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THE CHEMISTRY OF HETERO-ALLENE AND -ALLYLIC DERIVATIVES WITH RHODIUM

I. THE REACTION OF RHODIUM(I)-HETERO-ALLYLIC COMPOUNDS WITH HETERO-ALLENES; A. ISOTHIOCYANATES [1]

D.H.M.W. THEWISSEN * and H.L.M. VAN GAAL

Department of Inorganic Chemistry Catholic University, Toernooiveld, 6525 ED Nijmegen (The Netherlands)

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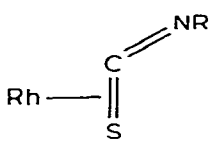
Summary

The reaction of the rhodium(I) complexes $Rh[X—C(Z)—Y](PPh_3)_2$, in which $[X—C(Z)—Y]^-$ is an unsaturated hetero-allylic chelate coordinating via two of the three hetero atoms (X, Y, Z = N, P or S), with an excess of the hetero-allene molecule R—N=C=S (R = Ph, Me) leads to the formation of the isocyanide—dithiocarbonimidato complexes $Rh[X—C(Z)—Y](RNC)(RNCS_2)(PPh_3)_2$ by disproportionation of the isothiocyanates. Evidence is presented that this disproportionation reaction proceeds in three consecutive steps. Initially a cumulene molecule is coordinated side-on by the C=S double bond to Rh. This is followed by attack of the carbon atom of a second hetero-allene at the endocyclic nucleophile of the moiety



i.e., sulphur, which results in an immediate template dimerisation of the isothiocyanates. In the subsequent step elimination of CNR occurs, leading to the final rhodium(III)—isocyanide—dithiocarbonimidato complexes. The Rh(III)-$(RNC)(RNCS_2)$ complexes react with PPh_3 by sulfur abstraction from $(RNCS_2)^{2-}$, resulting in $Rh[X—C(Z)—Y](RNC)(PPh_3)$, which is readily oxygenated to $Rh[X—C(Z)—Y](RNC)(PPh_3)(O_2)$.

Introduction

The chemistry of hetero-allenes X′=C=Y′ (X′, Y′ = S, NR, O or CR_2) with transition metals has been the subject of several investigations. Often the

hetero-allene molecule is bonded via an η^1-coordination of one of the hetero atoms [2—4]. Insertion into a M—L bond (L = H, R, SR, PR_2, NR_2, PR_3, halide etc.) may give pseudo-allylic derivatives [2—10]. With low-valent metal complexes, η^2-(side on) coordination occurs. This mode of coordination is fairly easily realised for the C=S fragment of the heterocumulene [2,11—13].

In this paper the reaction of rhodium(I)—hetero-allylic chelate complexes $Rh[X—C(Z)—Y](PPh_3)_2$ with an excess of R—N=C=S (R = Ph, Me) is described. Their reaction with CS_2 will be reported later [19].

In 1967 it was reported [13] that the reaction of CS_2 and of RNCS with $RhCl(PPh_3)_3$ leads to $RhCl(\sigma\text{-}CS_2)(\pi\text{-}CS_2)(PPh_3)_2$ (A) and $RhCl(\sigma\text{-}RNCS)(\pi\text{-}RNCS)(PPh_3)_2$ (B), respectively. Recently Powell et al. [14] investigated the latter reaction. They obtained rhodium(III)—isonitrile—dithiocarbonimidato complexes and reformulated complex (B) as $RhCl(RNC)(RNCS_2)(PPh_3)_2$. They also studied the reaction of RNCS with $Ru(CO)_2(PPh_3)_3$ in which ruthenium(II)—isonitrile—dithiocarbonimidato complexes were formed. Earlier, the dithiocarbonimidato complex $Pt(RNCS_2)(PPh_3)_2$ (R = Ph, Me) was obtained as the major product in the reaction of $Pt(PPh_3)_4$ or $Pt(\pi\text{-}RNCS)(PPh_3)_2$ with excess RNCS [15]. Itoh et al. [16,18] isolated the complex $Pd[EtC(O)NCS_2](PPh_3)_2$ from the reaction of $Pd(PPh_3)_4$ with EtC(O)NCS. $RhCl(PPh_3)_3$ was found to react with two molecules PhC(O)NCS [17] and three molecules EtOC(O)NCS [18]. The X-ray structure of the resulting complexes were determined. The reaction of anionic Mn—carbonyl complexes with RNCS were described by Knox et al. [40].

Similar reactions were reported of NR and O containing heterocumulenes. Dimerisation of CO_2 [20] and of $Ph_2C=C=O$ [21,22] to chelating ligands and catalytic trimerisation of isocyanates [23] were published. The reactions of PhNCO with iron—carbonyl complexes [24,25] and $Pd(PPh_3)_4$ and $RhCl(PPh_3)_3$ [26] gave deprotonated urea $[RNC(O)NR]^{2-}$ derivates, whereas $Fe(CO)_5$ and RNCNR reacted to give deprotonated guanidine compounds $[RNC(NR)NR]^{2-}$ [27].

Experimental

IR spectra were measured on a Perkin—Elmer 283 spectrophotometer (4000—200 cm^{-1}). $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL 100-FT spectrometer at 40.5 MHz, using the deuterated solvent as internal lock. Solutions for NMR measurements were prepared in a glove-box. C, H and N analyses were carried out at the Microanalytical Department of this University; other analyses and molecular weight determinations were performed by Prof. Dr. H. Malissa, Mikroanalytisches Laboratorium, Elbach über Engelskirchen, G.F.R. Analytical data are given in Table 1.

Reactions were carried out in analytical grade solvents under nitrogen. $RhCl(PPh_3)_3$ [28] and $Rh[X—C(Z)—Y](PPh_3)_2$ [29,30] were prepared according to literature procedures.

$RhCl(PhNC)(PhNCS_2)(PPh_3)_2$ (Ia)

This complex was prepared as described by Powell et al. [15].

$RhCl(MeNC)(MeNCS_2)(PPh_3)_2$ (Ib)

The procedure followed was analogous to that for Ia. MeNCS was used in excess. Yield: 70%.

$Rh[SC(S)NEt_2](RNC)(RNCS_2)(PPh_3)$ (IIa: R = Ph; IIb: R = Me)

An excess of oxygen-free RNCS was added to a solution of 300 mg $Rh[SC(S)NEt_2](PPh_3)_2$ in 50 ml benzene. The mixture was stirred and heated at 60°C for 2 h. After cooling to room temperature, n-hexane was added and the orange precipitate filtered off, washed with ethanol and diethyl ether, and dried under vacuum. Yield: IIa, 60%; IIb, 70%. Mol. wt. IIa in acetone: found, 806; calcd., 783.

$Rh[PhNC(S)NMe_2](RNC)(RNCS_2)(PPh_3)$ (IIIa: R = Ph; IIIb: R = Me)

An excess of RNCS was added to a solution of 300 mg $Rh[PhNC(S)NMe_2](PPh_3)_2$ in 50 ml benzene or toluene. The mixture was heated at 60°C for 2 h. The orange complex was precipitated with n-hexane, washed with ethanol and diethyl ether and dried under vacuum. Yield: IIIa, 75%; IIIb, 70%.

$Rh[Ph_2PC(S)NPh](PhNC)(PhNCS_2)(PPh_3)$ (IVa: R = Ph; IVb: R = Me)

A mixture containing 300 mg $Rh[Ph_2PC(S)NPh](PPh_3)_2$, excess RNCS and 50 ml benzene or toluene was heated at 60°C during 3 h. After precipitation with n-hexane, the yellow complex was washed with ethanol and diethyl ether and dried in vacuo. Yield: IVa, 45%; IVb, 40%.

$Rh[Ph_2P(S)C(S)NPh](PhNC)(PhNCS_2)(PPh_3)$ (Va)

300 mg $Rh[Ph_2P(S)C(S)NPh](PPh_3)_2$ was dissolved in 50 ml toluene and an excess of PhNCS was added. After heating the mixture for 3 h at 60°C, the complex was precipitated with n-hexane, washed with ethanol and diethyl ether, and dried in vacuo. Yield: 50%.

$RhCl(PhNC)(PPh_3)_2(O_2)$ (VIa)

200 mg of complex Ia was dissolved in toluene and an excess of PPh_3 was added. The mixture was refluxed for 2 h. The brown product was precipitated with n-hexane and washed with diethyl ether. Yield: 70%.

Results

Reactions and products

The starting compounds are rhodium(I) complexes of the type $Rh[X—C(Z)—Y](PPh_3)_2$. $[X—C(Z)—Y]^-$ represents a uninegative bidentate ligand (Fig. 1), in which three hetero atoms, X, Y and Z, are bonded to the central carbon atom. These ligands are often termed pseudo- or hetero-allyls, because of their electronic resemblance to the allylic anion [31].

The rhodium(I) complexes were reported previously [1,29]. On treating the rhodium(I) complexes with an excess of RNCS (R = Ph, Me) we obtained the rhodium(III)—isocyanide—dithiocarbonimidato complexes shown in Fig. 2.

IR spectra

The IR spectra of the orange air-stable complexes I—V exhibit absorptions

TABLE 1

ANALYTICAL DATA

Calculated values in parentheses

Code	Compound	C (%)	H (%)	N (%)	S (%)	Colour
Ia	$RhCl(PhNC)(PhNCS_2)(PPh_3)_2$	63,8	4,4	2,8		orange
		(64,3)	(4,3)	(3,0)		
Ib	$RhCl(MeNC)(MeNCS_2)(PPh_3)_2$	59,5	4,5	3,5		yellow-orange
		(59,4)	(4,1)	(3,5)		
IIa	$Rh[SC(S)NEt_2](PhNC)(PhNCS_2)(PPh_3)$	56,7	4,7	5,5		orange-red
		(56,7)	(4,5)	(5,4)		
IIb	$Rh[SC(S)NEt_2](MeNC)(MeNCS_2](PPh_3)$	48,9	4,7	6,1		yellow-orange
		(49,2)	(4,5)	(6,4)		
IIIa	$Rh[PhNC(S)NMe_2](PhNC)(PhNCS_2)(PPh_3)$	60,3	4,7	6,6	11,7	orange
		(60,4)	(4,5)	(6,9)	(11,8)	
IIIb	$Rh[PhNC(S)NMe_2](MeNC)(MeNCS_2)(PPh_3)$	54,1	4,7	7,6		yellow
		(53,9)	(4,7)	(8,1)		
IVa	$Rh[Ph_2PC(S)NPh](PhNC)(PhNCS_2)(PPh_3)$	63,2	4,7	4,3		yellow-orange
		(64,1)	(4,2)	(4,4)		
IVb	$Rh[Ph_2PC(S)NPh](MeNC)(MeNCS_2)(PPh_3)$	57,2	4,3	4,9		yellow
		(59,2)	(4,4)	(5,1)		
Va	$Rh[Ph_2P(S)C(S)NPh](PhNC)(PhNCS_2)(PPh_3)$	60,3	4,1	4,0		orange-red
		(62,0)	(4,1)	(4,3)		
VIa	$RhCl(PhNC)(PPh_3)_2(O_2)$	63,5	4,6	1,9		brown
		(64,7)	(4,4)	(1,8)		

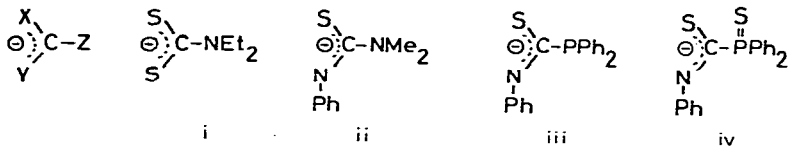


Fig. 1 The unsaturated hetero-allylic chelating ligands i to iv.

in the region 2230—2130 cm^{-1} attributed to ν(C≡N) of the coordinated isocyanide and 1578—1537 cm^{-1} and 927—915 cm^{-1} assigned to ν(C=N) and ν(C⋯S), respectively, of the bidentate dithiocarbonimidato ligand. The ν(C=N) values for the $(RNCS_2)^{2-}$ ligands of the complexes I—V are similar to the ν(C=N) values of $(RNCS_2)^{2-}$ found for the complexes $RhCl(RNC)(RNCS_2)(PPh_3)_2$, [14], $Pt(RNCS_2)(PPh_3)_2$ [15] and $Ru(CO)(RNC)(RNCS_2)(PPh_3)_2$ [14]. The C⋯S absorption is 30—40 cm^{-1} lower than in the complexes of analogous *N*-cyano-carbimato ligands $[NC—N=CS_2]^{2-}$ [32,33].

The stretching vibration frequency of the exocyclic C⋯N of the chelating hetero-allylic ligand does not differ significantly between the rhodium(III) complexes and the rhodium(I) starting compounds. This indicates that the mode of coordination of the ambidentate ligands in the rhodium(I) compounds remains unchanged in the rhodium(III) complexes. The most important IR absorptions are shown in Table 2.

^{31}P $\{^1H\}$ *NMR spectra*

The values of the parameters of the recorded ^{31}P $\{^1H\}$ NMR spectra are summarised in Table 3. For solubility reasons not all spectra could be measured.

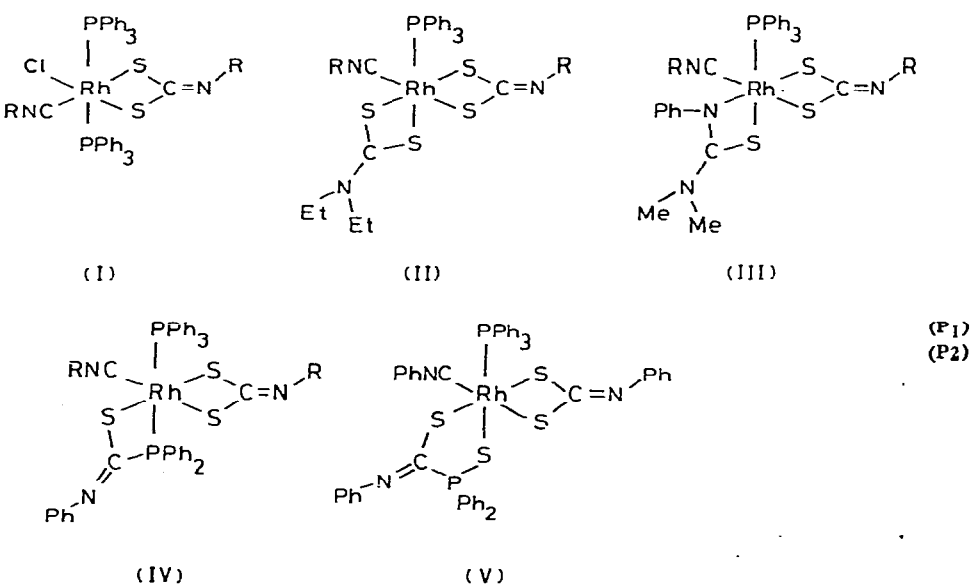


Fig. 2 Probable structures of the rhodium(III) complexes (R = Ph, Me).

TABLE 2

IR ABSORPTIONS (cm^{-1})

All spectra measured in CsI pellets

Code	Compound	(RNC)	$(RNCS_2)^{2-}$		$[X-C(Z)-Y]^-$
		ν(C≡N)	ν(C=N)	ν(C⋯S)	ν(C=N)
Ia	$RhCl(PhNC)(PhNCS_2)(PPh_3)_2$	2165s	1557vs	927w	
Ib	$RhCl(MeNC)(MeNCS_2)(PPh_3)_2$	2230s	1560vs	n.o.	
IIa	$Rh[SC(S)NEt_2](PhNC)(PhNCS_2)(PPh_3)$	2152s	1537vs	915m	1497vs
IIb	$Rh[SC(S)NEt_2](MeNC)(MeNCS_2)(PPh_3)$	2215s	1578vs	915w	1493vs
IIIa	$Rh[PhNC(S)NMe_2](PhNC)(PhNCS_2)(PPh_3)$	2154s	1555(sh)	927m	1535vs
IIIb	$Rh[PhNC(S)NMe_2](MeNC)(MeNCS_2)(PPh_3)$	2210s	1572(sh)	923w	1535vs
IVa	$Rh[Ph_2PC(S)NPh](PhNC)(PhNCS_2)(PPh_3)$	2163s	1550vs	927m	1563(sh)
IVb	$Rh[Ph_2PC(S)NPh](MeNC)(MeNCS_2)(PPh_3)$	2217s	1570(sh)	924m	1552vs
Va	$Rh[Ph_2P(S)C(S)NPh](PhNC)(PhNCS_2)(PPh_3)$	2130s	1545(sh)	921m	1566vs

The ^1J(Rh—P) values of 89—115 Hz for PPh_3 and of 64 and 70 Hz for $[Ph_2PC(S)NPh]^-$ are consistent with a six-coordination of the rhodium [39]. In Ia the two PPh_3 groups are in transposition to each other. The spectrum of IIb indicates that there exist two isomers. In the spectrum of IVa the value of $^2J(P_1—P_2)$ (518 Hz) points to a *trans* configuration of the phosphine ligands. In Va the PPh_3 and $—SPPh_2$ groups are *trans* ligands, as is indicated by the value of $^3J(P_1—P_2)$ (9 Hz). This value is almost the same as that of $^3J(P_1—P_3)$-*trans* in $Rh[Ph_2P(S)C(S)NPh](PPh_3)_2$, the structure of which has been established on other grounds (to be published).

The reactivity of some rhodium(III)—isocyanide—dithiocarbonimidato complexes towards PPh_3

The $(RNCS_2)^{2-}$ fragment is susceptible to sulphur abstraction by phosphine. Powell et al. [14] obtained $SPPh_3$ and $RhCl(PhNC)(PPh_3)_2$ from the reaction of PPh_3 with $RhCl(PhNC)(PhNCS_2)(PPh_3)_2$, which points to the formation of PhNCS.

We treated the rhodium(III)—isocyanide—dithiocarbonimidato complexes Ia and IVb with excess PPh_3 in refluxing toluene, and observed the formation of

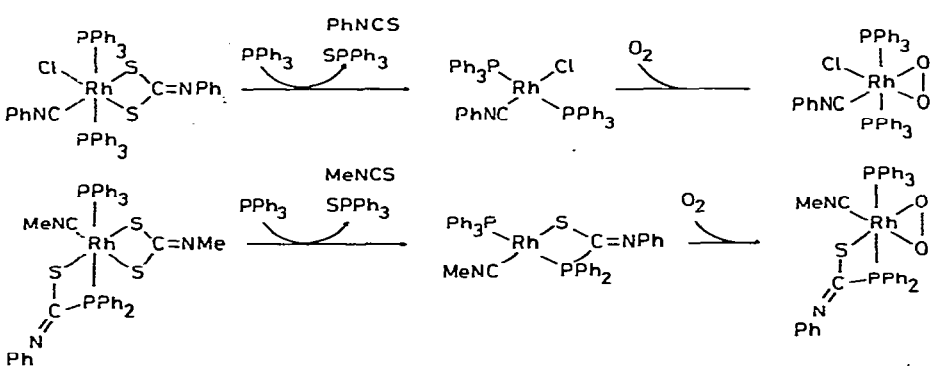


Fig. 3 Sulphur abstraction reaction by PPh_3, followed by uptake of a dioxygen molecule.

TABLE 3. ^{31}P $\{^1H\}$ NMR PARAMETERS OF Rh(RNC)(RNCS$_2$) COMPLEXES

δ in ppm relative to O=P(OMe)$_3$ (TMP), internal reference; upfield = +; J in Hz. *All* spectra were recorded in CD_2Cl_2, the spectrum of Rh[$Ph_2P(S)C(S)NPh$]-(PPh_3)$_2$ was measured in C_6D_6.

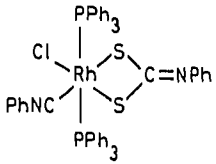
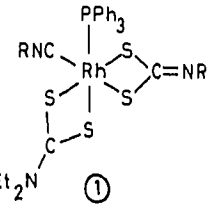
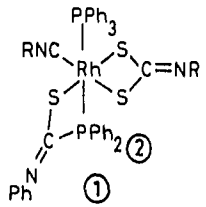
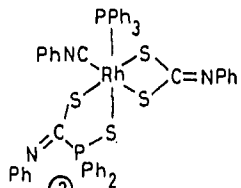
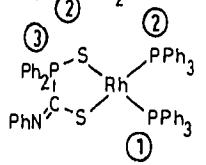
Code	Complex	PPh_3			$-PPh_2/-SPPh_2$		
		δ	^1J(Rh—P)	Group *trans*	δ	^1J(Rh—P)	$^nJ(P_i—P_j)$
Ia		−11.2	91	PPh_3			
IIa, R = Ph		−28.6	101				
IIb, R = Me		−33.8 −28.0	113 115				
IVa, R = Ph		−24.3	89	$-PPh_2$	+24.0	70	518 $^2J(P_1—P_2)$
IVb, R = Me		−24.5	87	$-PPh_2$	+21.8	64	480 $^2J(P_1—P_2)$
Va		−26.3	104	$-SPPh_2$	+8.0		9 $^3J(P_1—P_2)$
Ref. 30		−45.8 (P_1) −39.3 (P_2)	186 161	$-SPPh_2$ SC(NPh)—	−37.7		43 $^2J(P_1—P_2)$ *cis* 3 $^3J(P_1—P_3)$ *trans* 36 $^3J(P_2—P_3)$ *cis*

TABLE 4

IR ABSORPTIONS (cm^{-1})

All spectra were measured in C_6H_6 solution.

Code	Compound	(RNC)	(O_2)	$[X—C(Z)—Y]^-$
		ν(C≡N)	ν(O—O)	ν(C=N)
VII	$RhCl(PhNC)(PPh_3)_2$	2090s		
VIa	$RhCl(PhNC)(PPh_3)_2(O_2)$	2150s	891w—m	
VIII1	$Rh[Ph_2PC(S)NPh](MeNC)(PPh_3)$	2130s(br)		}1546vs
VIII2	$Rh[Ph_2PC(S)NPh](MeNC)(PPh_3)(O_2)$	2182s	n.o.	
VIII3	$Rh[Ph_2PC(S)NPh](PhCH_2NC)(PPh_3)$	2128s		}1550vs
VIII4	$Rh[Ph_2PC(S)NPh](PhCH_2NC)(PPh_3)(O_2)$	2184s	890w	

$RhCl(PhNC)(PPh_3)_2$ and $Rh[Ph_2PC(S)NPh](MeNC)(PPh_3)$ with liberation of RNCS. These complexes can be detected by an intense ν(C≡N), typical for rhodium(I)(RNC) complexes [37,38]. The formed rhodium(I)(RNC) complexes easily coordinate dioxygen, resulting in $RhCl(PhNC)(PPh_3)_2(O_2)$ and $Rh[Ph_2PC(S)NPh](MeNC)(PPh_3)(O_2)$. We have prepared $Rh[Ph_2PC(S)NPh](PhCH_2NC)(PPh_3)$ and $Rh[Ph_2PC(S)NPh](PhCH_2NC)(PPh_3)(O_2)$ by an independent route from $Rh[Ph_2PC(S)NPh](PPh_3)_2$ and $PhCH_2NC$ in benzene. The IR parameters of the compounds are given in Table 4.

A different behaviour, however, was observed with the complexes IIa and IIb. On refluxing these compounds with an excess of PPh_3 in toluene a substitution occurs, in which the coordinated isocyanide ligand is displaced by PPh_3. The dithiocarbonimidato ligand remains unaffected. The resulting compounds are not yet fully characterized.

Discussion

The reaction may proceed in three consecutive steps (Fig. 4).

(a) Initial step: uptake of one RNCS molecule to form an η^2-RNCS complex.

(b) Second step: uptake of another RNCS molecule followed by dimerisation of the two RNCS molecules.

(c) Final step: elimination of RNC to give the rhodium(III)—isocyanide—dithiocarbonimidato complex.

The overall reaction can be regarded as a disproportionation of the heterocumulene.

In the initial step $Rh[X—C(Z)—Y](PPh_3)_2$ takes up one molecule of RNCS to form a square planar rhodium(I) derivative (C) in which the heterocumulene molecule is coordinated side-on. Such four-coordinate Rh complexes with side-on coordinated hetero-allenes have been identified previously in the case of $RhCl(PCy_3)_2$(cumulene). The bulkiness of PCy_3 permits isolation of these intermediates [11]. We have found similar intermediates in the reaction of CS_2 with the rhodium(I) complexes $Rh[X—C(Z)—Y](PPh_3)_2$ of ligands $[X—C(Z)—Y]^-$ (i) to (iv) [19]. We did not observe such intermediates in the present reactions.

The complex (C) reacts rapidly in the second step with another molecule of RNCS leading to a dimerisation of the hetero-allene molecules at the rhodium

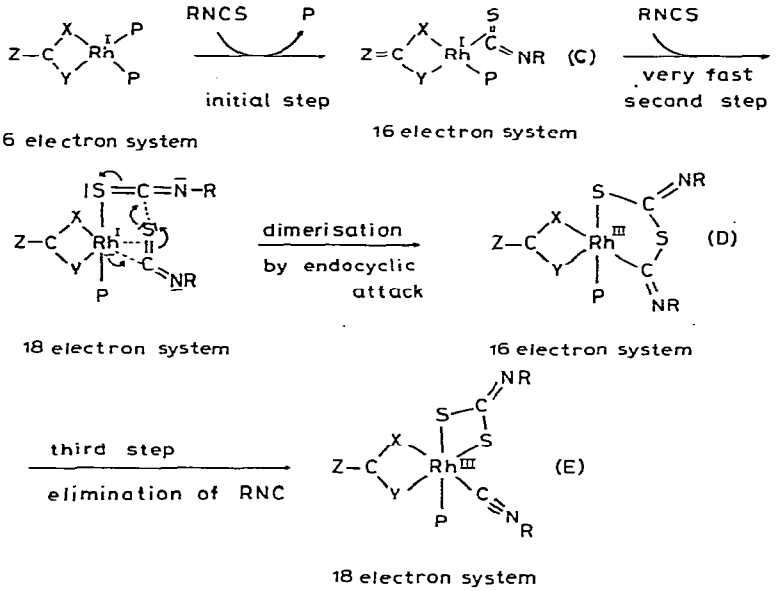


Fig. 4 The proposal scheme for the reaction between rhodium(I) complexes and RNCS molecules (R = Ph, Me).

Fig. 5.

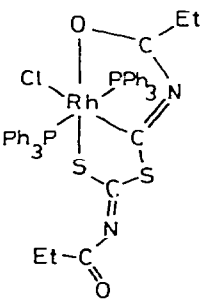


Fig. 5 The structure of $RhCl[EtC(O)NCS]_2(PPh_3)_2$.

center (D). This dimerisation may be seen as an electrophilic attack on the endocyclic nucleophile of the η^2-coordinated RNCS, i.e. sulphur, by the central carbon atom of the second molecule. Probably the second molecule is coordinated to Rh before the attack takes place, so that this reaction is a template process. This is supported by the behaviour of $RhCl(PCy_3)(RNCS)$. In this compound a second RNCS molecule cannot occupy a coordination site because of steric hindrance caused by the PCy_3 ligands, but it is expected to be able to approach an exposed coordinated sulphur atom. The bulky complex does not react, however, which favours a template mechanism for the dimerisation step. Examples of such compounds, in which the hetero-allenes are present as dimerised ligand, have been reported in the literature [20—22]. The complex $RhCl(PPh_3)_2[SCNC(O)R]_2$ is especially remarkable, as the Rh—SCSC five membered ring, postulated in (D), is stabilised by a chelate interaction of an acyl oxygen [17,34] (see Fig. 5). Seen from the metal this dimerisation is an oxidative coupling [35].

The final step is elimination of RNC (E), which can be regarded as a sulphur abstraction reaction, in which the sulphur is transferred from one RNCS molecule to another.

Note that in three stages of the reaction sulphur abstraction might occur: (a) From coordinated RNCS, during the disproportionation, by a second RNCS molecule; (b) from coordinated RNCS by PPh_3 [36]; (c) from coordinated $(RNCS_2)^{2-}$ by PPh_3. In the present reactions (a) and (c) have been observed, but not (b).

In the dimerisation an electrophilic attack on coordinated heterocumulenes

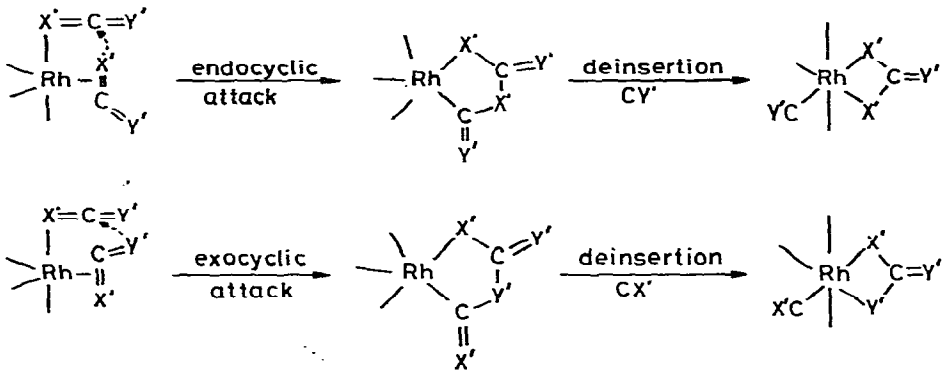


Fig. 6 Endocyclic and exocyclic attack pathways, and the complexes which result from two routes.

is postulated. This electrophilic attack appears to take place on the endocyclic, not the exocyclic nucleophile. Which atom is endocyclic may be deduced from the preference for side-on coordination in X'=C=Y'. This order is now established to be (X' > Y') : S > NR > O > CR_2. In Fig. 6 the endocyclic and exocyclic pathways of the formation of five membered rings by dimerisation of the hetero-allenes, as well as the resulting complexes after elimination are given.

Conclusion

All complexes reported to be formed by dimerisation of hetero-allenes have five-membered rings of the type M—X'C(Y')X'C=Y', resulting from an endocyclic attack, and the ligands formed by elimination of CY' are of the type $(X'_2C{=}Y')^{2-}$, in which C=X' is preferred over C=Y' for η^2-coordination. In agreement with this, the liberated CY' always contains the hetero atom which is less prone to η^2-coordination.

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