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Preliminary Communication

Some η^5-Cyclohexadienyl Complexes of Ruthenium.

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Summary:- The compounds $[(\eta^5 C_6H_6Y)Ru(PR_3)(N\text{-}N)]PF_6$ ($Y^- = H^-, CN^-, OH^-$; $PR_3 = PMe_2Ph, PMePh_2$; N-N = 1,10-phenanthroline, 2,2'-bipyridyl), $[(\eta^5\text{-}C_6Me_3H_4)Ru(PMe_2Ph)phen]PF_6$ and $[\eta^5 C_6H_7Ru\eta^5 C_5H_5]$ have been isolated and some evidence found for other unstable cyclohexadienyl or 1,3 cyclohexadiene compounds on addition of nucleophiles to a variety of cationic areneruthenium(II) complexes.

Although reactions of nucleophiles with complexes containing carbocyclic rings have been studied extensively, 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 [1]. In this note, we now report some results of our studies on the reactions of nucleophiles with various cationic areneruthenium(II) compounds where, in some instances, stable η^5-cyclohexadienyl complexes were obtained.

Thus, if $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = C_6H_6, $C_6Me_3H_3$) is stirred in methanol with excess 1,10-phenanthroline or 2,2'-bipyridyl (N-N) for ca 1 hour, and then NH_4PF_6 is added, the bright yellow solids $[(\eta^6\text{-arene})RuCl(N\text{-}N)]PF_6$ (I)[†] are precipitated. All these compounds then reacted with tertiary phosphines in methanol to give the pale yellow dicationic complexes $[(\eta^6\text{-arene})Ru(PR_3)(N\text{-}N)]\text{-}(PF_6)_2$(II) ($PR_3$ = PMe_2Ph, $PMePh_2$).[†] The analogous $[(\eta^5C_5Me_5)RhCl(N\text{-}N)]PF_6$ and $[(\eta^5\text{-}C_5Me_5)Rh(PR_3)(N\text{-}N)](PF_6)_2$ compounds have also been synthesised starting from $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$.[†]

Reaction of compounds (II) (arene = C_6H_6) with various nucleophiles Y^- (Y^- = H^-, CN^-, OH^-) produced intensely coloured solutions from which the η^5-cyclohexadienyl cationic compounds $[(\eta^5\text{-}C_6H_6Y)Ru(PR_3)(N\text{-}N)]PF_6$[†] were readily isolated. Similarly, $[(\eta^6\text{-}C_6Me_3H_3)Ru(PMe_2Ph)(phen)](PF_6)_2$ reacted with $NaBH_4$ to give $[(\eta^5\text{-}C_6Me_3H_4)Ru(PMe_2Ph)(phen)]PF_6$ and, as for other methyl substituted arene compounds [2], nmr evidence suggested that nucleophilic attack has occurred at one of the unsubstituted positions.

Although reaction of compounds (I) with the above nucleophiles also produced rapid colour changes, facile decomposition occurred and no clean products could be isolated. This rapid decomposition reaction was a characteristic of other monocationic areneruthenium(II) compounds such as $[\eta^6\text{-}C_6H_6RuClL_2]PF_6$ (L = PR_3, $AsPh_3$ etc) and $[\eta^6\text{-}C_6H_6Ru(S_2PPh_2)\text{-}PR_3]PF_6$ on treatment with $NaBH_4$. Similar very unstable products have been reported [1] when $[\eta^6\text{-}C_6H_6RuCl_2]_2$ was reacted with either KCN or NaOH in $d^6\text{-}(CH_3)_2SO$ and here ^1H nmr studies indicated that

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[†] All these compounds have been fully characterised by elemental analyses, conductivity measurements, infrared, ^1H and ^{13}C nmr spectroscopy.

substituted η^5-cyclohexadienyl compounds were initially formed.

For the mixed sandwich compound [η^6-$C_6H_6Ru\eta^5C_5H_5$]Cl, however, (made by reaction of [η^6-$C_6H_6RuCl_2]_2$ with TlC_5H_5[3]) small amounts of the neutral η^5-cyclohexadienyl complex [$\eta^5C_6H_7Ru\eta^5C_5H_5$] could be isolated from the reaction mixture obtained on addition of $NaBH_4$. ^1H nmr studies also indicated the formation of some [(η^5-C_6H_6OMe)-$Ru\eta^5$-C_5H_5] on addition of NaOMe, but with NaOH and KCN, nmr studies suggested that ring displacement reactions were more important.

Finally, preliminary studies on the reaction of the triple hydroxide bridged compound [$C_6H_6Ru(OH)_3RuC_6H_6$]BPh_4 [4] with $NaBH_4$ indicated that two hydride ions may have added to one benzene ring to produce a 1,3 cyclohexadiene ruthenium compound. Similar double hydride ion additions have been observed for the [(η^6-$C_6H_6)_2Ru]^{2+}$ cation forming [$\eta^6C_6H_6Ru\,\eta^4C_6H_8$] [5] and in the reaction of [η^6-$C_6H_6RuCl_2]_2$ with $NaBH_4$ in d^6-$(CH_3)_2SO$, transient 1,3 cyclohexadiene complexes were detected by nmr spectroscopy [1].

Further studies on these and other cationic areneruthenium(II) compounds with a wider range of nucleophiles are now in progress.

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