RHODIUM(I) PHOSPHINE COMPLEXES CONTAINING BIDENTATE UNSATURATED THIO LIGANDS

II *. REACTIONS WITH O_2 AND H_2

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Summary

The rhodium(I) complexes $(Ph_3P)_2Rh[Me_2NC(S)NC(S)NMe_2]$, $(Ph_3P)_2Rh[SC(S)NMe_2]$ and $(Ph_3P)_2Rh[PhNC(S)NMe_2]$ react with O_2 to give 1/1 dioxygen adducts. In solution, trans-$(Ph_3P)_2Rh(O_2)[Me_2NC(S)NC(S)NMe_2]$, cis- and trans-$(Ph_3P)_2Rh(O_2)[SC(S)NMe_2]$ and cis- and trans-$(Ph_3P)_2Rh(O_2)[PhNC(S)-NMe_2]$ are observed. For $(Ph_3P)_2Rh(O_2)[PhNC(S)NMe_2]$, there is a solvent effect on the initial cis—trans ratio and the rate of $O=PPh_3$ formation. In C_6H_6, $O=PPh_3$ formation from $(Ph_3P)_2Rh(O_2)[PhNC(S)NMe_2]$ is inhibited by additional PPh_3.

The reaction of $(Ph_3P)_2Rh[Ph_2PC(S)NPh]$ with O_2 in the presence of additional PPh_3 gives $O=PPh_3$ and cis-$(Ph_3P)_2Rh(O_2)[Ph_2P(O)C(S)NPh]$ as the only products. The same complex also can be prepared from $(Ph_3P)_2Rh[Ph_2P(O)C(S)NPh]$ and O_2.

Only $(Ph_3P)_2Rh[PhNC(S)NMe_2]$ reacts with H_2 at room temperature to give $(Ph_3P)_2RhH_2[PhNC(S)NMe_2]$, which is a catalyst for cyclohexene hydrogenation.

Introduction

Although a number of studies on the subject have been made, the reaction of $RhCl(PPh_3)_3$ with molecular oxygen is still not satisfactorily understood [2—4]. The reaction is important because of the increase of catalytic ability of $RhCl(PPh_3)_3$ in various reactions by traces of oxygen [5—7] and because of the catalytic activity of $RhCl(PPh_3)_3$ in olefin autoxidation [3,8,9]. One of the reasons for the complexity of the reaction between $RhCl(PPh_3)_3$ and O_2 is the

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* For part I see ref. 1.

ready dissociation of PPh$_3$ (either as PPh$_3$ or as O=PPh$_3$) and consequent dimeri-
sation to acquire coordinative saturation [16].

We have investigated the reactivity towards O$_2$ of the related rhodium(I)
complexes (Ph$_3$P)$_2$Rh[Me$_2$NC(S)NC(S)NMe$_2$] (IA) *, (Ph$_3$P)$_2$Rh[SC(S)NMe$_2$]
(IIA), (Ph$_3$P)$_2$Rh[PhNC(S)NMe$_2$] (IIIA) and (Ph$_3$P)$_2$Rh[Ph$_2$PC(S)NPh] (VA),
which contain only two PPh$_3$ groups and a bidentate unsaturated ligand L—L'.
The structures of the oxygen adducts (Ph$_3$P)$_2$Rh(O$_2$)(L—L') and their tendency
towards O=PPh$_3$ formation have been studied by IR, ^{1}H NMR and ^{31}P {^{1}H}
NMR. VA contains three phosphorus donor atoms, like RhCl(PPh$_3$)$_3$, and in addi-
tion to O=PPh$_3$ formation, oxidation of the P,S-coordinated Ph$_2$PC(S)NPh to Ph$_2$P-
(O)C(S)NPh is expected. Therefore, we also investigated the reaction between
O$_2$ and (Ph$_3$P)$_2$Rh[Ph$_2$P(O)C(S)NPh] (VIA).

The reactivities of the complexes IA—IIIA and VA towards H$_2$ have been
compared.

Experimental

IR spectra were obtained with Perkin—Elmer 257 and 283 spectrophotom-
eters. ^{1}H NMR spectra were recorded on a Bruker WH-90-FT and ^{31}P {^{1}H}
NMR spectra on a Varian XL-100-FT spectrometer. Relative concentrations
of O=PPh$_3$ and the dioxygen adducts were determined by ^{31}P NMR with a total
measuring time of 15 (1000 transients) or 30 minutes (2000 transients). The
observed peak heights, which result from integration over the total measuring
time, have been taken proportional to the peak heights at the mid-time of the
measurement.

The synthesis of the rhodium(I) complexes (Ph$_3$P)$_2$Rh(L—L') (IA—IIIA, VA
and VIA) has been described in part I [1]. C, H, and N analyses were performed
by the micro-analytical department of this university. Analytical values are given
in Table 1.

(A) Dioxygen adducts

Synthesis and isolation
*(Ph$_3$P)$_2$Rh(O$_2$)[Me$_2$NC(S)NC(S)NMe$_2$] (I) and (Ph$_3$P)$_2$Rh(O$_2$)[PhNC(S)NMe$_2$]
(III)*. The dioxygen adducts were prepared from (Ph$_3$P)$_2$Rh(L—L'), generated in
situ in O$_2$-free benzene by oxidative addition of Me$_2$NC(S)N(H)C(S)NMe$_2$ and
HN(Ph)C(S)NMe$_2$ to RhCl(PPh$_3$)$_3$ and subsequent dehydrohalogenation with
Et$_3$N, as described in part I [1]. Et$_3$NHCl was filtered off from the solution,
which was red in the first case and orange in the second. On passing through O$_2$, the
colour immediately changed to dark red-brown. Rapid precipitation by addi-
tion of n-hexane gave an ochre-yellow powder of I or III. I: ν(O—O) 883(s) cm^{-1},
ν(CNMe$_2$) 1503(s, br) cm^{-1}; II: ν(O—O) 871(s) cm^{-1}, ν(CNMe$_2$) 1562 (s, br)
cm^{-1}. Recorded in CsI.

(Ph$_3$P)$_2$Rh(O$_2$)[SC(S)NMe$_2$] (II). On passing dioxygen through a suspension
of 0.2 mmol (Ph$_3$P)$_2$Rh[SC(S)NMe$_2$] in 10 ml of O$_2$-free benzene, the solution

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* The codes used are the same as in part I [1].

TABLE 1

ANALYTICAL DATA

No.	Compound	Colour	Analysis (Found (calcd.) (%))		
			C	H	N
I	$(Ph_3P)_2Rh(O_2)[Me_2NC(S)NC(S)NMe_2]$	ochre-yellow	60.9	5.3	4.9
			(59.4)	(5.0)	(4.9)
II	$(Ph_3P)_2Rh(O_2)[SC(S)NMe_2]$	green-yellow	60.3	4.9	1.7
			(60.1)	(4.7)	(1.8)
III	$(Ph_3P)_2Rh(O_2)[PhNC(S)NMe_2]$	ochre-yellow	(65.2)	(5.1)	(3.4)
			(64.5)	(4.9)	(3.3)
VII	$(Ph_3P)_2RhH_2[PhNC(S)NMe_2]$	white	66.9	5.6	3.5
			(66.9)	(5.4)	(3.5)

turned dark red-brown. Rapid precipitation with n-hexane gave a green-yellow powder of II. $\nu(O—O)$ 881(m, br) cm^{-1}, $\nu(CNMe_2)$ 1529(s, br) cm^{-1}. Recorded in CsI.

(Ph₃P)₂Rh(O₂)[Ph₂P(O)C(S)NPh] (VI). This complex has been characterised in solution as the product of the reaction of $(Ph_3P)_2Rh[Ph_2PC(S)NPh]$ with O_2 as well as of the reaction of $(Ph_3P)_2Rh[Ph_2P(O)C(S)NPh]$ with O_2.

The solid dioxygen adducts I—III decompose very slowly in the air. Only after some weeks are $O=PPh_3$ absorptions observed in the IR.

Preparation of solution samples. NMR solution samples of the dioxygen adducts were prepared by dissolving the starting complex $(Ph_3P)_2Rh(L—L')$ in the O_2-free solvent in a glove-box and sealing with a silicone rubber cap. After freezing of the solution, the NMR tube was evacuated via a thin capillary through the rubber cap and one or more equivalents of O_2 were introduced with a syringe. (One equivalent = one mol of O_2 per mol of $(Ph_3P)_2Rh(L—L')$). The frozen solution was rapidly warmed to room temperature and shaken vigorously, resulting in an almost immediate change of colour to orange-brown or red-brown. Solution samples for IR were prepared similarly.

(B) Reactivity of the complexes (Ph₃P)₂Rh(L—L') towards H₂

(Ph₃P)₂RhH₂[PhNC(S)NMe₂] (VII). On passing H_2 through a O_2-free solution of $(Ph_3P)_2Rh[PhNC(S)NMe_2]$ in benzene at room temperature, the colour of the solution darkened. After 15 min, the Schlenk vessel was closed, and stirring was continued under hydrogen. After 35 min, a white precipitate began to form, and after 5 h the white precipitate of VII was filtered off. $\nu(M—H)$ 2018(m) and 2060(m) cm^{-1}, $\nu(CNMe_2)$ 1562 (s, br) cm^{-1}. Recorded in CsI. The complex is poorly soluble in the common organic solvents. In a similar procedure with Ia, IIa and VA no reaction was observed.

(C) Catalytic activity of VII in cyclohexene hydrogenation

25.5 mg of VII was dissolved in a mixture of 35 ml of benzene and 25 ml of cyclohexene. At 40°C and $p(H_2)$ 1.4 ATA the hydrogen uptake was 3.1 ml/min, from which a turnover number (*TN*) of 8.5 × 10^{-2} sec^{-1} was calculated.

Results and discussion

A. Reaction of (Ph₃P)₂Rh(L—L') with O₂

A. Reaction of (Ph₃P)₂Rh(L—L') with O₂

On powdering the rhodium(I) complexes IA, IIa, IIIA and VIA under atmospheric conditions, partial formation of the dioxygen adducts occurs, as evidenced by the appearance of a weak broad IR absorption due to $\nu(O_2)$, the position of which is in agreement with that observed for $\nu(O_2)$ in the dioxygen adducts isolated in the solid state (I, II, III), and for the dioxygen adducts prepared in situ in solution (Table 2). To study the structure of the dioxygen adducts $(Ph_3P)_2Rh(O_2)(L—L')$ and their tendency towards O=PPh₃ formation, they were generated in situ in solution from $(Ph_3P)_2Rh(L—L')$ and one equivalent of O_2 (Experimental).

The ^{31}P {^1H} NMR spectra indicate complete conversion of rhodium(I) complexes IA, IIA, IIIA and VIA into the dioxygen adducts I, II, III and VI by reaction with one equivalent of O_2. Besides the formation of O=PPh₃, the formation of *trans* *-(Ph₃P)₂Rh(O₂)[Me₂NC(S)NC(S)NMe₂] (*trans*-I), *cis*-(Ph₃P)₂Rh(O₂)-[SC(S)NMe₂] (*cis*-II) and a mixture of *cis*- and *trans*-(Ph₃P)₂Rh(O₂)[PhNC(S)-NMe₂] (*cis*-III and *trans*-III) is observed, in CD_2Cl_2 or in C_6D_6 (Fig. 1A, B). The reaction of VIA with one equivalent of O_2, which has only been investigated in CD_2Cl_2, gives *cis*-(Ph₃P)₂Rh(O₂)[Ph₂P(O)C(S)NPh] (*cis*-VI) as the only isomer (Fig. 2). In CH_2Cl_2 slow formation of O=PPh₃ occurs for all four O_2-adducts as is demonstrated by the increase of the sharp O=PPh₃ absorption at δ 24.9 ppm. No other phosphorous resonances of appreciable intensity are observed.

III, for which the *cis*- and *trans*-isomer are initially present in comparable concentrations, has been investigated in more detail. A solvent effect on both the initial *cis—trans* ratio and the rate of O=PPh₃ formation is observed. In C_6H_6, *cis*-III is formed in a relative higher concentration than in CH_2Cl_2 and an increased tendency towards O=PPh₃ formation is found (Fig. 1A, B). As judged from the relative peak heights of O=PPh₃ and *cis*-III and *trans*-III in CD_2Cl_2, 20 min after preparation of the solution about 5% of III has decomposed, and in C_6D_6 about 15%. After 45 min in CD_2Cl_2 no further decomposition has occurred, whereas in C_6D_6 about 50% has decomposed. The absence of phosphorous resonances other than those of O=PPh₃ and *cis*- and *trans*-III, and the simultaneous decrease and increase, respectively, in intensity of the resonances of III and O=PPh₃ suggest a simultaneous transfer of both O atoms to both PPh₃ groups. The nature of the rhodium complex formed by this "dissociative oxygen insertion" [10] is unknown. If the reaction of IIIA with one equivalent of O_2 in C_6H_6 is performed in the presence of two moles of PPh₃ per mol of III, remarkable inhibition of O=PPh₃ formation occurs: even after 45 min, no O=PPh₃ is observed in the ^{31}P NMR. Under these conditions, isomerisation of *cis*-III to the apparently more stable *trans*-III is observed. Similarly, *cis*-II in C_6H_6 in the presence of 2 mol of PPh₃, isomerises to *trans*-II.

Although the presence of two equivalents of PPh₃ lowers the intensity of O=PPh₃ absorption, the ^{31}P NMR spectrum of VI, formed by reaction of VIA with one equivalent of O_2 in CD_2Cl_2 does not show the pronounced inhibition of O=PPh₃ formation observed for III. Within four hours, the initially formed *cis*-

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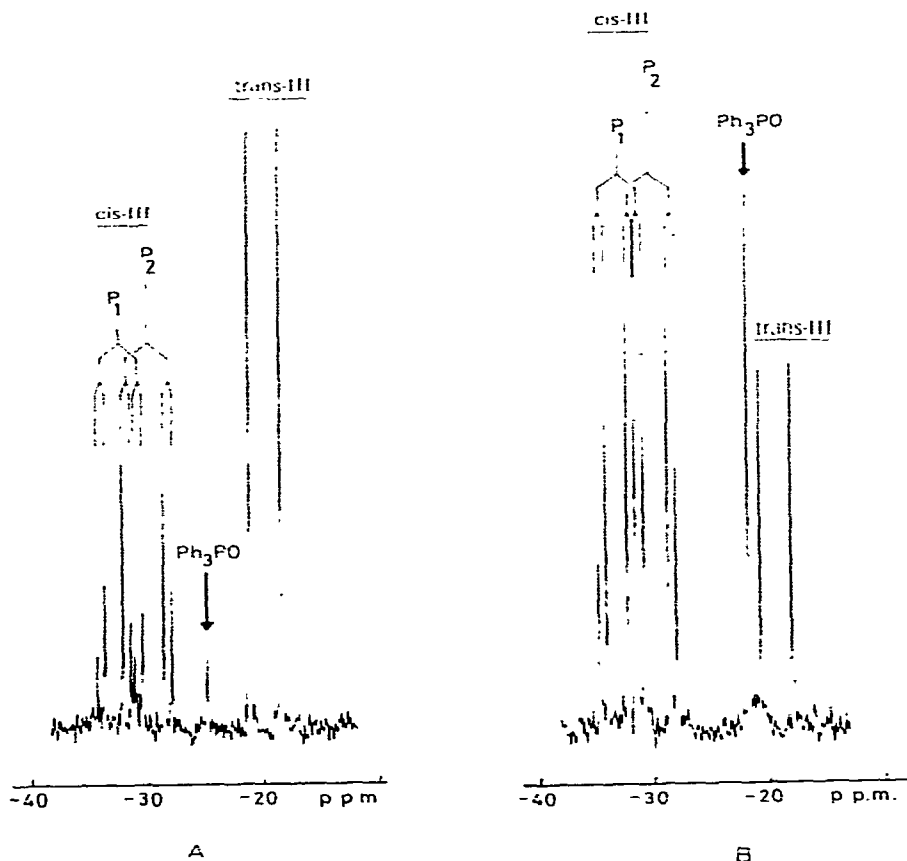* *cis* and *trans* indicate relative position of both PPh₃ groups.

Fig. 1. ^{31}P$\{^1$H$\}$ NMR spectrum of cis- and trans-(Ph$_3$P)$_2$Rh(O$_2$)[PhNC(S)NMe$_2$] (cis-III and trans-III). 20 min after preparation of the solution; (A) in CD$_2$Cl$_2$, (B) in C$_6$D$_6$ (numbering of the P atoms as in Table 2).

VI is completely converted into the parent rhodium(I) complex VIA and O=PPh$_3$, as can be seen from the change in colour from orange-brown to intense bright-red and can be followed by IR and ^{31}P NMR. The observed change in the IR spectrum is shown in Fig. 3. Cis-VI can also be obtained by reaction of VA with O$_2$ in CH$_2$Cl$_2$ in the presence of additional PPh$_3$. Six mol of PPh$_3$ per mol of VA have been used. The orange-yellow solution immediately turns orange-brown upon contact with O$_2$. The amount of O$_2$ necessary varied somewhat from one experiment to another. Generally three to four equivalents of O$_2$ were necessary for complete conversion of the starting complex VA to cis-VI. No other phosphorus resonances of appreciable intensity were observed (Fig. 4). Upon prolonged standing of the solution of cis-VI so obtained, conversion to VIA and O=PPh$_3$ is observed, as for cis-VI prepared directly from VIA. Fig. 5. summarizes the observed reactions of VA and VIA with O$_2$. Apparently the proposed initially-formed O$_2$ adduct (Ph$_3$P)$_2$Rh(O$_2$)[Ph$_2$PC(S)NPh] (V) is too labile to be detected.

TABLE 2

SPECTROSCOPIC PARAMETERS OF THE O_2-COMPLEXES IN SOLUTION

No.	Complex	Solvent	IR $\nu(O_2)$ (cm⁻¹)	$^{31}P\{^1H\}$ NMR δ [a] (ppm)	$^1J(Rh-P)$ [b] (Hz)	Atom or group trans	$^2J(P(1)-P(2))_{cis}$ [b]	^1H NMR $\tau(NMe_2)$ [c] (ppm)
I	trans-(Ph₃P)₂Rh(O₂)[Me₂NC(S)N-C(S)NMe₂]	CD₂Cl₂		−24.6	101	PPh₃		7.29(s)
II	trans-(Ph₃P)₂Rh(O₂)[SC(S)NMe₂] [d]	C₆D₆	878	−24.2	102	PPh₃		
III	trans-(Ph₃P)₂Rh(O₂)[PhNC(S)NMe₂]	C₆D₆		−20.7	104	PPh₃		7.93(s)
		CD₂Cl₂	870 [e]	−19.0	100	PPh₃		
		C₆D₆	866	−19.5	110			
II	cis-(Ph₃P)₂Rh(O₂)[SC(S)NMe₂]	CD₂Cl₂		−23.5 [d]	132	S	15	7.67(s)
				−42.2	143	O	15	
III	cis-(Ph₃P)₂Rh(O₂)[PhNC(S)NMe₂]	CD₂Cl₂		−32.4 [f]	131 (P(1)) [g]	S or NPh	28	7.48(s)
				−30.1	142 (P(2))	O	28	
		C₆D₆	870 [e]	−32.7 [f]	130 (P(1))		28	
				−30.2	143 (P(2))		28	
VI	cis-(Ph₃P)₂Rh(O₂)[Ph₂P(O)C(S)NPh]	CD₂Cl₂	869	−37.6	142 (P(1)) [h]	O	29	
				−30.3	140 (P(2))	O	29	
				−31.6 (O=PPh₂)				
	O=PPh₃	CD₂Cl₂		−24.9				
		C₆D₆		−21.0				

[a] Rel. to O=P(OMe)₃(TMP) int. ref.; values ±0.2 ppm, but relative shifts between two P atoms in the same complex ±0.03 ppm. [b] J values ±1 Hz. [c] Rel. to TMS int. ref.; s = singlet. [d] Observed in the presence of two equivalents of PPh₃. [e] To a C₆D₆ solution of cis- and trans-(Ph₃P)₂Rh(O₂)[PhNC(S)NMe₂] and two equivalents of PPh₃ only one $\nu(O_2)$ could be assigned. [f] ³¹P NMR parameters result from ABX analyses. [g] Numbering of the P atoms as in Fig. 1A and 1B. [h] Numbering of the P atoms as in Fig. 2 and 4.
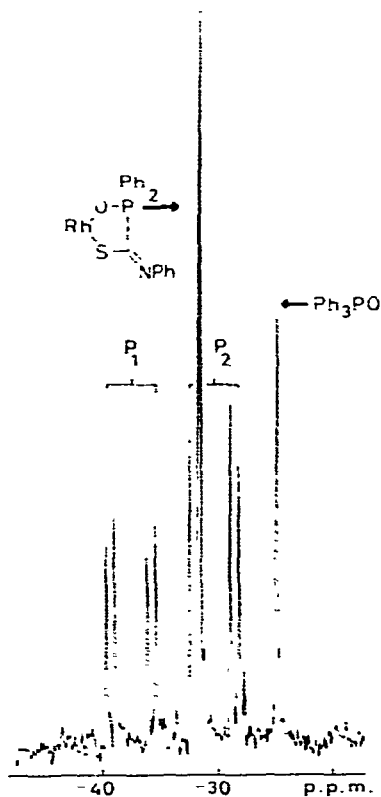
Fig. 2. ^{31}P {^{1}H} NMR spectrum of *cis*-(Ph$_3$P)$_2$Rh(O$_2$)[Ph$_2$P(O)C(S)NPh] (*cis*-VI) in CD$_2$Cl$_2$. Prepared from (Ph$_3$P)$_2$Rh[Ph$_2$P(O)C(S)NPh] (VIA). 20 min after preparation of the solution (numbering of P atoms as in Table 2).

and a very fast transfer of oxygen to Ph$_3$P as well as Ph$_2$P occurs. If both O atoms are indeed simultaneously transferred to two coordinating P atoms, two routes (A and B in Fig. 5) can be distinguished. If only transfer of oxygen via route A occurs, a maximum of two equivalents of O$_2$ would be absorbed. The high intensity of the O=PPh$_3$ resonance (Fig. 4) and the need for three to four equivalents of O$_2$ to obtain quantitative conversion seem to indicate that route B also occurs to some extent.

B. Spectra and structures of (Ph$_3$P)$_2$Rh(O$_2$)(L—L')

The IR, ^{31}P NMR and some ^{1}H NMR parameters of the O$_2$ adducts are given in Table 2. In the IR the observed values of ν(O$_2$) in solution are as expected for a five coordinate TBP rhodium(I) complex of class T [11], for which values of ν(O$_2$) ranging from 833—890 cm^{-1} [12,13] have been reported. For the square planar RhCl(PCy$_3$)$_2$(O$_2$) (class S), the much higher ν(O$_2$) of 993 cm^{-1} has been ascribed to a weaker M—O$_2$ π-backbonding in the square-planar geometry [11]. The chelate absorptions in solution are virtually the same as those assigned to
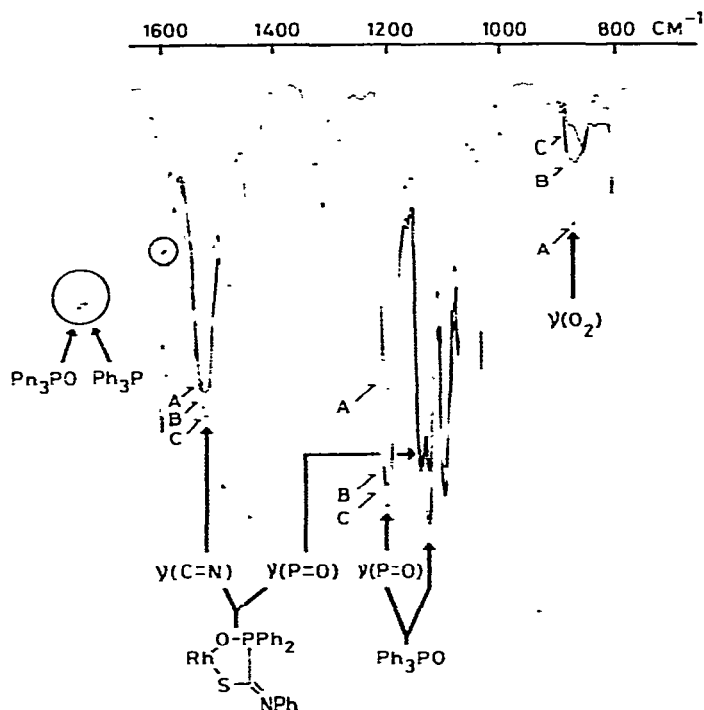
Fig. 3. Formation of (Ph₃P)₂Rh[Ph₂P(O)C(S)NPh] (VIA) from *cis*-(Ph₃P)₂Rh(O₂)[Ph₂P(O)C(S)NPh]-(*cis*-VI) and two moles of PPh₃ in CD₂Cl₂. Time dependent IR spectrum: A = 70 min., B = 150 min. and C = 220 min. after sampling (temp. = 40°C). ν(C=N) in *cis*-VI = 1525 cm⁻¹. ν(C=N) in VIA = 1511 cm⁻¹. ν(P=O) in *cis*-VI = 1130 cm⁻¹: ν(P=O) in VIA = 1133 cm⁻¹. r(PCS) is obscured by solvent absorption. O=PPh₃ absorptions increase (1592, 1192 and 1119 cm⁻¹) and ν(O₂) decreases.

the bidentate chelates L—L' in the parent rhodium(I) complexes. ν(P=O) in *cis*-VI (1130 cm⁻¹, CH₂Cl₂) (Fig. 3) indicates O-coordination of Ph₂P(O)C(S)-NPh as in VIA (ν(P=O) = 1133 cm⁻¹, CH₂Cl₂) for which O-coordination has been discussed in part I [1].

In the observed *trans*-isomers both Ph₃P groups are equivalent, and one doublet due to coupling with Rh (I = 1/2, 100% abundance) is observed (Table 2). In the *cis*-isomers both Ph₃P groups (P(1) and P(2)) are inequivalent, and two pairs of doublets are observed due to ¹J(Rh—P) and ²J(P(1)—P(2))$_{cis}$ (Fig. 1 and 2). In *cis*-VI the ³¹P absorption of the O-coordinated O=PPh₂ group coincides with one of the Ph₃P lines (Fig. 2). Its position is only slightly different from that observed in (Ph₃P)₂Rh[Ph₂P(O)C(S)NPh] (δ —28.6 ppm) and (CO)-(Ph₃P)Rh[Ph₂P(O)C(S)NPh] (δ —33.1 ppm). For III and VI two *cis*-isomers are possible (neglecting different enantiomers). Figure 6 summarizes the structures. The observed isomerization is also indicated. Because within the rhodium(I) complex (Ph₃P)₂Rh[Ph₂P(O)C(S)NPh] [1] the value of ¹J(Rh—P) for Ph₃P *trans* to O (202 Hz) is larger than for Ph₃P *trans* to S (170 Hz), we tentatively assign ¹J(Rh—P) ~140 Hz to Ph₃P *trans* to O and ¹J(Rh—P) ~130 Hz to P *trans*
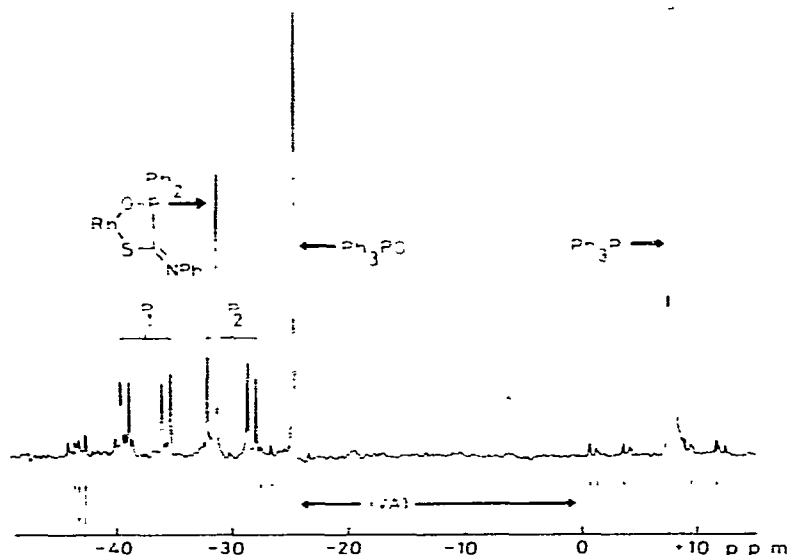
Fig. 4. ^{31}P $\{^1$H$\}$ NMR spectrum of cis-(Ph$_3$P)$_2$Rh(O$_2$)[Ph$_2$P(O)C(S)NPh] (cis-VI) in CD$_2$Cl$_2$. Prepared from (Ph$_3$P)$_2$Rh[Ph$_2$PC(S)NPh] (VA) and six moles of PPh$_3$. 20 min. after preparation of the solution. Unreacted VA is indicated (numbering of P atoms as in table 2).

to S (or NPh in cis-III). This implies that in cis-VI both Ph$_3$P groups have O trans (isomer (a), Fig. 6). This assignment is in accord with the absence of a ^3J(P—Rh—O—PPh$_2$) expected for P trans to S in isomer (b), by analogy to (Ph$_3$P)$_2$Rh[Ph$_2$P(O)C(S)NPh] [1]. So (a) is the most probable structure for cis-VI.
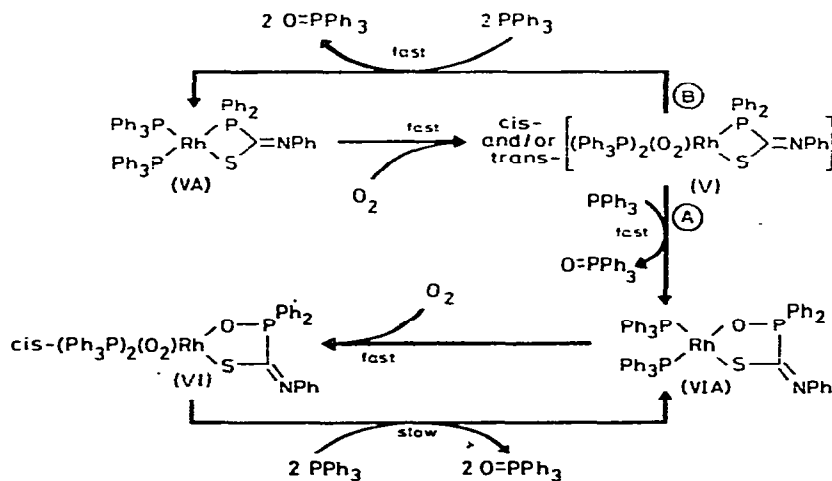
Fig. 5. The formation of cis-(Ph$_3$P)$_2$Rh(O$_2$)[Ph$_2$P(O)C(S)NPh] (cis-VI) from (Ph$_3$P)$_2$Rh[Ph$_2$PC(S)NPh] (VA) and (Ph$_3$P)$_2$Rh[Ph$_2$P(O)C(S)NPh] (VIA): reaction scheme.
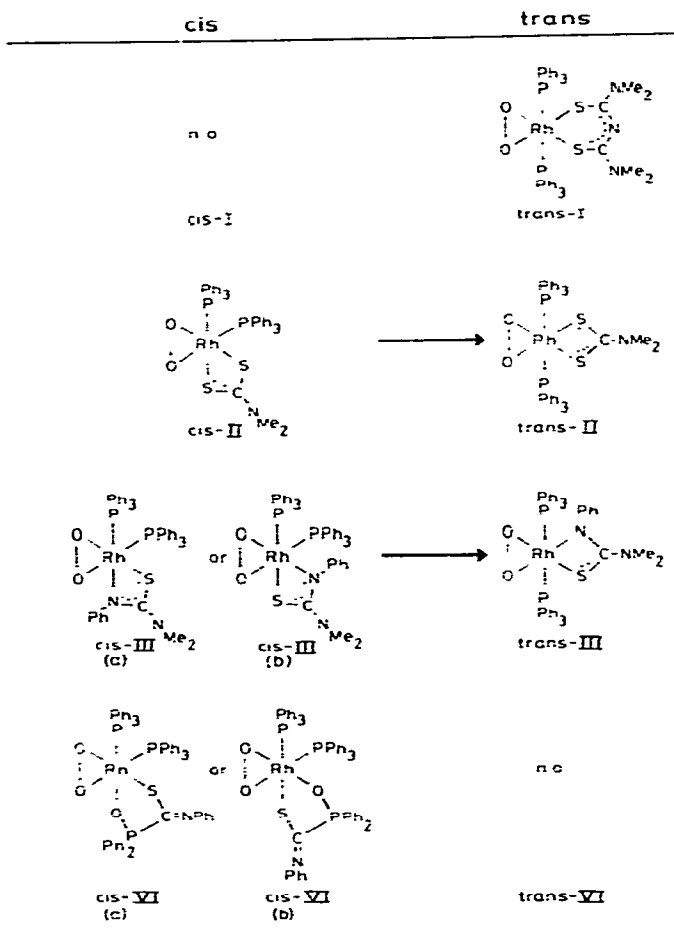
Fig. 6. Structures and observed isomerisation of the dioxygen adducts (n.o. = not observed).

C. Reaction of (Ph₃P)₂Rh(L—L') with H₂

Of the complexes investigated, only IIIA reacts with H_2 at room temperature. The two ν(Rh—H) absorptions (2060, 2018 cm^{-1}, CsJ) in (Ph₃P)₂RhH₂[PhNC-(S)NMe₂] (VII) indicate a *cis*-psoition for both hydrides. The observed chelate absorptions, except for ν(CNMe₂) (1525 cm^{-1}, CsI), are virtually the same as for PhN, S-coordinated thioureide in (Ph₃P)₂Rh[PhNC(S)NMe₂]. (ν(CNMe₂) = 1548 cm^{-1}, CsI). Because of the low solubility no useful NMR spectrum could be obtained. By analogy to the earlier reported *trans*-(Ph₃P)₂-RhH₂(ArNNNAr) and *trans*-(Ph₃P)₂RhH₂(O₂CR), both Ph₃P groups probably will be in *trans* position [14,15]. VII is not sensitive to O_2 in solution. Stirring VII in an ethylene-saturated solution results in hydrogenation and formation of (Ph₃P)₂Rh[PhNC(S)NMe₂]. The activity of the complex in cyclohexene hydrogenation (*TN* 8.5 × 10^{-2} sec^{-1}) is about 16% of that we have found for RhCl-

$(PPh_3)_3$ under the same conditions. Activity in olefin hydrogenation also has been reported for trans-$(Ph_3P)_2RhH_2(PhNNNPh)$ and trans-$(Ph_3P)_2RhH_2(O_2CR)$ [13,15].

D. Conclusions

The investigated complexes $(Ph_3P)_2Rh(L—L')$ are more reactive towards O_2 than H_2. Replacement of PhN in $(Ph_3P)_2Rh[PhNC(S)NMe_2]$ (IIIA) by S to give $(Ph_3P)_2Rh[SC(S)NMe_2]$ (IIA) makes the Rh centre unreactive towards H_2 at room temperature. The replacement of PhN by S also has an effect on the cis—trans ratio observed for the dioxygen adduct.

In the case of IIIA, cis- and trans-III are formed initially, whereas IIA initially forms only cis-II. We think this is a kinetic effect, because in both cases the trans-isomer if found to be the most stable. The stability of the trans-isomer is probably related to the relief of steric hindrance between both Ph_3P groups in this isomer. A marked effect of L—L' on the lability of $(Ph_3P)_2Rh(O_2)(L—L')$ towards O=PPh_3 formation is observed: for L—L' = $Ph_2PC(S)NPh$ the intially formed dioxygen adduct is too labile to be detected and oxygen transfer to Ph_3P as well as $Ph_2PC(S)NPh$ is found.

The nature of the inhibition of O=PPh_3 formation from cis-III by additional PPh_3 will be subject of further investigations.

Acknowledgement

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