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Studies on some mixed-ligand complexes of ruthenium(II) involving dithiocarboxylates, dithiocarbamates, triphenylphosphine and bipyridine

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Abstract—Ruthenium(II) complexes $[Ru(R\text{-}acda)_2(PPh_3)_2]$ (**1a–e**), $[Ru(R\text{-}acda)(bpy)_2](ClO_4)$(**2a–d**), $[Ru(R\text{-}acda)(phen)_2](ClO_4)$(**2e–g**), $[Ru(R_2\text{-}dtc)(bpy)_2](ClO_4)$(**3a, b**) and $[Ru(R_2\text{-}dtc)(phen)_2](ClO_4)$(**3c, d**) (where R-acdaH = 2-alkylamino-1-cyclopentene-1-dithicarboxylic acid, R_2-dtcNa = sodium *N,N'*-dialkyl dithiocarbamate, bpy = 2,2′-bipyridine and phen = 1,10-phenanthroline) have been synthesized and characterized. The ^1H NMR spectra of the phosphine complexes (**1a–e**) show that, with the increase in the chain length of the alkyl group of R-acda$^-$, the N-alkylamino proton becomes more deshielded and is accompanied by a shift of the NH stretching frequency ν(NH) to lower energy. A linear relationship is obtained between the chemical shift δ(NH) and ν(NH). All the complexes exhibit absorption bands due to $d\pi \rightarrow \pi^*$ (bpy, phen or PPh_3), $d\pi \rightarrow \pi^*$ (R-acda$^-$ or R_2-dtc$^-$) charge transfer transitions and $\pi \rightarrow \pi^*$ intraligand transition. Complexes **1a–e** undergo two irreversible oxidations, $Ru^{II} \rightarrow Ru^{III}$ and $Ru^{III} \rightarrow Ru^{IV}$, while the other complexes (**2, 3**) exhibit one reversible (Ru^{II}/Ru^{III}) and one irreversible ($Ru^{III} \rightarrow Ru^{IV}$) oxidation process. Copyright © 1996 Elsevier Science Ltd

Keywords: Ru^{II} complexes; mixed-ligand Ru^{II} complexes; dithiocarboxylates of Ru^{II}; dithiocarbamates of Ru^{II}; thioacid ligands; electrochemistry of Ru^{II}.

Mononuclear ruthenium(II) polypyridine complexes have been the focus of attention because of their unique chemical stability and interesting redox properties [1–5]. However, the chemistry of mixed-ligand mononuclear ruthenium(II) complexes containing polypyridine and dithiocarboxylates or dithiocarbamates has not been studied much. Herein, we report the synthesis, characterization and electrochemical behaviour of a series of monomeric mixed-ligand ruthenium(II) complexes (**1a–e, 2a–g, 3a–d**) derived from the (S, S$^-$) donor ligands HL [1–5], NaL [6, 7] and using PPh_3, 2,2′-bipyridine and 1,10-phenanthroline as co-ligands.

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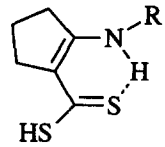
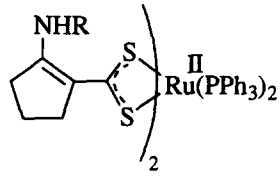
EXPERIMENTAL

Physical measurements

IR spectra were recorded on a Perkin–Elmer 783 spectrophotometer using KBr discs and electronic spectra on a Shimadzu UV-160 spectrophotometer. The electrochemical data were obtained with a BAS 100B electrochemistry system. A three-electrode assembly (BAS) comprising a platinum working electrode, a platinum auxilliary electrode and an Ag–AgCl reference electrode was used. The concentration of the supporting electrolyte tetraethylammonium perchlorate (TEAP) was maintained at 0.1 mol dm^{-3}. ^1H NMR spectra were obtained in $CDCl_3$ solutions on a 270 MHz Bruker WH 270 spectrometer using $Si(CH_3)_4$ ($\delta H = 0$) as the internal standard. Carbon,

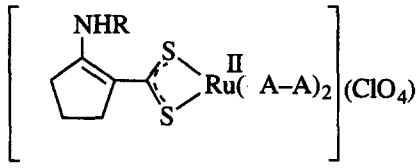


HL^{1-5}(R–acda H; R = H, Me, Et, Bu, C_6H_{11})



1a–1e

R = H(a), Me(b), Et(c), Bu(d), C_6H_{11}(e)



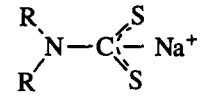
2a–2g

	R	(A–A)
2a:	H	bpy
2b:	Me	bpy
2c:	Et	bpy
2d:	Bu	bpy
2e:	H	phen
2f:	Me	phen
2g:	Et	phen

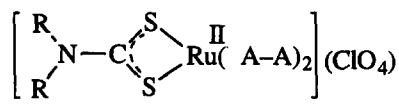
hydrogen and nitrogen analyses were carried out on a Perkin–Elmer 240C elemental analyser.

Materials

All reagents and solvents were purchased from chemical sources and used as received. 2-Alkylamino-1-cyclopentene-1-dithiocarboxylic acids were prepared by reported methods [6,7]. $Ru(bpy)_2Cl_2$, $Ru(phen)_2Cl_2$ and $Ru(PPh_3)_3Cl_2$ were prepared by the published methods [8,9]. Silver perchlorate was prepared from silver carbonate and perchloric acid, and recrystallized from benzene [10].



Na $L^{6,7}$(R_2dtc^-; R = Et, Pr)



3a–3d

	R	(A–A)
3a:	Et	bpy
3b:	Pr	bpy
3c:	Et	phen
3d:	Pr	phen

CAUTION! Silver perchlorate and the other perchlorate salts described below are potentially explosive. Although $AgClO_4$ was recrystallized in gram quantities without any difficulty, **extreme caution should be exercised in handling this material.**

Preparation of the complexes

All the reactions were carried out under nitrogen using dry solvents.

General procedure for the synthesis of the complexes $[Ru(R\text{-}acda)_2(PPh_3)_2]$ (**1a–e**). A typical procedure for the preparation of **1a** is given below.

$[Ru(H\text{-}acda)_2(PPh_3)_2]$(**1a**). To a stirred suspension of $Ru(PPh_3)_3Cl_2$(0.96 g, 1 mmol) in C_6H_6 (25 cm^3) was added a C_6H_6 solution (10 cm^3) of H-acdaH (0.32 g, 2.0 mmol). The mixture was stirred at room temperature for 5 h, during which time a clear solution was obtained. The solution was concentrated on a rotary evaporator to a small volume (*ca* 5 cm^3) and added dropwise to 50 cm^3 vigorously stirred petroleum ether (b.p. 40–60°C). The product precipitated was collected by filtration and purified by column chromatography using neutral alumina and C_6H_6 as the eluant; yield 0.75 g (80%).

General method for the preparation of $[Ru(A\text{-}A)_2(L^{1-4,6,7})](ClO_4)$ (A-A = bpy *or* phen) *complexes.* $[Ru(Me\text{-}acda)(bpy)_2](ClO_4)$ (**2b**). A stirred suspension of $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (0.26 g, 0.5 mmol) in EtOH (40 cm^3) was treated with $AgClO_4$ (0.21 g, 1 mmol) and filtered after 2 h to remove the AgCl precipitated. To the filtrate was added Me-acdaH (0.08 g, 0.5 mmol) dissolved in EtOH (10 cm^3). The solution was stirred at room temperature for 10 h, during which time the product deposited as microcrystals. These were collected by filtration and recrystallized from EtOH; yield 0.25 g (75%).

In the case of complexes **3a–d** the sodium salts of dialkyldithiocarbamates were used instead of Me-acdaH.

RESULTS AND DISCUSSION

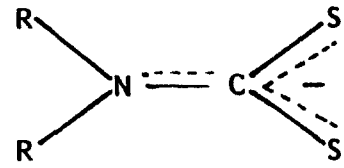
The synthetic routes involved in the formation of the phosphine complexes (**1a–e**) and polypyridine complexes (**2a–g, 3a–d**) are given by Eqs (1) and (2), respectively:

$$Ru(PPh_3)_3Cl_2 \xrightarrow[C_6H_6]{\text{R-acdaH}} [Ru(\text{R-acda})_2(PPh_3)_2]$$

$$[Ru(bpy)_2Cl_2/Ru(phen)_2Cl_2] \xrightarrow[\text{(ii) R-acdaH/Na[R}_2\text{dtc]}]{\text{(i) AgClO}_4\text{, EtOH}} \textbf{(1a–e)} \quad (1)$$

$$[Ru(\text{R-acda/R}_2\text{-dtc})\langle(bpy)_2/(phen)_2\rangle](ClO_4) \quad \textbf{(2a–g, 3a–d)} \quad (2)$$

All the complexes have been isolated in good yield and their microanalytical data (Table 1) confirm the composition given. The IR spectra of the phosphine complexes exhibit three NH stretching frequencies between 3400 and 3200 cm^{-1} for **1a**, while for complexes **1b–e** only a single ν(NH) vibration is observed. Significantly, the ν(NH) frequencies of these compounds, 3250 (**1b**), 3240 (**1c**), 3230 (**1d**) and 3220 (**1e**) cm^{-1}, are progressively shifted to lower energy with the increase in size of the alkyl group R of R-acda$^-$. Complexes **1a–e** show a characteristic sharp band at about 820 cm^{-1} which has previously been assigned to $\nu_{as}(CS_2^-)$ [6,11–13]. Three diagnostic IR bands for the dithiocarbamate complexes **3a–d** are observed due to ν(C---N), $\nu_{as}(CS_2^-)$ and $\nu_s(CS_2^-)$ vibrations of the delocalized ligand moiety at about



1500, 1280 and 780 cm^{-1}, respectively [10]. Although the ν(CN) frequency of these complexes at 1500 cm^{-1} is almost independent of the substituents, it is shifted to a higher energy relative to those of the free ligands (*ca* 1480 cm^{-1}) due to the increased double bond character upon coordination to the metal centre [14,15]. All the perchlorate complexes show a broad band at about 1100 cm^{-1} and a sharp band at 620 cm^{-1}, indicating the presence of free ClO_4^- anion.

The UV–vis spectra data of the complexes are given in Table 2. All the phosphine complexes (**1a–e**) have similar spectra, exhibiting three bands. The lowest energy band observed at 460 nm may be attributed to a $d\pi \rightarrow \pi^*$ (PPh_3) metal-to-ligand charge transfer (MLCT) transition. The next highest energy band, observed at about 380 nm, is also an MLCT $d\pi \rightarrow \pi^*$ (R-acda$^-$) transition [16,17]. The intra-ligand transition occurs at about 330 nm.

Complexes **2a–g** also exhibit two MLCT bands at 490 and 350 nm, and an intra-ligand transition at 330 nm, of which the 490 nm band is assignable to a $d\pi \rightarrow \pi^*$ (bpy or phen) transition and the band at 350 nm to a $d\pi \rightarrow \pi^*$ (R-acda$^-$) transition. It may be mentioned that the MLCT transition of $[Ru(bpy)_3](ClO_4)_2$ occurring at 452 nm [18] is displaced to lower energies on substituting bpy with one or two ligands [19]. In the case of complexes **3a–d** the two MLCT bands are shifted to relatively higher wavelengths, 515 and 460 nm.

The ^{1}H NMR spectral data of the phosphine–R-acdaH complexes (**1a–e**) are given in Table 3. The spectrum of complex **1b** shows two overlapping but discernible singlets at 2.85 and 2.87 ppm for the methyl

Table 1. Analytical data[a] for some selected complexes

Complex	Analysis (%)		
	C	H	N
1a	63.5 (63.6)	5.4 (5.1)	2.8 (2.7)
1b	62.5 (61.9)	5.5 (5.2)	2.9 (2.9)
1c	62.3 (62.5)	5.8 (5.4)	3.1 (2.8)
1d	64.8 (63.8)	6.7 (5.9)	2.9 (2.7)
1e	65.8 (65.1)	6.2 (6.0)	2.6 (2.5)
2a	46.0 (46.1)	3.9 (4.0)	9.2 (9.9)
2c	46.7 (46.9)	4.2 (4.2)	9.1 (9.7)
2d	45.5 (45.0)	4.6 (5.0)	7.9 (8.7)
3a	43.5 (44.1)	4.1 (4.1)	10.4 (10.3)
3b	46.8 (47.0)	4.3 (4.3)	9.9 (10.1)
3c	48.7 (49.3)	4.0 (4.2)	9.5 (9.3)

[a]Calculated values are given in parentheses.

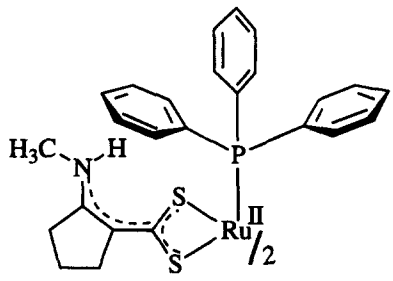
Table 2. UV–vis data for the complexes

Complex	λ_{max} (nm)/ε ($M^{-1}cm^{-1}$)		
1a	460 (16,400),	370 (14,800),	320 (18,000)
1b	460 (15,100),	380 (11,000),	330 (16,500)
1c	460 (13,300),	380 (10,000),	325 (16,000)
1d	460 (17,000),	380 (15,700),	300 (13,000)
1e	470 (18,000),	385 (22,000),	330 (15,000)
2a	490 (18,500),	350 (21,000),	300 (30,000)
2b	485 (18,200),	350 (20,800),	300 (28,000)
2c	485 (21,000),	350 (22,000),	300 (29,000)
2d	490 (21,500),	350 (20,500),	300 (32,000)
2e	490 (16,500),	400 (14,700),	345 (16,000)
2f	490 (20,000),	400 (16,500),	350 (22,700)
2g	490 (18,200),	400 (9500),	350 (15,000)
3a	520 (9600),	460 (6400),	350 (14,500)
3b	520 (9400),	475 (9600),	360 (12,400)
3c	510 (9800),	460 (10,000),	265 (35,000)
3d	515 (9700),	450 (9000),	265 (34,000)

Table 3. ^{1}H NMR ($CDCl_3$) spectral data for some complexes

Complex	δ(ppm)
1a	1.59–1.72 (m, 4H, 4-CH_2), 2.38–2.50 [m, 8H, (3, 5)-CH_2], 6.14 (s, 4H, NH_2), 7.02–7.08 (m, 12H, *m*-Ph), 7.14–7.19 (m, 6H, *p*-Ph), 7.29–7.38 (m, 12H, *o*-Ph)
1b	1.57–1.72 (m, 4H, 4-CH_2), 2.37–2.61 [m, 8H, (3, 5)-CH_2], 2.85, 2.87 (s, 6H, N-CH_3), 7.01–7.07 (m, 12H, *m*-Ph), 7.13–7.18 (m, 6H, *p*-Ph), 7.29–7.41 (m, 12H, *o*-Ph), 8.25–8.30 (t, 2H, NH)
1c	1.11–1.16 (t, 6H, 7-Ch_3), 1.56–1.76 (m, 4H, 4-CH_2), 2.32–2.61 [m, 8H, (3, 5)-CH_2], 3.13–3.22 (m, 4H, 6-CH_2), 7.01–7.06 (m, 12H, *m*-Ph), 7.12–7.23 (m, 6H, *p*-Ph), 7.28–7.42 (m, 12H, *o*-Ph), 8.37–8.39 (t, 2H, NH)
1d	0.77–0.96 (m, 6H, 9-CH_3), 1.25–1.36 (m, 4H, 8-CH_2), 1.40–1.52 (m, 4H, 7-CH_2), 1.57–1.70 (m, 4H, 4-CH_2), 2.43–2.57 [m, 8H, (3, 5)-CH_2], 3.09–3.16 (m, 4H, 6-CH_2], 7.00–7.05 (m, 12H, *m*-Ph), 7.12–7.17 (m, 6H, *p*-Ph), 7.28–7.39 (m, 12H, *o*-Ph), 8.46–8.50 (m, 2H, NH)
1e	1.17–1.52 [m, 10H, (7–11)-CH_2], 1.58–1.82 (m, 4H, 4-CH_2), 2.45–2.64 [m, 8H, (3, 5)-CH_2], 3.24–3.25 (m, 2H, 6-CH), 6.99–7.05 (m, 12H, *m*-Ph), 7.11–7.16 (m, 4H, *p*-Ph), 7.30–7.36 (m, 12H, *o*-Ph), 8.64 (br, 2H, NH)

group of Me-acda, indicating the presence of two structural isomers. The occurrence of the two isomers can be rationalized by taking into consideration the restricted rotation of the N-methyl group of Me-acda in the delocalized structure **1** [6]. From the almost identical heights of the two peaks it may be concluded that the two isomers are present in a 1 : 1 ratio. In the case of **1c**, a broad multiplet due to the —CH_2— group of the N-ethyl moiety of Et-acda is observed between 3.13 and 3.22 ppm. Although a quartet is expected for a single isomer, the broad multiplet again indicates the presence of two isomers.



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Another interesting aspect of the NMR spectra is that, with the increase in chain length of the alkyl group (cyclohexyl derivative included) in complexes **1b–e**, the chemical shift due to the NH proton increases. In other words, the NH proton becomes more deshielded as the substituent R of R-acda$^-$ is changed in the order Me, Et, Bu and cyclohexyl. Furthermore, with the increase in chain length of the alkyl group of R-acda$^-$, the NH stretching frequency is also shifted to a lower energy. Indeed, a linear correlation is obtained in a ν(NH) *vs* δ(NH) plot (Fig. 1). This observation indicates that along the series **1b–e**, a gradual change of the N—H bond distance probably occurs. However, in the absence of crystallographic results, it is not possible to ascertain the cause of such variation. It is important to note that the observed effect contradicts the trend expected purely on the basis of inductive influence of the alkyl groups. We note that Cole-Hamilton and Stephenson have reported the stereochemical features of $[Ru(PR_3)_2(S_2CNMe_2)_2]$ complexes [20].

The redox properties of the complexes were studied by cyclic voltammetry and differential pulse voltammetry, and the results are given in Table 4. The cyclic voltammograms of the phosphine complexes (**1a–e**) are consistent with two stepwise irreversible metal-centred oxidations, as shown in Eqs (3) and (4).

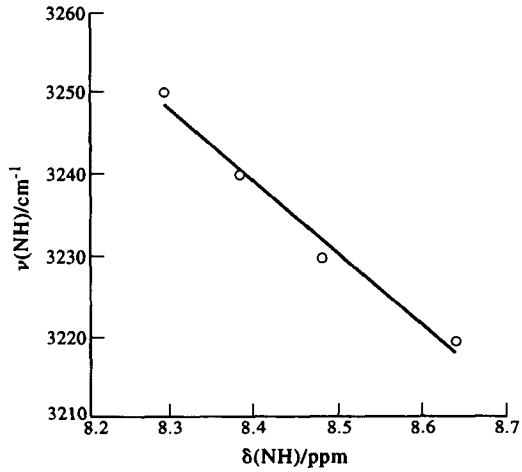

Fig. 1. Plot of chemical shift δ(NH) *vs* the stretching frequency ν(NH) of the phosphine complexes **1b–e**.

Table 4. Electrochemical data for the complexes

Complex	$E^1_{1/2}$(V)	ΔE_p (mV)	E^1_{pa}(V)	E^2_{pa}(V)
1a			0.26	0.72
1b			0.22	0.67
1c			0.24	0.67
1d			0.24	0.69
1e			0.23	0.69
2a	0.49	65		1.25
2b	0.45	64		1.15
2c	0.46	65		1.26
2d	0.45	63		1.26
2e	0.49	64		1.28
2f	0.45	64		1.20
2g	0.45	65		1.20
3a	0.56	60		1.60
3b	0.53	61		1.59
3c	0.55	63		1.57
3d	0.53	61		1.57

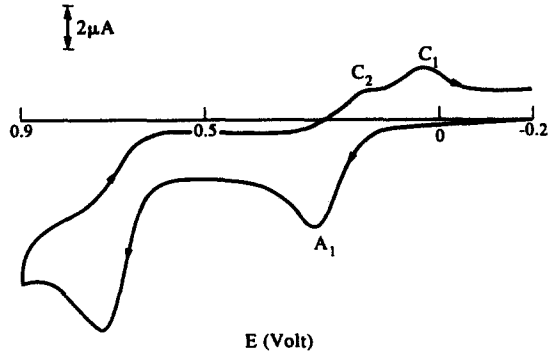

Fig. 2. Cyclic voltammogram of **1a** in CH_3CN with a platinum electrode at a scan rate of 100 mV s^{-1}. Concentration of the complex: 1.0×10^{-3} mol dm^{-3}; concentration of supporting electrolyte, $[Et_4N](ClO_4)$: 0.1 mol dm^{-3}.

$$[Ru^{II}(R\text{-acda})_2(PPh_3)_2]^0 \xrightarrow{E^1_{pa}} [Ru^{III}(R\text{-acda})_2(PPh_3)_2]^+ \quad (3)$$

$$[Ru^{III}(R\text{-acda})_2(PPh_3)_2]^+ \xrightarrow{E^2_{pa}} [Ru^{IV}(R\text{-acda})_2(PPh_3)_2]^{2+} \quad (4)$$

The E^1_{pa} and E^2_{pa} values of **1a** and **1b** are 0.26 and 0.72 V, and 0.21 and 0.67 V, respectively, indicating that the oxidation of **1a** is relatively somewhat more difficult than that of **1b**. This observation is in agreement with the greater electron-releasing ability of the methyl group in **1b** as compared to the hydrogen atom in **1a**. A similar trend is also observed for the oxidation of $R^{III} \rightarrow R^{IV}$ (E^2_{pa}). E^1_{pa} values for all substituted complexes (**1b–e**) lie in the narrow range of 0.21–0.24 V.

Recently, Chakravorty and co-workers have made extensive studies on the reactivities of ruthenium(II) complexes with S,S^- donor ligands containing phosphine and its derivatives, and have observed that the preferred geometries of these complexes are *cis* for ruthenium(II) and *trans* for ruthenium(III) [21–23]. They have demonstrated that at a lower temperature, *cis*-Ru^{II} oxidizes to *cis*-Ru^{III}, which, being unstable, isomerizes to stable *trans*-Ru^{III}. In the reverse scan, *trans*-Ru^{III} is reduced to *trans*-Ru^{II}, which is also unstable and isomerizes to *cis*-Ru^{II} [21–24].

The cyclic voltammogram of **1a** (Fig. 2) shows an indication of isomerism even at room temperature. As may be noted, the anodic peak $A_{(1)}$ has two components in the return sweep, $C_{(1)}$ and $C_{(2)}$, of which $C_{(1)}$ may be considered as due to *trans*-Ru^{II}, which then isomerizes to the more stable *cis*-Ru^{II}, which is indicated by $C_{(2)}$. Clearly, the isomerization rate is slow on the cyclic voltammetric time scale (100 mV s^{-1}).

Cyclic voltammograms of the mixed-ligand complexes (**2a–g**) exhibit reversible and irreversible metal-centred oxidation processes and two reversible reductions of bpy or phen. Thus, while the Ru^{II}/Ru^{III} couple is reversible, the conversion of $Ru^{III} \rightarrow Ru^{IV}$ takes place irreversibly. The criteria of reversibility were checked by observing the constancy of peak separation ($E_{pa} - E_{pa} = 60$–65 mV) and the ratio of peak heights ($i_{pa}/i_{pc} \approx 1$) with the variation of scan rates (50–500 mV s^{-1}). It may be noted that the $E^1_{1/2}$ value of **2a** (0.49 V) is again somewhat higher than the other alkyl derivatives **2b–d** (0.45 V); the latter compounds show practically no dependence on the substituents.

The reduction of bpy and phen in all the complexes occurs in two steps according to Eqs (5) and (6), typically at about −1.50 and −1.80 V:

$$[Ru(R\text{-acda})(bpy)_2]^+ + e \rightleftharpoons [Ru(R\text{-acda}(bpy)(bpy^{\cdot-})] \quad (5)$$

$$[Ru(R\text{-acda})(bpy)(bpy^{\cdot-})] + e \rightleftharpoons [Ru(R\text{-acda})(bpy^{\cdot-})_2] \quad (6)$$

Inasmuch as each bpy or phen can accept two electrons in this lowest unoccupied molecular orbital [25, 26], one should expect to observe four such reduction steps in the series **2a–g** and **3a–d**. The observation of only two couples up to −2.0 V was limited by the cut-off potential of the supporting electrolyte (TEAP) in acetonitrile.

Complexes **3a–d**, similar to **2a–g**, undergo reversible and irreversible meter-centred oxidation processes. The reduction behaviours of bpy or phen in these compounds are very similar to the preceding series. The $E^1_{1/2}$ values of **3a–d** (0.52–0.56 V) show a small substitutional effect.

A comparison of the electrochemical data for Ru^{II}/Ru^{III} in the three series of compounds (Table 4) reveals that the phosphine–R–acda$^-$ complexes (series **1**) are most easily oxidized relative to those of series **2** and **3**. The most important factor that contributes to the easier oxidation of the compounds of series **1** is

that they are uncharged, while those belonging to series **2** and **3** are monocationic. Another important difference lies in the number of (S,S^-) ligands attached, which is two for series **1** and one for series **2** and **3**. Between series **2** and **3,** the greater stability of ruthenium(II) in series **3** can be attributed to greater σ-donor capacity of the dithiocarbamate ligands relative to R-acda$^-$.

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