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Preliminary Communication:

Some reactions of the $[(\eta\text{-C}_6\text{H}_6)\text{Ru}(\text{OH})_3\text{Ru}(\eta\text{-C}_6\text{H}_6)]^+$ cation

D.R. Robertson and T.A. Stephenson*

Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

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Summary:— Reaction of $[(\eta\text{-C}_6\text{H}_6)\text{Ru}(\text{OH})_3\text{Ru}(\eta\text{-C}_6\text{H}_6)]\text{BPh}_4$ (I) with aqueous solutions of NH_4PF_6 gives $[\text{Ru}(\text{NH}_3)_3(\text{C}_6\text{H}_6)](\text{PF}_6)_2$ (II) whereas refluxing (I) in ROH (R = Me, Et) produced the triple alkoxide-bridged cations $[(\eta\text{-C}_6\text{H}_6)\text{Ru}(\text{OR})_3\text{Ru}(\eta\text{-C}_6\text{H}_6)]\text{BPh}_4$ (III); in contrast, no reaction between (I) and various tertiary phosphines was observed.

Recently, we reported that reaction of $[\{\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2\}_2]$ with an excess of either aqueous sodium hydroxide or carbonate gave the triple hydroxy-bridged cation $[(\text{C}_6\text{H}_6)\text{Ru}(\text{OH})_3\text{Ru}(\text{C}_6\text{H}_6)]\text{Cl}\cdot 3\text{H}_2\text{O}$ [1,2]. However, although $[\text{Ru}_2(\text{C}_6\text{H}_6)_2(\text{OH})_3]\text{BPh}_4$ (I) can be readily isolated by addition of NaBPh_4 to aqueous solutions of the chloride salt, attempts to trap-out the PF_6^- salt by addition of excess of NH_4PF_6 gave, after several days, a yellow nitrogen-containing solid (ca. 40% yield). On the basis of elemental analysis, conductivity measurements in nitromethane, i.r. and ^1H nmr spectral studies, this is best formulated as the trisamine dication $[\text{Ru}(\text{NH}_3)_3(\text{C}_6\text{H}_6)](\text{PF}_6)_2$ (II). A related complex to (II), namely, $[\text{Ru}(\text{NH}_3)_2(\text{C}_6\text{H}_6)\text{Cl}]\text{Cl}_3(\text{PF}_6)_3\text{NH}_4\text{PF}_6$ has been obtained in small yield from the reaction of $[\{\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2\}_2]$ with hot water, followed by addition of NH_4PF_6 [3]. Presumably, (II) is formed from the reaction of $[\text{Ru}_2(\text{C}_6\text{H}_6)_2(\text{OH})_3]^+$ with ammonium ion which can act as a weak acid, protonating the OH^- bridges to form the trisaqua intermediate $[\text{Ru}(\text{H}_2\text{O})_3(\text{C}_6\text{H}_6)]^{2+}$, which could then undergo replacement of water by ammonia groups (cf the related reactions of $[\text{Ru}_2(\text{OH})_3(\text{PMe}_2\text{Ph})_6]^+$ with acids in various solvents (S) which gave $[\text{RuS}_3(\text{PMe}_2\text{Ph})_3]^{2+}$ species [4]).

If (I) is refluxed in methanol for 3 hours, a yellow crystalline solid (III) is deposited on cooling. The ir spectrum of (III) shows no bands at ca 3500 cm^{-1} (νOH) but a strong band at 1050 cm^{-1} indicates the presence of -OMe groups (cf $\text{Ti}(\text{OMe})_4$ with $\nu(\text{O}-\text{C})$ 1032 cm^{-1} [5]). Since the ^1H nmr spectrum in $(\text{CD}_3)_2\text{CO}$ consists of BPh_4^- multiplets at ca 6.90 and 7.30 δ , a $\eta^6\text{-C}_6\text{H}_6$ peak at 5.48 δ and a singlet at 4.42 δ (assigned to -OMe protons) in the intensity ratio 20; 12; 9 respectively, (III) is formulated as the triple methoxide bridged complex $[(\text{C}_6\text{H}_6)\text{Ru}(\text{OMe})_3\text{Ru}(\text{C}_6\text{H}_6)]\text{BPh}_4^-$. This formulation is supported by elemental analyses and detailed conductivity measurements in nitromethane indicating a 1:1 electrolyte. Similarly, $[\text{Ru}_2(\text{C}_6\text{H}_6)_2(\text{OEt})_3]\text{BPh}_4^-$ was obtained by refluxing (I) in ethanol. Again, the mechanism of formation presumably involves protonation of the OH^- bridges by the weak acid ROH to form the $[\text{Ru}(\text{H}_2\text{O})_3(\text{C}_6\text{H}_6)]^{2+}$ cation which could then react rapidly with OR^- to give monomeric alkoxide compounds such as $[\text{Ru}(\text{H}_2\text{O})(\text{C}_6\text{H}_6)\text{OR}]^+$ and $[\text{Ru}(\text{H}_2\text{O})(\text{C}_6\text{H}_6)(\text{OR})_2]$. As discussed elsewhere for the analogous $[\text{Ru}_2(\text{C}_6\text{H}_6)_2\text{Cl}_3]^+$ [6] and $[\text{Ru}_2\text{Cl}_3(\text{PR}_3)_6]^+$ [7] cations, facile intermolecular coupling reactions of these solvated monomers would then give the $[\text{Ru}_2(\text{C}_6\text{H}_6)_2(\text{OR})_3]^+$ cations.

These alkoxide cations could also be synthesised by reaction of $[\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2]_2$ with freshly prepared NaOR (R = Me, Et) in alcoholic solvents, and, unlike the corresponding $[\text{Ru}_2(\text{C}_6\text{H}_6)_2(\text{OH})_3]^+$, their PF_6^- salts are readily isolated by addition of NH_4PF_6 to the above reaction mixtures.

Finally, although the analogous $[\text{Ru}_2(\text{C}_6\text{H}_6)_2\text{Cl}_3]^+$ cation undergoes facile bridge cleavage reactions with a variety of Lewis bases to give monomeric compounds of type $[\text{Ru}(\text{C}_6\text{H}_6)\text{ClL}_2]\text{PF}_6$, $[\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2\text{L}]$ and/or $[\text{RuCl}_2\text{L}_4]$ (L = $\text{C}_5\text{H}_5\text{N}$, Et_2S , $(\text{CH}_3)_2\text{SO}$, PR_3 etc) [1,6], $[\text{Ru}_2(\text{C}_6\text{H}_6)_2(\text{OH})_3]\text{BPh}_4^-$ does not react with excess of tertiary phosphines in acetone, even under reflux conditions for prolonged periods, (cf. $[\text{Pt}(\text{OH})(\text{PR}_3)_2]_2(\text{BF}_4)_2$ also does not react with more PR_3 [8]), the only product isolated being $[\text{Ru}_2(\text{C}_6\text{H}_6)_2(\text{OH})_3]\text{BPh}_4^-(\text{CH}_3)_2\text{CO}$.

Further studies on a wider range of these triple bridged hydroxo and alkoxide ruthenium(II) arene complexes are now in progress.

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