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Multistep redox sequences of azopyridyl (L) bridged reaction centres in stable radical complex ions $\{(\mu\text{-L})[\mathrm{MCl}(\eta^5\text{-}\mathrm{C_5Me_5})]_2\}^{\bullet +}$, M = Rh or Ir: spectroelectrochemistry and high-frequency EPR spectroscopy

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The dinuclear complex cations $\{(\mu\text{-L})[\mathrm{MCl}(\eta^5\text{-}\mathrm{C_5Me_5})]_2\}^n$, M = Rh or Ir and L = abpy (= 2,2′-azobispyridine) or abcp (= 2,2′-azobis(5-chloropyrimidine)), could be isolated as paramagnetic hexafluorophosphates ($n = 1+$) or, for M = Ir, as diamagnetic bis-hexafluorophosphates ($n = 2+$). In addition to the reversible one-electron process as indicated by this convertibility there are two successive chloride-releasing reduction steps, separated by unusually large potential differences ΔE_{EC} between 0.75 V ($\mathrm{Rh_2}$/abpy) and 1.14 V ($\mathrm{Ir_2}$/abcp), leading to the spectroelectrochemically characterised complexes $\{[(\eta^5\text{-}\mathrm{Me_5C_5})\mathrm{M}](\mu\text{-L})[\mathrm{MCl}(\eta^5\text{-}\mathrm{C_5Me_5})]\}^+$ and $(\mu\text{-L})[\mathrm{M}(\eta^5\text{-}\mathrm{C_5Me_5})]_2$. This large splitting of ΔE_{EC} establishes the capability of azopyridyl bridges for mediating efficient metal–metal communication beyond mere electron transfer. The neutral complexes $(\mu\text{-L})[\mathrm{M}(\eta^5\text{-}\mathrm{C_5Me_5})]_2$ are distinguished by a series of intense absorption bands in the near infrared, the lowest absorption energies being displayed by the $\mathrm{Ir_2}$/abcp combination. The stable electron reservoir intermediates $\{(\mu\text{-L})[\mathrm{MCl}(\eta^5\text{-}\mathrm{C_5Me_5})]_2\}^+$ were identified as complexes of $\mathrm{L}^{\bullet -}$ anion radicals *via* their small g anisotropy as measured through high-frequency (>200 GHz) EPR spectroscopy.

Introduction

The coupling of inorganic,[1,2] organometallic[3,4] or main group element[5,6] electron transfer centres through π-conjugated molecular bridges has much contributed to the understanding of electron transfer reactivity, treating it as a structurally (coordinatively) controlled degenerate *intra*molecular phenomenon instead of an intermolecular process.[7] As a side effect of such studies new stable mixed-valent intermediates[1,2,8] were obtained which owe their existence to strong electronic communication between the electron transfer centres *via* mediating molecular bridges: two degenerate half-wave potentials E for two chemically identical such centres may thus split into two different values E_1 and E_2 (eqn. (1)),

$$\underset{\text{Red}}{\mathrm{M}^n\text{-L-}\mathrm{M}^n} \underset{(E_1)}{\underset{+e^-}{\overset{-e^-}{\rightleftharpoons}}} \underset{\text{Int}}{\mathrm{M}^n\text{-L-}\mathrm{M}^{n+1}} \underset{(E_2)}{\underset{+e^-}{\overset{-e^-}{\rightleftharpoons}}} \underset{\text{Ox}}{\mathrm{M}^{n+1}\text{-L-}\mathrm{M}^{n+1}} \qquad (1)$$

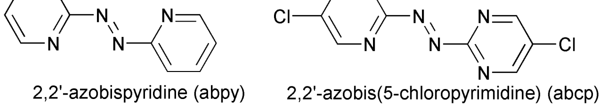
the separation $\Delta E = E_2 - E_1$ relating to the comproportionation constant K_c (eqn. (2)).[1,8]

$$K_c = \frac{[\mathrm{Int}]^2}{[\mathrm{Red}][\mathrm{Ox}]} = 10^{\Delta E/59\ \mathrm{mV}} \qquad (2)$$

In an effort to extend this concept to *reaction centres*, *i.e.* to molecular fragments which do not only undergo electron transfer processes (E) but electron transfer *and* chemical transformations (*e.g.* bond breaking) we have used[9,10] organometallic reaction centres $[(\mathrm{C_5Me_5})\mathrm{ClM}]^+$, M = Rh or Ir, from hydride transfer catalysis[11] which typically undergo a two-electron ECE reaction to $[(\mathrm{C_5Me_5})\mathrm{M}]$, involving the reversible loss of chloride (C process). As bridging systems we have so far used bis-chelating acceptors such as 2,2′-bipyrimidine (bpym),[10] 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz)[9] or 2,5-bis(imino)pyrazine ligands.[9]

We now describe the coupling of the $[(\mathrm{C_5Me_5})\mathrm{ClM}]^+$/$[(\mathrm{C_5Me_5})\mathrm{M}]$ system (M = Rh or Ir) in dinuclear complexes $\{(\mu\text{-L})[\mathrm{MCl}(\eta^5\text{-}\mathrm{C_5Me_5})]_2\}^n$ with the very strongly metal–metal coupling azopyridine[12] ligands L = 2,2′-azobispyridine (abpy) and 2,2′-azobis(5-chloropyrimidine) (abcp, Fig. 1).

2,2′-Azobispyridine can be conveniently synthesised by oxidative coupling of 2-aminopyridine and was early recognised[13] to exhibit strong interactions with low-valent metal centres such as iron(II) and to have a potential for several different coordination modes.[12,13] The structurally established alternatives include mono- and di-nuclear coordination situations with five-membered chelate ring formation NNCNM.[12] The ability of the abpy ligand to bridge two metal centres at a distance of about 5 Å,[14] the rather small size of its π system, and the low-lying π* orbital[15] make it a very special ligand, suitable for studying metal–metal interactions across an unsaturated molecular bridge.[12] 2,2′-Azobis(5-chloropyrimidine) was obtained in a similar way through chlorinating oxidative coupling of 2-aminopyrimidine;[16] it was shown to be an even better π acceptor ligand than abpy.[16,17]



2,2'-azobispyridine (abpy)   2,2'-azobis(5-chloropyrimidine) (abcp)

Fig. 1 The bridging ligands in their bis-chelating conformations.

The compounds studied are the dinuclear $\{(\mu\text{-L})[\mathrm{MCl}(\eta^5\text{-}\mathrm{C_5Me_5})]_2\}(\mathrm{PF_6})_n$, M = Rh or Ir, and L = abpy or abcp, which were initially isolated as stable one-electron reduced (radical) species ($n = 1$) but could be converted preparatively into the diamagnetic forms ($n = 2$) for M = Ir through chemical oxidation.

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Cyclic voltammetry, variable frequency EPR (9.5, 230, 285 GHz) and the spectroelectrochemical (UV/Vis) characterisation of the intermediates will be described, the results obtained shall be compared with those of the previously studied analogues of bpym,[10] bpip and bptz.[9] For complexes $\{(\mu\text{-L})[\mathrm{MCl}(\eta^5\text{-}\mathrm{C_5Me_5})]_2\}^n$ **1**^{n}: L = abpy, M = Rh; **2**^{n}: L = abpy, M = Ir; **3**^{n}: L = abcp, M = Rh; **4**^{n}: L = abcp, M = Ir.

Experimental

Instrumentation

X-Band EPR spectra at about 9.5 GHz were recorded on a Bruker System ESP 300 equipped with a Bruker ER035M gaussmeter and a HP 5350B microwave counter. High frequency EPR spectroscopy above 200 GHz was performed using a multifrequency spectrometer at 5 K.[18] Gunn diodes operating at 95 GHz and 115 GHz and equipped with a second and third harmonic generator have been used as a radiation source. An InSb bolometer (QMC Instruments) was used for detection. The main magnetic field was provided by a superconducting magnet (Cryogenics Consultant) which generates fields up to 12 T. Owing to different field sweep conditions the absolute values of the *g* components were obtained by calibrating the precisely measured *g* anisotropy data with the isotropic *g* value from X-band measurements. While this procedure does not account for the temperature dependence of *g*, the values extracted are identical with those obtained using an added standard. ^{1}H-NMR spectra were taken on a Bruker AC 250 spectrometer. UV/Vis absorption spectra were recorded on a Bruins Instruments Omega 10 spectrophotometer. Cyclic voltammetry was carried out in 0.1 M $\mathrm{Bu_4NPF_6}$ solutions, using a three-electrode configuration (glassy carbon or Pt working electrode, Pt counter electrode, Ag/AgCl reference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium couple served as internal reference. UV/Vis/NIR spectroelectrochemical measurements were performed using an optically transparent thin-layer electrode (OTTLE) cell.[19]

Syntheses

$\{(\mu\text{-abpy})[\mathrm{RhCl(C_5Me_5)}]_2\}(\mathrm{PF_6})$. To a suspension of 150 mg (0.25 mmol) of $[(\mathrm{C_5Me_5})\mathrm{Cl_2Rh}]_2$[20] in 30 mL acetone were added two equivalents (125 mg, 0.5 mmol) of $\mathrm{AgPF_6}$. After two hours the mixture was filtered through Celite and the solution treated with 46 mg (0.25 mmol) of abpy. After 5 hours heating to reflux 196 mg (0.50 mmol) $\mathrm{Bu_4NPF_6}$ were added to the greenish-brown solution. The solution was evaporated to dryness, the solid redissolved in 10 mL dichloromethane and the product precipitated by addition of 30 mL n-hexane. The green precipitate was collected and recrystallized from methanol to yield 164 mg (75%) of green microcrystals. Anal. calcd for $\mathrm{C_{30}H_{38}Cl_2F_6N_4PRh_2}$ (876.35): C, 41.12; H, 4.37; N, 6.39. Found: C, 40.29; H, 4.33; N, 6.05%. The complex could not be oxidised with $\mathrm{NOPF_6}$ to a wholly persistent species like the diiridium compound.

$\{(\mu\text{-abpy})[\mathrm{IrCl(C_5Me_5)}]_2\}(\mathrm{PF_6})$. To a suspension of 99.8 mg (0.125 mmol) of $[(\mathrm{C_5Me_5})\mathrm{Cl_2Ir}]_2$[21] in 50 mL acetone were added two equivalents (63.35 mg, 0.25 mmol) of $\mathrm{AgPF_6}$. After two hours the mixture was filtered through Celite and the solution treated with 23 mg (0.125 mmol) of abpy. After 10 hours heating to reflux 196 mg (0.50 mmol) $\mathrm{Bu_4NPF_6}$ were added to the reddish-brown solution. Partial removal of the solvent afforded a dark brown precipitate which was recrystallised from methanol (94 mg, 70%). Anal. calcd for $\mathrm{C_{30}H_{38}Cl_2F_6Ir_2N_4P}$ (1054.97): C, 34.16; H, 3.63; N, 5.31. Found: C, 34.29; H, 3.82; N, 5.38%.

$\{(\mu\text{-abpy})[\mathrm{IrCl(C_5Me_5)}]_2\}(\mathrm{PF_6})_2$. A cooled (0 °C) solution of 29.1 mg (0.028 mmol) of $\{(\mu\text{-abpy})[\mathrm{IrCl(C_5Me_5)}]_2\}(\mathrm{PF_6})$ in 10 mL $\mathrm{CH_3CN}$ was treated with 12.9 mg (0.11 mmol) of solid $\mathrm{NOPF_6}$ for 3 hours under a slight argon flow. After the colour change to dark green the solvent was removed, the residue redissolved in an ethanol/acetone (1/1) mixture and a saturated solution of $\mathrm{Bu_4NPF_6}$ in ethanol added. A dark-green precipitate was collected after partial removal of the solvent, it was washed with diethyl ether and dried under vacuum (31.2 mg, 95%). Anal. calcd for $\mathrm{C_{30}H_{38}Cl_2F_{12}Ir_2N_4P_2}$ (1199.95): C, 30.03; H, 3.19; N, 4.67. Found: C, 30.33; H, 2.97; N, 4.61%. ^{1}H-NMR ($\mathrm{CD_3CN}$): δ = 1.80 (s, 30H, $\mathrm{CH_3}$), 8.23 (ddd, 2H, $\mathrm{H^{5,5'}}$), 8.60 (ddd, 2H, $\mathrm{H^{4,4'}}$), 8.71 (dd, 2H, $\mathrm{H^{3,3'}}$), 9.02 (dd, 2H, $\mathrm{H^{6,6'}}$) ppm. $^3J(\mathrm{H^3H^4})$ = 8.3 Hz, $^3J(\mathrm{H^4H^5})$ = 7.5 Hz, $^3J(\mathrm{H^5H^6})$ = 5.6 Hz.

$\{(\mu\text{-abcp})[\mathrm{RhCl(C_5Me_5)}]_2\}(\mathrm{PF_6})$. A suspension of 110 mg (0.18 mmol) $[(\mathrm{C_5Me_5})\mathrm{Cl_2Rh}]_2$[20] in 30 mL acetone was stirred for 2 hours in the dark with 90 mg (0.36 mmol) $\mathrm{AgPF_6}$. The yellow solution was filtered twice over Celite, added to 49 mg (0.18 mmol) abcp and stirred for 3 hours at room temperature. The purple solution was evaporated to dryness. The product was dissolved in 40 mL of a mixture of hexane/dichloromethane (3/1) and cooled to −25 °C. After some hours the deep purple precipitate was filtered off, dried under vacuum and recrystallised from 7 mL hot methanol to yield 136 mg (80%) of the product. Anal. calcd. for $\mathrm{C_{28}H_{34}Cl_4F_6N_6PRh_2}$ (947.21): C, 35.51; H, 3.62; N, 8.87. Found: C, 34.25; H, 3.85; N, 8.44%.

$\{(\mu\text{-abcp})[\mathrm{IrCl(C_5Me_5)}]_2\}(\mathrm{PF_6})$. A suspension of 145 mg (0.22 mmol) $[(\mathrm{C_5Me_5})\mathrm{Cl_2Ir}]_2$[21] in 30 mL acetone was stirred for 2 hours in the dark with 100 mg (0.40 mmol) $\mathrm{AgPF_6}$. The light yellow solution was filtered twice over Celite, added to 56 mg (0.22 mmol) abcp and heated to reflux for 4 hours. The purple solution was evaporated to dryness. The product was dissolved in 40 mL of a mixture of hexane/dichloromethane (3/1) and cooled to −25 °C. After some hours the deep purple precipitate was filtered off, dried under vacuum and recrystallised from 8 mL hot methanol to yield 188 mg (75%) of the product. Anal calcd. for $\mathrm{C_{28}H_{34}Cl_4F_6Ir_2N_6P}$ (1125.83): C, 29.87; H, 3.04; N, 7.46. Found: C, 29.86; H, 2.93; N, 7.26%.

$\{(\mu\text{-abcp})[\mathrm{IrCl(C_5Me_5)}]_2\}(\mathrm{PF_6})_2$. 15 mg of $\{(\mu\text{-abcp})[\mathrm{IrCl(C_5Me_5)}]_2\}(\mathrm{PF_6})$ were dissolved in 5 mL acetonitrile and cooled to 0 °C. About 4 mg of $\mathrm{NOPF_6}$ were added to the solution that immediately turned from purple to green. The solution was immediately evaporated to dryness and the product redissolved for ^{1}H-NMR spectroscopy without any further purification. ^{1}H-NMR ($\mathrm{CD_3CN}$): δ = 1.79 (s, 30H, $\mathrm{CH_3}$), 9.06 (d, 2H, $\mathrm{H^{6,6'}}$), 9.37 (d, 2H, $\mathrm{H^{4,4'}}$) ppm. $^4J(\mathrm{H^6H^4})$ = 2.6 Hz.

Results and discussion

Synthesis and configuration

The compounds $\{(\mu\text{-L})[\mathrm{MCl}(\eta^5\text{-}\mathrm{C_5Me_5})]_2\}(\mathrm{PF_6})$ were obtained as air-stable species by reaction of the azopyridyl ligands with $[(\mathrm{C_5Me_5})\mathrm{Cl_2M}]_2$ in acetone. The rather positive reduction potentials of the dinuclear systems (*cf.* below) caused the initial formation of the paramagnetic one-electron reduced species from which the diamagnetic $\{(\mu\text{-L})[\mathrm{MCl}(\eta^5\text{-}\mathrm{C_5Me_5})]_2\}(\mathrm{PF_6})_2$, M = Ir, could be obtained by oxidation with $\mathrm{NOPF_6}$ ($E_{1/2}$ = 0.87 V *vs.* $\mathrm{Fc^{+/0}}$ in $\mathrm{CH_3CN}$).[22] The paramagnetic dirhodium complexes also underwent colour changes on reaction with $\mathrm{NOPF_6}$, however, persistent compounds $\{(\mu\text{-L})[\mathrm{RhCl(C_5Me_5)}]_2\}(\mathrm{PF_6})_2$ could not be isolated. The oxidised products of the initial reactions (high-valent rhodium or iridium species) have not been established.

As outlined previously,[9,10] such dinuclear systems can exist as diastereoisomers with the two chloride ligands in either *syn* (*cis*) or *anti* (*trans*) position, relative to the plane of the bridging ligand. For a related bis(arene)osmium(II) derivative of bpym the *anti* (*trans*) isomer was established crystallographically.[23] The complex dications of $\{(\mu\text{-L})[\mathrm{IrCl(C_5Me_5)}]_2\}^{2+}$ were isolated in only one configuration according to the ^{1}H-NMR spectra; by analogy and considering the typically smaller metal–metal distances d < 5.1 Å in abpy-bridged dimers[12,14] relative to bpym-bridged dinuclear species (*ca.* 5.6 Å)[24] we assume these to be the *anti* isomers (Fig. 2). No statements can be made on the configuation of the radical species, EPR and UV/Vis spectra of *syn*/*anti* isomers may not differ greatly. The *anti* isomers would be the *meso* forms as the metals are centers of chirality; the strongly electron accepting azo nitrogen atoms are electronically quite different from the more basic but less π acidic pyridyl or pyrimidyl nitrogen atoms.[12]

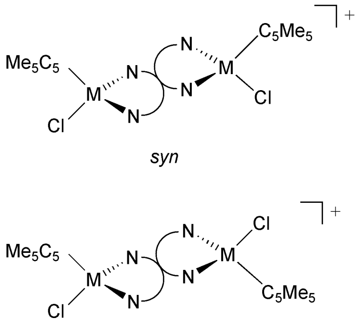


Fig. 2 Possible *syn* and *anti* isomers of dinuclear complexes.

Reduction of the complexes

Except for system **3**^{n} (L = abcp, M = Rh) the dinuclear complex ions $\{(\mu\text{-L})[\mathrm{MCl}(\eta^5\text{-C}_5\mathrm{Me}_5)]_2\}^n$ exhibit reversible one-electron transfer at relatively positive potentials *E*1 between the forms with $n = 2+$ and $n = 1+$. Consumption of 1e per molecule was verified coulometrically. Further reduction at *E*2 results in a chloride-dissociative quasi-reversible (*i.e.* slow) EC process to yield the two-electron mixed-valent species $[(\mathrm{C}_5\mathrm{Me}_5)\mathrm{ClM}(\mu\text{-L})\mathrm{M}(\mathrm{C}_5\mathrm{Me}_5)]^+$. In that respect, the dinuclear compounds are qualitatively similar to their mononuclear analogues[25] except for the less negative potentials, less facile chloride dissociation and thus higher stability of the paramagnetic "electron-reservoir" intermediate.[9,10] A typical cyclic voltammogram is shown in Fig. 3, the data according to Scheme 1 are summarised in Table 1. Small irregularities, *i.e.* features on plateaus behind the main peaks occurring at higher scan rates are ascribed to adsorption or isomerisation effects. Distortion of the anodic peak *E*2 can arise due to an insufficiently mobile chloride-dissociation equilibrium. In addition to a CE reoxidation mechanism (chloride association followed by electron transfer) at potential *E*2, a fraction of the chloride-free species can also be reoxidized *via* an EC mechanism at a slightly more positive potential.

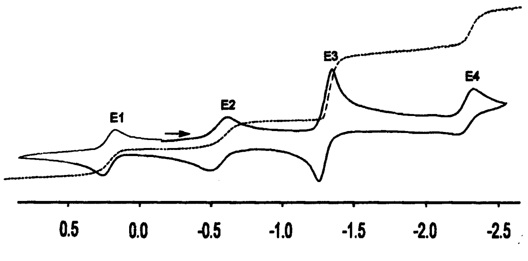
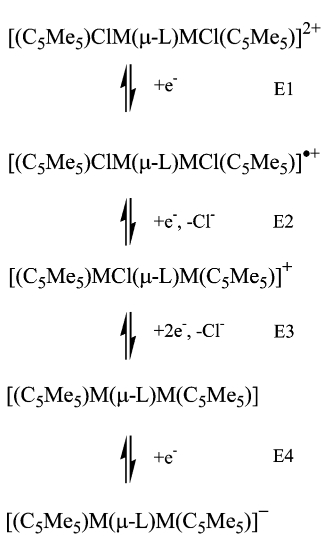


Fig. 3 Cyclic voltammogram of (**1**)(PF_6) in $\mathrm{CH}_3\mathrm{CN}$/0.1 mol dm^{-3} $\mathrm{Bu}_4\mathrm{NPF}_6$ at 50 mV s^{-1} (full line) and voltammogram at rotating Pt-disk electrode (dotted).



Scheme 1

Table 1 Electrochemical half-wave potentials[a] from cyclic voltammetry[b]

	*E*1	*E*2	*E*3	*E*4
(**1**)(PF_6)	0.24	− 0.51	− 1.26	− 2.34[d]
(**2**)(PF_6)	0.24	− 0.47	− 1.50	− 2.49[d]
(**3**)(PF_6)	0.51[c]	− 0.24	− 1.18	− 2.00
(**4**)(PF_6)	0.46	− 0.21	− 1.35	− 2.16[d]

[a] In V *vs.* ferrocene$^{0/+}$, determined as $(E_\mathrm{pc} + E_\mathrm{pa})/2$ (see Scheme 1). [b] At 100 mV s^{-1} scan rate in $\mathrm{CH}_3\mathrm{CN}$/0.1 mol dm^{-3} $\mathrm{Bu}_4\mathrm{NPF}_6$. [c] Anodic peak potential for irreversible oxidation. [d] Cathodic peak potential for irreversible reduction.

Table 2 Cathodic peak potentials[a] E_EC for chloride-dissociative EC steps in coupled dinuclear complexes $\{(\mu\text{-L})\mathrm{MCl}(\mathrm{C}_5\mathrm{Me}_5)]_2\}^n$

L	M	E_EC (1)	E_EC (2)[b]	ΔE_EC	Ref.
bpym	Rh	(−0.82)[b]	−1.33	(0.51)[b]	10
	Ir	−1.25[c]	−1.61[c]	0.36	10
bpip	Rh	−0.76	−1.25	0.49	9
	Ir	−0.83	−1.54	0.71	9
bptz	Rh	−1.06	−1.37	0.31	9
	Ir	−0.97	−1.48	0.51	9
abpy	Rh	−0.55	−1.30	0.75	This work
	Ir	−0.51	−1.53	1.02	This work
abcp	Rh	−0.27	−1.22	0.95	This work
	Ir	−0.25	−1.39	1.14	This work

[a] In V in $\mathrm{CH}_3\mathrm{CN}$/0.1 mol dm^{-3} $\mathrm{Bu}_4\mathrm{NPF}_6$ at 298 K. [b] Two-electron process. [c] In DMF/0.1 mol dm^{-3} $\mathrm{Bu}_4\mathrm{NPF}_6$ at 258 K.

The second metal reduction *E*3 proceeds in the chloride-releasing two-electron fashion as familiar from simple mononuclear species such as $[(\mathrm{C}_5\mathrm{Me}_5)\mathrm{ClM}(\mathrm{bpy})]^+$.[11,26] These processes leading to neutral compounds $\{(\mu\text{-L})[\mathrm{M}(\mathrm{C}_5\mathrm{Me}_5)]_2\}$ occur quasi-reversibly at rather negative potentials, causing effective splittings $\Delta E_\mathrm{EC} = E2 - E3$ from 0.75 V (Rh_2/abpy) to 1.14 V (Ir_2/abcp) between the first and the second *chemical* (EC) steps at the chosen scan rate of 100 mV s^{-1}. This splitting is much larger than the ΔE_EC values previously measured for bpym-, bpip- or bptz-bridged systems (Table 2).[9,10] Both the closer metal–metal distance and the more efficient metal–metal interaction mediation by the azopyridyl ligands[12] can be considered responsible for this effect; in agreement with previous results[27] we assume that the latter is more important. The special mediating capability of azopyridyl bridges as demonstrated in mixed-valence chemistry[27,28] is attributable to the low lying π* LUMO (b_g) which has about 80% contribution from the nitrogen atoms interfacing with the metal centres in dinuclear compounds.[12,15]

A further partially reversible one-electron reduction was observed for all systems at very negative potentials (*E*4) to yield the anionic $\{(\mu\text{-L})[\mathrm{M}(\mathrm{C}_5\mathrm{Me}_5)]_2\}^-$ (Fig. 3, Table 1). Characteristically,[9,25,26] these potentials are much lower than those of free abpy at −1.46 V or free abcp at −1.01 V,[12,16] confirming the substantial metal-to-ligand electron transfer in the ground state of neutral $\{(\mu\text{-L})[\mathrm{M(C_5Me_5)}]_2$. Supporting this interpretation, the EPR signal reported for mononuclear $[(\mathrm{abpy})\mathrm{Rh(C_5Me_5)}]^-$ ($g_1 = 2.16$, $g_2 = 2.002$, $g_3 = 1.945$) has shown substantial metal contributions according to the oxidation state description $[(\mathrm{abpy}^{-\mathrm{II}})\mathrm{Rh^{II}(C_5Me_5)}]^-$.[25]

In agreement with the better π acceptor properties of abcp *vs.* abpy[12,16,17,31] the complexes **3** and **4** display generally higher potentials E_n (Table 1) as well as larger splittings $\Delta E_{\mathrm{EC}} = E2 - E3$ (Table 2) and $E(\text{free ligand}) - E4$.

A comparison between dirhodium and diiridium analogues reveals that the latter are slightly easier to reduce with regard to the first EC step ($E2$) but exhibit more negative values $E3$ and $E4$, signifying the stronger donor effect of $\mathrm{Ir(C_5Me_5)}$.[26]

The stability of various redox states of the complexes, especially the isolability of the one-electron reduced forms, allowed us to carry out more detailed investigations by EPR at variable frequencies and by UV/Vis/NIR spectroelectrochemistry.

Information on the metal contribution to the singly occupied molecular orbitals (SOMOs) of radical complexes $\mathbf{1}^{\bullet+}$–$\mathbf{4}^{\bullet+}$ was expected from the g anisotropy determined at low-temperatures in frozen solution.[9] However, the X-band EPR spectra (9.5 GHz) were not sufficiently resolved, especially in the case of the rhodium compounds. No hyperfine coupling could be detected. We therefore resorted to EPR spectroscopy at high frequencies (>200 GHz) which helped to considerably separate the g components (Fig. 4). The EPR data are summarised in Table 3.

Table 3 EPR data of isolated radical complexes[a]

	g_1	g_2	g_3	Δg[b]	g_{iso}
(**1**)(PF$_6$)	1.996	1.993	1.990	0.006	1.993
(**2**)(PF$_6$)	1.979	1.971	1.954	0.025	1.968
(**3**)(PF$_6$)	1.997	1.997	1.994	0.003	1.996
(**4**)(PF$_6$)	2.002	1.976	1.945	0.057	1.974

[a] g Tensor components from high frequency (285 GHz) measurements at 5 K in toluene/dichloromethane, g_{iso} values from X-band EPR at 295 K in CH$_3$CN. [b] $\Delta g = g_1 - g_3$.

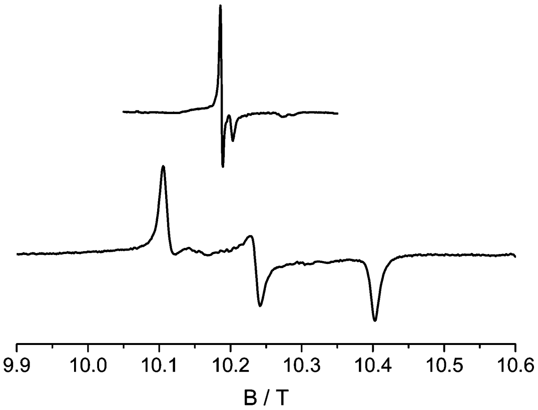


Fig. 4 285 GHz EPR spectra of (**3**)(PF$_6$) (top) and (**4**)(PF$_6$) (bottom) at 5 K in toluene/dichloromethane.

The illustration in Fig. 4 and the results from Table 3 show a very pronounced difference between corresponding dirhodium and diiridium complexes. The g anisotropy $\Delta g = g_1 - g_3$ is much larger for the complexes of the heavier (5d) homologue, an effect, which has been observed to a similar extent for other species $\{(\mu\text{-L}')[\mathrm{MCl}(\eta^5\text{-}\mathrm{C_5Me_5})]_2\}^{\bullet+}$, L′ = bpip, bptz.[9] Tentatively, we assume that this unusually large difference is not only due to the higher spin–orbit coupling constant of Ir *vs.* Rh[9,29,30] but also due to enhanced metal participation in the case of $\mathbf{2}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$. The Δg values for the dirhodium complexes $\mathbf{1}^{\bullet+}$ and $\mathbf{3}^{\bullet+}$ are particularly small which may be attributed to a virtual lack of Rh$^{\mathrm{III}}$–ligand π interaction. This hypothesis will have to be verified by appropriate calculations[31] in order to quantify the amount of the metal participation at the SOMO and to rationalise the deviation of g factors to values slightly below 2. However, the relatively small g anisotropies Δg determined for $\mathbf{1}^{\bullet+}$–$\mathbf{4}^{\bullet+}$ in comparison to mixed-valent dirhodium or diiridium species with largely metal-centered spin[9,30] clearly points to a radical formulation $\mathrm{M^{III}(L^{\bullet-})M^{III}}$ with the spin residing in the largely azo-localised π* MO of the azopyridyl bridging ligands.[31,32] The distinctly higher Δg value for the abcp/Ir$_2$ complex confirms the higher π acceptor capacity of that ligand[12,16,17] in relation to abpy, a result which has similarly been observed and theoretically confirmed for the complexes $\{(\mu\text{-L})[\mathrm{Re(CO)_3Cl}]_2\}^{\bullet-}$.[31] However, steric factors may also play a role in

Table 4 Absorption data[a] from spectroelectrochemistry[b]

	L = abpy		L = abcp	
	M = Rh	M = Ir	M = Rh	M = Ir
$\{(\mu\text{-L})[\mathrm{MCl(C_5Me_5)}]_2\}^{2+}$	340 (11.9)		342 (11.9)	323 (16.2)
	370sh	390sh, 405 (12.0), 430sh		395sh, 419 (9.5), 450sh
	550sh		490sh	
		631 (7.5)		694 (7.0)
$\{(\mu\text{-L})[\mathrm{MCl(C_5Me_5)}]_2\}^{\bullet+}$	345 (9.7), 370 (10.5)	334 (9.5), 366 (9.7)	360sh, 373 (14.0)	310 (15.6), 358 (16.5)
	433 (5.5)			
	570sh, 680sh, 940sh	458 (7.6)	474 (4.5)	510 (6.2)
		515sh, 575sh, 730 (1.8)	570 (4.3)	560sh, 630sh, 790sh
			750sh	
$[\mathrm{(C_5Me_5)M(\mu\text{-}L)MCl(C_5Me_5)}]^+$		357 (8.6)	340 (19.1), 353 (20.7), 370sh	349 (21.2)
	460sh			
	680 (8.5)	546 (13.0)		540 (4.4)
			570 (2.3)	
$\{(\mu\text{-L})[\mathrm{M(C_5Me_5)}]_2\}$			325 (14.2)	
	320 (19)	345sh	345 (14.0), 390sh	373 (16.3)
	575 (5.5)	628 (8.0)		750 (8.0)
	830sh	900sh	640sh, 718 (7.3)	1160sh
	960	993 (10.0)	1045 (5.0)	1298 (5.9)
			1175 (5.3)	
$\{(\mu\text{-L})[\mathrm{M(C_5Me_5)}]_2\}^-$	342 (12.5)	n.d.	351 (13.3)	366 (18.1)
	495 (4.8)		512 (3.4)	520sh, 700sh

[a] λ_{max} in nm; ε (in parentheses) in $10^3\ \mathrm{mol^{-1}\ dm^3\ cm^{-1}}$. [b] In CH$_3$CN/0.1 mol dm^{-3} Bu$_4NPF_6$.

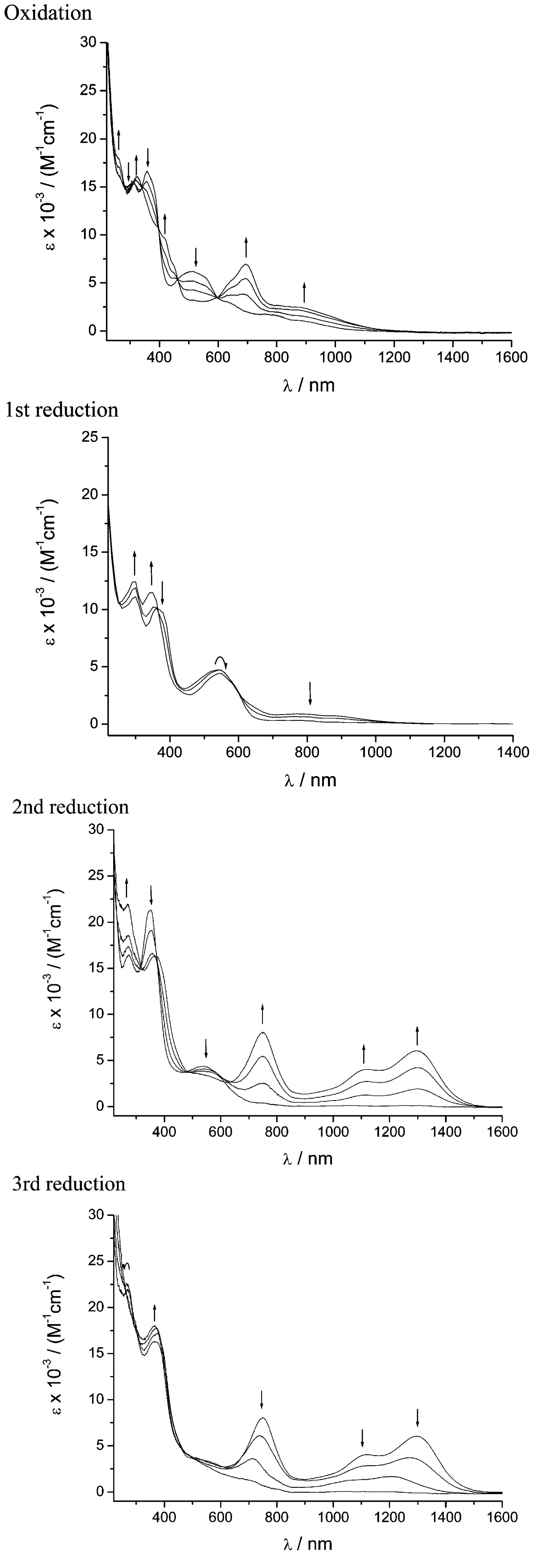


Fig. 5 Spectroelectrochemical oxidation and stepwise reduction of (**4**)(PF_6) in CH_3CN/0.1 mol dm^{-3} Bu_4NPF_6.

metal/ligand orbital mixing which would explain the higher *g* anisotropies[9c] of complexes $\{(\mu\text{-bpip})[MCl(C_5Me_5)]_2\}^{\bullet+}$ despite the poorer π acceptor capacity of the bpip (= 2,5-bis(1-phenyliminoethyl)pyrazine) ligand.[33] Mixed-valence complexes $\{(\mu\text{-L})[M(C_5Me_5)]_2\}^+$ which were observable for L = bpip with large *g* factor splittings $\Delta g > 0.2$[9] could not be detected here for L = abpy or abcp.

UV/Vis/NIR spectroelectrochemistry using an OTTLE cell was used to characterise not only $\mathbf{1}^{2+}$–$\mathbf{4}^{2+}$ and $\mathbf{1}^{\bullet+}$–$\mathbf{4}^{\bullet+}$ but also the two- and four-electron reduced species (Scheme 1, Fig. 5, Table 4). The spectra of the (2+) ions are dominated, especially for the diirdidium species, by ligand-to-metal charge transfer transitions from M–Cl bonds to the π* MO of the acceptor bridge. Recently obtained calculation results for the model system $[(bpy)IrCl(C_5H_5)]^+$ support this interpretation.[34]

Reduction of the dications at *E*1 results in a shift and partial intensity loss of the CT bands while features between about 430 and 510 nm, attributed to intraligand transitions of the azopyridyl radical anions,[12,34] become observable. The first EC reduction (at *E*2) to the formally dimetal(I,III) species $[(C_5Me_5)M(\mu\text{-L})MCl(C_5Me_5)]^+$ produces spectra with the expected[9,26,34] intense bands in the visible between about 540 and 680 nm which are further intensified and bathochromically shifted to between 960 and 1300 nm after the next (*E*3) two-electron process (Fig. 5, Tab. 4), leading to the "dimetal(I)" systems $(\mu\text{-L})[M(C_5Me_5)]_2$. There appears to be vibrational structuring of these intense bands ($\Delta\nu \approx 1000$ cm^{-1}) in agreement with previous observations on related species.[9,26] There is also a second intense band between 575 and 750 nm which, like the first, is attributed to a transition between strongly mixed metal d_π orbitals and the π* MO of the acceptor ligand. Two transitions are expected for a three-centre system M(L)M with three mixed orbitals and four electrons.

It is remarkable that these transitions lie at lower energies for the complexes with the stronger donor $(Me_5C_5)Ir$ and the better acceptor ligand L = abcp, which would be compatible with an MLCT situation.[35] The reverse is observed for the mixed compounds $\{(Me_5C_5)ClM(\mu\text{-L})M(C_5Me_5)]\}^+$ and for mononuclear species.[25,26]

Conclusions

Summarising, we have shown that the combination of two $[(Me_5C_5)ClM]^+$ or $(Me_5C_5)M$ systems (M = Rh or Ir) with the unique bridging azopyridyl acceptors abpy and abcp yields a number of unusual results such as isolable radical complexes $\mathbf{1}^{\bullet+}$–$\mathbf{4}^{\bullet+}$ with small *g* anisotropies as the most stable products, very large potential separations ΔE_{EC} between the chloride-productive EC steps, and intense near-infrared absorptions for the spectroelectrochemically studied four-electron reduced neutral species $(\mu\text{-L})[M(C_5Me_5)]_2$. Although efforts to structurally characterise these particular species have not yet been successful such attempts will continue to possibly gain further information on such organometallic redox pairs.[36] The suitability of azo-containing ligands to form stable radical complexes is once more confirmed[16,31,32,37] as is the use of high frequency EPR spectroscopy[31] in organometallic redox chemistry.

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