

## COUPLING OF ELECTRON TRANSFER AND BOND DISSOCIATION PROCESSES IN DINUCLEAR COMPLEXES WITH RHODIUM AND IRIIDIUM REACTION CENTRES BRIDGED BY 2,2'-BIPYRIMIDINE

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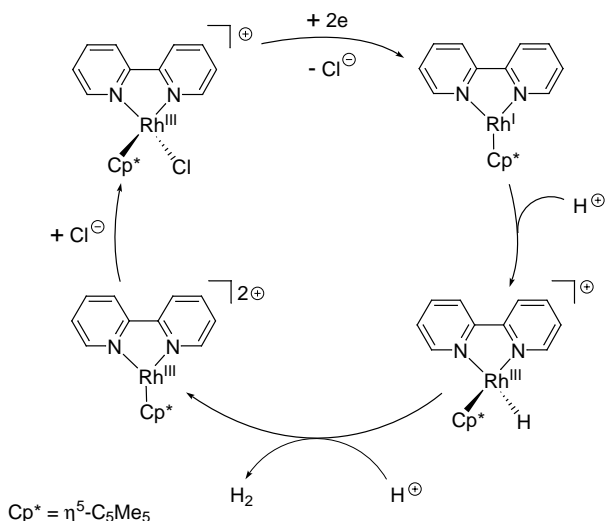
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*Dedicated to the memory of the late Professor Antonín A. Vlček.*

The complexes  $\{[MCl(\eta^5-C_5Me_5)]_2(\mu-bpym)\}(PF_6)_2$ ,  $bpym = 2,2'$ -bipyrimidine and  $M = Rh$  or  $Ir$ , were obtained as isomerically pure species ( $M = Ir$ ) or as mixtures of *cis/trans* isomers ( $M = Rh$ ). Even though these compounds undergo partial dissociation into the mononuclear  $bpym$ - and solvento-complexes in DMF or acetonitrile, cyclic voltammetry and, in part, spectroscopy (NMR, EPR, UV-VIS) could be used to analyze their reduction with up to five electrons. In acetonitrile at room temperature, the dirhodium compound displays two sequential chloride-dissociative two-electron cathodic steps, leading to the very reactive  $[Rh(\eta^5-C_5Me_5)]_2(\mu-bpym)$ . At  $-15$  °C in DMF, the diiridium compound was found to be sufficiently inert towards dissociation; it is then reversibly reduced to an EPR-detectable radical cation  $[IrCl(\eta^5-C_5Me_5)]_2(\mu-bpym)]^{*+}$  before two separated chloride-dissociative steps occur.

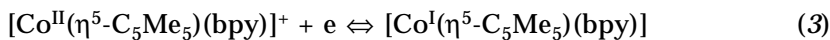
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Hydride transfer catalysis<sup>1</sup> is important for the generation of fuels (e.g.  $H_2$  from  $H^+$ , ref.<sup>2</sup>) and for the regeneration of NADH from  $NAD^+$  in biotechnological processes<sup>3</sup>. One of the well investigated catalysts is  $[RhCl(\eta^5-C_5Me_5)(bpy)]^+$  ( $bpy = 2,2'$ -bipyridine) which is reductively converted in a two-electron step to the highly reactive  $[Rh(\eta^5-C_5Me_5)(bpy)]$  (refs<sup>2,4</sup>). This compound reacts readily with  $H^+$  to form an active hydride intermediate  $[RhH(\eta^5-C_5Me_5)(bpy)]^+$ , the actual hydride transferring species in the hydrogen-producing catalytic cycle of Scheme 1 (refs<sup>1,2,4</sup>).



SCHEME 1

The intermediates of Scheme 1 can be stabilized through replacement of Rh with Ir ( $\rightarrow$  stable hydride form)<sup>5</sup> and through changing the chelate ligand to sterically shielding 1,4-diaza-1,3-butadienes ( $\rightarrow$  stable neutral form)<sup>6</sup>. In all instances ( $\text{N}^{\wedge}\text{N} = 2,2'$ -bipyridines<sup>2-5</sup>, bidiazines<sup>4</sup> or 1,4-diaza-1,3-butadienes<sup>6,7</sup>), however, the activation step is a two-electron process (1) as analyzed electrochemically; only with cobalt instead of rhodium or iridium a cobalt(II) intermediate was established<sup>8</sup> within the EC + E sequence according to Eqs (2) and (3), respectively.



The coupling of such reaction centres through conjugated bridging ligands BL has recently been described for BL = 2,5-bis[2-(phenylimino)ethyl]pyrazine (bpip) and derivatives, and for 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine<sup>9</sup> (bptz). This coupling extends the concept of metal-metal communication

from mere electron transfer<sup>10</sup> processes to chemically more relevant and potentially catalytic bond-breaking reactions.

However, dinuclear complexes  $[\text{MCl}(\eta^5\text{-C}_5\text{Me}_5)]_2(\mu\text{-BL})]^{2+}$  with the commercially available and extensively used<sup>11</sup> bridging ligand 2,2'-bipyrimidine have not yet been reported, although mononuclear forms, such as  $[\text{RhCl}(\eta^5\text{-C}_5\text{Me}_5)(\text{bpym})](\text{PF}_6)$ , are known<sup>4a</sup>. As will be described in this article, the studies of the dinuclear species (Fig. 1) are complicated owing to their dissociation in donor solvents such as DMF or acetonitrile, commonly used in electrochemistry.

## EXPERIMENTAL

### Instrumentation

EPR spectra were recorded in the X-band on a Bruker System ESP 300 equipped with a Bruker ER035M gaussmeter and a HP 5350B microwave counter. <sup>1</sup>H NMR spectra were taken on a Bruker AC 250 spectrometer. UV-VIS-NIR absorption spectra were recorded on Shimadzu UV160 and Bruins Instruments Omega 10 spectrophotometers. Cyclic voltammetry was carried out in 0.1 M  $\text{Bu}_4\text{NPF}_6$  solutions, using a three-electrode configuration (glassy carbon working, Pt counter and Ag/AgCl reference electrodes) connected to a PAR Model 273 potentiostat and function generator. The ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) couple served as internal reference. Spectroelectrochemical measurements were performed using an optically transparent thin-layer electrode (OTTLE) cell<sup>13</sup> for UV-VIS spectra and a two-electrode capillary for EPR studies<sup>14</sup>.

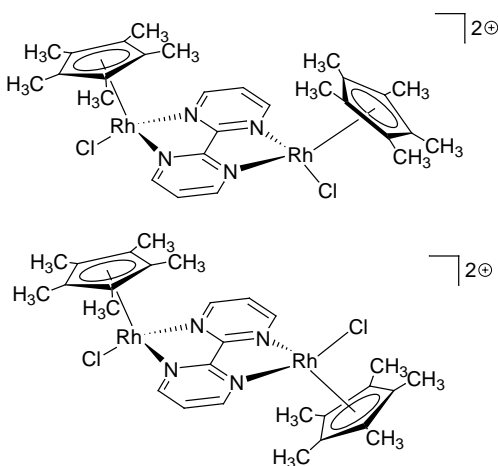


FIG. 1

*Cis*- and *trans*-isomers of  $[\text{RhCl}(\eta^5\text{-C}_5\text{Me}_5)]_2(\mu\text{-bpym})]^{2+}$

## Syntheses

All reactions were carried out in dried solvents under nitrogen.

$\{[RhCl(\eta^5-C_5Me_5)]_2(\mu-bpym)](PF_6)_2$  (*cis/trans* mixture, Fig. 1). A suspension of 250 mg (0.405 mmol)  $\{[RhCl(\eta^5-C_5Me_5)]Cl\}_2$  (ref. <sup>12a</sup>) in 50 ml acetone was stirred in the dark with 205 mg (0.81 mmol) of  $AgPF_6$  for 30 min. After removal of  $AgCl$  by filtration, 620 mg (1.60 mmol) of  $Bu_4NPF_6$  were added and then 50.5 mg (0.32 mmol) of *bpym*, dissolved in 10 ml acetone. Stirring at ambient temperature for 6 h, reduction of volume to about 20 ml, addition of pentane and washing with diethyl ether gave the yellow product in 85% yield (270 mg). For  $C_{28}H_{36}Cl_2F_{12}N_4P_2Rh_2 \cdot 0.5(CH_3)_2CO$  (1 024.3) calculated: 34.61% C, 3.84% H, 5.46% N; found: 34.22% C, 3.89% H, 4.91% N.

$\{[IrCl(\eta^5-C_5Me_5)]_2(\mu-bpym)](PF_6)_2$ . A suspension of 91.1 mg (0.114 mmol)  $\{[IrCl(\eta^5-C_5Me_5)]Cl\}_2$  (ref. <sup>12b</sup>) in 30 ml acetone was stirred in the dark with 57.8 mg (0.228 mmol) of  $AgPF_6$  for 3 h. After removal of  $AgCl$  by filtration over celite, 620 mg (1.60 mmol) of  $Bu_4NPF_6$  were added and then 18 mg (0.114 mmol) of *bpym*, dissolved in 5 ml acetone. After reduction of the volume to about 20 ml, an orange-red precipitate was collected in 60% yield (81.6 mg). For  $C_{28}H_{36}Cl_2F_{12}Ir_2N_4P_2$  (1 173.9) calculated: 28.65% C, 3.09% H, 4.77% N; found: 29.24% C, 3.29% H, 4.53% N.

$\{[Rh(\eta^5-C_5Me_5)]_2(\mu-bpym)]$ . A suspension of 50 mg (0.050 mmol)  $\{[RhCl(\eta^5-C_5Me_5)]_2(\mu-bpym)](PF_6)_2$  in THF was brought into contact with a potassium mirror, generated from 50 mg (1.28 mmol) potassium. Immersion into an ultrasonic bath for 10 min produced a colour change from light yellow to deep purple. Filtration, removal of the solvent from the filtrate and extraction with benzene gave 22 mg (70%) of purple microcrystals. Elemental analysis was not possible due to the extreme air-sensitivity.

## RESULTS AND DISCUSSION

*Syntheses, Stability and Isomerism*

The complexes  $\{[MCl(\eta^5-C_5Me_5)]_2(\mu-bpym)](PF_6)_2$  were obtained through standard procedures using  $\{[MCl(\eta^5-C_5Me_5)]Cl\}_2$  precursor compounds<sup>12</sup>. They are insoluble in acetone, THF or dichloromethane and dissociate partially in acetonitrile or DMF (*cf.* Eq. (4)); in  $CD_3NO_2$  they could be analyzed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (Fig. 2, Tables I and II).

The dirhodium compound is formed as a mixture in 4 : 5 molar ratio of *cis*- and *trans*-isomers with respect to the relative positions of Cl or  $C_5Me_5$  ligands above or below the central molecular plane (Fig. 1). The diiridium analogue is obtained as a pure isomer, we tentatively assume the *trans*-form, based on a previous<sup>11d</sup> crystal structure of the related  $\{[OsCl(p-cymene)]_2(\mu-bpym)](PF_6)_2$ . After heating for a few minutes in boiling methanol, the NMR spectrum shows the presence of two isomers in 1 : 1 ratio (equilibration).

In  $CD_3CN$  or  $DMF-d_7$  both complexes dissociate according to Eq. (4).

TABLE I  
 $^1\text{H}$  NMR chemical shifts<sup>a</sup> of bpym and its complexes

Compound	$\delta$ , ppm				Solvent
	H(4,4')	H(5,5')	H(6,6')	$\eta^5\text{-C}_5\text{Me}_5$	
bpym	8.95	7.51	8.95	–	$\text{CD}_3\text{CN}$
bpym	9.04	7.62	9.04	–	$\text{CD}_3\text{NO}_2$
bpym	8.35	6.28	8.35	–	$\text{C}_6\text{D}_6$
$\{[\text{RhCl}(\eta^5\text{-C}_5\text{Me}_5)_2](\mu\text{-bpym})\}(\text{PF}_6)_2^b$	9.57	8.51	9.57	1.95	$\text{CD}_3\text{NO}_2$
$\{[\text{RhCl}(\eta^5\text{-C}_5\text{Me}_5)_2](\mu\text{-bpym})\}(\text{PF}_6)_2^c$	9.60	8.56	9.60	1.90	$\text{CD}_3\text{NO}_2$
$[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)_2](\mu\text{-bpym})$	8.73	5.95	8.73	1.87	$\text{C}_6\text{D}_6$
$\{[\text{IrCl}(\eta^5\text{-C}_5\text{Me}_5)_2](\mu\text{-bpym})\}(\text{PF}_6)_2^d$	9.56	8.51	9.56	1.94	$\text{CD}_3\text{NO}_2$
$\{[\text{IrCl}(\eta^5\text{-C}_5\text{Me}_5)_2](\mu\text{-bpym})\}(\text{PF}_6)_2^e$	9.61	8.58	9.61	1.90	$\text{CD}_3\text{NO}_2$
$[\text{RhCl}(\eta^5\text{-C}_5\text{Me}_5)(\text{bpym})](\text{PF}_6)^f$	9.13	7.93	9.26	1.72	$\text{CD}_3\text{CN}$
$[\text{IrCl}(\eta^5\text{-C}_5\text{Me}_5)(\text{bpym})](\text{PF}_6)$	9.21	7.98	9.30	1.74	$\text{CD}_3\text{CN}$

<sup>a</sup> Coupling patterns and coupling constants are as expected:  $^3J(\text{H}(4)/\text{H}(5)) \approx ^3J(\text{H}(5)/\text{H}(6)) \approx 5.5$  Hz,  $^4J(\text{H}(4)/\text{H}(6)) < 2$  Hz. <sup>b</sup> Major isomer (isomer ratio 5 : 4). <sup>c</sup> Minor isomer. <sup>d</sup> Kinetic isomer (initial reaction product). <sup>e</sup> Second isomer (formed after thermal equilibration). <sup>f</sup> From ref.<sup>4a</sup>

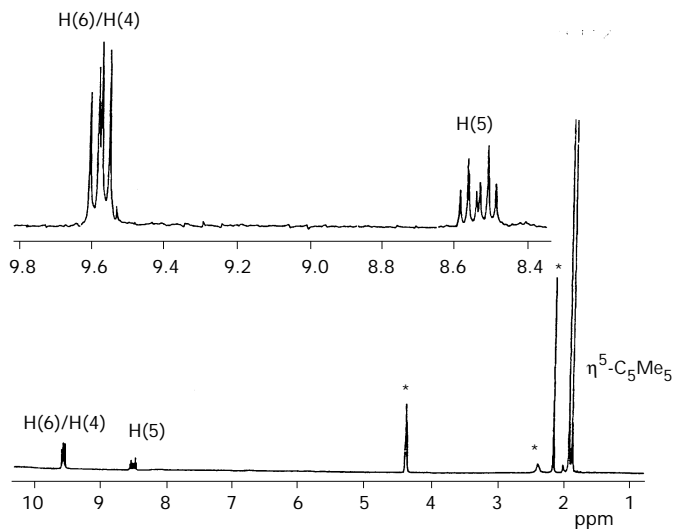
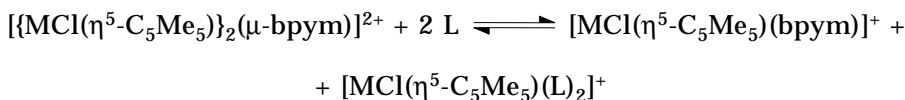


FIG. 2  
 $^1\text{H}$  NMR spectrum of  $\{[\text{RhCl}(\eta^5\text{-C}_5\text{Me}_5)_2](\mu\text{-bpym})\}(\text{PF}_6)_2$  (*cis/trans* mixture) in  $\text{CD}_3\text{NO}_2$  (\* solvent, water and acetone signals)



Interestingly, there is only one isomer detectable in the mixture (Eq. (4)) with M = Rh and L = CD<sub>3</sub>CN, we assume that the *cis*-isomer dissociates much more rapidly than the *trans*-form. Nevertheless, in CD<sub>3</sub>CN there is sufficient dirhodium compound left to study it by cyclic voltammetry (see below). In DMF-*d*<sub>7</sub> at -15 °C, the diiridium compound turned out to be fairly inert towards the dissociation (Eq. (4)). We thus chose those conditions for cyclic voltammetry.

The dissociative lability of the bpym-bridged dinuclear species is unusual when compared with the more stable systems with less basic bptz, bpip or abpy (abpy = azobipyridine) bridging ligands<sup>9,15</sup>. We attribute this lability to the strain in the N-C-C-N-M chelate rings:

Structure analysis of an unhindered ring in mononuclear [IrCl(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(Xyl-DAB)]PF<sub>6</sub>, Xyl-DAB = 1,4-bis(2,6-dimethylphenyl)-1,4-diaza-1,3-butadiene, has shown an N-C-C internal angle of about 115° (ref.<sup>6</sup>). This value is somewhat smaller than that of ca 117° required for a bpym-bridged dinuclear complex such as [{OsCl(*p*-cymene)}<sub>2</sub>(μ-bpym)](PF<sub>6</sub>)<sub>2</sub>

TABLE II  
<sup>13</sup>C NMR data of bpym and rhodium complexes

Compound	δ, ppm					Solvent
	C(2,2')	C(4,4')	C(5,5')	C(6,6')	η <sup>5</sup> -C <sub>5</sub> Me <sub>5</sub>	
bpym	161.5	160.5	126.5	162.2	–	CD <sub>3</sub> NO <sub>2</sub>
bpym	164.5	157.3	120.7	157.3	–	C <sub>6</sub> D <sub>6</sub>
[RhCl(η <sup>5</sup> -C <sub>5</sub> Me <sub>5</sub> )(bpym)](PF <sub>6</sub> )	161.5	160.1	126.7	162.2	9.3/99.7 <sup>a</sup>	CD <sub>3</sub> NO <sub>2</sub>
[{RhCl(η <sup>5</sup> -C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> (μ-bpym)](PF <sub>6</sub> ) <sub>2</sub> <sup>b</sup>	161.0	161.6	129.7	161.6	9.5/100.8 <sup>a</sup>	CD <sub>3</sub> NO <sub>2</sub>
[{RhCl(η <sup>5</sup> -C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> (μ-bpym)](PF <sub>6</sub> ) <sub>2</sub> <sup>c</sup>	161.0	161.8	129.8	161.8	9.4/100.6 <sup>a</sup>	CD <sub>3</sub> NO <sub>2</sub>
[Rh(η <sup>5</sup> -C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> (μ-bpym)]	137.5	143.5	106.3	143.5	9.9/88.2 <sup>d</sup>	C <sub>6</sub> D <sub>6</sub>

<sup>a</sup> <sup>2</sup>J(Rh/C) = 8.6 Hz. <sup>b</sup> Isomer A. <sup>c</sup> Isomer B. <sup>d</sup> <sup>2</sup>J(Rh/C) = 7.3 Hz.

(ref.<sup>11d</sup>). The relief of that strain by converting to the mononuclear arrangement with only one, relaxed five-membered chelate ring accounts for the dissociative lability of the dinuclear bpym-bridged compounds.

For reference purposes, we also synthesized the very reactive deep-purple  $\{[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)]_2(\mu\text{-bpym})\}(\text{PF}_6)_2$  from the precursor  $\{[\text{RhCl}(\eta^5\text{-C}_5\text{Me}_5)]_2(\mu\text{-bpym})\}(\text{PF}_6)_2$  by reduction with potassium. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (Tables I and II) confirm the composition through the observed symmetry and through the high field shifts of the H(5,5') nuclei. This result confirms the established<sup>4a,4b,5f,6,16</sup> strong  $\pi$ -back-donation from the  $\text{Rh}^{\text{I}}(\eta^5\text{-C}_5\text{Me}_5)$  fragments to  $\alpha$ -diimines and illustrates the large LUMO coefficients in 5,5'-positions relative to those in the 4,4',6,6'-positions<sup>11a,11b</sup> (Fig. 3).

### *Electrochemistry and Spectroelectrochemistry (UV-VIS, EPR)*

#### Dirhodium Compounds

The cyclic voltammogram of  $\{[\text{RhCl}(\eta^5\text{-C}_5\text{Me}_5)]_2(\mu\text{-bpym})\}(\text{PF}_6)_2$  in acetonitrile/0.1 M  $\text{Bu}_4\text{NPF}_6$  is shown in Fig. 4. In accordance with the NMR results (Eq. (4)), the waves from both the dinuclear and the (known<sup>4a</sup>) mononuclear species (peaks labelled with asterisk in Fig. 4) are observed. The cathodic wave for the dinuclear complex ( $E_1$ ) occurs at less negative potential, as expected. The observed peak current is rather low, revealing extensive dissociation of the parent dinuclear complex in MeCN solution. However, the shape of the peak pair  $E_1$  and  $E_2$ , clearly shows that this is a consecutive two-electron wave, coupled with the familiar<sup>2,4-9</sup> loss of chloride (ECE/EEC processes); both the addition of the mononuclear complex and increasing the substrate concentration caused an increased intensity of the current at  $E_1$  associated with the dinuclear form. Varying the scan rate between 50 and 500  $\text{mV s}^{-1}$  did not change the cyclic voltammogram sub-

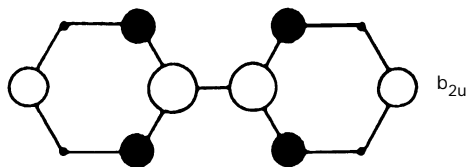


FIG. 3  
Representation of the lowest unoccupied  $\pi$ -MO of bpym

stantially. On reduction of the mononuclear bpym complex to  $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{bpym})]$  (ref. <sup>4a</sup>), its increased basicity at the free coordination site, coupled with the probably more relaxed strain in the now rhodium(I)-containing chelate ring, allows for the formation of more dinuclear compound, as evident from intensified signals for the second two-electron reduction to  $\{[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)]_2(\mu\text{-bpym})\}$  at  $E_3$  and for the reoxidation of  $\{[\eta^5\text{-C}_5\text{Me}_5]\text{Rh}(\mu\text{-bpym})\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}\}^+$  ( $E_{2'}$ ). Further indication for this rapid formation of the dinuclear species is that we could not detect the reduction of the second monomolecular species  $[\text{RhCl}(\eta^5\text{-C}_5\text{Me}_5)(\text{MeCN})_2]^+$  in MeCN solution. The latter complex should have a reduction potential slightly more negative than the mononuclear bpym complex.

Cyclic voltammetry of the product  $\{[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)]_2(\mu\text{-bpym})\}$  (Fig. 5), prepared by chemical reduction of  $\{[\text{RhCl}(\eta^5\text{-C}_5\text{Me}_5)]_2(\mu\text{-bpym})\}(\text{PF}_6)_2$  with potassium metal in THF (see Experimental), confirms the assignments in Table III (Fig. 5): Reversible two-electron ( $E_{1+2}$ ) oxidation and reversible one-electron reduction ( $E_4/E_4'$ ) are observed; further oxidation beyond the dicationic state ( $E_{2''}$ ) becomes reversible in the absence of charge-stabilizing chloride ions. Despite the apparent two-electron nature of the oxidation  $\{[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)]_2(\mu\text{-bpym})\}^{0\rightarrow 2+}$ , there is EPR-spectroscopic evidence for a  $\text{Rh}^{\text{I}}/\text{Rh}^{\text{II}}$  mixed-valent intermediate  $\{[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)]_2(\mu\text{-bpym})\}^+$ : the  $g$  values of  $g_1 = 2.177$ ,  $g_2 = 2.041$  and  $g_3 = 1.951$  in frozen THF solution at 4 K are similar to those for related species reported recently<sup>9d</sup>. The formation of

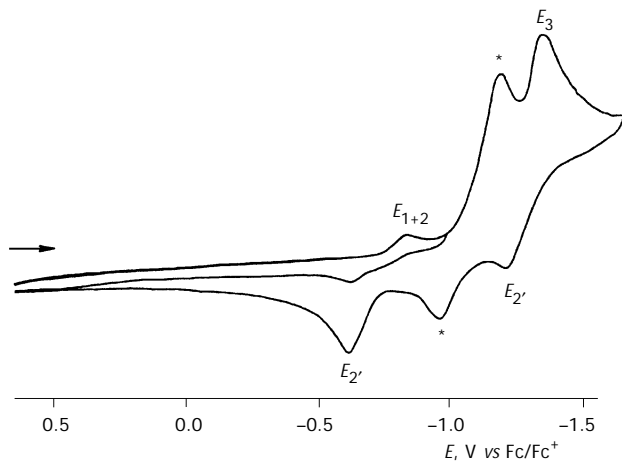


FIG. 4

Cyclic voltammogram of  $\{[\text{RhCl}(\eta^5\text{-C}_5\text{Me}_5)]_2(\mu\text{-bpym})\}(\text{PF}_6)_2$  (partially dissociated) in  $\text{CD}_3\text{CN}/0.1 \text{ M Bu}_4\text{NPF}_6$  at 298 K ( $100 \text{ mV s}^{-1}$  scan rate; potentials  $E$  in V vs  $\text{Fc}/\text{Fc}^+$ ). Peaks due to the mononuclear complex  $[\text{RhCl}(\eta^5\text{-C}_5\text{Me}_5)(\text{bpym})]^+$  are marked with asterisks



TABLE III  
 Electrochemical potentials  $E_n^a$  of dinuclear complexes  $[\{\text{MCl}(\eta^5\text{-C}_5\text{Me}_5)\}_2(\mu\text{-bpym})](\text{PF}_6)_2$

$E_n$	M	
	Rh <sup>b</sup>	Ir <sup>c</sup>
$E_1$	-0.82	-0.74
$E_{1'}$	-	-0.67
$E_2$	-0.82	-1.25
$E_{2'}$	-0.62	-0.50
$E_3$	-1.33	-1.61
$E_{3'}$	-1.21	-1.15
$E_4$	-2.59	-2.67
$E_{4'}$	-2.50	-2.54

<sup>a</sup> Peak potentials from cyclic voltammetry at 100 mV s<sup>-1</sup> scan rate, potentials in V vs ferrocene/ferrocenium (cf. Scheme 2). <sup>b</sup> In CH<sub>3</sub>CN/0.1 M Bu<sub>4</sub>NPF<sub>6</sub> at 298 K in the presence of mononuclear complex. <sup>c</sup> In DMF/0.1 M Bu<sub>4</sub>NPF<sub>6</sub> at 258 K.

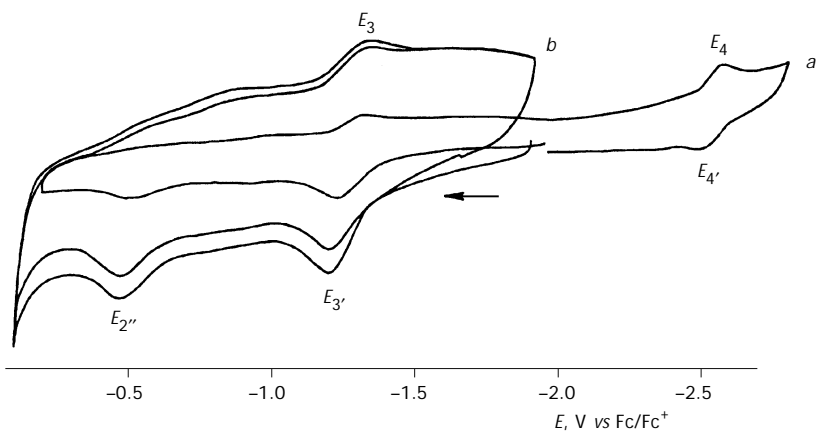


FIG. 5  
 Cyclic voltammogram of two-electron reduced  $[\{\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)\}_2(\mu\text{-bpym})]$  in THF/0.1 M Bu<sub>4</sub>NPF<sub>6</sub> at 298 K (100 mV s<sup>-1</sup> scan rate (a) and two cycles with 500 mV s<sup>-1</sup> (b); potentials  $E$  in V vs Fc/Fc<sup>+</sup>)

$\{[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-bpym})]^-$  at very negative potentials is as expected<sup>9</sup> and will be discussed below, together with the results for the diiridium derivative.

In agreement with the cyclovoltammetric results, UV-VIS spectroelectrochemistry of the equilibrium given by Eq. (4),  $M = \text{Rh}$ , in an OTTLE cell produces the species  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\mu\text{-bpym})\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}]^+$  and  $\{[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-bpym})]$  (Fig. 6). In the long-wavelength region the charge transfer absorptions from the formally  $d^8$ -species  $\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)$  to the  $\pi$ -acceptor ligand dominate. Whereas the mixed complex exhibits a spectrum not very different from that of  $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{bpym})]$  (ref.<sup>4b</sup>), the neutral dinuclear compound is distinguished by intense bands at very long wavelengths (Fig. 6, Table IV).

Similar such MLCT bands were observed<sup>17</sup> for  $\{[\text{Mo}(\text{CO})_2(\text{PBU}_3)_2]_2(\mu\text{-bpym})]$  at  $\lambda_{\text{max}} = 1\,212$  nm. In contrast, the bpym-bridged dimetal(III) precursor complexes exhibit no distinct absorption features in the visible region (Table IV).

### Diiridium Compounds

The more inert diiridium complex  $\{[\text{IrCl}(\eta^5\text{-C}_5\text{Me}_5)]_2(\mu\text{-bpym})\}(\text{PF}_6)_2$  could be studied in non-dissociated form at  $-15$  °C in DMF/0.1 M  $\text{Bu}_4\text{NPF}_6$ . Under these conditions, it exhibits a reversible one-electron reduction (Fig. 7, Table III) to the UV-VIS and EPR-detectable radical complex  $\{[\text{IrCl}(\eta^5\text{-C}_5\text{Me}_5)]_2(\mu\text{-bpym})\}^+$ .

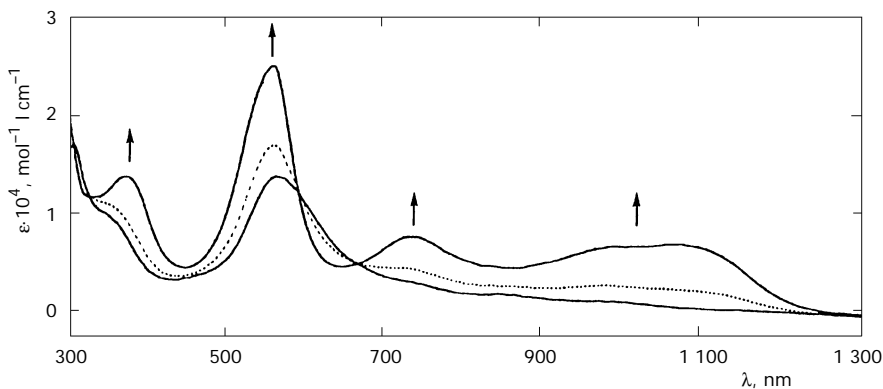


FIG. 6

UV-VIS spectroelectrochemistry of the transition  $\{[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\mu\text{-bpym})\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}]^+ \rightarrow \{[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-bpym})]$  in  $\text{CH}_3\text{CN}/0.1$  M  $\text{Bu}_4\text{NPF}_6$  at 298 K

Room temperature OTTLE spectroelectrochemistry in  $\text{CH}_3\text{NO}_2/0.1 \text{ M Bu}_4\text{NPF}_6$  produced an UV-VIS spectrum typical for platinum metal complexes with the  $[\text{bpym}]^-$  ligand<sup>4a,4b,18</sup>. Vibrationally split absorptions at long wavelengths and a prominent band around 510 nm can be assigned to forbidden and allowed transitions, respectively, involving the singly occupied MO (ref.<sup>18</sup>). The EPR spectrum of the radical cation obtained in the course of low-temperature ( $-15 \text{ }^\circ\text{C}$ ) electrolysis in  $\text{DMF}/0.1 \text{ M Bu}_4\text{NPF}_6$ , gave only an unresolved broad signal at  $g = 1.9767$ . In glassy-frozen solution at 110 K, a rhombic signal is obtained with  $g_1 = 2.0029$ ,  $g_2 = 1.9849$  and  $g_3 = 1.9451$  (Fig. 8).

Despite the rather distinct  $g$  anisotropy  $\Delta g = g_1 - g_3 = 0.0578$  and the low  $g(\text{av}) = 1.978$  we still interpret these results as indicating predominantly ligand-based spin<sup>19</sup>. The large spin-orbit coupling constant of iridium(III)<sup>20</sup> and the special  $g$  factor lowering, generally observed for  $[\text{bpym}]^-$ -bridged dinuclear complexes<sup>11a</sup>, are held responsible for the strong deviation of  $g$  from the free electron value of 2.0023 (ref.<sup>19</sup>).

Addition of another electron to  $[\{\text{IrCl}(\eta^5\text{-C}_5\text{Me}_5)\}_2(\mu\text{-bpym})]^{+}$  is electrochemically irreversible and produces  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\mu\text{-bpym})\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}]^+$  upon loss of one chloride ligand (Scheme 2). This reaction sequence implies electron-reservoir behaviour as observed previously<sup>9</sup>, by which the first electron is first stored in the ligand  $\pi$ -system before it combines with the second electron in a chemically productive step at one of the metal reac-

TABLE IV  
UV-VIS absorption data of complexes

Compound	$\lambda_{\text{max}}(\epsilon)^a$
$[\{\text{RhCl}(\eta^5\text{-C}_5\text{Me}_5)\}_2(\mu\text{-bpym})](\text{PF}_6)_2^b$	375 (4 000), 309 (4 000)
$[\{\text{RhCl}(\eta^5\text{-C}_5\text{Me}_5)\}\{\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-bpym})\}]^{+b}$	1 161 (600), 986 (1 300), 856 (1 800), 742 (2 900), 562 (12 000), 334 (9 000)
$[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-bpym})^b$	1 082 (8 000), 977 (7 000), 733 (13 000), 555 (29 000), 372 (25 000)
$[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-bpym})^c$	1 082, 983sh, 724, 552, 366
$[\{\text{IrCl}(\eta^5\text{-C}_5\text{Me}_5)\}_2(\mu\text{-bpym})](\text{PF}_6)_2$	520sh, 340
$[\{\text{IrCl}(\eta^5\text{-C}_5\text{Me}_5)\}_2(\mu\text{-bpym})^{+d}$	832sh, 760sh, 685sh, 605sh, 510, 390sh

<sup>a</sup> Wavelengths  $\lambda$  in nm, molar extinction coefficients  $\epsilon$  in  $\text{l mol}^{-1} \text{ cm}^{-1}$ . <sup>b</sup> In  $\text{CH}_3\text{CN}/0.1 \text{ M Bu}_4\text{NPF}_6$  (spectroelectrochemistry). <sup>c</sup> In THF. <sup>d</sup> In  $\text{CH}_3\text{NO}_2/0.1 \text{ M Bu}_4\text{NPF}_6$  (spectroelectrochemistry).

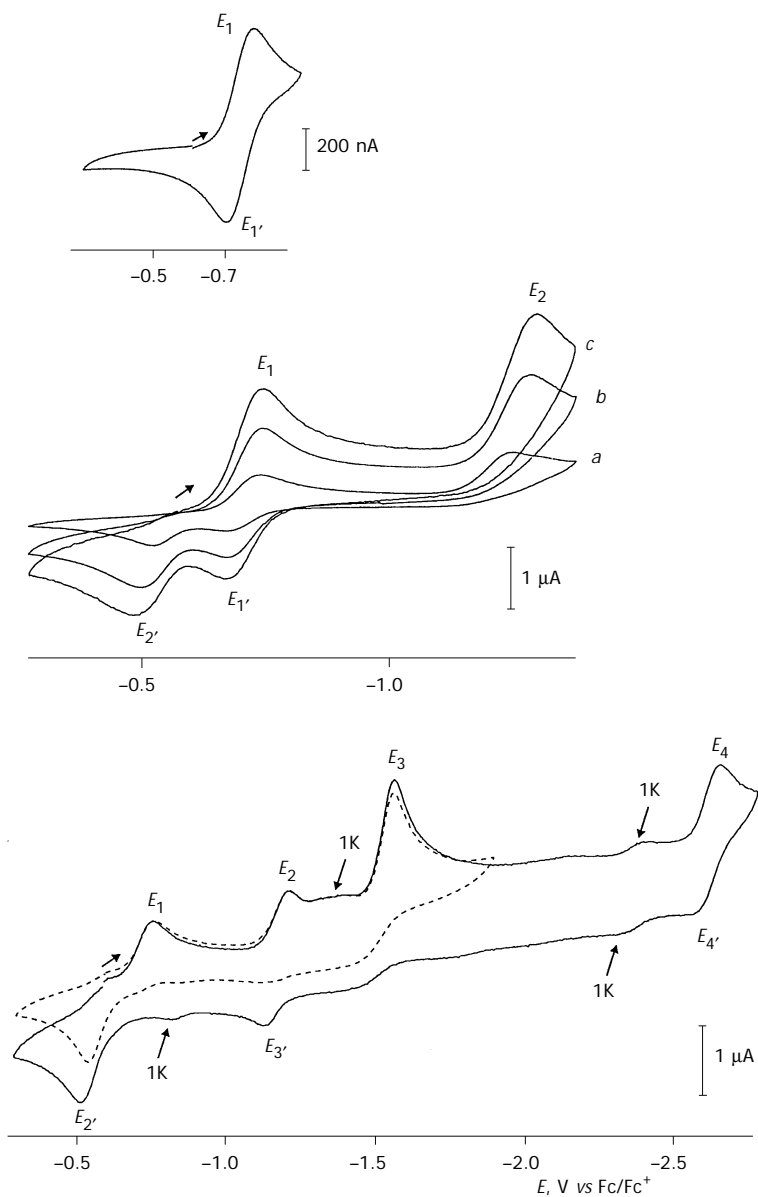
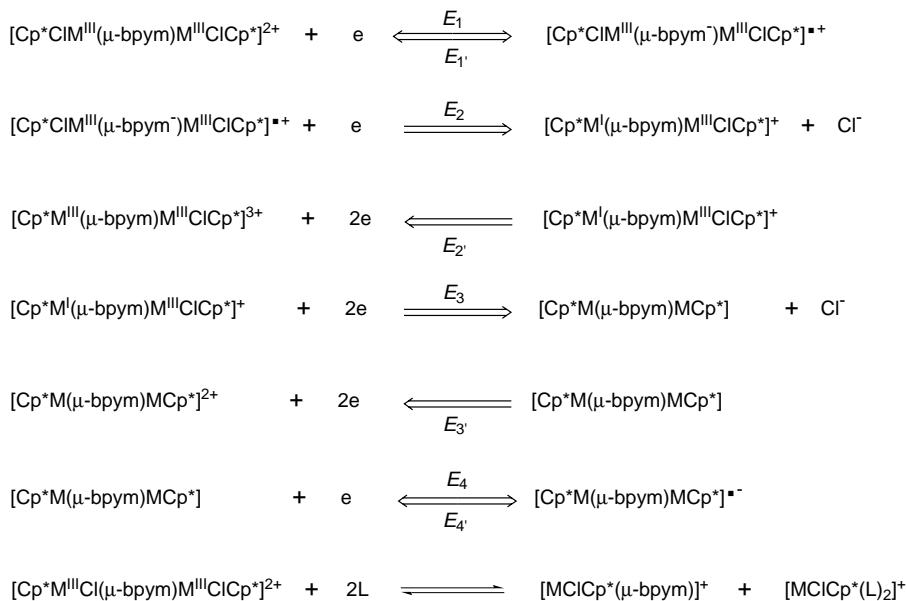


FIG. 7

Cyclic voltammograms of  $\{[\text{IrCl}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-bpym})](\text{PF}_6)_2$  (pure isomer) in DMF/0.1 M  $\text{Bu}_4\text{NPF}_6$  at 258 K. Top:  $100 \text{ mV s}^{-1}$  scan rate; centre: 100 (a), 500 (b) and 1 000 (c)  $\text{mV s}^{-1}$ ; bottom:  $200 \text{ mV s}^{-1}$ . The symbol 1K denotes waves due to the mononuclear complex. Potentials  $E$  in V vs  $\text{Fc}/\text{Fc}^+$

tion centres. The chloride dissociation at the other organometal site occurs in the familiar two-electron fashion for the diiridium system (Scheme 2).



L = solvent, Cp\* =  $\eta^5\text{-C}_5\text{Me}_5$

SCHEME 2

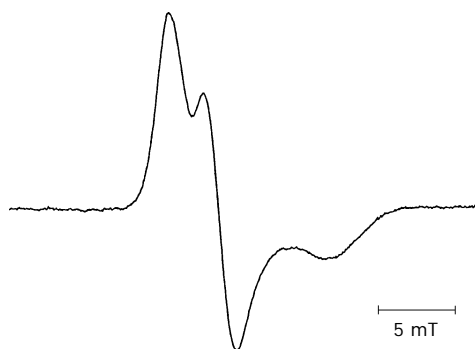


FIG. 8  
EPR spectrum of electrogenerated  $[\{\text{IrCl}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-bpym})\}^{*+}]$  in a glassy-frozen solution of DMF/0.1 M  $\text{Bu}_4\text{NPF}_6$  at 110 K

Electrochemical data for the mononuclear species  $[\text{MCl}(\eta^5\text{-C}_5\text{Me}_5)(\text{bpym})]\text{PF}_6$  are  $E_1 = -1.19$  V,  $E_1'/E_2' = -1.01$  V,  $E_4 = -2.29$  V and  $E_4' = -2.23$  V for  $\text{M} = \text{Rh}$  (ref.<sup>4a</sup>),  $E_1 = -1.28$  V,  $E_1'/E_2' = -0.89$  V,  $E_4 = -2.44$  V and  $E_4' = -2.36$  V for  $\text{M} = \text{Ir}$  (refs.<sup>5f,5g</sup>) (*cf.* Fig. 9). The potentials for the dinuclear species in Table III confirm that the cathodic peak potentials and the anodic reoxidation peak potentials of the mononuclear systems lie in between the (split) values for the dinuclear analogues, as expected for a ligand-coupled

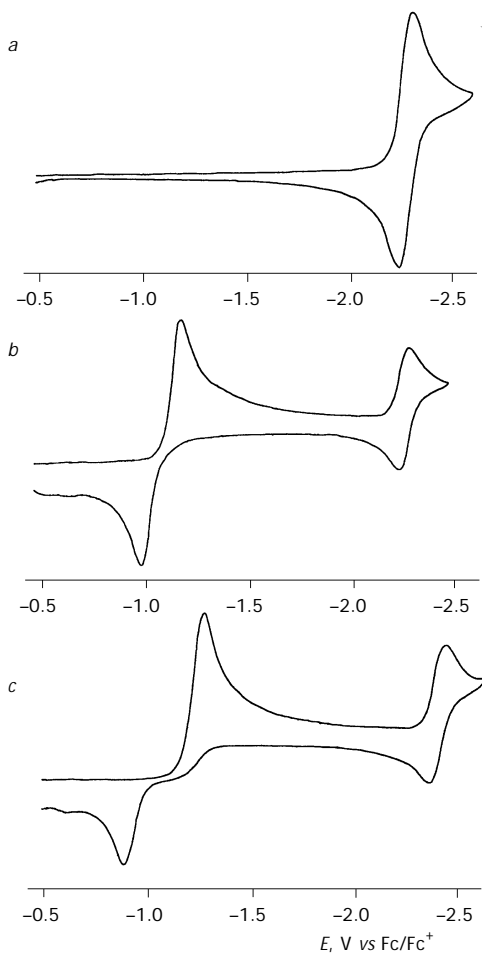


FIG. 9

Cyclic voltammograms of non-coordinated bpym (a),  $[\text{RhCl}(\eta^5\text{-C}_5\text{Me}_5)(\text{bpym})]\text{PF}_6$  (b) and  $[\text{IrCl}(\eta^5\text{-C}_5\text{Me}_5)(\text{bpym})]\text{PF}_6$  (c) in  $\text{CH}_3\text{CN}/0.1$  M  $\text{Bu}_4\text{NPF}_6$  at  $100$   $\text{mV s}^{-1}$  scan rate (potentials  $E$  in V vs  $\text{Fc}/\text{Fc}^+$ )

dimer with two-electron transfer centres<sup>21</sup>. Of course, the potential values for irreversible processes depend on the individual rates, so that there is no numerically exact averaging. The splitting  $\Delta E = E_2 - E_3$  of the chloride-dissociative cathodic processes in the dinuclear compounds is  $\Delta E = 0.51$  V for M = Rh (in CH<sub>3</sub>CN/298 K) and  $\Delta E = 0.36$  V for M = Ir (in DMF/258 K). The corresponding numbers for the reoxidation processes are 0.59 V for M = Rh and 0.65 V for M = Ir. These values appear fairly large when compared with  $\Delta E < 0.3$  V for pure electron transfer centres bridged with 2,2'-bipyrimidine<sup>21</sup>. However, a comparable value of 0.42 V was obtained with a complex that had two organoosmium reaction centres coupled by bpym<sup>11d</sup>.

Further reduction of the neutral dinuclear species  $[\{M(\eta^5-C_5Me_5)\}_2(\mu\text{-bpym})]$  occurs at more negative potentials  $E_4$  than the reduction of the mononuclear systems  $[M(\eta^5-C_5Me_5)(\text{bpym})]$  (cf. above) or bpym itself ( $E_{pc} = -2.21$  V, see Fig. 9). This result illustrates the exceedingly strong  $\pi$ -back-donation from one or, even stronger, two complex fragments  $M(\eta^5-C_5Me_5)$  to  $\pi$ -acceptor systems<sup>4a,4b,5f,6,16</sup>. The iridium(I) system exhibits a more pronounced effect than the rhodium analogue, and, in agreement with these results, the highly reduced forms are less stable for the iridium analogues.

Summarizing, despite the disturbing dissociative tendencies of complex ions  $[\{MCl(\eta^5-C_5Me_5)\}_2(\mu\text{-bpym})]^{2+}$ , M = Rh or Ir, we could study the electrochemical coupling phenomena for these organometallic reaction centres via the 2,2'-bipyrimidine bridge. Low-temperature techniques and the increased complex stability on reduction helped in analyzing the electron transfer and bond dissociation processes. Although bpym is a relatively weak mediator of metal-metal interactions<sup>21</sup>, the phenomena observed are qualitatively similar to those reported for much stronger  $\pi$ -acceptor bridging ligands<sup>9</sup>.

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