Metal Complexes of Sulphur Ligands. Part 16.[1] Reaction of *mer*-Trichlorotris(dimethylphenylphosphine)ruthenium and Dichlorotris(triphenylphosphine)ruthenium with Sodium and Ammonium Monothiobenzoates, and the Crystal and Molecular Structure of (4-Amino-2-imino-4-methylpentane)bis(dimethylphenylphosphine)bis(monothiobenzoato)ruthenium(II)

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Reaction of $[RuCl_2(PPh_3)_3]$ with an excess of Na[SOCPh] or $[NH_4]$[SOCPh] in either acetone or methanol and *mer*-$[RuCl_3(PMe_2Ph)_3]$ with Na[SOCPh] in acetone gives six-co-ordinate $[Ru(SOCPh)_2(PR_3)_2]$ [PR_3 = PPh_3 (1) or PMe_2Ph (2)] shown by i.r. and ^1H and ^{31}P n.m.r. studies to contain *trans*- and *cis*-PR_3 groups respectively. Support for these conclusions comes from the reactions of (1) and (2) with various Lewis bases which give $[Ru(SOCPh)_2(PR_3)_2L_2]$ [PR_3 = PPh_3, L = CO or NH_3 (3a); PR_3 = PMe_2Ph, L = CO, NH_3, or NH_2Et (3b)], shown by spectroscopic methods to have *trans*-*S*-bonded $[SOCPh]^-$ groups with *trans*-PPh_3, *trans*-L (3a), and *cis*-PMe_2Ph, *cis*-L (3b) groups respectively. In contrast, reaction of *mer*-$[RuCl_3(PMe_2Ph)_3]$ with excess of $[NH_4]$[SOCPh] in acetone gives a nitrogen-containing product (4) shown by *X*-ray analysis to be $[Ru(SOCPh)_2\{HNC(Me)CH_2CMe_2NH_2\}(PMe_2Ph)_2]$. The crystals are orthorhombic, space group $Pna2_1$ with a = 23.899(2), b = 11.163(1), and c = 13.889(3) Å. Finally, a mechanism of formation of (4) is suggested involving condensation of the diammine complex (3b) with mesityl oxide.

In Parts 5[2] and 6[3] of this series the reaction of various tertiary phosphine complexes of ruthenium(III) and ruthenium(II) with dithioacid ligands was reported to give the six-co-ordinate $[Ru(S\text{-}S)_2(PR_3)_2]$ ($S\text{-}S^-$ = $[S_2PR_2]^-$ or $[S_2CNR_2]^-$). Detailed variable-temperature ^1H n.m.r. studies indicated a *cis* configuration in most instances (mixture of enantiomers), and the rates of interconversion of these enantiomers were measured and a general mechanism of rearrangement deduced. Some reactions of these complexes with Lewis bases such as carbon monoxide were also examined.

We now report the results of the reaction of *mer*-$[RuCl_3(PMe_2Ph)_3]$ and $[RuCl_2(PPh_3)_3]$ with sodium and ammonium monothiobenzoates where, to our initial surprise, the nature of the cation sometimes plays an important role in determining the form of the reaction product. The reactions of the products with some unidentate Lewis bases were also examined.

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[1] Part 15, D. R. Robertson, and T. A. Stephenson, *J.C.S. Dalton*, 1978, 486.

[2] D. J. Cole-Hamilton and T. A. Stephenson, *J.C.S. Dalton*, 1974, 739.

[3] D. J. Cole-Hamilton and T. A. Stephenson, *J.C.S. Dalton*, 1974, 754.

RESULTS AND DISCUSSION

When $[RuCl_2(PPh_3)_3]$ was heated under reflux with an excess of Na[SOCPh] or $[NH_4]$[SOCPh] in either acetone or methanol solvent an orange-yellow non-conducting solid of composition $[Ru(SOCPh)_2(PPh_3)_2]$ (1) was isolated in 90% yield.* Similarly, reaction of *mer*-$[RuCl_3(PMe_2Ph)_3]$ at room temperature or under reflux in methanol with either $[NH_4]$[SOCPh] or Na[SOCPh] or in acetone with excess of Na[SOCPh] gave the reddish brown product $[Ru(SOCPh)_2(PMe_2Ph)_2]$ (2). These complexes were characterised by elemental analysis, and i.r. (Table 1), ^1H n.m.r. (Table 2), and ^{31}P n.m.r. spectroscopy, and their monomeric nature was established by mass spectroscopy and osmometric molecular-weight measurements in chloroform.

TABLE 1

Mull i.r. spectra of various monothiobenzoate complexes of ruthenium(II)

Compound	PhCOS vibrations (cm^{-1}) ν(CO)	PhCOS vibrations (cm^{-1}) ν(CS)	Other useful bands (cm^{-1})
Na[SOCPh]	1 500	960	
$[Ru(SOCPh)_2(PPh_3)_2]$	1 500	965	
$[Ru(SOCPh)_2(NH_3)_2$-$(PPh_3)_2]$	1 550 †	935	
$[Ru(SOCPh)_2(CO)_2$-$(PPh_3)_2]$	1 590, 1 570	935	1 950[ν(CO)]
$[Ru(SOCPh)_2(PMe_2Ph)_2]$	1 470	965	
$[Ru(SOCPh)_2(CO)_2$-$(PMe_2Ph)_2]$	1 600, 1 570	945	2 025, 2 005[ν(CO)]
$[Ru(SOCPh)_2(NH_2Et)_2$-$(PMe_2Ph)_2]$	1 525 †	935	
$[Ru(SOCPh)_2$-$\{HNC(Me)CH_2$-$CMe_2NH_2\}(PMe_2Ph)_2]$	1 530 †	935	3 350—3 000[$\nu(NH_2)$] 1 660[ν(CN)(imine)] 1 585[$\delta(NH_2)$]

† Low values of ν(CO) attributed to intramolecular hydrogen bonding between carbonyl groups and the amine group (see text).

TABLE 2

Hydrogen-1 n.m.r. data in $CDCl_3$ for some ruthenium(II) monothiobenzoate complexes

Complex	T/K	$\delta \pm 0.01$ p.p.m.[a] Methyl of phosphine	$\delta \pm 0.01$ p.p.m.[a] Other ligand resonances
$[Ru(SOCPh)_2(PMe_2Ph)_2]$	300	1.42(pt), 1.57(t)	7.00—8.00(m) [b]
	260	1.32(pt), 1.46(pt), 1.57(t)	
$[Ru(SOCPh)_2(NH_3)_2(PMe_2Ph)_2]$	300	1.75(pt)	7.00—8.00(m) [b]
$[Ru(SOCPh)_2(CO)_2(PMe_2Ph)_2]$	300	1.60(pt)	7.00—8.00(m) [b]
	260	1.60(pt)	
$[Ru(SOCPh)_2(NH_2Et)_2(PMe_2Ph)_2]$	300	1.74(pt)	7.00—8.30(m) [b]
$[Ru(SOCPh)_2\{HNC(Me)CH_2CMe_2NH_2\}(PMe_2Ph)_2]$	300	1.43(d), 1.86(d)	7.00—8.00)m),[d] 1.06(s),[d] 1.58(s),[d] 2.31(s),[d] 5.80(br) [e]
	250	1.03(d), 1.20(d), 1.95(t) [c]	

[a] s = Singlet, d = doublet, t = triplet, pt = pseudo-triplet, and m = multiplet. [b] Phenyl resonances. [c] Overlapping doublet of doublets. [d] *gem*-Methyls, imine-*C*-methyl, and methylene protons from $HNC(Me)CH_2CMe_2NH_2$ ligand. [e] NH_2 protons.

Identification of the positions of the C–O and C–S stretching frequencies in the i.r. spectra is the best way of determining the mode of bonding of the monothiobenzoate ligand. Earlier, Savant *et al.*[5] assigned these vibrations in Na[SOCPh] to the bands at 1 500 and 960 cm^{-1} respectively and then, by comparison with these values, elucidated the mode of bonding in a series of metal monothiobenzoate complexes. Thus, for bidentate co-ordination both ν(CO) and ν(CS) remain almost unaffected but, as the interaction through sulphur becomes more important than that through oxygen, ν(CS) decreases and ν(CO) increases. Hence, examination of Table 1 clearly shows that only bidentate $[SOCPh]^-$ co-ordination is present in complexes (1) and (2).

Although the ^1H n.m.r. spectrum of (1) is of no use for obtaining structural information, the ^{31}P-$\{^1H\}$ spectrum (singlet at δ 59.9 p.p.m.) indicates that only a single isomer which contains magnetically equivalent phosphines is formed. The ^1H n.m.r. spectrum of complex (2) in $CDCl_3$ at 300 K (methyl region) consists of a strong 'pseudo-triplet' † at δ 1.42 p.p.m. and a much weaker 'virtually coupled' triplet at 1.57 p.p.m. By comparison with earlier studies,[2,6] these patterns are indicative of the presence of two isomers containing *cis*- and *trans*-PMe_2Ph groups respectively. Furthermore, phosphorus-31 decoupling studies confirm that these two signals arise from different species, and in keeping with this the ^{31}P-$\{^1H\}$ n.m.r. spectrum of (2) at 303 K consists of a strong resonance at δ 39.0 p.p.m. and a very weak signal at 4.6 p.p.m.

Variable-temperature ^1H n.m.r. studies on (2) reveal that at lower temperatures the 'pseudo-triplet' signal broadens and at 260 K the spectrum consists of two 'pseudo-triplets' centred at δ 1.32 and 1.46 p.p.m. This behaviour, which is concentration-independent and

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* The analogous $[Ru(SOCMe)_2(PPh_3)_2]$ has been very briefly reported elsewhere.[4]

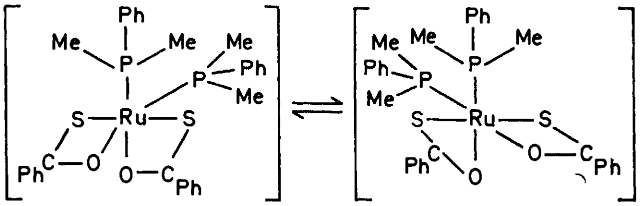
† A 'pseudo-triplet' pattern consists of a sharp doublet with a broad hump of comparable intensity situated between the doublet, and signifies a relatively large $J(PP')$ compared to the $|J(PH) + J(PH')|$ value {*cf.*[2] *cis*-$[Ru(S_2PMe_2)_2(PMe_2Ph)_2]$}.

[4] J. D. Gilbert and G. Wilkinson, *J. Chem. Soc.* (*A*), 1969, 1749.

[5] V. V. Savant, J. Gopalakrishnan, and C. C. Patel, *Inorg. Chem.*, 1970, **9**, 748.

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

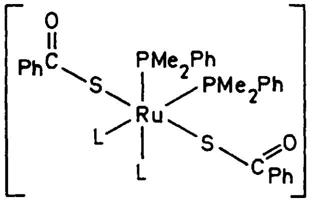
reversible with temperature, is analogous to that observed earlier for [M(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$] (M = Ru [2,3] or Os [7]) and is likewise attributed to rapid interconversion on the n.m.r. time scale of two optical isomers of (2) * [see equation (1)]. As expected for an isomer containing *trans*-PMe$_2$Ph groups, there is no apparent change in the shape of the ' virtually coupled ' triplet at δ 1.57 p.p.m. on changing the temperature.



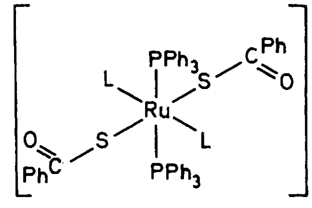
(1)

Further information about the detailed structures of complexes (1) and (2) has been obtained from an examination of their reactions with carbon monoxide. Thus, reaction with carbon monoxide gave lemon-yellow and pale cream products respectively which both analysed for [Ru(SOCPh)$_2$L$_2$(PR$_3$)$_2$] [L = CO; PR$_3$ = PPh$_3$ (3a) or PMe$_2$Ph (3b)]. The Nujol i.r. spectra of both these complexes revealed that an increase in the ν(CO) (SOCPh) and a decrease in the ν(CS) band positions, compared to those of (1) and (2), had occurred (Table 1) indicative of unidentate co-ordination of the [SOCPh]$^-$ groups through sulphur in both cases. However, the i.r. spectrum of (3a) contained only a single terminal ν(CO) absorption band at 1 950 cm^{-1} whereas that of (3b) had two ν(CO) bands at 2 025 and 2 005 cm^{-1} suggesting *trans* and *cis* carbonyl-group arrangements respectively.

The ^{1}H n.m.r. spectrum of (3b; L = CO) in CDCl$_3$ (methyl region) at 240—300 K exhibited a single ' pseudo-triplet ' pattern at δ 1.60 p.p.m. and the ^{31}P-{^{1}H} n.m.r. spectrum at 303 K contained a singlet at −10.8 p.p.m. This large change in ^{31}P n.m.r. chemical shift on going from (2) to (3b) suggests that substitution of the carbonyl groups occurs *trans* to the PMe$_2$Ph groups. Therefore, this n.m.r. and i.r. evidence indicates that complex (3b; L = CO) has a structure containing *cis*-carbonyls, *cis*-PMe$_2$Ph, and *trans*-*S*-bonded [SOCPh]$^-$ groups. This is consistent with the geometrical isomer postulated earlier for the major isomer of complex (2) [equation (1)] and with the expected most ready point of cleavage in (2), *viz*. the Ru–O rather than the Ru–S bonds.



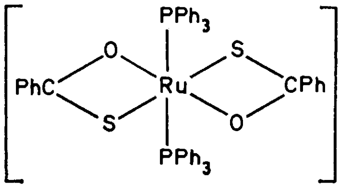
(3b) L = CO, NH$_3$, or NH$_2$Et



(3a) L = CO or NH$_3$

The ^{31}P-{^{1}H} n.m.r. spectrum of complex (3a; L = CO) consists of a singlet at δ 42.8 p.p.m. The relatively small change in ^{31}P n.m.r. chemical shifts on going from (1) to (3a) (L = CO) together with the i.r. data given above is consistent with a structure containing *trans*-carbonyls, *trans*-PPh$_3$, and *trans*-*S*-bonded [SOCPh]$^-$ groups. In support of this conclusion, the reaction of all-*trans*-[RuCl$_2$(CO)$_2$(PPh$_3$)$_2$] [8] and [NH$_4$][SOCPh] in acetone under reflux also gave a high yield of complex (3a; L = CO).

Therefore, this evidence strongly suggests that complex (1) has a structure with *trans*-PPh$_3$ groups {*cf*. the minor isomer of [Ru(SOCPh)$_2$(PMe$_2$Ph)$_2$]}. Presumably, the larger size of the PPh$_3$ groups facilitating formation of *trans* rather than *cis* isomers, allied with the high *trans* effect of PMe$_2$Ph groups favouring a *cis* rather than a *trans* configuration, is the main reason for this difference in stereochemistry between complexes (1) and (2).



(1)

Further support for this conclusion is that reaction of (1) with gaseous ammonia gives a yellow solid of composition [Ru(SOCPh)$_2$(NH$_3$)$_2$(PPh$_3$)$_2$]. Again, i.r. studies indicate the presence of unidentate *S*-bonded [SOCPh]$^-$ groups (Table 1) and the ^{31}P-{^{1}H} n.m.r. spectrum shows a singlet at δ 46.3 p.p.m. consistent with structure (3a; L = NH$_3$). In contrast, reaction of complex (2) with ammonia yields a product *in situ* whose ^{1}H n.m.r. spectrum in CDCl$_3$ exhibits a ' pseudo-triplet ' at δ 1.75 p.p.m. and whose ^{31}P-{^{1}H} n.m.r. spectrum contains a singlet at 23.7 p.p.m. Unfortunately, attempts to isolate a solid product in the latter case were unsuccessful although with NH$_2$Et, complex (2) gave the yellow-brown solid [Ru(SOCPh)$_2$(NH$_2$Et)$_2$(PMe$_2$Ph)$_2$] whose ^{1}H and ^{31}P n.m.r. spectra were also consistent with structure (3b; L = NH$_2$Et). Thus, the low sensitivity of the position of the ^{31}P n.m.r. resonance signals to a change in Lewis base for the PPh$_3$ compared to the PMe$_2$Ph complexes adds further support to the structural assignments made above.

Unlike the reactions of [RuCl$_2$(PPh$_3$)$_3$] with either [NH$_4$][SOCPh] or Na[SOCPh] in methanol or acetone which yielded the same product (1), the reaction of *mer*-[RuCl$_3$(PMe$_2$Ph)$_3$] with [NH$_4$][SOCPh] in acetone, either

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* Unlike [M(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$], two geometrical (and hence four optical) isomers containing magnetically equivalent *cis*-PMe$_2$Ph groups are possible here. However, the major isomer of complex (2) is assigned a structure with oxygens rather than sulphur atoms *trans* to PMe$_2$Ph groups, on the basis of its reaction with various Lewis bases (see later).

[7] D. J. Cole-Hamilton and T. A. Stephenson, *J.C.S. Dalton*, 1976, 2396.

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

at ambient temperature or under reflux, did not give (2) but, instead, an orange-brown non-conducting solid (4) containing 3.3% nitrogen. The i.r. spectrum of (4) showed a *small* increase in the position of the band assigned to ν(CO) (1 530 cm^{-1}) and a decrease in that for ν(CS) (935 cm^{-1}), compared to the values for complex (2), which again suggests the presence of unidentate *S*-bonded $[SOCPh]^-$ groups. The mass spectrum of (4), like that of (2), shows a strong peak at *m/e* 652 (^{102}Ru isotope) corresponding to $[Ru(SOCPh)_2(PMe_2Ph)_2]^+$ and the same fragmentation pattern for *m/e* values >100 which correspond to loss and subsequent breakdown of $[SOCPh]^-$ and PMe_2Ph groups. However, a number of extra peaks compared to (2) appear at *m/e* 97, 58, 42, and 15.

The ^1H n.m.r. spectrum of (4) is quite different to (2) comprising, at 300 K in $CDCl_3$, for δ values <5 p.p.m., two doublets [*J*(PH) 8.0 Hz] centred at 1.86 and 1.43 p.p.m. and three singlets at 2.31, 1.58, and 1.06 p.p.m. On decreasing the temperature, the doublets first broaden and then at 250 K each is resolved into two doublets (see Table 2) indicative of the presence of four magnetically inequivalent methyl groups. The three singlet resonances show no significant variation with temperature. The ^{31}P-{^1H} n.m.r. spectrum at 303 K in $CDCl_3$ consists of an AB pattern centred at δ 19.9 p.p.m. [*J*(PP) 32.9 Hz, δ(PP) 251.7 Hz] suggesting two magnetically inequivalent PMe_2Ph groups. Furthermore, the magnitude of the coupling constant suggests a *cis* orientation of these groups.[9]

A suitable single crystal of (4) was selected of dimensions 0.3 × 0.1 × 0.05 mm, and an *X*-ray structural analysis (see below) showed it to contain a co-ordinated 4-amino-2-imino-4-methylpentane molecule.

Crystal Data for (4).—$C_{36}H_{46}N_2O_2P_2RuS_2$, $M = 765$, reddish brown prismatic crystals, $a = 23.899(2)$, $b = 11.163(1)$, $c = 13.889(3)$ Å, $U = 3\,705$ Å^3, $D_m = 1.34$, $Z = 4$, $D_c = 1.37$ g cm^{-3}, $F(000) = 1\,592$, space group $Pna2_1$ (no. 33), Cu-K_α radiation, $\lambda = 1.541\,8$ Å, μ(Cu-K_α) = 56.2 cm^{-1}.

Structure determination. Photographic equi-inclination Weissenberg data were collected for layers $h0\rightarrow8l$ and $hk0\rightarrow6$. Cell dimensions were determined by the α_1–α_2 splitting method applied to 23 zero-layer reflections with $\theta \geqslant 75°$. All the films were scanned by the S.R.C. Microdensitometer Service and, after merging, 2 249 independent data were obtained, significant above background. No absorption corrections were applied. The *x* and *y* co-ordinates of the ruthenium atom were readily determined from the Patterson function. The subsequent difference Fourier, phased with these co-ordinates and an arbitrary *z*, is pseudo-centric, and some difficulty was experienced in choosing suitable S and P co-ordinates to break this symmetry. Eventually, all the non-hydrogen atoms were found. The structure was refined by block-diagonal least squares. In the last few cycles a weighting scheme was used of the form $W = XY$ with $X = (\sin\theta)/0.3$ for $\sin\theta < 0.3$ and 1.0 otherwise, and $Y = 35/|F_o|$ for $|F_o| > 35$ and 1.0 otherwise. Ruthenium, S, and P atoms were given anisotropic temperature factors, but hydrogen atoms were not included in the refinement. At convergence, $R = 0.065$. Final values of fractional parameters are given in Table 3. A structure-factor table, thermal parameters, and important interatomic distances and angles are deposited as Supplementary Publication No. SUP 22243 (13 pp.).*

The structure. A view of the complex molecule is given in the Figure. The complex shows only slight deviations from ideal octahedral angles about the ruthenium atom. In the imino-amino-ligand the imine C(32)–N(1) bond [1.333(26) Å] is a significant 0.15 Å shorter than the amine C(31)–N(2) distance [1.482(26) Å] and the Ru–N(1) bond length [2.151(15) Å] is 0.12 Å shorter than the Ru–N(2) distance [2.271(15) Å]. Similarly, in $[Cu\{HNC(Me)CH_2CMe_2NH_2\}_2][NO_3]_2$, made by reaction of $Cu[NO_3]_2$ and ammonia in acetone, *X*-ray analysis[10] showed C=NH 1.30, C–NH_2 1.51, Cu–NH 1.98, and Cu–NH_2 2.01 Å.

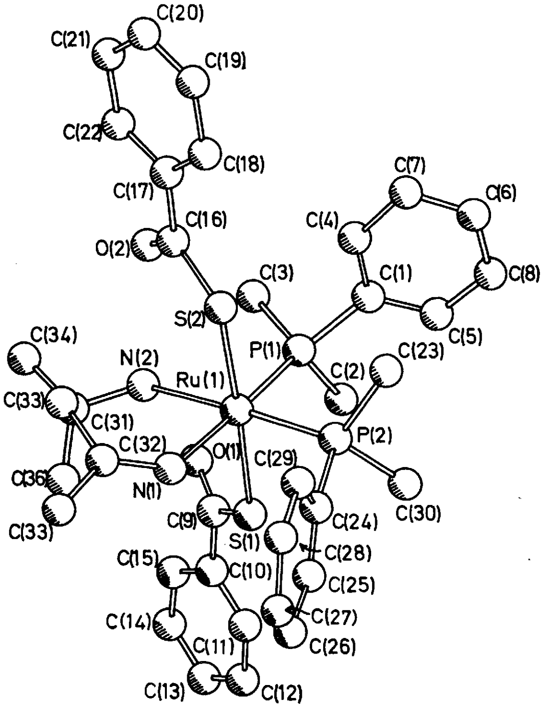

FIGURE A perspective view of (4)

An interesting feature of the structure is the orientation of the $[SOCPh]^-$ ligands, which brings the carbonyl oxygens within hydrogen-bonding distances (2.870 and 2.851 Å) of the amine nitrogen. In one case this results in the Ru atom being non-coplanar with the SOC group: Ru–S(1)–C(9)–O(1) 14°. Such hydrogen bonding presumably lends stability to the molecule and may

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[9] See P. R. Hoffman and K. G. Caulton, *J. Amer. Chem. Soc.*, 1975, **97**, 4221 and refs. therein.

[10] F. Hanic and M. Serator, *Chem. Zvesti*, 1964, **18**, 572.

explain the unexpectedly low value of the ν(CO) wavenumber (1 530 cm^{-1}) in the i.r. spectrum of (4) and also in that of [Ru(SOCPh)$_2$(NH$_2$Et)$_2$(PMe$_2$Ph)$_2$] (Table 1).

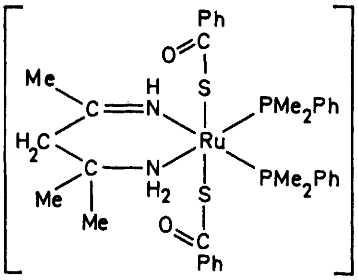
TABLE 3

Atomic positional parameters (× 10^4) for (4) with estimated standard deviations in parentheses

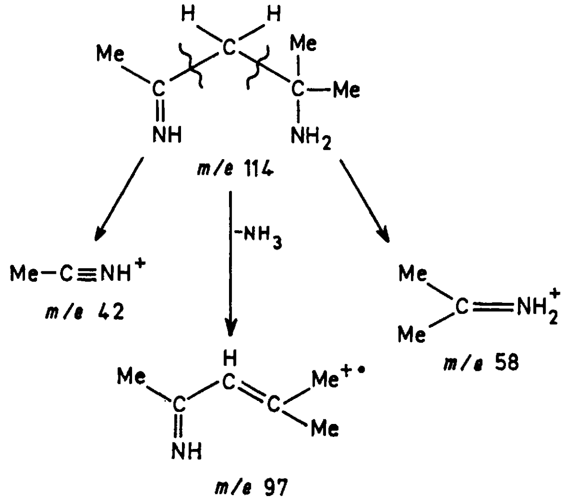
Atom	*x*/*a*	*y*/*b*	*z*/*c*
Ru	1 574.6(4)	695.3(10)	5 000
P(1)	2 062(2)	−793(4)	5 786(4)
P(2)	1 345(2)	1 660(4)	6 406(4)
S(1)	691(2)	−318(4)	5 106(5)
S(2)	2 375(2)	1 985(4)	4 842(4)
O(1)	1 098(5)	−2 174(11)	4 162(9)
O(2)	2 919(6)	474(13)	3 680(12)
N(1)	1 108(6)	2 007(13)	4 197(12)
N(2)	1 767(6)	−174(13)	3 560(11)
C(1)	2 512(7)	335(15)	6 783(14)
C(2)	1 651(9)	−2 000(20)	6 363(18)
C(3)	2 556(8)	−1 702(17)	5 079(22)
C(4)	2 992(9)	324(21)	6 614(19)
C(5)	2 378(9)	−576(20)	7 745(17)
C(6)	3 163(10)	615(24)	8 262(19)
C(7)	3 360(10)	846(22)	728(18)
C(8)	2 705(9)	−100(22)	8 476(19)
C(9)	676(7)	−1 716(16)	4 448(13)
C(10)	143(7)	−2 290(16)	4 388(13)
C(11)	−323(6)	−2 044(14)	4 928(20)
C(12)	−835(7)	−2 650(17)	4 829(17)
C(13)	−883(8)	−3 573(19)	4 159(16)
C(14)	423(9)	−3 814(20)	3 617(17)
C(15)	88(7)	−3 219(18)	3 741(16)
C(16)	2 931(7)	1 474(17)	4 146(14)
C(17)	3 439(7)	2 148(16)	4 118(14)
C(18)	3 544(8)	3 161(19)	4 706(16)
C(19)	4 039(10)	3 799(21)	4 616(18)
C(20)	4 447(10)	3 458(22)	3 951(19)
C(21)	4 358(9)	2 497(21)	3 365(18)
C(22)	3 850(8)	1 822(18)	3 432(16)
C(23)	1 890(8)	2 420(18)	7 105(15)
C(24)	834(8)	2 876(17)	6 187(15)
C(25)	290(8)	2 699(18)	6 096(16)
C(26)	−94(10)	3 653(22)	5 910(19)
C(27)	120(10)	4 779(22)	5 799(19)
C(28)	660(11)	4 996(24)	5 869(21)
C(29)	1 058(10)	4 101(23)	6 039(20)
C(30)	982(8)	804(20)	7 341(16)
C(31)	1 578(9)	338(18)	2 630(16)
C(32)	1 174(8)	2 331(17)	3 280(15)
C(33)	792(9)	3 302(19)	2 858(18)
C(34)	2 009(10)	−87(22)	1 879(20)
C(35)	1 632(8)	1 770(18)	2 661(15)
C(36)	977(9)	−50(21)	2 454(18)

Similarly in the i.r. spectra of both [Ni(O$_2$CMe)$_2$]·4H$_2$O [11] and [Pd(O$_2$CMe)$_2$(NHEt$_2$)$_2$] [12] the low value of ν_{asym}(CO$_2$) is attributed to intramolecular hydrogen bonding between the unco-ordinated oxygens of the carboxylate groups and water or amine groups respectively.

The three singlets in the ^{1}H n.m.r. spectrum are assigned to *gem*-methyl groups (δ 1.06 p.p.m.), the imino-*C*-methyl group (1.58 p.p.m.), and to the methylene protons (2.31 p.p.m.) (*cf.*[13] the related signals in [Ni{HNC(Me)CH$_2$CMe$_2$NH$_2$}$_2$][BF$_4$]$_2$). There is also a weak broad resonance at 5.80 p.p.m. which may be due to the hydrogens bound to nitrogen. If the solid-state structure of (4) is retained in solution, four magnetically inequivalent methyl groups are expected (and observed) in the ^{1}H n.m.r. spectrum because the bidentate ligand is both asymmetric and has a puckered conformation. At higher temperatures averaging of the signals from the methyl groups on the *same* phosphorus atoms occurred probably because of ready inversion of the chelate ring on the n.m.r. time scale. In the mass spectrum of (4) the additional peaks *m*/*e* <100 correspond to the fragmentation pattern of the 4-amino-2-imino-4-methylpentane molecule (Scheme 1) and we have observed the same pattern in the mass spectrum of [Ni{HNC(Me)-CH$_2$CMe$_2$NH$_2$}$_2$][BF$_4$]$_2$. In neither spectrum however is the parent-ion peak observed at *m*/*e* 114 and attempts to isolate such a molecule in the free state, either by displacement from (4) with various Lewis bases or protonation of (4) with gaseous HCl, were unsuccessful {although with CO, [Ru(SOCPh)$_2$(CO)$_2$(PMe$_2$Ph)$_2$] (3b) was obtained}. This failure is not surprising because of the known instability of compounds containing imine groups which readily rearrange or polymerise.[14]



(4)



SCHEME 1 Fragmentation pattern of the 4-amino-2-imino-4-methylpentane molecule

Finally, it is of some interest to speculate briefly on possible mechanisms for this reaction. As mentioned

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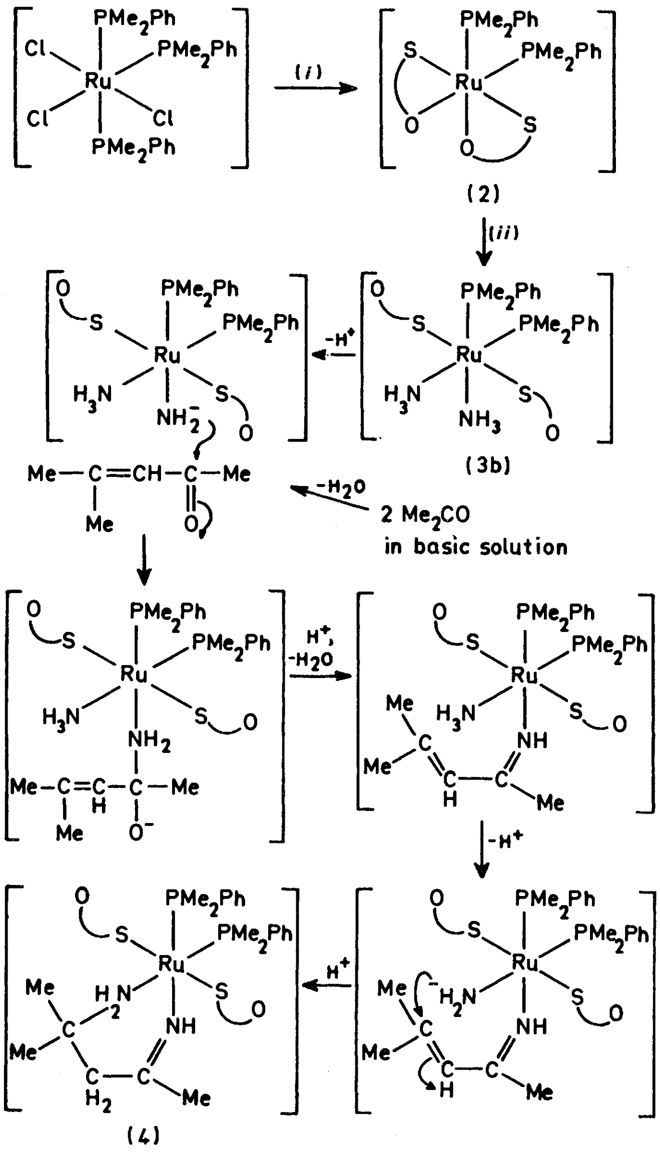
[11] K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, *J. Amer. Chem. Soc.*, 1957, **79**, 4904.

[12] T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 1965, 3632.

[13] N. J. Rose, M. S. Elder, and D. H. Busch, *Inorg. Chem.*, 1967, **6**, 1924.

[14] See R. O. C. Norman, 'Principles of Organic Synthesis,' Methuen, London, 1968, ch. 10, pp. 312—313.

earlier, [Ru(SOCPh)$_2$(NH$_3$)$_2$(PMe$_2$Ph)$_2$] can be prepared *in situ* and this readily reacts with either acetone or mesityl oxide at room temperature to give high yields of (4). This strongly suggests that the reaction path involves initial formation of [Ru(SOCPh)$_2$(PMe$_2$Ph)$_2$] (2) followed by reaction with ammonia to give the diammine species. Since reaction of [Ru(SOCPh)$_2$(PMe$_2$Ph)$_2$] (2) with either [NH$_4$][PF$_6$] or [NH$_4$][SOCPh] in acetone did *not* give any (4), it is clear that, in the original preparation of (4), deprotonation of the ammonium ion by the free PMe$_2$Ph released in the reaction is a key step in the formation of this diammine complex. A possible method of condensing mesityl oxide (the self-condensation product of acetone) with the diammine complex to give (4) is shown in Scheme 2. This is similar to a mechanism proposed elsewhere [15] to explain the formation of ruthenium imine complexes from reaction of ruthenium ammine and various organic carbonyl-containing compounds. An added attraction of the mechanism shown in this Scheme is that *cis*-ammine groups are essential for formation of the imino-amino chelating ligand and therefore this provides a good rationale for the inability to form the corresponding species starting from either [RuCl$_2$(PPh$_3$)$_3$] or [Ru(SOCPh)$_2$(NH$_3$)$_2$(PPh$_3$)$_2$] (3a).



SCHEME 2 Possible mechanism of formation of [Ru(SOCPh)$_2${HNC(Me)CH$_2$CMe$_2$NH$_2$}(PMe$_2$Ph)$_2$] (4). (*i*) [SOCPh]$^-$; (*ii*) NH$_3$

However, attempts to condense acetone (or mesityl oxide) with [Ru(SOCPh)$_2$(NH$_2$Et)$_2$(PMe$_2$Ph)$_2$] or ethyl methyl ketone with [Ru(SOCPh)$_2$(NH$_3$)$_2$(PMe$_2$Ph)$_2$] were also unsuccessful suggesting that steric constraints are another important consideration.

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} region 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$_3$PO$_4$). Mass spectra were obtained on an A.E.I. MS9 spectrometer. Melting points were determined with a Kofler hot-stage microscope and are uncorrected. Crystallographic calculations were made using the '*X*-RAY '72' system [16] as implemented at the Edinburgh Regional Computing Centre. Ruthenium(III) trichloride trihydrate (Johnson, Matthey Ltd.), carbon monoxide (Air Products), triphenylphosphine (B.D.H.), dimethylphenylphosphine (Maybridge Chemical Company), and monothiobenzoic acid (Aldrich) were obtained as indicated. The salts [NH$_4$][SOCPh] and Na[SOCPh] were prepared by reaction of PhCOSH with ammonia gas in benzene and Na$_2$[CO$_3$] in water respectively. The complexes [RuCl$_2$(PPh$_3$)$_3$],[8] *mer*-[RuCl$_3$(PMe$_2$Ph)$_3$],[17] and all-*trans*-[RuCl$_2$(CO)$_2$(PPh$_3$)$_2$] [8] were prepared as described earlier. All the solutions were degassed before use and reactions were carried out under a nitrogen atmosphere.

Bis(monothiobenzoato)bis(triphenylphosphine)ruthenium(II).—The compounds [RuCl$_2$(PPh$_3$)$_3$] (0.20 g) and Na[SOCPh] (0.40 g) were heated under reflux in degassed acetone (50 cm^3) for 3 h. The resulting orange-yellow *product* was filtered off and washed with acetone and diethyl ether (0.15 g, 88%), m.p. 218—220 °C (Found: C, 65.7; H, 4.7. Calc. for C$_{50}$H$_{40}$O$_2$P$_2$RuS$_2$: C, 66.7; H, 4.4%). The same product can also be obtained by reaction of [NH$_4$][SOCPh] with [RuCl$_2$(PPh$_3$)$_3$]. ^{31}P-{^{1}H} n.m.r. spectrum in CDCl$_3$ at 303 K: δ 59.9 (s) p.p.m.

Diamminebis(monothiobenzoato)bis(triphenylphosphine)-

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[15] I. P. Evans, G. W. Everett, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1976, **98**, 8041 and refs. therein.

[16] *X*-Ray Program System, Technical Report TR 192, Computer Science Center, University of Maryland, version of June 1972.

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

ruthenium(II).—Ethanol (20 cm^3) was saturated with ammonia gas and then [Ru(SOCPh)$_2$(PPh$_3$)$_2$] (0.10 g) was added. The suspension was stirred at room temperature for 3 h and the resulting bright yellow *product* was filtered off and washed with acetone and diethyl ether (0.09 g, 86%), m.p. 205—208 °C (Found: C, 64.5; H, 5.0; N, 2.7. Calc. for $C_{50}H_{46}N_2O_2P_2RuS_2$: C, 64.4; H, 4.9; N, 3.0%). ^{31}P-{^{1}H} n.m.r. spectrum in CDCl$_3$ at 303 K: δ 46.3 (s) p.p.m.

Dicarbonylbis(monothiobenzoato)bis(triphenylphosphine)-ruthenium(II).—*Method* (*a*). The complex [Ru(SOCPh)$_2$-(PPh$_3$)$_2$] (0.10 g) was suspended in ethanol (50 cm^3) and heated under reflux under carbon monoxide gas for 3 h. The bright lemon-yellow *product* was separated from starting material by dissolving it in dichloromethane, filtering, and recrystallising the product, m.p. 235—239 °C (Found: C, 65.2; H, 4.7. Calc. for $C_{52}H_{40}O_4P_2RuS_2$: C, 65.3; H, 4.2%). ^{31}P-{^{1}H} n.m.r. spectrum in CDCl$_3$ at 303 K: δ 42.8 (s) p.p.m.

Method (*b*). The compounds all-*trans*-[RuCl$_2$(CO)$_2$-(PPh$_3$)$_2$] (0.05 g) and [NH$_4$][SOCPh] (0.05 g) were heated under reflux in acetone (50 cm^3) for 2 h. The resulting bright yellow solution was filtered while hot, the volume was reduced, and light petroleum (b.p. 40—60 °C) was added. The lemon-yellow *product* was then filtered off.

Bis(dimethylphenylphosphine)bis(monothiobenzoato)-ruthenium(II).—The compounds *mer*-[RuCl$_3$(PMe$_2$Ph)$_3$] (0.20 g) and Na[SOCPh] (0.20 g) were heated under reflux in acetone (50 cm^3) for 3 h. The solution was filtered while hot, the volume was reduced, and water was added to yield a red-brown *precipitate* which was filtered off and dried *in vacuo* over calcium chloride (0.17 g, 70%), m.p. 169—171 °C (Found: C, 55.5; H, 5.0%; *M*(CHCl$_3$) 636. Calc. for $C_{30}H_{32}O_2P_2RuS_2$: C, 55.3; H, 4.9%; *M* 651). ^{31}P-{^{1}H} n.m.r. spectrum in CDCl$_3$ at 303 K: δ 39.0 (s) and 4.6 (m) p.p.m. The complex can also be prepared as above using Na[SOCPh] or [NH$_4$][SOCPh] in methanol as solvent.

Diamminebis(dimethylphenylphosphine)bis(monothiobenzoato)ruthenium(II).—The complex [Ru(SOCPh)$_2$(PMe$_2$Ph)$_2$] (0.20 g) was dissolved in chloroform (10 cm^3) and ammonia gas was bubbled through the solution at room temperature for 10 min to give a yellow-brown solution. The product was not isolated but was identified by ^{1}H and ^{31}P n.m.r. studies using a sample prepared in CDCl$_3$ (see Discussion section). Attempts at isolation were unsuccessful. ^{31}P-{^{1}H} n.m.r. spectrum in CDCl$_3$ at 303 K: δ 23.7 (s) p.p.m.

Dicarbonylbis(dimethylphenylphosphine)bis(monothiobenzoato)ruthenium(II).—The complex [Ru(SOCPh)$_2$(PMe$_2$Ph)$_2$] (0.10 g) was dissolved in ethanol (30 cm^3) and then carbon monoxide gas was bubbled through the solution at room temperature for 1 h to give a pale yellow solution. The volume of the solution was reduced and it was cooled over ice to yield a pale cream crystalline *powder* which was filtered off and dried *in vacuo* (0.06 g, 51%), m.p. 153—155 °C (Found: C, 53.8; H, 4.6. Calc. for $C_{32}H_{32}O_4P_2RuS_2$: C, 54.2; H, 4.5%). ^{31}P-{^{1}H} n.m.r. spectrum in CDCl$_3$ at 303 K: δ 10.8 (s) p.p.m.

Bis(dimethylphenylphosphine)bis(ethylamine)bis(monothiobenzoato)ruthenium(II).—The complex [Ru(SOCPh)$_2$-(PMe$_2$Ph)$_2$] (0.10 g) was heated under reflux in chloroform (20 cm^3) with ethylamine (0.50 cm^3; 70% aqueous solution) for 1 h. Ethanol (10 cm^3) was then added and the chloroform was evaporated off to yield a yellow-brown crystalline *powder* which was filtered off and washed with cold ethanol (0.10 g, 93%), m.p. 177—180 °C (Found: C, 54.0; H, 6.0; N, 3.7. Calc. for $C_{34}H_{46}N_2O_2P_2RuS_2$: C, 55.1; H, 6.2; N, 3.8%). ^{31}P-{^{1}H} n.m.r. spectrum in CDCl$_3$ at 303 K: δ 22.3 (s) p.p.m.

(*4-Amino-2-imino-4-methylpentane*)*bis(dimethylphenylphosphine)bis(monothiobenzoato)ruthenium*(II).—*Method* (*a*). The compounds *mer*-[RuCl$_3$(PMe$_2$Ph)$_3$] (0.30 g) and [NH$_4$]-[SOCPh] (0.30 g) were dissolved in the minimum volume of acetone (20 cm^3), and the solution was filtered and left to stand at room temperature under nitrogen for 72 h, after which time clear orange-brown *crystals* were removed from the flask. The complex was also prepared by refluxing the above reaction mixture in acetone (50 cm^3) for 2 h, reducing the volume of the solution, and then cooling it in ice to yield a yellow *powder* which was filtered off and recrystallised from chloroform (0.26 g, 72%), m.p. 208—210 °C (Found: C, 54.4; H, 5.6; N, 3.3%; *M*(CHCl$_3$) 724. Calc. for $C_{36}H_{46}N_2O_2P_2RuS_2$: C, 56.5; H, 6.0; N, 3.7%; *M* 765).

Method (*b*). The complex [Ru(SOCPh)$_2$(PMe$_2$Ph)$_2$] (0.10 g) in chloroform (10 cm^3) was treated with ammonia gas to give the diammine complex *in situ* (see earlier). Acetone (30 cm^3) was then added and the solution was left to stand for 3 h at room temperature when the complex was obtained as a yellow powder as in method (*a*). Similarly, [Ru-(SOCPh)$_2$(PMe$_2$Ph)$_2$] (0.10 g) in chloroform (10 cm^3) treated with ammonia gas and then with mesityl oxide (5 cm^3) yielded the complex after standing at room temperature. The complex was also obtained in both cases when the solutions were heated under reflux. ^{31}P-{^{1}H} n.m.r. spectrum in CDCl$_3$ at 303 K: δ 19.9 (q) p.p.m. [*J*(PP) 32.9 Hz, δ(PP) 251.7 Hz].

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