# ELECTROCHEMICAL STUDY OF DINUCLEAR RUTHENIUM(II)-ARENE COMPOUNDS: ELECTROGENERATION OF Ru(II)-Ru(I) SPECIES

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Abstract—The preparation and characterization of Ru(II)—arene compounds [{RuCl<sub>2</sub>(pcym)}<sub>2</sub>( $\mu$ -L-L)] where p-cym = p-MeC<sub>6</sub>H<sub>4</sub>CHMe<sub>2</sub>; and L-L = diphenylphosphinomethane (I), 1,1'-bisdiphenylphosphinoferrocene (II), pyrazine (III) and 4,4'-bipyridine (IV), are described. Electrochemical data for these compounds obtained by cyclic voltammetry and coulometry are reported. The electrochemical reduction of compounds I or II yields ruthenium(0) species. However, compounds III or IV containing ligands with delocalized  $\pi$  orbitals undergo one-electron reduction. The ESR signal detected during the electrolysis of compounds III or IV is consistent with one delocalized electron through the whole dinuclear unit.

The electrochemical oxidation of dinuclear Ru(II)– Ru(II) compounds has been extensively studied.<sup>1-3</sup> In some cases two single-electron transfer processes are observed and the mixed valence compound Ru(II)–Ru(III) can be isolated.<sup>1</sup> The electrochemical reduction which would generate *a priori* Ru(II)–Ru(I) or Ru(I)–Ru(I) species has been studied much less.

We have recently described how the electrochemical reduction of compounds of the type  $\{RuCl_2(arene)\}_2$  generates Ru(I) compounds of only limited stability in solution at room temperature.<sup>4</sup> The number of Ru(I) compounds described in the literature is very limited and in all the cases where a metal-metal bond is present.<sup>5</sup>

The electrochemical generation of Ru(I) species seems to be possible only if a metal-metal bond can be formed. We assumed that by using adequate bridging ligands we could stabilize binuclear Ru(I)-Ru(I) compounds. So we have prepared and studied the electrochemical properties of several new dinuclear ruthenium compounds containing phosphorus bridging ligands. Other compounds containing nitrogen ligands with delocalized  $\pi$  orbitals are also studied.

## **EXPERIMENTAL**

All solvents were reagent grade and were degassed and dried prior to use by standard procedures. All the reactions were carried out under argon using the Schlenk technique, although the isolated compounds were air-stable.

### Preparation of the compounds

 ${RuCl_2(p-cym)}_2$ ,  ${RuCl_2(p-cym)}_2$ dppe and  $[{Ru_2Cl_3(p-cym)_2}BPh_4]$  were prepared by literature methods.<sup>6-8</sup>

(a) [{RuCl<sub>2</sub>(p-cym)}<sub>2</sub>( $\mu$ -dppm)] (I). A solution of dppm (77 mg, 0.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>) was added to a solution of {RuCl<sub>2</sub>(p-cym)}<sub>2</sub> (122 mg,

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0.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>). The solvent was evaporated under reduced pressure and upon addition of hexane a red precipitate was formed. The precipitate was filtered, washed with hexane and dried *in vacuo*. Yield 72%. Found: C, 50.3; H, 4.9%. Calc. for C<sub>45</sub>H<sub>50</sub>Cl<sub>4</sub>P<sub>2</sub>Ru<sub>2</sub> · CH<sub>2</sub>Cl<sub>2</sub>: C, 51.0; H, 4.7%.

(b) [{RuCl<sub>2</sub>(p-cym)}<sub>2</sub>{ $\mu$ -Fe(C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>}] (II). A solution of Fe(C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub> (73 mg, 0.13 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 cm<sup>3</sup>) was added to a solution of {RuCl<sub>2</sub>(p-cym)}<sub>2</sub> (80 mg, 0.13 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (6 cm<sup>3</sup>). Hexane was added and the solvent evaporated under reduced pressure. The red precipitate was filtered, washed with hexane and dried *in vacuo*. Yield 87%. Found: C, 56.1; H, 5.1%. Calc. for C<sub>54</sub>H<sub>56</sub>Cl<sub>4</sub>FeP<sub>2</sub>Ru<sub>2</sub>: C, 55.6; H, 4.8%.

(c) [{RuCl<sub>2</sub>(p-cym)}<sub>2</sub>( $\mu$ -pyz)] (III). A solution of pyrazine (16 mg, 0.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 cm<sup>3</sup>) was added to a solution of {RuCl<sub>2</sub>(p-cym)}<sub>2</sub> (122 mg, 0.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>). At 10 min the solution was cloudy and in 1 h the precipitation of an orange-yellow compound was completed. The precipitate was filtered, washed with CH<sub>2</sub>Cl<sub>2</sub> and dried *in vacuo*. Yield 70%. Found: C, 39.8; H, 4.6; N, 3.7%. Calc. for C<sub>24</sub>H<sub>32</sub>Cl<sub>4</sub>N<sub>2</sub>Ru<sub>2</sub>: C, 41.0; H, 4.5; N, 4.0%.

(d) [{RuCl<sub>2</sub>(p-cym)}<sub>2</sub>( $\mu$ -4,4'-bipy)]. (IV). A solution of 4,4'-bipyridine (39 mg, 0.25 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>) was added to a solution of {RuCl<sub>2</sub>(p-cym)}<sub>2</sub> (153 mg, 0.25 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 cm<sup>3</sup>). The solution was stirred for 2 h at room temperature, during which a yellow precipitate was formed. The precipitate was filtered, washed with CH<sub>2</sub>Cl<sub>2</sub> and dried *in vacuo*. Yield 76%. Found: C, 46.3; H, 4.6; N, 3.3%. Calc. for C<sub>30</sub>H<sub>36</sub>Cl<sub>4</sub>N<sub>2</sub>Ru<sub>2</sub>: C, 46.8; H, 4.6; N, 3.6%.

### Instrumental

IR spectra were recorded on a Pye-Unicam SP-2000 spectrometer. NMR spectra were recorded on a Brucker AC-200 spectrometer. ESR spectra were recorded on a Varian E-12 spectrometer provided with a 100 kHz field modulation. The g factor was obtained by means of relation  $g = 0.714484\nu$ (MHz)/H(G) where the magnetic field H (in Gauss) at the sample was measured using a Gaussmeter and the microwave frequency ( $\nu$ ) (in MHz) was measured with a high precision frequency meter.

For complicated spectra the hyperfine coupling constants were obtained by comparing experimental and computer-simulated spectra, assuming a Lorentzian line-shape.

The electrochemical experiments were carried out in a three-electrode cell. The working and auxiliary electrodes were platinum, the reference was a saturated calomel electrode, electrically connected to the non-aqueous solution by a "saltbridge" containing the non-aqueous solvent and the supporting electrolyte.

Cyclic voltammograms were obtained with a programming function generator 305 H.Q. Instruments which was connected to a 552 Amel potentiostat and recorded with a Riken-Denshi F 35 x-y recorder.

The solvents were THF, freshly distilled over Na-benzophenone and DMSO dried by elution through a column of activated alumina and distilled under reduced pressure. The supporting electrolyte was  $Bu_4NPF_6$  recrystallized from ethanol and dried at 80°C in vacuo for 48 h.

In order to prove the presence of paramagnetic binuclear Ru(II)-Ru(I) species, we carried out simultaneous ESR and electrochemical experiments. The electrolysis is performed by placing a special flat cell inside the microwave cavity of the X-band spectrometer. We used the Willmad and Glass Co. Electrolytic Cell Assembly for ESR studies.

To obtain ESR spectra with high resolution, we prepared dilute solution of the studied compounds (1 mM) and used very low microwave power (2-5 mW). The solutions were degassed for 30 min to avoid the scavenging effect of dissolved oxygen. All the electrochemical experiments were carried out under an inert atmosphere.

## **RESULTS AND DISCUSSION**

Compounds I-IV are prepared by reacting  $\{RuCl_2(p-cym)\}_2$  with a stoichiometric amount of the ligand L-L in  $CH_2Cl_2$  at room temperature. Compounds III and IV are of limited solubility in  $CH_2Cl_2$  or THF and all the spectroscopic and electrochemical measurements have been performed in DMSO. The compounds are non-electrolytes in solution. (The measurements of conductivity were carried out in  $CH_2Cl_2$  for compounds I or II and in DMSO for compounds III or IV.)

<sup>1</sup>H and <sup>31</sup>P NMR spectra support the dinuclear stoichiometry  $[(p-cym)RuCl_2(\mu-L-L)RuCl_2(p-cym)]$  proposed for these compounds (Table 1). Compounds I and II show singlet signals in the <sup>31</sup>P NMR spectra at 21.1 and 18.3 ppm, respectively, indicating that both phosphorus nuclei are coordinated.

The four protons of the pyrazine ligand in compound III are equivalent and they appear as a sharp resonance at  $\delta = 9.03$  ppm. Both C<sub>5</sub>H<sub>4</sub>N moieties of the bipy ligand in compound IV give two doublets in the <sup>1</sup>H NMR spectrum at 9.1 and 7.4 ppm (J = 7 Hz). All the proton resonances corresponding to the *p*-cymene ligand are also observed for compounds I-IV.

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	<sup>1</sup> H NMR <sup>c46</sup>			ر
Compound	Co-ordinated arene protons	Others	<sup>31</sup> P NMR <sup>e</sup>	$(cm^{-1})$
$[{RuCl}_2(p-cym)]_2(\mu-dppm)]$	5.15, 4.90 (H <sub>A</sub> , H <sub>B</sub> , J 6); 2.47 (sp, CHCH <sub>3</sub> )	7.6(m), 7.2(m)	21.1(s)	292
	1.90(s, CH <sub>3</sub> ); 0.93 (d, CHCH <sub>3</sub> , J 7)	4.5(t)		281
$[{RuCl_2(p-cym)}_2{\mu-Fe(C_5H_4PPh_2)_2}]$	4.16, 3.87 (H <sub>A</sub> , H <sub>B</sub> , J 6); 2.52 (sp, CHCH <sub>3</sub> )	7.37, 7.73	18.3(s)	296
	1.70(s, CH <sub>3</sub> ); 0.95 (d, CHCH <sub>3</sub> , J 7)	5.06		280
$[{\mathbf{RuCl}}_2(p-{\rm cym})]_2(\mu-{\rm pyz})]'$	5.43, 5.27 (H <sub>A</sub> , H <sub>B</sub> , J 6); 3.02 (sp, CHCH <sub>3</sub> )	9.03(s)		288
	1.58 (s, CH <sub>3</sub> ); 1.28 (d, CHCH <sub>3</sub> , J 8)			284
$[{RuCl_2(p-cym)}_2(\mu-4,4'-bipy)]'$	5.49, 5.29 (H <sub>A</sub> , H <sub>B</sub> , J 6); 3.07 (sp, CHCH <sub>3</sub> )	9.16 (d, J 7)		291
	1.58 (s, CH <sub>3</sub> ); 1.25 (d, CHCH <sub>3</sub> , J 8)	7.45 (d, J 7)		281
"Measured in CDCl <sub>3</sub> at room temperatu	ure.			
<sup>b</sup> Abbreviations: s, singlet; d, doublet; t, t	triplet; sp, septet; m, multiplet.			
"Chemical shifts relative to Me <sub>4</sub> Si.	•			
J in Hz.				
<sup>e</sup> Chemical shifts relative to H <sub>3</sub> PO <sub>4</sub> .				
$f$ Measured in $(d_6)$ DMSO.				
<sup>#</sup> Labelling of <i>p</i> -cymene protons: H <sub>A</sub>	H <sub>B</sub>			

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Assignment of resonances to  $H_A$  and  $H_B$  is arbitrary.

Table 1. Spectroscopic data for the compounds<sup>ab</sup>

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	Ered		Epox
Compound	$A_1$	$A_2$	$A'_3$
$[\{RuCl_2(p-cym)\}_2(\mu-dppm)]^a$	- 1.64°		1.40ª
$[\{\operatorname{RuCl}_2(p-\operatorname{cym})\}_2(\mu-\operatorname{dppe})]^a$	- 1.58°	-1.70 <sup>c</sup>	1.14 <sup>d</sup>
$[{RuCl_2(p-cym)}_2{\mu-Fe(C_5H_4PPh_2)_2}]^{a}$	- 1. <b>92</b> °		0.64 <sup>d</sup>
$[\{\operatorname{RuCl}_2(p\operatorname{-cym})\}_2(\mu\operatorname{-pyz})]^b$	-1.30°	-2.12 <sup>c</sup>	
$[{RuCl_2(p-cym)}_2(\mu-4,4'-bipy)]^b$	- 1.28°	- 1.86°	
$[{Ru_2Cl_3(p-cym)_2}BPh_4]^a$	-0.74		

Table 2. Electrochemical parameters for the compounds

<sup>a</sup>Conditions: 0.1 M  $Bu_4NPF_6$  in THF; scan rate 100 mV s<sup>-1</sup>.

<sup>b</sup>Conditions: 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in DMSO; scan rate  $100 \text{ mV s}^{-1}$ .

'Irreversible cathodic peak.

<sup>d</sup>Reversible anodic peak.

A compound of stoichiometry  $[RuCl_{2(p}-cym)]$  (dppm)] has been previously described,<sup>9</sup> suggesting that the phosphine coordinates to the ruthenium atom only through one phosphorus atom. We have repeated the reported preparative method, obtaining the same spectroscopic and analytical results as for compound I. The bidentate coordination of dppm ligand is evident from the analytical data and from the integration of the <sup>1</sup>H NMR signals which fit better a bimetallic stoichiometry.

#### Electrochemical data

Table 2 summarizes the electrochemical data for compounds I-IV as well as for  $[{RuCl_2(p-cym)}_2 (\mu-dppe)]$  (V) and  $[{Ru_2(Cl_3(p-cym)_2)BPh_4}]$  (VI). Compounds containing phosphorus ligands reduce at higher potential values.  $Fe(C_5H_4PPh_2)_2$  behaves as a stronger electron donor ligand than dppm or dppe and consequently compound II reduces with more difficulty than compounds I or V. Only one reduction peak is observed for compounds I-IV, while compound V shows some splitting in the first process.

Potential-controlled electrolysis on the plateau of peak  $A_1$  gives a consumption of  $4 \text{ F mol}^{-1}$  for compounds I, II and V. This indicates that in  $A_1$ a complicated process yielding Ru(0) species takes place.

According to this, these three compounds do not show any clear tendency to stabilize the oxidation state (I) as observed for  $\{RuCl_2(p-cym)\}_2$ . They behave like other mononuclear compounds such as  $RuCl_2(p-cym)PPh_3$ . This compound shows two close reduction peaks,  $A_1$  (-1.54 V) and  $A_2$ (-1.64 V) each corresponding to one-electron transfer processes.

Compounds I, II and V oxidize reversibly with II showing the lowest oxidation potential.

Another aspect related to the electrochemical behaviour of  $\{RuCl_2(p-cym)\}_2$  is the fact that the first reduction peak  $A_1$  at -0.98 V corresponds to the simultaneous reduction of both Ru atoms. No evidence of an intermediate Ru(II)-Ru(I) species has been observed.

We considered the cationic species  ${Ru_2Cl_3(p-cym)_2}^+$  an interesting compound to generate Ru(II)-Ru(I) species. As cationic compounds usually reduce at lower potentials than neutral ones with the same oxidation state, we should expect  $\{Ru_2Cl_3(p-cym)_2\}^+$  to show a separate reduction peak corresponding to Ru(II)-Ru(II)  $\rightarrow$  Ru(II)-Ru(I) process. This compound reduces at -0.74 V. The exhaustive electrolysis at this potential value gives a consumption of  $1 \text{ F mol}^{-1}$ . From the resulting solution,  $\{RuCl_2(p-cym)\}_2$  can be isolated in a low yield. This indicates that the product of the reduction is not stable and shows a chemical evolution, probably such as  $Ru(II)-Ru(I) \rightarrow Ru(II)-Ru(II) + Ru(I)-Ru(I)$ . EPR measurements on the reduced solution of  $\{Ru_2Cl_3(p-cym)\}^+$  fail to show any evidence of a paramagnetic species in solution.

Another possible way to stabilize mixed valence species might be the use of bridging ligands capable of delocalizing electron density as pyrazine or 4,4'bipyridine.

The complexes  $[\{\operatorname{RuCl}_2(p\operatorname{-cym})\}_2(\mu\operatorname{-pyz})]$  and  $[\{\operatorname{RuCl}_2(p\operatorname{-cym})\}_2(\mu\operatorname{-4},4'\operatorname{-bipy})]$  show a monoelectronic reduction peak at -1.28 V assignable to the Ru(II)-Ru(II)  $\rightarrow$  Ru(II)-Ru(I) process. This reduction peak is in both cases irreversible. A second reduction peak is also observed for each compound. The potential values for the second peak are very similar to the reduction potential values of the corresponding ligands pyz and 4,4'bipy.

The reduced species are fairly stable in solution and have been detected by ESR spectroscopy. The



Fig. 1. EPR spectrum of reduced [{ $RuCl_2(p-cym)$ }\_2( $\mu$ -pyz)].



Fig. 2. EPR spectrum of reduced [{ $RuCl_2(p-cym)$ }\_2( $\mu$ -4,4'-bipy)].

ESR spectra obtained are shown in Figs 1 and 2. These spectra are very well resolved and show a metal-ligand isotropic superhyperfine interaction. The spectrum of the reduced complex  $[{RuCl_2(p-cym)}_2(\mu-pyz)]$  is composed of two quintets with the following hyperfine splittings:  $a_N = 7.20$  G and  $a_H = 2.65$  G (pyrazine ring protons). Its g factor is 2.0036.

The spectrum of the reduced complex  $[{RuCl_2(p-cym)}_2(\mu-4,4'-bipy)]$  is complicated and from its analysis by simulation assuming Lorentzian line-shape, three hyperfine coupling constants were obtained, whose values (in G) are: 3.50(Q, 1:2:3:2:1), 2.35 (Q, 1:4:6:4:1) and 0.45 (Q, 1:4:6:4:1). The first quintet corresponds to the nitrogen splittings and we assign the quintets with 2.35 and 0.45 G to the ortho and meta protons of the bipyridine rings, respectively. This assignment is based on the analysis of the canonical structure of this compound. Its g factor is 2.0030. Further studies of these and other related ruthenium arene complexes containing ligands with delocalized  $\pi$  orbitals are in progress.

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