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Preliminary communication

Electrochemical Studies on Neutral Triple-Bridged Di-Ruthenium Compounds.

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Summary

Voltammetric studies reveal that, like $[Ru_2Cl_4(PPh_3)_4(CO)]$, triply-bridged complexes $[Ru_2Cl_4L_5]$ (L = $PClPh_2$, $PMePh_2$, PEt_2Ph) are reversibly oxidized to $[Ru_2Cl_4L_5]^+$. The mixed valence complexes $[Ru_2Cl_5L_3Y]$ (L = PPh_3, $P(tol)_3$; Y = CO, CS) undergo a corresponding reduction to $[Ru_2Cl_5L_3Y]^-$; whereas $[Ru_2Cl_5L_4]$ (L = PEt_2Ph, $As(tol)_3$) and $[Ru_2Cl_6(AsPh_3)_3]$ are both reduced and oxidised in reversible one-electron steps. For the bridging $(RuCl_3Ru)^{z+}$ moiety, the redox series z = 1, 2, 3, 4 is established.

Recently we drew attention to the fact that the known triply-chloro-bridged di-ruthenium complexes range in oxidation level from di-Ru(II) to di-Ru(III) systems, suggesting the possibility of stepwise bridge-based

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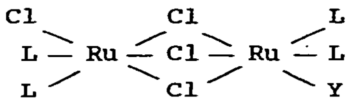
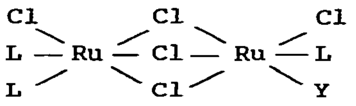
redox equilibria (equation 1), and went on to report the reversible one-electron oxidation of $[Ru_2Cl_4(PPh_3)_4(CO)]$ and its analogues (I) to the corresponding mixed valence cations [1].

$$(RuCl_3Ru)^{+} \rightleftharpoons (RuCl_3Ru)^{2+} \rightleftharpoons (RuCl_3Ru)^{3+} \qquad (1)$$

New voltammetric studies at a platinum electrode in CH_2Cl_2 establish that complexes $[Ru_2Cl_4(PR_3)_5]$ (II) likewise undergo a single reversible one-electron oxidation in the accessible potential range.† The electrode potential is seen to be markedly dependent on the nature of the phosphine (Table) with the more basic phosphines promoting readier oxidation.



I II



III IV

I L = PPh_3,$Ptol_3$; Y = CO,CS III L = PPh_3,$Ptol_3$; Y = CO,CS

II L = Y = $PClPh_2$,$PMePh_2$,PEt_2Ph IV L = Y = PEt_2Ph,$Astol_3$

Neutral mixed-valence complexes $[Ru_2Cl_5L_4]$, where L represents a soft neutral ligand, should offer the best opportunity for observing both redox steps within one molecule [1], and earlier synthetic work provides a systematic route to such compounds through HCl treatment

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[†] All the 'reversible' waves reported here satisfy the appropriate criteria of diffusion controlled electrode reversibility on Pt for cyclic voltammetry (CV) and alternating current voltammetry (acV) over widely varying CV scan rate ν(50-500mVsec^{-1}), and acV frequency ω (20-400Hz). Thus $\Delta E_{pp}(CV)$ - 60mV, $i_c = i_a \propto \nu^{\frac{1}{2}}$, $E_{\frac{1}{2}}(CV) = E_p(acV)$, $i_p(acV) \propto \omega^{\frac{1}{2}}$.

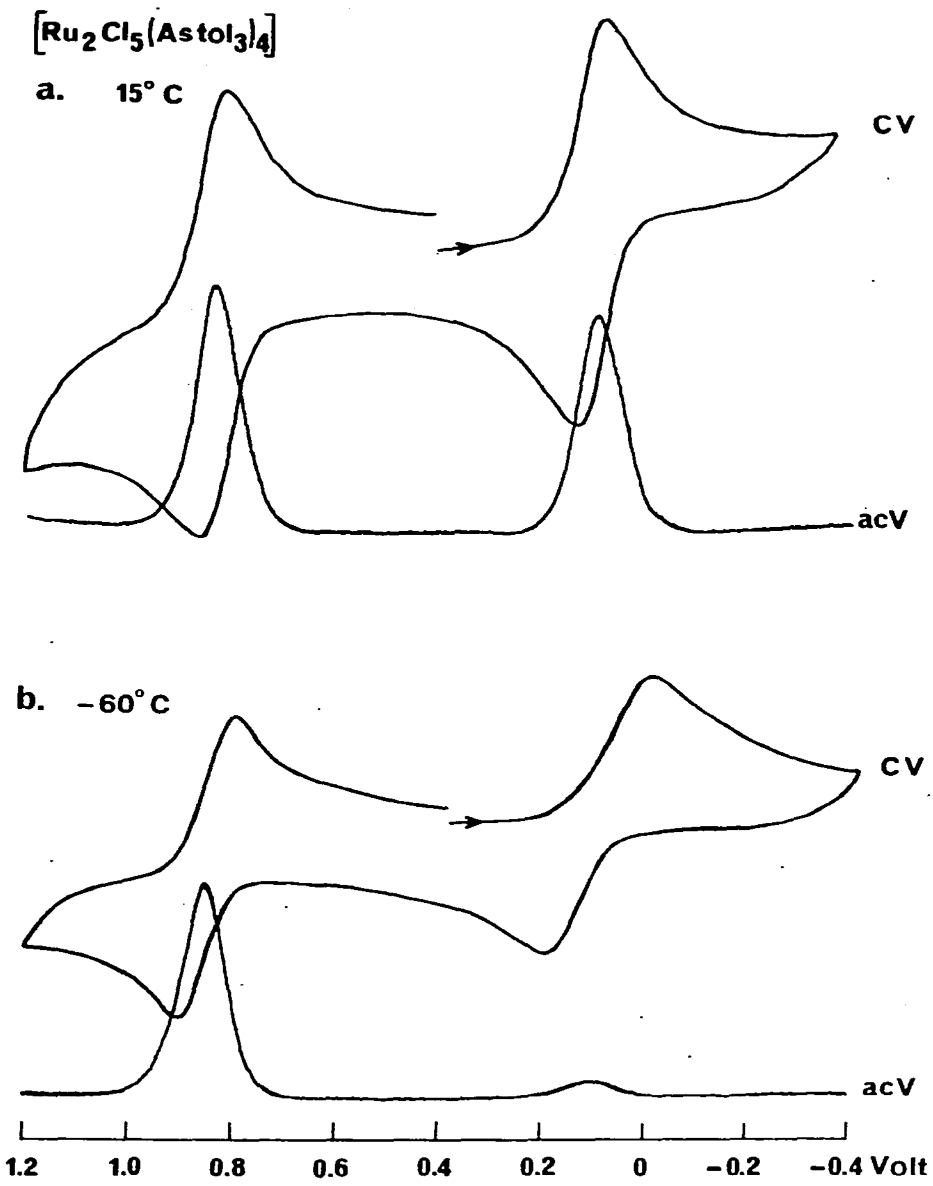

Fig. 1. Voltammetry of [$Ru_2Cl_5(Astol_3)_4$] *vs* Ag/AgI in CH_2Cl_2: a) at 15°C, b) at -60°C.

of [$Ru_2Cl_4L_5$] [2]. Accordingly, [$Ru_2Cl_5(PPh_3)_3(CS)$] and its analogues (III) were examined and found to undergo a reversible one-electron reduction to the corresponding di-Ru(II) mono-anion (Table). However, in these compounds

TABLE

Reversible Electrode Potentials for Binuclear Ruthenium Complexes

$E_{\frac{1}{2}}$ (volts) at 20°C in CH_2Cl_2/0.5$\underline{M}$ Bu_4NBF_4 [a]

Complex	II,II/II,III	II,III/III,III	III,III/III,IV
$[Ru_2Cl_4(CO)(PPh_3)_4]$	+0.75		
$[Ru_2Cl_4(CS)(PPh_3)_4]$	+0.74		
$[Ru_2Cl_4(CO)(Ptol_3)_4]$	+0.65		
$[Ru_2Cl_4(CS)(Ptol_3)_4]$	+0.64		
$[Ru_2Cl_4(PClPh_2)_5]$	+1.20		
$[Ru_2Cl_4(PMePh_2)_5]$	+0.75		
$[Ru_2Cl_4(PEt_2Ph)_5]$	+0.47		
$[Ru_2Cl_5(CO)(PPh_3)_3]$	+0.03		
$[Ru_2Cl_5(CS)(PPh_3)_3]$	+0.02		
$[Ru_2Cl_5(CO)(Ptol_3)_3]$	-0.06		
$[Ru_2Cl_5(PEt_2Ph)_4]$	-0.28	+1.27	
$[Ru_2Cl_5(Astol_3)_4]$	+0.10	+0.83	
$[Ru_2Cl_6(AsPh_3)_3]$		-0.37	+0.67

[a] versus a Ag/AgI/0.5M Bu_4NBF_4/CH_2Cl_2 reference electrode, at which ferrocene is oxidized at +0.60V. This electrode is shifted by 0.2V w.r.t. the Bu_4NClO_4-containing electrode used previously[1].

the anticipated anodic couple is not observed before the onset of multi-electron oxidation at extreme potentials.

In contrast, the symmetrical complexes (IV) exhibit one-electron reduction <u>and</u> oxidation steps which are both reversible in CH_2Cl_2 at room temperature (Table, Figure 1a), thus providing the first clear example of the predicted stepwise redox equilibria. Complementary studies on oxidation of harder systems such as $[Ru_2Cl_3(H_2O)_6]^{3+}$

and $[Ru_2Cl_3(NH_3)_6]^{3+}$ have been reported [3,4]. Interestingly, the measured separation of the two couples is very wide (~1.5V) for $[Ru_2Cl_5(PEt_2Ph)_4]$ whereas both couples occur at relatively modest potentials in $[Ru_2Cl_5(Astol_3)_4]$, implying that the coordinated arsine facilitates both oxidation and reduction. Intuitively this versatility is appropriate for the more polarisable π-acid ligand.

Voltammetry of the related di-Ru(III) complex $[Ru_2Cl_6(AsPh_3)_3]$ reveals a single reversible one-electron reduction. Further reduction would not be expected in the available cathodic range. Remarkably however, $[Ru_2Cl_6(AsPh_3)_3]$ also shows a reversible one-electron oxidation to form a unique Ru(III)/Ru(IV) binuclear cation, extending the sequence of equation 1. These observations have prompted a comparative study on monomeric ruthenium complexes which is reported separately [5]. Among the binuclear compounds of varying stoichiometry, replacement of a neutral ligand by Cl^- is accompanied by a shift of roughly -0.7V in the II,III/III,III redox couple.

The structural and spectroscopic changes accompanying stepwise electron-transfer in the bridged complexes are of considerable interest, expecially since it seems that the degree of metal-metal interaction in 35e and 34e systems may vary in apparently analogous complexes, depending on the identity of the bridging groups and terminal ligands. Strikingly, low temperature voltammetric studies on $[Ru_2Cl_5(Astol_3)_4]$ show that at -40°C the cathodic couple involves slow charge-transfer at the electrode although the anodic couple remains fully reversible (Figure 1b). A sluggish structural rearrangement accompanying the reduction is implied and it is exciting to speculate that this might be related to loss of a metal-metal bond. Preliminary controlled potential electrosyntheses confirm the indefinite stability of species such as $[Ru_2Cl_4(PPh_3)_4(CO)]^+$ and $[Ru_2Cl_5(Astol_3)_4]^-$ at low temperature and work in this area is continuing.

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