

COMMUNICATION

RUTHENIUM(II) COMPLEXES CONTAINING THE TRIDENTATE LIGAND 4,4',4''-TRI-TERT-BUTYL-TERPYRIDINE: SYNTHESIS AND ISOMERISATION STUDY OF *trans*-(trpy*)RuCl₂(L) [L = CO, PR₃, P(OR)₃]

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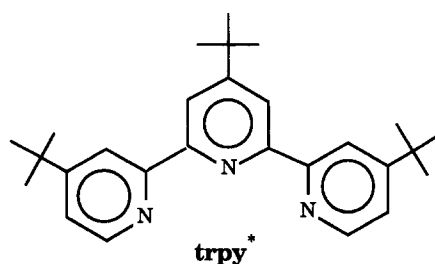
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Abstract—The synthesis and characterisation of a series of (trpy*)RuCl₂(L) complexes [where trpy* = 4,4',4''-tri-tert-butyl-2,2'-6',2''-terpyridine and L = CO, PPh₃, PMe₃, PMe₂Ph, P(OPh)₃, P(OMe)₃] are described together with a preliminary study of their *trans* → *cis* thermal and photochemical isomerisation.

The chemical, spectral and redox properties of ruthenium(II) complexes containing the tridentate ligand 2,2'-6',2''-terpyridine (trpy) have been widely studied.¹ For example, the synthesis and reactivity of *trans* and *cis* complexes of general formula (trpy)Ru^{II}Cl₂(L) have been extensively investigated.²⁻⁶ Recently we reported the preparation of cationic ruthenium complexes containing the new tridentate 4,4',4''-tri-tert-butyl-2,2'-6',2''-terpyridine (trpy*).⁷ We pointed out that the presence of the hydrophobic *tert*-butyl substituents considerably increases the solubility of the resulting complexes in non-polar solvents and enhances the electron donating influence of the trpy ligand. We now describe the synthesis and characterisation of new *trans*-(trpy*)RuCl₂(L) complexes containing a

variety of ligands L such as carbonyl, phosphines and phosphites. In addition, we report the preliminary study of their *trans* → *cis* isomerisation.

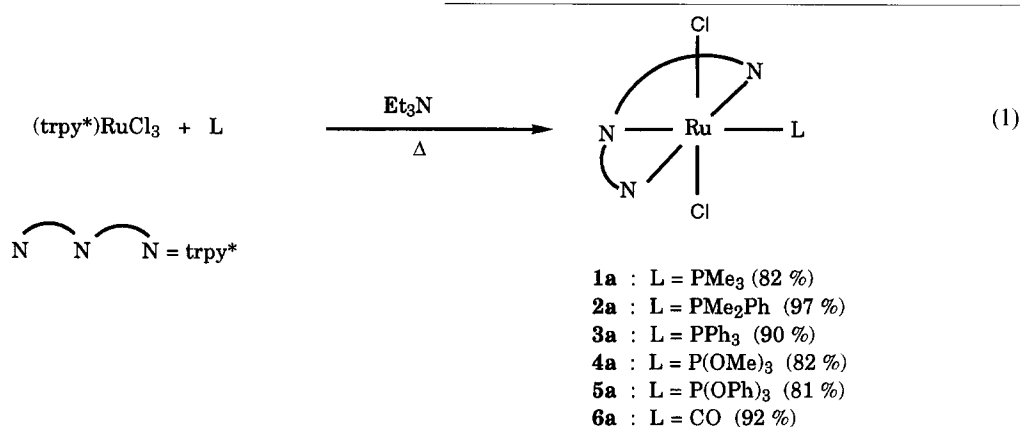


The complexes *trans*-(trpy*)RuCl₂(L) (**1a–5a**) were readily obtained in 81–97% yield by reacting (trpy*)RuCl₃, the phosphorus ligands L and an excess of triethylamine as reductant in refluxing chloroform [eq. (1)]. Similarly *trans*-(trpy*)RuCl₂(CO) (**6a**) was prepared in high yield (92%)

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under CO pressure (5 atm) in refluxing dichloroethane.

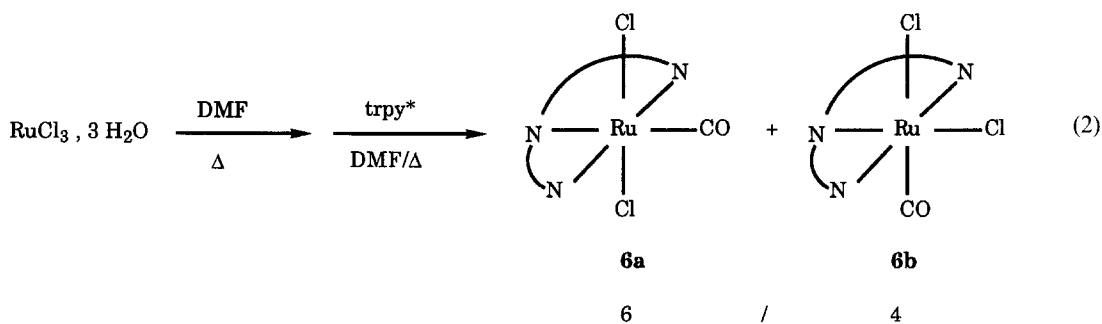
tammetry.[†] The ¹H NMR spectra display two typical resonances^{7b} in the ratio 1:2 between 1.6



Another convenient source of CO for the synthesis of carbonyl complex is dimethylformamide.³ Thus, heating the red ruthenium solution (obtained from RuCl₃ · 3H₂O in refluxing dimethylformamide) with trpy* in refluxing dimethylformamide produced **6**, in 96% yield, as a mixture of *trans* and *cis* isomers **6a** and **6b** in *ca* 60:40 ratio [eq. (2)]. No further *trans* → *cis* isomerisation was observed after prolonged heating. The IR spectrum of the mixture showed two strong absorption bands at 1946 and 1917 cm⁻¹ due to the ν_{CO} frequencies of the *trans* and *cis* isomers **6a** and **6b**, respectively.

and 1.3 ppm corresponding to the central and to the two lateral tert-butyl groups, respectively. Cyclic voltammetry of **1a–6a** in dichloromethane shows for all complexes reversible Ru^{III}/Ru^{II} couples (Table 1). The increase in Ru^{III}/Ru^{II} potentials follows the decrease in σ-donor ability of the ligands L, *i.e.* PMe₃ > PMe₂Ph > PPh₃ > P(OMe)₃ > P(OPh)₃ >> CO. Thus the easy introduction of ligands L allows the fine tune of the redox properties of such complexes over a relatively broad range (600 mV).

The *trans* → *cis* isomerisation of **1a–6a** was studied



Complexes **1a–6a** were characterised by elemental analysis, NMR spectroscopy, and cyclic vol-

under thermal and photochemical conditions and monitored by cyclic voltammetry. Whereas the

[†] Selected analytical and spectroscopical data: **3a**: Calc (Found) for C₄₅H₅₀N₃RuCl₂P: C, 64.7 (64.8); H, 6.0 (6.2); N, 5.0 (5.0); ¹H NMR (300 MHz, CD₂Cl₂, 297 K) δ 8.18 (d, 2H, *J* = 5.86 Hz); 8.17 (d, 2H, *J* = 0.88 Hz); 8.05 (d, 2H, *J* = 2.05 Hz); 7.88–7.20 (m, 15H, C₆H₅); 1.58 (s, 9H, *t*-Bu); 1.36 (s, 18H, *t*-Bu); ³¹P NMR (CD₂Cl₂, 121.5 MHz, 297 K) δ 46.45 (s, PPh₃). **3b**: Calc (Found) for C₄₅H₅₀N₃RuCl₂P: C, 64.7 (63.8); H, 6.0 (6.2); N, 5.0 (4.9); ¹H NMR (300 MHz, CD₂Cl₂, 297 K) δ 8.97 (d, 2H, *J* = 5.75 Hz); 7.58 (s, 2H); 7.50 (s, 2H); 7.20 (d, 2H, *J* = 6.46 Hz); 7.12 (m, 15H, C₆H₅); 1.34 (s, 9H, *t*-Bu); 1.23 (s, 18H, *t*-Bu); ³¹P NMR (CD₂Cl₂, 121.5 MHz, 297 K) δ 44.59 (s, PPh₃).

Table 1. Cyclic voltammetry data [$E_{1/2}$ (Ru^{III}/Ru^{II})] of complexes 1–6^a

Complex	L	<i>Trans</i> a	<i>Cis</i> b
1	PMe ₃	0.32	0.46
2	PMe ₂ Ph	0.34	0.49
3	PPh ₃	0.41	0.55
4	P(OMe) ₃	0.46	—
5	P(OPh) ₃	0.58	—
6	CO	0.93	1.02

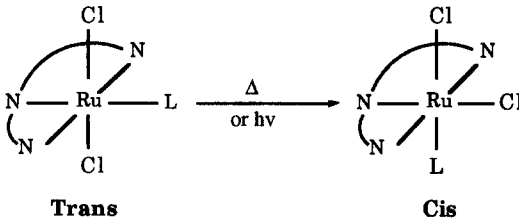
^a 0.1 M Bu₄NPF₆ in CH₂Cl₂; Pt working electrode; scan rate 200 mV s⁻¹.

phosphite and carbonyl complexes 4a–6a were thermally stable, the phosphine complexes 1a–3a slowly isomerised and led to a mixture of *trans* and *cis* isomers 1b–3b, after heating at reflux in dichloroethane for 16 h (Table 2). These results con-

trast with the quantitative thermal conversion of the analogous *trans* unsubstituted terpyridine complexes (L = triphenylphosphine) to their *cis* isomers upon refluxing in dichloroethane for 9–10 h.² The *cis*:*trans* ratio displayed in Table 2 indicates that the thermal isomerisation appears to be influenced by the nature of the ligand L, the formation of *cis* isomers being favoured by basic and sterically hindered ligands such as triphenylphosphine. Complexes 1a–3a were more easily and completely converted to 1b–3b upon irradiation at room temperature in dichloromethane (Hg lamp, pyrex). The isomerisation was clean and no side products could be observed. However under the same conditions, the carbonyl complex 6a was found to be photochemically stable whereas phosphite complexes 4a and 5a led to decomposition (Table 2). The Ru^{III}/Ru^{II} couples for *cis* compounds 1a–3a were found at *ca* 140 mV more anodic potentials than the *trans* isomers, an effect that has been already observed for the unsubstituted trpy analogues.^{2,5}

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Table 2. *Trans*:*cis* ratio obtained under thermal^a and photochemical^b conditions

			
Complex	L	Δ^a <i>cis</i> : <i>trans</i>	$h\nu^b$ <i>cis</i> : <i>trans</i>
1	PMe ₃	44:56	100:0
2	PMe ₂ Ph	40:60	100:0
3	PPh ₃	70:30	100:0
4	P(OMe) ₃	0:100	^c
5	P(OPh) ₃	0:100	^c
6	CO	0:100	0:100

^a Refluxing 1,2-dichloroethane for 16 h.

^b Dichloromethane at room temperature for 4 h.

^c Decomposition.

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