Complexes of the Platinum Metals
Part 35*. 4,6-Dimethylpyrimidine-2-thiol Derivatives of Ruthenium, Osmium, Rhodium and Iridium

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Abstract

Reactions of 4,6-dimethylpyrimidine-2-thiol (Me_2pymSH) and its oxidation product bis(4,6-dimethylpyrimidine-2-yl)disulphide (Me_2pymSSpymMe_2) with a range of platinum metal complexes are described. The chlorohydrides $[MHCl(CO)(PPh_3)_3]$ (M = Ru, Os) react with Me_2pymSH in refluxing toluene to afford $[RuCl(Me_2pymS)(CO)(PPh_3)_2]$ and $[OsH(Me_2pymS)(CO)(PPh_3)_2]$ (two isomers). A similar reaction in cold benzene affords the substitution product $[RuH(Cl)(Me_2pymSH)(CO)(PPh_3)_2]$ (two isomers). Reaction of the precursors $[MH_2(CO)(PPh_3)_3]$ (M = Ru, Os) and $[Ru(CO)_3(PPh_3)_2]$ in boiling toluene afford $[MH(Me_2pymS)(CO)(PPh_3)_2]$ (two isomers) and $[Ru(Me_2pymS)_2(CO)(PPh_3)]$ (two isomers) respectively whilst the reaction of $[Ru(CO)_3(PPh_3)_2]$ with Me_2pymSSpymMe_2 yields a mixture of $[Ru(Me_2pymS)_2(CO)_2(PPh_3)]$ and $[Ru(Me_2pymS)_2(CO)(PPh_3)]$. In the presence of the base (NEt_3) the dichlorides $[MCl_2(PPh_3)_3]$ (M = Ru, Os) react with Me_2pymSH to afford the bis-chelates $[M(Me_2pymS)_2(PPh_3)_2]$. Reactions between Me_2pymSH and the precursors $[IrCl(CO)(PPh_3)_2]$ and $[IrH(CO)(PPh_3)_3]$ at ambient temperature or below afford $[IrH(Cl)(Me_2pymS)(CO)(PPh_3)_2]$ and $[IrH_2(Me_2pymS)(CO)(PPh_3)_2]$ respectively, the same ligand reacts with $[RhCl(PPh_3)_3]$ and *mer*-$[IrH_3(PPh_3)_3]$ in refluxing benzene to afford $[RhH(Cl)(Me_2pymS)(PPh_3)_2]$, $[Rh(Me_2pymS)_3(PPh_3)]$, and $[IrH_2(Me_2pymS)(PPh_3)_2]$. The new complexes have been characterised by infrared and NMR [^1H, $^{31}P\{^1H\}$] spectroscopy, and shown to contain monodentate (S-bonded) or chelate (N,S-bonded) Me_2pymS ligands.

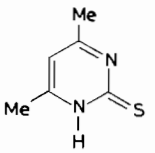
Introduction

As part of a study of the cyclic ligands containing the tautomeric grouping

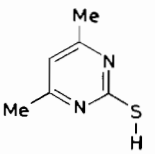
$$-NH-C(S)- \rightleftharpoons -N=C(SH)-$$

we have previously reported on the synthesis and characterisation of platinum group metal derivatives of pyridine-2-thiol [2]. In this paper we describe the extension of our work in this area to cover derivatives of the closely related pyrimidine-2-thiol system, and have chosen as our example 4,6-dimethylpyrimidine-2-thiol a molecule with a simple but informative ^1H NMR spectrum. Pyrimidine thiols are of interest because of their close relationship to sulphur analogues of the DNA bases and because their substituted derivatives find application as anti-tumour [3] and anti-thyroid agents [4]. 4,6-Dimethylpyrimidine-2-thiol contains two heterocyclic nitrogen atoms, and it was thought that some complexes of the anion might exhibit tautomeric character through interchange of monodentate (S-bonded) and monodentate (N-bonded) coordination modes through a bidentate (N,S-bonded) intermediate, or fluxional behaviour by exchange of one bidentate (N,S-bonded) form with an equivalent bidentate form involving bonding through the other nitrogen atom. The methyl groups at the 4 and 6 positions provide a convenient proton NMR label to afford evidence of the bonding mode or to demonstrate fluxional behaviour.

Me_2pymSH is a weak acid (pK_a 8.5) [5] for which two tautomeric forms are possible **Ia** and **Ib**. Pyrimidine-2-thiol (pymSH) has been predicted by quantum mechanical calculations [6] to exist mainly in the thione form, and this has been confirmed by infrared [7], ultraviolet [8] and ^{13}C NMR [9] spectroscopy. A ^{13}C NMR study has indicated that



Ia



Ib

*Part 34 is ref. 1.
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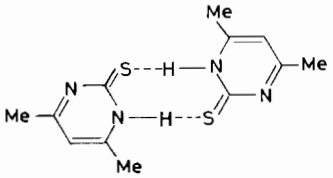
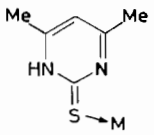
4,6-dimethylpyrimidine-2-thiol (Me_2pymSH) is also present in the thione form (**Ia**) in solution [10].

There is no published crystal structure for pyrimidine-2-thione or a substituted pyrimidine-2-thione, however a crystal structure for pyrimidine-2-one [11] clearly shows N--H--O hydrogen bonding in the solid state and a similar situation would be expected to pertain with pyrimidine-2-thiol. NMR evidence (see below) shows that the NH proton of Me_2pymSH is involved in hydrogen bonding and Me_2pymSH may be present in solution as hydrogen bonded dimers (**II**).

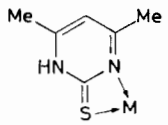


II

Me_2pymSH can coordinate to metals as a neutral species (Me_2pymSH) or as the conjugate base (Me_2pymS$^-$). In common with pyridine-2-thiol the neutral Me_2pymSH would be expected to coordinate through sulphur in the thione form (**III**) or as an N,S-chelate (**IV**). There is, unfortunately, no crystallographic evidence to support this; however infrared evidence seems to establish that the neutral species (Me_2pymSH) bonds as a monodentate S-donor [12, 13] or N,S-chelate [12, 14, 15].

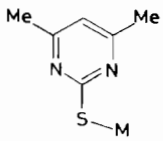


III

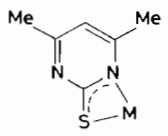


IV

The anionic Me_2pymS$^-$ would be expected to coordinate through sulphur as the thiolate (**V**) or as a chelate through nitrogen and sulphur (**VI**). Bonding as an N,S-chelate has been demonstrated in three crystal structures [16–18], monodentate S-bonding has not been demonstrated in the solid state but with unsubstituted pyrimidine-2-thiol (pymS$^-$) in solution there is NMR evidence for monodentate bonding through sulphur [19, 20]. There are also two examples of pymS$^-$ acting as a bridging ligand between two metal centers [21, 22].



V



VI

There is only one example in the literature of complexes of 4,6-dimethylpyrimidine-2-thiol with platinum group metals namely [Pt(Me_2pymS)$_2$] [22], but a few more with pyrimidine-2-thiol have been reported. Two ruthenium species [Ru(diene)(pymS)$_2$] and [Ru(cod)(pymS)(μ-I)]$_2$ have been described [23]. Platinum species reported include [Pt(pymSH)$_4$][PtCl$_6$] [24], [Pt(pymS)$_2$I]$_2$ and [Pt(pymS)$_2$]$_2$ [21], and [Pt(pymSH)$_2$Br$_2$][Pt(pymSH)$_2$Br$_4$] [25].

Experimental

For general experimental and instrumental details see Part 29 [2]. 4,6-Dimethylpyrimidine-2-thiol was obtained from Aldrich Chemical Co. and was used without further purification. Bis(4,6-dimethylpyrimidine-2-yl)disulphide was prepared from 4,6-dimethylpyrimidine-2-thiol according to a literature procedure [26]. References to light petroleum in the experimental details are to 60/80° light petroleum. Spectroscopic data are recorded in Tables 1–4.

Synthesis of Carbonylhydrido(4,6-dimethylpyrimidine-2-thiolato)bis(triphenylphosphine)-ruthenium

A mixture of carbonyldihydridotris(triphenylphosphine)ruthenium (0.367 g, 0.40 mmol) and 4,6-dimethylpyrimidine-2-thiol (0.056 g, 0.40 mmol) in benzene (50 cm^3) was heated under reflux for 30 min. The initial cloudy yellow solution cleared as the reaction proceeded. The cooled, filtered solution was evaporated to dryness under reduced pressure to yield a yellow residue which afforded yellow microcrystals from chloroform–light petroleum. The product was filtered off, washed with light petroleum and diethyl ether and dried *in vacuo*. This was identified by spectroscopic methods as a *c.* 80:20 mixture of two geometrical isomers of [RuH(Me_2pymS)(CO)(PPh_3)$_2$]. Yield 0.22 g (69%). *Anal.* Found: C, 64.8; H, 4.8; N, 3.5. Calc. for $C_{43}H_{38}N_2OP_2RuS$: C, 65.1; H, 4.8; N, 3.5%.

An alternative recrystallisation from dichloromethane–diethyl ether afforded a pure sample of the major isomer. Yield 0.13 g (41%), melting point (m.p.) 240/2 °C.

Synthesis of Carbonylchlorohydrido(4,6-dimethylpyrimidine-2-thiol)bis(triphenylphosphine)-ruthenium

A mixture of carbonylchlorohydridotris(triphenylphosphine)ruthenium (0.381 g, 0.40 mmol) and 4,6-dimethylpyrimidine-2-thiol (0.055 g, 0.392 mmol) in benzene (50 cm^3, 0–5 °C) was stirred for 6 h. The resultant cloudy yellow solution was evaporated to dryness under reduced pressure, without the application of heat. The yellow residue obtained was

TABLE 1. ^{1}H NMR data[a]

Compound	δ (MH) (ppm)	^2J (PH) (Hz)	δ (Me) (ppm)	δ (ArH) (ppm)
[Me_2pymSH] [b]			2.46	6.52
[Me_2pymSSpymMe_2]			2.40	6.77
[RuH(Me_2pymS)(CO)(PPh_3)$_2$] [c]	−11.51(t)	19	2.07, 0.98	5.53
[RuH(Me_2pymS)(CO)(PPh_3)$_2$]	−11.74(t)	20	1.96, 1.43	5.61
[Ru(Me_2pymS)$_2$(CO)(PPh_3)] [c]			2.51, 2.31 2.15, 1.92	6.39 5.95
[Ru(Me_2pymS)$_2$(CO)(PPh_3)]			2.39, 2.20 1.91, 1.49	6.44 6.03
[RuHCl(Me_2pymSH)(CO)(PPh_3)$_2$] [c] [RuHCl(Me_2pymSH)(CO)(PPh_3)$_2$] [d]	−11.85(t)	19	2.18, 1.55	5.66
			2.20, 1.09	5.56
[RuCl(Me_2pymS)(CO)(PPh_3)$_2$]			2.04, 1.26	5.53
[Ru(Me_2pymS)$_2$(CO)$_2$(PPh_3)$_2$]			2.12, 2.07 2.32	6.16 6.48
[Ru(Me_2pymS)$_2$(PPh_3)$_2$]			2.17, 2.06	5.79
[OsH(Me_2pymS)(CO)(PPh_3)$_2$] [c]	−13.23(t)	17	2.10, 0.91	5.64
[OsH(Me_2pymS)(CO)(PPh_3)$_2$]	−12.83(t)	19	2.02, 1.37	5.72
[Os(Me_2pymS)$_2$(PPh_3)$_2$]			2.21, 2.14	5.84
[RhHCl(Me_2pymS)(PPh_3)$_2$]	−17.12(dt)	10[e]	2.00, 1.46	5.56
[Rh(Me_2pymS)$_3$$PPh_3$)]			2.54, 2.300 2.29, 2.12 2.304	6.42 6.02 6.31
[IrH_2(Me_2pymS)(CO)(PPh_3)$_2$]	−9.31(td) −14.31(td)	17[f] 14	2.07	6.14
[IrHCl(Me_2pymS)(CO)(PPh_3)$_2$]	−12.95(t)	10	2.16, 1.65	6.67
[IrH(Me_2pymS)$_2$(PPh_3)$_2$]	−21.09(t)	14	1.72, 1.80 2.03	5.78 5.96
[IrH_2(Me_2pymS)(PPh_3)$_2$]	−19.93(td) −20.77(td)	16[g] 17	2.12, 0.98	5.71

[a]In $CDCl_3$ solution unless otherwise indicated: dt = doublet of triplets, t = triplet, td = triplet of doublets. [b]δ (SH) 13.81 ppm (broad). [c]Major isomer. [d]See 'Discussion'. [e] ^1J(RhH) 13 Hz. [f] ^2J(HH) 4 Hz. [g] ^2J(HH) 6 Hz.

recrystallised from chloroform–hexane. The pale greenish yellow precipitate obtained was filtered off, washed with hexane, ethanol and diethyl ether and dried *in vacuo*. This was identified by spectroscopic methods as a mixture of two geometrical isomers of [RuHCl(Me_2pymSH)(CO)(PPh_3)$_2$]. Yield 0.08 g (24%). *Anal.* Found: C, 63.1; H, 4.7; N, 3.4. Calc. for $C_{43}H_{39}ClN_2OP_2RuS$: C, 62.2; H, 4.7; N, 3.4%.

Synthesis of Carbonylchloro(4,6-dimethylpyrimidine-2-thiolato)bis(triphenylphosphine)ruthenium

A mixture of carbonylchlorohydridotris(triphenylphosphine)ruthenium (0.381 g, 0.40 mmol) and 4,6-dimethylpyrimidine-2-thiol (0.055 g, 0.392 mmol) in benzene (50 cm^3) was heated under reflux for 30 min. The yellow solution became greenish yellow as the reaction proceeded. The reaction mixture was cooled, filtered and evaporated to dryness under reduced pressure. The residue was recrystallised from dichloromethane–methanol to afford [RuCl(Me_2pymS)(CO)(PPh_3)$_2$] as yellow microcrystals which were filtered off, washed with methanol and diethyl ether, and dried *in vacuo*. Yield 0.28 g (84%), m.p. >250 °C. *Anal.* Found: C, 62.1; H, 4.4; N, 3.3. Calc. for $C_{43}H_{37}ClN_2OP_2RuS$: C, 62.3; H, 4.5; N, 3.4%.

Synthesis of Carbonylbis(4,6-dimethylpyrimidine-2-thiolato)(triphenylphosphine)ruthenium

A mixture of tricarbonylbis(triphenylphosphine)-ruthenium (0.284 g, 0.40 mmol) and 4,6-dimethylpyrimidine-2-thiol (0.280 g, 2.0 mmol) in toluene (50 cm^3) was heated under reflux for 6 h. The initial greenish yellow suspension cleared to a yellow solution as the reaction proceeded. The solution was cooled, filtered, and evaporated to dryness under reduced pressure. The yellow residue obtained was recrystallised from chloroform–hexane. The yellow precipitate obtained was filtered off, washed with hexane and diethyl ether, and dried *in vacuo* to afford two isomers of [Ru(Me_2pymS)$_2$(CO)(PPh_3)]. Yield 0.17 g (63%). *Anal.* Found: C, 55.3; H, 4.3; N, 8.3. Calc. for $C_{31}H_{29}N_4OPRuS_2$: C, 55.6; H, 4.4; N, 8.4%.

TABLE 2. $^{13}C\{^1H\}$ NMR of 4,6-dimethylpyrimidine-2-thiolate complexes[a]

Compound	4,6-Dimethylpyrimidine-2-thiol				Triphenylphosphine				Carbonyl δ(CO)
	δC2	δC5	δC4 and δC6	δMe	δC1	δC2 and C6	δC3 and C5	δC4	
Me_2pymSH at 304 K	180.7(s)	111.2(s)	*c.* 165vb	*c.* 22vb					
at 233 K	179.7(s)	111.5(s)	173.2b 156.9b	25.2b, 18.4b					
$Me_2pymSSpymMe_2$	168.8(s)	117.2(s)	167.6(s)	23.9(s)					
PPh_3 [b]					137.2(d) (11)	133.6(d) (20)	128.4(d) (7)	128.5(s)	
$[Ru(Me_2pymS)_2(CO)(PPh_3)]$ [c]	187.3(s) 186.1(s)	114.2(s) 114.9(d) (2)	165.8(s) 166.8(s) 167.9(s) 168.0(d) (3)	23.9(s), 23.6(s), 22.9(s), 21.8(s)	133.5(d) (49)	133.5(d) (10)	128.0(d) (10)	129.9(d) (1)	202.8(d) (20)
$[Ru(Me_2pymS)_2(PPh_3)_2]$	188.7(s)	113.7(s)	168.2(s)[d] 164.1(s)[d]	23.3(s), 22.5(s)	136.3(m)[e] (40)	134.1(t) (8)	126.9(t) (8)	128.4(s)	
$[Os(Me_2pymS)_2(PPh_3)_2]$	193.0(s)	113.7(2)	167.9(s)[d] 163.5(s)[d]	23.3(s), 22.4(s)	137.1(m)[e] (48)	134.0(t) (8)	126.8(t) (8)	128.2(t)	
$[IrH_2(Me_2pymS)(PPh_3)_2]$	187.8(s)	110.3(s)	162.6(s)[d] 164.6(s)[d]	23.5(s), 21.8(s)	135.4(m)[e] (52)	134.0(t) (12)	127.6(t) (9)	129.3(s)	

[a]In $CDCl_3$. All chemical shifts in ppm, b = broad, vb = very broad, d = doublet, s = singlet, t = triplet. Figures in parentheses are coupling constants (Hz) to ^{31}P. [b]Ref. 27. [c]See 'Discussion'. [d]Assignments may be reversed. [e]Separation quoted is between intense pair of lines and is equivalent to $|^nJ_{PC} + {}^{n+2}J_{PC}|$, see ref. 32.

TABLE 3. $^{31}P\{^1H\}$ NMR[a] and infrared data[b]

Compound	$\delta(PPh_3)$ (ppm)	$\nu(CO)$ (cm^{-1})	$\nu(MH)$ (cm^{-1})
$[RuH(Me_2pymS)(CO)(PPh_3)_2]$ [c]	48.0(s)	1919	1965
$[RuH(Me_2pymS)(CO)(PPh_3)_2]$	50.4(s)		
$[Ru(Me_2pymS)_2(CO)(PPh_3)]$ [c]	57.0(s)	1936	
$[Ru(Me_2pymS)_2(CO)(PPh_3)]$	54.1(s)		
$[RuHCl(Me_2pymSH)(CO)(PPh_3)_2]$ }[c]	49.1(s)	1919	
$[RuHCl(Me_2pymSH)(CO)(PPh_3)_2]$ }	47.0(s)	1924	
$[RuCl(Me_2pymS)(CO)(PPh_3)_2]$	35.0(s)	1934	
$[Ru(Me_2pymS)_2(CO)_2(PPh_3)]$	39.7(s)	2051, 1998 [d]	
$[Ru(Me_2pymS)_2(PPh_3)_2]$	48.7(s)		
$[OsH(Me_2pymS)(CO)(PPh_3)_2]$ [c]	19.0(s)	1902	2056
$[OsH(Me_2pymS)(CO)(PPh_3)_2]$	21.0(s)	1907	2059
$[Os(Me_2pymS)_2(PPh_3)_2]$	−9.9(s)		
$[RhHCl(Me_2pymS(PPh_3)_2]$	40.1(d)[e]	2040	
$[Rh(Me\ pymS)_3(PPh_3)]$	28.9(d)[f]		
$[IrH_2(Me_2pymS)(CO)(PPh_3)_2]$	8.9(s)	1997	2138, 2115
$[IrHCl(Me_2pymS)(CO)(PPh_3)_2]$	6.7(s)	2033	2174
$[IrH(Me_2pymS)_2(PPh_3)_2]$	9.4(s)		2145
$[IrH_2(Me_2pymS)(PPh_3)_2]$	19.2(s)		2137, 2098

[a]In $CDCl_3$ solution. [b]Nujol mulls unless otherwise indicated. [c]Major isomer. [d]$CHCl_3$ solution (Nujol mull: 3 peaks 2045, 1992, 1980). [e] $^1J(Rh-P)$ 107 Hz. [f] $^1J(Rh-P)$ 122 Hz.

TABLE 4. ^1H NMR phenyl proton resonance separation in C_6D_6

Complex	Shift relative to C_6H_6 (ppm)		Separation (ppm)
	ortho	*meta/para*	
$[Ru(Me_2pymS)_2(PPh_3)_2]$	+0.47	−0.32	0.79
$[Os(Me_2pymS)_2(PPh_3)_2]$	+0.43	−0.32	0.75
$[IrH_2(Me_2pymS)(PPh_3)_2]$	+0.75	−0.19	0.94

Synthesis of Dicarbonylbis(4,6-dimethylpyrimidine-2-thiolato)(triphenylphosphine)ruthenium

A solution of tricarbonylbis(triphenylphosphine)-ruthenium (0.426 g, 0.60 mmol) in toluene (80 cm^3) was heated to reflux. Bis(4,6-dimethylpyrimidine-2-yl)disulphide (0.167 g, 0.60 mmol) was rapidly introduced and the mixture heated under reflux for 8 min. The orange–yellow solution became orange during this time. The reaction mixture was then rapidly cooled (water *c.* 15 °C) and evaporated to dryness under reduced pressure without the application of heat. The orange residue obtained was recrystallised from dichloromethane–diethyl ether. The yellow precipitate was filtered off and washed with light petroleum and diethyl ether, and dried *in vacuo* to afford $[Ru(Me_2pymS)_2(CO)_2(PPh_3)]$. Yield 0.13 g (31%), m.p. 194/5 °C, effervescence 183/4 °C. *Anal.* Found: C, 54.2; H, 4.2; N, 8.1. Calc. for $C_{32}H_{29}N_4O_2PRuS_2$: C, 55.1; H, 4.2; N, 8.0%.

Synthesis of Bis(4,6-dimethylpyrimidine-2-thiolato)-bis(triphenylphosphine)ruthenium

4,6-Dimethylpyrimidine-2-thiol (0.126 g, 0.90 mmol) followed by dichlorotris(triphenylphosphine)-ruthenium (0.288 g, 0.30 mmol) was added to refluxing, degassed toluene (50 cm^3). Triethylamine (1 cm^3) was added and the whole refluxed for 4 h. The initial cloudy red solution cleared to a dark orange solution as the reaction proceeded. The cooled, filtered solution was evaporated to dryness under reduced pressure, and the orange residue obtained recrystallised from dichloromethane–diethyl ether to afford $[Ru(Me_2pymS)_2(PPh_3)_2]$. Yield 0.18 g (66%), m.p. > 250 °C. *Anal.* Found: C, 63.3; H, 4.9; N, 6.2. Calc. for $C_{48}H_{44}N_4P_2RuS_2$: C, 63.8; H, 4.9; N, 6.2%.

Synthesis of Carbonylhydrido(4,6-dimethylpyrimidine-2-thiolato)bis(triphenylphosphine)-osmium

A mixture of carbonyldihydridotris(triphenylphosphine(osmium (0.302 g, 0.30 mmol) and 4,6-dimethylpyrimidine-2-thiol (0.126 g, 0.90 mmol) in toluene (50 cm^3) was heated under reflux for 15 h. The initial cloudy yellow suspension cleared to a yellow solution. The mixture was cooled, filtered and

evaporated to dryness under reduced pressure. The residue was recrystallised from dichloromethane–methanol to afford two isomers of $[OsH(Me_2pymS)(CO)(PPh_3)_2]$ in a 80:20 ratio. Yield 0.24 g (70%). *Anal.* Found: C, 58.3; H, 4.3; N, 3.2. Calc. for $C_{43}H_{38}N_2OOsP_2S$: C, 58.5; H, 4.3; N, 3.2%.

The same products were similarly obtained from carbonylchlorohydridotris(triphenylphosphine)-osmium. Yield 68%. *Anal.* Found: C, 57.8; H, 4.3; N, 3.2%. Careful recrystallisation from dichloromethane–methanol yields a pure sample of the minor isomer, m.p. 218/20 °C.

Synthesis of Bis(4,6-dimethylpyrimidine-2-thiolato)-bis(triphenylphosphine)osmium

4,6-Dimethylpyrimidine-2-thiol (0.210 g, 1.50 mmol) followed by dichlorotris(triphenylphosphine)-osmium (0.314 g, 0.30 mmol) was added to refluxing, degassed toluene (50 cm^3). Triethylamine (1 cm^3) was added, and the colour of the solution changed from brown to green. The mixture was refluxed for 3 h and the cooled, filtered solution evaporated to dryness under reduced pressure. The green residue obtained was recrystallised from dichloromethane–methanol. The clear green solution changed colour to an orange solution overnight and deposited orange crystals, which were filtered off, washed with methanol and light petroleum, and dried *in vacuo* to afford $[Os(Me_2pymS)_2(PPh_3)_2]$. Yield 0.21 g (71%), m.p. > 250 °C. *Anal.* Found C, 57.9; H, 4.4; N, 5.6. Calc. for $C_{48}H_{44}N_4OsP_2S_2$, C, 58.0; H, 4.5; N, 5.6%.

Synthesis of Chlorohydrido(4,6-dimethylpyrimidine-2-thiolato)bis(triphenylphosphine)rhodium

4,6-Dimethylpyrimidine-2-thiol (0.049 g, 0.350 mmol) followed by chlorotris(triphenylphosphine)-rhodium (0.34 g, 0.367 mmol) were added to degassed, refluxing benzene (50 cm^3) and heated under reflux for 20 min to form a red solution. The cooled, filtered solution was evaporated to *c.* 10 cm^3 under reduced pressure and light petroleum added (10 cm^3). The yellow precipitate produced was filtered off, washed with light petroleum and diethyl ether, and dried *in vacuo* to afford $[RhHCl(Me_2pymS)(PPh_3)_2]$. Yield 0.19 g (64%), m.p. 158/60 °C. *Anal.* Found: C, 63.1; H, 4.8; N, 3.3. Calc. for $C_{42}H_{38}ClN_2P_2RhS$: C, 62.8; H, 4.8; N, 3.5%.

Synthesis of Tris(4,6-dimethylpyrimidine-2-thiolato)-(triphenylphosphine)rhodium

Chlorotris(triphenylphosphine)rhodium (0.740 g, 0.80 mmol) was added to degassed refluxing benzene (50 cm^3), and a degassed solution of 4,6-dimethylpyrimidine-2-thiol in ethanol (40 cm^3) was added dropwise over *c.* 15 min; the mixture was then refluxed for a further 90 min. The orange solution formed became yellow during this period. The cooled, filtered solution was evaporated to dryness under reduced pressure. The residue obtained was extracted with ethanol (50 cm^3). The ethanol soluble portion was concentrated to *c.* 20 cm^3 under reduced pressure and water (10 cm^3) added to produce an orange precipitate, which was filtered off and washed with water, light petroleum and hexane, and dried *in vacuo* to afford $[Rh(Me_2pymS)_3(PPh_3)]$. Yield 0.13 g (21%), m.p. 242/4 °C. *Anal.* Found: C, 55.2; H, 4.5; N, 10.8. Calc. for $C_{36}H_{36}N_6PRhS_3$: C, 55.2; H, 4.6; N, 10.7%.

Synthesis of Carbonyldihydrido(4,6-dimethylpyrimidine-2-thiolato)bis(triphenylphosphine)-iridium

A mixture of carbonylhydridotris(triphenylphosphine)iridium (0.30 g, 0.297 mmol) and 4,6-dimethylpyrimidine-2-thiol (0.0417 g, 0.297 mmol) in chloroform (50 cm^3, 0–5 °C) was stirred for 3 h. The pale yellow solution was reduced in volume to *c.* 10 cm^3, and hexane (20 cm^3) added, and the mixture cooled at 0 °C for 2 h. A pale yellow precipitate formed which was filtered off and washed with hexane to afford $[IrH_2(CO)(Me_2pymS)(PPh_3)_2]$. Yield 0.22 g (83%), m.p. 146/8 °C. *Anal.* Found: C, 56.8; H, 4.3; N, 3.2. Calc. for $C_{43}H_{39}IrN_2OP_2S$: C, 58.3; H, 4.4; N, 3.2%.

Synthesis of Carbonylchlorohydrido(4,6-dimethylpyrimidine-2-thiolato)bis(triphenylphosphine)-iridium

A mixture of *trans*-carbonylchlorobis(triphenylphosphine)iridium (0.312 g, 0.40 mmol), 4,6-dimethylpyrimidine-2-thiol (0.056 g, 0.399 mmol) and triphenylphosphine (0.525 g, 2.0 mmol) in benzene (50 cm^3) was stirred at ambient temperature for 3 h. The cloudy yellow solution cleared and then a white precipitate separated out. The solution was filtered and the precipitate washed with benzene and light petroleum, and dried *in vacuo* to afford $[IrHCl(Me_2pymS)(CO)(PPh_3)_2]$. Yield 0.24 g (65%). *Anal.* Found: C, 55.3; H, 4.2; N, 3.0. Calc. for $C_{43}H_{38}ClIrN_2OP_2S$: C, 56.1; H, 4.2; N, 3.0%.

The same product was obtained from a reaction of a mixture of *trans*-carbonylchlorobis(triphenylphosphine)iridium (0.312 g, 0.40 mmol), bis(4,6-dimethylpyrimidine-2-yl)disulphide (0.111 g, 0.40 mmol), and triphenylphosphine (0.525 g, 2.0 mmol) which were stirred in benzene (50 cm^3) at ambient temperature for 3 h. The cloudy yellow suspension cleared to a pale yellow solution. Light petroleum (20 cm^3) was added and a pale yellow precipitate separated out. The precipitate was filtered off, washed with light petroleum and diethyl ether, and dried *in vacuo* to afford $[IrHCl(Me_2pymS)(CO)(PPh_3)_2]$. Yield 0.14 g (33%), m.p. 212/4 °C. *Anal.* Found: C, 55.6; H, 4.4; N, 3.2%.

Synthesis of Hydridobis(4,6-dimethylpyrimidine-2-thiolato)bis(triphenylphosphine)iridium

A mixture of *trans*-carbonylchlorobis(triphenylphosphine)iridium (0.312 g, 0.40 mmol), 4,6-dimethylpyrimidine-2-thiol (0.168 g, 1.20 mmol) in toluene (50 cm^3) was heated under reflux for 4 h. The yellow solution darkened as the reaction proceeded. The cooled, filtered solution was evaporated to dryness under reduced pressure. The yellow residue obtained was recrystallised from dichloromethane/methanol to afford $[IrH(Me_2pymS)_2(PPh_3)_2]$ as yellow microcrystals. Yield 0.11 g (28%), m.p. 194/7 °C. *Anal.* Found: C, 57.6; H, 4.5; N, 5.5. Calc. for $C_{48}H_{45}IrN_4P_2S_2$: C, 57.9; H, 4.6; N, 5.6.

Synthesis of Dihydrido(4,6-dimethylpyrimidine-2-thiolato)bis(triphenylphosphine)iridium

mer-Trihydridotris(triphenylphosphine)iridium (0.393 g, 0.40 mmol) and 4,6-dimethylpyrimidine-2-thiol (0.168 g, 1.20 mmol) in benzene (50 cm^3) were heated under reflux for 3 h to form a yellow solution. The cooled solution was stood overnight, filtered and evaporated to dryness under reduced pressure. The yellow residue was recrystallised from dichloromethane–methanol and afforded $[IrH_2(Me_2pymS)(PPh_3)_2]$ as white microcrystals. Yield 0.29 g (84%), m.p. >250 °C. *Anal.* Found C, 59.6; H, 4.7; N, 3.4. Calc. for $C_{42}H_{39}IrN_2P_2S$: C, 58.8; H, 4.6; N, 3.3%.

Results and Discussion

NMR of 4,6-Dimethylpyrimidine-2-thiol

The ^1H NMR of Me_2pymSH exhibits a single methyl peak demonstrating that the methyls are equivalent. The labile NH proton is shifted significantly downfield (δ 13.82). We attribute this large shift to intermolecular hydrogen bonding; a non-hydrogen bonded thiol proton would be expected to resonate at *c.* 3–4 ppm (e.g. thiophenol δ 3.39). A non-hydrogen bonded unsaturated heterocyclic nitrogen proton usually occurs at *c.* 7–8 ppm (e.g. pyrrole δ 7.99). The concentration dependence of the NH proton signal (0.4 M, δ 13.82; 0.01 M, δ 12.68) provides further evidence of intermolecular H bonding. The $^{13}C\{^1H\}$ NMR shows sharp signals for C_2 and C_5, a broad peak for the two methyls and a very broad hump for C_4 and C_6; on cooling to 233 K the methyl peak separates into two discrete resonances and C_4 and C_6 can now be seen as fairly sharp signals.

The methyls are clearly not equivalent at low temperature, and this together with the likelihood of intermolecular hydrogen bonding, leads us to suggest that Me_2pymSH exists as rapidly interchanging dimers (**II**) in solution at 25 °C as has been found for pyridine-2-thiol [28].

Reactions with Ruthenium Precursors

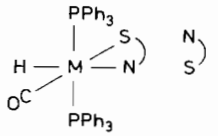
With $[RuH_2(CO)(PPh_3)_3]$

Treatment of $[RuH_2(CO)(PPh_3)_3]$ with Me_2pymSH in refluxing benzene for 30 min affords an 80:20 mixture of isomers of the 2,4-dimethylpyrimidine-2-thiolate chelate $[RuH(Me_2pymS)(CO)(PPh_3)_2]$. NMR data (Table 1) indicate that both isomers have a pair of equivalent ^{31}P nuclei *cis* to the hydride and thus establish that the phosphines are *trans* to each other. We therefore assign the stereochemistry indicated (**VII a/b**) to this pair. Hydride ligands *trans* to N- or S-donors have similar NMR chemical shifts and it is therefore not easy to differentiate between the isomers on this basis. The major isomer can be isolated by careful recrystallisation from dichloromethane–diethyl ether.

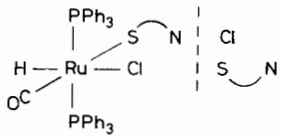
The isomers of $[RuH(Me_2pymS)(CO)(PPh_3)_2]$ were shown by $^{31}P\{^1H\}$ NMR to react further in the presence of excess Me_2pymSH to afford the bis-chelate $[Ru(Me_2pymS)_2(CO)(PPh_3)]$. This is observed as one isomer, and can also be obtained from $[Ru(CO)_3(PPh_3)_2]$ when it is observed as the major member of an isomer pair (see below).

With $[RuHCl(CO)(PPh_3)_3]$

Treatment of $[RuHCl(CO)(PPh_3)_3]$ with Me_2pymSH (1:1) in cold benzene yields a yellow air stable solid containing a mixture of two components in a 60:40 ratio. We formulate these as two geometric isomers of $[RuHCl(CO)(Me_2pymSH)(PPh_3)_2]$. The possibility that these involve linkage isomerism (N- or S-bonded Me_2pymSH) seems unlikely for the reasons discussed at length in our paper on the related pyridine-2-thiol system [2]. We therefore assign stereochemistry (**VIII a/b**) to this pair. The ^1H NMR spectrum of this mixture clearly shows the presence of four methyl resonances indicating that rotation about the Ru–S=C bonds is restricted, possibly due to hydrogen bonding between the NH proton and the adjacent chloride. The NH protons were not observed, this could be due to a broadening of the resonance for these protons caused by the hydrogen bonding and/or the N quadrupole moment.

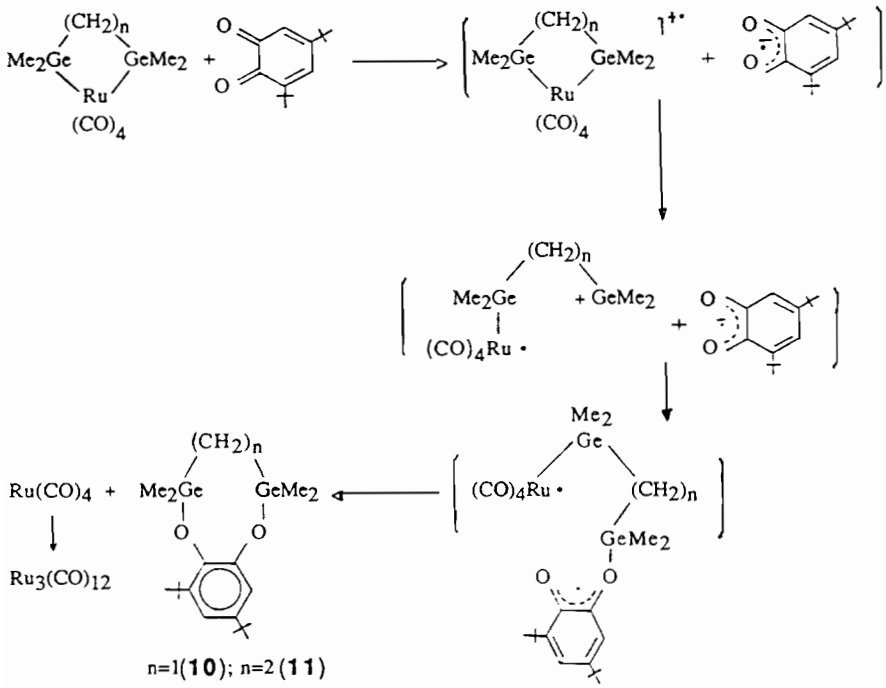


VII a/b



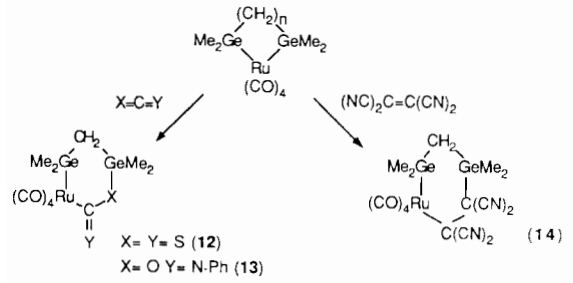
VIII a/b

The hydride portion of the spectrum shows a triplet pattern for the major isomer but the other hydride signal is very broad and appears underneath the first signal at room temperature. On cooling in CD_2Cl_2 the combined hydride resonance is observed



2) with quinones. The transient semiquinonic radical involved can be detected by ESR spectroscopy either as the anion radical or ion paired with the metal ($g = 2.0029$, a^H 2.8 G).

Compound **1** reacts at room temperature with CS_2, PhNCO and $(NC)_2C{=}C(CN)_2$ to give heterocyclic expansion reactions. Adducts **12–14** are stable at ambient temperature and characterized by NMR, IR and mass spectrometry analyses. ^1H NMR data (C_6D_6): **12**: δ 0.58 (s, CH_3GeRu), 0.44 (s, CH_3GeS) and 0.75 (s, CH_2) ppm; **13**: δ 0.14 (s, CH_3GeRu), 0.60 (s, CH_3GeO), 1.45 (s, CH_2) and 7.4 (C_6H_5) ppm; **14**: δ 0.12 (s, CH_3GeRu), 0.50 (s, CH_3GeC), 1.20 (s, CH_2) ppm. IR data (C_6H_6): **12**: νCO cm^{-1} 2080(m), 2010(f), 2000(F), 1990(F); νCS cm^{-1} 1500(m). **13**: νCO cm^{-1} 2080(m), 2060(f), 2000(F), 1960(F), 1650(f); νCN cm^{-1} 1600. **14**: νCO cm^{-1} 2080(m), 2020(f), 1990(F), 1960(F); νCN cm^{-1} 2160(m).



The new metalla heterocycles **12** and **13** decompose thermally to form the previously reported heterocycles $(Me_2GeX)_3$ and $Me_2\overline{GeCH_2Ge(Me_2)}CH_2$ suggestive of $Me_2\overline{GeCH_2Ge(Me_2)}X$ (X = O, S) and then, as observed, $[Me_2Ge{=}X]$ and $[Me_2Ge{=}CH_2]$ intermediates [9, 12, 15].

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$[OsH(Me_2pymS)(CO)(PPh_3)_2]$ as a mixture of two isomers **VII a/b.**

With [OsHCl(CO)(PPh$_3$)$_3$]

Treatment of $[OsHCl(CO)(PPh_3)_3]$ with Me_2pymSH (1:1) in boiling benzene for 30 min affords a 60:40 mixture of the two isomers of $[OsH(Me_2pymS)(CO)(PPh_3)_2]$. The minor isomer can be isolated by recrystallisation. Reactions of $[OsHCl(CO)(PPh_3)_3]$ with Me_2pymSH in the cold also afford $[OsH(Me_2pymS)(CO)(PPh_3)_2]$ as the major product. This is in contrast to the reaction with the ruthenium analogue where $[RuHCl(Me_2pymSH)(CO)(PPh_3)_2]$ is formed, the difference may be that an oxidative addition is involved and the relative inaccessibility of Ru(IV) as an intermediate means that $[RuHCl(Me_2pymSH)(CO)(PPh_3)_2]$ is kinetically more stable than the osmium analogue. ^{31}P NMR shows the presence of a signal at δ 12.8 which may be due to $[OsCl(Me_2pymS)(CO)(PPh_3)_2]$ but it was not possible to isolate as it appears to be converted to the hydride product rapidly.

With [OsCl$_2$(PPh$_3$)$_3$]

Treatment of $[OsCl_2(PPh_3)_3]$ with Me_2pymSH (1:5) in boiling toluene for 3 h in the presence of excess triethylamine affords $[Os(Me_2pymS)_2(PPh_3)_2]$ as dark orange crystals. The ^{1}H NMR in C_6D_6 shows a shift separation of the phenyl protons [30] ($\Delta\delta$) of *c.* 0.71 ppm indicating that in solution at least the phosphines are mutually *trans*. The ^{13}C NMR spectrum, which is essentially the same as that found for the analogous ruthenium complex (see above), provides further evidence of a *trans* arrangement of the phosphines in solution.

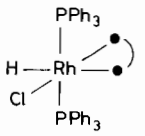
Reactions with Rhodium Precursors

With [RhCl(PPh$_3$)$_3$]

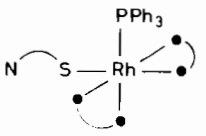
Treatment of $[RhCl(PPh_3)_3]$ with Me_2pymSH in boiling degassed benzene for 20 min affords $[RhHCl(Me_2pymS)(PPh_3)_2]$. The ^{31}P NMR is observed as a doublet due to coupling with the rhodium nucleus, this shows that the phosphines are equivalent and therefore must be mutually *trans*. In the ^{1}H NMR the hydride is observed as a doublet of triplets exhibiting coupling both to the rhodium nucleus and a pair of phosphines *cis* to the hydride. The methyl region displays two different methyl resonances indicating a chelate-N,S structure **XIII**.

Treatment of $[RhCl(PPh_3)_3]$ with Me_2pymSH (1:4) in benzene/ethanol for 1½ h yields a mixture containing 3 products. The major product was isolated and found to be $[Rh(Me_2pymS)_3(PPh_3)]$.

The ^{1}H NMR spectrum in $CDCl_3$ at 55 °C shows five methyl signals; four of which (δ 2.52, 2.28, 2.27 and 2.12) integrate for three protons each and one (δ 2.30) which integrates for six protons. We take



XIII



XIV

this to indicate two ligands chelated through N and S, and one monodentate ligand undergoing free rotation about the Rh–S–C bond and thus exhibiting equivalent methyl signals (**XIV**).

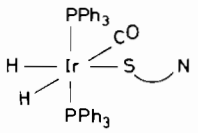
When the ^{1}H NMR is observed in d_6-DMSO the signals for one chelated ligand (δ 2.05 and 2.15) remain sharp when the temperature is raised from 298 to 378 K. The signals at δ 2.27 (6 protons) and δ 2.25 (3 protons) merge into a broad envelope at 358 K whilst at 378 K the signal at δ 2.42 is also broadened and overlaps the envelope for the 9 protons. This would appear to indicate that one chelated ligand is rigid but that there is a tendency for the non-coordinated N of the monodentate ligand to exchange with the coordinated N of the other chelated ligand.

Reactions with Iridium Precursors

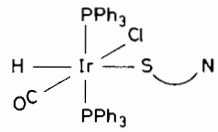
With [IrH(CO)(PPh$_3$)$_3$]

Treatment of $[IrH(CO)(PPh_3)_3]$ with Me_2pymSH in cold chloroform for 3 h affords $[IrH_2(Me_2pymS)(CO)(PPh_3)_2]$. The hydride portion of the ^{1}H NMR spectrum consists of two triplets of doublets exhibiting $^2J(PH)_{cis}$ and $^2J(HH)$ coupling which indicates the presence of two hydrides in different environments which are both *cis* to two equivalent phosphines. The ^{31}P NMR spectrum is a singlet thus demonstrating that the phosphines are mutually *trans*, and hence we assign the stereochemistry **XV**.

The other two coordination sites are occupied by a carbonyl and a Me_2pymS anion. There is only one resonance in the methyl region of the ^{1}H NMR and we therefore conclude that the anion is bonded in a monodentate fashion through S.



XV



XVI

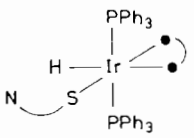
With trans-[IrCl(CO)(PPh$_3$)$_2$]

Treatment of *trans*-$[IrCl(CO)(PPh_3)_2]$ with Me_2pymSH (1:1) in benzene at ambient temperature for 3 h in the presence of an excess (5 equivalents) of PPh_3 affords $[IrHCl(Me_2pymS)(CO)(PPh_3)_2]$ (**XVI**)

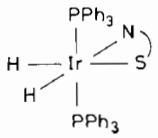
as a white precipitate. The ^{31}P NMR is a singlet indicating equivalent phosphines. The ^{1}H NMR exhibits a triplet hydride signal indicating a hydride ligand *trans* to sulphur rather than chloride or carbonyl thus confirming stereochemistry **XVI**.

The methyl region of the ^{1}H NMR spectrum shows two methyl peaks. This could indicate that the anion is bonded through N thus giving rise to two different methyl environments; but we believe that S bonding is more likely and that the two methyl signals arise from restricted rotation about the Ru–S–C bond.

Treatment of *trans*-$[IrCl(CO)(PPh_3)_2]$ with Me_2pymSH (1:3) in refluxing toluene for 4 h yields a dark yellow solution. Spectroscopic examination revealed the presence of $[IrH(Me_2pymS)_2(PPh_3)_2]$ **(XVII)** plus several minor components. The major component was isolated by crystallisation. The ^{31}P NMR consists of a singlet indicating equivalent phosphines. The ^{1}H NMR exhibits a triplet hydride signal demonstrating a hydride *cis* to two mutually *trans* phosphines.



XVII



XVIII

There are two signals for the aromatic pyrimidine protons which indicate that the two pyrimidines are not equivalent. The methyl region consists of three methyl peaks, one integrating for six protons (δ 2.03) and two which integrate for three protons each (δ 1.72 and 1.80). This indicates that one anion is bonded in a monodentate fashion through S, whilst the other is chelated through N and S.

Treatment of *trans*-$[IrCl(CO)(PPh_3)_2]$ with Me_2pymSSpymMe_2 (1:1) in benzene at ambient temperature for 3 h in the presence of an excess (5 equivalents) of PPh_3 yields a clear yellow solution, on addition of 60/80° light petroleum $[IrHCl(Me_2pymS)(CO)(PPh_3)_2]$ separates as a pale yellow precipitate.

Reactions with mer-$[IrH_3(PPh_3)_3]$

Treatment of *mer*-$[IrH_3(PPh_3)_3]$ with Me_2pymSH (1:3) in boiling benzene for 3 h yields $[IrH_2(Me_2pymS)(PPh_3)_2]$. The ^{1}H NMR exhibits two triplets of doublets in the hydride region, indicating two hydrides in different environments which are *cis* to each other and *cis* to two mutually *trans* phosphines. We therefore assign the stereochemistry **XVIII**. There is no evidence that either of the hydride signals is broadened by the nitrogen quadrupole.

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