Electrochemical, spectroscopic and EPR study of transition metal complexes of dipyrido[3,2-*a*:2′,3′-*c*]phenazine

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The electronic structures of the complexes $[Ru(dppz)_3]^{2+}$ and $(dppz)ML_n$, $ML_n = [Ru(bpy)_2]^{2+}$, $[Os(phen)_2]^{2+}$, $[Cu(PPh_3)_2]^+$, $Re(CO)_3Cl$, $Mo(CO)_4$, $PtPh_2$ or $Pt(Mes)_2$ (Mes = 2,4,6-trimethylphenyl), have been compared, based on cyclic voltammetry and spectroscopic studies (UV/vis, EPR of paramagnetic states). According to all experimental evidence, the lowest lying π^* orbital of dppz which is singly occupied in complexes of the dppz radical anion is localised almost exclusively in the phenazine part of the ligand. Amongst the consequences of this situation are a very weak coupling of the first three reduction processes of $[Ru(dppz)_3]^n$, very little difference in the reduction potentials and in the EPR spectra of the radical complexes $(dppz^{\cdot-})ML_n$, and absorption spectra with the intense MLCT transitions to higher lying α-diimine orbitals.

There has been much recent interest in the study and possible application of small, functionally active transition metal co-ordination compounds which can interact in a site-specific manner with DNA.[1–4] Amongst the the most frequently used components of such systems have been complexes of ruthenium(II),[5,6] osmium(II),[7,8] rhenium(I),[6e,9–11] copper(I),[11] nickel(II)[12] and cobalt(III)[12] with the dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz) ligand.

The heterocyclic π system of dppz combines the chelating function of α-diimines ("polypyridines" such as 2,2′-bipyridine, bpy, or 1,10-phenanthroline, phen)[13,14] with the electron transfer/proton transfer capacity of 1,4-diazines (pyrazines, quinoxalines, phenazines, *etc.*).[15,16] Molecular orbital calculations and experiments with $[Ru(bpy)_2(dppz)]^n$ have shown that the particular connection between both functions in dppz leads to the controlled access of H^+ to the $N^{9,14}$ (1,4-diazine) sites which are also the centres of one- or two-electron reduction.[6d] The α-diimine π acceptor site can interact with the π electron rich ruthenium(II) center in the established manner,[14] however the α-diimine acceptor orbitals $b_1(\psi)$ and $a_2(\chi)$[13,17] were shown

to lie *above* the phenazine-based π^* MO, $b_1(phz)$, and the latter seemed to have very little contribution from the α-diimine π centers.
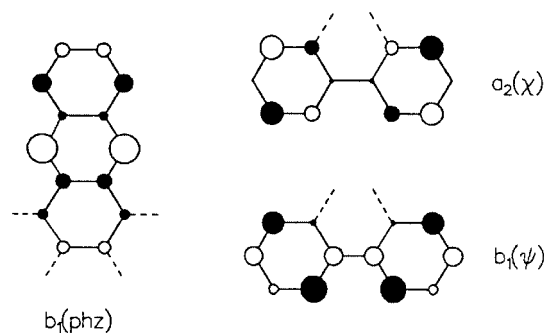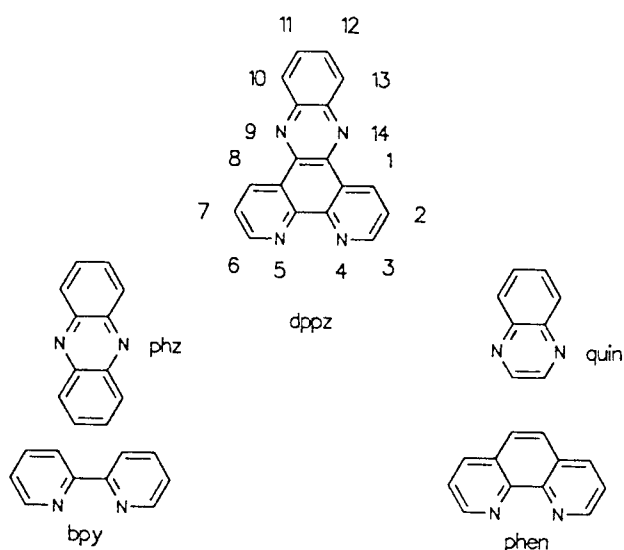
In combination with the potentially intercalating behaviour of dppz,[5,7] this special electronic constellation can be exploited by using $[Ru(bpy)_2(dppz)]^{2+}$ and derivatives as "molecular light switches":[5a] The metal-to-ligand charge transfer (MLCT) luminescence is quenched in water but not in aqueous solutions of micelles[6c] or DNA[5] due to a possibly specific intercalation of the phenazine portion of dppz into a hydrophobic pocket.

Previous studies on complexes such as $[Ru(bpy)_2(dppz)]^{2+}$ have revealed the divergence between "redox" and "optical" π acceptor orbitals.[6a–d] In order to add experimental evidence to the existing concept of the electronic structure of dppz and its co-ordination compounds we have now studied the complexes $[Ru(dppz)_3]^{2+}$ and $(dppz)ML_n$, $ML_n = [Ru(bpy)_2]^{2+}$, $[Os(phen)_2]^{2+}$, $[Cu(PPh_3)_2]^+$, $Re(CO)_3Cl$, $Mo(CO)_4$, $PtPh_2$ or $Pt(Mes)_2$ (Mes = mesityl = 2,4,6-trimethylphenyl). The latter, heteroleptic compounds were investigated with respect to their absorption spectroscopy and one-electron reduction (cyclic voltammetry, EPR); nuclei such as $^{63,65}Cu$, ^{189}Os, $^{185,187}Re$ or ^{195}Pt with large magnetic moments and isotropic hyperfine constants[18] should reveal any significant metal participation at the singly occupied MO (SOMO) in radical complexes.[19–22] Furthermore, organometallic fragments such as $Re(CO)_3Cl$ or PtR_2 are well known to facilitate the reduction of co-ordinated α-diimine ligands, if there is any significant orbital overlap at

Table 1 Cyclic voltammetry[a] data of complexes (dppz)ML$_n$

ML$_n$	E_{ox}	E_{red1}	E_{red2}	E_{red3}	E_{red4}	Solvent[b]
—	n.d.	−1.60	−2.49	−2.99(irr.)[c]		DMF[d]
[Ru(bpy)$_2$]$^{2+}$	0.85[e]	−1.36	−1.79	−1.99	−2.31	DMF[d]
[Os(phen)$_2$]$^{2+}$	0.40	−1.42	−1.67	−1.96(irr.)[c]		DMF
Re(CO)$_3$Cl	0.92[e,f]	−1.42	−2.00	−2.66(irr.)[c]		THF
[Cu(PPh$_3$)$_2$]$^+$	1.20[f,g]	−1.45	−2.09	−2.42(irr.)[c]		THF
Mo(CO)$_4$	n.d.	−1.54	−2.37	−2.82(irr.)[c]		THF
PtPh$_2$	0.69[f]	−1.54	−2.29			THF
Pt(Mes)$_2$	0.49	−1.50	−2.24			THF

[a] At 100 mV s^{-1} scan rate, potentials in V vs. ferrocenium–ferrocene. [b] In 0.1 mol dm^{-3} Bu$_4$NPF$_6$. [c] Peak potential for irreversible reduction. [d] From ref. 6(d). [e] In acetonitrile (ref. 6(d)). [f] Peak potentials for irreversible oxidation. [g] In DMF.
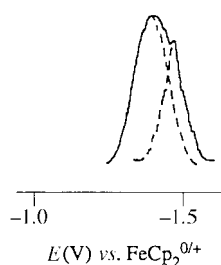

Fig. 1 Differential pulse polarogram (——) of [Ru(dppz)$_3$][PF$_6$]$_2$ in DMF–0.1 mol dm^{-3} Bu$_4$NPF$_6$ at 2 mV s^{-1} and 12.5 mV modulation (----: deconvolution).

the metal/ligand interface.[21,22] The homoleptic complex [Ru(dppz)$_3$]$^{2+}$, on the other hand, raises the question[14,23,24] of metal-mediated interaction between the three equivalent but only indirectly connected phenazine moieties.

Results and discussion

The compounds [Ru(dppz)$_3$][PF$_6$]$_2$ and [Mo(CO)$_4$(dppz)] were obtained from dppz and complementary fragments according to established procedures for the synthesis of α-diimine complexes.[14,23,25] The known compounds [Ru(bpy)$_2$(dppz)][PF$_6$]$_2$, [Os(phen)$_2$(dppz)][PF$_6$]$_2$, [Cu(PPh$_3$)$_2$(dppz)][BF$_4$], [Re(CO)$_3$Cl(dppz)], [PtPh$_2$(dppz)] and [Pt(Mes)$_2$(dppz)] were prepared as reported.[6d,7,11,22b]

The electrochemically active compounds were studied using cyclic voltammetry (Table 1) and, in the case of [Ru(dppz)$_3$]-[PF$_6$]$_2$, differential pulse polarography (DPP); the latter technique was used because of its superior resolution (Fig. 1). All complexes (dppz)ML$_n$ show *one* first reversible one-electron reduction wave at about −1.45 V vs. ferrocenium–ferrocene, slight differences correlating with the charge at the metal centre. In contrast, the homoleptic complex [Ru(dppz)$_3$]$^{2+}$ exhibits three very close reduction processes in DMF–0.1 mol dm^{-3} Bu$_4$NPF$_6$ which could be resolved into a two-electron wave at −1.35 V and a one-electron process at −1.42 V *via* the DPP experiment (Fig. 1).

In less congested form, such a pattern with increasing potential separation for the reduction of equivalent ligands is common for tris(ligand)ruthenium(II) complexes;[23,24] it reflects the Coulombic (charge) effects on successive electron addition. The localisation of charge on the peripheral phenazine "tails" of the dppz ligands (cf. below) is responsible for the very small separation $\Delta = E_{red}^{(2+/+)} - E_{red}^{(0/-)}$ of only 70 mV; other tris-(α-diimine)ruthenium(II) complexes exhibit separations $\Delta = 300$–900 mV.[23,24] Unfortunately, the following reduction processes for [Ru(dppz)$_3$]$_n$, beginning with $E_{pc}^{(-/2-)} = -2.07$ V, are not fully reversible.

While the similarity of the first reduction potential of all complexes confirms the phenazine-based b$_1$ π orbital as the lowest unoccupied MO, the second reduction is dppz based for the complexes of Pt^{II}, Mo^0, Cu^I and Re^I ($E_{red1} - E_{red2} > 0.58$ V)
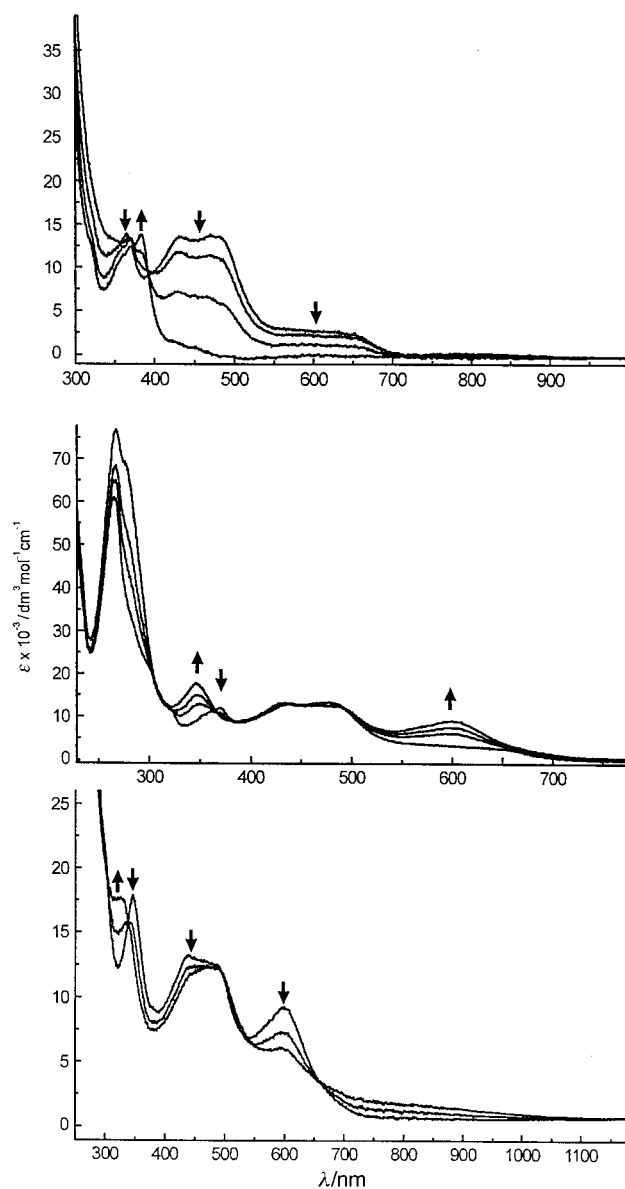

Fig. 2 Spectroelectrochemical response of [Os(phen)$_2$(dppz)]$^{n+}$ on one-electron oxidation (top, ($n = 2$) ⟶ ($n = 3$)) and two one-electron reduction processes (center, ($n = 2$) ⟶ ($n = 1$) and bottom, ($n = 1$) ⟶ ($n = 0$)) in CH$_3$CN–0.1 mol dm^{-3} Bu$_4$NPF$_6$.

but centered on the α-diimine co-ligand for [Ru(bpy)$_2$(dppz)] and [Os(phen)$_2$(dppz)].[6d,7] Oxidation potentials for reversible processes could be determined only for three systems, *i.e.* for Ru^{II}–Ru^{III}, Os^{II}–Os^{III} and Pt^{II}–Pt^{III} couples (Table 1).

The UV/vis spectra of the dppz complexes and of some of their reduction products from present (Figs. 2,3) or earlier[6d,11] spectroelectrochemical studies are listed in Table 2.

Table 2 Absorption spectral data of complexes $(dppz)ML_n$

Compound	$\lambda_{max}\ (\varepsilon)^a$	Solvent
dppz	379, 367 (sh); 359, 350 (sh), 340 (sh)	DMF[b]
dppz˙⁻	572, 545; 450; 384, 363	DMF[b]
dppz²⁻	719; 475 (sh), 456; 367	DMF[b]
$[Ru(bpy)_2(dppz)]^{2+}$	451, 435 (sh); 367, 357	DMF[b]
$[Ru(bpy)_2(dppz)]^{˙+}$	650 (sh), 588; 456, 435 (sh); 347	DMF[b]
$[Ru(bpy)_2(dppz)]$	588, 535, 495, 460 (sh); 360 (sh), 347	DMF[b]
$[Ru(dppz)_3]^{2+}$	460 (sh), 436 (18), 369 (37), 360 (36); 320 (sh), 282 (135)	DMF
$[Ru(dppz)_3]^{˙-}$	594 (34), 563 (sh); 464 (32); 382 (sh), 350 (70), 300 (75)	DMF
$[Os(phen)_2(dppz)]^{2+}$	600 (sh); 470 (13.2), 430 (13.2); 370 (12.6)	CH_3CN
$[Os(phen)_2(dppz)]^{3+}$	385 (13.2), 370 (12.6)^c	CH_3CN
$[Os(phen)_2(dppz)]^{˙+}$	600 (11.4); 470 (15.3); 430 (13.2); 350 (21)	CH_3CN
$[Os(phen)_2(dppz)]$	600 (7.8); 485 (15.3), 440 (14.0); 320 (21)	CH_3CN
$[Re(CO)_3Cl(dppz)]$	378 (sh), 360	CH_2Cl_2
	360 (13.8)	$CH_2Cl_2{}^d$
$[Re(CO)_3Cl(dppz)]^{˙-}$	584 (9.5), 336 (21.8)	$CH_2Cl_2{}^d$
$[Cu(PPh_3)_2(dppz)]^+$	375, 360 (sh)	CH_2Cl_2
	364 (8.6)	$CH_2Cl_2{}^d$
$[Cu(PPh_3)_2(dppz)]^{˙}$	587 (4.5); 335 (13.1)	$CH_2Cl_2{}^d$
$[Mo(CO)_4(dppz)]$	472; 373, 355	CH_2Cl_2
$[PtPh_2(dppz)]$	483 (2.83), 463 (2.79); 379 (12.3), 363 (12.1), 348 (10.9)	Toluene
$[Pt(Mes)_2(dppz)]$	581 (sh), 513, 471 (sh); 378, 362, 345	Toluene

^{a} λ_{max} values in nm, molar absorption coefficients in $10^3\ dm^3\ mol^{-1}\ cm^{-1}$. ^{b} From ref. 6($d$); for ε values see figures therein. ^{c} Very weak additional bands in the visible region. ^{d} From ref. 11.
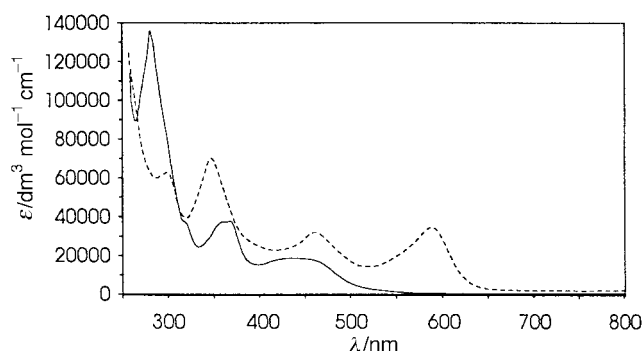
Fig. 3 Spectroelectrochemical response of $[Ru(dppz)_3][PF_6]_2$ (——) on three-electron reduction (----) in DMF–0.1 mol dm^{-3} Bu$_4$NPF$_6$.

The ligand dppz is a prototypical acceptor with different "redox" and "optical" π* orbitals.[6a–d] Specifically, the lowest lying unoccupied π MO of b_1(phz) symmetry is phenazine based (*cf.* electrochemistry and EPR) with very little contributions and effects from the α-diimine chelate site and the metal co-ordinated there. MLCT Transitions to that b_1(phz) MO are therefore very weak and usually not detectable. Observable MLCT transitions based on sizeable d(M)/π* overlap can occur between d_π orbitals of the chelated metal and higher lying α-diimine-based unoccupied MOs of the $b_1(\psi)$ and $a_2(\chi)$ type.[6d] In agreement with other, related α-diimine complexes,[14,22,23,26] intense singlet MLCT absorption bands in the 400–500 nm region of the visible were observed for complexes between dppz and Mo⁰, Ru[II], Os[II] and Pt[II], whereas the compounds $[Cu(PPh_3)_2(dppz)][BF_4]$ and $[Re(CO)_3Cl(dppz)]$ exhibit only MLCT shoulders around 370 nm which overlap with the typical[6d] strong intraligand (π ⟶ π*) absorption of dppz. The lower intensity and higher energy of MLCT bands of complexes (α-diimine)ML$_n$ with M = Cu[I] and Re[I] is established.[21,27,28] More than one MLCT band is observed for the complexes of square planar[6j] platinum(II) because of the closeness of several transitions from one of the four filled d levels (d⁸ situation) and because of the rigidity and reduced number of vibrating (and thus band-broadening) ligands.[22] Close-lying but still separable singlet MLCT transitions are possible to both dppz and the α-diimine co-ligands in $[Ru(bpy)_2(dppz)]^{2+}$ and $[Os(phen)_2(dppz)]^{2+}$. The osmium(II) complex is further

distinguished by additional weak long-wavelength features around 600 nm (Fig. 2) which we attribute to triplet MLCT absorptions because of the very high spin–orbit coupling of osmium(II).[7]

dppz-Centered reduction always produces a long-wavelength band between 570 and 600 nm (Figs. 2,3, Table 2) from an intraligand (IL) π ⟶ π* transition.[6d] Further reduction of the osmium compound involves one of the 1,10-phenanthroline co-ligands as evident from the remaining IL band of dppz˙⁻. Oxidation to the osmium(III) compound removes the MLCT bands from the visible to the ultraviolet region; very weak, broad features remaining in the visible part of the spectrum are attributed to Laporte-forbidden ligand-field (LF, d ⟶ d) transitions of the 5d⁵ system $[Os(phen)_2(dppz)]^{3+}$.

Following the reversible one-electron reduction processes of the complexes with dppz, the paramagnetic reduction products were studied by EPR. All complexes (dppz˙⁻)ML$_n$ gave essentially similar EPR spectra (Fig. 4) which are dominated by a quintet ($a \approx 0.5$ mT), caused by the coupling of the unpaired electron with two equivalent ¹⁴N centers. Smaller coupling can be accounted for by two sets of pairs of ¹H nuclei in some instances, however no metal isotope coupling could be detected in any case (Table 3) despite the large isotropic hyperfine constants a_0 of *e.g.* ¹⁸⁵,¹⁸⁷Re ($a_0 = 1253.60$ and 1266.38 mT, respectively) or ¹⁹⁵Pt ($a_o = 1227.84$ mT) nuclei (Fig. 4).[18] As the comparison with the "free ligand" radical anion shows, this hyperfine splitting pattern resembles the orbital composition of the b_1(phz) MO. Only the increased linewidths and the slight variations of a(¹⁴N) and g reflect the marginal participation (<1%) of the co-ordinated heavy transition metals at the singly occupied MO. The somewhat lowered nitrogen coupling for the Ru(bpy)$_2$ and Os(phen)$_2$ complexes may reflect strong π back donation from those metal centres or the closeness of the π* MOs of the co-ligands 2,2′-bipyridine or 1,10-phenanthroline, respectively (*cf.* Table 1). The g factor deviation from the ligand radical value is largely determined by the spin–orbit coupling constant[18] of the transition metal.[29] In agreement with their relatively high oxidation state and position in the third row of the d block elements, the osmium(II) and platinum(II) systems exhibit the most notable effects on g. Nevertheless, the small g anisotropy observed for the platinum systems (none detected for $[Os(phen)_2(dppz)]^{˙+}$ in the X band) confirms the very small participation of the metal at the singly occupied MO.

Reduction of $[Ru(dppz)_3]^{2+}$ yields only a broad, unresolved

Table 3 EPR Data of complexes (dppz$^{\cdot-}$)ML$_n$[a]

ML$_n$	g	a[b]				Solvent
		N[9,14]	H[10,13]	N[4,5]	H	
—	2.0032	0.505	0.183	0.021	[c]	THF
[Ru(bpy)$_2$]$^{2+}$	2.00336	0.48	0.13	0.07	0.07[d]	CH$_2$Cl$_2$
[Os(phen)$_2$]$^{2+}$	2.00395	0.45		Not resolved		CH$_3$CN
Re(CO)$_3$Cl	2.00346	0.497	0.149	0.065	0.065[e]	CH$_2$Cl$_2$
[Cu(PPh$_3$)$_2$]$^+$	2.00339	0.54		Not resolved		CH$_2$Cl$_2$
Mo(CO)$_4$	2.00333	0.52		Not resolved		THF
PtPh$_2$	2.0039[f]	0.50		Not resolved		DCE
Pt(Mes)$_2$	2.0035	0.52		Not resolved		DCE

[a] From cathodic reduction in CH$_2$Cl$_2$, DCE (1,2-dichloromethane) or CH$_3$CN–0.1 mol dm^{-3} Bu$_4$NPF$_6$ or reaction with K in THF. [b] Coupling constants in mT. [c] Additional hydrogen coupling constants 0.143, 0.094 and 0.056 mT (ref. 6(d)). [d] Additional hydrogen coupling constants (ref. 6(d)). [e] Additional hydrogen coupling constants. [f] $g_\parallel = 2.0084$, $g_\perp = 2.0018$ at 110 K.
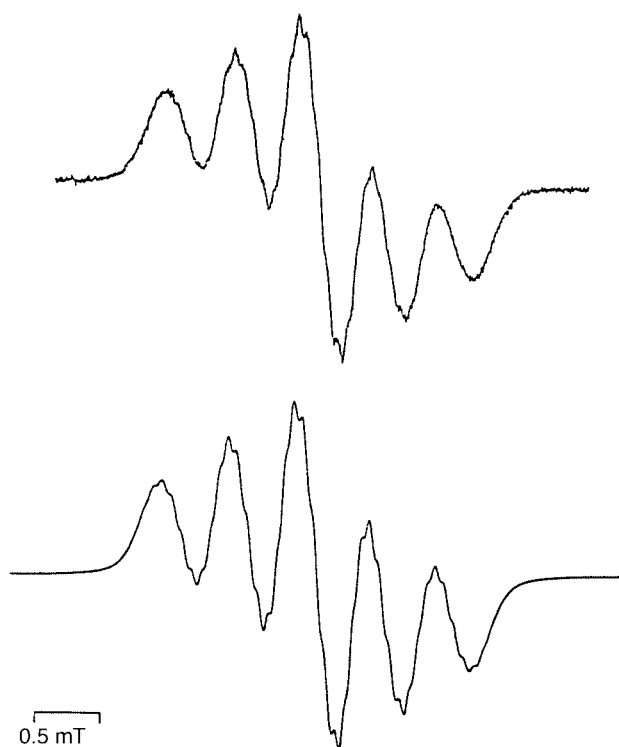

Fig. 4 The EPR spectrum of [Re(CO)$_3$Cl(dppz)]$^{\cdot-}$, generated by electrochemical reduction of the precursor at 293 K in CH$_2$Cl$_2$–0.1 mol dm^{-3} Bu$_4$NPF$_6$ with computer simulation (0.09 mT linewidth).

EPR signal at $g = 2.0031$ which indicates little or no participation of the metal and possible migration of the unpaired electron between the separated π^* sites as is well known from other such paramagnetic tris(ligand)ruthenium(II) compounds.[30,31]

Summarising, all complexes between dppz and the relatively low-valent metal centres described in this work have the phenazine-based b$_1$(phz) orbital as the lowest-lying MO which is occupied on electron addition. The planar phenazine part of the complexes is also the one that engages in π intercalation e.g. with DNA[1–5,7] and in intramolecular association as apparent from available crystal structures.[5c,j,6i,j,9] The situation in dppz complexes with higher-valent reducible metals such as e.g. rhodium(III) or iridium(III) remains to be studied.

Experimental

The compounds dppz, [Ru(bpy)$_2$(dppz)][PF$_6$]$_2$, [Os(phen)$_2$(dppz)][PF$_6$]$_2$, [Cu(PPh$_3$)$_2$(dppz)][BF$_4$], [Re(CO)$_3$Cl(dppz)], [PtPh$_2$(dppz)] and [Pt(Mes)$_2$(dppz)] were synthesized according to literature procedures.[6d,7,11,22b]

Tetracarbonyl(dipyrido[3,2-a:2′,3′-c]phenazine)molybdenum

Solutions of 20 mg (0.070 mmol) [Mo(CO)$_4$(nbd)] (nbd = norbornadiene) and 20 mg (0.070 mmol) dppz in THF were combined and stirred for 15 min at ambient temperature. n-Heptane was added to the red solution and the more volatile THF removed under vacuum. After decanting n-heptane the remaining solid was recrystallised from dichloromethane–n-hexane to yield 20 mg (51%) of CH$_2$Cl$_2$ containing product. Found: C, 48.09; H, 1.98; N, 10.01. C$_{22}$H$_{10}$N$_4$O$_4$·CH$_2$Cl$_2$ requires C, 48.02; H, 2.10; N, 9.74%. $\tilde{\nu}_{CO}$/cm^{-1} (THF): 2000s, 1895vs, 1880s and 1835(sh).

Tris(dipyrido[3,2-a:2′,3′-c]phenazine)ruthenium(II) bis(hexafluorophosphate)[6a]

A solution of 60 mg (0.125 mmol) [Ru(DMSO)$_4$]Cl$_2$[32] and 105 mg (0.375 mmol) dppz in 50 ml ethanol was heated to reflux for 3 h. Addition of 163 mg (1 mmol) NH$_4$PF$_6$ in 50 ml ethanol, volume reduction to about 1/4 and slow addition of toluene yielded the complex which was chromatographed on neutral alumina, 200 mesh, with ethanol–acetonitrile (5:1) as eluent. The orange-red fraction gave 80 mg (52%) of [Ru(dppz)$_3$][PF$_6$]$_2$ as its ethanolate. Found: C, 52.25; H, 3.06; N, 12.55. C$_{54}$H$_{30}$F$_{12}$N$_{12}$P$_2$Ru·2C$_2$H$_5$OH requires C, 52.33; H, 3.15; N, 12.63%.

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, infrared spectra using a Perkin-Elmer 684 instrument and UV/Vis/NIR absorption spectra on Shimadzu UV160 and Bruins Instruments Omega 10 spectrophotometers. Cyclic voltammetry was carried out at 100 mV s^{-1} scan rate in 0.1 mol dm^{-3} Bu$_4$NPF$_6$ solutions using a three-electrode configuration (glassy carbon working electrode, platinum counter electrode, Ag–AgCl reference) and a PAR 273 potentiostat and function generator. The ferrocene–ferrocenium couple served as internal reference. Differential pulse polarography was carried out with a PA-3 potentiostat from Laboratorni pristoje Praha (Czech Republic) at a mercury drop electrode. Spectroelectrochemical measurements were performed using an optically transparent thin-layer electrode (OTTLE) cell[33] for UV/Vis spectra and a two-electrode capillary for EPR studies.[31]

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