

# Mono and dinuclear arene ruthenium complexes containing 6,7-dimethyl-2,3-di(pyridine-2-yl)quinoxaline as chelating ligand: Synthesis and molecular structure

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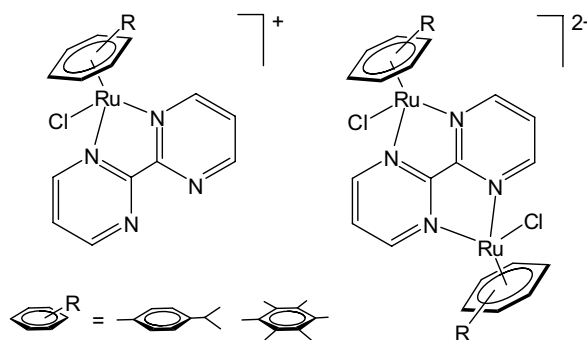
## Abstract

The mononuclear cations of the general formula  $[(\eta^6\text{-arene})\text{RuCl}(\text{dpqMe}_2)]^+$  ( $\text{dpqMe}_2 = 6,7\text{-dimethyl-2,3-di(pyridine-2-yl)quinoxaline}$ ; arene =  $\text{C}_6\text{H}_6$ , **1**;  $\text{C}_6\text{H}_5\text{Me}$ , **2**;  $p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me}$ , **3**;  $\text{C}_6\text{Me}_6$ , **4**) as well as the dinuclear dication  $[(\eta^6\text{-arene})_2\text{Ru}_2\text{Cl}_2(\mu\text{-dpqMe}_2)]^{2+}$  (arene =  $\text{C}_6\text{H}_6$ , **5**;  $\text{C}_6\text{H}_5\text{Me}$ , **6**;  $p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me}$ , **7**;  $\text{C}_6\text{Me}_6$ , **8**) have been synthesised from 6,7-dimethyl-2,3-di(pyridine-2-yl)quinoxaline ( $\text{dpqMe}_2$ ) and the corresponding chloro complexes  $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$ ,  $[(\eta^6\text{-C}_6\text{H}_5\text{Me})\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$ ,  $[(\eta^6\text{-}p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me})\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$  and  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$ , respectively. The X-ray crystal structure analyses of **[1][PF<sub>6</sub>]**, **[3][PF<sub>6</sub>]** and **[6][PF<sub>6</sub>]** reveal a typical piano-stool geometry around the metal centre; in the dinuclear complexes the two chloro ligands, with respect to each other, are found to be *trans* oriented.

**Keywords:** Arene ligands; Dinuclear complexes; N ligands; Ruthenium; Transfer hydrogenation

## 1. Introduction

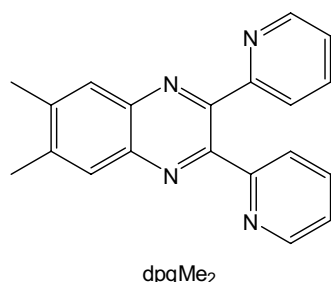
Polypyridyl complexes of ruthenium have received considerable attention owing to their photochemical properties [1], catalytic activities [2], electrochemical behaviour [3] and in the design of new materials [4]. Recently, we have shown that mono and dinuclear arene ruthenium complexes containing 2,2'-bipyrimidine as terminal or bridging chelate ligand catalyse the transfer hydrogenation of acetophenone with formic acid in aqueous solution to give phenylethanol and carbon dioxide [5].



Interestingly, an increase of the catalytic activity by three to five times in going from the mononuclear to the dinuclear complexes was observed. The higher catalytic activity of the dinuclear arene ruthenium complexes was accounted for by a synergistic electronic effect in the intact dinuclear moieties. The molecular structures of

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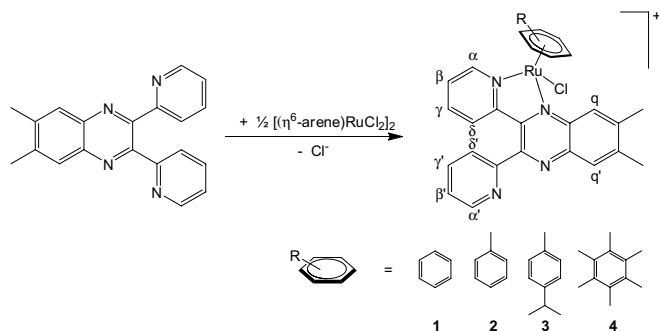
various dinuclear arene ruthenium and osmium complexes containing 2,2'-bipyrimidine as bridging chelate ligand have shown that the two chloro ligands can be found in both *cis* and *trans* orientations [6]. Therefore, in order to determine if the increase in the catalytic activity is correlated to the *cis-trans* conformations, we prepared a series of exclusively *trans* oriented dinuclear arene ruthenium complexes with the sterically hindered chelate ligand, 6,7-dimethyl-2,3-di(pyridine-2-yl)quinoxaline (dpqMe<sub>2</sub>). The catalytic activity of the dinuclear complexes and of their corresponding mononuclear congeners for the transfer hydrogenation of aromatic ketones to give the corresponding secondary alcohol with sodium formate as the hydrogen donor in aqueous solution is reported. We also present the single-crystal X-ray structure analysis of some representatives.



## 2. Results and discussion

### 2.1. Synthesis of the mononuclear complexes 1–4 as hexafluorophosphate salts

The arene ruthenium complexes  $[(\eta^6\text{-arene})\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$  (arene = C<sub>6</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>5</sub>Me, *p*-Pr<sup>*i*</sup>C<sub>6</sub>H<sub>4</sub>Me, C<sub>6</sub>Me<sub>6</sub>) react with 2 equiv. of 6,7-dimethyl-2,3-di(pyridine-2-yl)quinoxaline (dpqMe<sub>2</sub>) in methanol at 50 °C in the presence of KPF<sub>6</sub> to form the cationic arene ruthenium complexes  $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}(\text{dpqMe}_2)]^+$  (**1**),  $[(\eta^6\text{-C}_6\text{H}_5\text{Me})\text{RuCl}(\text{dpqMe}_2)]^+$  (**2**),  $[(\eta^6\text{-}p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me})\text{RuCl}(\text{dpqMe}_2)]^+$  (**3**) and  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}(\text{dpqMe}_2)]^+$  (**4**), which are isolated as their hexafluorophosphate salts (Scheme 1). The hexafluoro-



Scheme 1. Synthesis of cations 1–4.

phosphate salts of complexes 1–4 are red-purple, non-hygroscopic, air-stable, crystalline solids. They are sparingly soluble in methanol and chloroform, but well soluble in dichloromethane, acetone and acetonitrile. All compounds have been characterised on the basis of elemental analysis, <sup>1</sup>H NMR, IR, UV–Vis and mass spectroscopy.

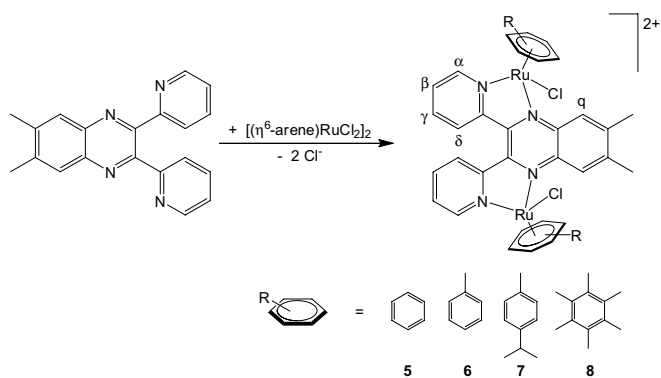
In the mass spectra they give rise to the corresponding  $[\text{M}]^+$  molecular peaks  $m/z$  at 527, 541, 583 and 611, respectively. The <sup>1</sup>H NMR spectra of 1–4 exhibit, other than the signals corresponding to the aromatic ligand, a characteristic set of 12 independent signals for the diastereotopic protons of the dpqMe<sub>2</sub> ligand. The ruthenium atom is stereogenic due to the coordination of four different ligand atoms. Upon coordination to the ruthenium atom, the aromatic protons of the dpqMe<sub>2</sub> ligand are shifted downfield, especially the H<sub>α</sub> of the coordinated pyridyl group which is observed at  $\delta \sim 9.4$  ppm, while the H<sub>α'</sub> of the non-coordinated pyridyl group is observed at only 8.65 ppm. Accordingly, the aromatic protons of the quinoxaline moiety are observed at  $\delta \sim 8.6$  (H<sub>q</sub>) and 8.1 (H<sub>q'</sub>), respectively. The <sup>1</sup>H NMR spectrum of 3 exhibits two doublets for the diastereotopic methyl protons of the isopropyl group. Likewise, the diastereotopic CH protons of the *p*-cymene ligand give rise to four doublets observed between  $\delta = 5.7\text{--}6.1$  ppm. A septet at  $\delta = 2.51$  ppm is observed for the CH proton of the isopropyl group. Similarly, the aromatic protons of the toluene ligand in 2 give rise to five multiplets observed between  $\delta = 5.7\text{--}6.2$  ppm and a singlet at  $\delta = 2.36$  ppm for the methyl group.

The UV–Vis data of complexes 1–4 have been recorded in acetonitrile. The electronic spectra display a medium intensity band in the visible region at  $\sim 385$  nm and an intense band at  $\sim 280$  nm. The low intensity band at  $\sim 385$  nm is assigned to the metal-to-ligand charge transfer transition (MLCT), while the high-energy band at  $\sim 280$  nm is assigned to intra-ligand  $\pi\text{-}\pi^*$  transitions [7].

### 2.2. Synthesis of the dinuclear complexes 5–8 as hexafluorophosphate salts

The reaction of the dimeric chloro complexes  $[(\eta^6\text{-arene})\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$  (arene = C<sub>6</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>5</sub>Me, *p*-Pr<sup>*i*</sup>C<sub>6</sub>H<sub>4</sub>Me, C<sub>6</sub>Me<sub>6</sub>) with 1 equiv. of 6,7-dimethyl-2,3-di(pyridine-2-yl)quinoxaline (dpqMe<sub>2</sub>) in refluxing methanol in the presence of KPF<sub>6</sub> results in the formation of the red-purple coloured, air-stable dinuclear complex dication  $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}]_2(\mu\text{-dpqMe}_2)^{2+}$  (**5**),  $[(\eta^6\text{-C}_6\text{H}_5\text{Me})\text{RuCl}]_2(\mu\text{-dpqMe}_2)^{2+}$  (**6**),  $[(\eta^6\text{-}p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me})\text{RuCl}]_2(\mu\text{-dpqMe}_2)^{2+}$  (**7**) and  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}]_2(\mu\text{-dpqMe}_2)^{2+}$  (**8**), which can be isolated as their hexafluorophosphate salts (Scheme 2).

Complexes 5–8 have been characterised by mass, UV–Vis, <sup>1</sup>H NMR spectroscopy and elemental analysis. In the mass spectra the hexafluorophosphate salts give rise to two main peaks; a minor peak with an approximately 50% intensity attributed to  $[\text{M}^{2+} + \text{PF}_6^-]^+$  at  $m/z$  887, 915, 999 and 1055, respectively, and a major peak which corresponds after decomplexation of an  $[(\text{arene})\text{RuCl}]^+$

Scheme 2. Synthesis of the dications **5–8**.

fragment to the mononuclear cations **1–4** at  $m/z = 527$ , 541, 583 and 611, respectively. The UV–Vis data of complexes **5–8** in acetonitrile show that the position of the MLCT transitions of the dinuclear complexes **5–8** is significantly red shifted ( $\sim 490$  nm) as compared to their mononuclear congeners.

The  $^1\text{H}$  NMR spectra of **5–8** exhibit, other than the signals corresponding to the aromatic ligand, a characteristic set of six signals for the protons of the  $\text{dpqMe}_2$  ligand. Despite the fact that the two ruthenium atoms are stereogenic and therefore should generate a mixture of *rac* and *meso* diastereoisomers, only the *rac* isomer is observed. The sterically hindered  $\text{dpqMe}_2$  ligand forces the chloro ligands to adopt exclusively a *trans* orientation, thus giving rise to only the (*R,R*) and (*S,S*) enantiomers and consequently six signals for the  $\text{dpqMe}_2$  bridging ligand. As observed in **1–4**, the aromatic protons of the  $\text{dpqMe}_2$  ligand are shifted downfield, especially the  $\text{H}_\alpha$  of the pyridyl groups which are observed at  $\delta \sim 9.4$  ppm, while the aromatic protons of the quinoxaline moiety are observed at  $\delta \sim 8.7$  ppm.

### 2.3. Crystal structure analysis of $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}(\text{dpqMe}_2)][\text{PF}_6]$ (**[1][PF<sub>6</sub>]**), $[(\eta^6\text{-}p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me})\text{RuCl}(\text{dpqMe}_2)][\text{PF}_6]$ (**[3][PF<sub>6</sub>]**) and $[(\eta^6\text{-C}_6\text{H}_5\text{Me})\text{RuCl}(\mu\text{-dpqMe}_2)][\text{PF}_6]_2$ (**[6][PF<sub>6</sub>]<sub>2</sub>**)

The molecular structures of  $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}(\text{dpqMe}_2)]^+$  (**1**) and  $[(\eta^6\text{-}p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me})\text{RuCl}(\text{dpqMe}_2)]^+$  (**3**) have been established by single-crystal X-ray structure analysis of their hexafluorophosphate salts. Both complexes show a typical piano-stool geometry with the metal centres coordinated by the arene ligand, a terminal chloride and the chelating  $\text{dpqMe}_2$  ligand. The molecular structures of **[1][PF<sub>6</sub>]** and **[3][PF<sub>6</sub>]** are presented in Figs. 1 and 2, respectively, while selected geometrical parameters are presented in Table 1.

In the mononuclear complexes **1** and **3**, the metal centre is stereogenic. However, since none of the ligand contains a chiral information, **1** and **3** are obtained as racemic mixtures and crystallised in the centrosymmetric space group  $C2/c$  and  $P2_1/n$ , respectively.

The Ru–N bond distances ranging from 2.057(3) to 2.118(2) Å in **1** and **3** are comparable to those in  $[(\eta^6\text{-}p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me})\text{RuCl}(2,3\text{-bis}(2\text{-pyridyl})\text{pyrazine})][\text{BF}_4]$  [8] and  $[(\eta^6\text{-}p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me})\text{RuCl}(2,3\text{-bis}(\alpha\text{-pyridyl})\text{quinoxaline})][\text{PF}_6]$  [9a]. Accordingly, there is no significant difference in the Ru–Cl bond length in **1** or **3** [2.389(1) and 2.3878(9) Å] and reported values [9–11]. The N(1)–Ru(1)–N(2) bond angle in complexes **1** [76.04(15)°] and **3** [76.33(10)°] are similar to those of complexes  $[(\eta^6\text{-}p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me})\text{RuCl}(2,3\text{-bis}(2\text{-pyridyl})\text{pyrazine})]^+$  [N(1)–Ru(1)–N(2) = 76.5(2)°] [8] and  $[(\eta^6\text{-}p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me})\text{RuCl}(2,3\text{-bis}(\alpha\text{-pyridyl})\text{quinoxaline})]^+$  [N(1)–Ru(1)–N(2) = 76.2(2)°] [9a].

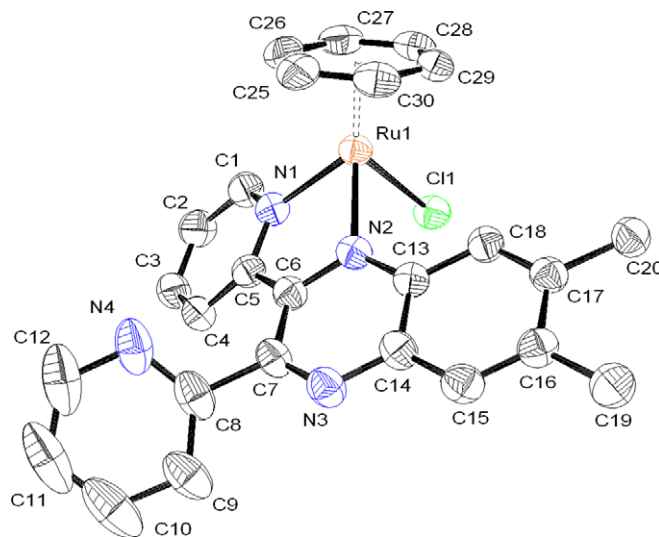
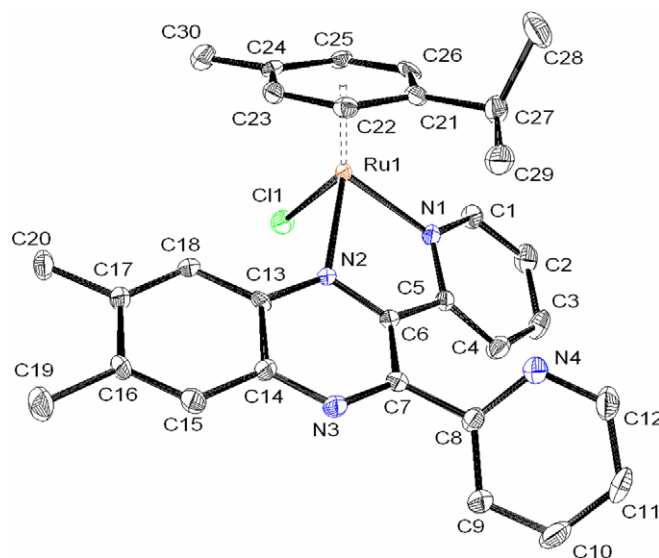
Fig. 1. Molecular structure of **1** at 50% probability level with hydrogen atoms, acetonitrile molecules and hexafluorophosphate anion being omitted for clarity.Fig. 2. Molecular structure of **3** at 50% probability level with hydrogen atoms, acetonitrile molecule and hexafluorophosphate anion being omitted for clarity.

Table 1  
Selected bond lengths (Å) and angles (°) for [1][PF<sub>6</sub>], [3][PF<sub>6</sub>] and [6][PF<sub>6</sub>]<sub>2</sub>

	[1][PF <sub>6</sub> ]	[3][PF <sub>6</sub> ]	[6][PF <sub>6</sub> ] <sub>2</sub>	
			Ru1	Ru2
<i>Interatomic distances</i>				
Ru1–N1 (Ru2–N3)	2.067(4)	2.057(3)	2.083(6)	2.109(5)
Ru1–N2 (Ru2–N4)	2.108(4)	2.118(2)	2.115(6)	2.063(6)
Ru1–Cl1 (Ru2–Cl2)	2.389(1)	2.3878(9)	2.393(2)	2.384(2)
Ru–centroid (arene)	1.692	1.694	1.698	1.695
C5–C6	1.472(6)	1.466(4)	1.482(9)	
C7–C8	1.509(7)	1.467(5)	1.473(10)	
<i>Angles and torsion angles</i>				
N1–Ru1–N2 (N3–Ru2–N4)	76.04(15)	76.33(10)	76.3(2)	76.4(2)
N1–Ru1–Cl1 (N3–Ru2–Cl2)	85.93(11)	86.08(7)	85.51(19)	88.48(17)
N2–Ru1–Cl1 (N4–Ru2–Cl2)	85.55(10)	88.27(7)	88.47(18)	86.29(19)
N1–C5–C6–N2	–11.2(6)	14.7(4)	16.5(9)	
N3–C7–C8–N4	131.8(5)	–131.2(3)	12.5(10)	
C5–C6–C7–C8	–23.1(8)	18.3(4)	32.9(12)	

In the crystal packing of [1][PF<sub>6</sub>]·2CH<sub>3</sub>CN, two molecules of **1** form a dimer through  $\pi$ -stacking interactions, see Fig. 3. The centroid–centroid separations are 3.73 and 4.32 Å. The distance observed between the  $\pi$ - $\pi$  interacting systems is in accordance with the theoretical value calculated for this stacking mode [10].

Cation **6** crystallises in the space group P-1 with both enantiomers *R,R*-**6** and *S,S*-**6** being present in the crystal. As mentioned earlier, the sterically hindered dpqMe<sub>2</sub> ligand forces the chloro atoms to adopt a *trans* orientation, thus generating only the *rac* isomers. An ORTEP drawing with the atom labelling scheme for **6** is shown in Fig. 4 and the selected geometrical parameters are presented in Table 1. As expected, cation **6** contains two metal centres bonded to  $\eta^6$ -C<sub>6</sub>H<sub>5</sub>Me and chloro ligands and bridged by a dpqMe<sub>2</sub> ligand through its nitrogen atoms. The distance

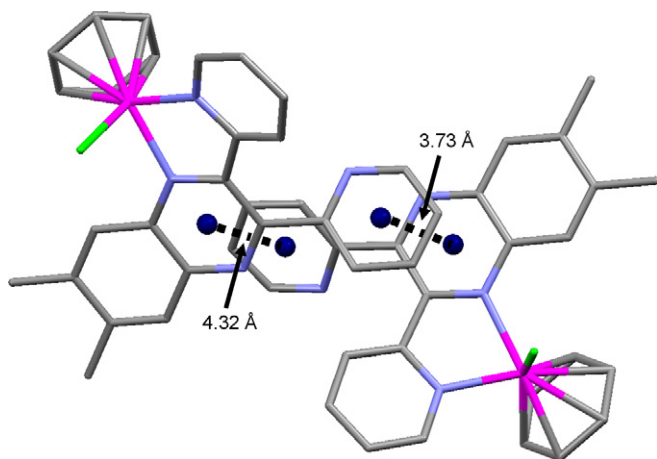


Fig. 3. Dimeric structure of **1** showing the intermolecular  $\pi$ -stacking interactions.

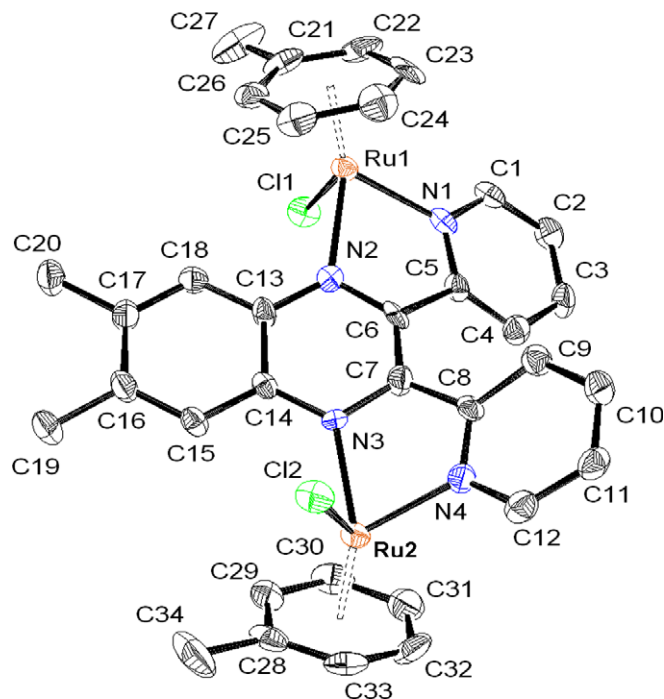


Fig. 4. Molecular structure of **6** at 50% probability level with hydrogen atoms, acetonitrile molecules and hexafluorophosphate anions being omitted for clarity.

between the ruthenium atoms is 6.96 Å, which is in accordance with the metal–metal distances observed in the homo-bimetallic complex  $[(\eta^6\text{-}p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me})_2\text{Ru}_2\text{Cl}_2(\mu\text{-}2,3\text{-di(pyridine-2-yl)pyrazine})][\text{PF}_6]_2$  (Ru–Ru distance = 6.84 Å) [9b] and in the hetero-bimetallic dpqMe<sub>2</sub> complex  $[(\text{bipy})_2\text{Ru}(\mu\text{-dpqMe}_2)\text{Cu}(\text{PPh}_3)_2][\text{BF}_4]_3$  (bipy = 2,2'-bipyridine) (Ru–Cu distance = 6.82 Å) [11].

Upon formation of mono or dinuclear complexes, the bond lengths between the connecting carbon atoms between the pyridyl and the quinoxaline moieties of the dpqMe<sub>2</sub> ligand are slightly reduced. Indeed, as compared to the free 6,7-dimethyl-2,3-di(pyridine-2-yl)quinoxaline in which the C–C distances (C5–C6 and C7–C8) are both at 1.493 Å [12], the corresponding C–C distances in the mononuclear complexes **1** and **3** are 1.472(6) and 1.466(4) Å, respectively, while in the dinuclear complex **6** the distances are 1.473(10) and 1.482(9) Å. These bond length changes are in agreement with a back-donation from the metallic fragments to the dpqMe<sub>2</sub> system, thus increasing the inter-ring bond order [6,13].

The major distortion imposed on the dpqMe<sub>2</sub> structure upon coordination is encountered by the pyridyl groups, see Fig. 5. In the free ligand the two pyridyl groups are twisted by 39.6° relative to the plane of the quinoxaline moiety. However, in **1** and **3** the twist of the coordinated pyridyl unit is 26.0(2) and 28.1(1)°, respectively, while the non-coordinated pyridyl unit remains at 41.7(1) and 41.1(1)°, respectively. Finally, the twist imposed on the pyridyl rings is raised to a maximum at 28.8(3) and 29.4(3)° in **6**.

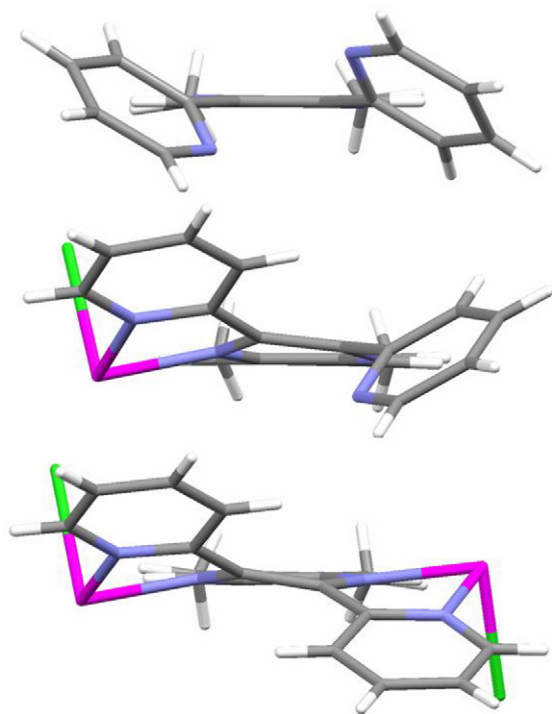
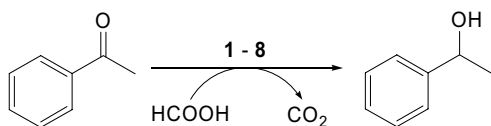


Fig. 5. Axial views of the free dpqMe<sub>2</sub> ligand (top), the mononuclear cation **3** (middle) and the dinuclear dication **6** (bottom). The quinoxaline moiety points away and the arene ligands are omitted for clarity.

#### 2.4. Catalytic evaluation of **1–8** for the transfer hydrogenation of acetophenone in aqueous solution

Based on the pioneering study of Ogo et al. on the use of 2,2'-bipyridine complexes  $[(\eta^6\text{-C}_6\text{Me}_6\text{Ru})(\text{bipy})(\text{OH}_2)]^+$  [14] and  $[(\eta^5\text{-C}_5\text{Me}_5\text{Ir})(\text{bipy})(\text{OH}_2)]^+$  [15] and on our previously reported results on arene ruthenium phenanthroline (phen) complexes  $[(\eta^6\text{-arene})\text{Ru}(\text{phen})(\text{OH}_2)]^+$  (arene = C<sub>6</sub>H<sub>6</sub>, *p*-Pr<sup>i</sup>C<sub>6</sub>H<sub>4</sub>Me, C<sub>6</sub>Me<sub>6</sub>) [16], the catalytic potential of the 6,7-dimethyl-2,3-di(pyridine-2-yl)quinoxaline complexes **1–8** was evaluated for the transfer hydrogenation of acetophenone in water using formic acid as hydrogen source (Table 2).



All complexes were found to poorly catalyse the transfer hydrogenation of acetophenone to give phenylethanol in aqueous solution at pH 4, which corresponds to the  $pK_a$  of the formic acid (3.77). In the best cases (complexes **6** and **7**, entries 6 and 7) the conversion of acetophenone does not exceed 6% within 16 h. This means that, in comparison to the corresponding 2,2'-bipyrimidine complexes [5], the introduction of a sterically hindered ligand system

Table 2

Catalytic transfer hydrogenation of acetophenone using the mononuclear  $[(\eta^6\text{-arene})\text{RuCl}(\text{dpqMe}_2)]^+$  (**1–4**) and dinuclear complexes  $\{[(\eta^6\text{-arene})\text{RuCl}]_2(\mu\text{-dpqMe}_2)\}^{2+}$  (**5–8**) as catalysts and formate as hydrogen donor in water<sup>a</sup>

Entry	Catalyst	( $\eta^6\text{-arene}$ )Ru	Conversion % (h) <sup>b</sup>	TOF (h <sup>-1</sup> ) <sup>c</sup>
1	<b>1</b>	(C <sub>6</sub> H <sub>6</sub> )Ru	<1 (15)	
2	<b>2</b>	(C <sub>6</sub> H <sub>5</sub> Me)Ru	<1 (15)	
3	<b>3</b>	( <i>p</i> -Pr <sup>i</sup> C <sub>6</sub> H <sub>4</sub> Me)Ru	<1 (15)	
4	<b>4</b>	(C <sub>6</sub> Me <sub>6</sub> )Ru	<1 (15)	
5	<b>5</b>	{(C <sub>6</sub> H <sub>6</sub> )Ru} <sub>2</sub>	2 (15)	0.1
6	<b>6</b>	{(C <sub>6</sub> H <sub>5</sub> Me)Ru} <sub>2</sub>	5 (15)	0.3
7	<b>7</b>	{( <i>p</i> -Pr <sup>i</sup> C <sub>6</sub> H <sub>4</sub> Me)Ru} <sub>2</sub>	6 (16)	0.4
8	<b>8</b>	{(C <sub>6</sub> Me <sub>6</sub> )Ru} <sub>2</sub>	1 (15)	0.1

<sup>a</sup> Conditions: Reactions carried out at 50 °C, at pH = 4, in 5 mL of water, acetophenone (0.64 mmol), the ratio catalyst/substrate/formate being 1:100:500.

<sup>b</sup> Determined by gas chromatography.

<sup>c</sup> TOF: turnover frequencies are expressed in mol of product/(mol of Ru · h).

which forces the dinuclear complexes to adopt a *trans* configuration causes a pronounced drop in the catalytic activity.

### 3. Experimental

#### 3.1. General

6,7-Dimethyl-2,3-di(pyridine-2-yl)quinoxaline (dpqMe<sub>2</sub>) and KPF<sub>6</sub> were purchased from Aldrich and used as received.  $[\text{Ru}(\eta^6\text{-arene})(\mu\text{-Cl})\text{Cl}]_2$  (arene = C<sub>6</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>5</sub>Me, *p*-Pr<sup>i</sup>C<sub>6</sub>H<sub>4</sub>Me, C<sub>6</sub>Me<sub>6</sub>) were prepared according to published methods [17]. The NMR spectra were recorded on a Varian Gemini 200 MHz spectrometer using the residual protonated solvent as internal standard. Infrared spectra were recorded as KBr pellets on a Perkin–Elmer FTIR 1720-X spectrometer. UV–Vis absorption spectra were recorded on an Uvikon 930 spectrophotometer. Microanalyses were performed by the Laboratory of Pharmaceutical Chemistry, University of Geneva (Switzerland). Electro-spray mass spectra were obtained in positive-ion mode with an LCQ Finnigan mass spectrometer.

#### 3.2. Preparation of the mononuclear complexes **1–4**

##### 3.2.1. $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}(\text{dpqMe}_2)][\text{PF}_6]$ (**1**) $[\text{PF}_6]$

In a typical experiment,  $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$  (100 mg, 0.20 mmol) is dissolved in methanol (50 mL). The resulting solution is added dropwise to a two-necked flask equipped with a reflux condenser and containing a methanol solution (50 mL) of dpqMe<sub>2</sub> (125 mg, 0.40 mmol) and KPF<sub>6</sub> (73.6 mg, 0.40 mmol). The mixture is heated to 50 °C and stirred for 24 h. After cooling to room temperature, the volume is reduced and the product is precipitated by addition of diethylether. The yellow-orange solid is filtered, washed with *n*-pentane and dried under vacuum to give  $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}(\text{dpqMe}_2)][\text{PF}_6]$  (80 mg, 0.12 mmol, yield 30%). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  (ppm) =

9.40 (d, 1H,  $^3J = 7.8$  Hz,  $H_{\text{pyr}}$ ), 8.65 (d, 1H,  $^3J = 7.5$  Hz,  $H_{\text{pyr}}$ ), 8.63 (s, 1H,  $H_{\text{qnox}}$ ), 8.11 (m, 2H,  $H_{\text{pyr}}$ ), 8.08 (s, 1H,  $H_{\text{qnox}}$ ), 7.77 (dd, 1H,  $H_{\text{pyr}}$ ), 7.62 (m, 2H,  $H_{\text{pyr}}$ ), 7.06 (d, 1H,  $^3J = 7.1$  Hz,  $H_{\text{pyr}}$ ), 6.13 (s, 6H,  $H_{\text{ar}}$ ), 2.74 (s, 3H,  $\text{Me}_{\text{qnox}}$ ), 2.65 (s, 3H,  $\text{Me}_{\text{qnox}}$ ); IR (KBr,  $\text{cm}^{-1}$ ): 840  $\nu(\text{P-F})$ ; 558 m. UV-Vis ( $1.19 \times 10^{-5}$  M,  $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  386 nm ( $\epsilon = 2.07 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), 274 nm ( $\epsilon = 3.78 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ). ESI-MS ( $m/z$ ): 527 [ $\text{M}^+$ ]; *Anal. Calc.* for  $\text{C}_{26}\text{H}_{22}\text{N}_4\text{ClF}_6\text{PRu}$ : C, 46.47; H, 3.30; N, 8.34. Found: C, 46.12; H, 3.69; N, 7.77%.

### 3.2.2. $[(\eta^6\text{-C}_6\text{H}_5\text{Me})\text{RuCl}(\text{dpqMe}_2)][\text{PF}_6]$ (**[2]**)[ $\text{PF}_6$ ]

The compound is prepared by the same procedure as described above for **[1]**[ $\text{PF}_6$ ] using  $[(\eta^6\text{-C}_6\text{H}_5\text{Me})\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$  (100 mg, 0.19 mmol),  $\text{dpqMe}_2$  (118.2 mg, 0.38 mmol) and  $\text{KPF}_6$  (69.7 mg, 0.38 mmol) and affording  $[(\eta^6\text{-C}_6\text{H}_5\text{Me})\text{RuCl}(\text{dpqMe}_2)][\text{PF}_6]$  (140 mg, 0.20 mmol, yield 54%).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  (ppm) = 9.32 (d, 1H,  $^3J = 7.1$  Hz,  $H_{\text{pyr}}$ ), 8.66 (d, 1H,  $^3J = 7.4$  Hz,  $H_{\text{pyr}}$ ), 8.55 (s, 1H,  $H_{\text{qnox}}$ ), 8.13 (m, 2H,  $H_{\text{pyr}}$ ), 8.08 (s, 1H,  $H_{\text{qnox}}$ ), 7.77 (dd, 1H,  $^3J = 8.3$  Hz,  $H_{\text{pyr}}$ ), 7.61 (m, 2H,  $H_{\text{pyr}}$ ), 7.07 (d, 1H,  $^3J = 9.5$  Hz,  $H_{\text{pyr}}$ ), 6.16 (dd, 1H,  $H_{\text{ar}}$ ), 5.99 (dd, 1H,  $^3J = 5.9$  Hz,  $H_{\text{ar}}$ ), 5.92 (d, 1H,  $^3J = 6.1$  Hz,  $H_{\text{ar}}$ ), 5.74 (d, 1H,  $H_{\text{ar}}$ ), 5.68 (dd, 1H,  $^3J = 5.8$  Hz,  $H_{\text{ar}}$ ), 2.73 (s, 3H,  $\text{Me}_{\text{qnox}}$ ), 2.65 (s, 3H,  $\text{Me}_{\text{qnox}}$ ), 2.36 (s, 3H,  $\text{Me}_{\text{ar}}$ ); IR (KBr,  $\text{cm}^{-1}$ ): 840s  $\nu(\text{P-F})$ ; 558 m. UV-Vis ( $1.16 \times 10^{-5}$  M,  $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  385 nm ( $\epsilon = 4.46 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), 278 nm ( $\epsilon = 8.82 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ). ESI-MS ( $m/z$ ): 541 [ $\text{M}^+$ ]; *Anal. Calc.* for  $\text{C}_{27}\text{H}_{24}\text{N}_4\text{ClF}_6\text{PRu}$ : C, 47.27; H, 3.53; N, 8.17. Found: C, 47.00; H, 3.70; N, 8.19%.

### 3.2.3. $[(\eta^6\text{-}p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me})\text{RuCl}(\text{dpqMe}_2)][\text{PF}_6]$ (**[3]**)[ $\text{PF}_6$ ]

The compound is prepared by the same procedure as described above for **[1]**[ $\text{PF}_6$ ] using  $[(\eta^6\text{-}p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me})\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$  (100 mg, 0.16 mmol),  $\text{dpqMe}_2$  (102.0 mg, 0.32 mmol) and  $\text{KPF}_6$  (60.1 mg, 0.32 mmol) and affording  $[(\eta^6\text{-}p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me})\text{RuCl}(\text{dpqMe}_2)][\text{PF}_6]$  (150 mg, 0.20 mmol, yield 63%).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  (ppm) = 9.37 (d, 1H,  $^3J = 7.1$  Hz,  $H_{\text{pyr}}$ ), 8.69 (d, 1H,  $^3J = 6.5$  Hz,  $H_{\text{pyr}}$ ), 8.52 (s, 1H,  $H_{\text{qnox}}$ ), 8.09 (m, 2H,  $H_{\text{pyr}}$ ), 8.06 (s, 1H,  $H_{\text{qnox}}$ ), 7.70 (m, 2H,  $H_{\text{pyr}}$ ), 7.60 (dd, 1H,  $H_{\text{pyr}}$ ), 7.00 (d, 1H,  $H_{\text{pyr}}$ ), 6.09 (d, 1H,  $^3J = 6.9$  Hz,  $H_{\text{ar}}$ ), 5.85 (m, 2H,  $H_{\text{ar}}$ ), 5.72 (d, 1H,  $^3J = 6.6$  Hz,  $H_{\text{ar}}$ ), 2.73 (s, 3H,  $\text{Me}_{\text{qnox}}$ ), 2.64 (s, 3H,  $\text{Me}_{\text{qnox}}$ ), 2.51 (sept, 1H,  $^3J = 6.9$  Hz,  $\text{CH}_{\text{ar}}\text{Me}_2$ ), 2.36 (s, 3H,  $\text{Me}_{\text{ar}}$ ), 1.11 (d, 3H,  $\text{CH}_{\text{ar}}\text{Me}_2$ ), 1.04 (d, 3H,  $\text{CH}_{\text{ar}}\text{Me}_2$ ); IR (KBr,  $\text{cm}^{-1}$ ): 840 s  $\nu(\text{P-F})$ ; 557 m. UV-Vis ( $5.50 \times 10^{-6}$  M,  $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  436 nm ( $\epsilon = 19695.82 \text{ M}^{-1} \text{ cm}^{-1}$ ), 387 nm ( $\epsilon = 8.53 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), 278 nm ( $\epsilon = 17.55 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ). ESI-MS ( $m/z$ ): 583 [ $\text{M}^+$ ]; *Anal. Calc.* for  $\text{C}_{30}\text{H}_{30}\text{N}_4\text{ClF}_6\text{PRu}$ : C, 49.49; H, 4.15; N, 7.70. Found: C, 49.17; H, 4.66; N, 7.47%.

### 3.2.4. $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}(\text{dpqMe}_2)][\text{PF}_6]$ (**[4]**)[ $\text{PF}_6$ ]

The compound is prepared by the same procedure as described above for **[1]**[ $\text{PF}_6$ ] using  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$  (100 mg, 0.15 mmol),  $\text{dpqMe}_2$  (93.4 mg, 0.30 mmol) and

$\text{KPF}_6$  (55.1 mg, 0.30 mmol) and affording  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}(\text{dpqMe}_2)][\text{PF}_6]$  (145 mg, 0.20 mmol, yield 64%).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  (ppm) = 8.77 (d, 1H,  $^3J = 7.7$  Hz,  $H_{\text{pyr}}$ ), 8.65 (d, 1H,  $^3J = 7.4$  Hz,  $H_{\text{pyr}}$ ), 8.29 (s, 1H,  $H_{\text{qnox}}$ ), 8.17 (m, 2H,  $H_{\text{pyr}}$ ), 8.05 (s, 1H,  $H_{\text{qnox}}$ ), 7.75 (dd, 1H,  $H_{\text{pyr}}$ ), 7.60 (m, 2H,  $H_{\text{pyr}}$ ), 7.07 (d, 1H,  $^3J = 7.5$  Hz,  $H_{\text{pyr}}$ ), 2.67 (s, 3H,  $\text{Me}_{\text{qnox}}$ ), 2.62 (s, 3H,  $\text{Me}_{\text{qnox}}$ ), 2.20 (s, 18H,  $\text{Me}_{\text{ar}}$ ); IR (KBr,  $\text{cm}^{-1}$ ): 843 s  $\nu(\text{P-F})$ ; 558 m. UV-Vis ( $1.06 \times 10^{-5}$  M,  $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  377 nm ( $\epsilon = 3.15 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), 281 nm ( $\epsilon = 7.89 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ). ESI-MS ( $m/z$ ): 611 [ $\text{M}^+$ ]; *Anal. Calc.* for  $\text{C}_{32}\text{H}_{34}\text{N}_4\text{ClF}_6\text{PRu}$ : C, 50.83; H, 4.53; N, 7.41. Found: C, 50.94; H, 4.62; N, 7.42%.

## 3.3. Preparation of the dinuclear complexes 5–8

### 3.3.1. $[\{(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}\}_2(\mu\text{-dpqMe}_2)][\text{PF}_6]_2$ (**[5]**)[ $\text{PF}_6]_2$ )

In a typical experiment,  $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$  (150 mg, 0.30 mmol),  $\text{dpqMe}_2$  (93.6 mg, 0.30 mmol) and  $\text{KPF}_6$  (110.0 mg, 0.60 mmol) are dissolved in methanol (30 mL). The resulting solution is heated to 60 °C and stirred for 4 h. After cooling to room temperature, the volume is reduced and the product is precipitated by addition of diethylether. The red solid is filtered, washed with *n*-pentane and dried under vacuum to give  $[\{(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}\}_2(\mu\text{-dpqMe}_2)][\text{PF}_6]_2$  (150 mg, 0.14 mmol, yield 48%).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  (ppm) = 9.43 (d, 2H,  $^3J = 6.4$  Hz,  $H_{\text{pyr}}$ ), 8.69 (s, 2H,  $H_{\text{qnox}}$ ), 8.56 (d, 2H,  $^3J = 8.2$  Hz,  $H_{\text{pyr}}$ ), 8.08 (dd, 2H,  $^3J = 7.8$  Hz,  $H_{\text{pyr}}$ ), 7.81 (dd, 2H,  $^3J = 6.9$  Hz,  $H_{\text{pyr}}$ ), 6.15 (s, 12H,  $H_{\text{ar}}$ ), 2.80 (s, 6H,  $\text{Me}_{\text{qnox}}$ ); IR (KBr,  $\text{cm}^{-1}$ ): 840 s  $\nu(\text{P-F})$ ; 559 m. UV-Vis ( $6.20 \times 10^{-5}$  M,  $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  486 nm ( $\epsilon = 0.53 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), 330 nm ( $\epsilon = 2.25 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ). ESI-MS ( $m/z$ ): 887 [ $\text{M} + \text{PF}_6$ ] $^+$ ; 527 [ $\text{M} - \{(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}\}^+$ ]; *Anal. Calc.* for  $\text{C}_{32}\text{H}_{28}\text{N}_4\text{Cl}_2\text{F}_{12}\text{P}_2\text{Ru}_2$ : C, 37.26; H, 2.74; N, 5.43. Found: C, 36.98; H, 3.23; N, 5.51%.

### 3.3.2. $[\{(\eta^6\text{-C}_6\text{H}_5\text{Me})\text{RuCl}\}_2(\mu\text{-dpqMe}_2)][\text{PF}_6]_2$ (**[6]**)[ $\text{PF}_6]_2$ )

The compound is prepared by the same procedure as described above for **[5]**[ $\text{PF}_6]_2$  using  $[(\eta^6\text{-C}_6\text{H}_5\text{Me})\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$  (530 mg, 0.1 mol),  $\text{dpqMe}_2$  (312 mg, 0.1 mol) and  $\text{KPF}_6$  (368 mg, 0.2 mol) and affording  $[\{(\eta^6\text{-C}_6\text{H}_5\text{Me})\text{RuCl}\}_2(\mu\text{-dpqMe}_2)][\text{PF}_6]_2$  (990 mg, 0.09 mol, yield 94%).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  (ppm) = 9.34 (d, 2H,  $^3J = 5.5$  Hz,  $H_{\text{pyr}}$ ), 8.57 (s, 2H,  $H_{\text{qnox}}$ ), 8.52 (d, 2H,  $^3J = 8.1$  Hz,  $H_{\text{pyr}}$ ), 8.07 (dd, 2H,  $^3J = 6.6$  Hz,  $H_{\text{pyr}}$ ), 7.80 (dd, 2H,  $^3J = 6.6$  Hz,  $H_{\text{pyr}}$ ), 6.20 (dd, 2H,  $^3J = 5.9$  Hz,  $H_{\text{ar}}$ ), 5.94 (m, 4H,  $H_{\text{ar}}$ ), 5.77 (d, 2H,  $^3J = 5.9$  Hz,  $H_{\text{ar}}$ ), 5.67 (dd, 2H,  $H_{\text{ar}}$ ), 2.76 (s, 6H,  $\text{Me}_{\text{qnox}}$ ), 2.45 (s, 6H,  $H_{\text{ar}}$ ); IR (KBr,  $\text{cm}^{-1}$ ): 843 s  $\nu(\text{P-F})$ ; 558 m. UV-Vis ( $3.77 \times 10^{-6}$  M,  $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  492 nm ( $\epsilon = 0.95 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), 327 nm ( $\epsilon = 4.43 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ). ESI-MS ( $m/z$ ): 915 [ $\text{M} + \text{PF}_6$ ] $^+$ ; 541 [ $\text{M} - \{(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}\}^+$ ]; *Anal. Calc.* for  $\text{C}_{34}\text{H}_{32}\text{N}_4\text{Cl}_2\text{F}_{12}\text{P}_2\text{Ru}_2$ : C, 38.54; H, 3.04; N, 5.29. Found: C, 38.21; H, 2.94; N, 5.11%.

### 3.3.3. $[(\eta^6\text{-}p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me})\text{RuCl}]_2(\mu\text{-dpqMe}_2)[\text{PF}_6]_2$ $([7][\text{PF}_6]_2)$

The compound is prepared by the same procedure as described above for  $[\mathbf{5}][\text{PF}_6]_2$  using  $[(\eta^6\text{-}p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me})\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$  (200 mg, 0.33 mmol),  $\text{dpqMe}_2$  (76.5 mg, 0.33 mmol) and  $\text{KPF}_6$  (90.2 mg, 0.66 mmol) and affording  $[(\eta^6\text{-}p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me})\text{RuCl}]_2(\mu\text{-dpqMe}_2)[\text{PF}_6]_2$  (270 mg, 0.24 mmol, yield 72%).  $^1\text{H NMR}$  (400 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  (ppm) = 9.38 (d, 2H,  $^3J = 7.7$  Hz,  $\text{H}_{\text{pyr}}$ ), 8.59 (s, 2H,  $\text{H}_{\text{qnox}}$ ), 8.39 (d, 2H,  $^3J = 8.1$  Hz,  $\text{H}_{\text{pyr}}$ ), 8.10 (dd, 2H,  $^3J = 7.7$  Hz,  $\text{H}_{\text{pyr}}$ ), 7.84 (dd, 2H,  $^3J = 6.9$  Hz,  $\text{H}_{\text{pyr}}$ ), 6.10 (d, 4H,  $\text{H}_{\text{ar}}$ ), 5.81 (d, 4H,  $^3J = 6.3$  Hz,  $\text{H}_{\text{ar}}$ ), 2.78 (s, 6H,  $\text{Me}_{\text{qnox}}$ ), 2.73 (sept, 2H,  $^3J = 6.9$  Hz,  $\text{CH}_{\text{ar}}\text{Me}_2$ ), 1.41 (s, 6H,  $\text{Me}_{\text{ar}}$ ), 1.13 (d, 6H,  $\text{CH}_{\text{ar}}\text{Me}_2$ ), 0.87 (d, 6H,  $\text{CH}_{\text{ar}}\text{Me}_2$ ); IR (KBr,  $\text{cm}^{-1}$ ): 842 s  $\nu(\text{P-F})$ ; 558 m. UV-Vis ( $7.35 \times 10^{-5}$  M,  $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  508 nm ( $\epsilon = 0.43 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), 327 nm ( $\epsilon = 1.68 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ). ESI-MS ( $m/z$ ): 999  $[\text{M}+\text{PF}_6]^+$ ; 583  $[\text{M}-\{(\eta^6\text{-}p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me})\text{RuCl}\}]^+$ ; Anal. Calc. for  $\text{C}_{40}\text{H}_{44}\text{N}_4\text{Cl}_2\text{F}_{12}\text{P}_2\text{Ru}_2$ : C, 42.00; H, 3.88; N, 4.90. Found: C, 39.95; H, 3.79; N, 4.60%.

### 3.3.4. $[(\eta^6\text{-}C_6\text{Me}_6)\text{RuCl}]_2(\mu\text{-dpqMe}_2)[\text{PF}_6]_2$ $([8][\text{PF}_6]_2)$

The compound is prepared by the same procedure as described above for  $[\mathbf{5}][\text{PF}_6]_2$  using  $[(\eta^6\text{-}C_6\text{Me}_6)\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$  (200 mg, 0.30 mmol),  $\text{dpqMe}_2$  (93.4 mg, 0.30 mmol) and  $\text{KPF}_6$  (110 mg, 0.60 mmol) and affording  $[(\eta^6\text{-}C_6\text{Me}_6)\text{RuCl}]_2(\mu\text{-dpqMe}_2)[\text{PF}_6]_2$  (145 mg, 0.12 mmol,

yield 40%).  $^1\text{H NMR}$  (400 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  (ppm) = 8.77 (d, 2H,  $^3J = 7.9$  Hz,  $\text{H}_{\text{pyr}}$ ), 8.65 (d, 2H,  $^3J = 7.5$  Hz,  $\text{H}_{\text{pyr}}$ ), 8.05 (s, 2H,  $\text{H}_{\text{qnox}}$ ), 7.75 (dd, 2H,  $^3J = 8.3$  Hz,  $\text{H}_{\text{pyr}}$ ), 7.64 (dd, 2H,  $^3J = 7.6$  Hz,  $\text{H}_{\text{pyr}}$ ), 3.29 (s, 6H,  $\text{Me}_{\text{qnox}}$ ), 2.63 (s, 18H,  $\text{Me}_{\text{ar}}$ ); IR (KBr,  $\text{cm}^{-1}$ ): 844 s  $\nu(\text{P-F})$ ; 558 m. UV-Vis ( $5.30 \times 10^{-5}$  M,  $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  551 nm ( $\epsilon = 0.58 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), 403 nm ( $\epsilon = 1.49 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), 328 nm ( $\epsilon = 2.45 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ). ESI-MS ( $m/z$ ): 1055  $[\text{M}+\text{PF}_6]^+$ ; 611  $[\text{M}-\{(\eta^6\text{-}p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me})\text{RuCl}\}]^+$ ; Anal. Calc. for  $\text{C}_{44}\text{H}_{52}\text{N}_4\text{Cl}_2\text{F}_{12}\text{P}_2\text{Ru}_2$ : C, 44.04; H, 4.37; N, 4.67. Found: C, 42.29; H, 4.60; N, 4.26%.

### 3.4. Single-crystal X-ray structure analyses

Crystals of complexes  $[\mathbf{1}][\text{PF}_6] \cdot 2\text{CH}_3\text{CN}$ ,  $[\mathbf{3}][\text{PF}_6] \cdot \text{CH}_3\text{CN}$  and  $[\mathbf{6}][\text{PF}_6]_2 \cdot 2\text{CH}_3\text{CN}$  were mounted on a Stoe Image Plate Diffraction system equipped with a  $\phi$  circle goniometer, using Mo K $\alpha$  graphite monochromated radiation ( $\lambda = 0.71073 \text{ \AA}$ ) with  $\phi$  range 0–200°. The structures were solved by direct methods using the program SHELXS-97 [18]. Refinement and all further calculations were carried out using SHELXL-97 [18]. The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on  $F^2$ . Crystallographic details are summarised in Table 3. Figs. 1, 2 and 4 were drawn with ORTEP [19] and Figs. 3 and 5 with the software MERCURY [20].

Table 3

Crystallographic and selected experimental data for  $[\mathbf{1}][\text{PF}_6] \cdot 2\text{CH}_3\text{CN}$ ,  $[\mathbf{3}][\text{PF}_6] \cdot \text{CH}_3\text{CN}$  and  $[\mathbf{6}][\text{PF}_6]_2 \cdot 2\text{CH}_3\text{CN}$

	$[\mathbf{1}][\text{PF}_6] \cdot 2\text{CH}_3\text{CN}$	$[\mathbf{3}][\text{PF}_6] \cdot \text{CH}_3\text{CN}$	$[\mathbf{6}][\text{PF}_6]_2 \cdot 2\text{CH}_3\text{CN}$
Chemical formula	$\text{C}_{30}\text{H}_{28}\text{ClF}_6\text{N}_6\text{PRu}$	$\text{C}_{32}\text{H}_{33}\text{ClF}_6\text{N}_5\text{PRu}$	$\text{C}_{38}\text{H}_{38}\text{Cl}_2\text{F}_{12}\text{N}_6\text{P}_2\text{Ru}_2$
Formula weight	754.07	769.12	1141.72
Crystal system	monoclinic	monoclinic	triclinic
Space group	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
Crystal colour and shape	red rod	red block	red block
Crystal size	$0.2 \times 0.2 \times 0.1$	$0.3 \times 0.3 \times 0.15$	$0.4 \times 0.4 \times 0.2$
$a$ (Å)	34.208(4)	14.450(3)	13.003(1)
$b$ (Å)	7.4461(5)	8.370(2)	13.340(1)
$c$ (Å)	29.870(3)	27.320(5)	14.516(2)
$\alpha$ (°)			111.43(1)
$\beta$ (°)	124.652(6)	97.16(3)	106.64(1)
$\gamma$ (°)			100.00(1)
$V$ (Å <sup>3</sup> )	6258.9(10)	3278.5(12)	2133.8(4)
$Z$	8	4	2
$T$ (K)	173(2)	173(2)	173(2)
$D_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	1.601	1.558	1.777
$\mu$ ( $\text{mm}^{-1}$ )	0.705	0.674	0.998
Scan range (°)	$1.45 < \theta < 25.17$	$2.55 < 2\theta < 26.15$	$2.42 < 2\theta < 25.97$
Unique reflections	5558	6176	7760
Observed reflections [ $I > 2\sigma(I)$ ]	4125	4407	4876
$R_{\text{int}}$	0.0985	0.0358	0.1736
Final $R$ indices [ $I > 2\sigma(I)$ ] <sup>a</sup>	0.0549, $wR_2$ 0.1427	0.0341, $wR_2$ 0.0776	0.0603, $wR_2$ 0.1597
$R$ indices (all data)	0.0690, $wR_2$ 0.1477	0.0532, $wR_2$ 0.0822	0.0976, $wR_2$ 0.2007
Goodness-of-fit	0.948	0.897	1.022
Maximum, minimum $\Delta\rho$ ( $\text{e \AA}^{-3}$ )	1.465, $-1.279$	0.473, $-1.484$	1.315, $-1.755$

<sup>a</sup> Structures were refined on  $F_o^2$ :  $wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}$ , where  $w^{-1} = [\sum(F_o^2) + (aP)^2 + bP]$  and  $P = [\max(F_o^2, 0) + 2F_c^2] / 3$ .

### 3.5. Transfer hydrogenation catalysis

The transfer hydrogenation reactions of acetophenone (0.64 mmol) using **1–8** as their hexafluorophosphate salts (6.4  $\mu$ mol) with formate (3.2 mmol) are carried out in water (5 mL) using a buffer of HCOOH/HCOONa at pH 4 under inert atmosphere. The reaction is quenched by cooling the mixture to 0 °C. The products are extracted by Et<sub>2</sub>O and identified (and turnover determined) by gas chromatography. The pH is monitored using a pH meter (Mettler Toledo InLab<sup>®</sup> 413).

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### Appendix A. Supplementary material

CCDC 641057, 641058 and 641059 contain the supplementary crystallographic data for [**1**][PF<sub>6</sub>] $\cdot$ 2CH<sub>3</sub>CN, [**3**][PF<sub>6</sub>] $\cdot$ CH<sub>3</sub>CN and [**6**][PF<sub>6</sub>]<sub>2</sub> $\cdot$ 2CH<sub>3</sub>CN. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.05.005.

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