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Redox potentials and electronic structures of organic complexes of ruthenium and rhodium

T V Magdesieva, K P Butin

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Abstract. The redox properties of mononuclear and polynuclear rhodium and ruthenium complexes are examined. Attention is concentrated on the possible locations of the electronic changes in the redox transitions. The relation between the electrochemical parameters of the complexes and electronic spectroscopic data is traced. Extensive reference data are presented on the oxidation and reduction potentials of mononuclear and polynuclear rhodium and ruthenium complexes. The bibliography includes 133 references.

I. Introduction

Transition metal dinuclear and polynuclear complexes in which the central ions are linked to one another by different bridging ligands (inorganic ligands of the type of CN, SCN, OCN, etc. and organic ligands of the type of polyazabiphenyls and polyazaterphenyls) have been investigated very vigorously during the last decade. This applies particularly to ruthenium(II) compounds, which have proved extremely useful in many applied investigations. Such complexes are employed widely as photoluminescent substances, mediators of photochemical processes,[1, 2] and materials for non-linear optics.[3, 4]

In essence, the polynuclear complexes can be regarded as mononuclear complexes which contain organometallic ligands. For example, in the compound $L_nM^1CN \rightarrow M^2L_n$ one of the ligands is L_nM^1CN. Such ligands are of undoubted interest, since they contain transition metal atoms and tend to undergo redox transitions. In our view, the polynuclear complexes can serve as convenient models for the study of intramolecular electron transfer (charge transfer) processes from the metal (in the above example this is M^2) to the ligand (L_nM^1CN) (MLCT) or from the ligand to the metal (LMCT) both under the conditions of photochemical excitation and in electrochemical or chemical oxidation-reduction reactions.[5, 6]

Complexes of rhodium and ruthenium, the organometallic compounds of which have been investigated most widely, are considered in the present review. The theoretical ideas concerning the structure of transition metal complexes are discussed briefly in the first part within the framework of the molecular orbital method. The redox and spectroscopic properties of mononuclear complexes of ruthenium and rhodium are considered next, since such data are essential for the subsequent analysis of the electronic structures of the polynuclear bridged metal complexes to which the next section is devoted. In conclusion, tables giving compilations of the experimental oxidation and reduction potentials of mononuclear and polynuclear ruthenium and rhodium complexes are presented with an indication of specific experimental conditions (electrode material, solvent, supporting electrolyte, reference electrode) and also of the most probable locations of the electronic changes in the involved molecules of the complexes occurring in redox transitions (in those cases where such assignment to particular locations is possible). We suggest that such data will be useful to a wide range of chemists as regards comparison of the reactivities of these compounds in homogeneous reactions of different nature and not only in electronic processes.

T V Magdesieva, K P Butin Department of Organic Chemistry, Faculty of Chemistry, Lomonosov Moscow State University, Leninskie Gory, 119899 Moscow. Fax (7-095) 939-01 26

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II. Theoretical ideas on the structures of transition metal complexes

1. The redox levels of the octahedral complexes

The highly symmetrical transition metal complexes with six identical monodentate ligands L, for example $[Co(NH_3)_6]^{3+}$ or $Cr(CO)_6$, have the structure of a regular octahedron. If the metal–ligand bond is formed exclusively by the lone pair of the ligand and the π orbitals are not involved in the bonding, then the perturbation of the nine atomic orbitals (*d*, *s*, *p*) of the metal by the six group orbitals of the L_6 ensemble, having the O_h symmetry, results in the formation of the following energy levels of the complex ML_6 in the octahedral field: six bonding levels (σ), six antibonding levels (σ*), and three degenerate non-bonding levels (t_{2g}) corresponding to the d_{xy}, d_{yz}, and d_{xz} orbitals of the metal, which are relatively little perturbed as regards energy and form (Fig. 1).[7] In the 18-electron complexes, all the bonding σ orbitals and t_{2g} orbitals are fully occupied. Consequently, in the simplest case, where the ligand is exclusively the donor of the lone pair of electrons and the molecular orbitals of the ligand (for example, π-type orbitals) not involved in bonding have low energies, the redox levels responsible for the oxidation potential (E^{Ox}, Fig. 1*c*) are the t_{2g} levels, which are the highest occupied molecular orbitals (HOMO) of the complex. Since the t_{2g} orbitals are largely located on the metal, it is usual to say that in the oxidation of ML_6 the electronic changes are 'localised on the metal atom'.

The position of the t_{2g} levels depends not only on the nature of the metal and its oxidation state but also on the donor strength of the ligands: if the ligands are strong donors (Fig. 1*a*) then the t_{2g} levels are raised, whilst in the case where they are weak donors (Fig. 1*b*) they are lowered, which is reflected in the oxidation potentials of the complexes.

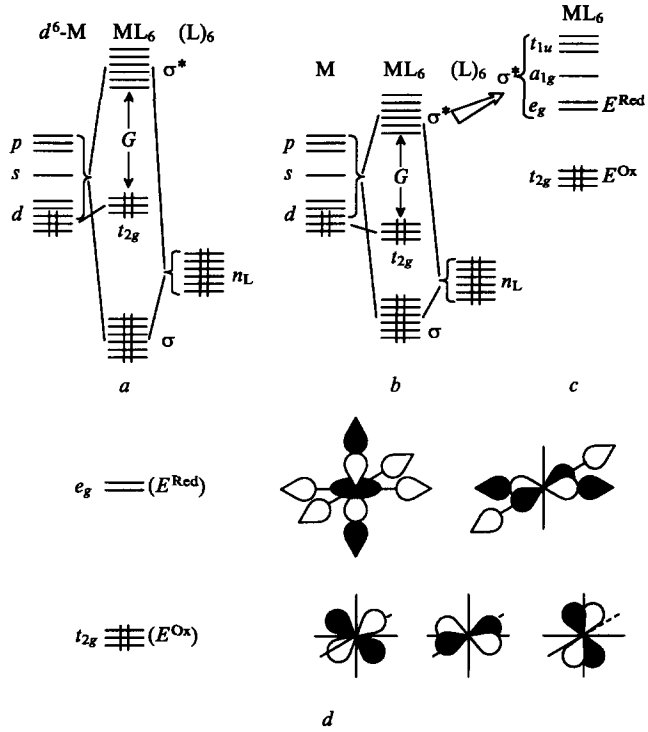


Figure 1. Energy levels of the octahedral complexes: (*a*) strong *n*-donor ligands; (*b*) weak *n*-donor ligands; (*c*) redox levels (t_{2g} and e_g) of the octahedral complex;[7] (*d*) the form of the frontier orbitals of the complex ML_6.

The six antibonding levels of the σ* type are divided into three blocks (Fig. 1*c*): the three degenerate t_{1u} orbitals have the highest energy, the a_{1g} orbital has a lower energy, and the two degenerate e_g levels have the lowest energy. The last levels are the redox levels responsible for the reduction of the complex (E^{Red}, Fig. 1*c*).

The form of the e_g orbitals is such that it is impossible to state *a priori* where the electronic changes during reduction are located: 'on the metal' or 'on the ligand', since, in contrast to the t_{2g} orbitals, the contributions of the ligand orbitals to the e_g levels can be significant. Therefore a special discussion of this problem is necessary in each specific case. The position of the e_g levels depends on the electron-donating capacity of the ligands. If the ligands are strong donors (Fig. 1*a*), then the splitting of the levels into the σ and σ* blocks is much more pronounced than in the case of weak donor ligands (Fig. 1*b*). As a result, the energy gap *G* between the highest occupied (t_{2g}) and lowest unoccupied (e_g) levels in the case of weak donor ligands is smaller than for the ligands with a greater electron-donating capacity. The chemical consequences of the change in the donor strength of the ligands are well known. Thus the octahedral complexes ML_6 with weak donor ligands are thermodynamically less stable and they pass more readily to paramagnetic moderate-spin or high-spin states, absorb light at longer wavelengths, etc. From the standpoint of redox chemistry, the transition from strong to weak ligands is expressed by a decrease in the electrochemical gap *G*,[8-10] defined as the difference between the redox potentials E^{Ox} and E^{Red} of the given compound.

$$ML_6^{\cdot+} \underset{E^{Ox}}{\overset{-\bar{e}}{\rightleftarrows}} ML_6 \underset{E^{Red}}{\overset{+\bar{e}}{\rightleftarrows}} ML_6^{\cdot-},$$

$$G = E^{Ox} - E^{Red}.$$

The quantity *G* is related to the constant for the equilibrium between the 17-electron radical-cation and the 19-electron radical-anion derived from the ML_6 molecule.

$$ML_6^{\cdot+} + ML_6^{\cdot-} \overset{K}{\rightleftarrows} 2ML_6;$$

$$\ln K = -(F/RT)G.$$

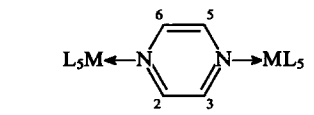
With decrease in *G*, *K* also diminishes, i.e. the equilibrium shifts to the left. This means that the 17-electron radical-cation (RC) and the 19-electron radical-anion (RA) are no longer quite so strongly destabilised relative to the 18-electron neutral complex ML_6 as in the case of compounds with large values of *G*. A complex with a narrow electrochemical gap, particularly in the case where it is uncharged and contains no strongly polar groups, i.e. has a moderate 'absolute electronegativity',[11] should be characterised by a tendency to enter into radical reactions. Similar considerations have been used in the classification of organomercury compounds in terms of their electrochemical potentials.[8]

Since the e_g levels of strong [donor?] ligands lie above those for the weak ligands, their complexes are reduced with a greater difficulty (i.e. the potentials E^{Red} have high negative values) and the 19-electron radical-anions formed, with an unpaired electron and a σ* orbital of the e_g type, are less stable.

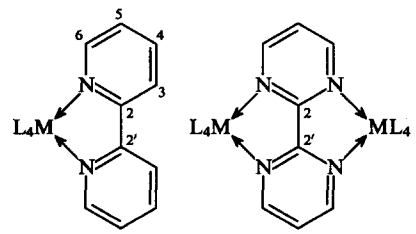
There exists a whole range of experimental evidence concerning the instability of 19-electron radical-anions in the case of strong donor ligands. For example, since CO is a strong *n*-donor, on bombardment with electrons in an argon matrix at −196 °C $Cr(CO)_6$ affords the 17-electron radical-anion $Cr(CO)_5^{\cdot-}$ as the main product,[12] while $Co(NH_3)_6^{3+}$ (NH_3 is a weaker donor than CO) combines with an electron to form the high-spin 19-electron $Co(NH_3)_6^{2+}$ cation, which does not decompose.[13]

2. Bidentate chelating and bridge-forming nitrogen-containing heterocycles

Pyrazine (pz) **1** is a bridge-forming ligand, 2,2′-bipyridyl (bpy) **2** is a chelating ligand, and 2,2′-bipyrimidyl (bpm) **3** is both a bridge-forming and a chelating ligand.



1



2 **3**

These and similar ligands form stable complexes with many transition metals: their structures can be readily modified by introducing various substituents altering the σ-donor and π-acceptor properties of the molecules. An appreciable proportion of the present review is devoted to the description of complexes with precisely these or similar ligands.

In the pyrazine molecule, the two lone pairs of the nitrogen atoms, directed to the opposite sides, interact with one another in such a way that they become non-equivalent. This is manifested by the fact that the ionisation potential of one lone pair is higher by 1.72 eV than that of the other.[14] Ideas concerning the interaction of electron pairs 'through space' and 'through the bond' are usually employed to account for this effect.[15-18] Direct interaction through space leads to the formation of symmetrised n_+ and n_- levels, the energies of which differ little owing to the

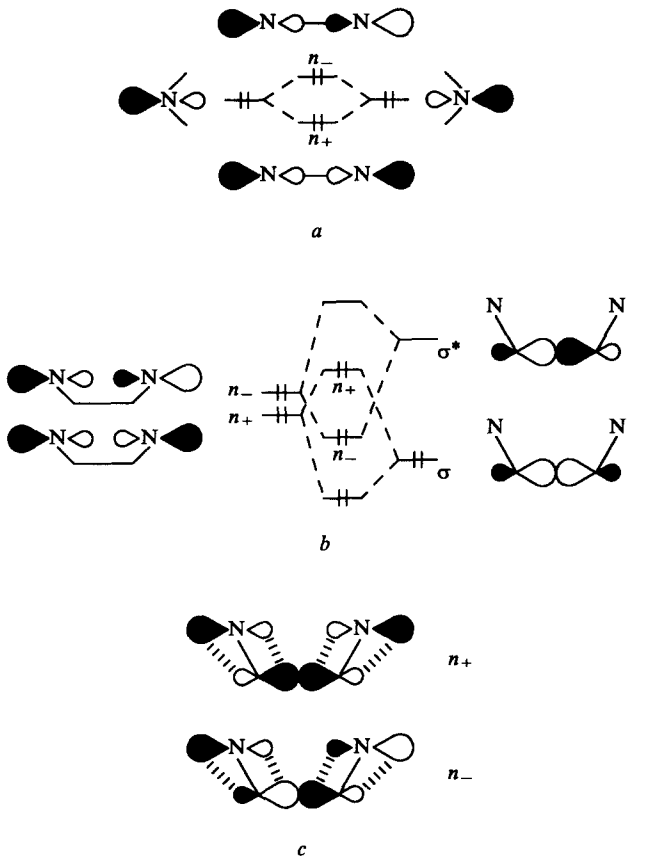


Figure 2. Interaction of the orbitals of the lone pairs of the nitrogen atoms in the pyrazine molecule: (*a*) through space; (*b*) through the C(2)–C(3) bond; (*c*) the form of the n_- and n_+ orbitals.

weak overlap as a consequence of the relatively large distance between the nitrogen atoms (Fig. 2*a*). We suggest that, as usual, combination in phase (n_+) has a lower energy than combination in antiphase (n_-). However, calculations and experiment have shown that the splitting between the levels n_+ and n_- is much greater than expected and moreover the n_+ level lies not below but above the n_- level by 1.72 eV.[7] Such an 'unnatural' order in the disposition of the levels can be explained by the fact that the lone pairs of the nitrogen atoms interact not only through space but also through C–C σ-bonds. Fig. 2*b* illustrates the interaction of the n_+ and n_- orbitals with the σ and σ* orbitals of the C(2)–C(3) bond in the pyrazine molecule. Compared with the weak 1,4-interaction between the nitrogen centres, the above 1,2-interactions of ($n_+ \pm \sigma$) and ($n_- \pm \sigma$) are strong. This leads to a greater splitting of the n_+ and n_- levels and to a change in their sequence. A similar interaction takes place with participation of the C(5)–C(6) bonds.

The molecular orbitals of complex **1** are constructed by a linear combination of the n_- and n_+ orbitals of pyrazine with the frontier orbitals of the two ML_5 fragments obtained by removing one ligand from the octahedral complex ML_6. The frontier orbital of the ML_5 fragment has the form shown in Fig. 3*a*.[7] On combining the bonding (M_+) and antibonding (M_-) combinations of the two frontier orbitals with the M_+ and M_- orbitals of the pyrazine lone pairs respectively, we obtain the pattern in the splitting of the levels shown in Fig. 3*b*. Since the M_+ and n_+ orbitals have more similar energies than the M_- and n_- orbitals, the M_+/n_+ splitting is greater than the M_-/n_- splitting. This renders the two M–N bonds in complex **1** equivalent, although in the pyrazine molecule the energies of the two electron pairs differ by 1.72 eV (see above).

Fig. 4 presents orbital diagrams for the chelate complex **2**: $L_4M(bpy)$. The ML_4 fragment has two almost degenerate frontier orbitals,[7] which are designated by the symbols M_+ and M_-

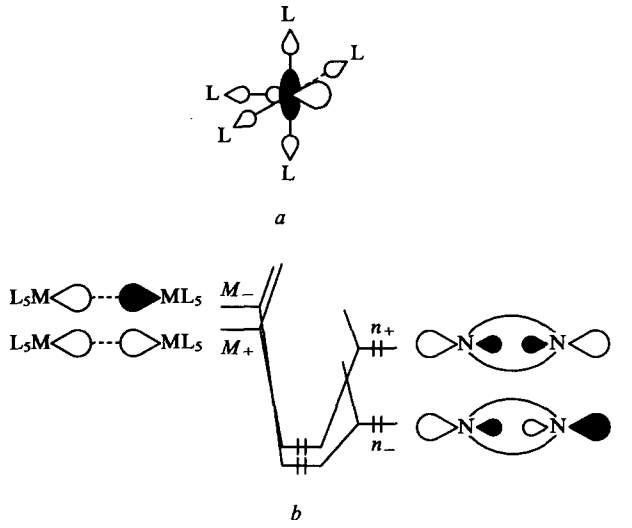


Figure 3. The form of the frontier orbital of the ML_5 fragment (*a*) and the orbital diagram for the interaction of the combination of two frontier orbitals in phase (M_+) and out of phase (M_-) with the n_+ and n_- orbitals of the lone pairs of pyrazine (*b*).

(Fig. 4*a*). In the 2,2′-bipyridyl molecule, the nitrogen *n* orbitals interact with one another through space and through the C(2)–C(2′) bonds similarly to the interaction of the orbitals in pyrazine. This interaction differs quantitatively from that in pyrazine, since the nitrogen lone pairs in the bipyridyl molecule are directed at an angle of 60° to one another and to the C(2)–C(2′)–L bond line. However, the qualitative pattern in the splitting of the levels of the lone pairs in he 2,2′-bipyridyl and pyrazine molecules is the same. The interaction of the M_+ and M_- orbitals with the n_+ and n_- orbitals (Fig. 4*b*) leads to strong chelate bonding (Fig. 4*c*).

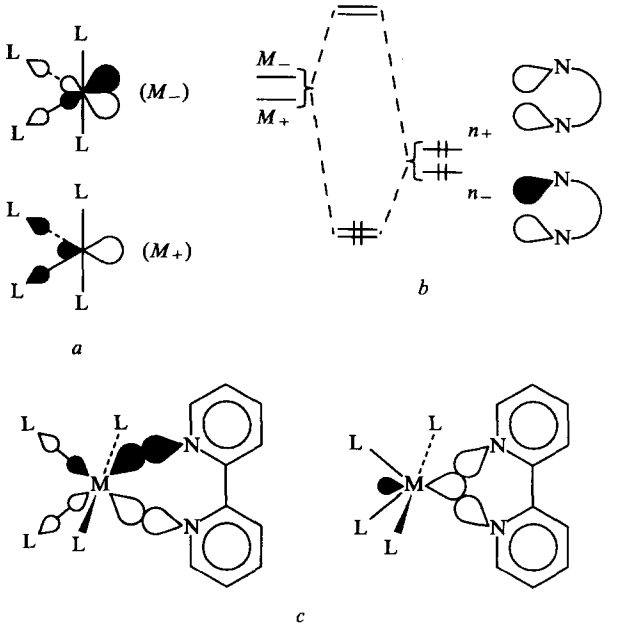
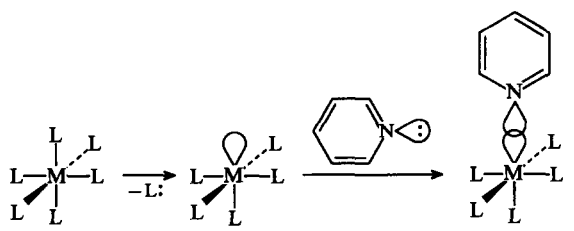


Figure 4. The form of the frontier orbitals of the ML_4 fragment (*a*), the diagram for the interaction of the frontier orbitals with the n_+ and n_- orbitals of the lone pairs in the 2,2′-bipyridyl molecule (*b*), and the form of the bonding molecular orbitals in the $L_4M(bpy)$ molecule (*c*).

3. The π-bonds in the octahedron

On passing from simple Lewis ligands of the type of NH_3, aliphatic amines, and phosphines to ligands containing p or π orbitals (these comprise CO, CN^-, SCN^-, Cl^-, and many organic ligands, including nitrogen-containing heterocycles) the positions of the redox levels can change greatly. We shall consider, for example the situation where one, two, or three of the simple ligands L in the octahedral complex ML_6 are replaced by pyridine molecules.



The pyridine nitrogen atom has a lone pair located in the plane of the ring. This pair participates in the formation of the usual coordinate bond in the complex L_5MPy (Py = pyridine). Pyridine (photochemical ionisation potential IP = 9.7 eV[18]) is a stronger lone pair donor than NH_3 (IP = 10.9 eV) but weaker than $N(CH_3)_3$ (IP = 8.5 eV), i.e. in the series of nitrogen-containing bases it is a moderately strong donor. However, in contrast to NH_3 and NR_3, there is a π-system in the pyridine molecule which can interact with the t_{2g} levels of the complex.

Fig. 5 illustrates the form of the two highest occupied and the two lowest unoccupied π orbitals of pyridine. Evidently in the coordinated pyridine molecule there is a possibility of interaction of the occupied d_{yz} level of the metal with the π LUMO and the π-bonding pyridine orbital, lying a little below the HOMO, because all three orbitals have the same symmetry b_1. This results in the stabilisation of both the π-bonding and d_{yz} levels, which increases the stability of the complex compared with the complex in which there is no π bonding.

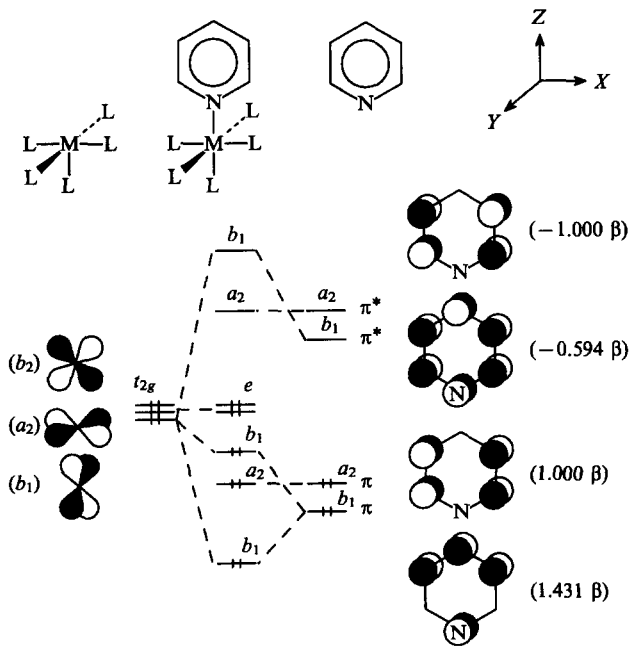
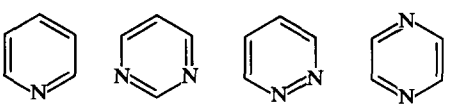


Figure 5. The π levels of the octahedral complex $L_5M(Py)$. The energies of the two highest occupied and the two lowest unoccupied π levels of the pyridine molecule, calculated by the Hückel method, are indicated in brackets.

The diagram in Fig. 5 corresponds to the case where the perturbation exerted by the π* molecular orbital of the ligand (reducing the energy of the t_{2g} level) is greater than the perturbation by the π molecular orbital (which increases the energy of the level). This type of splitting is more pronounced the lower the energy of the $\pi(b_1)$ orbital and the smaller the difference between the energies of the $\pi^*(b_1)$ and t_{2g} orbitals. In the series of free ligands pyridine, pyrimidine, pyridazine, and pyrazine, the ionisation potentials for the n and $\pi(b_1)$ levels, determined experimentally by photoelectron spectroscopy in the gas phase,[19] as well as the half-wave potentials $E_{1/2}$ for reduction in dimethylformamide (DMF), characterising the position of the $\pi^*(b_1)$ level,[20] vary as follows:

		Pyridine	Pyrimidine	Pyridazine	Pyrazine
					
IP/eV	n:	9.7	9.7	9.3	9.3
	$\pi(b_1)$:	10.5	10.5	11.3	13.3
$-E^{Red}_{1/2}$/ V (n.c.e.):		2.20	1.82	1.66	1.51

Evidently, on passing from pyridine to pyrimidine, the stabilising π-acceptor effect of the ligand should change little, but for pyridazine and pyrazine the effect intensifies, since the energy of the destabilising $\pi(b_1)$ orbital and of the stabilising $\pi^*(b_1)$ orbital diminishes. Compared with pyridine and pyrimidine, pyridazine and pyrazine also have higher n levels, which is indicated by the corresponding ionisation potentials, i.e. they are stronger Lewis bases. Consequently the stability of the pyridazine and pyrazine complexes increases as a result of the intensification of not only the π-acceptor but also of the σ-donor properties.

The π-bonding of two or three azine molecules, located at the vertices of the same face of the octahedron entails a decrease in two or three t_{2g} levels of the metal (Fig. 6). This means that, if the

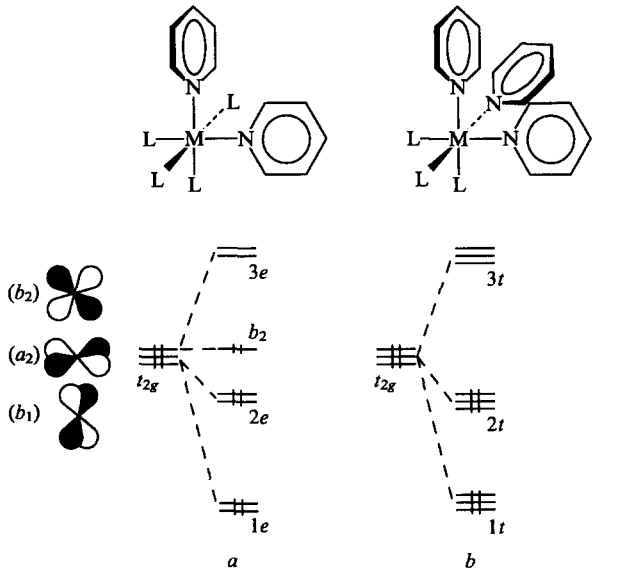
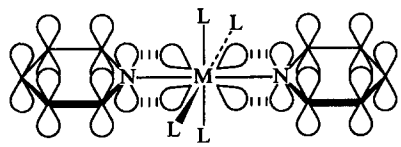


Figure 6. The π-bonding in the coordination of two (*a*) and three (*b*) pyridine molecules in orthogonal planes.

redox levels in the oxidation of the complexes are t_{2g} orbitals, then the oxidation potential of the complex $ML_3(azine)_3$ should increase relative to the oxidation potential of ML_6 (the oxidation should be hindered). A further increase in the number of ligands to six in the complex $M(azine)_6$ does not introduce significant changes into the perturbation pattern, since the π-systems of the two *trans*-ligands interact with only one of the t_{2g} orbitals, for example:

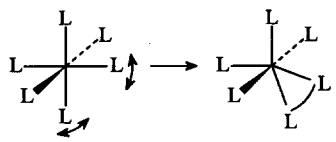


The positions of the $2t$ levels apparently change little (Fig. 6*b*).

If the ligand has fairly low acceptor π* orbitals but exhibits a π- or *p*-donor function, then the energy of the corresponding (in terms of symmetry) t_{2g} level increases, which destabilises the complex and diminishes its oxidation potential. Such ligands include, for example, Cl^- and other halide ions, ethers, or organic ligands of the Lewis *n*-type, which have electron-donating π-subsystems, in particular 4-mercaptopyridine.[21]

4. Geometrical distortions in the octahedron

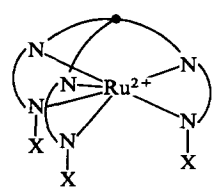
On coordination to bidentate ligands L–L, the structure of the regular octahedron is geometrically distorted when the length of the bridge is inadequate or the bridge is insufficiently flexible. These distortions are illustrated below schematically by arrows:



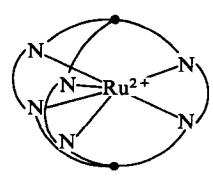
Analysis of the influence of the change in the bond angles between the L–M–L *cis*- and *trans*-bonds (see, for example Albright et al.[7] and the literature quoted therein) shows that the degenerate t_{2g} and e_g levels are lowered in the distorted octahedron. It was stated above that π-acceptor or π-donor ligands also create energy differences between the levels of the t_{2g} set. Since π overlap is a function of angular changes, the distortions in the octahedron also alter the degree of π bonding in the octahedron.

Geometrical distortions play an important role in 16-electron octahedral complexes ML_6. In order that such molecules should be in a low spin state, it is necessary that one of the t_{2g} levels should lie appreciably above the other two. This is achieved as a result of the combination of π bonding (if it is possible) with the geometrical distortions in the octahedron.

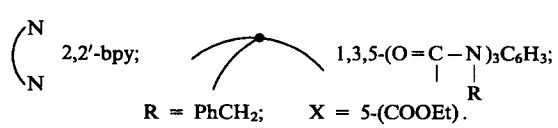
Particularly pronounced geometrical changes in the octahedron are observed in the case of the so called 'capped' ligands as well as ligands of the 'bicapped' type. The origin of these terms is clear from the three-dimensional formulae of compounds **4** and **5**, investigated by Barigelletti et al.,[22] presented below.



4
'capped'



5
'bicapped'



In this case, the six nitrogen atoms are arranged around the central metal ion, forming a trigonal prism. The six *n* orbitals of nitrogen, directed towards the centre of symmetry (D_{3h}), form six symmetrised group orbitals, the conventional representations of which are given in Fig. 7.

Fig. 7 shows that there is no fundamental difference between the octahedral and prismatic complexes: in both cases, the occupied t_{2g} levels (a_{1g} + e_{2g}) play the role of the HOMO, while the unoccupied e_g levels play the role of the LUMO.

Distortions can also arise owing to the rigidity of the bridging bidentate ligand. Thus the pyridine rings in 2,2'-bipyridyl cannot be located in the same plane owing to the repulsion of the hydrogen atoms in the 3- and 3'-positions, i.e. the molecule is twisted relative to the C(2)–C(2') axis; this alters the symmetry of the complex and the strength of bonding with the central metal ion.

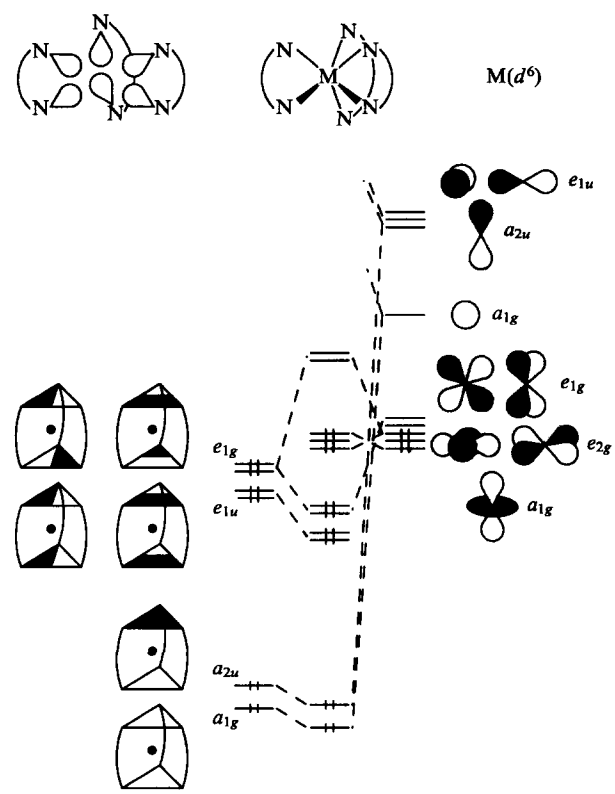


Figure 7. Molecular σ orbitals of the 'capped' and 'bicapped' complexes **4** and **5**.

5. Electrochemistry and photochemistry

In the general case, the electronic transitions in the spectra of transition metal complexes ML_6 can be divided into three types:[23]

(1) transitions between levels located predominantly on the metal, for example, the familiar d–d transition;

(2) transitions between levels predominantly located on ligands (for example, the π–π* transitions in aromatic ligands);

(3) transitions in which an electron is transferred from the metal to the ligand (MLCT) or, conversely, from the ligand to the metal (LMCT).

The possible electronic transitions for the symmetrical octahedral complex ML_6, in which the ligands L have π-systems, are illustrated schematically in Fig. 8. We may note that in the 17-electron complexes there is a possibility, apart from the transitions shown in Fig. 8, also of the $\pi L \rightarrow M(t_{2g})$ and $\sigma L \rightarrow M(t_{2g})$ transitions, while in the 19-electron complexes $M(e_g) \rightarrow \pi^* L$ transitions are possible. Among the transitions shown in Fig. 8, three (*c*, *d*, and *f*) correspond to the charge-transfer (CT) bands. In the spectra of 18-electron d^6 complexes with azine ligands, the

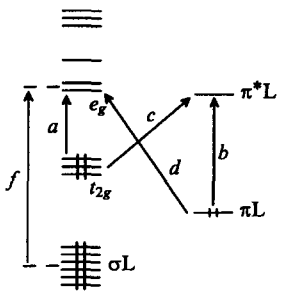


Figure 8. Schematic illustration of the main electronic transitions in the spectra of the complex of ML_6 with π-ligands. Transitions: (*a*) *d*–*d*; (*b*) πL→π*L; (*c*) $M(t_{2g})$→π*L(MLCT); (*d*) πL→$M(e_g)$ (LMCT); (*f*) σL→$M(e_g)$.

longest-wavelength band corresponds as a rule to the MLCT transition[1] $M(t_{2g})$→π*L, since the π and π* orbitals of these ligands are fairly low. This band usually has a low intensity, rarely exceeding 10^4 litre mol^{-1} s^{-1}, and in terms of this feature it can be distinguished from the more intense π→π* band. Thus the frontier orbitals of the azine complexes are $M(t_{2g})$ (HOMO) and π*L (LUMO).

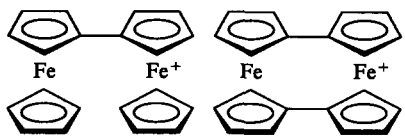
For this reason, one can assume that in the general case the electronic changes occurring on electrochemical oxidation of such complexes should be localised 'on the metal', while in the electrochemical reduction they should be localised 'on the azine ligand'. Naturally, one is dealing with the so called 'primary electronic changes'. Electron transfer may be followed by intramolecular electron transfer (IET), as a result of which the electron in the radical-cation or radical-anion formed may be located in a region completely different from that to which it was initially transferred.

Dinuclear compounds of the type M^1–μ-L–M^2, where μ-L is a bridging ligand, for example, pyrazine, 4,4′-bipyridyl, cyanide, etc. while M^1 and M^2 are two different or identical organometallic residues, are of great interest. As a rule, complexes in which M^1 and M^2 are in oxidation states differing by unity are the most important. If the two metallic centres can interact with one another via a bridge, then there is a possibility of an IET process, which in the given instance is referred to as an intervalence [mixed valence ? Ed.] transition:

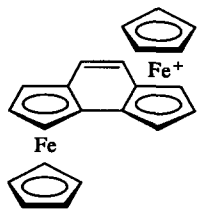
$$(M^1)^+ - \mu\text{-L} - M^2 \longrightarrow M^1 - \mu\text{-L} - (M^2)^+ .$$

Robin and Day[24] proposed that mixed-valence complexes be divided into three classes in terms of the degree of delocalisation of the valence electrons. Compounds in which there is no interaction of any kind between centres with different oxidation states, i.e. the valences are fixed, are referred to as class I and the properties of these complexes are simply the sum of the properties of the two different centres. The fully delocalised systems, in which the two centres with different oxidation states are indistinguishable by methods with characteristic times greater than the time required for electron transfer, are referred to as class III. Compounds of class II occupy an intermediate position between classes I and III. In this case, there is a weak interaction between M^1 and M^2.

The intervalence transitions are usually investigated by spectroscopic methods. The biferrocenyl cations **6** and **8** and a number of others were particularly thoroughly investigated (see Richardson[6] and the references quoted therein). The electronic spectrum of the cation **6** in acetonitrile contains absorption bands at 545, 840, and, which is particularly important, at 1800 nm (ε = 750) in the near infrared. The 1800 nm band is not observed in the spectra of either Fc–Fc or Fc^+–Fc^+. On this basis, it was attributed to an intervalence or IET transition occurring as a consequence of optical excitation. The Mössbauer spectrum shows clearly that the cation **6** contains iron(II) and iron(III) and that a thermal electron exchange takes place at a rate of about 10^7 s^{-1}. Thus the ion **6** belongs to class II in terms of the classification of Robin and Day.



6 **7**

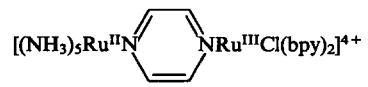


8

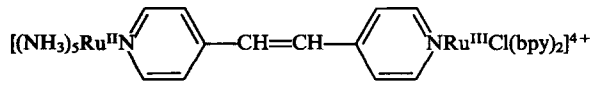
Electrochemical measurements have also shown that the cation **6** contains divalent and trivalent iron. Oxidation (E^{Ox} = 0.64 V in CH_3CN) and reduction (E^{Red} = 0.31 V) involve iron(II) and iron(III) respectively.[25]

Thus in the mixed-valence complexes the redox centres in the anodic and cathodic processes are different metal ions. However, in dinuclear bridged complexes of the type L_nM–μ-L–ML_n with two identical metals in the same oxidation state and with the same ligand environment, the electronic changes on reduction may be localised on the bridging or terminal ligand.

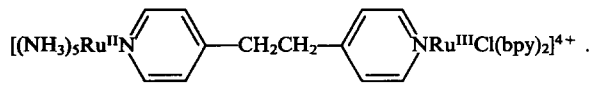
The band in the near infrared corresponds to charge transfer between two metallic centres (MMCT). It has been observed for many bridged bimetallic ruthenium complexes, for example, for the pyrazine and dipyridylethylene complexes presented below (the extinction coefficients are given in brackets):[26]



960 nm (530)



680 nm (< 300)



MMCT (band absent)

However, on passing to the dipyridylethane bridge, the MMCT band vanishes as a consequence of the absence of conjugation between the pyridine rings.

It is natural to expect that there should be a linear correlation between the energy of the long-wavelength charge-transfer band and the electrode potentials of the complexes, because the same frontier orbitals are involved both in photo-excitation and in electrode processes. The correlation equation is

$$G = ah\nu_{CT} + b, \qquad (1)$$

where *G* is the 'electrochemical gap' (in volts), defined as the difference between the oxidation (E^{Ox}) and reduction (E^{Red}) potentials of the given complex ($G = E^{Ox} - E^{Red}$), $h\nu_{CT}$ is the energy of the charge-transfer band or the 'spectral gap' (in eV), and *a* and *b* are constants. From general considerations, it is to be expected that *a* should be close to unity.

There have been a number of studies in which measurements were made of three parameters simultaneously ($h\nu_{CT}$, E^{Ox}, and E^{Red}) in fairly wide series of ruthenium complexes.[27–37]

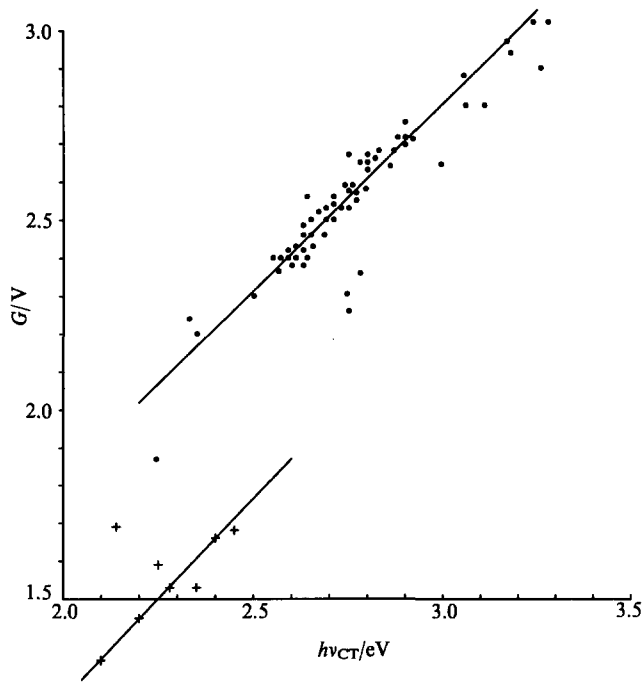
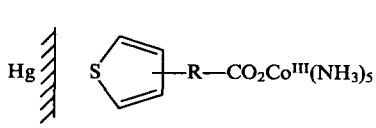


Figure 9. Relation between G and $h\nu_{CT}$ for ruthenium(II) complexes based on data in Refs 27–33.

Fig. 9 presents the relation between the spectral and electrochemical gaps for ruthenium(II) complexes constructed on the basis of the results of these studies. Evidently there is a linear relation between G and $h\nu_{CT}$ with a slope close to unity. A number of points deviate from the overall straight line, the deviation of the points in the lower left-hand corner of the diagram, designated by crosses, being most pronounced. They form their own straight line with a slope which is also close to unity. The reason for this is apparently that the majority of the 70 points plotted on the graph correspond to compounds with bidentate ligands of the type of α,α′-bipyridyl, 2,2′-bipyrimidyl, and similar compounds. On the other hand, the crosses correspond to compounds with six monodentate ligands, for example, $Ru(NH_3)_5L$, $(Py)Ru(NH_3)_4L$, $(3\text{-ClPy})Ru(NH_3)_4L$ (where L = 4-cyano-*N*-methylpyridinium), etc.[28] The shift of the points is caused by the change in the constant b in Eqn. (1). This constant probably depends largely on solvation. Indeed, it has been shown that MLCT depends exceptionally strongly on the solvent [nitromethane, acetonitrile, propylene carbonate, acetone, DMF, and dimethyl sulfoxide (DMSO) have been investigated] and this solvatochromism cannot be accounted for simply in terms of the dielectric properties of the solvents. There is evidence that the charge transfer depends on the specific interaction of the solvent with a coordinated NH_3 molecule.

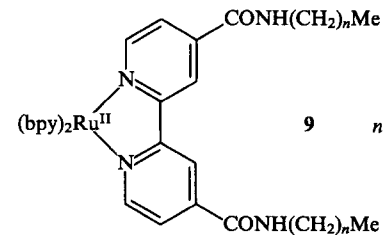
When the redox properties of the complexes are considered, it is essential to take into account primarily also the possibility of the specific interaction with the electrode material. For example, the pentamminecobalt(III) complex containing a carboxylate ion with a thienyl substituent as the sixth ligand is reduced at a mercury cathode not at the metal atom but initially at the thienyl group with subsequent electron transfer to the metal via the IET process described above.[38] This is associated with the strong specific interaction of the sulfur atom with mercury, which is responsible for the following orientation on the electrode:



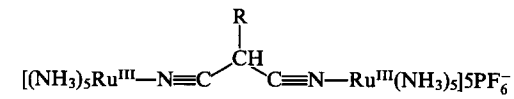
III. Electrochemical properties of ruthenium and rhodium complexes

1. Mononuclear ruthenium complexes

There has been a particular growth of interest in the chemistry of ruthenium complexes in recent years because ruthenium compounds have been finding increasing application in various fields. For example, since complexes containing ruthenium in different oxidation states are more stable than the analogous iron complexes, they can serve as a convenient model for the study of various redox reactions in biological systems where a ruthenium atom replaces an iron atom. In this connection, studies have been made[39] on the redox properties of tetra(*o*-aminophenyl)porphyrins containing ruthenium(II) combined with various axial ligands. Certain ruthenium compounds are of interest as nonlinear optical materials. Thus ruthenocene and its derivatives exhibit a second-order nonlinear optical effect.[3] Similar properties have been observed in recent years also in other ruthenium complexes, in particular those containing bipyridyl (compound **9**) and bridging (compound **10**) ligands.[4, 40]



9 $n = 1, 5, 11, 15, 17$



10

R = H, Bu^t

Considerable attention has been devoted to the study of polypyridylruthenium(II) complexes (Tables 1 and 2). More than 200 bidentate (LL) polypyridyl ligands used in the chemistry of ruthenium(II) have been examined in a review,[2] which also presents the oxidation-reduction potentials of a large number of the homoleptic complexes $Ru(LL)_3^{2+}$ synthesised. It is important to note that the different one-electron transitions observed on cyclic voltammograms for the ruthenium(II) complexes can be readily related in many instances to specific donor or acceptor orbitals.

Polypyridylruthenium(II) complexes are oxidised with participation of the t_{2g} orbitals d_{xy}, d_{xz}, and d_{yz}, which are located on the metal atom. This results in the formation of low-spin ruthenium(III) complexes with the $4d^5$ configuration, which are resistant to ligand substitution. This has been confirmed with the aid of orbital diagrams.[41]

$$[Ru^{II}(LL)_3]^{2+} \rightleftharpoons [Ru^{III}(LL)_3]^{3+} + \bar{e}\,.$$

It has been established that the Ru(II)/Ru(III) redox transitions in complexes with polypyridyl ligands lie within a narrow range of potentials [about 1.53 V relative to the saturated calomel electrode (s.c.e.)]. The replacement of one or several polypyridyl ligands can significantly alter these potentials. Thus the substitution of one bpy in $Ru(bpy)_3^{2+}$ by two chloride ions affords $Ru(bpy)_2Cl_2$ and lowers the oxidation potential to 0.63 V, while the introduction of two CO molecules instead of bpy increases the oxidation potential of $[Ru(bpy)_2(CO)_2]^{2+}$ to 2.18 V.

Table 1. Data on the electrochemical oxidation of mononuclear ruthenium complexes.

Complex[a]	E/V	ECLS[b]	Conditions[c]	Ref.
4 ('capped')	1.54	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	22
5 ('bicapped')	1.55	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, Ag	22
$Ru(bpy)_3^{2+}$	1.26	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, Ag	2, 44
$[Ru(5,5'\text{-}(EtO_2C)_2bpy)_3]^{2+}$	1.55	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, Ag	22
$[Ru(bpy)_2bpt]^+$	0.85	$Ru^{II/III}$	CG, MeCN, Bu_4NClO_4, n.h.e.	1
$Ru(2,3\text{-}dpp)(CO)_2Cl_2$	1.90	$Ru^{II/III}$	Pt, MeCN, Et_4NClO_4, s.c.e.	106
$Ru(2,5\text{-}dpp)(CO)_2Cl_2$	1.86	$Ru^{II/III}$	Pt, MeCN, Et_4NClO_4, s.c.e.	106
$[Ru(bpy)(biq)(Me_2bpy)]^{2+}$	1.30	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	42
$[Ru(bpy)(biq)(phen)]^{2+}$	1.35	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	42
$[Ru(bpy)(biq)(pq)]^{2+}$	1.39	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	42
$[Ru(bpy)(biq)(i\text{-}biq)]^{2+}$	1.29	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	42
$[Ru(bpy)(biq)(pzpm)]^{2+}$	1.42	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	42
$[Ru(bpy)(biq)(biImH_2)]^{2+}$	1.09	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	42
$[Ru(bpy)(biq)(bpm)]^{2+}$	1.46	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	42
$[Ru(bpy)(biq)(taphen)]^{2+}$	1.46	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	42
$[Ru(bpy)(biq)(dinapy)]^{2+}$	1.27	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	42
$[Ru(dinapy)_3]^{2+}$	1.01	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	44
$[Ru(bpy)_2(biBzImH)_2]^{2+}$	1.12	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	101
$Ru(chd)_3(BPh)$	1.22	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NBF_4, s.c.e.	70
$Ru(chd)_3(BBu^n)$	1.17	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NBF_4, s.c.e.	70
$Ru(chd)_3(BOMe)$	1.14	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NBF_4, s.c.e.	70
$Ru(chd)_3(BF)$	1.33	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NBF_4, s.c.e.	70
$Ru(chd)_3(BOMe)$	1.21	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NBF_4, s.c.e.	70
$Ru(chd)_3(BOEt)$	1.20	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NBF_4, s.c.e.	70
$Ru(chd)_3(BOPr^n)$	1.20	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NBF_4, s.c.e.	70
$Ru(chd)_3(BOPr^i)$	1.20	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NBF_4, s.c.e.	70
$Ru(chd)_3(BOBu^n)$	1.21	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NBF_4, s.c.e.	70
$Ru(chd)_3(BOn\text{-}C_5H_{11})$	1.21	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NBF_4, s.c.e.	70
$Ru(chd)_3(BOn\text{-}C_{10}H_{21})$	1.22	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NBF_4, s.c.e.	70
$Ru(dpg)(BBu^n)$	1.34	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NBF_4, s.c.e.	70
$Ru(dpg)(BOMe)$	1.43	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NBF_4, s.c.e.	70
$Ru(dmg)(BBu^n)$	1.15	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NBF_4, s.c.e.	70
$Ru(dmg)(BOMe)$	1.23	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NBF_4, s.c.e.	70
$[RuBr(CO)_2(\eta^5\text{-}C_5Ph_5)]$	1.76	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NPF_6, s.c.e.	68
$[RuMe(CO)_2(\eta^5\text{-}C_5Ph_5)]$	1.49	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NPF_6, s.c.e.	68
$[RuBr(CO)(PPh_3)L]$	1.07	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NPF_6, s.c.e.	68
$L = \eta^5\text{-}C_5Ph_5$				
$[RuBr(CO)(PEt_3)L]$	1.01	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NPF_6, s.c.e.	68
$L = \eta^5\text{-}C_5Ph_5$				
$[RuBr(CO)\{P(OMe)_3\}L]$	1.12	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NPF_6, s.c.e.	68
$L = \eta^5\text{-}C_5Ph_5$				
$[RuMe(CO)(PEt_3)L]$	0.73	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NPF_6, s.c.e.	68
$L = \eta^5\text{-}C_5Ph_5$				
$[RuEt(CO)(PEt_3)L]$	0.71	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NPF_6, s.c.e.	68
$L = \eta^5\text{-}C_5Ph_5$				
$[Ru(COMe)(CO)(PEt_3)L]$	0.67	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NPF_6, s.c.e.	68
$L = \eta^5\text{-}C_5Ph_5$				
$[Ru(CMe{=}CMe_2)(CO)(PEt_3)L]$	0.59	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NPF_6, s.c.e.	68
$L = \eta^5\text{-}C_5Ph_5$				
$[Ru(salen)(Ph_3P)]Cl$	0.49	$Ru^{III/IV}$	CG, MeCN, Bu_4NClO_4, $Ag/AgNO_3$	129
$[Ru(salen)(Py)]ClO_4$	0.76	$Ru^{III/IV}$	CG, MeCN, Bu_4NClO_4, $Ag/AgNO_3$	129
$[Ru(salen)(N_3)]$	0.48	$Ru^{III/IV}$	CG, MeCN, Bu_4NClO_4, $Ag/AgNO_3$	129
$[Ru(salen)(Ph_3P)(oTs]$	0.76	$Ru^{III/IV}$	CG, MeCN, Bu_4NClO_4, $Ag/AgNO_3$	129
$[Ru(salen)(CN)_2]^-$	0.37	$Ru^{III/IV}$	CG, MeCN, Bu_4NClO_4, $Ag/AgNO_3$	129
$[(bpy)(tpy)Ru(H_2O)]^{2+}$	0.80	$Ru^{II/IV}$	Pt, H_2O, Bu_4NOH, s.c.e.	130
$RuCl_2(Bu^tCN)_4$	0.99	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	131
$RuCl_2(2,4,6\text{-}Me_3C_6H_2CN)_4$	1.26	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	131
$RuCl_2(4\text{-}Br\text{-}2,6\text{-}Me_2C_6H_2)_4$	1.20	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	131
$RuCl_2(Bu^tCN)_2(Ph_3P)_2$	0.79	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	131
$RuCl_2L_2(Ph_3P)_2$	0.85	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	131
$L = 2,4,6\text{-}Me_3C_6H_2$				
$Ru(phen)_3^{2+}$	1.31	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	117
$Ru(dpp)_3^{2+}$	1.68	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	117
$Ru(dpq)_3^{2+}$	1.65	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	117
$Ru(phen)_2(dpq)^{2+}$	1.42	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	117
$Ru(phen)_2(dpp)^{2+}$	1.39	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	117
$Ru(bpy)_2(dpp)^{2+}$	1.33	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	117
$Ru(dpk)_2Cl_2$	0.61	$Ru^{II/III}$	CG, DMF, Bu_4NClO_4, s.c.e.	132
$Ru(dpk)(CO)Cl_2$	0.88	$Ru^{II/III}$	CG, DMF, Bu_4NClO_4, s.c.e.	132

Table 1. (continued)

Complex [a]	E/V	ECLS [b]	Conditions [c]	Ref.
$[Ru(dpk)(MeCN)_2]^{2+}$	1.31	$Ru^{II/III}$	CG, DMF, Bu_4NClO_4, s.c.e.	132
$[Ru(bpy)_2(dpk)]^{2+}$	1.34	$Ru^{II/III}$	CG, DMF, Bu_4NClO_4, s.c.e.	132
$Ru(o\text{-}NH_2)TPP(CO)$	0.88	$Ru^{II/III}$	Pt, MeCN, Et_4NClO_4, Ag/AgCl	39
	1.20			
$Ru(o\text{-}NH_2)TPP(Py)_2$	0.15		Pt, MeCN, Et_4NClO_4, Ag/AgCl	39
	0.38			
$Ru(o\text{-}NH_2)TPP(MeCN)_2$	0.12		Pt, MeCN, Et_4NClO_4, Ag/AgCl	39
	0.28			
$Ru(dmqH)_2(Ph_3P)_2$	0.44	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	76
	1.00	$Ru^{III/IV}$		
	0.40	$Ru^{II/III}$	Au, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	
	1.00	$Ru^{III/IV}$		
	0.40	$Ru^{II/III}$	CG, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	
	1.00	$Ru^{III/IV}$		
$Ru(dpqH)_2(Ph_3P)_2$	0.57	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	76
	1.13	$Ru^{III/IV}$		
	0.58	$Ru^{II/III}$	Au, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	
	1.12	$Ru^{III/IV}$		
	0.58	$Ru^{II/III}$	CG, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	
	1.14	$Ru^{III/IV}$		
$Ru(chdH)_2(Ph_3P)_2$	0.37	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	76
	0.96	$Ru^{III/IV}$		
	0.38	$Ru^{II/III}$	Au, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	
	0.98	$Ru^{III/IV}$		
	0.38	$Ru^{II/III}$	CG, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	
	0.99	$Ru^{III/IV}$		
$Ru(dmgH)_2(Ph_3P)(Py)$	0.42	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	76
	0.89	$Ru^{III/IV}$		
$Ru(quin)_2(Ph_3P)_2$	0.14	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	76
	1.15	$Ru^{III/IV}$		
$Ru(bgdH)_2(Ph_3P)_2$	0.23	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	76
	0.78	$Ru^{III/IV}$		
	1.04			
$Ru(bgdH)_2(Ph_3P)(MeIm)$	0.23	$Ru^{II/III}$	Pt, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	76
	0.73	$Ru^{III/IV}$		
	0.95			
$[Ru(NH_3)_5(Py)]^{2+}$	0.29	$Ru^{II/III}$	GG, H_2O, CF_3COOH/CF_3COONa, n.h.e.	59–61
	0.30	$Ru^{II/III}$	GG, H_2O, $MeC_6H_4OSO_3H/MeC_6H_4OSO_3K$, n.h.e.	59
$[Ru(NH_3)_5(isn)]^{2+}$	0.38	$Ru^{II/III}$	GG, H_2O, $MeC_6H_4OSO_3H/MeC_6H_4OSO_3K$, n.h.e.	59
$[Ru(NH_3)_5(4\text{-}acpy)]^{2+}$	0.39	$Ru^{II/III}$	GG, H_2O, $MeC_6H_4OSO_3H/MeC_6H_4OSO_3K$, n.h.e.	59
(E)-$[Ru(NH_3)_4(4\text{-}pic)_2]^{2+}$	0.42	$Ru^{II/III}$	GG, H_2O, CF_3COOH/CF_3COONa, n.h.e.	61
(E)-$[Ru(NH_3)_4(4\text{-}pic)(Py)]^{2+}$	0.45	$Ru^{II/III}$	GG, H_2O, CF_3COOH/CF_3COONa, n.h.e.	61
(E)-$[Ru(NH_3)_4(4\text{-}pic)(isn)]^{2+}$	0.50	$Ru^{II/III}$	GG, H_2O, CF_3COOH/CF_3COONa, n.h.e.	61
(Z)-$[Ru(NH_3)_4(4\text{-}pic)(isn)]^{2+}$	0.54	$Ru^{II/III}$	GG, H_2O, CF_3COOH/CF_3COONa, n.h.e.	61
(E)-$[Ru(NH_3)_4(4\text{-}pic)(pz)]^{2+}$	0.61	$Ru^{II/III}$	GG, H_2O, CF_3COOH/CF_3COONa, n.h.e.	61
(E)-$[Ru(NH_3)_4(4\text{-}pic)L]^{2+}$ L = 4-acpy	0.52	$Ru^{II/III}$	GG, H_2O, CF_3COOH/CF_3COONa, n.h.e.	61
(E)-$[Ru(NH_3)_4(Py)_2]^{2+}$	0.49	$Ru^{II/III}$	GG, H_2O, $MeC_6H_4OSO_3H/MeC_6H_4OSO_3K$, n.h.e.	59
(Z)-$[Ru(NH_3)_4(Py)_2]^{2+}$	0.51	$Ru^{II/III}$	GG, H_2O, $MeC_6H_4OSO_3H/MeC_6H_4OSO_3K$, n.h.e.	59
(E)-$[Ru(NH_3)_4(Py)(isn)]^{2+}$	0.55	$Ru^{II/III}$	GG, H_2O, CF_3COOH/CF_3COONa, n.h.e.	61
(Z)-$[Ru(NH_3)_4(Py)(isn)]^{2+}$	0.58	$Ru^{II/III}$	GG, H_2O, CF_3COOH/CF_3COONa, n.h.e.	61
(E)-$[Ru(NH_3)_4(Py)(pz)]^{2+}$	0.65	$Ru^{II/III}$	GG, H_2O, CF_3COOH/CF_3COONa, n.h.e.	61
(E)-$[Ru(NH_3)_4(4\text{-}acpy)(Py)]^{2+}$	0.55	$Ru^{II/III}$	GG, H_2O, CF_3COOH/CF_3COONa, n.h.e.	61
(E)-$[Ru(NH_3)_4(pz)(isn)]^{2+}$	0.70	$Ru^{II/III}$	GG, H_2O, CF_3COOH/CF_3COONa, n.h.e.	61
(Z)-$[Ru(NH_3)_4(Py)(isn)]^{2+}$	0.75	$Ru^{II/III}$	GG, H_2O, CF_3COOH/CF_3COONa, n.h.e.	61
(E)-$[Ru(NH_3)_4(isn)L]^{2+}$ L = 4-acpy	0.61	$Ru^{II/III}$	GG, H_2O, CF_3COOH/CF_3COONa, n.h.e.	61
(Z)-$[Ru(NH_3)_4(isn)L]^{2+}$ L = 4-acpy	0.66	$Ru^{II/III}$	GG, H_2O, CF_3COOH/CF_3COONa, n.h.e.	61
(E)-$[Ru(NH_3)_4(pz)L]^{2+}$ L = 4-acpy	0.74	$Ru^{II/III}$	GG, H_2O, CF_3COOH/CF_3COONa, n.h.e.	61
(E)-$[Ru(NH_3)_4(4\text{-}acpy)_2]^{2+}$	0.60	$Ru^{II/III}$	GG, H_2O, CF_3COOH/CF_3COONa, n.h.e.	61
(E)-$[Ru(NH_3)_4(pz)_2]^{2+}$	0.78	$Ru^{II/III}$	GG, H_2O, NaCl, n.h.e.	61
(Z)-$[Ru(NH_3)_4(pz)_2]^{2+}$	0.86	$Ru^{II/III}$	GG, H_2O, NaCl, n.h.e.	61
$[Ru(NH_3)_5(pz)]^{2+}$	0.49	$Ru^{II/III}$	GG, H_2O, NaCl, n.h.e.	61
$[Ru(bpy)_2(biImH_2)]^{2+}$	1.04	$Ru^{II/III}$	Pt, MeCN, Bu_4NBF_4, s.c.e.	50
$[Ru(bpy)_2(biBzImH_2)]^{2+}$	1.12		Pt, MeCN, Bu_4NBF_4, s.c.e.	50
$[Ru(bpy)_2(PBzImH)]^{2+}$	1.17		Pt, MeCN, Bu_4NBF_4, s.c.e.	50
$[Ru(bpy)_2(OBzImH)]^{2+}$	0.39		Pt, MeCN, Bu_4NBF_4, s.c.e.	50

Table 1. (continued)

Complex [a]	E/V	ECLS [b]	Conditions [c]	Ref.
$[Ru(bpy)_2(PBzIm)]^+$	0.72		Pt, MeCN, Bu_4NBF_4, s.c.e.	50
$[Ru(bpy)_2(biBzImH)]^+$	0.72		Pt, MeCN, Bu_4NBF_4, s.c.e.	50
$[Ru(bpy)_2(biBzIm)]$	0.43		Pt, MeCN, Bu_4NBF_4, s.c.e.	50
$[Ru(bpy)_2(OBzIm)]^+$	0.09		Pt, MeCN, Bu_4NBF_4, s.c.e.	50
$[Ru(2,3\text{-dpp})(bpy)_2]^{2+}$	1.31	$Ru^{II/III}$	Pt, MeCN, Et_4NClO_4, s.c.e.	103

Note. [a] The abbreviations of the ligand names are given in the text of the corresponding sections. Those not mentioned in the text are as follows: dpk = 2,2'-bipyridyl ketone; R_2dsc = dialkyl-substituted diselenocarbamate; (o-NH_2)TPP = tetra-o-aminophenylporphyrin; tpy = 2,2',6',2''-terpyridine; PBzImH = 2-(2-pyridyl)benzimidazole; OBzImH = 2-(o-hydroxyphenyl)benzimidazole; PImH = 2-(2-pyridyl)imidazole; $Fc^{+/0}$ = ferrocene-ferrocenium cation redox couple.

[b] ECLS denotes the most probable sites where the electronic changes are localised in the redox transitions. An empty column means that the assignment is difficult. The symbol L indicates that the reduction involves one of the ligands.

[c] In all tables, the conditions in the electrochemical measurements are listed in the following order: material of the working electrode, solvent, supporting electrolyte, reference electrode.

Table 2. Data on the electrochemical reduction of mononuclear ruthenium complexes.

Complex	$-E$/V	ECLS	Conditions	Ref.
4 ('capped')	0.86	L	Pt, MeCN, Bu_4NClO_4, s.c.e.	22
	0.99			
	1.17			
5 ('bicapped')	1.01	L	Pt, MeCN, Bu_4NClO_4, Ag	22
	1.20			
	1.38			
$[Ru(bpy)_3]^{2+}$	1.35	L	Pt, MeCN, Bu_4NClO_4, Ag	2, 44
	1.54			
	1.79			
$[Ru(5,5'\text{-}(EtO_2C)_2bpy)_3]^{2+}$	0.74	L	Pt, MeCN, Bu_4NClO_4, Ag	22
	0.86			
	1.03			
$[Ru(bpy)_2bpt]^+$	1.46	bpy	CG, MeCN, Bu_4NClO_4, n.h.e.	1
	1.72			
	2.28			
	2.45			
	2.52			
$Ru(2,3\text{-dpp})(CO)_2Cl_2$	1.04	dpp	Pt, MeCN, Et_4NClO_4, s.c.e.	106
$Ru(2,5\text{-dpp})(CO)_2Cl_2$	0.93	dpp	Pt, MeCN, Et_4NClO_4, s.c.e.	106
$[Ru(bpy)(biq)(Me_2bpy)]^{2+}$	0.92	biq	Pt, MeCN, Bu_4NClO_4, s.c.e.	42
	1.39	bpy		
	1.72	Me_2bpy		
$[Ru(bpy)(biq)(phen)]^{2+}$	0.90	biq	Pt, MeCN, Bu_4NClO_4, s.c.e.	42
	1.38	bpy		
	1.68	phen		
$[Ru(bpy)(biq)(pq)]^{2+}$	0.88	biq	Pt, MeCN, Bu_4NClO_4, s.c.e.	42
	1.19	pq		
	1.62	bpy		
$[Ru(bpy)(biq)(i\text{-biq})]^{2+}$	0.92	biq	Pt, MeCN, Bu_4NClO_4, s.c.e.	42
	1.39	bpy		
	1.66	i-biq		
$[Ru(bpy)(biq)(pzpm)]^{2+}$	0.89	biq	Pt, MeCN, Bu_4NClO_4, s.c.e.	42
	1.38			
	1.65			
$[Ru(bpy)_2(dinapy)]^{2+}$	1.66	dinapy	Pt, MeCN, Bu_4NClO_4, s.c.e.	42
	1.26			
	1.83			
$[Ru(bpy)(biq)(bpm)]^{2+}$	0.82	biq	Pt, MeCN, Bu_4NClO_4, s.c.e.	42
	1.10	bpm		
	1.56	bpy		
$[Ru(bpy)(biq)(taphen)]^{2+}$	0.65	taphen	Pt, MeCN, Bu_4NClO_4, s.c.e.	42
	1.00	biq		
	1.51	bpy		
$[Ru(bpy)(biq)(dinapy)]^{2+}$	0.66	dinapy	Pt, MeCN, Bu_4NClO_4, s.c.e.	42, 44, 53
	0.99	biq		
	1.71	bpy		
$[Ru(dinapy)_3]^{2+}$	0.82	dinapy	Pt, MeCN, Bu_4NClO_4, s.c.e.	44
	1.07			
	1.40			

Table 2. (continued)

Complex	$-E$/V	ECLS	Conditions	Ref.
$[Ru(salen)(Ph_3P)Cl]$	0.52	$Ru^{III/II}$	CG, MeCN, Bu_4NClO_4, $Ag/AgNO_3$	129
$[Ru(salen)(Ph_3P)(Py)]^+$	0.47	$Ru^{III/II}$	CG, MeCN, Bu_4NClO_4, $Ag/AgNO_3$	129
$[Ru(salen)(Ph_3P)(N_3)]$	0.64	$Ru^{III/II}$	CG, MeCN, Bu_4NClO_4, $Ag/AgNO_3$	129
$[Ru(salen)(Ph_3P)(PBu_3)]^+$	0.47	$Ru^{III/II}$	CG, MeCN, Bu_4NClO_4, $Ag/AgNO_3$	129
$[Ru(salen)(Ph_3P)(OTs)]$	0.65	$Ru^{III/II}$	CG, MeCN, Bu_4NClO_4, $Ag/AgNO_3$	129
$[Ru(salen)(CN)_2]^-$	1.06	$Ru^{III/II}$	CG, MeCN, Bu_4NClO_4, $Ag/AgNO_3$	129
$[Ru(bpy)_2(CO)_2]^{2+}$	1.03	$Ru^{II/I}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	128
$[Ru(phen)_2(CO)_2]^{2+}$	1.07	$Ru^{II/I}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	128
$[Ru(dmbpy)_2(CO)_2]^{2+}$	1.13	$Ru^{II/I}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	128
$[Ru(phen)_3]^{2+}$	1.34	phen	Pt, MeCN, Bu_4NClO_4, s.c.e.	117
	1.47			
$[Ru(dpp)_3]^{2+}$	0.95	dpp	Pt, MeCN, Bu_4NClO_4, s.c.e.	117
	1.12			
	1.39			
$[Ru(dpq)_3]^{2+}$	0.62	dpq	Pt, MeCN, Bu_4NClO_4, s.c.e.	117
	1.80			
	1.06			
$[Ru(phen)_2(dpp)]^{2+}$	1.07	dpp	Pt, MeCN, Bu_4NClO_4, s.c.e.	117
	1.35	phen		
$[Ru(bpy)_2(dpp)]^{2+}$	1.06	dpp	Pt, MeCN, Bu_4NClO_4, s.c.e.	117
	1.48	bpy		
$[Ru(phen)_2(dpq)]^{2+}$	0.79	dpq	Pt, MeCN, Bu_4NClO_4, s.c.e.	117
	1.50	phen		
$Ru(dpk)_2Cl_2$	1.06	dpk	CG, DMF, Bu_4NClO_4, s.c.e.	132
$Ru(dpk)(CO)Cl_2$	0.79	dpk	CG, DMF, Bu_4NClO_4, s.c.e.	132
$[Ru(dpk)_2(MeCN)_2]^{2+}$	0.81	dpk	CG, DMF, Bu_4NClO_4, s.c.e.	132
$[Ru(bpy)_2(dpk)]^{2+}$	1.06	dpk	CG, DMF, Bu_4NClO_4, s.c.e.	132
$Ru(bqdH)_2(Ph_3P)_2$	1.18		Pt, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	76
	1.14		Au, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	
	1.16		CG, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	
$Ru(bqdH)_2(Ph_3P)(MeIm)$	1.13		Pt, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	76
	1.13		Au, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	
	1.12		CG, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	
$[Ru(bpy)_2(biImH_2)]^{2+}$	1.66	bpy	Pt, MeCN, Bu_4NClO_4, s.c.e.	50
	1.96			
$[Ru(bpy)_2(biBzImH_2)]^{2+}$	1.60	bpy	Pt, MeCN, Bu_4NClO_4, s.c.e.	50
	1.90			
$[Ru(bpy)_2(PBzImH)]^{2+}$	1.49	bpy	Pt, MeCN, Bu_4NClO_4, s.c.e.	50
	1.76			
$[Ru(bpy)_2(OBzImH)]^{2+}$	1.67	bpy	Pt, MeCN, Bu_4NClO_4, s.c.e.	50
	2.00			
$[Ru(bpy)_2(PBzIm)]^+$	1.46	bpy	Pt, MeCN, Bu_4NClO_4, s.c.e.	50
	1.70			
$[Ru(bpy)_2(biBzImH)]^+$	1.53	bpy	Pt, MeCN, Bu_4NClO_4, s.c.e.	50
	1.86			
$[Ru(bpy)_2(biBzIm)]$	1.58	bpy	Pt, MeCN, Bu_4NClO_4, s.c.e.	50
	1.87			
$[Ru(bpy)_2(OBzIm)]^+$	1.63	bpy	Pt, MeCN, Bu_4NClO_4, s.c.e.	50
	1.94			
$Ru(2,3\text{-dpp})(bpy)_2^{2+}$	1.06	dpp	Pt, MeCN, Et_4NClO_4, s.c.e.	103
	1.50			

Polypyridylruthenium(II) complexes can be reduced with participation of orbitals located both on the metal atom and on the ligand. If the ligand field is strong and (or) the ligands are readily reducible, then the reduction proceeds with participation of the π^* orbital of the ligand. A similar picture is usually observed for polypyridylruthenium(II) complexes.[1, 2, 35, 41, 42, 44] The reduced form retains the low-spin $4d^6$ configuration and the reduction process is reversible:

$$[Ru^{II}(LL)_3]^{2+} + \bar{e} \rightleftharpoons [Ru^{II}(LL)_2(LL^-)]^+ .$$

Thus the additional electron is localised on a specific ligand. It is of interest that the complex $[Ru(bpy)_3]^{2+}$ may be reduced with consumption of $6\bar{e}$, affording $[Ru^{II}(bpy)_3]^{4-}$. If the complex is heteroleptic, then the ligands are reduced consecutively in a sequence determined by the energies of their π^* orbitals.

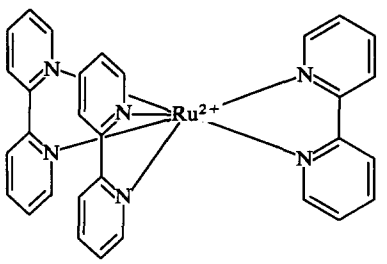
If the ligand field is weak, and (or) the ligands are difficult to reduce, then the e_g orbital, with an octahedral symmetry and largely located on the metal ion, may assume the role of the LUMO. In this case, the reduction product is an unstable low-spin d^7 system, in which one ligand is rapidly split off, which makes the reduction process irreversible:

$$[Ru^{II}(LL)_3]^{2+} + \bar{e} \rightleftharpoons [Ru^{I}(LL)_3]^+ \longrightarrow [Ru^{I}(LL)_2]^+ + LL.$$

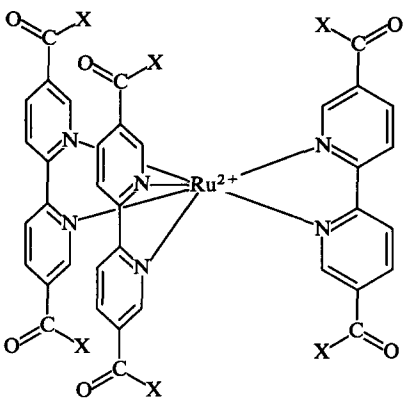
However, such processes are uncharacteristic of polypyridylruthenium complexes.

The electrochemical behaviour of the 'capped' (compound **4**) and 'bicapped' (compound **5**) see above) polypyridylruthenium(II) complexes and the comparison with their initial $Ru(bpy)_3^{2+}$ **11** and $Ru[5,5'\text{-}(EtO_2C)_2bpy]_3^{2+}$ **12**, a characteristic feature of which

is the distortion of the octahedral coordination sphere of the metal, are of interest.[22]



11

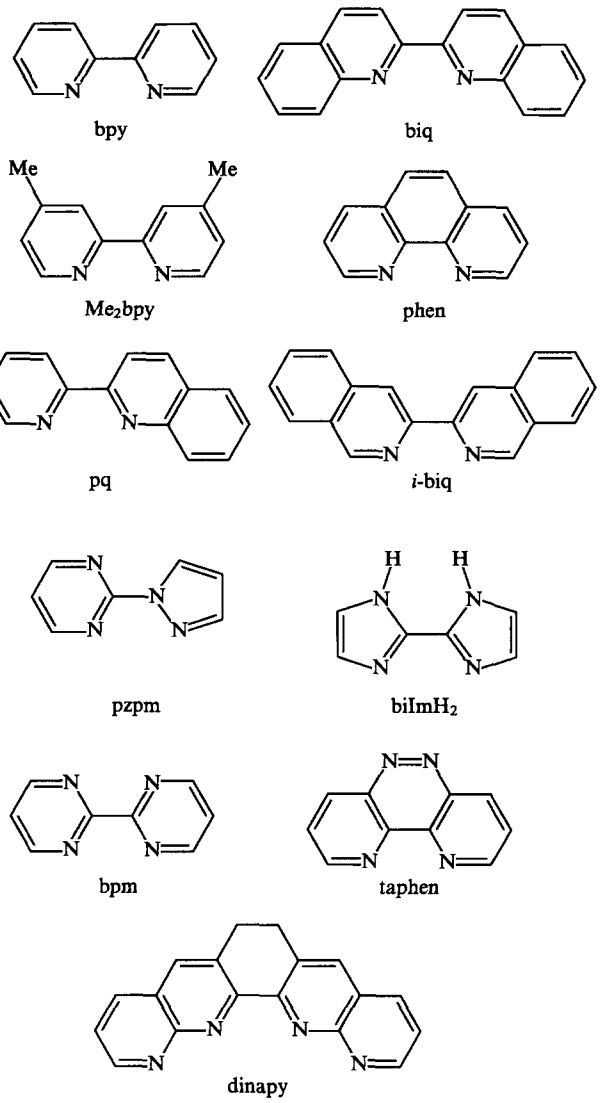


12

X = OC_2H_5

Complexes **4** and **5** are oxidised with one one-electron wave corresponding to oxidation 'at the metal atom' and are reduced with three one-electron waves corresponding to the reduction of the three bidentate ligands. The observed redox processes are reversible with the exception of the oxidation of compound **5**, as a result of which the process is kinetically controlled (i.e. the electron transfer is slow) even though stable species are formed. The low rate of electron transfer in the oxidation of compound **5** has been explained by steric hindrance, which precludes the approach of the metal atom to the electrode surface. Complexes **4**, **5**, and **12** are oxidised at identical potentials, which are more positive than for complex **11**. The equality of the oxidation potentials of compound **5** and **12** is surprising. In this case, one should apparently take into account the difference between the solvation energies of the oxidised and reduced forms and also the strain in the metal–ligand bonds due to the presence of the cage structure.

Electrochemical and spectroscopic data for the trisheteroleptic complexes $[Ru(LL)(LL')(LL'')]^{2+}$ are very rarely encountered in the literature. The electrochemical behaviour of a series of nine recently synthesised complexes of the type $[Ru(bpy)(biq)(LL)]^{2+}$ (LL = Me_2bpy, phen, pq, *i*-biq, pzpm, $biImH_2$, bpm, taphen, and dinapy) has been investigated.[42] These complexes are especially interesting because the redox processes in them proceed with participation of orbitals located on four different centres: M, LL, LL', and LL''. The electrochemical behaviour of $[Ru(bpy)(biq)(LL)]^{2+}$ is qualitatively similar to that of other polypyridylruthenium(II) complexes:[2, 41, 43] a single metal oxidation wave and a series of three waves corresponding to the reduction of the ligands are observed on the cyclic voltammogram. In order to assign the reduction waves to a particular ligand, a comparison was made with the known reduction potentials of homoleptic[2, 29, 33, 41, 44–49] and bisheteroleptic[2, 29, 33, 44–47, 49–51] complexes. For LL = Me_2bpy and phen, the first reduction wave was attributed to biq, the second to bpy, and the third to the LL ligands. For LL = pq, the order in which the ligands are reduced is as follows: biq is reduced initially, is followed by pq, and finally bpy is reduced. In the case of LL = *i*-biq, the interpretation of the first two waves (biq and bpy)

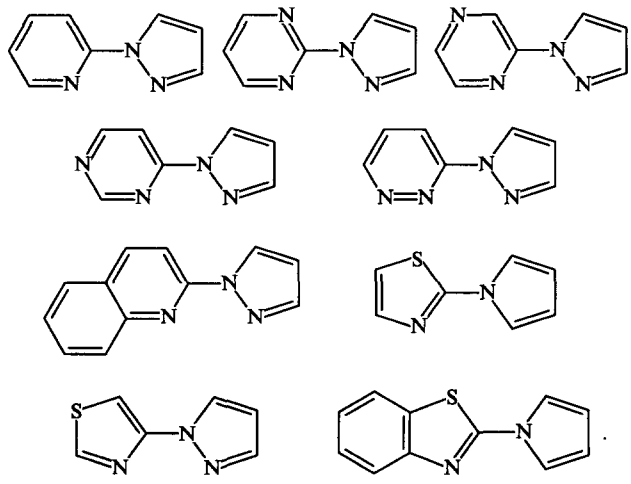


is not open to doubt, while the third wave may correspond both to the second stage of the reduction of biq and to the reduction of *i*-biq. For LL = pzpm, data on homoleptic complexes were not obtained. However, examination of the correlations between the spectroscopic and electrochemical quantities leaves no doubt that the biq ligand is the first to be reduced. Clear-cut data have not been obtained for LL = $biImH_2$, but it is clear from the first reduction potential (−1.66 V relative to the s.c.e.) of $[Ru(bpy)_2(biImH_2)]^{2+}$ that $biImH_2$ is reduced with more difficulty than bpy.[50] The first reduction potential of $[Ru(bpy)(biq)(biImH_2)]^{2+}$ was therefore attributed to the biq ligand. For LL = bpm, the sequence of the reduction waves is probably as follows: biq, bpm, bpy. The taphen ligand is very unusual, its π^* orbital being located mainly on the peripheral nitrogen atoms and having a low energy.[52] The most probable sequence in the reduction of the ligands of $[Ru(bpy)(biq)(taphen)]^{2+}$ is as follows: taphen is reduced initially and is followed by biq and bpy. Judging from the homoleptic complexes,[44, 53] dinapy is reduced more readily than biq, so that the order of the reduction of the ligands in $[Ru(dinapy)(biq)(bpy)]^{2+}$ should be as follows: dinapy, biq, bpy.

It has been shown[42, 54, 55] that in the polypyridylruthenium(II) complexes reduction involves in the first place the π^* orbital, with which the appearance in the spectra of the band due to charge transfer from the metal to the ligand (MLCT) is also associated. One can therefore expect a linear correlation[2, 29, 30, 33, 42, 45, 56, 57] between the energy of the absorption (or emission) maximum and the electrochemical gap $G = [E_{1/2}Ru(LL)_3^{III/II} - E_{1/2}Ru(LL)_3^{II/I}]$, which is a measure of the difference between the energies of

the HOMO and the LUMO of the ruthenium(II) complexes. Such correlation has indeed been observed for a series of polypyridyl complexes investigated (Fig. 9), with the exception of $[Ru(taphen)_3]^{2+}$.[42, 45] For this complex, both the long-wavelength absorption band and the emission band correspond to excited states with a higher energy than might have been expected on the basis of the reduction potential. This can be accounted for by the participation of the ligand biq in the spectral transitions, whereas the π^* orbital of the ligand taphen, localised mainly on the peripheral nitrogen atoms, participates in the redox transition. It is not clear why emission takes place from a high (with participation of biq) charge-transfer state and not from a low state (with participation of taphen).[42, 52] It may be that ligand–ligand interactions occur in the complexes investigated, which may be due both to electronic perturbations, transmitted mainly by the metal, and steric interactions of ligands such as biq.

The majority of studies devoted to the polypyridylruthenium(II) complexes constitute in essence attempts to select the necessary properties of the ground and excited states of the complexes by replacing one or several bpy ligands by other nitrogen-containing chelating ligands, mainly by six-membered aromatic nitrogen-containing heterocycles (azines). Electrochemical studies on complexes containing five-membered aromatic heterocycles (azoles) have been recently initiated.[32] It has been shown[32] that such ligands modify to a greater extent the properties of ruthenium complexes, since the π-excess azoles differ radically from the π-deficient azines. The study of various heteroleptic complexes $[Ru(bpy)_2(LL')]^{2+}$ and homoleptic complexes $[Ru(LL')_3]^{2+}$ showed that the reduction involves the ligand and is almost always reversible.[32] In this case, the symbol LL′ designates bidentate ligands containing five- and six-membered heterocycles having the following structures:



For the series of complexes $[Ru(bpy)_{3-x}(LL')_x]^{2+}$, the dependence of E^{Ox} on x is linear for a wide range of LL′. The slope of the straight line can be used to estimate the relative contributions of the π-donor and π-acceptor properties of the ligands LL′.[32, 58]

In the study of the redox transitions of $[Ru(NH_3)_5L]^{III/II}$ (L = py-X; X = Me, Cl, $CONH_2$, CF_3, COMe, CHO, COOH, H),[59] it was noted that complexes with unsaturated π-ligands have appreciably more positive reduction potentials than the hexammine or aquo-complexes. The electron-accepting substituents X in $[Ru(NH_3)_5(py\text{-}X)]^{2+}$ increase the formal potentials E_f, i.e. the π-acceptor properties of the ligands facilitate the reduction of the oxidised complex. If yet another ammonia molecule in the complex is replaced by the ligand L′, with strong π-acceptor and weak σ-donor properties, the ruthenium(II) complex is stabilised relative to the ruthenium(III) complex, which means that the redox transition in $[Ru(NH_3)_4LL']^{III/II}$ is facilitated.[60] This is confirmed by the results of a study[61] in which measurements were made of the reduction potentials of a series of *trans*-$[Ru(NH_3)_4LL']^{3+}$ [L,L′ = pyridine, 4-picoline (4-pic), isonicotanimide (isn), 4-acetylpyridine (4-acpy), pyrazine (pz), or pyrazinium (pzH^+)] with a fixed ligand L. In terms of their ability to facilitate the reduction of the ruthenium complex, the ligands investigated can be arranged in the sequence pz > 4-acpy > isn > py > 4-pic. Comparison of the redox potentials of *cis*- and *trans*-$[Ru(NH_3)_4(isn)L]^{2+}$ showed that the *cis*-isomers are reduced more readily than their *trans*-analogues. Taking into account the fact that only one of the *d* orbitals of the metal participates in the bonding to both heterocyclic ligands, one may conclude that the heterocyclic ligands in *trans*-$[Ru(NH_3)_4(isn)L]^{2+}$ are coplanar.

The ruthenium and rhodium complexes are interesting because they can serve as convenient models for the study of the influence of the metal atom coordination on the properties of the ligands. For example, by comparing the rate of the alkaline hydrolysis of the CN group in the pentammine complexes $[M(NH_3)_5(RCN)]^{n+}$ (M = Ru, Rh; R = Me, Ph; n = 2, 3), it is possible to estimate the electronic influence of the central atom on the organic ligand.[62] The ruthenium(II) and rhodium(III) complexes are isoelectronic ($4d^6$) and differ only in the charge, while the ruthenium(III) and rhodium(III) complexes have the same charge but differ in the number of *d* electrons of the metal [Ru(III)—$4d^5$]. It was found that complexes containing ruthenium(III) are hydrolysed much more readily than their $4d^6$ rhodium(III) and ruthenium(II) analogues. This is due to the ability of ruthenium(III) to function as a π-acceptor (by virtue of the t_{2g} vacancy in the *d* orbitals) and to stabilise the negative charge arising when the nitrile carbon atom is attacked by the OH group. The ruthenium(II) complex hardly undergoes alkaline hydrolysis, since it is an electron donor in relation to the π-acceptor unsaturated organic ligands.

The capacity of ruthenium(III) for reverse π-bonding has been confirmed also by electrochemical studies on pentammineruthenium(II) complexes containing quinone diimine ligands.[63] Thus the abstraction of one electron alters radically the influence of the metal atom on the ligands. The determination of the potentials and of the nature of the redox transitions can therefore be extremely useful for the elucidation of the change in the electronic properties of the central metal atom and the ligands bound to it.

The olefin complexes of ruthenium(II) have been investigated.[64–66] $[Ru(CO)_2L(\eta^4\text{-cot})]^{2+}$ (where L = CO or PPh_3 and cot = cyclooctatetraene) is oxidised at a platinum electrode in a single irreversible one-electron stage.[64] Complexes of the type $[Ru(NH_3)_5(olefin)]^{2+}$, where styrene, *p*-vinylbenzoic acid, cyclohexa-1,3-diene, and a number of others were used as the olefins, have been investigated by cyclic voltammetry.[65] The introduction of substituents into the aromatic rings of the ligands does not affect the electrochemical oxidation potential, while the pentammine environment is more likely to compensate for the charge on the ruthenium centre than a polycarboxylate environment.

The electrochemistry of the mixed-ligand ruthenium(II) and ruthenium(III) complexes containing various β-diketonate ligands has been studied.[67] The *d*-π molecular orbitals, formed from the t_{2g} orbitals d_{xy}, d_{xz}, and d_{yz} of ruthenium, assume the role of the HOMO and the LUMO of the tris(β-diketonato)ruthenium complexes. Linear correlations have been found[67] between the ligand composition and the $E_{1/2}$ for the oxidation and reduction of the complexes. For example, the reduction potentials of the mixed-ligand complexes can be estimated from these linear relations when the $E_{1/2}$ for the reversible redox transitions in the corresponding homoleptic complexes are known:

$$E^{III/II}(L''_nL'_{3-n}) = (n/3)E^{III/II}(L''_3) + (1-n/3)E^{III/II}(L'_3)\ .$$

The ligand η^5-C_5Ph_5 is known to stabilise paramagnetic complexes, which makes it possible to investigate[68] by cyclic voltammetry the ruthenium(II) complexes containing this ligand, in particular $[RuBr(CO)_2(\eta^5\text{-}C_5Ph_5)]$, $[RuBr(CO)L(\eta^5\text{-}C_5Ph_5)]$ [where L = PPh_3, PEt_3, $P(OMe)_3$], $[Ru(CO)LL'(\eta^5\text{-}C_5Ph_5)]^+$

[where L = PEt_3 or $P(OMe)_3$; L′ = CO, C_2H_4, PEt_3, MeHC=CHMe, $P(OMe)_3$], [$RuMe(CO)_2(\eta^5\text{-}C_5Ph_5)$], and [$RuR(CO)(PEt_3)(\eta^5\text{-}C_5Ph_5)$] (where R = Me, Et, COMe, CH=CHMe). It is seen from the analysis of the oxidation potentials that:

(1) the C_5Ph_5 ligands stabilise the cations [$Ru^{III}Br(CO)L(\eta^5\text{-}C_5Ph_5)]^+$ [L = PPh_3, PEt_3, $P(OMe)_3$] and [$Ru^{III}R(CO)(PEt_3)$. .$(\eta^5\text{-}C_5Ph_5)]^+$(R = Me, Et, COMe);

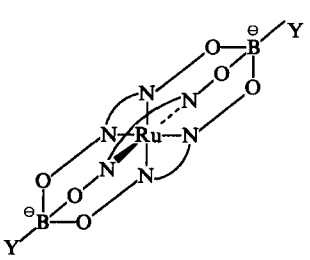
(2) the substitution of CO by L lowers the equilibrium potentials E^0;

(3) bromides are oxidised with greater difficulty than complexes containing σ-bound organic groups;

(4) the π-donor properties of the ligand have little influence on E^0.

The oxidation of sandwich complexes having the composition ($\eta^5\text{-}C_9H_7$)Ru(η^5-L) (L = C_5H_5, C_5Me_5, C_9H_7) has been investigated.[69] The reversible transfer of one electron leads to the formation of 17-electron radical-cations, the stability of which depends on the properties of the η-ligand and the nucleophilicity of the medium.

The influence of the steric and electronic effects on the stability of boron-containing ruthenium(II) and ruthenium(III) complexes has been investigated.[70] The cathodic (I_{pc}) and anodic (I_{pa}) currents have been determined by cyclic voltammetry for the quasi-equilibrium couple Ru(II/III); their ratio I_{pc}/I_{pa} served as a criterion of the stability of the ruthenium(III) complex. The increase in I_{pc}/I_{pa} for a series of substituents Y, i.e. n-$C_{10}H_{21}O$ > n-$C_5H_{11}O$ > Bu^nO > Pr^nO > EtO > MeO ≃ Pr^iO, permits the conclusion that the stability of the ruthenium(III) complex increases with increase in the length of the chain of the alkoxy-groups. However, it is believed that this effect is not related to the electronic or steric effects of the alkoxy-substituents, whereas the decrease in I_{pc}/I_{pa} on passing from $Ru(chd)_3(BOPr^n)_2$ to $Ru(chd)_3(BOPr^i)_2$ indicates a decrease in the stability of the high-valence complex with increase in the bulk of the alkoxy-groups.



Here O—N N—O is

(1) a 1,2-cyclohexanone dioxime residue (chd) with Y = Ph, Bu^n, Me, F or OR (R = Me, Et, Pr^n, Bu^n, n – C_5H_{11}, n – $C_{10}H_{21}$),

(2) a diphenyl-glyoxime residue (dpg) with Y = Bu^n or OMe, or

(3) a dimethyl-glyoxime residue (dmg) with Y = Bu^n or OMe.

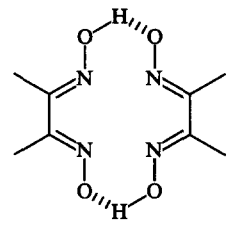
The study of the high-valence ruthenium(IV) complexes is of special interest, since they may prove to be promising catalysts (see, for example, Refs 71–73). The ruthenium(IV) complexes are relatively rare, and only a few of them have been reliably characterised (see Refs 74–76 and the literature quoted therein).

Ruthenium(II) complexes containing macrocyclic ligands which are difficult to oxidise can be readily oxidised at platinum, gold, or carbon glass electrodes with formation of hexacoordinate complexes formally corresponding to ruthenium(III) and ruthenium(IV), for example:[76]

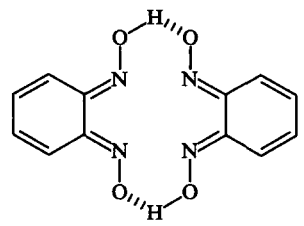
$$Ru(dmgH)_2(PPh_3)_2 \rightleftharpoons [Ru(dmgH)_2(PPh_3)_2]^+ + \bar{e},$$

$$[Ru(dmgH)_2(PPh_3)_2]^+ \rightleftharpoons [Ru(dmgH)_2(PPh_3)_2]^{2+} + \bar{e}.$$

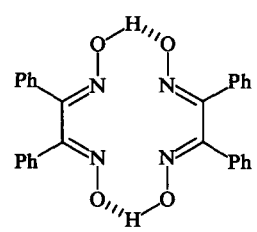
The ruthenium(III) complexes are relatively stable at room temperature, while the formation of the formally tetravalent ruthenium(IV) complexes frequently requires cooling to −78 °C.



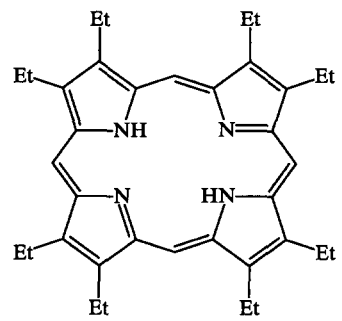
$(dmgH)_2$



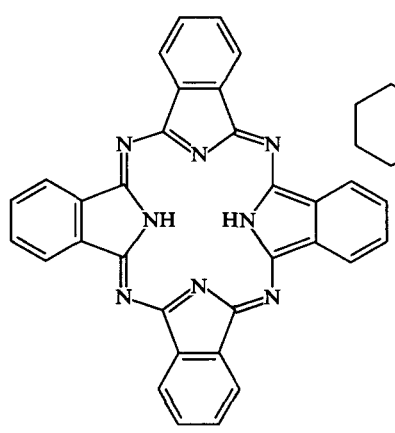
$(bgdH)_2$



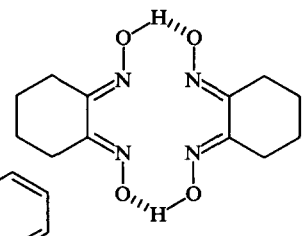
$(dpgH)_2$



P_0



P_c



$(chdH)_2$

It has been shown[76] that the stability of the ruthenium(IV) complexes increases significantly on replacement of nitrogen- or oxygen-containing donors (*N*-methylimidazole, DMSO, pyridine, etc.) by phosphine ligands. However, the formation of a high-valence ruthenium(IV) complex on oxidation of the complex $[Ru(bpy)_2(biBzIm)]^{2+}$ (where $biBzImH_2$ = 2,2′-bibenzimidazole) can be observed by cyclic voltammetry at a carbon glass (CG) electrode at a potential scanning rate $>5\ V\ s^{-1}$.[77] In contrast to the complex $[Ru(bpy)_3]^{2+}$, for which the second anodic wave corresponds to the oxidation of the ligand,[78] it was shown in this case[77] that the oxidation takes place at the ruthenium atom and that a low-spin d^5 [ruthenium(III)] complex is indeed formed.

The replacement of the nitrogen-containing macrocyclic system by other ligands, for example, 8-hydroxyquinoline, lowers the stability of the ruthenium(IV) complexes. The ability of nitrogen-containing macrocycles to stabilise metals in high oxidation states is known. For example, the complex $[Hg^{III}(N_4)]^{3+}$ (where N_4 = 1, 4, 8, 11-tetraazacyclotetradecane) with a lifetime of about 5 s at −78 °C has been obtained by electrochemical oxidation.[79, 80] Ruthenium(IV) complexes not containing macrocyclic ligands could not be isolated, although electrochemical evidence for their formation has been obtained.[81, 82] It is noteworthy that a true ruthenium(IV) complex is obtained only

if the ligand is not oxidised. In certain cases, the ligand may be oxidised after the electron transfer from the metal atom, i.e. there is a possibility of an intramolecular reaction involving electron transfer from the ligand to the metal, which means that the ruthenium(IV) complex cannot be claimed to be the final product of the electron transfer. The involvement of ligands such as dimethylglyoxime and its derivatives in such processes is unlikely, so that complexes containing them are extremely convenient for the synthesis of ruthenium(IV) compounds. There exists another point of view, according to which ruthenium(IV) complexes may be regarded as ruthenium(III) radicals.[77] The oxidation of the complex $Ru(dtc)_3$ (where dtc = dithiocarbamate) leads to the formation of heptacoordinate ruthenium(IV) complexes of the type $[Ru(dtc)_3Solv]^{2+}$ (Solv = solvent molecule)[83] or dimeric ruthenium(III) complexes. Similarly the oxidation of ruthenocene affords $[Ru^{IV}Cp_2Solv]^{2+}$.[84] The heptacoordinate ruthenium(IV) complexes are more stable than the hexacoordinate complexes.[76]

In conclusion one should note that, in order to be able to compare the electronic properties of different compounds on the basis of electrochemical parameters (current, potential), one has to be sure that the diffusion coefficient is constant for the given series of compounds. Measurements have been made[85] of the diffusion coefficients of a large series of ruthenium(II) complexes in solution in acetonitrile using a rotating disc electrode and it was shown that the diffusion coefficient remains almost constant, while the rate of electron transfer increases with decrease in the redox potential.

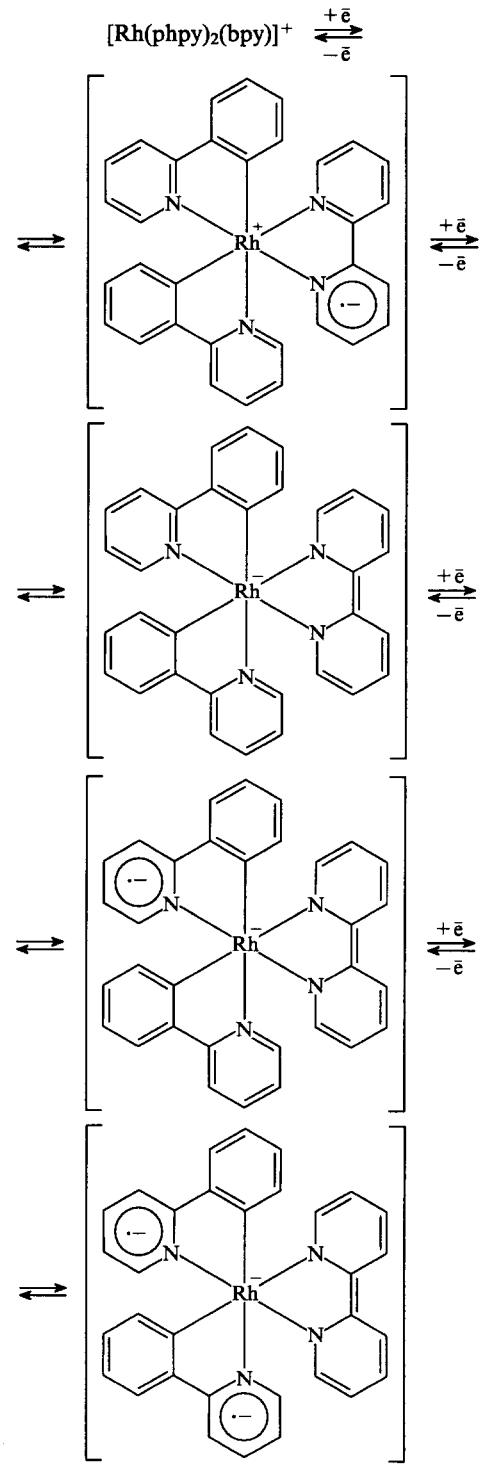
2. Electrochemical properties of mononuclear rhodium complexes

Comparison of the electrochemical properties of complexes containing metal atoms in the d^6 and d^8 configurations, for example, ruthenium(II) (d^6) and rhodium(I) (d^8) compounds, is of definite interest from the theoretical point of view. The energy difference between HOMO and LUMO is much smaller if the central metal atom has the d^8 configuration and not the d^6 one. This is apparently due to the fact that in the former case the unoccupied orbital is a ligand orbital, whilst the HOMO is localised on the metal atom.[86] For metal complexes with the d^6 configuration, both the HOMO and the LUMO are localised on the metal. This is confirmed, for example, by data on the electrochemical oxidation and reduction of dienerhodium(I) complexes containing cycloocta-1,5-diene (cod) or norbornadiene (nbd) ligands with 2,2′-bipyrimidine (bpym) (Tables 3 and 4).[86]

Extensive studies have been made on rhodium(III) complexes containing bipyrimidine and a number of other ligands capable of forming ortho-metallated derivatives, for example $[Rh(phpy)_2(phen)]^+$, $[Ru(thpy)_2(phen)]^+$, $[Rh(phpy)_2(biq)]^+$, $[Rh(phpy)_2(bpy)]^+$, and $[Rh(thpy)_2(bpy)]^+$, where phen = 1,10-phenanthroline, biq = 2,2′-biquinoline, and $phpy^-$ and $thpy^-$ denote the *ortho*-C-deprotonated forms of 2-phenylpyridine and 2-(2-thienyl)pyridine.[87–90] The *ortho*-metallated complexes constitute a new potential class of mediators for photochemical and chemiluminescence reactions. Four reversible waves are observed in the reduction of $[Rh(phpy)_2(bpy)]^+$ at a platinum disc electrode and a mercury dropping electrode in DMF at a low temperature (−54 °C).[87, 89] On the basis of the behaviour of the homoleptic complexes $Ru(bpy)_3^{2+}$,[33, 43] $Ir(bpy)_3^{3+}$, and $Ir(phpy)_3$,[89] as well as the dimer $[Ru(phpy)_2Cl]_2$,[91] one may conclude that the appearance of such a large number of reduction waves should be associated not only with ligand orbital association processes but also with the acceptor orbitals localised on the pyridine rings of the individual ligands. The first wave has been attributed to the reduction of the ligand bpy, while the group of three closely spaced waves is associated with the reduction of the two $phpy^-$ ligands and the second stage of the reduction of bpy (Scheme 1).

Three reversible waves are observed in the electrochemical reduction of $[Rh(phpy)_2phen]^+$ and $[Rh(phpy)_2(biq)]^+$. Thus each heteroleptic complex has virtually the same set of reduction waves regardless of whether the ligands are linked to a

Scheme 1



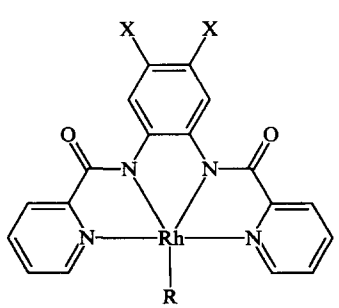
rhodium(III) atom or to, for example, an iridium(III) atom and the process proceeds consecutively with respect to each of the pyridine rings present in the molecule;[87] the difference between the wave [half-wave?] potentials is 0.2–0.3 V. The oxidation of rhodium(III) complexes listed above, with *ortho*-metallated nitrogen-containing ligands, takes place at the metal atom.

The correlations between the electrochemical parameters and electronic spectroscopic data for rhodium complexes have been examined.[87, 92–94] Cyclic voltammetric data[87] have shown that N,N-coordinated ligands are reduced more readily than the N,C-coordinated ones (for example, $phpy^-$). This shows that the π^* LUMO is to a large extent associated with the N,N-coordinated ligands. However, it follows from the absorption spectra[87] that the MLCT band with minimum energy corresponds to the electron transfer from the metal to the N,C-coordinated ligands and not to

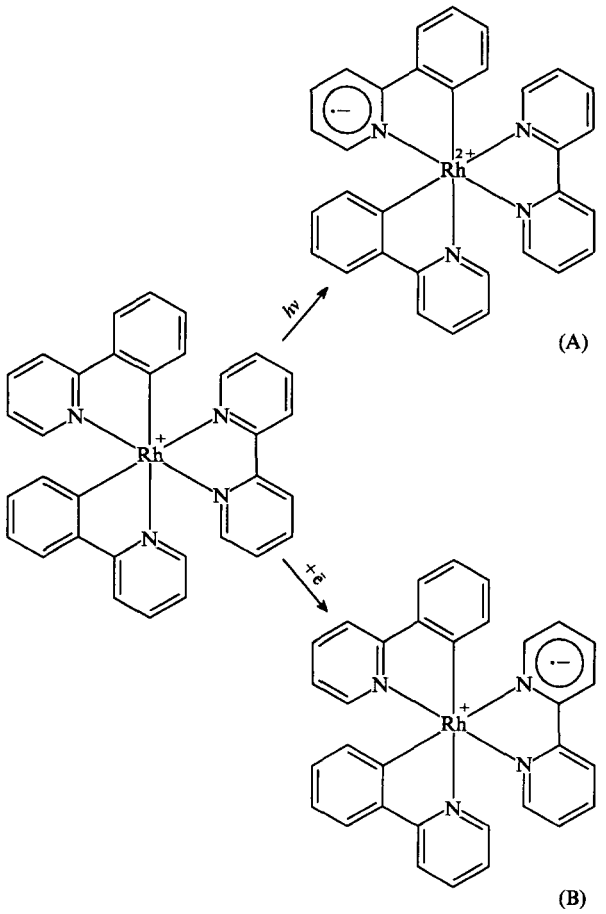
Table 3. Data on the electrochemical oxidation of mononuclear rhodium complexes.

Complex	E/V	ECLS	Conditions	Ref.
$[N(CH_2CH_2PPh_2)_3Rh(CN)]$	−0.19	$Rh^{I/II}$	Pt, CH_2Cl_2, Bu_4NClO_4, s.c.e.	93
	0.23	$Rh^{II/III}$		
	−0.19	$Rh^{I/II}$	Pt, THF, Bu_4NClO_4, s.c.e.	
	0.19	$Rh^{II/III}$		
$[P(CH_2CH_2PPh_2)_3Rh(CN)]$	−0.13	$Rh^{I/II}$	Pt, CH_2Cl_2, Bu_4NClO_4, s.c.e.	93
	0.38	$Rh^{II/III}$		
	−0.12	$Rh^{I/II}$	Pt, THF, Bu_4NClO_4, s.c.e.	
	0.34	$Rh^{II/III}$		
$[N(CH_2CH_2PPh_2)_3Rh(C\equiv CPh)]$	−0.45	$Rh^{I/II}$	Pt, CH_2Cl_2, Bu_4NClO_4, s.c.e.	93
	0.02	$Rh^{II/III}$		
	−0.39	$Rh^{I/II}$	Pt, THF, Bu_4NClO_4, s.c.e.	
	0.02	$Rh^{II/III}$		
$[P(CH_2CH_2PPh_2)_3Rh(C\equiv CPh)]$	−0.29	$Rh^{I/II}$	Pt, CH_2Cl_2, Bu_4NClO_4, s.c.e.	93
	0.38	$Rh^{II/III}$		
	−0.27	$Rh^{I/II}$	Pt, THF, Bu_4NClO_4, s.c.e.	
	0.31	$Rh^{II/III}$		
$[P(CH_2CH_2PPh_2)_3Rh(C\equiv C-CO_2Et)]$	−0.21	$Rh^{I/II}$	Pt, CH_2Cl_2, Bu_4NClO_4, s.c.e.	93
	0.33	$Rh^{II/III}$		
	−0.18	$Rh^{I/II}$	Pt, THF, Bu_4NClO_4, s.c.e.	
	0.28	$Rh^{II/III}$		
$[Rh(bpb)Me]\cdot H_2O$	0.31	$bpb^{0/+}$	CG, MeCN, Bu_4NBF_4, $Fc^{+/0}$	95
	0.81			
$[Rh(bpb)Et]\cdot H_2O$	0.31		CG, MeCN, Bu_4NBF_4, $Fc^{+/0}$	95
	0.82			
$[Rh(bpb)Cl_2]^-$	0.35		CG, MeCN, Bu_4NBF_4, $Fc^{+/0}$	95
	0.91			
$[Rh(bpb)(Py)]^+$	0.77		CG, MeCN, Bu_4NBF_4, $Fc^{+/0}$	95
	1.21			
$[Rh(bpb)(PPh_3)]^+$	0.70		CG, MeCN, Bu_4NBF_4, $Fc^{+/0}$	95
	1.25			
$[Rh(bpc)Me]\ H_2O$	0.48	$bpc^{0/+}$	CG, MeCN, Bu_4NBF_4, $Fc^{+/0}$	95
	0.94			
$[Rh(bpc)Cl_2]^-$	0.50		CG, MeCN, Bu_4NBF_4, $Fc^{+/0}$	95
	0.99			
$[Rh(bpb)(CN)_2]^-Na^+$	0.61		CG, MeCN, Bu_4NBF_4, $Fc^{+/0}$	95
	1.07			
$[Rh(ppz)_2bpy]^+$	1.27	$Rh^{III/IV}$	Pt, DMF, Et_4NClO_4, s.c.e.	88
$[Rh(3\text{-}Clppz)_2(bpy)]^+$	1.25		Pt, DMF, Et_4NClO_4, s.c.e.	88
$[Rh(4\text{-}NO_2ppz)_2(bpy)]^+$	1.24		Pt, DMF, Et_4NClO_4, s.c.e.	88
$[Rh(ppz)_2(biq)]^+$	1.20		Pt, DMF, Et_4NClO_4, s.c.e.	88
$[Rh(4\text{-}NO_2ppz)_2(biq)]^+$	1.09		Pt, DMF, Et_4NClO_4, s.c.e.	88
$[(NP_3)Rh(C\equiv CPh)]$	−0.45	$Rh^{I/II}$	Pt, CH_2Cl_2, Bu_4NClO_4, s.c.e.	94
$[(NP_3)Rh(C\equiv CCOOEt)]$	−0.26		Pt, CH_2Cl_2, Bu_4NClO_4, s.c.e.	94
$[(PP_3)Rh(C\equiv CPh)]$	−0.29		Pt, CH_2Cl_2, Bu_4NClO_4, s.c.e.	94
$[(PP_3)Rh(C\equiv CCOOEt)]$	−0.21		Pt, CH_2Cl_2, Bu_4NClO_4, s.c.e.	94
$[(NP_3)RhCN]$	−0.19		Pt, CH_2Cl_2, Bu_4NClO_4, s.c.e.	94
$[(PP_3)RhCN]$	−0.30		Pt, CH_2Cl_2, Bu_4NClO_4, s.c.e.	94
$[Rh(cod)(bpym)]^+$	0.96	$Rh^{I/II}$	Pt, MeCN, Et_4NClO_4, s.c.e.	86
$[Rh(nbd)(bpym)]^+$	1.10		Pt, MeCN, Et_4NClO_4, s.c.e.	86
$[Rh(R_2dtc)_3]$				
R = Me	1.13		Pt, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	133
Et	1.12			
Pr	1.02			
$[Rh(Et_2dsc)_3]$	0.78		Pt, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	133

the more readily reducible N,N-coordinated ligands. The reasons why the energies of the Rh→N,C and Rh→N,N transitions do not reflect the energies of the corresponding π^* orbitals are probably as follows. First, the octahedral t_{2g} d orbitals of the metal are split in different ways owing to the different electron-donating capacities of the N,N- and N,C-ligands and the d orbitals of the metal participating in the Rh→N,C transitions have a higher energy than the d orbitals involved in the Rh→N,N transitions. Secondly, owing to the different nature of the Rh–N,C and Rh–N,N bonds, the interaction between the outer electron shells in the excited state (A) and in the radical (B) may differ greatly, so that on photoexcitation the radical cation (A) is more stable while on electrochemical reduction radical (B) is more stable (see over).

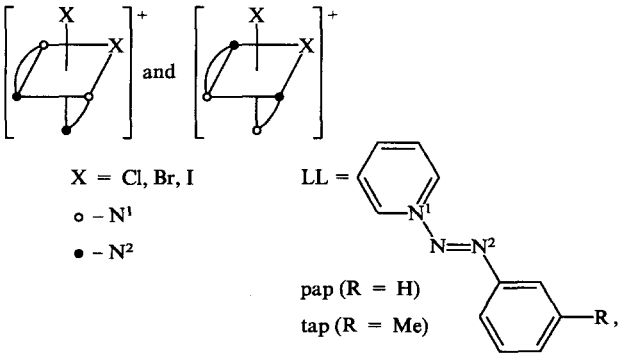


X = H, Cl;
R = Me, Et, Pr.



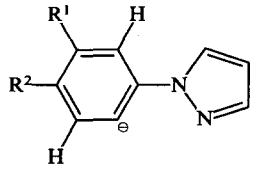
The dianionic amide chelating ligands containing a pyridine fragment are capable of stabilising transition metals in high oxidation states, which makes it possible to obtain fairly stable rhodium(IV) complexes. The electrochemical oxidation of such complexes has been investigated,[95] but the attempts to find a correlation between λ_{max} in the electronic absorption spectra of these compounds and their oxidation potentials were also unsuccessful. Thus the simplified picture of the 'localisation of the electronic changes' associated with the spectroscopic and electrochemical transitions ('on the metal' or 'on the ligand'), widely used for transition metal compounds, does not always yield a satisfactory description, particularly in the case of systems containing *ortho*-metallated ligands, where the metal–ligand bonds are significantly covalent.

The redox properties of 2-arylazopyridinerhodium(III) complexes $[RhX_2(LL)_2]ClO_4$, having the structure



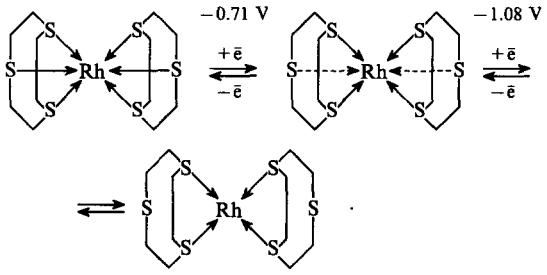
have been investigated by cyclic voltammetry at a platinum electrode.[96] The studies were carried out over a wide range of potentials: from 2.0 to −1.5 V. Three cathodic waves were observed, but the reduction products were unstable and were not isolated in a pure form. The EPR spectra of the electrolysis products at a reduced temperature (−13 °C) showed that the unpaired electron in the reduction products $[RhCl_2(LL)_2]$ and $[RhCl_2(LL)_2]^-$ is located on orbitals with a predominant ligand character, i.e. reduction takes place 'at the azo-group'.

The electrochemical behaviour of mixed-ligand rhodium(II) complexes containing neutral pyridine (bpy) and quinoline (biq) as well as anionic 1-phenylpyrazole ligands substituted in the benzene ring has been studied.[97] The results are in many respects similar to those observed for other cyclo-metallated rhodium(III) complexes:[88, 92] the reduction proceeds in the first place at the bpy ligand, while the oxidation is irreversible and belongs to processes 'localised on the metal'.



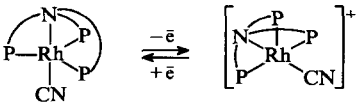
ppz⁻ (R^1 = R^2 = H)
(3-Clppz)⁻ (R^1 = Cl, R^2 = H)
(4-NO_2ppz)⁻ (R^1 = H, R^2 = NO_2)

Cyclic voltammetry at a platinum electrode of the homoleptic hexathia-coordinate complex $[Rh(LLL)_2](PF_6)_3$ (LLL = 1,4,7-trithiacyclononane) indicates the occurrence of two chemically reversible reduction processes, corresponding to the redox transitions Rh(III/II) and Rh(II/I). The cathodic reactions can be represented schematically as follows:[98]



The 19-electron complexes $[Rh(LLL)_2]^{2+}$ are less stable than the corresponding complexes $[Pd(LLL)_2]^{3+}$, which also have a central atom with the d^7 configuration. This is associated with the smaller formal charge on the rhodium atom. In the rhodium(I) complex, the metal has so many electrons that it is coordinated to only four and not six sulfur atoms. The cation $(Rh(LL)_2]^+$ is a very powerful reductant.

The redox properties of 18-electron pentacoordinate trigonal-bipyramidal rhodium(I) complexes containing σ-cyanide and σ-acetylide ligands, [(LLLL)Rh(CN)] and [(LLLL)Rh(C ≡ CPh)] [where LLLL = $N(CH_2CH_2PPh_2)_3$ or $P(CH_2CH_2PPh_2)_3$], were subjected to a comparative analysis.[93] It was found that there is little difference in the electrochemical behaviour of these complexes. π- and σ-bonding with the transition metal atom is characteristic of the cyanide and acetylide ligands. As a result of the one-electron oxidation of the above complexes, a stable paramagnetic rhodium(II) complex having the structure of a square pyramid is formed, for example:



Further oxidation of the rhodium(II) complex leads to the unstable rhodium(III) species, which rapidly decompose with formation of dicyanide complexes:

$$2[(LLLL)Rh(CN)]^{2+} \longrightarrow [(LLLL)Rh(CN)_2]^+ + [(LLLL)Rh]^{3+}.$$

Table 4. Data on the electrochemical reduction of mononuclear rhodium complexes.

Complex	$-E$/V	ECLS	Conditions	Ref.
$[Rh(phpy)_2(bpy)]^+$	1.84	bpy	Pt, DMF, Et_4NOH, $Ag/AgNO_3$	87, 89
	2.49			
	2.76			
$[Rh(phpy)_2(phen)]^+$	1.43	phen	Pt, DMF, Et_4NOH, $Ag/AgNO_3$	87
	2.12			
	2.42			
$[Rh(phpy)_2(bic)]^+$	1.00	bic	Pt, DMF, Et_4NOH, $Ag/AgNO_3$	87
	1.60			
	2.40			
$[RhCl_2(pap)_2]ClO_4 \cdot H_2O$	0.02	pap	Pt, MeCN, Et_4NOH, s.c.e.	96
	0.34			
	1.05			
$[RhCl_2(tap)_2]ClO_4 \cdot H_2O$	0.03	tap	Pt, MeCN, Et_4NOH, s.c.e.	96
	0.24			
	1.36			
[Rh(bpb)Me] H_2O	2.16	$Rh^{III/II}$	CG, MeCN, Bu_4NBF_4, $Fc^{+/0}$	95
[Rh(bpb)Et] H_2O	2.20		CG, MeCN, Bu_4NBF_4, $Fc^{+/0}$	95
$[Rh(bpb)Cl_2]^-$	1.98		CG, MeCN, Bu_4NBF_4, $Fc^{+/0}$	95
$[Rh(bpb)(Py)]^+$	1.70		CG, MeCN, Bu_4NBF_4, $Fc^{+/0}$	95
$[Rh(bpb)(Ph_3P)]^+$	1.30		CG, MeCN, Bu_4NBF_4, $Fc^{+/0}$	95
[Rh(bpc)Me] H_2O	2.15		CG, MeCN, Bu_4NBF_4, $Fc^{+/0}$	95
$[Rh(bpc)Cl_2]^-$	1.51		CG, MeCN, Bu_4NBF_4, $Fc^{+/0}$	95
$[Rh(bpc)(CN)_2]^-$	2.33		CG, MeCN, Bu_4NBF_4, $Fc^{+/0}$	95
$[Rh(ppz)_2(bpy)]^+$	1.46	bpy	Pt, DMF, Et_4NClO_4, s.c.e.	88
	2.09			
$[Rh(3\text{-}Clppz)_2(bpy)]^+$	1.42		Pt, DMF, Et_4NClO_4, s.c.e.	88
	2.02			
$[Rh(4\text{-}NO_2ppz)_2(bpy)]^+$	1.16		Pt, DMF, Et_4NClO_4, s.c.e.	88
	1.50			
$[Rh(ppz)_2(biq)]^+$	1.02	biq	Pt, DMF, Et_4NClO_4, s.c.e.	88
	1.64			
$[Rh(4\text{-}NO_2ppz)_2(biq)]^+$	0.92	biq	Pt, DMF, Et_4NClO_4, s.c.e.	88
	1.18	ppz		
	1.33			
	1.72			
$[Rh(cod)(bpym)]^+$	0.83	bpym	Pt, MeCN, Et_4NClO_4, s.c.e.	86
	0.90			
$[Rh(nbd)(bpym)]^+$	0.83		Pt, MeCN, Et_4NClO_4, s.c.e.	86
	0.91			
$Rh(Me_2dtc)_3$	2.02		Pt, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	133
	1.90		Hg, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	133
$Rh(Et_2dtc)_3$	2.11		Pt, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	133
	1.97		Hg, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	133
$Rh(Pr_2dtc)_3$	2.23		Pt, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	133
	2.10		Hg, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	133
$Rh(Et_2dsc)_3$	2.13		Pt, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	133
	1.99		Hg, CH_2Cl_2, Bu_4NClO_4, Ag/AgCl	133

Without knowing the structures of the intermediates, it is difficult to explain the pathway leading to the formation of the final dicyanide complex. The initial dimerisation with formation of a bridged tetracation $[(LLLL)Rh(\mu\text{-}CN)_2Rh(LLLL)]^{4+}$ and its subsequent decomposition appear most likely. Dicationic rhodium(III) acetylide complexes are more stable than the cyanide complexes. As expected, the acetylide ligands proved to be better donors, although not very much better, than the cyanide ions.

Terminal rhodium(II) and rhodium(III) complexes of acetylene have been obtained[94] by electrolysis at a controlled oxidation potential of the neutral rhodium(I) complexes $[(LLLL)Rh(C{\equiv}CR)]$, where R = Ph, COOEt, or CHO. Comparison of the stretching vibration frequencies of the C≡C bond in a series of complexes $[(LLLL)Rh(C{\equiv}CR)]^{n+}$ (n = 0–2) or of the redox potentials in a series of complexes [(LLLL)RhX] (X = Cl, H, C ≡ CR, CN or CO) indicates a fairly considerable interaction between the d–π-orbital of the metal and the π* orbital of the acetylide. Such interaction is reflected in the properties of the carbon–metal bond in the rhodium(I) and rhodium(II) complexes. On passing from ligands without π-acceptor properties (H, Cl) to strong π-acceptors, the potential E_0 of the Rh(I)/Rh(II) redox couple increases in the sequence Cl > H > C≡CR > CN > CO. The σ-acetylide compounds lie halfway between the hydride and cyanide complexes, E^0 depending on the electronic properties of the substituent at the C≡C bond.

The study of the electrochemical properties of the porphyrins[99] made it possible to deduce a series of empirical rules whereby it is possible to determine the direction of the redox process. According to one of them, the electronic changes involve the ligand environment if in the electrochemical reduction process the difference between $E_{1/2}$ for the metalloporphyrin and $E_{1/2}$ for the free porphyrin is negative. This conclusion is based on the hypothesis that the metal exerts a positive inductive effect and therefore shifts the σ-electron density closer to the ligand. A similar approach has been used in an electrochemical study of tetra(3,5-di-*tert*-butyl-4-hydroxyphenyl)dodecachlorophthalocyanine complexes

of various metals, including rhodium and ruthenium.[100] The oxidation and reduction processes can be described by means of the following scheme:

$$PcMX_n \begin{cases} \overset{+\bar{e}}{\rightleftharpoons} (PcMX_n)^- \overset{+\bar{e}}{\rightleftharpoons} (PcMX_n)^{2-} \\ \underset{-\bar{e}}{\rightleftharpoons} (PcMX_n)^+ \overset{-\bar{e}}{\rightleftharpoons} (PcMX_n)^{2+} \end{cases}$$

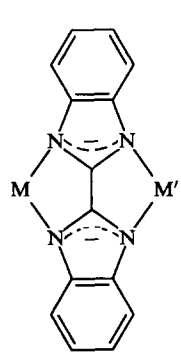
Pc = phthalocyanine, X = axial ligand.

It was shown that the magnesium, zinc, copper, and nickel complexes are oxidised and reduced with participation of the ligand, while the rhodium, ruthenium, osmium, cobalt, palladium, and platinum complexes are oxidised 'at the ligand' and their reduction takes place with participation of the metal ion.

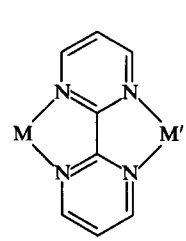
3. Polynuclear ruthenium and rhodium complexes

The redox chemistry of polymetallic complexes containing different bridging ligands is of special interest. Many natural products contain such fragments. By varying the structure of the bridging ligand, it is possible to alter the degree of metal–metal interaction and also the rate of the inner-sphere electron transfer. Complexes of metals in the same valence state as well as mixed-valence bimetallic complexes are known. Despite the fact that the study of the electrochemical properties of homonuclear and heteronuclear polymetallic complexes with organic ligands was begun comparatively recently, numerous interesting data, significantly expanding our ideas concerning their structure and properties, have already been obtained. The key component in such systems is the bridging ligand, since many properties of the complexes depend on the size, form, and electronic nature of the bridge; in certain cases, the bridge participates directly in electrochemical and photochemical processes.

Investigations of a series of 2,2′-bibenzimidazolyl (biBzIm) bridged homobinuclear and heterobinuclear complexes $[(bpy)_2M(biBzIm)M'(bpy)_2]^{n+}$ (n = 2–4; M = Ru, Os; M′ = Ru) and their fragments (mononuclear complexes) $[M(bpy)_2(biBzImH_2)]^{2+}$, $[M(bpy)_2(biBzIm)]$, and $[M'(bpy)_3]^{2+}$ have been performed.[101] The 2,2′-bibenzimidazolyl bridging ligand is structurally similar to the 2,2′-bipyrimidyl (bpm) ligand.



M(biBzIm)M′



M(bpm)M′

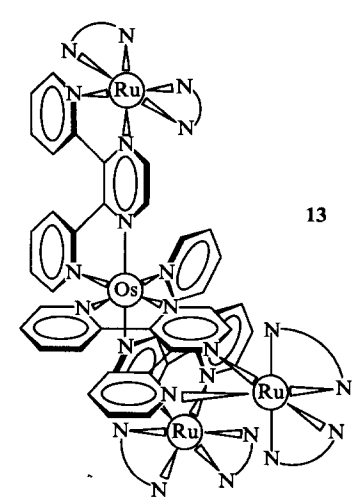
The distance between the metallic centres in these two complexes is in fact the same but the charges on the ligands are different; biBzIm has a charge of 2–, while bpm is neutral. All the dinuclear bisimidazolyl complexes investigated (with the exception of the ruthenium-nickel complex) give rise to two one-electron reversible waves on oxidation, whilst the complex containing ruthenium and nickel gives rise to one wave corresponding to the Ru(II)/Ru(III) transition. The potentials of the two oxidation waves of the heterobinuclear [Ru, Os] and [Ru, Co] complexes were compared with the potentials of the corresponding mononuclear complexes $[M(bpy)_3]^{2+}$, which made it possible to attribute the first electrode process (at the lower potential) to the Os(II)/Os(III) and Co(II)/Co(III) transitions and the second to the Ru(II)/Ru(III) transition. Comparison of the oxidation potentials of the dinuclear and mononuclear complexes $[M(bpy)_2(biBzImH_2)]^{2+}$ shows that the first oxidation potentials of the dinuclear complexes $[(bpy)_2M(biBzIm)M'(bpy)_2]^{n+}$ are lower by 0.3 V than the potentials of the corresponding mononuclear complexes. Hence it was concluded[101] that biBzIm exhibits electron-donating properties in the dinuclear complexes. On the other hand, the first oxidation potential of the dinuclear complex $[(bpy)_2Ru(bpm)Ru(bpy)_2]^{4+}$ is higher by 0.4 V than that of the corresponding mononuclear complex, which indicates the electron-accepting character of the bmp bridge. The potential of the Ru(II)/Ru(III) redox transition in the dinuclear complexes depends only on the charge of the second metal ion. This made it possible to conclude that the electron delocalisation via the biBzIm bridge is relatively slight and that electrostatic interactions have become an important potential-determining factor. Knowing the difference between the potentials of the different redox couples, it is possible to calculate the comproportionation constant (K_{com}).

$$[M^{II}-biBzIm-M^{II}]^{2+} + [M^{III}-biBzIm-M^{III}]^{4+} \rightleftharpoons \rightleftharpoons 2[M^{II}-biBzIm-M^{III}]^{3+}$$

For example, $K_{com} = 8.2 \times 10^4$ for M = $Ru(bpy)_2$.[101]

2,3-Di(2-pyridyl)pyrazine (dpp) is an interesting nitrogen-containing bridging ligand. The complex $[Ru(dpp)_3]^{2+}$ is of great practical importance,[102] since it is capable of forming polymetallic chains, which makes it possible to obtain a new class of polynuclear complexes capable of accumulating solar energy. The strength of the electronic interaction between the metal atoms in the ground state of the bimetallic and polymetallic complexes depends on the distance between the metal atoms and on the degree of conjugation in the π-system of the bridging ligand. The transmission of the influence along the bridge can be estimated by comparing the potentials E^{Ox} of complexes of the type $[(LL)_2Ru^{II}(\mu\text{-}L)]^{2+}$ (LL = bpy or phen and μ-L = dpp, dpq, or bpm is the bridging ligand) with the first oxidation potentials of the corresponding complexes $[(LL_2Ru^{II})_2(\mu\text{-}L)]^{4+}$. The small difference between the oxidation potentials of the monometallic and bimetallic complexes (eg. ΔE = 10 mV) indicates an insignificant change in the energy of the t_{2g} orbitals and hence a weak interaction between the two metallic centres in the bimetallic complex. If the interaction had been stronger, the bimetallic complex would have been oxidised at more positive potentials and ΔE could have reached several hundreds of millivolts.

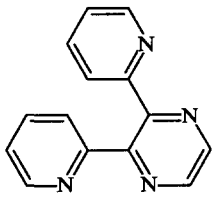
The redox properties of the heterometallic complex $Os[(\mu\text{-}2,3\text{-}dpp)Ru(bpy)_2]_3^{8+}$ **13**,[103] its homometallic analogue $Ru[(\mu\text{-}2,3\text{-}dpp)Ru(bpy)_2]_3^{8+}$ **14**,[102] and also the mononuclear



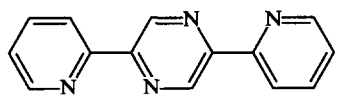
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complexes $[Ru(2,3\text{-dpp})(bpy)_2]^{2+}$ **15**[104, 105] and $[Os(2,3\text{-dpp})_3]^{2+}$ **16**[105] have been investigated by cyclic voltammetry. A single one-electron reversible wave, attributed to the oxidation of the metal, was observed in the electrochemical oxidation of the mononuclear complexes. When the homotetrametallic complex **14** is oxidised, it gives rise to a three-electron wave corresponding to the oxidation of the peripheral ruthenium atoms. Oxidation at the central ruthenium atom is not observed, since the atom is bound to three strong π-acceptor dpp bridging ligands. In the oxidation of compound **13**, a one-electron reversible wave followed by a three-electron quasi-reversible wave is observed. The first anodic process was attributed to the oxidation of the osmium atom and the second to the oxidation of the three ruthenium atoms. In the reduction of compounds **13**, **14**, and **16**, three one-electron waves, associated with the reduction of the three dpp ligands (since they are reduced much more readily than bpy), were observed. It has been noted[102, 103] that the bridging ligands are as a rule reduced more readily to an extent of approximately 0.4 V than the structurally similar terminal ligands. The several indistinct waves observed at potentials more negative than −1.35 V probably correspond to further reduction of dpp and the one-electron reduction of the bpy ligands. The sequence in the reduction of the ligands in complex **15** is similar: dpp followed by bpy. On the basis of the reversibility of all three reduction waves for the tetrametallic complexes, one may postulate that these systems can serve as multielectron oxidising agents in the ground state.

A study[106] of the mononuclear and dinuclear ruthenium(II) complexes $[Ru(L)(CO)_2Cl_2]$ and $(\mu\text{-}L)[Ru(CO)_2Cl_2]_2$, containing the 2,3- and 2,5-isomers of di(2-pyridyl)pyrazine (dpp) as the bridging ligands, showed that the interaction between the metallic centres depends not only on the structure of the bridge but also on the nature of the ligands bound to the metal.



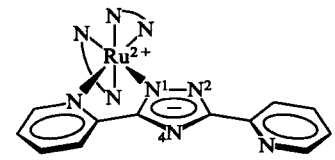
2,3-dpp



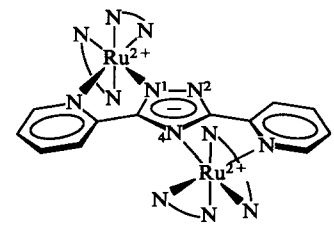
2,5-dpp

Monometallic and bimetallic complexes were oxidised with a single irreversible wave at a potential of about 2.0 V. Since the oxidation waves were observed only for the complexes and not for the free ligands, they apparently correspond to the oxidation of the metal ion. The high positive oxidation potentials agree well with the electron-accepting character of the CO ligands. The oxidation potentials of the monometallic and bimetallic complexes are similar, whence one may conclude that the bond between the two metallic centres is very weak. This can be accounted for by the strong mesomeric effect of the CO ligands. The first reduction wave for all the compounds of the given series is reversible and corresponds to the reduction of the aromatic ligand (dpp). Its potential diminishes in the sequence free ligand, mononuclear complex, dinuclear complex. This is associated with the fact that the electron density on the ligands diminishes on coordination to the electron-deficient ruthenium atom. A satisfactory linear correlation has been observed between the reduction potentials and the energies of the MLCT bands in the electronic spectra (see Section II.5).

The electrochemical behaviour at the carbon glass electrode of the polypyridine bisheteroleptic complexes has been investigated:[1, 107, 108] the mononuclear complex $[Ru(bpy)_2(bpt)]^+$ **17** and the dinuclear $[Ru(bpy)_2]_2(bpt)^+$ **18** [bpt = anion of 3,5-bis(2-pyridyl)-1,2,4-triazole].



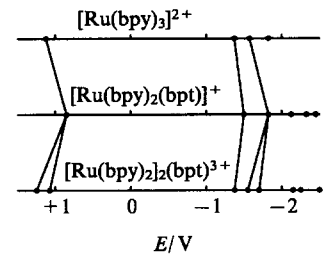
17



18

The anion bpt^- is particularly interesting, because, in contrast to the majority of other polypyridine bridging ligands, it carries a negative charge and exhibits a high σ-donor and low π-acceptor capacity. The redox potentials were measured using differential pulse polarography. The mononuclear complex **17** gives rise to one oxidation wave[107] and five reduction waves.[1, 108] The dinuclear complex **18** is oxidised in two stages,[107] while on reduction it gives rise to six waves, the first of which is a two-electron wave.[108] The protonated bpt^- anion (Hbpt) is not reduced at potentials up to −2.8 V. Scheme 2 illustrates the changes in E^{Red} and E^{Ox} on passing from $[Ru(bpy)_3]^{2+}$ to $[Ru(bpy)_2(bpt)]^+$ and then to the dinuclear complex.

Scheme 2



In particular, it follows from the analysis of Scheme 2 that, by virtue of the non-equivalence of the disposition of the two $[Ru(bpy)_2]^{2+}$ fragments relative to the bridge, two well-separated oxidation waves are obtained for the dinuclear complex, the difference between the potentials of which is 0.32 V. This permits the calculation of the comproportionation constant by using the equation $RT\ln K_{com} = F(\Delta E)$.

$$[M^{III}, M^{III}] + [M^{II}, M^{II}] \overset{K_{com}}{\rightleftharpoons} 2[M^{II}, M^{III}] .$$

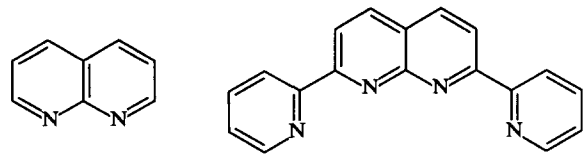
The value $K_{com} = 2.4 \times 10^5$ obtained indicates a fairly strong interaction between the metallic centres.

The first and second reduction potentials of $[Ru(bpy)_2bpt]^+$ are satisfactorily correlated with the corresponding reduction potentials of $[Ru(bpy)_3]^{2+}$ and hence can be attributed to the reduction of the coordinated bpy ligands.

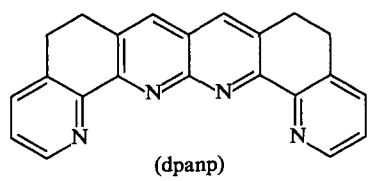
The splitting of the waves on passing from the mononuclear to the dinuclear compound in the reduction process is much smaller than the splitting observed in the oxidation process, so that the two centres involved in the reduction (ligands) are further apart than the two centres involved in the oxidation.

Detailed analysis of the electrochemical data obtained led to the conclusion[107] that the bridging bpt^- ligand hardly participates in the formation of the π LUMO of the complex.

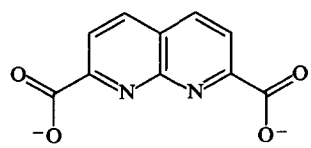
There exists a series of dinuclear copper, nickel, rhodium, and ruthenium complexes in which 1,8-naphthyridine (np) and its derivatives participate as the bridging ligands.[109, 110]



(np) (dpnp)



(dpanp)



$(dcnp)^{2-}$

These complexes are remarkable, because the small distance between the two metal nuclei leads to synergistic effects,[111, 112] especially in the homogenous catalysis.[113, 114] The oxidation of the rhodium complexes proceeds with participation of the orbitals localised on the metallic centres, while the reduction involves the ligand. It is of interest to note that the 2Ru(III)/Ru(III), Ru(II) transition in the complex $[Ru_2(OAc)_3(dcnp)]$ takes place very readily (0.33 V), while the Ru(III), Ru(II)/2Ru(II) transition is fairly difficult to achieve (−1.11 V), which indicates a greater stability of the system of the $[Ru^{III}, Ru^{II}]$ type. The stability of the $[Ru^{III}, Ru^{II}]$ complex can be estimated with the aid of the comproportionation constant

$$[Ru^{II}, Ru^{II}]+[Ru^{III}, Ru^{III}] \overset{K_{com}}{\rightleftharpoons} 2[Ru^{II}, Ru^{III}],$$

$$\ln K_{com} = \frac{F}{RT}(E_2^0 - E_1^0),$$

where E_2^0 and E_1^0 are the potentials of the 2Ru(III)/Ru(III), Ru(II) and Ru(III), Ru(II)/2Ru(II) redox transitions.

$K_{com} = 2.5 \times 10^{24}$ for the $[Ru_2(OAc)_3(dcnp)]$ complex,[110] which is one of the most stable mixed-valence complexes. For the analogous complex containing chloride instead of acetate ligands, $K_{com} = 3.5 \times 10^{23}$.[115] For comparison, we may point out that, for example, in the case of bimetallic ruthenium complexes, containing the bidentate bridging ligands 2,3-dpp and 2,3-di(2-pyridyl)quinoxaline (2,3-dpq), the comproportionation constant is of the order of 10^3. This value is the most typical for systems of this kind.[116]

It also follows from the electrochemical data[110] that the interaction between the metal atoms in the isovalent $[Ru^{II}, Ru^{II}]$ complex containing the dpp and dpq ligands is weak. The data presented indicate the important role of the aromatic bridging ligands in the redistribution of electrons between the two metallic centres.

The irreversible reduction wave of the complex $[Ru_2(OAc)_3(dcnp)]^-$ [formally corresponding to the 2Ru(II)/Ru(II)Ru(I) transition] is observed at very high cathodic potentials and has been attributed[110] to electron transfer to an orbital localised on the $(dcnp)^{2-}$ ligand.

The dependence of the distribution of electron density between the metal and the ligands on the introduction of a second substituent into the molecule has been investigated in relation to dienerhodium complexes containing bipyrimidine ligands.[86] Comparison of the spectroscopic and electrochemical properties of the mononuclear and dinuclear complexes $[Rh(nbd)(bpym)]^+$, $[Rh(cod)(bpym)]^+$, $[Rh(nbd)]_2(bpym)^{2+}$, and $[Rh(cod)]_2(bpym)^{2+}$ (where nbd = norbornadiene and cod = cycloocta-1,5-diene) showed[86] that in all cases the lowest excited state corresponds to the MLCT transition (Rh→bpym), while reduction involves in the first place the bpym ligand. The energy levels participating in the MLCT transition and also those associated with one-electron oxidation and reduction are very similar for the mononuclear and dinuclear complexes.

However, luminescence is observed for the mononuclear complexes but not for the dinuclear one. The reason for this is apparently the interaction of the two metallic centres. We may note that the potentials of the first and second reduction waves for $[Rh(cod)]_2(bpym)^{2+}$ are approximately equal to the reduction potential of the mononuclear complex (Tables 4 and 6), which shows that the introduction of the second Rh atom does not induce an appreciable change in the π^* level (b_1) of the bridging bipyrimidyl ligand. The dinuclear complexes are oxidised ($E_{1/2}$ = 1.0 V) with somewhat more difficulty than the mononuclear ones, which agrees fully with the electrostatic requirements. The potential of the second oxidation wave of the dinuclear rhodium complex is more positive by 0.42 V than that of the first wave. For the polynuclear ruthenium(II) complexes, the quantity $\Delta E_{1/2} = E^2_{1/2} - E^1_{1/2}$ can be regarded as a quantitative measure of the interaction between the two metallic centres.[117] Using a similar test, one may conclude that the interaction of the two rhodium(I) atoms in the $[Rh(cod)]_2(bpym)^{2+}$ ion is very significant.

In order to investigate the nature of the bonding in the cyanide-bridged rhodium and ruthenium complexes having the general formula $M^1-CN\rightarrow(M_2)^+$ [where M^1 and(or) M^2 = (η^5-C_5H_5)Rh(η^3-C_3H_5) or (η^6-Ph)Ru(η^3-C_3H_5)], a study was made of their oxidation and reduction reactions and also of the corresponding characteristics of their mononuclear fragments.[118] All the complexes are reduced in the first place at the 'cationic' fragment (M^{2+}). This results in the formation of the cyanide M^1CN, which is reduced in the second stage:

$$M^1-CN\rightarrow(M^2)^+ \xrightarrow{+\bar{e}} M^1CN \xrightarrow{+2\bar{e}} \text{products} + CN^-.$$

The fact that the first electron transfer is followed by the chemical stage involving the cleavage of the bridge has been confirmed by the irreversible nature of the reduction process and also by the very great similarity between the potential of the second stage in the reduction of the bridged complex and the potential E^{Red} of the mononuclear cyanide complex forming part of its composition. The mechanism of the oxidation of complexes of this type is much more complex. The number of electrons involved in the oxidation depends greatly on the structure of the complex. The irreversibility of all the oxidation waves shows that the radical-cation formed initially undergoes rapid consecutive reactions. Detailed analysis of the electrochemical parameters showed that the centres at which the electronic changes are localised in the oxidation of the complexes can be different, but the bridge is not cleaved in the oxidation of any of the complexes investigated.[118] This demonstrates a fairly high strength of the $N\rightarrow M^+$ bond and the delocalisation of the charge on the cationic fragment over the entire $M^1-C\equiv N\rightarrow(M^2)^+$ chain. The oxidation at the 'cationic' metal atom observed for the complexes $RhCNRu^+$ and RhCNRh, which at first sight appears unlikely, can be accounted for by the charge redistribution. Comparison of the spectroscopic and electrochemical data has shown[118] that linear correlations between the electrochemical potentials and the frequency of the CN group stretching vibrations occur for a series of compounds in which the electronic changes are localised at the same centre.

The electrochemical behaviour of the mixed-valence cyanide-bridged complexes $[(NH_3)_5RuCNRu(bpy)_2CN]^{3+}$ and $[(NH_3)_5RuCNRu(bpy)_2CNRu(NH_3)_5]^{6+}$, which can be designated by [3.2] and [3.2.3] in conformity with the oxidation state of the ruthenium atoms, has been investigated[34] by polarographic and cyclic voltammetric methods and by electrolysis at a controlled potential. The oxidation potentials of the complexes [3.2] and

Table 5. Data on the electrochemical oxidation of dinuclear ruthenium and rhodium complexes.

Complex	E/V	ECLS	Conditions	Ref.
$Os[(\mu\text{-}2,3\text{-}dpp)Ru(bpy)_2]_3^{8+}$	1.25	$Os^{II/III}$	Pt, MeCN, Et_4NClO_4, s.c.e.	103
	1.55	$Ru^{II/III}$		
$Ru[(\mu\text{-}2,3\text{-}dpp)Ru(bpy)_2]_3^{8+}$	1.50	$Ru^{II/III}$	CG, MeCN, Bu_4NClO_4, s.c.e.	102
$[Ru(bpy)_2]_2(bpt)]^+$	1.04	$Ru^{II/III}$	CG, MeCN, Bu_4NClO_4, s.c.e.	107, 108
	1.34			
$(\mu\text{-}2,3\text{-}dpp)[Ru(CO)_2Cl_2]_2$	2.00	$Ru^{II/III}$	Pt, MeCN, Et_4NClO_4, s.c.e.	106
$(\mu\text{-}2,5\text{-}dpp)[Ru(CO)_2Cl_2]_2$	1.92	$Ru^{II/III}$	Pt, MeCN, Et_4NClO_4, s.c.e.	106
$(fulv)Ru_2(CO)_4$	1.05	$Ru_2^{I/II}$	Pt, THF, Bu_4NBF_4, n.h.e.	125
$(fulv)RuMo(CO)_5$	1.03	$Ru^{I/II}$	Pt, THF, Bu_4NBF_4, n.h.e.	125
$[(bpy)_2Ru(BiBzIm)Ru(bpy)_2]^{2+}$	0.77	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	101
	1.06	$Ru^{II/III}$		
$[(bpy)_2Ru(BiBzIm)Os(bpy)_2]^{2+}$	1.01	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	101
	0.39	$Os^{II/III}$		
$[(bpy)_2Ru(BiBzIm)Co(bpy)_2]^{2+}$	1.01	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	101
	0.37	$Co^{II/III}$		
$[(bpy)_2Ru(BiBzIm)Ni(bpy)_2]^{2+}$	0.78	$Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	101
$[(Rh\,cod)_2bpym]^{2+}$	1.00	Rh^{I}, $Rh^{I/II}$	Pt, MeCN, Et_4NClO_4, s.c.e.	86
	1.42	Rh^{II}, $Rh^{I/II}$		
$[Ru(phen)_2]_2(dpp)^{4+}$	1.41	Ru^{II}, $Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	117
$[Ru(bpy)_2]_2(dpp)^{4+}$	1.44	Ru^{II}, $Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	117
	1.65	Ru^{III}, $Ru^{II/III}$		
$[(phen)_2Ru(dpp)Ru(bpy)_2]^{4+}$	1.41	Ru^{II}, $Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	117
	1.61	Ru^{III}, $Ru^{II/III}$		
$[Ru(bpy)_2]_2(dpq)^{4+}$	1.48	Ru^{II}, $Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	117
	1.64	Ru^{III}, $Ru^{II/III}$		
$[Ru(phen)_2]_2(dpq)^{4+}$	1.47	Ru^{II}, $Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	117
	1.62	Ru^{III}, $Ru^{II/III}$		
$[(phen)_2Ru(dpq)Ru(bpy)_2]^{4+}$	1.51	Ru^{II}, $Ru^{II/III}$	Pt, MeCN, Bu_4NClO_4, s.c.e.	117
	1.69	Ru^{III}, $Ru^{II/III}$		
$Ru_2(CO)_6L$	1.24		Pt, MeCN, Et_4NClO_4, s.c.e.	126
L = [C(Me) = C(Ph)COC(Me) = C(Ph)]	1.38		Pt, CH_2Cl_2, Et_4NClO_4, s.c.e.	126
$Ru_2(CO)_6L$	1.27		Pt, MeCN, Et_4NClO_4, s.c.e.	126
L = [C(Ph) = C(Ph)COC(Ph) = C(Ph)]				
$Ru_2(CO)_5(Ph_3P)L$	1.03		Pt, MeCN, Et_4NClO_4, s.c.e.	126
L = [C(Ph) = C(Me)COC(Ph) = C(Me)]	1.16		Pt, CH_2Cl_2, Et_4NClO_4, s.c.e.	126
$Ru_2(CO)_5(Ph_3As)L$	1.05		Pt, MeCN, Et_4NClO_4, s.c.e.	126
L = [C(Ph) = C(Me)COC(Ph) = C(Me)]	1.29		Pt, CH_2Cl_2, Et_4NClO_4, s.c.e.	126
$Ru_2(CO)_5(Ph_3Sb)L$	1.07		Pt, MeCN, Et_4NClO_4, s.c.e.	126
L = [C(Ph) = C(Me)COC(Ph) = C(Me)]	1.24		Pt, CH_2Cl_2, Et_4NClO_4, s.c.e.	126
$\{[(tpy)ClRu]_2(dpp)\}^{2+}$	0.94	$Ru^{II/III}$	Pt, MeCN, Bu_4NPF_6, s.c.e.	102
$\{Ru[(dpp)Ru(dpy)_2]_3\}^{8+}$	1.50	$Ru^{II/III}$	Pt, MeCN, Bu_4NPF_6, s.c.e.	102
$\{Ru[(dpp)Ru(phen)_2]_3\}^{8+}$	1.43	$Ru^{II/III}$	Pt, MeCN, Bu_4NPF_6, s.c.e.	102
$\{Ru[(dpp)Ru(tpy)Cl]_3\}^{5+}$	1.06	$Ru^{II/III}$	Pt, MeCN, Bu_4NPF_6, s.c.e.	102
$Rh_2(hp)_4$	0.82		Pt, MeCN, Bu_4NBF_4, Ag, $AgCl/Cl^-$	122
$Rh_2(chp)_4$	1.43		Pt, MeCN, Bu_4NBF_4, Ag, $AgCl/Cl^-$	122
$Rh_2(mhp)_4$	1.16		Pt, MeCN, Bu_4NBF_4, Ag, $AgCl/Cl^-$	122

Table 6. Data on the electrochemical reduction of dinuclear ruthenium and rhodium complexes.

Complex	$-E$/V	ECLS	Conditions	Ref.
$Os[(\mu\text{-}2,3\text{-}dpp)Ru(bpy)_2]_3^{8+}$	0.55	dpp	Pt, MeCN, Et_4NClO_4, s.c.e.	103
	0.65			
	0.77			
$Ru[(\mu\text{-}2,3\text{-}dpp)Ru(bpy)_2]_3^{8+}$	0.56	dpp	Pt, MeCN, Et_4NClO_4, s.c.e.	103
	0.74			
	0.89			
$[Ru(bpy)_2]_2(bpt)]^+$	1.40	bpy	CG, MeCN, Bu_4NClO_4, s.c.e.	108
	1.63			
	1.67			
	2.23			
	2.33			
	2.74			
$(\mu\text{-}2,3\text{-}dpp)[Ru(CO)_2Cl_2]_2$	0.62	dpp	Pt, MeCN, Et_4NClO_4, s.c.e.	106
$(\mu\text{-}2,5\text{-}dpp)[Ru(CO)_2Cl_2]_2$	0.38	dpp	Pt, MeCN, Et_4NClO_4, s.c.e.	106
$(fulv)Ru_2(CO)_4$	1.65	$Ru^{I/II}$	Pt, THF, Bu_4NBF_4, n.h.e.	125

Table 6 (continued).

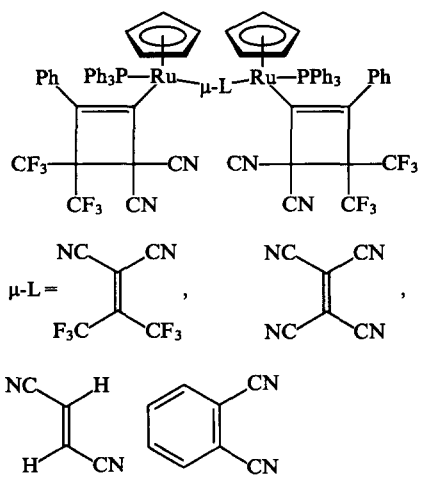
Complex	$-E$/V	ECLS	Conditions	Ref.
$[(triphos)RhH(\mu\text{-}Cl)_2HRh(triphos)]^{2+}$	0.84	$Rh^{III/II}$	Pt, DMF, Et_4NClO_4, s.c.e.	123
$[(triphos)Rh(\mu\text{-}S)_2Rh(triphos)]^{2+}$	0.45	$Rh^{II/I}$, Rh^{II}	Pt, CH_2Cl_2, Et_4NClO_4, s.c.e.	123
	1.00	Rh^{I}, $Rh^{II/I}$		
$[(triphos)Rh(\mu\text{-}S)_2Co(triphos)]^{2+}$	0.06	$Rh^{II/I}$, Co^{II}	Pt, CH_2Cl_2, Et_4NClO_4, s.c.e.	123
	0.98	Rh^{I}, $Co^{II/I}$		
$[Ru_2(OAc)_3(dcnp)]^{+}$	1.28	$Ru^{III/II}$, Ru^{II}	Pt, MeCN, Et_4NClO_4, s.c.e.	110
	0.57	$Ru^{II/I}$, Ru^{II}		
	1.21	Ru^{I}, $Ru^{II/I}$		
$[Rh_2(OAc)_4(MeCN)_2]$	1.00	$Rh^{III/II}$, Rh^{II}	Pt, MeCN, Et_4NClO_4, s.c.e.	110
	1.08	Rh^{II}, $Rh^{II/I}$		
$[Rh_2(OAc)_3(dpanp)]^{+}$	1.33	$Rh^{III/II}$, Rh^{II}	Pt, MeCN, Et_4NClO_4, s.c.e.	110
	0.68	Rh^{II}, $Rh^{II/I}$		
	1.36	Rh^{I}, $Rh^{II/I}$		
$[Rh_2(OAc)_3(dcnp)]^{-}$	0.98	$Rh^{III/II}$, Rh^{II}	Pt, MeCN, Et_4NClO_4, s.c.e.	110
	0.95	Rh^{II}, $Rh^{II/I}$		
	1.80	Rh^{I}, $Rh^{II/I}$		
$[Ru_2(dpnp)(bpy)_2Cl_2]^{2+}$	1.34	Ru^{III}, $Ru^{III/II}$	Pt, MeCN, Et_4NClO_4, s.c.e.	110
	0.64	$Ru^{III/II}$, Ru^{II}		
	0.76	Ru^{II}, $Ru^{II/I}$		
	1.35	Ru^{I}, $Ru^{II/I}$		
$[Ru_2(dpnp)(OAc)_3]^{+}$	0.72	$Ru^{III/II}$, Ru^{II}	Pt, MeCN, Et_4NClO_4, s.c.e.	110
	0.62	Ru^{II}, $Ru^{II/I}$		
	1.37	Ru^{I}, $Ru^{II/I}$		
$[Ru_2(dcnp)(OAc)_3]^{-}$	0.33	Ru^{III}, $Ru^{III/II}$	Pt, MeCN, Et_4NClO_4, s.c.e.	110
	1.11	$Ru^{III/II}$, Ru^{II}		
	1.86	Ru^{II}, $Ru^{II/I}$		
$\{[Rh(cod)]_2(bpym)\}^{2+}$	0.82	bpym	Pt, MeCN, Et_4NClO_4, s.c.e.	86
$\{[Ru(phen)_2]_2(dpp)\}^{4+}$	0.78		Pt, MeCN, Et_4NClO_4, s.c.e.	117
	1.41			
$\{[Ru(bpy)_2]_2(dpp)\}^{4+}$	0.64		Pt, MeCN, Et_4NClO_4, s.c.e.	117
	1.13			
	1.40			
$[(phen)_2Ru(dpp)Ru(bpy)_2]^{4+}$	0.60		Pt, MeCN, Et_4NClO_4, s.c.e.	117
	1.15			
	1.40			
$\{[Ru(bpy)_2]_2(bpq)\}^{4+}$	0.40		Pt, MeCN, Et_4NClO_4, s.c.e.	117
	1.09			
	1.40			
$\{[Ru(phen)_2]_2(dpq)\}^{4+}$	0.37		Pt, MeCN, Et_4NClO_4, s.c.e.	117
	1.10			
$[(phen)_2Ru(dpq)Ru(bpy)_2]^{4+}$	0.36		Pt, MeCN, Et_4NClO_4, s.c.e.	117
	1.08			
	1.41			
$Ru_2(CO)_6L$	1.25		Pt, MeCN, Et_4NClO_4, s.c.e.	126
L = [C(Me)=C(Ph)COC(Me)=C(Ph)]	1.39		Pt, CH_2Cl_2, Et_4NClO_4, s.c.e.	126
$Ru_2(CO)_6L$	1.12		Pt, MeCN, Et_4NClO_4, s.c.e.	126
L = [C(Ph)=C(Ph)COC(Ph)=C(Ph)]				
$Ru_2(CO)_5(Ph_3P)L$	1.45		Pt, MeCN, Et_4NClO_4, s.c.e.	126
L = [C(Ph)=C(Me)COC(Ph)=C(Me)]	1.57		Pt, CH_2Cl_2, Et_4NClO_4, s.c.e.	126
$Ru_2(CO)_5(Ph_3As)L$	1.36		Pt, MeCN, Et_4NClO_4, s.c.e.	126
L = [C(Ph)=C(Me)COC(Ph)=C(Me)]	1.51		Pt, CH_2Cl_2, Et_4NClO_4, s.c.e.	126
$Ru_2(CO)_5(Ph_3Sb)L$	1.35		Pt, MeCN, Et_4NClO_4, s.c.e.	126
L = [C(Ph)=C(Me)COC(Ph)=C(Me)]	1.47		Pt, CH_2Cl_2, Et_4NClO_4, s.c.e.	126
$[(tpy)ClRu]_2(dpp)^{2+}$	0.85	dpp	Pt, MeCN, Bu_4NPF_6, s.c.e.	102
	1.32			
	1.60	tpy		
$Ru[(dpp)Ru(bpy)_2]_3^{8+}$	0.56	dpp	Pt, MeCN, Bu_4NPF_6, s.c.e.	102
	1.12			
	1.24	bpy		
$Ru[(dpp)Ru(tpy)Cl]_3^{5+}$	0.60	dpp	Pt, MeCN, Bu_4NPF_6, s.c.e.	102
	0.72			
	0.84			
$[(triphos)Rh(\mu\text{-}S)_2Rh(triphos)]^{2+}$	0.45	Rh^{II}, $Rh^{II/I}$	Pt, CH_2Cl_2, Et_4NClO_4, s.c.e.	124
	1.10	Rh^{I}, $Rh^{II/I}$		
$[(triphos)Rh(\mu\text{-}S)_2Rh(triphos)]^{2+}$	0.06	Rh^{II}, $Co^{II/I}$	Pt, CH_2Cl_2, Et_4NClO_4, s.c.e.	124
	0.98	Co^{I}, $Rh^{II/I}$		

[3.2.3] are similar to the corresponding potentials for $[Ru(bpy)_2(CN)]^{2+}$, while the reduction potentials are virtually identical with the cathodic potentials of the pentammineruthenium(III) complexes. The compound [3.2] undergoes one-electron reversible reduction, while in the reduction of the compound [3.2.3] two consecutive one-electron reversible transitions are observed. These have similar standard potentials and lead to the formation of the complexes [3.2.2] and [2.2.2]. The comproportionation constant, determined electrochemically for the equilibrium

$$[3.2.3]+[2.2.2] \overset{K_{com}}{\rightleftharpoons} 2[3.2.2],$$

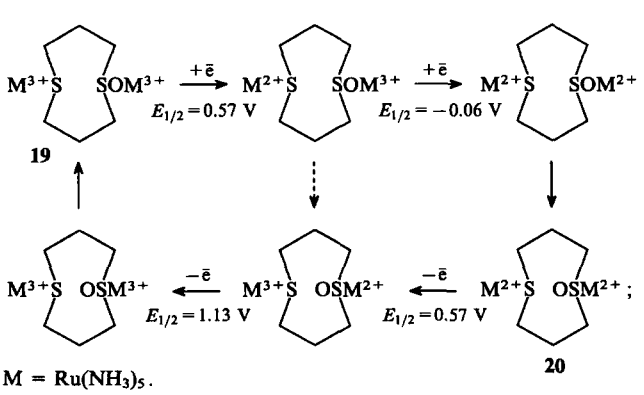
is 24, whence it follows that the amount of the complex [3.2.2] in the half-electrolysed [3.2.3] solution is about 70%.

Dinuclear complexes containing complex nitrile bridges as well as their constituent mononuclear fragments have also been investigated by cyclic voltammetry.[119]



Two reversible one-electron oxidation waves, corresponding to the Ru(II)/Ru(III) transitions, were observed for the dinuclear complex in which the bridging group is $(CN)_2C=C(CF_3)_2$. When the two rhodium atoms are linked by phthalodinitrile, a single two-electron oxidation wave is observed. The waves observed on reduction of dinuclear complexes of this type are quasi-reversible and correspond to the transfer of one electron to the nitrile ligand. The electron transfer in the dinuclear complex may be accompanied by isomerisation. The redox properties of (1,5-dithiacyclooctane 1-oxide)bis(pentammine)ruthenium(II) **19** may serve as one of the striking examples of such a process.[120] The electrochemical behaviour of the dinuclear system is presented in Scheme 3.

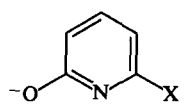
Scheme 3



M = $Ru(NH_3)_5$.

Evidently there are two types of mixed-valence complexes, one of which may be obtained only by the reduction of the stable form **19**, while the other can be obtained only by the oxidation of the stable form **20**.

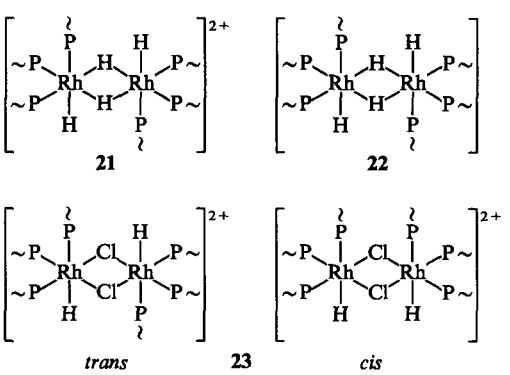
The electrochemical oxidation and reduction of the dinuclear rhodium, manganese, and cobalt complexes containing the methylene bridge has been studied.[121] The oxidation of the dirhodium complexes $Rh_2(hp)_4$, $Rh_2(chp)_4$, and $Rh_2(mhp)_4$ containing substituted *o*-hydroxypyridyl anions as the ligands has been investigated[122] by cyclic and a.c. voltammetry.



hp (X = H)
chp (X = Cl)
mhp (X = Me)

The oxidation potentials of the dirhodium fragment in such complexes depend not only on the nature of the substituent in the pyridine rings of the ligands but also on the solvent. They shift to the more cathodic with increase in the electron-donating strength of the solvent. A correlation has been found[124] between the oxidation potentials of these three complexes and the Taft resonance parameters of the substituents in the pyridine ring. The products of the one-electron oxidation of complexes containing the $[Rh_2]^{4+}$ fragments have been characterised spectroelectrochemically.

It is of interest to compare the electrochemical properties of complexes containing different inorganic bridging ligands. The electrochemical reduction of the dinuclear rhodium complexes $[(triphos)RhH(\mu\text{-}X)_2RhH(triphos)]^{n+}$ [X = H, Cl; *n* = 2, 0; triphos = $MeC(CH_2PPh_2)_3$], containing two hydride or chloride bridges, has been investigated.[123]

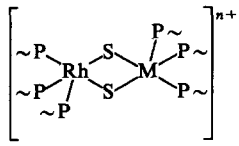


Complex **21** is reduced at the platinum electrode in two reversible one-electron stages:

$$[(triphos)RhH(\mu\text{-}H)_2RhH(triphos)]^{2+} \overset{+\bar{e}}{\underset{-\bar{e}}{\rightleftharpoons}} [(triphos)RhH(\mu\text{-}H)_2RhH(triphos)]^{+} \overset{+\bar{e}}{\underset{-\bar{e}}{\rightleftharpoons}} [(triphos)RhH(\mu\text{-}H)_2RhH(triphos)].$$

The complete electrochemical reversibility of these redox transitions shows that a significant structural reorganisation does not take place within the limits of the skeleton of the complex. As was to be expected, the oxidation potentials of complex **22** are identical with the potentials of the reduction wave of complex **21**. The presence of chloride bridges in the molecule alters sharply its redox properties and reversible electron transfer becomes impossible. The cyclic voltammogram for complex **23** shows a two-electron reduction peak, while the presence of several small anodic peaks, revealed by reverse scanning, indicates the occurrence of rapid fragmentation reactions accompanying the electron transfer.

Homobinuclear and heterobinuclear complexes having the general formula $[(triphos)Rh(\mu\text{-}S)_2M(triphos)]^{n+}$ (M = Rh, Co, n = 2; M = Pt or Fe, n = 1), and containing sulphide bridges have been investigated.[124]



Two consecutive cathodic processes were observed in all cases, the species formed in each stage being relatively stable:

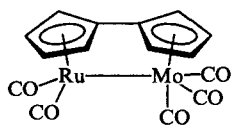
$$[Rh^{III}, M^{III}] \underset{-\bar{e}}{\overset{+\bar{e}}{\rightleftharpoons}} [Rh^{III}, M^{II}] \underset{-\bar{e}}{\overset{+\bar{e}}{\rightleftharpoons}} [Rh^{II}, M^{II}] .$$

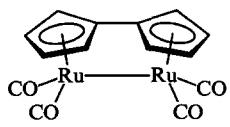
The difference between the potentials of the redox transitions in the two stages makes it possible to calculate[124] the compro-portionation constant:

$$[Rh^{III}, M^{III}] + [Rh^{II}, M^{II}] \overset{K_{com}}{\rightleftharpoons} 2[Rh^{III}, M^{II}] .$$

It is equal to 2×10^9 for the dirhodium complex, while in the case where M = Co we have $K_{com} = 3 \times 10^{15}$. The coordination polyhedron of each metal atom does not change and there is only some increase in the distance between the metal atoms in the consecutive reduction stages.[124]

Yet another type of dinuclear complex exists which contains simultaneously both a bridging ligand and a direct metal–metal bond. The bimetallic fulvalene complexes of ruthenium and molybdenum belong to this class.[125]

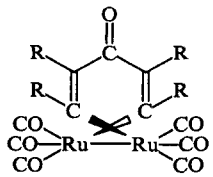




These complexes are oxidised in one two-electron irreversible stage. The irreversibility of the wave can be explained by the reaction of the dication formed with the solvent. The oxidation potentials of these and similar complexes with other metals are between 1.0 and 1.1 V (relative to the normal hydrogen electrode) regardless of the nature of the metals in the complexes. This led to the conclusion that an electron is removed from the orbital localised on the ligand. The reduction of the complexes depends greatly on the nature of the metal. Cyclic voltammetric and coulometric data support the *ece*-mechanism of the reduction process, (i.e. the alternation of stages: electrochemical, chemical, electrochemical — see diagram at the top of the next column).

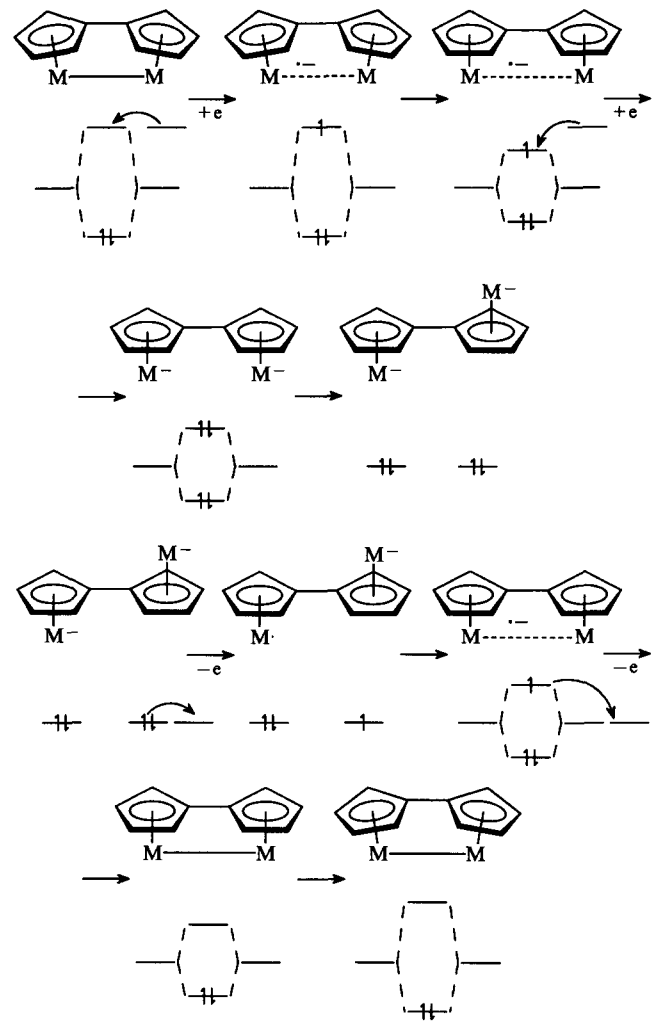
Presumably the first electron, transferred to the antibonding orbital of the M–M bond, lowers its order; this entails the initial formation of a radical-anion, the steric structure of the species changes, and the latter is reduced more readily than the initial complex.

The electrochemical behaviour of 'flyover-bridged' ruthenium complexes having the structure



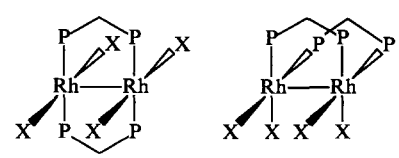
R = Alk, Ph.

has been investigated.[126] Both the anodic and cathodic processes take place with participation of one electron. The presence of



ligands having a higher ratio of the σ-donor and π-acceptor properties than CO renders the reduction process thermo-dynamically harder and favours oxidation.

Dirhodium complexes containing the $[Rh_2]^{4+}$ fragments are used widely as catalysts.[111, 112] The electrochemical properties of the complexes $Rh_2Cl_2(OOCMe)_2(dppm)_2$ and $Rh_2Cl_4(dppm)_2$ (dppm = diphenylphosphinomethane) have been investigated. The existence of structures of two types is possible for such complexes:



X = Cl, MeCOO.

Both complexes are oxidised and reduced irreversibly and their potentials E^{Red} and E^{Ox} differ very significantly. The difficulty of obtaining the $[Rh_2^{5+}]$ species, indicated by the oxidation potentials of these compounds (1.47 and 1.44 V respectively), is apparently due to the fact that the diphenylphosphinomethane and chloride ligands stabilise fairly effectively the $[Rh_2^{4+}]$ fragment. The complex $Rh_2Cl_2(dppm)_2(Ph_2PC_6H_4)_2$ is oxidised much more readily (0.86 V relative to Ag/AgCl) than the first two.

The relative ease of the $Rh_2^{4+} \rightarrow Rh_2^{5+}$ oxidative transition for the third complex suggests that $[Rh_2Cl_2(dppm)_2(Ph_2PC_6H_4)_2]^+$ can be readily obtained chemically, which was in fact subsequently achieved using NO^+ as the oxidising agent.[127]

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