Inorganica Chimica Acta, 62 (1982) 117–122

Influence of Organic Ligands and fac–mer Isomerization on the Redox Behaviour of Ru(III) Chloro Complexes

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Received February 19, 1982

*Ruthenium(III) complexes of the type $RuCl_3L_3$ (L_3 = (*ortho-*tolunitrile)$_3$, (*meta-*tolunitrile)$_3$, (pyridine)$_3$, (*ortho-*tolunitrile)$_2CH_3CN$, (*ortho-*tolunitrile)$_2$pyridine) were studied on platinum electrodes in organic solvents. The complexes undergo a reversible one-electron reduction near 0 V/SCE, corresponding to the Ru(II)/Ru(III) couple in all studied solvents. In CH_3CN, the complexes are reversibly oxidized into Ru(IV). The fac isomers are more difficult to reduce than the mer isomers. The effect of ligand exchange and of fac–mer isomerization upon the Ru(II)/Ru(III) redox potential is analysed, and an electrochemically-enhanced lability is evidenced in fac complexes.*

Introduction

Ruthenium chloro complexes $RuCl_XL_Y$ (X = 2, 3, 4; Y = 2, 3, 4; L: two electrons donor ligand) are known to undergo ligand exchange when dissolved in certain solvents. Thus, the interaction of $Ru^{(II)}Cl_2(PPh_3)_3$ with MeCN leads to the species $Ru^{(II)}Cl_2(MeCN)_2(PPh_3)_2$ [1]. Modifications of the complexes after dissolution in an organic solvent can be followed *in situ* by electrochemical methods, but electrochemical studies of halogeno complexes of ruthenium in organic media are still scarce [2].

Recent studies have been devoted to the electrochemical reduction of Ru(II) halogeno complexes to Ru(0) complexes. For instance, $Ru^{(II)}Cl_2(PPh_3)_3$ led to Ru(0) species according to the following reaction scheme [1]:

$$\begin{tikzcd}
Ru^{(II)}Cl_2(PPh_3)_3 \arrow[r, "MeCN", "-PPh_3"'] & Ru^{(II)}Cl_2(MeCN)_2(PPh_3)_2 \arrow[d, "+2e"] \\
Ru^{(0)}(MeCN)(PPh_3)_3 & (Ru^{(0)}(MeCN)_2(PPh_3)_2) \arrow[l, "PPh_3"'] \\
& +2Cl^-
\end{tikzcd}$$

Similarly [3]:

$$Ru^{(II)}Cl_2(PPh_3)_4 + 2e \xrightarrow{MeCN} Ru^{(0)}(PPh_3)_4(MeCN)_2 + \text{products}$$

Electroreduction of the complex $(Ru^{(II)}Cl(DPP)_2)PF_6$ (DPP = bis diphenylphosphinopropane) leads [4] to $Ru^{(I)}$ and $Ru^{(0)}$ species, in two distinct one-electron steps, as follows:

$$\begin{tikzcd}
(Ru^{(II)}Cl(DPP)_2)^+ \arrow[r, shift left, "+e"] & (Ru^{(I)}Cl(DPP)_2) \arrow[l, shift left, "-e"] \arrow[r, shift left, "+e"] & (Ru^{(0)}Cl(DPP)_2)^- \arrow[l, shift left, "-e"] \arrow[d] \\
& & \text{products}
\end{tikzcd}$$

Also, $(RuNO(DPP)_2)^+$ was shown [5] to undergo two reversible one-electron reductions.

Most of the electrochemical data on Ru complexes have been obtained in aqueous solutions [2], where it is known that $Ru^{(II)}$ complexes are unstable intermediates in the reduction of $Ru^{(III)}$ species [6]. The standard potential of the $Ru^{(II)}/Ru^{(III)}$ couple has been determined [7] as –0.2487 V for the reaction:

$$Ru^{2+} + H^+ \rightleftharpoons Ru^{3+} + 1/2H_2$$

in water at 25 °C.

The situation is quite different in organic media where solvent molecule(s) acting as ligand(s) may significantly stabilize low oxidation states of ruthenium. Recently, Stephenson *et al.* [8] reported voltammetric studies on monomeric $Ru^{(II)}$ and $Ru^{(III)}$ complexes of type $RuCl_3L_3$, $(RuCl_4L_2)^-$, $RuCl_2L_4$, where L are phosphines, arsines and other ligands. In this study [8], the $Ru^{(III)}$ oxidation and reduction half-wave potentials are given in $CH_2Cl_2/0.5\,M$ Bu_4NBF_4 at Pt electrode. With $RuCl_3L_3$, for which the nature of the isomer studied (fac or mer) was not given, the half-wave reduction potentials are not

0020-1693/82/0000-0000/$02.75

TABLE I. Electrochemical Reduction and Oxidation of $Ru^{(III)}Cl_3L_3$ Electrode: Pt; Solvent: CH_2Cl_2 or CH_3CN.

Compound	CH_2Cl_2 + 0.1 *M* THAP						CH_3CN + 0.1 *M* THAP	
	Stationary voltammetry				Cyclic voltammetry		Stationary voltammetry	
	$E_{1/2}^{cath}$ V/SCE	Slope mV	$E_{1/2}^{an}$ V/SCE	Slope mV	E_{p_c} (at 100 mV s^{-1})	ΔE_p (mV) ($E_{p_c} - E_{p_a}$)	$E_{1/2}^{cath}$ V/SCE	$E_{1/2}^{an}$ V/SCE
mer-$RuCl_3Py_3$	−0.26	100	+1.53	98	−0.30	95	−0.16	+1.55
mer-$RuCl_3$ (*m*-MePhCN)$_3$	+0.10	100	a		+0.08	70	+0.15	+1.83
mer-$RuCl_3$ (*o*-MePhCN)$_3$	+0.10	64	a		+0.07	90	+0.15	+1.81
mer-$RuCl_3$ (*o*-MePhCN)$_2CH_3CN$	+0.06	100	a		+0.01	100	+0.15	+1.80
mer-$RuCl_3$ (*o*-MePhCN)$_2$Py	+0.00	87	a		−0.05	80	+0.06	+1.75
fac-$RuCl_3$ (*m*-MePhCN)$_2$MeOH	−0.24				−0.28			
fac-$RuCl_3$ (*o*-MePhCN)$_2$MeOH	−0.24	64	a		−0.29	130	Solvent substitution	
fac-$RuCl_3$ (*o*-MePhCN)$_2H_2O$	−0.24				−0.28			

[a] No defined wave observable in that solvent.

far from 0 V *vs.* Ag/Ag I electrode, (+0.60 V *vs.* Ferrocene/Ferricinium) the electron transfer being reversible. At variance with $Ru^{(II)}/Ru^{(III)}$, the couple $Ru^{(III)}/Ru^{(IV)}$ is in most cases irreversible, with anodic $E_{1/2}^{Ox}$ values lying between +1.56 and +1.70 V *vs.* Ag/Ag I. For $Ru^{(III)}$ complexes, the difference $E_{1/2}^{an} - E_{1/2}^{cath}$ between their oxidation and their reduction half-wave potentials ranges from 1.37 to 1.56 V.

In the present paper a recently prepared series of $Ru^{(III)}Cl_3L_3$ complexes has been studied in organic media, on platinum electrodes, by stationary voltammetry (S.V.), cyclic voltammetry (C.V.) and controlled potential coulometry. In these complexes L was either pyridine, acetonitrile or *ortho*- and *meta*-tolunitrile. The complexes were mer-isomers [9–11], except for $RuCl_3$ (*o*-MePhCN)$_2$MeOH which was a fac-isomer.

Experimental

$RuCl_3L_3$ complexes were synthesized according to published procedures [9–11]. The three-electrode cell included a working platinum ring disk electrode (area 3.14 mm^2), a saturated calomel electrode (SCE) as reference, and a platinum wire as an auxiliary electrode. For S.V. measurements the rotation rate of the working electrode was 2000 rpm. Solvents were purified before use, as described elsewhere [12]. Tetra n-hexylammonium perchlorate (THAP) twice recrystallized was used as supporting electrolyte. In these experimental conditions, $E_{1/2}$ of the ferrocene/ferricinium redox couple used as internal standard [13] was +0.40 V *vs.* S.C.E. on Pt electrode in CH_2Cl_2 containing 0.1 *M* THAP. The electroactivity range available in CH_3CN (−2 to +2V *vs.* S.C.E.) was larger than in CH_2Cl_2 (−1.5 to +1.6 V *vs.* SCE).

Results

The electrochemical behaviour of a series of complexes mer-$RuCl_3L_3$ involving ligands L of different donicities (L_3 = Py_3, (*o*-MePhCN)$_3$, (*m*-MePhCN)$_3$, (*o*-MePhCN)$_2CH_3CN$, (*o*-MePhCN)$_2$Py), was studied on a platinum electrode. For comparison, results on fac-$RuCl_3$ (*o*-MePhCN)$_2$MeOH, fac-$RuCl_3$ (*o*-MePhCN)$_2H_2O$ and fac-$RuCl_3$ (*m*-MePhCN)$_2$MeOH are also reported in the present paper (Table I).

mer-$Ru^{(III)}Cl_3Py_3$

In CH_2Cl_2 containing 0.1 *M* THAP, mer-$Ru^{(III)}Cl_3$-Py_3 exhibits two waves in stationary voltammetry:

(i) a cathodic wave at $E_{1/2}^{cath}$ = −0.26 V/S.C.E.

(ii) an anodic wave at $E_{1/2}^{an}$ = +1.53 V/S.C.E., both waves being of equal heights.

A slope of 100 mV results from the logarithmic analysis of each wave, the corresponding limiting

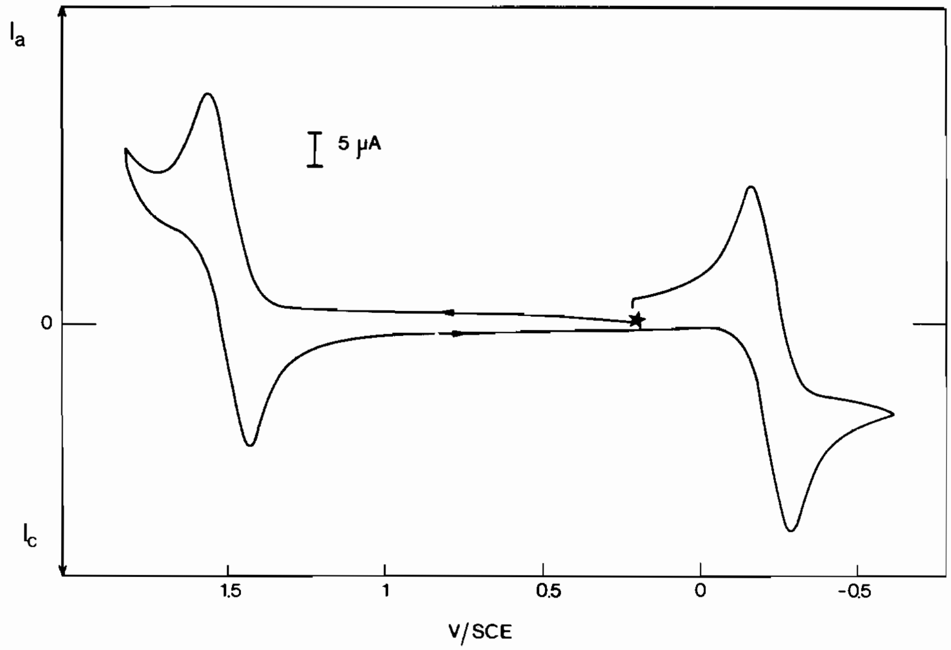

Fig. 1. Cyclic voltammetry of mer-$Ru^{(III)}Cl_3Py_3$ (10^{-3} *M*) in CH_2Cl_2 (+0.1 *M* THAP). scan rate = 0.1 V/s; Pt electrode.

currents being proportional to the concentration of the electroactive species mer-$Ru^{(III)}Cl_3Py_3$. Also the dependence of the limiting currents on the rotation rate of the electrode demonstrates that these limiting currents are diffusion controlled.

Cyclic voltammetry (potential scan rates between 20 mV. s^{-1} and 1 V. s^{-1}) reveals one oxidation and one reduction step on the studied complex (Fig. 1). For each step, the current peak ratio (I_{pa}/I_{pc}) is about unity. Also the difference $\Delta E_p = E_{pc} - E_{pa}$ increases with potential scan rates, from 70 mV (at 20 mV. s^{-1}) to 220 mV (at 1 V. s^{-1}) for the cathodic process, from ΔE_p = 80 mV (20 mV. s^{-1}) to 320 mV (at 1 V. s^{-1}) for the anodic process. Controlled potential coulometry gave n = 1 for each of the two processes. Therefore, these monoelectronic reductions and oxidations are diffusion controlled, electrochemically reversible, and moderately fast on the electrochemical time scale. The following scheme summarizes the corresponding sequence of the observed steps:

$$(Ru^{(IV)}Cl_3Py_3)^+ \underset{-e}{\overset{+e}{\rightleftharpoons}} \text{mer-}Ru^{(III)}Cl_3Py_3 \underset{-e}{\overset{+e}{\rightleftharpoons}} (Ru^{(II)}Cl_3Py_3)^-$$

$(Ru^{(II)}Cl_3Py_3)^-$ was identified in solution by its electronic spectrum (single band at λ = 400 nm) [11], whereas the unstability of generated $(Ru^{(IV)}Cl_3Py_3)^+$ prevented such characterization. Attempts to detect the presence of free Cl^- in solution after exhaustive oxidation or reduction of $Ru^{(III)}Cl_3Py_3$ failed. In solvents other than CH_2Cl_2, namely CH_3CN and propylene carbonate, qualitatively similar results were obtained and close $E_{1/2}$ values were measured, indicating that the redox process is not solvent dependent and in particular that no ligand exchange occurs between Py and the solvent in this complex. Thus mer-$RuCl_3Py_3$ is particularly inert towards ligand exchange with the solvent, in CH_2Cl_2, CH_3CN and in propylene carbonate.

mer-$Ru^{(III)}Cl_3$ (m-MePhCN)$_3$

This complex was studied in several solvents: CH_2Cl_2, CH_3CN, propylene carbonate, dimethylformamide, pyridine, with 0.1 *M* THAP as supporting electrolyte. The electrochemical behaviour is strongly solvent dependent, as evidenced from the following results:

- In CH_2Cl_2 only one reversible cathodic wave (Table I) is observed at $E_{1/2}^{cath}$ = +0.10 V/SCE ($E_{1/2}$ invariant with time).
- In CH_3CN monoelectronic oxidation and reduction are detected at respectively $E_{1/2}^{an}$ = +1.83 and $E_{1/2}^{cath}$ = +0.15 V/SCE.

However, as previously demonstrated [11], the complex mer-$Ru^{(III)}Cl_3$ (*m*-MePhCN)$_3$, is rapidly converted into mer-$Ru^{(III)}Cl_3$ (*m*-MePhCN)$_2$$CH_3CN$, in the presence of CH_3CN. Thus, the above potentials characterize the electrochemical behaviour of mer-$Ru^{(III)}Cl_3$ (*m*-MePhCN)$_2$$CH_3CN$.

- In propylene carbonate, the limiting current of the initial reduction wave ($E_{1/2}$ = +0.15 V *vs.* SCE) decreases with time whereas a new cathodic wave ($E_{1/2}$ = –0.17 V *vs.* SCE) increases, the total height of the two waves remaining constant (Fig.

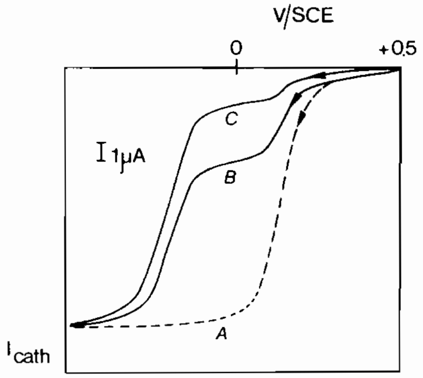

Fig. 2. Reduction of mer-$Ru^{(III)}Cl_3$ (*m*-$MePhCN)_3$ in propylene carbonate. Evolution of the stationary voltammogram with time elapsed after dissolution, at the beginning of the scan:

curve A = t = 0
curve B = t = 38 mn
curve C = t = 48 mn

PC + 0.1 *M* THAP
$RuCl_3$ (*m*-$MePhCN)_3$ in satured solution
Rotating Pt electrode 2000 rpm, area 3.14 mm^2.

2). After one hour, the initial wave (A) disappeared, and the color of the solution changed from red to yellow.

- In DMF, the same behaviour is observed as in propylene carbonate, but the initial cathodic wave (at $E_{1/2}$ = +0.14 V *vs.* SCE) disappears a few minutes after solubilization of the electroactive species and a new wave rises at $E_{1/2}$ = –0.23 V *vs.* SCE.
- In pyridine, cyclic voltammetry at 0.1 V. s^{-1} reveals that the initial reduction peak around 0 V *vs.* SCE is replaced, after few minutes, by a new peak at –0.25 V *vs.* SCE.

Thus, on the cathodic step, no time dependence is observed for the polarographic wave in CH_2Cl_2 on the electrochemical time scale, whereas significant changes are observed in more basic solvents. It is reasonable to ascribe these effects to ligand exchange and/or to mer–fac isomerization in the studied complexes. The latter aspect has been analysed independently by u.v. measurements as discussed below. The observed changes in the redox reactivity of the studied complexes are paralleled with a change in the color of the solution. On the other hand, electrochemical oxidation of mer-$RuCl_3$ (*m*-$MePhCN)_3$ is a reversible process only in CH_3CN.

mer-$RuCl_3$ (o-$MePhCN)_3$

The electrochemical behaviour of this complex is quite similar to that of the corresponding species with *meta*-MePhCN (see above), as shown in the Table. The one-electron oxidation signal is only observable in CH_3CN, owing to the limited electroactivity range available in CH_2Cl_2.

mer-$RuCl_3$ (o-$MePhCN)_2L$ (L = CH_3CN or Py)

Substitution of one (*o*-MePhCN) by a ligand CH_3CN or Py induces slight but significant changes in the electrochemical behaviour of the complexes: increasing basicity of the coordinated ligand renders the complex more difficult to reduce and easier to oxidize (Table I).

Discussion

In order to rationalize the experimental results, two processes occurring when the complexes are dissolved in an organic solvent, are to be taken into account:

(i) the mer–fac isomerization [11]
(ii) the possibility of ligand exchange between the complexes and the donor solvent.

The complexes mer-$Ru^{(III)}Cl_3(RCN)_2L$ (R = MePh) are red and exhibit a characteristic absorption at 420 nm (probably due to a charge transfer from ligand to metal) when L = Py, CH_3CN, RCN, whereas the complexes with L = MeOH, H_2O, DMF are yellow with an electronic absorption band near 370 nm. It has been demonstrated [14] that the red complexes have a mer-(*trans*, C_2v) structure, while the yellow complexes exhibit a fac (*cis*, C_3v) configuration. It is possible to convert the complex from a mer to a fac isomer: for instance, a few drops of MeOH added to a solution of mer-$RuCl_3$ (*m*-$MePhCN)_3$ in CH_2Cl_2 transforms the complex from mer (red) to fac (yellow) (Fig. 3). The complex thus obtained could be isolated and characterized as fac-$RuCl_3$ (*m*-$MePhCN)_2MeOH$ [11]. Also, this conversion in CH_2Cl_2 or red mer-$RuCl_3$ (*m*-$MePhCN)_3$ into yellow fac-$RuCl_3$ (*m*-$MePhCN)_2MeOH$ by addition of MeOH was followed by electrochemical measurements: on cyclic voltammograms the current peak corresponding to the reduction of the mer complex (at +0.08 V *vs.* SCE) disappears whilst a new peak corresponding to the fac isomer rises at potentials 300 mV more cathodic (at –0.28 V *vs.* SCE). In this conversion, previous studies [9–11] revealed that isomerization and ligand exchange occur simultaneously on the time scale of spectral observations. Similar complexes were described previously with L = $PhSPr^i$ [15] or PPh_3, $AsPh_3$ [16] instead of (MePhCN), but their isomerization was not discussed.

All the complexes studied above are mer isomers. In order to study also the redox behaviour of fac complexes, fac-$Ru^{(III)}Cl_3$ (*o*-$MePhCN)_2MeOH$ was examined. This complex is reduced at $E_{1/2}$ = –0.24 V vs. SCE in CH_2Cl_2 (Table I). The corresponding fac-$Ru^{(III)}Cl_3$ (*o*-$MePhCN)_2H_2O$ is reduced at the same

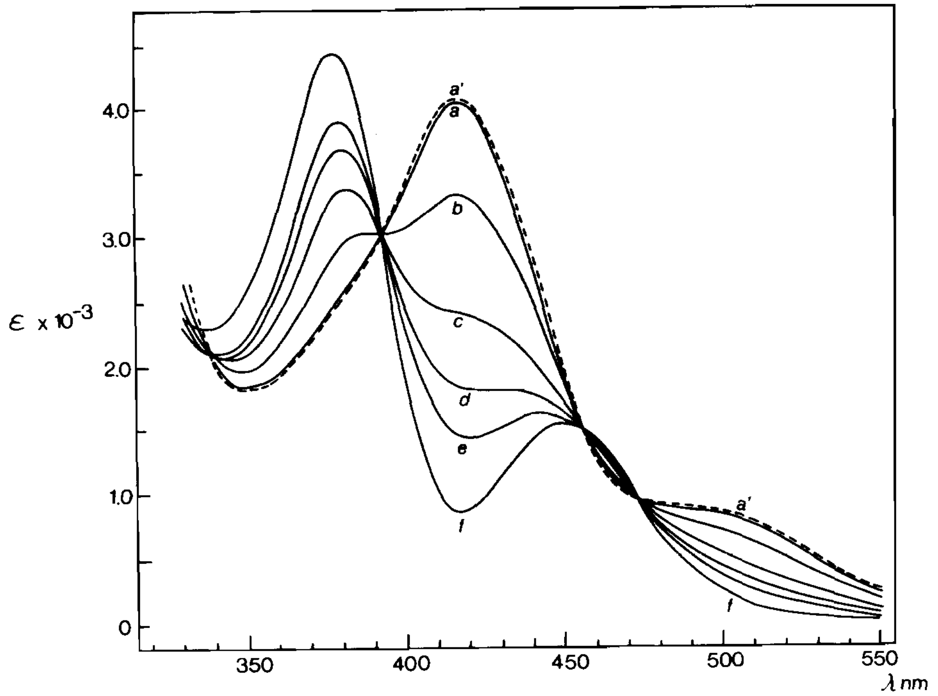

Fig. 3. Conversion of mer-$RuCl_3$ (*m*-MePhCN)$_3$ to fac-$RuCl_3$ (*m*-MePhCN)$_2$MeOH by addition of MeOH in a solution of mer-isomer in CH_2Cl_2. Initial solution: $RuCl_3L_3$ in CH_2Cl_2–MeOH; L = *o*-MePhCN.

a′: before addition of MeOH (time independent)
a : 5 minutes
b : 10 minutes
c : 20 minutes
d : 30 minutes
e : 40 minutes
f : 270 minutes
} after dissolution

potential as the potential observed at the end of the mer–fac evolution described above in the presence of MeOH (Table I). When CH_3CN is added to a CH_2Cl_2 solution of fac-$Ru^{(III)}Cl_3$ (*o*-MePhCN)$_2$MeOH, a slow exchange of CH_3CN occurs with MeOH, this exchange being complete in about a day. However, cyclic voltammetry at v = 0.1 V. s^{-1} revealed that this CH_3CN to MeOH substitution occurs very rapidly on the reduced form of ($Ru^{(III)}Cl_3$ (*o*-MePhCN)$_2$MeOH): the reoxidation peak of the reduced form of fac-$Ru^{(III)}Cl_3$ (*o*-MePhCN)$_2$MeOH, at –0.16 V/SCE, is indeed replaced by a new anodic peak at +0.11 V/SCE which was previously observed in the reoxidation of the species generated in the reduction of mer-$Ru^{(III)}Cl_3$ (*o*-MePhCN)$_2CH_3CN$ at +0.01 V/SCE (Table I). The latter reduction peak was assigned to mer-$RuCl_3$ (*o*-MePhCN)$_2CH_3CN$ by comparison with the behaviour of an authentic sample prepared independently (Table I). Thus, in contrast to the other compounds studied in this work, $Ru^{(III)}Cl_3$ (*o*-MePhCN)$_2$MeOH illustrates an electrochemically induced ligand lability in the ruthenium coordination sphere and the above results demonstrate the possibility to monitor reversibly the fac-mer interconversion. Furthermore, these results suggest that isomerization is responsible for the shift observed between the reduction potentials of the two isomers. A recent study of the oxidation of mer and fac-($ReCl(CO)_3$-$(PMe_2Ph)_2$) reported a difference in peak potential of 250 mV between the isomers [17].

In order to evaluate the influence of the ligand basicity on the reduction potential of a given isomeric series, the donor number [18] of the ligands has been plotted versus the measured potentials. The linear plot obtained with the mer isomers (Fig. 4) illustrates the additivity of the donating effects of the basic ligands: the most difficult reduction is observed with $Ru^{(III)}Cl_3Py_3$, in agreement with the highest donicity (DN = 33.1) of the ligand Py in the series.

It results from the above studies of octahedric complexes of ruthenium that one two-electron donor ligand is more labile than the others, and is easily exchanged with an other coordinating base (the solvent for instance). In this ligand exchange, and for the studied series of complexes, the geometry remains unaltered for mer-isomers whereas the ligand

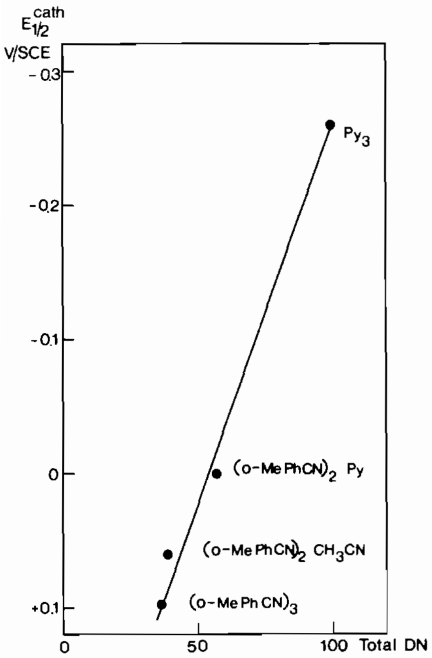

Fig. 4. Reduction of mer-$Ru^{(III)}Cl_3L_3$ in CH_2Cl_2 (+0.1 *M* THAP): effect of the donor number [18] of L upon the reversible cathodic $E_{1/2}^{cath}$. L_3 = Py_3, (o-MePhCN)$_2$CH$_3$CN, (o-MePhCN)$_2$Py, (o-MePhCN)$_3$. Total D.N. = overall D.N. of the L_3 ligands.

exchange isomerises the fac species to the corresponding mer complex.

As to the effects of these coordination changes on the redox reactivity of the complexes, we emphasize that:

(i) there is a HAMMETT type correlation between the ligand basicity and the reduction potentials of the complexes

(ii) for a given complex, the mer isomer is easier to reduce than the corresponding fac-form. This is documented for instance by the reduction potentials ($E_{1/2}^{cath}$) of mer-$RuCl_3$ (o-MePhCN)$_2$CH$_3$CN (+0.06 V/SCE) and of fac-$RuCl_3$ (o-MePhCN)$_2$-H_2O (−0.24 V/SCE): owing to the quasi-identical donicities of CH_3CN [1, 14] and of H_2O [18], the inductive effects of these ligands on reduction potentials are very close, so that the difference between these cathodic $E_{1/2}$ may be ascribed to the different conformations of the complexes.

Acknowledgements

The Laboratoire de Chimie de Coordination is grateful to CdF Chimie for a generous loan of ruthenium trichloride.

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