.97 (s)	4.00 (s)
[(C ₆ H ₃ Me ₃)Ru(OH) ₃ Ru(C ₆ H ₃ Me ₃)]BPh ₄	(CD ₃) ₂ CO	5.08 (s) (H); 2.16 (s) (Me)	4.36 (s)

^a Reference standard-internal Me₄Si lock unless otherwise stated. ^b Where appropriate BPh₄⁻ multiplets observed between 6.90–7.60 ppm. ^c These samples contain small amounts of appropriate triple hydroxo-bridged cation [arene Ru(OH)₃Ru arene]⁺ (Y = BPh₄⁻, Cl⁻ or Br⁻) whose NMR parameters are not given (see Experimental section for values). ^d Reference standard-external Me₄Si capillary. [N.B. As discussed earlier [10], the high frequency shift of the η -arene resonances here compared to those in the corresponding BPh₄⁻ salts is attributed mainly to the change of reference from internal Me₄Si to external Me₄Si capillary. ^e Not observed. ^f Labelling of *p*-xylylene protons:



Chemical shift difference calculated from line positions using formula $\Delta(H_A H_B) = [(v_1 - v_4)(v_2 - v_3)]^{1/2}$ since an AB pattern was observed. ^g Partially masked by BPh₄⁻ resonances. ^h Midpoint of AB resonance is quoted. ⁱ Partially masked by BPh₄⁻ resonances. ^j s (singlet); d (doublet); t (triplet); q (quartet); sp (septet); m (multiplet).

substitution of the arene ring, the greater the tendency to form the triple hydroxo-bridged complex, although it is likely that kinetically labile double hydroxo bridged complexes analogous to IIb are involved in the reaction.

Finally, attempts to isolate the cations IIa and IIb as their hexafluorophosphate salts by addition of NH_4PF_6 to the yellow solution obtained by reacting $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2]$ with aqueous NaOH, yielded an unexpected product. No precipitate was found immediately on addition of NH_4PF_6 , but on standing for several days, a yellow crystalline solid was deposited whose IR spectrum showed a series of sharp intense bands at 3095, 3210, 3300, and 3365 cm^{-1} . These were assigned to $\nu(\text{NH})$ stretching frequencies, whilst the broad absorptions at 1660 cm^{-1} (with shoulders at 1670 and 1630 cm^{-1}) and 452 cm^{-1} could be attributed to $\delta(\text{NH})$ deformations and $\nu(\text{Ru-N})$ stretches, respectively (cf. the vibrational modes associated with Ru-NH_3 for the cation $[\text{Ru}(\eta\text{-C}_6\text{H}_6)(\text{NH}_3)_2\text{Cl}]^+$ [13]). Also, no bands attributable to $\nu(\text{RuCl})$ stretching modes were observed in the IR spectrum. The ^1H NMR spectrum of this solid in $(\text{CD}_3)_2\text{CO}$ contained one $\eta\text{-C}_6\text{H}_6$ signal at δ 5.99 ppm plus a broad hump centred at δ 3.79 ppm (NH_3 protons). The intensity ratio from the ^1H NMR spectrum indicated three ammonia groups per coordinated benzene ring which, together with elemental analysis figures suggested the formulation $[\text{Ru}(\eta\text{-C}_6\text{H}_6)(\text{NH}_3)_3](\text{PF}_6)_2$. The molar conductivity of this complex in CH_3NO_2 was 178 $\text{S cm}^2 \text{mol}^{-1}$ (for a $10^{-3} \text{ mol dm}^{-3}$ solution) and a plot of $\Lambda_0 - \Lambda_e$ vs. $C_e^{1/2}$ gave a slope of 437, both consistent with that expected for a 1 : 2 electrolyte (cf $[\text{Ni}(\text{phen})_3]\text{Cl}_2$, $\Lambda_m = 118 \text{ S cm}^2 \text{mol}^{-1}$; slope = 420 [14]).

Presumably this trisammine complex is formed from the reaction of the cations IIa and/or IIb with ammonium ion which can act as a weak acid protonating the OH^- bridges to form the trisqua intermediate $[\text{Ru}(\eta\text{-C}_6\text{H}_6)(\text{H}_2\text{O})_3]^{2+}$ which might then undergo substitution of water by ammonia groups. (cf. the related reactions of $[\text{Ru}_2(\text{OH})_3(\text{PMe}_2\text{Ph})_6]^+$ with acids in various solvents (S) which gave $[\text{Ru}(\text{S})_3(\text{PMe}_2\text{Ph})_3]^{2+}$ species [7]). Alternatively since excess NaOH is present, H^+ may be removed by OH^- , but this would have to be followed by bridge cleavage and replacement of OH^- groups by NH_3 , which seems unlikely in view of the apparent stability of these hydroxo bridges towards Lewis bases (see below).

b) Synthesis of binuclear alkoxo-bridged complexes

Earlier, we showed that the $[\text{Ru}_2(\eta\text{-C}_6\text{H}_6)_2\text{Cl}_3]^+$ cation underwent facile bridge cleavage reactions with a variety of Lewis bases to give monomeric compounds of type $[\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{ClL}_2]\text{PF}_6$, $[\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\text{L}]$ and/or $[\text{RuCl}_2\text{L}_4]$ ($\text{L} = \text{C}_5\text{H}_5\text{N}$, Et_2S , Me_2SO , PR_3 etc). In contrast, product II ($[\text{C}_6\text{H}_6(\text{OH})\text{Ru}(\text{OH})_2\text{Ru}(\text{H}_2\text{O})\text{C}_6\text{H}_6]\text{BPh}_4$ and $[\text{Ru}_2(\eta\text{-C}_6\text{H}_6)_2(\text{OH})_3]\text{BPh}_4$) does not react with an excess of tertiary phosphines ($\text{PR}_3 = \text{PPh}_3$, PMe_2Ph , PEt_2Ph) in acetone, even under reflux conditions for prolonged periods, (cf. $[\{\text{Pt}(\text{OH})(\text{PR}_3)_2\}_2](\text{BF}_4)_2$ does not react with more PR_3 [5]), the only product isolated being $[\text{Ru}_2(\eta\text{-C}_6\text{H}_6)_2(\text{OH})_3]\text{BPh}_4\text{Me}_2\text{CO}$ (IIb).

However, refluxing $[\text{Ru}_2(\eta\text{-C}_6\text{H}_6)_2(\text{OH})_3]\text{BPh}_4\text{Me}_2\text{CO}$ (IIb) in methanol produced a yellow solution which deposited a yellow crystalline solid on cooling. The IR spectrum of this solid showed no bands at ca. 3600 cm^{-1} but the presence of a strong broad band at 1050 cm^{-1} indicated the presence of methoxide

groups (cf. $\text{Ti}(\text{OMe})_4$ with $\nu(\text{O}-\text{C})$ 1032 cm^{-1} [15]). Since the ^1H NMR spectrum in $(\text{CD}_3)_2\text{CO}$ consisted of BPh_4^- multiplets centred at ca. δ 6.90 and 7.30 ppm, a $\eta\text{-C}_6\text{H}_6$ peak at δ 5.48 ppm and a singlet at δ 4.42 ppm (assigned to $-\text{OMe}$ protons) in the intensity ratio 20 : 12 : 9 respectively, this compound was formulated as the triple methoxo-bridged complex $[\text{Ru}_2(\text{C}_6\text{H}_6)_2(\text{OMe}_3)]\text{-BPh}_4$. This formulation was supported by elemental analyses and conductivity measurements in CH_3NO_2 which indicated a 1 : 1 electrolyte. The ethoxo complex $[\text{Ru}_2(\eta\text{-C}_6\text{H}_6)_2(\text{OEt})_3]\text{BPh}_4$ was also prepared by refluxing IIb in ethanol (see Tables 1 and 2 for characterisation). Like the $[\text{Ru}(\eta\text{-C}_6\text{H}_6)(\text{NH}_3)_3]^{2+}$ cation discussed earlier, these alkoxo compounds are probably formed via protonation of the hydroxo bridges by the weak acid ROH to form the $[\text{Ru}(\eta\text{-C}_6\text{H}_6)(\text{H}_2\text{O})_3]^{2+}$ cation, which can then react rapidly with OR^- to give monomeric alkoxo species such as $[\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{OR}(\text{H}_2\text{O})_2]^+$ and $[\text{Ru}(\eta\text{-C}_6\text{H}_6)(\text{OR})_2\text{H}_2\text{O}]$. As discussed elsewhere for the analogous $[\text{Ru}_2(\eta\text{-C}_6\text{H}_6)_2\text{Cl}_3]^+$ [10] and $[\text{Ru}_2\text{Cl}_3(\text{PR}_3)_6]^+$ [11] cations, facile intermolecular coupling reactions of these solvated monomers would then give the $[\text{Ru}_2(\eta\text{-C}_6\text{H}_6)_2(\text{OR})_3]^+$ cations.

These alkoxo cations have also been prepared by reaction of $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{-Cl}_2\}_2]$ with freshly prepared NaOR ($\text{R} = \text{Me}, \text{Et}$) in alcoholic solvents followed by addition of NaBPh_4 . Unlike the binuclear hydroxo-bridged cations, their PF_6^- salts were readily isolated by addition of NH_4PF_6 to the above reaction mixture. Likewise reaction of $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2]$ with NaOPh in methanol and then addition of NaBPh_4 gave the triple phenoxo-bridged cation $[\text{Ru}_2(\eta\text{-C}_6\text{H}_6)_2\text{OPh}]_3\text{BPh}_4$. In fact, the following compounds have been successfully synthesised by reaction of $[\{\text{M}(\text{arene})\text{Cl}_2\}_2]$ with NaOMe ; $[\text{Ru}_2(\eta\text{-C}_6\text{H}_3\text{Me}_3)_2(\text{OMe})_3]\text{BPh}_4$; $[\text{Os}_2(\eta\text{-C}_6\text{H}_6)_2(\text{OMe})_3]\text{BPh}_4$ and $[\text{Ru}_2(\eta\text{-C}_6\text{Me}_6)_2(\text{OMe})_3]\text{BPh}_4$ (see Experimental section and Tables 1 and 2 for details).

However, attempts to synthesise longer chain alkoxides such as $i\text{-PrO}$ or $n\text{-BuO}$ using either the $[\text{Ru}_2(\eta\text{-C}_6\text{H}_6)_2(\text{OH})_3]\text{BPh}_4\text{Me}_2\text{CO}/\text{ROH}$ or $[\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2]/\text{NaOR}$ routes were unsuccessful since extensive decomposition occurred and no ruthenium complexes could be isolated from the reaction mixture. This decomposition is believed to occur via ruthenium hydride formation, generated by facile β -elimination steps from intermediate alkoxo species. Good evidence for hydride formation comes from a recent communication on the isolation of the complexes $[\text{Ru}_2(\eta\text{-arene})_2\text{X}(\text{H})_2]\text{PF}_6$ ($\text{X} = \text{Cl}^-$, arene = C_6Me_6 ; $\text{C}_6\text{H}_3\text{Me}_3$; $\text{X} = \text{H}^-$, arene = $\text{C}_6\text{H}_3\text{Me}_3$), obtained by reaction of $[\{\text{Ru}(\eta\text{-arene})\text{Cl}_2\}_2]$ with aqueous solutions containing isopropoxide ions [16]. Similar hydride complexes are probably formed in reactions between the benzene complexes and longer chain alkoxides, but due to the comparative weakness of the ruthenium-benzene bonds, loss of benzene and subsequent product decomposition results.

Finally, preliminary studies indicate that the binuclear hydroxo- and alkoxo-bridged complexes described in this paper react with a wide range of weak acids and other reagents [17] and these studies will be described in a future publication.

Experimental

Microanalyses were by the University of Edinburgh Chemistry Department. Infrared spectra were recorded in the region 4000–250 cm^{-1} on Perkin Elmer 447 and 557 grating spectrometers using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Hydrogen-1 NMR spectra were obtained on Varian Associates HA-100 and EM-360 spectrometers and carbon-13 NMR spectra on a Varian CFT 20 spectrometer operating at 20 MHz (^{13}C chemical shifts are quoted in ppm to high frequency of TMS). Melting points were determined with a Köfler hot stage microscope and are uncorrected. Conductivity measurements were made at 303 K using a model 310 Portland Electronics conductivity bridge. Conductivity vs. concentration data were obtained over a range of concentrations (2×10^{-3} to 5×10^{-3} dm^{-3} mol) for several of the compounds and a plot of Λ_e (equivalent conductance) vs. $C_e^{1/2}$ (concentration in equivalents dm^{-3}) gave a straight line which on extrapolation to $C_e^{1/2} = 0$ gave Λ_0 . A subsequent plot of $\Lambda_0 - \Lambda_e$ vs $C_e^{1/2}$ gave a straight line whose slope is a function of the ionic charges [9]. Thus, the slopes obtained for various samples were compared with those for known 1 : 1 and 2 : 1 electrolytes and hence the electrolyte type could be determined.

Materials

Ruthenium trichloride trihydrate and sodium hexachloroosmate(IV) (Johnson Matthey Ltd.), α -phellandrene (5-isopropyl-2-methylcyclohexa-1,3-diene) (Eastman Chemicals) CD_3NO_2 , cyclohexa-1,3-diene hexamethyl benzene (Aldrich Chemicals); NaOH, NaBPh₄ (BDH); sodium metal (Fisons); NH_4PF_6 , AgPF_6 (Alfa). The compounds 1,3,5-trimethylcyclohexa-1,4-diene, and cyclohexa-1,4-diene were prepared by the standard Birch reduction of the corresponding arenes [18]. The compounds [$\{\text{Ru}(\eta\text{-arene})\text{Cl}_2\}_2$] (arene = C_6H_6 , $\text{C}_6\text{H}_3\text{Me}_3$, $p\text{-MeC}_6\text{H}_4\text{CHMe}_2$) were prepared as described elsewhere [1c] using purified " $\text{RuCl}_3 \cdot x \text{H}_2\text{O}$ ". The compound [$\{\text{Os}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2$] was prepared in low yield (33%) from $\text{Na}_2[\text{OsCl}_6]$ and 1,3-cyclohexadiene in ethanol [1c] and [$\{\text{Ru}(\eta\text{-C}_6\text{Me}_6)\text{Cl}_2\}_2$] by reaction of [$\{\text{Ru}(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Cl}_2\}_2$] with C_6Me_6 [19]. All reactions were carried out under an atmosphere of nitrogen. Analytical and conductivity data for some of the binuclear compounds are given in Table 1 and ^1H NMR data in Table 2.

"Di- μ -hydroxo(aqua)hydroxobis[(η -benzene)ruthenium(II)] tetraphenylborate"

Method A. Addition of an excess of NaBPh₄ (0.20 g; 0.60 mmol) in water (5 cm^3) to the yellow solution obtained from the reaction of [$\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2$] (0.10 g; 0.20 mmol) and NaOH (0.15 g; 4.0 mmol) in warm water (20 cm^3) gave a yellow precipitate which was filtered off and air-dried. The filtrate deposited more of the complex if left to stand (0.09 g, 65%) m.p. 190°C (decomp) [$\nu(\text{OH})$ 3520, 3615 cm^{-1} ; $\delta(\text{Ru}-\text{OH})$ 1135 cm^{-1} ; $\nu(\text{RuO})$ 490 cm^{-1} (mull)] [^{13}C - ^1H] NMR in CD_3NO_2 (298 K): δ 77.8 (s) ppm, δ 121–136 ppm (BPh_4^-) slope of $\Lambda_0 - \Lambda_e$ vs $C_e^{1/2}$ plot in $\text{CH}_3\text{NO}_2 = 214$.

A small amount of tri- μ -hydroxobis[(η -benzene)ruthenium(II)] tetraphenylborate was also precipitated from this solution as evidenced by infrared [$\nu(\text{OH})$ 3530 cm^{-1} (mull)] ^1H NMR (CD_3NO_2): δ 5.56 (s) ppm (weak)] and ^{13}C - ^1H

NMR [δ 79.4 ppm; δ 121–136 ppm (BPh_4^-) data. Recrystallisation of this product from acetone gives a pure sample of tri- μ -hydroxobis[(η -benzene)-ruthenium(II)] tetraphenylborate acetone solvate (1 : 1) (m.p. 185° C (decomp)) [$\nu(\text{OH})$ 3530 cm^{-1} ; $\nu(\text{CO})$ 1695 cm^{-1} ; $\delta(\text{RuOH})$ 1135 cm^{-1} ; $\nu(\text{RuO})$ 510 cm^{-1} (mull)], ^{13}C - $\{^1\text{H}\}$ NMR in CD_3NO_2 (298 K): δ 79.4 (s) ppm. Similarly prepared was “di- μ -hydroxo(aqua)hydroxo bis[(η -benzene)osmium(II) tetraphenylborate” from [$\{\text{Os}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2$] and excess of NaOH followed by addition of NaBPh_4 (m.p. 195° C (decomp)) (60%) [$\nu(\text{OH})$ 3580, 3530 cm^{-1} ; $\delta(\text{OsOH})$ 1135 cm^{-1} (mull)]. A small amount of [$\text{Os}_2(\eta\text{-C}_6\text{H}_6)_2(\text{OH})_3$] BPh_4 was also precipitated from solution [$\nu(\text{OH})$ 3495 cm^{-1}] ^1H NMR in $(\text{CD}_3)_2\text{CO}$ at 298 K: δ 6.13 (s) ppm.

Method B. The complex [$\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2$] (0.10 g; 0.20 mmol) was dissolved in warm water (5 cm^3) and filtered. The orange solution was shaken with an excess of Na_2CO_3 (0.20 g; 2.0 mmol) for 2 hours to give a yellow solution, which on addition of NaBPh_4 (0.20 g; 0.60 mmol) gave the complex as a yellow precipitate (0.08 g, 59%). Recrystallisation from acetone then gave [$\text{Ru}_2(\eta\text{-C}_6\text{H}_6)_2(\text{OH})_3$] $\text{BPh}_4 \cdot \text{Me}_2\text{CO}$.

Di- μ -deuteroxo(deuterium oxide)deuteroxo bis[(η -benzene)ruthenium(II)] tetraphenylborate

As for method B above but using D_2O instead of H_2O to give a yellow solid, m.p. 200° C (decomp) [$\nu(\text{OD})$ 2595, 2670 cm^{-1} ; $\nu(\text{RuO})$ 475 cm^{-1} (mull)]. A small amount of tri- μ -deuteroxobis[(η -benzene)ruthenium(II)] tetraphenylborate is also precipitated ($\nu(\text{OD})$ 2600 cm^{-1}) and this can be obtained in a pure state (as an acetone solvate) by recrystallisation from $(\text{CD}_3)_2\text{CO}$.

Di- μ -hydroxo(aqua)hydroxobis[(η -benzene)ruthenium(II)] chloride hydrate (1/2)

The compound [$\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2$] (0.10 g; 0.20 mmol) was dissolved in water (10 cm^3) with NaOH (0.15 g; 4.0 mmol). The solution was warmed giving a yellow solution, filtered and left to stand under vacuo (water pump) for 2 hours to give a yellow solid (0.04 g, 42%) (m.p. 132° C (decomp)) [$\nu(\text{OH})$ 3300(br) cm^{-1} ; $\delta(\text{HOH})$ 1620 cm^{-1} ; $\nu(\text{RuO})$ 495 cm^{-1} (mull)]. Addition of NaBPh_4 to a concentrated aqueous solution of this compound gave “[$\text{Ru}_2(\text{C}_6\text{H}_6)_2(\text{OH})_3\text{H}_2\text{O}$] BPh_4 ” [$\nu(\text{OH})$ 3520, 3615 cm^{-1} (mull)] and a small amount of [$\text{Ru}_2(\text{C}_6\text{H}_6)_2(\text{OH})_3$] BPh_4 [$\nu(\text{OH})$ 3530 cm^{-1}].

Di- μ -hydroxo(aqua)hydroxo bis[(η -benzene)ruthenium(II)] bromide hydrate (1/3)

As above from [$\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Br}_2\}_2$] and excess of NaOH (m.p. 150° C (decomp)) [$\nu(\text{OH})$ 3250(br) cm^{-1} ; $\delta(\text{HOH})$ 1650 cm^{-1} ; $\nu(\text{RuO})$ 460 cm^{-1} (mull)].

Tri- μ -hydroxobis[(η -mesitylene)ruthenium(II)] tetraphenylborate

Method A. Addition of an excess of NaBPh_4 (0.20 g; 0.60 mmol) in water (5 cm^3) to the yellow solution obtained from the reaction of [$\{\text{Ru}(\eta\text{-C}_6\text{H}_3\text{Me}_3)\text{Cl}_2\}_2$] (0.12 g; 0.20 mmol) and NaOH (0.15 g; 4.0 mmol) in warm water (20 cm^3) gave a yellow precipitate which was filtered off and air dried. (0.20 g;

67%) (m.p. 110–111°C) [$\nu(\text{OH})$ 3600 cm^{-1} $\delta(\text{RuOH})$ 1149 cm^{-1} , $\nu(\text{RuO})$ 490 cm^{-1} (mull)].

Tri- μ -hydroxobis[(η -mesitylene)ruthenium(II)] chloride hydrate (1/3)

The compound [$\{\text{Ru}(\eta\text{-C}_6\text{H}_3\text{Me}_3)\text{Cl}_2\}_2$] (0.12 g; 0.20 mmol) was dissolved in water (10 cm^3) with NaOH (0.15 g; 4.0 mmol). The solution was warmed to give a yellow solution, filtered and left to stand under vacuo (water pump) for two hours to give a yellow crystalline solid, m.p. 185°C (decomp) [$\nu(\text{OH})$ 3300 cm^{-1} ; $\delta(\text{HOH})$ 1670 cm^{-1} ; $\nu(\text{RuO})$ 489 cm^{-1} (mull)].

*Tri- μ -hydroxobis[(η -*p*-cymene)ruthenium(II)] tetraphenylborate*

Method A. The compound [$\{\text{Ru}(\eta\text{-}i\text{-p-MeC}_6\text{H}_4\text{CHMe}_2)\text{Cl}_2\}_2$] (0.25 g; 0.40 mmol) was dissolved in water (10 cm^3) and NaOH (0.15 g; 4.0 mmol) was added. The solution was stirred and gently warmed for two hours. It was then filtered and excess NaBPh₄ (0.20 g; 0.60 mmol) in water (5 cm^3) was added to give a gummy precipitate. Vigorous stirring for several hours gave a yellow powdery precipitate which was filtered off and washed with water and light petroleum (b.p. 60–80°C) (0.11 g; 32%) [$\nu(\text{OH})$ 3550 cm^{-1} (mull)] ¹³C-¹H NMR CDCl₃ (298 K): δ 121–136 ppm (BPh₄⁻), δ 96.4 (A), 93.0 (B), 77.4 (C), 74.8 (D), 31.1 (E), 22.4 (F), 17.9 (G) ppm*.

Method B. As above but using an excess of Na₂CO₃ rather than NaOH (0.26 g; 75%) slopes of $\Lambda_0 - \Lambda_e$ vs $C_e^{1/2}$ in CH₃NO₂ = 100.

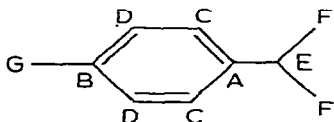
Tri- μ -hydroxobis[(η -hexamethyl)benzene)ruthenium(II)] chloride hydrate (1/4)

Method A. The compound [$\{\text{Ru}(\eta\text{-C}_6\text{Me}_6)\text{Cl}_2\}_2$] (0.10 g; 0.15 mmol) was dissolved in hot water (20 cm^3). The solution was filtered, an excess of NaOH (0.30 g; 8.0 mmol) added and the solution refluxed for two hours. On cooling a pale green solid was deposited which was filtered off, washed with water and air dried (0.08 g; 78%) (m.p. 192–195°C) [$\nu(\text{OH})$ 3420 cm^{-1} ; $\delta(\text{HOH})$ 1660 cm^{-1} ; $\nu(\text{RuO})$ 500 cm^{-1}].

Tris(ammine)(η -benzene)ruthenium(II) hexafluorophosphate

The compound [$\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2$] (0.02 g; 0.40 mmol) was dissolved in water (10 cm^3) with NaOH (0.15 g; 4.0 mmol) and warmed. Addition of an excess of NH₄PF₆ (0.16 g; 1.0 mmol) gave a yellow crystalline precipitate after 3 days (m.p. >240°C (decomp)) (0.15 g, 36%) [$\nu(\text{NH})$ 3095; 3210; 3300, 3365 cm^{-1} ; $\delta(\text{NH})$ 1670, 1660, 1630 cm^{-1} ; $\nu(\text{RuN})$ 452 cm^{-1} (mull)]. Found: C, 14.1; H, 2.9; N, 8.1. Calcd. for C₆H₁₅F₁₂N₃P₂Ru: C, 13.8; H, 2.9; N, 8.1%. Conductivity in CH₃NO₂ at 303 K: Λ_m (10⁻³ mol dm⁻³) = 178 S cm² mol⁻¹; Slope of $\Lambda_0 - \Lambda_e$ vs $C_e^{1/2}$ plot = 437 ¹H NMR in (CD₃)₂CO (298 K) δ 5.99 (s) ($\eta\text{-C}_6\text{H}_6$), 3.79 ppm (br) (NH₃).

* Labelling of *p*-cymene carbons



Tri- μ -methoxobis[(η -benzene)ruthenium(II)] tetraphenylborate

Method C. The compound [$\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2$] (0.10 g; 0.20 mmol) was added to a freshly prepared solution of NaOMe [Na (ca. 0.10 g) in MeOH (10 cm³)] and the solution was gently warmed to give a yellow solution which deposited a yellow solid on addition of NaBPh₄ and which was washed with methanol and air-dried. (0.12 g; 81%) (m.p. 198°C (decomp)) [$\nu(\text{CO})$ 1050 cm⁻¹; $\delta(\text{Ru}-\text{O}-\text{C})$ 1145 cm⁻¹; $\nu(\text{RuO})$ 550 cm⁻¹ (mull)]. Similarly prepared from [$\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2$] and NaOEt was tri- μ -ethoxobis[(η -benzene)ruthenium(II)] tetraphenylborate; m.p. 220°C (decomp) [$\nu(\text{CO})$ 1050 cm⁻¹; $\nu(\text{RuO})$ 570 cm⁻¹ (mull)]. If NH₄PF₆ is used instead of NaBPh₄, the complexes tri- μ -methoxobis[(η -benzene)ruthenium(II)] hexafluorophosphate (m.p. 200°C (decomp)) [$\nu(\text{CO})$ 1040 cm⁻¹; $\delta(\text{RuOC})$ 1150 cm⁻¹ (mull)] (slope of $\Lambda_0 - \Lambda_e$ vs. $C_e^{1/2}$ in CH₃NO₂ = 245) and Tri- μ -ethoxobis[(η -benzene)ruthenium(II)] hexafluorophosphate (m.p. 190°C (decomp)) [$\nu(\text{CO})$ 1050 cm⁻¹; $\delta(\text{RuOC})$ 1150 cm⁻¹] could be prepared.

Method D. The complex [$\text{Ru}_2(\eta\text{-C}_6\text{H}_6)_2(\text{OH})_3$]BPh₄Me₂CO (0.20 g; 0.30 mmol) was refluxed in methanol (10 cm³) for 3 hours. The yellow solution was filtered hot and deposited a yellow crystalline solid on cooling which was identified as [$\text{Ru}_2(\eta\text{-C}_6\text{H}_6)_2(\text{OMe})_3$]BPh₄ (0.20 g; 90%). Similarly prepared from ethanol and [$\text{Ru}_2(\eta\text{-C}_6\text{H}_6)_2(\text{OH})_3$]BPh₄Me₂CO was [$\text{Ru}_2(\eta\text{-C}_6\text{H}_6)_2(\text{OEt})_3$]BPh₄.

Tri- μ -phenoxobis[(η -benzene)ruthenium(II)] tetraphenylborate

By method C, using [$\{\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2$] (0.10 g; 0.20 mmol) and an excess of freshly prepared NaOPh in methanol (10 cm³) (made from NaOMe and excess phenol in methanol). This mixture was gently heated to give a yellow solution and addition of NaBPh₄ (0.07 g, 0.20 mmol) gave a yellow solid which was washed with methanol and air dried (0.10 g; 52%) (m.p. 195–196°C) [$\nu(\text{CO})$ 1065 cm⁻¹; $\nu(\text{RuO})$ 490 cm⁻¹ (mull)].

Tri- μ -methoxobis[(η -benzene osmium(II)] tetraphenylborate

By method C using [$\{\text{Os}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2\}_2$] (0.10 g; 0.15 mmol) and a freshly prepared solution of NaOMe in methanol (10 cm³). The mixture was stirred and heated gently to give a clear solution and then addition of NaBPh₄ (0.07 g; 0.20 mmol) gave a microcrystalline white solid which was washed with methanol and air dried (0.06 g; 39%) (m.p. 174–176°C) [$\nu(\text{CO})$ 1048 cm⁻¹; $\nu(\text{OsO})$ 400 cm⁻¹].

Tri- μ -methoxobis[(η -hexamethylbenzene)ruthenium(II)] tetraphenylborate

By method C using [$\{\text{Ru}(\eta\text{-C}_6\text{Me}_6)\text{Cl}_2\}_2$] (0.10 g; 0.15 mmol) and freshly prepared NaOMe [Na (0.10 g) in MeOH (15 cm³)]. The mixture was stirred and heated gently to give a yellow solution and addition of NaBPh₄ (0.07 g; 0.20 mmol) gave a yellow solid which was filtered off and washed with methanol (0.07 g; 47%) (m.p. 168–172°C) [$\nu(\text{CO})$ 1050 cm⁻¹; $\nu(\text{RuO})$ 495 cm⁻¹ (mull)].

Tri- μ -methoxobis[(η -mesitylene)ruthenium(II)] tetraphenylborate

By method C, using [$\{\text{Ru}(\eta\text{-C}_6\text{H}_3\text{Me}_3)\text{Cl}_2\}_2$] (0.12 g; 0.20 mmol) and freshly prepared NaOMe [Na (0.10 g) in methanol (10 cm³)]. The resulting orange solution was filtered and an excess of NaBPh₄ (0.20 g; 0.60 mmol) in methanol

added to give a copious yellow precipitate which was filtered and washed with methanol and diethylether (0.12 g; 65%) (m.p. 203–205°C) [$\nu(\text{CO})$ 1025 cm^{-1}]. ^{13}C - $\{^1\text{H}\}$ NMR in $(\text{CD}_3)_2\text{CO}$ (298 K): δ 121–136 ppm (BPh_4^-); δ 91.4 (CMe), 77.7 (CH), 67.2 (OMe), 17.4 (Me) ppm. Slope of $\Lambda_0 - \Lambda_e$ vs. $C_e^{1/2}$ plot in $\text{CH}_3\text{NO}_2 = 176$.

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References

- 1 (a) See R.O. Gould, W.J. Sime and T.A. Stephenson, *J. Chem. Soc. Dalton Trans.*, (1978) 76; (b) T. Arthur and T.A. Stephenson, *J. Organometal. Chem.* 168 (1979) C39; (c) *ibid.*, 208 (1981) 369, and references therein.
- 2 Preliminary communications 3: (a) D.R. Robertson and T.A. Stephenson, *J. Organometallic Chem.*, 116 (1976) C29; (b) R.O. Gould, C.L. Jones, D.R. Robertson and T.A. Stephenson, *J. Chem. Soc. Chem. Commun.*, (1977) 222; (c) D.R. Robertson and T.A. Stephenson, *J. Organometal. Chem.*, 157 (1978) C47.
- 3 J.W. Kang and P.M. Maitlis, *J. Organometal. Chem.*, 30 (1971) 127.
- 4 R.A. Zelonka and M.C. Baird, *Canad. J. Chem.*, 50 (1972) 3063.
- 5 G.W. Bushnell, K.R. Dixon, R.G. Hunter and J.J. McFarland, *Canad. J. Chem.*, 50 (1972) 3694.
- 6 P.M. Treichel, W.K. Dean and J.C. Calabrese, *Inorg. Chem.*, 12 (1973) 2908.
- 7 T.V. Ashworth, M.J. Nolte and E. Singleton, *J. Chem. Soc. Chem. Commun.*, (1977) 936.
- 8 R.O. Gould and C.L. Jones, private communication.
- 9 R.D. Feltham and R.G. Hayter, *J. Chem. Soc.*, (1964) 4587.
- 10 D.R. Robertson, T.A. Stephenson and T. Arthur, *J. Organometal. Chem.*, 162 (1978) 121.
- 11 W.J. Sime and T.A. Stephenson, *J. Organometal. Chem.*, 161 (1978) 245.
- 12 J. Cook, J.E. Hamlin, A. Nutton and P.M. Maitlis, *J. Chem. Soc. Chem. Commun.*, (1980) 144.
- 13 (a) R.O. Gould, C.L. Jones, D.R. Robertson and T.A. Stephenson, *Cryst. Struct. Commun.*, 7 (1978) 27; (b) D.R. Robertson, PhD Thesis, University of Edinburgh, 1978, p. 67.
- 14 R.C. Hayter and F.S. Humiec, *Inorg. Chem.*, 2 (1963) 306.
- 15 H. Kriegman and E. Licht, *Z. Electrochem.*, 62 (1958) 1163.
- 16 M.A. Bennett, T.N. Huang and T.W. Turney, *J. Chem. Soc. Chem. Commun.*, (1979) 312.
- 17 D.A. Tocher, unpublished work.
- 18 A.J. Birch and G. Subba Rao, *Adv. Org. Chem.*, 8 (1972) 1.
- 19 M.A. Bennett, T.W. Matheson, G.B. Robertson, A.K. Smith and P.A. Tucker, *Inorg. Chem.*, 19 (1980) 1014.