Metal Complexes of Sulphur Ligands. Part VI.[1,2] Studies of Facile Optical Isomerism Reactions in Dimethylphosphinodithioato-complexes of Ruthenium(II)

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Rate constants and associated activation parameters for the optical isomerisation reactions of *cis*-[Ru(S_2PMe_2)$_2L_2$] [L = PPh_3, $PMePh_2$, PMe_2Ph, $P(OMe)_3$, $P(OPh)_3$], *cis*-[Ru(S_2PMe_2)$_2$(PPh_3)($P\{OPh\}_3$)] and *cis*-[Ru(S_2PMe_2)$_2$-(PPh_3)CO] have been determined by line-shape analyses of their temperature-dependent ^1H n.m.r. spectra. Consideration of various bond-rupture and twist mechanisms for this inversion process strongly suggests that the only mechanism compatible with the overall experimental data is one involving a solvent-assisted cleavage of a ruthenium–sulphur bond *trans* to L.

For the analogous *cis*-[Ru(S_2CNMe_2)$_2L_2$] [L = PPh_3, PMe_2Ph, $P(OPh)_3$] and *cis*-[Ru(S_2CNMe_2)$_2$(PPh_3)-($P\{OPh\}_3$)] complexes, line shape studies suggest that their temperature dependent ^1H n.m.r. spectra arise from restricted rotation about the CN bonds and not a facile inversion process.

In Part V of this series,[1] the preparation, reactions, and spectroscopic properties of the compounds *cis*-[Ru(S_2PR_2)$_2L_2$] (L = tertiary phosphine or phosphite) were presented and discussed. In that paper, the variation with temperature of the ^1H n.m.r. spectra of these compounds and some of their derivatives was noted and ascribed to rapid interconversion of the two possible optical enantiomers, rather than a reversible *cis–trans* isomerism. A great deal of interest has been shown in recent years in the mechanism of interconversion of optical isomers of metal complexes and, in particular, of the nature of the first step in the reaction. However, most of the publications on this topic have been confined to studies of tris-chelate complexes [3a] and relatively few have discussed detailed mechanisms of optical isomerism in complexes of type *cis*-[M(chelate)$_2X_2$].[3b] Furthermore, with the exception of a very recent note on variable temperature ^1H n.m.r. studies of [Ru(S_2CNRR^1)$_3$] (R = Me, R^1 = $PhCH_2$),[4] this paper represents the only other published work on the facile interconversion of optical isomers in ruthenium chemistry.

Two main first-step mechanisms involving either a twist of the molecule or rupture of a metal–ligand bond have been postulated. In this paper, presentation of the kinetic results is followed by a consideration of these various methods of optical inversion in an attempt to determine which mechanism is most energetically feasible for these compounds.

RESULTS

(i) *Dimethylphosphinodithioato-complexes.*—Typical variable temperature ^1H n.m.r. spectra for compounds of type *cis*[Ru(S_2PMe_2)$_2L_2$] are illustrated in Figure 1 (Part V) for *cis*-[Ru(S_2PMe_2)$_2$(PMe_2Ph)$_2$] and the proton resonance positions in the fast and slow exchange limits for other compounds of this type are given in Table 5 (Part V). These spectra all show two $^-S_2PMe_2$ methyl doublets at low temperatures and a single doublet at higher temperatures. Thus, these n.m.r. changes, which are independent of complex concentration, are amenable to a detailed kinetic line-shape analysis and some of the results obtained from this are presented graphically (Figure 1) and the rates and calculated activation parameters at 298 K listed in Table 1.

For the mixed ligand complexes *cis*-[Ru(S_2PMe_2)$_2$LL'] (L = tertiary phosphine, L' = tertiary phosphite) and *cis*-[Ru(S_2PMe_2)$_2$L(CO)], four methyl doublets are expected although in some instances, two of the doublets are accidentally superimposed. For *cis*-[Ru(S_2PMe_2)$_2$(PPh_3)-($P\{OPh\}_3$)] (where four methyl doublets are observed at low temperatures) inversion rates and activation parameters were determined by separate line shape analysis on the exchange of the inner methyl doublets g and f and the outer doublets e and h (see Figure 3, Part V, for stereochemical assignment of these methyl groups). The close similarity of the calculated values for these rates and activation parameters (see Table 1) indicates that the same kinetic process is probably responsible for the interchange of the chemical environments of these two sets of methyl protons. For *cis*-[Ru(S_2PMe_2)$_2$(PPh_3)CO], the activation parameters given in Table 1 were calculated by using rate data obtained from the exchange of both the inner and outer doublets respectively which again suggests that a common kinetic process is in operation.

From Table 1, several other points of importance emerge which must be considered when contemplating possible mechanisms of inversion. For example, Table 1 reveals

[1] Part V, D. J. Cole-Hamilton and T. A. Stephenson, preceding paper.

[2] Preliminary communication: D. J. Cole-Hamilton, P. W. Armit, and T. A. Stephenson, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 917.

[3] For detailed references see N. Serpone and D. G. Bickley in *Progr. Inorg. Chem.*, 1972, **17** (Part II) (a) pp. 416—500, (b) 500—542.

[4] L. H. Pignolet, D. J. Duffy, and L. Que, jun., *J. Amer. Chem. Soc.*, 1973, **95**, 295.

TABLE 1

Rates and activation parameters obtained by line shape analysis for the inversion process *cis*-Δ ⇌ *cis*-Λ in some ruthenium(II) dimethylphosphinodithioate complexes

Compound	Solvent	$\log_{10}k_{298}$ [a]	E_a [b]	ΔH^*_{298} [b]	ΔS^*_{298} [c]	ΔG^*_{298} [b]
cis-[Ru(S$_2$PMe$_2$)$_2$(PPh$_3$)$_2$]	$CDCl_3$	3·53 ± 0·02	49·6 ± 1	47·1 ± 1	−19 ± 3	52·8 ± 0·1
cis-[Ru(S$_2$PMe$_2$)$_2$(PMePh$_2$)$_2$]	$CDCl_3$	2·78 ± 0·02	60·5 ± 2	58·0 ± 2	3 ± 7	57·1 ± 0·2
cis-[Ru(S$_2$PMe$_2$)$_2$(P{OMe}$_3$)$_2$]	$CDCl_3$	2·23 ± 0·34	67·8 ± 2	65·3 ± 2	17 ± 13	60·3 ± 2
cis-[Ru(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$]	$CDCl_3$	1·61 ± 0·12	62·0 ± 1	59·6 ± 1	−15 ± 4	63·8 ± 0·1
	C_6H_5Cl	1·01 ± 0·01	69·7 ± 1	67·2 ± 1	0 ± 4	67·2 ± 0·1
	C_6H_6	0·04 ± 0·12	126 ± 4	123·5 ± 4	170 ± 11	72·7 ± 0·1
cis-[Ru(S$_2$PMe$_2$)$_2$(P{OPh}$_3$)$_2$]	$CDCl_3$	0·41 ± 0·01	73·7 ± 2	71·2 ± 2	2 ± 8	70·6 ± 0·1
cis-[Ru(S$_2$PMe$_2$)$_2$(PPh$_3$)(P{OPh}$_3$)]	CH_2Cl_2	1·69 ± 0·05 [d]	47·3 ± 4 [d]	44·8 ± 4 [d]	−62 ± 15 [d]	63·3 ± 0·3 [d]
		1·62 ± 0·03 [e]	42·5 ± 3 [e]	40·0 ± 3 [e]	−80 ± 9 [e]	63·7 ± 0·2 [e]
cis-[Ru(S$_2$PMe$_2$)$_2$(PPh$_3$)CO] [f]	C_6H_5Cl	−1·90 ± 0·08 [g]	121·8 ± 2 [g]	119·3 ± 2 [g]	119 ± 7 [g]	83·8 ± 0·4 [g]

[a] Units of k, s^{-1}. [b] Units, kJ mol^{-1}. [c] Units, JK^{-1} mol^{-1}. [d] Obtained from analysis of exchange of inner doublets g and f. [e] Obtained from analysis of exchange of outer doublets e and h. [f] For *cis*-[Ru(S$_2$PMe$_2$)$_2$(CO)$_2$], no scrambling of methyl groups at 330 K. [g] Obtained from analysis of exchange of inner and outer doublets.

that the rate and the associated activation parameters are dependent on the solvent media in which the measurements are made. For *cis*-[Ru(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$], measurements in C_6H_6, C_6H_5Cl, and $CDCl_3$ respectively (Figure 2) show an increasing inversion rate accompanied by a substantial decrease in ΔH^* and ΔS^* values, particularly on changing from C_6H_6 to C_6H_5Cl (or $CDCl_3$). In addition, measuring the inversion rate (by line-shape analysis) at 301 K for CS_2–$CDCl_3$ solutions of *cis*-[Ru(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$], in which the $CDCl_3$ component is increased from 0 to *ca.* 40% reveals a first order dependence

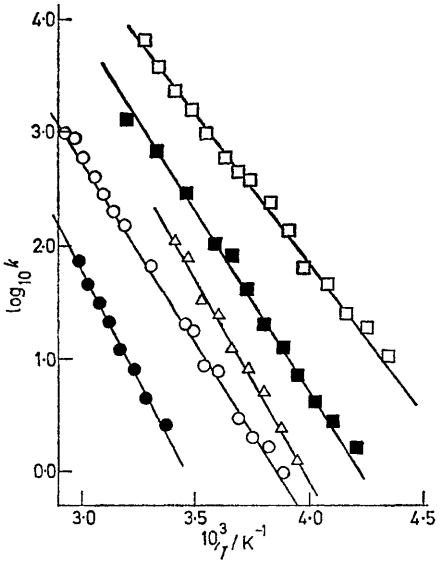

FIGURE 1 Arrhenius plots ($\log_{10}k$ *vs.* $1/T$) for various *cis*-[Ru(S$_2$PMe$_2$)$_2$L$_2$] compounds in $CDCl_3$: □, L = PPh_3; ■, L = $PMePh_2$; △, L = $P(OMe)_3$; ○, L = PMe_2Ph; ●, L = $P(OPh)_3$

on $CDCl_3$concentration (Figure 3). In a given solvent ($CDCl_3$), the inversion rate is also dependent on the group L, the relative order being $PPh_3 > PMePh_2 > P(OMe)_3 > PMe_2Ph > P(OPh)_3 \gg CO$. It is also of interest that the rate of oxidation of *cis*-[Ru(S$_2$PMe$_2$)$_2$L$_2$] as a function of L and solvent composition (see Part V) parallels these inversion rates in a semi-quantitative manner.

Finally, for the compounds *cis*-[Ru(S$_2$PR$_2$)$_2$(PMe$_2$Ph)$_2$] (R = Me, Ph) the two pseudo-triplets arising from the PMe_2Ph methyl groups at low temperature in $CDCl_3$ are separated by 13 and 8 Hz, and these coalesce at *ca.* 278 and 273 K respectively. From this data, the free energies of activation for this averaging process are estimated to be 57·4 and 58·6 kJ mol^{-1} respectively.[5] Comparison with

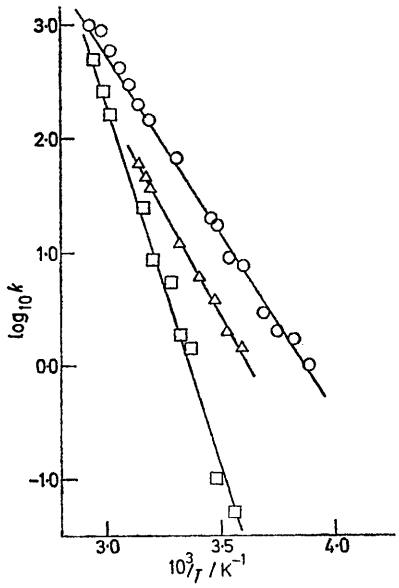

FIGURE 2 Arrhenius plots ($\log_{10}k$ *vs.* $1/T$) for *cis*-[Ru(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$] in various solvents: ○, in $CDCl_3$; △, in C_6H_5Cl; □, in C_6H_6

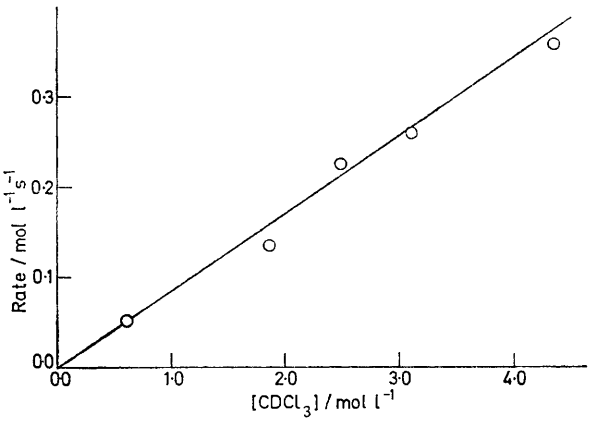

FIGURE 3 Rate of inversion of *cis*-[Ru(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$] (0·015 g ml^{-1}) in CS_2–$CDCl_3$ solution at 301 K as a function of $CDCl_3$ concentration

[5] For method see J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High Resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1959, p. 223.

ΔG^* obtained from the $^-S_2PMe_2$ signals of *cis*-$[Ru(S_2PMe_2)_2(PMe_2Ph)_2]$ by line shape analysis at 273 K (63·4 kJ mol^{-1}) indicates that these PMe_2Ph methyl protons are not averaged by the inversion process, since the observed ΔG^* is lower than that of the inversion process. Therefore, the only reasonable explanation for these n.m.r. changes is to postulate rapid rotation at higher temperatures about the ruthenium–phosphorus bonds.

(ii) NN-*Dimethyldithiocarbamato-complexes.*—For *cis*-$[Ru(S_2CNMe_2)_2L_2]$ [L = PMe_2Ph, PPh_3, $P(OPh)_3$], the low temperature ^1H n.m.r. spectra consists of two $^-S_2CNMe_2$ methyl singlets which coalesce at higher temperatures signals are independent of each other and the best explanation of this that we can offer is that these n.m.r. changes are produced by fast rotation about the ^-CN bonds of the $^-S_2CNMe_2$ groups *syn* to the PPh_3 and $P(OPh)_3$ groups respectively and *not* by a facile inversion process. In support of this conclusion, the two sets of activation parameters found for the PPh_3–$P(OPh)_3$ complex are reasonably similar to those found for the bis-PPh_3 and bis-$P(OPh)_3$ compounds respectively. The large difference in ΔS^* values for the ^-CN bond rotation process is tentatively attributed to substantial differences in the degree of solvation of the PPh_3 and $P(OPh)_3$ complexes, which might

TABLE 2

Rates and activation parameters obtained by line shape analysis for the interchange of methyl groups in some ruthenium(II) *NN*-dimethyldithiocarbamato-complexes

Compound	Solvent	$\log_{10}k_{298}$ [a]	E_a [b]	ΔH^*_{298} [b]	ΔS^*_{298} [c]	ΔG^*_{298} [b]
cis-$[Ru(S_2CNMe_2)_2(PMe_2Ph)_2]$	$CDCl_3$	0·71 ± 0·01	94·0 ± 2	91·5 ± 2	75 ± 7	69·0 ± 0·02
cis-$[Ru(S_2CNMe_2)_2(PPh_3)_2]$	$CDCl_3$	0·22 ± 0·02	105·7 ± 2	103·2 ± 2	105 ± 6	71·7 ± 0·2
cis-$[Ru(S_2CNMe_2)_2(P\{OPh\}_3)_2]$	$CDCl_3$	0·01 ± 0·02	79·2 ± 3	76·7 ± 3	12 ± 9	73·0 ± 0·07
cis-$[Ru(S_2CNMe_2)_2(PPh_3)(P\{OPh\}_3)]$	$CDCl_3$	0·23 ± 0·01 [d]	109·9 ± 2 [d]	107·4 ± 2 [d]	120 ± 5 [d]	71·7 ± 0·07 [d]
		0·15 ± 0·05 [e]	57·8 ± 3 [e]	55·3 ± 3 [e]	−60 ± 11 [e]	73·2 ± 0·7 [e]

[a] Units of k, s^{-1}. [b] Units, kJ mol^{-1}. [c] Units, J K^{-1} mol^{-1}. [d] Obtained from exchange of high field pair of singlets. [e] Obtained from exchange of low field pair of singlets.

TABLE 3

Assignment of methyl group stereochemistries for *cis*-Δ-$[Ru(S_2PMe_2)_2LL']$ after twisting and bond rupture operations

		Methyl group stereochemistries [b]			
For *cis*-Δ isomer [a]		*syn* (*to L*)	*anti* (*to L*)	*syn* (*to L'*)	*anti* (*to L'*)
Established experimentally [c] for *cis*-Δ ⇌ *cis*-Λ		e	g	f	h
		e ⇌ h	g ⇌ f	f ⇌ g	h ⇌ e
		Methyl group stereochemistries of product			
Operation [d] (on *cis*-Δ)	Product	*syn* (*to L*)	*anti* (*to L*)	*syn* (*to L'*)	*anti* (*to L'*)
(a) i-$C_3(1)^+$	*trans*-isomer	e,h	g,f	g,f	e,h
i-$C_3(1)^-$	*cis*-Λ	e	g	f	h
(b) i-$C_3(2)^+$	*				
i-$C_3(2)^-$	*cis*-Λ	f	h	g	e
(c) i-$C_3(3)^+$	*				
i-$C_3(3)^-$	*cis*-Λ	h	f	e	g
(d) i-$C_3(4)^+$	*cis*-Λ	f	h	e	g
i-$C_3(4)^-$	*				
Bond rupture mechanism (Figure 6)	*cis*-Λ	h	f	g	e

[a] Δ and Λ Isomers defined on basis of rules suggested by I.U.P.A.C. commission (see *Inorg. Chem.*, 1970, **9**, 1). [b] See Figure 4 for assignment of e, g, f, and h groups in *cis*-Δ isomer. [c] By variable temperature ^1H n.m.r. studies for *cis*-$[Ru(S_2PMe_2)_2(PPh_3)(\{POPh\}_3)]$ see Part V. [d] See Figures 4 and 5. * These twist operations are sterically impossible since they produce a configuration in which a $^-S_2PMe_2$ group would have to span *trans*-positions.

(see Table 5, Part V). The rates and activation parameters at 298 K for this process are given in Table 2. The room temperature ^1H n.m.r. spectrum of *cis*-$[Ru(S_2CNMe_2)_2(PPh_3)(P\{OPh\}_3)]$ consists of three methyl singlets of intensity ratio 1 : 2 : 1 indicating accidental superposition of two of the methyl resonances. At higher temperatures, the highest field singlet at τ 7·37 and one of the superimposed resonances at τ 7·13 coalesce to give a signal at τ 7·23 (T_c = 318 K) whilst the lowest field signal at τ 6·86 and the remaining resonance at τ 7·13 broaden considerably and move towards each other (see Table 5, Part V). Thus, the high field pair of singlets and the low field pair of singlets are undergoing exchange and the rates and activation parameters at 298 K for these exchange processes are given in Table 2. This data clearly shows that although the rates are fairly similar at 298 K, the activation parameters are very different. This can only mean that the kinetic processes exchanging these two sets of methyl arise as a consequence of replacing phenyl with phenoxy groups.

Finally for *cis*-$[Ru(S_2CNMe_2)_2(PMe_2Ph)_2]$, the estimated free energy of activation [5] for averaging the two pseudo-triplets of the PMe_2Ph methyl groups is 54·0 kJ mol^{-1} (at T_c = 253 K) which is again attributed to rapid rotation at higher temperatures about the ruthenium–phosphorus bonds.

DISCUSSION

Possible Mechanisms of the Inversion Process in Dimethylphosphinodithioato-complexes.—The possible mechanisms for the inversion process in these complexes will now be considered, starting with intramolecular twisting mechanisms.

(i) *Bailar (or trigonal) twists.*[6] In this mechanism,

[6] J. C. Bailar, jun., *J. Inorg. Nuclear Chem.*, 1958, **8**, 165.

the three atoms comprising one face of these octahedral complexes are rotated through 120° about the imaginary three-fold axis (i-C_3) whilst keeping the opposite face fixed. In the complexes *cis*-[Ru(S_2-PMe_2)$_2$LL'], there are four such axes as illustrated in Figure 4 and diagrams of the complex as viewed along these axes are given in Figure 5. The positions of the methyl groups e, f, g, and h shown in these Figures are

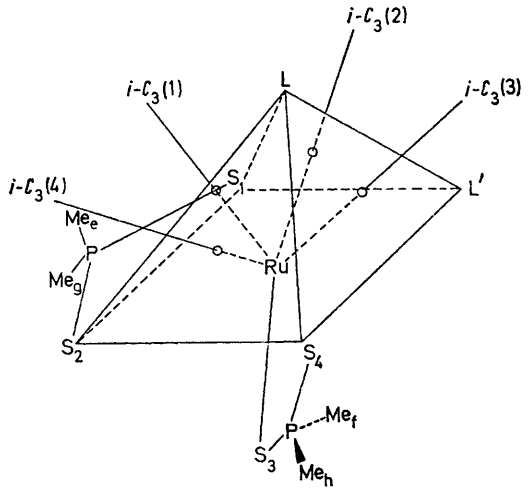

FIGURE 4 Labelling of the four imaginary three-fold axes (i-C_3) for the *cis*-Δ-[Ru(S_2PMe_2)$_2$LL'] complex: i-C_3(1), axis through plane of atoms S_1,L,S_2; i-C_3(2), axis through plane of atoms L',L,S_1; i-C_3(3), axis through plane of atoms S_4,L,L'; i-C_3(4), axis through plane of atoms S_2,L,S_4

consistent with the detailed assignments made in Part V for L = PPh_3, L' = $P(OPh)_3$ and the starting configuration arbitrarily chosen is designated *cis*-Δ on the basis of rules suggested by the recent I.U.P.A.C. commission.[7]

The problem is now to consider the effect of a trigonal twist around each axis in turn (clockwise and anticlockwise) in order to determine if such a process gives the optical isomer and also interchanges only the chemical environments of the methyl groups e,h and g,f respectively. Examination of Figure 5a and Table 3 shows that rotation about the i-C_3(1) axis in a clockwise direction gives the *trans* isomer whereas an anticlockwise twist gives the *cis*-Λ isomer. However, the $^-S_2PMe_2$ methyl groups will finish in the same chemical environment as they started and hence this twisting motion predicts inversion without any scrambling of methyl resonances. Rotation about i-C_3(2) or i-C_3(3) in a clockwise direction is impossible because it leads to a configuration in which a $^-S_2PMe_2$ group would have to span *trans* positions. Anticlockwise rotation about these axes gives the optical isomer together with scrambling of *all* methyl groups. Hence, if this were the inversion mechanism, a single methyl resonance should be observed at elevated temperatures and careful experiments with *cis*-[Ru(S_2PMe_2)$_2$(PPh_3)-($P\{OPh\}_3$)] and *cis*-[Ru(S_2PMe_2)$_2$(PPh_3)CO] (see Part V) show that this is not the case. Finally, rotation about

[7] For details see *Inorg. Chem.*, 1970, **9**, 1.

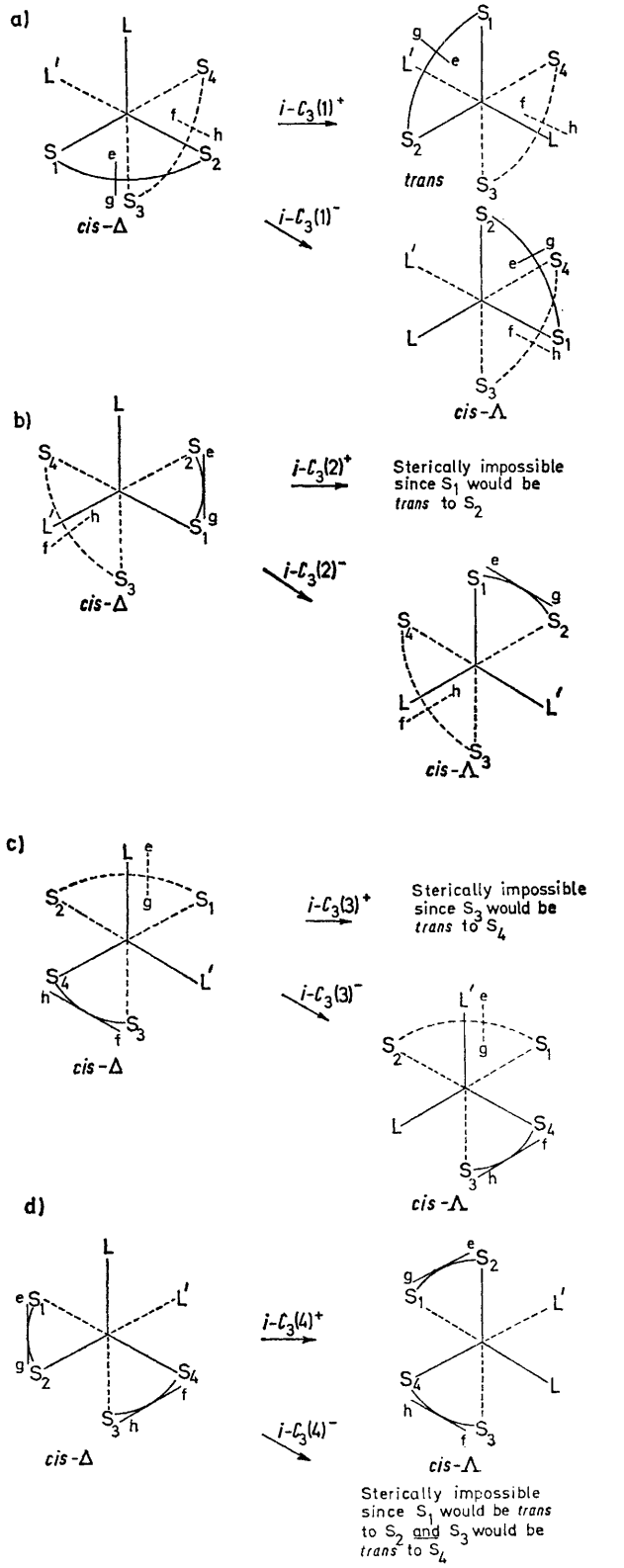

FIGURE 5 Bailar (trigonal) twists for a *cis*-Δ-[Ru(S_2PMe_2)$_2$LL'] compound about the four i-C_3 axes in clockwise (+) and anticlockwise (−) directions. For ease of interpretation, the direction of the P–Me bonds are drawn as the same as those of the Ru–L (or L') bonds to which they are *syn* or *anti*

i-C_3(4) is sterically impossible in an anticlockwise direction but in a clockwise direction gives the *cis*-Λ isomer and only partial scrambling of methyl groups. Thus, groups e,f and g,h respectively are interchanged (Figure 5d and Table 3). However, examination of Figure 4 shows that for L = L′, groups e and f and groups g and h are chemically equivalent and, therefore, if this were the inversion mechanism, the ^{1}H n.m.r. spectra of the compounds *cis*-[Ru(S_2PMe_2)$_2$$L_2$] should be temperature invariant. This is not the case and therefore a mechanism involving a trigonal twist about this axis is also rejected.

(ii) *Rây–Dutt (or rhombic) twist.*[8] For *cis*-[Ru(S_2-PMe_2)$_2$$L_2$], this inversion mechanism may be visualised as follows. The two L groups remain fixed while the two chelate rings rotate in their planes in different directions through an angle of 90° about axes which are perpendicular to their respective planes and pass through the ruthenium ion. For *cis*-[Ru(S_2PMe_2)$_2$$L_2$] this does not produce any scrambling of the methyl resonances and so this twisting mechanism can also be discarded.

Final rejection of a trigonal or rhombic twist mechanism comprising rotation about one or *several* of these axes is based on a consideration of steric effects on the expected trigonal prismatic transition state. If a twisting mechanism is important, the activation energy for the process should be dependent on the size of L, being higher the bulkier the ligand.[9] However, the results given in Table 1 reveal no apparent correlation with the size of L *e.g.* the bis-PPh_3 complex has a smaller activation energy than the bis-PMe_2Ph complex which is smaller than the bis-$P(OPh)_3$ compound. The large dependence of rate and associated activation parameters on solvent composition is also not compatible with a twist mechanism.

Therefore, it is necessary next to consider inversion mechanisms arising from initial cleavage of a ruthenium–ligand bond.

(iii) *Cleavage of a ruthenium–phosphorus bond.* Since the activation energies for the optical isomerism of the compounds *cis*-[Ru(S_2PMe_2)$_2$$L_2$] depend on the ligand L, it seems reasonable, at first sight, to postulate that the inversion mechanism might involve dissociation of a phosphorus ligand to give a square pyramidal or trigonal bipyramidal intermediate followed by recombination as the optical isomer. However, if this were the mechanism, then a ^{1}H n.m.r. spectrum of a mixture of two complexes containing different L groups should show scrambling of all the methyl resonances of the $^-S_2PMe_2$ groups. This is not the case for a mixture of *cis*-[Ru(S_2PMe_2)$_2$(PPh_3)$_2$] and *cis*-[Ru(S_2PMe_2)$_2$-(PMe_2Ph)$_2$] in $CDCl_3$ which shows only the unchanged ^{1}H n.m.r. spectral patterns of the two components. Furthermore, the ^{1}H n.m.r. spectrum of a mixture of *cis*-[Ru(S_2PMe_2)$_2$(PMe_2Ph)$_2$] and free PMe_2Ph in $CDCl_3$ at *ca.* 330 K indicates no exchange of free and bound phosphine. Thus, cleavage of a ruthenium–phosphorus bond may be eliminated as a possible first step in the inversion process.

(iv) *Complete dissociation of a dithioacid group.* If this was an important process, then a mixture of the two compounds *cis*-[Ru(S_2PR_2)$_2$$L_2$] and *cis*-[Ru($S_2$-$PR_2'$)$_2$$L_2$] should give some of the mixed species *cis*-[Ru(S_2PR_2)(S_2PR_2')L_2] under exchange conditions. This does not occur and therefore, the racemisation mechanism cannot involve complete dissociation of a dithioacid ligand.

(v) *Cleavage of a ruthenium–sulphur bond.* In the symmetrical complexes *cis*-[Ru(S_2PR_2)$_2$$L_2$], there are two types of ruthenium–sulphur bond; those which are *trans* to another sulphur atom and those *trans* to a phosphorus ligand. If optical isomerism occurred *via* cleavage of a ruthenium–sulphur bond *trans* to another sulphur atom, then the activation energy for the reaction would be relatively insensitive to changes in L. Thus, if this mechanism is correct, it must involve cleavage of a ruthenium–sulphur bond which is *trans* to a phosphorus ligand. This statement can be rationalised on the basis that the larger *trans* influence * of the phosphorus ligands, compared to the $^-S_2PR_2$ groups, should preferentially weaken the ruthenium–sulphur bonds *trans* to them. This suggestion is supported by the bond lengths found in *cis*-[Ru(S_2PEt_2)$_2$(PMe_2-Ph)$_2$] where the Ru–S bonds *trans* to the PMe_2Ph groups are *ca.* 0·2 Å longer than those *trans* to another sulphur atom.[10]

A possible mechanism of inversion of the compounds *cis*-[Ru(S_2PMe_2)$_2$LL′] which involves two ruthenium–sulphur bond cleavage sub-steps is outlined in Figure 6. It now remains to examine this mechanism to see if it is consistent with the experimental results presented earlier.

First, it is important to note that this overall mechanism not only leads to optical isomerism but also interchanges the chemical environments of methyl groups e,h and f,g respectively. Also, the mechanism as written is symmetrical (since *cis*-Δ ⇌ *cis*-Λ) and it obeys the Principle of Microscopic Reversibility. Furthermore, the solvent-assisted bond rupture step (1) is consistent with the observed first order dependence on $CDCl_3$ concentration in CS_2–$CDCl_3$ solutions.† On changing to a less solvating medium such as benzene, step (1) should be slower and the overall inversion rate should decrease as is observed experimentally (Table 1). Although there is no obvious correlation of rate

* The *trans* influence of a ligand is defined as the extent to which that ligand weakens the bond *trans* to itself in the equilibrium state of a substrate.[11]

† This does not necessarily mean that step (1) is rate-determining since for consecutive reactions of the type shown in Figure 6, (assuming steady state conditions), it can be shown that the overall rate expression involves a first order dependence on $CDCl_3$ concentration irrespective of the size of the relative rate constants of sub-steps (1) and (2).[12]

[8] P. Rây and N. K. Dutt, *J. Indian Chem. Soc.*, 1943, **20**, 81.
[9] E. L. Muetterties, *J. Amer. Chem. Soc.*, 1968, **90**, 5097.
[10] J. D. Owen and (in part) D. J. Cole-Hamilton, Part VII to be published.
[11] See A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc. (A)*, 1966, 1707.
[12] For method see A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' 2nd edn., Wiley, 1961, ch. 8.

with the size of L, there is a good correlation between rate and the *trans* influence of L as established independently by ^1H n.m.r. and i.r. studies [13] *viz.* $PPh_3 > PMePh_2 > PMe_2Ph > P(OMe)_3 \simeq P(OPh)_3 > CO$. This provides a reasonable explanation of the observed rate dependence if either sub-step (1) and/or sub-step (2) are contributing to the overall rate. The anomalous position of $P(OMe)_3$ compared with *trans* influence predictions could perhaps be explained by its small steric size having different effects in sub-steps (1) and (2) which we tentatively suggest below are associative and dissociative processes respectively.

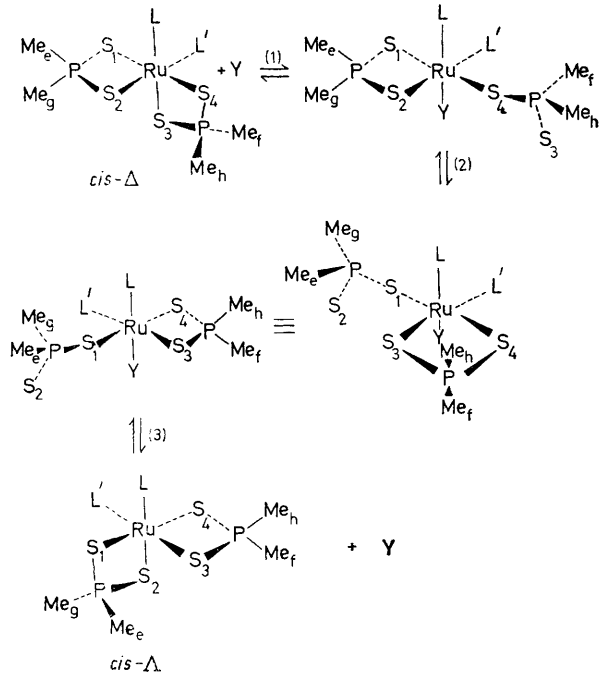

FIGURE 6 Proposed solvent-assisted bond rupture mechanism for the optical isomerisation reaction *cis*-Δ-$[Ru(S_2PMe_2)_2LL']$ ⇌ *cis*-Λ-$[Ru(S_2PMe_2)_2LL']$ (Y = $CDCl_3$ or C_6H_5Cl). [For clearer presentation, after step (2), the molecule is rotated by 90° in an anticlockwise direction about the L–Ru-Y axis]

Therefore, the overall mechanism depicted in Figure 6 is able to account for many of the experimental observations. However, there still remains the question of the relative importance of sub-steps (1) and (2) in the inversion rates of these bis-L_2, -LL', and -LCO complexes [it can be assumed that sub-step (3) is always rapid] and the nature of the activation parameters for these sub-steps. An explanation for the large change in activation parameters, which occurs on changing from $CDCl_3$ (or C_6H_5Cl) to C_6H_6 is also required. Although with the information at present available, it is impossible to provide completely satisfactory (or unambiguous) answers, we nevertheless feel that some speculation on these matters is justified in this instance.

From Table 1, the activation parameters for *cis*-$[Ru(S_2PMe_2)_2(PPh_3)CO]$ in C_6H_5Cl are ΔH^*, 119·3 kJ mol^{-1}; ΔS^*, 119 JK^{-1} mol^{-1}. In terms of the proposed mechanism, step (1) must involve cleavage of the Ru–S bond *trans* to PPh_3 (highest *trans* influence ligand) and step (2), that of the Ru–S bond *trans* to CO. Furthermore, it is reasonable to expect the rate of step (1) to be comparable to that in *cis*-$[Ru(S_2PMe_2)_2(PPh_3)_2]$. This compound has overall activation parameters of 47·1 kJ mol^{-1} (ΔH^*) and −19 JK^{-1} mol^{-1} (ΔS^*) in $CDCl_3$. However, since the overall rate constant is considerably higher for the bis-PPh_3 compound, compared to the phosphine carbonyl complex, this can only mean that the observed rate and activation parameters for *cis*-$[Ru(S_2PMe_2)_2(PPh_3)CO]$ correspond mainly to the rate and activation parameters of step (2). Thus, in this instance, step (2) is characterised by large positive ΔH^* and ΔS^* values. For ligands of higher *trans* influence than CO, it is reasonable to infer much lower ΔH^* values for step (2) but ΔS^* should remain fairly insensitive to the nature of L (or L'). These inferred values for ΔH^* and ΔS^* would be consistent with a dissociative mechanism [14] for step (2) in which bond-breaking of the Ru–S bond *trans* to L' is the rate-determining step.

However, because the ΔS^* term for (2) is probably fairly insensitive to the nature of L, this suggests that the inversion rates for all the bis-L_2 compounds in $CDCl_3$ (or C_6H_5Cl) must have an appreciable contribution from sub-step (1) since they all have activation parameters in the range 47 to 71 kJ mol^{-1} (ΔH^*) and 17 to −19 JK^{-1} mol^{-1} (ΔS^*). Thus, it seems reasonable to propose that in solvents such as $CDCl_3$ and C_6H_5Cl, step (1) is characterised by relatively low ΔH^* values and negative ΔS^* values. These values are indicative of an associative process which is to be expected for a solvent-assisted bond rupture step.

For *cis*-$[Ru(S_2PMe_2)_2(PPh_3)(P\{OPh\}_3)]$, the activation parameters are found to be ΔH^*, 44·8 kJ mol^{-1}, ΔS^*, −62 JK^{-1} mol^{-1} and again step (1) must involve cleavage of the Ru–S bond *trans* to PPh_3 and step (2) that of the Ru–S bond *trans* to $P(OPh)_3$. In this instance, the overall rates of inversion for the bis-PPh_3 and bis-$P(OPh)_3$ compounds are more comparable than that estimated for the bis-CO compound (no exchange even at 330 K). Therefore, although step (2) is probably slower than (1), we propose that both steps contribute to the observed rate.

The overall rate decrease, accompanied by substantial increases in ΔH^* and ΔS^*, which is observed when *cis*-$[Ru(S_2PMe_2)_2(PMe_2Ph)_2]$ is examined in C_6H_6 rather than $CDCl_3$ (or C_6H_5Cl) is explicable on the basis that in such a poor solvating medium, step (1) not only becomes considerably slower because it is no longer a solvent-assisted process but it also becomes dissociative in nature. However, the similarity of the high temperature n.m.r. spectrum of *cis*-$[Ru(S_2PMe_2)_2(PPh_3)(P\{OPh\}_3)]$ in C_6H_6 and C_6H_5Cl (two methyl doublets) is consistent with retention of the same overall inversion mechanism.

[13] M. J. Church and M. J. Mays, *J. Chem. Soc.* (*A*), 1968, 3074; H. C. Clark and J. D. Ruddick, *Inorg. Chem.*, 1970, **9**, 1226.

[14] A. Y. Girgis and R. C. Fay, *J. Amer. Chem. Soc.*, 1970, **92**, 7061.

Finally, the apparent inability of the corresponding *cis*-$[Ru(S_2CNMe_2)_2L_2]$ compounds to undergo inversion, even at elevated temperatures, is consistent with the stronger nucleophilicity of $^-S_2CNR_2$ compared to $^-S_2PR_2$ [15] which will lead to prohibitively high activation energies for sub-steps (1) and (2).

EXPERIMENTAL

All the compounds used in the line shape studies were prepared as described earlier.[1]

Kinetic Line Shape Analysis.—^{1}H N.m.r. spectra were measured on a Varian Associates HA 100 Spectrometer with variable temperature attachment. Accurate temperatures were determined using the separation of the two resonances of methanol (low temperature) and ethylene glycol (high temperature). Spectra were simulated using a computer programme based on that of Nakagawa.[16] The exchange process was considered for the purpose of computation as consisting of n two site exchanges where n is the multiplicity of the resonance being monitored. The single line simulated spectra were then superimposed with suitable weighting for intensities and the results plotted out on the line printer. Thus, in this work, a doublet is considered as two two-site exchanges of intensity ratio 1 : 1. The experimental spectra were fitted to the computed spectra either by finding the best fit between the ratio of maximum to minimum heights in the doublets (above and below coalescence) or the width of the signal at half height (around coalescence). Spin–spin relaxation times (T_2) were obtained for each compound by measurement of peak width at half height under slow exchange conditions. The same value of T_2 was used for all line-shape calculations on a given compound because, for L = PMe_2Ph and $P(OMe)_3$, the widths at half height in the slow and fast exchange limits differed by less than 0·25 Hz.

Lifetimes obtained by these fitting procedures were then used to construct Arrhenius plots ($\log_{10}k$ *vs.* $1/T$) in which straight lines were fitted by the least squares method. Activation parameters at 298 K, calculated from standard equations are shown in Tables 1 and 2 together with assessed error limits.

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[15] See D. F. Steele and T. A. Stephenson, *J.C.S. Dalton*, **1973**, 2124 and references therein.
[16] T. Nakagawa, *Bull. Chem. Soc. Japan*, 1966, **39**, 1006.