Metal Complexes of Sulphur Ligands. Part 20.[1] Reaction of Bis(dimethylphenylphosphine)bis(monothiobenzoato)ruthenium(II) with some Bidentate Nitrogen-donor Lewis Bases and *X*-Ray Structural Analyses on Two Isomers of Bis(dimethylphenylphosphine)bis(monothiobenzoato)(1,10-phenanthroline)ruthenium(II)

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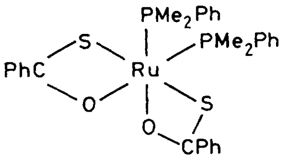
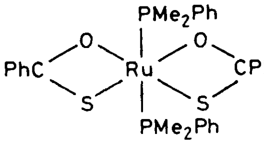
Reaction of [Ru(SOCPh)$_2$(PMe$_2$Ph)$_2$] (1) with ethylenediamine (en) in ethanol (1 : 1 molar ratio) gives [Ru(SOCPh)$_2$(en)(PMe$_2$Ph)$_2$] (3), shown by i.r., ^{1}H and ^{31}P-{^{1}H} n.m.r. studies to contain *trans* *S*-bonded $^-$SCOPh and *cis*-PMe$_2$Ph groups. Reaction of (1) with 2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen) also gives the six-co-ordinate [Ru(SOCPh)$_2$(N–N)(PMe$_2$Ph)$_2$] complexes but spectroscopic and *X*-ray analyses (for N–N = phen) reveal that the major product has the *cis,cis,cis* configuration (4). The crystals are monoclinic, space group $P2_1/c$, with a = 15.710(1), b = 13.729(2), c = 17.482(2) Å, and β = 90.79(1)°. A minor product shown by *X*-ray analysis to be *cis,cis,trans*-[Ru(SOCPh)$_2$(phen)(PMe$_2$Ph)$_2$] (5) is also formed. The crystals are monoclinic, space group $P2_1/c$, with a = 16.896(4), b = 10.754(2), c = 21.332(2) Å, and β = 94.92(1)°.

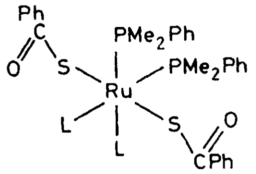
RECENTLY we reported that reaction of *mer*-[RuCl$_3$(PMe$_2$Ph)$_3$] with Na[SOCPh] in acetone or methanol gave the six-co-ordinate [Ru(SOCPh)$_2$(PMe$_2$Ph)$_2$] as a mixture of *cis* (1a) and *trans* (1b) isomers. Reaction of this compound with various unidentate Lewis bases such as CO, NH$_3$, and NH$_2$Et produced monomeric complexes [Ru(SOCPh)$_2$L$_2$(PMe$_2$Ph)$_2$] (2) suggesting cleavage of the Ru–O bonds in the major isomer (1a) of the starting material had occurred.[2] In this paper, the results of extending these reactions to bidentate nitrogen-donor bases such as ethylenediamine (en), 2,2′-bipyridyl (bipy), and 1,10-phenanthroline (phen) are described.



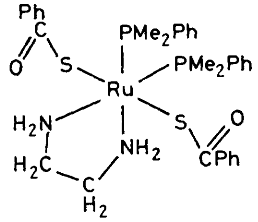
(1a)



(1b)



(2) L = CO, NH$_3$, or NH$_2$Et



(3)

RESULTS AND DISCUSSION

(*a*) *Reaction of* [Ru(SOCPh)$_2$(PMe$_2$Ph)$_2$] *with Ethylenediamine.*—When [Ru(SOCPh)$_2$(PMe$_2$Ph)$_2$] was reacted with a 1 : 1 molar ratio of ethylenediamine in ethanol a product was obtained which analysed for [Ru(SOCPh)$_2$(en)(PMe$_2$Ph)$_2$] (3) and, as expected, its i.r. spectrum, with ν(CS) at 930 cm^{-1}, indicated that the monothiobenzoate groups were bound through sulphur only.[3] However, ν(CO) at 1 515 cm^{-1} is lower than might be expected, an observation which seems to be characteristic of $^-$SOCPh complexes when there is scope for hydrogen bonding of the unco-ordinated oxygen to neighbouring ligands or cocrystallised solvent molecules; in this case the co-ordinated primary amine groups {*cf.* [Ru(SOCPh)$_2$(NH$_2$Et)$_2$(PMe$_2$Ph)$_2$], ν(CO) at 1 525 cm^{-1}; [Ru(SOCPh)$_2${HNC(Me)CH$_2$CMe$_2$NH$_2$}(PMe$_2$Ph)$_2$], ν(CO) at 1 530 cm^{-1} (ref. 2)}.

In the ^{1}H n.m.r. spectrum of (3) (see Table 1) a ' pseudo-triplet ' † is observed at δ 1.69 p.p.m. and this pattern is preserved unchanged at lower temperatures, indicating, as for the [Ru(SCOPh)$_2$L$_2$(PMe$_2$Ph)$_2$] complexes discussed earlier,[2] that (3) contains a plane of symmetry which makes the methyl groups on each phosphine magnetically equivalent at all temperatures. The pseudo-triplet decouples when irradiated at a frequency

TABLE 1

Hydrogen-1 n.m.r. data in CDCl$_3$ at 300 K for some ruthenium(II) monothiobenzoate complexes containing bidentate nitrogen-donor Lewis bases

	δ ±0.01 p.p.m.[a]	
Complex	Methyl of phosphine	Other ligand resonances
[Ru(SOCPh)$_2$(en)(PMe$_2$Ph)$_2$]	1.69 (pt)	7.00—7.60 [b]
[Ru(SOCPh)$_2$(bipy)(PMe$_2$Ph)$_2$]	1.37 (d), 1.38 (d), 1.98 (d), 2.04 (d)	7.00—7.50 [b] 7.76 (m), 8.02 (m), 8.32 (m), 8.56 (d), 9.50 (d) [c]
[Ru(SOCPh)$_2$(phen)(PMe$_2$Ph)$_2$]	1.25 (d), 1.34 (d), 1.50 (t), 2.06 (d), 2.14 (d)	7.00—7.50,[b] 7.96 (m), 8.05 (m), 8.37 (m), 8.89 (m), 9.75 (m) [d]

[a] d = Doublet, t = triplet, pt = pseudo-triplet, and m = multiplet. [b] Phenyl resonances. [c] Protons of 2,2′-bipyridyl; for assignments see Figure 1(*b*). [d] Protons of 1,10-phenanthroline; for assignments see Figure 2(*b*).

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† A ' pseudo-triplet ' pattern consists of a sharp doublet with a broad hump of comparable intensity situated between the components of the doublet and signifies a relatively large J(PP′) compared to the $|J(\text{PH}) + J(\text{PH}')|$ value.

equivalent to a ^{31}P chemical shift of *ca.* 26 p.p.m., in agreement with the ^{31}P-{^{1}H} n.m.r. spectrum of (**3**) which consists of a singlet at δ 21.7 p.p.m. Thus, the spectroscopic properties of (**3**) are similar to those of the unidentate Lewis-base adducts discussed earlier [2] and it can be assigned an analogous structure.

(*b*) *Reaction of* [$Ru(SOCPh)_2(PMe_2Ph)_2$] *with* 2,2′-*Bipyridyl and* 1,10-*Phenanthroline*.—When [$Ru(SOCPh)_2(PMe_2Ph)_2$] was treated in 1 : 1 molar ratio with L_2 = 2,2′-bipyridyl or 1,10-phenanthroline, products analysing for [$Ru(SOCPh)_2(L_2)(PMe_2Ph)_2$] were obtained as dark red crystals. Examination of the i.r. spectra indicated that, in each case, the $^{-}SOCPh$ groups were co-ordinated in unidentate fashion through sulphur. Since these bidentate ligands both form five-membered rings on co-ordination, and the aromaticity of the 1,10-phenanthroline molecule will in any case constrain it to remain planar, the familiar temperature-independent ' pseudo-triplet ' pattern was anticipated in the ^{1}H n.m.r. spectra. However, the spectra obtained for both species (Table 1) exhibited four doublets in the methyl region indicative of inequivalent methyl groups on *cis*-bonded phosphines. In the case of [$Ru(SOCPh)_2(bipy)(PMe_2Ph)_2$] the four doublets all have *J*(PH) = 8.0 Hz and all decouple when irradiated at a frequency equivalent to a ^{31}P chemical shift of *ca.* 12 p.p.m. In the ^{31}P-{^{1}H} n.m.r. spectrum a singlet is observed at δ 14.0 p.p.m. (300 K) which shifts to 15.3 p.p.m. (223 K) with no sign of splitting into more than one resonance. In the ^{1}H n.m.r. spectrum of [$Ru(SOCPh)_2(phen)(PMe_2Ph)_2$] four doublets appear at δ 1.25, 1.34 p.p.m. [*J*(PH) = 9.0 Hz] and at δ 2.06, 2.14 p.p.m. [*J*(PH) = 8.0 Hz] and there is a small virtually coupled 1 : 2 : 1 triplet at δ 1.50 p.p.m. The doublets are attributed to the methyl groups on *cis*-bonded phosphines and all decouple at a ^{31}P chemical shift of *ca.* 13 p.p.m. The 1 : 2 : 1 triplet is attributed to a species containing *trans* phosphines, and decouples at a ^{31}P chemical shift of *ca.* 6 p.p.m. In the ^{31}P-{^{1}H} n.m.r. spectrum an AB pattern centred at δ 12.9 p.p.m. is observed, which clearly arises from the complex containing inequivalent *cis* phosphines, and a singlet appears at δ 5.7 p.p.m. arising from the *trans*-phosphine species.

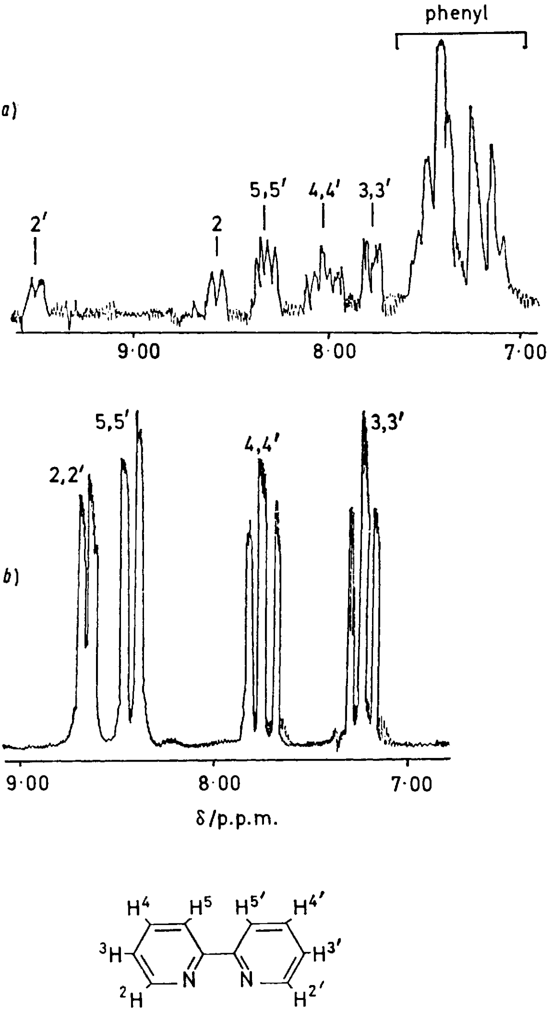


FIGURE 1 Hydrogen-1 n.m.r. spectrum in $CDCl_3$ at 300 K of (*a*) [$Ru(SOCPh)_2(bipy)(PMe_2Ph)_2$] and (*b*) 2,2′-bipyridyl

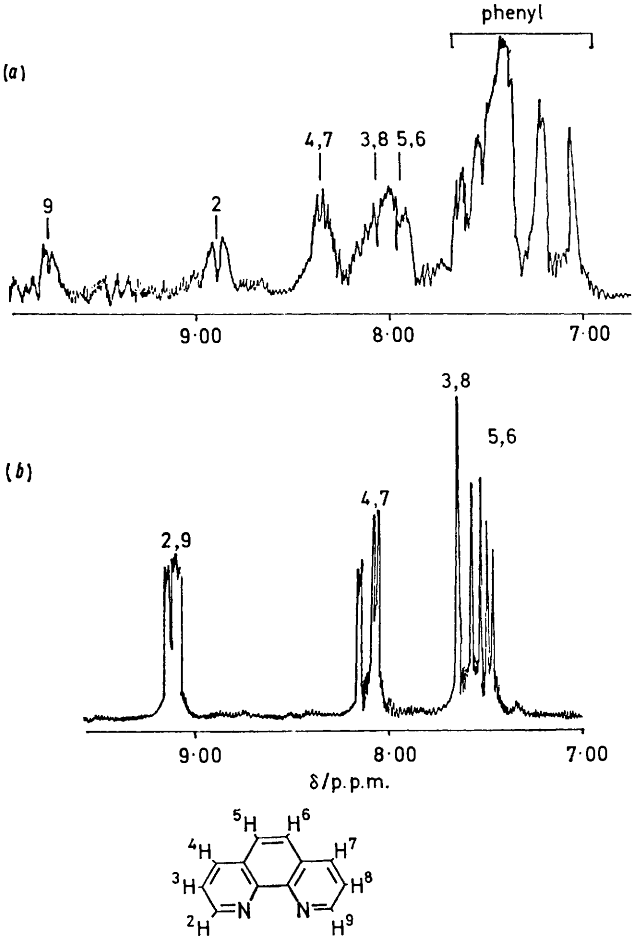
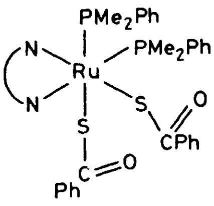
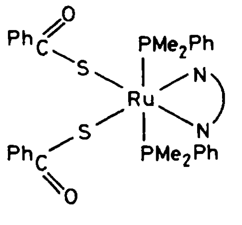


FIGURE 2 Hydrogen-1 n.m.r. spectrum in $CDCl_3$ at 300 K of (*a*) [$Ru(SOCPh)_2(phen)(PMe_2Ph)_2$] and (*b*) 1,10-phenanthroline

In the aromatic region of the ^{1}H n.m.r. spectra of the two complexes, resonances arising from the phenyl rings on the phosphines and the monothiobenzoate groups are superimposed between δ 7.00 and 7.60 p.p.m. Resonances from the 2,2′-bipyridyl and 1,10-phenanthroline ligands are also observed, and in each case the protons on the α-carbon atoms have become inequivalent (Table 1 and Figures 1 and 2). Unco-ordinated or symmetrically co-ordinated 2,2′-bipyridyl and 1,10-phenanthroline each shows four resonances arising from four pairs of symmetry-related protons [Figures 1(*b*) and 2(*b*) respectively]. However, when co-ordinated in an unsymmetrical environment, the symmetry is partially broken and the 2 and 2′ protons in the bipyridyl, or the 2 and 9 protons in the phenanthroline, become inequivalent and give rise to separate resonances [Figures 1(*a*) and 2(*a*) respectively]. This behaviour has been observed in some tin[4] and ruthenium[5] complexes where the effect has been attributed to the influence of bulky neighbouring groups. In this instance, the inequivalence of the *cis* phosphines in the *principal* isomer of [Ru(SOCPh)$_2$(phen)(PMe$_2$Ph)$_2$] suggests that, in the phenanthroline adduct at least, the effect is due to actual inequivalence of the co-ordinated nitrogens and taken together with the rest of the spectroscopic evidence indicates that these bulkier bidentate ligands form adducts of an unexpected stereochemistry containing inequivalent *cis*-bonded phosphines in the major species (4).



(4)



(5)

N-N = bipy or phen

The apparent equivalence of the phosphines in the ^{31}P-{^{1}H} n.m.r. spectrum of [Ru(SOCPh)$_2$(bipy)(PMe$_2$Ph)$_2$] must be ascribed to *accidental* coincidence of the chemical shifts of the phosphorus *trans* to sulphur and that *trans* to nitrogen. The inequivalence of the phosphine methyl groups and of the α-protons in the bipyridyl ligand give ample evidence that the anticipated structure containing *cis* phosphines, both *trans* to nitrogen, is not present. A minor species of [Ru(SOCPh)$_2$(phen)(PMe$_2$Ph)$_2$] (5) containing *trans* phosphines gives rise to the triplet in the ^{1}H n.m.r. and the singlet in the ^{31}P n.m.r. spectra.

The *cis* stereochemistry proposed above for (4) and the co-ordination of the *trans* isomer (5) have both been confirmed by *X*-ray structure determinations carried out on crystals of [Ru(SOCPh)$_2$(phen)(PMe$_2$Ph)$_2$]. The two isomers crystallised separately on cooling the reaction mixture, and examples of each suitable for data collection were selected and their structures solved.

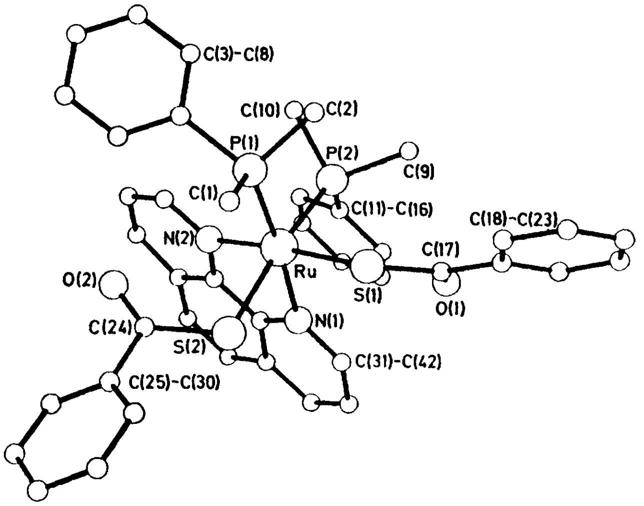


FIGURE 3 Molecular structure of *cis,cis,cis*-[Ru(SOCPh)$_2$(phen)(PMe$_2$Ph)$_2$] (4)

(*c*) *Crystal Structures of cis,cis,cis- and cis,cis,trans-*[Ru(SOCPh)$_2$(phen)(PMe$_2$Ph)$_2$].—Crystal data for both compounds are summarised in Table 2, final positional parameters for non-hydrogen atoms in Table 3, selected bond lengths and angles in Table 4, and perspective views in Figures 3 and 4. In both cases, the co-ordination of the ruthenium atom is distorted from octahedral by the narrow bite of the chelated 1,10-phenanthroline ligand. The *trans* influence of the tertiary phosphine groups is marked, as it is in the comparable *trans,cis,cis*-[Ru(SOCPh)$_2${HNC(Me)CH$_2$CMe$_2$NH$_2$}(PMe$_2$Ph)$_2$][2] (6). Over the three compounds, the mean distances *trans*

TABLE 2

Crystal data for (4) and (5)

Molecular formula	$C_{42}H_{40}N_2O_2P_2RuS_2$	$C_{42}H_{40}N_2O_2P_2RuS_2$
Space group	$P2_1/c$	$P2_1/c$
a/Å	15.710(1)	16.896(4)
b/Å	13.729(2)	10.754(2)
c/Å	17.482(2)	21.332(2)
β/°	90.79(1)	94.92(1)
U/Å^3	3 770	3 862
D_m/g cm^{-3}	1.451	1.423
D_c/g cm^{-3}	1.465	1.431
μ(Mo-K_α)/cm^{-1}	6.4	6.3
Independent observations	2 782	2 896
R	0.049	0.061

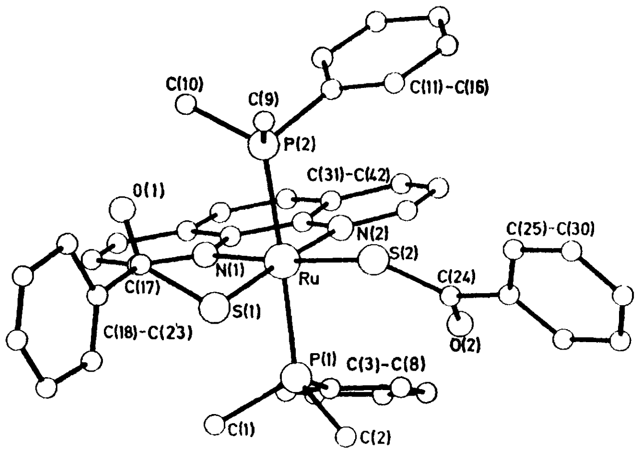


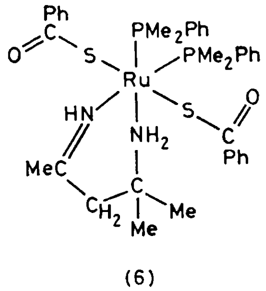
FIGURE 4 Molecular structure of *cis,cis,trans*-[Ru(SOCPh)$_2$(phen)(PMe$_2$Ph)$_2$] (5)

TABLE 3

Fractional co-ordinates for (4) and (5)

		(4)			(5)		
		10^4x	10^4y	10^4z	10^4x	10^4y	10^4z
Ru		2 238(1)	2 276(1)	815(1)	2 164(1)	2 562(1)	2 898(1)
P(1)		3 487(2)	1 849(2)	1 485(1)	2 355(2)	386(3)	2 776(1)
C(1)	methyl	4 398(7)	1 600(8)	867(6)	1 428(7)	−478(12)	2 637(6)
C(2)	methyl	3 966(6)	2 799(9)	2 075(6)	2 826(8)	−548(13)	3 413(6)
C(3)	phenyl	3 574(6)	788(7)	2 132(5)	2 879(6)	−27(10)	2 087(5)
C(4)		3 644(7)	−134(8)	1 849(6)	3 697(6)	−34(11)	2 122(5)
C(5)		3 711(7)	−945(8)	2 334(6)	4 096(7)	−295(12)	1 589(6)
C(6)		3 702(7)	−817(9)	3 115(7)	3 683(8)	−467(13)	1 037(6)
C(7)		3 622(8)	92(9)	3 402(7)	2 900(9)	−435(14)	979(7)
C(8)		3 556(6)	906(8)	2 927(6)	2 466(8)	−217(12)	1 510(6)
P(2)		1 646(2)	3 089(2)	1 852(1)	1 925(2)	4 722(3)	2 967(1)
C(9)	methyl	1 968(7)	4 301(8)	2 161(6)	1 792(7)	5 371(12)	3 743(6)
C(10)	methyl	1 719(6)	2 462(8)	2 764(6)	1 101(7)	5 365(12)	2 467(6)
C(11)	phenyl	491(6)	3 225(7)	1 737(5)	2 762(6)	5 637(10)	2 716(5)
C(12)		−76(6)	2 553(7)	2 055(5)	3 421(7)	5 838(11)	3 128(5)
C(13)		−939(6)	2 591(6)	1 892(6)	4 082(8)	6 437(13)	2 913(6)
C(14)		−1 263(7)	3 295(8)	1 416(6)	4 093(8)	6 778(12)	2 304(6)
C(15)		−730(7)	3 961(8)	1 092(6)	3 431(8)	6 608(12)	1 898(6)
C(16)		134(6)	3 943(7)	1 247(6)	2 765(7)	6 036(11)	2 103(6)
S(1)		3 091(2)	3 620(2)	402(1)	1 238(2)	1 948(3)	3 635(1)
C(17)		2 612(6)	4 765(7)	449(5)	372(7)	2 778(11)	3 626(5)
O(1)		1 831(4)	4 898(5)	479(4)	210(6)	3 702(10)	3 308(5)
C(18)	phenyl	3 193(6)	5 637(7)	442(5)	−219(7)	2 363(14)	4 091(6)
C(19)		2 824(7)	6 544(8)	417(6)	−626(10)	3 397(17)	4 362(8)
C(20)		3 315(7)	7 384(9)	452(7)	−1 223(13)	2 957(22)	4 804(10)
C(21)		4 181(7)	7 309(9)	510(7)	−1 299(14)	1 805(25)	4 853(11)
C(22)		4 544(7)	6 437(8)	533(6)	−921(14)	871(23)	4 702(11)
C(23)		4 066(6)	5 568(8)	515(6)	−310(10)	1 207(17)	4 245(8)
S(2)		2 760(2)	1 547(2)	−369(1)	3 062(2)	2 802(3)	3 822(1)
C(24)		2 914(5)	291(6)	−333(5)	3 971(6)	2 092(10)	3 806(5)
O(2)		2 740(4)	−221(5)	217(4)	4 168(4)	1 447(8)	3 360(4)
C(25)	phenyl	3 251(6)	−161(7)	−1 053(5)	4 562(6)	2 247(10)	4 361(4)
C(26)		2 928(6)	−1 060(7)	−1 273(5)	4 535(6)	3 199(10)	4 804(5)
C(27)		3 200(7)	−1 514(8)	−1 904(6)	5 121(7)	3 281(11)	5 299(5)
C(28)		3 787(7)	−1 062(8)	−2 293(6)	5 718(6)	2 456(13)	5 360(5)
C(29)		4 131(7)	−184(8)	−2 174(6)	5 763(8)	1 508(14)	4 941(7)
C(30)		3 851(6)	277(7)	−1 513(5)	5 184(7)	1 423(12)	4 436(6)
N(1)		1 161(4)	2 572(5)	108(4)	1 409(4)	2 481(9)	2 074(4)
N(2)		1 408(4)	1 124(6)	1 104(4)	2 963(4)	2 950(7)	2 227(4)
C(31)		1 066(5)	3 272(7)	−415(5)	629(6)	2 307(11)	2 009(5)
C(32)		305(7)	3 401(8)	−836(6)	194(7)	2 263(12)	1 416(6)
C(33)		−367(6)	2 785(8)	−716(6)	590(7)	2 397(14)	892(6)
C(34)		−291(6)	2 026(7)	−185(6)	1 399(6)	2 601(12)	924(5)
C(35)		−955(7)	1 350(8)	−1(6)	1 883(7)	2 774(12)	406(5)
C(36)		−839(7)	644(8)	503(6)	2 643(7)	3 012(12)	488(6)
C(37)		−45(6)	529(7)	912(6)	3 054(6)	3 127(10)	1 089(5)
C(38)		115(7)	−181(8)	1 458(6)	3 854(6)	3 437(11)	1 208(5)
C(39)		882(7)	−255(8)	1 802(6)	4 180(6)	3 513(10)	1 813(5)
C(40)		1 524(6)	397(7)	1 605(6)	3 724(6)	3 256(10)	2 310(5)
C(41)		630(6)	1 176(7)	752(5)	2 629(6)	2 902(9)	1 622(4)
C(42)		510(6)	1 940(7)	222(5)	1 800(6)	2 655(10)	1 537(4)

to phosphorus are Ru–P 2.372 and Ru–S 2.450, those *trans* to sulphur are Ru–P 2.333 and Ru–S 2.402, and those *trans* to N are Ru–P 2.315 and Ru–S 2.400 Å.



(6)

The 1,10-phenanthroline ligands are essentially planar, the root-mean-square (r.m.s.) deviations of the atoms from a plane being 0.02 Å in (4) and 0.04 Å in (5). In both cases, the ruthenium atom lies 0.14 Å out of this plane. The conformations of the unidentate monothiobenzoate groups show considerable variations over (4), (5), and (6). The variations may be expressed in terms of the Ru–S–C–O torsion angles and the angles between the planes of the S–C–O and phenyl groups. The interplanar angles vary between 7 and 37°, and the magnitudes of the torsion angles between 2 and 20°. There does not appear to be any correlation between values, and the ruthenium atom may be either closer to or further from the plane of the phenyl ring than is the sulphur atom.

The formation of *cis,cis,trans*-$[Ru(SOCPh)_2(phen)(PMe_2Ph)_2]$ (5) from the *trans*-phosphine isomer (1b) of $[Ru(SOCPh)_2(PMe_2Ph)_2]$ is possible by a simple Ru–O bond-rupture mechanism without further rearrangement; thus the minor isomer of the product can be formed from the minor isomer of the starting material. The *cis,cis,cis*

TABLE 4

Selected bond distances and angles for (4) and (5)

Atoms	(4)	(5)
	Distance/Å	
Ru–P(1)	2.346(2)	2.380(3)
Ru–P(2)	2.333(2)	2.365(3)
Ru–S(1)	2.399(2)	2.404(3)
Ru–S(2)	2.450(3)	2.398(2)
Ru–N(1)	2.122(7)	2.082(7)
Ru–N(2)	2.114(8)	2.091(8)
P(1)–C(1)	1.836(11)	1.823(13)
P(1)–C(2)	1.819(11)	1.819(13)
P(1)–C(3)	1.848(10)	1.833(12)
P(2)–C(9)	1.820(11)	1.827(13)
P(2)–C(10)	1.813(10)	1.818(12)
P(2)–C(11)	1.832(9)	1.840(12)
S(1)–C(17)	1.744(9)	1.712(12)
C(17)–O(1)	1.244(12)	1.22(2)
C(17)–C(18)	1.505(13)	1.52(2)
S(2)–C(24)	1.743(9)	1.717(11)
C(24)–O(2)	1.225(11)	1.246(13)
C(24)–C(25)	1.506(12)	1.491(13)
	Angle/°	
P(1)–Ru–P(2)	94.1(1)	176.8(4)
P(1)–Ru–S(1)	82.8(1)	84.4(1)
P(1)–Ru–S(2)	91.8(1)	96.5(1)
P(1)–Ru–N(1)	173.7(2)	86.9(3)
P(1)–Ru–N(2)	102.0(2)	91.1(2)
P(2)–Ru–S(1)	95.5(1)	96.0(1)
P(2)–Ru–S(2)	173.4(2)	86.6(1)
P(2)–Ru–N(1)	92.2(2)	90.0(3)
P(2)–Ru–N(2)	85.3(2)	88.3(2)
S(1)–Ru–S(2)	82.2(1)	83.8(1)
S(1)–Ru–N(1)	97.0(2)	98.9(2)
S(1)–Ru–N(2)	175.0(4)	175.4(4)
S(2)–Ru–N(1)	81.9(2)	175.8(4)
S(2)–Ru–N(2)	96.4(2)	98.1(2)
N(1)–Ru–N(2)	78.1(3)	79.4(3)
Ru–S(1)–C(17)	115.8(3)	116.9(4)
Ru–S(2)–C(24)	114.9(3)	116.1(4)
S(1)–C(17)–O(1)	124.1(7)	125.5(10)
S(2)–C(24)–O(2)	124.6(7)	124.1(8)

isomer is presumably formed from the major *cis*-phosphine isomer (1a) of the starting material, but since simple rupture of the Ru–O bonds would give the isomer of type (3) with *trans* $^{-}$SOCPh groups, and equivalent *cis* phosphines {*cf.* [Ru(SOCPh)$_2$(en)(PMe$_2$Ph)$_2$]}, a rearrangement has clearly taken place. Examination of a molecular model for a structure of type (3) shows that there are severe steric problems in accommodating two PMe$_2$Ph groups in the same plane as a chelated 2,2′-bipyridyl or 1,10-phenanthroline ligand. The problem is less severe when one of the PMe$_2$Ph groups changes places with a $^{-}$SOCPh group but, even so, the $^{-}$SOCPh group is twisted away from its preferred co-ordination geometry. Thus, it seems that the *cis,cis,cis* isomer is more thermodynamically stable than the predicted *trans,cis,cis*-[Ru(SOCPh)$_2$(N–N)(PMe$_2$Ph)$_2$] (3; N–N = bipy or phen) and it is probably produced by ready rearrangement of such an intermediate.

EXPERIMENTAL

Microanalyses were by the University of Edinburgh Chemistry Department. 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 HA-100 spectrometer equipped with a variable-temperature probe, and proton-noise-decoupled ^{31}P n.m.r. spectra on a Varian XL 100 spectrometer operating in the pulse and Fourier-transform modes at 40.5 MHz (^{31}P chemical shifts quoted in p.p.m. to high frequency of 85% H_3PO_4). Heteronuclear-decoupling experiments were carried out on the HA-100 spectrometer using a second radiofrequency field provided by the Schlumberger FS30 frequency synthesiser. Melting points were determined with a Köfler hot-stage microscope and are uncorrected.

Ruthenium(III) trichloride trihydrate (Johnson, Matthey Ltd.), dimethylphenylphosphine (Maybridge Chemical Company), monothiobenzoic acid (Aldrich), 2,2′-bipyridyl, and 1,10-phenanthroline (B.D.H.) were obtained as indicated. All the solutions were degassed before use and reactions were carried out under a nitrogen atmosphere.

Bis(dimethylphenylphosphine)(ethylenediamine)bis(monothiobenzoato)ruthenium(II).—The compound [Ru(SOCPh)$_2$(PMe$_2$Ph)$_2$] (0.10 g) was refluxed in ethanol (50 cm^3) with ethylenediamine (0.10 cm^3) for 1 h. The volume of the solution was reduced and the yellow-brown microcrystalline *product* was filtered off (0.08 g, 73%), m.p. 238—240 °C (Found: C, 53.4; H, 5.7; N, 4.0. Calc. for $C_{32}H_{40}N_2O_2P_2RuS_2$: C, 53.9; H, 5.6; N, 3.9%). Mull i.r. spectrum: ν(CO) at 1 515, ν(CS) at 930 cm^{-1}. ^{31}P-{^{1}H} n.m.r. spectrum in CDCl$_3$ at 300 K: δ 21.7(s) p.p.m.

2,2′-Bipyridylbis(dimethylphenylphosphine)bis(monothiobenzoato)ruthenium(II).—The compound [Ru(SOCPh)$_2$(PMe$_2$Ph)$_2$] (0.07 g) was refluxed in ethanol (30 cm^3) with 2,2′-bipyridyl (0.05 g) for 2 h. The volume of the solution was reduced and after standing for some hours the dark red crystalline *product* was filtered off (0.07 g, 82%), m.p. 182—185 °C (Found: C, 59.4; H, 5.0; N, 3.5. Calc. for $C_{40}H_{40}N_2O_2P_2RuS_2$: C, 59.5; H, 5.0; N, 3.5%). Mull i.r. spectrum: ν(CO) at 1 550 cm^{-1}, ν(CS) at 925 cm^{-1}. ^{31}P-{^{1}H} n.m.r. spectrum in CDCl$_3$: 300 K, δ 14.0(s) p.p.m.; 223 K, 15.3(s) p.p.m.

Bis(dimethylphenylphosphine)bis(monothiobenzoato)(1,10-phenanthroline)ruthenium(II).—The compound [Ru(SOCPh)$_2$(PMe$_2$Ph)$_2$] (0.05 g) was refluxed in ethanol with 1,10-phenanthroline hydrate (0.05 g) for 2 h. The volume of the solution was reduced, and after standing for some hours the dark red crystalline *product* was filtered off (0.06 g, 94%), m.p. 216—218 °C (Found: C, 60.4; H, 4.9; N, 3.5. Calc. for $C_{42}H_{42}N_2O_2P_2RuS_2$: C, 60.5; H, 4.8; N, 3.4%). Mull i.r. spectrum: ν(CO) at 1 550, ν(CS) at 927 cm^{-1}. ^{31}P-{^{1}H} n.m.r. spectrum in CDCl$_3$: at 300 K, δ 5.7(s), 12.9(q) [*J*(PP) 30.8 Hz, δ (PP) 47.5 Hz]; at 233 K, 12.6(q) p.p.m. [*J*(PP) 31.4 Hz, δ(PP) 88.1 Hz]. Parameters were obtained by refinement using the LAOCOON program.

Determination of the Crystal Structures of cis,cis,cis- *and* cis,cis,trans-[Ru(SOCPh)$_2$(phen)(PMe$_2$Ph)$_2$].—Data were collected on Enraf–Nonius diffractometers, using monochromatised Mo-K_α radiation ($\lambda = 0.710\,69$ Å). The crystals were small, having maximum dimension 0.3 mm, and no absorption corrections were applied. One unique set of data to $\theta = 22°$ was collected for each compound, and those reflections with $I \geqslant 3\sigma(I)$ were used for the solution and refinement of the structures. The structure of (4), in which the ruthenium atoms lie on fully general positions, was solved without difficulty by the heavy-atom technique. In the case of (5) it was not possible in the Patterson to distinguish between two possible positions for the ruthenium: 0.22, 0.25, 0.04, and the correct 0.22, 0.25, 0.29. In either case, the set of ruthenium atoms generated by the space-group symmetry make no significant contribution to reflections with $l = 2n + 1$. The incorrect solution was tried first, using the DIRDIF-A procedure[6] to assign probable phases to the $l = 2n + 1$ reflections. The resulting Fourier map gave sensible positions for the RuS_2P_2 moiety and for the entire 1,10-phenanthroline ligand, but no further progress could be made. The entire fragment was then shifted by 0.25 in z, when a difference Fourier revealed all other non-hydrogen atoms.

The Ru, S, and P atoms were refined anisotropically, while the O, N, and C atoms were restrained to be isotropic. In both structures most hydrogen atoms could be identified in a partially refined difference Fourier, and they were included in fixed idealised positions (C–H 1.1 Å, geometry trigonal or tetrahedral as appropriate, and $U = 0.05$ Å^2) for the last cycles of refinement. In both structures, reflections with $\sin\theta < 0.22$ were given weights of $(\sin\theta)/0.22$, and all other reflections were given unit weight. At the end of the refinement no parameter shift exceeded one standard deviation, and there was no substantial variation of $w\Delta F^2$ with $|F_o|$ or $\sin\theta$.

Calculations were made using the ' *X*-RAY '72 ' system[7] as implemented at the Edinburgh Regional Computing Centre. Observed and calculated structure factors, thermal parameters, and hydrogen-atom positions are deposited as Supplementary Publication No. SUP 22715 (34 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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