Metal Complexes of Sulphur Ligands. Part V.[1,2] Dialkyl-, Diaryl-phosphinodithioato-and *NN*-Dialkyldithiocarbamato-complexes of Ruthenium(II)

By **David J. Cole-Hamilton** and **T. Anthony Stephenson**,* Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

Complexes of general formula $[Ru(S-S)_2L_2][(S-S)^- = {}^-S_2PR_2$ (R = Me, Et, Ph), $^-S_2CNMe_2$; L = PPh_3, PMe_2Ph, $PMePh_2$, $P(OPh)_3$ *etc.*] have been synthesised by the reaction of various ruthenium(II) and (III) tertiary phosphine and phosphite complexes with Na(S–S). For $(S-S)^- = {}^-S_2PR_2$, these compounds are readily carbonylated to give the monocarbonyls $[Ru(S_2PR_2)_2L(CO)]$. However, the dicarbonyls can be synthesised directly, from ruthenium carbonyl halides and NaS_2PR_2. Although the corresponding dithiocarbamates are resistant to carbonylation, all these compounds undergo ligand exchange reactions with ligands of greater basicity (L′) to give either $[Ru(S-S)_2LL']$ and/or $[Ru(S-S)_2L'_2]$. All these compounds have been thoroughly examined by i.r., mass, and ^1H n.m.r. spectroscopy and the latter indicates a *cis*-configuration. Most of these compounds also show temperature variable ^1H n.m.r. spectra, attributable to facile interconversion of optical enantiomers (for the $^-S_2PR_2$ compounds), restricted rotation about the –CN bond (for the $^-S_2CNMe_2$ compounds), and, in some cases, hindered rotation about the ruthenium–phosphorus bonds.

Finally, for $[Ru(S_2PR_2)_2(PMe_2Ph)_2]$, carbonylation gives, in addition to $[Ru(S_2PR_2)_2(PMe_2Ph)CO]$, two isomers of formula $[Ru(S_2PR_2)_2(PMe_2Ph)_2CO]$. The structures of these compounds have been established by ^1H, ^{31}P n.m.r., and double resonance studies and a general mechanism of carbonylation for these compounds is proposed.

IN Parts I—IV of this series, the results of a thorough investigation of the reactions of the square-planar $[M(S-S)_2]$ compounds [M = Pt, Pd; $(S-S)^- = {}^-S_2PR_2$ (R = Me, Et, Ph), $^-S_2CNR_2$ (R = Me, Et), $^-S_2COEt$, and $^-S_2P(OEt)_2$] with ligands containing Group VB donor atoms (L) have been presented.[1,3] A detailed analysis, utilising *X*-ray diffraction, spectroscopic, and chemical techniques, revealed that reaction occurs by stepwise cleavage of the metal–sulphur bonds of *one* dithio-ligand, giving the compounds $[M(S-S)_2L]$ and $[M(S-S)L_2]$ (S–S) with unidentate–bidentate and bidentate–ionic co-ordination respectively. In addition, these compounds were shown to exhibit several different types of intra- and inter-molecular rearrangement reactions, depending on the nature of the dithio-ligand, the solvent, and the temperature at which the reactions were studied.[1,3]

In view of these unusual results, it was decided to extend the investigation to a study of other platinum metal dithioacid complexes and in this and the following papers,[4] we wish to report the full results of our recent ruthenium–sulphur studies. Later papers [5] will discuss related investigations into rhodium– and osmium–sulphur chemistry.

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[1] Part IV, D. F. Steele and T. A. Stephenson, *J.C.S. Dalton*, 1973, 2124.

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

[3] (*a*) T. A. Stephenson and B. D. Faithful, *J. Chem. Soc.* (*A*), 1970, 1504; (*b*) (Miss) J. M. C. Alison, T. A. Stephenson, and (in part) R. O. Gould, *J. Chem. Soc.* (*A*), 1971, 3690; (*c*) (Miss) J. M. C. Alison and T. A. Stephenson, *J.C.S. Dalton*, 1973, 254.

[4] (*a*) D. J. Cole-Hamilton and T. A. Stephenson, Part VI, following paper; (*b*) J. D. Owen, T. A. Stephenson, and (in part) D. J. Cole-Hamilton, Part VII, *J.C.S. Dalton*, submitted for publication.

[5] D. J. Cole-Hamilton and T. A. Stephenson, to be published.

RESULTS AND DISCUSSION

Although there has recently been an increasing interest in the chemistry of ruthenium as well as in the chemistry of complexes of sulphur-containing ligands with various metals, research into ruthenium complexes containing dithioacid ligands has been confined to relatively few papers and most of these have been concerned with complexes containing *NN*-dialkyldithiocarbamato-groups. Thus, complexes such as $[Ru(S_2CNRR')_3]$ ($R = R' = Me, Et, Bu^n$;[6] $R = Me, R' = PhCH_2$[7]), $[Ru(S_2CN\{PhCH_2\}_2)_2(CO)_2]Cl$,[8] $[Ru(S_2CNR_2)_2CO]$ ($R = Me, Et$),[8] $[Ru(S_2CNR_2)_2(CO)_2]$ ($R = Me, PhCH_2$),[8] $[Ru(S_2CNR_2)_2(PPh_3)_2]$ ($R = Me, Et, Ph$),[9] $[Ru(S_2CNEt_2)_2(Me_2SO)_2]$,[10] $[Ru(S_2CNRR')_2(S_2C_2\{CF_3\}_2)]$ ($R = R' = Me, Et$; $R = Me, R' = Ph$),[11] and $[RuNO(S_2CNR_2)_3]$ ($R = Me, Et$)[12] have been reported but the last is the only example to date of a ruthenium compound containing a dangling dithioacid group. Related 1,2-dithiolene complexes of ruthenium of type $[Ru(S_2C_2\{CF_3\}_2)(CO)_n(ER_3)_{3-n}]$ ($n = 1, 0$; $E = P, As$) have also been recently reported.[13]

In contrast, apart from brief references to the synthesis of $[Ru(S_2PR_2)_3]$ ($R = Et$,[14] Ph[15]), no investigation of ruthenium dialkyl (or diaryl)phosphinodithioates has been made.

By analogy with our earlier palladium and platinum studies,[1,3] our first attempts to synthesise a range of ruthenium dithioacid compounds were made either by reacting tertiary phosphines directly with $[Ru(S_2PR_2)_3]$ or by refluxing an ethanolic solution of $RuCl_3,nH_2O$, NaS_2PR_2, and PMe_2Ph. In both cases, the main product was $[Ru(S_2PR_2)_3]$, which provides an effective demonstration of the substitutional inertness of the ruthenium(III) (d^6) co-ordination sphere in this instance. Therefore, we tried another method, which has been successfully used to prepare other metal dithioacid complexes; namely, direct reaction between metal halogeno-complexes and an alkali metal salt of the appropriate dithioacid.

e.g.[9]
$$(h^5-C_5H_5)Fe(CO)_2Cl + NaS_2CNMe_2 \longrightarrow (h^5-C_5H_5)Fe(CO)_2S_2CNMe_2 + NaCl$$

Thus, when $[RuCl_2(PPh_3)_{3\ \mathrm{or}\ 4}]$,[16] $[RuCl_3(PPh_3)_2MeNO_2]$,[17] $[RuCl_2(PEtPh_2)_3]$,[18a] $[Ru_2Cl_3(PMePh_2)_6]Cl$,[19] or *mer*-$[RuCl_3(PMe_2Ph)_3]$[20] are gently refluxed in ethanol with an excess of NaS_2PR_2 ($R = Me, Et, Ph$) for *ca.* two hours orange solutions are formed. On cooling these solutions and after filtering off any precipitate of sodium chloride red or orange crystals of composition $[Ru(S_2PR_2)_2L_2]$ (A) (L = tertiary phosphine) are deposited in high yield.* Similar products are formed using acetone or methanol as solvent, except for $[Ru_2Cl_3(PMePh_2)_6]Cl$ in methanol when a red solid, believed to be of composition $[Ru_2Cl_3(PMePh_2)_5(S_2PR_2)]$ is also precipitated. Similar compounds can be obtained by pyrolysis of $[Ru_2Cl_3(PR_3)_6]S_2PR_2$ (*cf.* the pyrolysis of $[Ru_2Cl_3(PEt_2Ph)_6]Cl$ giving $[Ru_2Cl_4(PEt_2Ph)_5]$[21]) and these will be discussed in more detail in a later publication.[18b] In this instance, the dimer is readily separated from $[Ru(S_2PR_2)_2(PMePh_2)_2]$ by the technique of dry column chromatography.[22] For $[RuCl_2(PPh_3)_3]$ and NaS_2PPh_2, $[Ru(S_2PPh_2)_2(PPh_3)_2]$ is only obtained in pure form in the presence of an excess of triphenylphosphine; with no added triphenylphosphine, analytical and molecular weight data (see Experimental section) indicate that a mixture of $[Ru(S_2PPh_2)_2(PPh_3)_2]$ and $[Ru(S_2PPh_2)_2PPh_3]$ is probably formed. (*Cf.* the formation of mono- and bis-carbonyldithiocarbamato-ruthenium complexes[8] and $[RuCl_2(PPh_3)_n]$ (n = 3 or 4)[16] by slight changes in the experimental conditions.) However, by reaction in the presence of an excess of sulphur (an efficient tertiary phosphine scavenger), pure $[Ru(S_2PPh_2)_2PPh_3]$ can be isolated.

Compounds (A) have been characterised by elemental analyses (Table 1) and the usual spectroscopic methods (see later), and the monomeric formulation confirmed by osmometry and by an *X*-ray analysis[4b] on $[Ru(S_2PEt_2)_2(PMe_2Ph)_2]$. The compounds are non-electrolytes and diamagnetic (by Evans' method),[23] and exhibit sharp ^1H n.m.r. resonances. However, exposure of the solutions to air rapidly produces broadening of the n.m.r. signals which is attributed to facile oxidation to paramagnetic ruthenium(III) species. The rate of oxidation, which can be substantially reduced by

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* Shorter reaction times with stoicheiometric amounts of NaS_2PR_2 give paramagnetic species which have not been completely characterised to date.

[6] L. Malatesta, *Gazzetta*, 1938, **68**, 195; L. Cambi and L. Malatesta, *Chem. Ber.*, 1937, **70**, 2067.

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

[8] J. V. Kingston and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1966, **28**, 2709.

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[12] L. Cambi and L. Malatesta, *Rend. Ist. Lombardo Sci.*, 1938, **71**, 118 (*Chem. Abs.*, 1940, **34**, 3201–1); A. Domenicano, A. Vaciago, L. Zambonelli, P. L. Loader, and L. M. Venanzi, *Chem. Comm.*, 1966, 476; R. Davis, M. N. S. Hill, C. E. Holloway, B. F. G. Johnson, and K. H. Al-Obaidi, *J. Chem. Soc.* (*A*), 1971, 994.

[13] J. S. Miller and A. L. Balch, *Inorg. Chem.*, 1971, **10**, 1410; I. Bernal, A. Clearfield, E. F. Epstein, J. S. Ricci, jun., A. L. Balch, and J. S. Miller, *Chem. Comm.*, 1973, 39.

[14] See W. Kuchen and H. Hertel, *Angew. Chem. Internat. Edn.*, 1969, **8**, 89.

[15] E. B. Switkes, L. Ruiz-Ramirez, T. A. Stephenson, and (in part) J. Sinclair, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 593; L. Ruiz-Ramirez, T. A. Stephenson, and E. S. Switkes, *J.C.S. Dalton*, 1973, 1770.

[16] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.* 1966, **28**, 945.

[17] T. A. Stephenson, *J. Chem. Soc.* (*A*), 1970, 889.

[18] (*a*) P. W. Armit and T. A. Stephenson, *J. Organometallic Chem.*, 1973, **57**, C80; (*b*) P. W. Armit and T. A. Stephenson, unpublished work.

[19] J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 1961, 896.

[20] J. Chatt, G. J. Leigh, D. M. P. Mingos, and R. J. Paske, *J. Chem. Soc.* (*A*), 1968, 2636.

[21] R. H. Prince and K. A. Raspin, *J. Inorg. Nuclear Chem.*, 1969, **31**, 695; *J. Chem. Soc.* (*A*), 1969, 612; N. W. Alcock and K. A. Raspin, *ibid.*, 1968, 2108.

[22] For details see: B. Loev and M. M. Goodman, *Chem. and Ind.*, 1967, 2026.

[23] D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

addition of an excess of tertiary phosphine, is also dependent on the nature of L, a qualitative order being $PPh_3 > PMePh_2 > PMe_2Ph$. The solvent medium is also important, since studies indicate that increasing the percentage of $CDCl_3$ in $CDCl_3$–CS_2 mixtures increases the rate of oxidation.

In the reaction of $[\mathrm{RuCl_2(P\{OPh\}_3)_4}]$ [24] with an excess of NaS_2PR_2, the product formed depends critically upon both reaction time and solvent medium. Thus, in refluxing ethanol for one hour, reaction with an excess of NaS_2PMe_2 gives a sample of $[\mathrm{Ru(S_2PMe_2)_2(P\{OPh\}_3)_2}]$. However, if refluxing is continued for a further hour, a mixture of products is obtained which proved impossible to separate by chromatographic or sublimation techniques. However, the mass spectrum of the mixture reveals the parent ion and fragmentation pattern peaks expected for $[\mathrm{Ru(S_2PMe_2)_2(P\{OEt\}\{OPh\}_2)_2}]$ together with a peak at *m/e* 780 (^{102}Ru isotope) which can only arise from the species $[\mathrm{Ru(S_2PMe_2)_2(P\{OEt\}_2OPh)_2}]$ since there is no way of obtaining a fragment of this mass number by degradation of $[\mathrm{Ru(S_2PMe_2)_2(P\{OEt\}\{OPh\}_2)_2}]$. Consistent with this interpretation, the ^{1}H n.m.r. spectrum of the mixture shows two sets of ethyl resonances of approximate intensity 3 : 1 (the ratio varied from sample to sample) attributable to the mono- and bis-ethoxy phosphite complexes respectively. The experimental carbon and hydrogen percentages for the mixture are also in good agreement with calculated data based on this ratio.

TABLE 1

Analytical data for some ruthenium complexes

Complex	Colour	M.p. (°C)	Found %				Required %			
			C	H	Others	*M*	C	H	Others	*M*
cis-$[\mathrm{Ru(S_2PPh_2)_2(PPh_3)_2}]$	Red	193—195	64·2	4·7			64·1	4·5		
cis-$[\mathrm{Ru(S_2PPh_2)_2(PMePh_2)_2}]$	Orange	116—118	60·1	4·4			60·1	4·6		
cis-$[\mathrm{Ru(S_2PPh_2)_2(PMe_2Ph)_2}]$	Orange	247—248	54·7	4·7	S, 14·8; P, 14·2		54·7	4·8	S, 14·6; P, 14·2	
cis-$[\mathrm{Ru(S_2PMe_2)_2(PPh_3)_2}]$	Red-brown	139—142	54·7	4·7			54·9	4·8		
cis-$[\mathrm{Ru(S_2PMe_2)_2(PMePh_2)_2}]$	Orange	279—280(d)	47·8	5·0			47·9	5·1		
cis-$[\mathrm{Ru(S_2PMe_2)_2(PMe_2Ph)_2}]$	Orange	212(d)	38·3	5·2	S, 20·6; P, 19·6	618 [a]	38·3	5·4	S, 20·6; P, 19·8	627
cis-$[\mathrm{Ru(S_2PMe_2)_2(P\{OPh\}_3)_2}]$	Yellow	145—147	49·3	4·6		973 ± 5 [b]	49·4	4·3		971
cis-$[\mathrm{Ru(S_2PMe_2)_2(P\{OMe\}_3)_2}]$	Yellow	213—214 [c]	20·1	5·0		599 [b]	20·0	5·0		599
cis-$[\mathrm{Ru(S_2PMe_2)_2(PEtPh_2)_2}]$	Orange	158	48·7	5·6			49·3	5·4		
cis-$[\mathrm{Ru(S_2PEt_2)_2(PMe_2Ph)_2}]$	Red	156—157	42·7	6·1	S, 18·9		42·2	6·1	S, 18·7	
cis-$[\mathrm{Ru(S_2PEt_2)_2(PPh_3)_2}]$	Red	124—126	56·3	5·3			56·7	5·4		
cis-$[\mathrm{Ru(S_2CNMe_2)_2(PPh_3)_2}]$,$Me_2CO$	Yellow	168—169	58·1	4·8	N, 3·3		58·3	4·9	N, 3·2	
cis-$[\mathrm{Ru(S_2CNMe_2)_2(PMe_2Ph)_2}]$	Yellow	204—206	42·8	5·5	N, 4·7; S, 20·6; P, 10·1		42·8	5·5	N, 4·5; S, 20·7; P, 10·0	
trans-$[\mathrm{Ru(S_2CNMe_2)_2(PMe_2Ph)_2}]$	Yellow		42·8	5·5	N, 4·8		42·8	5·5	N, 4·5	
cis-$[\mathrm{Ru(S_2CNMe_2)_2(P\{OPh\}_3)_2}]$	Yellow	150—152	51·7	4·5	N, 2·9		52·4	4·4	N, 2·9	
cis-$[\mathrm{Ru(S_2PMe_2)_2(PPh_3)(P\{OPh\}_3)}]$	Orange	182—184	51·1	4·5			52·0	4·6		
cis-$[\mathrm{Ru(S_2PMe_2)_2(PMe_2Ph)(P\{OPh\}_3)}]$	Orange	124—125	44·4	4·7			45·0	4·8		
cis-$[\mathrm{Ru(S_2PPh_2)_2(PMe_2Ph)(P\{OPh\}_3)}]$	Orange	182—184	56·9	4·6			57·3	4·4		
cis-$[\mathrm{Ru(S_2CNMe_2)_2(PPh_3)(P\{OPh\}_3)}]$	Yellow	201—204	55·0	4·6	N, 3·1		55·2	4·6	N, 3·1	
cis-$[\mathrm{Ru(S_2PPh_2)_2(PMe_2Ph)CO}]$	Orange	194—195	51·6	4·0		763 ± 3 [b]	51·7	4·1		766
cis-$[\mathrm{Ru(S_2PMe_2)_2(PPh_3)CO}]$	Orange	123—125	43·3	4·3		720 [a] 638 ± 3 [b]	43·1	4·2		641
cis-$[\mathrm{Ru(S_2PMe_2)_2(PMePh_2)CO}]$	Orange	161—163	37·3	4·4		579 ± 1 [b]	37·3	4·3		579
cis-$[\mathrm{Ru(S_2PMe_2)_2(PMe_2Ph)CO}]$	Yellow	43—44	30·2	4·6		478 [a] 517 ± 1 [b]	30·2	4·5		517
cis-$[\mathrm{Ru(S_2PMe_2)_2(P\{OPh\}_3)CO}]$	Yellow	193—194	40·0	3·9		689 ± 1 [b]	40·1	3·9		689
cis-$[\mathrm{Ru(S_2PMe_2)_2(P\{OMe\}_3)CO}]$	Yellow	117—119	19·3	4·4		502 ± 1 [b]	19·1	4·2		503
cis-$[\mathrm{Ru(S_2PMe_2)_2(AsPh_3)CO}]$	Orange	104—106	40·8	4·3		687 ± 2 [b]	40·3	3·9		685
$[\mathrm{Ru(S_2PPh_2)_2(PMe_2Ph)_2CO}]$ [d]	Yellow	95—115(d)	53·9	4·7			54·5	4·7		
$[\mathrm{Ru(S_2PMe_2)_2(PMe_2Ph)_2CO}]$ [d]	Yellow	134—135(d)	38·2	5·2			38·5	5·2		
$[\mathrm{Ru(S_2PMe_2)_2(PMe_2Ph)_2CO}]$ [e]	Yellow	102—118(d)	38·7	5·1			38·5	5·2		
cis-$[\mathrm{Ru(S_2PPh_2)_2(CO)_2}]$	Yellow	89—90	47·8	3·2		655 ± 1 [b]	47·6	3·1		655
cis-$[\mathrm{Ru(S_2PMe_2)_2(CO)_2}]$	Yellow	159—160	17·9	3·0		407 ± 1 [b]	17·7	2·9		407
cis-$[\mathrm{Ru(S_2CNMe_2)_2(CO)_2}]$	Yellow	230—231 [f]	24·5	3·1	N, 7·2		24·8	3·0	N, 7·1	

[a] Molecular weight measured osmometrically at 37° in benzene. [b] Molecular weight from parent ion peak (^{101}Ru isotope) in mass spectrum. [c] Sublimes at 160 °C. [d] Configuration C. [e] Configuration D. [f] Sublimes at 170 °C.

Further refluxing (24 h) gives a yellow solution from which no solid product could be isolated but a mass spectrum of the resultant oil shows peaks attributable to $[\mathrm{Ru(S_2PMe_2)_2(P\{OEt\}_3)_2}]$, together with a number of other tertiary phosphite compounds (see Experimental section). However, if the reaction between $[\mathrm{RuCl_2(P\{OPh\}_3)_4}]$ and excess NaS_2PMe_2 is carried out in refluxing methanol, even for comparatively short reaction times, a pure sample of $[\mathrm{Ru(S_2PMe_2)_2(P\{OMe\}_3)_2}]$ can be isolated and phenol and trimethyl phosphite can be identified in the filtrate. All these phosphite compounds are more resistant to oxidation in solution than the corresponding tertiary phosphine complexes.

Muetterties *et al.*[25] have reported that triphenyl phosphite, when co-ordinated to ruthenium, does not

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[24] J. J. Levison and S. D. Robinson, *J. Chem. Soc.* (*A*), 1970, 639.

[25] D. H. Gerlach, W. G. Peet, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1972, **94**, 4545.

appear to undergo transesterification by alcohols, whereas such reactions readily occur with the free ligands. Therefore, at first sight, the transesterification of the tertiary phosphite groups in $[Ru(S_2PMe_2)_2(P\{OPh\}_3)_2]$ appears surprising. However, since the starting material has four phosphites per ruthenium and the product only two, then two must be released during the reaction, presumably as free tertiary phosphite. This free triphenyl phosphite may then be transesterified giving, in the case where methanol is solvent, trimethyl phosphite. The trimethyl phosphite, being a stronger nucleophile than its triphenyl analogue[26] (as well as less bulky), can then replace the co-ordinated $P(OPh)_3$ groups to give $[Ru(S_2PMe_2)_2(P\{OMe\}_3)_2]$. This conclusion is supported by the observation that $[Ru(S_2PMe_2)_2(P\{OPh\}_3)_2]$ may be recovered unchanged after refluxing in degassed methanol for 24 h.* Presumably the ease of formation of the $P(OMe)_3$ complex, compared with the $P(OEt)_3$ complex, is a reflection of the greater nucleophilicity of the methoxide ion compared to the ethoxide ion.

Finally, reaction of *mer*-$[RuCl_3(PMe_2Ph)_3]$ with an excess of NaS_2CNMe_2 gives $[Ru(S_2CNMe_2)_2(PMe_2Ph)_2]$, analogous to the triphenylphosphine complex reported elsewhere.[9]

Reactions of $[Ru(S\text{–}S)_2L_2]$ *Complexes*.—All the compounds of type (A) readily react with carbon monoxide under very mild conditions to give the monocarbonyl species $[Ru(S_2PR_2)_2L(CO)]$ (B). For L = PPh_3, $AsPh_3$; R = Me, the same compounds are also formed by prolonged interaction of *cis*-$[RuCl_2(CO)_2L_2]$[16] with NaS_2PMe_2. In contrast, in agreement with earlier work,[9] attempted carbonylation of the corresponding $[Ru(S_2CNR_2)_2(PR'_3)_2]$ compounds ($PR'_3 = PMe_2Ph$, PPh_3), even under pressure, gives only unchanged starting material. Furthermore, attempts to displace the remaining L group from $[Ru(S_2PR_2)_2L(CO)]$ to give $[Ru(S_2PR_2)_2(CO)_2]$ have also proved unsuccessful. However, the dicarbonyl complexes $[Ru(S_2PR_2)_2(CO)_2]$ (R = Me, Ph) have been synthesised from $Cs_2[RuCl_4(CO)_2]$,[27] NaS_2PMe_2 and from $[Ru_3(CO)_{12}]$,† Ph_2PS_2H combinations respectively. Similarly, reaction of $[Ru_3(CO)_{12}]$ with tetramethylthiuram disulphide gives the previously characterised[8] $[Ru(S_2CNMe_2)_2(CO)_2]$. A small amount of this product is also formed by prolonged reaction of *cis*-$[RuCl_2(CO)_2(PPh_3)_2]$ with NaS_2CNMe_2. Although $[Ru(S_2CNR_2)_2(CO)_2]$ does not react with PR'_3, the corresponding $[Ru(S_2PR_2)_2(CO)_2]$ are readily converted to $[Ru(S_2PR_2)_2(PR'_3)CO]$. Thus, it appears that the products $[Ru(S_2PR_2)_2L(CO)]$ are thermodynamically very stable, being readily formed from $[Ru(S_2PR_2)_2L_2]$ or $[Ru(S_2PR_2)_2(CO)_2]$, whereas with $(S\text{–}S)^- = {}^-S_2CNR_2$ no evidence has been found for the mixed species. For L = PMe_2Ph, reaction of $[Ru(S_2PR_2)_2(PMe_2Ph)_2]$ and carbon monoxide gives, in addition to $[Ru(S_2PR_2)_2(PMe_2Ph)CO]$, two other complexes which both analyse for $[Ru(S_2PR_2)_2(PMe_2Ph)_2CO]$. Compounds of this type have not been observed with other tertiary phosphines. A detailed spectroscopic analysis of these compounds, together with proposed structures and a possible general mechanism for these carbonylation reactions are presented later in this paper.

All the $[Ru(S\text{–}S)_2L_2]$ compounds undergo ligand exchange reactions with other phosphorus ligands of greater basicity. Thus, for $[Ru(S_2PR_2)_2L_2]$ where L = PPh_3 or $PMePh_2$, reaction with $PMe_2Ph(L')$ gives $[Ru(S_2PR_2)_2L'_2]$; similarly, both L groups are displaced by L' when L = PPh_3, L' = $PMePh_2$ and also with $[Ru(S_2CNMe_2)_2(PPh_3)_2]$ and an excess of PMe_2Ph, $[Ru(S_2CNMe_2)_2(PMe_2Ph)_2]$ is exclusively formed. These results can be readily rationalised on the basis that the compounds $[Ru(S\text{–}S)_2L'_2]$ are both sterically and electronically favoured compared with the mixed ligand complexes $[Ru(S\text{–}S)_2LL']$. However, when the phosphine complexes are treated with $P(OPh)_3$, steric effects become more important. Thus, $[Ru(S_2PR_2)_2(PMe_2Ph)_2]$ and $P(OPh)_3$, give only the mixed ligand complex $[Ru(S_2PR_2)_2(PMe_2Ph)(P\{OPh\}_3)]$ whereas with $[Ru(S\text{–}S)_2(PPh_3)_2]$ ($S\text{–}S^- = {}^-S_2PMe_2$, ${}^-S_2CNMe_2$), both $[Ru(S\text{–}S)_2(PPh_3)(P\{OPh\}_3)]$ and $[Ru(S\text{–}S)_2(P\{OPh\}_3)_2]$ can be isolated, the amount of each depending on the conditions employed. This is presumably because there is a fine balance between the large difference in basicity of PPh_3 and $P(OPh)_3$ (which will favour the bis-phosphite complex) and the greater steric crowding in the bis-phosphite complex compared to the mixed phosphine–phosphite species.

Spectroscopic Properties of Dithioacid Complexes.—(a) *Infrared spectra*. The i.r. spectra of all the complexes reported are rather complicated, showing absorptions due to the tertiary phosphine or phosphite groups, as well as the phosphinodithioate ligands. However, a recent paper from this laboratory[3b] indicates that for platinum and palladium(II) diphenylphosphinodithioate complexes there appears to be an empirical i.r. method of distinguishing between bidentate, ionic, and unidentate co-ordination of the ${}^-S_2PPh_2$ group. Thus, bidentate co-ordination is characterised by two bands at 603,570 cm^{-1}; ionic, 650,560 cm^{-1}; and unidentate, 645,540 cm^{-1}. Similarly, platinum and palladium(II) dimethylphosphinodithioates have characteristic bands at 570—585 cm^{-1} (bidentate); 610 cm^{-1} (ionic); and 600 cm^{-1} (unidentate). In this instance, the lower energy band (*ca.* 500 cm^{-1}) is masked by strong ligand vibrations.[1]

An examination of Table 2 reveals that all the [Ru-

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* In a recent paper (*Inorg. Chem.*, 1972, **11**, 749) Roundhill *et al.* suggest that transesterification of tertiary phosphites occurs when the phosphites are co-ordinated to platinum. However, since in each case where transesterification occurs, there is free phosphite present in the system, a better explanation (in view of Muetterties' work[25]) might be that the free phosphite is transesterified and then this replaces a bound phosphite which is, in turn, transesterified *etc.*

† We thank Dr. J. R. Jennings of I.C.I. Ltd. for a sample of this compound.

[26] P. G. Douglas and B. L. Shaw, *J. Chem. Soc.* (*A*), 1970, 1556, and references therein.

[27] R. Colton and R. H. Farthing, *Austral. J. Chem.*, 1967, **20**, 1283; M. J. Cleare and W. P. Griffith, *J. Chem. Soc.* (*A*), 1969, 372.

$(S_2PR_2)_2L_2]$ and $[Ru(S_2PR_2)_2LL']$ complexes contain only i.r. absorptions characteristic of bidentate $^-S_2PR_2$ co-ordination. Similarly, in spite of complications arising from the presence of carbonyl bending modes [δ(CO)] in the region 600—500 cm^{-1}, all the compounds of type $[Ru(S_2PR_2)_2L(CO)]$ and $[Ru(S_2PR_2)_2(CO)_2]$ show only 'bidentate' $^-S_2PR_2$ co-ordination. The latter also have two ν(CO) bands indicating a *cis*-configuration. For the compounds $[Ru(S_2PR_2)_2(PMe_2Ph)_2CO]$, in addition to the 'bidentate' bands, there are absorptions at 645,540 cm^{-1} (S_2PPh_2) and *ca.* 600 cm^{-1} (S_2PMe_2), indicative of unidentate co-ordination although the presence of a carbonyl bending vibration in this region is a complicating factor. However, in spite of this, the data in Table 2 clearly indicate the generality of these empirical methods for distinguishing between different types of $^-S_2PR_2$ co-ordination in platinum metal complexes.

TABLE 2

Infrared spectra of various ruthenium dithioacid complexes (shoulders in italics)

Complex	$^-S_2PR_2$ bands (cm^{-1})		ν(CO)(cm^{-1})	δ(CO)(cm^{-1})
	Bidentate	Unidentate		
cis-$[Ru(S_2PMe_2)_2(PPh_3)_2]$	583			
cis-$[Ru(S_2PMe_2)_2(PMePh_2)_2]$	587			
cis-$[Ru(S_2PMe_2)_2(PMe_2Ph)_2]$	588			
cis-$[Ru(S_2PMe_2)_2(P\{OPh\}_3)_2]$	589			
cis-$[Ru(S_2PMe_2)_2(P\{OMe\}_3)_2]$	589			
cis-$[Ru(S_2PMe_2)_2(PPh_3)(P\{OPh\}_3)]$	589			
cis-$[Ru(S_2PMe_2)_2(PMe_2Ph)CO]$	570		1933 (1945) [a]	564
$[Ru(S_2PMe_2)_2(PMe_2Ph)_2CO]$ [b]	589, 579	600	1939, *1929*, (1940) [a]	569
$[Ru(S_2PMe_2)_2(PMe_2Ph)_2CO]$ [c]	580	598	1961, 1944, (1967) [a]	569
cis-$[Ru(S_2PMe_2)_2(PPh_3)CO]$	581		1934	569
cis-$[Ru(S_2PMe_2)_2(PMePh_2)CO]$	581		1930	569
cis-$[Ru(S_2PMe_2)_2(P\{OMe\}_3)CO]$	581		*1955*, 1938	563
cis-$[Ru(S_2PMe_2)_2(CO)_2]$	582		2045, 1989, 1970 (2042, 1967) [a]	610, 562
cis-$[Ru(S_2PPh_2)_2(PPh_3)_2]$	606, 572, 568			
cis-$[Ru(S_2PPh_2)_2(PMePh_2)_2]$	609, 570			
cis-$[Ru(S_2PPh_2)_2(PMe_2Ph)_2]$	611, 573			
cis-$[Ru(S_2PPh_2)_2(PMe_2Ph)(P\{OPh\}_3)]$	609, 572, 568			
cis-$[Ru(S_2PPh_2)_2(PMe_2Ph)CO]$			1920 (1948) [d]	568
$[Ru(S_2PPh_2)_2(PMe_2Ph)_2CO]$ [b]	611, 570	645, 540	1939 (1946) [d]	579
$[Ru(S_2PPh_2)_2(PMe_2Ph)_2CO]$ [c]	607, 565	645, 542	1989 (1984) [d]	551
cis-$[Ru(S_2PPh_2)_2(CO)_2]$	608, 568		(2030, 1960) [a]	612, *560*

[a] Measured in $CHCl_3$ solution. [b] Configuration C. [c] Configuration D. [d] Measured in $CDCl_3$ solution.

(b) *Mass spectra.* The complexes of formula $[Ru(S_2PR_2)_2(PR'_3)_2]$ are all of high m.p. and decompose at low enough temperatures to make it impossible to obtain mass spectra for these complexes. However, the phosphine–phosphite and bis-phosphite compounds are more volatile and excellent mass spectra may be recorded at *ca.* 440 K. These consist of well defined parent ion peaks together with fragmentation patterns *e.g.* the spectrum of $[Ru(S_2PMe_2)_2(P\{OMe\}_3)_2]$ (Table 3) which shows successive loss of methyl groups and oxygen atoms from the phosphite groups.

The carbonyl-containing compounds $[Ru(S_2PR_2)_2L(CO)]$ and $[Ru(S_2PR_2)_2(PMe_2Ph)_2CO]$ are also more volatile than their bis-phosphine parent compounds and thus give reasonable mass spectra. For L = tertiary phosphine, parent ion peaks together with fragmentation patterns corresponding to loss of carbonyl, loss of tertiary phosphine, and loss of both carbonyl and phosphine groups are observed. There are also metastable ions corresponding to the loss of carbonyl groups and, in some cases, doubly positively charged species $[Ru(S_2PR_2)_2L]^{2+}$ are observed. For the $[Ru(S_2PR_2)_2(PMe_2Ph)_2CO]$ compounds, exactly the same parent ion and fragmentation pattern is observed as for $[Ru(S_2PR_2)_2(PMe_2Ph)CO]$ due to ready loss of a PMe_2Ph group. The phosphite complexes containing a carbonyl group give more complicated mass spectra *e.g.* the spectrum of $[Ru(S_2PMe_2)_2(P\{OPh\}_3)CO]$ (Table 4) which shows successive loss of carbonyl, phenoxo-, and $^-S_2PMe_2$ groups.

TABLE 3

Main peaks in the mass spectrum of $[Ru(S_2PMe_2)_2(P\{OMe\}_3)_2]$

Mass no. of ^{102}Ru peak [a]	Probable ion
600	$[Ru(S_2PMe_2)_2(P\{OMe\}_3)_2]^+$
585	$[Ru(S_2PMe_2)_2P\{OMe\}_3)(P\{OMe\}_2O)]^+$
569	$[Ru(S_2PMe_2)_2(P\{OMe\}_3)(P\{OMe\}_2)]^+$
507	$[Ru(S_2PMe_2)_2(P\{OMe\}_3)P]^+$
492	$[Ru(S_2PMe_2)_2(P\{OMe\}_2O)P]^+$
476	$[Ru(S_2PMe_2)_2P\{OMe\}_3]^+$ *or* $[Ru(S_2PMe_2)_2P\{OMe\}_2P]^+$
461	$[Ru(S_2PMe_2)_2P\{OMe\}_2O]^+$ *or* $[Ru(S_2PMe_2)_2P\{OMe\}OP]^+$
445	$[Ru(S_2PMe_2)_2P\{OMe\}_2]^+$ *or* $[Ru(S_2PMe_2)_2(P\{OMe\})P]^+$
383	$[Ru(S_2PMe_2)_2P]^+$
377 (metastable)	$600 \longrightarrow 476$
352	$[Ru(S_2PMe_2)_2]^+$

[a] All peaks show the characteristic ruthenium isotopic pattern.

(c) ^1H *N.m.r. spectra.** (i) *Complexes of formula* $[Ru(S_2PR_2)_2L_2]$. For L = $PMePh_2$ or PMe_2Ph, the room temperature resonance arising from the methyl groups on the phosphines (a $H_nPP'H'_n$ second-order type

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* Because of the complexity of the ^1H n.m.r. spectra of the $^-S_2PEt_2$ compounds, the n.m.r. studies have been confined to the dimethyl (and diphenyl)phosphinodithioato-complexes.

spectrum $n = 3$ or 6 [28]) consists of a sharp doublet with a broad hump situated between the doublet * (see Figure 1b). Comparison with other similar ruthenium tertiary phosphine complexes is of interest. Thus, for *trans*-$[RuCl_2CO(PMe_2Ph)_3]$, the ^1H n.m.r. spectrum consists of a ' virtually ' coupled 1,2,1 triplet from the *trans* phosphines and a doublet arising from the *cis*-phosphine, due to the fact that in this compound *J*(PP)(*trans*) is very large and *J*(PP)(*cis*) is effectively zero.[29] However, in some complexes, where the *cis*-phosphines are in equivalent chemical environments *e.g.* $[Ru_2Cl_3(PMe_2Ph)_6]Cl$, and *cis*-$[RuCl_2(PMe_2Ph)_4]$,[18a] the methyl ^1H n.m.r. signal is a pseudo-triplet, very similar in shape to those observed here for $[Ru(S_2PR_2)_2L_2]$ (L = PMe_2Ph, $PMePh_2$). This however is not true in every case, *e.g.* the *cis*-phosphines in *cis*-$[RuH_2(PMe_2Ph)_4]$ (which are also in equivalent chemical environments) give rise to a single sharp doublet [30] [*i.e.* *J*(PP) is effectively zero]. Thus, the pseudo-triplet pattern could arise either from *cis*-phosphines with a relatively large *J*(PP) or *trans* phosphines with a relatively low *J*(PP) [28] and hence no definitive conclusion about stereochemistry can be drawn from these peak contours at room temperature.

TABLE 4

Main peaks in the mass spectrum of $[Ru(S_2PMe_2)_2(P\{OPh\}_3)CO]$

Mass no. of ^{102}Ru peak [a]	Probable ion
690	$[Ru(S_2PMe_2)_2(P\{OPh\}_3)CO]^+$
662	$[Ru(S_2PMe_2)_2(P\{OPh\}_3)]^+$
635 (metastable)	$690 \longrightarrow 662$
597	$[Ru(S_2PMe_2)_2(P\{OPh\}_2)CO]^+$
569	$[Ru(S_2PMe_2)_2(P\{OPh\}_2)]^+$
537	$[Ru(S_2PMe_2)(P\{OPh\}_3)]^+$
476	$[Ru(S_2PMe_2)_2(P\{OPh\})]^+$
435 (metastable)	$662 \longrightarrow 537$
412	$[Ru(P\{OPh\}_3)]^+$
380	$[Ru(S_2PMe_2)_2CO]^+$
352	$[Ru(S_2PMe_2)_2]^+$
331	$[Ru(S_2PMe_2)_2(P\{OPh\}_3)]^{2+}$

[a] All peaks show the characteristic ruthenium isotopic pattern.

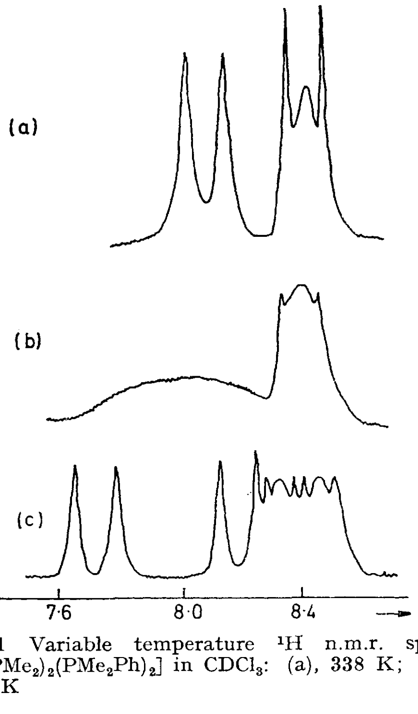

FIGURE 1 Variable temperature ^1H n.m.r. spectrum of $[Ru(S_2PMe_2)_2(PMe_2Ph)_2]$ in $CDCl_3$: (a), 338 K; (b), 301 K; (c), 253 K

However, on cooling the PMe_2Ph complex, the methyl resonance signal broadens and at 250 K consists of two pseudo-triplets separated by *ca.* 13 Hz (Figure 1c); raising the temperature reverses the process. The best explanation for these observations is that the complex has a *cis*-configuration and at lower temperatures rotation about the ruthenium–phosphorus bond is slowed down sufficiently for the inequivalence of the chemical environments of the two methyl groups (a and b) to be seen in the n.m.r. spectrum (Figure 2). This phenomenon has also been noted for the *trans* phosphines of *cis*-$[RuCl_2(CO)(PMe_2Ph)_3]$.[29] If (A; L = PMe_2Ph) had a *trans*-configuration, then the two methyl groups on the one PMe_2Ph ligand would be in identical chemical environments, giving rise to one resonance, irrespective of the rate of rotation about the ruthenium–phosphorus bond. For L = $PMePh_2$, the similarity of the shape of the pseudo-triplet to that for L = PMe_2Ph, and for L = $P(OMe)_3$, the close similarity of the observed second-order spectrum with that obtained for *cis*-$[PtX_2(P\{OMe\}_3)_2]$ [31] is further evidence for *cis*-stereochemistry in these compounds.

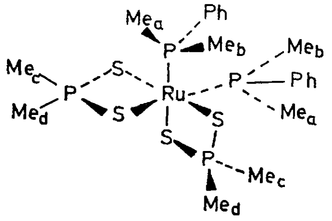

FIGURE 2 Diagrammatic representation of *cis*-configuration for $[Ru(S_2PMe_2)_2(PMe_2Ph)_2]$

However, full confirmation of *cis* stereochemistry for *all* these tertiary phosphine and phosphite complexes comes from an examination of the low temperature ^1H n.m.r. spectra of the methyl groups of the $^-S_2PMe_2$ ligands. For *cis*-$[Ru(S_2PMe_2)_2L_2]$, two types of inequivalent dithioacid methyl groups (c and d in Figure 2) are present, which should give two signals, each split into a doublet by the ^{31}P nuclei, whereas for *trans* stereochemistry only one doublet should be observed. Experimentally, the low temperature ^1H n.m.r. spectra of all the bis-phosphine and -phosphite compounds consists of two doublets, indicative of *cis* stereochemistry,

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* Referred to hereafter as a ' pseudo-triplet ' pattern.

[28] R. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

[29] J. M. Jenkins, M. S. Lupin, and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1787.

[30] K. C. Dewhirst, W. Keim, and C. A. Reilly, *Inorg. Chem.*, 1968, 546.

[31] M. J. Church and M. J. Mays, *J. Inorg. Nuclear Chem.*, 1971, **33**, 253.

at least at low temperature.* (See Figure 1c and Table 5.)

However, on warming to room temperature or above, these two doublets first coalesce and then sharpen to a single doublet [with a very similar $J(PH)$] (Figure 1a and Table 5). This process, which occurs at different rates for different L, is completely reversible. At first sight, these observations are consistent with either a reversible *cis–trans* isomerism or a rapid interconversion of the two possible optical enantiomers of the *cis* compounds at elevated temperatures. There are several reasons why the latter explanation is preferred. First, the shape of the resonance due to the methyl groups on the phosphines remains almost unchanged throughout the temperature changes whereas *cis–trans* isomerism should produce large changes in $J(PP)$ and hence in the shape of this resonance.[28] In general, it has been found that the more stable isomers of ruthenium complexes have a *cis*-configuration and that quite often on heating, the ***trans*** isomer undergoes an irreversible conversion to the *cis* isomer.[16,34] This is the reverse of the behaviour found in these complexes. Furthermore, the related $[Ru(S_2PR_2)_2(CO)_2]$ complexes, which have a *cis* configuration in both solid and solution state [two ν(CO)], show no evidence for formation of the ***trans*** isomer at higher temperatures (no change in i.r. spectra). Finally, the high temperature doublet is approximately halfway between the positions of the low temperature doublets, irrespective of L (Table 5). This phenomena is characteristic of a process such as rapid inversion which averages the two chemical environments of methyl groups c and d but not of an interconversion of geometrical isomers where it is extremely unlikely that the chemical shift of the methyl groups of the ***trans*** isomer will always coincide with the mean of those of the *cis* isomer.

Therefore, all the evidence suggests that the variation in ^1H n.m.r. spectra of the complexes *cis*-$[Ru(S_2PR_2)_2L_2]$ with temperature is due to the facile interconversion of optical isomers and the mechanism of this process is discussed in detail in Part VI.[4a]

The chemical shifts of the methyl resonances of the dithio-ligands are also of interest in that the position of the lower field doublet remains almost unaltered by changing L whereas that of the higher field doublet is very sensitive to changes in L, varying from τ 8·08 (L = P{OMe}$_3$) to τ 8·94 (L = PPh$_3$) (Table 5). A possible explanation of this is that the lower field doublet arises from the methyl groups *anti* to the phosphorus ligands (d in Figure 2) and the higher field doublet from the methyl groups (c) *syn* to the phosphorus ligands. Then, the *syn* methyl groups will be influenced by the ring currents of the phenyl rings on the phosphine, causing them to be more shielded than the *anti* methyl groups which would account for their higher field position. Furthermore, increasing the number of phenyl groups on the tertiary phosphine will lead to increased shielding of the *syn* methyls, making them resonant at even higher fields. Similar effects have been observed in the compounds $[M(S-S)(PR'_3)_2]BPh_4$ (M = Pt, Pd) ($S-S^- = {}^-S_2PR_2$, S_2CNR_2) where the R and R' resonances are shifted τ *ca.* 0·2—0·4 upfield with respect to their positions in the corresponding PF_6^- and Cl^- salts,[1,3c] and also in recent studies on the interaction of benzene with arsenic, antimony, and bismuth dithiocarbamates.[35] For L = P(OPh)$_3$, the higher field doublet resonates at τ 8·35. This is lower than that in the PPh$_3$ complex, presumably because the phenyl groups are further away from the *syn* methyl groups, producing less efficient shielding.

(ii) *Complexes of formula* $[Ru(S_2PR_2)_2L(CO)]$ *and* $[Ru(S_2PR_2)_2LL']$. In all the $[Ru(S_2PR_2)_2L(CO)]$ complexes the methyl group(s) of the phosphorus ligand produce a single doublet at high temperature in the ^1H n.m.r., an observation consistent with either *cis* or ***trans*** stereochemistry. However, for L = PMe$_2$Ph, cooling produces broadening and then splitting into two overlapping doublets, a fact attributable to a *cis*-configuration and to slow rotation about the ruthenium–phosphorus bond at low temperatures. For the compounds $[Ru(S_2PR_2)_2LL']$, the methyl groups on the phosphine exhibit a single sharp doublet, which is temperature invariant [except for R = Ph, L = PMe$_2$Ph, L' = P(OPh)$_3$] (Table 5). However, as for the $[Ru(S_2PR_2)_2L_2]$ compounds, examination of the $^-S_2PMe_2$ resonances provides an unequivocal demonstration of *cis*-stereochemistry. If the complexes $[Ru(S_2PMe_2)_2LL']$ or $[Ru(S_2PMe_2)_2L(CO)]$ had a ***trans*** configuration, the methyl groups of the dithioacid ligands would occupy two different chemical environments either *syn* to the ligand L or *syn* to L' (or CO), which would give rise to two signals each split into a doublet by coupling with a ^{31}P nucleus. For a *cis* configuration, all four methyl groups will be in different chemical environments (Figure 3) and four resonances (each a doublet) should appear in the ^1H n.m.r. spectrum.

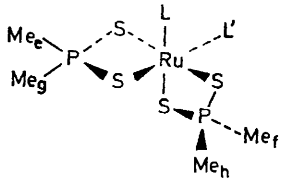

FIGURE 3 Diagrammatic representation of *cis*-configuration for $[Ru(S_2PMe_2)_2LL']$: (a), L = PMe$_2$Ph, L' = P{OPh}$_3$; (b), L = P{OMe}$_3$, L' = CO; (c), L = PPh$_3$, L' = P{OPh}$_3$

At low temperature, the ^1H n.m.r. spectra of all these complexes (with the exception of $[Ru(S_2PMe_2)_2(PMe_2Ph)(P\{OPh\}_3)]$ and $[Ru(S_2PMe_2)_2(P\{OMe\}_3)CO]$) consists of four doublets arising from the $^-S_2PMe_2$ groups.

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* *X*-Ray analysis has confirmed the *cis*-configuration for $[Ru(S_2PEt_2)_2(PMe_2Ph)_2]$[4b] and the related compounds $(Ru(HCS_2)_2(PPh_3)_2]$[32] and $[Ru(pyS)_2(PPh_3)_2]$[33] (pyS = pyridine-2-thiolato) also possess *cis* stereochemistry in the solid state.

[32] R. O. Harris, L. S. Sadavoy, S. C. Nyburg, and F. H. Pickard, *J.C.S. Dalton*, 1973, 2646.

[33] S. R. Fletcher and A. C. Skapski, *J.C.S. Dalton*, 1972, 635.

[34] B. E. Prater, *J. Organometallic Chem.*, 1972, **34**, 379.

[35] G. E. Manoussakis and C. A. Tsipis, *Z. anorg. Chem.*, 1973, **398**, 88.

TABLE 5

^{1}H N.m.r. data for various ruthenium dithioacid complexes

Complex	Solvent	Temp. (T/K)	Dithioligand (Me groups) τ Value [a] [(JPH)] [b]	T_c/K [c]	Me(phosphorus ligand) τ Value [a]	T_c/K [d]	Phenyl groups τ Value [a]
cis-$[Ru(S_2PMe_2)_2(PPh_3)_2]$	$CDCl_3$	319	8·34 (12·0)	256			2·4—3·1
		215	7·73 (12·0), 8·94 (12·0)				
cis-$[Ru(S_2PMe_2)_2(PMePh_2)_2]$	$CDCl_3$	329	8·28 (12·5)	278	8·05 [e] (8·0) [f]		2·4—3·0
		213	7·83 (12·5), 8·61 (12·5)		8·01 [e]		
cis-$[Ru(S_2PMe_2)_2(PMe_2Ph)_2]$	$CDCl_3$	341	8·01 (12·5)	298	8·38 [e] (9·0) [f]	278	2·7—3·1
		232	7·69 (13·0), 8·14 (12·0)		8·30 [e] (9·0) [f], 8·43 [e] (9·0) [f]		
cis-$[Ru(S_2PMe_2)_2(P\{OPh\}_3)_2]$	$CDCl_3$	297	7·95 (12·5), 8·35 (12·5)	330			2·6—3·1
cis-$[Ru(S_2PMe_2)_2(P\{OMe\}_3)_2]$	$CDCl_3$	301	8·03 (12·5)	278	6·27 [e] (10·0) [f]		
		243	7·89 (12·5), 8·08 (12·5)		6·27 [e] (10·0) [f]		
cis-$[Ru(S_2PPh_2)_2(PMePh_2)_2]$	$CDCl_3$	301			8·08 [e] (8·0) [f]		2·2—3·1
cis-$[Ru(S_2PPh_2)_2(PMe_2Ph)_2]$	CH_2Cl_2	301			8·45 [e] (8·0) [f]	273	2·0—3·2
		253			8·41 [e] (8·0), [f] 8·49 [e] (8·0) [f]		
cis-$[Ru(S_2PMe_2)_2(AsPh_3)CO]$	$CDCl_3$	298	7·90 (13·0), 7·96 (13·0), 8·00 (12·5), 9·07 (12·5)	>330			2·4—2·9
cis-$[Ru(S_2PMe_2)_2(PMePh_2)CO]$	$CDCl_3$	301	7·88 (13·0), 7·94 (13·0), 8·05 (13·0), 8·62 (13·0)	>330	7·83 [g] (9·0) [h]		2·2—3·0
cis-$[Ru(S_2PMe_2)_2(PMe_2Ph)CO]$	$CDCl_3$	301	7·83 (13·0), 7·96 (13·0), 8·06 (12·5), 8·33 (12·5)	>330	8·11 [g] (9·5) [h]	263	2·2—2·8
		243	7·80 (13·0), 7·94 (13·0), 8·05 (12·5), 8·35 (12·5)		8·10 [g] (9·5) [h] 8·12 [g] (10·0) [h]		
cis-$[Ru(S_2PMe_2)_2(P\{OPh\}_3)CO]$	$CDCl_3$	301	7·89 (13·0), 7·96 (13·0), 8·09 (13·0), 8·20 (12·5)	>330			2·6—3·0
cis-$[Ru(S_2PMe_2)_2(P\{OMe\}_3)CO]$	$CDCl_3$	301	7·91 [i] (12·5), 8·00 (12·5), 8·10 (13·0)	>330	6·25 [g] (10·5) [h]		
cis-$[Ru(S_2PMe_2)_2(CO)_2]$	$CDCl_3$	301	7·86 (12·5,) 7·99 (12·5)	>330			
cis-$[Ru(S_2PPh_2)_2(PMe_2Ph)CO]$	$(CD_3)_2CO$	>333			8·19 [g] (10·0) [h]	333	2·0—3·0
		301			8·16 [g] (10·0), [h] 8·21 [g] (10·0) [h]		
cis-$[Ru(S_2PMe_2)_2(PPh_3)CO]$	C_6H_5Cl	373	8·21, [j] 8·68 [k]	353 [l]			2·3—2·8
	C_6H_5Cl	301	8·10 [i] (13·0), 8·33 (12·5), 9·26 (12·5)	368 [m]			2·3—2·8
	$CDCl_3$	301	7·94 (13·0), 8·00 (13·0), 8·04 (12·5), 9·04 (12·5)				
cis-$[Ru(S_2PMe_2)_2(PPh_3)(P\{OPh\}_3]$	C_6H_5Cl	363	8·32 [j] (12·5), 8·45 [k] (12·5)	287 [l]			2·2—3·3
	CH_2Cl_2	298	8·28 [n]	313 [m]			
	CH_2Cl_2	233	7·83 (13·0), 8·12 (13·0), 8·45 (12·5), 8·97 (12·5)				
cis-$[Ru(S_2PMe_2)_2(PMe_2Ph)(P\{OPh\}_3)]$	$CDCl_3$	333	8·19 (12·5)	301 [o]	8·05 [g] (9·5) [h]		2·3—3·2
		253	7·86 (8·0), 8·03 (8·0), 8·41 [i] (12·5)		7·99 [g] (8·0) [h]		
cis-$[Ru(S_2PPh_2)_2(PMe_2Ph)(P\{OPh\}_3)]$	$CDCl_3$	301			8·04 [g] (9·0) [h]	268	2·1—3·2
		233			7·99 [g] (9·0), [h] 8·02 [g] (9·0) [h]		
$[Ru(S_2PMe_2)_2(PMe_2Ph)_2CO]$ (configuration C)	$CDCl_3$	301	8·11 (12·5), 8·91 (12·5)		7·86 [p] (8·0), [f] 7·90 [p] (9·0) [f]		2·2—2·8
$[Ru(S_2PMe_2)_2(PMe_2Ph)_2CO]$ (configuration D)	$CDCl_3$	273	7·80 (12·5), 7·87 (12·5) 7·93 (12·5), 8·36 (11·8)		8·24 [g] (8·0), [h] 8·26 [g] (8·0), [h] 8·43 [g] (9·5), [h] 8·48 [g] (10·0) [h]		2·4—3·0
$[Ru(S_2PPh_2)_2(PMe_2Ph)_2CO]$ (configuration C)	$(CD_3)_2CO$	333			8·34 [p] (7·0) [f]	301	1·8—3·0
		273			8·34 [p] (7·0), [f] 8·39 [p] (7·0) [f]		
$[Ru(S_2PPh_2)_2(PMe_2Ph)_2CO]$ (configuration D)	$CDCl_3$	301			8·25 [g] (7·0), [h] 8·33 [g] (9·0) [h] 8·34 [g] (9·0), [h] 8·36 [g] (8·0) [h]		1·8—3·0
cis-$[Ru(S_2CNMe_2)_2(PPh_3)_2],Me_2CO$ [q]	$CDCl_3$	333	7·14 [r]	318			2·3—3·2
		288	7·06, [r] 7·25 [r]				
cis-$[Ru(S_2CNMe_2)_2(PMe_2Ph)_2]$	$CDCl_3$	313	6·76 [r]	303	8·51 [e] (8·0) [f]	253	2·7—3·0
		240	6·67, [r] 6·75 [r]		8·48 [e] (8·0), [f] 8·53 [e] (8·0) [f]		

TABLE 1 (*Continued*)

Complex	Solvent	Temp. (T/K)	Dithioligand (Me groups) τ Value[a] [(JPH)][b]	T_c/K[c]	Me(phosphorus ligand) τ Value[a]	T_c/K[d]	Phenyl groups τ Value[a]
trans-[$Ru(S_2CNMe_2)_2(PMe_2Ph)_2$]	$CDCl_3$	313	7·20[r]		8·27[s]		2·3—3·0
		330	7·10[r]				
cis-[$Ru(S_2CNMe_2)_2(P\{OPh\}_3)_2$]	$CDCl_3$			325			2·7—3·2
		301	7·07,[r] 7·20[r]				
		330	6·94, 7·10, 7·23[v]				
cis-[$Ru(S_2CNMe_2)_2(PPh_3)(P\{OPh\}_3)$]	$CDCl_3$			318[w]			2·0—3·2
		301	6·86,[r] 7·13,[t] 7·37[r]				
cis-[$Ru(S_2CNMe_2)_2(CO)_2$]	$CDCl_3$	298	6·72,[r] 6·75[r]				

[a] ±0·01. [b] Doublet; J(PH) in parentheses (±0·2 Hz). [c] Coalescence temperature of dithioacid methyl resonances. [d] Coalescence temperature of methyl groups attached to phosphorus ligands. [e] $H_nPP'H'_n$ Type spectrum (pseudo-triplet). [f] $|J(PH) + J(PH')|$ In parentheses (±0·2 Hz). [g] Doublet. [h] J(PH) In parentheses (±0·2 Hz). [i] Two doublets superimposed. [j] Doublet from coalescence of inner doublets. [k] Doublet from coalescence of outer doublets. [l] Coalescence temperature for inner doublets. [m] Coalescence temperature for outer doublets. [n] Broadened doublet superimposed on broad signal. [o] Coalescence temperature for doublets at τ 8·03, 8·41 and τ 7·86, 8·41. [p] 'Virtually-coupled' 1,2,1 triplet. [q] Methyl singlet (acetone) at τ 7·86. [r] Singlet. [s] Broad singlet. [t] Two singlets superimposed. [v] Singlet from coalescence of peaks at τ 7·13 and 7·37. [w] Coalescence temperature for resonances at τ 7·13 and 7·37.

For [$Ru(S_2PMe_2)_2(PMe_2Ph)(P\{OPh\}_3)$] the two higher field doublets are superimposed (Table 5). These two resonances presumably arise from the methyl groups *syn* to the phosphine and *syn* to the phosphite ligands (e and f respectively—Figure 3a). In this instance, although the PMe_2Ph group has fewer phenyl rings than $P(OPh)_3$, those on the phosphite are further removed from the methyl group f by the presence of the oxygen atoms, thus producing similar shielding effects and hence identical chemical shifts for e and f. This conclusion is supported, in part, by the observation that the chemical shifts of the methyl groups (c) in the bis-PMe_2Ph and bis-$P(OPh)_3$ complexes are fairly close, being τ 8·14 and 8·35 respectively.

For [$Ru(S_2PMe_2)_2(P\{OMe\}_3)CO$], the two lower field doublets are superimposed (*i.e.* g and h in Figure 3b). This is not unexpected since the chemical shifts of the low field doublets in the bis-$P(OMe)_3$ and bis-carbonyl compounds occur at τ 7·89 and 7·86 respectively (Table 5). In support of this interpretation, heteronuclear phosphorus–hydrogen spin decoupling experiments confirm that the two methyl groups attached to different phosphorus atoms are accidently superimposed.

The methyl resonances of the dithio-ligands of the *cis*-[$Ru(S_2PMe_2)_2L(CO)$] and *cis*-[$Ru(S_2PMe_2)_2(CO)_2$] complexes, are temperature invariant up to *ca.* 330 K (although measurements on *cis*-[$Ru(S_2PMe_2)_2(PPh_3)(CO)$] at higher temperatures in chlorobenzene indicate similar behaviour to that described below for [$Ru(S_2PMe_2)_2(PPh_3)(P\{OPh\}_3)$]. However, those of the [$Ru(S_2PMe_2)_2LL'$] compounds show marked changes at lower temperatures. For example, on warming [$Ru(S_2PMe_2)_2(PPh_3)(P\{OPh\}_3)$], the four methyl doublets present at low temperature (Figure 4a) begin to broaden, the inner two coalescing at *ca.* 280 K (Figure 4b) and the outer two continuing to broaden until at 320 K the spectrum consists of a slightly broadened doublet superimposed on a broad signal which represents the coalesced peak of the outer doublets (Figure 4c). At even higher temperatures (in chlorobenzene), the spectrum consists of two doublets situated halfway between the original inner and outer doublet positions respectively (Figure 4d) (Table 5). This behaviour is attributed to the facile interconversion of optical isomers at higher temperatures, the different coalescence temperatures for the two pairs of doublets being due to their different separations.

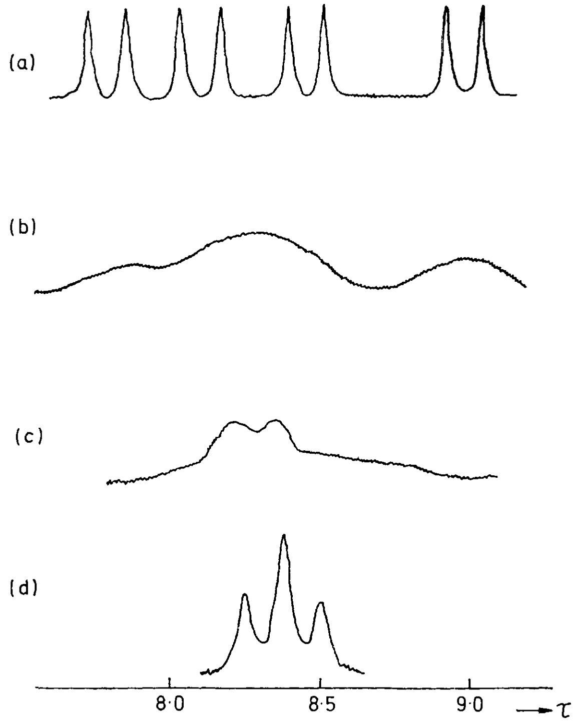

FIGURE 4 Variable temperature ^1H n.m.r. spectrum of [$Ru(S_2PMe_2)_2(PPh_3)(P\{OPh\}_3)$]: (a), 233 K in CH_2Cl_2; (b), 283 K in CH_2Cl_2; (c), 310 K in CH_2Cl_2; (d), 363 K in C_6H_5Cl

At this juncture, it is of interest to consider which resonances in the low temperature spectrum of this compound correspond to which methyl groups of the complex because such information will be important when the detailed mechanism of the inversion process is considered. According to the theory propounded earlier in which the ring currents of the phenyl rings on L (or L') shield the methyl groups nearest to them, the methyl resonances of [$Ru(S_2PMe_2)_2(PPh_3)(P\{OPh\}_3)$] are assigned as h, g, f, and e respectively (Figure 3c) in ascending order of chemical shift (Figure 4a). This is based on the fact that methyl groups e and g are closer to the PPh_3 group (which has the greater shielding effect) than are f and h. These conclusions are supported by the fact that irradiating the phosphorus spectrum at 40 481 983 Hz collapses the doublets labelled e and g whereas irradiation at 40 482 100 Hz decouples f and h. This confirms that the methyl groups giving rise to resonances e and g are attached to the same phosphorus atom whereas those giving rise to resonances f and h are attached to the other phosphorus atom. Thus at higher temperature, the chemical environments of groups h,e and of g,f are interchanged but there is no exchange between any of the other environments.* A possible interpretation of these observations is presented in Part VI.

(iii) *Complexes of formula* $[Ru(S_2CNMe_2)_2L_2]$. It was reported earlier [9] that the ^1H n.m.r. spectrum of $[Ru(S_2CNMe_2)_2(PPh_3)_2],Me_2CO$ shows $^-S_2CNMe_2$ methyl resonances at τ 7·18 and 7·30 (with an intensity ratio of 1 : 2). The authors concluded that the structure was *trans*, attributing the methyl group splitting to different orientations of the methyl groups, which they suggested is probably caused by steric effects emanating from the bulky PPh_3 groups. However, on repeating this experiment (in both cold and refluxing acetone), we have obtained a crystalline yellow solid, analysing for $[Ru(S_2CNMe_2)_2(PPh_3)_2],Me_2CO$, whose n.m.r. spectrum contains two methyl resonances of the *same* intensity at τ 7·06 and 7·25; there is also a peak at τ 7·86 (acetone). This spectrum is consistent with a *cis*-configuration. Similarly, for $[Ru(S_2CNMe_2)_2(PMe_2Ph)_2]$, prepared from *mer*-$[RuCl_3(PMe_2Ph)_3]$, the low temperature ^1H n.m.r. spectrum consists of two pseudo-triplets (PMe_2Ph groups) and two singlets ($^-S_2CNMe_2$ groups) which is indicative of a *cis*-configuration. At higher temperatures, coalescence to a single pseudo-triplet occurs at *ca.* 250 K and the methyl doublet coalesces to a singlet at *ca.* 300 K. A similar behaviour is observed at 318 K for the bis-PPh_3 complex (Table 5). For these compounds, coalescence of the pseudo-triplets is again attributed to the onset of free rotation around the Ru–P bonds. However, the process equilibrating the methyl groups at higher temperatures is probably due to facile –CN bond rotation rather than inversion of optical isomers. This conclusion is based on the results of a kinetic line shape analysis on the compound $[Ru(S_2CNMe_2)_2(PPh_3)(P\{OPh\}_3)]$ which reveals different activation parameters for the rates of exchange of the two sets of methyl groups. This is discussed in more detail in Part VI.

Finally, the reaction of *cis*-$[Ru(S_2CNMe_2)_2(PPh_3)_2]$ with an excess of PMe_2Ph in ethanol gives two products which both analyse for $[Ru(S_2CNMe_2)_2(PMe_2Ph)_2]$. The ^1H n.m.r. spectrum of the more soluble species (71% yield) is identical to that obtained from *mer*-$[RuCl_3(PMe_2Ph)_3]$ and NaS_2CNMe_2 (*i.e.* the *cis* isomer). However, the ^1H n.m.r. spectrum of the minor product (21%), which is temperature invariant up to 315 K, has a single sharp peak at τ 7·20 ($^-S_2CNMe_2$ groups) and a broader peak of the same intensity at τ 8·27 (PMe_2Ph groups), indicative of a *trans* configuration. On further heating, this compound rearranges irreversibly to the *cis* isomer. Therefore, in this instance, there is evidence for the irreversible *trans* $\longrightarrow$ *cis* isomerism found elsewhere,[16,34] and on this evidence, it is also possible to interpret the ^1H n.m.r. spectrum of $[Ru(S_2CNMe_2)_2(PPh_3)_2]$ observed earlier [9] as a 50 : 50 *cis–trans* mixture of isomers with the *trans* methyl resonance accidentally superimposed on one of the *cis* methyl resonances.

Mechanism of Carbonylation of cis-$[Ru(S_2PR_2)_2(PMe_2Ph)_2]$.—When *cis*-$[Ru(S_2PR_2)_2(PMe_2Ph)_2]$ (A) (R = Me, Ph) is carbonylated in refluxing ethanol or acetone for a prolonged period, a mixture of *cis*-$[Ru(S_2PR_2)_2(PMe_2Ph)CO]$ (B) and $[Ru(S_2PR_2)_2(PMe_2Ph)_2CO]$ (C) is always formed although these can be separated by dry column chromatography. However, when C is redissolved, partial rearrangement to B slowly occurs whereas if the reaction of A and CO is carried out in the presence of an excess of sulphur, only B is formed. Conversely, reaction of A and CO in the presence of an excess of PMe_2Ph gives pure C. In addition, another complex of formula $[Ru(S_2PR_2)_2(PMe_2Ph)_2CO]$ (D) may be isolated if the carbonylation reaction is carried out in the cold for a very short time (*ca.* one minute). In solution, D slowly and irreversibly gives first B and then some of C. This process can be monitored by both ^1H n.m.r. (since all the compounds have different spectra) or by observing the change in ν(CO) position since for R = Ph: ν(CO)(D) = 1984; ν(CO)(B) = 1948; ν(CO)(C) = 1946 cm^{-1} (all measured in $CDCl_3$). Measurement of the rate of loss of the carbonyl band intensity for D gives a rate constant for this rearrangement reaction of $1{\cdot}7 \times 10^{-4}\ s^{-1}$ at 323 K ($t_{\frac{1}{2}}$ = 65 min) and also confirms that the process is first order with respect to D.

Thus, these observations are consistent with the carbonylation mechanism shown below: *viz.* facile formation of D followed by a slower conversion to B which then undergoes a partial reversible rearrangement to C. It now only remains to determine the structures of C and D in order to establish the stereochemical pathway of the mechanism.

Assuming that ruthenium(II) retains its usual six-co-ordinate stereochemistry,† and we therefore have unidentate and bidentate $^-S_2PR_2$ groups,‡ there are four possible isomers for compounds of formula $[Ru(S_2PR_2)_2(PMe_2Ph)_2CO]$ (Figure 5). For R = Me, the

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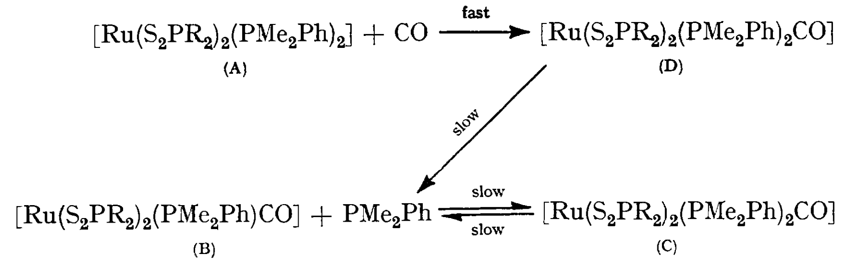
* *Note added in proof:* In support of this conclusion, homonuclear double resonance experiments (S. Forsen and R. A. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 2892) confirm that exchange only occurs between groups h, e and g, f respectively.

† A reasonable assumption since to our knowledge only one ruthenium(II) seven-co-ordinate compound has been claimed, *i.e.* $[RuCl_2(CO)_2(MeC\{SEt\}_3)]$.[36]

‡ This is suggested by the i.r. spectra of C and D (see earlier) (*cf.* $[Ru(NO)(S_2CNR_2)_3]$ [12]).

[36] J. Chatt, G. J. Leigh, and A. P. Storace, *J. Chem. Soc.* (*A*), 1971, 1380.



room temperature ^{1}H n.m.r. spectrum of C consists of two doublets (from the $^-S_2PMe_2$ groups) and a 1,3,3,1 quartet for the PMe_2Ph groups (*i.e.* two overlapping 1,2,1 ' virtually-coupled ' triplets as is seen for R = Ph) (Table 5). At higher temperatures, these collapse to a single triplet although a detailed observation of this process is obscured (for R = Me) by the increased tendency to rearrange to compound B at these higher temperatures. In contrast, the two $^-S_2PMe_2$ doublets are almost temperature invariant, except for a slight broadening at *ca.* 330 K which again is obscured because of the facile rearrangement to B at this temperature. Examination of Figure 5 reveals that this n.m.r. spectrum corresponds to that expected for structure (I) *i.e.* *trans* PMe_2Ph groups with slow exchange of uni/bidentate $^-S_2PR_2$ groups. Assignment of this structure to C would also account for the similarity in the position of ν(CO) to that observed for B (Table 2) since in each case the carbonyl group is situated *trans* to a sulphur atom of a bidentate dithioacid ligand.*

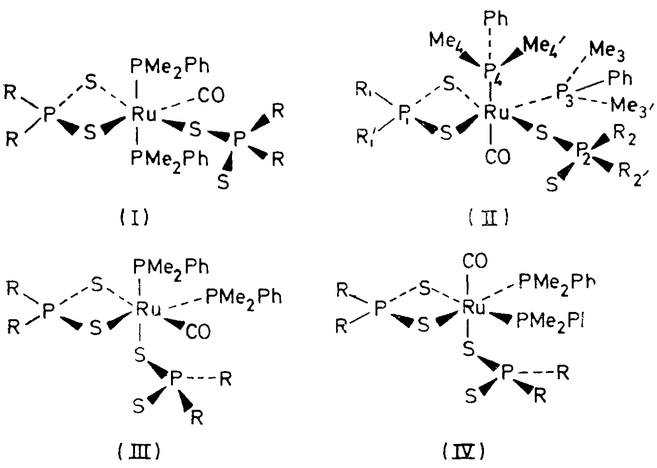


FIGURE 5 Possible isomeric forms for $[Ru(S_2PR_2)_2(PMe_2Ph)_2CO]$ assuming bidentate and unidentate $^-S_2PR_2$ co-ordination

The ^{1}H n.m.r. spectrum of D (R = Me), which is temperature invariant from 220 to 320 K (although over longer periods, it slowly converts to a mixture of B and C) consists of fourteen lines (Figure 6). By means of heteronuclear spin decoupling experiments it can be shown that the four phosphorus atoms in the molecule are all in inequivalent chemical environments and this is confirmed by measuring the proton noise decoupled ^{31}P n.m.r. spectrum of the complex (Figure 7). The decoupling studies (see Figure 6) also indicate that the 14 line ^{1}H n.m.r. spectrum is comprised of 8 doublets (with four of the doublets partially superimposed). [NB: The irradiation frequencies given in Figure 6 are different from the frequencies of the phosphorus nuclei obtained from the Fourier transform spectrum (Figure 7) because the former are obtained from the HA 100 spectrometer (with Schlumberger FS30 frequency synthesiser attachment) whereas the

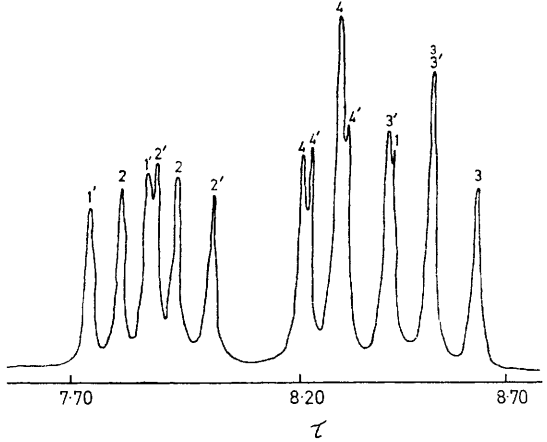


FIGURE 6 ^{1}H N.m.r. spectrum of $[Ru(S_2PMe_2)_2(PMe_2Ph)_2CO]$ (D) [methyl region] at 273 K; irradiating at 40 482 120 Hz decouples 1 and 1′, at 40 480 770 Hz decouples 2 and 2′, at 40 478 777 Hz decouples 3 and 3′, and at 40 477 700 Hz decouples 4 and 4′ (*note* Assignments of 2 and 2′, 3 and 3′, 4 and 4′ are arbitrary.)

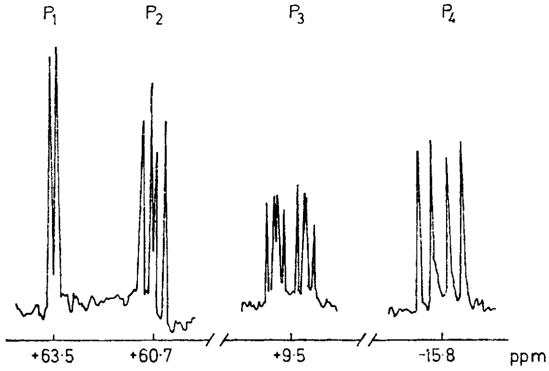


FIGURE 7 ^{31}P N.m.r. spectrum of $[Ru(S_2PMe_2)_2(PMe_2Ph)_2CO]$ (D) gives $J(P_1P_2)$ 0·0; $J(P_1P_3)$ 7·6; $J(P_1P_4)$ 0·0 ; $J(P_2P_3)$ 10·0; $J(P_2P_4)$ 14·9; $J(P_3P_4)$ 32·5 Hz. Chemical shifts are in p.p.m. to high frequency of 85% H_3PO_4, *cf.* $[Ru(S_2PMe_2)_2(CO)_2]$ + 92·6, $[Ru(S_2PMe_2)_2(PMe_2Ph)_2]$ + 88·1 and +21·4

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* A recent note (S. D. Robinson and M. F. Uttley, *Chem. Comm.*, 1972, 1047) reports the synthesis of the analogous $[Ru(OCOMe)_2(PPh_3)_2CO]$ compound with uni/bidentate acetato-groups but the detailed stereochemistry is not given. *Added in proof:* In the full paper (*J.C.S. Dalton*, 1973, 1912) the analogous carboxylato-complex is arbitrarily assigned a structure of type (I).

latter are directly measured on the XL 100 machine and these have slightly different reference frequencies.] Thus, all the methyl groups are in inequivalent chemical environments, and there is restricted rotation (even at 320 K) about the Ru–P bonds. This n.m.r. evidence is, in fact, compatible with a seven-co-ordinate complex with only bidentate dithioacid groups. However, addition of methyl iodide to a dichloromethane solution of D produces an immediate increase in conductivity. A similar increase is observed for $[Pt(S_2PMe_2)_2(PMe_2Ph)]$ (where uni/bidentate co-ordination is well established) and compound C, but with $[Pt(S_2PMe_2)_2]$ and $[Ru(S_2PMe_2)_2(PMe_2Ph)_2]$ there is no change. This conductivity increase is attributed to the formation of the complex $[Ru(S_2PMe_2)(MeS_2PMe_2)(PMe_2Ph)_2CO]I$ by methylation of the unco-ordinated sulphur atom. Furthermore, the ^1H n.m.r. spectrum of the conducting solution is not significantly different from that of D, except for extra signals at τ 6·96 (–SMe group) and τ 7·93 (excess of MeI) which strongly suggests that MeI is not reacting with a bound sulphur atom of a labile seven-co-ordinate species.

Examination of Figure 5 indicates that neither structure (I) (already assigned to C) nor structure (IV) (which has a plane of symmetry making the PMe_2Ph groups equivalent) fit the ^1H and ^{31}P n.m.r. data. However, (II) and (III) are both possible structures since in both cases hindered rotation about the ruthenium–phosphorus bonds is reasonable on steric grounds and furthermore the ruthenium atom is potentially a chiral centre and thus, no matter how rapid the rotation about the Ru–S bond of the unidentate $^-S_2PMe_2$ ligand, the two Me groups will always remain inequivalent. However, (III) would be expected to have a ν(CO) band in a similar position to that found in compounds B and C since the CO group is *trans* to a sulphur atom of a bidentate $^-S_2PR_2$ ligand whereas (II) should have a higher ν(CO) since the CO group is *trans* to a stronger π-acceptor ligand and hence back donation into the π^* orbitals of the CO group will be reduced. The latter is experimentally the case (Table 2) and hence structure (II) is preferred.

The heteronuclear decoupling information given in Figure 6 determines which sets of methyl protons in D are attached to phosphorus atoms 1—4 [which are labelled in the order they occur in the ^{31}P n.m.r. spectrum (Figure 7)]. Assuming structure (II) is more feasible than (III), then these phosphorus atoms can be assigned as follows: P_1 and P_2 belong to the $^-S_2PMe_2$ groups and P_3 and P_4 to the PMe_2Ph groups. This assignment is based on the chemical shift positions of the ^{31}P nuclei compared to those in $[Ru(S_2PMe_2)_2(CO)_2]$ and $[Ru(S_2PMe_2)_2(PMe_2Ph)_2]$ (see Figure 7) together with the fact that the lower field methyl doublets (which correspond to the $^-S_2PMe_2$ methyl resonances) are decoupled by irradiating at frequencies corresponding to phosphorus atoms P_1 and P_2. In $[Ru(S_2PMe_2)_2(PMe_2Ph)CO]$, the separation between the methyl dithioacid group *syn* to PMe_2Ph and that *syn* to CO is 33 Hz, which is close in value to the separation of the methyl groups 1 and 1′ attached to P_1 (44 Hz). In contrast, those attached to P_2 (2 and 2′) are only separated by 6 Hz. We therefore assign P_1 to the phosphorus atom of the bidentate $^-S_2PMe_2$ group and P_2 to the unidentate $^-S_2PMe_2$ group. Finally, since P_3 couples to P_1 whereas P_4 does not (Figure 7) it seems likely that P_3 is more nearly *trans* to P_1 than is P_4 and therefore P_3 and P_4 are assigned accordingly [see Figure 5, structure (II)].

The stereochemical pathway of the carbonylation mechanism is given in Figure 8. Thus, D is formed by cleavage of the weakest Ru–S bond *i.e.* that *trans* to a PMe_2Ph group. This is consistent with the bond lengths found in *cis*-$[Ru(S_2PEt_2)_2(PMe_2Ph)_2]$,[4b] where the Ru–S bonds *trans* to the PMe_2Ph groups are *ca.* 0·2 Å longer than those *trans* to another sulphur atom. This, incidentally, is another reason why structure (II) rather than (III) is preferred for D since to form the latter the Ru–S bond *trans* to a sulphur atom must be broken. Next, the combination of two high *trans* effect ligands such as CO and PMe_2Ph situated *trans* to each other, together with the favourable energy change associated with the conversion of unidentate to bidentate $^-S_2PMe_2$ co-ordination, results in the expulsion of a PMe_2Ph group and the formation of B. Finally, the high affinity of PMe_2Ph for ruthenium(II)[26] is demonstrated by its attack on the Ru–S bond *trans* to PMe_2Ph to give C. As was inferred earlier for the ligand exchange reactions of $[Ru(S_2PR_2)_2L_2]$ compounds, these favourable electronic changes are reinforced by favourable steric changes on progressing from A to D to B to C. The inability of *cis*-$[Ru(S_2PR_2)_2(PMe_2Ph)CO]$ to give *cis*-$[Ru(S_2PR_2)_2(CO)_2]$ is presumably a reflection

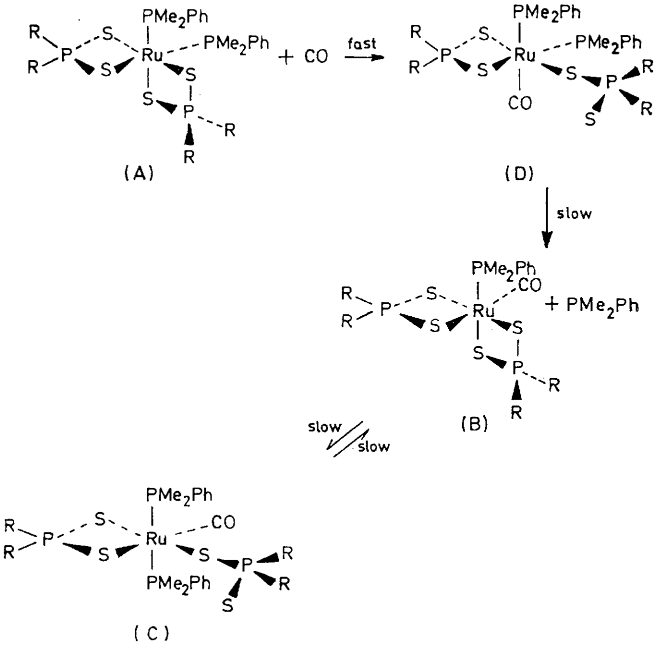

FIGURE 8 Proposed mechanism of carbonylation for $[Ru(S_2PMe_2)_2(PMe_2Ph)_2]$

of the fact that the favourable steric change is more than offset by the unfavourable electronic change of replacing a $Ru{-}PMe_2Ph$ bond with a $Ru{-}CO$ bond. This rationale is supported by the fact that *cis*-$[Ru(S_2PMe_2)_2(CO)_2]$ reacts with an excess of PMe_2Ph, even in the presence of CO, to give C and with an excess of PPh_3 to give *cis*-$[Ru(S_2PMe_2)_2(PPh_3)CO]$. The failure to observe compounds of type C or D with ligands other than PMe_2Ph * is probably due to the smaller *trans* effects (tertiary phosphites) and nucleophilicities (tertiary phosphines) towards ruthenium(II) of these other ligands compared to PMe_2Ph,[26] although, doubtless, a similar mechanism of carbonylation is applicable. It is also reasonable to postulate a similar mechanistic scheme for formation of the mixed ligand species $[Ru(S_2PR_2)_2LL']$ although, again, no intermediates of type D (or C) have been observed.

Finally, the unsuccessful attempts to carbonylate the *cis*-$[Ru(S_2CNR_2)_2L_2]$ complexes are probably due to the stronger nucleophilicity of $^-S_2CNR_2$ compared to $^-S_2PR_2$ (see reference 1), preventing formation of a compound of type D.

EXPERIMENTAL

Microanalyses were by the National Physical Laboratory, Teddington, A. Bernhardt, West Germany, and the University of Edinburgh Chemistry Department. Molecular weights were determined on a Perkin-Elmer–Hitachi 115 osmometer at 37°. I.r. spectra were recorded in the region 4000—250 cm^{-1} on a Perkin-Elmer 457 grating spectrometer using Nujol mulls on caesium iodide plates. Solution spectra were run in potassium bromide cells. Mass spectra were obtained on an A.E.I. MS9 spectrometer and conductivity measurements on a Portland electronics 310 conductivity bridge. ^1H N.m.r. spectra and solution magnetic moments (Evans' method) [23] were obtained on a Varian Associates HA 100 spectrometer and ^{31}P n.m.r. spectra on a Varian XL 100 spectrometer operating in the Pulse and Fourier Transform mode at 40·5 MHz. Heteronuclear decoupling experiments were carried out on the HA 100 spectrometer using a second radio frequency field provided by the Schlumberger FS 30 frequency synthesiser. M.p.s were determined with a Kofler hot-stage microscope and are uncorrected.

Materials.—Ruthenium trichloride trihydrate (Johnson Matthey); triphenylphosphine, dimethylphenylphosphine; triphenyl phosphite (B.D.H.); methyldiphenylphosphine (Strem); $PEtPh_2$ was made by a standard literature method; carbon monoxide (Air products); NaS_2CNMe_2, $2H_2O$ (Ralph Emanuel). Sodium diethyl- and dimethyl-phosphinodithioates were prepared as described earlier [37,38] and ammonium diphenylphosphinodithioate from Ph_2PS_2H and ammonia in benzene.[38] Operations involving free tertiary phosphines and phosphites [with the exception of $P(OPh)_3$ and PPh_3] were carried out under nitrogen.

The various ruthenium(II) and (III) tertiary phosphine and phosphite complexes which were used as starting materials were synthesised by published methods.

cis-*Bis(diphenylphosphinodithioato)bis(triphenylphosphine)ruthenium*(II).—$[RuCl_2(PPh_3)_3]$ (0·10 g), $NH_4S_2PPh_2$ (0·20 g), and PPh_3 (0·20 g) were shaken in acetone (25 ml) for 30 min and then the resulting red *crystals* filtered off, washed with water, acetone and n-pentane (yield: 0·10 g, 85%). However, if the reaction was carried out in the absence of an excess of PPh_3, the resulting red crystalline precipitate gave a consistently low analysis for the bis-phosphine complex [Found: C, 60·1; H, 4·2. $[Ru(S_2PPh_2)_2(PPh_3)_2]$ requires C, 64·1; H, 4·5% and *bis(diphenylphosphinodithioato)(triphenylphosphine)ruthenium*(II), 0·5 *acetone* requires C, 58·6; H, 4·3%]. Furthermore, the molecular weight of the product in benzene, over a short period of time, decreased from 697 to 649, values indicative of the facile dissociation of $[Ru(S_2PPh_2)_2(PPh_3)_2]$ (*M*, 1123) to $[Ru(S_2PPh_2)_2PPh_3]$ (*M*, 861) and free PPh_3 in solution. However, by refluxing a mixture of $[RuCl_2(PPh_3)_3]$ (0·10 g), $NH_4S_2PPh_2$ (0·12 g), and sulphur (0·003 g) in acetone, a pure sample of $[Ru(S_2PPh_2)_2PPh_3]$ (0·06 g, 72%) was isolated [Found: C, 58·1; H, 4·1%].

cis-*Bis(dimethylphosphinodithioato)bis(triphenylphosphine)ruthenium*(II).—$[RuCl_3(PPh_3)_2MeNO_2]$ (0·04 g), NaS_2PMe_2 (0·04 g), and PPh_3 (0·04 g) were shaken overnight in ethanol (10 ml). The resultant brown crystalline precipitate was filtered off, washed with water, ethanol, and n-pentane to give red-brown needles of the *complex* (0·04 g, 90%). The same compound was also prepared from $[RuCl_2(PPh_3)_3]$ (0·25 g) and NaS_2PMe_2 (0·15 g) in acetone solution (0·21 g, 92%). Similarly, cis-*bis(diethylphosphinodithioato)bis(triphenylphosphine)ruthenium*(II) was prepared from $[RuCl_2(PPh_3)_3]$ (0·25 g) and NaS_2PEt_2 (0·12 g).

cis-*Bis(dimethylphosphinodithioato)bis(ethyldiphenylphosphine)ruthenium*(II).—$[RuCl_2(PEtPh_2)_3]$ [18a] was shaken in ethanol for 12 h with a three-fold excess of NaS_2PMe_2 to give the orange crystalline *complex* (73%).

The compounds tabulated below were prepared by the following general method. The starting materials were refluxed in ethanol for the time shown and then the solution cooled and filtered. The crystals obtained were washed with water, ethanol, n-pentane and dried *in vacuo* (40°).

If $[Ru_2Cl_3(PMePh_2)_6]$ Cl (0·60 g) and NaS_2PMe_2 (0·30 g) are refluxed in methanol (15 ml) for 24 h, an orange crystalline solid is precipitated. Dissolution in a minimum volume of benzene and chromatography on a dry alumina column [22] gives an orange and a red band. The orange band was extracted with diethyl ether, evaporated to dryness, and recrystallised from CH_2Cl_2–n-pentane giving *cis*-$[Ru(S_2PMe_2)_2(PMePh_2)_2]$ (0·10 g, 20%). The red band was also eluted with diethyl ether, evaporated to dryness, and recrystallised from CH_2Cl_2–pentane to give $[Ru_2Cl_3(PMePh_2)_5S_2PMe_2]$ (0·07 g, 11%) (Found: C, 56·1; H, 5·0. Required C, 56·1; H, 5·0%). cis-*Bis(dimethylphosphinodithioato)bis(methyldiphenylphosphine)ruthenium*(II) may also be prepared by the reaction of *cis*-$[Ru(S_2PMe_2)_2(PPh_3)_2]$ (0·05g) with $PMePh_2$ (0·10 ml) in refluxing ethanol (15 ml) for 12 h. Cooling the solution gives orange crystals of the *complex* (0·03 g; 70%). cis-*Bis(dimethylphosphinodithioato)bis(dimethylphenylphosphine)ruthenium*(II) may be prepared in two other ways: (a) *cis*-$[Ru(S_2PMe_2)_2(PMePh_2)_2]$ (0·05 g) and PMe_2Ph (0·05 ml) were refluxed in ethanol (20 ml) for 4 h. Cooling the solution and partial

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* The one possible exception is with $[Ru(S_2PMe_2)_2(P\{OMe\}_3)_2]$ where carbonylation gives a transient species with $\nu(CO)$ 1997 cm^{-1} (type D!) but unfortunately this could not be separated from starting material.

[37] W. Kuchen, W. Strolenberg, and J. Metten, *Chem. Ber.*, 1963, **96**, 1733.

[38] R. G. Cavell, W. Byers, and E. D. Day, *Inorg. Chem.*, 1971, **10**, 2710.

Starting materials	Volume of EtOH	Reaction time	Yield	Product
mer-$[RuCl_3(PMePh_2)_3]$ (0·20 g) and $NH_4S_2PPh_2$ (0·25 g)	50 ml	4 h	0·14 g (56%)	*cis*-$[Ru(S_2PPh_2)_2(PMePh_2)_2]$
$[Ru_2Cl_3(PMePh_2)_6]Cl$ (0·08 g) and NaS_2PMe_2 (0·10 g)	20 ml	1 h	0·05 g (62%)	*cis*-$[Ru(S_2PMe_2)_2(PMePh_2)_2]$
mer-$[RuCl_3(PMe_2Ph)_3]$ (0·5 g) and $NH_4S_2PPh_2$ (1·0 g)	70 ml	3 h	0·70 g (100%)	*cis*-$[Ru(S_2PPh_2)_2(PMe_2Ph)_2]$
mer-$[RuCl_3(PMe_2Ph)_3]$ (0·70 g) and NaS_2PMe_2 (0·70 g)	70 ml	15 m	0·70 g (100%)	*cis*-$[Ru(S_2PMe_2)_2(PMe_2Ph)_2]$
$[RuCl_2(P\{OPh\}_3)_4]$ (0·80 g) and NaS_2PMe_2 (0·60 g)	20 ml	1 h	0·25 g (46%)	*cis*-$[Ru(S_2PMe_2)_2(P\{OPh\}_3)_2]$
mer-$[RuCl_3(PMe_2Ph)_3]$ (0·50 g) and NaS_2PEt_2 (0·90 g)	25 ml	3 h	0·39 g (71%)	*cis*-$[Ru(S_2PEt_2)_2(PMe_2Ph)_2]$

removal of solvent gave orange crystals of the *complex* which were filtered off, washed with n-pentane, and dried *in vacuo* (0·02 g; 48%); (b) *cis*-$[Ru(S_2PMe_2)_2(PPh_3)_2]$ (0·10 g) and PMe_2Ph (0·03 ml) were refluxed in acetone for 1 h. Removal of the solvent gave an orange oil from which the *product* was obtained by recrystallisation from CH_2Cl_2–n-pentane (0·05 g; 70%).

Reaction of $[RuCl_2(P\{OPh\}_3)_4]$ (0·60 g) and NaS_2PMe_2 (0·48 g) in ethanol (25 ml) under reflux for 5 h gave a yellow solution. The solution was filtered hot, concentrated, and allowed to crystallise overnight to give a yellow *solid*. Mass spectrum: *m/e* 876, (^{102}Ru isotope) $[Ru(S_2PMe_2)_2(P\{OPh\}_2OEt)_2]^+$; 828, $[Ru(S_2PMe_2)_2(P\{OPh\}_2OEt)(P\{OPh\}(OEt)_2]^+$; 780, $[Ru(S_2PMe_2)_2(P\{OEt\}_2OPh)_2]^+$ *etc.* ^{1}H N.m.r. spectrum (223 K): $[Ru(S_2PMe_2)_2(P\{OPh\}_2OEt)_2]$, τ 7·89 (12·5); 8·20 (12·5) $[^-S_2PMe_2]$; τ 6·08; 8·97 (6·0) [Et groups]; $[Ru(S_2PMe_2)_2(POPh\{OEt\}_2)_2]$, τ 7·91, 8·13 ($^-S_2PMe_2$); τ 5·93; 8·80 (6·0) [Et groups] intensity ratio 6 : 1 (Found: C, 42·9; H, 4·9. $[Ru(S_2PMe_2)_2(P\{OPh\}_2OEt)_2]$ requires C, 43·9; H, 4·8. $[Ru(S_2PMe_2)_2(POPh\{OEt\}_2)_2$ requires C, 37·0; H, 5·4. For 6 : 1 ratio, calculated analysis is C, 42·9; H, 4·9%).

Reactions of $[RuCl_2(P\{OPh\}_3)_4]$ with NaS_2PMe_2 in refluxing ethanol for 24 h gives, on solvent removal, an oil with mass spectral peaks *m/e* 828, $[Ru(S_2PMe_2)_2(P\{OPh\}_2OEt)_2]^+$; 780, $[Ru(S_2PMe_2)_2(P\{OEt\}_2OPh)_2]^+$; 732, $[Ru(S_2PMe_2)_2(P\{OEt\}_2OPh)(P\{OEt\}_3)]^+$; 684, $[Ru(S_2PMe_2)_2(P\{OEt\}_3)_2]^+$ *etc.* cis-*Bis*(*dimethylphosphinodithioato*)*bis*(*trimethyl phosphite*)*ruthenium*(II): $[RuCl_2(P\{OPh\}_3)_4]$ (0·50 g) and NaS_2PMe_2 (0·30 g) were refluxed in methanol (30 ml) for 3 h. The resultant yellow solution was filtered hot, and, after concentration, allowed to slowly crystallise at 273 K for 10 days. The orange *crystals* so formed were filtered and washed with water, methanol, and n-pentane (0·06 g; 28%). On further solvent removal from the filtrate, an oily white solid was deposited which on recrystallisation was identified as phenol (by its ^{1}H n.m.r. spectrum). The ruthenium complex rapidly decomposed on air exposure to give a black solid.

cis-*Bis*(*dimethylphosphinodithioato*)(*triphenylphosphine*)(*triphenyl phosphite*)*ruthenium*(II).—*cis*-$[Ru(S_2PMe_2)_2(PPh_3)_2]$ (0·08 g) and $P(OPh)_3$ (0·05 ml) were refluxed in ethanol (15 ml) for 3 h. The solution was cooled and the precipitated orange *solid* was washed with ethanol and n-pentane (yield, 0·03 g, 35%). The yellow filtrate was allowed to crystallise overnight to give a sample of *cis*-$[Ru(S_2PMe_2)_2(P\{OPh\}_3)_2]$ (0·04 g, 45%).

cis-*Bis*(*dimethylphosphinodithioato*)(*dimethylphenylphosphine*)(*triphenyl phosphite*)*ruthenium*(II).—*cis*-$[Ru(S_2PMe_2)_2(PMe_2Ph)_2]$ (0·20 g) was refluxed with $P(OPh)_3$ (1·2 ml) in ethanol for 1 h. Then, after concentration and standing for two days at 273 K, orange *crystals* were deposited which were filtered off and washed with ethanol and n-pentane (0·10 g; 39%).

cis-*Bis*(*diphenylphosphinodithioato*)(*dimethylphenylphosphine*)(*triphenyl phosphite*)*ruthenium*(II).—*cis*-$[Ru(S_2PPh_2)_2(PMe_2Ph)_2]$ (0·20 g) and $P(OPh)_3$ (0·3 ml) were shaken in dichloromethane (20 ml) for 7 days. After filtration and addition of n-pentane, the resultant orange solution was concentrated until orange *crystals* were deposited. These were filtered off and washed with n-pentane (0·07 g, 29%).

cis-*Bis*(*dimethylphosphinodithioato*)*carbonyl*(*triphenylphosphine*)*ruthenium*(II).—(a) *cis*-$[Ru(S_2PMe_2)_2(PPh_3)_2]$ (0·10 g) and PPh_3 (0·40 g) were carbonylated in refluxing ethanol for two hours. The resulting orange solution was evaporated to dryness and the residue recrystallised from CH_2Cl_2–light petroleum (b.p. 60—80°) to give orange crystals of the *complex* (0·03 g, 41%).

(b) *cis*-$[Ru(S_2PMe_2)_2(CO)_2]$ (0·02 g) and PPh_3 (0·04 g) were refluxed in ethanol (25 ml) for two hours. Removal of solvent gave an orange oil which was redissolved in diethyl ether and after leaving at 273 K for 12 h, orange crystals of the *product* were deposited (0·03 g, 92%).

(c) *cis*-$[RuCl_2(CO)_2(PPh_3)_2]$ (0·13 g) and NaS_2PMe_2 (0·26 g) were refluxed in acetone (20 ml) for 60 h. The resultant solution was filtered, evaporated to dryness, and then chromatographed on a dry silica column,[22] using benzene as eluant. One orange band was observed and the central portion of this band was extracted with diethyl ether. The resulting yellow solution was evaporated to dryness and the residue recrystallised from CH_2Cl_2–n-pentane to give orange crystals of the *complex* (0·08 g, 73%).

cis-*Bis*(*dimethylphosphinodithioato*)*carbonyl*(*triphenylarsine*)*ruthenium*(II).—*cis*-$[RuCl_2(CO)_2(AsPh_3)_2]$ (0·06 g) and NaS_2PMe_2 (0·09 g) were refluxed in acetone (25 ml) for 4 days with no apparent reaction. The mixture was then shaken for 3 weeks to give an orange solid and a white precipitate. After filtration, the solution was evaporated to dryness and the resulting orange oil chromatographed on a dry alumina column [22] using benzene as eluant and washing off the orange band with diethyl ether. Evaporation of the ether solution and recrystallisation from CH_2Cl_2–n-pentane gave the orange *complex* (0·03 g, 61%).

cis-*Bis*(*dimethylphosphinodithioato*)*carbonyl*(*methyldiphenylphosphine*)*ruthenium*(II).— *cis*-$[Ru(S_2PMe_2)_2(PMePh_2)_2]$ (0·10 g) was carbonylated in cold CH_2Cl_2 for one minute. The yellow-orange solution was evaporated to dryness and the product recrystallised from CH_2Cl_2–n-pentane to give the orange crystalline *complex* (0·03 g, 37%). Similarly, carbonylation of *cis*-$[Ru(S_2PMe_2)_2(P\{OMe\}_3)_2]$ (0·05 g) in CH_2Cl_2 for 10 min and recrystallisation from CH_2Cl_2–hexane gave yellow crystals of cis-*bis*(*dimethylphosphinodithioato*)*carbonyl*(*trimethyl phosphite*)*ruthenium*(II) (0·01 g, 25%) whereas carbonylation of *cis*-$[Ru(S_2PMe_2)_2(P\{OPh\}_3)_2]$ (0·07 g) in refluxing acetone for 4 h gave, after recrystallisation from CH_2Cl_2–n-pentane, yellow crystals of cis-*bis*(*dimethylphosphinodithioato*)*carbonyl*(*triphenyl phosphite*)*ruthenium*(II) (0·03 g, 60%).

cis-*Bis(dimethylphosphinodithioato)carbonyl(dimethylphenylphosphine)ruthenium*(II), (*B*) *and Bis(dimethylphosphinodithioato)carbonylbis(dimethylphenylphosphine)ruthenium*(II), (*C*).—*cis*-$[\mathrm{Ru(S_2PMe_2)_2(PMe_2Ph)_2}]$ (0·20 g) was carbonylated in refluxing acetone for *ca.* 1 h and the resulting solution evaporated to dryness. The residue was chromatographed on a dry alumina column using benzene and gave a yellow band (R_F value *ca.* 0·5) and an orange band (R_F value *ca.* 0·1)which were removed separately with diethyl ether, evaporated to dryness, and recrystallised from $\mathrm{CH_2Cl_2}$–pentane. The yellow band consisted of *cis*-$[\mathrm{Ru(S_2PMe_2)_2(PMe_2Ph)CO}]$ (0·01 g, 6%) and the orange $[\mathrm{Ru(S_2PMe_2)_2(PMe_2Ph)_2CO}]$ (configuration C) (0·15 g, 80%).

If *cis*-$[\mathrm{Ru(S_2PMe_2)_2(PMe_2Ph)_2}]$ (0·10 g) and sulphur (0·05 g) were carbonylated in refluxing benzene for 6 h, a t.l.c. of the resulting orange solution showed a single orange band together with a yellow band with the same R_F value as sulphur. The solution was evaporated to dryness to give an orange oil. This was dissolved in diethyl ether and after filtering off the excess of sulphur the solution was left overnight at 273 K when orange *crystals* of *cis*-$[\mathrm{Ru(S_2PMe_2)_2(PMe_2Ph)CO}]$ (0·05 g, 60%) were deposited. *cis*-$[\mathrm{Ru(S_2PMe_2)_2(CO)_2}]$ (0·10 g) was suspended in ethanol (50 ml), presaturated with carbon monoxide, and $\mathrm{PMe_2Ph}$ (0·14 ml) added. The solution was then refluxed in a stream of CO for 2 h to give an orange solution which on leaving overnight at 273 K gave only $[\mathrm{Ru(S_2PMe_2)_2(PMe_2Ph)_2CO}]$ (C) (0·08 g, 50%).

Bis(dimethylphosphinodithioato)carbonylbis(dimethylphenylphosphine)ruthenium(II), (*D*).—*cis*-$[\mathrm{Ru(S_2PMe_2)_2(PMe_2Ph)_2}]$ (0·20 g) was dissolved in $\mathrm{CH_2Cl_2}$ (10 ml) and carbon monoxide passed through the solution for 45 s. The resulting yellow solution was evaporated to dryness under vacuum at 273 K and the residue recrystallised by dissolving in a minimum amount of $\mathrm{CH_2Cl_2}$ and then adding an excess of diethyl ether (0·15 g, 80%).

cis-*Bis(diphenylphosphinodithioato)carbonyl(dimethylphenylphosphine)ruthenium*(II), (*B*).—*cis*-$[\mathrm{Ru(S_2PPh_2)_2(PMe_2Ph)_2}]$ (0·35 g) was dissolved in $\mathrm{CH_2Cl_2}$ (30 ml) and carbonylated for 1 h at room temperature. The yellow solution formed was evaporated to dryness and eluted from a dry silica column with $\mathrm{CH_2Cl_2}$. Two yellow bands were found and the first was extracted with $\mathrm{CH_2Cl_2}$ and the solution evaporated to dryness to give the crystalline *product* (0·04 g, 13%). The other band was removed with diethyl ether, the solution evaporated to dryness, and the residue recrystallised from $\mathrm{CH_2Cl_2}$–light petroleum (b.p. 40—60°) to give $[\mathrm{Ru(S_2PMe_2)_2(PMe_2Ph)_2CO}]$ (mixture of isomers C and D) (0·05 g, 14%).

Bis(diphenylphosphinodithioato)carbonylbis(dimethylphenylphosphine)ruthenium(II), (*C*).—*cis*-$[\mathrm{Ru(S_2PPh_2)_2(PMe_2Ph)_2}]$ (0·30 g) was carbonylated in refluxing ethanol (40 ml) for two hours to give a yellow solution. Concentration to dryness, followed by chromatography on a dry alumina column with benzene gave two bands. The first was eluted with diethyl ether, evaporated to dryness and the residue recrystallised from benzene–light petroleum (b.p. 100—120°) to give a very small amount of *cis*-$[\mathrm{Ru(S_2PPh_2)_2(PMe_2Ph)CO}]$. The second (more intense) orange band was also eluted with diethyl ether and after evaporation to dryness (in the cold) was recrystallised from benzene–n-pentane to give the required *product* (0·10 g, 31%).

Bis(diphenylphosphinodithioato)carbonylbis(dimethylphenylphosphine)ruthenium(II), (*D*).—*cis*-$[\mathrm{Ru(S_2PPh_2)_2(PMe_2Ph)_2}]$ (0·20 g) was carbonylated for one minute in cold $\mathrm{CH_2Cl_2}$. Then, pentane was added and the resulting orange solution evaporated to dryness and the orange *solid* collected without further purification (0·21 g, 100%).

cis-Bis(dimethylphosphinodithioato)bis(carbonyl)ruthenium(II).—*cis*-$\mathrm{Cs_2[RuCl_4(CO)_2]}$ (0·50 g) and $\mathrm{NaS_2PMe_2}$ (0·50 g) were refluxed in ethanol (20 ml) for six hours to give a yellow solution. After filtration, this was cooled giving yellow *crystals* which were washed with water, ethanol, and n-pentane (0·14 g, 39%).

cis-Bis(diphenylphosphinodithioato)bis(carbonyl)ruthenium(II).—$[\mathrm{Ru_3(CO)_{12}}]$ and an excess of $\mathrm{Ph_2PS_2H}$ were refluxed together in tetrahydrofuran for 18 h. The resulting yellow solution was evaporated to dryness, the residue extracted with diethyl ether and crystallised at 273 K to give the yellow *product*.

cis-*Bis(dimethyldithiocarbamato)bis(triphenylphosphine)ruthenium*(II)-*Acetone*.—$[\mathrm{RuCl_2(PPh_3)_3}]$ (0·26 g) and $\mathrm{NaS_2CNMe_2,2H_2O}$ (0·15 g) were shaken in acetone (25 ml) for two days. The solution was then filtered and the orange crystals washed with water, diethyl ether and dried in *vacuo* at 40°.

cis-*Bis(dimethyldithiocarbamato)bis(dimethylphenylphosphine)ruthenium*(II).—*mer*-$[\mathrm{RuCl_3(PMe_2Ph)_3}]$ (0·16 g) and $\mathrm{NaS_2CNMe_22H_2O}$ (0·16 g) were shaken in degassed $\mathrm{CH_2Cl_2}$ under nitrogen for eight hours. The resulting greenish yellow solution was filtered to remove any precipitated sodium chloride and evaporated to dryness. Chromatography on a dry alumina column with benzene gave an intense yellow band (*ca.* R_F value 0·6) together with a number of weaker bands of lower R_F value. The yellow band was removed with diethyl ether, giving on removal of solvent the yellow *product* (0·13 g, 88%).

trans-*Bis(dimethyldithiocarbamato)bis(dimethylphenylphosphine)ruthenium*(II).—*cis*-$[\mathrm{Ru(S_2CNMe_2)_2(PPh_3)_2}]$ (0·20 g) was refluxed with $\mathrm{PMe_2Ph}$ (0·15 ml) in ethanol (20 ml) for 12 h. The resulting yellow solution was filtered hot and allowed to crystallise. The first crop of yellow crystals were filtered off, and washed with ethanol and n-pentane to give the desired *product* (0·03 g, 21%). The yellow filtrate later deposited more crystals shown to be *cis*-$[\mathrm{Ru(S_2CNMe_2)_2(PMe_2Ph)_2}]$ (0·10 g, 71%).

cis-*Bis(dimethyldithiocarbamato)bis(triphenyl phosphite)ruthenium*(II).—$[\mathrm{RuCl_2(P\{OPh\}_3)_4}]$ (0·20 g) and $\mathrm{NaS_2CNMe_2,2H_2O}$ (0·16 g) were refluxed in ethanol (15 ml) for one hour. The resulting yellow solution was filtered hot and on cooling gave yellow crystals of the *product* (0·06 g, 41%).

cis-*Bis(dimethyldithiocarbamato)(triphenylphosphine)(triphenyl phosphite)ruthenium*(II).—*cis*-$[\mathrm{Ru(S_2CNMe_2)_2(PPh_3)_2}]$ (0·10 g) and $\mathrm{P(OPh)_3}$ (0·04 ml) in refluxing $\mathrm{CH_2Cl_2}$ gave an orange solution. Addition of ethanol and evaporation of $\mathrm{CH_2Cl_2}$ gave the yellow crystalline *product* which was washed with ethanol and n-pentane (0·07 g, 69%).

cis-*Bis(dimethyldithiocarbamato)bis(carbonyl)ruthenium*(II).—(a) $[\mathrm{Ru_3(CO)_{12}}]$ (0·20 g) and tetramethylthiuram disulphide (0·40 g) were refluxed in ethanol (15 ml) for 2 h. On cooling, the yellow solution gave the yellow crystalline *product* (0·20 g, 54%).

(b) *cis*-$[\mathrm{RuCl_2(CO)_2(PPh_3)_2}]$ (0·10 g) and $\mathrm{NaS_2CNMe_2,2H_2O}$ (0·20 g) were refluxed in ethanol (20 ml) for seven days. The resulting pale yellow solution was filtered, chromatographed on a dry alumina column with benzene, and the yellow band extracted with diethyl ether. Removal of solvent and recrystallisation from hexane gave the *product* (0·001 g, 2%).

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