Rhodium(III)-bis and -tris Hetero Allyl Complexes. Synthesis and Characterisation

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Rh(III)-bis- and Rh(III)-tris hetero allyl complexes can be prepared via ligand substitution starting from $RhCl_3 \cdot 3H_2O$ *and* $[X\text{–}C(Z)\text{–}Y]^-$ *or via oxidative addition starting from* $Rh(I)[X\text{–}C(Z)\text{–}Y]L_2$ *(*$L = C_8H_{14}$, PPh_3*) and suitable* $[X\text{–}C(Z)\text{–}Y]_2$ *or* $[X\text{–}C(Z)]_2Y$ *reagents. For these Rh(III) complexes different geometrical and optical isomers exist. The facial and the meridional forms of* $Rh[Me_2NC(S)NPh]_3$ *can be separated by fractional crystallisation. At elevated temperature the* mer *isomer is completely and irreversibly converted to the* fac *one. Rotation about the exocyclic C–N bonds is observed even at* $-60\ ^\circ C$.

$Rh[Ph_2PC(S)NR]_3$ *(R = Ph, Me) predominantly exists in the* mer *form. The* ^{31}P *NMR spectrum of this isomer at +11* $^\circ C$ *can be fitted for an ABXRh spectrum. The remarkable temperature dependence of the NMR parameters does not originate from interconversion of isomers but arises most probably from small changes in angles and bonding distances within the complex.*

Introduction

Hetero allyls $[X\text{–}C(Z)\text{–}Y]^-$ usuallly coordinate to a transition metal complex through two of the three hetero atoms, thus forming a chelate ring [1–3]. In this paper we report the syntheses and spectroscopic properties of Rh(III)-tris hetero allyl complexes containing equal or different ligands. The chelating anions used as ligands are given in Fig. 1.

The electrochemical oxidations and reductions of two of these complexes, $Rh[Ph_2PC(S)NR]_3$ (R = Ph, Me) and $Rh[Me_2NC(S)NPh]_3$ [4] as well as the synthesis and characterisation of some $Cu[R_2NC(S)NR']$-complexes [5] have been reported recently by us.

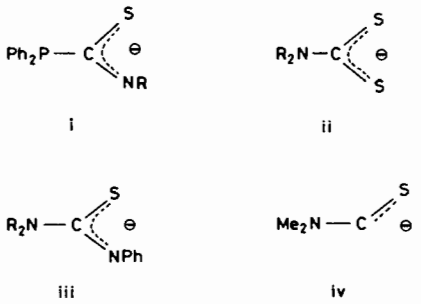

Fig. 1. The chelating ligands used in this paper. *i* = P,P-diphenyl-N-R-phosphinothioformamido (R = Ph,Me); *ii* N,N-di-R-dithiocarbamato (R = Me,Et); *iii* = N,N-di-R-N'-phenyl-(thio)ureido (R = Me, $R_2 = -(CH_2)_5-$); *iv* = N,N-dimethyl-thiocarboxamido.

The thiocarboxamido ligand $[Me_2NCS]^\ominus$, a pseudo-vinilyc anion, has also been included in this study because of its relationship with hetero allylic derivatives [6]. The coordination of this ligand to rhodium has been recently investigated and established to take place in an η^2 mode by C and S [7–9]. The Rh(III)-tris-hetero-allylic complexes have been prepared by ligand substitution starting from Rh(III) complexes and $[X\text{–}C(Z)\text{–}Y]^\ominus$ or by oxidative addition starting from $Rh(I)[X\text{–}C(Z)\text{–}Y]L_2$ ($L = C_8H_{14}$, PPh_3) and suitable [7, 10] compounds A–B, consisting of two hetero allyls or a combination of a hetero allyl and a pseudo vinyl. The compounds A–B are shown in Fig. 2.

Several geometrical, optical and rotational isomers of the Rh(III)-tris-hetero-allylic complexes are possible. Some of these undergo isomerisation under suitable conditions. For one of the complexes, *i.e.* $Rh[Me_2NC(S)NPh]_3$, the isomerisation processes have been closely investigated by means of temperature dependent ^1H NMR measurements. For $Rh[Ph_2PC(S)NPh]_3$ a remarkable temperature dependence of the ^{31}P NMR spectrum was observed. The results of these studies are reported in the present paper.

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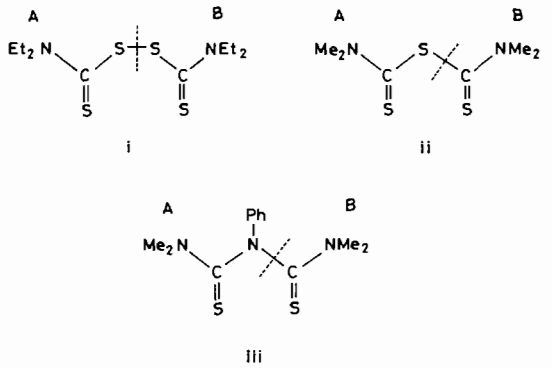

Fig. 2. The compounds A–B, used for oxidative additions. *i* = N,N,N′,N′-tetraethylthiuram disulfide; *ii* = N,N,N′,N′-tetra-methylthiuram monosulfide; *iii* = N,N,N′,N′-tetramethyl-N″-phenyl-dithiobiuret.

Experimental

IR spectra were measured on a Perkin-Elmer 283 spectrophotometer (400–200 cm^{-1}), in CsI pellets. ^1H and ^{31}P $\{^1H\}$ NMR spectra were recorded on a Bruker WH 90 spectrometer at 90 MHz and 36.44 MHz, respectively, and on a Varian SC 300 spectrometer at 300 MHz and 121 MHz, respectively, using the deuterated solvent as internal lock.

Elemental analyses were carried out at the element-analytical department of the Institute of Applied Chemistry TNO. Analytical data are given in Table I.

Reactions were carried out at room temperature in analytical grade solvents.

Starting material.

$RhCl_3 \cdot 3H_2O$ (reagent grade) was obtained from Drijfhout, $Et_2NC(S)SSC(S)NEt_2$ and $Me_2NC(S)SC(S)NMe_2$ from Fluka. $Me_2NC(S)NPhC(S)NMe_2$ [11], $Ph_2PC(S)NHR$ (R = Ph,Me) [12, 13], $Rh[Ph_2PC(S)NPh](PPh_3)_2$ [2], $Rh[Ph_2PC(N\text{-}p\text{-}tol)N\text{-}p\text{-}tol](PPh_3)_2$ and $Rh[Ph_2PC(NPh)O](PPh_3)_2$ [3] and $[RhCl(C_8H_{14})_2]_2$ [14] were prepared according to literature procedures. $Me_2NC(S)NHPh$ and $(CH_2)_5NC(S)NHPh$ were prepared by direct addition of Me_2NH and piperidine, respectively, to Ph–N=C=S in diethylether.

$Rh[Me_2NC(S)NPh]_3$ I

A suspension of 130 mg $RhCl_3 \cdot 3H_2O$ (0.5 mmol) and 260 mg $Me_2NC(S)NHPh$ (1.6 mmol) in 30 ml methanol was stirred vigorously. After 30 minutes a small excess of Et_3N was added. The colour of the mixture changed slowly from red to orange–red. After three hours the mixture contained an orange precipitate, which was filtered, washed with methanol and n-pentane and dried *in vacuo* (Ia). The filtrate was concentrated and toluene was added. After filtration the solution was extracted with distilled water to remove further $Et_3N \cdot HCl$. The toluene layer was dried on $MgSO_4$. Finally, the toluene was evaporated and on addition of n-pentane Ib was obtained.

$Rh[(CH_2)_5NC(S)NPh]_3$ II

The initial red solution from 130 mg $RhCl_3 \cdot 3H_2O$ and 350 mg $(CH_2)_5NC(S)NHPh$ in 30 ml ethanol changed slowly to red–orange upon addition of Et_3N. After three hours II was isolated and purified according to the procedure, followed for Ib. Separation of the geometrical isomers was not successful.

$Rh[Ph_2PC(S)NR]_3$ III (R = Ph); IV (R = Me)

0.3 mmol $RhCl_3 \cdot 3H_2O$ and 1.0 mmol $Ph_2PC(S)NHR$ were suspended in a mixture of 20 ml methanol and 20 ml toluene. Upon addition of Et_3N the colour changed to orange. After stirring for one hour and standing for one night, yellow crystals were formed. After filtration IIIb and IVb were washed with methanol and diethyl ether and dried *in vacuo*. On addition of n-pentane to both filtrates, mixtures of IIIa and IIIb, and of IVa and IVb, respectively, were obtained. Isolation of the geometrical isomers (IIIa and IVa) was not achieved.

$\{Rh[X\text{–}C(Z)\text{–}Y]_2Cl\}_2$ $[X\text{–}C(Z)\text{–}Y]^{\ominus} = [Me_2NC(S)NPh]^{\ominus}$ (V); $[(CH_2)_5NC(S)NPh]^{\ominus}$ (VI); $[Ph_2PC(S)NPh]^{\ominus}$ (VII); $[Ph_2PC(S)NMe]^{\ominus}$ (VIII)

0.5 mmol $RhCl_3 \cdot 3H_2O$ and 1.0 mmol of the protonated ligand were suspended in a mixture of 20 ml methanol and 20 ml toluene. After 30 minutes an excess of Et_3N was added. The solution was allowed to react for two more hours. After evaporation of methanol, toluene was added, and the suspension was filtered. The precipitate was washed with methanol, toluene and diethyl ether. V–VIII were dried *in vacuo*. Concentration of the filtrates gave considerable amounts of the $Rh[X\text{–}C(Z)\text{–}Y]_3$ products.

$Rh[Ph_2PC(S)NPh]_2[Me_2NC(S)NPh] \cdot 0.8C_6H_6$ IX

VII was reacted with an equimolar quantity of $Me_2NC(S)NHPh$ in the presence of Et_3N in benzene. After two hours IX was precipitated with n-pentane, washed with diethyl ether and dried *in vacuo*.

$Rh[Me_2NC(S)NPh]_2[Me_2NC(S)S] \cdot 0.5C_6H_6$ X

V was reacted with $NaSC(S)NMe_2$ in benzene. After two hours X was isolated according to the method, described for IX.

$Rh[Ph_2PC(S)NPh][Et_2NC(S)S]_2 \cdot 0.3C_7H_8$ XI

0.3 mmol $Rh[Ph_2PC(S)NPh](PPh_3)_2$ and 0.3 mmol $Et_2NC(S)SSC(S)NEt_2$ were dissolved in 30 ml oxygen-free toluene. The initial yellow colour changed to orange. After two hours the solution was diluted with n-hexane. Orange crystals were obtained.

Rh[$Ph_2PC(S)NPh$][$Me_2NC(S)S$][Me_2NCS]·0.3C_7H_8 XII

Synthesis from $Rh[Ph_2PC(S)NPh](PPh_3)_2$ and $Me_2NC(S)SC(S)NMe_2$ analogous to XI.

Rh[$Ph_2PC(S)NPh$][$Me_2NC(S)NPh$][Me_2NCS]·1.0C_6H_6 XIII

Synthesis from $Rh[Ph_2PC(S)NPh](PPh_3)_2$ and $Me_2NC(S)NPhC(S)NMe_2$ analogous to XI. Reaction was carried out in benzene.

Rh[$Me_2NC(S)S$][$Me_2NC(S)NPh$][Me_2NCS]·0.6C_6H_6 XIV

$Rh[Me_2NC(S)NPh](C_8H_{14})_2$ was prepared in situ by addition of 0.50 mmol $Me_2NC(S)NHPh$ to 0.25 mmol $[RhCl(C_8H_{14})_2]_2$ in the presence of Et_3N in 30 ml benzene. Subsequently 0.50 mmol $Me_2NC(S)SC(S)NMe_2$ were added. After dilution with n-hexane an orange precipitate was obtained.

Rh[$Me_2NC(S)NPh$]$_2$[Me_2NCS] XV

Synthesis from $Rh[Me_2NC(S)NPh](C_8H_{14})_2$ and $Me_2NC(S)NPhC(S)NMe_2$ anlogous to XIV.

Ir[$Ph_2PC(S)NPh$]$_3$ XVI

0.3 mmol $(NH_4)_3IrCl_6·H_2O$ and 1.0 mmol $Ph_2PC(S)NHPh$ were suspended in a mixture of 20 ml methanol and 20 ml toluene. On addition of NEt_3 the colour changed to orange–yellow. After stirring for one hour and on standing for one night yellow crystals of the *fac* and the *mer* isomer were formed.

Reactions and Products

The Rh(III) tris-hetero-allyl complexes are prepared either by substitution or by oxidative addition. Figures 3 and 4 summarize both synthetic routes.

TABLE I. Analytical Data. (Calculated values in parentheses).

Code	Compound	Colour	%C	%H	%N	%Cl	%S	Yield
Ia	*fac* $Rh[Me_2NC(S)NPh]_3$	orange–yellow	50.6 (50.6)	5.5 (5.2)	13.4 (13.1)			50%
Ib	*mer* $Rh[Me_2NC(S)NPh]_3$	orange–brown	50.7 (50.6)	5.2 (5.2)	12.8 (13.1)			20%
II	$Rh[(CH_2)_5NC(S)NPh]_3$	orange–yellow	56.8 (56.8)	6.0 (6.0)	11.2 (11.1)			80%
IIIb	*mer* $Rh[Ph_2PC(S)NPh]_3·C_7H_8$	yellow	66.3 (66.5)	4.7 (4.6)	3.6 (3.6)			75%
IVb	*mer* $Rh[Ph_2PC(S)NMe]_3$	yellow	58.0 (57.5)	4.7 (4.5)	4.4 (4.8)			70%
V	$\{RhCl[Me_2NC(S)NPh]_2\}_2$	brown	42.9 (43.5)	4.8 (4.5)	10.8 (11.3)	7.4 (7.2)		15%
VI	$\{RhCl[(CH_2)_5NC(S)NPh]_2\}_2$	yellow–brown	49.0 (50.0)	5.2 (5.3)	9.8 (9.7)	6.0 (6.2)		15%
VII	$\{RhCl[Ph_2PC(S)NPh]_2\}_2$	brown	57.8 (58.6)	4.0 (3.9)	3.4 (3.6)	4.5 (4.6)		10%
VIII	$\{RhCl[Ph_2PC(S)NMe]_2\}_2$	orange–brown	51.4 (51.3)	4.1 (4.0)	4.4 (4.3)			10%
IX	$Rh[Ph_2PC(S)NPh]_2[Me_2NC(S)NPh]·0.8C_6H_6$	orange	62.1 (63.1)	4.7 (4.7)	5.5 (5.7)	[a]	9.2 (9.8)	40%
X	$Rh[Me_2NC(S)NPh]_2[Me_2NC(S)S]·0.5C_6H_6$	orange–brown	46.5 (46.5)	5.4 (5.0)	11.3 (11.3)		20.2 (20.7)	40%
XI	$Rh[Ph_2PC(S)NPh][Et_2NC(S)S]_2·0.3C_7H_8$	yellow	49.2 (50.1)	5.3 (5.0)	5.6 (5.6)			90%
XII	$Rh[Ph_2PC(S)NPh][Me_2NC(S)S][Me_2NCS]·0.3C_7H_8$	orange	48.3 (48.5)	4.6 (4.6)	6.5 (6.5)			90%
XIII	$Rh[Ph_2PC(S)NPh][Me_2NC(S)NPh][Me_2NCS]·C_6H_6$	orange	57.7 (57.8)	5.3 (5.0)	7.2 (7.3)			90%
XIV	$Rh[Me_2NC(S)S][Me_2NC(S)NPh][Me_2NCS]·0.6C_6H_6$	orange–brown	41.1 (41.6)	5.3 (5.0)	10.6 (10.4)		23.6 (23.9)	60%
XV	$Rh[Me_2NC(S)NPh]_2[Me_2NCS]$	orange–brown	46.0 (45.9)	5.3 (5.1)	12.4 (12.8)		17.9 (17.5)	60%
XVI	$Ir[Ph_2PC(S)NPh]_3$	yellow	59.0 (59.4)	3.9 (3.9)	3.4 (3.6)			65%

[a] % P 6.1 (6.3).

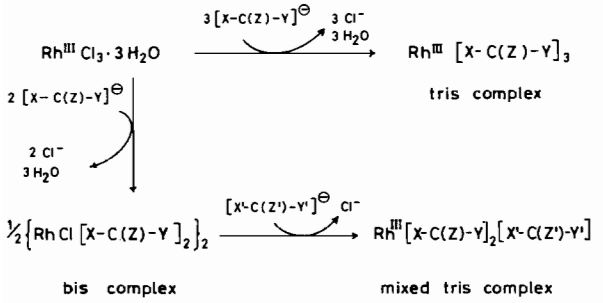

Fig. 3. Synthesis of Rh(III) tris-hetero-allyl complexes from $Rh^{III}Cl_3 \cdot 3H_2O$ *via* substitution.

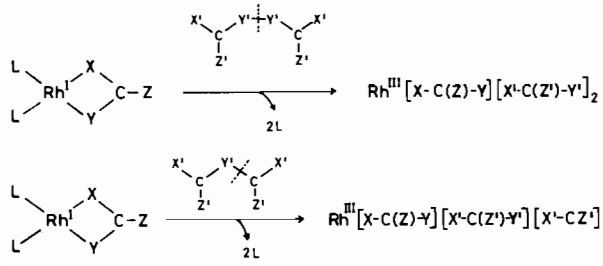

Fig. 4. Synthesis of Rh^{III} hetero allyl complexes *via* oxidative addition of A–B to $Rh^{I}[X\text{–}C(Z)\text{–}Y]L_2$ ($L = C_8H_{14}$, PPh_3) (see text).

The synthesis of the bis complexes $\{RhCl[X\text{–}C(Z)\text{–}Y]_2\}_2$ and the mixed tris complexes, according to Fig. 3, give only poor yields of the desired compounds, as a result of ligand scrambling. Moreover, it appears that in the substitution reactions generally a mixture of geometric isomers results. On the contrary most of the oxidative addition reactions starting from $Rh(I)[X\text{–}C(Z)\text{–}Y]L_2$ ($L = C_8H_{14}$, PPh_3) yield only one isomer. This suggests that metal–ligand bond formation and rearrangement of ligands in the complex proceed in a concerted fashion.

The two C_8H_{14} ligands are always easily displaced [15], whereas the second PPh_3 molecule can only be substituted if one of the hetero allyls possesses a PPh_2 group, implying that after oxidative addition the final complex still contains a coordinating phosphine ligand.

Results and Discussion

Rh[Me₂NC(S)NPh]₃

For $Rh[Me_2NC(S)NPh]_3$ two geometrical isomers exist, called facial and meridional, each having two optical isomers Λ and Δ. The Λ forms are shown in Fig. 5.

The *fac* isomer (orange) and the *mer* one (brown) can be separated by fractional crystallisation. The IR spectra of the two isomers show no significant differences (Table II).

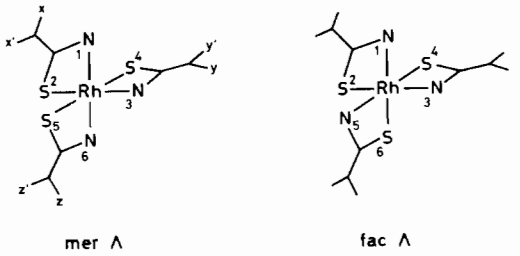

Fig. 5. The two geometrical isomers of $Rh[Me_2NC(S)NPh]_3$ (Λ forms).

The ^1H NMR spectra in the methyl region (1–4 ppm), recorded at various temperatures are shown in Fig. 6. The parameters are given in Table III. A permutational analysis of all intramolecular rearrangements of $M(AB)_3$, as performed by Eaton [16] and the effect of fast C–N rotation (of the exocyclic $C\text{–}NMe_2$ group) is given in Tables IV and V, for the *fac* and the *mer* isomer, respectively.

For the *fac* isomer only one methyl signal is observed throughout the whole temperature range, which implies, that only the rearrangements of type A_1, A_2, A_5 and A_6 in combination with a fast CN rotation can be active. However, A_2 and A_5 seem to be highly improbable permutations, because the physical mechanism corresponding to A_2 is a simultaneous 180° rotation of the three chelate rings via an approximately hexagonal transition state and

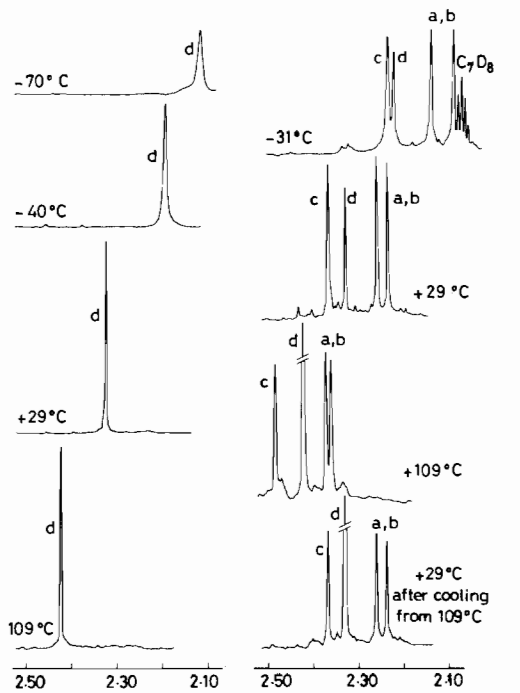

Fig. 6. Methyl region of the ^1H NMR spectra of *fac* (left) and *mer* (right) $Rh[Me_2NC(S)NPh]_3$ at various temperatures.

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

Code	Compound	$[Ph_2PC(S)NR]^{\ominus}$	$[R_2NC(S)S]^{\ominus}$	$[R_2NC(S)NPh]^{\ominus}$		$[R_2NCS]^{\ominus}$		$[X-C(Z)-Y]^{\ominus}$	νM–S
		ν(C=N)	ν(C=N)	$\nu(NCN)_{as}$	$\nu(NCN)_s$	ν(C=N)	ν(M<C,S>)	ν(C–S)	
Ia	*fac* $Rh[Me_2NC(S)NPh]_3$			1534 vs	1105 s			927 m	352 w
Ib	*mer* $Rh[Me_2NC(S)NPh]_3$			1537 s,br	1109 m			935 m	350 w
									327 w
II	$Rh[(CH_2)_5NC(S)NPh]_3$			1530 vs	1110 m			933 w	352 w
IIIb	*mer* $Rh[Ph_2PC(S)NPh]_3$	1548 vs						928 s	330 br
IVb	*mer* $Rh[Ph_2PC(S)NMe]_3$	1576 vs						911 m	322 w–m
V	$\{RhCl[Me_2NC(S)NPh]_2\}_2$			1537 s	1106 m			927 m	340 w
VI	$\{RhCl[(CH_2)_5NC(S)NPh]_2\}_2$			1523 vs,br	1108 m			937 w	340 w
					1129 m				328 w
VII	$\{RhCl[Ph_2PC(S)NPh]_2\}_2$	1562 vs						909 m	335 vw
VIII	$\{RhCl[Ph_2PC(S)NMe]_2\}_2$	1582 vs						914 m	337 w
IX	$Rh[Ph_2PC(S)NPh]_2[Me_2NC(S)NPh]$	1549 vs		1540 s,sh	1102 m			930 m	333 w
					1109 m				
X	$Rh[Me_2NC(S)NPh]_2[Me_2NC(S)S]$		1525 s,sh	1542 vs,br	1109 m			950 m	352 w–m
								908 m	
XI	$Rh[Ph_2PC(S)NPh][Et_2NC(S)S]_2$	1548 s	1502 s					920 m	352 w–m
								911 m	319 w–m
								902 m	
XII	$Rh[Ph_2PC(S)NPh][Me_2NC(S)S][Me_2NCS]$	1540 s	1511 s			1582 s	832 m	934 m	352 m
								918 m	311 w
XIII	$Rh[Ph_2PC(S)NPh][Me_2NC(S)NPh][Me_2NCS]$	1538 s		1532 s	1104 m	1592 s	833 s	924 sh	334 w,br
								919 m	314 w,br
XIV	$Rh[Me_2NC(S)S][Me_2NC(S)NPh][Me_2NCS]$		1518 s,sh	1532 vs,br	1105 s,br	1588 s,br	838 m	920 m	360 w,br
				1540 vs,sh					330 w,br
XV	$Rh[Me_2NC(S)NPh]_2[Me_2NCS]$			1540 vs,br	1107 s	1590 s	840 m	949 m	348 w
								921 m	
XVI	$Ir[Ph_2PC(S)NPh]_3$	1550 vs						930 s	310 br

TABLE III. ^{1}H NMR Parameters (alifatic region). δ in ppm Relative to TMS. s = singlet; m = multiplet; t = triplet; q = quartet.

Code	Compound	Solvent	Temp. (°C)	δ			Assignment[b]	Intensity ratio arom:alif
Ia	*fac* $Rh[Me_2NC(S)NPh]_3$	C_7D_8	29	2.32 s			d	5:6
			−70	2.10 s	(br)			
Ib	*mer* $Rh[Me_2NC(S)NPh]_3$	C_7D_8	29	2.36 s	(3H)		c	15:18
				2.33 s			d	
				2.26 s	(3H)		a,b	
				2.23 s	(3H)		a,b	
			−31	2.23 s			c	
				2.21 s			d	
				2.13 s			a,b	
				2.08 s			a,b	
			109	2.47 s			c	
				2.41 s			d	
				2.36 s			a,b	
				2.35 s			a,b	
II	$Rh[(CH_2)_5NC(S)NPh]_3$	$CDCl_3$	25	2.87 m	(12H)			15:30
				1.07 m	(18H)			
IVb	*mer* $Rh[Ph_2PC(S)NMe]_3$	$CDCl_3$	25	3.60 s	1			30:9
				3.58 s	2			
				3.56 s	2			
				3.40 s	2			
				3.37 s	2			
				3.34 s	1	relative		
				3.32 s	1	intensities		
				3.29 s	1			
				3.27 s	1			
				3.23 s	1			
				3.22 s	1			
				3.20 s	3			
				3.16 s	2			
VI	$\{RhCl[(CH_2)_5NC(S)NPh]_2\}_2$	$CDCl_3$	25	3.12 m	(8H)			10:20
				1.40 m	(12H)			
IX	$Rh[Ph_2PC(S)NPh]_2[Me_2NC(S)NPh]$[a]	$CDCl_3$	25	2.59 s				35:6
XI	$Rh[Ph_2PC(S)NPh][Et_2NC(S)S]_2 \cdot 0.3C_7H_8$	CD_2Cl_2	25	3.45 q	(4H)	$-CH_2-$		16:20
				0.99 t	(6H)	$-CH_3$		
				2.36 s	(1H)	toluene		

[a]This isomer ≈ 70% of total intensity. [b]The letters a,b,c and d refer to signals in Fig. 6.

because A_5 is only achieved by inversion. Permutation A_6 is achieved by a trigonal or Bailar twist mechanism, involving a trigonal prismatic intermediate. Such a twist movement is known to be operative in octahedral complexes. The distinction between A_1 or A_6, that is rigidity or Bailar twist, cannot be made. Due to the non-diasterotopic nature of the substituents, the active operation(s) cannot be selected.

The *mer* isomer measured contained a slight impurity of the *fac* isomer. Apart from a low intensity methyl signal of this isomer, at room temperature three methyl signals of equal intensity are observed. This signal multiplicity is to be expected, when A_1 and A_5 are operative. As A_5 corresponds to the highly improbable inversion, the conclusion is that apart from a rapid rotation about the CN bond, at room temperature the complex is stereochemically rigid. On increasing the temperature two signals shift towards each other and thereupon exhibit line-broadening, indicating the start of an exchange process of type A_2 and/or A_6. As mentioned above, A_2 is very improbable. By consequence an A_6 permutation, achieved by a Bailar twist, is then operative. The two methyl signals, predicted for the rapid exchange limit (2:1 intensity ratio) are, however, not obtained, probably because of the upper temperature limit, dictated by the solvent (toluene). Moreover, at 109 °C the *mer* isomer converts completely into the *fac* isomer, which is shown by the increasing

TABLE IV. Permutational Analysis for the CH_3 Signals of the ^1H NMR Spectra of *Fac*-Rh[$Me_2NC(S)NPh$]$_3$.

Operation	Averaging set	Net configurational change	Changes in signal multiplicity	Changes in signal multiplicity upon CN rotation
E	A_1	None	$2 \rightarrow 2^a$	$2 \rightarrow 1$
(12) (34) (56)	A_2	None	$2 \rightarrow 2^a$	$2 \rightarrow 1$
(12) (34) (56)	A_3	*Fac* $\rightarrow$ *Mer*	$2 \rightarrow 6^{b,d}$	$2 \rightarrow 3^{c,d}$
(12) (34) (34) (56) (12) (56)	A_4	*Fac* $\rightarrow$ *Mer*	$2 \rightarrow 6^{b,d}$	$2 \rightarrow 3^{c,d}$
E*	A_5	$\Delta \rightarrow \Lambda$	$2 \rightarrow 2^a$	$2 \rightarrow 1$
(12) (34) (56)*	A_6	$\Delta \rightarrow \Lambda$	$2 \rightarrow 2^a$	$2 \rightarrow 1$
(12)* (34)* (56)*	A_7	$\Delta \rightarrow \Lambda$ *Fac* $\rightarrow$ *Mer*	$2 \rightarrow 6^{b,d}$	$2 \rightarrow 3^{c,d}$
(12) (34)* (34) (56)* (12) (56)*	A_8	$\Delta \rightarrow \Lambda$ *Fac* $\rightarrow$ *Mer*	$2 \rightarrow 6^{b,d}$	$2 \rightarrow 3^{c,d}$

Intensity ratio: [a]1:1; [b]1:1:1:1:1:1; [c]1:1:1. [d]The maximum number of signals is only obtained when the *fac* isomer is completely and irreversibly converted into the *mer* isomer.

TABLE V. Permutational Analysis for the CH_3 Signals in the ^1H NMR Spectra of *Mer*-Rh[$Me_2NC(S)NPh$]$_3$.

Operation	Averaging set	Net configurational change	Net site interchange	Change in signal multiplicity	Changes in signal multiplicity upon CN rotation
E	A_1	None	None	$6 \rightarrow 6^a$	$6 \rightarrow 3^b$
(12) (34) (56)	A_2	None	(xy)	$6 \rightarrow 4^c$	$4 \rightarrow 2^d$
(12) (34) (56)	A_3	*Mer* $\rightarrow$ 1/3 *Fac* + 2/3 *Mer*	(yz) (xz)	$6 \rightarrow 2^e$	$2 \rightarrow 1$
(12) (34) (34) (56) (12) (56)	A_4	*Mer* $\rightarrow$ 1/3 *Fac* + 2/3 *Mer*	(xyz) (xzy)	$6 \rightarrow 2^e$	$2 \rightarrow 1$
E*	A_5	$\Delta \rightarrow \Lambda$	None	$6 \rightarrow 6^a$	$6 \rightarrow 3^b$
(12) (34) (56)*	A_6	$\Delta \rightarrow \Lambda$	(xy)	$6 \rightarrow 4^c$	$4 \rightarrow 2^d$
(12)* (34)* (56)*	A_7	$\Delta \rightarrow \Lambda$ *Mer* $\rightarrow$ 1/3 *Fac* + 2/3 *Mer*	(yx) (xz)	$6 \rightarrow 2^e$	$2 \rightarrow 1$
(12) (34)* (34) (56)* (12) (56)*	A_8	$\Delta \rightarrow \Lambda$ *Mer* $\rightarrow$ 1/3 *Fac* + 2/3 *Mer*	(xyz) (xzy)	$6 \rightarrow 2^e$	$2 \rightarrow 1$

Intensity ratio: [a]1:1:1:1:1:1; [b]1:1:1; [c]2:2:1:1; [d]2:1; [e]1:1.

intensity of the signals of the latter isomer at the expense of the former one. After heating a solution of *mer* Rh[$Me_2NC(S)NPh$]$_3$ for about one hour at 109 °C, the *mer* signals have completely vanished. This conversion is irreversible as can be seen after cooling the solution to room temperature. A conversion of the *fac* isomer into the *mer* form is not observed.

The enantiomerisation in Rh[$R_2NC(S)S$]$_3$ has been found to possess a high activation energy [17].

The assumption of such a high energy barrier may well explain, why a fast Bailar twist (A_6) for the *mer* isomer occurs at high temperatures only.

Fac and *mer* $Rh[(CH_2)_5NC(S)NPh]_3$ could not be separated and unfortunately, cannot be distinguished by spectroscopic techniques.

$Rh[Ph_2PC(S)NR]_3$ (R = Ph,Me)

This compound also occurs in two geometrical isomers: facial and meridional (see Fig. 7).

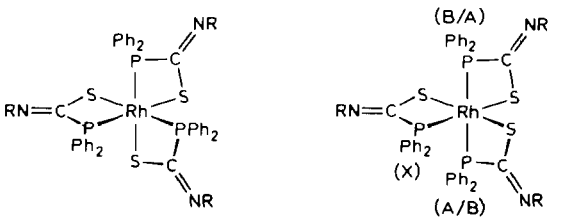

Fig. 7. *Fac* and *mer* $Rh[Ph_2PC(S)NR]_3$ (R = Ph,Me). The Δ isomers are shown.

Mer-$Rh[Ph_2PC(S)NR]_3$ is the main product from the reaction of $RhCl_3 \cdot 3H_2O$ with $[Ph_2PC(S)NR]^{\ominus}$. When rapidly precipitated the compounds always contain mixtures of the *fac* (±5%) and the *mer* (±95%) isomer. The values of ν(C=N) in the IR spectra of these compounds (see Table II) exclude N-coordination, so the ligand is coordinated by P and S.

The $^{31}P\{^1H\}$ NMR spectra of *mer*-$Rh[Ph_2PC(S)NR]_3$, recorded at 121 MHz in the temperature range of −49 °C to +104 °C are shown in Fig. 8. The values of the parameters are listed in Table VI. The note-worthy temperature dependence together with the multitude of δ and J parameters necessitates the application of a simulation program [18]. However, as $(\delta_A - \delta_B)$ is relatively small, the value of $^2J(A-B)_{trans}$ cannot be determined in all cases. From the spectrum measured at +11 °C a $^2J(A-B)_{trans}$ value of 475 Hz is found and a correct simulation of the spectrum for an ABXRh pattern is achieved (see Fig. 9), which leads to values for $^2J(A-X)_{cis}$ and $^2J(B-X)_{cis}$ of +22.5 Hz and −6.0 Hz, respectively. The variation of the contributions of metal s, p and d orbitals to $^2J(P-P)_{cis}$, arising from the slightly different P–M–P aperture angles [19] has been suggested as the cause for the striking difference between the values of the $^2J(P-P)_{cis}$ parameters which may even result in reversal of the sign [3]. Keeping the $^2J(A-B)_{trans}$-value as found for the +11 °C spectrum constant at all temperatures, the experimental and simulated spectra at other temperatures do not fully match. However, the data obtained from the simulations clearly reveal the following points:

– The δ_A and δ_B values diverge at increasing temperature, whereas isomerisation demands convergation of these values, at least towards a coalescence temperature. Line-broadening is not observed at any of the temperatures measured, further denying the presence of species being in equilibrium.

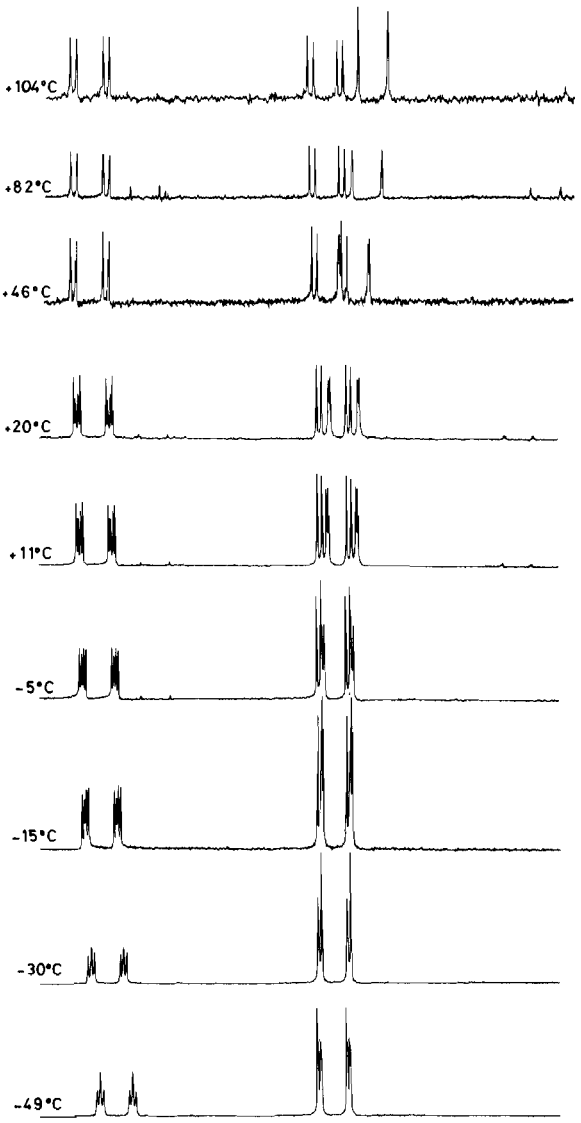

Fig. 8. Spectra of *mer* $Rh[Ph_2PC(S)NPh]_3$, recorded at various temperatures in C_7D_8 (+104, +82 and +46 °C) and $CDCl_3$ (other temperatures).

– δ_P and $^1J(Rh-P)$ values of all phosphino groups remain in the same range, confirming the preservation of the three chelates. The generation of any five coordinate species can therefore be excluded.

– No *mer* ⇔ *fac* isomerisation occurs, because a mixture of both isomers shows neither line-broadening, nor change in relative intensity ratios when measured at different temperatures. Intramolecular rearrangements with a net configurational change

TABLE VI. $^{31}P\{^{1}H\}$NMR Parameters. Spectra Recorded at Room Temperature (25 °C). δ in ppm relative to 80% H_3PO_4. $\delta_{TMP} - \delta_{H_3PO_4} = +2.3$ ppm. (Upfield = –); J in Hz. Data for complex IIIb are obtained by computer simulation. Data for the other complexes are obtained via first order calculations.

Code	Compound	Solvent	P_1			P_2			P_3			$^2J_{P_1-P_2}$	$^2J_{P_1-P_3}$	$^2J_{P_2-P_3}$
			δ_1	$^1J_{Rh-P}$	d	δ_2	$^1J_{Rh-P}$	d	δ_3	$^1J_{Rh-P}$	d			
IIIa	*fac* $Rh[Ph_2PC(S)NPh]_3$	$CDCl_3$[b,e]	−14.2	87.2	S									
IIIb	*mer* $Rh[Ph_2PC(S)NPh]_3$	$CDCl_3$[b,e]	−27.6	77.7	PPh_2	−28.8	79.3	PPh_2	−22.8	86.6	S	475 *trans*	22.5 *cis*	−6.0 *cis*
IVa	*fac* $Rh[Ph_2PC(S)NMe]_3$	$CDCl_3$[b]	−15.8	87.6	S									
IVb	*mer* $Rh[Ph_2PC(S)NMe]_3$	$CDCl_3$[b]	−30.2	78.5	PPh_2	−31.1	78.0	PPh_2	−24.2	84.8	S	470 *trans*	22.2 *cis*	−4.5 *cis*
VII	$\{RhCl[Ph_2PC(S)NPh]_2\}_2$	$CDCl_3$[a]	−17.2	98.9										
VIII	$\{RhCl[Ph_2PC(S)NMe]_2\}_2$	CD_2Cl_2[a]	−19.9	99.0										
IX	$Rh[Ph_2PC(S)NPh]_2[Me_2NC(S)NPh]$[c]	$CDCl_2$[a]	−17.3	87.9	S	−15.5	92.8	S				3.7 *cis*		
XI	$Rh[Ph_2PC(S)NPh][Et_2NC(S)S]_2$	CD_2Cl_2[a]	−11.2	94.6	S									
XII	$Rh[Ph_2PC(S)NPh][Me_2NC(S)S][Me_2NCS]$	CD_2Cl_2[a]	−13.2	93.4	S									
XIII	$Rh[Ph_2PC(S)NPh][Me_2NC(S)NPh][Me_2NCS]$	CD_2Cl_2[a]	−17.6	94.0	S									
Ref. [8]	$Rh[Ph_2PC(S)NPh][Me_2NCS]Cl(PPh_3)$	CD_2Cl_2[a]	−28.8 PPh_2	73.0	PPh_3	−19.8 PPh_3	101	PPh_2				518 *trans*		
XVIa	*fac* $Ir[Ph_2PC(S)NPh]_3$	$CDCL_3$[b]	−20.7											
XVIIb	*mer* $Ir[Ph_2PC(S)NPh]_3$	$CDCL_3$[b]	−25.4			−25.4			−23.9				15.0	15.0

[a]Recorded on a Bruker WH 90 spectrometer at 36.44 MHz. [b]Recorded on a Varian SC 300 spectrometer at 121 MHz. [c]The isomer, the parameters of which are given, is about 70% of the total intensity. [d]Group *trans*. [e]Measured at +11 °C.

like the Bailar twist seem to be most improbable because of steric hindrance.

– The positions (syn or anti) of the Ph or Me substituents, attached to the exocyclic N atoms (to be discussed below) have no observable influence upon the shape of the NMR signals.

The difference between the spectra, recorded at various temperatures cannot be explained in terms of a chemical process or isomerisation. The temperature dependence of some of the NMR parameters is possibly caused by the occurrence of relatively small changes within the molecule (distances, angles). An unambiguous trend in the temperature effect of the parameters (except those for δ_A and δ_B) is not observed.

Attempts to gain more information concerning the $^2J(A-B)_{trans}$ values by studying the spectra of the analogous Ir-complex failed. The $^{31}P\{^1H\}$ NMR spectrum of this complex likewise revealed the existence of a *fac* and a *mer* isomer, which do not undergo interconversion. However, the temperature dependent behaviour differs from that of the Rh-analogue.

The measured NMR parameters of $Rh[Ph_2PC(S)NR]_3$ are in the range as reported before [2, 3]. Predominantly the *trans* atom influences δ and

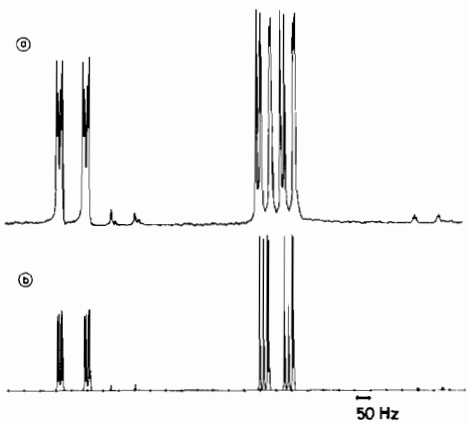

Fig. 9. $^{31}P\{^1H\}$ NMR spectrum of *mer* $Rh[Ph_2PC(S)NPh]_3$ at 121 MHz. *a* Measured at 11 °C in $CDCl_3$; *b* Simulated for an ABXRh pattern (see text).

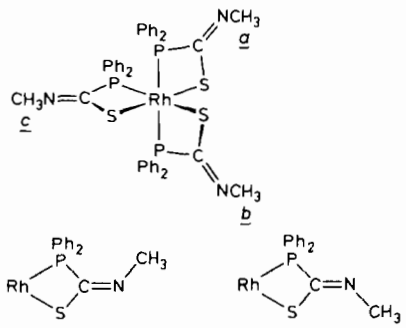

Fig. 10. *Mer* $Rh[Ph_2PC(S)NMe]_3$. *Syn* and *anti* positions of CH_3 group.

$^1J(Rh-P)$ as observed earlier [2]. When sulfur is the *trans* atom, δ varies from 14.2 to 24.2 ppm and $^1J(Rh-P)$ from 84.8 to 87.2 Hz. In the case of a *trans* Ph_2P-group, δ varies from 27.6 to 31.1 ppm and $^1J(Rh-P)$ from 77.7 to 79.3 Hz. The large $^2J(P_A-P_B)_{trans}$ coupling amounts to about 475 Hz.

The methyl groups in *mer* $Rh[Ph_2PC(S)NMe]_3$ can take *syn* or *anti* positions towards phosphorus. (See Fig. 10). When free rotation about the C–N bond is hindered, and there is no pronounced preference for one of the positions, the three different CH_3-groups give rise to eight conformational isomers, which would cause 24 lines in the ^1H NMR spectrum. However, two of the CH_3-groups will be nearly equivalent (a and b), which means a reduction to 14 lines. The actual NMR spectrum shows 13 lines. Even at 57 °C no line-broadening or change in signal multiplicity is observed. Therefore, free C–N rotation does not occur, confirming considerable π-electron density in the C–N bond.

$\{RhCl[X-C(Z)-Y]_2\}_2$

The dimeric species $\{RhCl]X-C(Z)-Y]_2\}_2$ show ligand adsorptions in the IR, comparable with those of the analogous tris complexes. ν(M–Cl) could not be assigned. In the ^{31}P NMR spectrum of VII and VIII δ is about 20 ppm and $^1J(Rh-P)$ amounts to 99.0 Hz, for the principal isomer (±60%), for which the structures are not yet clear. Mol. weights could not be determined because of the insufficient solubilities.

Mixed tris-complexes

For the complexes X, XIV and XV only the IR spectra have been recorded (see Table II). Several isomers are present. No assignments have been made.

The ^1H NMR and the ^{31}P NMR spectrum of IX indicate that also for this compound a number of geometrical isomers occurs. The principal isomer (about 70%) has δ_{Me} at 2.59 ppm (s) and $\delta(P_1)$ and $\delta(P_2)$ at about 17 ppm with $^1J(Rh-P_1)$ and $^1J(Rh-P_2)$ of nearly 90 Hz and $^2J(P_1-P_2)$ of 3.7 Hz. We cannot discriminate between P_1 and P_2. The phosphino groups take *cis*- positions to each other and have sulfur as *trans* ligands. (See Fig. 11).

For the complexes XI, XII and XIII, each having one Ph_2P-group, only one geometrical isomer occurs. δ_P varies from 11.2 to 17.6 ppm and $^1J(Rh-P)$ from 93.4 to 94.6 Hz. In these complexes the atom *trans* to phosphorus is always sulfur. The ^1H NMR spectra of compounds XI–XIII provide information concerning rotation about the exocyclic C–N bond. Like in $Rh[Me_2NC(S)NPh]_3$ free rotation takes place for the ligand $[Me_2NC(S)NPh]^-$, even at low temperature, but for the ligand $[Me_2NC(S)S]^-$ only at circa 50 °C. The ligand $[Me_2NCS]^-$ does not yet exhibit this

behaviour at 50 °C. The ^{1}H NMR and the IR ($\nu_{C=N}$ is about 1590 cm^{-1}) point out, that the $[Me_2NCS]^-$ entity is η^2 coordinated [10].

The probable structures of XI–XIII are given in Fig. 12.

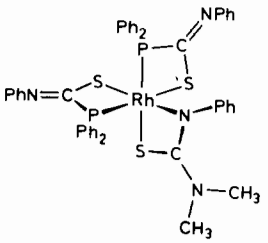

Fig. 11. The structure of $Rh[Ph_2PC(S)NPh]_2[Me_2NC(S)NPh]$, IX.

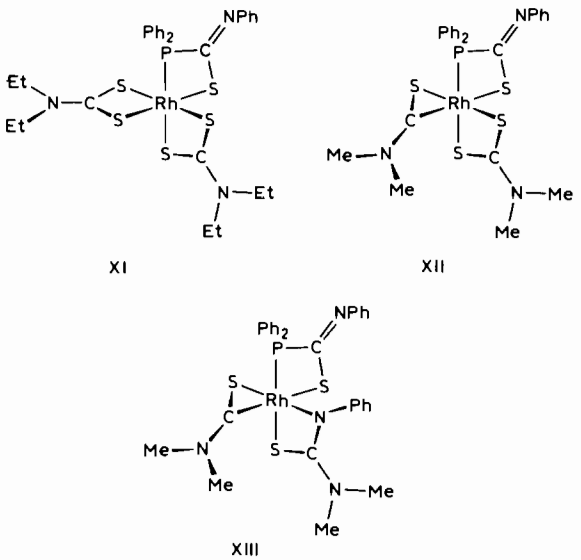

Fig. 12. The structure of XI. Possible structures of XII and XIII.

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