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SYNTHESIS OF TRIPLE HALIDE-BRIDGED ARENE COMPLEXES OF RUTHENIUM(II) AND OSMIUM(II)

T. ARTHUR and T.A. STEPHENSON *

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

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Summary

Reaction of $[\{M(\eta\text{-arene})X_2\}_2]$ (M = Ru; X = Cl^-, Br^-, I^-; M = Os, X = Cl^-) with C_5H_5N in methanol, followed by addition of NH_4PF_6 gives the monocations $[M(\eta\text{-arene})X(C_5H_5N)_2]PF_6$. Treatment of an equimolar mixture of these compounds and the corresponding $[M(\eta\text{-arene})X_2(C_5H_5N)]$ with HBF_4 in methanol then provides a high yield synthesis of the triple halide-bridged complexes $[M_2(\eta\text{-arene})_2X_3]BF_4$. Spectroscopic evidence for the formation of hetero-bridged, heteroarene and heteronuclear triple halide-bridged arene complexes of ruthenium(II) and osmium(II) using this synthetic route is also discussed.

Recently we reported that reaction of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ in methanol at ambient temperature with a slight excess of NH_4PF_6 for 24 hours gave, in high yield, $[\eta\text{-}C_6H_6RuCl_3Ru\eta\text{-}C_6H_6]PF_6$ (I). The most likely mechanism of formation of this cation was proposed to be by intermolecular coupling of the weakly solvated monomers $[Ru(\eta\text{-}C_6H_6)Cl_2MeOH]$ and $[Ru(\eta\text{-}C_6H_6)Cl(MeOH_2)]^+$. Unfortunately, attempts to prepare other triple halide-bridged cations $[Ru_2(\eta\text{-arene})_2X_3]^+$ (arene = 1,3,5-$C_6H_3Me_3$; X = Cl^-; arene = C_6H_6; X^- = Br^-, I^-, SCN^-) by reaction of the appropriate double halide-bridged dimers $[\{Ru(\eta\text{-arene})X_2\}_2]$ with NH_4PF_6 in methanol were unsuccessful, only $[\{Ru(\eta\text{-arene})X_2\}_2]$ being isolated. This failure was attributed to the very insoluble nature of these $[\{Ru(\eta\text{-arene})X_2\}_2]$ compounds which prevents formation of appreciable amounts of methanolate monomers [1].

In this paper, we now report the full results [2] of our attempts to develop more general, high yield, synthetic routes to these $[M_2(\eta\text{-arene})_2X_3]^+$ cations (M = Ru, Os).

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Results and discussion

(a) Syntheses and characterisation of [M(η-arene)X_2(C_5H_5N) and [M(η-arene)-X(C_5H_5N)$_2$]PF_6 complexes

Since the proposed mechanism of formation of compound I involves the coupling of the solvated monomers [Ru(η-C_6H_6)Cl_2MeOH] and [Ru(η-C_6H_6)Cl-(MeOH)$_2$]$^+$ [1], it was therefore considered that a good way of synthesising other complexes analogous to I would be by in situ generation of the appropriate solvated species. It was thought that this might be best accomplished by reaction of an equimolar mixture of [Ru(η-arene)X_2L] and [Ru(η-arene)X-(L)$_2$]PF_6 (where L is a ligand which can readily be protonated to give a good leaving group LH^+) with acids such as HBF_4 or HPF_6 which contain large, non-coordinating anions. Suitable complexes [Ru(η-arene)Cl_2(C_5H_5N)] [3] and [Ru(η-arene)Cl(N-N)]PF_6 (N-N = 2,2′-bipyridyl or 1,10-phenanthroline) [4] had already been synthesised but the bidentate ligands (N-N) proved very difficult to protonate completely (see later) and hence these could not be used successfully.

TABLE 1

ANALYTICAL DATA FOR SOME ARENE-RUTHENIUM(II) AND -OSMIUM(II) COMPOUNDS

Compound	Analysis (%) [a]			
	C	H	N	Halide
$Ru(C_6H_6)Cl_2(C_5H_5N)$	40.2(40.1)	3.4(3.4)	4.3(4.3)	—
$Ru(C_6H_6)Br_2(C_5H_5N)$	31.9(31.6)	2.7(2.7)	3.2(3.4)	—
$Ru(C_6H_3Me_3)Cl_2(C_5H_5N)$	45.3(45.3)	4.6(4.6)	3.8(3.8)	—
$[Ru(C_6H_6)Cl(C_5H_5N)_2]PF_6$	36.9(37.1)	3.0(3.1)	5.4(5.4)	—
$[Ru(C_6H_6)Br(C_5H_5N)_2]PF_6$	34.2(34.2)	2.8(2.9)	4.9(5.0)	—
$[Ru(C_6H_3Me_3)Cl(C_5H_5N)_2]PF_6$	40.6(40.8)	3.9(4.0)	4.9(5.0)	—
$[Ru(C_6H_3Me_3)Br(C_5H_5N)_2]PF_6$	37.3(37.8)	3.7(3.7)	5.3(4.6)	—
$[Ru(C_6H_3Me_3)I(C_5H_5N)_2]PF_6$	34.8(35.0)	3.4(3.4)	4.5(4.3)	—
$[Ru(p\text{-}MeC_6H_4CHMe_2)Cl(C_5H_5N)_2]PF_6$	41.6(41.9)	4.1(4.2)	4.8(4.9)	—
$[Os(C_6H_6)Cl(C_5H_5N)_2]PF_6$	31.8(31.7)	2.7(2.7)	4.7(4.6)	—
$[Os(p\text{-}MeC_6H_4CHMe_2)Cl(C_5H_5N)_2]PF_6$	36.2(36.2)	3.6(3.7)	4.3(4.2)	—
$[Ru_2(C_6H_6)_2Cl_3]BF_4$	26.0(26.1)	2.1(2.2)	—	18.6(19.3) [b]
$[Ru_2(C_6H_6)_2Br_3]BF_4$	21.3(21.0)	1.9(1.8)	—	32.7(35.0) [c]
$[Ru_2(C_6H_6)_2Cl_3]PF_6$	23.8(23.6)	2.0(2.0)	—	—
$[Ru_2(C_6H_6)_2Br_3]PF_6$	19.4(19.4)	1.6(1.6)	—	—
$[Ru_2(C_6H_6)_2I_3]PF_6$	16.3(16.3)	1.3(1.4)	—	—
"$[Ru_2(C_6H_6)_2BrCl_2]BF_4$"	24.2(24.2)	2.0(2.0)	—	12.1(11.9) [b]; 13.9(13.4) [c]
"$[Ru_2(C_6H_6)_2Br_2Cl]BF_4$"	22.6(22.5)	1.9(1.9)	—	5.5(5.5) [b]; 24.7(24.9) [c]
$[Ru_2(C_6H_3Me_3)_2Cl_3]BF_4$	33.8(34.0)	3.5(3.8)	—	—
$[Ru_2(C_6H_3Me_3)_2Br_3]BF_4$	27.9(28.1)	3.0(3.2)	—	—
$[Ru_2(C_6H_3Me_3)_2I_3]BF_4$	23.5(23.8)	2.6(2.7)	—	41.6(41.8) [d]
"$[Ru_2(C_6H_6)(C_6H_3Me_3)Cl_3]BF_4$" [e]	29.4(30.3)	2.9(3.0)	—	—
$[Ru_2(p\text{-}MeC_6H_4CHMe_2)_2Cl_3]PF_6$	33.3(33.3)	4.0(3.9)	—	—
$[Ru_2(p\text{-}MeC_6H_4CHMe_2)_2Br_3]PF_6$	27.9(28.1)	3.2(3.3)	—	—
$[Ru_2(p\text{-}MeC_6H_4CHMe_2)_2I_3]PF_6$	24.8(24.1)	2.8(2.8)	—	38.0(38.2) [d]
$[Os_2(C_6H_6)_2Cl_3]BF_4$	21.5(21.3)	2.0(1.8)	—	—
"$[OsRu(C_6H_6)_2Cl_3]BF_4$"	22.5(22.5)	1.8(1.9)	—	16.8(16.6) [a]

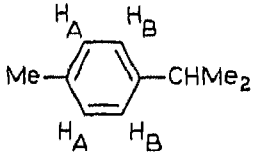
[a] Calculated figures in parentheses; [b] Chloride; [c] Bromide; [d] Iodide; [e] Product from reaction of $Ru(C_6H_6)C$ (C_5H_5N) and $[Ru(C_6H_3Me_3)Cl(C_5H_5N)_2]PF_6$.

TABLE 2

HYDROGEN-1 NMR DATA FOR SOME NEUTRAL AND CATIONIC PYRIDINE MONOMERIC COMPLEXES [a]

Compound	δ(ppm) [b]	
	Coordinated arene protons	Pyridine resonances
$Ru(C_6H_3Me_3)Cl_2(C_5H_5N)$	4.88(s)(H), 2.02(s)(Me)	9.02(m), 7.69(m), 7.29(m)
$Ru(C_6H_3Me_3)Br_2(C_5H_5N)$ [c]	4.96(s)(H), 2.15(s)(Me)	—
$Ru(C_6H_3Me_3)I_2(C_5H_5N)$	5.10(s)(H), 2.25(s)(Me)	9.40(m), 7.70(m), 7.25(m)
$[Ru(C_6H_6)Cl(C_5H_5N)_2]PF_6$	6.17(s)	8.85(m), 8.00(m), 7.45(m)
$[Ru(C_6H_6)Br(C_5H_5N)_2]PF_6$	6.22(s)	8.85(m), 8.04(m), 7.48(m)
$[Ru(C_6H_3Me_3)Cl(C_5H_5N)_2]PF_6$	5.49(s)(H), 1.96(s)(Me)	9.18(m), 8.06(m), 7.58(m)
$[Ru(C_6H_3Me_3)Br(C_5H_5N)_2]PF_6$	5.57(s)(H), 2.03(s)(Me)	9.16(m), 8.06(m), 7.59(m)
$[Ru(C_6H_3Me_3)I(C_5H_5N)_2]PF_6$	5.69(s)(H), 2.15(s)(Me)	9.10(m), 8.10(m), 7.60(m)
$[Ru(p\text{-}MeC_6H_4CHMe_2)Cl(C_5H_5N)_2]PF_6$ [d]	5.72(ΔH_AH_B 28.4 Hz, J = 6.0 Hz) 2.66(sp $CHMe_2$) 1.73(s, CH_3) 1.13(d, CH_3 of $CHMe_2$, J = 6.0 Hz)	8.88(m), 7.85(m), 7.42(m)
$[Os(C_6H_6)Cl_2(C_5H_5N)]PF_6$	6.38(s)	8.93(m), 8.10(m), 7.50(m)
$[Os(p\text{-}MeC_6H_4CHMe_2)Cl(C_5H_5N)_2]PF_6$ [d]	6.23(ΔH_AH_B 30.0 Hz, J = 6.0 Hz) 2.74(sp $CHMe_2$) 1.82(s, CH_3) 1.18(d, CH_3 of $CHMe_2$, J = 6.0 Hz)	8.90(m), 8.02(m), 7.48(m)
$[Ir(C_5Me_5)Cl(C_5H_5N)_2]PF_6$	1.55(s)(Me)	8.99(m), 8.09(m), 7.64(m)

[a] All neutral complexes run in $CDCl_3$ and cationic complexes in d6-Me_2CO at 298 K, s = singlet, d = doublet, sp = septet, m = multiplet. [b] Referenced to $SiMe_4$ (internal lock). [c] NMR of this compound obtained from mixture and therefore no pyridine resonances quoted. [d] Labelling of *p*-cymene protons.



Chemical shift difference calculated for line positions using formula $\Delta H_AH_B = [(\upsilon_1 - \upsilon_4)(\upsilon_2 - \upsilon_3)]^{1/2}$ since an AB rather than AA'BB' pattern was observed. Midpoint of AB resonance is quoted.

The complex $[Ru(\eta\text{-}C_6H_6)Cl(C_5H_5N)_2]PF_6$ is known [1], but since it was synthesised from the triple bridged complex I, this route could not be used to generate the analogous complexes $[Ru(\eta\text{-arene})X(C_5H_5N)_2]PF_6$ ($X = Br^-$, I^- etc) since the compounds $[Ru_2(\eta\text{-arene})_2X_3]PF_6$ were of course unknown. However, it has been reported that the complex $[Ru(\eta\text{-}C_6H_6)Cl(en)]BPh_4$ could be synthesised by reaction of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ with a slight excess of ethylenediamine (en) in methanol, followed by addition of an excess of $NaBPh_4$ [5]. We have found that reaction of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ with C_5H_5N in methanol followed by additions of NH_4PF_6 gave $[Ru(\eta\text{-}C_6H_6)Cl(C_5H_5N)_2]PF_6$ in high yield. This reaction was found to be quite general and the complexes $[Ru(\eta\text{-arene})X(C_5H_5N)_2]PF_6$ (M = Ru, $X = Br^-$, arene = C_6H_6; M = Ru, $X = Cl^-$, Br^-, I^-, arene = 1,3,5-$C_6H_3Me_3$; and M = Os, $X = Cl^-$, arene = C_6H_6, *p*-MeC_6H_4-$CH(Me)_2$ were prepared similarly. However, more forcing reaction conditions were required when M = Ru, $X = Br^-$, arene = C_6H_6 or when M = Os, $X = Cl^-$, arene = C_6H_6 and this is probably mainly due to the increased stability of the corresponding compounds $[\{M(\eta\text{-arene})X_2\}_2]$ towards bridge cleavage. This is further emphasised by the failure to generate the compounds $[Ru(\eta\text{-}C_6H_6)X(C_5H_5N)_2]PF_6$ ($X = I^-$, SCN^-) from the very insoluble complexes $[\{Ru(\eta\text{-}C_6H_6)X_2\}_2]$, even under very vigorous conditions, eg. refluxing in ethanol with a very high concentration of pyridine present. Another reaction designed to synthesise these complexes, namely treatment of $[Ru(\eta\text{-}C_6H_6)Cl(C_5H_5N)_2]PF_6$ with a 1 : 1 molar ratio of $AgPF_6$ in methanol to generate in situ the dication $[Ru(\eta\text{-}C_6H_6)(MeOH)(C_5H_5N)_2]^{2+}$, followed by addition of LiX ($X = I^-$ or SCN^-) also failed, since the products were identified as the dimeric complexes $[\{Ru(\eta\text{-}C_6H_6)X_2\}_2]$. Presumably, the driving force for the formation of these dimers is their extreme insolubility.

The complexes $[Ru(\eta\text{-arene})X(C_5H_5N)_2]PF_6$ were characterised by elemental analyses (Table 1), IR spectra, which showed the presence of C_5H_5N and PF_6^- vibrations, and ^1H NMR spectroscopy in $(CD_3)_2CO$ (Table 2), integration indicating two coordinated pyridine ligands for each η-arene ring.

As shown in Table 2, there is a shift to high frequency of the aromatic protons of the η-arene rings in the complexes $[Ru(\eta\text{-arene})X(C_5H_5N)_2]PF_6$ as the halide changes from Cl^- to Br^- to I^-. A similar deshielding trend has been observed for the complexes $[Ti(\eta\text{-}C_5H_5)_2X_2]$ ($X = Cl^-$, Br^-, I^-) [6] and this was attributed to the increase in double bond character of the Ti—X bond (the resonance effect). This suggests that the apparent electron-withdrawing power of the halides is in the order $I^- > Br^- > Cl^-$ which is the opposite of that expected on a purely inductive effect based on the electronegativity of the halide.

As reported earlier [3], the complexes $[Ru(\eta\text{-arene})X_2(C_5H_5N)]$ ($X = Cl^-$, Br^-, arene = C_6H_6; $X = Cl^-$, I^-, arene = $C_6H_3Me_3$) were synthesised by direct reaction of $[\{Ru(\eta\text{-arene})X_2\}_2]$ with pyridine. These were characterised by elemental analyses (Table 1), IR spectra which showed the presence of coordinated pyridine and, for arene = $C_6H_3Me_3$, the compounds were sufficiently soluble for ^1H NMR studies (Table 2). Integration of the ^1H NMR resonances confirmed the presence of one coordinated pyridine ligand for each η-$C_6H_3Me_3$ ring. As was observed for the bis-pyridine complexes, there is a shift to high frequency of the aromatic protons in the order $I^- > Br^- > Cl^-$ and a similar explanation can be invoked.

(b) Syntheses and characterisation of the symmetric triple bridged complexes $[M_2(\eta\text{-arene})_2X_3]Y$ *(M = Ru, X = Cl⁻, Br⁻; arene =* C_6H_6*, Y =* BF_4^-*; X = Cl⁻, Br⁻, I⁻; arene =* C_6H_6*, p-*$MeC_6H_4CHMe_2$*, Y =* PF_6^-*; X = Cl⁻, Br⁻, I⁻, arene =* $C_6H_3Me_3$*, Y =* BF_4^-*; M = Os, X = Cl⁻. arene =* C_6H_6*, Y =* BF_4^-*)*

The reaction of $[Ru(\eta\text{-}C_6H_6)Cl_2(C_5H_5N)]$ and $[Ru(\eta\text{-}C_6H_6)Cl(bipy)]PF_6$ (1 : 1 molar ratios) with HBF_4 in methanol gave, after removal of the solvent, an orange solid, shown by elemental analyses to contain small amounts of nitrogen. The ^1H NMR spectrum in CD_3NO_2 contained a strong signal at δ 5.93 ppm and a much weaker one at δ 6.30 ppm which were assigned to the benzene resonances of the triple bridge cation $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]^+$ and some unreacted $[Ru(\eta\text{-}C_6H_6)Cl(bipy)]^+$ cation, respectively. Furthermore, the yield of this product mixture was quite low and attempts to obtain the triple bridged complex in a pure state were unsuccessful.

If, however, $[Ru(\eta\text{-}C_6H_6)Cl(C_5H_5N)_2]PF_6$ was used in place of $[Ru(\eta\text{-}C_6H_6)Cl(bipy)]PF_6$, the reaction gave the triple bridged complex $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]BF_4$ in almost quantitative yields and in an analytically pure state. The mull IR spectrum of this complex was similar to that previously obtained for compound I [1], except for the bands attributable to BF_4^- as opposed to PF_6^-. The ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra in CD_3NO_2 at ambient temperature (Table 3) showed single resonances at δ 5.93 ppm and 82.0 ppm, respectively, assigned to the $\eta\text{-}C_6H_6$ groups (cf. the PF_6^- complex, which had ^1H and $^{13}C\text{-}\{^1H\}$ NMR signals at δ 5.90 ppm and 82.0 ppm, respectively). The analogous complexes $[Ru_2(\eta\text{-arene})_2X_3]BF_4$ (X = Br^-, arene = C_6H_6; X = Cl^-, I^-, arene = $C_6H_3Me_3$) were prepared and characterised similarly (see Experimental section and Tables 1 and 3). The complex $[Ru_2(\eta\text{-}C_6H_3Me_3)_2Cl_3]BF_4$ was also characterised by detailed conductivity measurements which showed that the molar conductance (Λ_m) in CH_3NO_2 was 90.5 S cm^2 mol^{-1} which lies within the range 75—95 S cm^2 mol^{-1} expected for 1 : 1 electrolytes in this solvent [7]. (See Experimental section for Λ_m values for other compounds). Furthermore, a plot of $\Lambda_0 - \Lambda_e$ vs $C_e^{1/2}$ [8] gave a straight line of slope 144 which is comparable to that obtained for other 1 : 1 electrolytes in CH_3NO_2, e.g. $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]PF_6$, Λ_m = 82 S cm^2 mol^{-1}, slope = 207 [1].

The observation that protonation of these monomers produces high yields of triple halide-bridged arene cations provides direct evidence for the postulated reaction pathway shown in the Scheme in ref. 1). It is not possible from these studies, however, to determine unequivocally whether the triple halide-bridged cation is formed by direct coupling of the solvated monomers or if a solvated, double halide-bridged cation (see Scheme, ref. [1]) is involved as a reaction intermediate. Good evidence that the latter is involved in provided by the observation that reaction of $[\{Ru(p\text{-}MeC_6H_4CHMe_2)X_2\}_2]$. (X = Cl^-, Br^-, I^-) with $AgPF_6$ (1 : 1 molar ratio) in acetone gives $[Ru_2(p\text{-}MeC_6H_4CHMe_2)_2X_3]PF_6$ in reasonable yield * (eqn. 1). Similarly $[Ru_2(\eta\text{-}C_6H_6)_2I_3]PF_6$ and $[Ru_2(\eta\text{-}C_6H_6)_2Br_3]PF_6$ were prepared by this route from $[\{Ru(\eta\text{-}C_6H_6)X_2\}_2]$ and $AgPF_6$ in CH_3NO_2. All these complexes were fully characterised by elemental

* Interestingly, attempts to synthesise these complexes starting from $[Ru(p\text{-}MeC_6H_4CHMe_2)X_2(C_5H_5N)]$, $[Ru(p\text{-}MeC_6H_4CHMe_2)X(C_5H_5N)_2]PF_6$ and HBF_4 were unsuccessful.

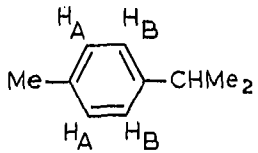
TABLE 3

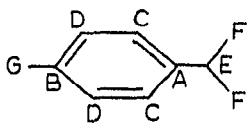
HYDROGEN-1 AND CARBON-13 NMR DATA FOR SOME BINUCLEAR COMPLEXES IN CD_3NO_2 AT 298 K

Compound	δ (ppm) [a]	
	^1H NMR	^{13}C-{^1H}NMR
$[Ru_2(C_6H_6)_2Cl_3]BF_4$	5.944(s) [b], 5.93(s) [c]	82.0
$[Ru_2(C_6H_6)_2Br_3]BF_4$	5.922(s) [b]	82.4
$[Ru_2(C_6H_6)_2Cl_3]PF_6$	5.90(s) [c]	82.0
$[Ru_2(C_6H_6)_2Br_3]PF_6$	5.92(s) [c]	82.3
$[Ru_2(C_6H_6)_2I_3]PF_6$	5.88(s) [c]	83.3
$[Ru_2(C_6H_6)_2BrCl_2]BF_4$ [d]	5.397(s) [b]	82.2
$[Ru_2(C_6H_6)_2Br_2Cl]BF_4$ [d]	5.929(s) [b]	82.3
$[Ru_2(C_6H_3Me_3)_2Cl_3]BF_4$	5.35(s)(H), 2.22(s)(Me)	102.0(*C*Me), 75.7(*C*H), 19.4(Me)
$[Ru_2(C_6H_3Me_3)_2Br_3]BF_4$	5.38(s)(H), 2.23(s)(Me)	100.3(*C*Me), 77.6(*C*H), 19.9(Me)
$[Ru_2(C_6H_3Me_3)_2I_3]BF_4$	5.52(s)(H), 2.30(s)(Me)	97.6(*C*Me), 81.7(*C*H), 20.7(Me)
$[Ru_2(C_6H_6)(C_6H_3Me_3)Cl_3]BF_4$ [d]	5.92(s), 5.37(s)(H), 2.20(s)(Me)	102.0(*C*Me), 82.0, 75.9(*C*H), 19.3(Me)
$[Os_2(C_6H_6)_2Cl_3]BF_4$	6.64(s)	73.6
$[OsRu(C_6H_6)_2Cl_3]BF_4$ [d]	6.46(s), 6.06(s)	82.3, 73.8
$[Ru_2(p\text{-}MeC_6H_4CHMe_2)_2Cl_3]PF_6$ [e,f]	5.70(ΔH_AH_B 19.4 Hz, J = 6.0 Hz) 2.84(sp *C*HMe_2), 2.23(s, CH_3) 1.32(d, CH_3 of $CHMe_2$, J = 6.0 Hz)	102.9(A), 99.0(B), 80.6(C), 79.4(D), 32.7(E), 22.4(F), 19.1(G)
$[Ru_2(p\text{-}MeC_6H_4CHMe_2)_2Br_3]PF_6$ [e,f]	5.64(ΔH_AH_B 21.2 Hz, J = 6.0 Hz), 2.84(sp *C*HMe_2(, 2.24(s, CH_3), 1.30(d, CH_3 of $CHMe_2$, J = 7.0 Hz)	103.9(A), 99.1(B), 80.2(C), 80.0(D), 32.8(E), 22.6(F), 19.7(G)
$[Ru_2(p\text{-}MeC_6H_4CHMe_2)_2I_3]PF_6$ [e,f]	5.66(ΔH_AH_B 20.1 Hz, J = 6.0 Hz) 2.90(sp *C*HMe_2), 2.34(s, CH_3), 1.30(d, CH_3 of $CHMe_2$, J = 7.0 Hz)	106.0(A), 99.6(B), 81.3(C), 80.5(D), 33.2(E), 22.9(F), 20.7(G)

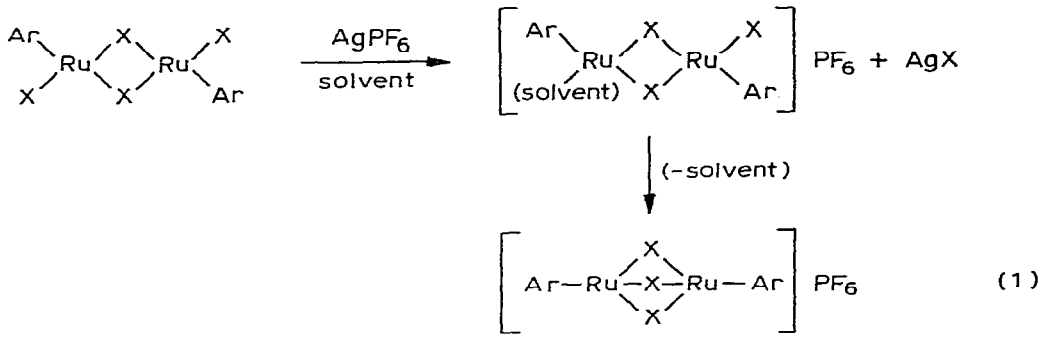
$[\{Ru(p\text{-}MeC_6H_4CHMe_2)Cl_2\}_2]$ [e,f,g]	5.45(ΔH_AH_B 12.0 Hz, J = 5.5 Hz) 2.93(sp C*H*Me$_2$), 2.17(s, CH_3), 1.29(d, CH_3 of $CHMe_2$, J = 6.0 Hz)	100.8(A), 96.5(B), 81.1(C), 80.3(D), 30.4(E), 21.9(F), 18.7(G)
$[\{Ru(p\text{-}MeC_6H_4CHMe_2)Br_2\}_2]$ [e,f,g]	5.43(ΔH_AH_B 11.2 Hz, J = 6.0 Hz) 2.95(sp C*H*Me$_2$), 2.20(s, CH_3) 1.26(d, CH_3 of $CHMe_2$, J = 7.0 Hz)	102.0(A), 96.7(B), 81.2(C), 81.1(D), 30.7(E), 22.2(F), 19.2(G)
$[\{Ru(p\text{-}MeC_6H_4CHMe_2)I_2\}_2]$ [e,f,g]	5.48(ΔH_AH_B 9.2 Hz, J = 6.0 Hz) 3.01(sp C*H*Me$_2$), 2.34(s, CH_3) 1.24(d, CH_3 of $CHMe_2$, J = 7.0 Hz)	104.2(A), 97.4(B), 82.4(C), 81.9(D) 31.3(E), 22.6(F), 20.1(G)
$[\{Os(p\text{-}MeC_6H_4CHMe_2)Cl_2\}_2]$ [e,f,g]	6.09(ΔH_AH_B 14.8 Hz, J = 6.0 Hz) 2.70(sp C*H*Me$_2$), 2.20(s, CH_3) 12.8(d, CH_3 of $CHMe_2$, J = 7.0 Hz)	92.5(A), 89.1(B), 74.0(C), 72.5(D), 31.3(E), 22.5(F), 19.4(G)

[a] Chemical shifts quoted to high frequency of $SiMe_4$ (internal lock), s = singlet, d = doublet, sp = septet. [b] Measured on XL100 NMR spectrometer. [c] Measured on HA100 NMR spectrometer. [d] NMR parameters of these compounds obtained from spectra of mixtures. [e] Labelling of *p*-cymene protons:





Chemical shift difference calculated from line positions using formula $\Delta(H_AH_B) = [(\upsilon_1 - \upsilon_4)(\upsilon_2 - \upsilon_3)]^{1/2}$ since an AB rather than AA'BB' pattern was observed. Midpoint of AB resonance is quoted. [f] Labelling of *p*-cymene carbons. [g] Spectra recorded in $CDCl_3$ at 298 K.



(1)

(Ar = p-$MeC_6H_4CHMe_2$, C_6H_6)

analyses, conductivity, ^1H and ^{13}C-{^1H} NMR studies (see Tables 1 and 3).

Furthermore, since protonation of the compounds [Ru(η-arene)X(C_5H_5N)$_2$]-PF_6 appears to generate the cations [Ru(η-arene)X(solv)$_2$]$^+$ in situ, it was hoped that in the absence of any [Ru(η-arene)X$_2$(solv)] intermediate, these monomeric solvated cationic intermediates would tetramerise with loss of coordinated solvent to give the novel cations [{Ru(η-arene)Cl}$_4$]$^{4+}$. The expected driving force for these reactions would be the formation of six strong ruthenium—ligand linkages since six coordinate Ru^{II} is a highly favoured stereochemistry [9]. A closely related complex [{Ru(η-C_6H_6)OH}$_4$]$(SO_4)_2$ 12 H_2O with a cubane-like structure has in fact been recently synthesised [10] and one proposed mechanism of formation was by facile tetramerisation of a [Ru(η-C_6H_6)OH(H_2O)$_2$]$^+$ cation. However, on reaction of [Ru(η-C_6H_6)Cl-(C_5H_5N)$_2$]PF_6 with HBF_4 in methanol, the only product isolated was the triple bridged complex [Ru$_2$(η-C_6H_6)$_2$Cl$_3$]BF_4. The failure of the cationic intermediate [Ru(η-C_6H_6)Cl(solv)$_2$]$^+$ to tetramerise is perhaps not surprising since on simple coulombic ideas, one would not expect four like charges to readily come together and form a complex of such high overall charge.

The only way to rationalise the formation of the triple bridged cation here is by postulating the occurrence of facile chloride exchange, enhanced by the addition of acid. This will generate some of the neutral species [Ru(η-C_6H_6)Cl_2-(MeOH)] which can then couple with the cation to give the triple bridged product. A "chloride deficient" product must also be formed but attempts to isolate this from solution were unsuccessful.

Although this facile chloride exchange probably prevents formation of any tetrameric cations, treatment of the compounds [M(η-arene)X(C_5H_5N)$_2$]PF_6 (M = Ru, X = Br^-, arene = $C_6H_3Me_3$; M = Os, X = Cl^-, arene = C_6H_6) with HBF_4 can be used to synthesise low yields of the corresponding triple bridged complexes [M$_2$(η-arene)$_2$X$_3$]BF_4. The reaction of the compound [Ru(p-MeC_6H_4-$CHMe_2$)Cl(C_5H_5N)$_2$]PF_6 with HBF_4 in methanol, however, does not give the corresponding triple bridged complex. No products could in fact be isolated from the reaction mixture and this is probably due to the high solubility of all the Ru(p-cymene) species *. This might also be the reason for the failure to

* As discussed earlier, however, triple halide-bridged cations containing this arene were isolated by treatment of [{Ru(p-$MeC_6H_4CHMe_2$)X$_2$}$_2$] with $AgPF_6$ in acetone.

synthesise the isoelectronic $[M_2(\eta\text{-}C_5Me_5)_2X_3]BF_4$ complexes (M = Rh, Ir) by reaction of $[M(\eta\text{-}C_5Me_5)X_2(C_5H_5N)]$ and $[M(\eta\text{-}C_5Me_5)X(C_5H_5N)_2]PF_6$ (X = Cl^-, I^-) with methanolic solutions of HBF_4.

(c) Syntheses and characterisation of the mixed complexes [MM'(arene)-(arene')X_2X']BF_4 (M = M' = Ru, X = Cl^-, Br^-, X' = Br^-, Cl^-, arene = arene' = C_6H_6; M = M' = Ru, X = X' = Cl^-, arene = C_6H_6, arene' = $C_6H_3Me_3$; M = Ru, M' = Os, X = X' = Cl^-, arene = arene' = C_6H_6)

Since the coupling reaction of $[M(\eta\text{-arene})X_2(C_5H_5N)]$ with $[M(\eta\text{-arene})X(C_5H_5N)_2]PF_6$ in HBF_4/MeOH was quite general, the possibility of using this route to synthesise hetero-bridged, hetero-arene and hetero-nuclear complexes was an obvious next step. Apart from some recent examples of mixed triple halide-bridged molybdenum complexes, e.g. $[Mo_2(\eta^7\text{-}C_7H_7)_2ClBr_2]$ [11] and the unsymmetrical complexes $[(\eta^7\text{-}C_7H_7)Mo(OR)_3Mo(\eta^3\text{-}C_7H_7)(CO)_2]$ [12] and $[(\eta^7\text{-}C_7H_7)Mo(ER)_3Mo(CO)_3]$ (E = S, Se) [13], no successful general syntheses of such compounds have been previously reported. Therefore, a number of reactions were carried out to try and remedy this deficiency.

Thus, the compounds $[Ru(\eta\text{-}C_6H_6)Cl_2(C_5H_5N)]$ and $[Ru(\eta\text{-}C_6H_6)Br(C_5H_5N)_2]PF_6$ (1 : 1 molar ratio) were reacted with HBF_4 in methanol and the product, which was isolated in high yield, analysed very closely for the mixed halide-bridged complex $[Ru_2(\eta\text{-}C_6H_6)_2Cl_2Br]BF_4$. The ^1H NMR spectrum in CD_3NO_2 on a wide spectral width (1000 Hz) showed a broadened resonance at δ 5.93 ppm. However, on a narrower spectral width (250 Hz) the resonance was seen to consist of several very closely separated peaks. A high resolution FT ^1H NMR spectrum at 298 K showed four resonances at δ 5.944, 5.937, 5.929 and 5.922 ppm of relative intensity 8 : 12 : 6 : 1. These were assigned to the $-(\mu Cl_3)-$, $-(\mu Cl)_2(\mu Br)-$, $-(\mu Cl)(\mu Br_2)-$ and $-(\mu Br)_3-$ cations respectively, since the triple chloro and triple bromo bridged cations have resonances at δ 5.944 and 5.922 ppm, respectively. Support for this conclusion comes from the observation that the experimental intensity ratio is that expected for a statistical mixture of these four products *. Furthermore, reaction of $[Ru(\eta\text{-}C_6H_6)Br_2(C_5H_5N)]$ and $[Ru(\eta\text{-}C_6H_6)Cl(C_5H_5N)_2]PF_6$ (1 : 1 molar ratio) with HBF_4/MeOH gave a product analysing for $[Ru_2(\eta\text{-}C_6H_6)_2ClBr_2]BF_4$ which showed the same four ^1H NMR resonances as above but now with relative intensities 1 : 6 : 12 : 8.

The fact that the complexes "$[Ru(\eta\text{-}C_6H_6)_2Cl_2Br]BF_4$" and "$[Ru_2(\eta\text{-}C_6H_6)_2ClBr_2]BF_4$" are a mixture of products in solution indicates that either the complexes are genuine single compounds in the solid state and rapidly rearrange when placed in solution, or that they are already a mixture of four triple halide-bridged complexes. If the latter is true, then facile halide exchange reactions must occur before and/or during and/or after the coupling process. There-

* The statistical probability of forming the following cations starting from $[Ru(\eta\text{-}C_6H_6)Cl_2(C_5H_5N)]$ and $[Ru(\eta\text{-}C_6H_6)Br(C_5H_5N)_2]PF_6$ (1 : 1 molar ratio) is as follows:
$[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]^+$ 2/3 × 2/3 × 2/3 = 8/27 = 8
$[Ru_2(\eta\text{-}C_6H_6)_2Cl_2Br]^+$ (2/3 × 2/3 × 1/3)3 = 12/27 = 12
$[Ru_2(\eta\text{-}C_6H_6)_2ClBr_2]^+$ (2/3 × 1/3 × 1/3)3 = 6/27 = 6
$[Ru_2(\eta\text{-}C_6H_6)_2Br_3]^+$ (1/3 × 1/3 × 1/3) = 1/27 = 1

fore, a number of further reactions were carried out in an attempt to clarify these interesting observations.

For example, it is readily demonstrated that facile halide exchange can occur prior to protonation since on mixing $[Ru(\eta\text{-}C_6H_6)Br(C_5H_5N)_2]PF_6$ and $[Ru(\eta\text{-}C_6H_6)Cl_2PPh_3]$ * in $(CD_3)_2CO$ at ambient temperature and leaving for a few minutes, ^1H NMR studies show that three new resonances at δ 6.18, 5.47 and 5.45 ppm are formed. These can be assigned to the complexes $[Ru(\eta\text{-}C_6H_6)Cl(C_5H_5N)_2]PF_6$, $[Ru(\eta\text{-}C_6H_6)Br_2PPh_3]$ and $[Ru(\eta\text{-}C_6H_6)ClBrPPh_3]$, respectively. This was accompanied by a decrease in the intensity of the resonance due to $[Ru(\eta\text{-}C_6H_6)Br(C_5H_5N)_2]PF_6$ (δ 6.22 ppm) and the complete disappearance of the resonance due to $[Ru(\eta\text{-}C_6H_6)Cl_2PPh_3]$ (δ 5.43 ppm). Similar facile halide exchange processes were observed on mixing solutions of $[Ru(\eta\text{-}C_6H_3Me_3)I(C_5H_5N)_2]PF_6$ and $[Ru(\eta\text{-}C_6H_3Me_3)Cl_2(C_5H_5N)]$, but, surprisingly, no halide exchange occurred between $[Ru(\eta\text{-}C_6H_3Me_3)Cl(C_5H_5N)_2]PF_6$ and $[Ru(\eta\text{-}C_6H_3Me_3)I_2(C_5H_5N)]$ under these conditions.

No halide exchange occurred when $[Ru(\eta\text{-}C_6H_5)Br(C_5H_5N)_2]PF_6$ was shaken with an excess of LiCl in $(CD_3)_2CO$ at ambient temperature for several hours. However, when the reverse reaction was carried out, i.e. $[Ru(\eta\text{-}C_6H_6)Cl(C_5H_5N)_2]PF_6$ plus an excess of LiBr, complete exchange readily occurred, as shown by the disappearance of the $\eta\text{-}C_6H_6$ resonance at δ 6.18 ppm (chloro complex) and the appearance of a resonance at δ 6.22 ppm (bromo complex) in the ^1H NMR spectrum of the solution.

Hence, all these results would appear to indicate that the Ru—X bonds of the cationic complexes are more labile than those of the corresponding neutral monomers and, furthermore, that the order of displacement is $I^- > Br^- > Cl^-$.

As discussed earlier, the synthesis of small amounts of $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]BF_4$ by protonation of $[Ru(\eta\text{-}C_6H_6)Cl(C_5H_5N)_2]PF_6$ alone clearly indicates that facile chloride ion exchange occurs as a result of protonation. Therefore, irrespective of the halide attached to ruthenium in the $[Ru(\eta\text{-arene})X(C_5H_5N)_2]^+$ cations, facile halide exchange will also occur on protonation, thus producing a complex mixture of solvated monomers (when the halide ions in the cationic and neutral monomers are, of course, different) which will then generate a statistical mixture of triple halide-bridged compounds by cross-coupling reactions.

However, further complications are introduced by the observation that mixing $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]BF_4$ and $[Ru_2(\eta\text{-}C_6H_6)_2Br_3]BF_4$ at ambient temperature in CD_3NO_2 and leaving for a few minutes produces a mixture of the $-(\mu Cl)_3-$, $-(\mu Cl_2)(\mu Br)-$, $-(\mu Cl)(\mu Br)_2-$ and $-(\mu Br)_3-$ cations (^1H NMR evidence). In other words, facile halide exchange can also occur after the formation of the triple bridged cations. For this reason, no attempts have been made to separate the various species by either chromatographic or fractional crystallisation techniques.

Possible mechanisms for this facile halide exchange reaction between the dimers are illustrated in Figure 1. The only difference between the proposals

* The complex $[Ru(\eta\text{-}C_6H_6)Cl_2PPh_3]$ was used because of the insolubility of $[Ru(\eta\text{-}C_6H_6)Cl_2(C_5H_5N)]$ in acetone.

is in the structure of the tetranuclear intermediate which either retains the triple halide interactions (Figure 1a) or undergoes partial solvent assisted bridge cleavage to give an intermediate with double halide bridges (Figure 1b). Insufficient evidence is available to distinguish between these possibilities, although a similar tetranuclear intermediate to that shown in Figure 1b has been postulated in the reaction of $[Pd_2Cl_4L_2]$ with $[Pt_2Cl_4L_2]$ which gives some $[PdPtCl_4L_2]$ (L = PEt_3, P-n-Pr_3, P-n-Bu_3) [14].

In an attempt to synthesise triple halide-bridged hetero-arene complexes an equimolar mixture of $[Ru(\eta\text{-}C_6H_6)Cl_2(C_5H_5N)]$ and $[Ru(\eta\text{-}C_6H_3Me_3)Cl(C_5H_5N)_2]PF_6$ was treated with HBF_4 in methanol. Although the product isolated analysed quite well for the mixed arene compound $[Ru_2(\eta\text{-}C_6H_6)(\eta\text{-}C_6H_3Me_3)Cl_3]BF_4$, the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra of this material in CD_3NO_2 showed it consisted of the three cations $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]^+$, $[Ru_2(\eta\text{-}C_6H_3Me_3)_2Cl_3]^+$ and $[Ru_2(\eta\text{-}C_6H_6)(\eta\text{-}C_6H_3Me_3)Cl_3]^+$ in intensity ratio 2 : 1 : 2, respectively (Table 3). When $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]^+$ and $[Ru_2(\eta\text{-}C_6H_3Me_3)_2Cl_3]^+$ are mixed in solution, ^1H NMR studies reveal that in contrast to the $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]^+/[Ru_2(\eta\text{-}C_6H_6)_2Br_3]^+$ system the mixed arene cation is formed very slowly (several days). The comparative slowness of this scrambling process does not, however, necessarily indicate that different mechanisms to those postulated in Figure 1 for halogen exchange are operating. The difference in rate may be due to unfavourable steric affects from the bulkier mesitylene rings which destabilises the proposed tetranuclear intermediates.

Reaction of $[Ru(\eta\text{-}C_6H_6)Cl_2(C_5H_5N)]$ with $[Os(\eta\text{-}C_6H_6)Cl(C_5H_5N)_2]PF_6$ and HBF_4 in MeOH gave an orange solid which analysed well for $[OsRu(\eta\text{-}C_6H_6)_2Cl_3]BF_4$. However, the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra in CD_3NO_2 at 298 K revealed that this product is a mixture of the complexes $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]BF_4$, $[Os_2(\eta\text{-}C_6H_6)_2Cl_3]BF_4$ and $[OsRu(\eta\text{-}C_6H_6)_2Cl_3]BF_4$ (Table 3). Rapid formation of this hetero-nuclear complex is found when solutions of $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]BF_4$ and $[Os_2(\eta\text{-}C_6H_6)_2Cl_3]BF_4$ are mixed, although a pure sample of the mixed species could not be generated. A general reaction scheme for the formation of hetero-bridged, hetero-arene and hetero-nuclear complexes starting from the two cations $[M_2(\eta\text{-arene})_2X_3]^+$ and $[M_2'(\eta\text{-arene}')_2X_3']^+$ is outlined in Figure 2.

Finally, as shown in Table 3, the variations in the chemical shifts of both the aromatic protons and their associated carbons depend on the halide in the triple bridge and on the arene. Thus, when the arene is benzene, there is a decrease in the proton chemical shift as the bridging halide changes from chloride to bromide to iodide and this is accompanied by an increase in the chemical shift of the tertiary ring carbons. However, when the arene is mesitylene there is an increase in the chemical shifts of the aromatic protons and a corresponding increase in the shift of the tertiary ring carbons for the same change of halide. When the arene is *p*-cymene, there is no overall trend in the proton shift, but an increase in the carbon chemical shifts is observed. Interestingly, when compounds of ruthenium and osmium are compared, changing from ruthenium to osmium produces a substantial shift to high frequency for the aromatic protons signal but a shift to low frequency for the ring carbon resonances. There are many different factors here which can influence the size and direction of NMR chemical shifts, e.g. inductive and resonance effects of the halide, ring current effects. changes in configuration of the rings with respect to

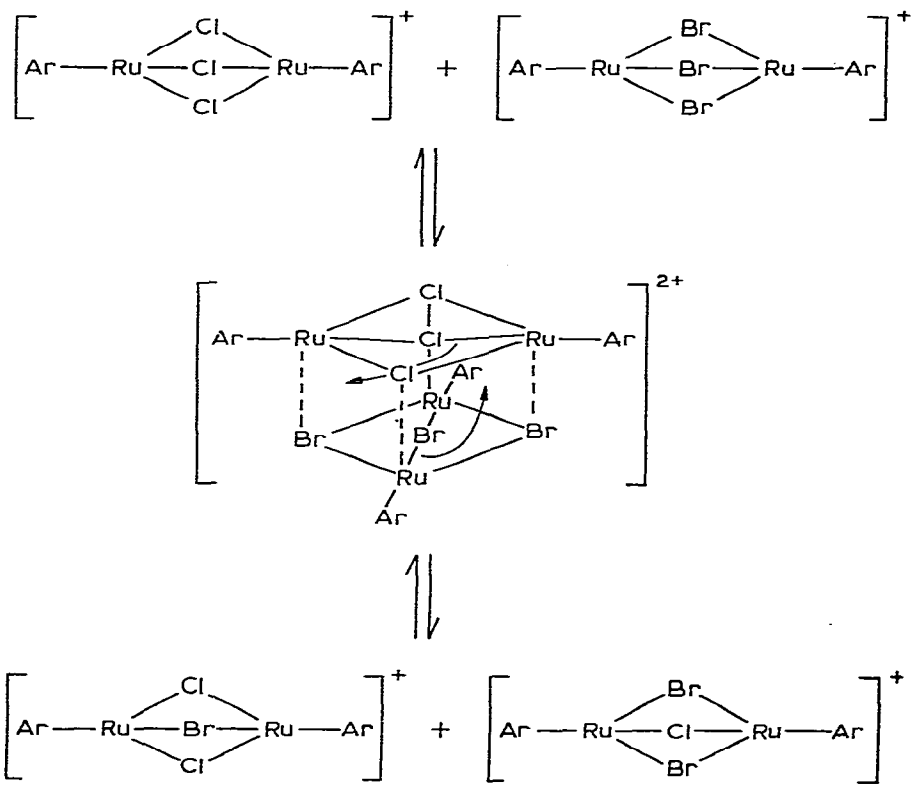
bridging groups etc. Since there is almost certainly a delicate balance between many of these factors, it is not feasible at this juncture to present a rationale for the observed trends.

Conclusion

A general route has been found for the syntheses of a variety of new triple halide-bridged arene cations including some with different arenes, different metals and different bridging groups. However, because of facile scrambling processes before, during and after coupling of the monomeric precursors, pure samples of the latter could not be isolated. Nevertheless much valuable spectroscopic information about these novel compounds has been ascertained and reaction schemes for the various scrambling processes have been inferred.

Experimental

Microanalyses were by B.M.A.C. and the University of Edinburgh Chemistry Department. Molecular weights were determined in C_6H_6 on a Perkin-Elmer-Hitachi osmometer (model 115). Infrared spectra were recorded in the region 4000—250 cm^{-1} on a Perkin-Elmer 457 grating spectrometer using Nujol mulls on caesium iodide plates. Hydrogen-1 NMR spectra were obtained on Varian



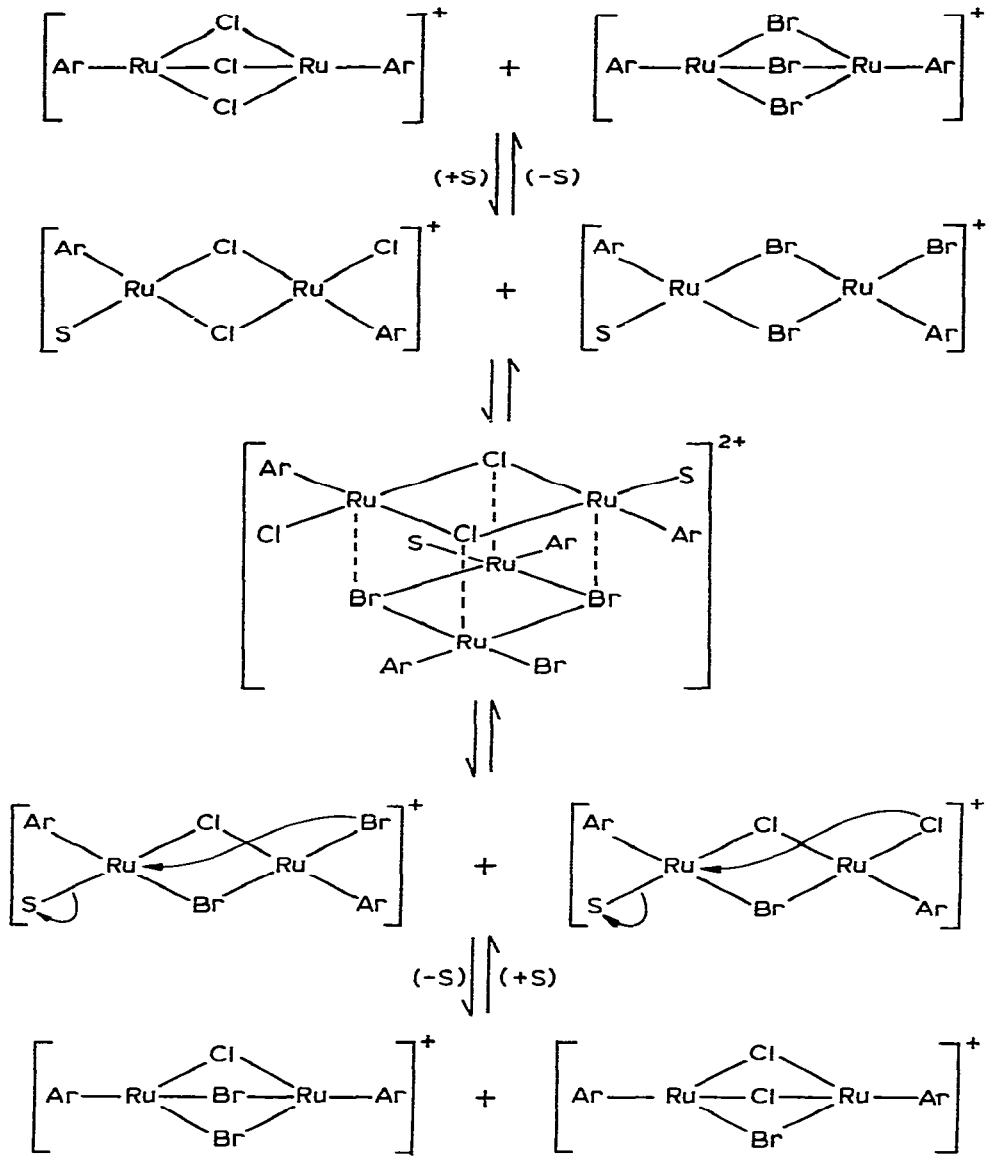


Fig. 1a and b. Possible mechanisms for halide exchange between the cations $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]^+$ and $[Ru_2(\eta\text{-}C_6H_6)_2Br_3]^+$.

Associates HA-100 and XL100 (FT) spectrometers. Carbon-13 NMR spectra were recorded on a Varian CFT 20 spectrometer operating at 20 MHz and ^{13}C chemical shifts are quoted in ppm to high frequency of TMS. Conductivity measurements were made at 303 K using a model 310 Portland Electronics conductivity bridge. Melting points were determined with a Köfler hot-stage microscope and are uncorrected.

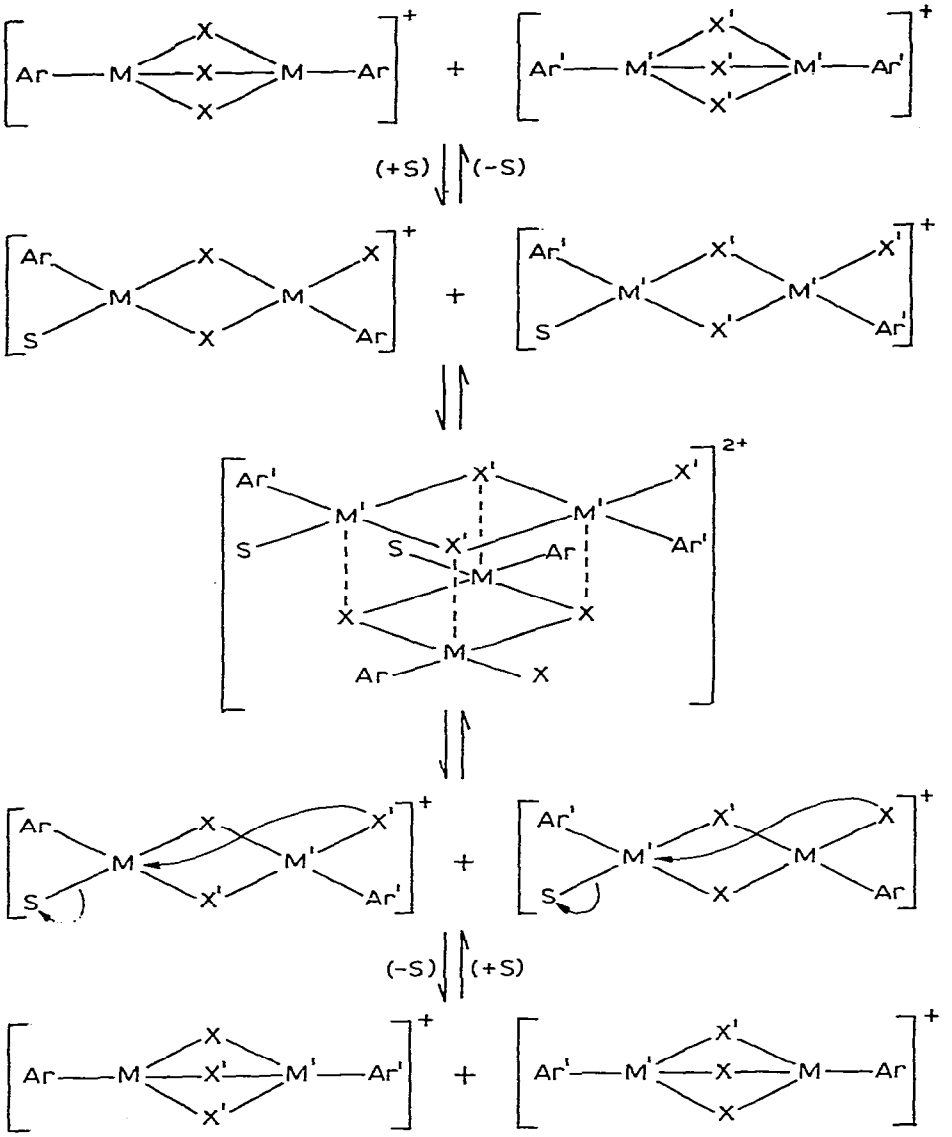


Fig. 2. General reaction scheme for the formation of heterobridged, heteroarene and heteronuclear cations starting from $[M_2(\eta\text{-arene})_2X_3]^+$ and $[M_2'(\eta\text{-arene}')_2X'_3]^+$.

Materials

Ruthenium trichloride trihydrate and sodium hexachloro-osmate(IV) (Johnson Matthey Ltd), α-phellandrene (5-isopropyl)-2-methylcyclohexa-1,3-diene) (Eastman Chemicals); CD_3NO_2, cyclohexa-1,3-diene (Aldrich Chemicals); LiBr, LiI, LiSCN (BDH); pyridine, tetrafluoroboric acid (40% aqueous solution) (Fisons); NH_4PF_6 and $AgPF_6$ (Alfa) were used as supplied. The compounds 1,3,5-trimethylcyclohexa-1,4-diene, 1-methoxycyclohexa-1,4-diene and cyclohexa-1,4-diene were prepared by the standard Birch reduction of the corre-

sponding arenes [15]. The compounds $[\{Ru(\eta\text{-arene})Cl_2\}_2]$ (arene = C_6H_6, 1,3,5-$C_6H_3Me_3$, p-$MeC_6H_4CH(Me)_2$ and C_6H_5OMe) were prepared by the following modifications of the literature methods [3,16]. Aqueous solutions of the commercial ruthenium trichloride (pH ~1.5) were first evaporated to dryness several times on a waterbath to remove most of the hydrochloric acid contaminant. This purified "$RuCl_3\ x\ H_2O$" was found to be much more reactive towards 1,3- or 1,4-cyclohexadienes, since refluxing it in degassed 90% aqueous ethanol with an excess of these dienes gave the complex $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ as a bright red precipitate after only 5—10 minutes. This is in marked contrast to the brown to red coloured solids isolated after three to four hours at 40°C using "unpurified" ruthenium trichloride [16]. Furthermore, the red $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ is much more reactive than the previously isolated brown material which may be polymeric rather than dimeric in nature. The reaction times with purified "$RuCl_3\ x\ H_2O$" and some substituted cyclohexadienes, e.g. 1-methoxycyclohexa-1,4 diene and α-phellandrene (5-isopropyl-2-methylcyclohexa-1,3-diene) were also greatly reduced from those quoted elsewhere [3]. However, the reaction with 1,3,5-trimethylcyclohexa-1,4-diene still took 16 hours for completion, as reported [3].

The complexes $[\{Ru(\eta\text{-arene})X_2\}_2]$ (X = Br^-, I^-, SCN^-; arene = C_6H_6, 1,3,5-$C_6H_3Me_3$, p-$MeC_6H_4CH(Me_2)$ were prepared by the addition of excess of LiX to saturated solutions of the corresponding chloro compounds in water [3,16]. The complex $[\{Os(\eta\text{-}C_6H_6)Cl_2\}_2]$ was prepared by reaction of 1,3-cyclohexadiene (10 cm^3) with $Na_2[OsCl_6]$ (1.00 g) in a minimum amount (10 cm^3) of degassed commercial ethanol. It was isolated as a yellow solid after refluxing the solution for 4 hours and then cooling in ice. The product was then washed with small amounts of water, ethanol, diethyl ether and dried in vacuo at 40°C [Found: C, 22.3; H, 2.2; Cl, 22.1. Calcd. for $[\{Os(C_6H_6)Cl_2\}_2]$ 0.5 EtOH; C, 22.3; H, 2.1, Cl, 20.3%] m.p. 164—166°C. (Yield 0.25 g, 33%).

Similarly, reaction of $Na_2[OsCl_6]$ (1.00 g) and α-phellandrene (10 cm^3) in degassed ethanol (10 cm^3) for 3 hours gave a deep yellow brown solution and a small amount of dark brown material with low carbon (1.3%) and hydrogen (0.3%) content. However, concentration of the filtrate on a rotary evaporator and storage for 24 hours at 0°C gave orange needle crystals of $[\{Os(p\text{-cymene})Cl_2\}_2]$ which were filtered off and washed with ethanol and diethyl ether and dried in vacuo at 40°C [Found: C, 30.7; H, 3.6; Cl, 17.7, M (osmometrically, C_6H_6) 837, Calcd. for $[\{Os(p\text{-cymene})Cl_2\}_2]$: C, 30.4; H, 3.5; Cl, 18.0% M, 790] m.p. 223—225°C (decomp) (Yield, 0.22 g, 20%).

The complexes $[\{M(\eta\text{-}C_5Me_5)X_2\}_2]$, $[M(\eta\text{-}C_5Me_5)X_2C_5H_5N]$ (M = Rh, Ir; X = Cl^-, Br^-, I^-), [17], $[M(\eta\text{-}C_5H_5)Cl(N\text{-}N)]PF_6$ [4a,18] and $[Ru(\eta\text{-}C_6H_6)Cl(N\text{-}N)]PF_6$ [4] (N-N = 2,2'-bipyridyl, 1,10 phenanthroline) were prepared as described earlier.

All reactions were carried out in degassed solvents under nitrogen. Analytical data for the new complexes are given in Table 1, hydrogen-1 NMR data for some monomeric pyridine complexes in Table 2 and hydrogen-1 and carbon-13 NMR data for some binuclear complexes in Table 3.

Synthesis of the pyridine monomers

η-Benzene dichloro(pyridine)ruthenium(II). The compound $[\{Ru(\eta\text{-}C_6H_6)$-

$Cl_2\}_2$] (0.20 g, 0.40 mmol) was shaken with pyridine (10 cm^3) for several days to give an orange solid. This was filtered off and washed with methanol and diethyl ether. (Yield 0.17 g; 65%) m.p. 245°C (decomp); ν(RuCl) 280 cm^{-1}.

The complexes η-benzene dibromo(pyridine)ruthenium(II) (0.15 g; 67%); η-mesitylene dichloro(pyridine)ruthenium(II) (0.09 g; 37%) m.p. 210°C (decomp) ν(RuCl) 277 cm^{-1}; η-mesitylene di(iodo)(pyridine)ruthenium(II) (0.14 g; 56%) m.p. 120°C (decomp), were prepared similarly starting from 0.20 g of [$\{Ru(\eta\text{-arene})X_2\}_2$].

η-Benzene(chloro)bis(pyridine)ruthenium(II) hexafluorophosphate. Method A: The compound [$\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2$] (0.20 g; 0.40 mmol) was stirred in methanol (10 cm^3) with pyridine (0.20 cm^3) to give a yellow solution. This was filtered and a solution of excess NH_4PF_6 in methanol (5 cm^3) was added to give a copious yellow precipitate. This was filtered off, washed with water, methanol and finally diethyl ether. (Yield 0.34; 82%) m.p. 227°C (decomp); ν(RuCl) 280 cm^{-1}, Λ_m (1×10^{-3} mol dm^{-3}) in CH_3NO_2 = 84 Scm^2 mol^{-1}. Method B: The filtrate from the reaction of the compound [$\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2$] with neat pyridine was concentrated and the residue dissolved in methanol. Addition of NH_4PF_6 as in Method A gave the compound [$Ru(\eta\text{-}C_6H_6)Cl(C_5H_5N)_2$]$PF_6$ in 10% yield.

η-Benzene(bromo)bis(pyridine)ruthenium(II) hexafluorophosphate. The compound [$\{Ru(\eta\text{-}C_6H_6)Br_2\}_2$] (0.20 g; 0.30 mmol) was refluxed in methanol/pyridine (1 : 1 v/v) (10 cm^3) for four hours. The orange solution was filtered to remove undissolved starting compound and then excess NH_4PF_6 was added to give an orange precipitate. This was filtered off and washed as for the corresponding chloro complex. (Yield 0.17 g; 50%); Λ_m (1×10^{-3} mol dm^{-3}) in CH_3NO_2 = 78 Scm^2 mol^{-1}.

The following compounds were synthesised via methods A and B using 0.20 g of [$\{Ru(\eta\text{-arene})X_2\}_2$]:

η-Mesitylene(chloro)bis(pyridine)ruthenium(II) hexafluorophosphate. Method A: (Yield 0.17 g; 45%); Method B: (0.23 g; 61%) m.p. 220°C (decomp), ν(RuCl) 295 cm^{-1}, Λ_m (1×10^{-3} mol dm^{-3}) in CH_3NO_2 = 71 Scm^2 mol^{-1}.

η-Mesitylene(bromo)bis(pyridine)ruthenium(II) hexafluorophosphate. Method A: (0.22 g; 71%); Method B: (0.03 g; 10%) m.p. 222°C (decomp); Λ_m (1×10^{-3} mol dm^{-3}) in CH_3NO_2 = 78 Scm^2 mol^{-1}.

η-Mesitylene(iodo)bis(pyridine)ruthenium(II) hexafluorophosphate. Method A: (0.15 g; 54%); Method B: (0.04 g; 14%) m.p. 220°C (decomp).

η-p-Cymene(chloro)bis(pyridine)ruthenium(II) hexafluorophosphate. The compound [$\{Ru(\eta\text{-}p\text{-cymene})Cl_2\}_2$] (0.10 g; 0.20 mmol) was shaken in pyridine (10 cm^3) to give an orange solution which was then concentrated to dryness. The residue was extracted with methanol to give an orange solid (impure [$Ru(\eta\text{-}p\text{-cymene})Cl_2(C_5H_5N)$] and an orange solution. Excess NH_4PF_6 was added to the solution which was then taken to dryness. The yellow residue was shaken with water and the yellow precipitate filtered off, washed with diethylether and dried in vacuo (0.08 g; 41%) ν(RuCl) 280 cm^{-1}.

η-Benzene(chloro)bis(pyridine)osmium(II) hexafluorophosphate. The compound [$\{Os(\eta\text{-}C_6H_6)Cl_2\}_2$] (0.10 g; 0.15 mmol) was refluxed in ethanol/pyridine (1 : 1 v/v) (20 cm^3) until a yellow solution had formed (2—3 h). This was then filtered and an excess of NH_4PF_6 in methanol added. The solution was

taken to dryness and the residue redissolved in methanol (5 cm^3) and on standing a yellow precipitate formed. This was filtered off, washed with water and diethylether (0.16 g; 90%) m.p. 225—227°C, ν(OsCl) 285 cm^{-1}.

η-p-Cymene(chloro)bis(pyridine)osmium(II) hexafluorophosphate. The compound $[\{Os(\eta\text{-}p\text{-cymene})Cl_2\}_2]$ (0.16 g; 0.20 mmol) was stirred in methanol (10 cm^3) with pyridine (0.20 cm^3) to give a yellow solution. An excess of NH_4PF_6 in methanol was added and the solution taken to dryness. The residue was extracted with acetone and filtered; concentration of the filtrate gave a yellow solid which was filtered and washed with water and diethylether (0.11 g; 32%) m.p. 175—177°C, ν(OsCl) 290 cm^{-1}, ν(CN) 1610 cm^{-1}.

η-Pentamethylcyclopentadienyl(chloro)bis(pyridine)iridium(III) hexafluorophosphate. By method A from 0.20 g of $[\{Ir(\eta\text{-}C_5Me_5)Cl_2\}_2]$ (0.28 g; 83%). Found: C, 36.0; H, 3.8; N, 4.1%. Calcd. for $C_{20}H_{25}ClF_6IrN_2P$: C, 36.1; H, 3.8; N, 4.2%.

Synthesis of triple halide-bridged, binuclear complexes

Tri-μ-chlorobis[(η-benzene)ruthenium(II)] tetrafluoroborate. Method C: The compounds $[Ru(\eta\text{-}C_6H_6)Cl_2(C_5H_5N)]$ (0.03 g; 0.10 mmol) and $[Ru(\eta\text{-}C_6H_6)Cl(C_5H_5N)_2]PF_6$ (0.05 g; 0.10 mmol) were suspended in methanol (10 cm^3). Tetrafluoroboric acid (40% aqueous solution) (1 cm^3) was added and the solution stirred vigorously. The suspended solids immediately dissolved to give an orange solution, from which an orange, microcrystalline solid was rapidly precipitated. The mixture was gently warmed for 1 hour and the solid was then filtered off. Concentration of the filtrate gave more of the orange compound. The solid was washed with methanol and diethylether (0.05 g; 92%) m.p. 270°C (decomp), ν(RuCl) 260 cm^{-1}. Λ_m (1×10^{-3} mol dm^{-3}) in CH_3NO_2 = 76 Scm^2 mol^{-1}. Method D: The compound $[Ru(\eta\text{-}C_6H_6)Cl(C_5H_5N)_2]$-$PF_6$ (0.15 g; 0.30 mmol) was suspended in methanol (10 cm^3) and HBF_4 (1 cm^3) was added as above. An orange solid was formed and isolated as for method C. This complex is identical to that formed by method C (0.02 g; 25%).

Tri-μ-bromo bis[(η-benzene)ruthenium(II)] tetrafluoroborate. This complex was synthesised by method C using the compounds $[Ru(\eta\text{-}C_6H_6)Br_2(C_5H_5N)]$ (0.08 g; 0.20 mmol) and $[Ru(\eta\text{-}C_6H_6)Br(C_5H_5N)_2]PF_6$ (0.11 g; 0.20 mmol); (0.11 g; 87%) m.p. 270°C (decomp). Λ_m (1×10^{-3} mol dm^{-3}) in CH_3NO_2 = 82 Scm^2 mol^{-1}.

Tri-μ-chloro bis[(η-mesitylene)ruthenium(II)] tetrafluoroborate. Method C (0.11 g; 86%) m.p. 280°C (decomp); ν(RuCl) 260 cm^{-1}, Λ_m (1×10^{-3} mol dm^{-3}) in CH_3NO_2 = 77 Scm^2 mol^{-1}.

Tri-μ-bromo bis[(η-mesitylene)ruthenium(II)] tetrafluoroborate. By method D using $[Ru(\eta\text{-}C_6H_3Me_3)Br(C_5H_5N)_2]PF_6$ (0.12 g; 0.20 mmol) (0.014 g; 18%), Λ_m (1×10^{-3} mol dm^{-3}) in CH_3NO_2 = 79 S cm^2 mol^{-1}.

Tri-μ-iodo bis[(η-mesitylene)ruthenium(II)] tetrafluoroborate. Method C (0.13 g; 71%) m.p. 260°C (decomp), Λ_m (1×10^{-3} mol dm^{-3}) in CH_3NO_2 = 88 Scm^2 mol^{-1}.

Tri-μ-chloro bis[(η-benzene)osmium(II)] tetrafluoroborate. By method D using $[Os(\eta\text{-}C_6H_6)Cl(C_5H_5N)_2]PF_6$ (0.08 g; 28%).

Tri-μ-bromo bis[(η-benzene)ruthenium(II)] hexafluorophosphate. The com-

pound [{Ru(η-C_6H_6)Br_2}$_2$] (0.13 g; 0.20 mmol) was suspended in nitromethane (10 cm^3) with $AgPF_6$ (0.05 g; 0.20 mmol). The mixture was stirred for several hours and the solution then filtered through celite to remove AgBr precipitate. The filtrate was taken to dryness and the residue washed with methanol to give an orange solid which was filtered off and washed with diethyl ether (0.05 g; 34%) m.p. 276°C (decomp), Λ_m (1×10^{-3} mol dm^{-3}) in CH_3NO_2 = 77 Scm^2 mol^{-1}. The following compounds were prepared similarly from 0.20 mmol of [{Ru(η-arene)X_2}$_2$]: tri-μ-iodo bis[(η-benzene)ruthenium(II)] hexafluorophosphate (0.06 g; 32%); tri-μ-chloro bis[(η-*p*-cymene)ruthenium(II)] hexafluorophosphate (in acetone) (0.07 g; 58%) m.p. 197—199°C, ν(RuCl) 260 cm^{-1}; tri-μ-bromo bis[(η-*p*-cymene)ruthenium(II)] hexafluorophosphate (in acetone) (0.13 g; 85%) m.p. 250—252°C, Λ_m (1×10^{-3} mol dm^{-3}) in CH_3NO_2 = 77 Scm^2 mol^{-1}; tri-μ-iodo bis[(η-*p*-cymene)ruthenium(II)] hexafluorophosphate (in acetone) (0.11 g; 54%) m.p. 265°C (decomp), Λ_m (1×10^{-3} mol dm^{-3}) in CH_3NO_2 = 74 Scm^2 mol^{-1}.

The following complexes were synthesised by method C using 0.20 mmol of reactants although as discussed in detail earlier, facile exchange processes lead to inseparable product mixtures. "μ-Bromo-di-μ-chloro bis[(η-benzene)ruthenium(II)] tetrafluoroborate" from the compounds [Ru(η-C_6H_6)Cl_2(C_5H_5N)] and [Ru(η-C_6H_6)Br(C_5H_5N)$_2$]PF_6 (0.10 g; 87%) Λ_m (1×10^{-3} mol dm^{-3}) in CH_3NO_2 = 79 S cm^2 mol^{-1}; "di-μ-bromo-μ-chloro bis[(η-benzene)ruthenium(II)] tetrafluoroborate" from the compounds [Ru(η-C_6H_6)Br_2(C_5H_5N)] and [Ru(η-C_6H_6)Cl(C_5H_5N)$_2$]PF_6 (0.11 g; 88%) Λ_m (1×10^{-3} mol dm^{-3}) in CH_3NO_2 = 74 Scm^2 mol^{-1}; "tri-μ-chloro(η-benzene)osmium(II)(η-benzene)-ruthenium(II) tetrafluoroborate" from the compounds [Ru(η-C_6H_6)Cl_2-(C_5H_5N)] and [Os(η-C_6H_6)Cl(C_5H_5N)$_2$]PF_6 (0.09 g; 70%); "tri-μ-chloro[(η-benzene)(η-mesitylene)diruthenium(II)] tetrafluoroborate" from the compounds [Ru(η-C_6H_6)Cl_2(C_5H_5N)] and [Ru(η-$C_6H_3Me_3$)Cl(C_5H_5N)$_2$]PF_6 (0.10 g; 86%) or [Ru(η-$C_6H_3Me_3$)Cl_2(C_5H_5N)] and [Ru(η-C_6H_6)Cl(C_5H_5N)$_2$]PF_6 (0.09 g; 73%) respectively, ν(RuCl) 260 cm^{-1}, Λ_m (1×10^{-3} mol dm^{-3}) in CH_3NO_2 = 78 Scm^2 mol^{-1}.

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