Synthesis and characterization of ruthenium(II) complexes containing the new tridentate ligand 4,4′,4″-tri-tert-butyl-terpyridine

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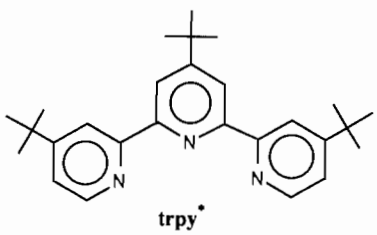
Abstract

The synthesis of coordination compounds of ruthenium(II) containing the new tridentate ligand 4,4′,4″,-tri-tert-butyl-terpyridine (trpy*) is reported. Trpy* has been prepared in up to 50% yield from tert-butyl-pyridine, and easily separated from 4,4′-di-tert-butyl-bipyridine (bpy*). A series of complexes $[(trpy^*)(L_2)RuX]^+$ (L_2 = bpy; bpy*; $X^- = Cl^-$, CF_3SO_3-) and $[(trpy^*)(L_2)RuOH_2]^{2+}$ (L_2bpy; bpy*) were obtained from $(trpy^*)RuCl_3$. Individual complexes have been characterized by elemental analyses, ^1H NMR and UV–Vis spectroscopies, and cyclic voltammetry.

Introduction

2,2′:6′,2″-Terpyridine (trpy) has been widely used as a tridentate chelating ligand in coordination chemistry [1] . In particular, the synthesis of trpy ruthenium(II) and trpy osmium(II) complexes, and their redox reactions have been extensively studied [2–8]. By contrast, the use of substituted terpyridines as metal-chelating agents so far has been restricted to aryl [9–13] and vinyl substituents [14]. The preparation of several 4,4′,4″-trialkyl-terpyridines (R = Me, Et, i-Pr, n-Bu, n-pent) has also been reported but the poor yields and their delicate separations from the main products, 4,4′-dialkyl-bipyridines, probably prevented their use as ligands [15]. In the present work we report (i) the first synthesis in good yield of 4,4′,4″-tri-tert-butyl-terpyridine (trpy*), which can conveniently by separated from 4,4′-di-tert-butyl-bipyridine (bpy*); and (ii) its application in the preparation of new polypyridyl ruthenium(II) complexes. We show that the presence of hydrophobic tert-butyl substituents increases the solubility of the resulting complexes and enhances the electron donating influence of the trpy ligand. A part of this work has already been published as a preliminary communication [16].



trpy*

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Experimental

Instrumentation

Elemental analyses were performed by the Service Central de Microanalyse du CNRS at Lyon, France. Mass spectra were obtained at 70 eV using a Varian MAT 311 mass spectrometer (Centre de Mesures Physiques, Rennes). ^1H NMR spectra were recorded on Bruker WP-80 and Bruker AM 300 spectrometers. UV–Vis electronic spectra were obtained with a Hitachi 100-60 spectrophotometer. Cyclic voltammograms were obtained with a EGG PAR model 362 scanning potentiostat and a XY recorder. A three electrode cell was used comprising a 2 mm Pt-disk working electrode, a 2 mm Pt-disk auxiliary electrode, and an aqueous saturated calomel (SCE) reference electrode. Purified Bu_4NPF_6 was used as electrolyte.

Preparation of 4,4′,4″-tri-tert-butyl-2,2′:6′,2″-terpyridine (trpy)*

2 g of palladium (10% on charcoal) were degassed overnight using an oil pump at 180 °C and then stored under argon at room temperature. 50 ml of freshly distilled 4-tert-butyl-pyridine were transferred with a

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canula into the Schlenk flask containing the palladium catalyst. The mixture was refluxed with stirring under argon for 6 days. After cooling, 150 ml of tetrahydrofuran were added and the mixture was filtered to remove the catalyst. The solvent was concentrated to *c.* 150 ml. 60 g of neutral alumina were added to the solution and the solvent was then evaporated. The resulting mixture was introduced into a flask equipped with a sublimator finger. The unreacted tert-butyl-pyridine (2–5 ml) was first eliminated under vacuum at 120–130 °C. A total of 27–30 g (52–56%) of 4,4'-di-tert-butyl-2,2'-bipyridine (bpy*) was then removed by sublimation at 180–190 °C. Finally extraction of the unsublimed residue from alumina with tetrahydrofuran followed by evaporation of the solvent to dryness gave 18–26 g (35–48%) of pure trpy* as a white powder. Melting point (m.p.) 240 °C. *Anal.* Calc. for $C_{27}H_{35}N_3$: C, 80.75; H, 8.78; N, 10.46. Found: C, 80.37; H, 8.73; N, 10.25%. Mass spectrum (*m/z*): calc. for M^+: 401.598; found: 401.279. UV–Vis (CH_2Cl_2), λ_{max} (nm): 284 sh, 276. ^1H NMR (80 MHz, $CDCl_3$, 309 K): δ 8.74 (dd, 2H, J_{HH} = 1.9 and 0.7 Hz); 8.62 (dd, 2H, J_{HH} = 5.1 and 0.7 Hz); 8.48 (s, 2H); 7.32 (dd, 2H, J_{HH} = 5.1 and 1.9 Hz); 1.46 (s, 9H); 1.42 (s, 18H).

4,4'-tri-tert-butyl-2,2'-bipyridine (bpy)*

Melting point (m.p) 156 °C. Mass spectrum (*m/z*): calc. for $C_{18}H_{24}N_2$ (M^+) 268.194; found: 268.194. UV–Vis (CH_2Cl_2), λ_{max} (nm): 282. ^1H NMR (80 MHz, $CDCl_3$, 309 K): δ 8.59 (dd, 2H, J_{HH} = 5.3 and 0.6 Hz); 8.42 (dd, 2H, J_{HH} = 2.0 and 0.6 Hz); 7.29 (dd, 2H, J_{HH} = 5.3 and 2.0 Hz).

Preparation of (trpy)$RuCl_3 \cdot 3H_2O$ (1)*

2.62 g (10 mmol) of $RuCl_3 \cdot 3H_2O$ and 4.02 g (10 mmol) of trpy* were combined in 80 ml of ethanol. The mixture was heated at reflux for 4 h and allowed to cool to room temperature. The solvent was evaporated to give a brown residue which was dissolved in acetone and precipitated with water. The greenish brown solid was then washed three times with diethyl ether and dried under vacuum. Yield 6.0 g (93%). *Anal.* Calc. for $C_{27}H_{39}Cl_3N_3O_2Ru$: C, 50.28; H, 6.09; N, 6.51; Cl, 16.49. Found: C, 50.87; H, 5.90, N, 6.74; Cl, 16.63%.

Preparation of [(trpy)(bpy)RuCl]PF_6 (2)*

A 6.4 g (10 mmol) quantity of **1** and 1.56 g of 2,2'-bpy (10 mmol) were heated at reflux for 4–6 h in 100 ml of a 1/1 solution of ethanol/water containing 2 g of lithium chloride and 2 ml of triethylamine as reductant. After this time the solvent was reduced with a rotary evaporator. The brown product **2** was precipitated as the PF_6^- salt by adding an NH_4PF_6 saturated water solution and purified by Soxhlet extraction in toluene. Yield 7.0 g (83%). *Anal.* Calc. for $C_{37}H_{43}ClF_6N_5PRu$: C, 52.95; H, 5.16; N, 8.34; Cl, 4.22. Found: C, 52.21; H, 5.26; N, 7.91; Cl, 4.07%. ^1H NMR (300 MHz, $CDCl_3$, 297 K): δ 10.23 (dd, 1H); 8.49 (d, 1H); 8.22 (s, 2H); 8.12 (dt, 1H); 8.07 (d, 2H); 7.74 (dt, 1H); 7.59 (dt, 1H); 7.42 (d, 2H); 7.13 (m, 4H); 6.99 (dt, 1H); 1.58 (s, 9H); 1.28 (s, 18H).

Preparation of [(trpy)(bpy*)RuCl]PF_6 (3)*

Using the same procedure as in the preparation of **2**, 9.0 g of **3** (94%) were obtained from 6.4 g (10 mmol) of **1**, 2.7 g (10 mmol) of bpy*, 2 g of LiCl and 2 ml of Et_3N. *Anal.* Calc. for $C_{45}H_{59}ClF_6N_5PRu$: C, 56.80; H, 6.25; N, 7.37; Cl, 3.73; P, 3.26. Found: C, 56.85: H, 6.28: N, 7.38; Cl, 3.83; P, 3.18%. ^1H NMR (300 MHz, $CDCl_3$, 297 K): δ 10.17 (d, 1H), 8.48 (s, 1H); 8.34 (s, 2H); 8.20 (d, 3H); 7.77 (d, 1H); 7.50 (d, 2H); 7.23 (m, 4H); 1.65 (s, 9H); 1.60 (s, 9H); 1.34 (s, 18H); 1.28 (s, 9H).

Preparation of [(trpy)(bpy)RuOSO$_2$CF$_3$]CF$_3$SO$_3$ (4)*

1.68 g (2 mmol) of **2** and an excess of trifluoromethanesulfonic acid (10 drops) were combined in 30 ml of dichloromethane under an inert atmosphere. The mixture was heated at reflux for 5 h. The orange solution was allowed to cool to room temperature, after which the volume was reduced *in vacuo*. The sample was triturated in hexane to afford an hygroscopic orange powder. Yield 1.77 g (85%). *Anal.* Calc. for $C_{39}H_{43}F_6N_5O_6RuS_2 \cdot CH_2Cl_2$: C, 46.10; H, 4.32; N, 6.72. Found: C, 44.80; H, 4.03; N, 6.60%.

Preparation of [(trpy)(bpy*)RuOSO$_2$CF$_3$]CF$_3$SO$_3$ (5)*

The same procedure was utilized as in the preparation of **4**. 0.91 g of **5** (74%) was obtained from 0.95 g of **3** (1 mmol) and 7 drops of trifluoromethanesulfonic acid. *Anal.* Calc. for $C_{47}H_{59}F_6N_5O_6RuS_2 \cdot CH_2Cl_2$: C, 49.91: H, 5.28; N, 6.07. Found: C, 50.00; H, 5.28; N, 6.05%.

Preparation of [(trpy)(bpy)RuOH$_2$](PF$_6$)$_2$ (6)*

3.36 g (4 mmol) of **3** and 2.06 g (8 mmol) of silver trifluoromethanesulfonate were heated at reflux for 5 h in 200 ml of a 3/1 solution of acetone/water. Silver chloride was filtered off and the volume was then reduced on a rotary evaporator to *c.* 30 ml. Addition of 30 ml of water containing an excess of ammonium hexafluorophosphate gave a brown precipitate. The solid was collected on a frit, washed with water (3×20 ml), and then dried *in vacuo*. Yield 2.97 g (76%). *Anal.* Calc.

for $C_{37}H_{43}F_{12}N_5OP_2Ru$: C, 45.96; H, 4.69; N, 7.24. Found: C, 46.07; H, 4.88; N, 7.85%.

Preparation of [(trpy)(bpy*)RuOH$_2$](PF$_6$)$_2$ (7)*

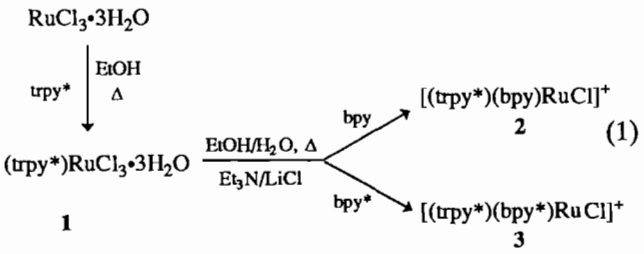
The same procedure was utilized as in the preparation of **6**. 1.90 g (88%) of **7** were obtained from 1.90 g (2 mmol) of **4** and 1.03 g (4 mmol) of silver trifluoromethanesulfonate. *Anal.* Calc. for $C_{45}H_{61}F_{12}N_5OP_2Ru$: C, 50.09; H, 5.70; N, 6.49. Found: C, 49.79; H, 5.75; N, 7.31%.

Results and discussion

Syntheses of ligands and complexes

Trpy* was synthesized on a preparative scale (15–25 g) and in good yield (35–50%) from 4-tert-butyl-pyridine by adapting the method of Rosevear and Sasse [15]. A mixture of trpy* and bpy* [17] was obtained. They were readily separated by sublimation that selectively removed the more volatile bpy*. Details of the procedure and physical and analytical data of trpy* are described in 'Experimental'.

Tri-tert-butyl-terpyridine ruthenium complexes **1**, **2** and **3** were obtained from ruthenium trichloride by adapting the procedures for the preparation of (trpy)RuCl$_3$ [2] and [(trpy)(bpy)RuCl]$^+$ [3] (eqn. (1)); (trpy*)RuCl$_3$ (**1**) was obtained in high yield (93%) by reaction of trpy* with RuCl$_3$·3H$_2$O in refluxing ethanol. The new chloro complexes of type [(trpy*)L$_2$RuCl]PF$_6$ (**2**: L$_2$=bpy; **3**: L$_2$=bpy*) were readily prepared by heating **1** and the ligands L$_2$ in aqueous ethanol containing an excess of lithium chloride and triethylamine as reductant, and precipitating the complex by addition of NH_4PF_6. Complex [(trpy)(bpy*)RuCl]PF$_6$ (**3'**) was also prepared in a similar manner from (trpy)RuCl$_3$ and bpy*. New complexes **2**, **3'**, and especially **3**, which contains five tert-butyl groups, are highly soluble in chlorinated hydrocarbon solvents and in THF, and even slightly soluble in toluene which allowed their purified by Soxhlet extraction.



Triflato complexes of polypyridyl d^6 metal centers have proved to be useful synthetic intermediates for the preparation of solvato, hydrido or nitro complexes [18–21]. The synthesis of the triflato ruthenium complexes **4** and **5** was readily accomplished by the reaction between an excess of triflic acid and chloro ruthenium complexes **2** and **3** in refluxing dichloromethane. The orange complexes **4** and **5** were obtained in 74–85% yield after precipitation by the slow addition of hexane. As expected these complexes showed a good propensity to ionize in polar solvents: addition of water to a dichloromethane solution of **4** and **5** rapidly gave the aquo-ruthenium **6** and **7** in 95% yield (eqn. (2)). These compounds were also made conveniently in one step and in high yield (76–88%) by the reaction between silver triflate and the corresponding chloro complexes **2** and **3** in refluxing acetone–water solution.

TABLE 1. Selected ^{1}H NMR spectral data for ligands and terpyridyl ruthenium complexes

Compound	δ t-Bu (ppm) (multiplicity, relative integration)	Solvent
bpy*	1.37 (s, 18H)	$CDCl_3$
trpy*	1.46 (s, 9H); 1.32 (s, 18H)	$CDCl_3$
[(trpy*)(bpy)RuCl]$^+$ (**2**)	1.58 (s, 9H); 1.28 (s, 18H)	$CDCl_3$
[(trpy*)(bpy*)RuCl]$^+$ (**3**)	1.65 (s, 9H); 1.60 (s, 9H) 1.34 (s, 18H); 1.28 (s, 9H)	$CDCl_3$
[(trpy)(bpy*)RuCl]$^+$ (**3'**)	1.72 (s, 9H); 1.32 (s, 9H)	$(CD_3)_2CO$
[(trpy*)(bpy)RuOSO$_2$CF$_3$]$^+$ (**4**)	1.67 (s, 9H); 1.36 (s, 18H)	CD_2Cl_2
[(trpy*)(bpy*)RuOSO$_2$CF$_3$]$^+$ (**5**)	1.63 (s, 9H); 1.61 (s, 9H) 1.42 (s, 18H); 1.30 (s, 9H)	CD_2Cl_2
[(trpy*)(bpy)RuOH$_2$]$^{2+}$ (**6**)	1.68 (s, 9H); 1.38 (s, 18H)	CD_2Cl_2
[(trpy*)(bpy*)RuOH$_2$]$^{2+}$ (**7**)	1.61 (s, 9H); 1.54 (s, 9H) 1.30 (s, 18H); 1.22 (s, 9H)	$CDCl_3$

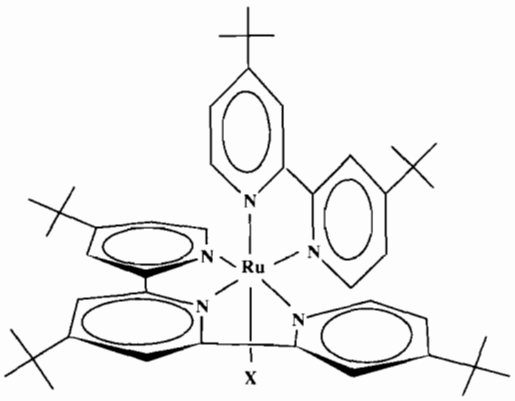
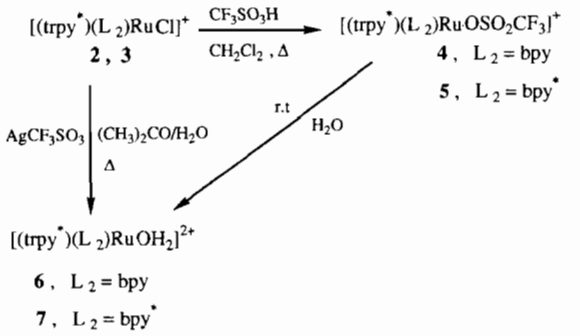


Fig. 1. Structure of $[(trpy^*)(bpy^*)RuX]^{n+}$ (**3**, **5**, **7**) in solution.



(2)

Spectroscopic and electrochemical properties

^1H NMR data

The most characteristic NMR data are indicated in Table 1. Tert-butyl groups are efficient NMR probes for elucidating the geometry of the molecules. As for the free trpy* ligand, complexes **2**, **4** and **6** of type $[(trpy^*)(bpy)RuX]^{n+}$ ($n=1$, 2) show two signals in the ratio 1:2 at *c.* 1.6 and 1.3 ppm corresponding to the central and to the two lateral tert-butyl groups, respectively. In complexes **3**, **5** and **7** of type $[(trpy^*)(bpy^*)RuX]^{n+}$, the tert-butyl groups give rise to four signals in the ratio 1:1:2:1 characteristic of a disymmetric 4,4′-tert-butyl-2,2′-bipyridine. These NMR data are in agreement with the structure represented in Fig. 1.

Electronic spectra

The UV–Vis spectra of these terpyridyl complexes (Table 2) are typical for complexes of this type [5, 22, 23]. They are dominated by metal-to-ligand charge transfer (MLCT) bands in the visible region. A shifting to higher energy normally occurs by replacing the chloro ligand by the triflato and aquo ligands. A similar assignment can be made for the shoulders observed at *c.* 350 nm [5]. Inspection of the absorption data for the chloro ruthenium series shows that the MLCT maxima are slightly affected by substitution: a progressive bathochromic shift is observed as electron donating substituents are introduced.

Electrochemical properties

The redox potentials of the various complexes were determined by cyclic voltammetry either in acetonitrile or in dichloromethane. These complexes each exhibit three reversible or quasi reversible waves, one at positive potentials due to the $Ru^{(II)}/Ru^{(III)}$ redox couple and two at negative potentials attributed to reduction of the coordinated bipyridine and/or terpyridine ligands. As an example the cyclic voltammogram of **3** is shown in Fig. 2. The $Ru^{(III)}/Ru^{(II)}$ potentials reported in Table 2 show that replacing hydrogen atoms by tert-butyl groups has a significative effect in stabilizing the Ru(III) oxidation state: the introduction of electron donating tert-butyl groups decreases the oxidation potentials by *c.* 25 mV per tert-butyl substituent (*e.g.* $[(trpy)(bpy)RuCl]^+$ versus $[(trpy^*)(bpy^*)RuCl]^+$: $\Delta E = 120$ mV for five tert-butyl groups).

Conclusions

In this paper we have reported the synthesis and characterization of a series of ruthenium(II) complexes containing the new 4,4′,4″-tri-tert-butyl-terpyridine li-

TABLE 2. Electronic and cyclic voltammetry data for terpyridyl ruthenium complexes

Complex	λ_{max} (nm) (10^{-3} ϵ (M^{-1} cm^{-1})[a]	$E_{1/2}$(ox) (V) vs. SCE (ΔE_p (mV))
$[(trpy)(bpy)RuCl]^+$	504 (8.1); 369sh (5.5)	0.81 (70)[b]
$[(trpy^*)(bpy)RuCl]^+$ (**2**)	511 (12.9); 372sh (12.1)	0.73 (60)[b]
$[(trpy^*)(bpy^*)RuCl]^+$ (**3**)	514 (14.4); 374sh (13.7)	0.69 (70)[b]
$[(trpy)(bpy^*)RuCl]^+$ (**3′**)	506 (9.6); 370sh (8.2)	0.76 (70)[b]
$[(trpy^*)(bpy)RuOSO_2CF_3]^+$ (**4**)	488; 371sh	1.07 (110)[c]
$[(trpy^*)(bpy^*)RuOSO_2CF_3]^+$ (**5**)	490; 375sh	1.04 (120)[c]
$[(trpy^*)(bpy)RuOH_2]^{2+}$ (**6**)	480 (11.8); 347sh (6.6)	1.12 (190)[c]
$[(trpy^*)(bpy^*)RuOH_2]^{2+}$ (**7**)	485 (11.6); 341sh (7.8)	1.02 (170)[c]

[a]In CH_2Cl_2; sh = shoulder. [b]0.1 M Bu_4NPF_6 in CH_3CN; Pt working electrode; scan rate 200 mV/s. [c]0.1 M Bu_4NPF_6 in CH_2Cl_2.

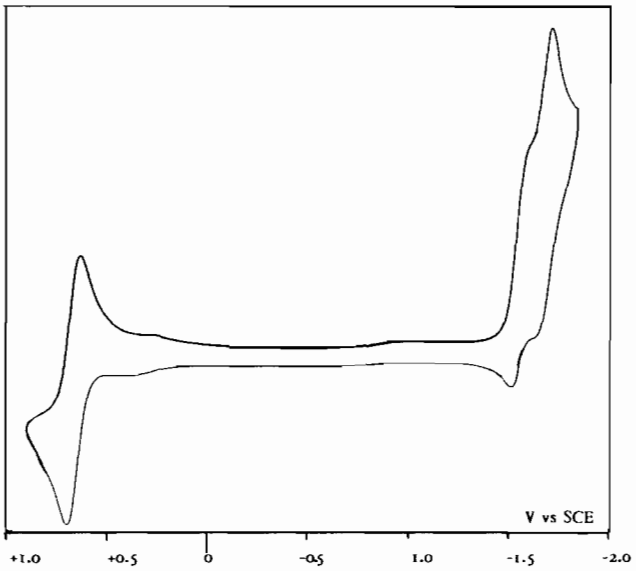


Fig. 2. Cyclic voltammogram of complex **3** in 0.1 M Bu_4NPF_6/CH_3CN. Scan rate = 200 mV/s.

gand. The complexes show significantly better solubility in non-polar solvents than the corresponding unsubstituted trpy analogues. In addition, we show that by varying the number of tert-butyl substituents we are able to 'tune' the redox properties of the complexes.

References

1 E. C. Constable, *Adv. Inorg. Chem. Radiochem., 30* (1986) 69.
2 B. P. Sullivan, J. M. Calvert and T. J. Meyer, *Inorg. Chem., 19* (1980) 1404.
3 K. J. Takeuchi, M. S. Thompson, D. W. Pipes and T. J. Meyer, *Inorg. Chem., 23* (1984) 1845.
4 G. B. Deacon, J. M. Patrick, B. W. Skelton, N. C. Thomas and A. H. White, *Aust. J. Chem., 37* (1984) 929.
5 M. J. Root and E. Deutsch, *Inorg. Chem., 24* (1985) 1464.
6 A. Llobet, P. Doppelt and T. J. Meyer, *Inorg. Chem., 27* (1988) 514.
7 H.-F. Suen, S. W. Wilson, M. Pomerantz and J. L. Walsh, *Inorg. Chem., 28* (1989) 786.
8 R. A. Leising, S. A. Kubow and K. J. Takeuchi, *Inorg. Chem., 29* (1990) 4569, and refs. therein.
9 F. Kröhnke, *Synthesis,* (1976) 1.
10 C. O. Dietrich-Buchecker, P. A. Marnot and J.-P. Sauvage, *Tetrahedron Lett.,* (1983) 5291.
11 W. Spahni and G. Calzaferri, *Helv. Chim. Acta. 67* (1984) 450.
12 M. Beley, J.-P. Colin, J.-P. Sauvage, H. Sugihara, F. Heisel and A. Miehé, *J. Chem. Soc., Dalton, Trans.,* (1991) 3157.
13 J.-P. Colin, S. Guillerez, J.-P. Sauvage, F. Barigelletti, L. De Cola, F. Flamigni and V. Balzani, *Inorg. Chem., 30* (1991) 4230.
14 K. T. Potts, D. A. Usifer, A. Guadalupe and H. D. Abruna, *J. Am. Chem. Soc., 109* (1987) 3961.
15 P. E. Rosevear and W. H. F. Sasse, *J. Heterocycl. Chem., 8* (1971) 483.
16 T. Ben Hadda and H. Le Bozec. *Polyhedron, 7* (1988) 575.
17 P. Belser and A. Von Zelewsky, *Helv. Chim. Acta, 63* (1980) 1675.
18 B. P. Sullivan and T. J. Meyer, *J. Chem. Soc., Chem. Commun.,* (1984) 403.
19 B. P. Sullivan and T. J. Meyer, *J. Chem. Soc., Chem. Commun.,* (1984) 1244.
20 C. M. Bolinger, N. Story, B. P. Sullivan and T. J. Meyer, *Inorg. Chem., 27* (1988) 4582.
21 M. A. Greaney, C. L. Coyle, M. A. Harmer, A. Jordan and E. I. Stiefel, *Inorg. Chem., 28* (1989) 912.
22 G. M. Bryant, J. E. Fergusson and H. K. Powell, *Aust. J. Chem., 24* (1971) 257.
23 N. R. Davies and T. L. Mullins, *Aust. J. Chem., 20* (1967) 657.