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Interaction of $Ph_2PC(S)NHR$ (R = Ph, Me) with $[Rh(CO)_2Cl]_2$. Modes of Coordination of $Ph_2PC(S)NHR$ and $[Ph_2PC(S)NR]^-$

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Upon reaction with $[Rh(CO)_2Cl]_2$, $Ph_2PC(S)NHR$ (R = Ph, Me) displaces one CO molecule and coordinates to the metal end-on (η^1) via P. All the complexes containing the protonated ligand rapidly eliminate HCl in the presence of a base. Generally, bidentate coordination via P and S is observed for the resulting deprotonated ligand. By loss of HCl coordinative unsaturation is generated. In some cases this results in the involvement of all three hetero atoms (P, S and N) in the coordination, as found in $\{Rh(CO)[Ph_2C(S)NR]\}_4$. The binuclear complex $\{Rh(\mu Cl)H(CO)[Ph_2PC(S)NHR]\}$ $\{Rh(\mu Cl)(CO)[Ph_2PC(S)NR]\}$ occurs in the tautomeric form, in which both metal centres possess the formal oxidation state II and exhibit a metal–metal interaction. The rhodiumhydride complex $RhH(CO)[Ph_2PC(S)NPh]_2$, which results from intramolecular oxidative addition in $Rh(CO)[Ph_2PC(S)NHPh][Ph_2PC(S)NPh]$ has been isolated.

The nitrogen analogue $Me_2NC(S)NHPh$ only reacts with $[Rh(CO)_2Cl]_2$ under basic conditions to yield $Rh(CO)_2[Me_2NC(S)NPh]$.

Introduction

$Ph_2PC(S)NHR$ is known to coordinate end-on (η^1) through P to Mo(II) [1]. As the functional group $-C(S)NHR$ does not take part in the coordination, the ligand behaves like an ordinary phosphine ligand.

Bidentate coordination through P and S is generally found to occur in Rh(I) phosphine complexes of the deprotonated $[Ph_2PC(S)NR]^-$; thus a stabilising chelate ring is formed in which the metal is incorporated [2, 3]. $\{Mo(CO)_2[Ph_2PC(S)NR]_2\}_2$ is the only example known so far, having a $[Ph_2PC(S)NR]^-$ ligand, which coordinates via all three hetero atoms [1]. In this paper, another example of a complex, in which both P, S and N in $[Ph_2PC(S)NR]^-$ are bonded to a metal, is presented.

Experimental

IR spectra were measured on a Perkin-Elmer 577 spectrometer (4000–200 cm^{-1}), mainly in KBr disks. ^1H and ^{31}P $\{^1H\}$ NMR spectra were recorded on a Bruker WH 90 spectrometer at 90 MHz and 36.44 MHz, respectively, using the deuterated solvent as internal lock.

Elemental analyses were performed at the element-analytical department of the Institute for Organic Chemistry TNO. Mol. weight determinations were carried out osmometrically by Prof. Dr. Dipl.-Ing. H. Malissa and G. Reuter, Mikroanalytisches Laboratorium, Elbach über Engelskirchen, W. Germany. Analytical data are given in Table I.

Reactions were carried out under nitrogen at room temperature in analytical grade solvents. $[Rh(CO)_2Cl]_2$ was commercially obtained from Strem Chemicals. $Ph_2PC(S)NHPh$ and $Ph_2C(S)NHMe$ were synthesized according to literature procedures [4, 5]. $Me_2NC(S)NHPh$ was prepared by direct addition of Me_2NH to PhN=C=S in diethyl ether.

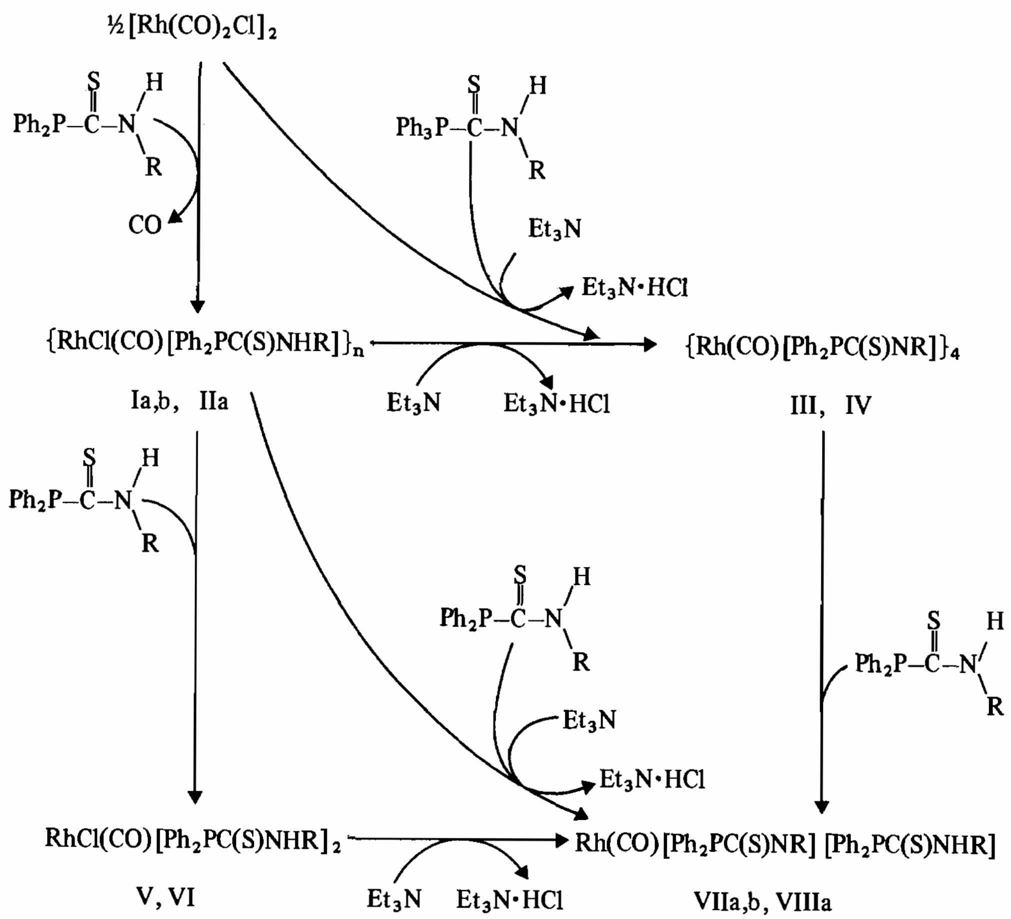
$\{Rh(CO)Cl[Ph_2PC(S)NHR]\}_n$ Ia (R = Ph, n = 2); Ib (R = Ph, n = 4); IIa (R = Me, n = 2)

On addition of 1.0 mmol $Ph_2PC(S)NHR$ to a suspension of 0.5 mmol $[Rh(CO)_2Cl]_2$ in 20 ml toluene, a fast CO evolution was observed. The mixture was stirred during two hours. Upon standing, an orange-brown precipitate (Ia and IIa) was obtained. The precipitate was filtered off, washed with toluene and diethyl ether and dried *in vacuo*. On standing for a longer time black metallic crystals (Ib) were formed. In solution Ia is slowly converted into Ib.

TABLE I. Analytical Data[a] (theoretical values in parentheses).

Code	Compound	Colour	%C	%H	%N	%Cl	%S	Mol. weight	Yield
Ia	$\{RhCl(CO)[Ph_2PC(S)NHPh]\}_2 \cdot 0.6C_7H_8$	orange-brown	51.48	3.71	2.58	6.66		983[b]	90%
			(51.49)	(3.60)	(2.72)	(6.89)		(1030)	
Ib	$\{RhCl(CO)[Ph_2PC(S)NHPh]\}_4 \cdot 0.4C_7H_8$	black	49.59	3.39	2.72	6.89		1400[c]	60%
			(50.00)	(3.41)	(2.82)	(7.28)		(1419)	
IIa	$\{RhCl(CO)[Ph_2PC(S)NMe]\}_2$	orange	42.62	3.28	3.07	8.07	7.17	–	80%
			(42.30)	(3.32)	(3.29)	(8.33)	(7.52)	(851)	
III	$\{Rh(CO)[Ph_2PC(S)NPh]\}_4 \cdot 0.4C_7H_8$	yellow	53.69	3.50	2.80			1250[d]	90%
			(53.98)	(3.46)	(3.04)			(1315)	
IV	$\{Rh(CO)[Ph_2PC(S)NMe]\}_4 \cdot 0.6C_7H_8$	yellow	56.95	4.59	3.32			–	80%
			(57.20)	(4.45)	(3.48)			(1611)	
V	$RhCl(CO)[Ph_2PC(S)NHPh]_2$	yellow	58.12	4.08	3.28	4.26		–	90%
			(57.88)	(3.99)	(3.46)	(4.39)		(809)	
VI	$RhCl(CO)[Ph_2PC(S)NHMe]_2 \cdot 0.05C_7H_8$	yellow	51.08	4.09	3.97	5.10	9.23	–	90%
			(51.11)	(4.15)	(4.06)	(5.15)	(9.29)	(689)	
VIIa	$Rh(CO)[Ph_2PC(S)NPh[Ph_2PC(S)NHPh] \cdot 0.3C_7H_8]$	yellow-orange	61.92	4.36	3.40			–	30%
			(61.68)	(4.21)	(3.50)			(800)	
VIIb	$Rh(CO)(H)[Ph_2PC(S)NPh]_2 \cdot 0.3C_7H_8$	brown-violet	61.53	4.01	3.34			–	60%
			(61.68)	(4.21)	(3.50)			(800)	
VIIIa	$Rh(CO)[Ph_2PC(S)NMe][Ph_2PC(S)NHMe] \cdot 0.1C_7H_8$	yellow-orange	54.13	4.24	4.21		9.58	636[b]	40%
			(54.23)	(4.26)	(4.26)		(9.74)	(657)	
IX	$Rh(CO)_2[Me_2NC(S)NPh]$	red-brown	38.87	3.44	8.12		9.00	–	75%
			(39.05)	(3.28)	(8.28)		(9.47)	(338)	

[a] The presence of C_7H_8 in these complexes was confirmed by ^1H NMR. [b] Determined in toluene. [c] Determined in acetone. Actual value observed: 1987. Value corrected for the presence of solvent: 1987/1.4 = 1419. [d] Determined in THF. Actual value observed: 1841. Value corrected for the presence of solvent: 1841/1.4 = 1315.



Scheme 1. Survey of the reactions of $[Rh(CO)_2Cl]_2$ with $Ph_2PC(S)NHR$ (R = Ph, Me) in the absence or the presence of Et_3N, discussed in this paper.

$\{Rh(CO)[Ph_2PC(S)NR]\}_4$ III (R = Ph); IV (R = Me)

On addition of a small excess of Et_3N to a solution of 0.5 mmol $[Rh(CO)_2Cl]_2$ and 1.0 mmol $Ph_2PC(S)NHR$ in 20 ml toluene, the initially brown-red colour changed to bright yellow. After stirring for two hours, the suspension was diluted with 10 ml n-pentane. The precipitate was filtered off, washed with small portions of 1-propanol to remove the $Et_3N \cdot HCl$ salt, and finally with n-pentane, and dried *in vacuo.*

$RhCl(CO)[Ph_2PC(S)NHR]_2$ V (R = Ph); VI (R = Me)

The reaction mixture, containing 0.5 mmol $[Rh(CO)_2Cl]_2$ and 2.1 mmol $Ph_2PC(S)NHR$ in 20 ml toluene, was stirred for two hours. The suspension was diluted with n-pentane. The yellow precipitate was filtered off, washed with diethyl ether and n-pentane and dried under vacuum.

$Rh(CO)[Ph_2PC(S)NR][Ph_2PC(S)NHR]$ VIIa,b (R = Ph); VIIIa (R = Me)

On addition of a small excess of Et_3N to a suspension of 0.5 mmol $[Rh(CO)_2Cl]_2$ and 2.1 mmol $Ph_2PC(S)NHR$ in 20 ml toluene, the yellow precipitate disappeared very fast to yield an orange suspension. After stirring for two hours and after filtration of $Et_3N \cdot HCl$, n-pentane was added dropwise. Cooling gave an orange-yellow precipitate of VIIa and VIIIa. Upon standing for a longer time the orange colour of the solution changed to brown-red. Precipitation with n-pentane gave a brown-violet solid of VIIb.

$Rh(CO)_2[Me_2NC(S)NPh]$ IX

Addition of 1.1 mmol $Me_2NC(S)NHPh$ to a suspension of 0.5 mmol $[Rh(CO)_2Cl]_2$ in 20 ml toluene showed no reaction. Upon injection of Et_3N no CO evolution was observed; the colour of the solution turned to orange-brown. After dilution with n-pentane, the precipitate was filtered off, washed with diethyl ether and dried *in vacuo.*

Results and Discussion

Scheme 1 summarizes the reactions of $[Rh(CO)_2Cl]_2$ with $Ph_2PC(S)NHR$ in the absence or the

TABLE II. IR Absorptions. Spectra Measured in KBr Pellets. Values in cm^{-1}.

Code	Compound	ν(C≡O)	Ligand absorptions			ν(M–S)	ν(M–Cl)	ν(M–H)	ν(N–H)
			ν(C=N)	ν(P–C–S)	Others				
Ia	$\{RhCl(CO)[Ph_2PC(S)NHPh]\}_2$	2040 s 2015 s	1590 s 1492 s	[a]	1309 m 1263 m	–	250 w–m	–	3275 m
Ib	$\{RhCl(CO)[Ph_2PC(S)NHPh]\}_4$	2030 s 1989 s	1551 s 1538 m,sh	919 m	–	333 w 310 w	274 w	2190 m	3285 w
IIa	$\{RhCl(CO)[Ph_2PC(S)NHMe]\}_2$	2030 s 2005 s	1595 s 1512 m	[a]	1307 w–m 1275 w	–	255 w–m	–	3305 m
III	$\{Rh(CO)[Ph_2PC(S)NPh]\}_4$	1972 vs	1580 m	910 m 876 m	–	[a]	–	–	–
IV	$\{Rh(CO)[Ph_2PC(S)NMe]\}_4$	1967 vs	1595 m	915 m 885 m	–	[a]	–	–	–
V	$RhCl(CO)[Ph_2PC(S)NHPh]_2$	2005 vs	1537 m	920 w–m	–	–	280 vw	–	3175 m 3115 w
VI	$RhCl(CO)[Ph_2PC(S)NHMe]_2$	1991 vs	1533 m–s	947 m	–	–	290 w	–	3202 s
VIIa	$Rh(CO)[Ph_2PC(S)NPh][Ph_2PC(S)NHPh]$	1973 vs	1551 s, br	924 m	–	330 w	–	–	3180 m
VIIb	$Rh(CO)(H)[Ph_2PC(S)NPh]_2$	1983 vs	1545 m–s, br	917 w–m	–	335 w	–	2165 m–s	–
VIIIa	$Rh(CO)[Ph_2PC(S)NMe][Ph_2PC(S)NHMe]$	1970 vs	1595 s 1504 m	909 m–s	–	343 w	–	–	3225 m
IX	$Rh(CO)_2[Me_2NC(S)NPh]$	2060 vs 2005 vs	1554 νNCN_{as} 1109 νNCN_s	–	–	350 m	–	–	–

[a] Not observed.

TABLE III. $^{31}P\{^1H\}$ NMR Parameters. Spectra recorded at −50 °C. Solvent: $CDCl_3$. δ in ppm relative to H_3PO_4 (85% solution) (Upfield = +); J in Hz.

Code	Compound	δ_1	$^1J(Rh-P_1)$	δ_2	$^1J(Rh-P_2)$	$^2J(P_1-P_2)$	$^2J(Rh-P_1)$	$^2J(Rh-P_2)$
Ia	$\{RhCl(CO)[Ph_2PC(S)NHPh]\}_2$ [a]	−65.5	122.7	−12.3	85.4	^3J 12.8	1.8	6.1
IIa	$\{RhCl(CO)[Ph_2PC(S)NHMe]\}_2$	−59.2	126.3	−10.7	85.8	^3J 12.7	2.5	6.5
III	$\{Rh(CO)[Ph_2PC(S)NPh]\}_4$	−7.2	132.5					
IV	$\{Rh(CO)[Ph_2PC(S)NMe]\}_4$	−5.4	134.2					
V	$RhCl(CO)[Ph_2PC(S)NHPh]_2$ [b]	−44.9	123.0					
VI	$RhCl(CO)[Ph_2PC(S)NHMe]_2$	−41.3	126.2					
VIIa	$Rh(CO)[Ph_2C(S)NPh][Ph_2PC(S)NHPh]$	−54.8	138.3	+6.3	98.3	305.0 *trans*		
VIIb	$Rh(CO)(H)[Ph_2PC(S)NHPh]_2$ [c,d]	+24.6	70.8	+27.3	70.8	[e]		
VIIIa	$Rh(CO)[Ph_2PC(S)NMe][Ph_2PC(S)NHMe]$	−51.3	141.6	+9.1	99.7	302.0 *trans*		

[a] The spectrum of Ib could not be measured, because Ib decomposes slowly in solution. [b] The spectrum of V, measured at −25 °C, shows one broad signal at about −42 ppm. [c] In the spectrum of VIIb no hydride-couplings are observed. [d] The spectrum of VIIb, measured at −25 °C, shows one broad signal at about +25 ppm. [e] The $^2J(P_1-P_2)_{trans}$ coupling could not be determined.

TABLE IV. ^1H NMR Parameters. δ in ppm relative to TMS. Measured in $CDCl_3$ at −50 °C.

Code	Compound	δ_{N-H}	R.I.[f]	Ligand δCH_3	R.I.	Toluene δCH_3	R.I.	Intensity	
								Arom.	Alif.
Ia	$\{RhCl(CO)[Ph_2PC(S)NHPh]\}_2 \cdot 0.6C_7H_8$	8.77	0.5			2.39	1.0	17	1
Ib	$\{RhCl(CO)[Ph_2PC(S)NHPh]\}_4 \cdot 0.4C_7H_8$	[a]				2.38	0.3	16	0.3
IIIa	$\{RhCl(CO)[Ph_2PC(S)NHMe]\}_2$ [b]	9.45	0.5	3.28 3.27	1.5 1.5			10	3
III	$\{Rh(CO)[Ph_2PC(S)NPh]\}_4 \cdot 0.4C_7H_8$ [c]					2.39	0.3	15.5	0.3
IV	$\{Rh(CO)[Ph_2PCl(S)NMe]\}_4 \cdot 0.6C_7H_8$	[a]		3.44	3	2.39	0.5	11	3.5
V	$RhCl(CO)[Ph_2PC(S)NHPh]_2$								
VI	$RhCl(CO)[Ph_2PC(S)NHMe]_2 \cdot 0.05C_7H_8$	8.02 br	2	3.29 3.28	3 3	2.39	0.2	21	6.2
VIIa	$Rh(CO)[Ph_2PC(S)NPh][Ph_2PC(S)NHPh] \cdot 0.3C_7H_8$	[a]				2.38	0.9	31.5	1
VIIb	$Rh(CO)(H)[Ph_2PC(S)NPh]_2 \cdot 0.3C_7H_8$ [d]					2.38	1.0	32	1
VIIIa	$Rh(CO)[Ph_2PC(S)NMe][Ph_2PC(S)NHMe] \cdot 0.1C_7H_8$	9.79	1	3.37 3.28	3 3	2.37	0.3	22	6.3
IX	$Rh(CO)_2[Me_2NC(S)NPh]$ [e]			2.83	6			5	6

[a] δ_{N-H} not observed. [b] Measured in acetone-d_6 at +25 °C. [c] Measured in $CDCl_3$ at +25 °C. [d] δ_{Rh-H} not observed in hydride range. [e] Measured in $CDCl_3$ at +25 °C. [f] R.I. = Relative intensity.

presence of a base. It appears that upon additon of $Ph_2PC(S)NHR$ CO evolution rather than breaking of the chloride bridges takes place. In the presence of Et_3N always HCl elimination occurs. However, $[Rh(CO)_2Cl]_2$ does not react with $Me_2NC(S)NHPh$ under the same conditions, unless Et_3N is added. In this reaction a CO ligand is not eliminated. The reaction of $[Rh(CO)_2Cl]_2$ with $Ph_2PC(S)NHR$ proceeds via the attachment of the Ph_2P group to the metal. Obviously, the Ph_2P group possesses such coordinating properties, that it is able to displace a CO molecule.

One equivalent of $[Rh(CO)_2Cl]_2$ reacts with two equivalents of $Ph_2PC(S)NHR$ to give compounds of the general composition $\{RhCl(CO)[Ph_2PC(S)]NHR]\}_n$. When R = Ph (I), two forms exist: an

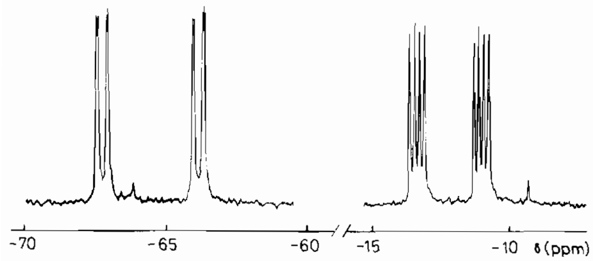


Fig. 1. The ^{31}P NMR spectrum of {Rh(μCl)H(CO)[Ph_2PC(S)NHPh]}{Rh(μCl)(CO)[Ph_2PC(S)NPh]}, (Ia).

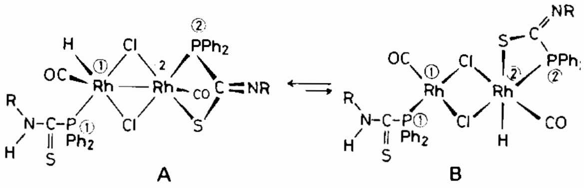


Fig. 2. The structure of Ia (R = Ph) and IIa (R = Me) (see text).

orange-brown species Ia (n = 2) and a black compound Ib (n = 4). Upon standing in solution Ia is slowly converted to Ib. Ib decomposes in chlorinated solvents. For II (R = Me) only the orange dimer has been prepared (IIa).

The IR spectra of Ia and IIa (see Table II) show ν(N–H) at about 3300 cm^{-1} and ν(Rh–Cl) at *ca.* 250 cm^{-1}, pointing to Cl bridges, whereas no ν(Rh–H) could be observed. Two carbonyl stretching frequencies are shown at about 2035 and 2000 cm^{-1}, indicating moderate back-bonding and therefore a fairly high oxidation state of both metals. With respect to the ligand skeletal vibrations two ($C\overset{\cdot\cdot}{-}N$) stretching frequencies are observed at about 1590 and 1500 cm^{-1} and two further absorptions at ±1308 and 1270 cm^{-1}. No (P–C–S) vibrations in the range 880–930 cm^{-1} are shown. From these absorptions it can be concluded that two differently coordinated phosphino ligands are present in the complex, one of which is coordinated end-on via P, whereas the other is bidentate bonded through P and S.

In the ^{1}H NMR spectra of Ia and IIa (see Table IV), a resonance is observed at $\delta \approx 9$ ppm. Based on the relative intensity of this signal it is concluded that only one of the two phosphino ligands present in the complex contains an N–H group. The spectrum of IIa exhibits two CH_3 signals at 3.27 and 3.38 ppm, respectively, further confirming the presence of two different types of phosphino ligands. Even when measured at low temperature, the NMR spectrum does not reveal a signal which can be assigned to a metal–hydride.

Deuteration of the ligand, yielding Ph_2PC(S)NDR, and subsequent reaction with [Rh$(CO)_2$Cl$]_2$ gives the analogous complex {RhCl(CO)D[Ph_2PC(S)NDR]}{RhCl(CO)[Ph_2PC(S)NR]}. In the IR and ^{1}H NMR spectra of the deuterated complex there is no evidence for a Rh–D bond.

The ^{31}P NMR spectra of Ia and IIa (Table III, Fig. 1) show two octets at about –60 ppm with ^{1}J(Rh–P) ≈ 124 Hz, arising from a monodentate P-coordinated ligand, and at –12 ppm with ^{1}J(Rh–P) ≈ 85 Hz, arising from a bidentate ligand, in which the Ph_2P group is incorporated in a four-membered chelate ring. This is in agreement with earlier assignments made for the compounds Rh$(PPh_3)_2$[Ph_2PC(S)NR] (R = Ph, Me) [2, 3].

Furthermore the spectra reveal J(P_1–P_2) of *ca.* 12 Hz, and J(Rh_1–P_2) and J(Rh_2–P_1) of about 6 and 2 Hz, respectively. The large values of these couplings strongly suggest that coupling does not take place via a Cl bridge, which would involve coupling over four and three bonds, respectively, but argues in favour of a direct Rh–Rh interaction, thus allowing coupling to take place over three bonds – ^{3}J(P_1–P_2) – and two bonds – ^{2}J(Rh_1–P_2) and ^{2}J(Rh_2–P_1) –, respectively.

In the ^{31}P NMR spectra of Ia and IIa no P–H couplings are observed.

Based on the spectroscopic data we propose for Ia and IIa structure A, as given in Fig. 2, with two six-coordinate Rh(II) centres having a direct bond. This type of d^7–d^7 metal–metal interaction has previously been suggested for the complex [IrH(μ-StBu)(CO)$(PR_3)]_2$ [6]. The fact that neither the IR nor the ^{1}H and ^{31}P NMR spectra provide indication for the presence of a Rh–H bond, may be explained by the assumption that the hydride displays fast dynamic behaviour, as a result of the tautomeric equilibrium A ⟷ B (Fig. 2). In structure B, which lacks a direct Rh–Rh interaction, the formal oxidation state of the two Rh centres is I (d^8) and III (d^6), respectively. Particularly in view of the values of ν(CO), ^{3}J(P_1–P_2), ^{2}J(Rh_1–P_2) and ^{2}J(Rh_2–P_1), this equilibrium is strongly situated to the left.

The IR spectrum of the tetranuclear compound Ib shows a Rh–hydride absorption at 2190 cm^{-1} and ν(N–H) at 3285 cm^{-1}. The values of ν($C\overset{\cdot\cdot}{-}N$) at 1551 and 1538 cm^{-1} are normal for a P- and a P,S-coordinated ligand, respectively. No vibrations at about 1310 and 1270 cm^{-1} are observed. For solubility reasons the ^{31}P NMR spectrum could not be measured, so that the structure of Ib is not clear at this time.

The IR spectra of the tetrameric compounds III and IV, {Rh(CO)[Ph_2C(S)NPh]}$_4$ display only one CO vibration at about 1970 cm^{-1}. No ν(N–H) is shown. The ligand skeletal absorptions deviate somewhat from the normal pattern. Apart from the fairly high value for ν($C\overset{\cdot\cdot}{-}N$) of ±1590 cm^{-1}, two other vibrations at *ca.* 910 and 880 cm^{-1} are observed, giving evidence for an unusual mode of coordination

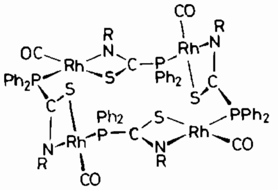


Fig. 3. The structure of $\{Rh(CO)[Ph_2PC(S)NR]\}_4$, III (R = Ph); IV (R = Me).

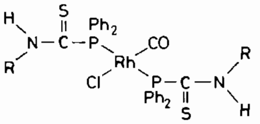


Fig. 4. The structure of $RhCl(CO)[Ph_2PC(S)NHR]_2$, V (R = Ph); VI (R = Me).

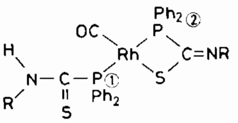


Fig. 5. The structure of $Rh(CO)[Ph_2PC(S)NR][Ph_2PC(S)NHR]$, VIIa (R = Ph): VIIIa (R = Me).

of the ligand. In the ^1H NMR spectrum of IV only one resonance for the CH_3 substituent is found. The ^{31}P NMR spectra show a doublet with $\delta \approx -6$ ppm and $^1J(Rh-P) \approx 133$ Hz. The value of $^1J(Rh-P)$ demonstrates that the ligand is end-on coordinated via P. However, there is a remarkable upfield shift in δ of 40–50 ppm in comparison with δ in complexes having an end-on P-coordinated $Ph_2PC(S)NHR$ ligand. This shielding effect affirms the participation of the other hetero groups in the interaction with rhodium. These observations are in good agreement with the spectroscopic data, reported for $\{Mo(CO)_2[Ph_2PC(S)NMe]_2\}_2$. The X-ray structural analysis of this compound has revealed two of the four hetero allyls to coordinate through P, S and N [1]. Based on these considerations we propose the structure of III and IV to be as given in Fig. 3.

Complexes V and VI show in the IR spectrum $\nu(N-H)$ at ± 3200 cm^{-1}, $\nu(CO)$ at ± 2000 cm^{-1} and $\nu(Rh-Cl)$ at ± 285 cm^{-1}. The ligand absorptions are normal for P-coordinated $Ph_2PC(S)NHR$. The values of the ^{31}P NMR parameters (doublet; $\delta \approx -43$ ppm, $^1J(Rh-P) \approx 125$ Hz) are in accordance with the values for the P-coördinated ligands in compounds Ia and IIa. At ambient temperature the spectra of V and VI show one broad signal as a result of dynamic behaviour of the phosphino ligands (see Fig. 4).

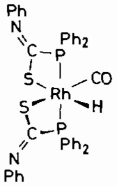


Fig. 6. The structure of $RhH(CO)[Ph_2PC(S)NPh]_2$, VIIb.

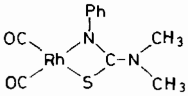


Fig. 7. The structure of $Rh(CO)_2[Me_2NC(S)NPh]$, IX.

The IR spectra of the monomeric complexes VIIa and VIIIa and the ^1H NMR spectrum of VIIIa point to the presence of one P-coordinated $Ph_2PC(S)NHR$ and one P,S-coordinated $[Ph_2PC(S)NR]^-$ ligand in these complexes. The ^{31}P NMR spectra of VIIa and VIIIa at -50 °C show a downfield quartet ($\delta \approx -53$ ppm) with $^1J(Rh-P) \approx 140$ Hz and an upfield quartet ($\delta \approx +7$ ppm) with $^1J(Rh-P_2) \approx 99$ Hz. The two phosphino groups are in *trans* position to each other, as indicated by the large value for $^2J(P_1-P_2)$ of *ca.* 304 Hz. At ambient temperature the phosphino ligands again display dynamic behaviour (see Fig. 5).

Under certain conditions intramolecular oxidative addition may occur, resulting in VIIb. $\nu(Rh-H)$ is observed at 2165 cm^{-1}. In the corresponding complex, obtained from the deuterated ligand $Ph_2PC(S)NDPh$, an absorption at this wavenumber is lacking). Nevertheless, $\delta(Rh-H)$ is not found in the ^1H NMR spectrum and no hydrido couplings are shown in the ^{31}P NMR spectrum. The almost equivalence of both P nuclei leads us to the structure given in Fig. 6.

Compared with $Ph_2PC(S)NHR$, the amino-analogue $Me_2NC(S)NHPh$ is much less reactive. It is not able to displace a CO ligand in $[Rh(CO)_2Cl]_2$. As indicated by its IR spectrum complex IX contains two inequivalent CO molecules and a S,N bidentate coordinated $[Me_2NC(S)Ph]^-$ ligand [3]. The spectral parameters and therefore the structure of IX and $Rh(CO)_2[Me_2NC(S)NPh]$ [7] resemble each other (Fig. 7).

In summary, three different modes of coordination for the $[Ph_2PC(S)NR]^-$ system occur:

(i) In its protonated form terminal coordination (η^1) via P takes place;

(ii) Bidentate coordination through P and S generally occurs for the deprotonated ligand;

(iii) If the metal centre is coordinatively unsaturated, the deprotonated ligand may coordinate via P, S and N.

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