Complexes of the Platinum Metals. Part 29.[1] Pyridine-2-thiolate Derivatives of Ruthenium and Osmium: *X*-Ray Crystal Structures of $[Ru(C_5H_4NS)_2(CO)_2(PPh_3)]$ and $[Ru(C_5H_4NS)_2(CO)(PPh_3)]$†

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Ruthenium and osmium precursors $[MH(Cl)(CO)(PPh_3)_3]$, $[MH_2(CO)(PPh_3)_3]$, $[Ru(CO)_3(PPh_3)_2]$, $[OsH_2(CO)_2(PPh_3)_2]$, $[RuH_2(PPh_3)_4]$, and $[OsH_4(PPh_3)_3]$ react with pyridine-2-thiol (pySH) or dipyridyl-2,2′-disulphide (pySSpy) in boiling benzene or toluene to afford a range of pyridine-2-thiolate complexes including $[MCl(pyS)(CO)(PPh_3)_2]$, (2 isomers), $[M(pyS)_2(CO)_2(PPh_3)]$, $[M(pyS)_2(CO)(PPh_3)]$, and $[M(pyS)_2(PPh_3)_2]$ in which the pyridine-2-thiolate ligands are bound in monodentate (S-bonded) or bidentate (N,S-chelated) mode. Similar products are obtained from $[RuCl_2(PPh_3)_3]$ and $[RuCl_2(CO)_2(PPh_3)_2]$ in the presence of triethylamine and pyridine-2-thiol. The new complexes have been characterised by i.r. and n.m.r. ($^{31}P-\{^1H\}$ and ^1H) spectroscopy; reaction pathways are discussed. The *X*-ray crystal structures of $[Ru(pyS)_2(CO)_2(PPh_3)]$ and $[Ru(pyS)_2(CO)(PPh_3)]$ have been determined. The dicarbonyl $[Ru(pyS)_2(CO)_2(PPh_3)]$, which undergoes facile conversion to $[Ru(pyS)_2(CO)(PPh_3)]$, displays structural evidence of incipient attack by the non-co-ordinated N atom of the monodentate pyridine-2-thiolate ligand on a carbonyl group [N ··· C 2.782(7) Å]. Crystals of $[Ru(pyS)_2(CO)_2(PPh_3)]$ are monoclinic, space group $P2_1/c$, with a = 11.307(2), b = 11.083(3), c = 24.090(5) Å, β = 109.47(2)°, and Z = 4. The structure, which has been refined to R = 0.045 for 4 375 observed reflections, consists of highly distorted octahedral ruthenium(II) molecules with monodentate (S-bonded) and bidentate (N,S-bonded) pyridine-2-thiolate ligands, a *cis* pair of carbonyl groups, and a triphenylphosphine ligand *trans* to the S-bonded pyridine-2-thiolate. Crystals of $[Ru(pyS)_2(CO)(PPh_3)]$ are triclinic, space group $P\bar{1}$, with a = 10.317(3), b = 11.749(3), c = 12.517(3) Å, α = 67.65(2), β = 70.55(2) γ = 86.43(2)°, and Z = 2. The structure, which has been refined to R = 0.040 for 12 196 observed reflections consists of highly distorted octahedral ruthenium(II) molecules with a *cis* pair of bidentate (N,S-bonded) pyridine-2-thiolate ligands (*trans* S atoms), a carbonyl group, and a triphenylphosphine ligand.

The many known cyclic molecules containing the tautomeric system shown below (X = O or S) include a number of important biological compounds, notably purine and pyrimidine bases and their sulphur-containing analogues. The co-ordination chemistry displayed by tautomeric ligands of this type is therefore of considerable current interest. As part of a wider investigation into the chelating ability of ligands containing these groups towards platinum metals we have examined the reactions of pyridine-2-thiol (pySH), one of the simplest examples, and its oxidation product, dipyridyl-2,2′-disulphide (pySSpy), with a range of ruthenium and osmium precursors, and have isolated a number of new pyridine-2-thiolate complexes. In this, the first of a series of papers on pyridine-2-thiolate and related complexes, a brief summary of the co-ordination chemistry of pyridine-2-thiol and its conjugate base, the pyridine-2-thiolate anion, seems appropriate. The weak acid pySH (pK_a 9.97)[2] exists in two tautomeric forms, the thione tautomer (**Ia**) which is thought to predominate in methanol or acetone solution[3] and the thiol tautomer (**Ib**) which appears to be favoured in dilute cyclohexane solution.[4] Electronic[4] and n.m.r. spectroscopic data [δ(N-*H* ··· *S*) = 13.48 p.p.m., $CDCl_3$ solution][5] have been taken to indicate that pyridine-2-thiol is present in cyclohexane and chloroform solutions as H-bonded dimers (**II**) particularly at high concentrations. Differences in i.r. data for pyridine-2-thiol in *dilute* carbon tetrachloride solution [ν(NH) = 3 376 cm^{-1}] and in the solid state [ν(NH) = 2 870 cm^{-1}] suggest that H-bonded dimers are also present in the latter phase.[6] This conclusion has recently been confirmed by *X*-ray and neutron diffraction studies which have established that the solid-state structure (**II**) is indeed correct [N–(H) ··· S 3.289(2) Å].[7]

$$-NH-C(X)- \rightleftharpoons -N{=}C(XH)-$$

Depending upon reaction conditions (notably the solution pH) employed, pyridine-2-thiol can co-ordinate to transition metals either as the free ligand (pySH) or as the conjugate base (pyS^-). The neutral pySH ligand can theoretically display any one of four monodentate co-ordination modes: two for the thione form, (**IIIa**) and (**IIIb**), and two for the thiol form, (**IIIc**) and (**IIId**). Previous authors have concluded that the S-co-ordinated thione form (**IIIb**) is dominant[8] and this conclusion is supported by the available *X*-ray crystallographic data[9,10] although in one case bond lengths have been interpreted in

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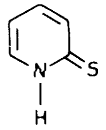
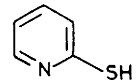
† Dicarbonyl(pyridine-2-thiolato-*S*)(pyridine-2-thiolato-*N*,*S*)(triphenylphosphine)ruthenium(II) and carbonylbis(pyridine-2-thiolato-*N*,*S*)(triphenylphosphine)ruthenium(II).

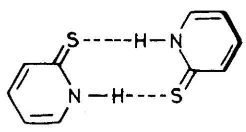
Supplementary data available (No. SUP 56269, 8 pp.): thermal parameters for all non-H atoms, positional parameters of H atoms. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.



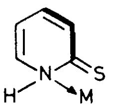
(Ia)



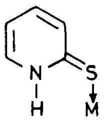
(Ib)



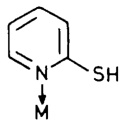
(II)



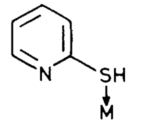
(IIIa)



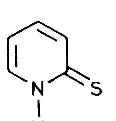
(IIIb)



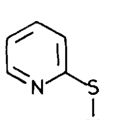
(IIIc)



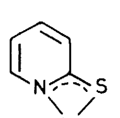
(IIId)



(IVa)



(IVb)



(IVc)

terms of a zwitterionic ($H\overset{+}{N}C_5H_4\overset{-}{S}$) contribution to the structure of the S-co-ordinated ligand.[9] The anionic pyS^- ligand can function as a monodentate N-, or preferably, S-bonded ligand, **(IVa)** and **(IVb)**, or as an N,S-donor chelate, **(IVc)**.[11-13] There is some evidence,[14] recently confirmed[15] that the pyS^- anion can also serve as an N,S-bonded bridging ligand between adjacent metal centres.

Complexes containing pySH or pyS^- ligands have been reported for *p*-block metals, notably zinc,[8,16,17] cadmium,[8] mercury,[8,18-20] tin,[8,12,21-24] lead,[18] and bismuth,[8] for *d*-block metals, including titanium,[25] molybdenum,[26,27] tungsten,[26] iron,[28,29] cobalt,[8,9,28,30,31] nickel,[8,28] copper,[10,28,30] silver,[28] and the platinum metals, and for at least one *f*-block metal, namely uranium.[32] Published work on pyridine-2-thiolate complexes of the platinum group metals, though fairly extensive, is rather fragmented, and no systematic study appears to have been attempted. The first example, $[RuCl(pyS)(pySH)(PPh_3)_2]$, was reported by Gilbert and Wilkinson[33] and formulated as a dimer; other ruthenium derivatives are $[Ru(pyS)_2(C_8H_{12})]$(C_8H_{12} = cyclo-octa-1,5-diene),[34,35] $[Ru(pyS)_2(C_7H_8)]$(C_7H_8 = norbornadiene),[35] $[\{RuI(pyS)(C_7H_8)\}_2]$,[35] $[\{RuCl_2(pySH)_2\}_n]$,[36] and $[Ru(pyS)_2(PPh_3)_2]$.[13,36,37] Two trinuclear osmium carbonyl clusters $[Os_3H(pyS)(CO)_{10}]$ and $[Os_3H(pyS)(CO)_9]$ have been formulated with edge- or face-bridging pyridine-2-thiolate ligands.[38] Attempts to displace acetate ligands from $[Rh_2(O_2CCH_3)_4]$ merely yielded the adduct $[Rh_2(O_2CCH_3)_4(pySH)_2]$,[28] however, treatment of $[Rh_2(O_2CCH_3)_4(MeOH)_2]$ with aqueous HBF_4 followed by pySH afforded a product formulated as $[Rh(pyS)_2(PPh_3)_2][BF_4]$.[39] The iridium hydrides $[IrH(pyS)_2(PPh_3)_n]$ (n = 1 or 2) have been described and their conversion to the corresponding ethyl derivatives $[Ir(C_2H_5)(pyS)_2(PPh_3)_n]$ under pressure of ethylene has been demonstrated.[40] Three palladium complexes $[Pd(pySH)_4Cl_2]\cdot EtOH$,[28] $[Pd(pyS)_2(pySH)]$,[28] and $[Pd(pyS)_2(PPh_3)_2]$[41] together with two platinum analogues $[Pt(pySH)_4Cl_2]$[8] and $[Pt(pyS)_2(PPh_3)_2]$[41] have been described. Other platinum derivatives include $[Pt(pyS)(NH_3)(H_2O)][NO_3]$, and $[Pt(pyS)_2(NH_3)(H_2O)]$, both of which have been screened for anti-tumour activity[42] and the binuclear complex $[Pt_2(pyS)_2(en)_2]Cl_2$ (en = ethylenediamine).[15,*]

Experimental

Platinum metal salts were supplied by Johnson Matthey. Pyridine-2-thiol (pySH) and dipyridyl-2,2′-disulphide (pySSpy) were obtained from the Aldrich Chemical Co., and were used without further purification. Reagent grade solvents, dried over molecular sieves, were used throughout. All reactions were performed under nitrogen but products were worked up in the open atmosphere. The precursors $[RuCl_2(CO)_2(PPh_3)_2]$, $[MH(X)(CO)(PPh_3)_3]$, $[MH_2(CO)(PPh_3)_3]$ (M = Ru or Os; X = Cl or Br), $[Ru(O_2CCF_3)_2(MeOH)(CO)(PPh_3)_2]$, $[Ru(CO)_3(PPh_3)_2]$, $[RuH_2(PPh_3)_4]$, and $[OsH_4(PPh_3)_3]$ were prepared by standard literature procedures.[43,44] $[RuCl_2(PPh_3)_3]$ was prepared by adding an ethanolic solution of $RuCl_3\cdot 3H_2O$ to a boiling solution of triphenylphosphine in the same solvent, and rapidly deposited as shiny black crystals. Product ratios for reaction solutions and product mixtures are based on $^{31}P-\{^1H\}$ n.m.r. spectra, integrals rounded to the nearest 5%; accuracy is *ca.* ± 5%. Microanalyses were performed by University College, London. Melting points were determined on a Buchi apparatus using samples sealed in capillaries under nitrogen. Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrometer using samples mulled in Nujol. Proton n.m.r. spectra were recorded in $CDCl_3$ solutions on a Bruker WM 250 (250.13 MHz) spectrometer using $SiMe_4$ as internal reference. Phosphorus-31 n.m.r. spectra were recorded in $CDCl_3$ on a Bruker HFX 90 (36.44 MHz) spectrometer using 85% H_3PO_4 as external reference. In each case positive chemical shifts are to low field of the reference. Spectroscopic data are recorded in Table 1.

Reactions of $[RuH_2(CO)(PPh_3)_3]$ *with Pyridine-2-thiol.*—A solution of the complex (0.40 g, 0.44 mmol) and pySH (0.048 g, 0.44 mmol) in toluene (60 cm^3) was heated under reflux for 30 min. During this time the colourless solution became pale yellow. The filtered solution was evaporated to dryness under reduced pressure to yield a pale yellow residue (0.42 g) which afforded cream microcrystals from chloroform–hexane. The product was identified by spectroscopic methods, including comparison with authentic samples (see below) as a *ca.* 80:20 mixture of two geometrical isomers of $[RuH(pyS)(CO)(PPh_3)_2]$, **(1)** and **(2)**; overall yield 0.29 g (87%). An alternative crystallisation from dichloromethane–methanol afforded a pure sample of isomer **(1)**; yield 0.27 g (80%), m.p. >250 °C.

Using a reflux time of 6 h and a metal:ligand ratio of 1:5 an orange solution was obtained; evaporation to dryness gave an orange-yellow residue which on crystallisation from chloroform–hexane afforded $[Ru(pyS)_2(CO)(PPh_3)]$ **(3)** in essentially quantitative yield as yellow microcrystals.

Reaction of $[RuH_2(CO)(PPh_3)_3]$ *with Dipyridyl-2,2′-disulphide.*—A solution of the complex (0.40 g, 0.44 mol) and pySSpy (0.097 g, 0.44 mmol) in toluene (60 cm^3) was heated under reflux for 30 min. During this time the colourless solution became yellow. The filtered solution was evaporated to dryness under reduced pressure and then extracted with methanol. The insoluble residue was further washed with methanol then dried *in vacuo* to yield pale yellow microcrystals. These were shown by spectroscopic methods to consist of a *ca.* 80:20 mixture of two geometrical isomers of $[RuH(pyS)(CO)(PPh_3)_2]$, **(1)** and **(2)**;

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* *Note added in proof:* A review (E. S. Raper, *Coord. Chem. Rev.*, 1985, **61**, 115), published after this manuscript was submitted, includes a section on pyridine-2-thiol complexes.

Table 1. Spectroscopic data

Complex	ν(CO)	ν(MH)	δ(MH)/p.p.m.	^{2}J(PH)/Hz	δ(NH)/p.p.m.	δ(PPh$_3$)/p.p.m.
(1) [RuH(pyS)(CO)(PPh$_3$)$_2$]	1 905	1 969	−12.28 (t)	20	—	49.7 (s)
(2) [RuH(pyS)(CO)(PPh$_3$)$_2$]	1 909	1 965	−11.55 (t)	20	—	51.0 (s)
(3) [Ru(pyS)$_2$(CO)(PPh$_3$)]	1 934	—	—	—	—	57.0 (s)
(4) [RuH(Cl)(pySH)(CO)(PPh$_3$)$_2$] ^{a}	1 922	1 989	−10.22 (t)	18	13.21 (s)	41.4 (s)
(5) [RuH(Cl)(pySH)(CO)(PPh$_3$)$_2$]	1 899	2 010	−14.72 (t)	17	13.77 (s)	40.9 (s)
(4a) [RuH(Br)(pySH)(CO)(PPh$_3$)$_2$] ^{a}	1 936	2 038	−10.50 (t)	17	12.75 (s)	39.3 (s)
(5a) [RuH(Br)(pySH)(CO)(PPh$_3$)$_2$]	1 932	2 043	−14.03 (t)	17	13.31 (s)	39.9 (s)
(6) [RuCl(pyS)(CO)(PPh$_3$)$_2$]	1 938	—	—	—	—	37.7 (s)
(7) [RuCl(pyS)(pySH)(CO)(PPh$_3$)$_2$]	1 922	—	—	—	15.20 (s)	33.1 (s)
(8) [Ru(pyS)$_2$(CO)$_2$(PPh$_3$)]	2 030, 1 976, 1942^{b}	—	—	—	—	41.1 (s)
(9) [Ru(pyS)$_2$(PPh$_3$)$_2$]	—	—	—	—	—	49.9 (s)
(10) [{RuCl(pyS)(pySH)(PPh$_3$)$_2$}$_n$]	—	—	—	—	13.22 (s)	32.1 (s)
(11) [Ru(O$_2$CCF$_3$)(pyS)(pySH)(CO)(PPh$_3$)$_2$]	1 940^{c}	—	—	—	—	32.75 (s)
(1′) [OsH(pyS)(CO)(PPh$_3$)$_2$]	1 888	2 070	−13.88 (t)	17	—	21.5 (s)
(2′) [OsH(pyS)(CO)(PPh$_3$)$_2$]	1 894	2 032 (sh)	−12.31 (t)	19	—	22.6 (s)
(3′) [Os(pyS)$_2$(CO)(PPh$_3$)]	1 917	—	—	—	—	12.8 (s)
(4′) [OsH(Cl)(pySH)(CO)(PPh$_3$)$_2$] ^{a}	1 912	2 093	−10.71 (t)	16	12.93 (s)	13.0 (s)
(5′) [OsH(Cl)(pySH)(CO)(PPh$_3$)$_2$]	1 869	2 091	−16.74 (t)	14	13.53 (s)	12.4 (s)
(4a′) [OsH(Br)(pySH)(CO)(PPh$_3$)$_2$] ^{a}	1 909 (sh)	2 010	−11.06 (t)	16	12.59 (s)	9.7 (s)
(5a′) [OsH(Br)(pySH)(CO)(PPh$_3$)$_2$]	1 896	1 984	−16.25 (t)	14	13.21 (s)	10.6 (s)
(6′) [OsCl(pyS)(CO)(PPh$_3$)$_2$]	1 911	—	—	—	—	8.6 (s)
(6a′) [OsBr(pyS)(CO)(PPh$_3$)$_2$]	1 912	—	—	—	—	7.6 (s)
(9′) [Os(pyS)$_2$(PPh$_3$)$_2$]	—	—	—	—	—	−4.0 (s)

[a] The i.r. spectra of these isomeric compounds were obtained using isomer mixtures; assignments may be transposed. [b] 2050 and 1997 cm^{-1} in CHCl$_3$ solution. [c] ν(CO$_2$) = 1 689 and 1 433 cm^{-1}.

yield 0.06 g (18%) (Found: C, 64.4; H, 4.5; N, 1.7. Calc. for $C_{42}H_{35}NOP_2RuS$: C, 66.0; H, 4.6; N, 1.8%).

The methanol extract was evaporated to dryness under reduced pressure and the residue recrystallised from chloroform–hexane to afford [Ru(pyS)$_2$(CO)(PPh$_3$)] **(3)** as yellow crystals (0.17 g, 64%), m.p. 190—194 °C (Found: C, 56.2 and 57.25; H, 3.8 and 4.0; N, 4.4 and 4.1. Calc. for $C_{29}H_{23}N_2OPRuS_2$: C, 56.9; H, 3.8; N, 4.6%).

Reactions of [RuH(Cl)(CO)(PPh$_3$)$_3$] *with Pyridine-*2*-thiol*.—(*a*) *In cold benzene*. A solution of the complex (0.3 g, 0.31 mmol) and pySH (0.035 g, 0.31 mmol) was stirred in cold benzene (0.5 °C, 40 cm^3) for 1 h. During this time the solution darkened from yellow to deep orange. The filtered solution was evaporated to dryness under reduced pressure and without application of heat to yield an orange residue which afforded orange microcrystals from chloroform–hexane. These were shown by spectroscopic methods to be a *ca*. 40 : 60 mixture of isomeric products of stoicheiometry [RuH(Cl)(pySH)(CO)(PPh$_3$)$_2$], **(4)** and **(5)**; yield 0.24 g (48%) (Found: C, 62.25; H, 4.45; N, 1.70. Calc. for $C_{42}H_{36}ClNOP_2RuS$: C, 62.95; H, 4.55; N, 1.75%).

(*b*) *In boiling benzene*. A similar reaction in boiling benzene (30 min) afforded a yellow residue, spectroscopic examination of which revealed the presence of a major (*ca*. 90%) component **(6)** and two minor components, [RuH(pyS)(CO)(PPh$_3$)$_2$], isomers **(1)** and **(2)**. Recrystallisation from chloroform–hexane afforded orange-yellow microcrystals of **(6)** which were identified by spectroscopic methods and comparison with an authentic sample (see below) as [RuCl(pyS)(CO)(PPh$_3$)$_2$] (89%).

Reactions of [RuH(Br)(CO)(PPh$_3$)$_3$] *with Pyridine-*2*-thiol*.—(*a*) *In cold benzene*. A mixture of the complex (0.40 g, 0.401 mmol) and pySH (0.0446 g, 0.401 mmol) was stirred in cold benzene (50 cm^3, 0—5 °C) for 3 h. The cloudy yellow solution which formed was evaporated to dryness under reduced pressure without application of heat to afford a yellow residue (0.42 g) which was shown by ^{31}P-{^{1}H} n.m.r. to be a 10:85:5 mixture comprising isomers of [RuH(Br)(CO)(pySH)(PPh$_3$)$_2$], **(4a)** and **(5a)**, together with [RuBr(pyS)(CO)(PPh$_3$)$_2$] **(6a)**. Crystallisation from chloroform–hexane yielded a mixture of [RuH(Br)(CO)(pySH)(PPh$_3$)$_2$] isomers, yield 0.10 g (30%) (Found: C, 58.8; H, 4.05, N, 1.50. Calc. for $C_{42}H_{36}BrNOP_2RuS$: C, 59.65; H, 4.30; N, 1.65%).

(*b*) *In boiling benzene*. A similar reaction in boiling benzene (30 min reflux) afforded an orange residue which was shown by ^{31}P-{^{1}H} n.m.r. spectroscopy to consist of a *ca*. 5:20:15:5:50:5 mixture comprising isomers of [RuH(Br)(CO)(pySH)(PPh$_3$)$_2$], **(4a)** and **(5a)**, and isomers of [RuH(pyS)(CO)(PPh$_3$)$_2$], **(1)** and **(2)**, together with [RuBr(pyS)(CO)(PPh$_3$)$_2$] **(6a)** and an unidentified minor product.

Reactions of [RuH(Cl)(CO)(PPh$_3$)$_3$] *with Dipyridyl-*2,2′*-disulphide*.—(*a*) *In cold benzene*. A mixture of the complex (0.286 g, 0.30 mmol) and pySSpy (0.066 g, 0.30 mmol) was stirred in benzene (50 cm^3, 0—5 °C) for 4 h to afford a clear yellow solution. This solution was reduced to dryness without application of heat and the yellow residue was shown by ^{31}P-{^{1}H} n.m.r. to consist of three components: [RuH(Cl)(CO)(pySH)(PPh$_3$)$_2$], isomers **(4)** and **(5)**, and [RuCl(pyS)(CO)(PPh$_3$)$_2$] **(6)** in the ratio 25:45:30 together with triphenylphosphine oxide.

(*b*) *In boiling benzene*. A solution of [RuH(Cl)(CO)(PPh$_3$)$_3$] (0.60 g, 0.63 mmol) and pySSpy (0.193 g, 0.63 mmol) in benzene (60 cm^3) was heated under reflux for 20 min. During this time the colour of the solution changed from yellow to orange-yellow. The filtered solution was evaporated to dryness under reduced pressure and the residue recrystallised from dichloromethane–methanol to afford [RuCl(pyS)(CO)(PPh$_3$)$_2$] **(6)** as orange-yellow microcrystals; yield 0.27 g (54%), m.p. 274—275 °C (decomp.) (Found: C, 62.8; H, 4.4; N, 2.0. Calc. for $C_{42}H_{34}ClNOP_2RuS$: C, 63.1; H, 4.3; N, 1.75%).

*Reaction of Dipyridyl-*2,2′*-disulphide with Water and Triphenylphosphine*.—A mixture of pySSpy (0.11 g, 0.5 mmol), PPh$_3$ (0.131 g, 0.5 mmol), and water (1.0 g, 55 mmol), and chloroform (40 cm^3) was stirred for 3 h at 0—5 °C. The solution was filtered and reduced to dryness to yield a yellow residue which was shown by n.m.r. spectroscopy to be a mixture of pyridine-2-thiol [δ(N*H*) = 14.1 p.p.m.] and triphenylphosphine oxide [$\delta(\mathrm{Ph_3}P\mathrm{O})$ = 29.2 p.p.m. (s)].

Reactions of [$\mathrm{Ru(CO)_3(PPh_3)_2}$] *with Pyridine-2-thiol.*—A solution of the complex (0.25 g, 0.35 mmol) and pySH (0.117 g, 1.05 mmol) in toluene (60 cm^3) was heated under reflux for 30 min. The yellow solution became darker during this time. The filtered solution was evaporated to dryness under reduced pressure to yield a dark brown residue (0.38 g). The ^{31}P n.m.r. spectrum of this product indicates the presence of four components: [$\mathrm{RuH(pyS)(CO)(PPh_3)_2}$], isomers (**1**) and (**2**), [$\mathrm{Ru(pyS)_2(CO)(PPh_3)}$] (**3**), and a new species (**8**) subsequently identified (see below) as [$\mathrm{Ru(pyS)_2(CO)_2(PPh_3)}$]. Product ratio *ca.* 20:5:70:5.

Using a Ru:pySH ratio of 1:3 and a reflux time of 3 h a dark yellow residue was obtained. Crystallisation from dichloromethane–methanol afforded a bright yellow microcrystalline material (0.23 g) identified by ^{31}P n.m.r. as a *ca.* 95:5 mixture of two components: [$\mathrm{Ru(pyS)_2(CO)(PPh_3)}$] (**3**) and [$\mathrm{Ru(pyS)_2(CO)_2(PPh_3)}$] (**8**). A futher crystallisation gave pure [$\mathrm{Ru(pyS)_2(CO)(PPh_3)}$] (**8**).

Reactions of [$\mathrm{Ru(CO)_3(PPh_3)_2}$] *with Dipyridyl-2,2′-disulphide.*—A solution of the complex (0.50 g, 0.70 mmol) and pySSpy (0.155 g, 0.70 mmol) in toluene (80 cm^3) was heated under reflux for 10 min and then rapidly cooled (water, 16 °C). The yellow solution was evaporated to dryness under reduced pressure to yield an orange-yellow residue which was identified by ^{31}P n.m.r. as a *ca.* 25:75 mixture of two components: [$\mathrm{Ru(pyS)_2(CO)(PPh_3)}$] (**3**) and [$\mathrm{Ru(pyS)_2(CO)_2(PPh_3)}$] (**8**). The crude product was extracted with methanol (3 × 8 cm^3) and the residue was crystallised from dichloromethane–methanol then chloroform–hexane to yield [$\mathrm{Ru(pyS)_2(CO)_2(PPh_3)}$] (**8**) as yellow microcrystals; yield 0.18 g (40%), m.p. 213—214 °C, effervescence 187—189 °C (Found: C, 56.10; H, 4.00; N, 4.40. Calc. for $\mathrm{C_{30}H_{23}N_2O_2PRuS_2}$: C, 56.35; H, 3.60; N, 4.40%). The methanol extract was concentrated to *ca.* 10 cm^3 under reduced pressure then allowed to stand whereupon yellow microcrystals (0.03 g, 5%) of [$\mathrm{Ru(pyS)_2(CO)(PPh_3)}$] (**3**) separated slowly.

When the reflux time was increased to 30 min a slightly higher proportion of (**3**) was obtained.

Conversion of [$\mathrm{Ru(pyS)_2(CO)_2(PPh_3)}$] *to* [$\mathrm{Ru(pyS)_2(CO)(PPh_3)}$].—A solution of the complex (0.10 g, 1.6 mmol) in chloroform–hexane (1:1, 10 cm^3) was allowed to stand at ambient temperature for 7 d then evaporated to dryness under reduced pressure to afford yellow microcrystals. These were purified by column chromatography [silica gel, 1 cm × 20 cm column, $\mathrm{CHCl_3}$–hexane (1:1) eluant]. The principal fraction was concentrated and then slowly evaporated to afford yellow crystals (0.057 g, 60%) of pure [$\mathrm{Ru(pyS)_2(CO)(PPh_3)}$]. The crystals were shown to be triclinic with the same unit cell and intensity values as an authentic sample.

Reaction of [$\mathrm{RuH_2(PPh_3)_4}$] *with Pyridine-2-thiol.*—A solution of the complex (0.576 g, 0.5 mmol) and pySH (0.167 g, 1.5 mmol) in benzene (120 cm^3) was heated under reflux for 2.5 h. During this time the yellow solution darkened to deep red. After evaporation under reduced pressure the residue was recrystallised from dichloromethane–methanol to afford [$\mathrm{Ru(pyS)_2(PPh_3)_2}$] (**9**) as orange microcrystals; yield 0.40 g (94%), m.p. 212—250 °C (decomp.) (Found: C, 65.9; H, 4.6; N, 3.0. Calc. for $\mathrm{C_{46}H_{38}N_2P_2RuS_2}$: C, 65.3; H, 4.5; N, 3.3%).

Reaction of [$\mathrm{RuCl_2(PPh_3)_3}$] *with Pyridine-2-thiol in the Presence of Triethylamine.*—A solution of the complex (0.288 g, 0.30 mmol), pySH (0.067 g, 0.60 mmol) and $\mathrm{NEt_3}$ (1 cm^3) in degassed benzene (50 cm^3) was heated under reflux for 24 h. The initial cloudy brown solution gradually cleared to afford a pale orange solution and a white precipitate ([$\mathrm{NHEt_3}$]Cl). The solution was cooled, filtered, concentrated to 15 cm^3 under reduced pressure, diluted with hexane (35 cm^3) and set aside for 12 h whereupon orange microcrystals separated. These were filtered off, washed with acetone, hexane, and diethyl ether then dried *in vacuo* and identified as [$\mathrm{Ru(pyS)_2(PPh_3)_2}$] (**9**) (0.16 g, 91%) by comparison with an authentic sample.

Reaction of [$\mathrm{RuCl_2(CO)_2(PPh_3)_2}$] *with Pyridine-2-thiol.*—A solution of the complex (0.226 g, 0.30 mmol) and pySH (0.10 g, 0.90 mmol) in toluene (50 cm^3) was heated under reflux for 3 h to afford an orange solution. Evaporation under reduced pressure left the crude product which was shown by ^{31}P-{^{1}H} n.m.r. spectroscopy to be a mixture of four components: [$\mathrm{Ru(pyS)_2(CO)(PPh_3)}$] (**3**), [$\mathrm{RuCl(pyS)(CO)(PPh_3)_2}$] (**6**), [$\mathrm{RuCl(pyS)(pySH)(CO)(PPh_3)_2}$] (**7**) and an unidentified species. Product ratio *ca.* 20:5:60:15. The crude material was washed with hexane and then extracted with methanol. The methanol extract was reduced to dryness and then recrystallised from chloroform–hexane to yield [$\mathrm{RuCl(pyS)(pySH)(CO)(PPh_3)_2}$] (**7**) as orange microcrystals (0.04 g, 15%) (Found: C, 61.0; H, 4.10; N, 3.35. Calc. for $\mathrm{C_{47}H_{39}ClN_2OP_2RuS_2}$: C, 62.0; H, 4.30; N, 3.10%).

Reaction of [$\mathrm{RuCl_2(CO)_2(PPh_3)_2}$] *with Pyridine-2-thiol in the Presence of Triethylamine.*—A solution of the complex (0.226 g, 0.30 mmol), pySH (0.10 g, 0.90 mmol), and $\mathrm{NEt_3}$ (1 cm^3) in toluene was heated under reflux for 3 h. A yellow solution and a white precipitate ([$\mathrm{NHEt_3}$]Cl) formed. The solution was cooled, filtered and evaporated to dryness under reduced pressure to leave a crude product which was shown by ^{31}P n.m.r. spectroscopy to be a *ca.* 45:55 mixture of two components: [$\mathrm{Ru(pyS)_2(CO)(PPh_3)}$] (**3**) and [$\mathrm{Ru(pyS)_2(CO)_2(PPh_3)}$] (**8**).

Reaction of [$\mathrm{Ru(O_2CCF_3)_2(MeOH)(CO)(PPh_3)_2}$] *with Pyridine-2-thiol.*—A mixture of the complex (0.271 g, 0.30 mmol) and pySH (0.067 g, 0.60 mmol) in benzene (50 cm^3) was heated under reflux for 2 h. The orange solution was cooled, filtered and reduced to dryness under reduced pressure. The residue was crystallised from methanol–water then washed with water, diethyl ether, and light petroleum (b.p. 60—80 °C) to yield orange microcrystals (0.20 g). This product was shown by spectroscopic methods to be a *ca.* 30:70 mixture of [$\mathrm{Ru(pyS)_2(CO)(PPh_3)}$] (**3**) and [$\mathrm{Ru(O_2CCF_3)(pyS)(pySH)(CO)(PPh_3)_2}$] (**11**). Recrystallisation of this mixture from chloroform–hexane followed by washing with light petroleum (b.p. 60—80 °C) and diethyl ether afforded [$\mathrm{Ru(O_2CCF_3)(pyS)(pySH)(CO)(PPh_3)_2}$] as yellow microcrystals; yield 0.09 g (34%), m.p. 203—205 °C (Found: C, 59.0; H, 3.90; N, 2.90. Calc. for $\mathrm{C_{49}H_{39}F_3N_2O_3P_2RuS_2}$: C, 59.55; H, 4.00; N, 2.85%).

Reaction of [$\mathrm{Ru(O_2CCF_3)(pyS)(pySH)(CO)(PPh_3)_2}$] *with Pyridine-2-thiol.*—A mixture of the complex (0.06 g, 0.008 mmol) and pySH (0.04 g, 0.36 mmol) in toluene (25 cm^3) was heated under reflux for 3 h. The solution was cooled and filtered then evaporated under reduced pressure to afford a yellow residue which was examined by ^{31}P-{^{1}H} n.m.r. and shown to be exclusively [$\mathrm{Ru(pyS)_2(CO)(PPh_3)}$] (**3**).

Carbonylation of [$\mathrm{RuCl(pyS)(pySH)(PPh_3)_2}$].—The complex (0.011 g, 0.012 mmol) was carbonylated (CO, 101 325 Pa) for 2 h in boiling benzene (25 cm^3). The yellow solution was cooled, filtered and then evaporated to dryness under reduced pressure.

The orange residue, after washing with hexane, was examined by ^{31}P n.m.r. and shown to be a *ca.* 50:40:10 mixture of [RuCl(pyS)(pySH)(CO)(PPh_3)$_2$] (**7**), [RuCl(pyS)(CO)(PPh_3)$_2$] (**6**), and [Ru(pyS)$_2$(CO)(PPh_3)] (**3**).

Reaction of [OsH_2(CO)(PPh_3)$_3$] *with Pyridine-2-thiol.*—A solution of the complex (0.30 g, 0.30 mmol) and pySH (0.10 g, 0.90 mmol) in toluene (50 cm^3) was heated under reflux for 12 h. During this time the solution changed from colourless to yellow. Evaporation of the filtered solution to dryness under reduced pressure followed by crystallisation of the residue from chloroform–hexane afforded yellow microcrystals; yield 0.09 g (35%). Spectroscopic (^{31}P-{^{1}H} n.m.r.) examination established the product as an 85:15 mixture of the *trans* phosphine isomers of [OsH(pyS)(CO)(PPh_3)$_2$] (**1′**) and (**2′**). An alternative crystallisation from CH_2Cl_2–MeOH afforded a pure sample of isomer (**1′**); yielded 0.08 g (31%), m.p. > 250 °C.

Reactions of [OsH_2(CO)(PPh_3)$_3$] *with Dipyridyl-2,2′-disulphide.*—A solution of the complex (0.96 g, 0.95 mmol) and dipyridyl-2,2′-disulphide (0.21 g, 0.95 mmol) in toluene (100 cm^3) was heated under reflux for 8 h. During this time the solution changed from colourless to lemon yellow. Concentrating the solution to 10 cm^3 under reduced pressure followed by cooling at 0 °C overnight afforded a pale yellow precipitate which was washed with methanol and hexane then dried *in vacuo* to yield pale yellow microcrystals. These were identified by their ^{31}P-{^{1}H} n.m.r. spectra as a *ca.* 80:20 mixture of [OsH(pyS)(CO)(PPh_3)$_2$], isomers (**1′**) and (**2′**); overall yield 0.41 g (50.5%) (Found: C, 58.3; H, 4.15; N, 1.2. Calc. for $C_{42}H_{35}NOOsP_2S$: C, 59.1; H, 4.15; N, 1.6%). When a 5-molar excess of pySSpy was used and the reflux time was extended to 36 h the solution changed from colourless to yellow then to deep orange. The cooled solution was evaporated to dryness under reduced pressure and the orange residue was extracted with methanol (3 × 25 cm^3). The extract was evaporated to dryness and the residue crystallised from chloroform–hexane to afford [Os(pyS)$_2$(CO)(PPh_3)] (**3′**) as orange microcrystals (0.28 g, 42%) (Found: C, 49.2; H, 3.3; N, 3.8. Calc. for $C_{29}H_{23}N_2OOsPS_2$: C, 49.7; H, 3.3; N, 4.00%).

Attempted Reactions with [OsH_2(CO)$_2$(PPh_3)$_2$].—Solutions of this complex (0.20 g, 0.26 mmol) when heated with pySH (0.086 g, 0.78 mmol) or pySSpy (0.17 g, 0.78 mmol) in toluene under reflux for 24 or 6 h, respectively, yielded essentially unchanged starting materials.

Reactions of [OsH(Cl)(CO)(PPh_3)$_3$] *with Pyridine-2-thiol.*—(*a*) *In cold benzene.* A suspension of the complex (0.25 g, 0.24 mmol) and pySH (0.0267 g, 0.24 mmol) was stirred in cold benzene (40 cm^3, 0—5 °C) for 1 h. During this time the suspension changed from yellow to orange. Evaporation to dryness under reduced pressure and without application of heat gave an orange-yellow residue (0.28 g) which was shown by ^{31}P-{^{1}H} n.m.r. spectroscopy to be a *ca.* 65:30:5 mixture of three components: [OsH(Cl)(pySH)(CO)(PPh_3)$_2$], isomers (**4′**) and **5′**), and [OsH(pyS)(CO)(PPh_3)$_2$] isomer (**2′**). Crystallisation from cold dichloromethane–methanol afforded [OsH(Cl)(pySH)(CO)(PPh_3)$_2$], mixed isomers (**4′**) and (**5′**) as yellow microcrystals: yield 0.16 g (75%) (Found: C, 57.3; H, 3.75; N, 1.35. Calc. for $C_{42}H_{36}ClNOOsP_2S$: C, 56.65; H, 4.05; N, 1.55%).

(*b*) *In boiling toluene.* A similar reaction in boiling toluene (18 h reflux) afforded after evaporation of the solvent a yellow residue which was shown by ^{31}P-{^{1}H} n.m.r. spectroscopy to contain three components: [OsH(pyS)(CO)(PPh_3)$_2$], isomers (**1′**) and (**2′**), and [OsCl(pyS)(CO)(PPh_3)$_2$] (**6′**) in the ratio 20:5:75.

Reaction of [OsH(Cl)(CO)(PPh_3)$_3$] *with Dipyridyl-2,2′-disulphide.*—A mixture of the complex (0.26 g, 0.25 mmol) and pySSpy (0.055 g, 0.25 mmol) in benzene (25 cm^3) was heated under reflux for 5 min to form an orange solution. Filtration followed by evaporation under reduced pressure yielded an orange yellow residue which, on crystallisation from dichloromethane–methanol, afforded [OsCl(pyS)(CO)(PPh_3)$_2$] (**6′**) as yellow microcrystals; yield 0.14 g (60%), m.p. > 300 °C (Found: C, 56.3; H, 4.00; N, 1.55. Calc. for $C_{42}H_{34}ClNOOsP_2S$: C, 56.8; H, 3.85; N, 1.60%).

Reactions of [OsH(Br)(CO)(PPh_3)$_3$] *with Pyridine-2-thiol.*—(*a*) *In cold benzene.* A solution of the complex (0.22 g, 0.203 mmol) and pySH (0.0225 g, 0.203 mmol) was stirred in cold benzene (50 cm^3, 0—5 °C) for 3 h. An initial yellow suspension gradually cleared to an orange–yellow solution, which was evaporated to dryness under reduced pressure without the application of heat to yield an orange-yellow residue (0.25 g). This was shown by spectroscopic methods to be a *ca.* 25:55:10:10 mixture containing the isomers of [OsH(Br)(pySH)(CO)(PPh_3)$_2$], (**4a′**) and (**5a′**), together with [OsBr(pyS)(CO)(PPh_3)$_2$] (**6a′**) and unchanged starting material.

(*b*) *In boiling toluene.* A similar reaction in boiling toluene (reflux time 3 h, three-fold excess of ligand) deposited, on evaporation of the solvent, an orange-yellow residue which, on crystallisation from dichloromethane–methanol, afforded [OsBr(pyS)(CO)(PPh_3)$_2$] (**6a′**) as pale yellow microcrystals (53%), m.p. > 300 °C (Found: C, 53.95; H, 4.10; N, 1.65. Calc. for $C_{42}H_{34}BrNOOsP_2S$: C, 54.1; H, 3.65; N, 1.50%).

Reaction of [OsH_4(PPh_3)$_3$] *with Pyridine-2-thiol.*—A solution of the complex (0.469 g, 0.48 mmol) and pySH (0.167 g, 1.5 mmol) in benzene (120 cm^3) was heated under reflux for 4 h. During this time the colour of the solution changed from yellow to red-brown. Evaporation of the filtered solution to dryness under reduced pressure and crystallisation of the residue from dichloromethane–methanol afforded [Os(pyS)$_2$(PPh_3)$_2$] (**9′**) as brown crystals; yield 0.35 g (78%) m.p. 232—233 °C (Found: C, 57.7; H, 4.0; N, 2.95. Calc. for $C_{46}H_{38}N_2OsP_2S_2$: C, 59.1; H, 4.1; N, 3.0%).

X-Ray Crystal Structure of [Ru(pyS)$_2$(CO)$_2$(PPh_3)].—*Crystal data.* $C_{30}H_{23}N_2O_2PRuS_2$, $M = 639.71$, monoclinic, a = 11.307(2), b = 11.083(3), c = 24.090(5) Å, β = 109.47(2)°, U = 2 846(1) Å^3, space group $P2_1/c$, Z = 4, D_c = 1.493, D_m = 1.48(1) g cm^{-3}. Yellow air-stable prisms obtained from chloroform–hexane, crystal dimensions 0.35 × 0.32 × 0.24 mm, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 7.65 cm^{-1}.

Data collection and processing. Nicolet *P3m* computer-controlled diffractometer. Unit cell determined by a least-squares procedure from the measured angular position of 15 reflections, θ range 5.35—16.36°. Max. value of sinθ/λ reached in intensity measurement 0.703 54 Å^{-1}, h = 0—15, k = 0—15, l = −33—33; 9 432 reflections recorded, 8 335 unique, 3 960 with $I < 4\sigma(I)$ classified as unobserved; $R_{\text{int.}}$ = 0.020. Data were processed as described by Bachechi *et al.*[45] with a value of the ignorance factor ρ = 0.000 202 and corrected for Lorentz and polarisation effects.

Structure analysis and refinement. Structure solved by Patterson and Fourier methods and refined by least-squares methods. The isotropic refinement converged at R = 0.096. In the subsequent least-squares cycles all non-hydrogen atoms were refined anisotropically. Hydrogen atoms included in the calculation with idealised positions [d(C–H) = 1.08 Å] and isotropic thermal parameters equal to those of the nearest carbon atoms. Convergence reached at R = 0.045 (R' = 0.054). Final refinement by full-matrix methods; function minimised $\Sigma w(|F_o| - |F_c|)^2$, with weights $w = 1/(\sigma^2|F_o| + b|F_o|^2)$ with b

Table 2. Positional parameters for non-hydrogen atoms, with estimated standard deviations in parentheses, for $[Ru(pyS)_2(CO)_2(PPh_3)]$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru	0.213 56(3)	0.685 27(4)	0.611 07(2)
S(1)	0.035 4(1)	0.811 6(1)	0.555 4(1)
S(2)	0.079 6(1)	0.618 1(1)	0.665 0(1)
P	0.324 4(1)	0.772 8(1)	0.553 4(1)
O(1)	0.162 6(5)	0.445 0(4)	0.548 8(2)
O(2)	0.458 5(4)	0.610 0(5)	0.701 6(2)
N(1)	0.208 5(4)	0.851 0(4)	0.653 7(2)
N(2)	0.248 7(4)	0.441 3(5)	0.704 6(2)
C(1)	0.182 9(5)	0.536 8(5)	0.570 7(3)
C(2)	0.364 3(5)	0.633 7(7)	0.669 0(3)
C(3)	0.103 4(5)	0.903 7(5)	0.617 2(3)
C(4)	0.062 1(6)	1.013 2(6)	0.629 6(4)
C(5)	0.132 5(7)	1.067 9(7)	0.683 1(4)
C(6)	0.234 8(7)	1.012 3(7)	0.720 8(4)
C(7)	0.271 2(6)	0.902 3(6)	0.704 5(3)
C(8)	0.150 3(5)	0.497 0(5)	0.710 4(2)
C(9)	0.094 6(7)	0.456 5(7)	0.752 0(3)
C(10)	0.147 0(9)	0.360 6(8)	0.787 8(3)
C(11)	0.249 8(9)	0.305 8(6)	0.783 6(3)
C(12)	0.298 1(8)	0.348 5(6)	0.741 2(3)
C(111)	0.251 0(4)	0.768 0(5)	0.473 1(2)
C(112)	0.145 1(6)	0.699 8(5)	0.446 4(3)
C(113)	0.095 7(7)	0.691 8(6)	0.385 6(3)
C(114)	0.151 2(6)	0.751 8(7)	0.350 5(3)
C(115)	0.253 3(7)	0.822 4(7)	0.375 8(3)
C(116)	0.306 4(6)	0.830 0(6)	0.437 5(3)
C(121)	0.354 8(5)	0.931 8(4)	0.571 9(2)
C(122)	0.271 3(6)	1.021 6(5)	0.539 8(3)
C(123)	0.284 0(8)	1.141 3(6)	0.560 3(3)
C(124)	0.379 1(8)	1.170 1(6)	0.612 3(4)
C(125)	0.459 1(7)	1.082 2(6)	0.643 9(3)
C(126)	0.447 4(6)	0.962 8(5)	0.623 9(2)
C(131)	0.479 7(4)	0.707 7(5)	0.563 6(2)
C(132)	0.497 1(5)	0.584 4(6)	0.572 1(3)
C(133)	0.613 1(6)	0.531 7(6)	0.578 6(3)
C(134)	0.710 6(6)	0.599 9(8)	0.577 2(3)
C(135)	0.693 8(6)	0.723 8(8)	0.566 5(3)
C(136)	0.579 9(5)	0.778 1(6)	0.560 0(3)

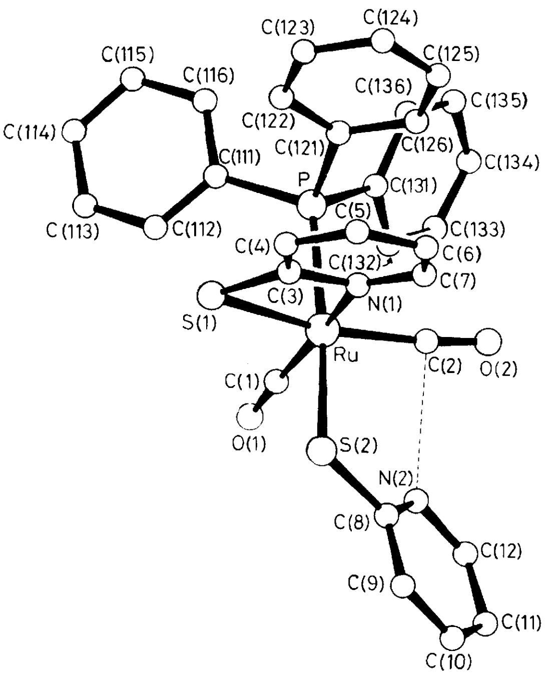


Figure 1. View of the molecular structure of $[Ru(pyS)_2(CO)_2(PPh_3)]$ showing the atomic numbering scheme

chosen so as to minimise the dispersion of the values of the minimised function over ranges of reflections ($b = 0.002\ 199$). Atomic scattering factors and anomalous dispersion terms were taken from International Tables.[46] Ratio of max. least-squares shift-to-error in final refinement cycle generally <0.05 for positional parameters and thermal parameters. Max. and min. height in final difference Fourier map 0.56 and -0.15 e Å^{-3}. Calculations performed on the UNIVAC 1110 computer of the University of Rome with SHELX 76 system of programs[47] and on the HP 21MX minicomputer of the C.N.R. Research Area of Rome using local programs.[48] Final positional parameters for non-H atoms are given in Table 2.

X-*Ray Crystal Structure of* $[Ru(pyS)_2(CO)(PPh_3)]$.—*Crystal data.* $C_{29}H_{23}N_2OPRuS_2$, $M = 611.70$, triclinic, $a = 10.317(3)$, $b = 11.749(3)$, $c = 12.517(3)$ Å, $\alpha = 67.65(2)$, $\beta = 70.55(2)$, $\gamma = 86.43(2)°$, $U = 1\ 319.6(6)$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_c = 1.539$, $D_m = 1.54(1)$ g cm^{-3}. Yellow air-stable prisms obtained from dichloromethane–methanol solution. Crystal dimensions $0.18 \times 0.48 \times 0.62$ mm, $\lambda(\text{Mo-}K_\alpha) = 0.710\ 69$ Å, $\mu(\text{Mo-}K_\alpha) = 8.19$ cm^{-1}.

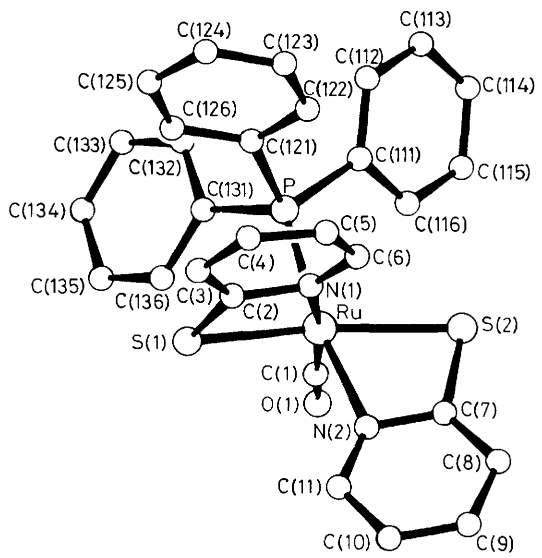


Figure 2. View of the molecular structure of $[Ru(pyS)_2(CO)(PPh_3)]$ showing the atomic numbering scheme

Data collection and processing. Nicolet *P*3*m* computer-controlled diffractometer. Unit cell determined by a least-squares procedure from the measured angular position of 15 reflections, θ range = 14.86—23.79°. Max. value of $\sin\theta/\lambda$ reached in intensity measurement 0.994 96 Å^{-1}, $h = 0$—20, $k = -23$—23, $l = -25$—25; 23 251 reflections recorded; after averaging 12 196 observed reflections with $I > 3\sigma(I)$, $R_{\text{int.}} = 0.0121$. For the three standard reflections recorded every 100 measurements only random deviations were found. Data processed as described by Bachechi *et al.*[45] with an ignorance factor $\rho = 0.000\ 056$, and corrected for Lorentz and polarisation effects.

Structure analysis and refinement. Structure solved by Patterson and Fourier methods, and refined by least-squares procedure. The isotropic refinement converged at $R = 0.103$. In

Table 3. Positional parameters for non-hydrogen atoms, with estimated standard deviations in parentheses, for [Ru(pyS)$_2$(CO)(PPh$_3$)]

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ru	−0.076 92(2)	0.203 72(2)	0.266 28(2)	C(111)	−0.134 7(3)	0.464 6(2)	0.345 7(3)
S(1)	−0.267 3(1)	0.047 0(1)	0.360 0(1)	C(112)	−0.206 6(4)	0.569 8(3)	0.343 0(4)
S(2)	0.110 2(1)	0.347 3(1)	0.105 0(1)	C(113)	−0.142 2(5)	0.674 5(3)	0.336 8(5)
P	−0.213 9(1)	0.318 4(1)	0.368 8(1)	C(114)	−0.007 3(5)	0.673 9(4)	0.334 2(4)
O(1)	0.088 6(3)	0.134 1(3)	0.434 5(3)	C(115)	0.065 0(4)	0.571 5(4)	0.334 7(4)
N(1)	−0.199 9(2)	0.228 5(2)	0.152 3(2)	C(116)	0.002 1(3)	0.466 5(3)	0.341 1(4)
N(2)	0.053 1(2)	0.124 4(2)	0.146 4(2)	C(121)	−0.369 6(2)	0.359 0(2)	0.328 5(3)
C(1)	0.021 8(3)	0.159 2(3)	0.372 9(3)	C(122)	−0.358 2(3)	0.445 8(3)	0.212 9(3)
C(2)	−0.299 3(3)	0.135 3(3)	0.226 0(3)	C(123)	−0.471 4(4)	0.467 2(4)	0.172 9(4)
C(3)	−0.410 5(4)	0.122 0(4)	0.189 9(4)	C(124)	−0.595 3(4)	0.402 2(5)	0.247 0(5)
C(4)	0.411 1(5)	0.203 7(5)	0.075 3(5)	C(125)	−0.608 9(3)	0.314 9(5)	0.362 7(4)
C(5)	−0.306 9(5)	0.290 3(5)	0.001 0(4)	C(126)	−0.495 7(3)	0.292 8(4)	0.403 9(3)
C(6)	−0.200 9(4)	0.302 9(3)	0.042 3(3)	C(131)	−0.279 5(3)	0.247 5(3)	0.536 6(2)
C(7)	0.142 8(3)	0.219 7(3)	0.063 7(3)	C(132)	−0.353 2(3)	0.315 1(3)	0.605 2(3)
C(8)	0.242 1(4)	0.210 1(4)	−0.040 1(4)	C(133)	−0.399 3(4)	0.261 3(4)	0.732 7(3)
C(9)	0.243 8(5)	0.097 1(4)	−0.052 6(4)	C(134)	−0.372 6(4)	0.141 0(4)	0.793 6(3)
C(10)	0.151 2(4)	0.001 4(4)	0.031 4(4)	C(135)	−0.300 2(4)	0.073 4(3)	0.727 1(3)
C(11)	0.054 9(3)	0.016 4(3)	0.132 8(3)	C(136)	−0.254 3(3)	0.126 5(3)	0.598 5(3)

the subsequent least-squares cycles all non-hydrogen atoms were refined anisotropically. Hydrogen atoms included in the calculation with idealised positions [*d*(C–H) = 1.08 Å] and isotropic thermal parameters equal to those of the nearest carbon atoms. Convergence reached at $R = 0.040$ ($R' = 0.057$). Final refinement by block diagonal least-squares methods; function minimised $\Sigma w(|F_o| - |F_c|)^2$, with weights $w = \sin\theta/\lambda$. Atomic scattering factors and anomalous dispersion terms were taken from International Tables.[46] Ratio of max. least-squares shift-to-error in final refinement cycle 0.02. Max. and min. height in final difference Fourier map 1.5 and −0.7 e Å^{-3}. Calculations performed on the HP 21MX minicomputer of the C.N.R. Research Area of Rome using local programs.[48] Final positional parameters for non-H atoms are given in Table 3.

Results and Discussion

Reactions with Ruthenium Precursors.—Reaction pathways and product stereochemistry are given in Scheme 1. Products are identified by the numbers (**1**)—(**11**).

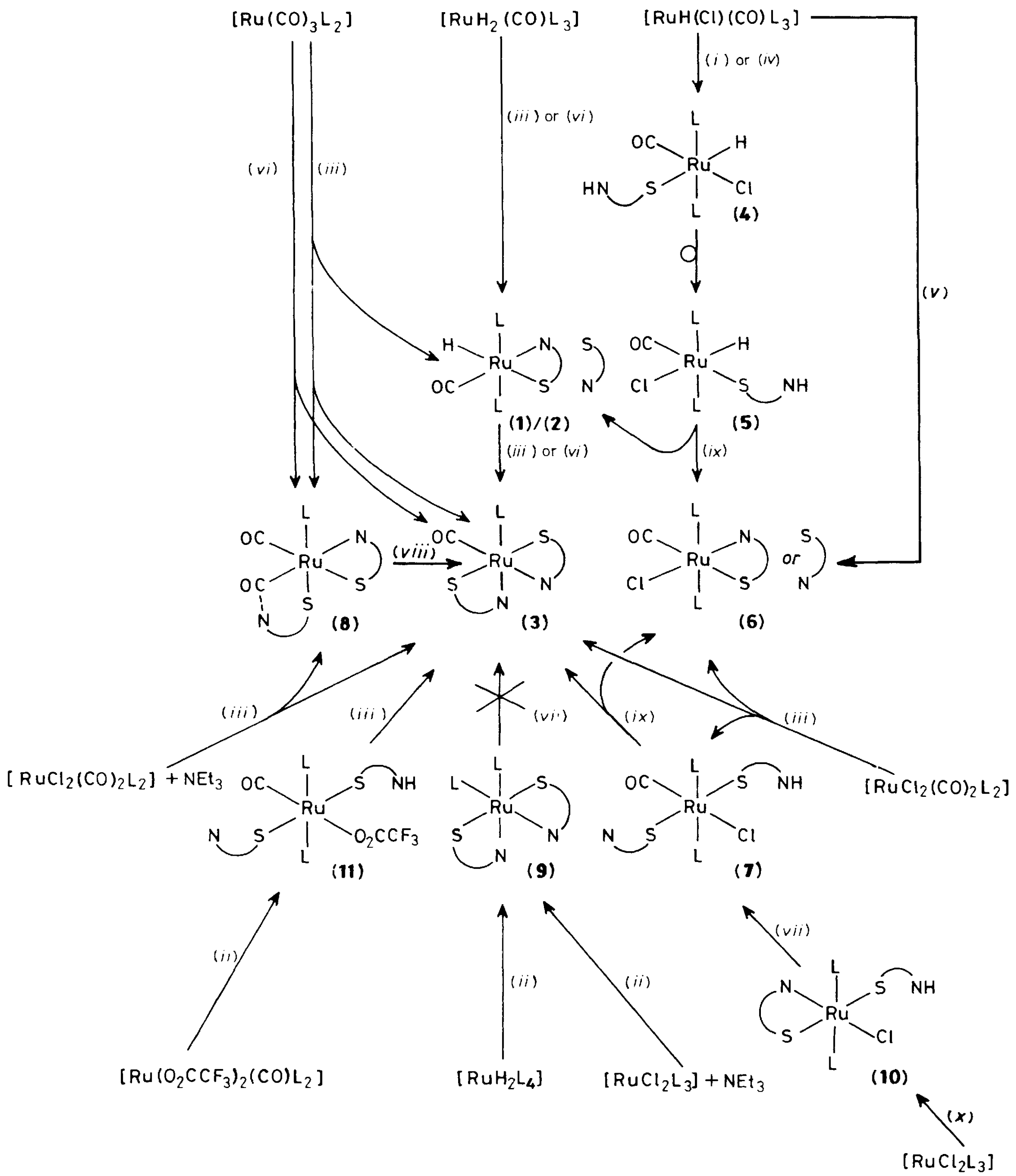
With [RuH$_2$(CO)(PPh$_3$)$_3$]. Treatment of [RuH$_2$(CO)(PPh$_3$)$_3$] with pySH or pySSpy in boiling toluene affords two isomeric products [RuH(pyS)(CO)(PPh$_3$)$_2$], (**1**) and (**2**), which react further in the presence of excess ligand to yield the bis-chelate [Ru(pyS)$_2$(CO)(PPh$_3$)] (**3**). N.m.r. data (Table 1) clearly indicate that isomers (**1**) and (**2**) each have a pair of equivalent ^{31}P nuclei *cis* to a hydride ligand and thus establish the *trans* phosphine structures shown in Scheme 1. Unfortunately hydride ligands *trans* to N-or S-donors of the type under discussion here have rather similar n.m.r. chemical shifts and it is therefore not easy to differentiate between isomers (**1**) and (**2**) on this basis. However, the high-field triplet signal (δ −11.55 p.p.m.) of the minor isomer shows a distinct broadening, relative to that of the major isomer, which we attribute to the presence of a small unresolved coupling ^4J(HH′) between the hydride ligand and the proton *ortho* to the nitrogen atom in the pyS ligand and which we take to be indicative of isomer (**2**) (hydride *trans* to N). It follows that the major isomer is (**1**) with hydride *trans* to S.

The formation of the isomer mixture (**1**)/(**2**) may be a kinetic phenomenon reflecting the reaction of tautomeric thione and thiol forms of pyridine-2-thiol with [RuH$_2$(CO)(PPh$_3$)$_3$]. However, given that the reaction of [RuH$_2$(CO)(PPh$_3$)$_3$] with dipyridyl-2,2′-disulphide affords the same isomer ratio it seems highly likely that we are observing a thermodynamically controlled isomer distribution.

The stereochemistry of [Ru(pyS)$_2$(CO)(PPh$_3$)] (**3**) cannot readily be deduced from spectroscopic data. However, an *X*-ray diffraction study (see below) confirmed the proposed stoicheiometry and established the stereochemistry shown in Scheme 1.

It is possible to formulate mechanisms for the formation of products (**1**)—(**3**) directly from pySSpy with concomitant liberation of pySH. However, in view of our later observation (see below) that pySSpy reacts readily with free triphenylphosphine in the presence of moisture to generate pySH it appears probable that an alternative mechanism involving pySH as reagent is also operative unless moisture is rigorously excluded from the system.

With [RuH(X)(CO)(PPh$_3$)$_3$] (X = Cl or Br). Treatment of [RuH(Cl)(CO)(PPh$_3$)$_3$] with pyridine-2-thiol (molar ratio 1:1) in cold benzene affords an orange air-stable two-component mixture which resisted attempts at separation. However, analytical and spectroscopic data were consistent with the presence of two isomeric products (**4**) and (**5**) with a common formulation [RuH(Cl)(pySH)(CO)(PPh$_3$)$_2$]. N.m.r. data (Table 1) indicate that each isomer possesses a pair of equivalent ^{31}P nuclei *cis* to a hydride ligand and are taken to indicate the structures shown. The possibility that linkage isomerism (*N*- or *S*-bonded pySH) is involved seems unlikely since the monofunctional N-donor ligands pyridine and piperidine each generate similar pairs of isomers [RuH(Cl)(L)(CO)(PPh$_3$)$_2$] {n.m.r. for L = C$_5$H$_5$N: δ(Ru*H*) = −13.51 [t, ^2J(PH) = 20 Hz], δ(*P*Ph$_3$) = 45.8 p.p.m. (s), δ(Ru*H*) = −12.41 [t, ^2J(PH) = 20 Hz], δ(*P*Ph$_3$) = 43.4 p.p.m. (s); for L = C$_5$H$_{11}$N: δ(Ru*H*) = −13.76 [t, ^2J(PH) = 18 Hz], δ(*P*Ph$_3$) = 46.9 p.p.m. (s), δ(Ru*H*) = −12.25 [t, ^2J(PH) = 20 Hz], δ(*P*Ph$_3$) = 44.6 p.p.m. (s)}. Unfortunately attempts to react monofunctional S-donor ligands [Pr^{i}NCS, thiophene, PPh$_3$S, (NH$_2$)$_2$CS, and PhSH] with [RuH(Cl)(CO)(PPh$_3$)$_3$] under mild conditions gave products too insoluble for n.m.r. spectra to be recorded. The isomeric products (**4**) and (**5**) cannot be halide-free cationic species, *i.e.* [RuH(CO)(pySH)$_2$(PPh$_3$)$_2$]$^+$, since the analogous products (**4a**) and (**5a**), obtained from [RuH(Br)(CO)(PPh$_3$)$_3$] under similar conditions, have significantly different n.m.r. parameters. The small chemical shifts observed in the high-field proton n.m.r. spectra when chloride is replaced by bromide are consistent with the presence of halide *cis* and *trans* to the hydride ligand in (**4**) and (**5**) respectively. As



Scheme 1. L = PPh_3. (*i*) pySH, C_6H_6; (*ii*) pySH, C_6H_6 (reflux); (*iii*) pySH, $C_6H_5CH_3$ (reflux); (*iv*) pySSpy, C_6H_6; (*v*) pySSpy, C_6H_6 (reflux); (*vi*) pySSpy, $C_6H_5CH_3$ (reflux); (*vii*) CO, C_6H_6 (reflux); (*viii*) $CHCl_3$, hexane, 25 °C; (*ix*) C_6H_6 (reflux); (*x*) pySH, Me_2CO (reflux)

noted above, it is not easy to distinguish, on the basis of high-field proton n.m.r. shifts, between hydride *trans* to N- or S-donors in the present systems. However, the shifts recorded for isomer (**4**) and its bromo-analogue (**4a**) (δ −10.22 and −10.50 p.p.m. respectively) tend to favour hydride *trans* to the softer S-donor rather than N-donor atom; this result is in keeping with the known tendency for pyridine-2-thiol to exist in the thione form and to co-ordinate as an S-donor. Thus it is possible to rationalise formation of products (**4**) and (**5**) in terms of a displacement of the labile triphenylphosphine ligand *trans* to hydride[49] by the thione form of the pySH ligand and subsequent partial isomerisation of the product (**4**) ⟶ (**5**).

A more prolonged treatment of [RuH(Cl)(CO)(PPh_3)$_3$] with pyridine-2-thiol gave a good yield of the expected product [RuCl(pyS)(CO)(PPh_3)$_2$] (**6**) together with small amounts (*ca.* 10%) of the isomeric hydrides [RuH(pyS)(CO)(PPh_3)$_2$], (**1**) and (**2**). The $^{31}P-\{^1H\}$ n.m.r. spectrum of (**6**) consists of a singlet indicative of equivalent and therefore mutually *trans* triphenylphosphine ligands. Given that (**6**) is formed by elimination of dihydrogen from the major isomer (**5**) it follows that (**6**) probably has the structure shown rather than the alternative arrangement with chloride and carbonyl ligands transposed.

The formation of products (**1**) and (**2**), albeit in small yield, in the reaction of [RuH(Cl)(CO)(PPh_3)$_3$] with pySH was not anticipated but with hindsight can be attributed to excess pySH functioning as a base to remove HCl from the intermediate [RuH(Cl)(pySH)(CO)(PPh_3)$_2$]. Complete conversion of [RuH(Cl)(pySH)(CO)(PPh_3)$_2$], isomers (**4**) and (**5**), to

$[RuH(pyS)(CO)(PPh_3)_2]$, isomers (**1**) and (**2**), under similar conditions but in the presence of added base (NEt_3) confirms this conclusion. The presence of intramolecular H-bonding (N–H ••• Cl) between pySH and chloride ligands in (**4**) and (**5**) may also facilitate the elimination of HCl to form (**1**) and (**2**). When $[RuCl(pyS)(CO)(PPh_3)_2]$ (**6**) is heated under reflux with excess pySH (benzene, 90 min) conversion to $[RuCl(pyS)(pySH)(CO)(PPh_3)_2]$ (**7**) and thence by HCl elimination to $[Ru(pyS)_2(CO)(PPh_3)]$ (**3**) occurs. N.m.r. data [$\delta(PPh_3)$ = 33.1 p.p.m. (s)] observed for (**7**) indicate a *trans* phosphine structure.

Treatment of $[RuH(Cl)(CO)(PPh_3)_3]$ with dipyridyl-2,2′-disulphide in cold benzene led to the unexpected formation of $[RuH(Cl)(pySH)(CO)(PPh_3)_2]$, isomers (**4**) and (**5**). Further investigation revealed that, in the presence of free triphenylphosphine {from $[RuH(Cl)(CO)(PPh_3)_3]$} and adventitious moisture, dipyridyl-2,2′-disulphide is reduced to pyridine-2-thiol which, in turn, affords the observed products (below).

$$[RuH(Cl)(CO)(PPh_3)_3] \longrightarrow [RuH(Cl)(CO)(PPh_3)_2] + PPh_3$$

$$pySSpy + H_2O + PPh_3 \longrightarrow 2\ pySH + PPh_3O$$

$$[RuH(Cl)(CO)(PPh_3)_2] + pySH \longrightarrow [RuH(Cl)(pySH)(CO)(PPh_3)_2]$$

Under more vigorous conditions the same reagents afford the expected product $[RuCl(pyS)(CO)(PPh_3)_2]$ (**6**) in good yield.

With $[Ru(CO)_3(PPh_3)_2]$. Pyridine-2-thiol reacts with $[Ru(CO)_3(PPh_3)_2]$ (molar ratio 3:1) in boiling toluene over a period of *ca.* 30 min to yield a mixture of four products: $[RuH(pyS)(CO)(PPh_3)_2]$, isomers (**1**) and (**2**), $[Ru(pyS)_2(CO)(PPh_3)]$ (**3**), and $[Ru(pyS)_2(CO)_2(PPh_3)]$ (**8**). After 3 h reflux the major product is $[Ru(pyS)_2(CO)(PPh_3)]$ (**3**) contaminated with *ca.* 5% of $[Ru(pyS)_2(CO)_2(PPh_3)]$ (**8**).

Treatment of $[Ru(CO)_3(PPh_3)_2]$ with dipyridyl-2,2′-disulphide (molar ratio 1:1) in boiling toluene for 10 min yielded a mixture of two products, $[Ru(pyS)_2(CO)(PPh_3)]$ (**3**) and $[Ru(pyS)_2(CO)_2(PPh_3)]$ (**8**). Extraction with methanol and repeated recrystallisation of the residue gave the major product (**8**) in pure form. An *X*-ray diffraction study (see below) confirmed the proposed stoicheiometry and established the stereochemistry shown in Scheme 1.

When allowed to stand for several days in chloroform–hexane solution at ambient temperature the dicarbonyl complex $[Ru(pyS)_2(CO)_2(PPh_3)]$ slowly loses carbon monoxide to form the monocarbonyl $[Ru(pyS)_2(CO)(PPh_3)]$. Likewise, on heating in the solid-state, effervescence attributable to carbon monoxide evolution (187—189 °C) preceded melting (213—214 °C). A possible explanation for the lability of the carbonyl ligand involving incipient nucleophilic attack by the nitrogen atom of the monodentate pyS ligand on the carbon atom of the carbonyl ligand is indicated by the results of the *X*-ray diffraction study, discussed below, which reveal a very short non-bonded distance between these two atoms.

With $[RuH_2(PPh_3)_4]$. This reaction has already been reported by Wilkinson and co-workers;[36,37] the product $[Ru(pyS)_2(PPh_3)_2]$ (**9**) has also been obtained from $[Ru_5Cl_{12}]^{2-}$ and pyridine-2-thiol,[36,37] and the *X*-ray crystal structure has been determined.[13] The compound has *cis*-phosphines in the solid state but adopts a *trans* structure in solution (see below). Attempts to convert $[Ru(pyS)_2(PPh_3)_2]$ to $[Ru(pyS)_2(CO)(PPh_3)]$ by carbonylation in boiling benzene were unsuccessful.

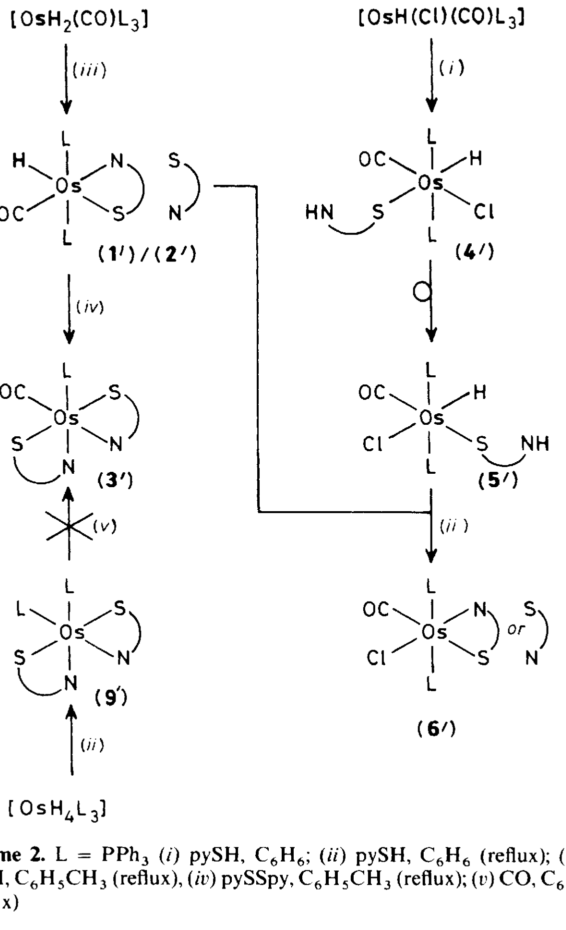
With $[RuCl_2(PPh_3)_3]$. Treatment of $[RuCl_2(PPh_3)_3]$ with pySH (molar ratio 1:2) and excess triethylamine in boiling benzene for 24 h gave $[Ru(pyS)_2(PPh_3)_2]$ (**9**), identical to the product mentioned above.

We have also repeated the reaction between $[RuCl_2(PPh_3)_3]$ and pySH, and isolated the product $[\{RuCl(pyS)(pySH)(PPh_3)_2\}_n]$ (**10**) previously obtained by Gilbert and Wilkinson.[33] However, in our hands, the complex is apparently monomeric [Found: *M* 650 ($CHCl_3$ solution); monomer requires *M* 887] and, given that the dimeric structure originally proposed is likely to be highly strained, a monomer appears more probable. Further evidence in favour of a monomeric formulation is provided by the proton n.m.r. spectrum which displays a *concentration independent* resonance at δ 13.22 p.p.m. attributable to an *intra*molecular rather than an *inter*molecular H-bonding interaction N–H ••• Cl.

Carbonylation (benzene, reflux, 2 h) of $[RuCl(pyS)(pySH)(PPh_3)_2]$ affords an orange microcrystalline solid which was shown by $^{31}P-\{^1H\}$ n.m.r. to consist of three components: $[RuCl(pyS)(pySH)(CO)(PPh_3)_2]$ (**7**), $[RuCl(pyS)(CO)(PPh_3)_2]$ (**6**), and $[Ru(pyS)_2(CO)(PPh_3)]$ (**3**).

With $[RuCl_2(CO)_2(PPh_3)_2]$. Treatment of $[RuCl_2(CO)_2(PPh_3)_2]$ (*cis* CO/*trans* PPh_3 isomer) with pyridine-2-thiol (molar ratio 1:3) in boiling toluene for 3 h affords a mixture containing four components: $[Ru(pyS)_2(CO)(PPh_3)]$ (**3**), $[RuCl(pyS)(CO)(PPh_3)_2]$ (**6**), $[RuCl(pyS)(pySH)(CO)(PPh_3)_2]$ (**7**) and an unidentified product (**12**). From this mixture the minor component (**7**) can be separated by extraction into methanol.

The same reaction performed in the presence of excess triethylamine affords an approximately equimolar mixture of $[Ru(pyS)_2(CO)(PPh_3)]$ (**3**) and $[Ru(pyS)_2(CO)_2(PPh_3)]$ (**8**) thus confirming the ability of the organic base to abstract HCl from these systems.



Scheme 2. L = PPh_3 (*i*) pySH, C_6H_6; (*ii*) pySH, C_6H_6 (reflux); (*iii*) pySH, $C_6H_5CH_3$ (reflux), (*iv*) pySSpy, $C_6H_5CH_3$ (reflux); (*v*) CO, C_6H_6 (reflux)

With $[Ru(O_2CCF_3)_2(MeOH)(CO)(PPh_3)_2]$. Pyridine-2-thiol reacts with $[Ru(O_2CCF_3)_2(MeOH)(CO)(PPh_3)_2]$ in boiling benzene to afford a mixture of $[Ru(O_2CCF_3)(pyS)(pySH)(CO)(PPh_3)_2]$ (**11**) and $[Ru(pyS)_2(CO)(PPh_3)]$ (**3**) from which the former product may be separated by fractional crystallisation. Spectroscopic data for (**11**) indicate monodentate trifluoroacetate [$\nu(OCO)$ = 1 689 and 1 433 cm^{-1}, KBr disc] and equivalent triphenylphosphine ligands [$\delta(PPh_3)$ = 32.75 p.p.m.] thus suggesting a *trans* phosphine structure analogous to that proposed (see above) for the corresponding chloro-complex (**7**). The shift in ν(CO) from 1 922 to 1 940 which accompanies the change from chloride to trifluoroacetate clearly implies that these anionic ligands are *trans* to carbonyl in their respective complexes, and thus establishes the stereochemical arrangements shown for (**7**) and (**11**) in Scheme 1. Under more vigorous conditions and in the presence of excess ligand, (**11**) is converted quantitatively into $[Ru(pyS)_2(CO)(PPh_3)]$ (**3**).

Reactions with Osmium Precursors.—Reaction pathways and product stereochemistries are given in Scheme 2. Products are identified by the numbers (**1′**)—(**9′**). The osmium-based reactions generally parallel those of their ruthenium counterparts but proceed more slowly.

With $[OsH_2(CO)(PPh_3)_3]$. Treatment of $[OsH_2(CO)(PPh_3)_3]$ with pyridine-2-thiol (molar ratio 1:1) in boiling toluene over a period of 4 h yields a dark yellow air-stable solid containing unreacted $[OsH_2(CO)(PPh_3)_3]$ (*ca.* 55%) and two isomeric products $[OsH(pyS)(CO)(PPh_3)_2]$, (**1′**) and (**2′**). A more prolonged reaction (12 h) gave the mixed isomers (**1′**) and (**2′**) free from starting material. The same mixture of isomers was obtained when $[OsH_2(CO)(PPh_3)_3]$ was heated with dipyridyl-2,2′-disulphide (1:1 molar ratio) in toluene for 8 h.

On the basis of ^1H and $^{31}P-\{^1H\}$ n.m.r. data (Table 1) and by the comparison with their ruthenium analogues the osmium products (**1′**) and (**2′**) can be assigned the structures shown in Scheme 2; (**1′**) is the major isomer (*ca.* 80%). A more prolonged reaction (refluxing toluene, 36 h) with excess pySSpy gave the bis-chelate $[Os(pyS)_2(CO)(PPh_3)]$ (**3′**) which is assigned the same stereochemistry as that established (see above) for the analogous ruthenium complex.

With $[OsH(X)(CO)(PPh_3)_3]$ (X = Cl *or* Br). Treatment of $[OsH(Cl)(CO)(PPh_3)_3]$ with pyridine-2-thiol (molar ratio 1 : 1) in cold benzene for 1 h gave an air-stable orange-yellow four-component mixture in which the major products, isomers of $[OsH(Cl)(pySH)(CO)(PPh_3)_2]$, (**4′**) and (**5′**), were contaminated with small amounts of $[OsH(pyS)(CO)(PPh_3)_2]$, isomer (**2′**), and an unidentified hydride-containing species. On the basis of ^1H and $^{31}P-\{^1H\}$ n.m.r. data, and by analogy with the corresponding ruthenium system, (**4′**) and (**5′**) are assigned the structures shown with (**4′**) as the major isomer.

In a similar reaction the bromide $[OsH(Br)(CO)(PPh_3)_3]$ affords three products: $[OsH(Br)(pySH)(CO)(PPh_3)_2]$, isomers (**4a′**) and (**5a′**), and $[OsBr(pyS)(CO)(PPh_3)_2]$ (**6a′**).

Reactions between $[OsH(X)(CO)(PPh_3)_3]$ and pyridine-2-thiol or dipyridyl-2,2′-disulphide in boiling benzene or toluene

Table 4. Selected bond distances (Å)* and angles (°) for $[Ru(pyS)_2(CO)_2(PPh_3)]$

Ru–S(1)	2.453(1)	S(1)–C(3)	1.757(6)	C(3)–C(4)	1.368(8	N(2)–C(12)	1.348(8)
Ru–S(2)	2.419(1)	S(2)–C(8)	1.747(6)	C(4)–C(5)	1.407(10)	C(8)–C(9)	1.423(7)
Ru–P	2.367(1)	O(1)–C(1)	1.133(6)	C(5)–C(6)	1.357(10)	C(9)–C(10)	1.373(10}
Ru–N(1)	2.114(4)	O(2)–C(2)	1.124(6)	C(6)–C(7)	1.384(9)	C(10)–C(11)	1.344(10)
Ru–C(1)	1.884(5)	N(1)–C(3)	1.353(7)	N(2)–C(8)	1.320(7)	C(11)–C(12)	1.392(10)
Ru–C(2)	1.895(5)	N(1)–C(7)	1.321(7)				

S(1)–Ru–S(2)	85.5(1)	S(2)–Ru–C(2)	94.7(2)	Ru–N(1)–C(3)	102.7(3)	Ru–S(2)–C(8)	109.6(2)
S(1)–Ru–P	86.8(<1)	N(1)–Ru–C(1)	168.4(2)	N(1)–C(3)–C(4)	122.1(6)	S(2)–C(8)–N(2)	121.3(4)
S(1)–Ru–N(1)	67.6(1)	P–Ru–N(1)	92.0(1)	S(1)–C(3)–N(1)	109.9(4)	N(2)–C(8)–C(9)	120.9(6)
S(1)–Ru–C(1)	103.9(2)	P–Ru–C(1)	95.6(2)	C(3)–C(4)–C(5)	116.9(7)	C(8)–C(9)–C(10)	119.1(6)
S(1)–Ru–C(2)	161.4(2)	P–Ru–C(2)	91.9(2)	C(4)–C(5)–C(6)	120.8(6)	C(9)–C(10)–C(11)	120.4(6)
S(2)–Ru–P	172.1(<1)	Ru–C(1)–O(1)	176.3(5)	C(5)–C(6)–C(7)	118.5(7)	C(10)–C(11)–C(12)	117.5(7)
S(2)–Ru–C(1)	88.2(2)	Ru–C(2)–O(2)	174.4(5)	C(6)–C(7)–N(1)	121.6(7)	C(11)–C(12)–N(2)	124.1(7)
		Ru–S(1)–C(3)	79.7(2)	C(7)–N(1)–C(3)	119.9(5)	C(12)–N(2)–C(8)	117.9(5)

* Non-bonded distance, N(2) ··· C(2) 2.782(7) Å.

Table 5. Selected bond distances (Å) and angles (°) for $[Ru(pyS)_2(CO)(PPh_3)]$

Ru–S(1)	2.429(1)	S(1)–C(2)	1.732(4)	C(2)–C(3)	1.403(5)	N(2)–C(11)	1.342(4)
Ru–S(2)	2.422(1)	S(2)–C(7)	1.744(3)	C(3)–C(4)	1.392(10)	C(7)–C(8)	1.400(7)
Ru–P	2.309(1)	O(1)–C(1)	1.146(4)	C(4)–C(5)	1.344(10)	C(8)–C(9)	1.393(7)
Ru–N(1)	2.138(2)	N(1)–C(2)	1.357(5)	C(5)–C(6)	1.392(6)	C(9)–C(10)	1.359(9)
Ru–N(2)	2.118(3)	N(1)–C(6)	1.324(6)	N(2)–C(7)	1.338(6)	C(10)–C(11)	1.392(7)
Ru–C(1)	1.844(3)						

S(1)–Ru–S(2)	157.96(3)	S(2)–Ru–C(1)	91.7(1)	S(1)–C(2)–N(1)	111.4(2)	Ru–N(2)–C(7)	102.2(2)
S(1)–Ru–P	88.90(3)	P–Ru–N(2)	170.8(1)	N(1)–C(2)–C(3)	120.1(4)	S(2)–C(7)–N(2)	110.0(3)
S(1)–Ru–N(1)	67.8(1)	P–Ru–N(1)	92.75(7)	C(2)–C(3)–C(4)	117.7(5)	N(2)–C(7)–C(8)	121.2(3)
S(1)–Ru–N(2)	96.46(8)	P–Ru–C(1)	90.9(1)	C(3)–C(4)–C(5)	120.9(4)	C(7)–C(8)–C(9)	117.1(5)
S(1)–Ru–C(1)	105.1(1)	N(1)–Ru–C(1)	172.0(1)	C(4)–C(5)–C(6)	119.4(6)	C(8)–C(9)–C(10)	121.2(5)
S(2)–Ru–P	105.22(3)	Ru–C(1)–O(1)	176.8(4)	C(5)–C(6)–N(1)	120.8(5)	C(9)–C(10)–C(11)	119.1(4)
S(2)–Ru–N(2)	67.51(9)	Ru–S(1)–C(2)	80.2(1)	C(6)–N(1)–C(2)	121.0(3)	C(10)–C(11)–N(2)	120.2(5)
S(2)–Ru–N(1)	94.2(1)	Ru–N(1)–C(2)	100.5(2)	Ru–S(2)–C(7)	80.2(2)	C(11)–N(2)–C(7)	121.2(4)

afford the products $[OsX(pyS)(CO)(PPh_3)_2]$ (**6′**) together with small amounts of $[OsH(pyS)(CO)(PPh_3)_2]$, isomers (**1′**) and (**2′**). From these mixtures the major products $[OsX(pyS)(CO)(PPh_3)_2]$ can be crystallised in pure form. On the basis of n.m.r. data and by analogy with the corresponding ruthenium complexes the products $[OsX(pyS)(CO)(PPh_3)_2]$ (**6′**) were tentatively assigned the stereochemistry shown in Scheme 2.

With $[OsH_4(PPh_3)_3]$. Treatment of $[OsH_4(PPh_3)_3]$ with pyridine-2-thiol (molar ratio 1:3) in boiling benzene for 4 h affords $[Os(pyS)_2(PPh_3)_2]$ (**9′**) as a brown microcrystalline solid. By analogy with the corresponding ruthenium complex,[36,37] for which structural data are available,[13] we assign the structure with *cis* triphenylphosphine ligands (Scheme 2) to the osmium complex. However, the ^1H n.m.r. spectra of $[Os(pyS)_2(PPh_3)_2]$ and its ruthenium analogue, both taken in C_6D_6 solution, are essentially identical, and each display an *ortho* to *meta*/*para* proton resonance separation of *ca.* 0.7 p.p.m. for the triphenylphosphine protons. Since we have previously shown chemical shift separations of this magnitude to be indicative of mutually *trans* triphenylphosphine ligands[50] these results clearly imply that dissolution of the complexes $[M(pyS)_2(PPh_3)_2]$ in deuteriochloroform is accompanied by a *cis* ⟶ *trans* isomerisation. In order to verify this conclusion we have examined the ^{13}C spectrum of the ruthenium complex. The presence in this spectrum of virtual coupling (triplet patterns) between the phenyl ^{13}C atoms and the ^{31}P atoms of the triphenylphosphine ligands strongly suggests that the complex does indeed adopt a *trans* phosphine configuration in solution.[51] Further support for this conclusion is provided by the absence of any coupling between the ^{13}C atoms of the pyS ligands and the ^{31}P atoms of the phosphine ligands. In the closely related complex $[Ru(pyS)_2(CO)(PPh_3)]$, where the phosphine is *trans* to a pyS ligand, small couplings of this type are clearly discernible under similar conditions. A detailed account of these and some related ^{13}C spectra will be published elsewhere.

X-Ray Crystal Structure of $[Ru(pyS)_2(CO)_2(PPh_3)]$.—The molecular structure is shown in Figure 1, molecular dimensions are given in Table 4. The monomeric complex has highly distorted octahedral co-ordination about the ruthenium(II) atom with a chelate (N,S-donor) pyS ligand *trans* to a *cis* pair of carbonyls and a monodentate (S-donor) pyS ligand *trans* to the triphenylphosphine ligand. The most interesting feature of the structure is the short non-bonded contact N(2)···C(2) between the nitrogen atom of the monodentate pyS ligand and the carbon atom of one of the carbonyl ligands. This close approach [2.782(7) Å], which is *ca.* 0.5 Å *less* than the sum of the van der Waals radii of the two atoms concerned, may simply arise from molecular packing interactions or stereochemical constraints within the ruthenium co-ordination sphere. However, given the remarkable lability of this carbonyl ligand, noted above, it seems highly probable that the close approach of N(2) to C(2) reflects an incipient nucleophilic attack by the pyridine nitrogen on the carbon atom of the carbonyl ligand. Such an interaction, which would be expected to feed electron density from the nitrogen lone pair into a π^* antibonding orbital on the carbonyl ligand to the detriment of the metal→carbonyl d_π–p_π back-bonding, should be reflected in the structural parameters of the carbonyl ligand. Unfortunately a comparison of the bond lengths and angles for the Ru–C(1)–O(1) group [Ru–CO 1.884(5), RuC–O 1.133(6) Å; Ru–C–O 176.3(5)°] with those of the Ru–C(2)–O(2) group [Ru–CO 1.895(5), RuC–O 1.124(6) Å; Ru–C–O 174.4(5)°] reveals differences which, though consistent with the effect of a nucleophilic attack on the carbon atom of the Ru–C(2)–O(2) carbonyl ligand, are too small to be statistically significant.

However, in view of the chemical evidence discussed above we stand by our conclusion[52] that the short non-bonding distance N(2)···C(2) is indeed indicative of such an attack. Other bond distances and angles are similar to those found in related structures involving octahedral ruthenium(II) and merit no special comment. A preliminary report on this structure and the labile carbonyl ligand has appeared elsewhere.[52]

X-Ray Crystal Structure of $[Ru(pyS)_2(CO)(PPh_3)]$.—The molecular structure is shown in Figure 2, molecular dimensions are given in Table 5. The monomeric complex has highly distorted octahedral co-ordination about the ruthenium(II) atom with two chelate pyS ligands (mutually *trans* S atoms, mutually *cis* N atoms), a carbonyl group, and a triphenylphosphine ligand. The structure closely parallels that previously found[13] for the related complex $[Ru(pyS)_2(PPh_3)_2]$ except that one of the phosphine ligands in the latter is replaced by a carbonyl. A comparison of salient bond distances and angles for the two structures reveals excellent correlation.

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