2,2′:6′,2″-Terpyridine (terpy) acting as a Fluxional Bidentate Ligand. Part 3.[1] Ruthenium Carbonyl Halide Complexes, $[RuX_2(CO)_2(terpy)]$ (X = Cl, Br or I) and Metal Tetracarbonyl Complexes $[M(CO)_4(terpy)]$ (M = Cr, Mo or W): Nuclear Magnetic Resonance Studies of their Solution Dynamics and Synthesis of *trans*-$[RuX_2(CO)(terpy)]$ (X = Cl, Br or I)

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Under mild conditions 2,2′:6′,2″-terpyridine reacted with $[\{RuX_2(CO)_2\}_n]$ (X = Cl, Br or I) and with $[M(CO)_4(nbd)]$ [M = Cr, Mo or W; nbd = norbornadiene (bicyclo[2.2.1]hepta-2,5-diene)] to form the octahedral complexes *trans, cis*-$[RuX_2(CO)_2(terpy)]$ and $[M(CO)_4(terpy)]$ respectively, in which the terpyridine acts as a bidentate chelate ligand. In solution these complexes are fluxional with the terpyridine oscillating between equivalent bidentate modes. Heating *trans,cis*-$[RuX_2(CO)_2(terpy)]$ (X = Cl, Br or I) in a high boiling solvent formed *trans*-$[RuX_2(CO)(terpy)]$ whereas *cis*-$[RuX_2(CO)(terpy)]$ was formed by heating the solid dicarbonyl complex.

2,2′:6′,2″-Terpyridine (terpy) has long been known to form stable complexes with transition metals, but in recent years there has been increased interest shown in the co-ordination compounds formed by terpy and other oligopyridines.[2] Attention has been particularly focused on complexes of ruthenium(II) because of the photochemical and electrochemical properties exhibited by some of these complexes.[3,4] Although terpy primarily functions as a terdentate ligand, a number of complexes have been reported in which it is acting as a bidentate ligand.[5-12]

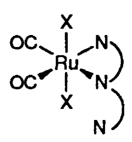
We have reported[13] our preliminary results of a detailed NMR study of some complexes of Pt^{IV}, Re^{I} and W^{0} with terpy and our completed results for trimethylplatinum halides[14] and rhenium pentacarbonyl halides.[1] In these studies it was shown that in solution terpy was definitely acting in a bidentate chelate mode and was also undergoing an oscillatory fluxional motion. We now report further examples of terpy behaving as a fluxional bidentate ligand in the areas of Ru^{II}, Cr^{0}, Mo^{0} and W^{0} complexes.

This paper describes the reactions of the polymeric ruthenium dicarbonyl halides $[\{RuX_2(CO)_2\}_n]$ (X = Cl, Br or I) and the tetracarbonyl norbornadiene [nbd (bicyclo[2.2.1]hepta-2,5-diene)] complexes $[M(CO)_4(nbd)]$ (M = Cr, Mo or W) with terpy, solution NMR studies of the dynamic stereochemistry of the resulting *trans,cis*-$[RuX_2(CO)_2(terpy)]$ **1** and $[M(CO)_4(terpy)]$ complexes respectively, and the conversions of **1** to *cis*- and *trans*-$[RuX_2(CO)(terpy)]$ **2** and **3**.

Experimental

Materials.—The compounds $[M(CO)_4(nbd)]$ (M = Cr or Mo[15] and W[16]), *trans,cis*-$[RuX_2(CO)_2(terpy)]$ (X = Cl or Br)[9] were prepared by previous methods with the modification for Ru complexes that the solutions were allowed to cool to approximately 40 °C before addition of the terpy. 2,2′:6′,2″-Terpyridine (terpy) was purchased from Aldrich.

Synthesis of Complexes.—All preparations were carried out using standard Schlenk techniques[17] under purified nitrogen using freshly distilled, dried and degassed solvents.



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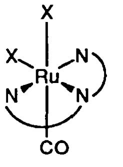

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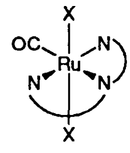

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Tetracarbonyl(2,2′:6′,2″-*terpyridyl*)*chromium*(0). The complex $[Cr(CO)_4(nbd)]$ (0.18 g, 0.70 mmol) was added to a stirred solution of terpyridine (0.15 g, 0.64 mmol) in hexane (30 cm^3). The pale yellow solution was protected from light and stirred for 3 to 4 d. The supernatant liquid was then decanted and the red precipitate was washed with hexane (3 × 10 cm^3) and dried under vacuum. Yield 0.03 g (12%). Because of its instability this compound was not obtained pure.

Tetracarbonyl(2,2′:6′,2″-*terpyridyl*)*molybdenum*(0). The complex $[Mo(CO)_4(nbd)]$ (0.13 g, 0.43 mmol) and terpyridine (0.1 g, 0.43 mmol) were heated in hexane (40 cm^3) under reflux for 2 h. The initially pale-yellow solution darkened to red-purple and a dark purple solid was precipitated. The solid was isolated by filtration, washed with hexane (2 × 10 cm^3) and recrystallised from dichloromethane–hexane to yield dark red, needle-like crystals. Yield 0.09 g (47%).

Tetracarbonyl(2,2′:6′,2″-*terpyridyl*)*tungsten*(0). The complex $[W(CO)_4(nbd)]$ (0.17 g, 0.43 mmol) and terpyridine (0.1 g, 0.43 mmol) were heated in hexane (30 cm^3) under reflux for 10 h to produce a mauve solution and a black precipitate. The solid was isolated by filtration, washed with hexane (2 × 10 cm^3) and recrystallised from dichloromethane–hexane to yield a dark red-purple crystalline solid. Yield 0.05 g (23%).

cis-*Dicarbonyl*-trans-*diiodo*(2,2′:6′,2″-*terpyridyl*)-*ruthenium*(II). The complex $[\{RuCl_2(CO)_2\}_n]$ (0.04 g, 0.18

Table 1 Synthetic and analytical data for the complexes $[M(CO)_4(terpy)]$ (M = Cr, Mo or W), $[RuX_2(CO)_2(terpy)]$ and *trans*-$[RuX_2(CO)(terpy)]$ (X = Cl, Br or I)

				Analysis[c] (%)		
Complex	Appearance	Yield[a] (%)	ν_{CO}[b]/cm^{-1}	C	H	N
$[Cr(CO)_4(terpy)]$	Red	12	2010 (s) 1832 (s) 1903 (vs) 1860 (sh)	—	—	—
$[Mo(CO)_4(terpy)]$	Red-purple	47	2015 (m) 1832 (s) 1905 (vs) 1885 (sh)	50.8 (51.7)	2.5 (2.5)	9.3 (9.5)
$[W(CO)_4(terpy)]$	Dark purple	23	2009 (s) 1826 (s) 1892 (vs) 1880 (sh)	42.4 (43.1)	2.2 (2.1)	7.4 (7.9)
trans,cis-$[RuCl_2(CO)_2(terpy)]$	Green-yellow	49	2066 (s) 2005 (s)	45.0 (44.3)	2.2 (2.4)	9.2 (9.1)
trans,cis-$[RuBr_2(CO)_2(terpy)]$	Red and yellow[d]	45	2064 (s) 2005 (s)	36.8 (37.1)	1.9 (2.0)	7.4 (7.6)
trans,cis-$[RuI_2(CO)_2(terpy)]$	Dark red	44	2058 (s) 2005 (s)	31.0 (31.7)	1.9 (1.7)	6.1 (6.5)
trans-$[RuCl_2(CO)(terpy)]$	Red	86	1966 (s)	45.0 (44.4)	2.6 (2.6)	9.8 (9.7)
trans-$[RuBr_2(CO)(terpy)]$	Brown-red	83	1968 (s)	36.2 (36.8)	2.1 (2.1)	7.5 (8.0)
trans-$[RuI_2(CO)(terpy)]$	Dark red	81	1965 (s)	32.8 (32.5)	2.1 (2.2)	6.3[e] (6.5)[e]

[a] Yield quoted relative to metal-containing reactant. [b] Recorded in CH_2Cl_2 solution; s = strong, v = very, m = medium, sh = shoulder. [c] Calculated values in parentheses. [d] Ref. 9. [e] Allows for $0.5Me_2CO$.

mmol) and LiI (0.2 g, 1.5 mmol) were heated in methanol (10 cm^3) under reflux for 3 h. The dark yellow solution was cooled to approximately 40 °C, terpyridine (0.05 g, 0.21 mmol) added and the resulting solution heated under reflux for 4 min. Cooling the solution produced a fine dark red solid which was washed with methanol (2 × 10 cm^3) and then recrystallised from hot methanol. Yield 0.05 g (44%).

trans-*Carbonyldihalogeno*(2,2′:6′,2″-*terpyridyl*)*ruthenium*(II). The chloro, bromo and iodo monocarbonyl complexes were prepared in a similar fashion by heating the dicarbonyl complexes in boiling tetrachloroethane for 3 to 4 h. The progress of the reaction was monitored using infrared spectroscopy, to note the disappearance of the carbonyl bands of the dicarbonyl species. The cooled solution was concentrated under reduced pressure to a low volume and the solid thus produced was isolated by decantation, washed with hexane (2 × 10 cm^3) and recrystallised from acetone. The synthetic and analytical data for the three complexes are given in Table 1.

Physical Methods.—Hydrogen-1 NMR spectra were recorded on Bruker AM250 or AC300 spectrometers operating at 250.13 and 300.13 MHz respectively. A standard B-VT1000 variable-temperature unit was used to control the probe temperature, the calibration of this unit being checked periodically against a Comark digital thermometer. The temperatures are considered accurate to ± 1 °C. Rate data were based on band-shape analysis of ^{1}H spectra using the authors' version of the standard DNMR program,[18] and activation parameters based on experimental rate data were calculated using the THERMO program.[19] Infrared spectra were recorded on a Perkin Elmer 881 spectrometer calibrated from the 1602 cm^{-1} signal of polystyrene, and on a Nicolet Magna IR 550 FT spectrometer. UV/VIS spectra were recorded on a Philips PU 8730 spectrophotometer. Elemental analyses were performed by Butterworth Laboratories Ltd., Teddington, Middlesex.

Results and Discussion

The complexes *trans,cis*-$[RuX_2(CO)_2(terpy)]$ **1** (X = Cl, Br or I) were readily obtained from $[\{RuX_2(CO)_2\}_n]$ and terpy by a modification of a previous method.[9] In solution the complexes show two strong carbonyl stretching bands (Table 1) which are indicative of a *cis* stereochemistry for the carbonyl groups and in agreement with the reported values.[9] NMR spectroscopy (see below) provided conclusive evidence for terpy acting as a bidentate chelate ligand in these complexes. The stereochemistry of these complexes has been established by X-ray crystallography.[9]

Previous work[9] has shown that decarbonylation of *trans,cis*-$[RuX_2(CO)_2(terpy)]$ with trimethylamine *N*-oxide produced *cis*-$[RuX_2(CO)(terpy)]$, the *cis* arrangement of halogens being confirmed by X-ray crystallography. We find that heating *trans,cis*-$[RuX_2(CO)_2(terpy)]$ in tetrachloroethane causes decarbonylation with the formation of *trans*-$[RuX_2(CO)(terpy)]$. This identification was based upon analytical data, IR data (a single carbonyl band) (Table 1), a ^{1}H NMR spectrum which comprised only six chemically shifted signals (Table 2) indicative of a terdentate terpy, and a visible absorption band at approximately 450 nm (Table 3) in agreement with reported values for the *trans* isomers.[9,20]

In contrast to this, heating solid *trans,cis*-$[RuX_2(CO)_2(terpy)]$ above 140 °C resulted in the formation of *cis*-$[RuX_2(CO)(terpy)]$. The stereochemical identification of these compounds was based on the observation of a band in the visible spectrum at approximately 415 nm which is in agreement with a previous report.[9] The far infrared data obtained for the *cis* and *trans* monocarbonyl compounds were also consistent with previous work (Table 3). The ^{1}H NMR spectra of these compounds were not recorded as they would not aid stereochemical assignment.

The complexes $[M(CO)_4(terpy)]$ (M = Cr, Mo or W) were prepared from $[M(CO)_4(nbd)]$ and terpy. These complexes, which are all air and light sensitive in solution, show four carbonyl stretching vibrations (Table 1), in agreement with a previous report and consistent with a $M(CO)_4$ moiety of C_{2v} symmetry. This implies a bidentate terpy and NMR spectroscopy (see below) provided confirmation of this conclusion.

Ambient and Above-ambient Temperature NMR Studies.—$[RuX_2(CO)_2(terpy)]$. At ambient temperature the ^{1}H NMR spectra of these complexes consisted of a complex pattern of

Table 2 Proton NMR chemical shift data [a] for terpy and its chromium(0), molybdenum(0), tungsten(0) and ruthenium(II) complexes

Compound	T/°C	Solvent	δ_{AE}	δ_{BF}	δ_{CG}	δ_{DH}	δ_J	δ_{KL}
terpy[b]	30	CD$_2$Cl$_2$	8.69	7.35	7.88	8.64	7.96	8.47
[Cr(CO)$_4$(terpy)][b]	30	CD$_2$Cl$_2$	9.27 (A)	7.35 (B)	7.85 (C)	8.12 (D)	8.00 (J)	8.10 (K)
			8.81 (E)	7.35 (F)	7.70 (G)	7.61 (H)		7.68 (L)
[Mo(CO)$_4$(terpy)][b]	−70	CD$_2$Cl$_2$	9.07 (A)	7.47 (B)	7.99 (C)	8.20 (D)	8.10 (J)	8.23 (K)
			8.73 (E)	7.42 (F)	7.91 (G)	7.68 (H)		7.68 (L)
[W(CO)$_4$(terpy)][b]	−30	CD$_2$Cl$_2$	9.22 (A)	7.46 (B)	8.02 (C)	8.26 (D)	8.12 (J)	8.23 (K)
			8.75 (E)	7.43 (F)	7.91 (G)	7.69 (H)		7.66 (L)
trans,cis-[RuCl$_2$(CO)$_2$(terpy)][c]	30	(CDCl$_2$)$_2$	9.15 (A)	7.68 (B)	8.16 (C)	8.28 (D)	8.19 (J)	8.28 (K)
			8.84 (E)	7.56 (F)	7.95 (G)	8.20 (H)		7.91 (L)
trans,cis-[RuBr$_2$(CO)$_2$(terpy)][c]	30	(CDCl$_2$)$_2$	9.15 (A)	7.66 (B)	8.14 (C)	8.27 (D)	8.18 (J)	8.28 (K)
			8.84 (E)	7.56 (F)	7.94 (G)	8.19 (H)		7.85 (L)
trans,cis-[RuI$_2$(CO)$_2$(terpy)][c]	30	(CDCl$_2$)$_2$	9.13 (A)	7.60 (B)	8.09 (C)	8.26 (D)	8.13 (J)	8.27 (K)
			8.82 (E)	7.53 (F)	7.91 (G)	8.15 (H)		7.73 (L)
trans-[RuCl$_2$(CO)(terpy)][c]	30	(CDCl$_2$)$_2$	9.02	7.67	8.27	8.61	8.55	8.95
trans-[RuBr$_2$(CO)(terpy)][c]	30	(CDCl$_2$)$_2$	8.83	7.67	8.28	8.62	8.60	8.75
trans-[RuI$_2$(CO)(terpy)][c]	30	(CDCl$_2$)$_2$	8.79	7.64	8.26	8.65	8.57	8.72

[a] Relative to SiMe$_4$ (internal) δ = 0. See Fig. 2 for hydrogen labelling. [b] Recorded at 250 MHz. [c] Recorded at 300 MHz.

Table 3 Spectroscopic data for *cis*- and *trans*-[RuX$_2$(CO)(terpy)] (X = Cl, Br or I)

Compound	UV/VIS[a] λ_{max}/nm	IR[b,c] (400–200)/cm^{-1}	Source
cis-[RuCl$_2$(CO)(terpy)]	417	318m, 278m, 255m	Ref. 9
cis-[RuCl$_2$(CO)(terpy)]	419	315m, 277m, 255m	Ref. 20
cis-[RuCl$_2$(CO)(terpy)]	415	320m, 261m, 240m	This work
cis-[RuBr$_2$(CO)(terpy)]	421	258m, 243w, 190m, 164w	Ref. 9
cis-[RuBr$_2$(CO)(terpy)]	417	250w	This work
cis-[RuI$_2$(CO)(terpy)]	413	—	This work
trans-[RuCl$_2$(CO)(terpy)]	461	315m, 302 (sh)	Ref. 20
trans-[RuCl$_2$(CO)(terpy)]	461	322m, 305 (sh)	This work
trans-[RuBr$_2$(CO)(terpy)]	455	248m	This work
trans-[RuI$_2$(CO)(terpy)]	451	—	This work

[a] Recorded in CH$_2$Cl$_2$ solution. [b] m = Medium, sh = shoulder, w = weak. [c] Recorded as CsI discs.

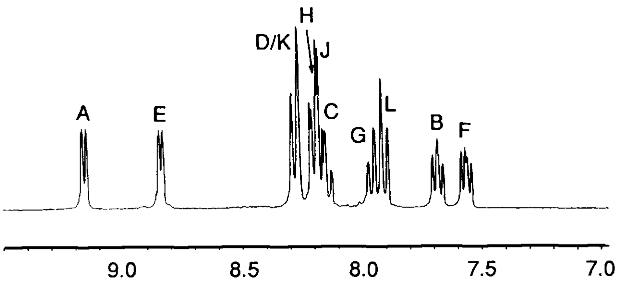


Fig. 1 300 MHz ^{1}H NMR spectrum of *trans,cis*-[RuCl$_2$(CO)$_2$(terpy)] in (CDCl$_2$)$_2$ at 30 °C. Signal labels refer to Fig. 2

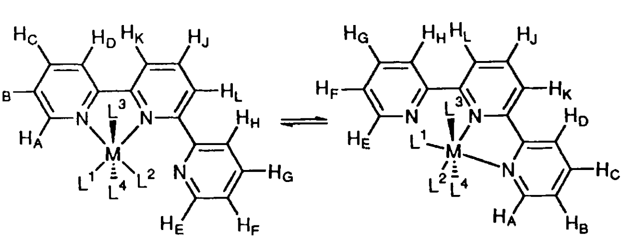


Fig. 2 Interconverting structures of the terpy complexes showing the hydrogen labelling: (*a*) M = Ru, L^1 = L^2 = CO, L^3 = L^4 = Cl, Br or I; (*b*) M = Cr, Mo or W, L^1 = L^2 = L^3 = L^4 = CO

overlapping signals which was clearly associated with an unsymmetrically co-ordinated terpyridine. The results for [RuCl$_2$(CO)$_2$(terpy)] will serve to demonstrate the analysis of the problem. The spectrum (Fig. 1) was fully assigned by a two-dimensional correlation spectroscopy (COSY) experiment to eleven non-equivalent protons labelled A to L in Figs. 1 and 2, and hence was clearly consistent with a bidentate terpyridine ligand. All chemical shift and coupling constant data are given in Tables 2 and 4. Hydrogens H$_A$ and H$_E$, alpha to the N atoms, give rise to signals at the highest frequencies, with H$_A$ experiencing an additional co-ordination-induced shift.

On increasing the solution temperature to *ca.* 70 °C extensive spectral changes took place as indicated in Fig. 3. Exchange broadening occurred between analogous pairs of protons namely H$_{A/E}$, H$_{B/F}$, H$_{C/G}$, H$_{D/H}$ and H$_{K/L}$. As observed previously [1,14] with compounds of Re^I and Pt^{IV} involving bidentate terpy, proton H$_J$ retained its triplet structure and did not undergo exchange. These exchange processes can be rationalised by the dynamic spin problems ABCD $\rightleftharpoons$ EFGH and JKL $\rightleftharpoons$ JLK.

At temperatures greater than 70 °C a new set of signals appeared amidst the broad coalescing signals of the bidentate terpy species. The intensity of these new signals increased rapidly with temperature (Fig.3) whilst the exchange-broadened signals decreased in intensity. The triplet structure of the signal due to H$_J$ also collapsed. At 110 °C six sharp well resolved chemically shifted signals were observed, which are indicative of terpy symmetrically bonded to Ru. On cooling the sample to ambient temperature the spectrum remained consistent with a symmetrical terpyridine and it indicated that only a trace amount of the starting complex involving a bidentate terpy was present. These spectral changes can be rationalised as arising from two processes, first the terpyridine being involved in a fluxional process in which the co-ordination complex is oscillating between two forms both of which involve terpy

Table 4 Proton NMR scalar coupling constant data[a] for $[M(CO)_4(terpy)]$ (M = Cr, Mo or W), $[RuX_2(CO)_2(terpy)]$ and *trans*-$[RuX_2(CO)(terpy)]$ (X = Cl, Br or I)

Complex	$^3J_{AB}/^3J_{EF}$	$^4J_{AC}/^4{}_{EG}$	$^3J_{BC}/^3J_{FG}$	$^4J_{BD}/^4J_{FH}$	$^3J_{CD}/^3J_{GH}$	$^3J_{JK}/^3J_{JL}$
$[Cr(CO)_4(terpy)]$	5.7/5.5	*b*	*b*	*b*	6.7/*b*	7.7/7.7
$[Mo(CO)_4(terpy)]$	5.3/4.5	*b*	7.5/7.2	*b*	8.8/7.8	7.9/7.8
$[W(CO)_4(terpy)]$	5.0/4.3	*b*	7.1/7.0	*b*	8.4/7.0	7.8/7.8
trans,cis-$[RuCl_2(CO)_2(terpy)]$	5.5/4.9	1.6/1.6	6.3/7.8	*b*	*b*/7.9	8.1/8.1
trans,cis-$[RuBr_2(CO)_2(terpy)]$	5.5/5.2	1.4/1.7	6.9/7.8	1.1/1.1	8.1/7.8	7.9/7.7
trans,cis-$[RuI_2(CO)_2(terpy)]$	5.4/4.9	1.5/1.7	5.8/7.8	1.2/1.0	8.0/7.9	7.9/7.7
trans-$[RuCl_2(CO)(terpy)]$	8.2	1.0	6.3	1.0	8.1	8.1
trans-$[RuBr_2(CO)(terpy)]$	8.0	1.3	6.0	1.2	8.0	7.6
trans-$[RuI_2(CO)(terpy)]$	8.1	1.1	5.9	1.2	8.0	7.7

[a] In Hz. See Fig. 2 for labelling of hydrogen atoms. [b] Not measured accurately. All five-bond couplings < 0.5 Hz.

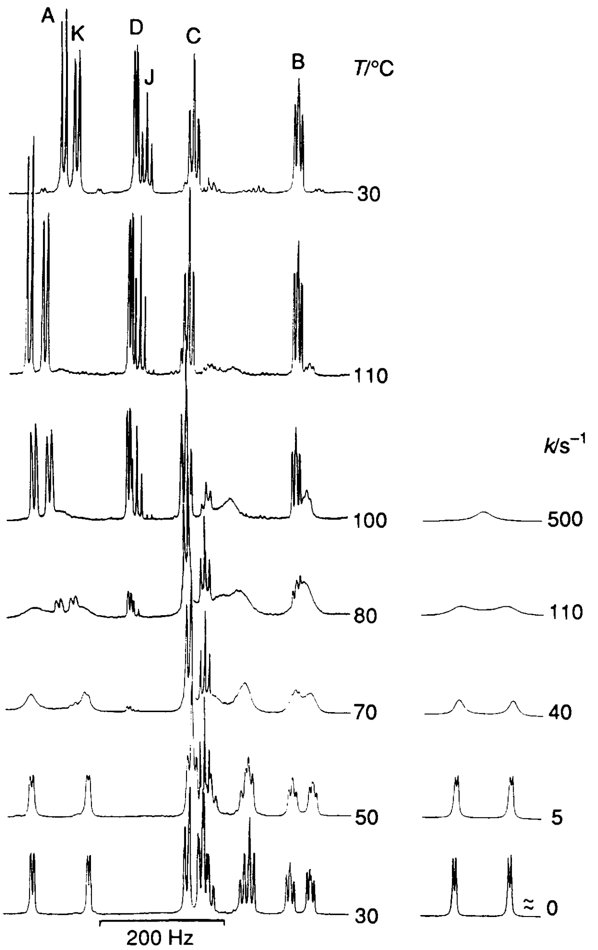


Fig. 3 300 MHz ^1H NMR spectra of $[RuCl_2(CO)_2(terpy)]$ in $(CDCl_2)_2$ in the temperature range 30–110 °C, illustrating the fluxional process and the formation of *trans* $[RuCl_2(CO)(terpy)]$. The uppermost spectrum was obtained after cooling the sample to 30 °C. Computer simulated spectra are shown on the right with 'best-fit' rate constants *k* for the fluxional process

functioning as a bidentate chelate ligand (Fig. 2), and secondly, at temperatures greater than 70 °C the simultaneous formation of a complex in which terpy is functioning as a terdentate ligand. The fluxionality of the terpyridine is analogous to that which we have reported for complexes involving Pt^{IV} and Re^I.

The energetics of the fluxional process were analysed by the application of standard band-shape analysis methods. Because of the formation of the terdentate complex at higher temperatures, studies were necessarily restricted to the temperature range 30–100 °C. As reported[1] for the Re complexes it was found to be sufficient to apply the method to the exchanging pairs of signals A and E and fitting the AE portion of the AB $\rightleftharpoons$ EF dynamic spectrum. The experimental and computed spectra are compared in Fig. 3. Analogous spectral changes were observed for the other two complexes $[RuX_2(CO)_2(terpy)]$ (X = Br or I).

$[M(CO)_4(terpy)]$. The ambient temperature ^1H NMR spectra of $[Mo(CO)_4(terpy)]$ and $[W(CO)_4(terpy)]$ both show six chemically shifted signals, three of which are strongly overlapping. Cooling the solutions to −70 °C and −30 °C respectively produced spectra containing eleven chemically shifted signals which could be unambiguously assigned by decoupling experiments and by comparison with the spectra of the analogous rhenium complexes *fac*-$[ReX(CO)_3(terpy)]$ (X = Cl, Br or I). Hence for these complexes the terpyridyl ligand is fully fluxional at ambient temperature but the motion can be arrested at low temperatures. The energetics of this process were calculated in a manner similar to that described for the ruthenium complexes.

The ambient temperature NMR spectrum of $[Cr(CO)_4(terpy)]$, although it contained some signals attributed to impurities because of the instability of the complex in solution, showed eleven chemically shifted signals all of which could be assigned to terpyridine in a bidentate non-fluxional bonding mode. Attempts to study any fluxional process by increasing the solution temperature led to rapid decomposition of the sample. Hence no quantitative information could be obtained but it can be inferred that the fluxional process in the Cr complex involves a greater activation energy than for the Mo and W complexes since the process is slow on the NMR time-scale at ambient temperature.

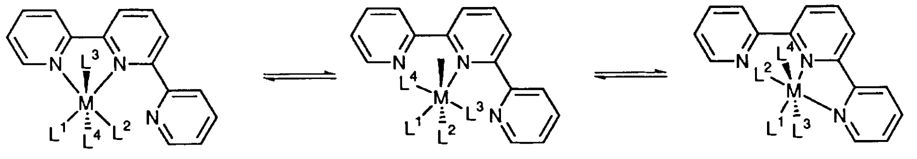
trans-$[RuX_2(CO)(terpy)]$. These complexes contained terdentate terpy and were stereochemically rigid, their ^1H NMR spectra consisting of six chemically shifted signals at all temperatures. Comparison of the data in Table 2 for terpy and $[RuX_2(CO)(terpy)]$ shows that on terdentate complexation hydrogens A/E, B/F, C/G, J and K/L all experience high frequency shifts ($\Delta\delta$ = 0.64–0.1) but hydrogens D/H experience a very small low frequency shift ($\Delta\delta$ = 0.03–0.01). The directions of these co-ordination-induced shifts are the same as observed for the Re complexes but the magnitudes differ as might be expected. The explanation for the observed high and low frequency shifts on complex formation is as described[1] for the Re complexes, and involves a combination of high frequency metal co-ordination shifts and the effects of the necessary reorientation of the pyridine rings into a *cis,cis* arrangement on terdentate complexation.

Energies and Mechanisms of the Fluxion in $[RuX_2(CO)_2(terpy)]$ *and* $[M(CO)_4(terpy)]$ *Complexes*.—The activation parameters for the fluxional process were calculated from 'best-fit' rate data and are listed in Table 5. Values for the Ru complexes range from 75.8 to 78.7 kJ mol⁻¹ and exhibit slight halogen dependence. The order Cl < Br < I is identical

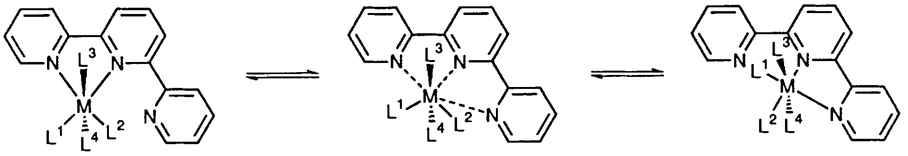
Table 5 Activation parameters for M–N fluxion in *trans,cis*-$[RuX_2(CO)_2(terpy)]$ and $[M(CO)_4(terpy)]$ complexes

Complex	Temperature range/°C	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}	$\Delta G^‡$*/kJ mol^{-1}
$[Mo(CO)_4(terpy)]$	−70 to 30	52.4 ± 1.6	13.3 ± 6.6	48.4 ± 0.4
$[W(CO)_4(terpy)]$	−30 to 40	69.7 ± 1.9	45.9 ± 6.7	56.0 ± 0.1
trans,cis-$[RuCl_2(CO)_2(terpy)]$	30–100	88.3 ± 1.4	41.8 ± 4.1	75.8 ± 0.2
trans,cis-$[RuBr_2(CO)_2(terpy)]$	30–100	86.2 ± 2.6	29.4 ± 7.5	77.4 ± 0.3
trans,cis-$[RuI_2(CO)_2(terpy)]$	30–100	83.1 ± 0.9	14.8 ± 2.6	78.7 ± 0.1

* At 298.15 K.



Mechanism (i)



Mechanism (ii)

Fig. 4 Two possible mechanisms for the M–N linkage fluxion for a bidentate terpy in an octahedral metal complex, namely the rotation mechanism (i) and the 'tick-tock' twist mechanism (ii)

to that observed for the terpy complexes of Re^I but is in contrast to that for Pt^{IV} where no halogen dependence was observed. The only values available for direct comparison are those from our work with the complexes $[PtXMe_3(terpy)]$ and $[ReX(CO)_3(terpy)]$ (X = Cl, Br or I) where the $\Delta G^‡$ values range from 61.5 to 62.5 and 70.3 to 73.0 kJ mol^{-1} respectively. Thus the ordering of $\Delta G^‡$ with respect to metal for these d^6 octahedral complexes is $Ru^{II} > Re^I > Pt^{IV} > W^0 > Mo^0$, for the metal–terpyridine commutation.

Although we were unable to obtain quantitative data for Cr^0, the qualitative observation of $\Delta G^‡$ values in the order Cr > W > Mo is in contrast to values for fluxional motions of $M(CO)_5$ moieties undergoing 1,2 or 1,3 shifts on N ligands[21,22] or on S ligands[23,24] where the orders are $W \approx Cr > Mo$ and $W > Cr > Mo$ respectively.

Two possible mechanisms for the terpy fluxion are illustrated in Fig. 4. Mechanism (i) involves a five-co-ordinate intermediate whereas mechanism (ii) involves a seven-co-ordinate intermediate. In the $[PtXMe_3(terpy)]$ complexes, mechanism (ii) was shown to operate since exchange of the equatorial (*trans*-N) Pt–Me environments occurred. When we reported our results[1] on the $[ReX(CO)_3(terpy)]$ complexes we were unable to deduce which mechanism was operating because of problems of solubility of the complexes. We have now overcome these problems and have been able to show by ^{13}C NMR spectroscopy that the equatorial (*trans*-N) carbonyl environments do exchange and hence mechanism (ii) is also operating in the rhenium complexes. In the present work we have been unable to deduce the precise mechanism because of a combination of insolubility, instability and conversion to terdentate ligand species. However in view of the structural similarity of the metal complexes involved, we believe that the 'tick-tock' mechanism (ii) is also operating in these Mo, W and Ru complexes. This postulate receives further support from the observation that for the Ru complexes the fluxion and the decarbonylation occur simultaneously and the *trans* orientation of the halogens is retained in the resulting terdentate terpy complex. If it is assumed that the fluxion and the decarbonylation involve the same intermediate, then the seven-co-ordinate intermediate of mechanism (ii) is favoured since the five-co-ordinate intermediate of mechanism (i) would be highly fluxional and probably result in the formation of *cis*- and *trans*-monocarbonyl products.

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