

Preliminary communication

CATIONIC AND ANIONIC COMPLEXES OF RUTHENIUM(II) CONTAINING η^6 -ARENE LIGANDS

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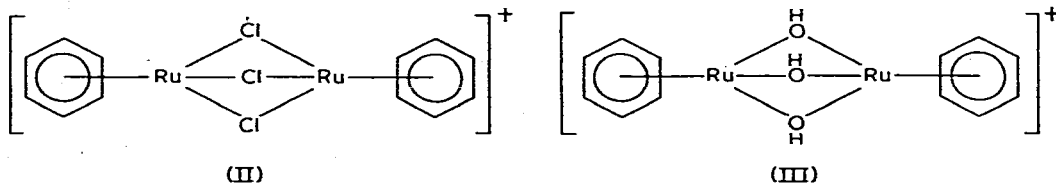
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Summary

Reaction of $[\eta^6\text{-C}_6\text{H}_6\text{RuCl}_2]_2$ (I) with NH_4PF_6 in methanol gives high yields of $[\text{Ru}_2\text{Cl}_3(\eta^6\text{-C}_6\text{H}_6)_2]\text{PF}_6$ whereas with aqueous NaOH , $[\text{Ru}_2(\text{OH})_3(\eta^6\text{-C}_6\text{H}_6)_2]\text{Cl} \cdot 3\text{H}_2\text{O}$ is formed; in contrast, reaction of I with CsCl/HCl gives $\text{Cs}[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_3]$.

Reaction of $[\eta^6\text{-C}_6\text{H}_6\text{RuCl}_2]_2$ (I) with hot water gives an orange solution from which NH_4PF_6 slowly precipitates an orange solid identified as $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_3\text{Ru}(\eta^6\text{-C}_6\text{H}_6)]\text{PF}_6$ (II) (yield ca.40%) [1]. From studies based on analogy with the isoelectronic $[\eta^5\text{-C}_5\text{Me}_5\text{RhCl}_2]_2$ [2], we have now found that II can be readily synthesised in high yield (>90%) by shaking I with an excess of NH_4PF_6 in methanol. However, attempts to synthesise new cationic complexes of type $[\text{L}_3\text{RuCl}_3\text{RuL}_3]\text{PF}_6$ by arene displacement from II by an excess of L (L = $\text{C}_5\text{H}_5\text{N}$, Me_2SO etc) were unsuccessful. For example, reaction with pyridine in ethanol either under reflux or by photolysis gives $[\eta^6\text{-C}_6\text{H}_6\text{RuCl}(\text{C}_5\text{H}_5\text{N})_2]\text{PF}_6$ and *trans*- $[\text{RuCl}_2(\text{C}_5\text{H}_5\text{N})_4]$ and no binuclear complexes. With PMe_2Ph , $[\text{Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6]\text{Cl}$ is isolated, but earlier studies [3] suggest that this is probably formed via *cis*- $[\text{RuCl}_2(\text{PMe}_2\text{Ph})_4]$.

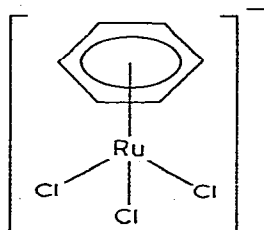


Reaction of $[\eta^5\text{-C}_5\text{Me}_5\text{RhCl}_2]_2$ with aqueous NaOH gave orange crystals of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{OH})_3\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)]\text{Cl} \cdot 4\text{H}_2\text{O}$ [2]. Similarly, reaction of I with aqueous NaOH gives a dark yellow solution from which on standing,

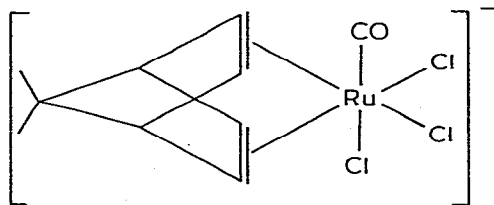
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$[\eta^6\text{-C}_6\text{H}_6\text{Ru}(\text{OH})_3\text{Ru}(\eta^6\text{-C}_6\text{H}_5)]\text{Cl} \cdot 3\text{H}_2\text{O}$ (III), is deposited as a crystalline yellow solid. Likewise, with $[\eta^6\text{-C}_6\text{Me}_3\text{H}_3\text{RuCl}_2]_2$ and NaOH, $[\eta^6\text{-C}_6\text{Me}_3\text{H}_3\text{Ru}(\text{OH})_3\text{Ru}(\eta^6\text{-C}_6\text{Me}_3\text{H}_3)]\text{Cl} \cdot 3\text{H}_2\text{O}$ can be isolated*.

In contrast, reaction of I with an excess of caesium chloride and concentrated HCl in ethanol gives an orange powder analysing closely for $\text{Cs}[\eta^6\text{-C}_6\text{H}_6\text{RuCl}_3]$ (IV), although it is always difficult to obtain this complex free of CsCl. This product, which is the first reported anionic ruthenium arene complex, is closely related to $\text{M}[\text{RuCl}_3\text{COC}_7\text{H}_8]$ (V) ($\text{M} = \text{Cs}, \text{Ph}_3(\text{PhCH}_2)\text{P}$; $\text{C}_7\text{H}_8 = \text{bicyclo}[2.2.1]\text{-hepta-2,5-diene(norbornadiene)}$) formed by reaction of $[\text{RuCl}_2\text{CO}(\text{C}_7\text{H}_8)]_2$ with MCl/HCl [4]. However, although V is a good precursor for synthesis of a range of anionic complexes of type $\text{Ph}_3(\text{PhCH}_2)\text{P}[\text{RuCl}_3\text{COL}_2]$ ($\text{L} = \text{AsPh}_3, \text{C}_5\text{H}_5\text{N}, \text{Me}_2\text{SO}$ etc.) [5], attempts to synthesise the unknown *fac*- $[\text{RuCl}_3\text{L}_3]$ by reaction of IV with an excess of L gave only the neutral $[\eta^6\text{-C}_6\text{H}_6\text{RuCl}_2\text{L}]$ compounds.



(IV)



(V)

Acknowledgement

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References

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*All these compounds have been characterised satisfactorily by elemental analysis, conductivity measurements, IR and ^1H NMR spectra.