

## Review

## Electrochemistry of metal-metal bonded diruthenium complexes

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## ABSTRACT

This review summarizes the known electrochemistry of metal-metal bonded diruthenium complexes containing an air-stable  $Ru_2^{4+}$ ,  $Ru_2^{5+}$  or  $Ru_2^{6+}$  core or an *in-situ* generated  $Ru_2^{2+}$ ,  $Ru_2^{3+}$ ,  $Ru_2^{7+}$  or  $Ru_2^{8+}$  core with O,O'-, N,O- or N,N'- donor bridging ligands. The majority of published studies have been carried out in nonaqueous media and involved compounds with a  $Ru_2^{5+}$  oxidation state and four anionic "ap" or "DPhF"-type bridging ligands where ap and DPhF are the 2-anilinopyridinate and N,N'-diphenylformamidinate anions, respectively. The potentials and mechanisms of electron transfer depend in part upon the properties of the electrochemical solvent and in part upon properties of the compound, the most important of which are the initial oxidation state of the air-stable dimetal unit, the number and type of axial ligands and the type of anionic bridging ligands. The vast majority of redox processes described to date for these compounds involve electron addition or abstraction at the diruthenium core, but redox reactions involving the bridging ligands or other electroactive groups on the molecule have also been observed. In most cases, the redox reactions were reversible on the cyclic voltammetry and spectroelectrochemical time-scale, thus enabling the *in-situ* generation of new compounds in both very low and high oxidation states with dimetal units ranging from  $Ru_2^{2+}$  to  $Ru_2^{8+}$ .

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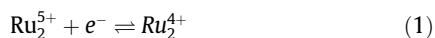
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## 1. Introduction

Ruthenium is an element with a rich chemistry [1–3] and applications of bimetallic compounds containing this element have been described in the areas of biochemistry [4–8], medicinal chemistry [9–14] and catalysis [9,15–24]. For instance, *in-vitro* studies have demonstrated the ability of diruthenium complexes to attack tumor cells [9–14], thus leading to an interest in these complexes as potential antitumor agents. Diruthenium compounds containing carboxylate and/or N,N'-bidentate ligands with a paddlewheel-type structure have also been found to be good catalysts for oxygen atom insertion, C–H insertion and C–H amination reactions [17,20–25] as well as molecular wires and memory devices [26–30]. Several reviews devoted to metal-metal bonded dinuclear complexes have discussed [2,4,9,31] the general electrochemical properties of diruthenium compounds, but a complete survey on the redox potentials and electrochemical reactivity of most known compounds as a function of the dimetal unit oxidation state and type of bridging or axial ligands has not appeared in the literature.

This is addressed in the current review which describes the known electrochemistry of metal-metal bonded diruthenium complexes starting with the first synthesis of these paddlewheel-type compounds by Stephenson and Wilkinson in 1966 [32]. These tetracarboxylate complexes are shown in Fig. 1 and formulated as Ru<sub>2</sub>(RCO<sub>2</sub>)<sub>4</sub>Cl where R is an alkyl group and the oxidation state of the metal core is Ru<sub>2</sub><sup>5+</sup>. Cotton and coworkers [33] later confirmed the proposed paddlewheel geometry via single crystal X-ray analysis of an analogous diruthenium complex which showed a short Ru–Ru bond distance of 2.281 Å, a value consistent with a multiple metal-metal bond. Moreover, a detailed theoretical analysis of a model Ru<sub>2</sub><sup>5+</sup> tetracarboxylate complex by Norman and coworkers [34] in 1979 assigned the electronic configuration of Ru<sub>2</sub><sup>5+</sup> as σ<sup>2</sup>π<sup>4</sup>–δ<sup>2</sup>π<sup>2</sup>δ\* (S = 3/2) where the π\* and δ\* orbitals were nearly degenerate, leading to the stability of the quartet ground state.

Early electrochemical studies of Ru<sub>2</sub>(RCO<sub>2</sub>)<sub>4</sub>Cl were limited to aqueous media due to poor solubility of the tetracarboxylate compounds in organic solvents and under these solution conditions only a single reduction assigned to the reversible Ru<sub>2</sub><sup>5+/4+</sup> electrochemical process (see Eq. (1)) was observed within the solvent potential window [9,31,32,35].



Following the initial electrochemical study of Ru<sub>2</sub>(CH<sub>3</sub>CO<sub>2</sub>)<sub>4</sub>Cl by Mukaida et al. in aqueous 0.5 M acetate buffer [35], the bridging acetate ligands were replaced by longer alkyl chain carboxylates, thus increasing the solubility in organic solvents and therefore

enabling electrochemical studies to be carried out in a nonaqueous solvent such as CH<sub>2</sub>Cl<sub>2</sub> [36]. A conversion of the Ru<sub>2</sub><sup>5+</sup> core to its Ru<sub>2</sub><sup>4+</sup> form was again observed but several redox active forms of the tetracarboxylate complexes could be generated within the solvent potential window [35,36]. Substituting the negatively charged chloride axial ligand on Ru<sub>2</sub>(RCO<sub>2</sub>)<sub>4</sub>Cl with small diatomic molecules such as CO or NO led to a stabilization of the lower oxidation states of the diruthenium unit, thus allowing access to additional oxidation states of the compounds when using cyclic voltammetry to investigate their electrochemistry [37].

Higher oxidation states of the diruthenium unit were electrochemically accessed by replacing the tetracarboxylate O,O'-bridging ligands with mono-anionic O,N- or N,N'-bridging ligands. The first of these compounds to be synthesized and electrochemically characterized were the tetraacetamidates and tetraoxopyridinate derivatives [38–42]. Electrochemistry of the diruthenium compounds containing four anionic acetamidate or oxopyridinate bridging ligands showed the presence of a reversible Ru<sub>2</sub><sup>5+/6+</sup> process (Eq. (2)) in addition to the earlier observed Ru<sub>2</sub><sup>5+/4+</sup> electrode reaction.



The acetamidate and oxopyridinate diruthenium complexes also showed other redox processes in addition to Ru<sub>2</sub><sup>5+/4+</sup> and Ru<sub>2</sub><sup>5+/6+</sup> when characterized by cyclic voltammetry [38,40,43] but an assignment of the electron transfer sites was not given in the initial publications and it was therefore not clear whether other oxidation states of the dimetal unit might also be accessible. An answer to this question, however, was clearly provided when the O,N-bridging ligands were replaced by N,N'-bridging ligands such as in the case of anilinopyridinate or diphenylformamidinate, giving a series of compounds which were investigated in both

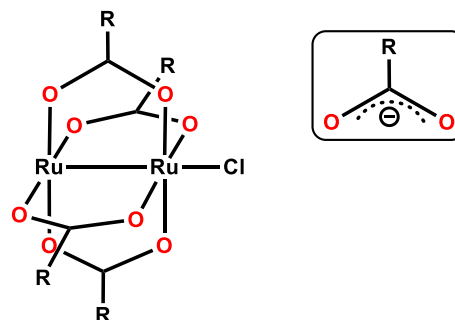
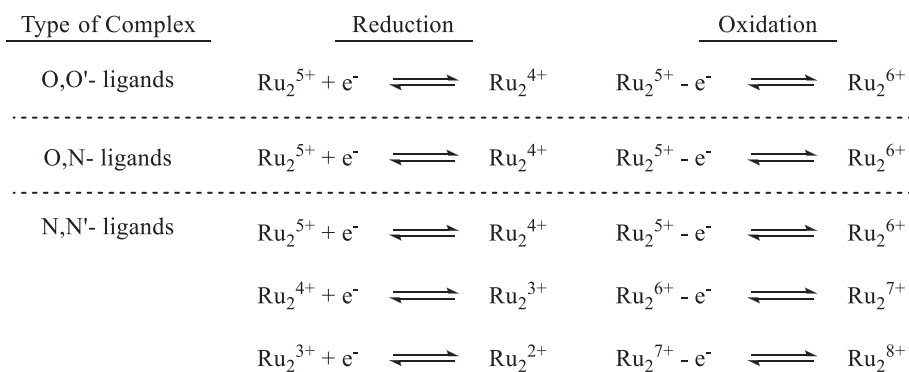


Fig. 1. Paddlewheel structure of metal-metal bonded diruthenium complexes containing a Ru<sub>2</sub><sup>5+</sup> core and four O,O'-bridging ligands where R is an alkyl group.



**Scheme 1.** Overview of the various diruthenium oxidation states reported for complexes containing O,O'-, O,N- and N,N'-bridging ligands.

the non-coordinating solvent  $\text{CH}_2\text{Cl}_2$  and the coordinating solvent PhCN [44]. The anilinoypyridinate or and diphenylformamidinate complexes exhibited two reversible oxidations in  $\text{CH}_2\text{Cl}_2$ , the second of which was assigned to  $\text{Ru}_2^{6+/7+}$  (see Eq. (3)). In PhCN, a reduction of the same complexes proceeded in two one-electron transfer steps, the second of which was clearly assigned as involving a  $\text{Ru}_2^{4+/3+}$  process (see Eq. (4)).



Diruthenium complexes containing a  $\text{Ru}_2^{5+}$  core and four identical N,N'-bridging ligands could also be converted to their  $\text{Ru}_2^{2+}$  forms under a CO atmosphere, the lower oxidation state being stabilized on the cyclic voltammetry timescale by axial coordination of two CO molecules [45–48]. The air-stable  $\text{Ru}_2^{6+}$  complexes were shown to undergo two one-electron oxidations, the second of which was attributed to a  $\text{Ru}_2^{7+/8+}$  redox process [49,50]. After publication of this study it became clear that up to four different diruthenium core oxidation states ( $\text{Ru}_2^{2+}$ ,  $\text{Ru}_2^{3+}$ ,  $\text{Ru}_2^{7+}$  or  $\text{Ru}_2^{8+}$ ) could be electrogenerated the exact number depending in large part upon the type of axial and bridging ligands.

In summary, the six possible electron transfer reactions which might be electrochemically detected for a given paddlewheel complex are summarized in Scheme 1. Not all processes are seen for a given compound and the electrogeneration of a specific high or low oxidation state derivative will depend upon several factors, the most important of which were the solution conditions, the initial oxidation state of the air-stable complex and the specific axial and bridging ligands coordinated to the dimetal core.

## 2. Voltammetric measurement techniques

This review summarizes the electrochemical data reported in the literature for metal-metal bonded diruthenium compounds by authors using a variety of solution conditions, electrochemical measurement techniques (cyclic voltammetry, polarography, differential pulse polarography) and reference electrodes (*i.e.* potentials are sometimes reported as V vs a saturated calomel electrode (SCE) vs Ag/AgCl or vs Fc/Fc<sup>+</sup>). No attempts were made in this review to convert data in the literature to a standard reference system, but to aid the reader a brief summary is given on the following pages on how solution conditions (solvent supporting electrolyte) and choice of reference electrode will effect a given reported value of reduction or oxidation potentials.

### 2.1. Selection of solvent and supporting electrolyte

Electrochemical studies of diruthenium complexes have been performed in a wide variety of nonaqueous solvents and some aqueous conditions as well. A number of early studies employed aprotic media such as dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), dimethylsulfoxide (DMSO), or acetonitrile ( $\text{CH}_3\text{CN}$ ) and in some cases weakly acidic aqueous media (pH = 5.0) [35–38,40,43,51]. Electrochemical data is now available in a number of nonaqueous solvents with the majority of recent data reported in the non-binding solvents, dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) and/or tetrahydrofuran (THF). An advantage of THF or  $\text{CH}_2\text{Cl}_2$  is the increased cathodic and anodic potential range which is close to 1.9 and  $-1.9$  V vs SCE for  $\text{CH}_2\text{Cl}_2$  and 1.7 to  $-2.4$  V vs SCE for THF [52–54]. This wide potential window enables the possible examination of multiple oxidations and reductions of a given compound under the same solution condition; however, it should be noted that THF is a fairly high resistance solvent as compared to dichloromethane, thus making  $\text{CH}_2\text{Cl}_2$  the preferable electrochemical solvent.

The majority of the above-mentioned electrochemical studies involving diruthenium paddlewheel complexes in nonaqueous media have utilized organic tetraalkylammonium salts as a supporting electrolyte while aqueous electrochemical investigations employ alkali metal salts or organic buffers. The most commonly employed nonaqueous supporting electrolyte are tetrabutylammonium perchlorate or tetrabutylammonium hexafluorophosphate salts (abbreviated as TBAP and TBAPF<sub>6</sub>), but other studies have also utilized tetrabutylammonium salts with BF<sub>4</sub><sup>-</sup> (TBABF<sub>4</sub>) or Cl<sup>-</sup> (TBACl). The consideration of supporting electrolyte concentration, and diruthenium anolyte concentration for that matter, is important in terms of interpreting specific values of reported half-wave potentials. Typically, electrochemical evaluations reported herein utilize solutions of 1 mM diruthenium anolyte and 0.1 M TBAX (X = ClO<sub>4</sub><sup>-</sup> (or P<sup>-</sup>), PF<sub>6</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup> or Cl<sup>-</sup>) whereas higher concentrations of 0.2 M TBAX have been often employed in high resistance solvents such as THF [52,54]. It should be noted that exact potentials and shape of the current-voltage curve measured in nonaqueous solutions containing 0.1 M TBAP, for example, are not identical to those measured with concentrations of 0.01 or 1.0 M in the same solvent due to several factors such as the formation of ion-pairs stabilizing the electrogenerated product or an equilibrium between some  $\text{Ru}_2$  complexes with specific anions [36,38,39,55,56].

### 2.2. Reporting measured redox potentials

As mentioned above, the majority of diruthenium redox reactions occur at the dimetal core and involve reversible electron transfers whose potentials are reported as  $E_{1/2}$  versus a standard

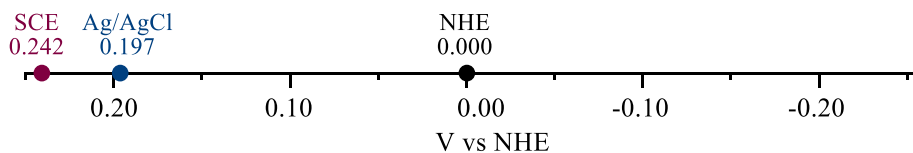


Fig. 2. Relationship between potentials on the Ag/AgCl and SCE scales in comparison to the Normal Hydrogen Electrode (NHE).

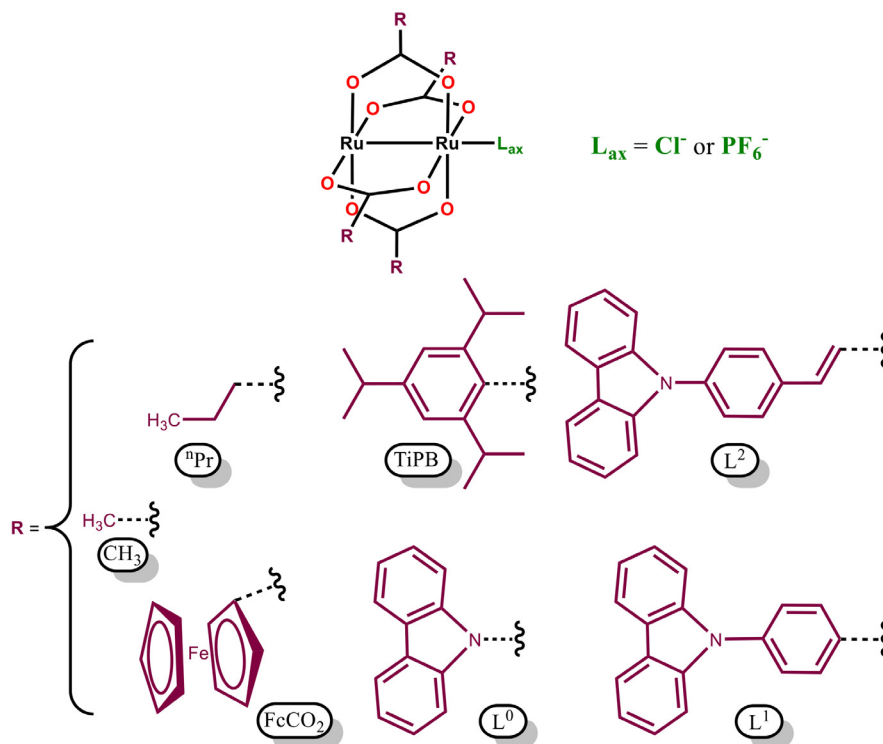


Fig. 3. Schematic representation of  $\text{Ru}_3^+$  complexes with O,O'-bridging ligands and a mono-anionic axial ligand.

reference electrode, of which the most commonly used has been a saturated calomel electrode (SCE) or an Ag/AgCl reference electrode. Some reversible potentials have been reported vs other less commonly used reference electrodes such as nonaqueous Ag/AgCl/ $\text{Cl}^-$ ,  $\text{CH}_2\text{Cl}_2$  (0.60 V vs  $\text{Fc}/\text{Fc}^+$ ) [39,57] while other  $E_{1/2}$  values are reported versus the ferrocene/ferrocenium couple ( $\text{Fc}/\text{Fc}^+$ ) in the same nonaqueous solvent.

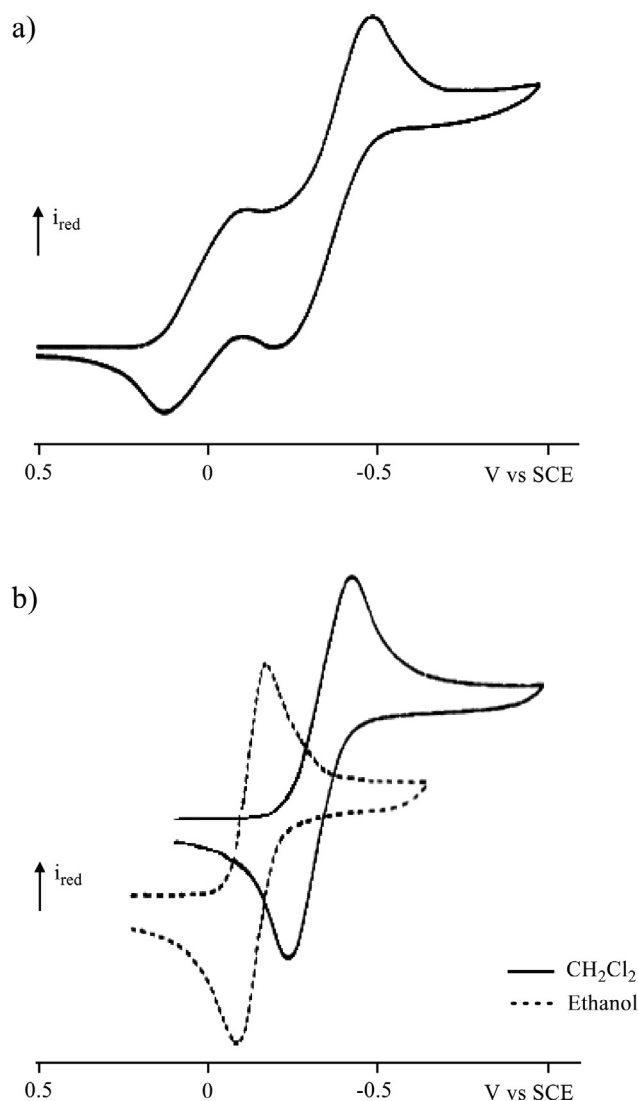
In addition to the above, the reported  $E_{1/2}$  values should include the voltammetric experimental conditions (such as scan rate, concentration of specific supporting electrolyte, etc.) and/or an illustration of the actual experimental data so as to avoid misinterpretations of the electrode reactions (i.e. reversible, irreversible or quasi-reversible). This is because an observed irreversible redox reaction might stem from a multitude of well-known factors [58–60] such as slow electron transfer kinetics or the occurrence of coupled chemical reactions, in which case the experimentally observed values could be significantly different from the thermodynamic important potentials.

In this review, all redox values are reported as given in the literature and the reference electrode for each is specified, no attempts were made to convert potentials measured against one reference electrode to another standard reference system. However, a depiction of the relationship between the standard reference electrodes is given in Fig. 2 and can be used to convert potentials at the readers discretion. It should be noted that potentials used for thermodynamic correlations must be reported versus

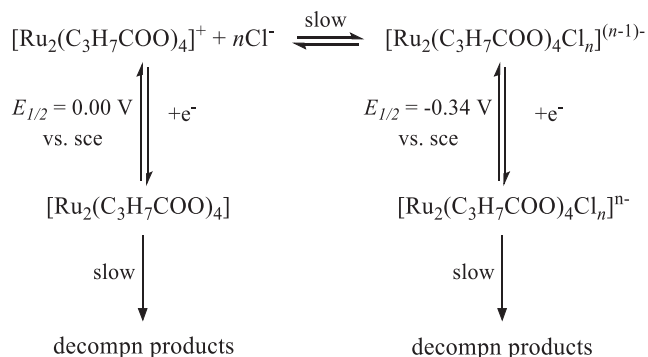
the  $\text{Fc}/\text{Fc}^+$  couple in order to minimize errors due to differences in liquid junction potential between different solvents and/or experimental conditions. The approximate value of the  $\text{Fc}/\text{Fc}^+$  couple generally ranges from 0.40 to 0.55 V vs SCE depending on the utilized electrochemical solvent and the experimental setup, but these quoted values must only be taken as a very rough approximation without making the exact experimental measurement [61,62].

### 2.3. Quantifying factors effecting potentials

Generally, the addition of electron-donating substituents to the bridging ligands of diruthenium paddlewheel complexes facilitate oxidation while making the reduction more difficult. In contrast, the addition of electron-withdrawing groups removes electron density from the dimetal core leading to easier reductions and harder oxidations. The magnitude of the shift in potentials for oxidation or reduction has often been related to the Hammett substituent constants [63] ( $\Sigma\sigma$ ) for electron-donating or electron-withdrawing groups on the bridging ligand and can provide valuable information regarding the electron transfer mechanism and the degree of interaction between the bridging ligand substituents and the dimetal core. This electronic effect of the bridging ligand substituents on the  $E_{1/2}$  values can be quantified through Hammett linear free energy relationships [64] as shown in Eq. (5), where  $E_{1/2}(\text{X})$  is the potential for each substituted bridging ligand deriva-



**Fig. 4.** Cyclic voltammograms showing reduction of an O,O'-type  $\text{Ru}_2^{5+}$  complex with formula  $\text{Ru}_2(\text{Pr}^n\text{CO}_2)_4\text{Cl}$  in a)  $\text{CH}_2\text{Cl}_2$ , 0.1 M TBAP and b)  $\text{CH}_2\text{Cl}_2$ , 0.1 M TEACl (—) and ethanol, 0.1 M TEACl (---) (adapted from reference [36]). See Scheme 2 for prevailing equilibrium observed in part a of the figure.



**Scheme 2.** Electron transfer processes of  $\text{Ru}_2(\text{Pr}^n\text{CO}_2)_4\text{Cl}$  in nonaqueous media (from reference [36]).

tive,  $E_{1/2}(\text{H})$  is the potential for the non-substituted bridging ligand and  $\rho$  is the reaction constant measuring the degree of interaction between the substituent and the site of electron transfer.

$$\Delta E_{1/2} = E_{1/2}(\text{X}) - E_{1/2}(\text{H}) = \Sigma \sigma \rho \quad (5)$$

The experimentally obtained value of  $\rho$  in Eq. (5) will depend on several factors, the most important of which include the site of electron transfer, the solvent, the supporting electrolyte and the temperature.

### 3. $\text{Ru}_2^{5+}$ complexes

#### 3.1. O,O'- bridging ligands

$\text{Ru}_2^{5+}$  complexes with carboxylate O,O' - bridging ligands are described by the formula  $\text{Ru}_2(\text{RCO}_2)_4\text{Cl}$  where R is an alkyl or aryl group (see Fig. 3). These compounds all exhibit a  $\text{Ru}_2^{5+/4+}$  process within the potential range of the solvent and examples of  $E_{1/2}$  values for this reaction are summarized in Table 1.

The potential of the one-electron reduction varies with the specific  $\text{Ru}_2^{5+}$  complex but a quantitative correlation of half-wave potential in the different studies is not so straightforward because different solvents and different reference electrodes were used in the different laboratories. For  $\text{Ru}_2(\text{CH}_3\text{CO}_2)_4\text{Cl}$  and  $\text{Ru}_2(\text{Pr}^n\text{CO}_2)_4\text{Cl}$ , the  $E_{1/2}$  of the  $\text{Ru}_2^{5+/4+}$  process ranges from +0.06 to -0.34 V (vs SCE) depending upon the solution conditions and the association or dissociation of the chloride axial ligands [35,36]. Cyclic voltammograms of  $\text{Ru}_2(\text{Pr}^n\text{CO}_2)_4\text{Cl}$  under different solution conditions are shown in Fig. 4 from a study by Cotton and Pedersen [36] and the proposed electron transfer processes given by the authors are shown in Scheme 2. The current-voltage curve obtained for reduction of  $\text{Ru}_2(\text{Pr}^n\text{CO}_2)_4\text{Cl}$  in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M TBAP is shown in Fig. 4a and was interpreted in terms of an equilibrium between the more easily reducible  $[\text{Ru}_2(\text{Pr}^n\text{CO}_2)_4]^+$  and  $[\text{Ru}_2(\text{Pr}^n\text{CO}_2)_4\text{Cl}_n]^{(n-1)-}$ , giving rise to a 'split reduction' wave where the latter form of the compound containing one or more axial chloride ligands is reduced at a more negative potential. Conversely, the two voltammograms in Fig. 4b were obtained under solution conditions where only one electroactive form of the compound was present.

Four compounds, formulated as  $\text{Ru}_2(\text{CH}_3\text{CO}_2)_2(\text{TiPB})_2\text{Cl}$ ,  $\text{Ru}_2(\text{CH}_3\text{CO}_2)_2(\text{TiPB})_2(\text{PF}_6)$ ,  $\text{Ru}_2(\text{TiPB})_4\text{Cl}$  and  $\text{Ru}_2(\text{TiPB})_4(\text{PF}_6)$  (see Fig. 3), were examined by Gracia *et al.* as to their electrochemical properties in  $\text{CH}_3\text{OH}$  containing 0.1 M  $\text{TBAPPF}_6$  (tetrabutylammonium hexafluorophosphate) [65]. For all these compounds, the  $\text{Ru}_2^{5+/4+}$  process was located close to 0.0 V (vs  $\text{Ag}/\text{Ag}^+$ ).  $[\text{Ru}_2(\text{FcCO}_2)_4]^+(\text{PF}_6)$  (see ligand structure in Fig. 3) was also examined as to its electrochemical properties in  $\text{CH}_2\text{Cl}_2$  containing  $[\text{TBA}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  as supporting electrolyte [66]. At a concentration of 0.5 mM, the examined compound was shown to undergo four well-defined ferrocenyl-based oxidations along with the expected reduction at the  $\text{Ru}_2^{5+}$  core. However, at a concentration of 1.0 mM, or in the presence of  $\text{TBAPPF}_6$ , the four ferrocenyl redox processes coalesced into two waves as a result of  $(\text{Fc})^+(\text{PF}_6)^-$  ion pairing. The  $\text{Ru}_2^{5+/4+}$  process of the dimetal unit was located at -0.49 V (vs  $\text{Fc}/\text{Fc}^+$ ) and this reaction was followed by a coating of the  $\text{Ru}_2^{4+}$  form of the compound on the electrode surface.

Three compounds formulated as  $\text{Ru}_2(\text{L}^0)_4\text{Cl}$ ,  $\text{Ru}_2(\text{L}^1)_4\text{Cl}$  and  $\text{Ru}_2(\text{L}^2)_4\text{Cl}$  (see structures in Fig. 3) were electrochemically investigated in DMF containing 0.1 M TBAP [67]. Each complex was shown to undergo a quasi-reversible one-electron oxidation assigned by the authors as  $\text{Ru}_2^{5+/6+}$ . The potential for this electrode reaction was shown to shift cathodically upon changing the bridging ligand from  $\text{L}^0$  to  $\text{L}^2$  (see Fig. 3) owing to a more extensive conjugation through the ligand and subsequent higher electron density on the  $\text{Ru}_2^{5+}$  core. It is worth noting that this was the only reported electrogenerated  $\text{Ru}_2^{5+}$  complex containing O,O' - bridging ligands until a 2019 report by Handa and coworkers which re-examined the electrochemistry of  $\text{Ru}_2(\text{Pr}^n\text{CO}_2)_4\text{Cl}$  in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M  $\text{TBABF}_4$  along with two new derivatives,



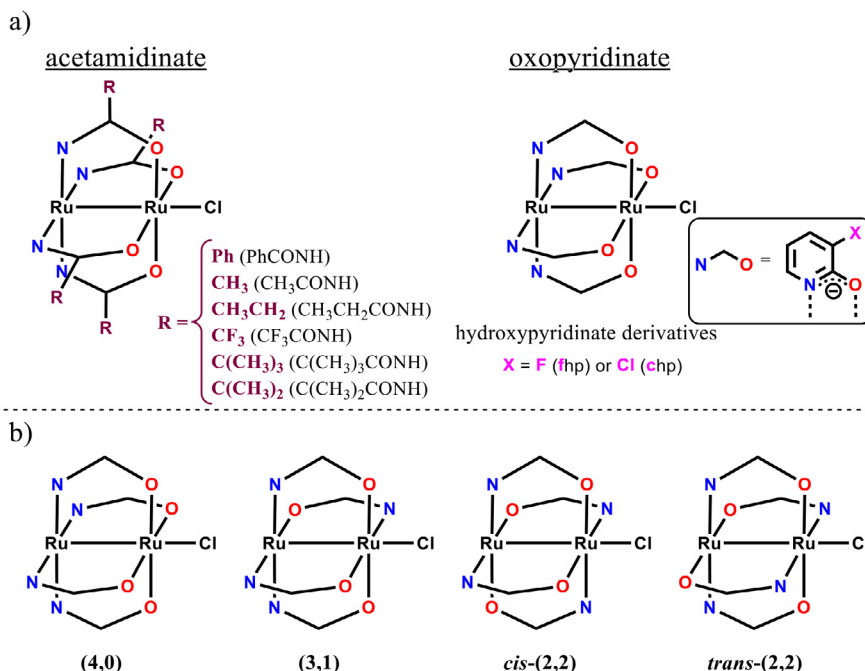


Fig. 5. Schematic representation of a)  $\text{Ru}_2^{5+}$  complexes with N,O-bridging ligands and b) possible structural isomers for these types of complexes.

$[\text{Ru}_2(\text{Pr}^i\text{CO}_2)_4\text{Cl}_2]\text{NBu}_4$  and  $[\text{Ru}_2(\text{Pr}^i\text{CO}_2)_4(\text{H}_2\text{O})_2]\text{BF}_4$  [68]. Under these solution conditions, each  $\text{Ru}_2^{5+}$  tetracarboxylate complex displayed identical 'split'  $\text{Ru}_2^{5+/4+}$  processes stemming from the aforementioned equilibrium as described by Cotton [36] as well as a  $\text{Ru}_2^{5+/6+}$  process located between 1.35 and 1.37 V vs SCE.

### 3.2. N,O-bridging ligands

Table 2 lists published  $E_{1/2}$  values for the one-electron  $\text{Ru}_2^{5+/6+}$  oxidation and one-electron  $\text{Ru}_2^{5+/4+}$  reduction of  $\text{Ru}_2^{5+}$  derivatives with anionic N,O-bridging ligands. Both processes can be observed for  $\text{Ru}_2^{5+}$  derivatives with acetamidinate or oxopyridinate N,O-bridging ligands (see Fig. 5), although in some studies only one of the two redox processes are discussed. The reported potentials for  $\text{Ru}_2^{5+/4+}$  varied between +0.34 V (vs Ag/Ag<sup>+</sup>) and -0.96 V (vs SCE) while  $E_{1/2}$  values for  $\text{Ru}_2^{5+/6+}$  were shown to range from +0.47 V (vs SCE) to +1.68 V (vs Ag/Ag<sup>+</sup>). As seen in Table 2, the potential gaps between the  $\text{Ru}_2^{5+/4+}$  and  $\text{Ru}_2^{5+/6+}$  processes varied between 1.23 and 1.69 V.

$\text{Ru}_2(\text{CF}_3\text{CONH})_4\text{Cl}$  [38] was shown to exhibit one, two or three redox processes, all assigned as  $\text{Ru}_2^{5+/4+}$  while  $\text{Ru}_2((\text{CH}_3)_3\text{CCONH})_4\text{Cl}$  [39] exhibited one, two or three  $\text{Ru}_2^{5+/6+}$  reactions depending upon the electrochemical solvent; this was explained by the presence of several forms of each compound in solution due to equilibria involving an associated or dissociated chloride axial ligand. Fig. 6 shows cyclic voltammograms of the tetraamidate diruthenium complex,  $\text{Ru}_2(\text{CF}_3\text{CONH})_4\text{Cl}$  (Fig. 5a), under different solution conditions, while Scheme 3 summarizes the proposed electron transfer processes of this compound under these solution conditions.  $\text{Ru}_2(\text{CH}_3\text{CONH})_4\text{Cl}$  [40] (Fig. 5a) was characterized as having one oxidation and two reductions. The first oxidation at 0.47 V and first reduction at -0.96 V (vs SCE) were assigned as  $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{5+/4+}$ , respectively, while the second reduction at -1.22 V was suggested to be a ligand-centered reaction [40]. A  $\text{Ru}_2^{5+}$  benzamidato complex was also characterized by two reductions at -0.66 and -1.09 V (vs SCE) in DMSO. The first electron addition was assigned as  $\text{Ru}_2^{5+/4+}$  while the second was said to be ligand-

centered [43]. It should be noted that of the earlier-reported tetraamidate  $\text{Ru}_2^{5+}$  complexes, only  $\text{Ru}_2(\text{PhCONH})_4\text{Cl}$  was structurally characterized [69] and found to exist as a *cis*-2,2 isomer (Fig. 5b) while others were proposed but not structurally proven to take on the *trans*-2,2 configuration. A more recent report by Handa and coworkers [70] reported the *cis*-2,2 regioisomer for  $[\text{Ru}_2(\text{PhCONH})_4(\text{BF}_4)(\text{H}_2\text{O})]$  which displayed similar redox behavior as  $\text{Ru}_2(\text{PhCONH})_4\text{Cl}$ .

*Cis*-2,2 isomers of  $\text{Ru}_2((\text{CH}_3)_2\text{CHCONH})_4\text{Cl}$  and  $\text{Ru}_2(\text{CH}_3\text{CH}_2\text{CONH})_4\text{Cl}$  were also examined as to their electrochemistry. Both derivatives undergo  $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{5+/4+}$  processes, but potentials for these reactions are more negative in the case of the former compound, thus indicating a difference of electron donor properties between the two sets of bridging ligands [22].

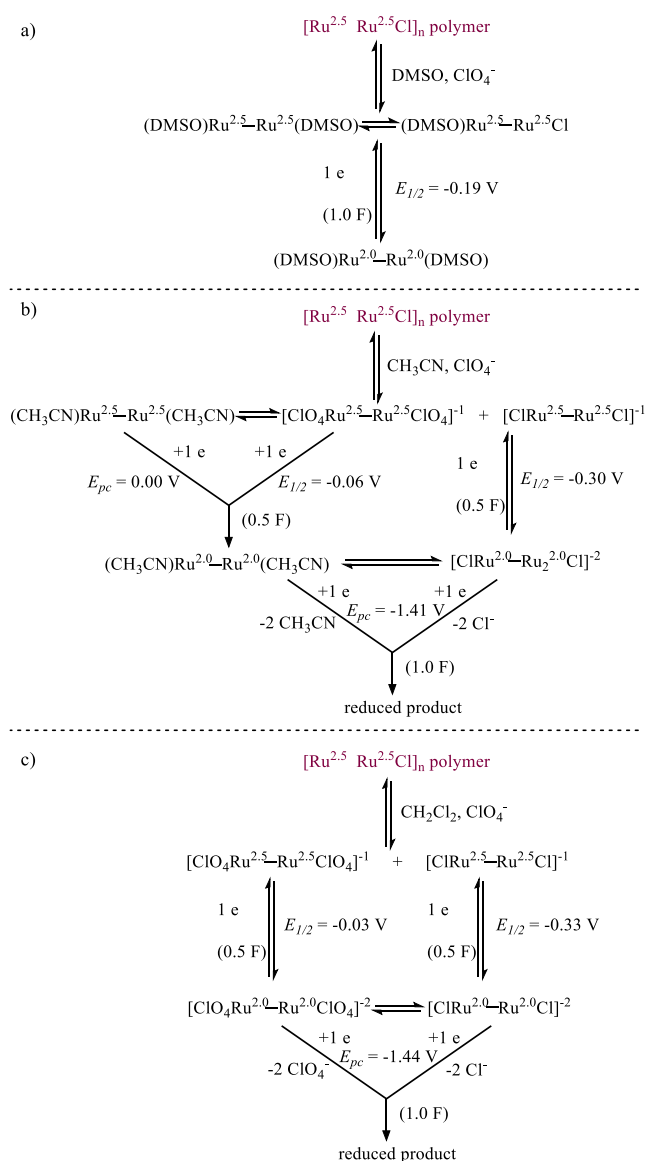
Two complexes with oxopyridinate bridging ligands,  $\text{Ru}_2(\text{fhp})_4\text{Cl}$  [41] and  $\text{Ru}_2(\text{chp})_4\text{Cl}$  [42] (see Fig. 5a), were examined as to their electrochemistry.  $\text{Ru}_2(\text{fhp})_4\text{Cl}$  exhibits only  $\text{Ru}_2^{5+/4+}$  and  $\text{Ru}_2^{5+/6+}$  processes, whereas one oxidation ( $\text{Ru}_2^{5+/6+}$ ) and several reductions are seen for  $\text{Ru}_2(\text{chp})_4\text{Cl}$ . The first two reductions were both assigned to  $\text{Ru}_2^{5+/4+}$ ; an assignment was not given for the third reduction.

### 3.3. N,N'-bridging ligands

The majority of electrochemically characterized  $\text{Ru}_2^{5+}$  complexes with N,N' bridging ligands are the anilinyridinate (ap) or formamidinate (DPHF) derivatives or their analogs, but a few diruthenium compounds with other N,N'-bridging ligands have also been reported as described below.

#### 3.4. Anilinyridinate (ap) bridging ligand

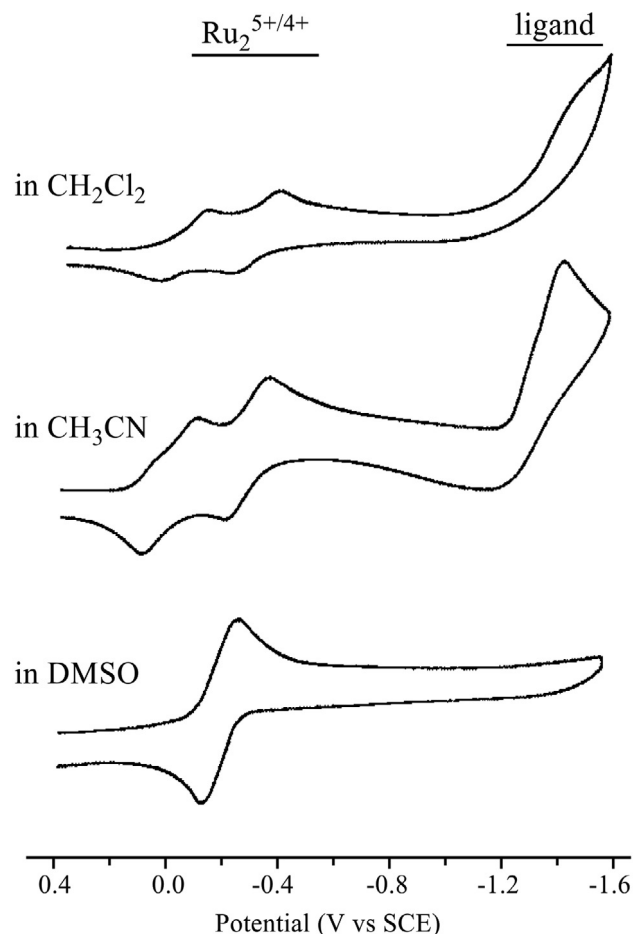
Most  $\text{Ru}_2^{5+}$  complexes containing ap or substituted-ap bridging ligands undergo reversible  $\text{Ru}_2^{5+/4+}$  reductions and  $\text{Ru}_2^{5+/6+}$  reversible oxidations. However, the electrogeneration of compounds with core oxidation states of  $\text{Ru}_2^{7+}$ ,  $\text{Ru}_2^{3+}$  and  $\text{Ru}_2^{2+}$  have also been demonstrated under some experimental conditions [44,47,48,71-73].



**Scheme 3.** Proposed electron transfer processes of  $\text{Ru}_2(\text{CF}_3\text{CONH})_4\text{Cl}$  represented as  $[\text{Ru}^{2.5}\text{-Ru}^{2.5}\text{Cl}]_n$  polymer in a) DMSO, b)  $\text{CH}_3\text{CN}$  and c)  $\text{CH}_2\text{Cl}_2$  all containing 0.1 M TBAP (from reference [38]).

Additional redox reactions were also sometimes seen for diruthenium and these processes were said to be a reduction or oxidation at the redox active bridging ligand [49,74,75].

The  $\text{Ru}_2^{5+/4+}$  and  $\text{Ru}_2^{5+/6+}$  processes of ap or “ap-type” diruthenium complexes with bound  $\text{Cl}^-$ , CN, NO or NCS axial ligands are all known but the majority of electrochemical data in the literature has involved compounds with a single chloride axial group (see Fig. 7a and Fig. 7b for schematic representation of the investigated compounds). The published half-wave potentials are summarized in Table 3 and vary between +0.28 and +1.14 V (vs SCE) for  $\text{Ru}_2^{5+/6+}$  and between -0.03 and -0.89 V (vs SCE) for  $\text{Ru}_2^{5+/4+}$ . The potential separations between  $E_{1/2}$  values for the  $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{5+/4+}$  processes generally varied from 1.08 to 1.36 V when the measurements were made in non-coordinating solvents but a smaller separation of 1.01 V and a larger separation of 1.55 V can also be seen from the data in Table 3. For these compounds, it should be noted that the 1.01 V separation between processes was obtained in  $\text{CH}_3\text{CN}$  which can bind to the  $\text{Ru}_2^{4+}$  form of the compound [48] while the larger 1.55 V value is most likely related to the fact that the compound undergoes a facile exchange of the



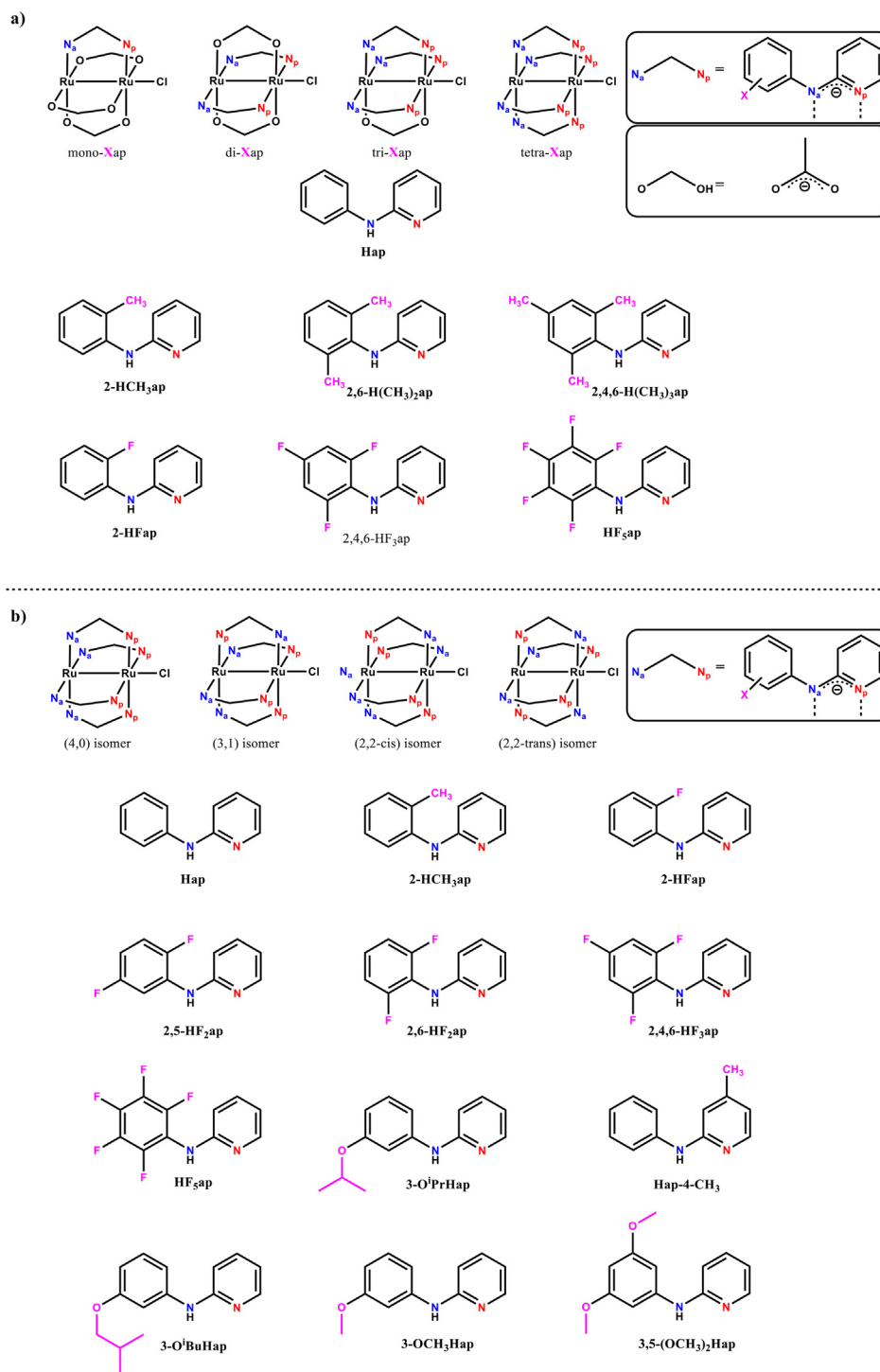
**Fig. 6.** Cyclic voltammograms of  $\text{Ru}_2(\text{CF}_3\text{CONH})_4\text{Cl}$  complexes with N,O bridging ligands in different nonaqueous solvents (all containing 0.1 M TBAP) (modified from reference [38]).

chloride axial ligand with the anion of the supporting electrolyte [55].

### 3.5. Electronic effect of regioisomer type and bridging ligands

The effect of regioisomer type and electronic effect of the bridging ligands on the redox behavior of  $\text{Ru}_2^{5+}$  complexes containing four identical “ap-type” bridging ligands and a chloride axial ligand was reported in several papers [44,71,73]. Diruthenium complexes with four identical unsymmetrical bridging ligands can theoretically exist in up to four different forms of geometric isomers which were labeled as (4,0), (3,1), (2,2)-*trans* and (2,2)-*cis* (see Fig. 7b). The (4,0), (3,1) and (2,2)-*trans* geometric isomers of  $\text{Ru}_2(\text{F}_5\text{ap})_4\text{Cl}$  ( $\text{F}_5\text{ap}$  = pentafluoroanilinopyridinate anion) were shown to exhibit reversible  $\text{Ru}_2^{5+/4+}$ ,  $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{6+/7+}$  processes all three of which are sensitive to the type of regioisomer (see Table 3 for the case of  $\text{Ru}_2^{5+/4+}$  and  $\text{Ru}_2^{5+/6+}$ ), but the largest shift in potential is seen for the  $\text{Ru}_2^{5+/6+}$  process as shown in Fig. 8. Processes 1 and 3 in Fig. 8 were said to involve a  $\pi^*$  orbital while process 2 was proposed to involve a  $\delta^*$  orbital [73,76].

A series of seven diruthenium compounds with the formulation  $\text{Ru}_2(\text{L})_4\text{Cl}$  ( $\text{L}$  = 2- $\text{CH}_3\text{ap}$ , 2,5- $\text{F}_2\text{ap}$ , 2,6- $\text{F}_2\text{ap}$  and 2,4,6- $\text{F}_3\text{ap}$ ) were examined as to their electrochemistry in  $\text{CH}_2\text{Cl}_2$  [71] and the data analyzed as a function of the isomer type, (4,0) or (3,1). Each compound was characterized by two reversible oxidations ( $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{6+/7+}$ ) and one reversible reduction ( $\text{Ru}_2^{5+/4+}$ ) in this solvent, after which the electronic effects of the bridging ligand substituents on



**Fig. 7.** Schematic representation of a)  $Ru_2(CH_3CO_2)_{4-n}(L)_nCl$  where  $n = 1, 2, 3$  or  $4$  and b)  $Ru_2(L)_4Cl$  where  $L$  is ap or a substituted ap bridging ligand.

the measured  $E_{1/2}$  values were quantified by the Hammet linear free energy relationship given in Eq. (5) (see Section 2.3).

The  $Ru_2^{5+/4+}$  and  $Ru_2^{6+/7+}$  processes were insensitive to the coordination type with both (4,0) and (3,1) isomers having nearly identical  $\rho$  values (slope of the  $E_{1/2}$  vs  $\Sigma\sigma$  plot) ranging from 111 to 100 mV for  $Ru_2^{5+/4+}$  and 43 to 41 mV for  $Ru_2^{6+/7+}$ . However, the (4,0) isomers exhibited a larger substituent effect than the (3,1) isomers for the  $Ru_2^{5+/6+}$  process, the  $\rho$  values in this case being 107 mV and 76 mV respectively. Changes in redox behavior among the seven compounds in the series appeared not to be related to changes in structural features of the diruthenium complexes nor

were there any differences in electronic configurations of the reduced or oxidized species. Fig. 9 shows cyclic voltammograms for selected diruthenium (3,1) isomers with “ap-type” bridging ligands in  $CH_2Cl_2$ . The electrode reactions corresponding to each redox process of the dimetal core is specified in the figure.

The combined electrochemical and UV-visible spectroelectrochemical data indicate a reversible conversion of  $Ru_2(ap-4-CH_3)_4Cl$ , where the methyl substituent is located at the *para* position of the pyridine ring as opposed to the aniline ring (see Fig. 7) to its  $Ru_2^{4+}$  form upon reduction and to its  $Ru_2^{6+}$  form upon oxidation [46]. The overall redox behavior of this compound



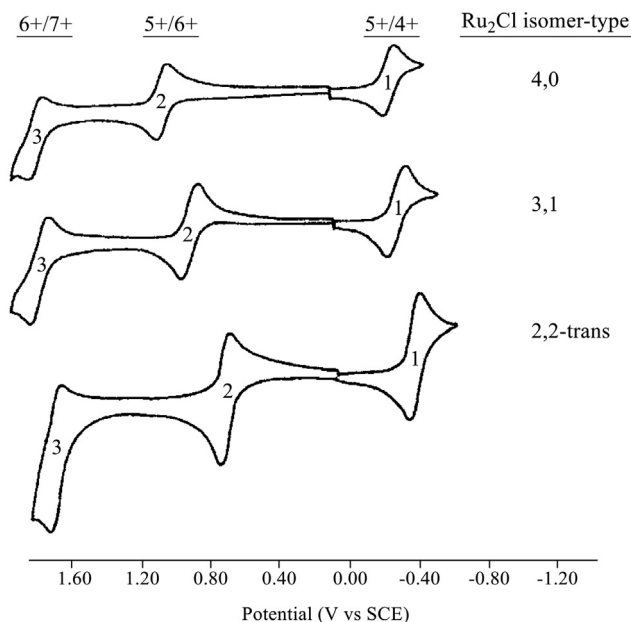


Fig. 8. Cyclic voltammograms of regioisomers of  $\text{Ru}_2^{3+}$  complexes with four "ap-type" bridging ligands (adapted from reference [73]).

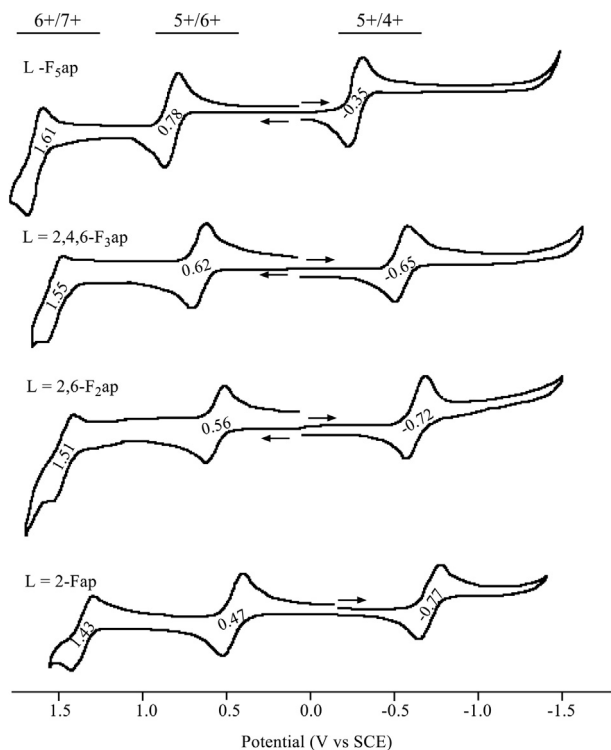


Fig. 9. Cyclic voltammograms of (3,1)  $\text{Ru}_2(\text{L})_4\text{Cl}$  where L is an "ap-type" bridging ligand. This figure also shows the electronic effect of equatorial ligands on the redox potentials (adapted from reference [71]).

resembled that of the analogous  $\text{Ru}_2(2\text{-CH}_3\text{ap})_4\text{Cl}$  species, but the half-wave potentials for oxidation and reduction were both shifted due to the methyl substituent on the bridging ligand with the largest shift in  $E_{1/2}$  being for oxidation. In addition, there was an increased lability of the axial  $\text{Cl}^-$  ligand in  $\text{Ru}_2(\text{ap-4-CH}_3)_4\text{Cl}$ , thus leading to a greater reactivity of the ap-4- $\text{CH}_3$  compound towards CO as compared to  $\text{Ru}_2(2\text{-CH}_3\text{ap})_4\text{Cl}$  and related compounds. The

substituents on the ap ligand were then modified, leading to  $\text{Ru}_2(\text{OCH}_3\text{ap})_4\text{Cl}$  [77],  $\text{Ru}_2((\text{OCH}_3)_2\text{ap})_4\text{Cl}$  [75],  $\text{Ru}_2(\text{O}^i\text{Prap})_4\text{Cl}$  [77], and  $\text{Ru}_2(\text{O}^i\text{Buap})_4\text{Cl}$  [78], each of which was characterized by one reduction and one oxidation in THF, these processes corresponding to  $\text{Ru}_2^{5+/4+}$  and  $\text{Ru}_2^{5+/6+}$ , respectively.

### 3.6. Effect of solvent and axial solvent coordination

The effect of solvent on the redox behavior of  $\text{Ru}_2(\text{L})_4\text{Cl}$  has been investigated by Kadish, Bear and coworkers [44,71] for three  $\text{Ru}_2^{5+}$  complexes, (4,0)  $\text{Ru}_2(2\text{-CH}_3\text{ap})_4\text{Cl}$ , (3,1)  $\text{Ru}_2(2\text{-Fap})_4\text{Cl}$  and (3,1)  $\text{Ru}_2(2,4,6\text{-F}_3\text{ap})_4\text{Cl}$ , each of which was examined as to their electrochemical properties in five different nonaqueous solvents (see Fig. 10). In the case of oxidation, only the  $\text{Ru}_2^{5+/6+}$  process was observed in THF, DMF or DMSO while both  $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{6+/7+}$  were accessible within the positive potential limit of  $\text{CH}_2\text{Cl}_2$  and PhCN (benzonitrile). Each compound also exhibited two one-electron reductions in PhCN which were assigned as  $\text{Ru}_2^{5+/4+}$  and  $\text{Ru}_2^{4+/3+}$  but in  $\text{CH}_2\text{Cl}_2$  only the first step was seen.

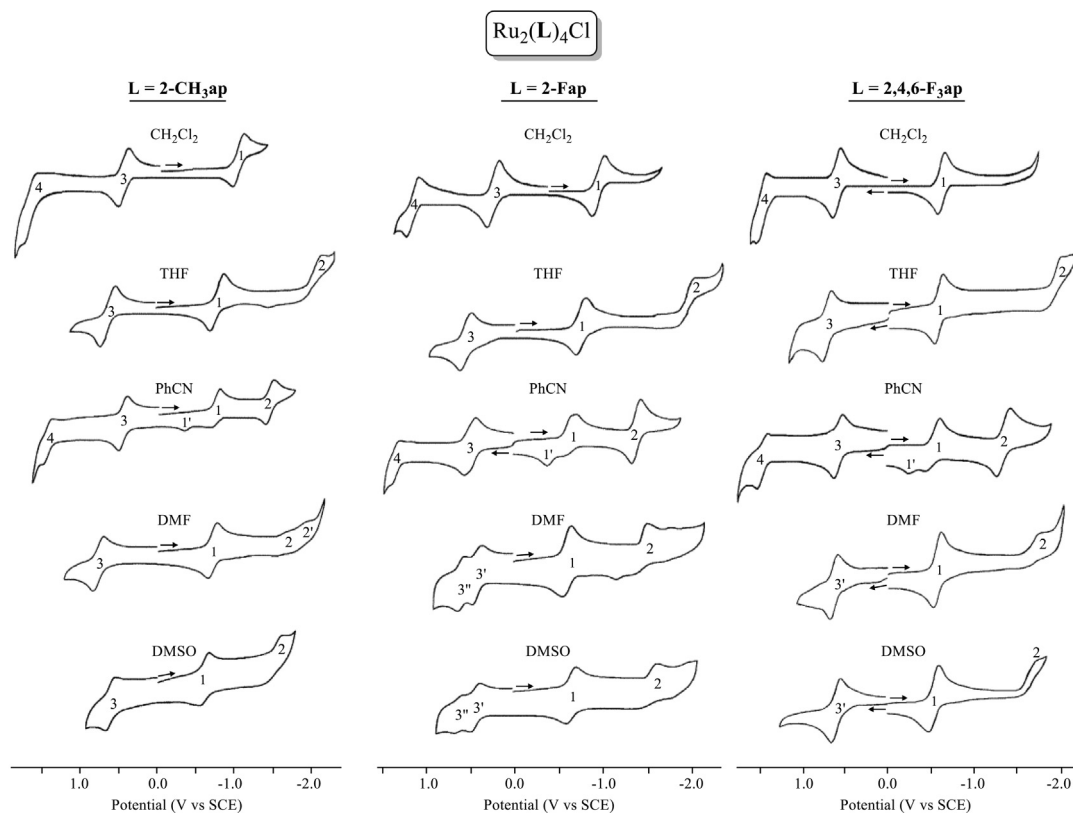
PhCN was shown not to bind to the  $\text{Ru}_2^{6+}$  form of any investigated diruthenium compound, but it did coordinate to the  $\text{Ru}_2^{4+}$  form of the complexes. The solvent binding properties of the singly reduced and singly oxidized forms of  $\text{Ru}_2(\text{L})_4\text{Cl}$  were also shown to depend upon the electronic effect of the bridging ligands.

### 3.7. Effect of axial group

The  $\text{Ru}_2^{5+/4+}$ ,  $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{6+/7+}$  redox processes of air-stable  $\text{Ru}_2^{5+}$  complexes containing "ap-type" bridging ligands are affected by the type of axial ligands on the dimetal unit. For instance, a cyclic voltammogram of  $\text{Ru}_2(2\text{-Fap})_4\text{Cl}(\text{NO})$  in  $\text{CH}_2\text{Cl}_2$  shows two reversible reductions and a single reversible one-electron oxidation at  $E_{1/2}$  values positively shifted as compared to those of  $\text{Ru}_2(2\text{-Fap})_4\text{Cl}$  [79]. Cyclic voltammograms of  $\text{Ru}_2(\text{L})_4(\text{CN})$  (L = ap, Fap, or  $\text{CH}_3\text{ap}$ ) in  $\text{CH}_2\text{Cl}_2$  show  $\text{Ru}_2^{5+/4+}$ ,  $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{6+/7+}$  processes [72], but a substitution of the  $\text{Cl}^-$  axial ligand by  $\text{CN}^-$  shifts  $\text{Ru}_2^{5+/4+}$  in a positive direction, with the magnitude of the shift depending upon the specific compound. This result was accounted for by  $\pi$ -back bonding between the  $\text{CN}^-$  axial ligand and the diruthenium core which leads to stabilization of the  $\text{Ru}_2^{4+}$  oxidation state in the compound. In contrast to this large effect on  $\text{Ru}_2^{5+/4+}$ , the replacement of  $\text{Cl}^-$  by  $\text{CN}^-$  produced only a small effect on the  $\text{Ru}_2^{5+/6+}$  process, consistent with the fact that the  $\text{Ru}_2^{5+/4+}$  and  $\text{Ru}_2^{5+/6+}$  processes involve different MO's, namely the  $\pi^*$  and  $\delta^*$  orbitals [71,72].

Kadish *et al.* [47] examined how the electrochemistry of the different isomers varied under a CO atmosphere. The examined compounds were  $\text{Ru}_2(\text{L})_4\text{Cl}$  complexes (L = 2- $\text{CH}_3\text{ap}$ , ap, 2-Fap, 2,3-F<sub>2</sub>ap, 2,4-F<sub>2</sub>ap, 2,5-F<sub>2</sub>ap, 3,4-F<sub>2</sub>ap, 3,5-F<sub>2</sub>ap, 2,4,6-F<sub>3</sub>ap or F<sub>5</sub>ap) which differed in their geometric isomeric forms, *i.e.* (4,0) or (3,1). The  $\text{Ru}_2^{5+/4+}$  and  $\text{Ru}_2^{4+/3+}$  processes were both irreversible under CO but  $\text{Ru}_2^{3+/2+}$  was reversible. The dependence of  $E_{1/2}$  on the electron-withdrawing or electron-donating properties of the ap-bridging ligand was quantified by the standard Hammett linear free energy relationship given in Eq. (5) (see Section 2.3). The  $\rho$  values (slope of the  $E_{1/2}$  vs  $\Sigma\sigma$  plot) were shown to depend upon the specific redox process as well as the type of geometric isomer. The behavior of regioisomers in their lower  $\text{Ru}_2^{4+}$  and  $\text{Ru}_2^{3+}$  oxidation states was discussed, and the UV-visible and IR spectra of the  $\text{Ru}_2^{4+}$  and  $\text{Ru}_2^{3+}$  complexes were both shown to be isomer dependent under a CO atmosphere [47].

An unusual isomeric conversion involving diruthenium compounds with an "ap-type" structure was reported by Kadish, Bear and coworkers [80]. The (3,1) isomer of  $\text{Ru}_2(\text{F}_3\text{ap})_4\text{Cl}$  is converted to the (4,0) isomeric form of  $\text{Ru}_2(\text{F}_3\text{ap})_4\text{Cl}$  in the presence of TBACl. The reversible  $\text{Ru}_2^{5+/6+}$  process of (3,1)  $\text{Ru}_2(\text{F}_3\text{ap})_4\text{Cl}$  at  $E_{1/2} = 0.62$  V



**Fig. 10.** Cyclic voltammograms of  $\text{Ru}_2(\text{L})_4\text{Cl}$  where  $\text{L} = 2\text{-CH}_3\text{ap}$ ,  $2\text{-Fap}$ , or  $2,4,6\text{-F}_3\text{ap}$  in five nonaqueous organic solvents containing 0.1 M TBAP as supporting electrolyte. Scan rate = 0.1 V/s. Processes 1 and 2 correspond to reductions and processes 3 and 4 to oxidations (adapted from reference [44]).

in  $\text{CH}_2\text{Cl}_2$ , 0.1 M TBAP first shifts to 0.29 V upon formation of (3,1)  $\text{Ru}_2(\text{F}_3\text{ap})_4\text{Cl}_2$  in solutions containing excess TBAP and then the potential shifts even further to 0.10 V after formation of (4,0)  $\text{Ru}_2(\text{F}_3\text{ap})_4\text{Cl}_2$  in solution. The 190 mV potential difference between  $\text{Ru}_2^{5+/6+}$  redox couples of the (3,1) and (4,0)  $\text{Ru}_2(\text{F}_3\text{ap})_4\text{Cl}_2$  isomers in chloride-containing media was much larger than the 60 mV potential difference between the same redox couples of (3,1) and (4,0)  $\text{Ru}_2(\text{F}_3\text{ap})_4\text{Cl}$ , a result accounted for by structural differences that were said to manifest themselves in different strengths of axial coordination to the  $\text{Ru}_2^{5+}$  form of the compounds.

Bear, Kadish and coworkers [81] reported the synthesis and electrochemical characterization of (3,1)  $\text{Ru}_2(2,4,6\text{-F}_3\text{ap})_4(\text{NCS})$  where  $\text{F}_3\text{ap}$  is the 2,4,6-trifluoroanilino-pyridinate anion. The compound exhibits one reduction and two oxidation in  $\text{CH}_2\text{Cl}_2$ , 0.1 M TBAP. The second oxidation is irreversible at a scan rate of 0.1 V/s. The  $\text{Ru}_2^{5+/6+}$  of  $\text{Ru}_2(\text{F}_3\text{ap})_4(\text{NCS})$  was shown to shift cathodically in solutions containing excess  $\text{SCN}^-$  [81], thus suggesting that the type of anionic ligand could be an important factor for controlling the electrochemical properties of this type of compound. However, each process involves the dimetal core and the change in axial ligand from  $\text{Cl}^-$  to  $\text{SCN}^-$  yields only a slight positive shift of potentials for the prevailing redox processes.

Further influence of the anionic axial ligand on the electrochemical properties of diruthenium complexes is given by the electrochemistry of  $\text{Ru}_2(\text{ap})_4\text{F}$ . The  $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{5+/4+}$  processes of this  $\text{Ru}_2^{5+}$  complex are cathodically shifted as compared to  $E_{1/2}$  values of  $\text{Ru}_2(\text{ap})_4\text{Cl}$ , with the magnitude of the shift being 0.08 V and 0.21 V, respectively. This led to an increased HOMO-LUMO gap of 130 mV for the fluoride bound  $\text{Ru}_2^{5+}$  complex as compared to the chloro derivative under the same solution conditions and this was ascribed to the stronger donor ability of the  $\text{F}^-$  axial ligand [77].

Ren and coworkers synthesized  $\text{Ru}_2(\text{ap})_4(\text{C}_6\text{H}_4\text{-}p\text{-X})$  where  $\text{X} = \text{N}(\text{CH}_3)_2$ ,  $\text{N,N}-(\text{C}_6\text{H}_4\text{-}4\text{-OCH}_3)_2$ ,  $t\text{Bu}$ ,  $\text{H}$ ,  $\text{Br}$  or  $\text{CF}_3$  [82].

Each compound showed the expected reversible  $\text{Ru}_2^{5+/4+}$  and  $\text{Ru}_2^{5+/6+}$  process. Additional oxidations were also observed and these were proposed to involve the amine group or possibly a  $\text{Ru}_2^{6+/7+}$  process. The  $\text{NR}_2$  group of the compound seemed to stabilize the  $\text{Ru}_2(\text{ap})_4$  core through extensive conjugation. The first reduction and first oxidation of the compounds were cathodically shifted by 300–350 mV as compared to the respective redox processes of  $\text{Ru}_2(\text{ap})_4\text{Cl}$ . In addition, the aryl derivatives were more difficult to reduce than their analogous alkynyl complexes, indicating a stronger electron donicity of the aryl groups as compared to the alkynyl ligands. The magnitude of the cathodic shift increased as the aryl ligand became increasingly more electron donating. A linear correlation was shown to exist between  $E_{1/2}$  of  $\text{Ru}_2^{5+/6+}$  and the Hammett substituent constants of the  $\sigma$ -bonded aryl axial group [82]. A follow up study by Raghavan, Yuan and Ren involving  $\text{Ru}_2(\text{ap})_4(\text{C}_6\text{H}_4\text{-}p\text{-N}(\text{CH}_3)_2)$  showed the ability of the complex to reversibly bind carbon monoxide, retaining its  $\text{Ru}_2^{5+}$  core oxidation state but altering the spin state from  $S = 3/2$  to  $S = 1/2$  for the CO adduct [83]. The CO-ligation and subsequent change in spin state upon formation of  $\text{Ru}_2(\text{ap})_4(\text{C}_6\text{H}_4\text{-}p\text{-N}(\text{CH}_3)_2)(\text{CO})$  resulted in a 230 mV easier  $\text{Ru}_2^{5+/4+}$  reduction and a 70 mV harder  $\text{Ru}_2^{5+/6+}$  oxidation as compared to the precursor,  $\text{Ru}_2(\text{ap})_4(\text{C}_6\text{H}_4\text{-}p\text{-N}(\text{CH}_3)_2)$  (see Table 4).

### 3.8. Complexes with mixed acetate/“ap-type” bridging ligands

Examples of diruthenium complexes with mixed “ap-type” bridging ligands are given by  $\text{Ru}_2(\text{CH}_3\text{CO}_2)_x(\text{Fap})_{4-x}\text{Cl}$  (where  $x = 1, 2$  or  $3$ ) [55],  $\text{Ru}_2(\text{CH}_3\text{CO}_2)_3(\text{L})\text{Cl}$  (where  $\text{L} = 2,3,4,5,6\text{-F}_5\text{ap}$ ,  $2,4,6\text{-F}_3\text{ap}$ ,  $\text{ap}$ ,  $2\text{-CH}_3\text{ap}$ ,  $2,6\text{-(CH}_3)_2\text{ap}$  or  $2,4,6\text{-(CH}_3)_3\text{ap}$ ) [84] and  $\text{Ru}_2(\text{CH}_3\text{CO}_2)_2(2,4,6\text{-(CH}_3)_3\text{ap})_2\text{Cl}$  [48].  $E_{1/2}$  values for the redox reactions of  $\text{Ru}_2(\text{CH}_3\text{CO}_2)_x(\text{Fap})_{4-x}\text{Cl}$  varied linearly with the number of Fap groups on the molecule for  $x = 0, 1$  and  $2$  [55] while for  $x = 3$  the electrochemical data was related to an equilibrium

involving association/dissociation of the chloride axial ligand.  $E_{1/2}$  values for the  $\text{Ru}_2^{5+/4+}$  process of  $\text{Ru}_2(\text{CH}_3\text{CO}_2)_3(\text{L})\text{Cl}$  also showed a linear free energy relationships with ligand substituents in aqueous solutions containing 0.1 M KCl and in DMSO containing 0.1 M TBAP.

The electrochemistry of  $\text{Ru}_2(\text{CH}_3\text{CO}_2)(2,4,6\text{-(CH}_3)_3\text{ap})_3\text{Cl}$  was investigated in  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  containing 0.1 M TBAP under a CO atmosphere [48]. Under  $\text{N}_2$ , the compound undergoes up to four one-electron redox processes involving the dimetal unit while under CO,  $[\text{Ru}_2(\text{CH}_3\text{CO}_2)(2,4,6\text{-(CH}_3)_3\text{ap})_3(\text{CO})\text{Cl}]^-$  and  $\text{Ru}_2(\text{CH}_3\text{CO}_2)(2,4,6\text{-(CH}_3)_3\text{ap})_3(\text{CO})$  were *in-situ* generated from the initial  $\text{Ru}_2^{5+}$  complex. The two CO bound species exhibited additional reductions yielding  $\text{Ru}_2^{3+}$  and  $\text{Ru}_2^{2+}$  forms of each compound, respectively.

### 3.9. “ap-type” complexes with an axial acetylide group

The effect of one axial acetylide group on the electrochemical properties of  $\text{Ru}_2^{5+}$  complexes with four “ap-type” bridging ligands has been reported in a very large number of papers [75,78,85–91]. Examples of investigated compounds are shown in Fig. 11 while representative cyclic voltammograms are shown in Fig. 12. Table 4 lists  $E_{1/2}$  values for the  $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{5+/4+}$  processes of acetylide diruthenium complexes with different anionic bridging ligands. As seen in the table, half-wave potentials for  $\text{Ru}_2^{5+/6+}$  range from +0.19 to +0.54 V while  $E_{1/2}$  values for  $\text{Ru}_2^{5+/4+}$  range from –0.50 to –1.10 V. The potential separation between the two redox processes range from 1.04 to 1.44 V (see values of  $\Delta$  in Table 4) and the overall data suggests that the reduction is more sensitive than the oxidation to the type of group (R) on the acetylide ligand.

The  $\text{Ru}_2^{5+/4+}$  and  $\text{Ru}_2^{5+/6+}$  processes of  $\text{Ru}_2(\text{ap})_4(\text{C}\equiv\text{CR})$  (R = H, Si(CH<sub>3</sub>)<sub>3</sub> or CH<sub>2</sub>OCH<sub>3</sub>) are cathodically shifted with respect to the same reactions of  $\text{Ru}_2(\text{ap})_4\text{Cl}$  (see Table 3) [85]. An additional oxidation is also observed for  $\text{Ru}_2(\text{ap})_4(\text{C}\equiv\text{C-4-C}_6\text{H}_4\text{-N}_3\text{Et}_2)$  in THF containing 0.2 M TBAPF<sub>6</sub> and this process was attributed to an electron abstraction from the triazene group [86].

$\text{Ru}_2(\text{Xap})_4(\text{C}\equiv\text{C-}p\text{-C}_6\text{H}_4\text{NH}_2)$  and  $\text{Ru}_2(\text{Xap})_4(\text{C}\equiv\text{C-}m\text{-C}_6\text{H}_4\text{NH}_2)$  (Xap = 2-anilino-pyridinate or 2-(3,5-dimethoxy)-anilino-pyridinate) were shown to undergo  $\text{Ru}_2^{5+/4+}$  and  $\text{Ru}_2^{5+/6+}$  processes in THF containing 0.2 M TBAPF<sub>6</sub> [87]. There was also an additional quasi-reversible oxidation which was attributed to the amino group, as in the case of  $\text{Ru}_2(\text{Xap})_4(\text{C}\equiv\text{C-}p\text{-C}_6\text{H}_4\text{NH}_2)$  [87]. DFT calculations were carried out to explain the electrochemical differences between the two investigated compounds [87]. The measured  $E_{1/2}$  values of  $\text{Ru}_2(\text{O}^i\text{Buap})(\text{C}\equiv\text{C-C}_6\text{H}_5)$  and  $\text{Ru}_2(\text{O}^i\text{Buap})_4(\text{C}\equiv\text{C-Si}^i\text{Pr}_3)$  in THF containing 0.2 M TBAPF<sub>6</sub> (see Table 4) were similar to values reported for  $\text{Ru}_2(\text{ap})_4$ -based compounds [78].

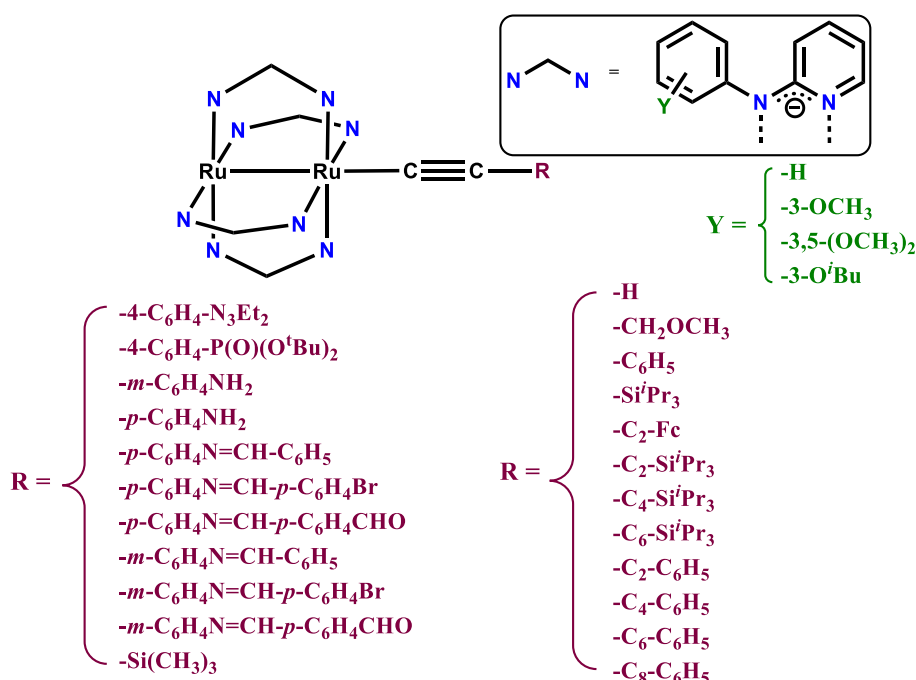


Fig. 11. Schematic representation of  $\text{Ru}_2(\text{L})_4(\text{C}\equiv\text{CR})$  where L is an “ap-type” bridging ligand.

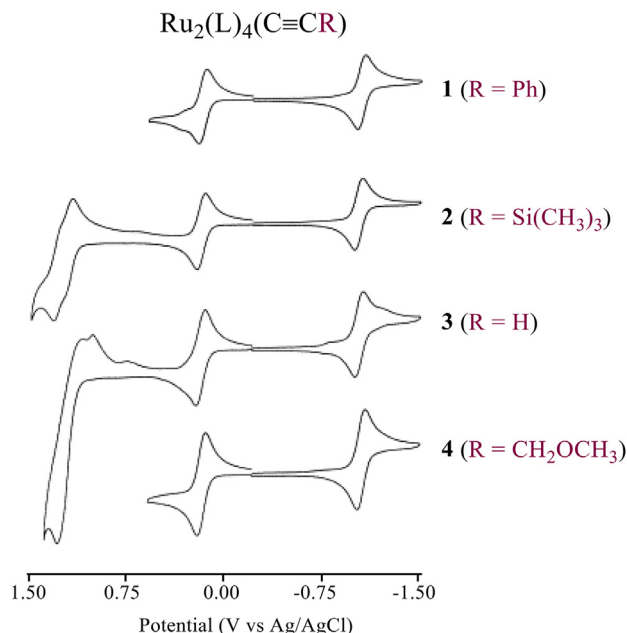


Fig. 12. Cyclic voltammograms of  $\text{Ru}_2(\text{L})_4(\text{C}\equiv\text{CR})$  where L is an “ap-type” bridging ligand and R = Ph (1), Si(CH<sub>3</sub>)<sub>3</sub> (2), H (3) and CH<sub>2</sub>OCH<sub>3</sub> (4) (adapted from reference [85]).

$E_{1/2}$  values for the  $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{5+/4+}$  processes of  $\text{Ru}_2(\text{ap})_4(\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{N}=\text{CH}-p\text{-C}_6\text{H}_4\text{R})$  and  $\text{Ru}_2(\text{ap})_4(\text{C}\equiv\text{C}-m\text{-C}_6\text{H}_4\text{N}=\text{CH}-p\text{-C}_6\text{H}_4\text{R})$  ( $\text{R} = \text{H}, \text{Br}$  or  $\text{CHO}$ ) in THF containing 0.1 M  $\text{TBAPF}_6$  vary little with changes in the R group of the  $\sigma$ -iminophenylacetylide ligand (see Table 4) [88]. Compounds with  $\text{R} = \text{H}$  and  $\text{R} = \text{Br}$  exhibited a single oxidation of the  $\text{Ru}_2$  core along with three reductions, two of which were proposed to involve the dimetal unit and one the imine group. The compounds with  $\text{R} = \text{CHO}$  were characterized by redox behavior similar to that for the derivatives with  $\text{R} = \text{H}$  or  $\text{R} = \text{Br}$ , but each compound also showed a fourth reduction assigned to the aldehyde functional group [88].

Ren and coworkers [89] showed that the electrochemical properties of  $\text{Ru}_2(\text{ap})_4(\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{-P}(\text{O})(\text{O}^t\text{Bu})_2)$  in THF containing 0.2 M  $\text{TBAPF}_6$  were essentially the same as for diruthenium compounds with unsubstituted aryl acetylide ligands, i.e. both were characterized by one reversible oxidation and one reversible reduction centered at the dimetal unit and both having similar potential separations between the two processes thus indicating a minimal effect of the phosphonate capping group.  $\text{Ru}_2(3\text{-OCH}_3\text{ap})_4(\text{L})$  ( $3\text{-OCH}_3\text{ap} = 2\text{-}(3\text{-methoxyanilino})\text{pyridinate}$  ion and  $\text{L} = (\text{C}\equiv\text{C})_2\text{-Si}(\text{CH}_3)_3$  or  $(\text{C}\equiv\text{C})_2\text{Fc}$  where Fc is the ferrocenyl group) and  $\text{Ru}_2(3,5\text{-}(\text{OCH}_3)_2\text{ap})_4(\text{L})$  ( $3,5\text{-}(\text{OCH}_3)_2\text{ap} = 2\text{-}(3,5\text{-dimethoxyanilino})\text{pyridinate}$  ion and  $\text{L} = ((\text{C}\equiv\text{C})_2\text{-Si}(\text{CH}_3)_3)$  were shown [75] to exhibit two reversible one-electron transfers assigned to  $\text{Ru}_2^{5+/4+}$  and  $\text{Ru}_2^{5+/6+}$ . Oxidation potentials for the  $\text{Ru}_2^{5+/6+}$  reactions were more positive than those for similar derivatives containing a  $\text{Cl}^-$  axial ligand (see Table 3). A  $\text{Fc}/\text{Fc}^+$  oxidation process was observed for  $\text{Ru}_2(3\text{-OCH}_3\text{ap})_4((\text{C}\equiv\text{C})_2\text{Fc})$ ; and this reaction occurred at 0.61 V vs  $\text{Ag}/\text{AgCl}$ , a value only 60 mV less

negative than that for the  $\text{Fc}/\text{Fc}^+$  redox couple of  $\text{Ru}_2(\text{ap})_4((\text{C}\equiv\text{C})_2\text{Fc})$ .

Ren and coworkers [90] electrochemically characterized compounds containing one cross-conjugated  $\sigma$ -geminal-diethynylethene ligand (*gem*-DEE) of the type  $\text{Ru}_2(\text{Xap})_4(\text{Y-gem-DEE})$  ( $\text{Xap} = \text{ap}$  or  $3,5\text{-}(\text{OCH}_3)_2\text{ap}$ ,  $\text{Y} = \text{Si}^i\text{Pr}_3$  or  $\text{H}$ ) (see Fig. 13). Each compound had one reversible oxidation ( $\text{Ru}_2^{5+/6+}$ ) and two reductions ( $\text{Ru}_2^{5+/4+}$  and  $\text{Ru}_2^{4+/3+}$ ) in THF but only the  $\text{Ru}_2^{5+/4+}$  process was reversible. There was a slight cathodic shift in the oxidation potential but virtually no change in the reduction potential as compared to the corresponding reactions of  $\text{Ru}_2(\text{ap})_4(\text{C}\equiv\text{CSi}^i\text{Pr}_3)$ , thus indicating that the *gem*-DEE ligands are slightly better donors than simple acetylides. In addition, potentials of the ap and  $3,5\text{-}(\text{OCH}_3)_2\text{ap}$  derivatives were virtually identical to each other, showing the equal donor strengths of these two ligands.

Each compound in the series of  $\text{Ru}_2(\text{ap})_4(\text{C}_{2(k-1)}\text{R})$  complexes ( $\text{R} = \text{Si}^i\text{Pr}_3$ ,  $\text{C}_6\text{H}_5$  or  $\text{H}$ ,  $k = 2\text{-}5$ ) displays  $\text{Ru}_2^{5+/4+}$  and  $\text{Ru}_2^{5+/6+}$  processes [91] and the potential separation between these two processes was linearly correlated with the number of acetylenic bonds within each series. The  $\text{Ru}_2^{5+/4+}$  reaction became less reversible as the number of acetylene bonds was increased; a trend based on the electron-deficiency character of the acetylene unit.

### 3.10. Axially linked $\text{Ru}_2^{5+}$ “ap-type” complexes

Several axially linked  $\text{Ru}_2^{5+}$  complexes (see Figs. 14 and 15) supported by ap or “ap-type” bridging ligands have been characterized and the electronic communication between the two diruthenium units elucidated [92–95]. In the case of linked dimeric units, two

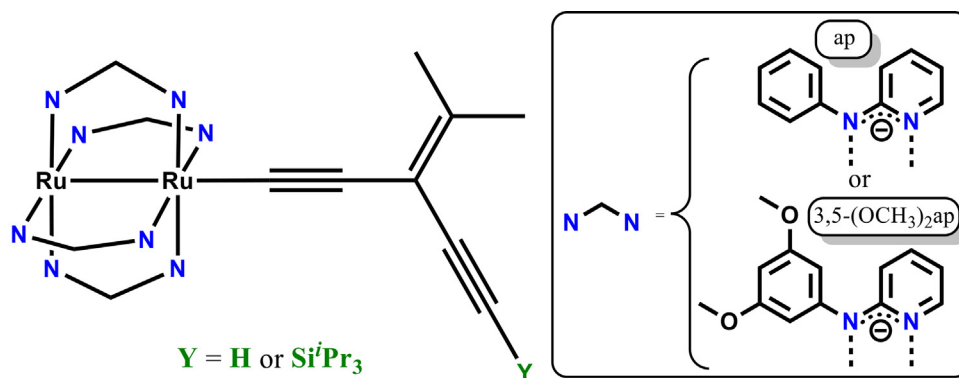


Fig. 13. Schematic representation of  $\text{Ru}_2(\text{ap})_4\text{-gem-DEE}$  compounds (adapted from reference [90]).

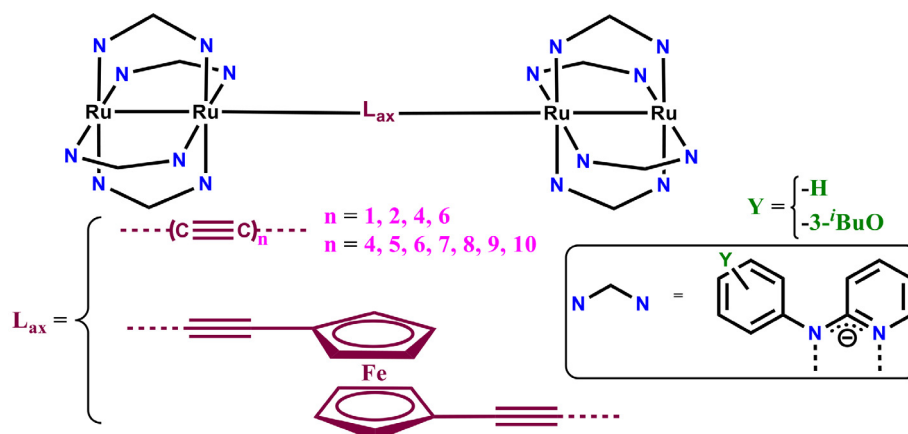
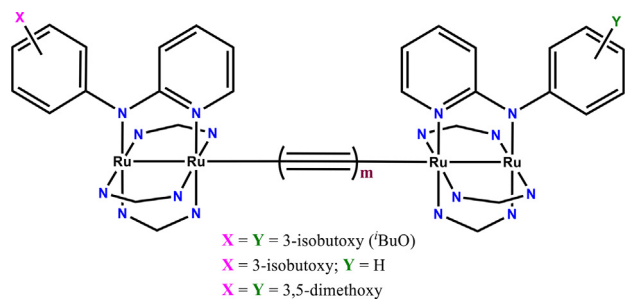


Fig. 14. Schematic representation of axially linked  $\text{Ru}_2^{5+}$  complexes with “ap-type” bridging ligands.



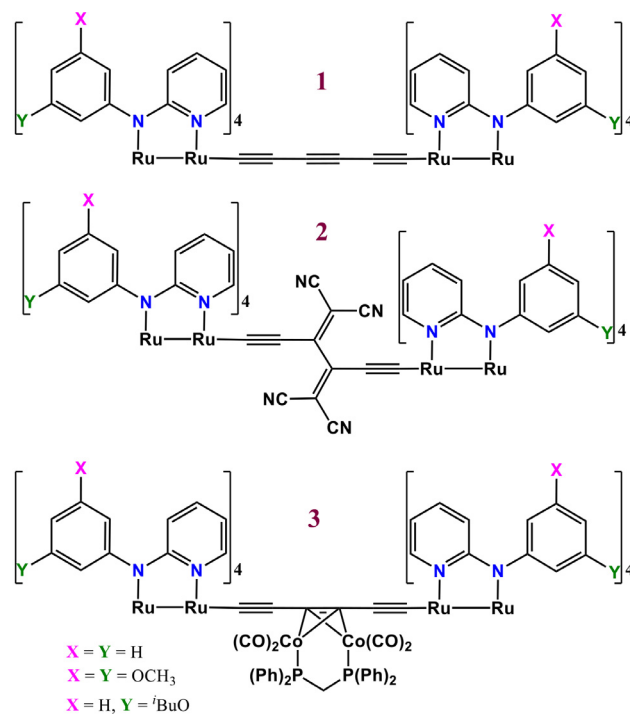


**Fig. 15.** Schematic representation of  $\text{Ru}_2$ -polyyn- $\text{Ru}_2$  complexes containing “ap type” bridging ligands where  $m = 4-8$  (see reference [95]).

extremes of redox behavior are known to occur [96,97]: one in which no electronic coupling exists between the two linked redox active units where two overlapping one-electron redox processes are observed and one in the case of equivalent and interacting dimeric units where two separate redox potentials are observed for a given electrode process. In the latter case, the magnitude of the separation between  $E_{1/2}$  or ( $E_p$ ) values will be larger with an increased degree of interaction.

Table 5 lists  $E_{1/2}$  values for the  $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{5+/4+}$  processes of several compounds in THF. The linear alkynyl chains of  $[(\text{ap})_4\text{Ru}_2](\text{C}\equiv\text{C})_n[\text{Ru}_2(\text{ap})_4]$  where  $n = 1, 2, 4$  or  $6$  mediate significant electronic communication between the two  $\text{Ru}_2^{5+}$  units of the compound, but this communication decreased as the length of the carbon chain was increased [92,93]. The  $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{5+/4+}$  processes in this series of compounds were both shifted towards more positive values as the size of the alkynyl chain was increased. Cyclic and differential pulse voltammetric data of  $1,1'-[\text{Ru}_2(\text{ap})_4(\text{C}\equiv\text{C})_2]\text{Fc}$  (Fc = ferrocene moiety) both suggested that the two  $\text{Ru}_2$  units in the “dimer-of-dimer” were weakly coupled in their reduced form [98]. Cyclic and differential pulse voltammetry measurements on a series of  $\text{Ru}_2(\text{Xap})_4$ -capped polyyn-diyl compounds of the type  $[(\text{Xap})_4\text{Ru}_2](\text{C}\equiv\text{C})_m[\text{Ru}_2(\text{Yap})_4]$  ( $X = Y$  or  $X \neq Y$ ) (Fig. 15) (Xap or Yap = 2-anilino-pyridine or its aniline substituted derivative) coupled with spectroelectrochemical data indicated that the reduced monoanions  $[\text{Ru}_2\text{-C}_{2m}\text{-Ru}_2]^-$  ( $m = 4-8$ ) could be described as Robin-Day class II mixed valent ions [95]. Electronic coupling between the  $\text{Ru}_2$  units was shown to depend upon the length of the alkyl chain group, with an attenuation constant estimated to be between 0.12 and 0.15 per angstrom. Spin-unrestricted DFT calculations provided insight into the nature of the orbitals that mediate the long-distance electronic coupling.

Fig. 17 shows differential pulse voltammograms (DPV) of three  $\text{Ru}_2$ -polyyn complexes in THF, 0.2 M TBAP<sub>6</sub>, namely  $[\text{Ru}_2(\text{Xap})_4]_2(\mu\text{-C}_6)$ ,  $[\text{Ru}_2(\text{Xap})_4]_2\{\mu\text{-C}\equiv\text{CC}(\text{C}(\text{CN})_2)\text{-C}(\text{C}(\text{CN})_2)\text{C}\equiv\text{C}\}$  and  $[\text{Ru}_2(\text{Xap})_4]_2(\mu\text{-C}_6)(\text{Co}_2(\text{dppm})(\text{CO})_4)$  (shown respectively in Fig. 16 as **1**, **2** and **3**) [94]. The redox processes in Fig. 17 are labeled as A, B, C, D, AB' and CD' and the assigned couples are summarized in the figure. Voltammetric and spectroelectrochemical data showed that the two  $\text{Ru}_2$  units were sufficiently coupled in the monoanion of  $[\text{Ru}_2(\text{Xap})_4]_2(\mu\text{-C}_6)$ , thus suggesting that the compound behaves as a Robin-Day class II/III mixed valence species. Coupling between the two  $\text{Ru}_2$  termini was still significant but somewhat weakened in  $[\text{Ru}_2(\text{Xap})_4]_2(\mu\text{-C}_6)(\text{Co}_2(\text{dppm})(\text{CO})_4)$  but was completely removed by insertion of a TCNE group in  $[\text{Ru}_2(\text{Xap})_4]_2\{\mu\text{-C}\equiv\text{CC}(\text{C}(\text{CN})_2)\text{-C}(\text{C}(\text{CN})_2)\text{C}\equiv\text{C}\}$ . The decrease in electronic coupling was further explored by X-ray diffraction and spin-unrestricted DFT calculations which showed that significant conformational changes in the TCNE linked diruthenium units hindered the superexchange pathway by forcing  $\pi$  orbitals of the TCNE linker to become quasi-orthogonal, thus effectively eliminating electronic coupling between two  $\text{Ru}_2$  termini [94].



**Fig. 16.** Schematic representation of  $[\text{Ru}_2(\text{Xap})_4]_2(\mu\text{-C}_6)$  (**1**),  $[\text{Ru}_2(\text{Xap})_4]_2\{\mu\text{-C}\equiv\text{CC}(\text{C}(\text{CN})_2)\text{-C}(\text{C}(\text{CN})_2)\text{C}\equiv\text{C}\}$  (**2**) and  $[\text{Ru}_2(\text{Xap})_4]_2(\mu\text{-C}_6)(\text{Co}_2(\text{dppm})(\text{CO})_4)$  (**3**) (adapted from reference [94]).

### 3.11. Diarylformamidinate (DARf) and amidinate bridging ligands

A recent review [4] discussed the electrochemical properties of diruthenium amidinate complexes containing DARf and “DARf-type” equatorial bridging ligands where Ar is a substituted phenyl ring (see Fig. 18). The  $\text{Ru}_2^{3+}$  formamidinate complexes typically undergo two oxidations processes, the first of which is reversible and leads to a  $\text{Ru}_2^{6+}$  complex, whereas the second is irreversible and described as  $\text{Ru}_2^{6+/7+}$ . Most of the compounds also showed two reductions assigned as  $\text{Ru}_2^{5+/4+}$  and  $\text{Ru}_2^{4+/3+}$ . The  $\text{Ru}_2^{5+/4+}$  processes of compounds initially containing a bound chloride or azide axial anion were usually accompanied by a loss of the ligand. Evidence for the loss of the axial ligand was given by the presence of a non-coupled reoxidation process on the reverse scan by cyclic voltammetry and an anodic peak located at a potential corresponding to the  $\text{Ru}_2^{5+/4+}$  reaction of the compound lacking an axial ligand [99]. The  $E_{1/2}$  values of the tetra-diarylformamidinate derivatives of  $\text{Ru}_2(\text{RNCHNR})_4(\text{N}_3)$  where R =  $p\text{-CH}_3\text{O-C}_6\text{H}_4$ ,  $p\text{-CH}_3\text{-C}_6\text{H}_4$ , Ph,  $m\text{-CH}_3\text{O-C}_6\text{H}_4$ ,  $p\text{-Cl-C}_6\text{H}_4$ ,  $m\text{-Cl-C}_6\text{H}_4$ ,  $m\text{-CF}_3\text{-C}_6\text{H}_4$ ,  $3,4\text{-Cl}_2\text{-C}_6\text{H}_3$  or  $3,5\text{-Cl}_2\text{-C}_6\text{H}_3$  shifted anodically with increasing electron withdrawing nature of the aryl substituents and these shifts in potential were quantified using Eq. (5) ( $\rho = 89$  mV) [100]. The mono-alkynyl  $\text{Ru}_2^{5+}$  complexes exhibited an irreversible oxidation and a reversible reduction with the potentials being cathodically shifted with respect to  $E_{1/2}$  values of the corresponding chloride-bound complexes [101].

A summary of  $E_{1/2}$  values for the  $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{5+/4+}$  processes of monomeric diruthenium complexes containing “DPHF-type” bridging ligands are listed in Table 6. The  $\text{Ru}_2^{5+/6+}$  reversible potentials were located between 0.29 and 1.35 V (vs Ag/AgCl) while  $E_{1/2}$  values for  $\text{Ru}_2^{5+/4+}$  varied between  $-0.11$  and  $-0.71$  V, thus suggesting that the oxidation was more affected by the type of bridging ligands and/or axial groups than the reduction. The potential separation between the oxidation and reduction ranged from 1.04 to 1.68 V, thus indicating that a significant tuning of the



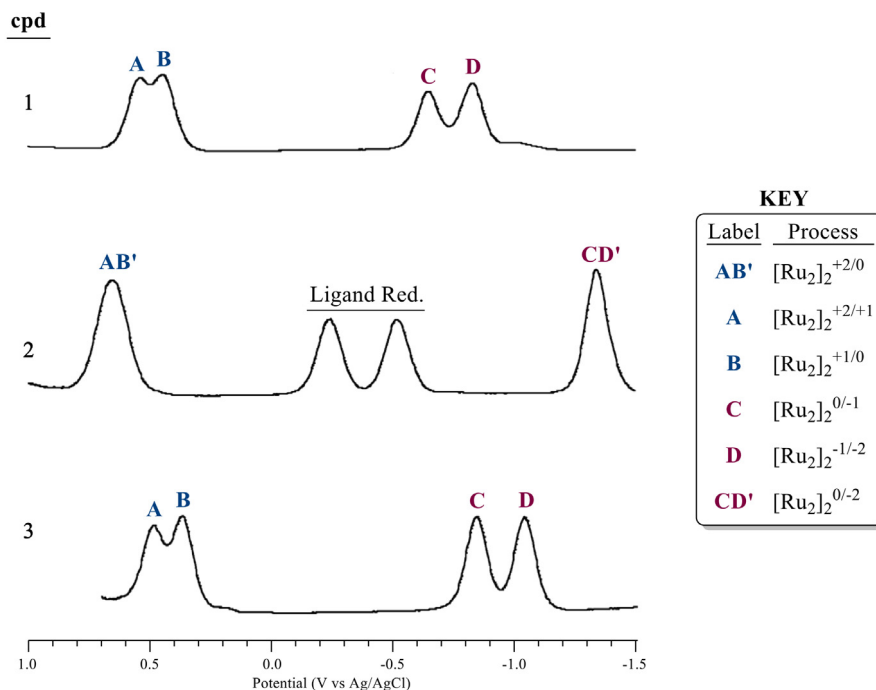


Fig. 17. Differential pulse voltammograms (DPV) of axially linked  $\text{Ru}_2^+$  complexes having an “ap-type” structure. Electrode processes labeled A, B, C, D, AB' and CD' above peak currents are summarized in the key, while the given compound numbers refer to the structures in Fig. 16 (adapted from reference [94]).

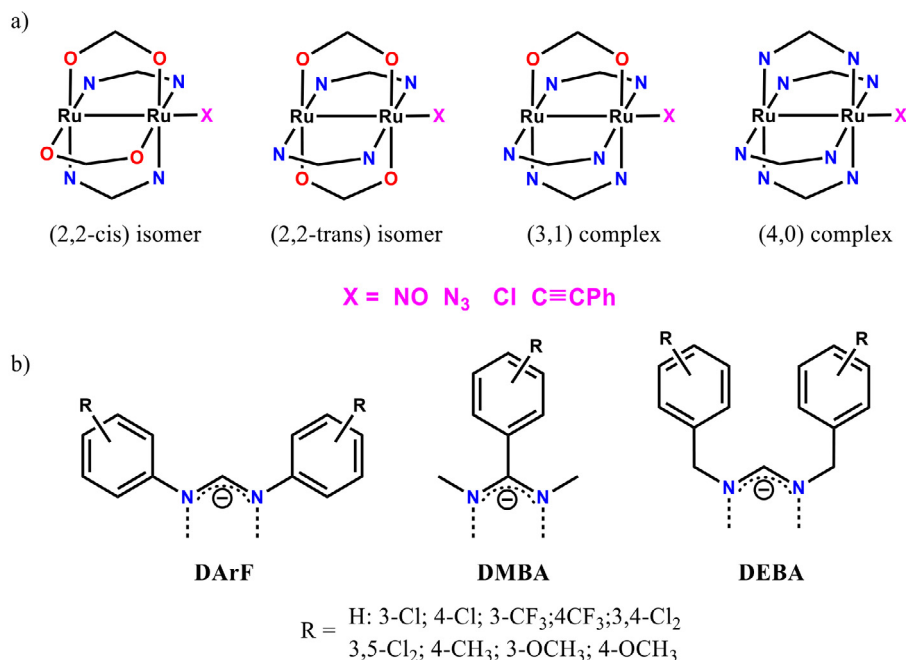


Fig. 18. Schematic representation of a)  $\text{Ru}_2(\text{L})_n(\text{O}_2\text{CCH}_3)_{4-n}\text{X}$  ( $n = 2, 3$  or  $4$  and  $\text{X} = \text{NO}, \text{N}_3, \text{Cl}$  or  $\text{C}\equiv\text{CPh}$ ) and b) DArF, DMBA and DEBA bridging ligands.

potential gap could be achieved by the choice of bridging and/or axial ligands.

### 3.12. Mixed acetato/“DPhF-type” complexes

$\text{Ru}_2(\text{D}(3,5\text{-Cl}_2\text{Ph})\text{F})_{4-n}(\text{O}_2\text{CFC})_n\text{Cl}$  and  $\text{Ru}_2(\text{DmAniF})_{4-n}(\text{O}_2\text{CFC})_n\text{Cl}$  ( $n = 1$  or  $2$ ) (see Fig. 19) were synthesized by Ren and coworkers [102,103] and electrochemically characterized (Fig. 20). The proposed sequence of redox processes is given in Scheme 4.  $\text{Ru}_2(\text{DmAniF})_3(\text{O}_2\text{CFC})\text{Cl}$  (Compound **3b** in Fig. 20) undergoes an

irreversible  $\text{Ru}_2^{5+/4+}$  process followed by a reversible  $\text{Ru}_2^{4+/3+}$ . This behavior is identical to that of the analogous,  $\text{Ru}_2(\text{DmAniF})_3(\text{O}_2\text{CCH}_3)\text{Cl}$  (Compound **1b**), thus showing no effect of the ferrocenyl group.  $\text{Ru}_2(\text{DmAniF})_2(\text{O}_2\text{CFC})_2\text{Cl}$  (**4b**) also exhibits a cathodic behavior similar to that of  $\text{Ru}_2(\text{DmAniF})_2(\text{O}_2\text{CCH}_3)_2\text{Cl}$  (**2b**). However, the  $\text{Ru}_2^{4+/3+}$  process of the former compound is irreversible suggesting decomposition after reduction.  $\text{Ru}_2(\text{DmAniF})_3(\text{O}_2\text{CFC})\text{Cl}$  (**3b**) displays two closely spaced quasi-reversible one electron oxidations. The first oxidation is assigned to the ferrocenyl group and the second to the diruthenium center of the compound. The  $\text{Ru}_2^{5+/6+}$

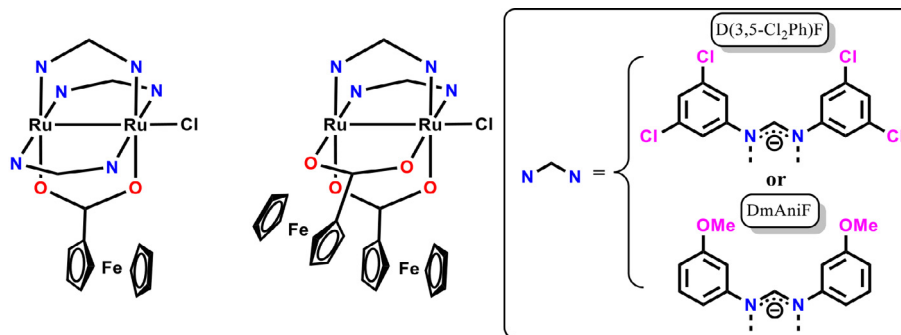


Fig. 19. Schematic representation of monomeric  $\text{Ru}_2^{2+}$  complexes containing "DPHF-type" and ferrocenyl bridging ligands.

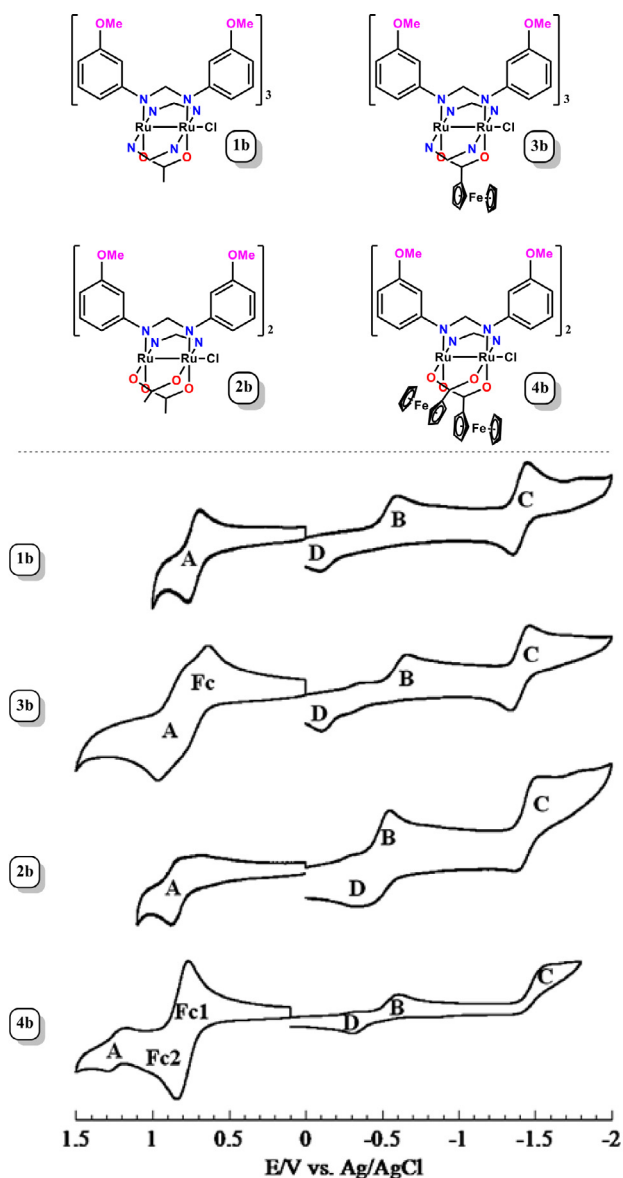
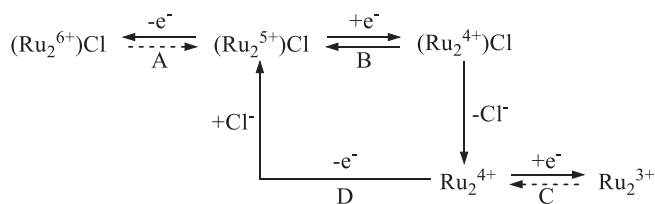


Fig. 20. Cyclic voltammograms of  $\text{Ru}_2(\text{DmAniF})_{4-n}(\text{O}_2\text{CCH}_3)_n\text{Cl}$  ( $n = 1$  or  $2$ ) and  $\text{Ru}_2(\text{DmAniF})_{4-n}(\text{O}_2\text{CFC}_2)_n\text{Cl}$  ( $n = 1$  or  $2$ ) in THF containing  $0.2 \text{ M TBAPF}_6$  (adapted from reference [102]).

process of  $\text{Ru}_2(\text{DmAniF})_3(\text{O}_2\text{CFC})\text{Cl}$  (**3b**) occurs at a slightly more positive potential than that of  $\text{Ru}_2(\text{DmAniF})_3(\text{O}_2\text{CCH}_3)\text{Cl}$  (**1b**) due to the added positive charge after oxidation of ferrocene in the former compound.



Scheme 4. Electron transfer processes of  $\text{Ru}_2^{5+}$  complexes with "DPHF-type" ligands (adapted from reference [102]).

The oxidation behavior of  $\text{Ru}_2(\text{DmAniF})_2(\text{O}_2\text{CFC})_2\text{Cl}$  (**4b**) is quite different from that of  $\text{Ru}_2(\text{DmAniF})_2(\text{O}_2\text{CCH}_3)_2\text{Cl}$  (**2b**). Three oxidations were observed, the first two of which were assigned to the two Fc groups and the third to the  $\text{Ru}_2^{5+/6+}$  core. Again, the  $\text{Ru}_2^{5+/6+}$  process of  $\text{Ru}_2(\text{DmAniF})_2(\text{O}_2\text{CFC})_2\text{Cl}$  (**4b**) is located at a much more positive potential than is seen for  $\text{Ru}_2(\text{DmAniF})_2(\text{O}_2\text{CCH}_3)_2\text{Cl}$  (**2b**). The fact that the oxidation of  $\text{Ru}_2(\text{DmAniF})_2(\text{O}_2\text{CFC})_2\text{Cl}$  (**4b**) consists of a pair of closely spaced electron transfers associated with each Fc group indicates the occurrence of electronic coupling between the two Fc centers in the mixed valence state ( $[\text{Fc}-\text{Fc}]^+$ ). The difference in peak potentials between the two processes in the differential pulse voltammogram was approximately  $71 \text{ mV}$ , as determined by differential pulse voltammetry (DPV). [103]

Several compounds containing acetato bridging ligands carrying olefin groups were examined as to their electrochemical properties [104]. Cyclic voltammograms of  $\text{Ru}_2(\text{D}(3,5\text{-Cl}_2\text{Ph})\text{F})_3(\text{L})\text{Cl}$  ( $\text{L} = 4\text{-vinylbenzoate}$ ,  $5\text{-hexenoate}$  and  $6\text{-heptenoate}$ ) and  $\text{cis-Ru}_2(\text{D}(3,5\text{-Cl}_2\text{Ph})\text{F})_2(4\text{-vinylbenzoate})_2\text{Cl}$  in THF containing  $\text{TBAPF}_6$  show  $\text{Ru}_2^{5+/6+}$ ,  $\text{Ru}_2^{5+/4+}$  and  $\text{Ru}_2^{4+/3+}$  processes. The two reductions involve a chloride-bound species, thus indicating that the electro-generated  $\text{Ru}_2^{4+}$  form of the compound does not readily lose  $\text{Cl}^-$  as is the case for  $\text{Ru}_2(\text{DmAniF})_3(\text{O}_2\text{C}(\text{CH}_2)_m\text{CH}=\text{CH}_2)\text{Cl}$  ( $m = 3, 4$  or  $8$ ),  $\text{Ru}_2(\text{DmAniF})_2(\text{O}_2\text{C}(\text{CH}_2)_m\text{CH}=\text{CH}_2)_2\text{Cl}$  ( $m = 3$  or  $8$ ) or  $\text{Ru}_2(\text{DmAniF})_2(\text{O}_2\text{C}(\text{CH}_2)_m\text{CH}=\text{CH}_2)\text{Cl}$  ( $m = 3$  or  $8$ ), all of which also carry terminal olefin groups [105].

Handa and coworkers [106] prepared  $\text{cis-}[\text{Ru}_2(4\text{-CH}_3\text{-pf})_2(\text{O}_2\text{CCH}_3)_2\text{Cl}]$  and  $\text{trans-}[\text{Ru}_2(2,6\text{-Et}_2\text{-pf})_2(\text{O}_2\text{CCH}_3)_2\text{Cl}]$  where  $4\text{-CH}_3\text{-pf}^-$  is the  $\text{N,N}'\text{-bis}(4\text{-methylphenyl})\text{formamidinate}$  ion and  $2,6\text{-Et}_2\text{-pf}^-$  is the  $\text{N,N}'\text{-bis}(2,6\text{-diethylphenyl})\text{formamidinate}$  ion. Both compounds exhibit the usual  $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{5+/4+}$  redox processes but the current-voltage curves are complicated due to association and/or dissociation of the chloride axial group.

The carbonyl complex,  $[\text{Ru}_2(\text{DPHF})_3(\text{CH}_3\text{CO}_2)(\text{CO})](\text{BF}_4)$ , and the nitrosyl complex,  $[\text{Ru}_2(\text{DPHF})_3(\text{CH}_3\text{CO}_2)(\text{NO})](\text{BF}_4)$  were prepared by Barral *et al.* [45] The carbonyl derivative displays two quasi-reversible cathodic processes assigned to the  $\text{Ru}_2^{5+/4+}$  process of two species in equilibrium, namely  $[\text{Ru}_2(\text{DPHF})_3(\text{CH}_3\text{CO}_2)(\text{CO})]^+$  and  $[\text{Ru}_2(\text{DPHF})_3(\text{CH}_3\text{CO}_2)(\text{BF}_4)(\text{CO})]$ . The nitrosyl compound undergoes one quasi-reversible cathodic process, a behavior analogous to that of  $\text{Ru}_2(\text{DPHF})_3(\text{CH}_3\text{CO}_2)\text{Cl}$  and  $\text{Ru}_2(\text{DPHF})_3(\text{PhCO}_2)\text{Cl}$ .

Substitution of the acetate bridging ligand in  $\text{Ru}_2(\text{DPhF})_3(\text{CH}_3\text{CO}_2)\text{Cl}$  by benzoate or substituted benzoate gives  $\text{Ru}_2(\text{DPhF})_3(\text{O}_2\text{CC}_6\text{H}_5)\text{Cl}$  and  $\text{Ru}_2(\text{DPhF})_3(\text{O}_2\text{CC}_6\text{H}_4\text{-pCN})\text{Cl}$ , respectively, both of which exhibit an irreversible  $\text{Ru}_2^{5+/4+}$  process but a reversible  $\text{Ru}_2^{5+/6+}$  reaction, as is the case for the parent compound [107].

An unusual compound containing two bridging DmAniF ligands and two chelating DmAniF groups bound to the diruthenium core (see Fig. 21) were reported by Ren and coworkers and formulated as  $\text{Ru}_2(\eta^2\text{-DmAniF})_2(\mu\text{-DmAniF})_2(\mu\text{-OAc})(\mu\text{-O})$  [108]. The diruthenium complex contains a formal  $\text{Ru}_2^{7+}$  core and undergoes a reversible reduction at  $-0.68$  V (vs Ag/AgCl) assigned to  $\text{Ru}_2^{7+/6+}$  and a reversible oxidation at  $0.38$  V (vs Ag/AgCl) assigned to  $\text{Ru}_2^{7+/8+}$ .

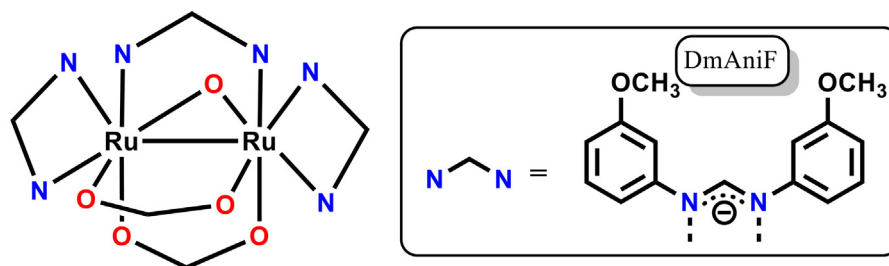


Fig. 21. Schematic representation of  $\text{Ru}_2(\eta^2\text{-DmAniF})_2(\mu\text{-DmAniF})_2(\mu\text{-OAc})(\mu\text{-O})$ .

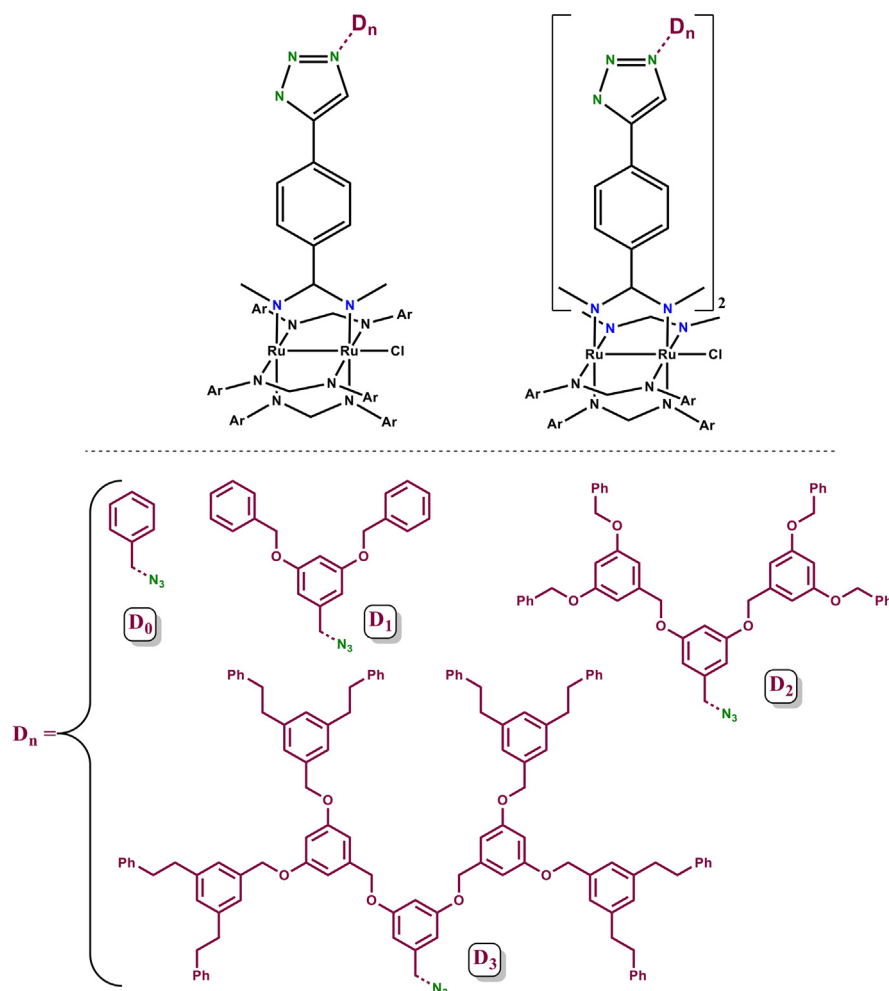


Fig. 22. Schematic representation of  $\text{Ru}_2^{5+}$  complexes with dendritic ( $\text{D}_n$ ) structures with the general formula  $\text{Ru}_2(\text{D}(3,5\text{-Cl}_2\text{Ph})\text{F})_3(\text{DMBA-N}_3\text{-D}_n)\text{Cl}$  or  $\text{Ru}_2(\text{D}(3,5\text{-Cl}_2\text{Ph})\text{F})_2(\text{DMBA-N}_3\text{-D}_n)_2\text{Cl}$  where  $n = 0, 1, 2$  or  $3$  (adapted from reference [109]).

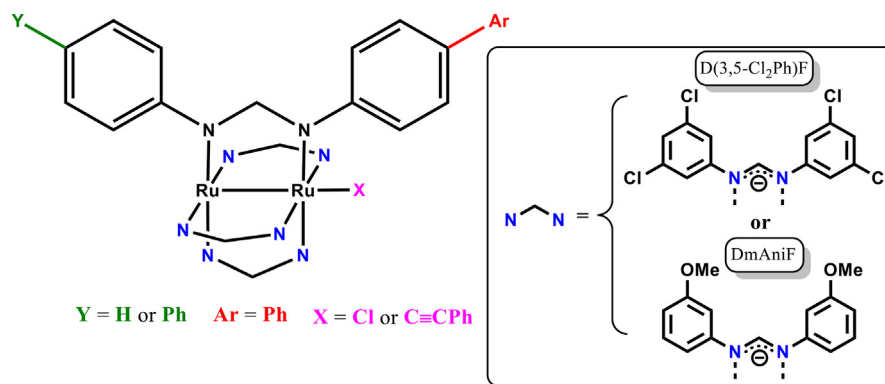


Fig. 23. Schematic representation of  $\text{Ru}_2(\text{DArF})_3(\text{L})\text{Cl}$  where L is a diarylformamidinate ligand containing one biphenyl group at the periphery.

Ren and coworkers also carried out the selective ligand modification on the periphery of diruthenium compounds [110]. In this study, three compounds,  $\text{Ru}_2(\text{DmAniF})_3(\text{O}_2\text{CCH}_3)\text{Cl}$ ,  $\text{Ru}_2(\text{DmAniF})_3(\text{DMBA-I})\text{Cl}$  and  $\text{Ru}_2(\text{DmAniF})_2(\text{DMBA-I})_2\text{Cl}$ , where DMBA is the dimethylbenzamidinate bridging ligand, were electrochemically investigated in THF containing TBAPF<sub>6</sub> as supporting electrolyte. Each diruthenium complex shows the  $\text{Ru}_2^{5+/6+}$ ,  $\text{Ru}_2^{5+/4+}$  and  $\text{Ru}_2^{4+/3+}$  processes.  $E_{1/2}$  values of the two DMBA compounds were cathodically shifted by 100 mV with respect to  $E_{1/2}$  values of  $\text{Ru}_2(\text{DmAniF})_3(\text{O}_2\text{CCH}_3)\text{Cl}$ , consistent with the fact that DMBA is a much stronger donor ligand than acetate. A similar conclusion was reached after comparing  $E_{1/2}$  values for reduction of  $\text{Ru}_2(\text{DmAniF})_3(\text{O}_2\text{CCH}_3)\text{Cl}$  and  $\text{Ru}_2(\text{DmAniF})_3(\text{DMBA-4-C}_2\text{Si}^i\text{Pr}_3)\text{Cl}$  [111]. The authors showed that the two Fc centers of *cis*- $\text{Ru}_2(\text{DmAniF})_2(\text{DMBA-4-C}_2\text{Fc})_2\text{Cl}$  were oxidized at exactly the same potential, indicating that they were not electronically coupled.

### 3.14. Compounds with different “DPHF-type” bridging ligands

Derivatives of  $\text{Ru}_2(\text{DArF})_3(\text{L})\text{Cl}$  and  $\text{Ru}_2(\text{DArF})_3(\text{L})(\text{C}\equiv\text{CPh})$ , synthesized from  $\text{Ru}_2(\text{DArF})_3(\text{O}_2\text{CCH}_3)\text{Cl}$ , where DArF is DmAniF or D(3,5-Cl<sub>2</sub>Ph)F and L is one of the diarylformamidinate ligands containing at least one biphenyl (see Fig. 23) gave voltammograms similar to those of the parent compounds, thus indicating a complete retention of the electronic properties of the diruthenium species upon peripheral modification [112].

### 3.15. Oligomeric compounds with “DPHF-type” bridging ligands

$E_{1/2}$  values for the  $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{5+/4+}$  processes of equatorially linked diruthenium complexes supported by “DPHF-type” bridging ligands [107,113,114] (see Fig. 24) are given in Table 7. As reviewed in the previous section, there is very little electronic communication between the diruthenium units due to the extended separation between the  $\text{Ru}_2$  moieties [4]. For instance, the cyclic voltammogram of  $[\text{Ru}_2(\text{D}(3,5\text{-Cl}_2\text{Ph})\text{F})_3\text{Cl}]_2(1,1'\text{-O}_2\text{CFCO}_2)$  closely resembles that of  $\text{Ru}_2(\text{D}(3,5\text{-Cl}_2\text{Ph})\text{F})_3(\text{O}_2\text{CCH}_3)\text{Cl}$  except that the peak currents are roughly doubled, thus indicating a lack of electronic coupling between the two diruthenium units [114]. A similar lack of electronic coupling has also been reported for  $[\text{Ru}_2(\text{DmAniF})_3\text{Cl}]_2(1,1'\text{-O}_2\text{CFCO}_2)$ ,  $[\text{Ru}_2(\text{D}(3,5\text{-Cl}_2\text{Ph})\text{F})_3\text{Cl}]_2(\text{O}_2\text{CCH}_2\text{CH}=\text{CHCH}_2\text{CO}_2)$ , and the *trans* and *cis* isomers of  $[\text{Ru}_2(\text{D}(3,5\text{-Cl}_2\text{Ph})\text{F})_3\text{Cl}]_2(\text{O}_2\text{C}(\text{CH}_2)_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{CO}_2)$  [113]. The equatorially linked bridged dimers,  $[\text{Ru}_2(\text{DPhF})_3(\text{H}_2\text{O})\text{Cl}]_2(\text{O}_2\text{C})_2$  and  $[\text{Ru}_2(\text{DPhF})_3\text{Cl}]_2(\text{C}_6\text{H}_4\text{-}p\text{-(CO}_2)_2)$ , and the trimers,  $[\text{Ru}_2(\text{DPhF})_3\text{Cl}]_3(\text{C}_6\text{H}_3\text{-1,3,5-(CO}_2)_3)$ ,  $[\text{Ru}_2(\text{DPhF})_3(\text{NCS})]_3(\text{C}_6\text{H}_3\text{-1,3,5-(CO}_2)_3)$  and  $[\text{Ru}_2(\text{DPhF})_3(\text{H}_2\text{O})(\text{SO}_3\text{CF}_3)]_3(\text{C}_6\text{H}_3\text{-1,3,5-(CO}_2)_3)$ , each having a structure similar to that shown in Fig. 24b, were electrochemi-

cally investigated by Barral and coworkers [107], and again there was no evidence of electronic interaction between the diruthenium units in either the dimers or the trimers.  $[\text{Ru}_2(\text{DPhF})_3(\text{H}_2\text{O})(\text{SO}_3\text{CF}_3)]_3(\text{C}_6\text{H}_3\text{-1,3,5-(CO}_2)_3)$  had an additional oxidation process attributed to the presence of two types of diruthenium compounds in equilibrium, rather than two consecutive reversible oxidations of the same compound. The charge delocalization along the equatorial direction thus appears less facile than that along the axial direction. However, there was a higher degree of electronic communication between  $\text{Ru}_2^{5+}$  units of equatorially bridged diruthenium tetrameric complexes containing shorter linkers, namely oxalate bridged networks, as compared to terephthalate linked tetramers [115].

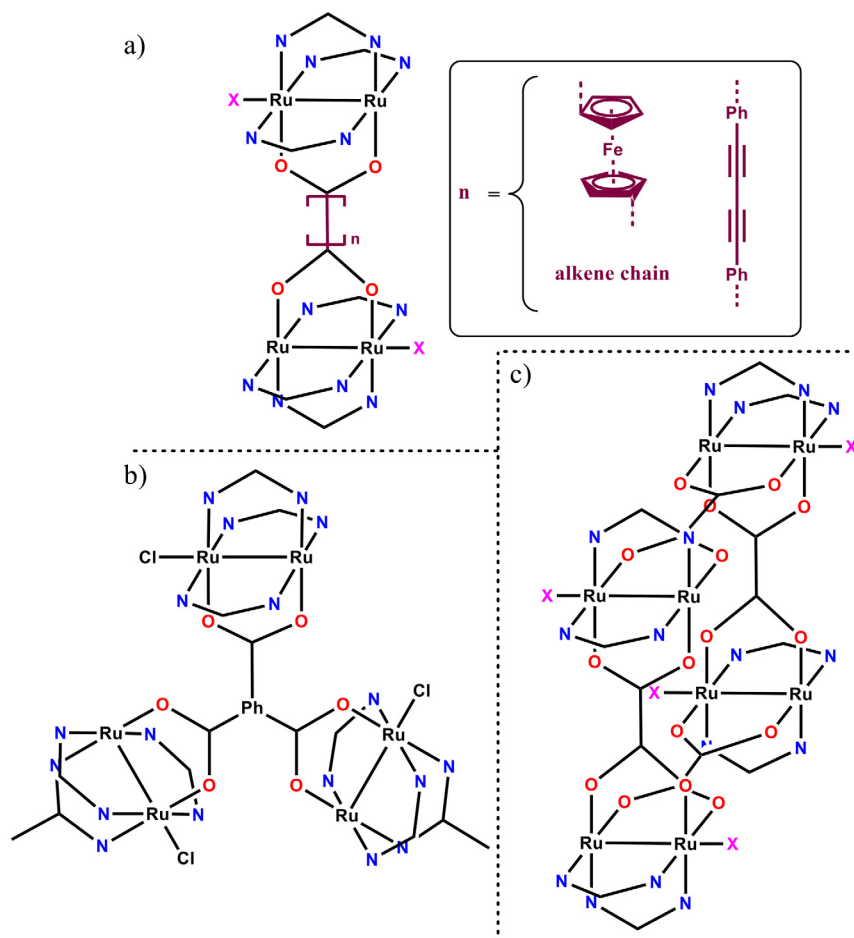
Voltammetric studies of symmetrical and unsymmetrical “dimer of dimers” based on  $\text{Ru}_2[\text{D}(3,5\text{-Cl}_2\text{Ph})\text{F}]_3(\text{DMBA-4-C}_2\text{H})$  type compounds (similar to Fig. 24a) show a lack of interaction between the  $\text{Ru}_2$  units in the symmetrical derivative but a weakly coupled push-pull effect between the two monomeric units in the unsymmetrical derivative [116]. Ren and coworkers synthesized diruthenium complexes with one (Fig. 24a) and two  $\omega$ -alkene- $\alpha$ -carboxylate (Fig. 24c) bridging ligands [113]. Cross metathesis was carried out between two monoolefin compounds, thus resulting in a symmetrical “dimer of dimers,” which, on the basis of voltammetric measurements, behaved as a monomeric system, i.e. there was no electronic coupling between the two monomeric units.

### 3.16. Other types of bridging ligands

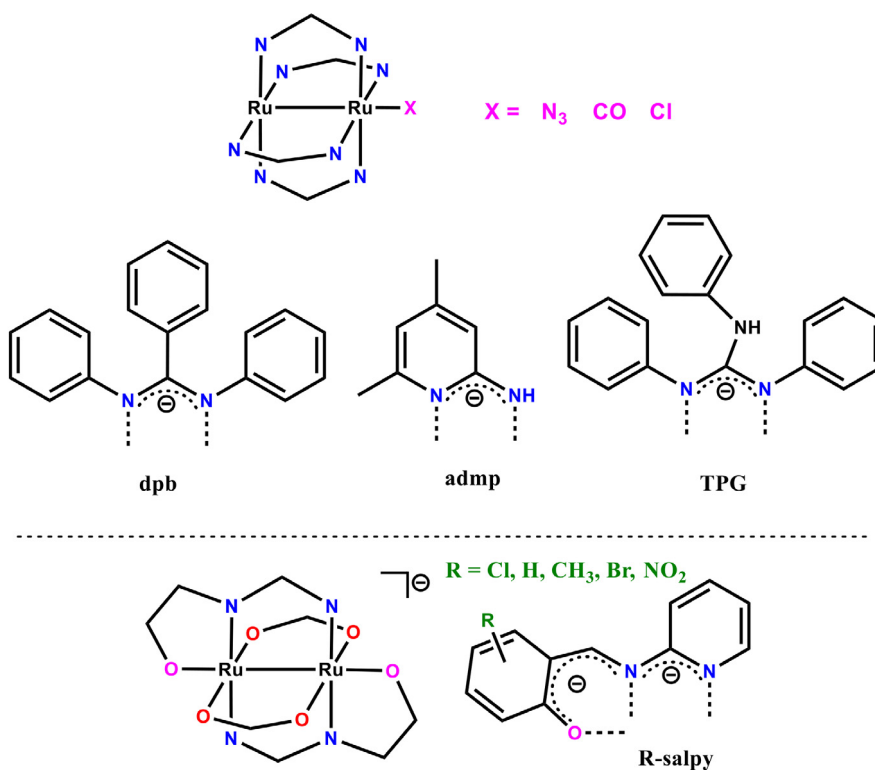
Table 8 lists  $E_{1/2}$  values for the  $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{5+/4+}$  processes of diruthenium complexes with bridging ligands other than “ap-type” or “DPHF-type” (see Fig. 25).

Berry and coworkers [56] characterized the chloro derivatives  $\text{Ru}_2(\text{CH}_3\text{CO}_2)(\text{TPG})_3\text{Cl}$  and  $\text{Ru}_2(\text{TPG})_4\text{Cl}$  as well as their azido analogues,  $\text{Ru}_2(\text{CH}_3\text{CO}_2)(\text{TPG})_3(\text{N}_3)$  and  $\text{Ru}_2(\text{TPG})_4(\text{N}_3)$  (TPG = N, N', N'' – triphenylguanidinate ion). Electrochemical properties of these compounds were examined in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M TBAPF<sub>6</sub>.  $\text{Ru}_2(\text{CH}_3\text{CO}_2)(\text{TPG})_3\text{Cl}$  displays both  $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{5+/4+}$  processes. The oxidation is reversible whereas the reduction is irreversible and involves a loss of the chloride axial ligand after electron transfer. The electrochemistry of  $\text{Ru}_2(\text{TPG})_4\text{Cl}$  in  $\text{CH}_2\text{Cl}_2$  containing TBAPF<sub>6</sub> as supporting electrolyte is more complicated due to an equilibrium involving the chloride axial ligand. Cyclic voltammograms were obtained in solutions containing excess chloride ion and an overall electron transfer mechanism was proposed.

Manowong *et al.* [117] described the spectroscopic and electrochemical properties of  $\text{Ru}_2(\text{dpb})_4\text{Cl}$ ,  $\text{Ru}_2(\text{dpb})_4(\text{CO})$  and  $\text{Ru}_2(\text{dpb})_4(\text{NO})$ .  $\text{Ru}_2(\text{dpb})_4\text{Cl}$  exists in different forms in solution, with each

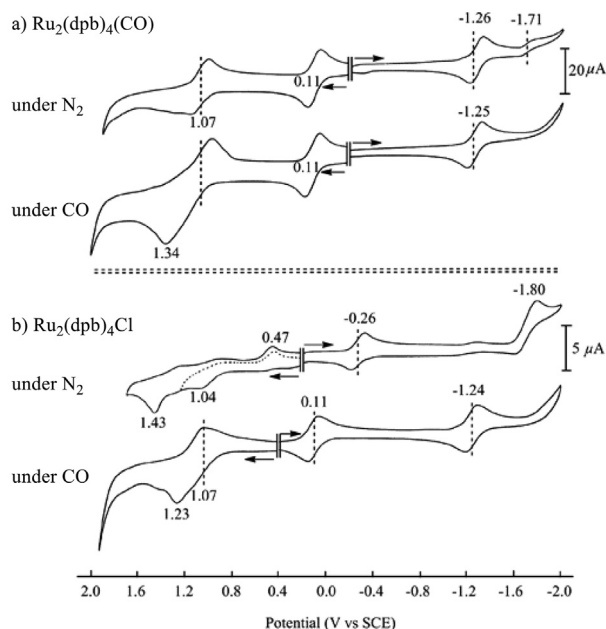


**Fig. 24.** Schematic representation of equatorially linked a) dimeric, b) trimeric and c) tetrameric diruthenium complexes supported by 'DPHF-type' bridging ligands where  $n$  is one of several linkers.



**Fig. 25.** Schematic representation of diruthenium complexes with  $dpb$ ,  $TPG$  and  $R\text{-salpy}$  bridging ligands.





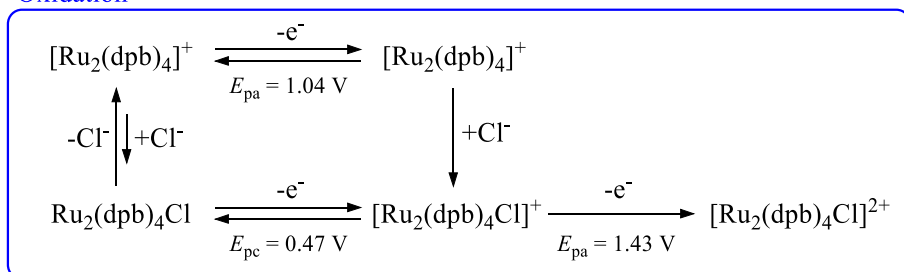
**Fig. 26.** Effect of CO on the cyclic voltammograms of a)  $\text{Ru}_2(\text{dpb})_4(\text{CO})$  and b)  $\text{Ru}_2(\text{dpb})_4\text{Cl}$  in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M TBAP (adapted from reference [117]).

electrode reaction depending upon the solvent and the bound axial group.  $\text{Ru}_2(\text{dpb})_4\text{Cl}$  was converted to  $[\text{Ru}_2(\text{dpb})_4(\text{CO})]^+$  by bubbling CO gas into the solution and the resulting CO adduct was shown to undergo several redox processes in  $\text{CH}_2\text{Cl}_2$ , 0.1 M TBAP under a  $\text{N}_2$  or CO atmosphere. Fig. 26 shows cyclic voltammograms of  $\text{Ru}_2(\text{dpb})_4(\text{CO})$  and  $\text{Ru}_2(\text{dpb})_4\text{Cl}$  under  $\text{N}_2$  and under CO, while Schemes 5 and 6 describe the electron transfer processes of  $\text{Ru}_2(\text{dpb})_4\text{Cl}$  under  $\text{N}_2$  and  $\text{Ru}_2(\text{dpb})_4(\text{CO})$  under CO.  $\text{Ru}_2(\text{dpb})_4(\text{NO})$  was characterized by two successive one-electron reductions and a single one-electron oxidation, all processes involving the diruthenium unit.

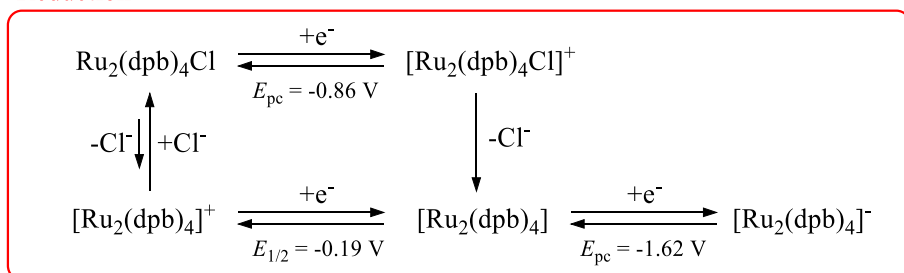
$\text{Ru}_2(\text{CH}_3\text{CO}_2)_3(\text{admpym})\text{Cl}(\text{CH}_3\text{OH})$ , where admpym is 2-amino-4,6-dimethylpyrimidine (see Fig. 27a), undergoes three one-electron transfers assigned to the  $\text{Ru}_2^{5+/6+}$ ,  $\text{Ru}_2^{5+/4+}$  and  $\text{Ru}_2^{4+/3+}$  reactions [118] whereas diruthenium complexes containing two carboxylate bridging ligands and two 5-R-salpy bridging ligands (Fig. 25) display four one-electron transfers attributed to  $\text{Ru}_2^{5+/4+}$ ,  $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{6+/7+}$  along with one ligand-based oxidation [119,120].

Each compound in the series of  $\text{Ru}_2(\text{CH}_3\text{CO}_2)_{4-x}(\text{admp})_x\text{Cl}$  complexes (where  $x = 1, 2, 3$  or 4) (see Fig. 27b), exhibits a one-electron oxidation and a one-electron reduction but this is not the case for  $\text{Ru}_2(\text{admp})_4\text{Cl}$  where only a single one-electron oxidation was observed [121]. This behavior was explained by a change in the magnetic state of the compound. The

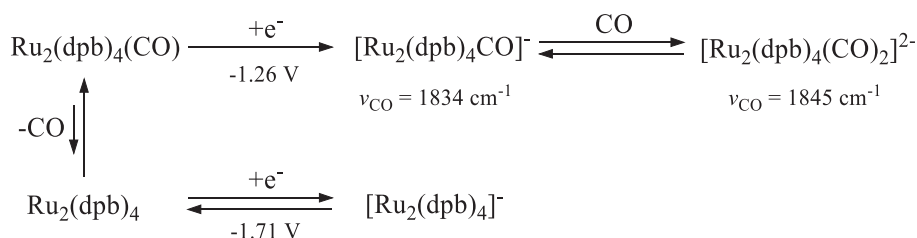
### Oxidation



### Reduction



**Scheme 5.** Electron transfer processes for oxidation and reduction of  $\text{Ru}_2(\text{dpb})_4\text{Cl}$  (adapted from reference [117]).



**Scheme 6.** Electron transfer reactions of  $\text{Ru}_2(\text{dpb})_4(\text{CO})$  under a CO atmosphere (from reference [117]).

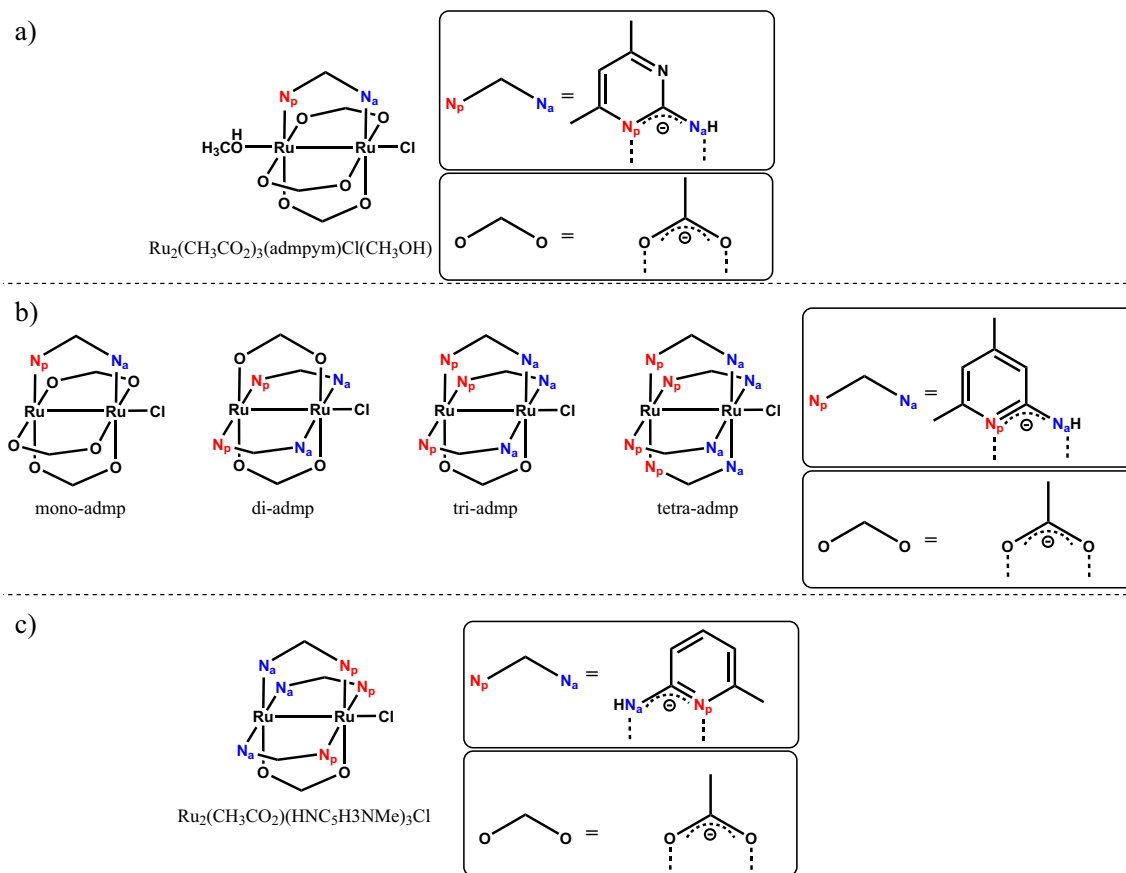


Fig. 27. Schematic representation of a)  $\text{Ru}_2(\text{CH}_3\text{CO}_2)_3(\text{admpym})\text{Cl}(\text{CH}_3\text{OH})$ , b)  $\text{Ru}_2(\text{CH}_3\text{CO}_2)_{4-x}(\text{admp})_x\text{Cl}$  (where  $x = 1, 2, 3$  or  $4$ ) and c)  $\text{Ru}_2(\text{CH}_3\text{CO}_2)(\text{HNC}_5\text{H}_3\text{NMe})_3\text{Cl}$ .

potentials for oxidation and reduction of compounds in the  $\text{Ru}_2(\text{CH}_3\text{CO}_2)_{4-x}(\text{admp})_x\text{Cl}$  series both shifted in an anodic direction upon going from  $x = 1$  to  $x = 3$ . The analogous mixed-ligand  $\text{Ru}_2^{5+}$  complex,  $\text{Ru}_2(\text{CH}_3\text{CO}_2)(\text{HNC}_5\text{H}_3\text{NMe})_3\text{Cl}$ , (see Fig. 27c) was, however, characterized by three metal-based redox processes assigned to  $\text{Ru}_2^{5+/6+}$  for the oxidation and  $\text{Ru}_2^{5+/4+}$  and  $\text{Ru}_2^{4+/3+}$  for the two reductions [57].

### 3.17. $\text{Ru}_2^{6+}$ complexes

Electrochemical data for stable  $\text{Ru}_2^{6+}$  compounds has been restricted to compounds containing N,N' - bridging ligands such as, anilinyridinate (ap), formamidinate (DPHF), benzamidinate (BA), dimethylbenzamidinate (DMBA) and guanidinate (hpp) anions. The majority of electrochemical data on these types of compounds has been reported for diruthenium complexes containing the dimethylbenzamidinate and anilinyridinate bridging ligands and in most cases two alkynyl groups were coordinated to the dimetal unit.

### 3.18. "ap-type" complexes

All reported  $\text{Ru}_2^{6+}$  derivatives with "ap-type" bridging ligands undergo  $\text{Ru}_2^{6+/7+}$ ,  $\text{Ru}_2^{6+/5+}$  and  $\text{Ru}_2^{5+/4+}$  processes and  $E_{1/2}$  values for the  $\text{Ru}_2^{6+/7+}$  and  $\text{Ru}_2^{6+/5+}$  processes of diruthenium complexes with this type of substituted bridging ligand are summarized in Table 9. The first oxidation ranges from  $E_{1/2} = 0.55$  to  $1.35$  V (vs SCE) while  $E_{1/2}$  values for the first reduction range from  $+0.22$  to  $-0.58$  V (vs SCE). This result shows that the  $\text{Ru}_2^{6+/7+}$  and  $\text{Ru}_2^{6+/5+}$  processes can both be significantly tuned by the type of bridging ligands and/or axial ligands because both processes cover a range of 800 mV. The potential separation between the  $\text{Ru}_2^{6+/7+}$  and  $\text{Ru}_2^{6+/5+}$  reactions varies between 0.95 and 1.26 V.

### 3.19. Compounds with alkynyl and cyano axial groups

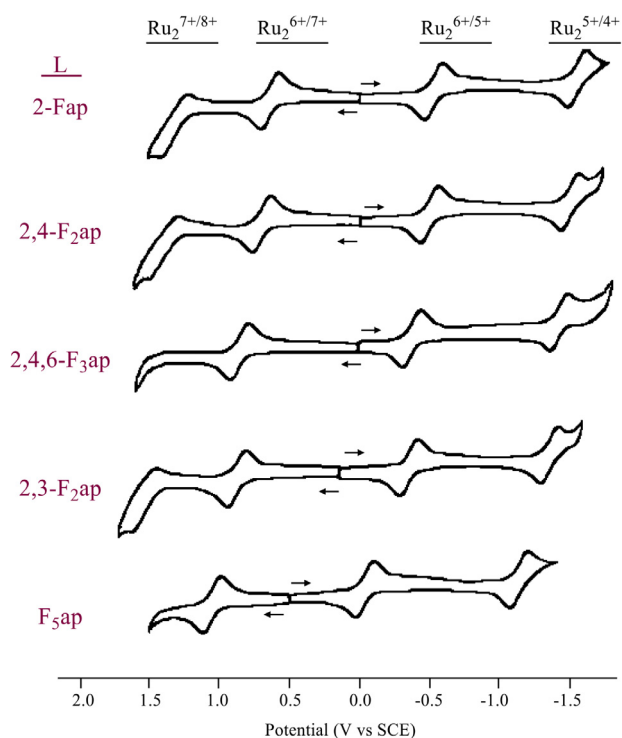
The *bis*-alkynyl [73] and *bis*-cyano [72] tetraanilinyridinate diruthenium complexes typically exhibit a single one-electron oxidation assigned to  $\text{Ru}_2^{6+/7+}$  and one or two one-electron reductions assigned to  $\text{Ru}_2^{5+/4+}$  and  $\text{Ru}_2^{4+/3+}$ . Several dissymmetrical *trans*-ethynyl butadiynyl adducts on a diruthenium core were examined by Ren [122] as to their electrochemical properties in THF. One or two reductions and a single oxidation were seen by cyclic voltammetry. The  $\text{Ru}_2^{6+/7+}$  and  $\text{Ru}_2^{5+/4+}$  reactions were both irreversible for derivatives containing an axial  $\text{C}\equiv\text{CH}$  group. In addition, the three examined compounds, (4,0)  $\text{Ru}_2(\text{F}_5\text{ap})_4(\text{C}\equiv\text{CPh})_2$ , (3,1)  $\text{Ru}_2(\text{F}_5\text{ap})_4(\text{C}\equiv\text{CPh})_2$  and (2,2)  $\text{Ru}_2(\text{F}_5\text{ap})_4(\text{C}\equiv\text{CPh})_2$ , show redox reactions which were sensitive to the type of regioisomer [73].

Ren and coworkers [123] also reported synthesis and electrochemical properties for a series of *trans*- $\text{XC}\equiv\text{C}-\text{Ru}_2(\text{ap})_4-\text{C}\equiv\text{C}-4-\text{C}_6\text{H}_4-\text{P}(\text{O})(\text{O}^i\text{Bu})_2$  complexes where  $\text{X} = \text{Si}(\text{CH}_3)_3$ ,  $\text{C}_2\text{Si}(\text{CH}_3)_3$ ,  $\text{C}_4\text{H}$ , or  $4-\text{C}_6\text{H}_4\text{C}_2\text{Si}(\text{CH}_3)_3$  and *trans*- $(^i\text{BuO})_2(\text{O})\text{P}-\text{C}_6\text{H}_4-4-\text{C}\equiv\text{C}-\text{Ru}_2(\text{ap})_4-\text{C}\equiv\text{C}-4-\text{C}_6\text{H}_4\text{SC}_2\text{H}_4\text{Si}(\text{CH}_3)_3$ . These compounds display at least one reversible oxidation and two reductions (one reversible and the other quasi-reversible) corresponding to  $\text{Ru}_2^{6+/7+}$ ,  $\text{Ru}_2^{6+/5+}$  and  $\text{Ru}_2^{5+/4+}$ , respectively. The derivative with  $\text{X} = \text{C}_4\text{H}$  exhibited an additional redox reaction assigned to the  $\text{Ru}_2^{4+/3+}$  redox couple. Introduction of an organophosphate substituent did not change substantially the redox behavior of the  $\text{Ru}_2$ -*bis*-alkynyl compounds.

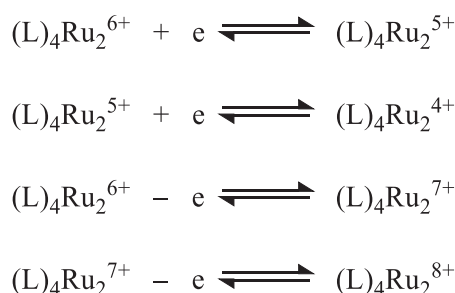
$\text{Ru}_2(\text{O}^i\text{Buap})_4(\text{C}\equiv\text{CPh})_2$  [78],  $\text{Ru}_2((\text{OCH}_3)_2\text{ap})_4((\text{C}\equiv\text{C})_2\text{Si}(\text{CH}_3)_3)_2$  [75] and  $\text{Ru}_2(\text{OCH}_3\text{ap})_4((\text{C}\equiv\text{C})_2\text{SiMe}_3)_2$  [75] (see schematic representation of the bridging ligands in Fig. 7b) exhibit one irreversible  $\text{Ru}_2$ -based oxidation and two reversible  $\text{Ru}_2$ -based reductions. (3,1)  $\text{Ru}_2(\text{ap})_4(\text{C}\equiv\text{CC}_5\text{H}_4\text{N})_2$  undergoes one reversible  $\text{Ru}_2$ -based oxidation and two reversible  $\text{Ru}_2$ -based reductions [80].  $\text{Ru}_2(\text{ap})_4(\text{C}\equiv\text{CR})(\text{C}\equiv\text{CR}')$  where  $\text{R} = 4-\text{Me}_3\text{Si}(\text{CH}_2)_2\text{S}-\text{Ph}$  and

R' = 4-Ph-P(O)(O<sup>t</sup>Bu)<sub>2</sub> displays one reversible oxidation and two reductions, only the first of which is reversible [89]. All of the observed electrode reactions were said to occur at Ru<sub>2</sub>-core.

Kadish, Bear and coworkers synthesized and electrochemically investigated a series of (4,0) and (3,1) derivatives formulated as Ru<sub>2</sub>(L)<sub>4</sub>(C≡CPh)<sub>2</sub> where L = 2-Fap, 2,3-F<sub>2</sub>ap, 2,4-F<sub>2</sub>ap, 2,5-F<sub>2</sub>ap, 3,4-F<sub>2</sub>ap or 2,4,6-F<sub>3</sub>ap [50]. Cyclic voltammograms for the (3,1) derivatives are shown in Fig. 28. Some of the compounds were characterized by two reversible reductions and two reversible oxidations while others displayed two reversible reductions and only a single reversible oxidation. This behavior was independent of the isomer type. A stepwise conversion between compounds with five different dimetal oxidation states Ru<sub>2</sub><sup>3+</sup>, Ru<sub>2</sub><sup>7+</sup>, Ru<sub>2</sub><sup>6+</sup>, Ru<sub>2</sub><sup>5+</sup> and Ru<sub>2</sub><sup>4+</sup>, was therefore electrochemically accomplished (see Scheme 7). The dependence of E<sub>1/2</sub> on the electronic effect of the anionic bridging ligand was quantified by Hammett linear free energy relationships for the two reductions and the first oxidation. The linearity in the slope of the E<sub>1/2</sub> vs Σσ plot (see Eq. (5), Section 2.3) suggested that the same electron transfer mechanism occurred for each redox



**Fig. 28.** Cyclic voltammograms of Ru<sub>2</sub><sup>6+</sup> complexes with the formula Ru<sub>2</sub>(L)<sub>4</sub>(C≡CC<sub>6</sub>H<sub>5</sub>) where L is a substituted ap bridging ligand (adapted from reference [50]).



**Scheme 7.** Electrode reactions of Ru<sub>2</sub><sup>6+</sup> complexes with “ap-type” bridging ligands (from reference [50]).

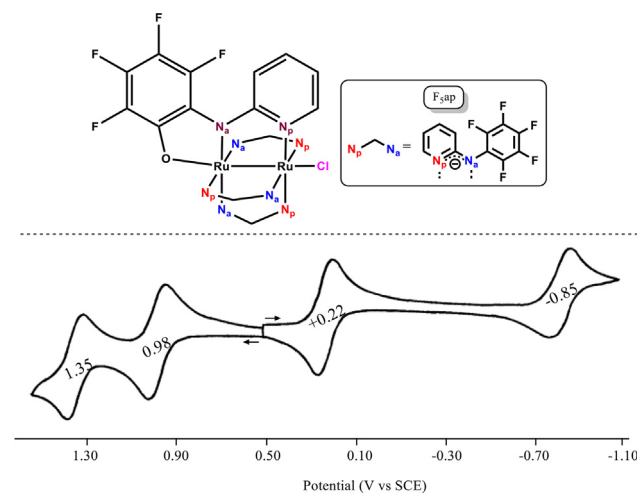
reaction in the two series of isomers. The reactivity constant (ρ) from the linear free-energy relationship for the Ru<sub>2</sub><sup>6+/7+</sup> and Ru<sub>2</sub><sup>5+/6+</sup> redox couples increases upon going from the (4,0) to the (3,1) isomers while the reaction constant for the Ru<sub>2</sub><sup>5+/4+</sup> process shows an opposite trend. The substituent effect on the energy level of the π\* orbital is more sensitive to the isomer type than the substituent effect on the energy level of the δ\* orbital. In addition, the redox reactions of Ru<sub>2</sub>(L)<sub>4</sub>(C≡CPh)<sub>2</sub> where L is an “ap-type” ligand appeared to be more sensitive to the substituent effect than those of Ru<sub>2</sub>(L)<sub>4</sub>(C≡CPh)<sub>2</sub> where L is a “DPHF-type” ligand.

### 3.20. Compounds with a quinone type structure

Several diruthenium complexes with a “quinone-type” bridging ligand, similar to those shown in Fig. 7b, were synthesized by Bear *et al.* [74] and characterized as to their electrochemical properties. For example, as seen in Fig. 29, (3,1) Ru<sub>2</sub>(F<sub>4</sub>Oap)(F<sub>5</sub>ap)<sub>3</sub>Cl [74] undergoes four reversible one-electron transfer reactions; two of which are oxidations and two reductions. Three of the four processes were assigned to the dimetal core while one of the two oxidations (unspecified in the report) was said to involve the bridging ligand due to the “quinone-type” structure of the compound. Two reductions and three oxidations were reported for Ru<sub>2</sub>(F<sub>4</sub>Oap)<sub>2</sub>(F<sub>5</sub>ap)<sub>2</sub> [49] and Ru<sub>2</sub>(F<sub>4</sub>Oap)(F<sub>4</sub>NcNap)(F<sub>5</sub>ap)<sub>2</sub> [49] while two reductions and two oxidations are observed for (3,1) Ru<sub>2</sub>(F<sub>3</sub>ap)<sub>3</sub>(F<sub>2</sub>Oap)(NCS) [81]. The two reductions of all three compounds were attributed to Ru<sub>2</sub><sup>6+/5+</sup> and Ru<sub>2</sub><sup>5+/4+</sup> processes. The first oxidations of Ru<sub>2</sub>(F<sub>4</sub>Oap)<sub>2</sub>(F<sub>5</sub>ap)<sub>2</sub> and Ru<sub>2</sub>(F<sub>4</sub>Oap)(F<sub>4</sub>NcNap)(F<sub>5</sub>ap)<sub>2</sub> were assigned as Ru<sub>2</sub><sup>6+/7+</sup>, but the first oxidation of (3,1) Ru<sub>2</sub>(F<sub>3</sub>ap)<sub>3</sub>(F<sub>2</sub>Oap)(NCS) was attributed to a one-electron abstraction from the dianionic bridging ligand. A similar assignment can also be made for the first oxidation of (3,1) Ru<sub>2</sub>(F<sub>4</sub>Oap)(F<sub>5</sub>ap)<sub>3</sub>Cl [74] since this compound has a chemical structure analogous to that of (3,1) Ru<sub>2</sub>(F<sub>3</sub>ap)<sub>3</sub>(F<sub>2</sub>Oap)(NCS).

### 3.21. Other Ru<sub>2</sub><sup>6+</sup> complexes containing “ap-type” bridging ligands

Kadish and Bear reported the synthesis and electrochemistry of bis-[PcRu(CO)]-[Ru<sub>2</sub>(ap)<sub>4</sub>(C≡CC<sub>5</sub>H<sub>4</sub>N)<sub>2</sub>] (Pc is the dianion of *tert*-butylphthalocyanine), a tetra-ruthenium complex containing two ruthenium(II) phthalocyanines and one metal-metal bonded Ru<sub>2</sub><sup>6+</sup> unit (see Fig. 30) [124]. Cyclic voltammograms of the triad in CH<sub>2</sub>Cl<sub>2</sub> or benzonitrile showed eight redox processes, four of



**Fig. 29.** Schematic representation of Ru<sub>2</sub>(F<sub>4</sub>Oap)(F<sub>5</sub>ap)<sub>3</sub>Cl which exists as the (3,1)-isomer and its corresponding voltammogram in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP (adapted from reference [74]).

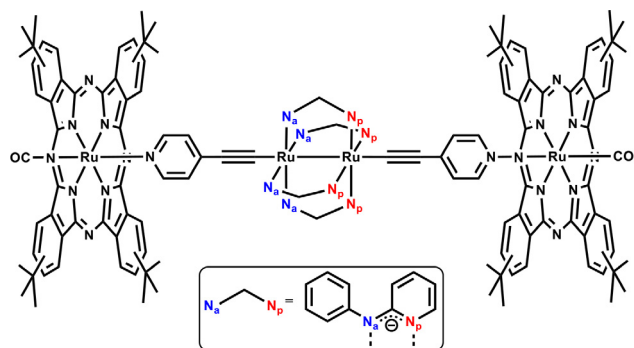


Fig. 30. Schematic representation of bis-[PcRu(CO)]-[Ru<sub>2</sub>(ap)<sub>4</sub>(C≡CC<sub>5</sub>H<sub>4</sub>N)<sub>2</sub>].

which were assigned to occur at the macrocycle of PcRu(CO) and four at the diruthenium unit. Little to no electronic interaction was observed between the diruthenium unit and the externally linked ruthenium phthalocyanines.

### 3.22. "DARF-type" or "DMBA-type" complexes

The formamidinate complexes, Ru<sub>2</sub>(DARF)<sub>4</sub>(C≡CPh)<sub>2</sub> exhibit reversible Ru<sub>2</sub><sup>6+/7+</sup>, Ru<sub>2</sub><sup>6+/5+</sup> and Ru<sub>2</sub><sup>5+/4+</sup> electrode processes [125] and linear correlations were observed between the E<sub>1/2</sub> values of each redox process and the Hammett constants corresponding to the bridging ligand substituents.

Dimethylbenzamidinate complexes containing Cl, BF<sub>4</sub>, NO<sub>3</sub> or an alkynyl group in the axial position were also examined as to their electrochemical properties [126–128]. A similar redox behavior was observed for each compound, independent of the axial ligand, i.e. three one-electron transfer processes assigned as Ru<sub>2</sub><sup>6+/7+</sup>, Ru<sub>2</sub><sup>6+/5+</sup> and Ru<sub>2</sub><sup>5+/4+</sup>. Fig. 31 gives examples of cyclic voltammograms and Scheme 8 illustrates the proposed electron transfer mechanisms of these compounds where processes A, B, C, D and E are shown in Fig. 31. In the case of Ru<sub>2</sub>(DMBA)<sub>4</sub>Cl<sub>2</sub>, the Ru<sub>2</sub><sup>5+/7+</sup> and Ru<sub>2</sub><sup>6+/5+</sup> processes are reversible while the Ru<sub>2</sub><sup>5+/4+</sup> reaction is

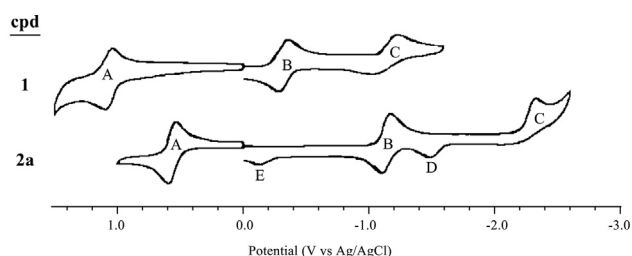
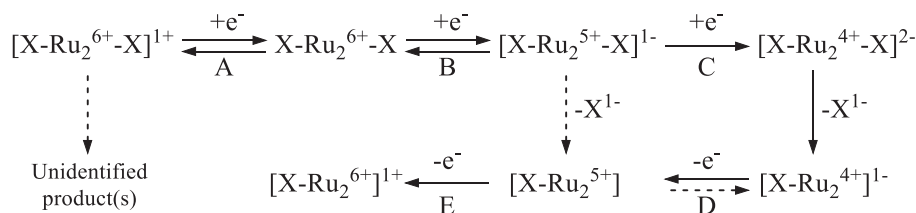


Fig. 31. Cyclic voltammograms of Ru<sub>2</sub><sup>5+</sup> complexes with "DMBA-type" structures where **cpd 1** is Ru<sub>2</sub>(DMBA)<sub>4</sub>Cl<sub>2</sub> and **cpd 2a** is Ru<sub>2</sub>(DMBA)<sub>4</sub>(C<sub>2</sub>Si(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub> (adapted from reference [126]).



Scheme 8. Electrode processes of Ru<sub>2</sub><sup>6+</sup> complexes with "DMBA-type" bridging ligands (from reference [126]).

quasi-reversible [126,127]. The E<sub>1/2</sub> value of each reaction depended on the type of axial ligand, i.e. Cl<sup>-</sup>, BF<sub>4</sub><sup>-</sup> or NO<sub>3</sub><sup>-</sup>.

E<sub>1/2</sub> values for the Ru<sub>2</sub><sup>6+/7+</sup> and Ru<sub>2</sub><sup>6+/5+</sup> reactions of Ru<sub>2</sub><sup>6+</sup> complexes with four "DMBA-type", "DARF-type" or mixed DARF/DMBA bridging ligands are listed in Table 10. Potentials for the Ru<sub>2</sub><sup>6+/7+</sup> processes ranged from E<sub>1/2</sub> = 0.32 to 1.74 V while reversible half-wave potentials for Ru<sub>2</sub><sup>6+/5+</sup> ranged from 0.19 to -1.15 V. The potential separation between the first reduction and first oxidation vary between 1.36 and 1.73 V.

Most electrochemically investigated compounds with a DMBA bridging ligand have been of the type Ru<sub>2</sub>(DMBA)<sub>4</sub>(C≡CAr)(C≡CAr') where Ar and Ar' represents an aryl group. Each compound was characterized by the expected Ru<sub>2</sub><sup>6+/7+</sup> and Ru<sub>2</sub><sup>6+/5+</sup> processes and additional electron transfer processes were also seen for the diruthenium complexes containing electroactive groups on the axial sites. Ru<sub>2</sub>(DMBA)<sub>4</sub>(C≡CAr)<sub>2</sub> where Ar = -4-C<sub>6</sub>H<sub>4</sub>-N<sub>3</sub>Et<sub>2</sub> [86], has a second irreversible oxidation that was proposed to be Ru<sub>2</sub><sup>7+/8+</sup>. Ru<sub>2</sub>(DMBA)<sub>4</sub>(X-gem-DEE)<sub>2</sub> shows an additional reduction beyond the Ru<sub>2</sub><sup>6+/5+</sup> process which was attributed to the Ru<sub>2</sub>-based reduction of a mono-gem-DEE Ru<sub>2</sub> complex generated in solution upon partial dissociation of the gem-DEE ligands after the Ru<sub>2</sub><sup>6+/5+</sup> reaction of the initial compound [129]. The compounds with ferrocenyl-substituted gem-DEE ligands showed additional oxidations assigned to Fc/Fc<sup>+</sup>, but no electronic coupling was observed between the two axial Fc units and the other redox active sites on the molecule as is the case for Ru<sub>2</sub>(DMBA)<sub>4</sub>(C<sub>2n</sub>Fc)-type compounds, thus suggesting that the cross conjugated nature of the gem-DEE linear severely limited the degree of electronic coupling. Oxidations attributed to a TTF moiety of Ru<sub>2</sub>(DMBA)<sub>4</sub>(C≡CTTF)<sub>2</sub> and Ru<sub>2</sub>(DMBA)<sub>4</sub>(C≡CTTF)<sub>2</sub> [130] were also observed in addition to the diruthenium-centered processes. Ru<sub>2</sub>(Y-DMBA)<sub>4</sub>((C≡C)<sub>m</sub>Fc)<sub>2</sub> (where m = 3 or 4 and Y-DMBA is a "DMBA-type" bridging ligand) undergoes one Ru<sub>2</sub>-based reduction and several oxidations, some of which were assigned to Fc/Fc<sup>+</sup> and others to Ru<sub>2</sub><sup>6+/7+</sup> [131]. Ru<sub>2</sub>(DmAniF)<sub>3</sub>(Y-DMBA)(C≡CR)<sub>2</sub> displays one irreversible Ru<sub>2</sub><sup>6+/7+</sup> reaction and two reversible Ru<sub>2</sub><sup>6+/5+</sup> and Ru<sub>2</sub><sup>5+/4+</sup> processes [110]. Ru<sub>2</sub>(DmAniF)<sub>2</sub>(Y-DMBA)<sub>2</sub>(C≡CR)<sub>2</sub> also exhibited these redox processes but they were usually less reversible than those of Ru<sub>2</sub>(DmAniF)<sub>3</sub>(Y-DMBA)(C≡CR)<sub>2</sub> [110].

Ru<sub>2</sub>(DMBA)<sub>4</sub>(L1Si<sup>1</sup>Pr<sub>3</sub>)<sub>2</sub>, Ru<sub>2</sub>(DMBA)<sub>4</sub>(L2Si<sup>1</sup>Pr<sub>3</sub>)<sub>2</sub>, Ru<sub>2</sub>(DMBA)<sub>4</sub>(L1H)<sub>2</sub> and Ru<sub>2</sub>(DMBA)<sub>4</sub>(L2H)<sub>2</sub> whose structures are shown Fig. 32 exhibit the usual Ru<sub>2</sub><sup>6+/7+</sup> and Ru<sub>2</sub><sup>6+/5+</sup> processes [132] but differences can be seen between the compounds in terms of their redox potentials when compared to that of Ru<sub>2</sub>(DMBA)<sub>4</sub>(C<sub>2</sub>SiEt<sub>3</sub>)<sub>2</sub>. Derivatives with the L1 ligand in Fig. 32 were ~200 mV easier to reduce and ~160 mV harder to oxidize than Ru<sub>2</sub>(DMBA)<sub>4</sub>(C<sub>2</sub>SiEt<sub>3</sub>)<sub>2</sub>, showing the electron withdrawing nature of L1. In contrast, the derivatives with an L2 ligand (see Fig. 32) have redox potentials slightly more negative than those of Ru<sub>2</sub>(DMBA)<sub>4</sub>(C<sub>2</sub>SiEt<sub>3</sub>)<sub>2</sub>, and significantly more negative than those of the complexes with the L1 group. The electron donicity thus follows the order: L2 > C<sub>2</sub>SiEt<sub>3</sub> >> L1. This result points out that the initial olefin unit insulates the Ru<sub>2</sub> center from the extended conjugated fragments of L2.

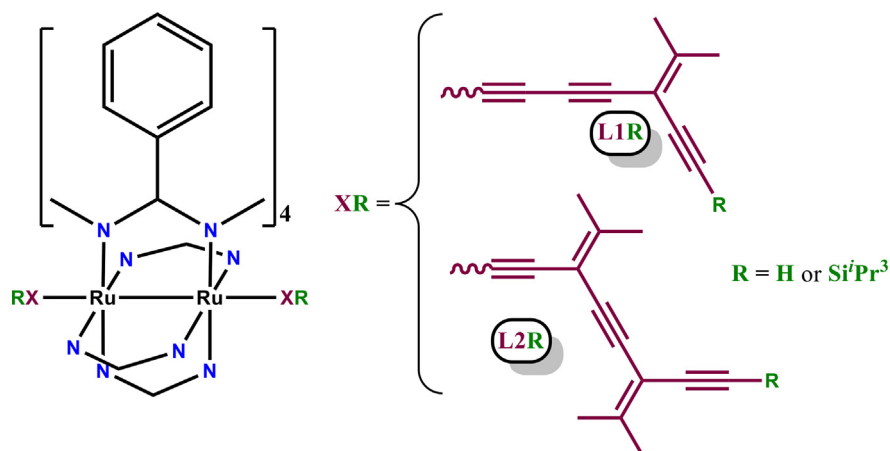


Fig. 32. Schematic representation of  $\text{Ru}_2(\text{DMBA})_4(\text{XR})_2$  where  $\text{X} = \text{L1}$  or  $\text{L2}$  and  $\text{R} = \text{H}$  or  $\text{Si}^i\text{Pr}_3$  (adapted from reference [132]).

Raghavan and Ren reported the synthesis of three bisaryl  $\text{Ru}_2^{\text{6+}}$  complexes of the type  $\text{Ru}_2(\text{DMBA})_4(\text{Ar})_2$  where  $\text{Ar} = \text{C}_6\text{H}_4\text{-4-}^t\text{Bu}$ ,  $\text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_3\text{-3,5-(OCH}_3)_2$  [133]. Each compound is characterized by two oxidations and one reduction. The first oxidation is reversible and assigned as  $\text{Ru}_2^{\text{6+}/7+}$  but the second is irreversible, thus suggesting that it might be an aryl-based process. The reduction is quasi reversible but became irreversible upon repetitive scans, most likely due to a degradation of the compound upon scanning. The  $\text{Ru}_2^{\text{6+}}$  complexes containing aryl groups are much stronger electron donors than their alkynyl counterparts, thus shifting the first oxidation of the aryl derivatives cathodically to a very low, negative potential ( $E_{1/2} = -0.53$  to  $-0.42$  V vs  $\text{Fc}/\text{Fc}^+$ ). Illustration of this effect was seen in the case of  $\text{Ru}_2(\text{DMBA})_4(\text{C}_6\text{H}_4\text{-4-}^t\text{Bu})_2$  which existed in both its  $\text{Ru}_2^{\text{6+}}$  and  $\text{Ru}_2^{\text{7+}}$  forms under ambient conditions.

Trimers containing two “ap-type” diruthenium complexes appended to one “DMBA-type” diruthenium complex have also been prepared [134]. These compounds are formulated as  $\text{Ru}_2(\text{XDMBA})_4(\text{C}\equiv\text{C-R-C}\equiv\text{C-Ru}_2(\text{Yap})_4)_2$  where  $\text{R} = \text{nothing}$ ,  $\text{C}_2$  or  $\text{C}_6\text{H}_4$ ,  $\text{X} = 3\text{-CH}_3\text{O}$  or  $3,5\text{-(CH}_3\text{O)}_2$  and  $\text{Y} = 3\text{-CH}_3\text{O}$  or  $3,5\text{-(CH}_3\text{O)}_2$ . The three compounds where  $\text{R}$  is either nothing or a  $\text{C}_2$  group exhibit pair-wise oxidations and reductions, *i.e.* overlapped electron transfer processes, indicating electron coupling between the two “ap-type”  $\text{Ru}_2$  termini. A slight decrease in the potential difference between the two processes is observed when  $\text{R}$  is a  $\text{C}_2$  group, consistent with an increase in the distance between the two diruthenium ap-type complexes. Electrochemical behavior of the compound with  $\text{R} = \text{C}_6\text{H}_4$  was different from that of the other compounds in that no stepwise oxidation or reduction process were

seen for this compound, thus showing that the introduction of a benzene ring into the molecule clearly diminished the electronic coupling within the trimeric unit.

### 3.2.3. Complexes containing hpp, amp and BAM bridging ligands

Bear, Kadish and coworkers showed that the tetraguanidinate complex,  $\text{Ru}_2(\text{hpp})_4\text{Cl}_2$  (see Fig. 33) undergoes a single one-electron oxidation at  $E_{1/2} = 0.55$  V and a single one electron reduction at  $E_{1/2} = -0.60$  V (vs SCE) which are attributed to  $\text{Ru}_2^{\text{6+}/7+}$  and  $\text{Ru}_2^{\text{6+}/5+}$ , respectively [135]. Those electrode reactions of the  $\text{Ru}_2^{\text{6+}}$  complexes were cathodically shifted with respect to the analogous redox reactions of the *bis*-chloro benzamidinates. Kataoka *et al.* [136] reported that  $\text{Ru}_2(\text{BAM})_4\text{Cl}_2$  (see Fig. 33) undergoes a single electrode reaction in  $\text{CHCl}_3$  at  $E_{1/2} = 0.23$  V (vs SCE). This process was assigned as  $\text{Ru}_2^{\text{6+}/5+}$  but no spectral data was given to confirm this assignment.

Handa and coworkers obtained two  $\text{Ru}_2^{\text{6+}}$  complexes formulated as  $\text{Ru}_2(\text{amp})_4\text{Cl}_2$  and  $\text{Ru}_2(\text{ammp})_4\text{Cl}_2$  (see Fig. 33 for ligand abbreviation) via a reaction between  $\text{Ru}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}$ , Hamp or Hammp and excess LiCl [137].  $\text{Ru}_2(\text{amp})_4\text{Cl}_2$  and  $\text{Ru}_2(\text{ammp})_4\text{Cl}_2$  compounds were both shown to undergo a single reduction at  $-0.08$  and  $-0.18$  V vs SCE in  $\text{CHCl}_3$  containing TBACl as supporting electrolyte. DFT calculations revealed that the reduced species in each complex had a quartet state ( $S = 3/2$ ), consistent with a reduction at the  $\text{Ru}_2$  core involving the  $\delta$  orbitals. A comparison of potentials for the above-mentioned  $\text{Ru}_2^{\text{6+}}$  complexes with hpp, amp, ammp or BAM bridging ligands is given in Table 11.

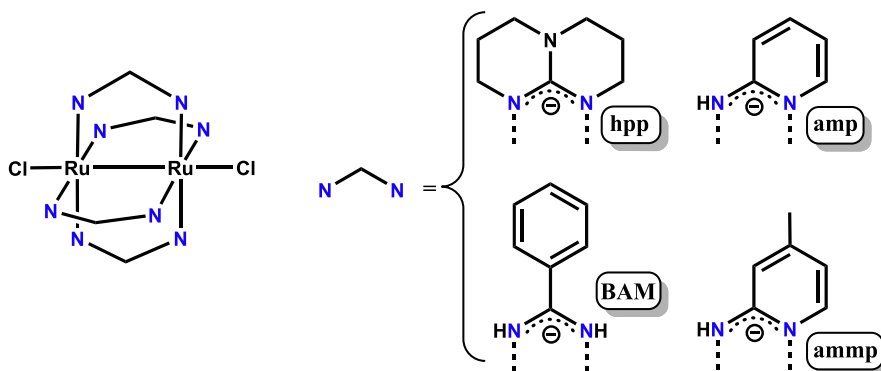


Fig. 33. Schematic representation of  $\text{Ru}_2(\text{L})_4\text{Cl}_2$  where  $\text{L} = \text{hpp}$ , BAM, amp or ammp.



### 3.24. Ru<sub>2</sub><sup>4+</sup> complexes

These diruthenium complexes have been electrochemically investigated for O,O' - and N,N' - bridging ligands, but most studies have involved the O,O' - bridging ligands. Table 12 lists  $E_{1/2}$  values for the Ru<sub>2</sub><sup>4+/5+</sup> process of these compounds. The easiest oxidation was for Ru<sub>2</sub>(CH<sub>3</sub>CO<sub>2</sub>)<sub>4</sub> at  $E_{1/2} = -0.05$  V (vs SCE) in THF containing 0.2 M TBAPF<sub>6</sub> as supporting electrolyte and the most difficult for Ru<sub>2</sub>(CF<sub>3</sub>CO<sub>2</sub>)<sub>4</sub> at  $E_{1/2} = +1.17$  V in CH<sub>2</sub>Cl<sub>2</sub>, 0.2 M TBAPF<sub>6</sub> (vs SCE).

### 3.25. O,O' - bridging ligands

Tetracarboxylate derivatives of the type Ru<sub>2</sub>(RCO<sub>2</sub>)<sub>4</sub> are easily converted to their Ru<sub>2</sub><sup>5+</sup> forms, a reversible or quasi-reversible one-electron oxidation is also at a potential close to where reduction of the related Ru<sub>2</sub><sup>5+</sup> species is observed [37]. The oxidation potentials of these compounds depend upon both properties of the solvent and the R group on the carboxylate bridging ligands. The oxidations are easier in donor solvents with a strong coordination ability and more difficult for compounds with strong electron withdrawing R substituents [51].

Miyasaka et al. tuned the Ru<sub>2</sub><sup>4+/5+</sup> reaction of diruthenium complexes using fluorine atoms on the benzoate ligands [138]. The investigated compounds were formulated as Ru<sub>2</sub>(F<sub>x</sub>PhCO<sub>2</sub>)<sub>4</sub>(THF)<sub>2</sub> where F<sub>x</sub>PhCO<sub>2</sub> is a fluorine-substituted benzoate ligand. The  $E_{1/2}$  for the Ru<sub>2</sub><sup>4+/5+</sup> reaction varied between  $-0.04$  V and  $+0.36$  V vs Ag/Ag<sup>+</sup> for compounds with fluorinated benzoate ligands. The  $E_{1/2}$  values in THF depend upon the electronic and not the structural effect of the *o*-F derivatives, although more than one substituent in the *m*- and *p*-positions shifted  $E_{1/2}$  to more positive potentials. The redox potentials of these complexes correlated well with the HOMO energy level and the electronic effect of F atoms was proposed the main factor controlling  $E_{1/2}$  values of the Ru<sub>2</sub><sup>4+/5+</sup> reaction of the complexes with ligands free from rotational constraint, i.e. complexes in solutions. In a series of *trans*-

heteroleptic (mixed ligand) carboxylate-bridged paddlewheel Ru<sub>2</sub><sup>4+</sup> complexes having the general formula [Ru<sub>2</sub>(2,6-(CF<sub>3</sub>)<sub>2</sub>PhCO<sub>2</sub>)(R-CO<sub>2</sub>)<sub>2</sub>(THF)<sub>2</sub>], (R = CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>, CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>, CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>, C(CH<sub>3</sub>)<sub>3</sub>, F<sub>4</sub>Ph) the type of RCO<sub>2</sub><sup>-</sup> ligands has been shown to strongly influence the redox properties of the complexes [139].

An additional study by Miyasaka and coworkers involving a series of *trans*-heteroleptic Ru<sub>2</sub><sup>4+</sup> complexes containing two 2,6-bis(trifluoromethyl)benzoate bridging ligands and two substituted benzoate bridging ligands, formulated as Ru<sub>2</sub>(2,6-(CF<sub>3</sub>)<sub>2</sub>PhCO<sub>2</sub>)<sub>2</sub>(*p*-RPhCO<sub>2</sub>)<sub>2</sub>(THF)<sub>2</sub>, (R = CF<sub>3</sub>, Cl, F, H, Ph, CH<sub>3</sub>, OCH<sub>3</sub>, OH) established linear relationships between  $E_{1/2}$  of the Ru<sub>2</sub><sup>4+/5+</sup> process and both the pK<sub>a</sub> of the substituted benzoic acids and the Hammett substituent constants of *p*-R group [140].

Ru<sub>2</sub>(CH<sub>3</sub>CO<sub>2</sub>)(TiPB)<sub>2</sub> and Ru<sub>2</sub>(TiPB)<sub>4</sub>, prepared by Patmore and coworkers [65] (see schematic representation of TiPB in Fig. 3), had Ru<sub>2</sub><sup>4+/5+</sup> processes at 0.04 and 0.02 V (vs Ag/AgCl), respectively, thus showing that the homoleptic complex is slightly easier to oxidize than the bis-bis analogue.

### 3.26. N,N' - bridging ligands

Ru<sub>2</sub><sup>4+</sup> complexes with formamidinate, triazenate and naphthyridinate ions as bridging ligands were examined as to their electrochemistry and the measured potentials are given in Table 12. A diamagnetic Ru<sub>2</sub><sup>4+</sup> di-*p*-tolylformamide derivative, Ru<sub>2</sub>(D(4-CH<sub>3</sub>Ph)F)<sub>4</sub> (see Fig. 34a), displays two redox reactions; a reversible oxidation at 1.16 V and a reversible reduction at  $-0.12$  V (vs SCE), but the origin of these two electron transfer processes was unclear [141]. In contrast, Ru<sub>2</sub>(N<sub>3</sub>Ph)<sub>4</sub> (see Fig. 34b) exhibits one reduction and two oxidations and a similar electrochemical behavior is also seen for its CO, NO and Bu<sup>+</sup>NC adducts [37]. The single reduction and first oxidation were one-electron transfers attributed to Ru<sub>2</sub><sup>4+/3+</sup> and Ru<sub>2</sub><sup>4+/5+</sup>, respectively. The second oxidation of these compounds was said to involve the bridging ligands. Ru<sub>2</sub><sup>4+</sup> complexes with naphthyridinate bridging ligands exhibit multiple

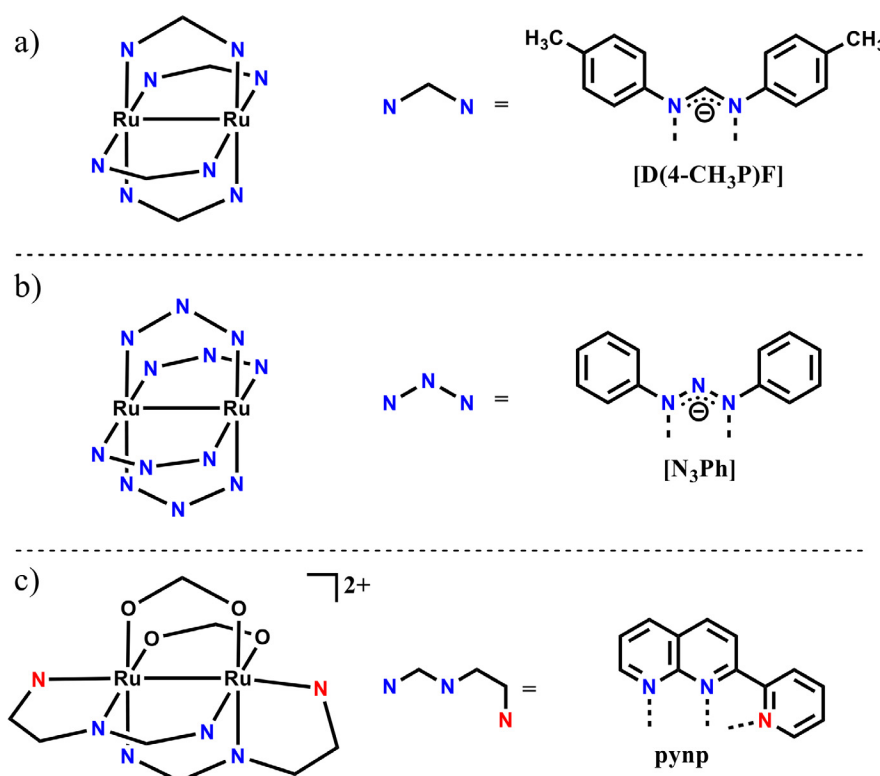
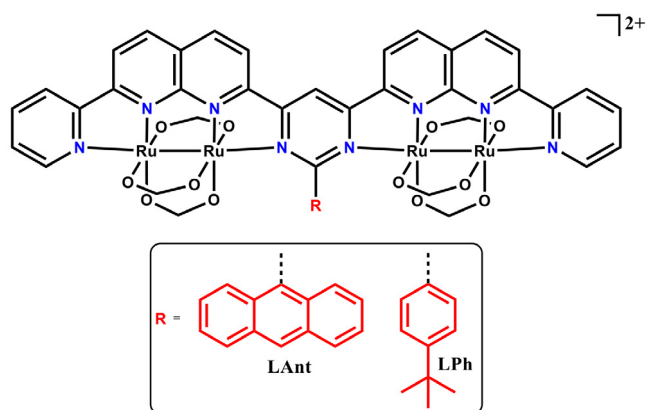


Fig. 34. Schematic representation of Ru<sub>2</sub><sup>4+</sup> complexes with a) formamidinate, b) triazenate and c) naphthyridinate bridging ligands.

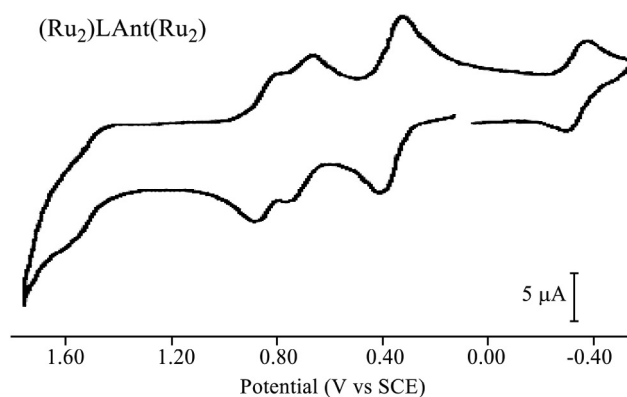
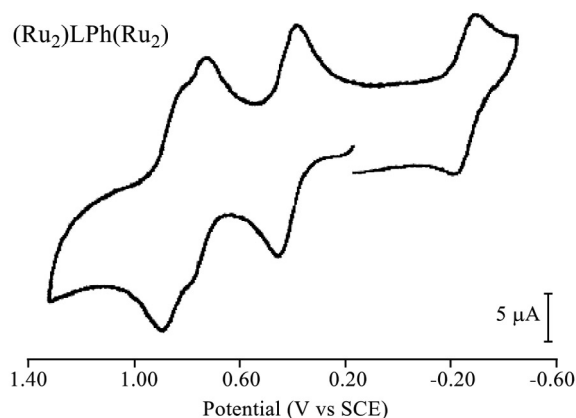


**Fig. 35.** Schematic representation of linked  $\text{Ru}_2^{4+}$  complexes with simplified formula  $[(\text{Ru}_2)\text{LPh}(\text{Ru}_2)]^{2+}$  and  $[(\text{Ru}_2)\text{LAnt}(\text{Ru}_2)]^{2+}$ .

redox processes due to both the dimetal core and the bridging ligands [142]. For example, *cis*- $[\text{Ru}_2(\text{O}_2\text{CCH}_3)_2(\text{pynp})_2](\text{PF}_6)_2$  (see Fig. 34c), undergoes four reversible one-electron ligand-based reductions and one irreversible one-electron metal-based oxidation.

Similar to the  $\text{Ru}_2^{4+}$  DARf derivative depicted in Fig. 34a, Patmore and coworkers examined an air-sensitive diamagnetic  $\text{Ru}_2(\text{Dmof})_4$  complex [143], synthesized from  $\text{Ru}_2(\text{O}_2\text{CCH}_3)_4$ , where Dmof = bis(3,5-dimethoxyphenyl)formamidine and reported two successive oxidations assigned to  $\text{Ru}_2^{4+/5+}$  and  $\text{Ru}_2^{5+/6+}$ . Moreover, spectroscopic techniques demonstrated dioxygen to reversibly bind to the  $\text{Ru}_2^{4+}$  core of  $\text{Ru}_2(\text{Dmof})_4$ .

Lehn and coworkers reported the synthesis and electrochemical characterization of two bridged bis-diruthenium complexes formulated as  $[(\text{Ru}_2)\text{LPh}(\text{Ru}_2)]^{2+}$  and  $[(\text{Ru}_2)\text{LAnt}(\text{Ru}_2)]^{2+}$  (see Fig. 35) [144]. The electrochemistry was examined in acetonitrile containing two different concentrations of TBAP. Fig. 36 shows cyclic voltammograms of the two compounds in  $\text{CH}_3\text{CN}$  at room temperature.  $[(\text{Ru}_2)\text{LPh}(\text{Ru}_2)]^{2+}$  exhibited two oxidations at +0.76 and +0.85 V vs SCE and one reduction at  $-0.31$  V vs SCE while  $[(\text{Ru}_2)\text{LAnt}(\text{Ru}_2)]^{2+}$  was characterized by two oxidations at +0.73 and +0.86 V and one reduction at  $-0.30$  V. There was also a third oxidation at +1.51 V. In both compounds, the first two oxidations were assigned to the  $\text{Ru}_2^{4+/5+}$  process of each interacting dimetallic unit. The third oxidation of  $(\text{Ru}_2)\text{LAnt}(\text{Ru}_2)$  was attributed to the anthracene moiety. The reduction of each compound is described as a bridging ligand-based process. The anthracene-derived ligands were shown to promote a larger electronic coupling than the 4-*tert*-butylphenyl-substituted ligand. The authors proposed that the anthracene moiety contributed to electronic coupling between the redox sites by opening up a new pathway for super-exchange, perhaps by mediating a through space interaction involving anthracene-based orbitals. Indeed, the anthracene based-HOMO was found to be very close in energy to the metal-centered orbitals,



**Fig. 36.** Cyclic voltammograms of linked  $\text{Ru}_2^{4+}$  complexes (adapted from reference [144]).

thus making quite possible a hole-transfer pathway involving the anthracene HOMO [144].

#### 4. Conclusion

It is clear that a significant amount of detailed electrochemical data on diruthenium paddlewheel complexes has been reported over the last six decades, and an organized compilation of this material is necessary for advancing the impact of these metal-metal bonded complexes. Electrochemical data alongside experimental information vital for comparisons from over 120 references have been summarized in tabular form, being organized on the basis of the  $\text{Ru}_2$  core oxidation state and, within this subset, on the basis of anionic bridging ligand type. It is hoped that this review will offer the reader a comprehensive summary regarding decades of diruthenium electrochemistry and provide a nexus for researchers in need of retrieving the desired information.

## 5. Tables of Potentials

**Table 1** $E_{1/2}$  values for the  $\text{Ru}_2^{5+/4+}$  process of  $\text{Ru}_2^{5+}$  complexes with O,O' - bridging ligands.

Compound	$\text{Ru}_2^{5+/4+}$	Solvent	Ref. electrode	Refs.
$\text{Ru}_2(\text{CH}_3\text{CO}_2)_4\text{Cl}$	+0.06	Acetato buffer	SCE	[35]
$\text{Ru}_2(\text{Pr}^n\text{CO}_2)_4\text{Cl}$	0.00, -0.34	$\text{CH}_2\text{Cl}_2$	SCE	[36]
$[\text{Ru}_2(\text{Pr}^n\text{CO}_2)_4\text{Cl}_2]\text{NBu}_4$	-0.46	$\text{CH}_2\text{Cl}_2$	SCE	[68]
$[\text{Ru}_2(\text{Pr}^n\text{CO}_2)_4(\text{H}_2\text{O})_2]\text{BF}_4$	-0.41	$\text{CH}_2\text{Cl}_2$	SCE	[68]
$\text{Ru}_2(\text{CH}_3\text{CO}_2)_2(\text{TiPB})_2\text{Cl}$	+0.05	$\text{CH}_3\text{OH}$	$\text{Ag}/\text{Ag}^+$	[65]
$\text{Ru}_2(\text{CH}_3\text{CO}_2)_2(\text{TiPB})_2(\text{PF}_6)$	+0.05	$\text{CH}_3\text{OH}$	$\text{Ag}/\text{Ag}^+$	[65]
$\text{Ru}_2(\text{TiPB})_4\text{Cl}$	+0.02	$\text{CH}_3\text{OH}$	$\text{Ag}/\text{Ag}^+$	[65]
$\text{Ru}_2(\text{TiPB})_4(\text{PF}_6)$	+0.02	$\text{CH}_3\text{OH}$	$\text{Ag}/\text{Ag}^+$	[65]
$\text{Ru}_2(\text{L}^0)_4\text{Cl}^a$	+0.43	DMF	$\text{Ag}/\text{Ag}^+$	[67]
$\text{Ru}_2(\text{L}^1)_4\text{Cl}^a$	+0.33	DMF	$\text{Ag}/\text{Ag}^+$	[67]
$\text{Ru}_2(\text{L}^2)_4\text{Cl}^a$	+0.18	DMF	$\text{Ag}/\text{Ag}^+$	[67]
$[\text{Ru}_2(\text{FcCO}_2)_4]^+(\text{PF}_6)$	-0.49	$\text{CH}_2\text{Cl}_2$	$\text{Fc}/\text{Fc}^+$	[66]

<sup>a</sup> See  $\text{L}^0$ ,  $\text{L}^1$  and  $\text{L}^2$  structure in Fig. 3; <sup>b</sup>  $E_p$  value at 0.05 V/s**Table 2** $E_{1/2}$  values for the  $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{5+/4+}$  processes of  $\text{Ru}_2^{5+}$  complexes with N,O - bridging ligands.

Compound	$\text{Ru}_2^{5+/6+}$	$\text{Ru}_2^{5+/4+}$	$\Delta^a$ (V)	Solvent	Ref. electrode	Refs.
$\text{Ru}_2((\text{CH}_3)_3\text{CCONH})_4\text{Cl}^c$	0.68, 0.93, 1.09			$\text{CH}_2\text{Cl}_2$	$\text{Ag}/\text{AgCl}/\text{Cl}^-$ , $\text{CH}_2\text{Cl}_2$	[39]
$\text{Ru}_2((\text{CH}_3)_3\text{CCONH})_4\text{Cl}^c$	0.85			DMSO	$\text{Ag}/\text{AgCl}/\text{Cl}^-$ , $\text{CH}_2\text{Cl}_2$	[39]
$\text{Ru}_2((\text{CH}_3)_3\text{CCONH})_4\text{Cl}^c$	1.01, 1.07			$\text{CH}_3\text{OH}$	$\text{Ag}/\text{AgCl}/\text{Cl}^-$ , $\text{CH}_2\text{Cl}_2$	[39]
$\text{Ru}_2(\text{CF}_3\text{CONH})_4\text{Cl}^d$		-0.03, -0.33		$\text{CH}_2\text{Cl}_2$	SCE	[38]
$\text{Ru}_2(\text{CF}_3\text{CONH})_4\text{Cl}^d$		0.00, -0.06, -0.30		$\text{CH}_3\text{CN}$	SCE	[38]
$\text{Ru}_2(\text{CF}_3\text{CONH})_4\text{Cl}^d$		-0.22		DMF	SCE	[38]
$\text{Ru}_2(\text{CH}_3\text{CONH})_4\text{Cl}$	0.47	-0.96	1.43	DMSO	SCE	[40]
$\text{Ru}_2(\text{PhCONH})_4\text{Cl}$		-0.66		DMSO	$\text{Ag}/\text{AgCl}$	[43]
$\text{Ru}_2(\text{PhCONH})_4(\text{BF}_4)(\text{H}_2\text{O})$	1.12	-0.5 <sup>b</sup>		$\text{CH}_2\text{Cl}_2$	SCE	[70]
$\text{Ru}_2((\text{CH}_3)_2\text{CHCONH})_4\text{Cl}^c$	0.53			$\text{CH}_3\text{CN}$	$\text{Ag}/\text{AgCl}$	[22]
$\text{Ru}_2(\text{CH}_3\text{CH}_2\text{CONH})_4\text{Cl}^c$	0.77			$\text{CH}_3\text{CN}$	$\text{Ag}/\text{AgCl}$	[22]
$\text{Ru}_2(\text{fhp})_4\text{Cl}$	1.68	-0.01	1.69	$\text{CH}_2\text{Cl}_2$	$\text{Ag}/\text{AgCl}$	[41]
$\text{Ru}_2(\text{chp})_4\text{Cl}$	1.13	0.10	1.23	$\text{CH}_2\text{Cl}_2$	$\text{Ag}/\text{AgCl}$	[42]
$\text{Ru}_2(\text{chp})_4\text{Cl}$	1.61 <sup>b</sup>	0.09, 0.34		$\text{CH}_3\text{CN}$	$\text{Ag}/\text{AgCl}$	[42]

<sup>a</sup> Potential difference between the  $\text{Ru}_2^{5+/4+}$  and  $\text{Ru}_2^{5+/6+}$  processes; <sup>b</sup>  $E_p$  value at 0.1 V/s; <sup>c</sup> Only the oxidation of the compound was examined; <sup>d</sup> Only reduction of the compound was examined.

**Table 3** $E_{1/2}$  values for the  $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{5+/4+}$  reactions of  $\text{Ru}_2^{5+}$  complexes with ap or substituted ap bridging ligands containing  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{CN}^-$ , NO or  $\text{NCS}^-$  as an axial ligand.

Compound	$\text{Ru}_2^{5+/6+}$	$\text{Ru}_2^{5+/4+}$	$\Delta^a$ (V)	solvent	Ref. electrode	Refs.
(4,0) $\text{Ru}_2(2\text{-CH}_3\text{ap})_4\text{Cl}$	0.41	-0.89	1.30	$\text{CH}_2\text{Cl}_2$	SCE	[71]
(4,0) $\text{Ru}_2(\text{ap})_4\text{Cl}$	0.37	-0.86	1.23	$\text{CH}_2\text{Cl}_2$	SCE	[71]
(4,0) $\text{Ru}_2(2,4,6\text{-F}_3\text{ap})_4\text{Cl}$	0.69	-0.67	1.36	$\text{CH}_2\text{Cl}_2$	SCE	[71]
(4,0) $\text{Ru}_2(2,5\text{-F}_2\text{ap})_4\text{Cl}$	0.65	-0.63	1.28	$\text{CH}_2\text{Cl}_2$	SCE	[71]
(4,0) $\text{Ru}_2(\text{F}_5\text{ap})_4\text{Cl}$	0.95	-0.35	1.30	$\text{CH}_2\text{Cl}_2$	SCE	[71]
(4,0) $\text{Ru}_2(3\text{-OCH}_3\text{ap})_4\text{Cl}$	0.56	-0.76	1.32	THF	Ag/AgCl	[77]
(4,0) $\text{Ru}_2(3,5\text{-(OCH}_3)_2\text{ap})_4\text{Cl}$	0.57	-0.75	1.32	THF	Ag/AgCl	[75]
(4,0) $\text{Ru}_2(3\text{-O}^i\text{Prap})_4\text{Cl}$	0.55	-0.77	1.32	THF	Ag/AgCl	[77]
(4,0) $\text{Ru}_2(3\text{-O}^t\text{Buap})_4\text{Cl}$	0.58	-0.77	1.35	THF	Ag/AgCl	[78]
(4,0) $\text{Ru}_2(\text{ap})_4\text{F}$	0.47	-0.98	1.45	THF	Ag/AgCl	[77]
(3,1) $\text{Ru}_2(2\text{-Fap})_4\text{Cl}$	0.47	-0.77	1.24	$\text{CH}_2\text{Cl}_2$	SCE	[71]
(3,1) $\text{Ru}_2(2,6\text{-F}_2\text{ap})_4\text{Cl}$	0.56	-0.72	1.28	$\text{CH}_2\text{Cl}_2$	SCE	[71]
(3,1) $\text{Ru}_2(2,4,6\text{-F}_3\text{ap})_4\text{Cl}$	0.62	-0.65	1.27	$\text{CH}_2\text{Cl}_2$	SCE	[71]
(3,1) $\text{Ru}_2(\text{F}_5\text{ap})_4\text{Cl}$	0.78	-0.35	1.14	$\text{CH}_2\text{Cl}_2$	SCE	[71]
(3,1) $\text{Ru}_2(\text{ap-4-CH}_3)_4\text{Cl}$	0.28	-0.83	1.11	$\text{CH}_2\text{Cl}_2$	SCE	[46]
(4,0) $\text{Ru}_2(\text{ap})_4(\text{CN})$	0.43	-0.73	1.16	$\text{CH}_2\text{Cl}_2$	SCE	[72]
(4,0) $\text{Ru}_2(\text{CH}_3\text{ap})_4(\text{CN})$	0.46	-0.73	1.19	$\text{CH}_2\text{Cl}_2$	SCE	[72]
(3,1) $\text{Ru}_2(\text{Fap})_4(\text{CN})$	0.52	-0.68	1.20	$\text{CH}_2\text{Cl}_2$	SCE	[72]
(3,1) $\text{Ru}_2(2\text{-Fap})_4\text{Cl}(\text{NO})$	1.14	-0.03	1.17	$\text{CH}_2\text{Cl}_2$	SCE	[79]
(3,1) $\text{Ru}_2(2,4,6\text{-F}_3\text{ap})_4(\text{NCS})$	0.72	-0.58	1.30	$\text{CH}_2\text{Cl}_2$	SCE	[81]
(2,2) trans $\text{Ru}_2(\text{F}_5\text{ap})_4\text{Cl}$	0.63	-0.45	1.08	$\text{CH}_2\text{Cl}_2$	SCE	[73]
$\text{Ru}_2(\text{CH}_3\text{CO}_2)_3(2\text{-Fap})\text{Cl}$	1.14	-0.41	1.55	$\text{CH}_2\text{Cl}_2$	SCE	[55]
$\text{Ru}_2(\text{CH}_3\text{CO}_2)_2(2\text{-Fap})_2\text{Cl}$	0.78	-0.55	1.33	$\text{CH}_2\text{Cl}_2$	SCE	[55]
$\text{Ru}_2(\text{CH}_3\text{CO}_2)(2\text{-Fap})_3\text{Cl}$	0.60	-0.72	1.32	$\text{CH}_2\text{Cl}_2$	SCE	[55]
$\text{Ru}_2(\text{CH}_3\text{CO}_2)(2,4,6\text{-(CH}_3)_3\text{ap})_3\text{Cl}$	0.48	-0.81	1.29	$\text{CH}_2\text{Cl}_2$	SCE	[48]
$\text{Ru}_2(\text{CH}_3\text{CO}_2)(2,4,6\text{-(CH}_3)_3\text{ap})_3\text{Cl}$	0.41	-0.60	1.01	$\text{CH}_3\text{CN}$	SCE	[48]
$\text{Ru}_2(\text{CH}_3\text{CO}_2)_3(\text{F}_5\text{ap})\text{Cl}$		-0.26		DMSO	SCE	[84]
$\text{Ru}_2(\text{CH}_3\text{CO}_2)_3(2,4,6\text{-F}_3\text{ap})\text{Cl}$		-0.31		DMSO	SCE	[84]
$\text{Ru}_2(\text{CH}_3\text{CO}_2)_3(\text{ap})\text{Cl}$		-0.36		DMSO	SCE	[84]
$\text{Ru}_2(\text{CH}_3\text{CO}_2)_3(2\text{-CH}_3\text{ap})\text{Cl}$		-0.38		DMSO	SCE	[84]
$\text{Ru}_2(\text{CH}_3\text{CO}_2)_3(2,6\text{-(CH}_3)_2\text{ap})\text{Cl}$		-0.39		DMSO	SCE	[84]
$\text{Ru}_2(\text{CH}_3\text{CO}_2)_3(2,4,6\text{-(CH}_3)_3\text{ap})\text{Cl}$		-0.40		DMSO	SCE	[84]

<sup>a</sup> Potential separation between the  $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{5+/4+}$  processes.

**Table 4** $E_{1/2}$  (V vs Ag/AgCl) values for the  $Ru_2^{5+/6+}$  and  $Ru_2^{5+/4+}$  processes of  $Ru_2^{5+}$  complexes with ap or substituted "ap-type" bridging ligands and an acetylide or aryl axial group.

Compound	$Ru_2^{5+/6+}$	$Ru_2^{5+/4+}$	$\Delta^a$ (V)	solvent	Refs.
$Ru_2(ap)_4(C\equiv C-p-C_6H_4-N_3Et_2)$	0.34	-1.10	1.44	THF	[86]
$Ru_2(ap)_4(C\equiv C-p-C_6H_4-P(O)(O^iBu)_2)$	0.48	-0.80	1.28	THF	[89]
$Ru_2(ap)_4(C\equiv C-m-C_6H_4NH_2)$	0.43	-0.88	1.31	THF	[87]
$Ru_2(ap)_4(C\equiv C-p-C_6H_4NH_2)$	0.39	-0.93	1.32	THF	[87]
$Ru_2(ap)_4(C\equiv C-p-C_6H_4N=CH-C_6H_5)$	0.44	-0.86	1.30	THF	[88]
$Ru_2(ap)_4(C\equiv C-p-C_6H_4N=CH-p-C_6H_4Br)$	0.44	-0.85	1.29	THF	[88]
$Ru_2(ap)_4(C\equiv C-p-C_6H_4N=CH-p-C_6H_4CHO)$	0.44	-0.85	1.29	THF	[88]
$Ru_2(ap)_4(C\equiv C-m-C_6H_4N=CH-C_6H_5)$	0.42	-0.86	1.28	THF	[88]
$Ru_2(ap)_4(C\equiv C-m-C_6H_4N=CH-p-C_6H_4Br)$	0.44	-0.87	1.31	THF	[88]
$Ru_2(ap)_4(C\equiv C-m-C_6H_4N=CH-p-C_6H_4CHO)$	0.44	-0.86	1.30	THF	[88]
$Ru_2(ap)_4(C\equiv C-Si(CH_3)_3)$	0.20	-1.02	1.22	$CH_2Cl_2$	[85]
$Ru_2(ap)_4(C\equiv C-H)$	0.20	-1.03	1.23	$CH_2Cl_2$	[85]
$Ru_2(ap)_4(C\equiv C-CH_2OCH_3)$	0.20	-1.05	1.25	$CH_2Cl_2$	[85]
$Ru_2(ap)_4(C\equiv C-C_6H_5)$	0.19	-1.04	1.23	$CH_2Cl_2$	[85]
$Ru_2(ap)_4(C\equiv C-Si^iPr_3)$	0.45	-0.88	1.33	THF	[91]
$Ru_2(ap)_4(C\equiv C-C_6H_5)$	0.44	-0.88	1.32	THF	[91]
$Ru_2(ap)_4((C\equiv C)_2Fc)$	0.48	-0.76	1.24	THF	[91]
$Ru_2(ap)_4((C\equiv C)_2-Si^iPr_3)$	0.49	-0.74	1.23	THF	[91]
$Ru_2(ap)_4((C\equiv C)_2-C_6H_5)$	0.48	-0.74	1.22	THF	[91]
$Ru_2(ap)_4((C\equiv C)_3-Si^iPr_3)$	0.51	-0.62	1.13	THF	[91]
$Ru_2(ap)_4((C\equiv C)_3-C_6H_5)$	0.50	-0.65	1.15	THF	[91]
$Ru_2(ap)_4((C\equiv C)_4-Si^iPr_3)$	0.54	-0.56	1.10	THF	[91]
$Ru_2(ap)_4((C\equiv C)_4-C_6H_5)$	0.54	-0.55	1.09	THF	[91]
$Ru_2(ap)_4((C\equiv C)_5-C_6H_5)$	0.54	-0.50	1.04	THF	[91]
$Ru_2(ap)_4(Si^iPr_3-gem-DEE)$	0.44	-0.86	1.30	THF	[90]
$Ru_2(ap)_4(H-gem-DEE)$	0.43	-0.87	1.30	THF	[90]
$Ru_2(3,5-(OCH_3)_2ap)_4(C\equiv C-p-C_6H_4NH_2)$	0.39	-0.91	1.30	THF	[87]
$Ru_2(3,5-(OCH_3)_2ap)_4(C\equiv C-m-C_6H_4NH_2)$	0.42	-0.87	1.29	THF	[87]
$Ru_2(3,5-(OCH_3)_2ap)_4((C\equiv C)_2-Si(CH_3)_3)$	0.49	-0.72	1.21	THF	[75]
$Ru_2(3,5-(OCH_3)_2ap)_4(H-gem-DEE)$	0.43	-0.87	1.30	THF	[90]
$Ru_2(3,5-(OCH_3)_2ap)_4(Si^iPr_3-gem-DEE)$	0.44	-0.86	1.30	THF	[90]
$Ru_2(3-OCH_3ap)_4((C\equiv C)_2-Si(CH_3)_3)$	0.50	-0.72	1.22	THF	[75]
$Ru_2(3-OCH_3ap)_4((C\equiv C)Fc)$	0.42	-0.89	1.31	THF	[75]
$Ru_2(3-O^iBuap)_4(C\equiv C-C_6H_5)$	0.45	-0.87	1.32	THF	[78]
$Ru_2(3-O^iBuap)_4(C\equiv C-Si^iPr_3)$	0.47	-0.87	1.34	THF	[78]
$Ru_2(ap)_4(C_6H_4-p-N(CH_3)_2)^b$	-0.38	-1.62	1.28	$CH_2Cl_2$	[82]
$Ru_2(ap)_4(C_6H_4-p-N,N-(C_6H_4-p-OCH_3)_2)^b$	-0.34	-1.58	1.24	$CH_2Cl_2$	[82]
$Ru_2(ap)_4(C_6H_4-p^iBu)^b$	-0.31	-1.57	1.26	$CH_2Cl_2$	[82]
$Ru_2(ap)_4(C_6H_4-p-H)^b$	-0.30	-1.56	1.26	$CH_2Cl_2$	[82]
$Ru_2(ap)_4(C_6H_4-p-Br)^b$	-0.29	-1.50	1.21	$CH_2Cl_2$	[82]
$Ru_2(ap)_4(C_6H_4-p-CF_3)^b$	-0.24	-1.47	1.23	$CH_2Cl_2$	[82]
$Ru_2(ap)_4(C_6H_4-p-N(CH_3)_2)^b$	-0.27	-1.62	1.35	THF	[83]
$Ru_2(ap)_4(C_6H_4-p-N(CH_3)_2)(CO)^b$	-0.34	-1.39	1.05	THF	[83]

<sup>a</sup> Potential separation between  $Ru_2^{5+/4+}$  and  $Ru_2^{5+/6+}$  processes. <sup>b</sup> Potential given as V vs  $Fc^{+/0}$ **Table 5** $E_{1/2}$  values (V vs Ag/AgCl) for the  $Ru_2^{5+/6+}$  and  $Ru_2^{5+/4+}$  processes of axially linked  $Ru_2^{5+}$  complexes with ap or substituted "ap-type" bridging ligand.

Compound	$Ru_2^{5+/6+}$	$Ru_2^{5+/4+}$	$\Delta^a$ (V)	solvent	Refs.
$1,1'-[Ru_2(ap)_4(C\equiv C)]_2Fc$	0.43	-0.88 <sup>b</sup>	1.31	THF	[98]
$[Ru_2(ap)_4](C\equiv C)[Ru_2(ap)_4]$	0.22, 0.51	-0.89, -1.56	1.11	THF	[92]
$[Ru_2(ap)_4](C\equiv C)_2[Ru_2(ap)_4]$	0.33, 0.49	-0.78, -1.17	1.11	THF	[92]
$[Ru_2(ap)_4](C\equiv C)_4[Ru_2(ap)_4]$	0.45, 0.54	-0.63, -0.78	1.08	THF	[93]
$[Ru_2(ap)_4](C\equiv C)_6[Ru_2(ap)_4]$	0.52	-0.49, -0.62	1.01	THF	[93]
$[Ru_2(3-O^iBuap)_4](C\equiv C)_4[Ru_2(3-O^iBuap)_4]$	0.54	-0.61, -0.77	1.15	THF	[95]
$[Ru_2(3-O^iBuap)_4](C\equiv C)_5[Ru_2(ap)_4]$	0.55	-0.54, -0.68	1.09	THF	[95]
$[Ru_2(3-O^iBuap)_4](C\equiv C)_6[Ru_2(3-O^iBuap)_4]$	0.58	-0.46, -0.59	1.04	THF	[95]
$[Ru_2(3-O^iBuap)_4](C\equiv C)_7[Ru_2(ap)_4]$	0.58	-0.42, -0.54	1.00	THF	[95]
$[Ru_2(3-O^iBuap)_4](C\equiv C)_8[Ru_2(3-O^iBuap)_4]$	0.58	-0.41, -0.51	0.99	THF	[95]
$[Ru_2(3-O^iBuap)_4](C\equiv C)_9[Ru_2(ap)_4]$	0.58	-0.38, -0.47	0.96	THF	[95]
$[Ru_2(3-O^iBuap)_4](C\equiv C)_{10}[Ru_2(3-O^iBuap)_4]$	0.59	-0.34, -0.43	0.93	THF	[95]
$[Ru_2(3,5-(OCH_3)_2ap)_4]_2(\mu-C_6)^c$	0.44, 0.54	-0.65, -0.83	1.09	THF	[94]
$[Ru_2(3-O^iBuap)_4]_2(\mu-C_6)^c$	0.44, 0.54	-0.67, -0.87	1.11	THF	[94]
$[Ru_2(ap)_4]_2(\mu-C_6) \{ \mu-C\equiv CC(C(CN)_2)-C(C(CN)_2)C\equiv C \}^c$	0.66 <sup>b</sup>	-1.32 <sup>b</sup>	1.98	THF	[94]
$[Ru_2(3,5-(OCH_3)_2ap)_4]_2(\mu-C_6) \{ \mu-C\equiv CC(C(CN)_2)-C(C(CN)_2)C\equiv C \}^c$	0.65 <sup>b</sup>	-1.34 <sup>b</sup>	1.99	THF	[94]
$[Ru_2(3-O^iBuap)_4]_2(\mu-C\equiv CC(C(CN)_2)-C(C(CN)_2)C\equiv C)^c$	0.66 <sup>b</sup>	-1.34 <sup>b</sup>	2.00	THF	[94]
$[Ru_2(ap)_4]_2(\mu-C_6)(Co_2(dppm)(CO)_4)^c$	0.37, 0.50	-0.86, -1.05	1.23	THF	[94]
$[Ru_2(3,5-(OCH_3)_2ap)_4]_2(\mu-C_6)(Co_2(dppm)(CO)_4)^c$	0.37, 0.49	-0.84, -1.04	1.21	THF	[94]
$[Ru_2(3-O^iBuap)_4]_2(\mu-C_6)(Co_2(dppm)(CO)_4)^c$	0.35, 0.49	-0.87, -1.07	1.22	THF	[94]

<sup>a</sup> Potential separation in V between the  $Ru_2^{5+/6+}$  and  $Ru_2^{5+/4+}$  processes. <sup>b</sup> Two-electron process. <sup>c</sup> Potentials measured from differential pulse (DPV).



**Table 6**  
E<sub>1/2</sub> values for the Ru<sub>2</sub><sup>5+/6+</sup> and Ru<sub>2</sub><sup>5+/4+</sup> processes of monomeric Ru<sub>2</sub><sup>5+</sup> complexes containing "DPHF-type" bridging ligands.

Compound	Ru <sub>2</sub> <sup>5+/6+</sup>	Ru <sub>2</sub> <sup>5+/4+</sup>	Δ <sup>a</sup> (V)	Solvent	Ref. elec.	Refs.
Ru <sub>2</sub> (DPhF) <sub>4</sub> Cl	0.54	-0.64 <sup>b</sup>		CH <sub>2</sub> Cl <sub>2</sub>	SCE	[99]
Ru <sub>2</sub> (D(4-OCH <sub>3</sub> Ph)F) <sub>4</sub> Cl	0.52	-0.75 <sup>b</sup>		CH <sub>2</sub> Cl <sub>2</sub>	Ag/AgCl	[100]
Ru <sub>2</sub> (D(4-CH <sub>3</sub> Ph)F) <sub>4</sub> Cl	0.57	-0.71 <sup>b</sup>		CH <sub>2</sub> Cl <sub>2</sub>	Ag/AgCl	[100]
Ru <sub>2</sub> (D(4-ClPh)F) <sub>4</sub> Cl	0.85	-0.41 <sup>b</sup>		CH <sub>2</sub> Cl <sub>2</sub>	Ag/AgCl	[100]
Ru <sub>2</sub> (D(3-ClPh)F) <sub>4</sub> Cl	0.95	-0.33 <sup>b</sup>		CH <sub>2</sub> Cl <sub>2</sub>	Ag/AgCl	[100]
Ru <sub>2</sub> (D(3-CF <sub>3</sub> Ph)F) <sub>4</sub> Cl	1.07	-0.34 <sup>b</sup>		CH <sub>2</sub> Cl <sub>2</sub>	Ag/AgCl	[100]
Ru <sub>2</sub> (D(3,4-Cl <sub>2</sub> Ph)F) <sub>4</sub> Cl	1.11	-0.25 <sup>b</sup>		CH <sub>2</sub> Cl <sub>2</sub>	Ag/AgCl	[100]
Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>4</sub> Cl	1.21	-0.23 <sup>b</sup>		CH <sub>2</sub> Cl <sub>2</sub>	Ag/AgCl	[100]
Ru <sub>2</sub> (DPhF) <sub>4</sub> (C≡CPh)	0.33	-0.89		CH <sub>2</sub> Cl <sub>2</sub>	SCE	[99]
Ru <sub>2</sub> (D(4-ClPh)F) <sub>4</sub> (C≡CPh)	0.64	-0.54		CH <sub>2</sub> Cl <sub>2</sub>	Ag/AgCl	[101]
Ru <sub>2</sub> (D(3-ClPh)F) <sub>4</sub> (C≡CPh)	0.72	-0.51		CH <sub>2</sub> Cl <sub>2</sub>	Ag/AgCl	[101]
Ru <sub>2</sub> (D(3-CF <sub>3</sub> Ph)F) <sub>4</sub> (C≡CPh)	0.81	-0.41		CH <sub>2</sub> Cl <sub>2</sub>	Ag/AgCl	[101]
Ru <sub>2</sub> (D(3,4-Cl <sub>2</sub> Ph)F) <sub>4</sub> (C≡CPh)		-0.30		CH <sub>2</sub> Cl <sub>2</sub>	Ag/AgCl	[101]
Ru <sub>2</sub> (D(3,4-Cl <sub>2</sub> Ph)F) <sub>4</sub> (C≡CPh)	1.00 <sup>b</sup>	-0.23		CH <sub>2</sub> Cl <sub>2</sub>	Ag/AgCl	[101]
Ru <sub>2</sub> (DPhF) <sub>3</sub> (O <sub>2</sub> CC <sub>6</sub> H <sub>5</sub> )Cl	0.76	-0.62 <sup>b</sup>		CH <sub>2</sub> Cl <sub>2</sub>	Ag/AgCl	[107]
Ru <sub>2</sub> (DPhF) <sub>3</sub> (O <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> -pCN)Cl	0.78	-0.56 <sup>b</sup>		CH <sub>2</sub> Cl <sub>2</sub>	Ag/AgCl	[107]
[Ru <sub>2</sub> (DPhF) <sub>3</sub> (CH <sub>3</sub> CO <sub>2</sub> )(CO)](BF <sub>4</sub> )	0.93	-0.11	1.04	CH <sub>2</sub> Cl <sub>2</sub>	SCE	[45]
Ru <sub>2</sub> (DPhF) <sub>4</sub> (N <sub>3</sub> )	0.43	-0.76 <sup>b</sup>		CH <sub>2</sub> Cl <sub>2</sub>	Ag/AgCl	[111]
Ru <sub>2</sub> (D(4-OCH <sub>3</sub> Ph)F) <sub>4</sub> (N <sub>3</sub> )	0.29	-0.86 <sup>b</sup>		CH <sub>2</sub> Cl <sub>2</sub>	Ag/AgCl	[111]
Ru <sub>2</sub> (D(4-CH <sub>3</sub> Ph)F) <sub>4</sub> (N <sub>3</sub> )	0.40	-0.82 <sup>b</sup>		CH <sub>2</sub> Cl <sub>2</sub>	Ag/AgCl	[111]
Ru <sub>2</sub> (D(3-OCH <sub>3</sub> Ph)F) <sub>4</sub> (N <sub>3</sub> )	0.46	-0.74 <sup>b</sup>		CH <sub>2</sub> Cl <sub>2</sub>	Ag/AgCl	[111]
Ru <sub>2</sub> (D(3-ClPh)F) <sub>4</sub> (N <sub>3</sub> )	0.71	-0.49 <sup>b</sup>		CH <sub>2</sub> Cl <sub>2</sub>	Ag/AgCl	[111]
Ru <sub>2</sub> (D(3-CF <sub>3</sub> Ph)F) <sub>4</sub> (N <sub>3</sub> )	0.79	-0.46 <sup>b</sup>		CH <sub>2</sub> Cl <sub>2</sub>	Ag/AgCl	[111]
Ru <sub>2</sub> (D(4-CF <sub>3</sub> Ph)F) <sub>4</sub> (N <sub>3</sub> )	0.80	-0.40 <sup>b</sup>		CH <sub>2</sub> Cl <sub>2</sub>	Ag/AgCl	[111]
Ru <sub>2</sub> (D(3,4-Cl <sub>2</sub> Ph)F) <sub>4</sub> (N <sub>3</sub> )	0.80	-0.40 <sup>b</sup>		CH <sub>2</sub> Cl <sub>2</sub>	Ag/AgCl	[111]
Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>4</sub> (N <sub>3</sub> )	0.93	-0.31 <sup>b</sup>		CH <sub>2</sub> Cl <sub>2</sub>	Ag/AgCl	[111]
Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>3</sub> (4-vinylbenzoate)Cl	1.09	-0.20	1.29	THF	Ag/AgCl	[104]
Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>3</sub> (5-hexenoate)Cl	1.11	-0.22	1.33	THF	Ag/AgCl	[104]
Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>3</sub> (6-heptenoate)Cl	1.10	-0.23	1.33	THF	Ag/AgCl	[104]
Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>3</sub> (O <sub>2</sub> CFC)Cl	1.16	-0.24	1.40	THF	Ag/AgCl	[102]
Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>3</sub> (O <sub>2</sub> CCH <sub>2</sub> CH = CH <sub>2</sub> )Cl	1.09	-0.21	1.30	THF	Ag/AgCl	[113]
Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>3</sub> (O <sub>2</sub> C(CH <sub>2</sub> ) <sub>2</sub> CH = CH <sub>2</sub> )Cl	1.10	-0.22	1.32	THF	Ag/AgCl	[113]
Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>3</sub> (D(4-I-Ph)F)Cl	1.02	-0.27 <sup>b</sup>		THF	Ag/AgCl	[112]
Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>3</sub> (D(4-Ph-Ph)F)Cl	1.00	-0.26 <sup>b</sup>		THF	Ag/AgCl	[112]
Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>3</sub> (D(4-CH <sub>3</sub> C(O)Ph-Ph)F)Cl	1.00	-0.24 <sup>b</sup>		THF	Ag/AgCl	[112]
[Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>3</sub> (D(4-I-Ph)F)](C≡CPh)	0.87	-0.30	1.17	THF	Ag/AgCl	[112]
[Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>3</sub> (D(4-Ph-Ph)F)](C≡CPh)	0.85	-0.34	1.19	THF	Ag/AgCl	[112]
[Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>3</sub> (D(4-CH <sub>3</sub> C(O)Ph-Ph)F)](C≡CPh)	0.86	-0.32	1.18	THF	Ag/AgCl	[112]
Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>2</sub> (O <sub>2</sub> CFC) <sub>2</sub> Cl	1.35	-0.33	1.68	THF	Ag/AgCl	[102]
Cis-Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>2</sub> (4-vinylbenzoate) <sub>2</sub> Cl	1.17	-0.27	1.44	THF	Ag/AgCl	[104]
Cis-Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>2</sub> (O <sub>2</sub> CCH <sub>2</sub> CH = CH <sub>2</sub> ) <sub>2</sub> Cl	1.15	-0.29	1.44	THF	Ag/AgCl	[113]
Cis-Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>2</sub> (O <sub>2</sub> C(CH <sub>2</sub> ) <sub>2</sub> CH = CH <sub>2</sub> ) <sub>2</sub> Cl	1.15	-0.30	1.45	THF	Ag/AgCl	[113]
Cis-Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>2</sub> (O <sub>2</sub> C(CH <sub>2</sub> ) <sub>3</sub> CH = CH <sub>2</sub> ) <sub>2</sub> Cl	1.15	-0.30	1.45	THF	Ag/AgCl	[113]
Cis-Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>2</sub> (O <sub>2</sub> C(CH <sub>2</sub> ) <sub>2</sub> CH = CH(CH <sub>2</sub> ) <sub>2</sub> CO <sub>2</sub> ) <sub>2</sub> Cl	1.13	-0.33	1.46	THF	Ag/AgCl	[113]
Cis-Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>2</sub> (O <sub>2</sub> C(CH <sub>2</sub> ) <sub>3</sub> CH = CH(CH <sub>2</sub> ) <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> Cl	1.13	-0.30	1.43	THF	Ag/AgCl	[113]
Ru <sub>2</sub> (DmAniF) <sub>3</sub> (O <sub>2</sub> CCH <sub>3</sub> )Cl	0.74	-0.52 <sup>b</sup>		THF	Ag/AgCl	[110]
Ru <sub>2</sub> (DmAniF) <sub>3</sub> (O <sub>2</sub> CFC)Cl	0.87	-0.61 <sup>b</sup>		THF	Ag/AgCl	[102]
Ru <sub>2</sub> (DmAniF) <sub>3</sub> (O <sub>2</sub> C(CH <sub>2</sub> ) <sub>3</sub> CH = CH <sub>2</sub> )Cl	0.73	-0.58 <sup>b</sup>		THF	Ag/AgCl	[105]
Ru <sub>2</sub> (DmAniF) <sub>3</sub> (O <sub>2</sub> C(CH <sub>2</sub> ) <sub>4</sub> CH = CH <sub>2</sub> )Cl	0.73	-0.57 <sup>b</sup>		THF	Ag/AgCl	[105]
Ru <sub>2</sub> (DmAniF) <sub>3</sub> (O <sub>2</sub> C(CH <sub>2</sub> ) <sub>8</sub> CH = CH <sub>2</sub> )Cl	0.74	-0.55 <sup>b</sup>		THF	Ag/AgCl	[105]
Ru <sub>2</sub> (DmAniF) <sub>3</sub> (DMBA-I)Cl	0.55	-0.67 <sup>b</sup>		THF	Ag/AgCl	[110]
Ru <sub>2</sub> (DmAniF) <sub>3</sub> (4-Ph-PhNCNPh)Cl	0.65	-0.65 <sup>b</sup>		THF	Ag/AgCl	[112]
Ru <sub>2</sub> (DmAniF) <sub>3</sub> (D(4-Ph-Ph)F)Cl	0.66	-0.59 <sup>b</sup>		THF	Ag/AgCl	[112]
Ru <sub>2</sub> (DmAniF) <sub>3</sub> (DMBA-4-C <sub>2</sub> Si <sup>1</sup> Pr <sub>3</sub> )Cl	0.57	-0.67 <sup>b</sup>		THF	Ag/AgCl	[110]
Ru <sub>2</sub> (DmAniF) <sub>3</sub> (DMBA-4-C <sub>2</sub> Fc)Cl	0.54	-0.73 <sup>b</sup>		THF	Ag/AgCl	[110]
[Ru <sub>2</sub> (DmAniF) <sub>3</sub> (D(4-I-Ph)F)](C≡CPh)	0.57	-0.68	1.25	THF	Ag/AgCl	[112]
[Ru <sub>2</sub> (DmAniF) <sub>3</sub> (D(4-Ph-Ph)F)](C≡CPh)	0.52	-0.71	1.23	THF	Ag/AgCl	[112]
Ru <sub>2</sub> (DmAniF) <sub>2</sub> (O <sub>2</sub> CFC) <sub>2</sub> Cl	1.23	-0.61 <sup>b</sup>		THF	Ag/AgCl	[102]
Ru <sub>2</sub> (DmAniF) <sub>2</sub> (O <sub>2</sub> C(CH <sub>2</sub> ) <sub>3</sub> CH = CH <sub>2</sub> ) <sub>2</sub> Cl	0.80	-0.54 <sup>b</sup>		THF	Ag/AgCl	[105]
Ru <sub>2</sub> (DmAniF) <sub>2</sub> (O <sub>2</sub> C(CH <sub>2</sub> ) <sub>8</sub> CH = CH <sub>2</sub> ) <sub>2</sub> Cl	0.86	-0.58 <sup>b</sup>		THF	Ag/AgCl	[105]
Ru <sub>2</sub> (DmAniF) <sub>2</sub> (O <sub>2</sub> C(CH <sub>2</sub> ) <sub>3</sub> CH = ) <sub>2</sub> Cl	0.80	-0.58 <sup>b</sup>		THF	Ag/AgCl	[105]
Ru <sub>2</sub> (DmAniF) <sub>2</sub> (O <sub>2</sub> C(CH <sub>2</sub> ) <sub>8</sub> CH = ) <sub>2</sub> Cl	0.85	-0.60 <sup>b</sup>		THF	Ag/AgCl	[105]
Cis-Ru <sub>2</sub> (DmAniF) <sub>2</sub> (DMBA-I) <sub>2</sub> Cl	0.41	-0.79 <sup>b</sup>		THF	Ag/AgCl	[110]
Cis-Ru <sub>2</sub> (DmAniF) <sub>2</sub> (DMBA-4-C <sub>2</sub> Fc) <sub>2</sub> Cl	0.39	-0.85 <sup>b</sup>		THF	Ag/AgCl	[110]
[Ru <sub>2</sub> (η <sup>2</sup> -DmAniF) <sub>2</sub> (μ-DmAniF) <sub>2</sub> (μ-OAc)(μ-O)]	0.38	-0.68	1.06	THF	Ag/AgCl	[108]
cis-[Ru <sub>2</sub> (4-CH <sub>3</sub> -pF) <sub>2</sub> (O <sub>2</sub> CCH <sub>3</sub> ) <sub>2</sub> Cl]	0.32 <sup>b</sup>	-1.33 <sup>b</sup>		THF	Fc/Fc <sup>+</sup>	[106]
trans-[Ru <sub>2</sub> (2,6-Et <sub>2</sub> -pF) <sub>2</sub> (O <sub>2</sub> CCH <sub>3</sub> ) <sub>2</sub> Cl]	0.55 <sup>b</sup>	-1.45 <sup>b</sup>		THF	Fc/Fc <sup>+</sup>	[106]
Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>3</sub> (DMBA-N <sub>3</sub> -D <sub>0</sub> )Cl <sup>c</sup>	0.90	-0.35	1.25	THF	Ag/AgCl	[109]
Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>3</sub> (DMBA-N <sub>3</sub> -D <sub>1</sub> )Cl <sup>c</sup>	0.91	-0.34	1.25	THF	Ag/AgCl	[109]
Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>3</sub> (DMBA-N <sub>3</sub> -D <sub>2</sub> )Cl <sup>c</sup>	0.88	-0.35	1.23	THF	Ag/AgCl	[109]
Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>3</sub> (DMBA-N <sub>3</sub> -D <sub>3</sub> )Cl <sup>c</sup>	0.90	-0.38	1.25	THF	Ag/AgCl	[109]
Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>2</sub> (DMBA-N <sub>3</sub> -D <sub>0</sub> ) <sub>2</sub> Cl <sup>c</sup>	0.86	-0.53	1.39	THF	Ag/AgCl	[109]
Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>2</sub> (DMBA-N <sub>3</sub> -D <sub>1</sub> ) <sub>2</sub> Cl <sup>c</sup>	0.87	-0.54	1.41	THF	Ag/AgCl	[109]
Ru <sub>2</sub> (D(3,5-Cl <sub>2</sub> Ph)F) <sub>2</sub> (DMBA-N <sub>3</sub> -D <sub>2</sub> ) <sub>2</sub> Cl <sup>c</sup>	0.90	-0.52	1.42	THF	Ag/AgCl	[109]

<sup>a</sup> Potential difference in V between the Ru<sub>2</sub><sup>5+/6+</sup> and Ru<sub>2</sub><sup>5+/4+</sup> processes. <sup>b</sup> E<sub>pc</sub> (or E<sub>pa</sub>) value at 0.1 V/s. <sup>c</sup> See Fig. 22 for structure of dendron (D<sub>n</sub>)

**Table 7** $E_{1/2}$  values (V vs Ag/AgCl) for the  $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{5+/4+}$  processes of equatorially linked  $\text{Ru}_2^{5+}$  complexes containing "DPhF-type" bridging ligands.

Compound	$\text{Ru}_2^{5+/6+}$	$\text{Ru}_2^{5+/4+}$	$\Delta^a$ (V)	Solvent	Refs.
$[\text{Ru}_2(\text{D}(3,5\text{-Cl}_2\text{Ph})\text{F})_3\text{Cl}]_2(1,1'\text{-O}_2\text{CFCO}_2)$	1.10	-0.22	1.32	THF	[114]
$[\text{Ru}_2(\text{D}(3,5\text{-Cl}_2\text{Ph})\text{F})_3\text{Cl}]_2(\text{O}_2\text{CCH}_2\text{CH}=\text{CHCH}_2\text{CO}_2)$	1.08	-0.21	1.29	THF	[113]
Trans- $[\text{Ru}_2(\text{D}(3,5\text{-Cl}_2\text{Ph})\text{F})_3\text{Cl}]_2(\text{O}_2\text{C}(\text{CH}_2)_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{CO}_2)$	1.07	-0.22	1.29	THF	[113]
Cis- $[\text{Ru}_2(\text{D}(3,5\text{-Cl}_2\text{Ph})\text{F})_3\text{Cl}]_2(\text{O}_2\text{C}(\text{CH}_2)_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{CO}_2)$	1.07	-0.22	1.29	THF	[113]
$[\text{Ru}_2(\text{DmAniF})_3\text{Cl}]_2(1,1'\text{-O}_2\text{CFCO}_2)$	0.74	-0.68	1.42	THF	[114]
$[\text{Ru}_2(\text{DPhF})_3(\text{H}_2\text{O})\text{Cl}]_2(\text{O}_2\text{C})_2$	0.80	-0.55 <sup>b</sup>		$\text{CH}_2\text{Cl}_2$	[107]
$[\text{Ru}_2(\text{DPhF})_3\text{Cl}]_2(\text{C}_6\text{H}_4\text{-p}-(\text{CO}_2)_2)$	0.77	-0.58 <sup>b</sup>		$\text{CH}_2\text{Cl}_2$	[107]
$[\text{Ru}_2(\text{DPhF})_3\text{Cl}]_3(\text{C}_6\text{H}_3\text{-1,3,5}-(\text{CO}_2)_3)$	0.77	-0.54 <sup>b</sup>		$\text{CH}_2\text{Cl}_2$	[107]
$[\text{Ru}_2(\text{DPhF})_3(\text{NCS})]_3(\text{C}_6\text{H}_3\text{-1,3,5}-(\text{CO}_2)_3)$	0.85			$\text{CH}_2\text{Cl}_2$	[107]
$[\text{Ru}_2(\text{DPhF})_3(\text{H}_2\text{O})(\text{SO}_3\text{CF}_3)]_3(\text{C}_6\text{H}_3\text{-1,3,5}-(\text{CO}_2)_3)$	0.79	-0.20	0.99	$\text{CH}_2\text{Cl}_2$	[107]
$\{[\text{cis-Ru}_2(\mu\text{-DAniF})_2\text{Cl}(\text{H}_2\text{O})](\mu\text{-oxalate})\}_4^c$	1.05, 0.87	-0.48, -0.70		$\text{CH}_2\text{Cl}_2$	[115]
$\{[\text{cis-Ru}_2(\mu\text{-DAniF})_2\text{Cl}(4\text{-Bu}^t\text{py})](\mu\text{-terephthalate})\}_4^c$	0.80	-0.58	1.38	$\text{CH}_2\text{Cl}_2$	[115]
$[\text{Ru}_2\text{Cl}(\text{D}(3,5\text{-Cl}_2\text{Ph})\text{F})_3]-(\text{DMBA-C}_4\text{-DMBA})-[\text{Ru}_2\text{Cl}(\text{D}(3,5\text{-Cl}_2\text{Ph})\text{F})_3]$	0.90 <sup>d</sup>	-0.36 <sup>d</sup>	1.26	THF	[116]
$[\text{Ru}_2\text{Cl}(\text{D}(3,5\text{-Cl}_2\text{Ph})\text{F})_3]-(\text{DMBA-C}_2\text{-DMBA})-[\text{Ru}_2\text{Cl}(\text{DmAniF})_3]$	0.89, 0.55	-0.42 <sup>b</sup> , -0.73 <sup>b</sup>		THF	[116]

<sup>a</sup> Potential separation in V between the  $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{5+/4+}$  processes. <sup>b</sup>  $E_{pc}$  at 0.1 V/s. <sup>c</sup> Potentials obtained from DPV. <sup>d</sup> two electron transfer process**Table 8** $E_{1/2}$  values for the  $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{5+/4+}$  processes of  $\text{Ru}_2^{5+}$  complexes with bridging ligands other than those with "ap-type" or "DPhF-type" bridging ligands.

Compound	$\text{Ru}_2^{5+/6+}$	$\text{Ru}_2^{5+/4+}$	$\Delta^a$ (V)	Solvent	Ref. electrode	Refs.
$\text{Ru}_2(\text{dpb})_4\text{Cl}$	+1.04 <sup>b</sup>	-0.26		$\text{CH}_2\text{Cl}_2$	SCE	[117]
$\text{Ru}_2(\text{dpb})_4(\text{CO})$	+1.07	+0.11	1.18	$\text{CH}_2\text{Cl}_2$	SCE	[117]
$\text{Ru}_2(\text{CH}_3\text{CO}_2)_3(\text{admpym})\text{Cl}(\text{CH}_3\text{OH})$	+0.72	-0.65	1.37	$\text{CH}_3\text{CN}$	Ag/AgCl	[118]
$\text{Ru}_2(\text{CH}_3\text{CO}_2)_3(\text{admp})\text{Cl}$	+1.11	-0.44	1.55	$\text{CH}_2\text{Cl}_2$	Ag/AgCl	[121]
$\text{Ru}_2(\text{CH}_3\text{CO}_2)_2(\text{admp})_2\text{Cl}$	+0.76	-0.71	1.47	$\text{CH}_3\text{CN}$	Ag/AgCl	[121]
$\text{Ru}_2(\text{CH}_3\text{CO}_2)(\text{admp})_3\text{Cl}$	+0.48	-1.00	1.48	$\text{CH}_3\text{CN}$	Ag/AgCl	[121]
$\text{Ru}_2(\text{admp})_4\text{Cl}$	+1.48			$\text{CH}_3\text{CN}$	Ag/AgCl	[121]
$\text{Ru}_2(\text{CH}_3\text{CO}_2)(\text{HNC}_5\text{H}_3\text{NCH}_3)_3\text{Cl}$	+0.64	-0.61	1.25	$\text{CH}_3\text{CN}$	Ag/AgCl/Cl <sup>-</sup>	[57]
$\text{Ru}_2(\text{TPG})_4\text{Cl}$	-0.05	-1.35 <sup>c</sup>		$\text{CH}_2\text{Cl}_2$	Fc/Fc <sup>+</sup>	[56]
$\text{Ru}_2(\text{CH}_3\text{CO}_2)(\text{TPG})_3\text{Cl}$	+0.06	$\approx -1.3^c$		$\text{CH}_2\text{Cl}_2$	Fc/Fc <sup>+</sup>	[56]
$\text{Ru}_2(\text{CH}_3\text{CO}_2)(\text{TPG})_3(\text{N}_3)$	+0.02	-1.46 <sup>c</sup>		$\text{CH}_2\text{Cl}_2$	Fc/Fc <sup>+</sup>	[56]
$[\text{Ru}_2(\text{CH}_3\text{CO}_2)_2(\text{Cl-salpy})_2]^-$	-0.24	-1.39	1.15	$\text{CH}_3\text{CN}$	Ag/AgCl	[119]
$[\text{Ru}_2(\text{CH}_3\text{CO}_2)_2(\text{H-salpy})_2]^-$	-0.33	-1.51	1.18	$\text{CH}_3\text{CN}$	Ag/AgCl	[120]
$[\text{Ru}_2(\text{CH}_3\text{CO}_2)_2(\text{Me-salpy})_2]^-$	-0.37	-1.50	1.13	$\text{CH}_3\text{CN}$	Ag/AgCl	[120]
$[\text{Ru}_2(\text{CH}_3\text{CO}_2)_2(\text{Br-salpy})_2]^-$	-0.23	-1.43	1.20	$\text{CH}_3\text{CN}$	Ag/AgCl	[120]
$[\text{Ru}_2(\text{CH}_3\text{CO}_2)_2(\text{NO}_2\text{-salpy})_2]^-$	-0.03	-1.28	1.25	$\text{CH}_3\text{CN}$	Ag/AgCl	[120]

<sup>a</sup> Potential difference between the  $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{5+/4+}$  processes; <sup>b</sup>  $E_{pa}$  at 0.1 V/s; <sup>c</sup>  $E_{pc}$  at 0.1 V/s

**Table 9**  
 $E_{1/2}$  values for the  $\text{Ru}_2^{6+/7+}$  and  $\text{Ru}_2^{6+/5+}$  processes of  $\text{Ru}_2^{6+}$  complexes with “ap-type” bridging ligands.

Compound	$\text{Ru}_2^{6+/7+}$	$\text{Ru}_2^{6+/5+}$	$\Delta^a$ (V)	Solvent	Ref. electrode	Refs.
(4,0) $\text{Ru}_2(\text{ap})_4(\text{C}\equiv\text{CPh})_2$	0.55	−0.54	1.09	$\text{CH}_2\text{Cl}_2$	SCE	[50]
(4,0) $\text{Ru}_2(\text{ap})_4((\text{C}\equiv\text{C})_2\text{Si}(\text{CH}_3)_3)(\text{C}\equiv\text{CSi}^i\text{Pr}_3)$	0.83	−0.37	1.20	THF	Ag/AgCl	[122]
(4,0) $\text{Ru}_2(\text{ap})_4((\text{C}\equiv\text{C})_2\text{Si}(\text{CH}_3)_3)(\text{C}\equiv\text{C}(\text{CH}_3)_3)$	0.83	−0.36	1.19	THF	Ag/AgCl	[122]
(4,0) $\text{Ru}_2(\text{ap})_4((\text{C}\equiv\text{C})_2\text{H})(\text{C}\equiv\text{CSi}^i\text{Pr}_3)$	0.84 <sup>b</sup>	−0.38		THF	Ag/AgCl	[122]
(4,0) $\text{Ru}_2(\text{ap})_4((\text{C}\equiv\text{C})_2\text{H})(\text{C}\equiv\text{CSi}(\text{CH}_3)_3)$	0.83 <sup>b</sup>	−0.38		THF	Ag/AgCl	[122]
(4,0) $\text{Ru}_2(\text{ap})_4((\text{C}\equiv\text{C})_2\text{H})(\text{C}\equiv\text{CH})$	0.83 <sup>b</sup>	−0.39		THF	Ag/AgCl	[122]
(4,0) $\text{Ru}_2(\text{ap})_4(\text{C}\equiv\text{C}-4-\text{C}_6\text{H}_4-\text{P}(\text{O})(\text{O}^t\text{Bu})_2)(\text{C}\equiv\text{CSi}(\text{CH}_3)_3)$	0.74	−0.38	1.12	THF	Ag/AgCl	[123]
(4,0) $\text{Ru}_2(\text{ap})_4(\text{C}\equiv\text{C}-4-\text{C}_6\text{H}_4-\text{P}(\text{O})(\text{O}^t\text{Bu})_2)((\text{C}\equiv\text{C})_2\text{Si}(\text{CH}_3)_3)$	0.86	−0.31	1.17	THF	Ag/AgCl	[123]
(4,0) $\text{Ru}_2(\text{ap})_4(\text{C}\equiv\text{C}-4-\text{C}_6\text{H}_4-\text{P}(\text{O})(\text{O}^t\text{Bu})_2)((\text{C}\equiv\text{C})_3\text{H})$	0.90	−0.25	1.15	THF	Ag/AgCl	[123]
(4,0) $\text{Ru}_2(\text{ap})_4(\text{C}\equiv\text{C}-4-\text{C}_6\text{H}_4-\text{P}(\text{O})(\text{O}^t\text{Bu})_2)(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\text{Si}(\text{CH}_3)_3)$	0.78	−0.37	1.15	THF	Ag/AgCl	[123]
(4,0) $\text{Ru}_2(\text{ap})_4(\text{C}\equiv\text{C}-4-\text{C}_6\text{H}_4-\text{P}(\text{O})(\text{O}^t\text{Bu})_2)(\text{C}\equiv\text{C}-4-\text{C}_6\text{H}_4\text{SC}_2\text{H}_4\text{Si}(\text{CH}_3)_3)$	0.74	−0.38	1.12	THF	Ag/AgCl	[123]
(3,1) $\text{Ru}_2(\text{ap})_4(\text{C}\equiv\text{CC}_5\text{H}_4\text{N})_2$	0.69	−0.52	1.21	$\text{CH}_2\text{Cl}_2$	SCE	[80]
(3,1) $\text{bis}[\text{PcRu}(\text{CO})][\text{Ru}_2(\text{ap})_4(\text{C}\equiv\text{CC}_5\text{H}_4\text{N})_2]$	0.74	−0.49	1.23	$\text{CH}_2\text{Cl}_2$	SCE	[124]
(4-(TMSE-S)-Ph-C≡C) $\text{Ru}_2(\text{ap})_4(\text{C}\equiv\text{C}-4-\text{Ph}-\text{P}(\text{O})(\text{O}^t\text{Bu})_2)$	0.75	−0.38	1.13	THF	Ag/AgCl	[89]
(4,0) $\text{Ru}_2(3,4-\text{F}_2\text{ap})_4(\text{C}\equiv\text{CPh})_2$	0.70	−0.45	1.15	$\text{CH}_2\text{Cl}_2$	SCE	[50]
(4,0) $\text{Ru}_2(2,5-\text{F}_2\text{ap})_4(\text{C}\equiv\text{CPh})_2$	0.76	−0.42	1.18	$\text{CH}_2\text{Cl}_2$	SCE	[50]
(4,0) $\text{Ru}_2(\text{F}_5\text{ap})_4(\text{C}\equiv\text{CPh})_2$	0.90	−0.05	0.95	$\text{CH}_2\text{Cl}_2$	SCE	[73]
(3,1) $\text{Ru}_2(2-\text{Fap})_4(\text{C}\equiv\text{CPh})_2$	0.62	−0.58	1.20	$\text{CH}_2\text{Cl}_2$	SCE	[50]
(3,1) $\text{Ru}_2(2,4-\text{F}_2\text{ap})_4(\text{C}\equiv\text{CPh})_2$	0.70	−0.56	1.26	$\text{CH}_2\text{Cl}_2$	SCE	[50]
(3,1) $\text{Ru}_2(2,4,6-\text{F}_3\text{ap})_4(\text{C}\equiv\text{CPh})_2$	0.78	−0.42	1.20	$\text{CH}_2\text{Cl}_2$	SCE	[50]
(3,1) $\text{Ru}_2(2,3-\text{F}_2\text{ap})_4(\text{C}\equiv\text{CPh})_2$	0.80	−0.40	1.20	$\text{CH}_2\text{Cl}_2$	SCE	[50]
(3,1) $\text{Ru}_2(\text{F}_5\text{ap})_4(\text{C}\equiv\text{CPh})_2$	1.00	−0.14	1.13	$\text{CH}_2\text{Cl}_2$	SCE	[73]
(2,2) $\text{trans Ru}_2(\text{F}_5\text{ap})_4(\text{C}\equiv\text{CPh})_2$	1.04	−0.18	1.22	$\text{CH}_2\text{Cl}_2$	SCE	[73]
(4,0) $\text{Ru}_2(\text{OCH}_3\text{ap})_4((\text{C}\equiv\text{C})_2\text{Si}(\text{CH}_3)_3)_2$	0.99	−0.25	1.24	THF	Ag/AgCl	[75]
(4,0) $\text{Ru}_2((\text{OCH}_3)_2\text{ap})_4((\text{C}\equiv\text{C})_2\text{Si}(\text{CH}_3)_3)_2$	0.92	−0.24	1.16	THF	Ag/AgCl	[75]
(4,0) $\text{Ru}_2(\text{O}^t\text{Buap})_4(\text{C}\equiv\text{CPh})_2$	0.77 <sup>b</sup>	−0.42		THF	Ag/AgCl	[78]
(4,0) $\text{Ru}_2(\text{ap})_4(\text{CN})_2$	1.02 <sup>b</sup>	−0.24		$\text{CH}_2\text{Cl}_2$	SCE	[72]
(3,1) $\text{Ru}_2(2-\text{Fap})_4(\text{CN})_2$	0.92	−0.21	1.13	$\text{CH}_2\text{Cl}_2$	SCE	[72]
(3,1) $\text{Ru}_2(\text{F}_4\text{Oap})(\text{F}_5\text{ap})_3\text{Cl}$	1.35 (0.98) <sup>c</sup>	0.22		$\text{CH}_2\text{Cl}_2$	SCE	[74]
(3,1) $\text{Ru}_2(\text{F}_3\text{ap})_3(\text{F}_2\text{Oap})(\text{NCS})$	1.34	0.14	1.20	$\text{CH}_2\text{Cl}_2$	SCE	[81]
(3,1) $\text{Ru}_2(\text{F}_4\text{Oap})_2(\text{F}_5\text{ap})_2$	1.20 (0.70) <sup>c</sup>	0.05		$\text{CH}_2\text{Cl}_2$	SCE	[49]
(3,1) $\text{Ru}_2(\text{F}_4\text{Oap})(\text{F}_4\text{NCNp})(\text{F}_5\text{ap})_2$	1.23 (0.84) <sup>c</sup>	0.20		$\text{CH}_2\text{Cl}_2$	SCE	[49]
$\text{Ru}_2(\text{ap})_4(\text{C}_6\text{H}_4-p-\text{N}(\text{CH}_3)_2)(\text{C}\equiv\text{CH})$	−0.11	−0.98	0.87	THF	Fc/Fc <sup>+</sup>	[83]
$\text{Ru}_2(\text{ap})_4(\text{C}_6\text{H}_4-p-\text{N}(\text{CH}_3)_2)(\text{CN})$	−0.21	−1.20	0.99	THF	Fc/Fc <sup>+</sup>	[83]

<sup>a</sup> Potential separation between the  $\text{Ru}_2^{6+/7+}$  and  $\text{Ru}_2^{6+/5+}$  processes; <sup>b</sup>  $E_{\text{pa}}$  at 0.1 V/s; <sup>c</sup> two oxidations reported but no definitive assignment of electron transfer site was made.

**Table 10** $E_{1/2}$  values (vs Ag/AgCl) for the  $Ru_2^{6+/7+}$  and  $Ru_2^{6+/5+}$  processes of  $Ru_2^{6+}$  complexes with “DMBA-type”, “DArF-type”, or mixed DArF/DMBA bridging ligands.

Compound	$Ru_2^{6+/7+}$	$Ru_2^{6+/5+}$	$\Delta^a$ (V)	Solvent	Refs.
$Ru_2(D(4-OCH_3Ph)F)_4(C\equiv CPh)_2$	0.77	-0.62	1.39	$CH_2Cl_2$	[125]
$Ru_2(D(4-CH_3Ph)F)_4(C\equiv CPh)_2$	0.94	-0.50	1.44	$CH_2Cl_2$	[125]
$Ru_2(D(4-CIPh)F)_4(C\equiv CPh)_2$	1.09	-0.26	1.35	$CH_2Cl_2$	[125]
$Ru_2(D(3-CIPh)F)_4(C\equiv CPh)_2$	1.11	-0.21	1.32	$CH_2Cl_2$	[125]
$Ru_2(D(3-CF_3Ph)F)_4(C\equiv CPh)_2$	1.22	-0.11	1.33	$CH_2Cl_2$	[125]
$Ru_2(D(3,4-Cl_2Ph)F)_4(C\equiv CPh)_2$	1.27	0.01	1.26	$CH_2Cl_2$	[125]
$Ru_2(D(3,5-Cl_2Ph)F)_4(C\equiv CPh)_2$	1.41 <sup>b</sup>	0.09		$CH_2Cl_2$	[125]
$Ru_2(DMBA)_4(C\equiv CPh)_2$	0.52	-1.10	1.62	THF	[126]
$Ru_2(DMBA)_4(C\equiv CTF1)_2$	0.61	-0.98	1.59	THF	[130]
$Ru_2(DMBA)_4(C\equiv CTF2)_2$	0.55	-0.91	1.46	THF	[130]
$Ru_2(DMBA)_4(H-gem-DEE)_2$	0.50	-1.15	1.65	THF	[129]
$Ru_2(DMBA)_4(Si^iPr_3-gem-DEE)_2$	0.50	-1.16	1.66	THF	[129]
$Ru_2(DMBA)_4(Fc-gem-DEE)_2$	0.47	-1.16	1.63	THF	[129]
$Ru_2(DMBA)_4(4-C_6H_4NO_2-gem-DEE)_2$	0.49			THF	[129]
$Ru_2(DMBA)_4(4-C_6H_4NMe_2-gem-DEE)_2$	0.45	-1.17	1.62	THF	[129]
$Ru_2(DMBA)_4(C\equiv CSi^iPr_3)_2$	0.59	-1.14	1.73	THF	[129]
$Ru_2(DMBA)_4(OPE_1-S-TMSE)_2$	0.52	-1.06	1.58	THF	[145]
$Ru_2(DMBA)_4(OPE_2-S-TMSE)_2$	0.48	-1.06	1.54	THF	[145]
$Ru_2(DMBA)_4(OPE_3-S-TMSE)_2$	0.53	-1.05	1.58	THF	[145]
$Ru_2(DMBA)_4(C\equiv CC_6H_2(OCH_3)_2(NO_2))_2$	0.60	-0.89	1.49	THF	[146]
$Ru_2(DMBA)_4(C\equiv CC_6H_4N(CH_3)_2)_2$	0.32	-1.16	1.48	THF	[146]
$Ru_2(DMBA)_4(C\equiv CC_5H_4N)_2$	0.69	-0.92	1.61	THF	[146]
$Ru_2(DMBA)_4(C\equiv CPh)(C\equiv CC_6H_4NO_2)$	0.69	-0.87	1.56	THF	[146]
$Ru_2(DMBA)_4(C\equiv CPh)(C\equiv CC_6H_4N(CH_3)_2)$	0.39	-1.10	1.49	THF	[146]
$Ru_2(DMBA)_4(C\equiv CC_6H_4N(CH_3)_2)(C\equiv CC_6H_4NO_2)$	0.60	-0.94	1.54	THF	[146]
$Ru_2(DMBA)_4(C\equiv CC_6H_4N(CH_3)_2)(C\equiv CC_6H_2(OCH_3)_2(NO_2))$	0.44	-1.00	1.44	THF	[146]
$Ru_2(OMe-DMBA)_4((C\equiv C)_3Fc)_2$	0.73	-0.75	1.48	THF	[131]
$Ru_2(OMe-DMBA)_4((C\equiv C)_4Fc)_2$	0.79	-0.65	1.44	THF	[131]
$Ru_2(DMBA)_4Cl_2$	1.06	-0.32	1.38	THF	[126]
$Ru_2(Br-DMBA)_4Cl_2$	1.12	-0.25	1.37	THF	[147]
$Ru_2(I-DMBA)_4Cl_2$	1.11	-0.26	1.37	THF	[147]
$Ru_2(DMBA)_4(C\equiv CSi(CH_3)_3)_2$	0.56	-1.14	1.70	THF	[126]
$Ru_2(DMBA)_4(C\equiv CH)_2$	0.57	-1.20 <sup>c</sup>		THF	[126]
$Ru_2(DMBA)_4((C\equiv C)_2Si(CH_3)_3)_2$	0.73	-0.90	1.63	THF	[126]
$Ru_2(DMBA)_4((C\equiv C)_2H)_2$	0.73	-0.92	1.65	THF	[126]
$Ru_2(DMBA)_4(BF_4)_2$	1.74	0.19	1.55	$CH_2Cl_2$	[128]
$Ru_2(DMBA)_4(NO_3)_2$	1.40	-0.07	1.47	$CH_2Cl_2$	[128]
$Ru_2(OMe-DMBA)_4Cl_2$	1.08	-0.32	1.40	$CH_2Cl_2$	[127]
$Ru_2((OMe)_2-DMBA)_4Cl_2$	1.11	-0.32	1.43	$CH_2Cl_2$	[127]
$Ru_2(DEBA)_4Cl_2$	1.20	-0.16	1.36	$CH_2Cl_2$	[127]
$Ru_2(DMBA)_4(C\equiv CSi(CH_3)_3)_2$	0.55	-1.15	1.70	$CH_2Cl_2$	[127]
$Ru_2(OCH_3-DMBA)_4(C\equiv CSi(CH_3)_3)_2$	0.56	-1.15	1.71	$CH_2Cl_2$	[127]
$Ru_2((OCH_3)_2-DMBA)_4(C\equiv CSi(CH_3)_3)_2$	0.56	-1.15	1.71	$CH_2Cl_2$	[127]
$Ru_2(DEBA)_4(C\equiv CSi(CH_3)_3)_2$	0.63	-1.09	1.72	$CH_2Cl_2$	[127]
$Ru_2(DMBA)_4((C\equiv C)_2Si(CH_3)_3)_2$	0.73	-0.90	1.63	$CH_2Cl_2$	[127]
$Ru_2(OMe-DMBA)_4((C\equiv C)_2Si(CH_3)_3)_2$	0.74	-0.88	1.62	$CH_2Cl_2$	[127]
$Ru_2((OMe)_2-DMBA)_4((C\equiv C)_2Si(CH_3)_3)_2$	0.73	-0.90	1.63	$CH_2Cl_2$	[127]
$Ru_2(DEBA)_4((C\equiv C)_2Si(CH_3)_3)_2$	0.78	-0.86	1.64	$CH_2Cl_2$	[127]
$Ru_2(DMBA)_4(C\equiv C-4-C_6H_4-N_3Et_2)_2$	0.45	-1.11	1.56	THF	[86]
$Ru_2(DMBA)_4(C\equiv C-4-C_6H_4-P(O)(O^tBu)_2)_2$	0.63	-0.99	1.62	THF	[89]
$Ru_2(DmAniF)_3(DMBA-4-C\equiv CSi^iPr_3)((C\equiv C)_2Si(CH_3)_3)_2$	1.07 <sup>b</sup>	-0.37		THF	[110]
$Ru_2(DmAniF)_3(DMBA-4-C\equiv CFC)((C\equiv C)_2Si(CH_3)_3)_2$	1.06 <sup>b</sup>	-0.39		THF	[110]
$Ru_2(DmAniF)_3(DMBA-1)((C\equiv C)_2Si(CH_3)_3)_2$	1.06 <sup>b</sup>	-0.37		THF	[110]
$Cis-Ru_2(DmAniF)_2(DMBA-4-C\equiv CFC)(C\equiv CPh)_2$	1.11 <sup>b</sup>	-0.67		THF	[110]
$Cis-Ru_2(DmAniF)_2(DMBA-1)_2(C\equiv CPh)_2$	0.80 <sup>b</sup>	-0.65		THF	[110]
$Ru_2(3-CH_3ODMBA)_4(C\equiv C-C_2-C\equiv C-Ru_2(3,5-(CH_3O)_2ap)_4)_2$	0.69	-1.29	1.98	THF	[134]
$Ru_2(3,5-(CH_3O)_2DMBA)_4(C\equiv C-C_2-C\equiv C-Ru_2(3,5-(CH_3O)_2ap)_4)_2$	0.69	-1.28	1.97	THF	[134]
$Ru_2(3,5-(CH_3O)_2DMBA)_4(C\equiv C-C_2-C\equiv C-Ru_2(3-CH_3Oap)_4)_2$	0.70	-1.26	1.96	THF	[134]
$Ru_2(3-CH_3ODMBA)_4(C\equiv C-C_6H_4-C\equiv C-Ru_2(3-CH_3Oap)_4)_2$	0.54	-1.13	1.67	THF	[134]
$Ru_2(DMBA)_4(L1Si^iPr_3)_2^d$	0.06	-1.54	1.60	THF	[132]
$Ru_2(DMBA)_4(L2Si^iPr_3)_2^d$	0.08	-1.52	1.61	THF	[132]
$Ru_2(DMBA)_4(L1H)_2^d$	-0.13	-1.82	1.69	THF	[132]
$Ru_2(DMBA)_4(L2H)_2^d$	-0.08 <sup>b</sup>	-1.81		THF	[132]
$Ru_2(DMBA)_4(C_6H_4-4-tBu)_2$	-0.53	-2.05	1.52	$CH_2Cl_2$	[133]
$Ru_2(DMBA)_4(C_6H_5)_2$	-0.47	-2.02	1.55	$CH_2Cl_2$	[133]
$Ru_2(DMBA)_4(C_6H_3-3,5-(OCH_3)_2)_2$	-0.42	-1.97	1.55	$CH_2Cl_2$	[133]

<sup>a</sup> Potential difference between the  $Ru_2^{6+/5+}$  and  $Ru_2^{6+/7+}$  processes; <sup>b</sup>  $E_{pa}$  values at 0.1 V/s; <sup>c</sup>  $E_{pc}$  values at 0.1 V/s; <sup>d</sup> Potential V vs  $Fc^{+/0}$ . <sup>e</sup> See Fig. 32 for structure.

**Table 11** $E_{1/2}$  values (V vs SCE) for the  $\text{Ru}_2^{6+/7+}$  and  $\text{Ru}_2^{6+/5+}$  processes of  $\text{Ru}_2^{6+}$  complexes containing hpp, amp, ammp or BAM bridging ligands.

Compound <sup>b</sup>	$\text{Ru}_2^{6+/7+}$	$\text{Ru}_2^{6+/5+}$	$\Delta^a$ (V)	Solvent	Refs.
$\text{Ru}_2(\text{hpp})_4\text{Cl}_2$	0.55	-0.60	1.15	$\text{CH}_2\text{Cl}_2$	[135]
$\text{Ru}_2(\text{BAM})_4\text{Cl}_2$		-0.23		$\text{CH}_3\text{Cl}$	[136]
$\text{Ru}_2(\text{amp})_4\text{Cl}_2$		-0.08		THF	[137]
$\text{Ru}_2(\text{ammp})_4\text{Cl}_2$		-0.18		THF	[137]

<sup>a</sup> Potential separation in V between the  $\text{Ru}_2^{5+/6+}$  and  $\text{Ru}_2^{5+/4+}$  processes. <sup>b</sup> See Fig. 33 for structures.**Table 12** $E_{1/2}$  values for the  $\text{Ru}_2^{4+/5+}$  process of  $\text{Ru}_2^{4+}$  complexes.

Compound	$\text{Ru}_2^{4+/5+}$	Solvent	Ref. Electrode	Refs.
$\text{Ru}_2(\text{HCO}_2)_4$	0.25	$\text{CH}_3\text{CN}$	SCE	[51]
$\text{Ru}_2(\text{HCO}_2)_4$	0.23	THF	SCE	[51]
$\text{Ru}_2(\text{CH}_3\text{CO}_2)_4$	0.00	$\text{CH}_3\text{CN}$	SCE	[51]
$\text{Ru}_2(\text{CH}_3\text{CO}_2)_4$	-0.05	THF	SCE	[51]
$\text{Ru}_2(\text{CH}_2\text{ClCO}_2)_4$	0.34	$\text{CH}_3\text{CN}$	SCE	[51]
$\text{Ru}_2(\text{CH}_2\text{ClCO}_2)_4$	0.29	THF	SCE	[51]
$\text{Ru}_2(\text{EtCO}_2)_4$	-0.02	$\text{CH}_3\text{CN}$	SCE	[51]
$\text{Ru}_2(\text{EtCO}_2)_4$	-0.03	THF	SCE	[51]
$\text{Ru}_2(\text{PhCO}_2)_4$	0.13	$\text{CH}_3\text{CN}$	SCE	[51]
$\text{Ru}_2(\text{PhCO}_2)_4$	0.07	THF	SCE	[51]
$\text{Ru}_2(\text{CF}_3\text{CO}_2)_4$	1.17	$\text{CH}_2\text{Cl}_2$	SCE	[37]
$\text{Ru}_2(\text{PhCO}_2)_4$	0.06	THF	Ag/Ag <sup>+</sup>	[138]
$\text{Ru}_2(o\text{-FPhCO}_2)_4$	0.04	THF	Ag/Ag <sup>+</sup>	[138]
$\text{Ru}_2(m\text{-FPhCO}_2)_4$	0.04	THF	Ag/Ag <sup>+</sup>	[138]
$\text{Ru}_2(p\text{-FPhCO}_2)_4$	-0.04	THF	Ag/Ag <sup>+</sup>	[138]
$\text{Ru}_2(2,6\text{-F}_2\text{PhCO}_2)_4$	0.05	THF	Ag/Ag <sup>+</sup>	[138]
$\text{Ru}_2(3,4\text{-F}_2\text{PhCO}_2)_4$	0.14	THF	Ag/Ag <sup>+</sup>	[138]
$\text{Ru}_2(3,5\text{-F}_2\text{PhCO}_2)_4$	0.18	THF	Ag/Ag <sup>+</sup>	[138]
$\text{Ru}_2(2,3,4\text{-F}_3\text{PhCO}_2)_4$	0.21	THF	Ag/Ag <sup>+</sup>	[138]
$\text{Ru}_2(2,3,6\text{-F}_3\text{PhCO}_2)_4$	0.34	THF	Ag/Ag <sup>+</sup>	[138]
$\text{Ru}_2(2,4,5\text{-F}_3\text{PhCO}_2)_4$	0.16	THF	Ag/Ag <sup>+</sup>	[138]
$\text{Ru}_2(2,4,6\text{-F}_3\text{PhCO}_2)_4$	0.10	THF	Ag/Ag <sup>+</sup>	[138]
$\text{Ru}_2(3,4,5\text{-F}_3\text{PhCO}_2)_4$	0.27	THF	Ag/Ag <sup>+</sup>	[138]
$\text{Ru}_2(2,3,4,5\text{-F}_4\text{PhCO}_2)_4$	0.31	THF	Ag/Ag <sup>+</sup>	[138]
$\text{Ru}_2(2,3,5,6\text{-F}_4\text{PhCO}_2)_4$	0.36	THF	Ag/Ag <sup>+</sup>	[138]
$\text{Ru}_2(\text{F}_5\text{PhCO}_2)_4$	0.36	THF	Ag/Ag <sup>+</sup>	[138]
$\text{Ru}_2(\text{TiPB})_4$	0.02	MeOH	Ag/Ag <sup>+</sup>	[65]
$\text{Ru}_2(\text{N}_3\text{Ph}_2)_4$	0.16	$\text{CH}_2\text{Cl}_2$	SCE	[37]
$\text{Ru}_2(\text{N}_3\text{Ph}_2)_4(\text{Bu}^t\text{NC})$	0.23	$\text{CH}_2\text{Cl}_2$	SCE	[37]
$\text{Ru}_2(\text{N}_3\text{Ph}_2)_4(\text{CO})_2$	0.59 <sup>a</sup>	$\text{CH}_2\text{Cl}_2$	SCE	[37]
$\text{Ru}_2(\text{CH}_3\text{CO}_2)_2(\text{TiPB})_2$	0.04	MeOH	Ag/Ag <sup>+</sup>	[65]
$[\text{Ru}_2(2,6\text{-}(\text{CF}_3)_2\text{PhCO}_2)_2(\text{CH}_3\text{CO}_2)_2(\text{THF})_2]$	0.02	THF	Ag/Ag <sup>+</sup>	[139]
$[\text{Ru}_2(2,6\text{-}(\text{CF}_3)_2\text{PhCO}_2)_2(\text{EtCO}_2)_2(\text{THF})_2]$	0.01	THF	Ag/Ag <sup>+</sup>	[139]
$[\text{Ru}_2(2,6\text{-}(\text{CF}_3)_2\text{PhCO}_2)_2(\text{PrCO}_2)_2(\text{THF})_2]$	0.02	THF	Ag/Ag <sup>+</sup>	[139]
$[\text{Ru}_2(2,6\text{-}(\text{CF}_3)_2\text{PhCO}_2)_2(\text{BuCO}_2)_2(\text{THF})_2]$	0.02	THF	Ag/Ag <sup>+</sup>	[139]
$[\text{Ru}_2(2,6\text{-}(\text{CF}_3)_2\text{PhCO}_2)_2(\text{t}^t\text{BuCO}_2)_2(\text{THF})_2]$	0.02	THF	Ag/Ag <sup>+</sup>	[139]
$[\text{Ru}_2(2,6\text{-}(\text{CF}_3)_2\text{PhCO}_2)_2(2,3,5,6\text{-F}_4\text{PhCO}_2)_2(\text{THF})_2]$	0.31	THF	Ag/Ag <sup>+</sup>	[139]
$[\text{Ru}_2(2,6\text{-}(\text{CF}_3)_2\text{PhCO}_2)_2(p\text{-CF}_3\text{PhCO}_2)_2(\text{THF})_2]$	0.24	THF	Ag/Ag <sup>+</sup>	[140]
$[\text{Ru}_2(2,6\text{-}(\text{CF}_3)_2\text{PhCO}_2)_2(p\text{-ClPhCO}_2)_2(\text{THF})_2]$	0.18	THF	Ag/Ag <sup>+</sup>	[140]
$[\text{Ru}_2(2,6\text{-}(\text{CF}_3)_2\text{PhCO}_2)_2(p\text{-FPhCO}_2)_2(\text{THF})_2]$	0.16	THF	Ag/Ag <sup>+</sup>	[140]
$[\text{Ru}_2(2,6\text{-}(\text{CF}_3)_2\text{PhCO}_2)_2(p\text{-HPhCO}_2)_2(\text{THF})_2]$	0.11	THF	Ag/Ag <sup>+</sup>	[140]
$[\text{Ru}_2(2,6\text{-}(\text{CF}_3)_2\text{PhCO}_2)_2(p\text{-PhPhCO}_2)_2(\text{THF})_2]$	0.11	THF	Ag/Ag <sup>+</sup>	[140]
$[\text{Ru}_2(2,6\text{-}(\text{CF}_3)_2\text{PhCO}_2)_2(p\text{-CH}_3\text{PhCO}_2)_2(\text{THF})_2]$	0.08	THF	Ag/Ag <sup>+</sup>	[140]
$[\text{Ru}_2(2,6\text{-}(\text{CF}_3)_2\text{PhCO}_2)_2(p\text{-OCH}_3\text{PhCO}_2)_2(\text{THF})_2]$	0.04	THF	Ag/Ag <sup>+</sup>	[140]
$[\text{Ru}_2(2,6\text{-}(\text{CF}_3)_2\text{PhCO}_2)_2(p\text{-OHPhCO}_2)_2(\text{THF})_2]$	-0.02	THF	Ag/Ag <sup>+</sup>	[140]
$[\text{Ru}_2(p\text{-CF}_3\text{PhCO}_2)_4(\text{THF})_2]$	0.12	THF	Ag/Ag <sup>+</sup>	[140]
$[\text{Ru}_2(p\text{-PhPhCO}_2)_4(\text{THF})_2]$	0.04	THF	Ag/Ag <sup>+</sup>	[140]
$[\text{Ru}_2(p\text{-OCH}_3\text{PhCO}_2)_4(\text{THF})_2]$	-0.18	THF	Ag/Ag <sup>+</sup>	[140]
$\text{Cis-}[\text{Ru}_2(\text{CH}_3\text{CO}_2)_2(\text{pynp})_2](\text{PF}_6)_2$	0.85	$\text{CH}_3\text{CN}$	Ag/Ag <sup>+</sup>	[142]
$[(\text{Ru}_2)\text{LPh}(\text{Ru}_2)](\text{PF}_6)_2$	0.76, 0.85	$\text{CH}_3\text{CN}$	SCE	[144]
$[(\text{Ru}_2)\text{LAnt}(\text{Ru}_2)](\text{PF}_6)_2$	0.73, 0.86	$\text{CH}_3\text{CN}$	SCE	[144]
$\text{Ru}_2(\text{D}(4\text{-CH}_3\text{Ph})\text{F})_4$	-0.12, 1.16 <sup>b</sup>	$\text{CH}_2\text{Cl}_2$	Ag/AgCl	[141]
$\text{Ru}_2(\text{Dmof})_4$	-0.58	$\text{CH}_2\text{Cl}_2$	Fc/Fc <sup>+</sup>	[143]

<sup>a</sup>  $E_{pa}$  at 0.1 V/s. <sup>b</sup> The origin of these two redox processes was not defined.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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