Metal Complexes of Sulphur Ligands. Part 21.[1] Reactions of [Ru($SOCPh)_2(PMe_2Ph)_2$] † with $Ph_2P(CH_2)_nPPh_2$ ($n = 1$ or 2) and PMe_2Ph and of *cis*-[$RuCl_2(PMe_2Ph)_4$] ‡ with Ammonium Monothiobenzoate. Crystal and Molecular Structure of [Ru($SOCPh)_2(PMe_2Ph)\{Ph_2P(CH_2)_2PPh_2\}$]·MeOH §

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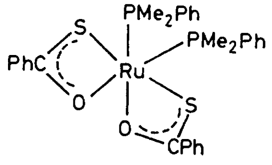
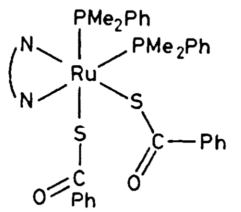
Whereas reaction of [Ru($SOCPh)_2(PMe_2Ph)_2$] (1) with $Ph_2PCH_2PPh_2$ (dppm) in ethanol (1 : 1 molar ratio) gives *mer*-[Ru($SOCPh)_2(PMe_2Ph)_3$]–dppm, the corresponding reaction with $Ph_2P(CH_2)_2PPh_2$ (dppe) gives, after recrystallisation from methanol, the product [Ru($SOCPh)_2(PMe_2Ph)$(dppe)]·MeOH. This has been shown by ^1H and ^{31}P-{^1H} n.m.r. spectroscopy to consist of two isomers (3a) and (3b) with bidentate and *S*-bonded ^-SCOPh groups and the structure of (3b) has been verified by *X*-ray analysis. The crystals are triclinic, space group $P\bar{1}$, with a = 10.01(1), b = 14.70(1), c = 18.52(1) Å, α = 75.2(3), β = 83.6(3), and γ = 73.5(3)°. Reaction of compound (1) with an excess of PMe_2Ph gives an isomeric mixture of *mer*-[Ru($SOCPh)_2(PMe_2Ph)_3$] whereas shaking *cis*-[$RuCl_2(PMe_2Ph)_4$] in benzene or methanol for short periods with [NH_4][SOCPh] gives the *facial* isomer. If *cis*-[$RuCl_2(PMe_2Ph)_4$] is shaken with [NH_4][SOCPh] in methanol for several hours, however, the cation [Ru(SOCPh)($PMe_2Ph)_4]^+$ can be isolated by addition of Na[BPh_4].

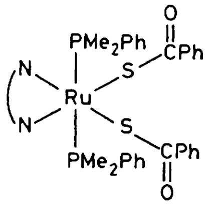
RECENTLY, we reported that reaction of *mer*-[$RuCl_3(PMe_2Ph)_3$] with Na[SOCPh] in acetone or methanol gave the six-co-ordinate complex [Ru($SCOPh)_2(PMe_2Ph)_2$] (1) as a mixture of *cis* and *trans* isomers. Reaction of this compound with various unidentate Lewis bases such as CO, NH_3, and NH_2Et (L) produced monomeric complexes [Ru($SOCPh)_2(PMe_2Ph)_2L_2$] containing *cis*-PMe_2Ph, *cis*-L, and *trans*-*S*-bonded ^-SCOPh ligands which suggested that cleavage of the Ru–O bonds in the major *cis* isomer of the starting material had occurred.[2] In contrast, reaction of (1) with bulky bidentate nitrogen-donor Lewis bases such as 2,2′-bipyridyl and 1,10-phenanthroline (N–N) gave a mixture of isomers [Ru($SOCPh)_2$(N–N)($PMe_2Ph)_2$] (2a) and (2b) in one of which, (2a), the sulphur atoms had rearranged from the *trans* stereochemistry of the starting material to a *cis* arrangement.[1] We have now extended these reactions to the unidentate and bidentate phosphorus-donor Lewis bases PMe_2Ph and $Ph_2P(CH_2)_nPPh_2$ ($n = 1$, dppm; $n = 2$, dppe) and have also investigated the reaction of *cis*-[$RuCl_2(PMe_2Ph)_4$] with [NH_4][SOCPh] under different experimental conditions.



(1)



(2a)



(2b)

RESULTS AND DISCUSSION

Reaction of [Ru($SOCPh)_2(PMe_2Ph)_2$] *with dppm and dppe.*—When [Ru($SOCPh)_2(PMe_2Ph)_2$] (1) was treated in ethanol with a 1 : 1 molar ratio of dppm a yellow product was obtained from a reaction mixture which smelt strongly of free tertiary phosphine; after recrystallisation from ethanol, the maximum yield was 38%. The i.r. spectrum (see Experimental section) indicated the presence of both bidentate and (*S*-bonded) unidentate monothiobenzoate groups,[1–3] and the complex analysed reasonably well for [Ru($SOCPh)_2(PMe_2Ph)_3$(dppm)]. The sharp melting point, which was quite different from that of [Ru($SOCPh)_2(PMe_2Ph)_3$] alone, suggested that it was not a simple mixture of [Ru($SOCPh)_2(PMe_2Ph)_3$] and dppm.

However, the ^{31}P-{^1H} n.m.r. spectrum at room temperature in $CDCl_3$ contains a strong singlet at δ −22.1 p.p.m. (the chemical shift of free dppm), three poorly resolved doublets between 1 and 5 p.p.m., and a broad triplet at 24.4 p.p.m. On cooling to 240 K the spectrum was resolved into three AX_2 patterns, identified as those characteristic of an isomeric mixture of *mer*-[Ru($SOCPh)_2(PMe_2Ph)_3$] (see later). A proposed overall mechanism for this reaction is shown in the Scheme, with dppm initially reacting with (1), shown as its major *cis* isomer, to form a chelated complex of the type [Ru($SOCPh)_2(PMe_2Ph)$(dppm)] by displacement of a dimethylphenylphosphine group (*cf.* the dppe product below). Two molecules of free PMe_2Ph then attack and displace the dppm to give the meridional isomers of

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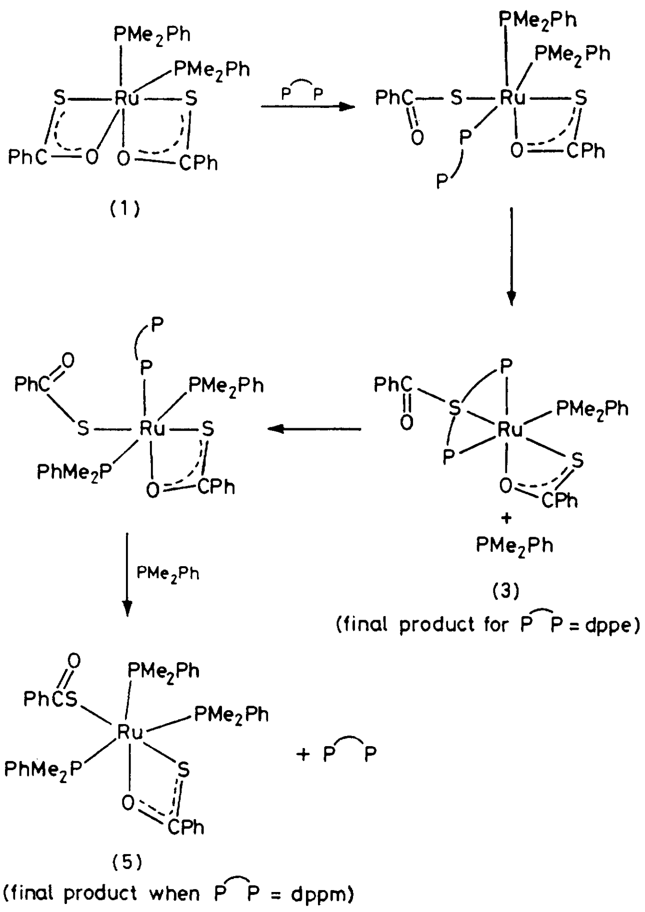
† Bis(dimethylphenylphosphine)bis(monothiobenzoato)ruthenium.
‡ *cis*-Dichlorotetrakis(dimethylphenylphosphine)ruthenium.
§ [1,2-Bis(diphenylphosphino)ethane](dimethylphenylphosphine)bis(monothiobenzoato)ruthenium–methanol (1/1).



SCHEME Proposed mechanism of reaction of $[Ru(SOCPh)_2(PMe_2Ph)_2]$ with $Ph_2P(CH_2)_nPPh_2$ (n = 1 or 2)

$[Ru(SOCPh)_2(PMe_2Ph)_3]$. This scheme is related to that proposed[4] for the reaction of *cis*-$[Ru(S_2PMe_2)_2(PMe_2Ph)_2]$ with carbon monoxide, in which a molecule of PMe_2Ph is first displaced and then re-attacks to break a Ru–S bond and give the final product $[Ru(S_2PMe_2)_2(CO)(PMe_2Ph)_2]$ containing *trans* phosphines. In the present case, the product isolated always contained dppm, although the $^{31}P-\{^1H\}$ n.m.r. spectrum showed that it was completely dissociated in solution. Two possible explanations can be suggested: either the product crystallised from ethanol as a clathrate containing a 1 : 1 molar ratio of ruthenium complex to dppm, or the dppm was bound in the complex and dissociated immediately on dissolving. Unfortunately, the spectroscopic evidence cannot distinguish between these two possibilities.

When compound (1) was treated with dppe in ethanol (1 : 1 molar ratio) a yellow-brown product was obtained, in *ca.* 70% yield, which, after recrystallisation from methanol, analysed for $[Ru(SOCPh)_2(PMe_2Ph)(dppe)]\cdot MeOH$. The compound gave a non-conducting solution in methylene chloride, and was shown by osmometric molecular-weight measurements to be monomeric in chloroform and acetone at several different concentrations. In the i.r. spectrum, ν(CO) was observed at 1 545 and 1 460 cm^{-1}, suggesting that both *S*-bonded unidentate and bidentate monothiobenzoate groups were present; the ν(CS) region was obscured by dppe vibrational modes.

The methyl region of the ^1H n.m.r. spectrum in $CDCl_3$ at 300 K (Table 1) showed four doublets at δ 1.25, 1.46 (two doublets superimposed, on the evidence of ^{31}P decoupling experiments), and 1.78 p.p.m. each with a J(PH) of 8.50 Hz and a small doublet splitting of 1.60 Hz on each peak. The $^{31}P-\{^1H\}$ n.m.r. spectrum (Table 2, Figure 1) consists of two first-order ABX patterns of approximately equal intensity. The A and B resonances in each spectrum arise from the two phosphorus atoms of the chelated dppe group, while the X resonance arises from the single PMe_2Ph group. The values of the coupling constants indicate that the PMe_2Ph group is in each case co-ordinated *trans* to the B phosphorus atom of the dppe, giving rise to the largest coupling constant, while comparison with the decoupling frequencies observed in the $^1H-\{^{31}P\}$ n.m.r. spectrum shows that the large and small J(PH) doublet splittings arise from coupling of the PMe_2Ph methyl protons to the PMe_2Ph

TABLE 1

Hydrogen-1 n.m.r. (and $^1H-\{^{31}P\}$) data in $CDCl_3$ for some new ruthenium(II) monothiobenzoate complexes

Compound	T/K	Proposed structure	δ^a/p.p.m. Methyl (phosphine)	 Others
$[Ru(SOCPh)_2(PMe_2Ph)(dppe)]$	300	(3b)	1.25 (dd), 1.46 (dd), ^2J(PH) 8.50 (3) [b], ^4J(PH) 1.60 (67) [b]	2.80—3.20 (u) [c]
		(3a)	1.46 (dd), 1.78 (dd), ^2J(PH) 8.50 (5) [b], ^4J(PH) 1.60 (67) [b]	6.80—7.50 (m) [d]
mer-$[Ru(SOCPh)_2(PMe_2Ph)_3]$	300	(5a)—(5c)	1.57 (t), ^2J(PH) + ^4J(PH′) [e] 7.0, 1.31 (u) (br)	7.00—8.00 (m) [d]
	250		1.57 (t), ^2J(PH) + ^4J(PH′) [e] 7.0 (6) [b]; 1.22 (d), J(PH) 9.0 (21) [b]	7.00—8.00 (m) [d]
fac-$[Ru(SOCPh)_2(PMe_2Ph)_3]$	300	(6)	1.55 (u) (br), 1.85 (d), J(PH) 9.0	7.00—8.00 (m) [d]
	240		1.14 (d), J(PH) 9.0 (16) [b]; 1.38 (d), J(PH) 9.0 (16) [b]; 1.94 (d), J(PH) 9.0 (27) [b]	7.00—8.00 (m) [d]
$[Ru(SOCPh)(PMe_2Ph)_4][BPh_4]$	300	(7)	1.21 (t), ^2J(PH) + ^4J(PH′) [e] 6.0 (1) [b]; 1.60 (d), J(PH) 8.0 (19) [b]; 1.86 (d), J(PH) 8.0 (9) [b]	7.00—8.00 (m) [d]
mer-$[Ru(SOCPh)_2(PMePh_2)_3]$ [f]	300	(5a)—(5c)	1.93 (t), ^2J(PH) + ^4J(PH′) [e] 7.5 (14) [b]; 1.89 (d), J(PH) 9.0 (30) [b]	7.00—8.00 (m) [d]

[a] ±0.01 p.p.m.; pt = pseudo-triplet (see ref. 7 for definition), u = unresolved. J values in Hz. [b] Approximate ^{31}P chemical shift in parentheses (in p.p.m. to higher frequency of 85% H_3PO_4) equivalent to the irradiation frequency which brings about collapse of splitting in ^1H n.m.r. spectrum. [c] Ethylenic protons of dppe. [d] Phenyl resonances. [e] 'Virtually coupled' 1 : 2 : 1 triplet. [f] Contains some *cis*-$[Ru(SOCPh)_2(PMePh_2)_2]$ [δ(PMe) 1.59 (pt), ^2J(PH) + ^4J(PH′) 9.0 Hz (46)].

TABLE 2

^{31}P-{^1H} n.m.r. data in $CDCl_3$ for some new ruthenium(II) monothiobenzoate complexes

Compound	T/K	Proposed structure	δ^a/p.p.m.	
			PR$_3$	Other
$[Ru(SOCPh)_2(PMe_2Ph)(dppe)]$ [b]	300	(3a)	5.1 (X), J(AX) 28.0, J(BX) 308.1	75.0 (A), 65.8 (B), J(AB) 15.6
		(3b)	3.4 (X′), J(A′X′) 26.2, J(B′X′) 318.6	66.2 (A′) 67.6 (B′), J(A′B′) 15.0
$[Ru(SOCPh)_2(PMe_2Ph)(dppe)(CO)]$ [c]	300	(4a)	−4.9 (X), J(AX) 31.7, J(BX) 276.9	34.3 (A), 52.7 (B), J(AB) 19.5
mer-$[Ru(SOCPh)_2(PMe_2Ph)_3]$	300	(5a)—(5c)	4.2 (u), 13.1 (u), 26.8 (u)	
	220 [d]	(5c)	5.1 (d), 18.1 (t), ^2J(PP) 30.0	
		(5b)	3.8 (d), 20.6 (t), ^2J(PP) 30.0	
		(5a)	5.3 (d), 28.6 (t), ^2J(PP) 33.0	
	220 [e]	(5b)	3.8 (d), 20.6 (t), ^2J(PP) 30.0	
fac-$[Ru(SOCPh)_2(PMe_2Ph)_3]$	240	(6)	11.7 (A), 15.8 (B), 28.2 (X),[f] J(AB) 26.2, J(AX) 32.3, J(BX) 30.4	
$[Ru(SOCPh)(PMe_2Ph)_4][BPh_4]$	300	(7)	0.6 (A), 8.3 (B), 19.7 (C),[g] J(AB) 26.8, J(AC) 31.2	
mer-$[Ru(SOCPh)_2(PMePh_2)_3]$	300	(5c)	13.9 (d), 20.4 (t), ^2J(PP) 27.6	
		(5a)	14.0 (d), 32.9 (t), J(PP) 32.5	
		(5b)	15.0 (d), 29.5 (t), ^2J(PP) 30.3	
cis-$[Ru(SOCPh)_2(PMePh_2)_2]$ [h]	300		45.6 (s)	

[a] Quoted in p.p.m. to high frequency of 85% H_3PO_4 (±0.05); u = unresolved. J values in Hz. [b] See Figure 1. [c] In mixture containing (3a) and (3b) (see text). [d] Fresh solution; relative intensities 1 : 4 : 3 for (5c), (5b), and (5a). [e] After storage for 5 d only (5b) was present. [f] ABX pattern; values obtained using computer program LAOCOON (R. K. Harris, S.R.C. N.M.R. Computer Program Library, University of East Anglia). [g] A_2BC pattern; values obtained using computer program NUMARIT (same ref. as in f). [h] In mixture containing *mer*-$[Ru(SOCPh)_2(PMePh_2)_3]$ isomers; assigned structure of type (1).

phosphorus, and to the *trans* phosphorus atom of dppe respectively. The two structures (3a) and (3b) are proposed for the two isomers of $[Ru(SOCPh)_2(PMe_2Ph)(dppe)]\cdot MeOH$ and isomer (3b) has been confirmed by X-ray structural analysis. Finally, if the assumption is made that the dppe phosphorus *trans* to oxygen in (3a) has a more positive chemical shift than that *trans* to sulphur in (3b) {see later discussion on $[Ru(SOCPh)_2(PMe_2Ph)_3]$ isomers}, then the ^{31}P-{^1H} ABX n.m.r. spectrum in Table 2 can be assigned to isomer (3a) and that of A′B′X′ to isomer (3b).

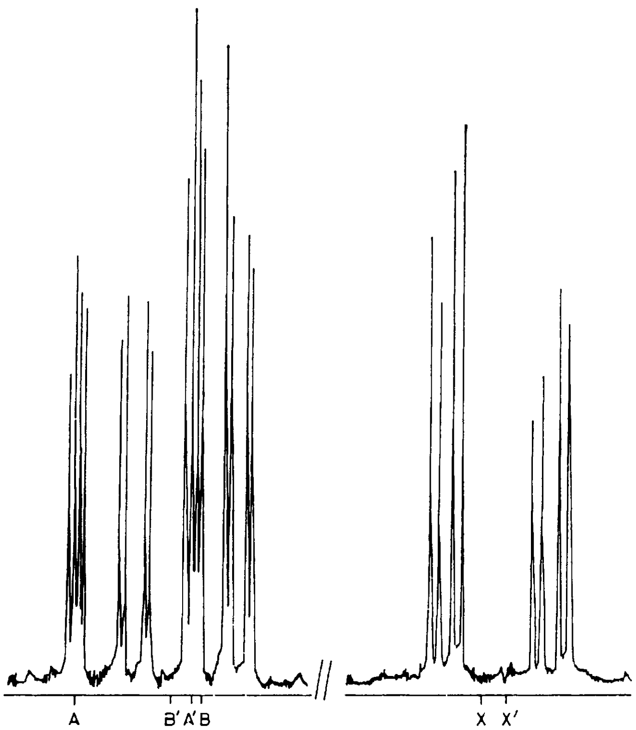
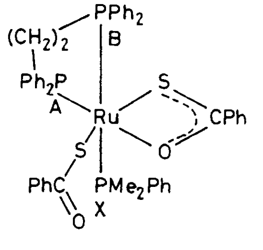
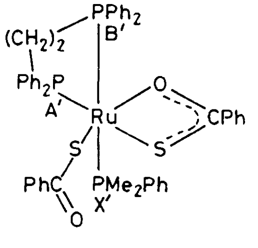


FIGURE 1 ^{31}P-{^1H} n.m.r. spectrum of $[Ru(SOCPh)_2(PMe_2Ph)(dppe)]\cdot MeOH$ in $CDCl_3$ at 300 K. Isomer (3a); δ 75.0 (A), 65.8 (B), and 5.1 p.p.m. (X). Isomer (3b); δ 66.2 (A′), 67.6 (B′), and 3.4 p.p.m. (X′)

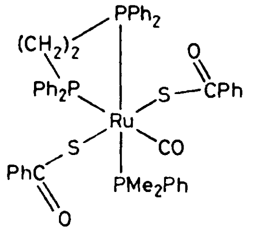
When (3) was treated with carbon monoxide, a product was obtained on removal of solvent which had one carbonyl stretching mode in its i.r. spectrum, at 1 990 cm^{-1}, and one new ν(CO)(acid) band at 1 560 cm^{-1} (indicative of S-bonded ^-SOCPh), together with the ν(CO)(acid) bands already observed for (3). In the ^{31}P-{^1H} n.m.r. spectrum, the two ABX patterns arising from the isomers of (3) were observed in the same relative proportions as before, but the strongest signals in the spectrum were those of a third ABX pattern. Clearly, the arrangement of phosphorus atoms was the same as in (3), and structure (4a) or (4b) is proposed for the CO adduct. The difference of almost 20 p.p.m. between the chemical shifts of the two dppe phosphorus atoms (Table 2) suggests that structure (4a), where the phosphorus atoms are *trans* to carbon and phosphorus, is the more likely. This isomer would be formed by cleavage of the Ru–O bond in isomer (3a) of the starting material, which is a reasonable suggestion since a bond *trans* to phosphorus, as in (3a), would be expected to be more labile than one *trans* to sulphur, as in (3b). The car-



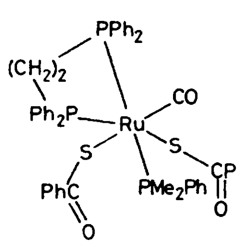
(3a)



(3b)



(4a)



(4b)

bonylation of (3) is by no means facile, since several hours refluxing in ethanol under carbon monoxide does not take the reaction to completion. This is probably due to simple steric reasons, since the co-ordination sphere of (3) is already extremely crowded (see Figure 2).

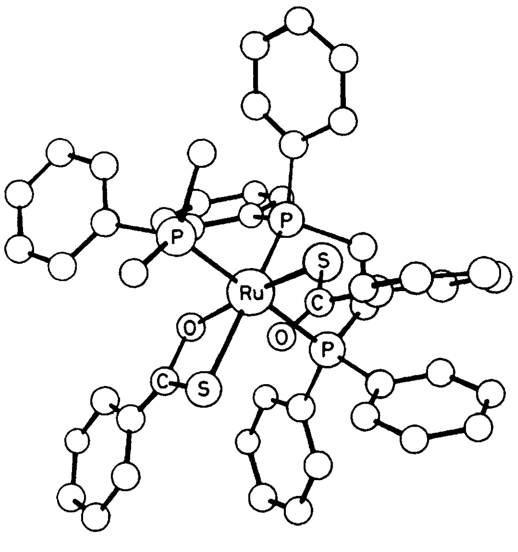


FIGURE 2 Molecular structure of [Ru(SOCPh)$_2$(PMe$_2$Ph)(dppe)]·MeOH (3b)

However, this does not explain why *both* isomers of the starting material are still present, in almost equal amounts, after the carbonylation reaction. The presence of only one isomer of the carbonylated product suggests *either* that the two isomers of (3) are in dynamic equilibrium in refluxing ethanol, possibly by a solvent-assisted mechanism, so that selective carbonylation of one isomer will always leave an isomeric mixture of unreacted starting material, *or* that the product is formed by the carbonylation of both isomers, followed by rearrangement to give but one isomer of the product. The spectroscopic evidence cannot distinguish between these two possibilities.

Crystal Structure of [Ru(SOCPh)$_2$(PMe$_2$Ph)(dppe)]·MeOH (3b).—Details of the solution of the structure are given in the Experimental section, selected bond distances and angles are in Table 3, and a view of the molecule in Figure 2. Despite the poor resolution of the structure, reflected in the large standard deviations in both distances and angles, the basic geometry of the complex is clear. The co-ordination about the ruthenium is distorted octahedral, with the largest deviation from ideal geometry arising from the small bite of the chelated monothiobenzoate ligand [S(1)–O(1) 2.54 Å, S(1)–Ru–O(1) 67.0°]. The unco-ordinated oxygen atom of the unidentate monothiobenzoate group is hydrogen-bonded to a molecule of methanol solvate (O–O *ca.* 3.0 Å). This interaction would account for the low value of the ν(CO) mode in the i.r. spectrum assigned to the unidentate acid ligand. The ligand is slightly twisted from its preferred conformation [Ru–S(2)–C(42)–O(2) 8°] which would also be explained by the hydrogen bond, and the general steric crowding in the co-ordination sphere.

TABLE 3

Interatomic distances and angles for compound (3b), with estimated standard deviations in parentheses

(*a*) Distances (Å)

Ru–P(1)	2.27(2)	Ru–O(1)	2.10(4)
Ru–P(2)	2.40(2)	Ru–S(2)	2.35(2)
Ru–P(3)	2.33(2)	Ru–O(2)	3.50(4)
Ru–S(1)	2.47(2)		

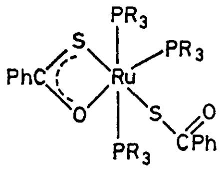
(*b*) Angles (°)

P(1)–Ru–P(2)	84.6(6)	P(2)–Ru–S(2)	88.7(7)
P(1)–Ru–P(3)	98.9(7)	P(3)–Ru–S(1)	91.2(7)
P(1)–Ru–S(1)	161.3(8)	P(3)–Ru–O(1)	95.2(11)
P(1)–Ru–O(1)	96.3(12)	P(3)–Ru–S(2)	87.3(7)
P(1)–Ru–S(2)	89.0(8)	S(1)–Ru–O(1)	67.0(12)
P(2)–Ru–P(3)	174.6(8)	S(1)–Ru–S(2)	107.2(7)
P(2)–Ru–S(1)	86.6(7)	O(1)–Ru–S(2)	173.7(10)
P(2)–Ru–O(1)	88.4(7)		

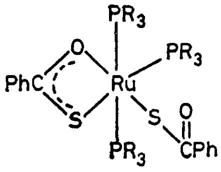
The proposed mechanism of formation of (3) is shown in the first part of the Scheme. The difference between the behaviour of dppm and dppe in this reaction, with dppm being displaced from the complex by free PMe$_2$Ph while dppe forms a stable chelate, is probably due to the difference in the bite of the two ligands. Dppm forms a strained four-membered ring on chelation in an octahedral or square-planar complex, and is known to have a preference for bridging rather than chelating co-ordination in square-planar platinum(II) complexes, in circumstances where dppe readily chelates.[5] In the present case, where bridging behaviour may be ruled out by steric factors, the dppm is simply displaced.

Reaction of [Ru(SOCPh)$_2$(PMe$_2$Ph)$_2$] (1) *with* PMe$_2$Ph *and of cis*-[RuCl$_2$(PMe$_2$Ph)$_4$] *with* [NH$_4$][SOCPh].—When compound (1) was treated in ethanol under reflux with an excess of dimethylphenylphosphine a yellow product was obtained which analysed well for [Ru(SOCPh)$_2$-(PMe$_2$Ph)$_3$], and whose i.r. spectrum (Experimental section) indicated the presence of both bidentate and *S*-bonded unidentate monothiobenzoate groups. The reaction of *cis*-[RuCl$_2$(PMe$_2$Ph)$_4$] with [NH$_4$][SOCPh] in ethanol under reflux gave a product of identical formulation, and the ^{1}H and ^{31}P-{^{1}H} n.m.r. spectra of the two compounds confirmed that in each case a mixture of meridional isomers of [Ru(SOCPh)$_2$(PMe$_2$Ph)$_3$] had been produced.

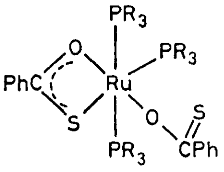
The ^{1}H n.m.r. spectrum of the product in CDCl$_3$ (Table 1) at room temperature showed a 1 : 2 : 1 'virtually coupled ' triplet * at δ 1.57 p.p.m. and on cooling to 250 K an additional doublet appeared at δ 1.22 p.p.m. The patterns collapsed to singlets on irradiation at frequencies equivalent to ^{31}P chemical shifts of *ca.* 6 p.p.m. (triplet) and *ca.* 21 p.p.m. (doublet). At 220 K, the ^{31}P-{^{1}H} n.m.r. spectrum (which was poorly resolved at room temperature) (see Table 2) exhibited three AX_2 patterns with the A triplets occurring between 3 and 6 p.p.m. in agreement with the decoupling frequencies found in the ^{1}H-{^{31}P} n.m.r. spectrum. Thus, the product consisted of a mixture of isomers, each containing a meridional arrangement of phosphines, with the triplet in the ^{1}H n.m.r. spectrum arising from the methyl groups of the *trans* phosphines. The relative intensities of the AX_2 patterns in the ^{31}P-{^{1}H} n.m.r. spectrum were approximately 1 : 3 : 4 in a freshly prepared solution (see Table 2). After storage for 3 d, the ^{31}P-{^{1}H} n.m.r. spectrum of the same solution exhibited only one AX_2 pattern, indicating slow isomerisation in solution to form the thermodynamically favoured isomer. A number of meridional isomers of [Ru(SOCPh)$_2$(PMe$_2$Ph)$_3$] can be envisaged, and three (5a—c) are proposed to account for the observed spectra. An isomer such as (5c), with a unidentate monothiobenzoate group bonded through oxygen, is unlikely to occur in large amounts, and its characteristic ν(CO) and ν(CS) modes [1-3] were not observed in the i.r. spectrum, but it may account for the weakest of the three AX_2 patterns. Isomers (5a) and (5b), both with a unidentate monothiobenzoate group bonded through sulphur, are proposed as the two major isomers, but there is no definite evidence as to which is the thermodynamically favoured form that predominates in aged solutions. However, comparison of the triplet chemical shifts in the ^{31}P-{^{1}H} n.m.r. spectrum (which arise from the unique phosphine *trans* to oxygen or sulphur) with the ^{31}P chemical shift observed for the major isomer of [Ru(SOCPh)$_2$(PMe$_2$Ph)$_2$] (1) (in which the phosphines are *trans* to oxygen) [2] suggests that the triplet at δ 28.6 p.p.m. [*cf.* 39.0 p.p.m. for (1)] is more likely to arise from a phosphine *trans* to oxygen than are those at δ 20.6 or 18.1 p.p.m. Thus, it is suggested that the spectrum of the aged solution, with its triplet at δ 20.6 p.p.m., arises from isomer (5b).



(5a)

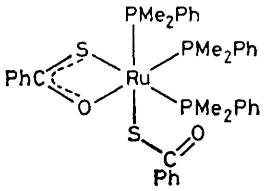


(5b)



(5c)

When *cis*-[RuCl$_2$(PMe$_2$Ph)$_4$] was shaken in benzene or methanol with [NH$_4$][SOCPh] at room temperature for short periods a bright yellow product, again analysing for [Ru(SOCPh)$_2$(PMe$_2$Ph)$_3$], was obtained. The i.r. spectrum was very similar to that of the product obtained in refluxing ethanol, but its ^{1}H and ^{31}P-{^{1}H} n.m.r. spectra were quite different. In particular, the ^{31}P-{^{1}H} n.m.r. spectrum (at 240 K) consisted of an ABX pattern in which all the coupling constants were of a size (*ca.* 30 Hz) typical of couplings between *cis* phosphines [6] attached to ruthenium(II) (Table 2). A facial arrangement of phosphines is proposed for this product (6). Here, one phosphine is *trans* to oxygen and can confidently be assigned the ^{31}P chemical shift of 28.2 p.p.m., while the two phosphines *trans* to sulphur are assigned the remaining shifts, which differ by only *ca.* 4 p.p.m. and could not be distinguished in the ^{1}H-{^{31}P} decoupling experiments. Furthermore, on refluxing in ethanol, the facial isomer (6) was converted into the meridional isomer (5b). Thus, it seems that the facial isomer was formed first in either polar or non-polar solvents, then rearranged at refluxing temperatures to give the thermodynamically preferred meridional form.



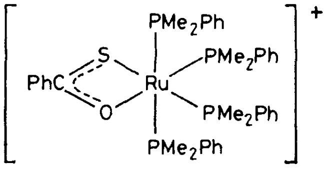
(6)

However, when *cis*-[RuCl$_2$(PMe$_2$Ph)$_4$] was shaken in methanol with [NH$_4$][SOCPh] for a few hours a product was isolated on addition of Na[BPh$_4$] which analysed for [Ru(SOCPh)(PMe$_2$Ph)$_4$][BPh$_4$], and which gave an i.r. spectrum indicating only bidentate co-ordination of the monothiobenzoate ligand. The same cation was also obtained by treating *fac*-[Ru(SOCPh)$_2$(PMe$_2$Ph)$_3$] with an excess of PMe$_2$Ph in methanol. In its ^{1}H n.m.r. spectrum in CDCl$_3$ at 300 K (Table 1) a ' virtually coupled ' 1 : 2 : 1 triplet was observed at δ 1.21 p.p.m. and two doublets at δ 1.60 and 1.86 p.p.m.; these patterns decoupled at frequencies equivalent to ^{31}P chemical shifts of *ca.* 1, 19, and 9 p.p.m. respectively. In the ^{31}P-{^{1}H} n.m.r. spectrum a second-order A_2BC pattern was observed (Table 2) and structure (7) is proposed for the cation, with the *trans* phosphines giving rise to the A resonance in the ^{31}P-{^{1}H} n.m.r. spectrum, and to the associated 1 : 2 : 1 triplet in the ^{1}H n.m.r. spectrum. The B and C resonances, with their associated ^{1}H n.m.r. doublets, arise from the two *cis* phosphines and, on the

* A ' virtually coupled ' 1 : 2 : 1 triplet arises in the spectra of complexes containing two equivalent methyl-bearing phosphines which are coupled such that $|J(PP')| \gg |J(PH) + J(PH')|$. It is usually characteristic of *trans* phosphines.

basis of the reasoning outlined earlier, the resonance at δ 19.7 p.p.m. can be assigned to the phosphine ***trans*** to oxygen and that at δ 8.3 p.p.m. to the one ***trans*** to sulphur.

Thus, it appears that reaction of *cis*-[$RuCl_2(PMe_2Ph)_4$] with an excess of [NH_4][SOCPh] under mild conditions leads to displacement of the chloride ions and one PMe_2-Ph ligand to give *fac*-[$Ru(SOCPh)_2(PMe_2Ph)_3$] (6). In polar media at ambient temperature in the presence of an excess of PMe_2Ph, this reacts to give the [Ru(SOCPh)-($PMe_2Ph)_4]^+$ cation (7), whereas refluxing (6) in ethanol leads to formation of the thermodynamically preferred meridional isomer (5b).



(7)

This reaction sequence is similar to that proposed earlier [7] for the reactions of [$RuCl_2(PR_3)_n$] ($n = 3$ or 4) with various dithioacid ligands except that, in this instance, there is no evidence for the further rearrangement of [$Ru(SOCPh)_2(PMe_2Ph)_3$] to [$Ru(SOCPh)_2$-($PMe_2Ph)_2$]. This is of course consistent with the reduced co-ordinating power towards Ru^{II} of oxygen compared to sulphur, coupled with the well known high affinity of PMe_2Ph for Ru^{II}.[8] In support of the latter statement, reaction of *trans*-[$RuCl_2(PMePh_2)_4$] with an excess of [NH_4][SOCPh] in ethanol under reflux gives an isomeric mixture of *mer*-[$Ru(SOCPh)_2(PMePh_2)_3$] complexes together with a small amount of *cis*-[$Ru(SOCPh)_2$-($PMePh_2)_2$] (Tables 1 and 2).

Finally, the inability to form [$Ru(SOCPh)_2(PMe_2Ph)_4$] with two *S*-bonded $^-$SOCPh groups {*cf.* [$Ru(SOCPh)_2$-($PMe_2Ph)_2L_2$] (L = CO, NH_3, or NH_2Et; L_2 = 2,2′-bipyridyl or 1,10-phenanthroline},[1,2] either by reaction of *cis*-[$RuCl_2(PMe_2Ph)_4$] with $^-$SOCPh or of [$Ru(SOCPh)_2$-($PMe_2Ph)_2$] with PMe_2Ph, must be mainly attributable to adverse steric constraints.

EXPERIMENTAL

Microanalyses were by the University of Edinburgh Chemistry Department. Molecular weights were determined on a Mechrolab vapour-pressure osmometer (model 301A) calibrated with benzil. Infrared spectra were recorded in the range 250—4 000 cm^{-1} on a Perkin-Elmer 557 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Hydrogen-1 n.m.r. spectra were obtained on a Varian Associates HA100 spectrometer equipped with a variable-temperature probe, and heteronuclear decoupling experiments were carried out using a second radiofrequency field provided by the Schlumberger FS30 frequency synthesiser. Proton noise-decoupled ^{31}P n.m.r. spectra were recorded on a Varian XL-100 spectrometer operating in the pulse and Fourier-transform modes at 40.5 MHz (^{31}P chemicals shifts quoted to high frequency of 85% H_3PO_4). Melting points were determined with a Kofler hot-stage microscope and are uncorrected.

Crystal-structure Determination of (3b).—*Crystal data.* $C_{49}H_{49}O_3P_3RuS_2$, $M = 944.0$, Triclinic, $a = 10.01(1)$, $b = 14.70(1)$, $c = 18.52(1)$ Å, $\alpha = 75.2(3)$, $\beta = 83.6(3)$, $\gamma = 73.5(3)^\circ$, $U = 2\,524$ Å^3, $D_m = 1.27$, $Z = 2$, $D_c = 1.24$ g cm^{-3}, Cu-K_α radiation, $\lambda = 1.541\,8$ Å, $\mu(\text{Cu-}K_\alpha) = 45.2$ cm^{-1}, space group $P\bar{1}$. Only small, poorly diffracting crystals were obtained. Cell dimensions were estimated from Weissenberg and precession photographs, and a crystal was mounted about the *c* axis for data collection on a Stadi-2 two-circle diffractometer. One unique set of data was collected to a resolution of 1.2 Å; 1 274 of the 1 640 measured data had $I > 3\sigma(I)$, and the solution and refinement of the structure were based on these. No measurable intensities were obtained at high resolution. No absorption corrections were made. The solution was obtained by the heavy-atom method, the position of the ruthenium atom having been determined from a Patterson synthesis. The other atoms were found in successive electron-density syntheses. The low resolution made it impossible to define single atoms of the phenyl rings, so these were refined as rigid groups with C–C 1.40 Å. Hydrogen atoms were not included in the refinement. Individual isotropic thermal parameters were included for all C and O atoms, and anisotropic parameters for Ru, S, and P. At convergence (unit weights), $R = 0.15$. Positional and thermal parameters and observed and calculated structure factors are deposited as Supplementary Publication No. SUP 23137 (11 pp.).* Crystallographic calculations made use of the '*X*-Ray' system of programs.[9]

Ruthenium(III) trichloride trihydrate (Johnson Matthey Ltd.), carbon monoxide (Air Products), dimethylphenylphosphine and methyldiphenylphosphine (Maybridge Chemical Company), and sodium tetraphenylborate (B.D.H.) were obtained as indicated. The compounds [$Ru(SOCPh)_2(PMe_2Ph)_2$],[2] *cis*-[$RuCl_2(PMe_2Ph)_4$],[10] and *trans*-[$RuCl_2(PMePh_2)_4$] [11] were prepared as described earlier. Bis(diphenylphosphino)methane was obtained by the method of Issleib and Müller [12] and 1,2-bis(diphenylphosphino)ethane by the method of Chatt and Hart.[13]

All the solutions were degassed before use and reactions were carried out under a nitrogen atmosphere. Hydrogen-1 n.m.r. data are given in Table 1 and $^{31}P\text{-}\{^1H\}$ n.m.r. data in Table 2.

Tris(dimethylphenylphosphine)bis(monothiobenzoato)-ruthenium(II)*-Bis(diphenylphosphino)methane.*—The compounds [$Ru(SOCPh)_2(PMe_2Ph)_2$] (0.10 g) and $Ph_2PCH_2PPh_2$ (0.06 g) were refluxed in ethanol (50 cm^3) for 2 h. The volume of the solution was reduced and on cooling the yellow ***product*** was filtered off and recrystallised from ethanol (0.06 g, 38%), m.p. 119—122 °C (Found: C, 65.6; H, 5.2. Calc. for $C_{63}H_{65}O_2P_5RuS_2$: C, 64.4; H, 5.5%). Mull i.r. spectrum: ν(CO) at 1 530—1 560, ν(CS) at 930 and 960 cm^{-1}.

[*1,2-Bis(diphenylphosphino)ethane*](*dimethylphenylphosphine*)*bis(monothiobenzoato)ruthenium*(II)*-Methanol* (1/1).—The compounds [$Ru(SOCPh)_2(PMe_2Ph)_2$] (0.10 g) and Ph_2-$PC_2H_4PPh_2$ (0.60 g) were refluxed in ethanol (50 cm^3) for 2 h. The volume of the solution was reduced and on cooling the yellow-brown ***product*** was filtered off and recrystallised from methanol (0.10 g, 73%), m.p. 107—109 °C (decomp.) [Found: C, 63.9; H, 5.1%; *M*(acetone) 896. Calc. for

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

$C_{49}H_{49}O_3P_3RuS_2$: C, 62.3; H, 5.2%; *M* 943]. Mull i.r. spectrum: ν(CO) at 1 545 and 1 460 cm^{-1}; ν(CS) obscured by dppe ligand vibrations.

Tris(*dimethylphenylphosphine*)*bis*(*monothiobenzoato*)-*ruthenium*(II).—*Meridional isomers.* The compound *cis*-[$RuCl_2(PMe_2Ph)_4$] (0.10 g) was refluxed in ethanol (50 cm^3) with [NH_4][SOCPh] (0.10 g) for 2 h. The solution was filtered hot to remove [NH_4]Cl, then the volume was reduced, and on cooling the orange *product* was filtered off (0.08 g, 76%), m.p. 176—179 °C (Found: C, 58.0; H, 5.6. Calc. for $C_{38}H_{43}O_2P_3RuS_2$: C, 57.8; H, 5.5%). Mull i.r. spectrum: ν(CO) at 1 575 and 1 540, ν(CS) at 960 and 930 cm^{-1}.

The same complex was also prepared by refluxing [$Ru(SOCPh)_2(PMe_2Ph)_2$] (0.10 g) in ethanol with PMe_2Ph (0.10 g) for 2 h, filtering, reducing the volume, and cooling.

Facial isomer. The compound *cis*-[$RuCl_2(PMe_2Ph)_4$] (0.10 g) was shaken in benzene (20 cm^3) with [NH_4][SOCPh] (0.10 g) at room temperature for 30 min. The solution was filtered and the volume reduced, then after standing for 3 h the yellow *product* was filtered off (0.07 g, 68%), m.p. 156—159 °C (Found: C, 57.1; H, 5.8. Calc. for $C_{38}H_{43}O_2P_3RuS_2$: C, 57.8; H, 5.5%). Mull i.r. spectrum: ν(CO) at 1 585 and 1 550, ν(CS) at 965 and 932 cm^{-1}. The complex was converted into the meridional isomer (5b) on refluxing in ethanol for 1 h.

Tetrakis(*dimethylphenylphosphine*)(*monothiobenzoato*)-*ruthenium*(II) *Tetraphenylborate.*—The compound *cis*-[$RuCl_2(PMe_2Ph)_4$] (0.10 g) was shaken in methanol (20 cm^3) with [NH_4][SCOPh] (0.10 g) for 30 min at room temperature, then Na[BPh_4] (0.05 g) was added and the solution allowed to stand for 4 h, when the pale yellow *product* was filtered off (0.08 g, 57%), m.p. 160—163 °C (Found: C, 68.1; H, 6.2. Calc. for $C_{63}H_{69}BOP_4RuS$: C, 68.2; H, 6.2%). Mull i.r. spectrum: ν(CO) at 1 490, ν(CS) at 956 cm^{-1}.

Tris(*methyldiphenylphosphine*)*bis*(*monothiobenzoato*)-*ruthenium*(II) (*Meridional Isomers*).—The compound *trans*-[$RuCl_2(PMePh_2)_4$] (0.10 g) was refluxed in ethanol (50 cm^3) with [NH_4][SCOPh] (0.10 g) for 2 h. The solution was filtered hot and the volume was reduced. On cooling, the orange *product* was filtered off (0.08 g, 81%), m.p. 98—100 °C (Found: C, 65.2; H, 5.1. Calc. for $C_{53}H_{49}O_2P_3RuS_2$: C, 65.2; H, 5.0%). Mull i.r. spectrum: ν(CO) at 1 550 and 1 480, ν(CS) at 960 and 925 cm^{-1}. N.m.r. studies (Tables 1 and 2) show that a small amount of *cis*-[$Ru(SOCPh)_2(PMePh_2)_2$] is also present.

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