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Preliminary communication

A CONVENIENT SYNTHETIC ROUTE TO 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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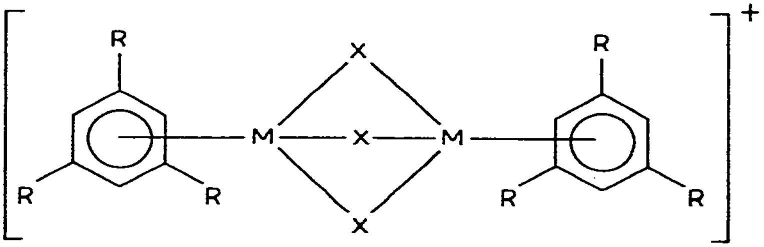
Summary

Protonation with HBF_4 of equimolar mixtures of $[M(arene)X_2(C_5H_5N)]$ and $[M(arene)X(C_5H_5N)_2]PF_6$ in methanol provides a convenient, high yield, synthetic route to the triple halide bridged arene complexes $[M_2(arene)_2X_3]BF_4$ (M = Ru; X = Cl, Br; arene = C_6H_6, 1,3,5-$C_6H_3Me_3$; M = Os, X = Cl, arene = C_6H_6).

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 h gave, in high yield, $[(\eta\text{-}C_6H_6)RuCl_3Ru(\eta\text{-}C_6H_6)]PF_6$. The most likely mechanism of formation of this cation was proposed to be by intermolecular coupling of the weakly solvated monomers $[Ru(C_6H_6)Cl_2(MeOH)]$ and $[Ru(C_6H_6)Cl(MeOH)_2]^+$. Unfortunately, attempts to prepare other triple halide bridged arene cations by reaction of the appropriate double halide bridged dimers with NH_4PF_6 in methanol were unsuccessful, probably because of the very insoluble nature of these $[\{Ru(arene)X_2\}_2]$ compounds [1].

We now wish to report a more convenient, high yield, synthetic route to these $[M_2(arene)_2X_3]^+$ cations (I). This involves the formation in situ of high equi-

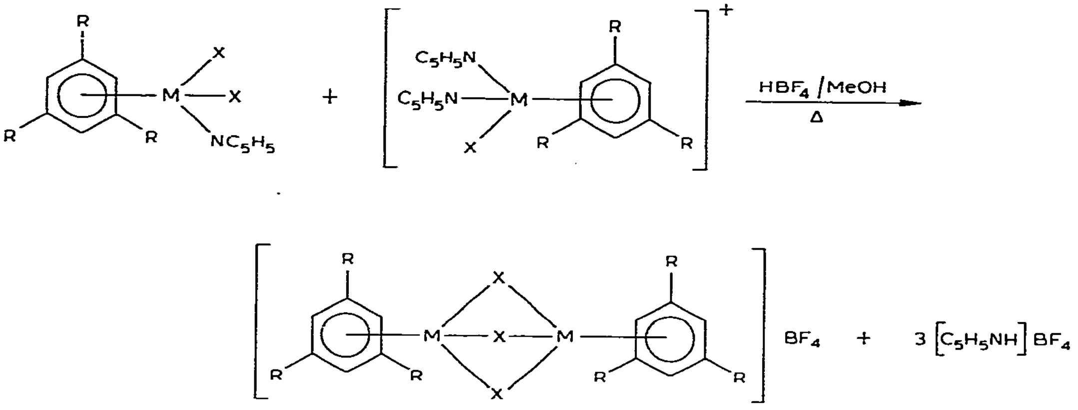


(I)

M = Ru, X = Cl, Br; R = H or Me

M = Os, X = Cl; R = H

molar concentrations of the solvated monomers [M(arene)X_2(MeOH)] and [M(arene)X$(MeOH)_2]^+$ by protonation in methanol of the corresponding pyridine complexes [M(arene)X_2(C_5H_5N)] and [M(arene)X$(C_5H_5N)_2$]PF_6 respectively.



Thus, for example, treatment of equimolar amounts of [Ru(C_6H_6)Cl_2(C_5H_5N)] [2] and [Ru(C_6H_6)Cl$(C_5H_5N)_2$]PF_6 [1,3] in methanol with a slight excess of HBF_4 gave, after gently refluxing the solution for one hour, an almost quantitative yield of [$Ru_2(C_6H_6)_2Cl_3$]BF_4. Similarly, reaction of [Ru(C_6H_6)Br_2(C_5H_5N)] and [Ru(C_6H_6)Br$(C_5H_5N)_2$]PF_6 [3] with HBF_4 gave [$Ru_2(C_6H_6)_2Br_3$]BF_4 and analogous reactions with the appropriate pyridine monomers gave [$Ru_2(C_6H_3Me_3)_2X_3$]BF_4 (X = Cl, Br).

As observed earlier for the $[Ru_2(C_6H_6)_2Cl_3]^+$ cation [1], all these compounds undergo facile bridge cleavage reactions in solvents such as H_2O and Me_2SO, but fortunately, they are all soluble and stable in CH_3NO_2. Thus, ^1H and ^{13}C-$\{^1H\}$ NMR studies in CD_3NO_2 (Table 1) together with analytical data, conductivity (all 1/1 electrolytes) and far infrared studies (only bridging ν(RuX) present) establish unequivocally the structure of the compounds.

In an attempt to make the mixed bridge compound [(C_6H_6)RuCl_2BrRu(C_6H_6)]-BF_4, equimolar amounts of [Ru(C_6H_6)Cl_2(C_5H_5N)] and [Ru(C_6H_6)Br$(C_5H_5N)_2$]-PF_6 were treated with HBF_4/MeOH. However, although the product analysed closely for "[$Ru_2(C_6H_6)_2Cl_2Br$]BF_4", its ^1H NMR spectrum in CD_3NO_2 showed

TABLE 1

^1H AND ^{13}C-$\{^1H\}$ NMR SPECTRA IN CD_3NO_2 OF SOME RUTHENIUM(II) AND OSMIUM(II) ARENE COMPLEXES

Compound	$^1H^a$	^{13}C- ^1H ^{a}
[$Ru_2(C_6H_6)_2Cl_3$]BF_4	5.944	82.04
[$Ru_2(C_6H_6)_2Br_3$]BF_4	5.922	82.37
"[$Ru_2(C_6H_6)_2Cl_2Br$]BF_4" "[$Ru_2(C_6H_6)_2ClBr_2$]BF_4"	5.944,5.937,5.929,5.922	—
[$Os_2(C_6H_6)_2Cl_3$]BF_4	6.64	73.55
[$RuOs(C_6H_6)_2Cl_3$]BF_4	6.46,6.06	82.21,73.82
[$Ru_2(C_6H_3Me_3)_2Cl_3$]BF_4	5.35(H),2.22(Me)	102.01($\underline{C}$Me),75.72($\underline{C}$H),19.42(Me)
[$Ru_2(C_6H_6)(C_6H_3Me_3)Cl_3$]$BF_4$	5.92,5.37(H),2.20(Me)	102.01($\underline{C}$Me),82.02,75.89($\underline{C}$H),19.28(Me)

^{a} Reference is $(CH_3)_4Si$; all singlets.

four η-C_6H_6 resonances at 5.944, 5.937, 5.929 and 5.922 ppm of relative intensity 8/12/6/1. The resonance at δ 5.944 ppm arises from $[Ru_2(C_6H_6)_2Cl_3]BF_4$ and that at δ 5.922 ppm from $[Ru_2(C_6H_6)_2Br_3]BF_4$. Conversely, reaction of $[Ru(C_6H_6)Br_2(C_5H_5N)]$ and $[Ru(C_6H_6)Cl(C_5H_5N)_2]PF_6$ (1/1 molar ratio) with HBF_4/MeOH gave a product analysing for "$[Ru_2(C_6H_6)_2ClBr_2]BF_4$" which showed the same four ^{1}H NMR η-C_6H_6 resonances but now with relative intensities 1/6/12/8. Thus, these experiments clearly show that statistical mixtures of $[Ru_2(C_6H_6)_2Cl_3]^+$, $[Ru_2(C_6H_6)_2Cl_2Br]^+$, $[Ru_2(C_6H_6)_2ClBr_2]^+$ and $[Ru_2(C_6H_6)_2Br_3]^+$ and $[Ru_2(C_6H_6)_2Br_3]^+$ cations are formed in these reactions.

It is readily demonstrated that this facile halide exchange can occur prior to protonation since on mixing $[Ru(C_6H_6)Cl_2(PPh_3)]$ * and $[Ru(C_6H_6)Br(C_5H_5N)_2]^+$ in acetone-d_6, ^{1}H NMR studies reveal that some $[Ru(C_6H_6)Br_2(PPh_3)]$ and $[Ru(C_6H_6)Cl(C_5H_5N)_2]^+$ are rapidly formed. However, the ^{1}H NMR spectrum of a mixture of $[Ru_2(C_6H_6)_2Cl_3]BF_4$ and $[Ru_2(C_6H_6)_2Br_3]BF_4$ in CD_3NO_2 after several minutes at ambient temperature shows four η-C_6H_6 resonances, indicating that facile halide exchange can also occur after formation of the dimers (cf. the formation of some $[PdPtCl_4L_2]$ from reaction of $[Pd_2Cl_4L_2]$ and $[Pt_2Cl_4L_2]$ [4]).

In an attempt to synthesise the tetrameric cation $[\{Ru(C_6H_6)Cl\}_4]^{4+}$ a suspension of $[Ru(C_6H_6)Cl(C_5H_5N)_2]PF_6$ in methanol was treated with HBF_4 but the only product isolated was $[Ru_2(C_6H_6)_2Cl_3]BF_4$ in low yield (ca. 25%). This clearly demonstrates that protonation removes some coordinated chloride as HCl which then reacts to form some $[Ru(C_6H_6)Cl_2MeOH]$. Similarly, protonation of $[Os(C_6H_6)Cl(C_5H_5N)_2]PF_6$ [3] gave $[Os_2(C_6H_6)_2Cl_3]BF_4$ whereas treatment of an equimolar mixture of $[Ru(C_6H_6)Cl_2(C_5H_5N)]$ and $[Os(C_6H_6)Cl(C_5H_5N)_2]PF_6$ with HBF_4/MeOH gave a statistical mixture of $[Ru_2(C_6H_6)_2Cl_3]BF_4$, $[Os_2(C_6H_6)_2Cl_3]BF_4$ and $[RuOs(C_6H_6)_2Cl_3]BF_4$. Mixing the pure ruthenium and osmium dimers at ambient temperature in CD_3NO_2 rapidly gave some $[RuOs(C_6H_6)_2Cl_3]^+$ cation.

Finally, using these methods, the $[(C_6H_6)RuCl_3Ru(C_6H_3Me_3)]^+$ cation can be generated, but not separated, from the $[Ru_2(C_6H_6)_2Cl_3]^+$ and $[Ru_2(C_6H_3Me_3)_2Cl_3]^+$ cations.

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*$[Ru(C_6H_6)Cl_2PPh_3]$ was used because of the insolubility of $[Ru(C_6H_6)Cl_2(C_5H_5N)]$ in acetone.