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Preliminary communication

THE PREPARATION AND REACTIONS OF CATIONIC RUTHENIUM(II) COMPLEXES CONTAINING 1,5-CYCLOOCTADIENE AND ACETONITRILE

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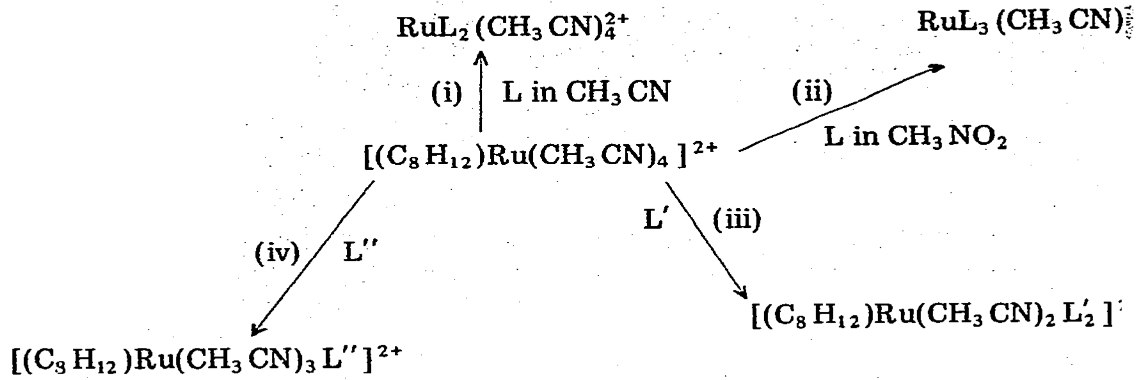
Summary

The polymer $[(C_8H_{12})RuCl_2]_x$, (C_8H_{12} = 1,5-cyclooctadiene, $x > 2$), dissolves in refluxing acetonitrile to form $[(C_8H_{12})RuCl(CH_3CN)_3]^+$ and, on treatment with $AgPF_6$, $[(C_8H_{12})Ru(CH_3CN)_4]^{2+}$; some reactions of these cations are described.

Few general methods have been reported for the preparation of a range of cationic ruthenium(II) complexes. Indirect methods [1,2] have utilised hydride abstraction from ruthenium(II) hydride and allyl—ruthenium(II) complexes producing $RuHL_4^+$ ($L = PPh_3$), $RuHL_5^+$ ($L = P(OMe)_2Ph$, $P(OEt)_2Ph$) [1], $[(diene)RuL_2L'_2]^{n+}$ ($L_2 = \pi$-allyl ($n = 1$), bipy, phen, diars ($n = 2$), $L' = CH_3CN$; $L = L' = CH_3CN$ ($n = 2$)), and $Ru(CH_3CN)_6^{2+}$ [2]. A cursory report [3] on the reaction of $[RuCl_2(DMSO)_4]$ with $AgNO_3$ in DMSO to give $Ru(DMSO)_6^{2+}$ has appeared as well as isolated cases [4] of the formation of ruthenium(II) cationic species but no reactions of these salts have been reported. We have been studying the formation and reactions of cationic diene—ruthenium(II) complexes and found [5] that the polymer $[(diene)RuCl_2]_x$, readily dissolves in methanol in the presence of hydrazine to form $[(diene)Ru(N_2H_4)]^{2+}$ which could only be isolated as the BPh_4^- salt. However, this salt suffers from the ready formation of the highly insoluble product of stoichiometry "diene $RuBPh_4$" when treated with bulky phosphine or phosphinite ligands. Furthering our attempts to utilise the readily available diene polymer as a precursor, we now wish to report a very simple general route to cationic dieneruthenium(II) species utilising acetonitrile as a ligand.

When a suspension of the polymer $[(C_8H_{12})RuCl_2]_x$ ($x > 2$) is refluxed in acetonitrile an orange solution results from which $[(C_8H_{12})RuCl(CH_3CN)_3]$-$PF_6$ (I) is obtained on addition of NH_4PF_6. If $AgPF_6$ is added to the orange solution the dicationic salt $[(C_8H_{12})Ru(CH_3CN)_4](PF_6)_2$ (II) [2] forms



(i) L = PPh_3, $PMePh_2$, PMe_2Ph, $P(OMe)_2Ph$ and $P(OMe)_3$
(ii) L = $P(OMe)_2Ph$ and $P(OMe)_3$
(iii) L′ = pyridine, propylamine and γ-picoline
(iv) L″ = diethyl sulphide

SCHEME 1

almost quantitatively. A limited series of reactions has, so far, been carried out on these products with a series of ligands of different steric and electronic properties to give a range of mixed ligand cationic ruthenium(II) complexes (Scheme 1).

Treatment of a solution of II in refluxing acetonitrile with L produced the compounds $[RuL_2(CH_3CN)_4](PF_6)_2$ (III), (L = PPh_3, $PMePh_2$, PMe_2Ph, $P(OMe)_2Ph$ and $P(OMe)_3$). When refluxing nitromethane was used as a solvent, II and L (L = $P(OMe)_2Ph$, $P(OMe)_3$) formed the trisubstituted salts $[RuL_3(CH_3CN)_3](PF_6)_2$ (IV) (L = $P(OMe)_2Ph$ and $P(OMe)_3$) whereas with the bulky ligand PPh_3 only III (L = PPh_3) was obtained.

The reaction of II in neat amine ligands, e.g. pyridine, propylamine and γ-picoline gave $[(C_8H_{12})Ru(CH_3CN)_2L'_2](PF_6)_2$ (V), (L′ = C_5H_5N, $C_3H_7NH_2$ and C_6H_8N) without substitution of the diene. Using the thioether $S(Et)_2$ as solvent only $[(C_8H_{12})Ru(CH_3CN)_3L''](PF_6)_2$ (VI), (L″ = $S(Et)_2$) is formed.

When the salt $[(C_8H_{12})RuCl(CH_3CN)_3]PF_6$ (I) is treated with phosphines in refluxing acetonitrile solution the products $[RuL_2Cl(CH_3CN)_3]PF_6$ (VII), (L = PPh_3, $PMePh_2$ and PMe_2Ph) are obtained. On addition of $AgPF_6$ to a suspension of II in methanol a yellow solution is formed containing the dicationic complex $[(C_8H_{12})Ru(MeOH)(CH_3CN)_3]^{2+}$. Reactions of this methanol-containing cation are being studied.

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