Reactions of 2-Thiopyridone Rhodium(III) Complexes with Tertiary Phosphines

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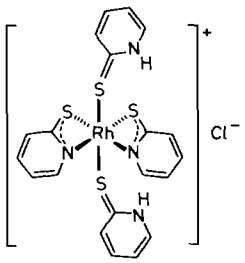
Abstract

The rhodium(III) complexes containing 2-thiopyridone (pySH) and its conjugate anion 2-thiopyridonato (pyS) as the only ligands, $[Rh(pyS)_2(pySH)_2]Cl$, $[Rh(pyS)_3(pySH)]$, and $[Rh(pyS)_3]$, react with the tertiary phosphines PMe_2Ph, PPh_3, $Ph_2PCH_2PPh_2$ (dppm), and $Ph_2PCH_2CH_2PPh_2$ (dppe) to give mixed pyS/tertiary phosphine complexes of the type $[Rh(pyS)_3L]$, $[Rh(pyS)_3L_2]$, and $[Rh(pyS)_2L_2]ClO_4$ where L represents a single phosphorus donor atom. These compounds were characterized mainly by ^1H and ^{31}P NMR spectroscopy.

Introduction

We recently described a series of rhodium(III) complexes (**1**–**3**) containing only 2-thiopyridone (pySH) and 2-thiopyridonato (pyS) as ligands [1, 2].



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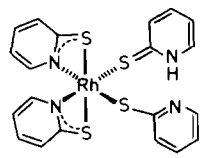

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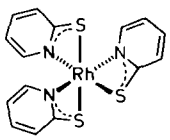

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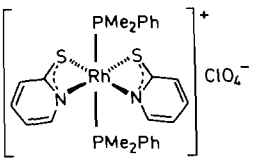
In examining the reactivity of these complexes we have synthesized several new phosphine complexes containing pyS. Mixed pyS/phosphine complexes have been reported previously by Wilkinson *et al.* [3–5] and by Robinson *et al.* [6, 7]. However, apart from an isolated report of $[Rh(pyS)_2(PPh_3)]BF_4$ [5], for which no spectroscopic data were given, there are no previous examples of rhodium(III) 2-thiopyridonato phosphine complexes. The synthetic route given here is particularly useful since in principle any tertiary phosphine (or other neutral ligand) might be introduced after the pyS or pySH ligands.

Results

Dimethylphenylphosphine

Treatment of $[Rh(pyS)_2(pySH)_2]Cl$ (**1**) with PMe_2Ph in refluxing 2-ethoxyethanol followed by treatment with $AgClO_4$ gave the bis chelate complex formulated as $[Rh(pyS)_2(PMe_2Ph)_2][ClO_4]$ (**4**). The ^1H NMR spectrum (Table I) shows a virtually coupled 1:2:1 triplet at δ 1.67 showing that the phosphines are mutually *trans*. Furthermore the Me groups are not diastereotopic and so there is a plane of symmetry through the metal phosphorus axis [8]. Hence **4** contains the two chelate ligands in a plane with the donor sulphur atoms *cis* to each other and likewise for the nitrogen atoms. The IR spectrum of $[Rh(pyS)_2(PMe_2Ph)_2][ClO_4]$ (**4**) shows an uncoordinated perchlorate absorption (1095 cm^{-1}), as expected for the formulation of the complex as a cation. The structure of **4** relates to that of the parent molecule (**1**) by simple replacement of the two *trans* monodentate pySH ligands by two PMe_2Ph ligands.



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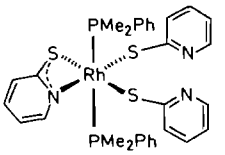

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Treatment of $[Rh(pyS)_3(pySH)]$ (**2**) with PMe_2Ph in refluxing toluene followed by column chromatography affords three major products identified as the tris-chelate complex (**3**) [1, 2], a bis-phosphine complex $[Rh(pyS)_3(PMe_2Ph)_2]$ (**5**), and a monophosphine complex $[Rh(pyS)_3(PMe_2Ph)]$ (**6**). The 200 MHz ^1H NMR spectrum of complex **5** shows two virtually-coupled triplets indicating that the phosphines are *trans* and the methyl groups diastereotopic. This is only consistent with the structure shown for **5**

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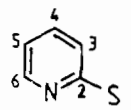
TABLE I. ^{1}H NMR Data for Rhodium(III) Thiopyridonato Phosphine Derivatives. Number Scheme:



Compound	Chemical shifts (δ)[a]
$[Rh(pyS)_2(PMe_2Ph)_2]ClO_4$ (4)	6.33(d) (H^3), 6.86(t) (H^5), 8.40(d) (H^6), 7.16(m), 7.31(m) (H^4 + Ph), 1.67(t) (PMe, J 7.0[b])
$[Rh(pyS)_3(PMe_2Ph)_2]$ (5)	5.80(t) (H^5), 6.25(d) (H^3), 7.53(d) (H^3), 8.08(d) (H^6), 8.20(d) (H^6), 6.78(m), 6.95(m), 7.16(m), 7.45(m) (other pyS signals + Ph), 1.72(t) (PMe, J 7.2[b]), 1.83(t) (PMe, J 7.2[b])
$[Rh(pyS)_3(PMe_2Ph)]$ (6)	6.26(t) (H^5), 6.59(d) (H^3), 6.70(t) (H^5), 7.59(d) (H^6), 8.17(t) (H^6), 8.26(d) (H^6), 6.80(m), 7.18(m), 7.25(m), 7.38(m) (other pyS signals + Ph), 1.89(d) (PMe, J 10.0), 1.93(d) (PMe, J 10.0)
$[Rh(pyS)_3(PPh_3)]$ (7)	6.30(m) (H^3, H^5), 8.14(d) (H^6), 8.16(d) (H^6), 6.60(m), 7.25(m), 7.60(m), 7.80(m) (other pyS signals + Ph)
$[Rh(pyS)_2(dppm)]ClO_4$ (8)	6.76(d) (H^3), 6.93(t) (H^5), 7.34(t) (H^4), 8.30(d) (H^6), 7.25(m), 7.48(m), 7.66(m) (Ph), 5.30(t) (CH_2)
$[Rh(pyS)_3(dppm)]$ (9)	6.20(t) (H^5), 6.33(d) (H^3), 8.12(d) (H^6), 8.30(d) (H^6), 7.25(m), 7.50(m), 7.80(m) (Ph), 3.60(m), 4.20(m) (CH_2)
$[Rh(pyS)_2(dppe)]ClO_4$ (10)	6.48(d) (H^3), 6.83(t) (H^5), 8.13(d) (H^6), 7.17(m), 7.26(m), 7.56(m) (other pyS signals + Ph), 2.80(m), 3.40(m) (CH_2CH_2)

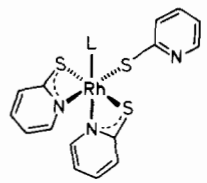
[a] In $CDCl_3$ at 200 MHz. J in Hz; assignable pyS signals given first; multiplicities are approximate. [b] $J_{obs} = {}^2J(PH) + {}^4J(PH)$.

which has two monodentate and one chelating pyS ligand in a square plane. The methyl groups in $[Rh(pyS)_3(PMe_2Ph)]$ (**6**) are also diastereotopic; the 400 MHz ^{1}H NMR spectrum has two methyl doublets. The molecule contains two chelating and one monodentate pyS ligands and the two monodentate ligands (pyS and PMe_2Ph) are *cis*. Four structures (**6a–6d**) with three non-equivalent pyS ligands are each consistent with the spectra. We favour structure **6a** because this relates directly to **2** with pySH replaced by PMe_2Ph but cannot distinguish these isomers experimentally.

Treatment of $[Rh(pyS)_3]$ with PMe_2Ph in refluxing toluene gives the same products as from a similar reaction of $[Rh(pyS)_3(pySH)]$ with this phosphine. Since the tris-chelate compound $[Rh(pyS)_3]$ is formed in significant quantities in the latter reaction, the most probable pathway involves the initial dissociation of pySH from $[Rh(pyS)_3(pySH)]$ and subsequent addition of PMe_2Ph.

Triphenylphosphine

$[Rh(pyS)_3(pySH)]$ reacts with PPh_3 in refluxing toluene to give the mono-phosphine complex $[Rh(pyS)_3(PPh_3)]$ (**7**) as the major product. The ^{1}H NMR spectrum is consistent with a structure like that of the PMe_2Ph analogue.



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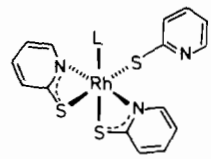

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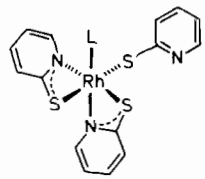

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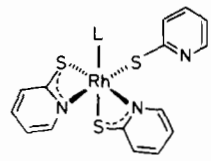


d

6 L = PMe_2Ph
7 L = PPh_3
9 L = η^1-dppm

Dppm

Reaction of $[Rh(pyS)_2(pySH)_2]Cl$ with $Ph_2PCH_2PPh_2$ (dppm) in refluxing 2-ethoxyethanol followed by the addition of $AgClO_4$ gives the cationic complex $[Rh(pyS)_2(dppm)]ClO_4$ (**8**). The pyS ligands are equivalent (^{1}H NMR evidence) (Table I). The $^{31}P\{^1H\}$ NMR spectrum (Table II) shows a single doublet [J(RhP) 96.3 Hz] consistent with the tris-chelate

TABLE II. $^{31}P\{^1H\}$ NMR Data for Rhodium(III) Thiopyridonato Phosphine Complexes[a]

Compound	δ[c] (ligand)	δ (complex)	Coordination shift (Δ)	^1J (RhP) (Hz)	*trans* ligand
$[Rh(pyS)_2(PMe_2Ph)_2]ClO_4$ (**4**)	−187.0	−137.6	+49.4	86.5	P
$[Rh(pyS)_3(PMe_2Ph)_2]$ (**5**)	−187.0	−142.2	+44.8	90.0	P
$[Rh(pyS)_3(PMe_2Ph)]$ (**6**)	−187.0	−125.7	+61.3	116.0	N
$[Rh(pyS)_3(PPh_3)]$ (**7**)	−148.0	−107.5	+40.5	121.0	N
$[Rh(pyS)_2(dppm)]ClO_4$ (**8**)	−163.2	−159.2	+4.0	96.5	N
$[Rh(pyS)_3(dppm)]$ (**9**)[b]	−163.2	−109.6	+53.6	118.5	N
$[Rh(pyS)_2(dppe)]ClO_4$ (**10**)	−154.2	−87.3	+66.9	112.5	N

[a]Referenced to $P(OMe)_3$ which is at 141 ppm relative to 85% H_3PO_4. [b]Non-coordinated P: δ −168.2. $^2J(PP) \approx 32$ Hz. [c]From ref. 8.

structure shown. The compound $[Rh(pyS)_3(dppm)]$ (**9**) is obtained from the treatment of $[Rh(pyS)_3(pySH)]$ with dppm in refluxing toluene. The $^{31}P\{^1H\}$ NMR spectrum shows two phosphine signals at δ −109.6 and −168.2, only the former showing $^{103}Rh-^{31}P$ coupling (118.7 Hz). The dppm ligand is therefore monodentate and the structure is probably analogous to that of $[Rh(pyS)_3(PMe_2Ph)]$ (**6**).

Dppe

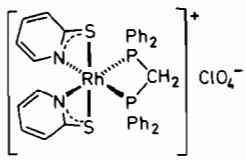
The reaction of $[Rh(pyS)_2(pySH)_2]Cl$ with dppe ($Ph_2PCH_2CH_2PPh_2$) in refluxing 2-ethoxyethanol followed by treatment with $AgClO_4$ gives $[Rh(pyS)_2(dppe)]ClO_4$ (**10**), the NMR spectra of which confirm the tris-chelate formulation (Table I).

Discussion

The smallest ^1J(RhP) values are for $[Rh(pyS)_3(PMe_2Ph)_2]$ (**5**) and $[Rh(pyS)_2(PMe_2Ph)_2]ClO_4$ (**4**) in which the phosphine ligands are mutually *trans* (Table II). Small metal–phosphorus coupling is normally associated with a high *trans*-influence ligand *trans* to phosphorus [9]. The ^1J(RhP) values are larger for $[Rh(pyS)_3L]$ in the order $PPh_3 > Ph_2PCH_2PPh_2 > PMe_2Ph$ which is consistent with previous observations that the value increases with aryl for alkyl substitution at phosphorus [10]. This has been attributed to increased π-acceptor properties [10] or to an increase in s-character at phosphorus on aryl substitution [11].

Chemical shifts on coordination (Δ) are positive and Mann *et al.* [12] have proposed that smaller Δ are associated with a smaller opening of R–P–R angles on coordination as expected for bulkier R groups. Hence for the monodentate ligands reported here the smallest Δ is for PPh_3 in compound **7**.

In chelating diphosphine complexes large positive Δ are normal for five-membered rings but four-membered rings give ^{31}P shifts at higher field than expected. That is Δ is very much smaller but still positive [13, 14]. Δ values for the diphosphine compounds **8** to **10** agree with these generalizations. In particular the differences in Δ between chelating and η^1 dppm are very clear and allow an easy assignment of structure.



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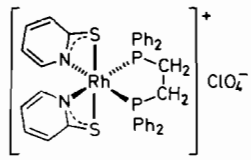

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The ^{13}C NMR spectra of the compounds $[Rh(pyS)_2(diphos)]ClO_4$ (**8** and **10**) do not show any long-range coupling between pyS carbon atoms and ^{31}P nuclei as observed for $[Ru(pyS)_2(CO)(PPh_3)]$ and related species [6, 7]. The observation of this would have allowed us to position P *trans* to N atoms with confidence. All the pyS carbon atoms, except for the *ipso*-carbon, appear as singlets; the small splitting of the *ipso*-carbon signal results from ^{103}Rh coupling. However, this certainly does not mean that the N atoms are mutually *trans* in the tris-chelate compounds. For steric reasons it is more probable that the S atoms are *trans* as found for the compounds **2** and $[RhPd_2(pyS)_4(C_4H_7)_2]BF_4$ [15].

Experimental

Compounds **1** to **3** were prepared as reported [1, 2].

Preparation of $[Rh(pyS)_2(PMe_2Ph)_2][ClO_4]$ (4)

A mixture of $[Rh(pyS)_2(pySH)_2]Cl$ (**1**) (0.100 g, 1.72×10^{-4} mol) and PMe_2Ph (0.05 g, 3.62×10^{-4} mol) in 2-ethoxyethanol (20 cm^3) was refluxed for 8h. The solvent was removed under vacuum and

replaced by acetone (5 cm^3). $AgClO_4$ (0.035 g, 1.68×10^{-4} mol) was added, the precipitated AgCl filtered off, and diethylether layered carefully over the acetone solution, and the mixture left to give yellow crystals. These were recrystallized from chloroform–diethylether mixtures to give **4** as fine yellow crystals. *Anal.* Found: C, 44.0; H, 4.3; N, 3.8; Cl, 5.3. Calc. for $C_{26}H_{30}N_2ClO_4P_2RhS_2$: C, 44.6; H, 4.3; N, 4.0; Cl, 5.1%.

Reaction of [Rh(pyS)$_3$(pySH)] (2) with PMe$_2$Ph

A mixture of compound **2** (0.136 g, 2.51×10^{-4} mol) and PMe_2Ph (0.038 g, 2.50×10^{-4} mol) in toluene (15 cm^3) was refluxed for 8 h. The solvent was removed under reduced pressure and the residue eluted through a 5% deactivated neutral alumina column with a dichloromethane/chloroform (10:1) mixture. Seven fractions were collected. The first gave *mer*-[Rh(pyS)$_3$] (**3**) (0.02 g, 18%): the third gave the bis-phosphine compound [Rh(pyS)$_3$(PMe$_2$Ph)$_2$] (**5**) (0.03 g, 18%). *Anal.* Found: C, 52.5; H, 4.9; N, 5.7. Calc. for $C_{31}H_{34}N_3P_2RhS_3$: C, 52.4; H, 4.8; N, 5.9; the fifth fraction gave the mono-phosphine compound [Rh(pyS)$_3$(PMe$_2$Ph)] (**6**) (0.05 g, 35%). *Anal.* Found: C, 48.3; H, 4.1; N, 7.2. Calc. for $C_{23}H_{23}N_3PRhS_3$: C, 48.3; H, 4.0; N, 7.4%. Both **5** and **6** gave red oils which slowly solidified. The other fractions were not characterized.

Preparation of [Rh(pyS)$_3$(PPh$_3$)] (7)

A suspension of [Rh(pyS)$_3$(pySH)] (**2**) (0.100 g, 1.84×10^{-4} mol) and PPh_3 (0.048 g, 1.83×10^{-4} mol) in toluene (15 cm^3) was refluxed for 8 h. The solvent was removed under reduced pressure and the residue eluted through a 5% deactivated alumina column with dichloromethane/chloroform (10:2 *v/v*) mixture. One of the several fractions gave [Rh(pyS)$_3$(PPh$_3$)] (**7**) (0.064 g, 50%). An analytically pure sample was not obtained but the compound was identified by comparison with compound **6**.

Preparation of [Rh(pyS)$_3$(dppm)] (9)

A suspension of [Rh(pyS)$_3$(pySH)] (**2**) (0.250 g, 4.60×10^{-4} mol) and dppm (0.176 g, 4.60×10^{-4} mol) in toluene (15 cm^3) was refluxed for 12 h. Work-up as above gave compound **9** as a salmon-pink solid (0.225 g, 60%) characterized by $^{31}P\{^1H\}$ and ^1H NMR spectra.

Preparation of [Rh(pyS)$_2$(dppe)]ClO$_4$ (10)

A suspension of [Rh(pyS)$_2$(pySH)$_2$]Cl (**1**) (0.100 g, 1.72×10^{-4} mol) and dppe (0.068 g, 1.71×10^{-4} mol) in 2-ethoxyethanol was refluxed for 8 h. The solvent was removed under vacuum and replaced with dichloromethane (10 cm^3). $AgClO_4$ (0.035 g, 1.68×10^{-4} mol) was added and the precipitate of AgCl filtered off. Diethylether was carefully layered over the dichloromethane solution which slowly deposited red crystals which were recrystallized from dichloromethane/diethylether to give compound **10** as orange crystals (0.05 g, 35%). *Anal.* Found: C, 50.45; H, 3.9; N, 3.3; Cl, 9.5. Calc. for $C_{36}H_{32}ClN_2O_4P_2RhS_2 \cdot 2/3CH_2Cl_2$: C, 50.2; H, 3.8; N, 3.2; Cl, 9.4%.

Preparation of [Rh(pyS)$_2$(dppm)]ClO$_4$ (8)

This compound was prepared similarly. The product was crystallized from dichloromethane/diethylether mixtures to give **8** as yellow crystals (39%). *Anal.* Found: C, 50.4; H, 3.7; Cl, 6.8. Calc. for $C_{35}H_{30}ClN_2O_4P_2RhS_2 \cdot 1/3CH_2Cl_2$: C, 50.8; H, 3.7; N, 3.4; Cl, 7.1%.

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