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Preliminary communication

ELECTROCHEMICAL STUDIES ON TRIPLE-BRIDGED DI-RUTHENIUM(II) COMPOUNDS

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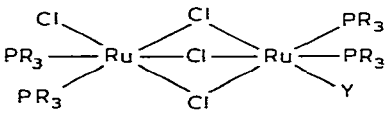
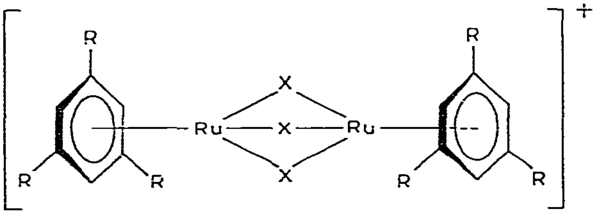
Summary

Voltammetric studies on $[(PR_3)_2ClRu^{II}Cl_3Ru^{II}Y(PR_3)_2]$ ($PR_3 = PPh_3$ or $Ptol_3$, Y = CO or CS) show a reversible one-electron oxidation to form $[(PR_3)_2ClRu^{III}Cl_3Ru^{II}Y(PR_3)_2]^+$ whereas the corresponding oxidation of di-ruthenium(II) mono-cations $[(PR_3)_3RuCl_3Ru(PR_3)_3]^+$ ($PR_3 = P(OMe)Ph_2$ or PMe_2Ph), $[(C_6H_6)RuCl_3Ru(C_6H_6)]^+$ and $[(C_6H_3R_3)Ru(OH)_3Ru(C_6H_3R_3)]^+$ (R = H or Me) is more difficult and also irreversible. For the $(RuCl_3Ru)^{z+}$ moiety, the redox series $z = 1, 2, 3$ is established.

Chatt and Hayter characterised the first triple chloro-bridged ruthenium(II) dimers, $[Ru_2Cl_3(PR_3)_6]Cl$, in 1961 [1], and there have been scattered subsequent examples [2]. In recent years a variety of triple bridged di-ruthenium(II) complexes have been synthesised including the thiocarbonyl complexes and their carbonyl analogues, I and II [3,4] and the μ-trichloro and μ-trihydroxy di-arenes, III and IV [5,6].



(I) Y = CS, R = Ph or tolyl
(II) Y = CO, R = Ph or tolyl



(III) X = Cl, R = H (PF_6^-)
(IV) X = OH, R = H or Me (BPh_4^-)

Interestingly, [$Ru_2Cl_4(CS)(PPh_3)_4$)] is readily oxidised by HCl to the mixed oxidation state complex [$Ru_2Cl_5(CS)(PPh_3)_3$] [3], which has one confirmed analogue [$Ru_2Cl_5(P$-n-$Bu_3)_4$] [7] and we have now isolated a di-ruthenium(III) complex [$Ru_2Cl_6(AsPh_3)_3$] [8]. Thus in such phosphine and arsine systems the common -$RuCl_3Ru$- bridging unit displays a sequence of oxidation levels, which suggests that in an individual complex the various levels might be accessible by one-electron transfer at an electrode.

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

Cyclic voltammetry (CV) and linear alternating current voltammetry (acV) of I and II in CH_2Cl_2/0.5 *M* n-Bu_4NClO_4 now establish that these complexes readily undergo oxidation at a stationary platinum electrode. For example [$Ru_2Cl_4(CO)(PPh_3)_4$] exhibits a well-defined wave at +0.56 V vs. Ag/AgI (Fig. 1), satisfying all the criteria of a one-electron fully-reversible diffusion-controlled step. No further oxidation is observed before the solvent limit (approximately +1.5 V) and the complex resists reduction until an irreversible multi-electron process at −1.65 V. Qualitatively identical behaviour is found for the other carbonyl and thiocarbonyl complexes and the results are summarised in Table 1.

Initial attempts to prepare [$Ru_2Cl_4Y(PR_3)_4$]$^+$ salts by chemical oxidation of I and II using I_2 or cerium(IV) led to product mixtures. However, [$Ru_2Cl_4(CO)(PPh_3)_4$]$^+$ has now been generated as a stable CH_2Cl_2 solution by controlled potential electrolysis (+1.0 V) on a platinum gauge electrode at −45°C, although the cation decomposes rapidly at room temperature. A market colour change from orange to brown accompanies the oxidation. Spectroscopic characterisation and attempts to isolate crystalline salts following electrosynthesis at low temperatures are now in progress.

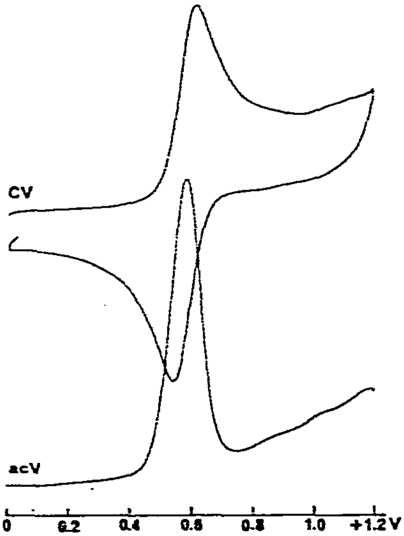


Fig. 1. Oxidation of [$Ru_2Cl_4(CO)(PPh_3)_4$] (CV = cyclic voltammogram, acV = linear alternating current voltammogram, vs. Ag/AgI in 0.5 *M* n-Bu_4NC1O_4/CH_2Cl_2).

TABLE 1

CYCLIC VOLTAMMETRY AND LINEAR ALTERNATING CURRENT VOLTAMMETRY FOR CARBONYL AND THIOCARBONYL DI-RUTHENIUM(II) COMPLEXES

Complex	Electrode potential $E_{1/2}$ (20°C)[a]			Solvent, Reference
$[Ru_2Cl_4(CS)(PPh_3)_4]$	+0.55 r	−1.5 i	(redn)	CH_2Cl_2, Ag/AgI
$[Ru_2Cl_4(CS)(Ptol_3)_4]$	+0.45 r	−1.7 i	(redn)	CH_2Cl_2, Ag/AgI
$[Ru_2Cl_4(CO)(PPh_3)_4]$	+0.56 r	−1.65 i	(redn)	CH_2Cl_2, Ag/AgI
$[Ru_2Cl_4(CO)(Ptol_3)_4]$	+0.46 r	−1.75 i	(redn)	CH_2Cl_2, Ag/AgI
$[Ru_2Cl_3(PMe_2Ph)_6]BPh_4$ [b]	+0.81 i	+1.16 r		CH_2Cl_2, Ag/AgI
$[Ru_2Cl_3(P(OMe)Ph_2)_6]BPh_4$	+0.86 i	+1.26 r		CH_2Cl_2, Ag/AgI
$[Ru_2Cl_3(C_6H_6)_2]PF_6$	+0.80 i	+1.17 i		CH_3CN, Ag/AgCl
$[Ru_2(OH)_3(C_6H_6)_2]BPh_4$	+1.05 i	+1.3 i	+1.47 i	CH_3CN, Ag/AgCl
$[Ru_2(OH)_3(C_6H_3Me_3)_2]BPh_4$	+1.02 i	+1.4 i	+1.54 i	CH_3CN, Ag/AgCl

[a] r = reversible wave, $E_{1/2}(CV) = E_p(acV)$, $\Delta E_{pp}(CV) \sim 60$ mV; i = irreversible wave, $E_{1/2}(CV)$ measured at 85% I_p (anodic scan). [b] SCN^- salt gives identical results.

In contrast to I and II, $[Ru_2Cl_3(PR_3)_6]BPh_4$ complexes ($PR_3 = P(OMe)Ph_2$ or PMe_2Ph [9,10]) in CH_2Cl_2 each undergo an irreversible oxidation (with no CV return wave); an additional reversible one-electron wave of similar CV height is observed at more positive potentials. Evidently the initially formed di-cation is unstable and reacts very rapidly to form an as yet unidentified oxidizable species. No reduction is observed to at least −2.0 V.

The diarene systems III and IV have been examined by CV in acetonitrile/ 0.3 *M* n-Bu_4NClO_4. In common with the previous cationic complexes they undergo a well-defined but irreversible oxidation at fairly positive potentials. Further irreversible waves are observed which again are due to unknown species arising by rapid reaction of the first-formed oxidation product.

The predicted capacity for oxidation is best demonstrated by the uncomplicated behaviour of the neutral complexes I and II, although only the first step can be observed. Interestingly the second redox couple (but not the first) has been identified previously in the case of harder supporting ligands since the mixed-valence species $[Ru_2Cl_3(H_2O)_6]^{2+}$ and $[Ru_2Cl_3(NH_3)_6]^{2+}$ undergo reversible one-electron oxidation, although their reduction is ill-defined and almost inaccessible [11,12]. Taken together, these observations establish that electrode-reversible one-electron transfers do connect the three oxidation levels of the bridged di-ruthenium system, as in eq. 1.

In I and II replacement of CO by CS has a negligible effect on the oxidation potential, although replacement of $Ptol_3$ by the less electron-donating PPh_3 causes a consistent increase of 0.1 V. These results, and the absence of a ready second step suggest localised oxidation of the harder $Cl(PR_3)_2Ru$ centre takes place to generate a true mixed-valence $Ru^{2+,3+}$ complex rather than an extensively delocalised $Ru^{2.5+}$ radical. However, X-ray studies on the analogous but symmetrically ligated $[Ru_2Cl_5(PBu_3)_4]$ gave no evidence of differing ruthenium valencies [13], and further evidence is required to specify the degree of metal—metal interaction in the various systems*.

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*Similar considerations apply to formally mixed oxidation state complexes such as $[(NH_3)_5Ru(\mu\text{-pyrazine})Ru(NH_3)_5]^{5+}$ which have been extensively discussed as models for intramolecular electron-transfer theory [19].

A striking aspect of the present results is the loss of reversibility accompanying the shift to higher oxidation potentials in the case of the cationic complexes (e.g. compare $[Ru_2Cl_4(CO)(PPh_3)_4]$ and $[Ru_2Cl_3(PMe_2Ph)_6]^+$). This may be correlated with the tendency of the preferred oxidation level to match the number of chloride ligands in the complexes as generally isolated. Thus the mono-cations $[Ru_2Cl_3L_6]^+$ and $[Ru_2Cl_4L_5]^+$, where L represents any soft neutral ligand, probably represent stable limits; $[Ru_2Cl_3L_6]^{2+}$ species are only formed at more positive potentials and decompose rapidly, as evidenced by our electrochemical studies. Clearly, complexes of stoichiometry $[Ru_2Cl_5L_4]$ provide the best chance of realizing the complete redox sequence (eq. 1) within one molecule, and a variety of these are now to be examined.

In EAN terms such a sequence ranges from 36 valence electrons (18 per Ru) to 34, permitting the formation of a metal—metal bond. Systematic spectroscopic and structural changes are known to accompany similar redox series in double- and single-bridged iron and manganese compounds [14,15], and comparison of the variously bridged clusters is of considerable interest. In the $(RuCl_3Ru)^+$ complexes the Ru—Ru distance might indeed contract upon oxidation (from ca. 3.4 Å [16,17]), since $[Ru_2Cl_5(P\text{-}n\text{-}Bu_3)_4]$ has an internuclear separation of 3.12 Å [13], and in diamagnetic $[Ru_2(S_2CNMe_2)_5]^+$ the relatively unconstrained ruthenium(III)—ruthenium(III) bond length is 2.79 Å [18]. However $[Ru_2Cl_3(AsPh_3)_6]$ is paramagnetic (μ_{eff} (293 K) 1.95 per Ru). Hopefully the present investigation will provide more coherent data on this point.

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