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RHODIUM(I) PHOSPHINE COMPLEXES CONTAINING BIDENTATE UNSATURATED THIO LIGANDS

I. SYNTHESIS AND CHARACTERISATION

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Summary

The rhodium(I) complexes $(Ph_3P)_2Rh(L—L')$, in which L—L' is an unsaturated chelate coordinating via L = S and L' = N, O, P or S, have been prepared from $RhCl(PPh_3)_3$ by two routes.

Direct substitution of one Ph_3P and Cl^- by the chelate anion gives $(Ph_3P)_2Rh[Ph_2PC(S)S]$ (L = S, L' = P). Oxidative addition of an N—H bond followed by reductive elimination of HCl results in $(Ph_3P)_2Rh[Me_2NC(S)NC(S)NMe_2]$ (L = S, L' = S), $(Ph_3P)_2Rh[PhNC(S)NMe_2]$ (L = S, L' = N), $(Ph_3P)_2Rh[Ph_2PC(S)NPh)$ (L = S, L' = P) and $(Ph_3P)_2Rh[Ph_2P(O)C(S)NPh]$ (L = S, L' = O).

Reaction of the complexes $(Ph_3P)_2Rh(L—L')$ with CO gives $(CO)(Ph_3P)Rh(L—L')$ with CO *trans* to the chelate donor atom with the lowest *trans*-influence. $Pt(PPh_3)_4$ reacts with $Me_2NC(S)N(H)C(S)NMe_2$ and $HN(Ph)C(S)PPh_2$, respectively, to give $H(Ph_3P)Pt[Me_2NC(S)NC(S)NMe_2]$ (L = S, L' = S) and $H(Ph_3P)Pt[Ph_2PC(S)NPh]$ (L = S, L' = P).

The coordinating atoms and their configurations have been assigned by IR ^{31}P NMR and ^1H NMR. Some trend in IR and ^{31}P NMR paramaters are discussed.

Introduction

We are interested in the variation of chemical and spectroscopic properties of the rhodium(I) complexes $(Ph_3P)_2Rh(L—L')$ as a function of the unsaturated chelate (L—L'). We have thus synthesized a number of such complexes containing the formally uninegative ligands (I—VI), which can all be regarded as derived from the dithiocarbamate ion II, for which S,S-coordination has been reported in $A(Ph_3P)Rh[SC(S)NMe_2]$ * (A = Ph_3P or CO) [1]. No rhodium(I) complexes

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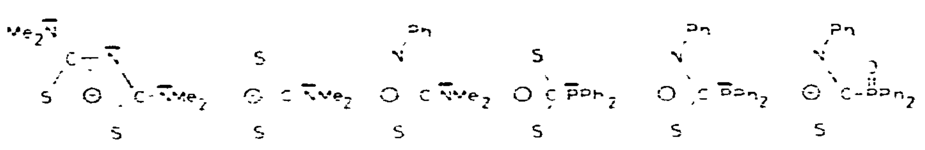
* To avoid confusion: except for I, the coordinating atoms L and L' of the chelate L—L' are placed in the formulas immediately before and after the central carbon atom, with the non-coordinating atom further away from the carbon atom, e.g. in $A(Ph_3P)Rh[SC(S)NMe_2]$ both S atoms coordinate to the metal centre and N of NMe_2 does not.

TABLE 1

ANALYTICAL VALUES AND MOLECULAR WEIGHTS [a]

No.	Compound	Colour	Analysis (Found (calcd.) (%))					
			%C	%H	%N	%P	%S	Mol. wt.
IA	$(Ph_3P)_2Rh[Me_2NC(S)NC(S)NMe_2]$	orange-red	59.1 (61.7)	5.2 (5.2)	5.4 (5.1)		8.2 (7.8)	752 [b] (817)
IIA	$(Ph_3P)_2Rh[SC(S)NMe_2]$	orange	62.0 (62.7)	5.0 (4.9)	1.8 (1.9)			
IIIA	$(Ph_3P)_2Rh[PhNC(S)NMe_2] \cdot C_6H_6$	orange	68.5 (69.2)	5.3 (5.4)	3.0 (3.2)		3.3 (3.6)	
IVA	$(Ph_3P)_2Rh[Ph_2PC(S)S]$	brick-red	65.9 (66.3)	4.8 (4.5)		9.9 (10.4)	6.9 (7.2)	600 [c] (888)
VA	$(Ph_3P)_2Rh[Ph_2PC(S)NPh]$	orange-yellow	70.0 (69.7)	5.1 (4.8)	1.4 (1.5)	9.5 (9.8)	3.2 (3.4)	915 [c] (947)
VIA	$(Ph_3P)_2Rh[Ph_2P(O)C(S)NPh]$	red	68.4 (68.5)	4.7 (4.7)	1.5 (1.5)	3.3 (3.3)	9.6 (9.6)	
IB	$(CO)(Ph_3P)Rh[Me_2NC(S)NC(S)NMe_2]$	orange-yellow	52.0 (51.5)	4.8 (4.7)	7.0 (7.2)			
IIB	$(CO)(Ph_3P)Rh[SC(S)NMe_2] \cdot (H_3CC(O)CH_3)$	yellow	53.3 (52.6)	4.7 (4.8)	2.5 (2.5)			
IIIB	$(CO)(Ph_3P)Rh[PhNC(S)NMe_2] \cdot C_6H_6$	yellow	63.2 (62.8)	5.1 (5.0)	4.1 (4.3)	4.8 (4.7)	4.9 (4.9)	686 [b] (650)
IVB	$(CO)(Ph_3P)Rh[Ph_2PC(S)S]$	red	58.5 (58.7)	3.8 (3.8)		9.5 (9.4)	9.8 (9.8)	627 [c] (654)
VB	$(CO)(Ph_3P)Rh[Ph_2PC(S)NPh]$	yellow	63.8 (64.0)	4.3 (4.2)	1.9 (2.0)	8.2 (8.6)	4.4 (4.5)	764 [c] (713)
VIB	$(CO)(Ph_3P)Rh[Ph_2P(O)C(S)NPh]$	yellow	62.5 (62.6)	4.3 (4.1)	1.8 (1.9)	8.5 (8.5)	4.3 (4.4)	718 [c] (730)
VII	$H(Ph_3P)Pt[Me_2NC(S)NC(S)NMe_2]$	pale-yellow	44.3 (44.4)	4.4 (4.4)	6.4 (6.5)			
VIII	$H(Ph_3P)Pt[Ph_2PC(S)NPh]$	pale-yellow	56.9 (57.1)	4.2 (4.0)	1.7 (1.8)			

[a] Osmometrically under N_2-atmosphere. [b] In C_6H_6. [c] In CH_2Cl_2.



(I) (II) (III) (IV) (V) (VI)

(I) *N,N,N′,N′*-tetramethyldithiobiuretato; (II) *N,N*-dimethyldithiocarbamato; (III) *N,N*-dimethyl-*N′*-phenyl-thioureido; (IV) *P,P*-diphenylphosphinodithioformato; (V) *P,P*-diphenyl-*N*-phenylphosphino-thioformamido; (VI) *P,P*-diphenyl-*N*-phenyl-phosphinylthioformamido.

containing the other ligands were previously known. I is expected to coordinate via S,S in a six-membered chelate ring [41]. III has been found NPh,S-coordinated to rhodium(III) [13,16]. In view of the reported tendency of IV towards P,S-coordination in case of a "soft" metal centre [35], P,S-coordination is expected for IV and P,S- or P,NPh-coordination for V. In VI, the oxidized form of V, S,NPh-coordination in a four-membered chelate ring as in III seems possible, but S,O- or NPh,O-coordination in a five-membered chelate ring is also conceivable. The coordinating atoms L,L′ have been assigned in both the $(Ph_3P)_2$-Rh(L—L′) and $(CO)(Ph_3P)Rh(L—L′)$ which result from the reaction of $(Ph_3P)_2$-Rh(L—L′) with CO. The complexes $H(Ph_3P)Pt(L—L′)$ with L—L′ being I and V, respectively, are also described.

Experimental

Reactions were performed at room temperature using Schlenk apparatus. Solutions for IR and NMR measurements were prepared in a glove-box. ^1H NMR spectra were recorded on a Varian T-60 and a Bruker WH-90-FT NMR spectrometer. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-100-FT at 40.5 MHz using the deuterated solvent as internal lock.

C, H and N analysis for the air-stable complexes were performed at the microanalytical department of this university. Other elemental analysis and molecular weight determinations were carried out by Alfred Bernhardt, Microanalytisches Laboratorium, Elbach über Engelskirchen, W.-Germany. The analytical results are given in Table 1. The molecular weight determination of the air-sensitive complexes $(Ph_3P)_2Rh(L—L′)$ are probably less accurate.

Starting materials

$NaS_2CNMe_2 \cdot 2H_2O$(II) (reagent grade) was obtained from Fluka. $Me_2NC(S)N(H)C(S)NMe_2$ (I-H) [2], $HN(Ph)C(S)NMe_2$ (III-H) [3], $HN(Ph)C(S)PPh_2$ (V-H) [4], $HN(Ph)C(S)P(O)Ph_2$ (VI-H) [5], $RhCl(PPh_3)_3$ [6] and $Pt(PPh_3)_4$ [7] were prepared by published procedures. $RhCl(CO)(PPh_3)_2$ was prepared from $RhCl(PPh_3)_3$ and CO.

$KS_2CPPh_2 \cdot 1$ dioxane (IV) was prepared by a modification of a published procedure [8]: the turbid red-brown THF solution obtained by addition of $KPPh_2$ to CS_2 in dry THF was diluted with an equal volume of dry ether and left for two days. The very air-sensitive yellow precipitate was centrifuged off and the residual solution evaporated in vacuo. On stirring the resulting red oil with dry 1,4-dioxane the orange-yellow $KS_2CPPh_2 \cdot 1$ dioxane precipitated.

Synthesis of the complexes $(Ph_3P)_2Rh(L—L')$

A. Oxidative addition of N—H bond

$(Ph_3P)_2Rh[Me_2NC(S)NC(S)NMe_2]$ (IA). Addition of 0.4 mmol of I-H to a stirred solution of 0.4 mmol $RhCl(PPh_3)_3$ in 10 ml of benzene * resulted in an orange solution and some orange precipitate. After 30 min a small excess of Et_3N was added to give a red solution. Stirring was continued for 15 min and the precipitate of Et_3NHCl was filtered off. Dilution with n-hexane and cooling gave orange-red crystals of IA. $\tau(NMe_2)(CD_2Cl_2)$ 7.00(12)s ppm **. By analogous procedures the following complexes were obtained:

$(Ph_3P)_2Rh[PhNC(S)NMe_2] \cdot C_6H_6$ (IIIA). The red-orange solution from $RhCl(PPh_3)_3$ and III-H changed to orange upon addition of Et_3N and orange crystals of IIIA were isolated. $\tau(NMe_2)(CD_2Cl_2)$ 7.48(6)s ppm. The presence of C_6H_6 was confirmed by the ^1H NMR spectrum.

$(Ph_3P)_2Rh[Ph_2PC(S)NPh]$ (VA). The initial bright-red solution changed to orange-yellow upon addition of Et_3N, and orange-yellow crystals of VA were isolated.

$(Ph_3P)_2Rh[Ph_2P(O)C(S)NPh]$ (VIA). The initial dark-red solution changed to intense bright-red upon addition of Et_3N. VIA was obtained as red crystals.

B. Substitution of Cl and Ph_3P.

$(Ph_3P)_2Rh[SC(S)NMe_2]$ (IIA). The complex was prepared by a modification of a literature procedure [1]. 0.4 mmol of II was added to a stirred solution of $RhCl(PPh_3)_3$ in 20 ml of acetone for 45 min. The spontaneously formed orange precipitate was washed with water (removal of NaCl), ethanol and n-hexane. Prepared in this way the complex was analytically pure and needed not to be chromatographed as reported by O'Connor et al. [1]. $\tau(NMe_2)(CD_2Cl_2)$ 6.90(6) s ppm.

$(Ph_3P)_2Rh[Ph_2PC(S)S]$ (IVA). 0.4 mmol of IV was stirred with 0.4 mmol $RhCl(PPh_3)_3$ in 15 ml of dry acetone during 15 h. The resulting brick-red precipitate of IVA was washed with water, ethanol and n-hexane.

All the complexes IA—VIA are moderately air-sensitive in the solid state and very air-sensitive in solution.

Synthesis of the complexes $(CO)(Ph_3P)Rh(L—L')$

A. Oxidative addition of N—H bond.

$(CO)(Ph_3P)Rh[Me_2NC(S)NC(S)NMe_2]$ (IB). 0.2 mmol of I-H was added to a stirred solution of 0.2 mmol $RhCl(CO)(PPh_3)_2$ in 10 ml of benzene. After 30 min, addition of a small excess of Et_3N resulted in the precipitation of Et_3NHCl. Filtration, dilution with n-hexane and cooling gave orange-yellow crystals of IB. $\tau(NMe_2)(CD_2Cl_2)$ 6.87(12) s(br) ppm.

$(CO)(Ph_3P)Rh[Ph_2PC(S)NPh]$ (VB) and $(CO)(Ph_3P)Rh[Ph_2P(O)C(S)NPh]$ (VIB). These complexes were prepared similarly. $RhCl(CO)(PPh_3)_2$ failed to react with III-H in benzene in the presence of Et_3N, even under reflux.

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[*] At the concentrations shown not all the $RhCl(PPh_3)_3$ immediately dissolved.

[**] Number of protons (from intensity ratio to Ph-resonances) between parenthesis; s, singlet; br, broad.

B. Substitution of Ph_3P by CO

$(CO)(Ph_3P)Rh[Me_2NC(S)NC(S)NMe_2]$ (IB). CO was passed through a solution of 0.2 mmol of IA in 10 ml of benzene. The solution turned orange-yellow in a few seconds. Dilution with n-hexane and cooling gave orange crystals of IB. $\tau(NMe_2)(CD_2Cl_2)$ 6.87(12) s(br) ppm.

In an analogous procedure $(CO)(Ph_3P)Rh[PhNC(S)NMe_2] \cdot C_6H_6$ (IIIB) $\tau(NMe_2)(CD_2Cl_2)$ 7.27(6) s ppm, $(CO)(Ph_3P)Rh[Sh_2PC(S)S]$ (IVB), $(CO)(Ph_3P)Rh[Ph_2PC(S)NPh]$ (VB) and $(CO)(Ph_3P)Rh[Ph_2P(O)C(S)NPh]$ (VIB) were prepared. IIIB is very soluble in benzene and difficult to precipitate and. The presence of C_6H_6 in IIIB was confirmed by ^1H NMR.

$(CO)(Ph_3P)Rh[SC(S)NMe_2] \cdot$ acetone (IIB). 0.4 mmol of II and 0.4 mmol $RhCl(PPh_3)_3$ were stirred in acetone. After 30 min NaCl was filtered off. On stirring for another 10 min an orange precipitate of $(Ph_3P)_2Rh[SC(S)NMe_2]$ appeared. On passing CO through the solution it turned from orange to yellow and the $(Ph_3P)_2Rh[SC(S)NMe_2]$ redissolved. Concentration of the solution and addition of n-hexane gave a yellow precipitate of IIB. $\tau(NMe_2)(CD_2Cl_2)$ 6.70(3)s, 6.86(3)s ppm. The presence of acetone was confirmed by ^1H NMR. (O'Connor et al. [1] reported a brown colour for this complex.)

The complexes IB—VIB are stable in the air for days as solids, and no air-sensitivity was found for the solutions.

Synthesis of the complexes $H(Ph_3P)Pt(L—L')$

$H(Ph_3P)Pt[Me_2NC(S)NC(S)NMe_2]$ (VII). 0.2 mmol $Pt(PPh_3)_4$ and 0.2 mmol of I-H were stirred in 20 ml of benzene for 24 h. Addition of n-hexane to the pale-yellow solution resulted in a pale-yellow precipitate of VII. $\tau(NMe_2)(CD_2Cl_2)$ 6.68(6) s(br) and 6.84(6) s ppm.

$H(Ph_3P)Pt[Ph_2PC(S)NPh]$ (VIII) was prepared similarly.

Under the same conditions $Pt(PPh_3)_4$ did not react with III-H.

Results and discussion

A. Synthetic routes; breaking of the N—H bond

Schemes 1—3 summarize the synthetic routes used for the rhodium(I) complexes. In the reaction of I-H, III-H, V-H and VI-H with $RhCl(PPh_3)_3$ formal oxidative addition of the N—H bond to rhodium(I) takes place. The initial change of colour upon interaction with the N—H containing molecules can be ascribed to the formation of a hydridochlororhodium(III) complex, which undergoes reductive elimination of HCl upon addition of Et_3N. When no Et_3N was present in the reaction of I-H with $RhCl(PPh_3)_3$ a mixture of products was isolated which displayed an absorption in the IR at 2132 cm^{-1} (CsJ), probably ν(Rh—H). We did not attempt to isolate the intermediates for III-H, V-H and VI-H.

Whereas $RhCl(PPh_3)_3$ reacts with all the molecules containing N—H bonds, $RhCl(CO)(PPh_3)_2$ reacts with I-H, V-H and VI-H, but not with III-H. Similarly $Pt(PPh_3)_4$ reacts with I-H and V-H and not with III-H *. If HCl is passed through a solution of $(CO)(PPh_3)Rh(L—L')$ with L—L' being I, III or V in the presence

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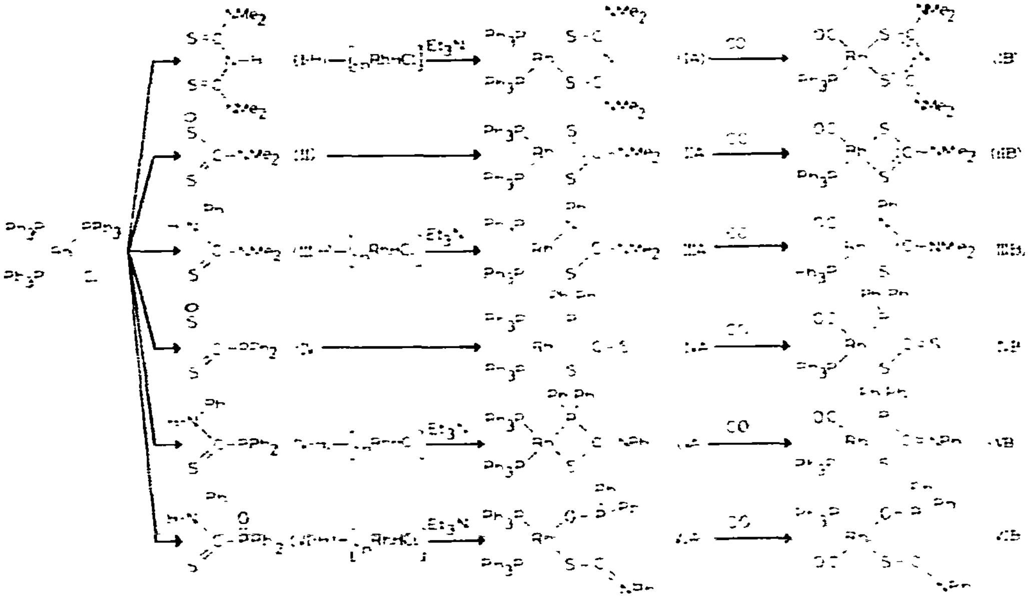
* The reaction of VI-H with $Pt(PPh_3)_4$ has not yet been investigated.

SCHEME 1. Synthesis and structures of the rhodium(I) complexes from $RhCl(PPh_3)_3$.

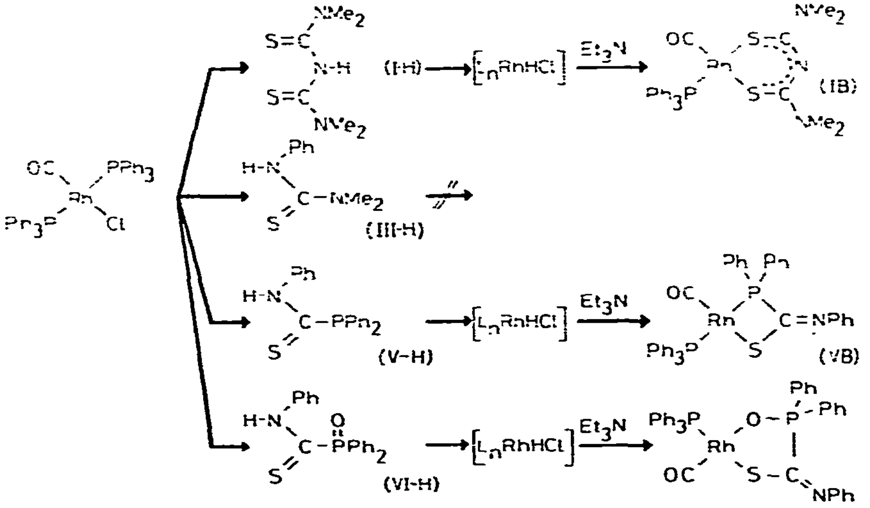


of one equivalent of PPh_3, $RhCl(CO)(PPh_3)_2$ (characterised by IR) is precipitated immediately. This suggests a rapid equilibrium, as represented by eq. 1.

$$\begin{array}{ccccc} RhCl(CO)(PPh_3)_2 & & (CO)(Ph_3P)_nRhHCl(L{-}L') & & (CO)(Ph_3P)Rh(L{-}L') \\ + & \rightleftharpoons & + & \rightleftharpoons & \\ L{-}L'{-}H & & (2-n)PPh_3 & & +\ HCl + PPh_3 \\ (L{-}L' = I, III \text{ or } V) & & (n = 1 \text{ or } 2) & & \end{array} \quad (1)$$

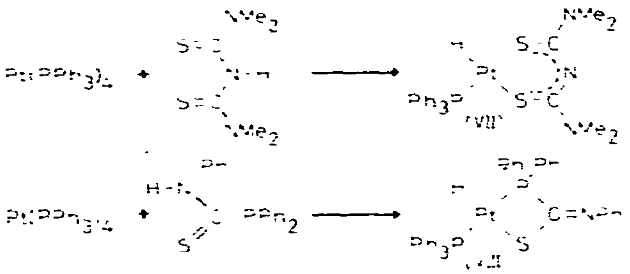
It seems that interaction of III-H with $RhCl(CO)(PPh_3)_2$ does not give the intermediate hydridochlororhodium(III) complex.

SCHEME 2. Synthesis and structures of the rhodium(I) complexes from $RhCl(CO)(PPh_3)_2$.



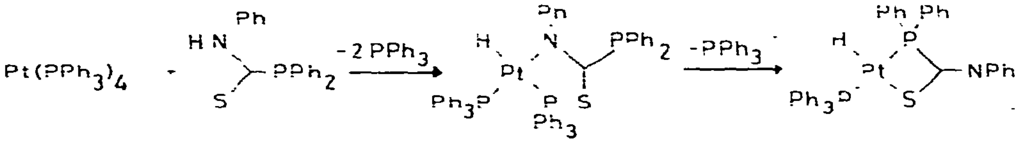
Further support for the idea of intermediate formation of $A(Ph_3P)_nRhHCl(L—L')$ ($A = CO, Ph_3P$) is found in the reactions of $Pt(PPh_3)_4$ with I-H and V-H to give the hydridoplatinum(II) complexes VII and VIII (Scheme 3). In both

SCHEME 3. Synthesis and structures of the platinum(II) complexes.



reactions the reaction mechanism must be rather complicated, because after the initial oxidative addition of the N—H bond, substitution of PPh_3 and rearrangement to S,S-coordination for VII and (P,S) coordination for VIII, must occur, as visualised for VIII (Scheme 4).

SCHEME 4. Formation of $H(Ph_3P)Pt[Ph_2PC(S)NPh]$ (possible reaction scheme).



Other examples of oxidative addition of N—H bonds to platinum(0) and palladium(0) have been reported. Oxidative addition of cyclic imides such as succinimide to $Pt(PPh_3)_4$ gave *trans*-$(Ph_3P)_2PtH$ (succinimido) [9]. However with $Pd(PPh_3)_4$, *trans*-$(Ph_3P)_2Pd$ (succinimido)$_2$ was obtained [9]. *Cis*- and *trans*-$(Ph_3P)_2M(ArNNNAr)_2$ (M = Pt and Pd) with monodentate triazenido groups are formed in the reaction of HN(Ar)NNAr with $M(PPh_3)_4$ [10,11]. These differences demonstrate the subtlety of the factors governing product formation. Oxidative addition of N—H bonds to rhodium is less well documented. The reaction of $RhCl(PPh_3)_3$ with HN(Ar)NNAr is reported to give $(Ph_3P)RhCl(ArNNNAr)_2$ [11]. In our case we did not detect any bis-complexes $(Ph_3P)RhCl(L—L')_2$.

B. Spectra and structures of rhodium complexes

IR spectra

The assigned chelate frequencies in the IR of CH_2Cl_2 solutions between 2000 and 700 cm^{-1} are shown in Tables 2A and 2B. We assign the intense absorption at ~1505 cm^{-1} in Ia, B to $\nu(C{\doteq}NMe_2)$. A number of complexes $M^{II}[Me_2NC(S)NC(S)NMe_2]_2$ have been reported recently [12] but no IR absorptions were given. The chelate absorptions assigned for IIA, B and IVA, B are as expected for S,S-coordinated $S_2CNMe_2^-$ [13—15] and S,NPh-coordinated $PhNC(S)NMe_2^-$ [13,16]. The two chelate absorptions assigned for IVA, B nearly coincide with

(continued on p. 366)

TABLE 2A

INFRARED ABSORPTIONS AND ASSIGNMENTS OF $A(Ph_3P)Rh(L-L')$ WITH A = CO, Ph_3P; COMPARISON WITH $[(Ph_3P)_2Pt(L-L')]^+$ (2000—700 cm^{-1} in CH_2Cl_2; NaCl-cells)

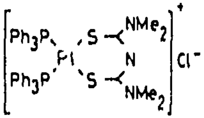
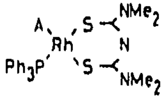
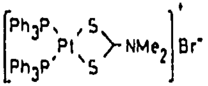
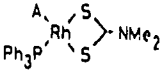
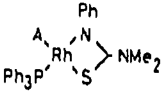
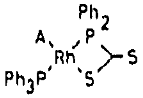
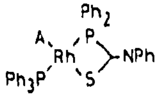
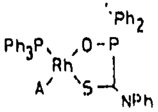
Complex	No.	A	$\nu(CO)$ [a]	Chelate absorptions									
				$\nu(C\equiv E)$ [a, b]		N–Ph	N–Me	N–Me		N–Me			
	d			1526vs	$\nu(C\equiv NMe_2)$		1400vw	1376s	1318s	1129s	912vw(br)		
	IB	CO	1976vs	1512vs	$\nu(C\equiv NMe_2)$		1396vw	1367s	1316s	1123s	915w		
	IA	Ph_3P		1499vs	$\nu(C\equiv NMe_2)$		1392vw	1358s	1318s	1127s	916w		
	d			1570vs [c]	$\nu(C\equiv NMe_2)$			1402s [c]	1234w [c]	1161m [c]	960w [c]		
	IIB	CO	1973vs	1538vs	$\nu(C\equiv NMe_2)$			1400s	1251m [c]	1152m	970m		
	IIA	Ph_3P		1525vs	$\nu(C\equiv NMe_2)$			1396s	1258m [c]	1146s	970m		
	IIIB	CO	1970vs	1549vs	$\nu(C\equiv NMe_2)$	1601m	1422(sh)	1364s	1205m	1108m	952w	847w	787w
	IIIA	Ph_3P		1537vs	$\nu(C\equiv NMe_2)$	1603m	1418(sh)	1357s	1201m	1109m	952w	840w	787w

TABLE 2B

Complex	No.	A	ν(CO)^a	Chelate absorptions				
				ν(C=E)^{a,b}		ν(P=O)	ν(PCS)	N—Ph
	IVB	CO	1984vs	1094vs	ν(C=S)		842m	
	IVA	Ph_3P		1082vs	ν(C=S)		847m	
	VB	CO	1975vs	1572vs	ν(C=N)		930m	803w
	VA	Ph_3P		1556vs	ν(C=N)		934m	802w
	VIB	CO	1980vs	1533s	ν(C=N)	1130s	968m	802m
	VIA	Ph_3P		1511s	ν(C=N)	1135s	968m	802w

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[a] ν(CE) and ν(CO) have been determined to ± 1 cm^{-1} by expanding the IR spectrum. [b] ν(C=E) is normal mode with stretching of exocyclic double bond as the main component; ν(C=E) is the same for the exocyclic partial double bond. [c] In CsI. [d] Synthesis of these complexes to be published.

TABLE 3

CHARACTERISTIC ABSORPTIONS FOR P,S-COORDINATION OF Ph_2PCS_2

Complex	Reference	Coordination mode	ν(C=S)	ν(PCS)	ν_{as}-(CS_2)	ν_s(CS_2)	Solvent
$(Ph_3P)_2Rh[Ph_2PC(S)S]$		P,S	1082vs	847m			CH_2Cl_2
$(CO)(Ph_3P)Rh[Ph_2PC(S)S]$		P,S	1094vs	842m			CH_2Cl_2
$Ni[Ph_2PC(S)S]_2$	17	P,S	1091vs	830s			KBr
$Mn[SC(S)PPh_2]_2 \cdot EtOH$	18	S,S			981s	891m	KBr
$KSC(S)PPh_2 \cdot$ dioxane		—			1000vs	853m	KBr

ν(C=S) and ν(PCS_2) for P,S-coordinated $S_2CPPh_2^-$ in $Ni[Ph_2PC(S)S]_2$ [17]. They are clearly different from the two absorptions of S,S-coordinated $S_2CPPh_2^-$ in $Mn[SC(S)PPh_2]$ · EtOH assigned as $\nu_{as}(CS_2)$ and $\nu_s(CS_2)$ [18]. This confirms P,S-coordination in IVA, B (Table 3).

Analogous to IVA, B we assign in VA, B the absorptions at ~1560 and ~930 cm^{-1} to ν(C=N) and ν(PCS) respectively. In support of our assignment, ν(C=S) and ν_{as}(SCS) in $Pt(S_2CS)_2^{2-}$ [42] are close to ν(C=S) and ν(PCS) in $Pt[Ph_2PC(S)S]_2$ [17] and the rhodium(I) complexes IVA, B. Similarly $\nu(CS_2)$ and ν(C=N) reported for $(Ph_3P)_2Pt(S_2CNPh)$ [43] are very close to ν(PCS) and ν(C=N) in VA, B.

The normal coordinate analyses of $Ni(S_2CS)_2^{2-}$ [19], $Ni(S_2C{=}N{-}CN)_2$ [20], $Ni(S_2CNMe_2)_2$ [14] and $Pt(S_2COMe)_2$ [21] demonstrate that although the ring vibrations ν(LCL′) (L and L′ are coordinating atoms) in four-membered unsaturated chelate rings sometimes couple strongly with other vibrations, a strong absorption can generally be assigned to a normal mode with ν(C=E) or ν(C$\overset{...}{=}$E) as the main component. (CE is the exocyclic double or partial double bond). Changes in ν(CE) reflect changes in CE bond order, and are informative about bonding. Table 2A, B shows that ν(CE) for the four-membered rings in IIA—VA as well as the five-membered ring in VIA and the six-membered ring in Ia, is raised by 10—20 cm^{-1} upon substitution of Ph_3P by CO and that ν(CE) is more sensitive than the other vibrations. A more pronounced increase in ν(CE) (~30 cm^{-1}) is observed for the change in the central metal in IA and IIA. Both shifts can be accounted for by the simple valence bond formalism as shown by the resonance structures for VA (Fig. 1). Lowering the π-electron density on the metal centre ($Ph_3P \rightarrow CO$) or raising its oxidation state (Rh^I, $d^8 \rightarrow Pt^{II}$, d^8) raises the relative importance of resonance structure 2.

In VI-H a strong vibration at 1184 cm^{-1} has been assigned to ν(P=O) [5]. The decrease in ν(P=O) of about 50 cm^{-1} found in VIA, B indicates coordination via the phosphinyl oxygen ($O{=}PPh_2$).

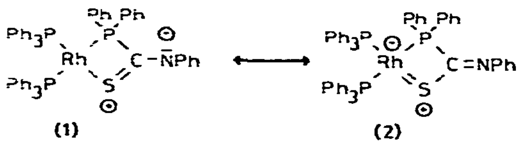


Fig. 1. Resonance structures for $(Ph_3P)_2Rh[Ph_2PC(S)NPh]$ (VA).

ν(CO) in IIB is different from the value of 1920 cm^{-1} assigned before to the same complex by O'Connor [1]. The values of ν(CO) in IB and IIB are comparable to those found in (CO)(Ph$_3$P)Rh(S$_2$PR$_2$) (R = OPh, ν(CO) = 1980 cm^{-1}; R = Cy, ν(CO) = 1972 cm^{-1}) [22].

^{31}*P NMR spectra*

Assignment. Table 4 summarizes the ^{31}P{^{1}H} NMR parameters. In this table the first order parameters are given except where two magnetically inequivalent P atoms are *trans* to each other and in case of VIB where the difference in chemical shift between both P atoms is very small (for details see footnotes to Table 4).

The view that *cis*-influences on the values of δ and ^1J(M—P) are smaller than *trans*-influences is supported by our results [23,24]. In IA and IIA both Ph$_3$P groups are equivalent and coupling with ^{103}Rh (100% abundance; I = 1/2) results in a doublet. The effect of ring size on ^1J(Rh—P) and δ for IA, IIA and IB, IIB is relatively small.

In the spectrum of Va (Fig. 2) the Ph$_3$P group and the Ph$_2$P group *trans* to it show a *trans*-coupling ^2J(P$_1$—P$_3$) of 330 Hz. In VB the *trans*-coupling (^2J(P$_1$—P$_2$) 332 Hz) is still observed, so in Va CO replaced Ph$_3$P *trans* to S(P$_2$). The spectrum of (Ph$_3$P)$_2$Rh[Ph$_2$PC(S)S] in CD$_2$Cl$_2$ reveals the presence of several species, including IVA, for which the absorptions were assigned by comparison with VA. The presence of the other unidentified species probably

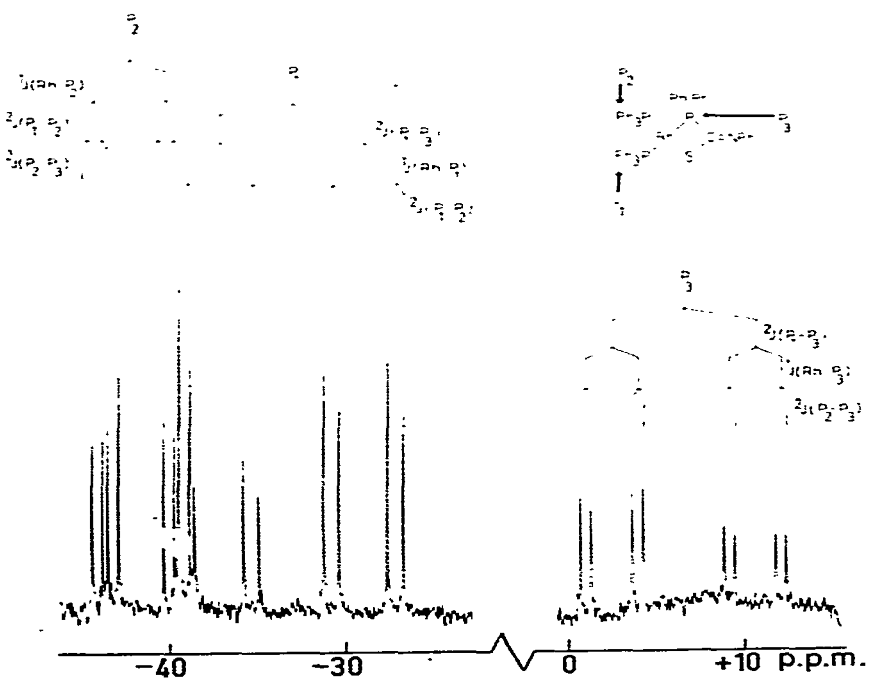
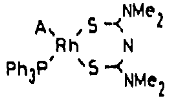
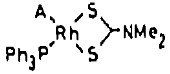
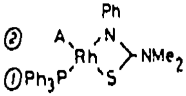
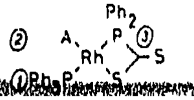


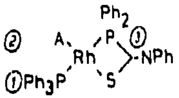
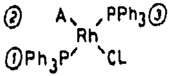
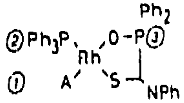
Fig. 2. ^{31}P{^{1}H} NMR spectrum of (Ph$_3$P)$_2$Rh[Ph$_2$PC(S)NPh] (VA) in CD$_2$Cl$_2$.

(continued on p. 370)

TABLE 4

^{31}P{^{1}H} NMR PARAMETERS[g] OF A(Ph$_3$P)Rh(L—L') WITH A = Ph$_3$P OR CO IN CD$_2$Cl$_2$ [a] (δ (ppm) relative to O=P(OMe)$_3$(TMP) internal reference; upfield = +; J (Hz))

Complex	No.	A	Ph$_3$P P-*trans* δ	 ^1J(Rh—P)	 S-*trans* δ	 ^1J(Rh—P)	 N,Cl,O-*trans* δ	 ^1J(Rh—P)	—PPh$_2$ δ	 ^1J(Rh—P)	^nJ(P$_i$—P$_j$)	Assignment
	IA IB	Ph$_3$P CO			−41.4 −36.5	170 151						
	IIA IIB	Ph$_3$P CO			−41.3 −40.3	177 158						
	IIIA IIIB	Ph$_3$P CO			−41.3	182	−55.8 −46.0	182 156			47	^2J(P(1)—P(2))*cis*
	IVA	Ph$_3$P [b]	−31.7	147	−41.1	165			+3.4(PPh$_2$)	117	34 24 315	^2J(P(1)—P(2))*cis* ^2J(P(2)—P(3))*cis* ^2J(P(1)—P(3))*trans*
	IVB	CO	−30.3	[f]					+8.4(PPh$_2$)	99	[f]	^2J(P(1)—P(3))*trans*

	VA	Ph_3P [b]	−32,6	148	−41,5	164			+6,0(PPh_2)	119	35 24 330	^2J(P(1)—P(2))*cis* ^2J(P(3)—P(3))*cis* ^2J(P(1)—P(3))*trans*
	VB	CO [c]	−31,2	136					+7,8(PPh_2)	102	332	^2J(P(1)—P(3))*trans*
		Ph_3P	−29,2	143			−45,9	196			38	^2J(P(1)—P(2))*cis*
		CO	−26,6	127								
	VIA	Ph_3P			−40,9	170	−54,8	202	−28,6($OPPh_2$)	3(^2J(Rh—P))	47 18	^2J(P(1)—P(2))*cis* ^3J(P(2)—P(3)))
	VIB	CO [d]			−36,6	152			−33,1($OPPh_2$)	4(^2J(Rh—P))	17	^3J(P(2)—P(3))
$K^+SC(S)PPh_2^-$									−40,2(PPh_2) [e]			
$HN(Ph)C(S)PPh_2$									−17,3(PPh_2)			
$HN(Ph)C(S)P(O)Ph_2$									−18,8($OPPh_2$)			

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[a] δ (TMP, int. ref.) − δ (85% H_3PO_4, ext. ref.) = +2,3 ppm. [b] Values of J and δ resulting from ABMX-analyses (X = Rh): J_{AX}, J_{BX} and J_{MX} have been given the same sign. [c] Values of J and δ resulting from ABX-analyses. J_{AX} and J_{BX} have been given the same sign. [d] ABX-analyses: best fit with observed intensities and most reasonable value of $^2J(Rh{-}P_3)$, comparable with $^2J(Rh{-}P_3)$ in VIA, when J_{AX} and J_{BX} were given the same sign. [e] Obtained from ref. 17: δ −42,5 (85% H_3PO_4, ext. ref.) in acetone. [f] Not observed due to line broadening. [g] Estimated accuracy in J: ±1 Hz. Estimated accuracy in δ: ±0,2 ppm.

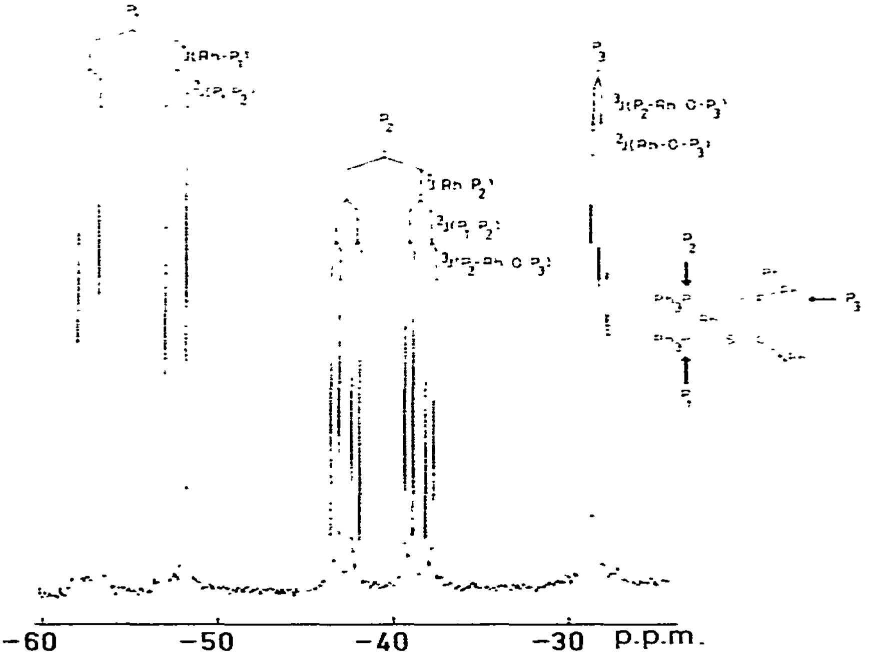


Fig. 3. $^{31}P\{^1H\}$ NMR spectrum of $(Ph_3P)_2Rh[Ph_2P(O)C(S)NPh]$ (VIA) in CD_2Cl_2.

explains the low molecular weight observed in CH_2Cl_2 (Table 1). Although the chemical shift values of IVB are in good agreement with those of VB the lines are broadened and no *trans*-coupling is observed.

VIA (Fig. 3) shows a $^2J(Rh-O-P_3)$ and a $^3J(P_2-Rh-O-P_3)$ coupling. No couplings of this type have been reported before. They are in accord with coordination via the O atom of the phosphinyl group. The values of δ −54.8 ppm and $^1J(Rh-P)$ 202 Hz are assigned to Ph_3P *trans* to O, in agreement with assignments made for $(Ph_3P)_2RhO_2CORh(PPh_3)_3$ [25]. For this P-atom (P(1)) no $^3J(P-Rh-O-P_3)$ is observed. The preservation of $^3J(P_2-Rh-O-P_3)$ in VIB suggests that in VIA P(1) *trans* to O is substituted by CO.

cis-Influence of Ph_3P and CO. For all P atoms coordinated to rhodium(I) an upfield shift and a decrease in $^1J(Rh-P)$ is observed upon replacement of Ph_3P by CO: a *cis*-influence. The magnitude of the changes in $\delta(\Delta\delta)$ and $^1J(Rh-P)$ (ΔJ) seems almost exclusively dependent on the nature of the *trans*-atom. For (IA, B), (IIA, B) and (VIA, B) with *P trans* to S $\Delta\delta \sim +5.3$ ppm and $\Delta J \sim -19$ Hz are found (Table 4). $\Delta\delta$ (+1.4 ppm) and ΔJ (−12 Hz) for VA, B suggest the difference in *cis*-influence between Ph_3P and CO to be smaller when P is *trans* than when S is *trans*. If the upfield shift upon replacement of *cis*-Ph_3P by CO is general the Ph_3P group at δ −46.0 ppm in IIIB must correspond with that at δ −55.8 ppm in IIIA. The observed $\Delta\delta$ (+9.8 ppm) and ΔJ (−26 Hz) are clearly different from those observed for Ph_3P *trans* to S. So we conclude that CO replaces Ph_3P *trans to* S in IIIA. A value of $\Delta\delta$ and ΔJ for P trans to O can be obtained by comparing $(Ph_3P)_2RhO_2CORh(PPh_3)_3$ [25] and $RhCO(acac)PPh_3$

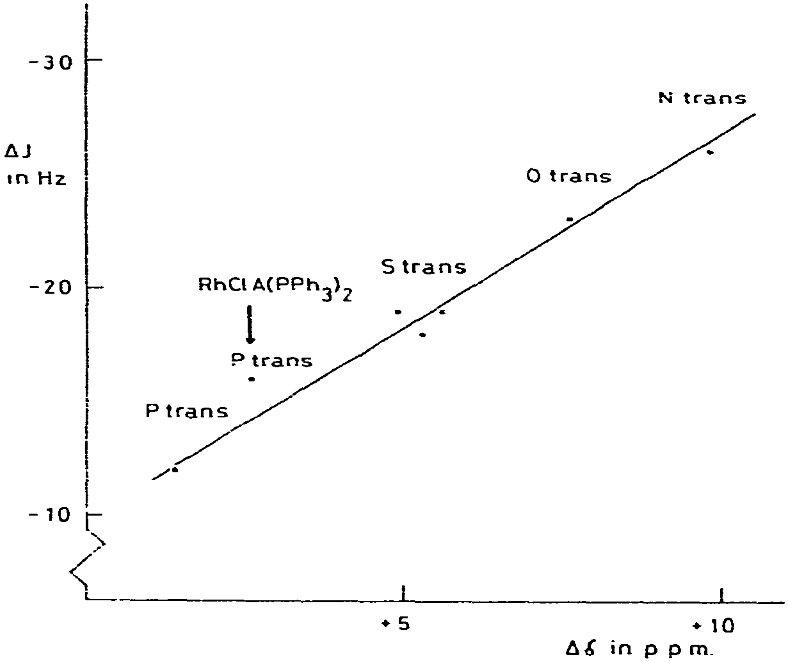


Fig. 4. The difference in *cis*-influence between CO and PPh$_3$ on ^1J(Rh—P) and δ (ppm) in square planar A(Ph$_3$P)Rh(L—L′) (A = CO, Ph$_3$P) as modified by the *trans*-atom. P *trans* (VA, B); S *trans* (IA, B), (IIA, B), (VIA, B); N *trans* (IIIA, B); O *trans*: see text.

[26] (Δδ +7.6 ppm; Δ*J* −23 Hz). As shown in Fig. 4 the relation between Δδ and Δ*J* is roughly linear. The non-chelate complexes RhClA(PPh$_3$)$_2$ (A = PPh$_3$ or CO) have been included. Although there is no obvious interpretation of the effect, it can be used in structural assignment, as above.

trans-Influence on ^1J(Rh—P). On comparing ^1J(Rh—P) within one bis-phosphine complex (Ph$_3$P)$_2$Rh(L—L′) with L ≠ L′ an order of increasing *trans*-influence on ^1J(Rh—P) can be obtained from Table 4: O < NPh, S < PPh$_2$. The small differences between IA, B and IIA, B and between RhCl(PPh$_3$)$_3$ and (Ph$_3$P)$_2$Rh-[Ph$_2$PC(S)NPh] suggest the effect of ring-size and ring-strain to be small, so comparison with non-chelate rhodium(I) complexes seems meaningfull. By comparing ^1J(Rh—P) in complexes in which only the atom *trans* to Ph$_3$P has been changed, a more complete *trans*-influence series is obtained: O, Cl, Br, I < NPh, S < CO, PPh$_2$, PPh$_3$. For this series in addition to the values in Table 4 also the values of ^1J(Rh—P) in RhX(PPh$_3$)$_3$ (X = Cl, Br, I) [28], Rh(CO)$_2$Cl(PPh$_3$), Rh(CO)(acac)(PPh$_3$) [26] and (Ph$_3$P)$_2$RhO$_2$CORh(PPh$_3$)$_3$ [25] have been used. The sequence found is in accordance with that for square planar platinum(II) complexes [27].

The generally accepted view is that ^1J(M—P) arises almost entirely from the Fermi-contact interaction [23,27] and the change in the total MO bond order between the *s*-orbitals on the coupled atoms $P'(s_M s_P)$ is mainly responsible for the changes in ^1J(M—P) induced by various *trans*-ligands [23,29]. Using a localised MO description, an increase in $P'(s_M s_P)$ can arise from an increase in the s-character of the metal hybride orbital as well as increasing covalency in the M—P σ-bond [27,29]. Both have been shown to give a stronger bond [30], so the magnitude of ^1J(Rh—P) can be used as a measure of the strength of the Rh—P bond. In IIIA the equal value of ^1J(Rh—P) for P *trans* to S and NPh probably indicates a very similar demand for the Rh hybride σ-orbital by both donor atoms.

Chemical shift ^1J(Rh—P) for PPh_2. The PPh_2 group in IV and V-H undergoes a remarkable upfield shift upon coordination (Table 4). Generally in alkyl- and aryl-phosphine-rhodium(I) and -rhodium(III) complexes a downfield coordination shift is observed [23, 31]. The upfield coordination shift in the four-membered Rh—P—C—S ring is probably related to the effect reported recently by Garrou [32], who showed that a P atom in a four-membered chelate ring is shifted upfield (+12 to +80 ppm, positive ring contribution) relative to a comparable P-atom not incorporated into a four-membered ring.

The ring-strain in IVA and VA, as evidenced by the crystal structure of $Ni(Cy_2PC(S)S]_2$ [34,35], results in a considerable smaller value of ^1J(Rh—P) for PPh_2 then for PPh_3 *trans* to it. A similar lowering of ^1J(M—P) is found in the four-membered rings in *trans*-$PtCl[P(t\text{-}Bu)_2Ph][OC_6H_4P(t\text{-}Bu)_2]$ [32] and *cis*-$Pt(Ph)_2(Ph_2PCH_2PPh_2)$ [33].

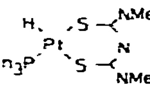
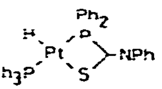
C. Spectra and structures of the platinum(II) complexes

Table 5 summarizes the IR and ^1H NMR parameters obtained for VII and VIII The values of ν(Pt—H), τ(Pt—H) and ^1J(Pt—H) of VIII are in accord with those observed for *trans*-$(Ph_3P)_2PtH(SC_6H_4Y)$ [36] (Y = a *para*-substituent) and *trans*-$(Ph_3P)_2Pt(H)[SC(O)CH_3]$ [37]. For H *trans* to PPh_3 in VIII both ν(Pt—H) and ^1J(Pt—H) are expected to be lower because of the higher *trans*-influence of Ph_3P compared to S [27]. In VII and VIII the assigned chelate absorptions in the IR are virtually the same as in the rhodium(I) complexes.

TABLE 5

SPECTRAL PARAMETERS OF THE Pt(II) COMPLEXES

I.R. frequencies in cm^{-1}, δ in ppm rel. to TMS, J in Hz.

Complex	No.	IR			^1H NMR (CD_2Cl_2)	
		Assignment	CsJ	CH_2Cl_2	τ(Pt—H) (ppm)	^1J(Pt—H) (Hz)
	VII	ν(Pt—H)	2142m	2110(br)	+20.7	1081 [a]
		δ(Pt—H)	838m	825(br)		
		ν(C⎓NMe₂)	1511vs	1518vs		
	VIII	ν(Pt—H)	2106s	2100(br)	+20.0	1152 [b]
		δ(Pt—H)	789m	[c]		
		ν(C=N)	1564vs	1568vs		
		ν(PCS)	927m	930m		

[a] $^2J(P\text{—}H)_{cis}$ 19 Hz. [b] $^2J(P\text{—}H)_{cis}$ not observed due to line-braodening. [c] Not observed.

D. Comparison of structures

For the complexes IA—VA, on reaction with CO, substitution of PPh_3 *trans* to S takes place, whereas in VIA Ph_3P *trans* to O is substituted. The very fast replacement of Ph_3P by CO in $(Ph_3P)_2Rh(L—L')$ and the observation of only one isomer for all complexes $(CO)(Ph_3P)Rh(L—L')$ suggests the isomers found to be the thermodynamically most stable. In IIIB, IVB, VB as well as $RhCl(CO)(PPh_3)_2$, where CO can choose between two different *trans*-atoms, the configuration with the least steric hindrance and with the atom or group with the lowest *trans*-influence (as determined from $^1J(Rh—P)$) in the *trans*-position is obtained. In VIB, in which no bulky substituent is present on one of the donor atoms (L,L'), CO is also found *trans* to the donor atom with the lowest *trans*-influence. So generally the configuration found is that in which the strongest σ-bond between rhodium(I) and CO can be formed. In IIIB where the *trans*-influences of both donor atoms (NPh,S) are comparable, minimalisation of steric hindrance could be decisive for the position of CO.

In VIII the configuration with the lowest steric hindrance and H *trans* to the atom with the lowest *trans*-influence is again found. The observed *trans*-position of both P-atoms is the same as in *trans*-$(Ph_3P)_2PtH(A)$, which results from oxidative addition of the weak acid HA to $Pt(PPh_3)_n$ ($n = 3, 4$) [36—38, 40].

In VIA,B no S,NPh-coordination is observed as in IIIA, B, and there is an unusual coordination via the oxygen of a phosphine oxide group stabilised by the chelate effect. The only well characterised R_3PO complex of rhodium(I) reported previously was *cis*-$RhCl(CO)_2(OPCy_3)$ [39].

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