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Cationic, Neutral and Anionic Complexes of Ruthenium(II) containing η^6-Arene Ligands

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Summary

Reaction of $[\{Ru(C_6H_6)Cl_2\}_2]$ with an excess of CsCl/HCl in ethanol gives the first anionic arene complex of ruthenium $Cs[Ru(C_6H_6)Cl_3]$ (II) although in aqueous solution this readily loses a chloride ion to give $[Ru(C_6H_6)Cl_2(H_2O)]$ and reactions with various Lewis bases give the compounds $[Ru(C_6H_6)Cl_2L]$ (L = C_5H_5N, Me_2SO, PR_3 etc). Reaction of $[\{Ru(C_6H_6)Cl_2\}_2]$ with NH_4PF_6 in methanol gives high yields of the triple chloride bridged complex $[Ru_2(C_6H_6)_2Cl_3]PF_6$(III) which, although stable in $MeNO_2$, readily undergoes bridge cleavage reactions in water and Me_2SO. Reaction of (III) with various Lewis bases produces the new monomeric, ruthenium(II), arene cations $[Ru(C_6H_6)ClL_2]PF_6$ (L = C_5H_5N, Et_2S, $AsPh_3$, PR_3 etc).

Introduction

In recent years, some reactions of the unusual η^6-arene complexes $[\{Ru(arene)X_2\}_2]$ (arene = C_6H_6, C_6H_5OMe, p- and m-$C_6H_4Me_2$, C_6H_5Me, 1,3,5-$C_6H_3Me_3$, p-$MeC_6H_4CHMe_2$; X = Cl or Br) have been investigated by several workers [1-7]. In particular, bridge cleavage reactions with a variety of Lewis bases to give the neutral, monomeric complexes $[Ru(arene)X_2L]$ (L = PR_3, $P(OR)_3$, AsR_3, C_5H_5N etc) are well documented [1-3].

In this paper, we now report the full results [8] of the formation of the benzene anion $[Ru(C_6H_6)Cl_3]^-$ and the triple chloride bridged cation $[C_6H_6RuCl_3RuC_6H_6]^+$ from $[\{Ru(C_6H_6)Cl_2\}_2]$, together with details of the reactions of these compounds with various Lewis bases.

Results and Discussion

a) Synthesis and reactions of $Cs[Ru(C_6H_6)Cl_3]$

As reported earlier [9], reaction of the compound $[\{Ru(CO)Cl_2(C_7H_8)\}_2]$ (C_7H_8 = bicyclo [2.2.1] hepta-2,5-diene) with MCl/HCl (M = $Ph_3(PhCH_2)P^+$, Cs^+) in degassed acetone gave a high yield of the first anionic diene complex of ruthenium $M[Ru(CO)Cl_3(C_7H_8)]$. An attempt has now been made to synthesise the first anionic η^6-arene ruthenium complex using a similar preparative route. Thus, shaking $[\{Ru(C_6H_6)Cl_2\}_2]$ (I) with a mixture of excess CsCl and concentrated HCl in ethanol for several days gave an orange powder analysing closely for $Cs[Ru(C_6H_6)Cl_3]$ (II) although it was always difficult to obtain this complex completely free of CsCl. The mull i.r. spectrum of (II) indicated the presence of coordinated benzene and contained a broad band at 280 cm^{-1} assigned to terminal $\nu(RuCl)$ stretching vibration(s). Since compound (II) posesses C_{3v} symmetry two $\nu(RuCl)$ bands were expected and thus, the broad band at 280 cm^{-1} might contain both the a_1 and e vibrational modes or a weak band at 298 cm^{-1} could be assigned to one of the $\nu(RuCl)$ bands. Unfortunately, attempts to make the corresponding $[Ru(C_6H_6)X_3]^-$ ($X = Br^-, I^-$) anions, either by reaction of $[\{Ru(C_6H_6)X_2\}_2]$ or $Cs[Ru(C_6H_6)Cl_3]$ with X^- were unsuccessful, only $[\{Ru(C_6H_6)X_2\}_2]$ being recovered from the reaction mixture in each case.

As expected, $Cs[Ru(C_6H_6)Cl_3]$ was more soluble in water than $[\{Ru(C_6H_6)Cl_2\}_2]$ and an aqueous solution of (II) was highly conducting (eg. for a 10^{-3} mol dm^{-3} solution, Λ_m = 374 S cm^2 mol^{-1}). Unfortunately the unavoidable presence of a small amount of CsCl, together with the fact that ^1H nmr studies on (II) in aqueous solution indicated that extensive dissociation of chloride ion occurred meant that no firm conclusion about electrolyte type could be drawn from these conductivity measurements.

The ^{1}H nmr spectrum of Cs[$Ru(C_6H_6)Cl_3$] in D_2O consisted of a single η^6-C_6H_6 resonance at 6.40δ whereas that of [{$Ru(C_6H_6)Cl_2$}$_2$] in D_2O showed two coordinated benzene resonances at 6.39(vs) and 6.50(w)δ which previous workers have assigned to either the aqua complexes [$Ru(C_6H_6)Cl(D_2O)_2$]$^+$ and [$Ru(C_6H_6)(D_2O)_3$]$^{2+}$ respectively or to a combination of one of these cations and the neutral complex [$Ru(C_6H_6)Cl_2D_2O$][1].* It is therefore very likely that the signal at 6.40δ observed for (II) in D_2O is due to an aqua complex formed by displacement of chloride ion, and by reference to the reactions of (II) with Lewis bases, (see below), this aqua complex is probably the neutral [$Ru(C_6H_6)Cl_2(D_2O)$]. In an attempt to suppress this dissociation process and obtain the ^{1}H nmr spectrum of (II), large amounts of CsCl/HCl were added to the D_2O solution of (II). Unfortunately, the residual water peak became more intense and shifted to higher frequencies (from 5.20 to 5.90δ), thus obscuring any new η^6-C_6H_6 resonance, and furthermore, slow precipitation of [{$Ru(C_6H_6)Cl_2$}$_2$] also occurred.

Earlier, $Ph_3(PhCH_2)P$[$Ru(CO)Cl_3(C_7H_8)$] was shown to be a good precursor for synthesising a wide range of anionic complexes of the type Ph_3PhCH_2P[$Ru(CO)Cl_3L_2$] (L = $AsPh_3$, C_5H_5N, Me_2S etc) via displacement of diene [10]. Attempts, however, to synthesise the unknown *fac*-[$RuCl_3L_3$]$^-$ anions by reaction of Cs[$Ru(C_6H_6)Cl_3$] with excess of various

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* Zelonka and Baird [1] quoted the resonance positions for [{$Ru(C_6H_6)Cl_2$}$_2$] in D_2O at 5.93 and 6.03δ. The discrepancy between their work and the chemical shifts given above probably arises from the fact that these chemical shifts are relative to an external TMS capillary whereas in ref [1] they are with respect to an internal TMS lock. Support for this explanation comes from the shift to high frequency observed for the coordinated η^6-C_6H_6 resonance in the ^{1}H nmr spectrum of [$Ru(C_6H_6)Cl_2(PMe_2Ph)$] when run in $CDCl_6$ with respect to an external TMS capillary (5.95δ) as opposed to an internal TMS reference (5.35δ). Also, the difference between the chemical shifts of the two η^6-C_6H_6 resonances of [{$Ru(C_6H_6)$-Cl_2}$_2$] in D_2O is very similar with respect to both the external TMS reference (0.11δ) and the internal TMS lock (0.10δ).

L gave only neutral complexes. Thus, either shaking or gently refluxing (II) with excess of pyridine in methanol gave a yellow solution, and the orange solid isolated from this by concentration followed by precipitation with diethyl ether analysed very closely for [$Ru(C_6H_6)Cl_2(C_5H_5N)$]. The compound was insoluble in most deuterated solvents except d^6-Me_2SO and its ^1H nmr spectrum in this solvent showed broad resonances at *ca*. 7.3 and 8.3δ (C_5H_5N) plus *two* η^6-C_6H_6 resonances at 5.65 and 5.90δ. The latter was assigned to the d^6-Me_2SO complex [$Ru(C_6H_6)Cl_2(d^6$-$Me_2SO)$], (reported in ref [1] to have an η^6-C_6H_6 ^1H nmr resonance at 5.93δ) and this was verified by synthesising [$Ru(C_6H_6)Cl_2(Me_2SO)$], either by refluxing [$Ru(C_6H_6)Cl_2(C_5H_5N)$] or Cs[$Ru(C_6H_6)Cl_3$] with excess Me_2SO in methanol. In contrast, prolonged refluxing of (II) in neat pyridine gave a mixture of [$Ru(C_6H_6)Cl_2(C_5H_5N)$] and the well-known [11] *trans*-[$RuCl_2(C_5H_5N)_4$].

The products from the reaction of compound (II) and tertiary phosphines were dependent both on the reaction conditions and the nature of the phosphine. Thus, if (II) was shaken with excess PR_3 in methanol (PR_3 = PPh_3, PMe_2Ph, $PMePh_2$) the previously reported [1-3] monomeric complexes [$Ru(C_6H_6)Cl_2(PR_3)$] were formed. Similarly, [$Ru(C_6H_6)$-$Cl_2(SbPh_3)$] was prepared by shaking (II) and excess $SbPh_3$ in methanol. However, under reflux conditions, the reaction with tertiary phosphines resulted in loss of the benzene ring from Cs[$Ru(C_6H_6)Cl_3$]. For example, refluxing (II) with excess of PMe_2Ph in methanol gave *cis*-[$RuCl_2(PMe_2Ph)_4$], previously synthesised either by reaction of excess PMe_2Ph with [$RuCl_2(PPh_3)_3$] in degassed light petroleum (bp 60 - 80°C) or with *mer*-[$RuCl_3(PMe_2Ph)_3$] in hexane [12]. In CH_2Cl_2, *cis*-[$RuCl_2(PMe_2Ph)_4$] readily rearranged to [$Ru_2Cl_3(PMe_2Ph)_6$]Cl [12]. In contrast, refluxing (II) with excess PPh_3 in methanol gave [$RuCl_2(PPh_3)_3$], previously prepared by refluxing "$RuCl_3xH_2O$" with excess of PPh_3 in methanol [13].

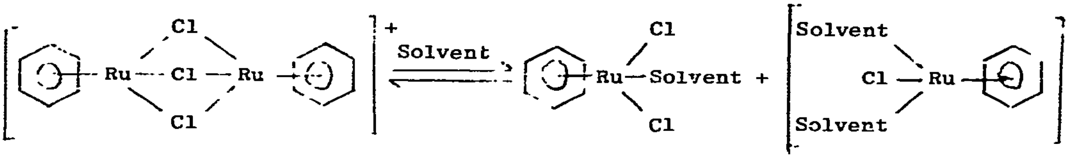
Hence, although the complex Cs[$Ru(C_6H_6)Cl_3$] is in itself of interest in so much as it represents the first anionic arene complex of ruthenium, the lability of the coordinated benzene group is very much less than that of the diene in $[Ru(CO)Cl_3(C_7H_8)]^-$. Thus, loss of chloride ion from $[Ru(C_6H_6)Cl_3]^-$ occurs much more readily than loss of the C_6H_6 ring and therefore, little is to be gained by using the $[Ru(C_6H_6)Cl_3]^-$ anion rather than $[\{Ru(C_6H_6)Cl_2\}_2]$ as a starting material.

b) Synthesis of $[C_6H_6RuCl_3RuC_6H_6]PF_6$

As reported earlier by Bennett and Smith [3], the reaction of $[\{Ru(C_6H_6)Cl_2\}_2]$ (I) with hot water gave an orange solution from which NH_4PF_6 slowly precipitated in *ca* 40% yield, an orange solid identified as $[Ru_2(C_6H_6)_2Cl_3]PF_6$ (IIIa). In our hands, however, this reaction produced only low variable yields (*ca*. 12%) of (IIIa) plus, on one occasion, a further product (see experimental section) shown by X-ray analysis [14] to be $[Ru(NH_3)_2(C_6H_6)Cl]_3(PF_6)_3NH_4PF_6$. Since the $[Ru_2(C_6H_6)_2Cl_3]^+$ cation is isoelectronic with $[Rh_2Cl_3(C_5Me_5)_2]^+$, which was isolated in high yield from reaction of $[\{RhCl_2(C_5Me_5)\}_2]$ with $NaBPh_4$ in methanol [15], a similar preparative route for (III) has been examined. Thus, stirring the dark red-brown $[\{Ru(C_6H_6)Cl_2\}_2]$ in methanol at ambient temperature with a slight excess of NH_4PF_6 for 24h gave, in high yield, (> 90%) a dark orange-yellow solid which analysed quite well for $[Ru_2(C_6H_6)_2Cl_3]PF_6$ (IIIb). No apparent reaction occurred in the absence of NH_4PF_6 or if methanol was replaced by acetone.

The mull ir spectrum of (IIIb) confirmed the presence of PF_6^- and in the far ir spectrum two intense bands at 276, 264 cm^{-1} were observed, indicative of bridging $\nu(RuCl)$ vibrations (*cf* in ref [3], $\gamma(RuCl)$ of (IIIa) quoted at 265 cm^{-1}). Compound (IIIb) gave conducting solutions in $MeNO_2$ with values characteristic of 1:1 electrolytes [16] (eg. for a 10^{-3} mol dm^{-3} solution, $\Lambda_m = 82$ S cm^2 mol^{-1}) and this was supported by $\Lambda_o - \Lambda_c$ *vs* $c^{\frac{1}{2}}$ plots over a range of concentrations which had a slope characteristic of 1:1 electrolytes (see experimental section). The ^1H and $^{13}C-\{^1H\}$ nmr spectra of (IIIb) in d^3-$MeNO_2$ at ambient temperature both showed a single sharp resonance for the η^6-C_6H_6 groups at 5.90δ and 82.0 ppm respectively, indicating that the dimeric unit remained intact in this solvent.

However, in other solvents such as D_2O and d^6-Me_2SO, more than one η^6-C_6H_6 resonance was observed. Thus, the ^1H nmr spectrum of (IIIa or b) in D_2O contained two η^6-C_6H_6 resonances at 6.35 and 6.48δ[†] of comparable intensity. These resonance positions are virtually identical to those found for [$\{Ru(C_6H_6)Cl_2\}_2$] dissolved in D_2O [6.39 and 6.50δ - see section a)] indicating facile bridge cleavage has occurred as shown in the equation.



In d^6-Me_2SO, three singlets were observed in the ^1H nmr spectrum of (IIIb) at 5.95(vs), 6.15(w) and 6.50(s) δ which corresponded closely to the quoted positions of the η^6-C_6H_6 resonances for the species [Ru-$(C_6H_6)Cl_2(d^6$-$Me_2SO)$] (5.93δ), [$Ru(C_6H_6)Cl(d^6$-$Me_2SO)_2$]$^+$ (6.12δ) and [$Ru(C_6H_6)(d^6$-$Me_2SO)_3$]$^{2+}$ (6.47δ) [1]. The relative intensities of these signals suggested that the monocation has reacted further with d^6-Me_2SO to give the dication.

As discussed elsewhere [17] for the closely related [$Ru_2Cl_3L_6$]$^+$ cations, (L = PR_3, $P(OR)Ph_2$, $P(OR)_2Ph$), the most likely mechanism of formation of [$Ru_2(C_6H_6)_2Cl_3$]$^+$ is by intermolecular coupling of the weakly solvated monomers [$Ru(C_6H_6)Cl_2$(solvent)] and [$Ru(C_6H_6)Cl$(solvent)$_2$]$^+$, the monomers being formed by reaction of [$\{Ru(C_6H_6)Cl_2\}_2$] with either

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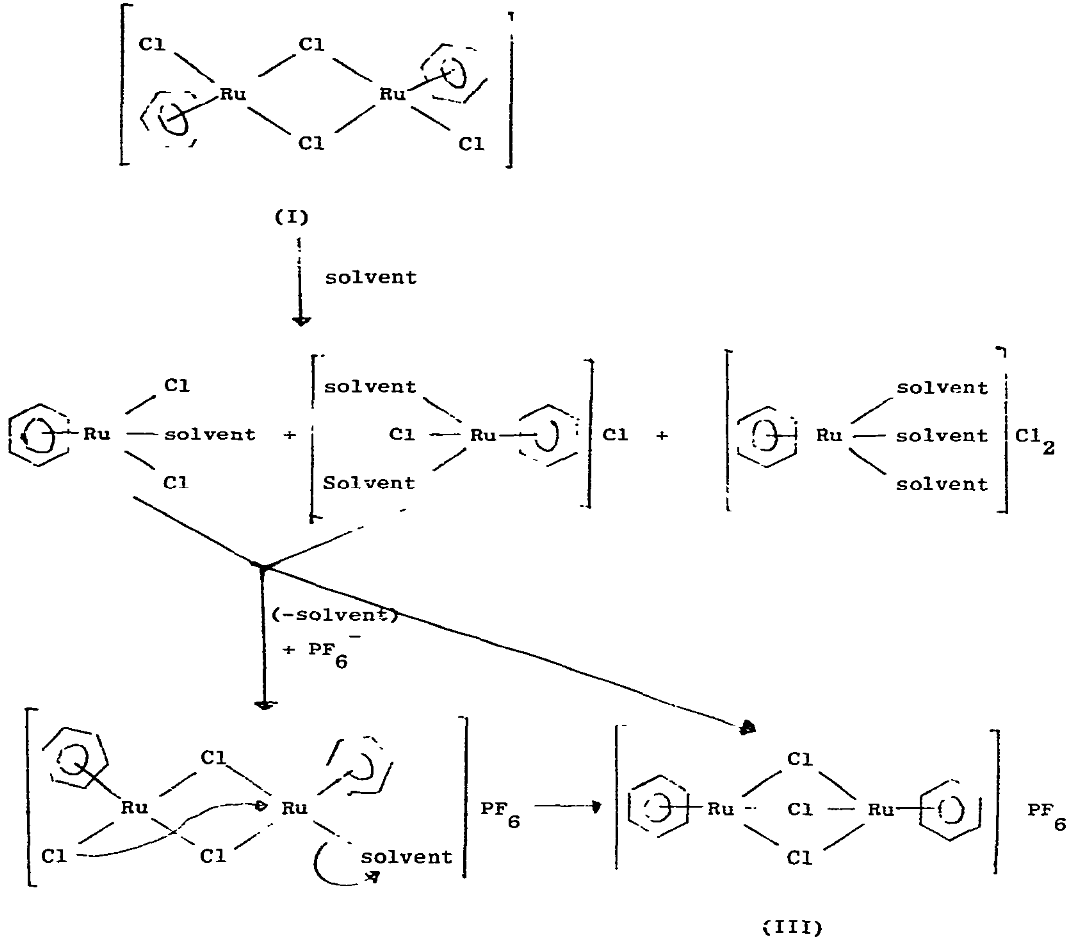
[†] Interestingly in ref [3], only a single resonance for (IIIa) in D_2O at 6.04δ was reported. As discussed earlier, the difference in chemical shift is probably due to the different references used but the observation of only one signal for (IIIa) in ref [3] is puzzling.



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methanol or hot water.* These may then couple to give the triple chloride bridged cation directly, or on the basis of evidence from earlier work with ruthenium ethyldiphenylphosphinite complexes [17], via the cationic, double chloride bridged solvated intermediate [(C_6H_6)-$ClRuCl_3Ru(solvent)(C_6H_6)]^+$ which then rearranges readily to (III) (Scheme).

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*Unfortunately, the solubility of $[\{Ru(C_6H_6)Cl_2\}_2]$ in methanol is too low to obtain ^1H nmr evidence for the formation of methanolate monomers although, of course, there is no doubt that analogous momomeric species are readily formed in D_2O and d^6-Me_2SO.

The low solubility of the PF_6^- salt of $[Ru_2(C_6H_6)_2Cl_3]^+$ in either methanol or water, together with the desire of ruthenium (II) to achieve six strong bonds is presumably the driving force for the combination of these intermediates.

Attempts to prepare other triple halide bridged cations $[Ru_2(arene)_2X_3]^+$ (arene = 1,3,5-$C_6H_3Me_3$; X = Cl^-; arene = C_6H_6, X = Br^-, I^-, SCN^-) by reaction of $[\{Ru(arene)X_2\}_2]$ with NH_4PF_6 in methanol were however unsuccessful, only $[\{Ru(arene)X_2\}_2]$ being isolated from the reaction mixture. This failure probably stems from the very insoluble nature of these $[\{Ru(arene)X_2\}_2]$ compounds which prevents formation of appreciable amounts of methanolate monomers.

c) Reactions of $[Ru_2(C_6H_6)_2Cl_3]PF_6$

Originally, it was hoped that this high yield synthesis of $[Ru_2(C_6H_6)_2Cl_3]PF_6$ (III) might provide a general route to the preparation of complexes such as $[Ru_2Cl_3L_6]^+$ (L = C_5H_5N, Me_2SO, RCN _etc_) _via_ displacement of η^6-C_6H_6 groups. However, as discussed above, the tendency of (III) to generate monomers by facile bridge cleavage proved greater than the desire to undergo replacement of the coordinated benzene rings. Thus, refluxing compound (III) with excess of pyridine in ethanol for _ca_ 4h gave an orange solution which on standing under nitrogen for a further 24h deposited an orange crystalline solid. On the basis of analytical data, together with ^1H nmr, ir and conductivity studies, this was best formulated as the monomeric cation $[Ru(C_6H_6)Cl(C_5H_5N)_2]PF_6$. Concentration of the remaining filtrate gave the non-conducting orange-solid _trans_-$[RuCl_2(C_5H_5N)_4]$. Attempts to retain the chloride bridges but induce replacement of η^6-C_6H_6 groups for pyridine by photolysis of the same reaction mixture also proved unsuccessful, only $[Ru(C_6H_6)Cl(C_5H_5N)_2]PF_6$ and _trans_-$[RuCl_2(C_5H_5N)_4]$ being isolated.

Reaction between compound (III) and Et_2S gave two compounds identified as $[Ru(C_6H_6)Cl(Et_2S)_2]PF_6$ and $[Ru(C_6H_6)Cl_2(Et_2S)]$. This bridge cleavage reaction also occurred with tertiary phosphines and arsines when (III) was shaken in methanol with excess of the ligand for short reaction times and this provided a route to the previously unknown cationic tertiary phosphine complexes $[Ru(C_6H_6)Cl(PR_3)_2]PF_6$ (PR_3 = PPh_3, PMe_2Ph, $PMePh_2$).

The reaction of (III) with excess of PR_3 under reflux conditions sometimes produced loss of the η^6-C_6H_6 groups. For example, refluxing (III) with excess of PPh_3 in methanol gave a mixture of $[Ru(C_6H_6)Cl(PPh_3)_2]$-PF_6 and $[RuCl_2(PPh_3)_3]$. In contrast, refluxing (III) with excess of PMe_2Ph in methanol gave a yellow solution from which only the triple chloride bridged complex $[Ru_2Cl_3(PMe_2Ph)_6]PF_6$ was isolated. As discussed earlier [12,17], this cation was most likely formed by rearrangement reactions of <u>cis</u>-$[RuCl_2(PMe_2Ph)_4]$, itself formed by bridge cleavage and η^6-C_6H_6 displacement from (III) by PMe_2Ph.

In conclusion, although reactions of $[Ru_2(C_6H_6)_2Cl_3]PF_6$ do not provide a route to the synthesis of new triple chloride bridged cations $[Ru_2Cl_3L_6]^+$, the facile bridge cleavage reaction does give a convenient synthetic route to new η^6-C_6H_6 cationic compounds of type $[Ru(C_6H_6)ClL_2]PF_6$. Recent work has shown that similar facile bridge cleavage reactions occur with other triple chloride bridged complexes. For example, reaction of $[Ru_2YCl_4(PPh_3)_4]$ (Y = CO,CS) with excess of $P(OR)Ph_2$ (R = Me,Et) in benzene gave a mixture of $[Ru(Y)Cl_2(P(OR)Ph_2)_3]$ and $[RuCl_2(P(OR)Ph_2)_3]$[18].

In view of this, it is surprising that the closely related $[Ru_2Cl_3$-$(PR_3)_6]^+$ cations do <u>not</u> undergo bridge cleavage reactions with excess of PR_3 [19], although this may be a result of the strong electron donating ability of the coordinated PR_3 groups which inhibits bridge cleavage by other nucleophiles (<u>cf</u> the inertness of $[Ru(C_6H_6)Cl_2(PR_3)]$ compounds towards nucleophilic attack on the ring [1]).

Experimental

Microanalyses were by B.M.A.C. and the University of Edinburgh Chemistry Department. Infrared spectra were recorded in the region 4000-250 cm^{-1} on a Perkin Elmer 457 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates and in the region 400-200 cm^{-1} on a Beckman RIIC IR 720 far ir spectrometer using pressed polythene discs. Hydrogen-1 nmr spectra were obtained on Varian Associates HA-100 and EM-360 spectrometers and ^{13}C-{^{1}H} nmr spectra on a Varian XL100 spectrometer operating at 25.2 MHz (^{13}C chemical shifts quoted in ppm to high frequency of SiMe$_4$). Conductivity measurements were made at 298K using a model 310 Portland Electronics conductivity bridge. As described earlier [17], plots of $\Lambda_o - \Lambda_c$ vs $c^{\frac{1}{2}}$ gave a straight line whose slope is a function of the ionic charges [20]. Melting points were determined with a Köfler hot-stage microscope and are uncorrected.

Materials

Ruthenium trichloride hydrate (Johnson Matthey); cyclohexa-1,3-diene, ammonium hexafluorophosphate and triphenylarsine (Ralph Emanuel Ltd); caesium chloride, triphenylphosphine and sodium tetraphenylborate (B.D.H.); methyldiphenylphosphine and dimethylphenylphosphine (Maybridge): nitromethane, pyridine, acetonitrile and mesitylene (Fisons); dimethylsulphoxide (Hopkins and Williams); triphenylstibine (Kodak). [{Ru(C$_6$H$_6$)Cl$_2$}$_2$] and [{Ru(C$_6$H$_3$Me$_3$)Cl$_2$}$_2$] were prepared as described earlier [1,3] from "RuCl$_3$xH$_2$O' cyclohexa-1,3-diene (or cyclohexa-1,4 diene) or 1,3,5-trimethylcyclohexa-1,4-diene respectively. [{Ru(C$_6$H$_6$)X$_2$}$_2$] (X = Br, I, SCN) were prepared by treating aqueous solutions of [{Ru(C$_6$H$_6$)Cl$_2$}$_2$] with an excess of LiX.

Analytical and conductivity data for the various compounds are given in Table 1 and Hydrogen-1 nmr data are listed in Table 2. Diagnostic ir bands are listed for each compound. All reactions were carried out in degassed solvents under an atmosphere of nitrogen and a medium pressure, Hanovia 1L mercury U.V. lamp was used for the photochemical reaction.

Caesium(benzene)(trichloro)ruthenate(II): The compound [{Ru(C$_6$H$_6$)Cl$_2$}$_2$] (0.20g,0.40 mmol) was shaken in ethanol (25 cm^3) with an excess of caesium chloride (0.40g) and concentrated hydrochloric acid (5 cm^3) for 5 days. The resulting orange suspension was decanted off and washed

TABLE 1

Analytical and Conductivity Data for some η^6-Areneruthenium(II) Complexes

Compound	Found %				Calculated %				Λ_m^a
	C	H	N	Cl	C	H	N	Cl	
$Cs[Ru(C_6H_6)Cl_3]$	16.9	1.4	-	25.2	17.2	1.4	-	25.5	37.4[b]
$[Ru(C_6H_6)Cl_2(C_5H_5N)]$	40.4	3.3	4.6	-	40.1	3.3	4.3	-	
$[Ru(C_6H_5)Cl_2(PPh_3)]$	56.6	4.3	-	-	56.3	4.1	-	-	
$[Ru(C_6H_6)Cl_2(PMePh_2)]$	49.9	4.1	-	-	50.7	4.2	-	-	
$[Ru(C_6H_6)Cl_2(Me_2SO)]$	28.8	3.6	-	-	29.2	3.2	-	-	
$[RuCl_2(PMe_2Ph)_4]$	52.4	6.1	-	-	53.0	6.1	-	-	30.0[c]
$[Ru_2(C_6H_6)_2Cl_3]PF_6$	23.8	1.9	-	16.2	23.6	1.9	-	17.4	82.0
$[Ru(C_6H_6)Cl(C_5H_5N)_2]PF_6$	37.0	3.0	5.3	-	37.1	3.1	5.4	-	84.0
$[Ru(C_6H_6)Cl_2(Et_2S)]$	34.9	4.6	-	-	35.3	4.7	-	-	
$[Ru(C_6H_6)Cl(Et_2S)_2]PF_6$	31.5	4.6	-	-	31.2	4.8	-	-	64.0
$[Ru(C_6H_6)Cl(PPh_3)_2]PF_6$	56.7	4.2	-	-	57.1	4.1	-	-	78.0
$[Ru(C_6H_6)Cl(AsPh_3)_2]PF_6$	51.6	3.7	-	-	51.9	3.7	-	-	75.0
$[Ru(C_6H_6)Cl(PMe_2Ph)_2]PF_6$	41.3	4.4	-	-	41.5	4.4	-	-	72.0
$[Ru(C_6H_6)Cl(PMePh_2)_2]PF_6$	50.5	4.8	-	-	50.6	4.2	-	-	67.0
$[Ru_2Cl_3(PMe_2Ph)_6]PF_6$	44.9	5.1	-	-	44.9	5.2	-	-	74.0
$[Ru(NH_3)_2(C_6H_6)Cl]_3(PF_6)_3 \cdot NH_4PF_6$	16.3	2.9	7.1	-	16.1	3.0	7.3	-	

[a] Equivalent conductivities (S cm^2 mol^{-1}) measured in nitromethane (unless stated) at 10^{-3} mol dm^{-3} concentration [b] measured in H_2O [c] measured in CH_2Cl_2 - rearranges to $[Ru_2Cl_3(PMe_2Ph)_6]Cl$.

with methanol and diethyl ether mp. 270°C (decomp) (Yield 0.31g,95%) ν(RuCl) 280 (broad) cm^{-1}.

Benzene(dichloro)pyridine ruthenium(II): The compound $Cs[Ru(C_6H_6)Cl_3]$ (0.10g;0.23 mmol) was shaken in methanol (10 cm^3) with excess of pyridine (1.0 cm^3) for *ca* 4h. Concentration of the resulting yellow solution and addition of diethyl ether gave an orange solid mp. 245°C (decomp) (0.07g, 86%) ν(RuCl) 280 cm^{-1}.

TABLE 2

Hydrogen-1 nmr data for some η^6-Areneruthenium(II) Complexes

		δ^a ppm	
Compound	Solvent	η^6-C_6H_6	other resonances
$[\{Ru(C_6H_6)Cl_2\}_2]$	D_2O^b	6.39^c;6.50^c	
$Cs[Ru(C_6H_6)Cl_3]$	D_2O^b	6.40^c	
$[Ru(C_6H_6)Cl_2(C_5H_5N)]$	d^6-Me_2SO	$5.65,5.90^d$	7.30,8.80(pyridine)
$[Ru(C_6H_6)Cl_2(Me_2SO)]$	$CDCl_3$	5.90	*ca* 2.70(br) (Me_2SO)
$[Ru(C_6H_6)Cl_2PPh_3]$	$CDCl_3$	5.40	7.50 (PPh_3)
$[Ru(C_6H_6)Cl_2(PMePh_2)]$	$CDCl_3$	5.40	7.65(Ph);1.95(d)($^2J_{PH}$ 12.0Hz)(Me)
$[Ru(C_6H_6)Cl_2(PMe_2Ph)]$	$CDCl_3$	5.35	7.50(Ph);1.85(d)($^2J_{PH}$ 12.0Hz)(Me)
	$CDCl_3{}^b$	5.95	8.03(Ph);2.48(d)($^2J_{PH}$ 12.0Hz)(Me)
$[Ru(C_6H_6)Cl_2(SbPh_3)]$	$CDCl_3$	5.68	7.40-7.70($SbPh_3$)
$[Ru(C_6H_6)Cl_2(AsPh_3)]$	$CDCl_3$	5.50	7.40-7.60($AsPh_3$)
$[Ru(C_6H_6)Cl_2(Et_2S)]$	$CDCl_3$	5.70	2.90(q);1.35(t) (Et_2S)
$[Ru_2(C_6H_6)_2Cl_3]PF_6$	d^3-$MeNO_2$	5.90	
	D_2O^b	6.35^c,6.48^c	
	d^6-Me_2SO	5.95^c,6.15^c,6.50^c	
$[Ru(C_6H_6)Cl(C_5H_5N)_2]PF_6$	d^6-Me_2CO	6.16	7.45,8.00,8.85(pyridine)
$[Ru(C_6H_6)Cl(Et_2S)_2]PF_6$	$CDCl_3$	5.95	3.00(q);1.45(t) (Et_2S)
$[Ru(C_6H_6)Cl(PPh_3)_2]PF_6$	$CDCl_3$	5.52	7.30(PPh_3)
$[Ru(C_6H_6)Cl(PMePh_2)_2]PF_6$	$CDCl_3$	5.75	7.20-7.60(Ph) 1.60(t) (Me)
$[Ru(C_6H_6)Cl(PMe_2Ph)_2]PF_6$	$CDCl_3$	5.87	7.50(Ph);1.64(t);2.12(t)(Me)
$[Ru(C_6H_6)Cl(AsPh_3)_2]PF_6$	$CDCl_3$	5.66	7.40-7.60($AsPh_3$)

d (doublet), t (triplet), q (quartet)

[a] Unless specified, reference is TMS(internal lock) [b] With respect to external TMS capillary. [c] See text for assignment of these resonances

[d] From $[Ru(C_6H_6)Cl_2(d^6\text{-}Me_2SO)]$

Benzene(dichloro)triphenylphosphine ruthenium(II): The compound Cs[$Ru(C_6H_6)Cl_3$] (0.10g; 0.23 mmol) was shaken with excess of PPh_3 (0.10g; 0.40 mmol) in methanol for *ca* 3h to give a dark red crystalline *solid* mp. 182°C (0.11g,91%)ν(RuCl) 295, 280 cm^{-1}.

Benzene(dichloro)methyldiphenylphosphine ruthenium(II): mp. 197°C (0.09g,82%) ν(RuCl) 290, 270 cm^{-1}; *benzene(dichloro)dimethylphenylphosphine-ruthenium(II)* mp. 175°C (0.07g; 78%) ν(RuCl) 290, 275 cm^{-1}; *benzene(dichloro)triphenylstibine ruthenium(II)* mp. 220-222°C ν(RuCl) 290, 269 cm^{-1} and *benzene(dichloro)dimethylsulphoxide ruthenium(II)* mp. 211°C ν(RuCl) 291, 272 cm^{-1} were similarly prepared.

Cis-dichlorotetrakis(dimethylphenylphosphine)ruthenium(II): The compound Cs[$Ru(C_6H_6)Cl_3$] (0.10g; 0.23 mmol) was refluxed in methanol with excess PMe_2Ph (0.50 cm^3) for 6h. The resulting yellow solution on standing gave a yellow, crystalline *solid* mp. 126°C (0.13g; 82%) ν(RuCl) 288, 241 cm^{-1}.

Tri-μ-chlorobis[(benzene)ruthenium(II)]hexafluorophosphate:- *Method A*: The complex [$\{Ru(C_6H_6)Cl_2\}_2$] (0.20g; 0.40 mmol) was heated under reflux with water (10 cm^3) for 2h. The orange solution was filtered and treated with a saturated aqueous solution of NH_4PF_6. After several days the orange *precipitate* was filtered off and washed with water and methanol mp. 255°C (decomp) (0.03g; 12%). On leaving the filtrate for another 7 days, another orange crystalline *solid* was deposited which was characterised by X-ray analysis [14] as [$Ru(NH_3)_2(C_6H_6)Cl]_3(PF_6)_3.NH_4PF_6$ (νRuCl 285 cm^{-1}; ν(NH) 3180, 3250, 3320, 3370 cm^{-1}; δ(NH) 1615, 1630 cm^{-1}; ν(Ru-N) 421, 440, 455 cm^{-1}). Unfortunately, subsequent attempts to prepare this latter compound were unsuccessful.

Method B: The complex [$\{Ru(C_6H_6)Cl_2\}_2$] (0.20g; 0.40 mmol) was stirred in methanol (25 cm^3) with excess of NH_4PF_6 (0.16g; 1.00 mmol) for 24h. The orange-yellow *solid* was filtered off and washed with water, methanol and diethyl ether mp. 280°C (decomp) (0.22g; 90%) ν(RuCl) 264, 276 cm^{-1}. Conductivity in $MeNO_2$ at 298K. Slope of $\Lambda_o - \Lambda_c$ vs $c^{\frac{1}{2}}$ plot = 207; for [$Ru_2Cl_3(PMe_2Ph)_6$]PF_6, slope = 190. ^{13}C-$\{^1H\}$nmr in d^3-$MeNO_2$ at 303K.

82.0 ppm (singlet). The compound is insoluble in $CHCl_3$, CH_2Cl_2, benzene and very sparingly soluble in acetone.

Benzene(chloro)bis(pyridine)ruthenium(II)hexafluorophosphate: The complex $[Ru_2(C_6H_6)_2Cl_3]PF_6$ (0.09g; 0.14 mmol) was refluxed in ethanol (30 cm^3) with pyridine (0.40 cm^3) for *ca* 6h. The yellow solution on standing for 24h gave a yellow crystalline *solid* mp. 227-229°C (0.05g; 66%) ν(RuCl) 285 cm^{-1}. Concentration of the filtrate from this reaction gave an orange solid *trans-dichlorotetrakis(pyridine)ruthenium(II)* mp. 255°C (decomp) (0.03g; 24%) ν(RuCl) 338 cm^{-1}.

Benzenedichloro(diethylsulphide)ruthenium(II): The complex $[Ru_2(C_6H_6)_2$-$Cl_3]PF_6$ (0.10g; 0.16 mmol) was refluxed in ethanol (30 cm^3) with Et_2S-(0.20 cm^3) for *ca* 3h. The orange solution was filtered and concentrated by evaporation of solvent under *vacuo*. The orange *precipitate* obtained was recrystallised from acetone/diethyl ether mp. 225°C (decomp) ν(RuCl) 283, 265 cm^{-1}). The filtrate from the above reaction gave an orange crystalline *solid* on standing for 24h identified as *benzene(chloro)bis-(diethylsulphide)ruthenium(II)hexafluorophosphate* mp. 175°C, ν(RuCl) 290 cm^{-1}.

Benzenechlorobis(triphenylphosphine)ruthenium(II)hexafluorophosphate: The complex $[Ru_2(C_6H_6)_2Cl_3]PF_6$ (0.20g; 0.32 mmol) was shaken in methanol (20 cm^3) with excess of PPh_3 (0.20g; 0.80 mmol). The red precipitate was filtered off from the yellow solution, recrystallised from CH_2Cl_2/hexane and identified as $[Ru(C_6H_6)Cl_2(PPh_3)]$. Addition of diethylether and hexane to the yellow filtrate gave the yellow crystalline *product* mp. 172°C (0.11g, 41%), ν(RuCl) 290 cm^{-1}. Similar reactions gave the yellow solids *benzenechlorobis(triphenylarsine)ruthenium(II)hexafluorophosphate* mp. 142°C, ν(RuCl) 310 cm^{-1}; *benzenechlorobis(methyldiphenylphosphine)ruthenium(II)hexafluorophosphate* mp. 158°C, ν(RuCl) 292 cm^{-1} and *benzenechlorobis(dimethylphenylphosphine)ruthenium(II)hexafluorophosphate* mp.209-211°C, ν(RuCl) 298 cm^{-1}.

Tri-μ-chlorobis[tris(dimethylphenylphosphine)ruthenium(II)]hexafluorophosphate:

The compound [$Ru_2(C_6H_6)_2Cl_3$]PF_6 (0.20g; 0.32 mmol) was refluxed in methanol (20 cm^3) with excess of PMe_2Ph (1 cm^3) for 5h. Addition of diethyl ether to the yellow solution gave a yellow crystalline solid mp. 238-239°C (0.37g, 92%).

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References

1. R.A. Zelonka and M.C. Baird, Canad. J. Chem., 50 (1972) 3063
2. ibid, J. Organometal Chem., 44 (1972) 383.
3. M.A. Bennett and A.K. Smith, J. Chem. Soc. Dalton Trans., (1974) 233.
4. A.S. Ivanov, A.Z. Rubezhov and S.P. Gubin, Izv. Acad. Nauk. S.S.S.R. Ser Khim, 4 (1974) 931.
5. D.F. Dersnah and M.C. Baird, J. Organometal Chem., 127 (1977) C55
6. H. Brunner and R.G. Gastinger, J.C.S. Chem. Comm., (1977) 488; ibid J. Organometal Chem., 145 (1978) 365.
7. R.H. Crabtree and A.J. Pearman, J. Organometal Chem., 141 (1977) 325.
8. Preliminary Communication, D.R. Robertson and T.A. Stephenson, J. Organometal Chem., 116 (1976) C29.
9. T.A. Stephenson, E.S. Switkes and L. Ruiz-Ramirez, J. Chem. Soc. Dalton Trans., (1973) 2112.
10. L. Ruiz-Ramirez and T.A. Stephenson, J. Chem. Soc. Dalton Trans., (1974) 1640.
11. E.W. Abel, M.A. Bennett and G. Wilkinson, J. Chem. Soc., (1959) 3178.
12. P.W. Armit, A.S.F. Boyd and T.A. Stephenson, J. Chem. Soc. Dalton Trans., (1975) 1663.
13. T.A. Stephenson and G. Wilkinson, J. Inorg. Nuclear Chem., 28 (1966) 945.
14. R.O. Gould, C.L. Jones, D.R. Robertson and T.A. Stephenson, Cryst. Struct. Comm., 7 (1978) 27.
15. J.W. Kang and P.M. Maitlis, J. Organometal Chem., 30 (1971) 127.

16. See W.J. Geary, Coord. Chem. Reviews, 7 (1971) 81.

17. W.J.Sime and T.A. Stephenson, J. Organometal Chem , submitted for publication.

18. W.J. Sime and T.A. Stephenson, J. Chem. Soc. Dalton Trans., submitted for publication.

19. J. Chatt, B.L. Shaw and A.E. Field, J. Chem. Soc., (1964) 3466

20. R.D. Feltham and R.G. Hayter, J. Chem. Soc., (1964) 4587.