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Preliminary communication

Electrochemical Studies on Monomeric Ruthenium Complexes.

R. Contreras, G.A. Heath*, A.J. Lindsay and T.A. Stephenson*.

Department of Chemistry, University of Edinburgh, Edinburgh
EH9 3JJ (G.B.)

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Summary

Voltammetric studies on monomeric Ru(II) and Ru(III) complexes establish *inter alia* reversible one-electron reduction and irreversible oxidation of [$RuCl_3L_3$] in contrast to [$RuCl_4L_2$]$^-$, and reversible one-electron oxidation of [$RuCl_2(CO)_xL_{4-x}$] (x = 1,2) for L = a variety of neutral ligands.

Recently we reported electrochemical studies which establish a variety of facile reversible one-electron redox steps in triply chloro-bridged binuclear ruthenium complexes [$Ru_2Cl_xL_{9-x}$] (x = 4,5,6), where L represents a variety of soft ligands [1,2]. To place these observations in context we have now extended our investigations to a range of monomeric ruthenium complexes containing similar ligands. The new data, obtained by cyclic voltammetry (CV) and alternating current voltammetry (acV) [1] at a Pt electrode in CH_2Cl_2 solution, are summarised in the Table.

Syntheses of a wide range of neutral Ru(III) monomers [$RuCl_3L_2L'$] and [$RuCl_3LL'_2$] where L = $AsPh_3$ or PPh_3 and L' = RCN, C_5H_5N and other Lewis bases have been reported previously [3,4]. Further examples including those with L = As(p-tolyl)$_3$ and L' = pyrazine, 1,4-dithian and 4,4'-bipyridyl [5], together with the well-known [$RuCl_3L_3$] (L = PMe_2Ph [6] and Me_2S [7]) were prepared in this study. All these compounds show a characteristic reversible one-electron reduction which provides a simple and general synthetic route to the hitherto rather inaccessible Ru(II) mono anions. In most instances the neutral Ru(III) complexes also undergo an irreversible one-electron oxidation; however dual pyridine-based ligands appear to confer at least transient stability on the novel Ru(IV) cations. Such behaviour is described herein as 'partly reversible'.† In contrast, the anions [$RuCl_4L_2$]$^-$ (L = PPh_3, $AsPh_3$ [8], and $Astol_3$ [5]) show only irreversible reduction, probably associated with loss of Cl^-. Partly reversible oxidation to short-lived Ru(IV) species [$RuCl_4L_2$] is observed for the arsine complexes only, confirming the ability of tertiary arsines to stabilise higher oxidation states of ruthenium, a trend already discerned in the binuclear complexes [2].

A similar survey of Ru(II) carbonyl-containing monomers [$RuCl_2(CO)_xL'_{4-x}$] (see Table) suggests that as a class they tend to have a difficult but reversible (or partly reversible) one-electron oxidation, which is substantially easier in the presence of ligands such as 2,2'-bipyridyl but inaccessible

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† i.e. in CV i_p(return)/i_p(forward) increases towards unity with increasing scan-rate, consistent with slow reaction of the electrode product following reversible charge-transfer; 'quasi-reversibility' refers strictly to sluggish charge transfer.

TABLE

ELECTRODE POTENTIALS FOR MONOMERIC RUTHENIUM COMPLEXES

$E_{\frac{1}{2}}$ (volts) at 20°C in CH_2Cl_2/0.5M $Bu_4N\ BF_4$

Complex	II/III	III/IV	$E_{Ox}-E_{red}$
$[RuCl_4(PPh_3)_2]^-$	−0.55 i	+1.05 i	1.60
$[RuCl_4(AsPh_3)_2]^-$	−0.54 i	+1.10 pr	1.64
$[RuCl_4(Astol_3)_2]^-$	−0.63 i	+1.02 pr	1.65
$[RuCl_3(AsPh_3)(pyr)_2]$	0.00 r	+1.56 i	1.56
$[RuCl_3(AsPh_3)(4\text{-}Me\text{-}pyr)_2]$	−0.02 r	+1.56 pr	1.58
[" $(4,4'\text{-}bipy)_2]$	+0.08 r	+1.61 pr	1.53
[" (O-phen)]	+0.06 r	+1.58 pr	1.52
[" (2,2'-bipy)]	+0.05 r	+1.56 pr	1.51
[" $(pyz)_2]1$	+0.27 r	+1.70 i	1.43
[" (1,4-dtn)]	+0.22 r	+1.58 i	1.37
$[RuCl_3(Astol_3)(1,4\text{-}dtn)]$	+0.16 pr	+1.55 i	1.39
$[RuCl_3(AsPh_3)_2(CH_3CN)]$	+0.12 r	+1.58 i	1.46
[" $(PhCH_2CN)]$	+0.15 r	+1.61 i	1.46
[" (PhCN)]	+0.17 r	+1.59 i	1.42
[" (pyr)]	+0.00 r	+1.55 i	1.46
$[RuCl_3(SMe_2)_3]$	+0.12 r	+1.65 i	1.53
$[RuCl_3(PMe_2Ph)_3]$	+0.14 r	-	
$[RuCl_3(CO)(PPh_3)_2]^-$	+0.93 r	-	
$[RuCl_2(CO)_2(PPh_3)_2]$	–		
$[RuCl_2(CO)_2(AsPh_3)_2]$	–		
$[RuCl_2(CO)(PMe_2Ph)_3]$	+1.18 r		
$[RuCl_2(CO)_2(quin)_2]$	+1.45 pr		
$[RuCl_2(CO)_2(PhNH_2)_2]$	+1.08 pr		
$[RuCl_2(CO)_2(O\text{-}phen)]$	+0.72 r		
$[RuCl_2(CO)_2(2,2'\text{-}bipy)]$	+0.73 r		

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[a] vs Ag/AgI reference electrode, at which ferrocene is oxidized at +0.60V.

[b] r = reversible, i = irreversible, pr = partly reversible

[d] abbreviations: bipy = bipyridyl, dtn = dithian, pyr = pyridine, pyz = pyrazine, phen = phenanthroline, quin = quinoline.

for L' = PPh_3 or $AsPh_3$. The reversible oxidation of $[RuCl_2(CO)(PMe_2Ph)_3]$ at +1.18 V illustrates both the importance of phosphine basicity and the effect of replacing Cl^- by CO. The general correlation between the number of chloride ligands and the nature of the II/III and III/IV redox couples is apparent from the Table. Clearly, binuclear ruthenium (II) and (III) complexes are more prone to ready reversible electron transfers than the related monomers [1,2], presumably because of greater opportunity for charge delocalisation.

For $[RuCl_3(AsPh_3)_2(MeOH)]$ however, within five minutes of the addition of the crystalline compound to the cell the expected single reversible reduction at -0.02 V gives way to new waves at +0.62V and -0.42V, which both approach half the initial height of the original wave and prove to be reversible one-electron reduction steps (Figure). Thus although the visible spectrum is virtually invariant the electrochemical study establishes unequivocally that a rapid transformation of the methanolate complex occurs in CH_2Cl_2. Manoharan _et al_ proposed a trigonal bipyramidal structure (D_{3h}) for desolvated $[RuCl_3(AsPh_3)_2]$

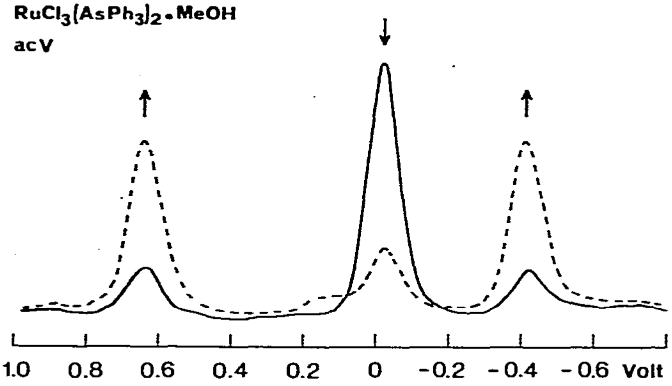
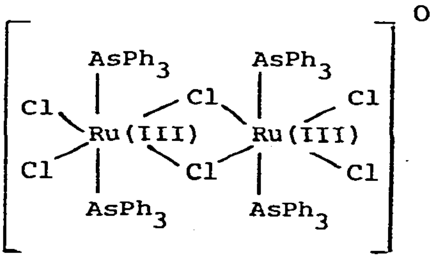


Figure 1. Time-dependent a.c. voltammograms of $RuCl_3(AsPh_3)_2$·MeOH dissolved in CH_2Cl_2, after 30 seconds (———) and 3 minutes (----), _vs_ Ag/AgI.

in CH_2Cl_2 based on the contrasting esr spectra of the methanolate in solid and solution phases [9]. However the electrochemical data strongly suggest that only a dinuclear Ru_2(III,III) species such as I could exhibit stepwise reversible reductions as observed.



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The proposed formation of [$Ru_2Cl_6(AsPh_3)_4$] from [$RuCl_3$—$(AsPh_3)_2$(MeOH)] is akin to the associative behaviour already established for various Ru(II) solvates in non-coordinating media [10]. We find that [$RuCl_3(Astol_3)_2$(MeOH)] behaves in an identical fashion, in joint contrast to the analogous but less labile complexes listed in the Table.

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