Metal Complexes of Sulphur Ligands. Part IX.[1] Synthesis of Dimethylphosphinodithioato-complexes of Ruthenium(II) containing Bidentate Donor Ligands

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The tris(chelate) complexes $[Ru(S_2PMe_2)_2(diene)]$ {diene $=$ bicyclo[2.2.1]hepta-2,5-diene (nbd) or cyclo-octa-1,5-diene (cot)} have been synthesised by the reaction of $[\{RuCl_2(diene)\}_n]$ with $Na[S_2PMe_2]\cdot 2H_2O$ in either ethanol or NN-dimethylformamide. The labile diene moiety is readily replaced by various chelating ligands to give $[Ru(S_2PMe_2)_2(L-L)]$ {L–L $=$ $Ph_2P[CH_2]_2PPh_2$ (dppe), $Ph_2PCH_2PPh_2$ (dppm), $C_6H_4(AsMe_2)_2$ (pdma)}. For L–L $=$ pdma, $trans$-$[Ru(S_2PMe_2)_2$ (pdma)$_2]$ is also formed. Unlike the corresponding cis-$[Ru(S_2PMe_2)_2L_2]$ [L $=$ PR_3 or $P(OR)_3$], all the tris(chelate) complexes exhibit very slow rates of optical inversion and this evidence is used to tentatively propose a modified inversion mechanism of that postulated earlier.

In a recent paper [2] we proposed that the temperature-variable ^1H n.m.r. spectra of complexes of the type cis-

$[Ru(S_2PMe_2)_2L_2]$ [L $=$ PPh_3, $PMePh_2$, PMe_2Ph, $P(OMe)_3$ or $P(OPh)_3$] are best explained in terms of rapid inter-

[1] Part VIII, J. D. Owen and D. J. Cole-Hamilton, *J.C.S. Dalton*, 1974, 1867.

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

conversion of the two possible optical isomers of these complexes and that, at least for cis-[Ru(S$_2$PMe$_2$)$_2$(L)L'] [L = PPh$_3$; L' = P(OPh)$_3$ or CO] in solvating media (CDCl$_3$ or PhCl) the mechanism of these inversion processes involves initial S_N2 solvent (Y)-assisted cleavage of the Ru–S bond trans to L, followed by exchange between uni- and bi-dentate sulphur ligands and finally recombination of a unidentate [Me$_2$PS$_2$]$^-$ group with concomitant loss of solvent to form the optical isomer [Scheme

producing [Ru(S$_2$PMe$_2$)$_2$(L–L)] {L–L = Ph$_2$P[CH$_2$]$_2$-PPh$_2$ (dppe), Ph$_2$PCH$_2$PPh$_2$ (dppm), or C$_6$H$_4$(AsMe$_2$)$_2$ (pdma)}, although when excess of pdma was used a complex of formula [Ru(S$_2$PMe$_2$)$_2$(pdma)$_2$] was formed. This may be converted into [Ru(S$_2$PMe$_2$)$_2$(pdma)] by recrystallisation from toluene. These tris(chelate) complexes may also be isolated in low yield by prolonged reaction of trans-[RuCl$_2$(L–L)$_2$] and Na[S$_2$PMe$_2$] heated under reflux in ethanol.
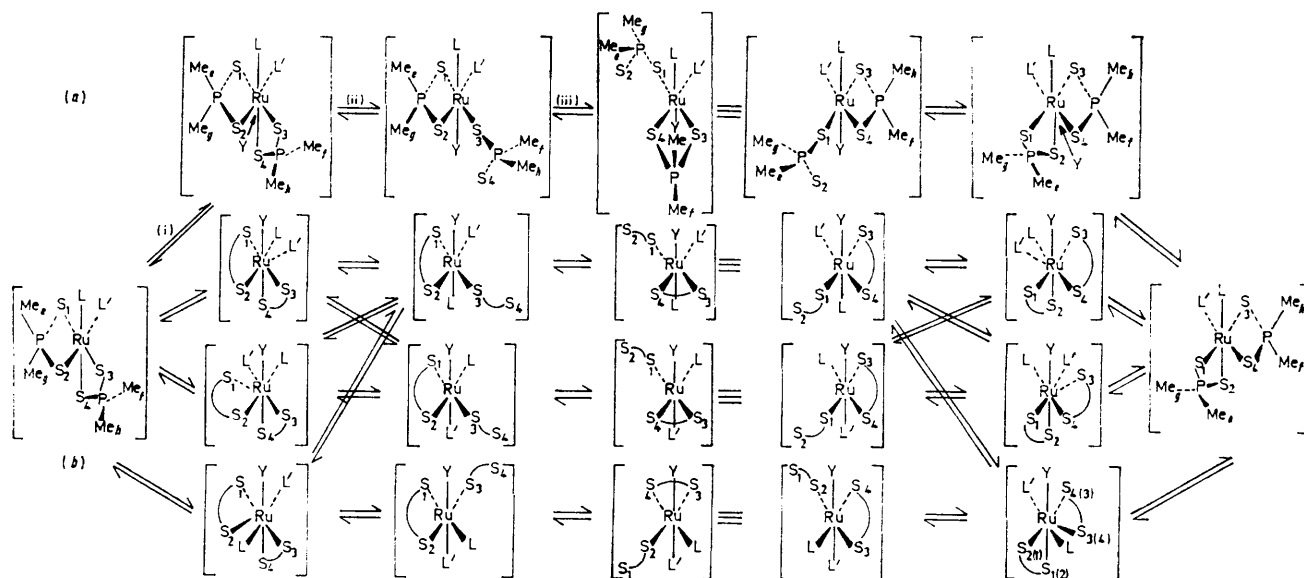
SCHEME 1   Possible solvent (Y)-assisted bond-rupture mechanism for inversion of cis-[Ru(S$_2$PMe$_2$)$_2$(L)L']:   (a) cis attack by solvent;   (b) trans attack by solvent

1(a)].   In a non-solvating media (C$_6$H$_6$) the mechanism is essentially the same except that the first step is dissociative with no solvent participation.   Furthermore, on the basis of the calculated activation parameters, we postulated that the exchange of uni- and bi-dentate sulphur ligands occurs via a dissociative mechanism irrespective of the solvent.   We have now synthesised some tris-(chelate) complexes [Ru(S$_2$PMe$_2$)$_2$(L–L)] {L–L = bicyclo-[2.2.1]hepta-2,5-diene (norbornadiene, nbd), cyclo-octa-1,5-diene (cot), Ph$_2$P[CH$_2$]$_2$PPh$_2$ (dppe), Ph$_2$PCH$_2$PPh$_2$ (dppm), or C$_6$H$_4$(AsMe$_2$)$_2$ (pdma)} and examined their variable-temperature ^{1}H n.m.r. spectra.   These studies provide more insight into possible mechanisms of the inversion process and the nature of the seven-co-ordinate intermediate.

RESULTS AND DISCUSSION

The reaction between [{RuCl$_2$(diene)}$_n$] (diene = nbd or cot) and Na[S$_2$CNMe$_2$] in hot NN-dimethylformamide has recently been shown to produce [Ru(S$_2$CNMe$_2$)$_2$-(diene)] in high yield.[3]   We have found that [Ru-(S$_2$PMe$_2$)$_2$(diene)] may be prepared in analogous fashion using Na[S$_2$PMe$_2$]·2H$_2$O and furthermore that the diene moiety is labile, being readily replaced by CO or PPh$_3$ to give the known cis-[Ru(S$_2$PMe$_2$)$_2$L$_2$] complexes [4] (L = CO or PPh$_3$).   Reaction of [Ru(S$_2$PMe$_2$)$_2$(diene)] in ethanol with chelating ligands also causes exchange

Spectroscopic Properties of [Ru(S$_2$PMe$_2$)$_2$(L–L)].—
I.r. spectra. The i.r. spectra of the complexes [Ru-(S$_2$PMe$_2$)$_2$(L–L)] all showed absorptions arising from the chelating L–L ligands and from the [Me$_2$PS$_2$]$^-$ groups. The bidentate nature of the latter is indicated in every case by the position of ν(PS) between 580 and 590 cm^{-1}.[4,5] However for [Ru(S$_2$PMe$_2$)$_2$(pdma)$_2$] the only peak in the region 500—700 cm^{-1} was a sharp absorption at 600 cm^{-1} with a shoulder at 595 cm^{-1} which suggests that both [Me$_2$PS$_2$]$^-$ groups are probably bound through only one sulphur atom.[4,5]   This observation is supported by ^{1}H n.m.r. data (see below).

^{1}H N.m.r. spectra. In all these tris(chelate) complexes the stereochemistry of the molecules is constrained to be cis and, although for L–L = cot the signals from the diene protons were difficult to see and for dppe only the phenyl resonances were clearly seen (on account of the low intensity and complicated nature of the ^{1}H n.m.r. signals arising from the expected H$_2$PP'H'$_2$ spin system), the resonances arising from L–L in the other complexes were readily distinguished and are all consistent with cis stereochemistry (Table 1).   Thus, for L–L = nbd, signals are assigned as arising from four olefinic protons

[3] P. Powell, J. Organometallic Chem., 1974, 65, 89.
[4] D. J. Cole-Hamilton and T. A. Stephenson, J.C.S. Dalton, 1974, 739.
[5] D. F. Steele and T. A. Stephenson, J.C.S. Dalton, 1973, 2124.

(τ 6·15), two methylene protons (τ 8·70), and two bridge-head protons (τ 5·90). For L–L = pdma, a poorly resolved AA′BB′ type spectrum arising from the phenylene protons was observed, centred at τ 2·40, whilst the methyl groups of pdma gave rise to two sharp singlets at τ 8·24 and 8·60. For L–L = dppm, apart from the phenyl resonances, a sharp triplet at τ 5·03 was seen, which arises from splitting of the methylene protons' resonance by the two chemically equivalent ^{31}P nuclei.

As for $[Ru(S_2PMe_2)_2L_2]$,[4] the methyl groups on the $[Me_2PS_2]^-$ ligands gave rise to two doublets for all $[Ru(S_2PMe_2)_2(L–L)]$ at low temperatures; however, in contrast to the behaviour of $[Ru(S_2PMe_2)_2L_2]$ [2] [L = PR_3 or $P(OR)_3$], these resonances remained sharp on warming to 373 K in PhCl. Above this temperature for L–L = diene the signals began to broaden but, since the b.p. of PhCl is 403 K, the condition of fast exchange of the $[Me_2PS_2]^-$ methyl groups is never reached.

high positive values found for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (Table 2) could be explained either by sub-step (i) or (iii) in the mechanism shown in Scheme (1a) being slow and rate determining.* That is either the chelating ligands have low *trans* influences, thus making step (iii) slow {as was proposed for cis-$[Ru(S_2PMe_2)_2(PPh_3)CO]$ and cis-$[Ru(S_2PMe_2)_2(CO)_2]$},[2] or they prevent the solvent from entering the co-ordination sphere for steric reasons, thus making step (i) dissociative and slow {as is found for cis-$[Ru(S_2PMe_2)_2(PMe_2Ph)_2]$ in a non-co-ordinating medium such as benzene}.[2]

The literature available on the *trans* influences of these ligands is somewhat erratic since, although dienes all appear to have low *trans* influences, dppe can apparently exhibit either a low or a high *trans* influence depending on how it is measured whereas pdma always appears to exhibit a high *trans* influence.[6] Hence, at least for $[Ru(S_2PMe_2)_2(pdma)]$, the observed low rate of inversion

TABLE 1

^{1}H N.m.r. data (τ) for complexes $[Ru(S_2PMe_2)_2(L–L)_n]$ ($n = 1$ or 2) in $CDCl_3$ at 301 K

Complex	$[Me_2PS_2]^-$ (Me group) [a,b]	L–L [a]	Phenyl or phenylene group [a]
$[Ru(S_2PMe_2)_2(nbd)]$	7·78 (12·5), 8·15 (13·0)	5·90, 6·15, 8·70 [c]	
$[Ru(S_2PMe_2)_2(cot)]$	8·20 (13·0), 8·75 (12·5)	6·35, 7·80	
$[Ru(S_2PMe_2)_2(dppe)]$	7·90 (13·0), 9·25 (13·0)	d	2·0—3·0
$[Ru(S_2PMe_2)_2(dppm)]$	7·85 (13·0), 8·88 (12·5)	5·03(t), (10·0)	2·0—3·0
$[Ru(S_2PMe_2)_2(pdma)]$	7·65 (13·0), 8·26 (12·5)	8·24(s), 8·60(s)	2·1—2·8
$trans$-$[Ru(S_2PMe_2)_2(pdma)_2]$	8·46 (12·0)	8·02(s)	2·1—2·6

s = Singlet, t = triplet.

[a] τ ±0·01. [b] Doublets; J(PH) in parentheses (±0·2 Hz). [c] See text for assignments. [d] C_2H_4 Protons too weak for accurate measurement.

TABLE 2

Rates and activation parameters for the inversion process cis Δ $\rightleftharpoons$ cis Λ for some ruthenium(II) dimethylphosphinodithioates

Complex	Solvent	$\log_{10}(k/s^{-1})$ at 298 K	$E^{\ddagger}$ kJ mol^{-1}	$\Delta H_{298}^{\ddagger}$ kJ mol^{-1}	$\Delta S_{298}^{\ddagger}$ J K^{-1} mol^{-1}	$\Delta G_{298}^{\ddagger}$ kJ mol^{-1}
$[Ru(S_2PMe_2)_2(dppe)]$	PhCl	-3.2 ± 0.30	113·4 ± 7	110·9 ± 7	65 ± 20	91·4 ± 2
cis-$[Ru(S_2PMe_2)_2(PPh_3)CO]$ *	PhCl	-1.90 ± 0.08	121·8 ± 2	119·3 ± 2	119 ± 7	83·8 ± 0·4
cis-$[Ru(S_2PMe_2)_2(PMe_2Ph)_2]$ *	PhCl	1.01 ± 0.01	69·7 ± 1	67·2 ± 1	0 ± 4	67·2 ± 0·1
cis-$[Ru(S_2PMe_2)_2(PMe_2Ph)_2]$ *	C_6H_6	0.04 ± 0.12	126 ± 4	123·5 ± 4	170 ± 11	72·7 ± 0·1

* See ref. 2.

Finally, $[Ru(S_2PMe_2)_2(pdma)_2]$ gave rise to a well resolved AA′BB′ type set of signals in the phenylene region, a sharp singlet from the pdma methyl groups at τ 8·02, and a sharp doublet from the methyl groups of the $[Me_2PS_2]^-$ ligands (τ 8·46). This spectrum was temperature invariant (233—333 K) and this is best explained if the two $[Me_2PS_2]^-$ ligands are both unidentate and mutually *trans* since, if they were *cis*, two resonances would be expected from the methyl groups of the pdma ligands.

Mechanistic Implications.—In Part VI of this series [2] we proposed that complexes $[Ru(S_2PMe_2)_2(L)L']$ invert by the solvent-assisted bond-rupture mechanism [Scheme 1(a)]. At first sight there seems no reason why the same mechanism of inversion should not apply for the tris-(chelate) complexes $[Ru(S_2PMe_2)_2(L–L)]$. Thus for $[Ru(S_2PMe_2)_2(dppe)]$ the very low rate constant and the

is incompatible with the known high *trans* influence of this ligand, which suggests that either the steric constraint proposed above or a *different* inversion mechanism to that given in Scheme 1(a) is responsible.

On further consideration there are a number of other possible microscopic paths for this inversion mechanism [Scheme 1(b)]. These are all consistent with the experimental data in Part VI apart from the last which causes exchange between the wrong pairs of methyl groups and hence does not explain the temperature-variable ^{1}H n.m.r. spectra of cis-$[Ru(S_2PMe_2)_2(PPh_3)\{P(OPh)_3\}]$. It is to be noted that whereas the mechanism shown in Scheme 1(a) involves attack of the solvent molecule (Y) in a position close to the Ru–S bond to be broken so that the solvent simply takes the place of the dissociating sulphur atom in the co-ordination sphere, those in 1(b) involve a pentagonal-bipyramidal intermediate in which the

* All the other tris(chelate) complexes have even *slower* inversion rates and thus insufficient data could be obtained for Arrhenius plots.

[6] T. G. Appleton, H. C. Clark, and L. E. Manzer, *Co-ordination Chem. Rev.*, 1973, 10, 335 and refs. therein.

leaving sulphur atom and the attacking solvent molecule are in the two axial positions. In these pentagonal bipyramids L and L' may either be adjacent to one another in the plane of the pentagon or may be separated by a sulphur atom and after cleavage of the Ru–S bond either L or L' may be *trans* to the co-ordinated solvent molecule.* Examination of the seven-co-ordinate intermediate in the last mechanism outlined in Scheme 1(*b*) reveals that L and L' are separated by a sulphur atom, and therefore if L and L' were joined together (as in a chelate molecule) any inversion mechanism involving this

region 4 000—250 cm⁻¹ on a Perkin-Elmer 457 grating spectrometer using Nujol mulls on caesium iodide plates. Mass spectra were obtained on an A.E.I. MS9 spectrometer and ¹H n.m.r. spectra on a Varian Associates HA-100 spectrometer with variable-temperature attachment. Accurate temperatures were determined using the separation of the two resonances of ethylene glycol. Spectra were simulated using a computer program based on that of Naka-gawa.[7] The exchange process was considered for the purpose of computation as consisting of two two-site exchanges of equal intensity and separated by the coupling constant of the doublets. Computed spectra were plotted on the
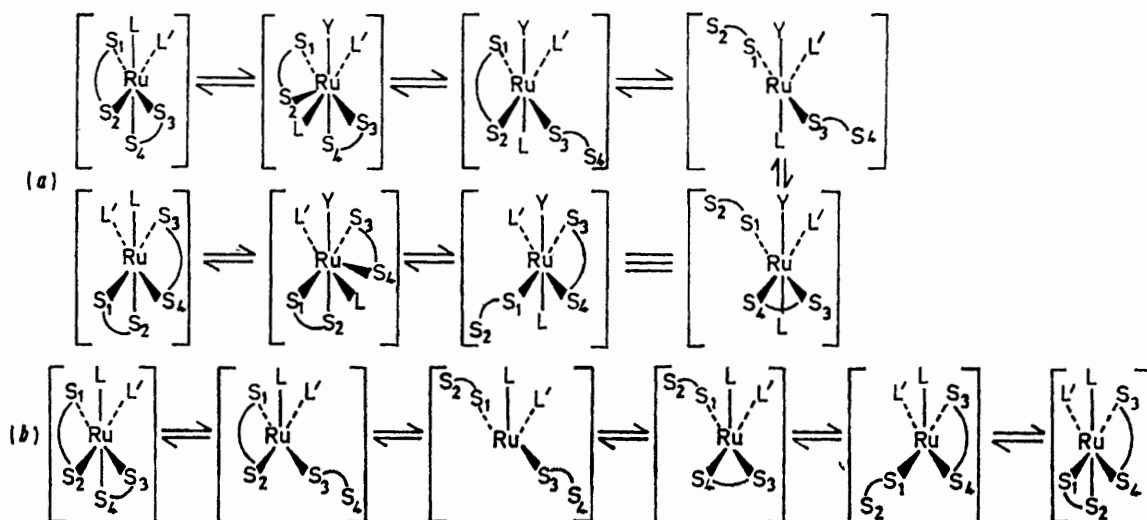
SCHEME 2 Postulated mechanisms of inversion for *cis*-[Ru(S₂PMe₂)₂(L)L']: (*a*) in a polar solvent; (*b*) in a non-polar solvent

seven-co-ordinate species would be very unfavourable on steric grounds as is experimentally observed.†

Thus we tentatively propose that the mechanism of inversion of complexes *cis*-[Ru(S₂PMe₂)₂L₂] and *cis*-[Ru(S₂PMe₂)₂(L)L'] in solvating media (CDCl₃ or PhCl) is that shown in Scheme 2(*a*), whereas in a non-solvating medium and for [Ru(S₂PMe₂)₂(L–L)] the mechanism is as in 2(*b*). However, although the mechanisms shown in Scheme 2 accommodate all the observations we have made in this paper and earlier work,[2] we cannot entirely rule out the possibility that different mechanisms of inversion operate for these different tris(chelate) complexes; *e.g.* for L–L = diene or dppm the mechanism *may* be that shown in Scheme 1 (*a*) where the low *trans* influences of these ligands are responsible for their very slow inversion rates, whereas for L–L = dppe or pdma their low inversion rates may be attributable to the steric constraints expected for a rigid bidentate ligand on the basis of the mechanism shown in Scheme 2(*a*).

EXPERIMENTAL

Microanalyses were by the University of Edinburgh Chemistry Department. I.r. spectra were recorded in the

line printer and experimental spectra were fitted to them by finding the best fit between the ratio of maximum to minimum heights in the doublets. Spin–spin relaxation times (T_2) were obtained by measurement of the peak width at half height under slow-exchange conditions. Life-times obtained by this fitting procedure were then used to construct an Arrhenius plot ($\log_{10}k$ against T^{-1}) to which a straight line was fitted by the least-squares method. Activation parameters at 298 K were obtained from standard equations. Analytical data for the new complexes are given in Table 3. M.p.s were determined on a Köfler hot-stage microscope and are uncorrected.

Materials.—Ruthenium trichloride trihydrate (Johnson Matthey), bicyclo[2.2.1]hepta-2,5-diene (nbd) (Koch–Light), cyclo-octa-1,5-diene (cot) (Ralph Emanuel), and *o*-phenylenebis(dimethylarsine) (pdma) (Aldrich) were obtained as indicated. 1,2-Bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), sodium dimethylphosphinodithioate, and ruthenium(II)-containing starting materials were prepared by standard literature methods. Operations were carried out under nitrogen and in degassed solvents.

(Bicyclo[2.2.1]hepta-2,5-diene)bis(dimethylphosphinodi-thioato)ruthenium(II).—(a) The complex [{RuCl₂(nbd)}ₙ][8] (0·20 g) and Na[S₂PMe₂]·2H₂O[9] (0·40 g) were heated under

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* If any of the sulphur atoms takes up a position *trans* to Y the mechanisms which result can all be shown to disobey the principle of microscopic reversibility.

† It should also be pointed out that this seven-co-ordinate intermediate is the least sterically hindered of the ones shown in Scheme 1.

[7] T. Nakagawa, *Bull. Chem. Soc. Japan*, 1966, **39**, 1006.

[8] E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 1959, 3178.

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

reflux in ethanol (25 cm³) for 5 h. After filtration and cooling, the complex precipitated as orange *crystals* (0·20 g, 60%).

(b) The complex [{RuCl₂(nbd)}ₙ] (0·26 g) was added to a hot solution of Na[S₂PMe₂]·2H₂O (0·29 g) in *NN*-dimethylformamide (8 cm⁻³). After cooling and addition

remove excess of *trans*-[RuCl₂(dppe)₂] and NaCl and, on cooling, the complex precipitated as orange *crystals* (0·06 g, 39%).

[1,2-*Bis*(*diphenylphosphino*)*methane*]*bis*(*dimethylphosphinodithioato*)*ruthenium*(ii).—The complex [Ru(S₂PMe₂)₂-(nbd)] (0·05 g) and dppm (0·10 g) were shaken in ethanol

TABLE 3

Analytical data for some ruthenium complexes

Complex	Colour	M.p. (θ_c/°C)	M *	Found C	Found H	Calc. C	Calc. H
[Ru(S₂PMe₂)₂(nbd)]	Orange	167—170	443 ± 1 (443)	29·9	4·6	29·8	4·5
[Ru(S₂PMe₂)₂(cot)]	Orange	184—185	459 ± 1 (459)	30·7	5·1	31·3	5·2
[Ru(S₂PMe₂)₂(dppe)]	Orange	228—230	749 ± 1 (749)	47·7	4·9	48·0	4·8
[Ru(S₂PMe₂)₂(dppm)]	Orange	230—233 (decomp.)		47·5	4·8	47·3	4·6
[Ru(S₂PMe₂)₂(pdma)]	Orange	238—240 (decomp.)		28·6	4·3	26·4	4·3
trans-[Ru(S₂PMe₂)₂(pdma)₂]	Pink	236—237 (decomp.)		31·3	4·9	31·2	4·8

* Molecular weight from parent-ion peak (¹⁰¹Ru isotope) in mass spectrum; calculated values are given in parentheses.

of water, the brown solid was filtered off and recrystallised from aqueous acetone as orange *crystals* (0·17 g, 41%).

(*Cyclo-octa*-1,5-*diene*)*bis*(*dimethylphosphinodithioato*)*ruthenium*(ii) was similarly prepared from [{RuCl₂(cot)}ₙ] [8] (0·28 g) and Na[S₂PMe₂]·2H₂O (0·29 g) as orange crystals.

[1,2-*Bis*(*diphenylphosphino*)*ethane*]*bis*(*dimethylphosphinodithioato*)*ruthenium*(ii).—(a) The complex [Ru(S₂PMe₂)₂-(nbd)] (0·11 g) was heated under reflux with dppe (0·10 g) in acetone for 24 h. Cooling and concentrating the solution then afforded the complex as orange *crystals* which were recrystallised from CH₂Cl₂-n-hexane (0·10 g, 58%).

(b) The complex *trans*-[RuCl₂(dppe)₂] [10] (0·20 g) and Na[S₂PMe₂]·2H₂O (0·20 g) were heated under reflux in ethanol (25 cm³) for 24 h. The solution was filtered hot to

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

(20 cm³) for 5 h. The orange *crystals* were filtered off and washed with water, ethanol, and n-pentane (0·13 g, 80%).

trans-*Bis*(*dimethylphosphinodithioato*)*bis*[*o*-*phenylenebis*-(*dimethylarsine*)]*ruthenium*(ii).—The complex [Ru(S₂PMe₂)₂-(nbd)] (0·05 g) and pdma (0·2 cm³) were heated under reflux in ethanol (10 cm³) for 10 min. The pink crystals were filtered off and washed with water, ethanol, and n-pentane (0·085 g, 97%). Recrystallisation from boiling toluene gave orange *crystals* of the product in 100% yield.