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COMMUNICATION

RUTHENIUM(II) COMPLEXES CONTAINING THE TRIDENTATE LIGAND 4,4′,4″-TRI-TERT-BUTYL-TERPYRIDINE: SYNTHESIS AND ISOMERISATION STUDY OF *trans*-(trpy*)$RuCl_2$(L) [L = CO, PR_3, $P(OR)_3$]

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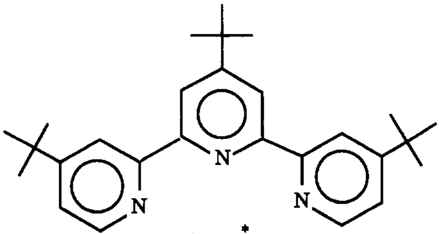
Abstract—The synthesis and characterisation of a series of (trpy*)$RuCl_2$(L) complexes [where trpy* = 4,4′,4″-tri-tert-butyl-2,2′-6′,2″-terpyridine and L = CO, PPh_3, PMe_3, PMe_2Ph, $P(OPh)_3$, $P(OMe)_3$] are described together with a preliminary study of their *trans* → *cis* thermal and photochemical 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) $Ru^{II}Cl_2$(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*)$RuCl_2$(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.



trpy*

The complexes *trans*-(trpy*)$RuCl_2$(L) (**1a**–**5a**) were readily obtained in 81–97% yield by reacting (trpy*)$RuCl_3$, the phosphorus ligands L and an excess of triethylamine as reductant in refluxing chloroform [eq. (1)]. Similarly *trans*-(trpy*) $RuCl_2$(CO) (**6a**) was prepared in high yield (92%)

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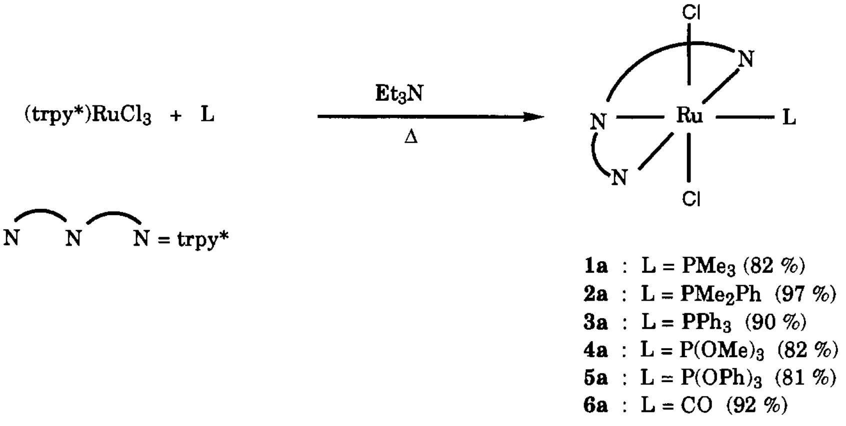
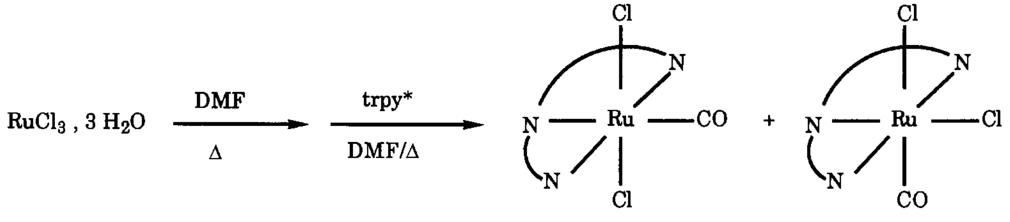
under CO pressure (5 atm) in refluxing dichloroethane.



(1)

1a : L = PMe3 (82 %)
2a : L = PMe2Ph (97 %)
3a : L = PPh3 (90 %)
4a : L = P(OMe)3 (82 %)
5a : L = P(OPh)3 (81 %)
6a : L = CO (92 %)

Another convenient source of CO for the synthesis of carbonyl complex is dimethylformamide.[3] Thus, heating the red ruthenium solution (obtained from $RuCl_3 \cdot 3H_2O$ 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.



(2)

6a **6b**

6 / 4

Complexes **1a**–**6a** were characterised by elemental analysis, NMR spectroscopy, and cyclic voltammetry.† The ^1H NMR spectra display two typical resonances[7b] in the ratio 1:2 between 1.6 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.* $PMe_3 > PMe_2Ph > PPh_3 > P(OMe)_3 > P(OPh)_3 \gg CO$. 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 under thermal and photochemical conditions and monitored by cyclic voltammetry. Whereas the

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† *Selected analytical and spectroscopical data*: **3a**: Calc (Found) for $C_{45}H_{50}N_3RuCl_2P$: C, 64.7 (64.8); H, 6.0 (6.2); N, 5.0 (5.0); ^1H NMR (300 MHz, CD_2Cl_2, 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, C_6H_5), 1.58 (s, 9H, t-Bu), 1.36 (s, 18H, t-Bu); ^{31}P NMR (CD_2Cl_2, 121.5 MHz, 297 K) δ 46.45 (s, PPh_3). **3b**: Calc (Found) for $C_{45}H_{50}N_3RuCl_2P$: C, 64.7 (63.8); H, 6.0 (6.2); N, 5.0 (4.9); ^1H NMR (300 MHz, CD_2Cl_2 297 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, C_6H_5), 1.34 (s, 9H, t-Bu), 1.23 (s, 18H, t-Bu); ^{31}P NMR (CD_2Cl_2, 121.5 MHz, 297 K) δ 44.59 (s, PPh_3).

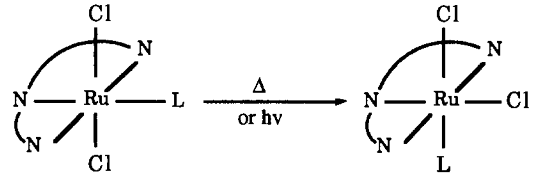
Table 1. Cyclic voltammetry data [$E_{1/2}$ (Ru^{III}/Ru^{II})] of complexes **1–6**[a]

Complex	L	*Trans* a	*Cis* b
1	PMe_3	0.32	0.46
2	PMe_2Ph	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 Bu_4NPF_6 in CH_2Cl_2; 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 contrast 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]

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



Trans **Cis**

Complex	L	Δ[a] *cis* : *trans*	*hν*[b] *cis* : *trans*
1	PMe_3	44 : 56	100 : 0
2	PMe_2Ph	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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