RUTHENIUM COMPLEXES CONTAINING GROUP VB DONOR LIGANDS

IX *. CATIONIC η^6-ARENE AND η^5-CYCLOHEXADIENYL COMPLEXES OF RUTHENIUM CONTAINING NITROGEN AND PHOSPHORUS DONOR LIGANDS

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Summary

Reaction of the compounds $[Ru(\eta^6\text{-}C_6H_6)PR_3(N\text{—}N)](PF_6)_2$ with various nucleophiles (Y^-) give the stable η^5-cyclohexadienyl complexes $[Ru(\eta^5\text{-}C_6H_6Y)\text{-}PR_3(N\text{—}N)]PF_6$ $(Y^- = H^-, CN^-, OH^-; PR_3 = PMe_2Ph, PMe_2; N\text{—}N = 1,10$ phenanthroline, 2,2'-bipyridyl) and reaction of $[Ru(\eta^6\text{-}C_6H_3Me_3)(PMe_2Ph)phen]\text{-}(PF_6)_2$ with $NaBH_4$ gives $[Ru(\eta^5\text{-}C_6H_4Me_3)(PMe_2Ph)phen]PF_6$. In contrast, reaction of these nucleophiles with other areneruthenium(II) cationic complexes such as $[Ru(\eta^6\text{-}C_6H_6)Cl(N\text{—}N)]PF_6$, $[Ru(\eta^6\text{-}C_6H_6)Cl(PMe_2Ph)_2]PF_6$ and $[Ru(\eta^6\text{-}C_6H_6)PMePh_2(S_2PPh_2)]PF_6$ leads to facile decomposition.

Introduction

Although reactions of nucleophiles with cationic complexes containing coordinated arenes have been studied extensively [2], very little work has been published on such reactions with areneruthenium(II) compounds. This is probably because, in most instances, addition to the coordinated ring gave products which were too unstable to be isolated [3]. In this paper, we now report our full studies [4] on the reactions of nucleophiles with various areneruthenium(II) compounds where, in some instances, stable η^5-cyclohexadienyl complexes are obtained.

Results and discussion

On stirring $[\{RuCl_2(\eta^6\text{-}C_6H_6)\}_2]$ in methanol with an excess of 1,10-phenanthroline (phen) for ca. 1 h, an orange-yellow solution is formed which

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* For part VIII see ref. 1.

TABLE 1

ANALYTICAL AND CONDUCTIVITY DATA FOR SOME η^6-ARENE AND η^5-CYCLOHEXA-DIENYL-RUTHENIUM COMPLEXES

Compound	M.p. (°C)	Analysis (Found(calcd.) (%)			Λ_m [a]
		C	H	N	
[Ru(C$_6$H$_6$)Cl(phen)]PF$_6$	222 (decomp)	39.9 (40.0)	2.6 (2.6)	5.3 (5.2)	71
[Ru(C$_6$H$_6$)Cl(bipy)]PF$_6$	275 (decomp)	37.2 (37.3)	2.7 (2.7)	5.5 (5.4)	88
[Ru(C$_6$H$_3$Me$_3$)Cl phen]PF$_6$	260 (decomp)	43.0 (43.3)	3.4 (3.4)	4.8 (4.8)	65
[Ru(C$_6$H$_5$OMe)Cl phen]PF$_6$	190 (decomp)	39.8 (40.0)	2.7 (3.0)	5.1 (4.9)	130 [b]
[Ru(C$_6$H$_5$OMe)Cl bipy]PF$_6$	220 (decomp)	37.2 (37.4)	2.8 (2.8)	5.1 (4.9)	128 [b]
[Ru(MeC$_6$H$_4$CHMe$_2$)Cl phen]PF$_6$	154 (decomp)	44.5 (44.3)	3.7 (3.7)	4.7 (4.7)	120 b
[Ru(C$_6$H$_6$)(PMe$_2$Ph)phen](PF$_6$)$_2$	245—247	39.4 (39.6)	3.2 (3.2)	3.5 (3.6)	158
[Ru(C$_6$H$_6$)(PMePh$_2$)phen](PF$_6$)$_2$	263—265 (decomp)	43.9 (43.8)	3.2 (3.2)	3.3 (3.3)	140
[Ru(C$_6$H$_6$)(PEt$_2$Ph)phen](PF$_6$)$_2$	267 (decomp)	41.4 (41.2)	3.7 (3.6)	3.4 (3.4)	174
[Ru(C$_6$H$_6$)(PMe$_2$Ph)bipy](PF$_6$)$_2$	227—229	37.5 (37.8)	3.3 (3.3)	3.7 (3.7)	215 [b]
[Ru(C$_6$H$_6$)(PMePh$_2$)(bipy)](PF$_6$)$_2$	255—257 (decomp)	42.3 (42.2)	3.2 (3.5)	3.5 (3.4)	220 [b]
[Ru(C$_6$H$_3$Me$_3$)(PMe$_2$Ph)phen](PF$_6$)$_2$	232—234	41.9 (42.0)	3.7 (3.7)	3.4 (3.4)	160
[Ru(C$_6$H$_5$OMe)(PMe$_2$Ph)bipy](PF$_6$)$_2$	221—224 (decomp)	37.6 (37.8)	3.3 (3.4)	3.7 (3.5)	215 [b]
[Ru(C$_6$H$_7$)(PMe$_2$Ph)phen]PF$_6$	162—165	48.2 (48.5)	4.1 (4.0)	4.3 (4.3)	73
[Ru(C$_6$H$_7$)(PMePh$_2$)phen]PF$_6$	178—179 (decomp)	52.8 (52.8)	4.1 (4.0)	4.0 (4.0)	135 [b]
[Ru(C$_6$H$_6$OH)(PMe$_2$Ph)phen]PF$_6$(acetone)	168—169	48.4 (48.5)	4.2 (4.4)	3.9 (3.9)	80
[Ru(C$_6$H$_6$CN)(PMe$_2$Ph)phen]PF$_6$	230 (decomp)	48.2 (48.5)	3.8 (3.7)	6.2 (6.3)	76
[Ru(C$_6$H$_6$OH)(PMePh$_2$)phen]PF$_6$(acetone)	110—113	53.0 (52.4)	4.3 (4.4)	3.5 (3.6)	128 [b]
[Ru(C$_6$H$_7$)(PMePh$_2$)bipy]PF$_6$	177—180 (decomp)	51.0 (51.1)	4.2 (4.1)	4.0 (4.1)	110 [b]
[Ru(C$_6$H$_6$CN)(PMe$_2$Ph)bipy]PF$_6$	170 (decomp)	45.6 (46.6)	3.6 (3.9)	5.7 (6.5)	130 [b]
[Ru(C$_6$H$_6$CN)(PMePh$_2$)bipy]PF$_6$	180—181 (decomp)	50.9 (51.0)	3.8 (3.8)	5.9 (5.9)	140 [b]
[Ru(C$_6$H$_4$Me$_3$)(PMe$_2$Ph)(phen)]PF$_6$	198—199	50.7 (50.8)	4.7 (4.7)	3.9 (4.1)	—

[a] Molar conductivities at 298 K in CH$_3$NO$_2$. [b] Molar conductivities at 298 K in acetone (S cm^2 mol^{-1}), measured at 10^{-3} mol dm^{-3} concentration.

deposits a bright yellow solid on addition of NH_4PF_6. The analysis figures for this solid (see Table 1) fit for the formulation [$Ru(C_6H_6)Cl(phen)PF_6$ and conductivity measurements in nitromethane agree with those expected for a 1/1 electrolyte (for a 10^{-3} mol dm^{-3} solution, the molar conductivity $\Lambda_m = 71$ S cm^2 mol^{-1} and a graph of $\Lambda_0 - \Lambda_e$ vs. $C_e^{1/2}$ gives a straight line of slope 233, which are characteristic values for 1/1 electrolytes [5,6]). The IR spectrum of this complex shows bands at 715, 776, 1090, 1135, 1211, 1430, 1520, 1579 and 1600 cm^{-1} which originate from vibrations associated with the heterocyclic and aromatic rings of the 1,10-phenanthroline ligand [7]. A band at 295 cm^{-1} can be assigned to the terminal $\nu(RuCl)$ stretching vibration whilst a band at 360 cm^{-1} may be due to a $\nu(Ru-N)$ stretch. The presence of PF_6^- is shown by IR absorptions at 835 and 560 cm^{-1}, with the former absorption obscuring the band normally found at ca. 800 cm^{-1} which arises from the coordinated benzene ring. However, the ^1H NMR spectrum at 298 K in $(CD_3)_2CO$ clearly shows a singlet at δ 6.33 ppm which lies within the region expected for a coordinated benzene ring whereas a series of multiplets centred at δ 8.20, 8.85 and 9.95 ppm confirms the presence of 1,10-phenanthroline (Table 2). Finally, the intensity ratio of these resonances is 6 and 8, respectively, which agrees with the formulation [$Ru(C_6H_6)Cl(phen)$]PF_6.

The analogous complexes [$Ru(arene)Cl(N-N)$]PF_6 (arene = $C_6H_3Me_3$, C_6H_5-OMe, p-MeC$_6$H$_4$CHMe$_2$; N—N = phen; arene = C_6H_6, C_6H_5OMe; N—N = 2,2'-bipyridyl(bipy)) have also been prepared by reaction of [{$RuCl_2$(arene)}$_2$] with an excess of phen or bipy under the same reaction conditions and characterised as above (see Tables 1 and 2).

However, if [{$RuCl_2(C_6H_6)$}$_2$] is refluxed with an excess of phen in methanol for ca. 8 h, loss of coordinated benzene occurs as well as bridge cleavage and halide replacement. Thus, the ^1H NMR spectrum of the orange solid isolated from this reaction mixture by addition of NH_4PF_6 does not show any coordinated benzene resonances and consists only of signals at δ 7.72, 8.43, 8.75 and 8.85 ppm which can be assigned to 1,10-phenanthroline. Analytical data suggests the formulation [$Ru(phen)_3$]$(PF_6)_2$ and this is supported by conductivity measurements in CH_3NO_2 which are characteristic of a 1/2 electrolyte $(\Lambda(1 \times 10^{-3}$ mol dm$^{-3}) = 161.0$ S cm^2 mol^{-1} [5]).

All the cationic complexes [$Ru(arene)Cl(N-N)$]PF_6 react readily with the tertiary phosphines PMe_2Ph, $PMePh_2$ or PEt_2Ph to give the dications [$Ru(arene)PR_3(N-N)$]$^{2+}$ which can be isolated as their hexafluorophosphate salts. Analytical (Table 1) and ^1H NMR (Table 2) data support this formulation and conductivity measurements (Table 1) confirm the dicationic character of the complexes, e.g. for [$Ru(C_6H_6)(PMe_2Ph)(phen)$]$(PF_6)_2$ in CH_3NO_2, $\Lambda_m = 158$ S cm^2 mol^{-1} and a graph of $\Lambda_0 - \Lambda_e$ vs. $C_e^{1/2}$ gives a straight line of slope 390, which are characteristic values for 1/2 electrolytes [5,6]. In contrast to recent reports involving addition of tertiary phosphines to cyclic organic ligands coordinated to manganese [8], iron [9] cobalt or rhodium [2] cations, no evidence for ring addition by PR_3 has been observed in these studies.

However, these dicationic complexes [$Ru(arene)PR_3(N-N)$]$(PF_6)_2$ readily undergo ring addition reactions with various other nucleophiles to give brightly coloured, air stable, η^5-cyclohexadienyl complexes. Thus, addition of $NaBH_4$ to a methanolic solution of the pale yellow complex [$Ru(C_6H_6)(PMe_2Ph)phen$]-

TABLE 2

HYDROGEN-1 NMR DATA FOR SOME η^6—ARENE- AND η^5-CYCLOHEXADIENYL RUTHENIUM COMPLEXES AT 298 K

Compound	Solvent	^{1}H NMR (δ, ppm) [a]						Others
		η^6-arene	η^5-cyclohexadienyl					
			H(1)(endo)	H(2,6)	H(3,5)	H(4)		
[Ru(C$_6$H$_6$)Cl(phen)]PF$_6$	Acetone-d_6	6.33s						8.20m, 8.85d, 9.95d [b]
[Ru(C$_6$H$_6$)Cl(bipy)]PF$_6$	DMSO-d_6	6.22s						7.78m, 8.30m, 8.60s, 9.75d [c]
[Ru(C$_6$H$_3$Me$_3$)Cl(phen)]PF$_6$	Acetone-d_6	2.32s, 5.68s [d]						8.00m, 8.22s, 8.85d, 9.80d [b]
[Ru(C$_6$H$_6$)(PMe$_2$Ph)(phen)](PF$_6$)$_2$	Acetone-d_6	6.75s						2.27d(11.0) [e,f], 6.30m [g], 8.05m, 8.75d, 9.65m [b]
[Ru(C$_6$H$_6$)(PMePh$_2$)(phen)](PF$_6$)$_2$	Acetone-d_6	6.80s						2.70d(12.0) [e,f], 7.08m [g], 8.05m, 8.85d, 10.0d [b]
[Ru(C$_6$H$_6$)(PEt$_2$Ph)(phen)](PF$_6$)$_2$	Acetone-d_6	6.72s						1.24dt(16.0) [e,h], 2.76m [i], 6.0—6.5m [g]; 8.05m, 8.78d, 9.65d [b]
[Ru(C$_6$H$_6$)(PMe$_2$Ph)bipy](PF$_6$)$_2$	Acetone-d_6	6.63s						2.25d(11.0) [e,f], 6.3—6.7m [g], 7.60m, 8.25d, 9.40d [c]
[Ru(C$_6$H$_6$)(PMePh$_2$)bipy](PF$_6$)$_2$	Acetone-d_6	6.73s						2.65d(11.0) [e,f], 7.30m [g], 7.85m, 8.25d, 9.62d [c]

Compound	Solvent						
[Ru(C₆H₃Me₃)(PMe₂Ph)phen](PF₆)₂	Acetone-d_6	2.36s, 5.80s [d]					2.49d(10.0) [e,f], 7.80m [g], 8.20m, 8.90d, 9.80d [b]
[Ru(C₆H₇)(PMe₂Ph)phen]PF₆	CDCl₃	2.38m	2.38m [j]	2.80m	4.78dd	5.79m	1.89d(br)(10.0) [e,f], 6.0m [g], 6.60m, 7.80m, 8.30m [b]
[Ru(C₆H₇)(PMePh₂)phen]PF₆	CDCl₃		2.16m [j]	2.72m	4.78br	5.84m	1.60s [f], 6.90m [g], 6.60m, 7.80m, 8.28m [b]
[Ru(C₆H₆OH)(PMe₂Ph)phen]PF₆(acetone)	CDCl₃		2.95m	3.05m	4.60dd	5.72m	1.65s [k], 1.88m [f], 2.00s [l], 6.10m, 6.60m, 7.78m, 8.30d, 8.50m [b,g]
[Ru(C₆H₆CN)(PMe₂Ph)phen]PF₆	CDCl₃		3.18m	3.80dd	5.18dd	6.10t	2.00d(11.0) [e,f], 6.15—6.80m, 7.98m, 8.52d, 8.70m [b,g]
[Ru(C₆H₇)(PMePh₂)bipy]PF₆	CDCl₃		2.10m [j]	2.55m	4.60br	5.78m	1.58br [f], 6.90—7.20m, 7.40m, 7.80m [c,g]
[Ru(C₆H₇)(PEt₂Ph)(phen)]PF₆	CDCl₃		ca. 2.40 [j,m]	2.80m	4.70dd	5.80m	1.10m [h], 2.40 [i], 6.30m, 7.70m, 8.30m [b,g]
[Ru(C₆H₆OH)(PMePh₂)phen]PF₆	CDCl₃		2.70m	2.90br	4.70br	5.82m	1.70br [f], 6.50—7.00m, 7.70m, 8.25d, 9.30m [b,g]
[Ru(C₆H₄Me₃)(PMe₂Ph)(phen)]PF₆	CDCl₃	1.30s [d], 1.45s [d]; other resonances at 1.70, 2.30 and 4.35 which may be due to ring II's					1.45d(9.0) [e,f], 6.70m [g], 6.20m, 8.00m, 9.00d, 9.75d

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[a] Internal reference (CH₃)₄Si, s(singlet); d(doublet); t(triplet); m(multiplet); br(broad). [b] Resonances due to 1,10-phenanthroline. [c] Resonances due to 2,2'-bipyridyl. [d] Methyl resonances of C₆H₃Me₃. [e] Numbers in round brackets indicate ²J(PH) in Hz. [f] PMe₂Ph or PMePh₂ resonance. [g] Phenyl resonance from phosphine group. [h] CH₂CH₃ resonance. [i] Methylene resonance of ethyl group. [j] II(1)(exo) probably superimposed on H(1)(endo) resonance. [k] Hydroxyl resonance. [l] Resonance due to solvated acetone. [m] Masked by methylene resonance of ethyl group.

$(PF_6)_2$ produced an immediate colour change to deep orange. Addition of water to this solution to destroy excess $NaBH_4$, followed by extraction with methylene chloride or chloroform and concentration of the organic extract leads to the orange product. This analysed well for $[Ru(\eta^5\text{-}C_6H_7)(PMe_2Ph)phen]$ PF_6 and conductivity measurements confirmed the compound is a 1/1 electrolyte (Table 1). The ^1H NMR spectrum of this material in $CDCl_3$ is very different from that of the starting material in that the coordinated benzene resonance at δ 6.75 ppm has disappeared completely and is replaced by weaker resonances at δ 2.38, 2.80, 4.78 and 5.79 ppm (relative intensity 2/2/2/1, respectively) which are consistent with the presence of a η^5-cyclohexadienyl ligand. These resonances are very similar to those observed for the reaction of $[\{Ru(C_6H_6)Cl_2\}_2]$ and KCN in $(CD_3)_2SO$. The cyclohexadienyl complex resulting presumably from the reaction of $Ru(C_6H_6)Cl_2(\{CD_3\}_2SO)$, $[Ru(C_6H_6)Cl\text{-}(\{CD_3\}_2SO)_2]^+$ or $[Ru(C_6H_6)(\{CD_3\}_2SO)_3]^{2+}$ [10] and CN^- has never been isolated but the reactions was followed by ^1H NMR spectroscopy [3]. The gradual growth of resonances at δ 2.88, 3.83, 5.05 and 6.00 ppm was observed and these were assigned to H(2) and H(6); H(1)(*endo*); H(3) and H(5); H(4), respectively (see Fig. 1). Homonuclear decoupling studies on $[Ru(\eta^5\text{-}C_6H_7)\text{-}$
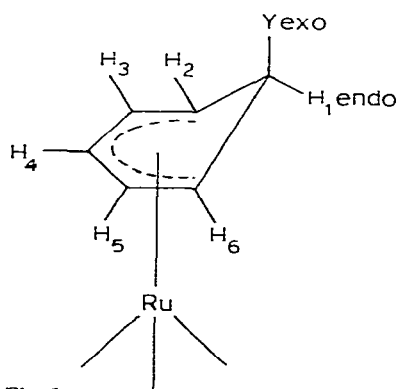

Fig. 1.

(PMe₂Ph)phen]PF₆, however, clearly show that irradiation of the resonance at δ 2.80 ppm collapses the doublet of doublets at δ 4.78 ppm to a doublet whereas irradiation at 2.30 produces no change in this resonance. Hence, for $[Ru(\eta^5\text{-}C_6H_7)(PMe_2Ph)phen]PF_6$, the resonances at δ 2.38, 2.80, 4.78 and 5.79 ppm are assigned to H(1) (*exo* and *endo*); H(2) and H(6); H(3) and H(5); H(4), respectively. A similar frequency order has recently been proposed for $[Rh(C_5Me_4Et)(\eta^5\text{-}C_6H_7)]PF_6$ [2]. Support for this conclusion comes from the ^1H NMR spectra of other η^5-C_6H_7 compounds (Table 2) and from the $^{13}C\text{-}\{^1H\}$ NMR spectra of $[Ru(C_6H_6)(PMe_2Ph)phen](PF_6)_2$ and $[Ru(\eta^5\text{-}C_6H_7)\text{-}(PMe_2Ph)phen]PF_6$, since the resonance at 93.8 ppm (η^6-C_6H_6) in the former is replaced in the latter by resonances at 27.5, 32.7, 75.9 and 96.1 ppm. By analogy with the $^{13}C\text{-}\{^1H\}$ NMR spectrum of $[Rh(C_5Me_4Et)(\eta^5\text{-}C_6H_7)]PF_6$ [2] these can be assigned to carbon atoms C(1), C(2, 5), C(4) and C(3, 5), respectively (Fig. 1). The IR spectrum of $[Ru(\eta^5\text{-}C_6H_7)(PMe_2Ph)phen]PF_6$ (KBr disc) shows an absorption band at 2820 cm^{-1} as observed in other η^5-C_6H_7 compounds (e.g. $Mn(\eta^5\text{-}C_6H_7)(CO)_3$ [11], $[Rh(C_5Me_4Et)(\eta^5\text{-}C_6H_7)]PF_6$ [2]) and

this is assigned to the $\nu(\text{C-H}_{exo})$ stretching vibration.

Similarly, facile reaction of various $[\text{Ru}(C_6H_6)(PR_3)(N\text{—}N)](PF_6)_2$ with other nucleophiles Y^- (Y^- = H^-, OH^-, CN^-) leads to formation and isolation of substituted cyclohexadienyl complexes, $[\text{Ru}(\eta^5\text{-}C_6H_6Y)(PR_3)(N\text{—}N)]PF_6$, characterised by elemental analysis, conductivity (Table 1) and ^1H NMR (Table 2) data. The compound $[\text{Ru}(C_6H_3Me_3)(PMe_2Ph)phen](PF_6)_2$ also reacts with $NaBH_4$ to give $[\text{Ru}(\eta^5\text{-}C_6H_4Me_3)(PMe_2Ph)phen]PF_6$. By analogy with related studies [2], stereospecific *exo* addition of the nucleophiles to the ring probably occurs since the IR spectra of the substituted cyclohexadienyl complex (i.e. $Y \neq H$) contain no characteristic $\nu(\text{C—H}_{exo})$ stretching vibrations at <2850 cm^{-1}. No evidence for further attack by these nucleophiles to give disubstituted cyclohexadiene complexes was observed, even under reflux conditions, and attempts to extend these studies to a wider range of nucleophiles such as $CH_3CO_2^-$, i-Pr_2NH, t-BuO^- and PhS^- were unsuccessful.

The reaction of the monocations $[\text{Ru}(arene)Cl(N\text{—}N)]PF_6$ with similar nucleophiles also results in immediate colour changes but rapid decomposition then occurs preventing isolation of any clean products. Attempts to follow these reactions by ^1H NMR spectroscopy were also unsuccessful since decomposition was too rapid. The instability of these complexes towards nucleophiles compared with the dicationic complexes may be due to competition between reactions involving addition to the coordinated six-membered ring and direct attack on the metal centre via substitution of chloride for H^-, OH^- or CN^- groups and/or ring displacement reactions. Similarly, the compounds $[\text{Ru}(C_6H_6)ClL_2]PF_6$ (L = PPh_3, PMe_2Ph, Et_2S, $AsPh_3$ etc) [10] decompose on addition of $NaBH_4$ although for L = PMe_2Ph, ^1H NMR resonances were observed at δ 3.38 and 3.95 ppm which might be due to the formation of some $\eta^5\text{-}C_6H_7$ complex but this could not be isolated. For cations of type $[\text{Ru}(C_6H_6)L(S_2PR_2)]^+$ [12] rapid decomposition occurred on addition of $NaBH_4$ although in these complexes the hydride ion probably attacks the $^-S_2PR_2$ ligand in preference to the coordinated benzene ring.

In conclusion, the ability of the $[\text{Ru}(arene)PR_3(N\text{—}N)]^{2+}$ cations to react with certain nucleophiles to produce stable η^5-cyclohexadienyl complexes can probably be attributed to the presence of strong metal—ligand bonds minimising the possibility of alternative reaction pathways and to the high formal positive charge favouring nucleophilic attack. The presence of such good π-acceptor ligands as PR_3 and phen (or bipy) will also render the coordinated arene more susceptible to nucleophilic attack.

Experimental

Microanalyses were by 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 or KBr discs. Hydrogen-1 NMR spectra were obtained on Varian Associates HA-100 and EM-360 spectrometers and ^{13}C-$\{^1H\}$ NMR spectra on a Varian CFT-20 spectrometer operating at 20 MHz (^{13}C chemical shifts quoted in ppm to high frequency of $SiMe_4$). Melting points were determined with a Köfler hot stage microscope and are uncorrected. Conductivity measure-

ments were made at 298 K using a model 310 Portland Electronics conductivity bridge. Conductivity vs. concentration data were obtained over a range of concentrations (1×10^{-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 equivalent dm^{-3}) gave a straight line whose slope is a function of the ionic charges. Thus, the slopes obtained for various samples were compared with those for known 1/1 and 1/2 electrolytes and hence the electrolyte type could be determined [6].

Materials

Ruthenium trichloride hydrate (Johnson Matthey); cyclohexa-1,3-diene, ammonium hexafluorophosphate (Ralph Emanuel Ltd); methyldiphenylphosphine, dimethylphenylphosphine, diethylphenylphosphine (Maybridge), 2,2'-bipyridyl, 1,10-phenanthroline, sodium borohydride, potassium cyanide (BDH); α-phellandrene (5-isopropyl-2-methyl-cyclohexa-1,3-diene) (Eastman Chemicals). Various cyclohexa-1,4-dienes were prepared by the Birch reduction of arenes [13] and then [{Ru(η-arene)Cl$_2$}$_2$] (arene = C$_6$H$_6$, 1,3,5-C$_6$H$_3$Me$_3$, C$_6$H$_5$OMe, p-MeC$_6$H$_4$CHMe$_2$) were synthesised as described earlier [3,14] from "RuCl$_3$ x H$_2$O" and the corresponding cyclohexa-1,4 diene (or if available cyclohexa-1,3-diene). Analytical and conductivity data for the various compounds are given in Table 1 and hydrogen-1 NMR data in Table 2. All reactions were carried out in degassed solvents under an atmosphere of nitrogen.

η^6-*Benzene(chloro)(1,10-phenanthroline)ruthenium(II) hexafluorophosphate*. The compound [{Ru(η-C$_6$H$_6$)Cl$_2$}$_2$] (0.20 g; 0.40 mmol) was stirred in methanol (25 cm^3) with an excess of 1,10-phenanthroline (0.18 g; 1.00 mmol) for ca. 1 h. The reaction mixture was filtered, and addition of excess NH$_4$PF$_6$ (0.30 g; 2.00 mmol) to the yellow/orange filtrate precipitated the product as a yellow solid, which was filtered off and washed thoroughly with water, methanol and diethyl ether (yield 0.35 g, 82%) ν(RuCl) 295 cm^{-1}.

If the reactants in this reaction are refluxed for ca. 8 h, an orange solution is produced which deposits an orange crystalline solid which was recrystallised from acetone/diethyl ether and identified as tris(1,10-phenanthroline)ruthenium(II) hexafluorophosphate diethyletherate. (Found: C, 45.6; H, 3.0; N, 7.9. C$_{40}$H$_{34}$F$_{12}$N$_6$OP$_2$Ru calcd.: C, 45.3; H, 3.2; N, 7.9%) (m.p. >290°C (decomp)), ν(C=N) 1600 cm^{-1}; Λ_m(1×10^{-3} mol dm^{-3} in CH$_3$NO$_2$) 161.0 S cm^2 mol^{-1}.

η^6-Benzene(2,2'-bipyridyl)chlororuthenium(II) hexafluorophosphate (nc) was prepared from [{Ru(η^6-C$_6$H$_6$)Cl$_2$}$_2$] (0.20 g; 0.40 mmol), 2,2'-bipyridyl (0.14 g; 1.00 mmol) and NH$_4$PF$_6$ (0.30 g; 2.00 mmol) under similar conditions to those described for the 1,10-phenanthroline complex (0.39 g, 85%) ν(RuCl) 295 cm^{-1}. Chloro(η^6-mesitylene)(1,10-phenanthroline)ruthenium(II) hexafluorophosphate (nc) ν(RuCl) 295 cm^{-1}, (η^6-anisole)chloro(1,10-phenanthroline)ruthenium(II) hexafluorophosphate (nc) (0.15 g; 35%) ν(RuCl) 300 cm^{-1}, η^6-anisole(2,2'-bipyridyl)chlororuthenium(II) hexafluorophosphate (nc) (0.16 g; 40%) ν(RuCl) 295 cm^{-1} and chloro(p-cymene)(1,10-phenanthroline)ruthenium(II) hexafluorophosphate (nc) (0.40 g; 68%) ν(RuCl) 295 cm^{-1} were similarly prepared.

η^6-*Benzene(dimethylphenylphosphine)(1,10-phenanthroline)ruthenium(II)* *hexafluorophosphate.* The complex [Ru(η-C_6H_6)Cl(phen)]PF_6 (0.10 g; 0.19 mmol) was suspended in methanol (20 cm³) and PMe_2Ph (0.10 cm³) was added. The solution was gently warmed until the yellow starting material had completely dissolved (15 min) and then NH_4PF_6 (0.18 g; 1.00 mmol) was added. On cooling, a very pale yellow crystalline solid was deposited which was filtered off and washed thoroughly with water, then diethyl ether and air dried. Evaporation of the solvent from the filtrate gave more of the complex which was washed with water to remove excess NH_4PF_6 and recrystallised from acetone/diethyl ether (yield 0.096 g; 66%).

The complexes η^6-benzene(methyldiphenylphosphine)(1,10-phenanthroline)-ruthenium(II) hexafluorophosphate (nc); η^6-benzene(diethylphenylphosphine)-(1,10-phenanthroline)ruthenium(II) hexafluorophosphate (nc); η^6-benzene-(2,2′-bipyridyl)(dimethylphenylphosphine)ruthenium(II) hexafluorophosphate (nc), η^6-benzene(2,2′-bipyridyl)methyldiphenylphosphine)ruthenium(II) hexafluorophosphate (nc) (60%) η^6-mesitylene(dimethylphenylphosphine)(1,10-phenanthroline)ruthenium(II) hexafluorophosphate (nc), and η^6-anisole(2,2′-bipyridyl)(dimethylphenylphosphine)ruthenium(II) hexafluorophosphate (nc) (62%) were prepared similarly from the appropriate chloro complex and tertiary phosphine.

η^5-*Cyclohexadienyl(dimethylphenylphosphine)(1,10-phenanthroline)ruthenium(II)* *hexafluorophosphate.* The compound [Ru(η^6-C_6H_6)(PMe_2Ph)phen]-(PF_6)$_2$ (0.10 g; 0.13 mmol) was dissolved in methanol (20 cm³). Addition of an excess of $NaBH_4$ (0.10 g; 2.60 mmol) gave an immediate orange/red colouration, and the reaction mixture was stirred for 30 min. Water (20 cm³) was added to destroy the excess of $NaBH_4$ and the resultant mixture was extracted with 2 × 50 cm³ portions of methylene chloride. The orange solution containing the product was dried (Na_2SO_4) and concentrated by evaporation of the methylene chloride in vacuo. Addition of light petroleum (b.p. 60—80°C) gave the product as an orange solid (0.04 g; 52%).

η^5-Cyclohexadienyl(methyldiphenylphosphine)(1,10-phenanthroline)ruthenium(II) hexafluorophosphate (nc) (60%), η^5-cyclohexadienyl(diethylphenyl-phosphine)(1,10-phenanthroline)ruthenium(II) hexafluorophosphate (nc) (45%), η^5-cyclohexadienyl(2,2′-bipyridyl)(methyldiphenylphosphine)ruthenium(II) hexafluorophosphate (nc) (70%) and η^5-1,3,5-trimethylcyclohexadienyl(dimethylphenylphosphine)(1,10-phenanthroline)ruthenium(II) hexafluorophosphate (nc) were similarly prepared from the appropriate [Ru(η^6-arene)(PR_3)(N—N)](PF_6)$_2$ and excess of $NaBH_4$.

η^5-*1-Hydroxocyclohexadienyl(dimethylphenylphosphine)(1,10-phenanthroline)ruthenium(II) hexafluorophosphate acetone solvate.* The complex [Ru(η^6-C_6H_6)(PMe_2Ph)phen](PF_6)$_2$ (0.10 g; 0.13 mmol) was stirred in a mixture of acetone (15 cm³) and water (5 cm³) with 1 pellet of NaOH (0.032 g; 0.80 mmol) for 1 h. The orange solid deposited was filtered off and washed thoroughly with water and diethyl ether (0.05 g; 58%) ν(CO) (acetone) 1705 cm⁻¹.

η^5-1-Hydroxocyclohexadienyl(methyldiphenylphosphine)(1,10-phenanthroline)ruthenium(II) (nc) was similarly prepared starting from [Ru(η^6-C_6H_6)-($PMePh_2$)phen](PF_6)$_2$ and NaOH (70%).

η⁵-1-Cyanocyclohexadienyl(dimethylphenylphosphine)(1,10-phenanthro-line)ruthenium(II) hexafluorophosphate. The complex [Ru(η^6-C_6H_6)-(PMe$_2$Ph)phen](PF$_6$)$_2$ (0.10 g; 0.13 mmol) was stirred in methanol (10 cm^3) with an excess of KCN (0.10 g; 1.50 mmol) for ca. 1 h. The bright yellow precipitate which had formed was filtered off and washed thoroughly with water and diethyl ether (0.055 g; 61%). Likewise, η⁵-1-cyanocyclohexadienyl(2,2'-bipyridyl)(dimethylphenylphosphine)ruthenium(II) hexafluorophosphate (nc) (50%) and η⁵-1-cyanocyclohexadienyl(2,2'-bipyridyl)(methyldiphenylphos-phine)ruthenium(II) hexafluorophosphate (nc) (80%) can be synthesised from the appropriate [Ru(C_6H_6)PR$_3$(bipy)](PF$_6$)$_2$ and KCN.

Acknowledgement

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