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Preliminary communication

SYNTHESIS AND CHARACTERISATION OF NEW TRIPLE HALIDE-BRIDGED MIXED VALENCE BINUCLEAR COMPLEXES OF RUTHENIUM AND OSMIUM

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Summary

Several isomers of the type $[M_2Cl_5L_4]$ (M = Ru, L = $AsPh_3$, As(*p*-tol)$_3$, As(*p*-PhCl)$_3$, PEt_2Ph, PMe_2Ph; L_2 = $Ph_2As(CH_2)_2AsPh_2$; M = Os, L = PPh_3, $AsPh_3$) have been synthesised by various routes and characterised by magnetic, ESR and electrochemical measurements, and for $[(PEt_2Ph)Cl_2RuCl_3Ru(PEt_2Ph)_3]$ by X-ray structural analysis.

It is well established that whereas the reaction of "$RuCl_3xH_2O$" with an excess of PPh_3 in refluxing methanol gives $[RuCl_2(PPh_3)_3]$ [1], a similar reaction with $AsPh_3$ [1] or As(*p*-tol)$_3$ [2] gives the ruthenium(III) methanolates $[RuCl_3(AsR_3)_2MeOH]$. Recent electrochemical studies on the latter [2] strongly indicate that facile rearrangement to the double chloride bridged complexes $[Ru_2Cl_6(AsR_3)_4]$ occurs at room temperature in CH_2Cl_2, whereas thermolysis in C_6H_6 (or treatment of $[Ru_2Cl_6(AsR_3)_4]$ with HBF_4), produced the triple chloride bridged complexes $[(AsR_3)_2ClRuCl_3RuCl_2(AsR_3)]$ [3] which are the most oxidized members of stepwise Ru_2(II,II) to Ru_2(III,III) electron-transfer series.*

In contrast, Poddar and Ugarwala [4] reported in 1973 that refluxing "$RuCl_3xH_2O$" and an excess of $AsPh_3$ in butan-2-ol for several hours under nitrogen gave a brown solid (A) of composition $[\{RuCl_2(AsPh_3)_2\}_n]$. On the basis of analytical and magnetic data, ESR and electrochemical evidence, we suggest that this product A should be reformulated as the binuclear $[Ru_2Cl_5$-

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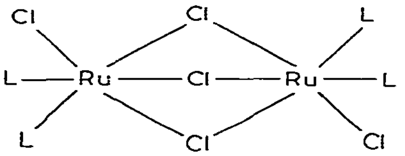
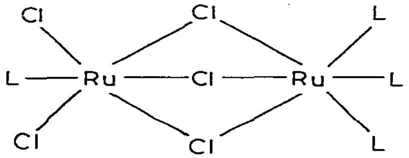
*Further electrochemical studies show that the two cyclic voltammetric waves observed at +0.62 and —0.44 V represent successive reductions of $[Ru_2Cl_6(AsPh_3)_3]$, rather than one-electron oxidation and one-electron reductions as first believed [3]. The behaviour of $[Ru_2Cl_6(As(p\text{-tol})_3)_3]$, reducing at +0.58 and −0.44 V, confirms this pattern.

$(AsPh_3)_4]$ complex with a formal II,III oxidation state. Thus, cyclic voltammetric (CV) and alternating current voltammetric (acV) studies on A in CH_2Cl_2/ 0.50 *M* Bu_4NBF_4 at 20°C unequivocally show a one-electron, reversible oxidation (+0.90 V)* and a one-electron reversible reduction (+0.14 V) step (separation 0.76 V), which are incompatible with the formation of a binuclear Ru_2-(II,II) complex. Magnetic measurements at ambient temperature give a value of μ_{eff} 1.75 BM corresponding to that expected for one unpaired electron/molecule. Furthermore, the product exhibits a strong rhombic ESR spectrum in CH_2Cl_2 at 77 K (g_1 2.32; g_2 2.03; g_3 1.76) which indicates the absence of a plane of symmetry in the complex and hence configuration I (L = $AsPh_3$) is proposed.



(I)



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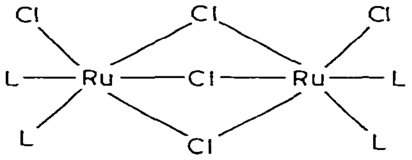

(III)

The analogous red-brown complex $[Ru_2Cl_5\{As(p\text{-tol})_3\}_4]$ (I, L = $Astol_3$) ($E_{1/2}$ +0.83 V (oxidation); +0.10 V (reduction); g_1 2.41; g_2 2.11; g_3 1.87) can be obtained as the major product** (A′) by reaction of "$RuCl_3xH_2O$" with an excess of $As(p\text{-tol})_3$ in ethanol. However, reaction of "$RuCl_3xH_2O$" with an excess of $As(p\text{-tol})_3$ in butan-2-ol yields a yellow-green product B, also of stoichiometry $[Ru_2Cl_5\{As(p\text{-tol})_3\}_4]$ (μ_{eff} = 2.27 BM at 291 K) which was shown by CV and acV studies to be quite distinct from A′ with more difficult one-electron reversible oxidation (+1.24 V) and reduction (—0.26 V) steps. Furthermore, the ESR spectrum of B at 77 K in CH_2Cl_2 revealed an axial *g*-value pattern ($g_\perp$ 2.54; $g_\parallel$ 1.63), indicative of a plane of symmetry in the complex which is compatible with either configuration II or III. Figure 1 emphasises the dramatic dependence of electrochemical behaviour on the isomer form of these mixed valence $[Ru_2Cl_5(As\text{-}p\text{-}tol_3)_4]$ compounds.

The $E_{1/2}$ values and separation between oxidation and reduction waves (1.50 V) for B are very similar to those found for the previously reported $[Ru_2Cl_5\text{-}(PEt_2Ph)_4]$ (+1.27 and —0.28 V, separation 1.55 V [3]); the latter also exhibits

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*All $E_{1/2}$ values are measured with respect to Ag/AgI reference electrode at which ferrocene is oxidised at +0.60 V.

**ESR and electrochemical studies also reveal that a small amount of isomer II (see text) is present in the reaction mixture.

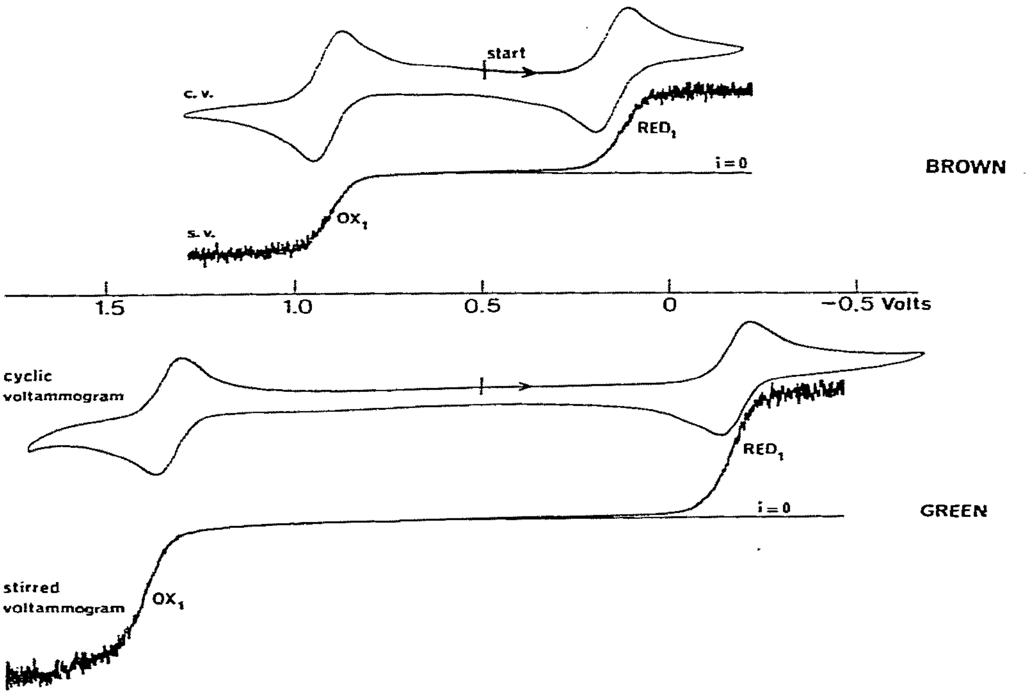

Fig. 1. Voltammetry of geometrical isomers of [$Ru_2Cl_5\{As(p\text{-tol})_3\}_4$] in CH_2Cl_2 /0.50 *M* Bu_4NBF_4 at 20°C vs. Ag/AgI. (Scan rate 100 mV s^{-1}).

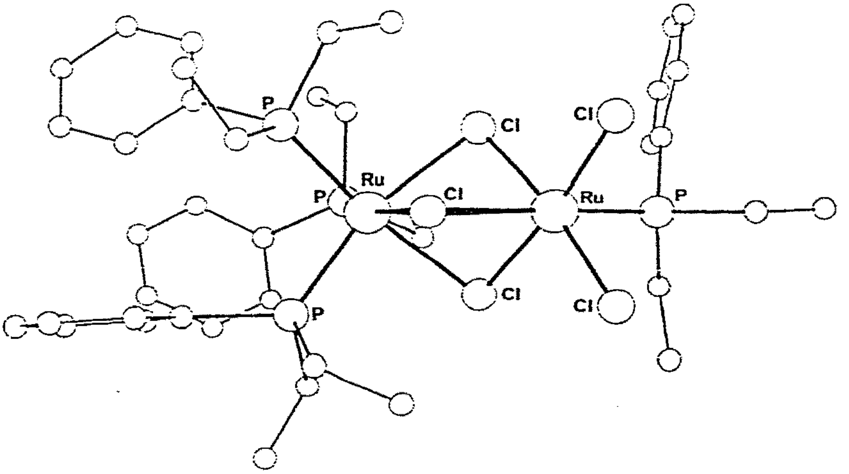

Fig. 2. Molecular geometry of [$(PEt_2Ph)Cl_2RuCl_3Ru(PEt_2Ph)_3$], Ru-Ru 3.28 Å, angle RuClRu 82.9°.

a two *g*-value ESR pattern ($g_\perp$ 2.46; $g_\parallel$ 1.63) with μ_{eff} 1.83 BM at 293 K. X-ray structural analysis of this compound has now confirmed this formulation and shows the asymmetrical structure II (Fig. 2) with three tertiary phosphines sharing a triangular face*. Since [$(PEt_2Ph)Cl_2RuCl_3Ru(PEt_2Ph)_3$] is synthesised

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*Crystal data for $Ru_2Cl_5(PPhEt_2)_4 \cdot MeNO_2$: triclinic, space group $P\bar{1}$: *a* 12.835, *b* 14.353, *c* 30.597 Å, α 75.04, β 76.46, γ 65.87°. There are two very similar molecules in the asymmetric unit.

by aerial oxidation of $[(PEt_2Ph)_2ClRuCl_3Ru(PEt_2Ph)_3]$ in hydrochloric acid/nitromethane, the exclusive formation of configuration II is indicative of selective oxidation of the "harder" $RuCl(PEt_2Ph)_2$ end of the Ru_2(II,II) binuclear compound, accompanied by substitution by further chloride.

Previously [3], we suggested that the large difference between the redox couples in $[Ru_2Cl_5\{As(p\text{-tol})_3\}_4]$ (I) and $[Ru_2Cl_5(PEt_2Ph)_4]$ (II) might be ascribed to the variations in the π-acid character of the $As(p\text{-tol})_3$ and PEt_2Ph ligands. However, now that it is appreciated that different isomeric forms are involved, the observed electrode potentials are understood to reflect quite simply the environment of the particular metal centre engaged in each Ru(II)/Ru(III) couple.

Similarly, the product from reaction of "$RuCl_3xH_2O$" with $As(p\text{-}PhCl)_3$ in methanol, of stoichiometry $[Ru_2Cl_5\{As(pPhCl)_3\}_4]$, shows a reversible oxidation at 1.26 V and a quasi-reversible reduction at −0.42 V (separation 1.68 V) and an axial ESR pattern ($g_\perp$ 2.48, $g_\parallel$ 1.76) indicative of configuration II, while aerial oxidation of $[Ru_2Cl_4(PMe_2Ph)_5]$ in HCl/CH_3NO_2 gives $[Ru_2Cl_5(PMe_2Ph)_4]$ (II) with $E_{1/2}$ +0.81, −0.76 V (separation 1.57 V).

Similar mixed-valence binuclear complexes can be obtained with bidentate ligands. For example, reaction of "$RuCl_3xH_2O$" with $Ph_2As(CH_2)_2AsPh_2$ (dpae) (1/1 molar ratios) in butan-2-ol gave a product analysing closely for $[Ru_2Cl_5(dpae)_2]$. Electrochemical studies showed two reversible oxidations at +0.10 and +0.26 V of unequal height with corresponding reversible reductions at −0.40 and −0.64 V. The separations between these redox couples are 0.50 V (major component) and 0.90 V, respectively, and the ESR spectrum of the product in CH_2Cl_2 at 77 K contains both a rhombic pattern (g_1 2.29, g_2 2.08, g_3 1.93) and a less prominent axial pattern ($g_\perp$ 2.29, $g_\parallel$ 1.74) thus strongly suggesting that both isomers I and III have been formed.

Finally, preliminary studies reveal that mixed valence binuclear complexes $[Os_2Cl_5L_4]$ ($L = PPh_3$, $AsPh_3$) can be formed from $Na_2[OsCl_6]$. Hence, reaction of $Na_2[OsCl_6]$ with an excess of PPh_3 in butan-2-ol gives first an orange-brown precipitate and later a green precipitate. The latter is the well-known $[OsCl_2(PPh_3)_3]$ [5] and the former, which analyses well for $[Os_2Cl_5(PPh_3)_4]$ (μ_{eff} 2.14 BM at 291 K), shows reversible one-electron reduction (−0.06 V) and one-electron oxidation (+0.50 V) waves. Unfortunately the ESR spectrum was uninformative due to the excessive line broadening characteristic of osmium even at 77 K but the small separation favours a configuration of type I or III.

Reaction of $Na_2[OsCl_6]$ with an excess of $AsPh_3$ in butan-2-ol also gave two products. The first orange-brown precipitate analysed for $[OsCl_4(AsPh_3)_2]$ and exhibited a reversible one electron reduction wave at +0.45 V. The second red-orange precipitate which analysed for $[Os_2Cl_5(AsPh_3)_4]$ (μ_{eff} 1.87 BM at 291 K) showed a reversible oxidation at +0.60 V and a reversible reduction step at −0.78 V. The large separation of 1.38 V would suggest that the asymmetrical isomer of type II has been formed but again ESR spectra were unhelpful.

Further work is now in progress to extend those studies to include other mono- and bi-dentate ligands and also to characterise and ultimately isolate some of these compounds in their less stable electrogenerated redox states.

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