Luminescent Metal Complexes. Part 3.[1] Electrochemical Potentials of Ground and Excited States of Ring-substituted 2,2′-Bipyridyl and 1,10-Phenanthroline Tris-complexes of Ruthenium

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$E_{\frac{1}{2}}$ values for 21 tris-complexes of substituted 2,2′-bipyridyls and 1,10-phenanthrolines with Ru^{II}–Ru^{III} in acetonitrile have been measured using cyclic voltammetry. A linear correlation exists between $E_{\frac{1}{2}}$ and the Hammett σ constant for data obtained from complexes of 4,4′-and 5,5′-disubstituted 2,2′-bipyridyls. The reduction potential for the couple $Ru(ligand)_3{}^{3+}$–$^*Ru(ligand)_3{}^{2+}$, where * refers to the excited state, have been calculated from the $E_{\frac{1}{2}}$ values and a combination of data collected from luminescence and magnetic circular dichroism measurements.

Ru^{II} tris-2,2′-bipyridyl complex, $Ru(bipy)_3{}^{2+}$, absorbs light in the visible region at about 450 nm to yield a set of metal–ligand charge-transfer excited states[2] denoted $^*Ru(bipy)_3{}^{2+}$, equation (1). These species are strong reducing agents, losing an electron to oxidizing substrates and generating Ru^{III} tris-2,2′-bipyridyl, $Ru(bipy)_3{}^{3+}$, equation (2). The latter, being a relatively strong oxidizing agent, may then be reduced to ground state $Ru(bipy)_3{}^{2+}$, equation (3). The three equations constitute a photo-driven cycle which it may be possible to exploit within schemes for the photochemical cleavage of water[3] and for the conversion of solar energy into electrical energy within a photogalvanic cell.[4]

$$Ru(bipy)_3{}^{2+} \xrightarrow{h\nu} {}^*Ru(bipy)_3{}^{2+} \qquad (1)$$

$$Ru(bipy)_3{}^{3+} + e \rightleftharpoons {}^*Ru(bipy)_3{}^{2+} \qquad {}^*E_{\frac{1}{2}} \quad (2)$$

$$Ru(bipy)_3{}^{3+} + e \rightleftharpoons Ru(bipy)_3{}^{2+} \qquad E_{\frac{1}{2}} \quad (3)$$

Recently, we have prepared and investigated the absorption and emission spectra of a wide range of Ru^{II} complexes of substituted 2,2′-bipyridyls and 1,10-phenanthrolines.[1,5,6] In the course of their preparation it was noted that some of the complexes were readily oxidized. It became clear that the $E_{\frac{1}{2}}$ values were spread over a wide range. Therefore we have carried out measurements of the formal $E_{\frac{1}{2}}$ potentials of selected examples, (**1**)—(**21**), in acetonitrile using cyclic voltammetry and have used the absorption and emission energies to derive the $^*E_{\frac{1}{2}}$ values. Both the $E_{\frac{1}{2}}$ and $^*E_{\frac{1}{2}}$ values vary over a range of about 1 V; the former values are closely correlated with the basicity of the ligand. The data extend significantly the range of reduction potentials previously reported within this class of metal complex.[7]

Table. Standard reduction potentials of the electronic ground state ($E_{\frac{1}{2}}$) and lowest excited state ($^*E_{\frac{1}{2}}$) of some tris-chelated Ru^{II}–Ru^{III} complexes

Compound No.	Substituents	$E_{\frac{1}{2}}$/ V	$^*E_{\frac{1}{2}}{}^a$/ V	$\lambda_{max.}$ emission/ nm	$^*E_{\frac{1}{2}}{}^b$/ V	σ^c
Bipyridyl series						
(**1**)	4,4′-diNEt_2	0.61	−1.30	700		−0.53
(**2**)	4,4′-diOEt	0.90	−1.09	670	−1.14	−0.24
(**3**)	4,4′-diOCH_2Ph	0.95	−1.07	670		
(**4**)	4,4′-diNHCOMe	0.97	−1.06	670		
(**5**)	4,4′-diOPh	1.05	−0.94	670		
(**6**)	4,4′-diMe	1.11	−0.95	640		−0.14
(**7**)	4,4′-diCH:CHPh	1.14	−0.82	680	−0.74	−0.07
(**8**)	5,5′-diMe	1.16	−0.98	620		−0.06
(**9**)	4,4′-diPh	1.20	−0.88	640	−0.86	−0.01[d]
(**10**)	5,5′-diNHCOMe	1.21	−0.90	630		0.14
(**11**)	$(4,4'\text{-diPh})_2$/none	1.22	−0.87	635		
(**12**)	4,4′-diPh/$(\text{none})_2$	1.24	−0.87	630		
(**13**)	none	1.28	−0.83	630	−0.86	0.0
(**14**)	4-Cl	1.33	−0.75	640		
(**15**)	4-Br	1.34	−0.74	640		
(**16**)	4,4′-diCl	1.44	−0.55	670		0.23[d]
(**17**)	4,4′-diBr	1.44	−0.58	660		0.23[d]
(**18**)	4,4′-diCO_2Et	1.56	−0.47	655	−0.49	0.44
Phenanthroline series						
(**19**)	4,7-di*p*MeC_6H_4	1.19	−0.99	620		
(**20**)	4,7-diPh	1.22	−0.96	620		
(**21**)	none	1.27	−0.94	610	−0.94	

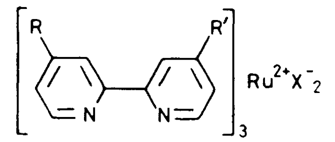
[a] Excited state reduction potentials calculated as described in text. [b] Excited state reduction potentials calculated from an estimation of the singlet-triplet energy using the low-temperature m.c.d. and emission spectra. [c] O. Exner, in 'Correlation Analysis in Chemistry—Recent Advances' eds. N. B. Chapman and J. Shorter, Plenum Press, New York, 1978, ch. 10, p. 439. [d] C. D. Johnson, 'The Hammett Equation,' Cambridge University Press, Cambridge 1973, ch. 1.

Experimental

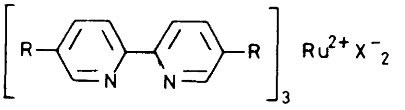
The preparation of substituted ligands and their Ru^{II} complexes has been described previously.[5,6] $E_{\frac{1}{2}}$ Values of each complex were determined using a polarographic analyser (model 174 A, Princeton Applied Research Corporation) and a programmer (model 175, P.A.R.) in the cyclic voltammetry mode. The electrochemical cell employed platinum working and auxiliary electrodes with a reference electrode of Ag–$AgNO_3$, 0.01M-$AgNO_3$, and 0.1M $(Bu^n)_4N{\cdot}BF_4$ in MeCN. The metal complexes were dissolved in MeCN at a concentration of 1×10^{-3}M plus a supporting electrolyte of 0.1M-anhydrous $NaClO_4$. At 20 °C the potential of the Ag–$AgNO_3$ electrode relative to the n.h.e. is 0.38 V. Cyclic voltammograms were recorded by oscilloscope at a current of *ca.* 1 mA and a sweep rate of 500 mV s^{-1}. Under these conditions all the complexes studied were electrochemically reversible.

Results and Discussion

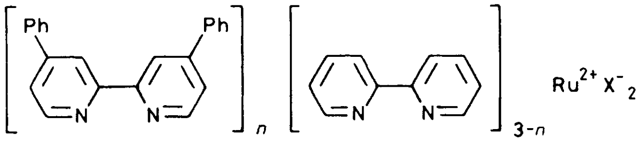
$E_{\frac{1}{2}}$ *Values.*—Results obtained in MeCN by cyclic voltammetry, see Table, show that the reduction potential within this series of compounds is highly sensitive to ligand substituent, varying between +0.61 and 1.56 V. The presence of electron-withdrawing groups stabilises the Ru^{II} state whereas electron-



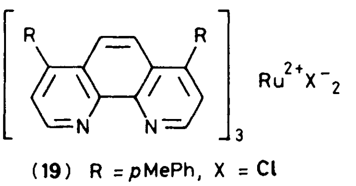
(1) R = R′ = NEt$_2$, X = Cl
(2) R = R′ = OEt, X = I
(3) R = R′ = OCH$_2$Ph, X = Cl
(4) R = R′ = NHCOMe, X = I
(5) R = R′ = OPh, X = Cl
(6) R = R′ = Me, X = I
(7) R = R′ = CH:CHPh(*E*), X = Cl
(9) R = R′ = Ph, X = Cl
(13) R = R′ = H, X = Cl
(14) R = Cl, R′ = H, X = I
(15) R = Br, R′ = H, X = I
(16) R = R′ = Cl, X = I
(17) R = R′ = Br, X = I
(18) R = R′ = CO$_2$Et, X = BF$_4$



(8) R = Me, X = Cl
(10) R = NHCOMe, X = I



(11) *n* = 2, X = I
(12) *n* = 1, X = I



(19) R = *p*MePh, X = Cl
(20) R = Ph, X = Cl
(21) R = H, X = Cl

donating substituents favour Ru^{III}. Comparison of data for the 4-chloro and 4-bromo derivatives (**14**) and (**15**) with those for the 4,4′-disubstituted analogues (**16**) and (**17**) shows that the introduction of the second halide substituent has a larger effect on $E_{\frac{1}{2}}$ than introduction of the first. A non-linear change in $E_{\frac{1}{2}}$ is also observed on sequential replacement of an unsubstituted ligand by 4,4′-diphenyl-2,2′-bipyridyl [series (**13**), (**12**), (**11**), and (**9**)]. In the series of 1,10-phenanthroline complexes, tolyl groups in the 4,7-positions reduce $E_{\frac{1}{2}}$ by 0.03 V more than phenyl groups.

In order to quantify the substituent effect a plot has been made, see Figure, of the $E_{\frac{1}{2}}$ values against the Hammett σ values, $\sigma_{p,m}$, for complexes of 4,4′- and 5,5′-disubstituted 2,2′-bipyridyls. A straight line with a correlation coefficient of 0.971 and slope of 0.984 is obtained for 11 compounds. There is doubt over the values of σ_p for OPh, OCH$_2$Ph, and NHCOMe so these have been omitted from the plot. It has been shown that substituent effects for pyridine protonation correlate with σ for all substituents other than $-M$, $-I$ groups. These correlate better with σ_I values.[8] The use of the σ_I value (0.34), rather than σ_p for the CO$_2$Et group in the Figure, leads to an improvement in the correlation (correlation coefficient 0.976, slope 1.051).

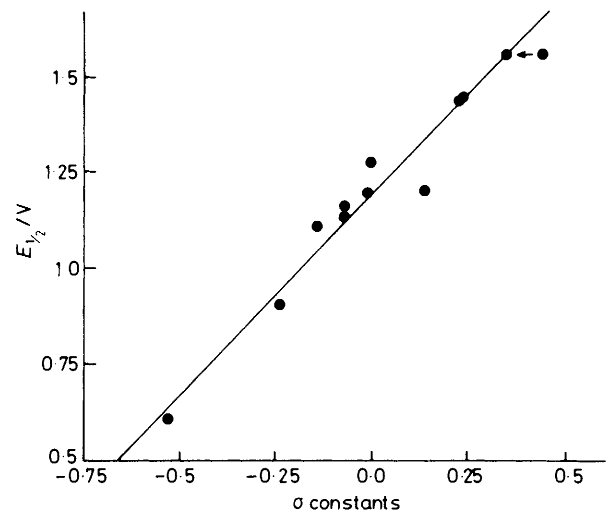


Figure. Plot of $E_{\frac{1}{2}}$ values against Hammett σ constants. Line corresponds to the improved correlation using σ_I for the CO$_2$Et group

$$\mathrm{Fe(bipy)_3}^{3+} + e \rightleftharpoons \mathrm{Fe(bipy)_3}^{2+} \qquad (4)$$

A relationship between the $E_{\frac{1}{2}}$ values of the couple in expression (4) for substituted bipyridyls and the pK_a values of the ligands has previously been noted.[9] An increase in basicity by *ca.* 2 pK_a units leads to a drop in $E_{\frac{1}{2}}$ values from *ca.* +1.2 to *ca.* 1.05 V. For the ruthenium complexes reported here the variation is in the same sense, *i.e.* an increase in ligand basicity leads to a drop in $E_{\frac{1}{2}}$ values. The magnitude of the swing in $E_{\frac{1}{2}}$ values is much greater because the range of ligand basicities is that much greater. Unfortunately there appear to be few pK_a values reported for the ligands shown in the Table. However, it is well established that the basicity of the series of nitrogen bases correlates well with σ. These correlations have been found not only for simple pyridines, referred to above, but also for mono-substituted 2,2′-bipyridyls[10] and 1,10-phenanthrolines.[10,11] Thus the Figure, in effect, provides a demonstration of the dependence of the $E_{\frac{1}{2}}$ values upon ligand basicity. From the pK_a values for 2,2′-bipyridyl (4.50) and 4,4′-dimethyl-2,2′-bipyridyl (5.45)[12] it seems likely that the aqueous-phase basicities of the substituted bipyridyl ligands plotted in the Figure vary over at least six pK_a units.

If we take the ligand pK_a value to reflect the σ-bonding ability of the ligand, then the correlation shown in the Figure demonstrates that as the σ-bonding strength of the ligand increases, the stability of the Ru^{III} complexes increases faster than the stability of the Ru^{II} complexes.

*$E_{\frac{1}{2}}$ *Values.*—The reduction potentials of the luminescent states can be calculated according to the method of Lin and Sutin[13] from the potential for the reduction of Ru(ligand)$_3^{3+}$ to Ru(ligand)$_3^{2+}$ and the free-energy change for the conversion of Ru(ligand)$_3^{2+}$ into *Ru(ligand)$_3^{2+}$. The enthalpy change

between the ground and excited states can be estimated from the average of the singlet–triplet absorption and emission bands. For the entropy change only that part due to the change in spin multipliciy, namely $R\ln3$, can be estimated. The term $T\Delta S$ then takes a value of *ca.* 0.03 eV at 300 K. The major problem arises in the estimation of the average energy of the singlet–triplet absorption and emission band, especially for a long series of compounds. This is because the energy of the triplet band in the absorption spectrum is not well defined, the absorption band being a rather broad tail to the main singlet band. We have adopted the following procedure. For six of the complexes listed in the Table we have previously measured the magnetic circular dichroism (m.c.d.) spectrum at 4.2 K of solutions in alcoholic glasses.[14] There are clearly resolved features in the m.c.d. spectrum underlying the singlet–triplet absorption making it possible to estimate the energy of the triplet state. Similarly we have measured the luminescence spectra at 4.2 K and obtained well resolved spectra such that the O–O vibrational band can be readily identified. Hence we can obtain the mean energy of the features measured in the m.c.d. and the luminescence spectra. The resulting $^*E_{\frac{1}{2}}$ values are given in column 4 of the Table.

For all the compounds listed in the Table we have previously reported the room-temperature luminescence spectra in ethanol–methanol (4 : 1) mixed solvent.[5,6] The wavelengths of the emission maxima, after correction for the spectral response of the monochromator–photomultiplier combination, are listed in the Table. The spectroscopic parameters for two of the compounds, **(9)** and **(13)**, were also measured in MeCN.[5] The $\lambda_{\text{max.}}$ values in the two solvents were the same. By using the energy of the emission maximum, an approximate value for the excited state reduction potential can be calculated. However, this number is slightly in error because it represents a Franck–Condon process, *i.e.* a vertical energy on the configuration co-ordinate diagram. In order to estimate the correction to these values we have taken the $^*E_{\frac{1}{2}}$ values evaluated by obtaining the energy of the singlet–triplet from the m.c.d. and emission spectra and compared them with the $^*E_{\frac{1}{2}}$ values calculated on the basis of the room-temperature emission maxima. It is found that there is a difference of between 0.1 and 0.2 eV for the five bipyridyl complexes: we use the mean value of 0.17 eV for the five compounds as a correction factor to compute the values of $^*E_{\frac{1}{2}}$ listed in column 2 of the Table, for complexes **(1)**—**(18)**. Using this procedure we estimate a value of -0.83 V as the $^*E_{\frac{1}{2}}$ for the parent complex **(13)**. This compares well with the value reported by Lin and Sutin[13] of -0.84 V and a value of -0.81 ± 0.02 V for the couple in Me_3CN containing 0.1M-tetra-n-propylammonium perchlorate obtained using rate comparisons.[15] For the phenanthroline complexes **(19)** and **(20)** we use a correction factor of 0.21 V, the value derived from data for compound **(21)**.

The variation in $^*E_{\frac{1}{2}}$ values with ligand substituents is almost 1 V, with $Ru(4,4'\text{-bisethoxycarbonylbipy})_3{}^{3+/2+}$ having the highest value of -0.47 V and $Ru[4,4'\text{-bis(diethylamino)bipy}]_3{}^{3+\;2+}$ the lowest at -1.30 V. We note that the Ru^{II} state of the latter is apparently the most powerful reducing agent in its luminescing state yet reported for this series of complexes. Qualitatively, the effect of substituents on $^*E_{\frac{1}{2}}$ is rather similar to their effect on $E_{\frac{1}{2}}$. However, as we pointed out earlier,[5] there is no simple relationship between the energy of the emission band and the Hammett substituent constant. Accordingly, no linear correlation is to be expected between $^*E_{\frac{1}{2}}$ and this parameter.

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References

1 Part 2, M. J. Cook, A. P. Lewis, G. S. G. McAuliffe, V. Skarda, A. J. Thomson, J. L. Glasper, and D. J. Robbins, preceding paper.
2 A. Ceulemans and L. G. Vanquickenborne, *J. Am. Chem. Soc.*, 1981, **103**, 2238.
3 See for example, N. Sutin, *J. Photochem.*, 1979, **10**, 19.
4 For a review see W. J. Albery and A. W. Foulds, *J. Photochem.*, 1979, **10**, 41.
5 M. J. Cook, A. P. Lewis, G. S. G. McAuliffe, V. Skarda, A. J. Thomson, J. L. Glasper, and D. J. Robbins, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1293.
6 M. J. Cook, A. P. Lewis, G. S. G. McAuliffe, V. Skarda, A. J. Thomson, J. L. Glasper, and D. J. Robbins, unpublished work.
7 J. V. Casper and T. J. Meyer, *Inorg. Chem.*, 1983, **22**, 2444; C. M. Elliott and E. J. Hershenhart, *J. Am. Chem. Soc.*, 1982, **104**, 7519; C.-T. Lin, W. Böttcher, M. Chou, C. Creutz, and N. Sutin, *ibid.*, 1976, **98**, 6536; T. Saji and S. Aoyagui, *J. Electroanal. Chem. Interfacial Electrochem.*, 1975, **58**, 401; N. E. Tokel-Takvoryan, R. E. Hemingway, and A. J. Bard, *J. Am. Chem. Soc.*, 1973, **95**, 6582.
8 G. B. Ellam and C. D. Johnson, *J. Org. Chem.*, 1971, **36**, 2284 and references cited therein.
9 C. S. G. Phillips and R. J. P. Williams, 'Inorganic Chemistry,' Oxford University Press, Oxford, 1966, vol. II, p. 315.
10 M. J. Cook, A. R. Katritzky, and S. Nadji, *J. Chem. Soc., Perkin Trans. 2*, 1978, 1215.
11 A. A. Schilt and G. F. Smith, *J. Phys. Chem.*, 1956, **60**, 1546.
12 B. R. James and R. J. P. Williams, *J. Chem. Soc.*, 1961, 2007.
13 C.-T. Lin and N. Sutin, *J. Phys. Chem.*, 1976, **80**, 97.
14 V. Skarda, A. J. Thomson, M. J. Cook, A. P. Lewis, G. S. G. McAuliffe, and D. J. Robbins, unpublished work.
15 C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, 1975, **97**, 2909.

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