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THE COORDINATION OF HETEROCUMULENES AND OTHER UNSATURATED MOLECULES TO $RhCl(P(C_6H_{11})_3)_2$

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Summary

$RhCl(PCy_3)_2$ (Cy = cyclohexyl) forms four-coordinated addition complexes with CS_2, COS, RNCS (R = methyl, allyl, phenyl and *p*-tolyl) in which the heterocumulene is side-on coordinated by S and C; and with *N,N'*-di-*p*-tolyl carbodiimide (TolNCNTol) and PhNCO, in which the heterocumulene is side-on coordinated by N and C. EtNCO and CO_2 do not react with $RhCl(PCy_3)_2$. $IrCl(PCy_3)_2(CS_2)$ and $IrCl(PCy_3)_2(PhNCS)$ are also described. By sulfur-abstraction from the CS_2-complexes $MCl(PCy_3)_2(CS)$ (M = Rh, Ir) is formed. Addition complexes of $RhCl(PCy_3)_2$ with acetylenes RC≡CR (R = phenyl, ethyl, H), SO_2 and nitrosobenzene are also described. $RhCl(PCy_3)_2(PhNO)$ contains an end-on coordinated nitrosobenzene. The ^{31}P NMR spectra of the various addition complexes show a Rh—P coupling constant which correlates with the π-acceptor properties of the added molecule.

Introduction

Heterocumulenes or pseudo-allenes (X=C=Y (X, Y = S, NR, O) and related compounds) have interesting bonding and reactivity properties as ligands. Often coordination occurs by the lone pair of the hetero-atom, resulting in h^1-coordination [1—3]. Insertion into a M—Z bond (Z = H, R, SR, halide etc.) may lead to a pseudo-allyl ligand [1—5]. Worth mentioning is the recent structure report of $[Ir(S_2CPPh_3)(PPh_3)_2(CO)]BF_4$ which revealed that a PPh_3 ligand had migrated to the carbon atom of the CS_2, resulting in the zwitterionic ligand $Ph_3P^+—CS_2^-$ [6]. Dimerisation of CO_2 to a chelating ligand [7] and catalytic trimerisation of isocyanates have also been reported [8]. With low-valent metal complexes, h^2-(side-on) coordination by one of the double bonds may occur. This mode of coordination is fairly easily realised for the C=S fragment of the heterocumulene [1,9], but relatively rare for C=N and C=O fragments. Examples of the latter two include h^2-coordination of azaallene $R_2C=N=CR_2$ to molybdenum (0) [10], of ketenimine $RN=C=CR_2$ to nickel (0) [11], iron (0) and cobalt (I) [12], of diphenylketene $Ph_2C=C=O$ to platinum (0) [13] and of carbon dioxide to nickel (0) [14], molybdenum (0) [15], rhodium (I) [16] and iridium (I) [7,16] complexes. Acyl isocyanates $RC(O)N=C=O$ have been found to coordinate either side-on or chelating to rhodium (I) [17,18] and iridium (I) [18,19].

The three-coordinated 14-electron complex $RhCl(PCy_3)_2$ [20] is a compound with a paradoxical reactivity. On the one hand, compared to $RhCl(PPh_3)_2$ and $[RhCl(PPh_3)_2]_2$ [21] it has by the absence of a fourth ligand an enhanced reactivity. This is demonstrated by its spontaneous coordination of molecular nitrogen [20]. On the other hand, the presence of two bulky tricyclohexylphosphine ligands excludes the addition of other bulky ligands to $RhCl(PCy_3)_2$, and restricts the addition of further ligands as soon as a 16-electron configuration has been achieved. This made it attractive to study the addition of heterocumulenes and other unsaturated molecules to $RhCl(PCy_3)_2$ and related compounds, which is the subject of this paper.

Experimental

IR spectra were measured on a Perkin—Elmer 257 spectrophotometer (4000—625 cm^{-1}) and a Hitachi EPI-L spectrophotometer (700—200 cm^{-1}) in KBr or CsI pellets. ^1H and ^{31}P NMR spectra were recorded on a Varian XL 100 spectrometer at 100 and 40.5 MHz. C, H and N analyses were carried out at the microanalytical department of this university; other analyses and molecular weight determinations by Dr. A. Bernhardt, Mikroanalytisches Lab., Elbach über Engelskirchen, Germany. Analytical data are given in Table 1.

Reactions were carried out under nitrogen at room temperature in analytical grade solvents. $[RhCl(C_8H_{14})_2]_2$ and $[IrCl(C_8H_{14})_2]_2$ were prepared as described in ref. 22, $RhCl(PCy_3)_2$ and $RhCl(PCy_3)_2L$ ($L = H_2$, O_2, C_2H_4, CO and N_2) as in ref. 20.

$RhCl(PCy_3)_2(S=C=X)$ ($X = S$, NPh, N(p-Tolyl), N-Allyl, NMe)

An excess of $S=C=X$ was added to a solution of 200 mg $RhH_2Cl(PCy_3)_2$ in 20 ml benzene. The solution was stirred for a few minutes and concentrated at reduced pressure to a small volume. Ethanol was added, and the precipitate was collected on a filter, washed with ethanol and dried under vacuum.

$RhCl(PCy_3)_2(S=C=O)$

SCO was passed through a solution of 200 mg $RhH_2Cl(PCy_3)_2$ for 30 sec. The solution was concentrated at reduced pressure, ethanol was added, the precipitate was filtered off, washed with ethanol and dried under vacuum.

$IrCl(PCy_3)_2(S=C=X)$ ($X = S$, NPh)

C_2H_4 was bubbled through a solution of 150 mg $[IrCl(C_8H_{14})_2]_2$ in 20 ml benzene, and 200 mg PCy_3 was added; the solution was stirred for 15 min and an excess of $S=C=X$ was added. The solution was stirred for another 5 min and concentrated at reduced pressure. Ethanol was added, the precipitate collected on a filter, washed with ethanol and dried under vacuum.

TABLE 1

ANALYTICAL DATA AND MOLECULAR WEIGHTS OF COMPLEXES (theoretical values in parentheses)

Compound	Colour	C (%)	H (%)	N (%)	S (%)	Mol. wt [a]	Decomp. temp. (°C)
$RhCl(PCy_3)_2(CS_2)$	ochre	57.3 (57.3)	8.65 (8.52)		7.57 (8.27)	810 (774)	235
$RhCl(PCy_3)_2(SCNMe)$	ochre	59.9 (59.1)	9.18 (9.01)	1.61 (1.81)		730 (772)	167
$RhCl(PCy_3)_2(SCNPh)$	ochre	61.1 (61.9)	8.45 (8.58)	1.72 (1.68)	3.63 (3.84)	830 (834)	140
$RhCl(PCy_3)_2(SCNTol)$	ochre	62.6 (62.3)	8.83 (8.67)	1.32 (1.65)			167
$RhCl(PCy_3)_2(SCNAllyl)$	ochre	59.6 (60.2)	9.00 (8.96)	1.87 (1.75)			146
$RhCl(PCy_3)_2(SCO)$	ochre	57.5 (58.5)	8.80 (8.76)				188
$IrCl(PCy_3)_2(CS_2)$	ochre	52.2 (51.4)	8.15 (7.69)		9.28 (7.42)		275
$IrCl(PCy_3)_2(SCNPh)$	ochre	54.7 (55.9)	8.15 (7.75)	1.66 (1.52)		1002 (924)	158
$RhCl(PCy_3)_2(CS)$	ochre	59.8 (59.8)	9.00 (8.95)		5.41 (4.31)	831 (743)	249
$RhCl(PCy_3)_2(PhNCO)$	yellow	63.1 (63.1)	8.91 (8.75)	1.73 (1.71)		817 (818)	172
$RhCl(PCy_3)_2(TolNCNTol)C_6H_6$	orange	68.2 (68.4)	9.17 (8.67)	2.72 (2.80)		940 (921)	164
$RhCl(PCy_3)_2(C_2Ph_2)$	yellow	67.7 (68.5)	8.2 (8.8)				
$RhCl(PCy_3)_2(C_2Et_2)$	yellow	63.7 (64.7)	9.6 (9.8)				
$RhCl(PCy_3)_2(C_2H_2)$	yellow	63.9 (62.9)	9.47 (9.45)				216
$RhCl(PCy_3)_2(SO_2)$	brown	57.2 (56.7)	8.92 (8.72)		4.09 (4.20)	711 (763)	192
$RhCl(PCy_3)_2(PhNO)$	yellow	63.5 (62.6)	8.87 (8.88)	1.63 (1.74)			153

[a] Osmometric in benzene.

$MCl(PCy_3)_2(CS)$ (M = Rh, Ir)

200 mg $MCl(PCy_3)_2(CS_2)$ and 80 mg PCy_3 in 20 ml benzene were stirred for 24 h. Ether was added, which precipitated $SPCy_3$. The solution was filtered, and hexane was added to the filtrate. The second precipitate was collected on a filter, washed with hexane and dried under vacuum.

$RhCl(PCy_3)_2(PhNCO)$

170 mg $[RhCl(C_8H_{14})_2]_2$ and 250 mg PCy_3 were stirred in 10 ml benzene for 45 min. Excess PhNCO was added. The solution was concentrated at reduced pressure, ethanol was added, the precipitate was filtered off, washed with ethanol and dried under vacuum. The compound has to be stored in the dark.

$RhCl(PCy_3)_2(TolNCNTol)$ (Tol = p-tolyl)

A freshly prepared portion of $RhCl(PCy_3)_2$ was dissolved in benzene (ca. 150 mg in 5 ml). Excess *N,N'*-di-*p*-tolyl carbodiimide was added and the solution stirred for 5 min. Ethanol was added, the precipitate was collected on a filter, washed with ethanol and dried under vacuum.

Attempted reaction of $RhCl(PCy_3)_2$ with CO_2 and EtNCO respectively

A freshly prepared portion of $RhCl(PCy_3)_2$ (ca. 150 mg) was dissolved in 5 ml benzene. The solution was saturated with CO_2, or, in the second case, had an excess of EtNCO added. The lilac color of $RhCl(PCy_3)_2$ persisted. When the solution was stirred for some days, $RhCl_2(PCy_3)_2$, the decomposition product of $RhCl(PCy_3)_2$ [20], was obtained.

$RhCl(PCy_3)_2(C_2Ph_2)$, $RhCl(PCy_3)_2(C_2Et_2)$ and $RhCl(PCy_3)_2(SO_2)$

These compounds were prepared similarly to $RhCl(PCy_3)_2(PhNCO)$; SO_2 was passed through the solution for about 30 sec.

$RhCl(PCy_3)_2(C_2H_2)$ and $RhCl(PCy_3)_2(PhNO)$

These compounds were prepared similarly to $RhCl(PCy_3)_2(TolNCNTol)$; C_2H_2 was passed through the solution for not longer than 1 min, and the work-up time was kept to a minimum. The compounds have to be stored under nitrogen at $-20°C$.

Results and discussion

Synthetic methods

Most addition complexes $RhCl(PCy_3)_2L$ with L = various ligands can be prepared by simple addition to $RhCl(PCy_3)_2$. Adducts with L = phenyl isocyanate, sulfur dioxide, tolane (= diphenylacetylene) and 3-hexyne may also be prepared using solutions of $[RhCl(C_8H_{14})_2]_2$ and the required equivalents of PCy_3, aged for one hour. In such a solution, the equilibrium $RhCl(PCy_3)_2(C_8H_{14}) \rightleftharpoons RhCl(PCy_3)_2 + C_8H_{14}$ lies to the left [20b]. Cyclooctene has to be removed for the reaction of $RhCl(PCy_3)_2$ with *N,N'*-di-*p*-tolyl carbodiimide, nitrosobenzene and acetylene, whereas even under these conditions ethyl isocyanate and carbon dioxide do not react.

With S=C-containing heterocumulenes, the adducts cannot be prepared by the above-mentioned method of direct addition to $RhCl(PCy_3)_2$. These reactions result in destruction of the heterocumulene. The dihydrido complex $RhH_2Cl(PCy_3)_2$, however, reacts smoothly with S=C=X ligands (X = S, O, NR) under formation of the adducts $RhCl(PCy_3)_2(SCX)$ and hydrogen replacement.

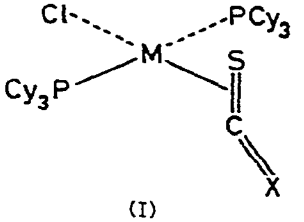
The reaction of $[IrCl(C_8H_{14})_2]_2$ [22] with PCy_3 leads to the formation of an oily product. $IrCl(C_2H_4)_4$ [24] gives with PCy_3 an orange solution, from which impure $IrCl(PCy_3)_2(C_2H_4)$ can be isolated. The solution reacts with carbon disulfide, carbonyl sulfide and phenyl isocyanate, but not with methyl and allyl isocyanate. The iridium—tricyclohexylphosphine system has not been investigated further.

S=C=X heterocumulenes (X = S, NR, O)

S=C=X heterocumulenes rapidly displace H_2 from $RhH_2Cl(PCy_3)_2$ to form the complexes $RhCl(PCy_3)_2(SCX)$ (X = S, NR, or O). $IrCl(PCy_3)_2(SCX)$ (X = S, NPh) has been obtained similarly from $IrCl(PCy_3)_2(C_2H_4)$ and S=C=X. In contrast with $RhCl(PPh_3)_3$ [9] two S=C=X molecules never coordinate to $RhCl(PCy_3)_2$.

The complexes are monomeric in benzene. The ^{31}P NMR spectra of the rhodium complexes (Table 2) all show a doublet arising from coupling of two equivalent phosphorus atoms with rhodium ($I = \frac{1}{2}$), which indicate square planar structures with *trans*-phosphines.

All complexes show IR absorptions (Table 3) characteristic for side-on C=S coordination [1] (I): one band between 603 and 649 cm^{-1}, which we attribute to a  ring vibration with $\nu(M—C)$ and $\nu(C—S)$ character, and another one between 275 and 292 cm^{-1}, which we attribute to a $\nu(M—S)$ vibration. $\nu(M—Cl)$ is found between 314 and 335 cm^{-1}.



(I)

M = Rh, X = S, O, NMe, N-Allyl, NPh, N(p-Tol); M = Ir, X = S, NPh.

$RhCl(PCy_3)_2(CS_2)$ shows $\nu(C=S)$ of the uncoordinated double bond at 1240 and 1186 cm^{-1}, and $IrCl(PCy_3)_2(CS_2)$ at 1264 and 1166 cm^{-1}. Baird et al. [9] explained the presence of two bands in this region by the possible occurrence of isomers. We think it more probable that the doubling is caused by Fermi reso-

TABLE 2

^{31}P NMR DATA OF ADDITION COMPLEXES OF $RhCl(PCy_3)_2$ (Room temperature, solvent benzene, reference $OP(OMe)_3$)

Compound	$^1J(P—Rh)$ (Hz)	δ (ppm)
(a) h^2-ligands		
$RhCl(PCy_3)_2(S=CNPh)$	104.4	—18.5
$RhCl(PCy_3)_2(S=CNTol)$	104.6	—17.5
$RhCl(PCy_3)_2(S=CO)$	104.9	—19.1
$RhCl(PCy_3)_2(O=O)$	106.3	—21.0
$RhCl(PCy_3)_2(S=CNMe)$	106.5	—17.8
$RhCl(PCy_3)_2(S=CS)$	106.6	—13.9
$RhCl(PCy_3)_2(S=CN—Allyl)$	106.6	—17.0
$RhCl(PCy_3)_2(PhN=CO)$	110.5	—24.4
$RhCl(PCy_3)_2(TolN=CNTol)$	110.6	—21.6
$RhCl(PCy_3)_2(PhC\equiv CPh)$	115.4	—21.8
$RhCl(PCy_3)_2(HC\equiv CH)$	116.0	—20.3
$RhCl(PCy_3)_2(H_2C=CH_2)$	118.6	—20.0
$RhCl(PCy_3)_2(EtC\equiv CEt)$	121.3	—22.1
(b) h^1-ligands		
$RhCl(PCy_3)_2(SO_2)$	107.6	—30.0
$RhCl(PCy_3)_2(CO)$	119.9	—11.9
$RhCl(PCy_3)_2(N_2)$	122.0	—27.6
$RhCl(PCy_3)_2(CS)$	132.1	—16.5
$RhCl(PCy_3)_2(PhNO)$	153.1	— 9.2

TABLE 3

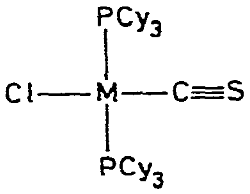
IR DATA OF THE COMPLEXES (cm^{-1})

Compound	ν(M–Cl)	ν(M–S)	$\nu(\mathrm{M}\overset{\mathrm{C}}{\underset{\mathrm{S}}{\langle}})$	ν(C=N)	ν(C=S)		others
RhCl(PCy$_3$)$_2$(CS$_2$)	329s	284s	610s		1240s 1186s		
IrCl(PCy$_3$)$_2$(CS$_2$)	323s		625s		1264s 1166s		
RhCl(PCy$_3$)$_2$(CS)	287s				1283vs		
RhCl(PCy$_3$)$_2$(SCNMe)	329s	277s	610m	1710vs			
RhCl(PCy$_3$)$_2$(SCNAllyl)	329m	275m	603m	1700s			1640m(νC=C)
RhCl(PCy$_3$)$_2$(SCNPh)	314m	285w	649s	1680vs			1582s, 1474s(Ph)
IrCl(PCy$_3$)$_2$(SCNPh)	314s		646m	1659vs			1584s, 1484s(Ph)
RhCl(PCy$_3$)$_2$(SCNTol)	335m	292m	644m	1690vs			1604s, 1572w 1503s(Tol)
RhCl(PCy$_3$)$_2$(SCO)	335s	285m	633s		1762s	ν(C=O)	
RhCl(PCy$_3$)$_2$(PhNCO)	326s			1333s	1842s		1589s, 1491s(Ph)
RhCl(PCy$_3$)$_2$(TolNCNTol)	321s			1375s 1742vs			1603s, 1502s, 1232s(Tol)
RhCl(PCy$_3$)$_2$(C$_2$Ph$_2$)	315s				1860m	ν(C=C)	
RhCl(PCy$_3$)$_2$(C$_2$Et$_2$)	308s				1943m		608m(νRh–C)
RhCl(PCy$_3$)$_2$(C$_2$H$_2$)	302s				1721m		651s(νRh–C)
RhCl(PCy$_3$)$_2$(SO$_2$)	292m	1266s, 1121s, 1111s, [ν(S=O)] 570vs [δ(S=O$_2$)]					
RhCl(PCy$_3$)$_2$(PhNO)	290w	1357s [ν(N=O)]					

nance of the overtone of the vibration near 620 cm^{-1}.

$RhCl(PCy_3)_2(SCO)$ has ν(C=O) at 1762 cm^{-1}; the isothiocyanate complexes $RhCl(PCy_3)_2(SCNR)$ (R = methyl, allyl, phenyl and p-tolyl) and $IrCl(PCy_3)_2(SCNPh)$ have ν(C=N) between 1659 and 1710 cm^{-1}. ν(CN) increases from phenyl to p-tolyl to allyl to methyl.

The CS_2-complexes decompose upon standing in solution by sulfur-abstraction. In contrast with $RhCl(PPh_3)_2(CS_2)_2$ [25], no polar co-solvent is needed for this sulfur-abstraction reaction. When extra PCy_3 is added to the solution, a high yield of the thiocarbonyl complexes $MCl(PCy_3)_2(CS)$ (M = Rh, Ir) is obtained. $IrCl(PCy_3)_2(CS)$ has been previously prepared from $IrCl(PPh_3)_2(CS)$ and PCy_3 [26]. The thiocarbonyl complexes are supposed to be structurally similar to $RhCl(PPh_3)_2(CS)$ [25], the crystal structure of which shows an end-on carbon-coordinated CS-group *trans* to the chlorine ligand (II).



(II)

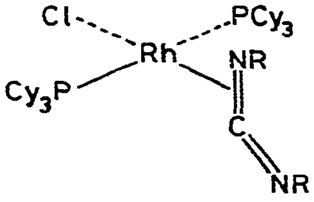
M = Rh, Ir

From a solution of $RhCl(PCy_3)_2(COS)$, $RhCl(PCy_3)_2(CO)$ is deposited upon standing. Only $IrCl(PCy_3)_2(CO)$ could be isolated from the reaction of $IrCl(PCy_3)_2(C_2H_4)$ and COS. No sulfur-abstraction from the isothiocyanate complexes has been noticed. These latter complexes are also rather resistant towards breaking of the R—N bond, a reaction observed during addition of RNCS towards $Pt(PPh_3)_3$ for various R [9].

RN=C=X heterocumulenes (X = NR, O) and CO_2

$RhCl(PCy_3)_2(PhNCO)$ and $RhCl(PCy_3)_2(TolNCNTol)$ are monomeric in benzene. The ^{31}P NMR spectra show a doublet for both compounds, indicative of two equivalent phosphorus atoms. The ^1J(Rh—P) coupling constants of the two complexes are nearly identical (110.5 and 110.6 Hz), which is indicative of a comparable bonding situation.

$RhCl(PCy_3)_2(TolNCNTol)$ has CN-stretching vibration bands at 1742 and 1375 cm^{-1}. These values agree with a h^2-coordination via C and one N of the carbodiimide, in which the bond order of one C=N bond is lowered upon coordination (see below). This is to our knowledge the first report of a h^2-coordinated carbodiimide (III). In $RhCl(CO)_2$(carbodiimide), the ligand is h^1-coordi-



(III)

nated via one of the N-atoms [27]. The difference in coordination behaviour must be attributed to the different basicities of the metal centers in the fragments $RhCl(PCy_3)_2$ and $RhCl(CO)_2$.

$RhCl(PCy_3)_2(PhNCO)$ has strong IR absorption bands at 1333 and 1842 cm^{-1}, attributable to the symmetric and antisymmetric stretching vibrations of the NCO moiety. These values agree with a h^2-coordination of phenyl isocyanate. The coordination is either by carbon and nitrogen or by carbon and oxygen.

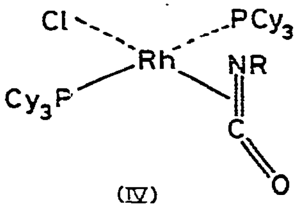
Solid $RhCl(PCy_3)_2(PhNCO)$ must be stored in the dark; under the influence of light it decomposes within a day. As a strong IR band at 1947 cm^{-1} is observed, the decomposition product may contain $RhCl(PCy_3)_2(CO)$ [20]. This implies that a nitrene entity NPh has been split off. The nitrene has, however, not been detected. The decarbonylation of organic isocyanates has recently been reviewed [28]; the example of $RhCl(PCy_3)_2(PhNCO)$ shows that this reaction most probably occurs by a C=N h^2-coordinated intermediate.

IR properties of coordinated cumulenes

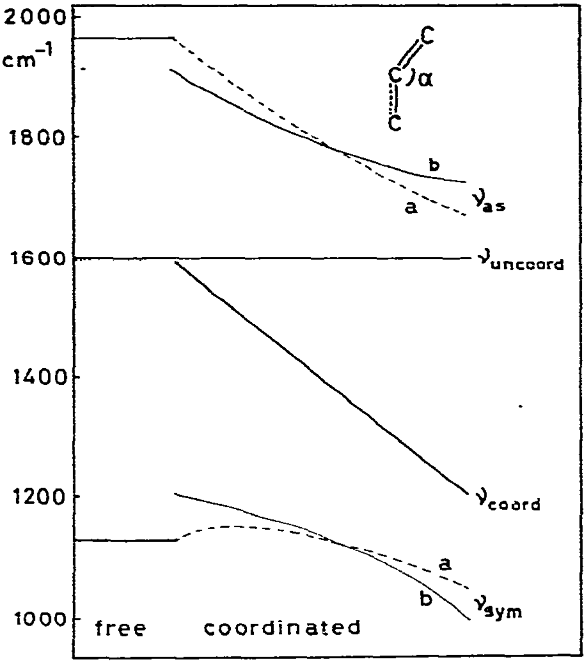
The stretching vibrations of the two double bonds of allene ($H_2C{=}C{=}CH_2$), carbodiimide and phenyl isocyanate are coupled in a symmetric vibration near 1200 cm^{-1} and an antisymmetric one near 2000 cm^{-1}. Upon side-on coordination the force constant of the coordinated C=X bond stretching is lowered. In addition, the angle at the central carbon atom is no longer 180°. These two effects alter the coupling between the two stretching vibrations. In Fig. 1 are given the calculated effects of coupling in coordinated allene. It can be seen that the antisymmetric vibration of the allene reflects the lowering of the force constant of the coordinated double bond. This is experimentally confirmed by the results, given in Fig. 2, where the IR data of a series of allene and diphenylacetylene complexes are compared. In the carbodiimide and phenyl isocyanate complexes both the symmetric (ν_{sym}) and the antisymmetric (ν_{as}) vibrations are found. This permits a rough calculation of the lowering of the frequency of the coordinated double bond (ν_{coord}), corrected for coupling with the uncoordinated double bond ($\nu_{uncoord}$), by the formula:

$$\nu_{as}^2 + \nu_{sym}^2 = \nu_{coord}^2 + \nu_{uncoord}^2$$

With the estimated values of $\nu_{uncoord}(CN) = 1650\ cm^{-1}$ and $\nu_{uncoord}(CO) = 1720\ cm^{-1}$, an approximate value of ν_{coord} may be calculated. For the carbodiimide, $\nu_{coord}(CN) = 1484\ cm^{-1}$ and the lowering of the CN frequency upon coordination is $\Delta\nu(CN) = 1650 - 1484\ cm^{-1} = 166\ cm^{-1}$. If, in the phenyl isocyanate complex, CN is coordinated, then $\nu_{coord}(CN) = 1487\ cm^{-1}$ and $\Delta\nu(CN) = 1650 - 1487\ cm^{-1} = 163\ cm^{-1}$; if CO is coordinated, then $\nu_{coord}(CO) = 1564\ cm^{-1}$ and $\Delta\nu(CO) = 1720 - 1564\ cm^{-1} = 156\ cm^{-1}$. These values are a rough measure of the interaction between the metal and the coordinated double bond.



(IV)



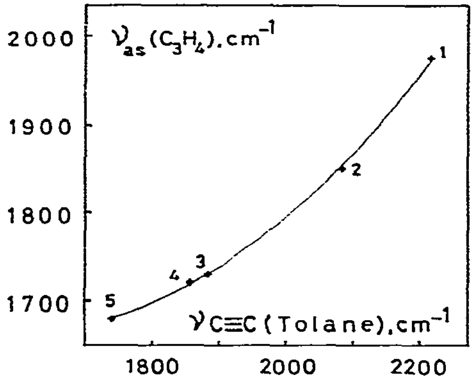


Fig. 1. Calculated coupling between ν_{coord} and $\nu_{uncoord}$ in allene, resulting in ν_{as} and ν_{sym} · ν_{coord} as variable; a: α changing linearly with ν_{coord}; b: $\alpha = 150°$. The figure shows that ν_{as} reflects the value of ν_{coord}.

Fig. 2. Comparison of IR data of allene and tolane complexes. Data from refs. 23, 29—32. (1) free ligand L (L = allene, tolane); (2) $[Pt(CH_3)(PPh_2Me)_2(allene)]^+$ versus $[Pt(CH_3)(AsMe_3)_2(tolane)]^+$; (3) $RhCl(PPh_3)_2L$; (4) $IrCl(PPh_3)_2L$; (5) $Pt(PPh_3)_2L$.

The calculated values of $\Delta\nu(CN) = 163$ cm^{-1} and $\Delta\nu(CO) = 156$ cm^{-1} do not furnish a decisive criterion about whether phenyl isocyanate is CN or CO coordinated. However, two other arguments point to CN coordination (IV): firstly the $^1J(Rh—P)$ value is equal for the PhNCO and the TolNCNTol complex; and secondly, neither ethyl isocyanate nor carbon dioxide coordinate to $RhCl(PCy_3)_2$, suggesting that both C=O and C=N h^2-coordination are unfavorable, and that C=N h^2-coordination is promoted by an electron-withdrawing aryl substituent.

Four-coordination

We mentioned that, because of coupling, the antisymmetric vibration frequency of the cumulene ligand measures roughly the interaction between the metal and the coordinated double bond. In sulfur-containing heterocumulenes, the coupling is expected to be weaker, because of the greater mass and/or the larger difference in uncoupled frequencies. Therefore, in sulfur-containing heterocumulenes ν_{as} reflects to a lesser extend the metal-ligand interaction than in allene and in N- and O-containing heterocumulenes. We find, nonetheless, that in the square planar rhodium and iridium PCy_3 complexes the ν_{as} are high, compared with the frequencies of platinum (0) three-coordinated and rhodium (I) and iridium (I) five-coordinated complexes of the same ligands (Table 4). This again illustrates that the coordination geometry has a definite influence on

TABLE 4

COMPARISON OF IR FREQUENCIES OF 3-, 4- and 5-COORDINATED COMPLEXES OF S=C=X HETEROCUMULENES

Compound (this work)	ν(C=X) (or mean value) (cm^{-1})		Compound (ref. 9)
	4-coord.	3/5-coord.	
$RhCl(PCy_3)_2(CS_2)$	1213	1024	$RhCl(PPh_3)_2(\pi\text{-}CS_2)(\sigma\text{-}CS_2)$
$IrCl(PCy_3)_2(CS_2)$	1215	1157	$IrCl(CO)(PPh_3)_2(CS_2)$
		1151	$Pt(PPh_3)_2(CS_2)$
$RhCl(PCy_3)_2(COS)$	1762	1727	$Pt(PPh_3)_2(COS)$
$RhCl(PCy_3)_2(PhNCS)$	1680	1540	$RhCl(PPh_3)_2(PhNCS)_2$
$IrCl(PCy_3)_2(PhNCS)$	1659	1643	$Pt(PPh_3)_2(PhNCS)$
$RhCl(PCy_3)_2(MeNCS)$	1710	1653	$Pt(PPh_3)_2(MeNCS)$

the bonding between the metal and a π-acceptor ligand, comparable with the influence of electron density variations, brought about by different ligands. This agrees with the theoretical expectation that trigonal bipyramidal and trigonal complexes have enhanced π-backbonding properties towards ligands in the trigonal plane by symmetry-allowed interplay of the π-acceptor orbitals with the σ-donor orbitals of the other ligands in the plane [33].

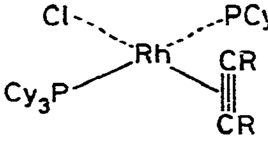
That $RhCl(PCy_3)_2$ does not react with CO_2 and EtNCO, but that $IrCl(PMe_3)_3$ [7] and $Ni(PCy_3)_2$ [14] do coordinate CO_2, may also be related to the coordination geometry: four-coordination is less favorable for π-backbonding than five- and three-coordination.

Acetylenes, sulfur dioxide and nitrosobenzene

Diphenylacetylene and diethylacetylene add rapidly to $RhCl(PCy_3)_2$. $RhCl(PCy_3)_2(PhC{\equiv}CPh)$ ($\nu(C{\equiv}C) = 1860$ cm^{-1}) shows as expected for tolane no tendency to react with a second molecule of tolane. $RhCl(PCy_3)_2(EtC{\equiv}CEt)$ ($\nu(C{\equiv}C) = 1943$ cm^{-1}) is the first isolated 3-hexyne complex of rhodium. That it does not react with a second molecule of 3-hexyne is attributed to the presence of the bulky phosphines. $RhCl(PCy_3)_2$, prepared in situ, reacts with acetylene, C_2H_2, but the reaction goes further, probably leading to a metallocyclopentadiene complex $RhCl(PCy_3)_2(C_4H_4)$ ($\nu(C{=}C) = 1615$ cm^{-1}), which cannot be isolated in pure form, due to a subsequent decomposition reaction. If cyclooctene is first removed from the $RhCl(PCy_3)_2$ solution, the addition of C_2H_2 is faster, which permits isolation of $RhCl(PCy_3)_2(C_2H_2)$ as a yellow compound ($\nu(C{\equiv}C) = 1712$ cm^{-1}). This compound, like $Pt(PPh_3)_2(C_2H_2)$ [34] ($\nu(C{\equiv}C) = 1700$ cm^{-1}), $Ir(SnCl_3)(PPh_3)_2(CO)(C_2H_2)$ [35] ($\nu(C{\equiv}C) = 1682$ cm^{-1}) and $Os(NO)(CO)(PR_3)_2(C_2H_2)$ [36] is among the few Group VIII metal complexes of unsubstituted acetylene. The iridium and osmium complexes have an 18-electron configuration which prevents further reaction. The platinum complex has as a three-coordinated complex an optimum for π-backbonding and has therefore not much tendency to coordinate a second acetylene. Furthermore the bulky phosphine in $RhCl(PCy_3)_2(C_2H_2)$ slows down sufficiently the addition of a second acetylene to permit isolation of the complex.

The single ν(Rh—Cl) and the doublet in the ^{31}P NMR spectrum are sufficient proof of a monomeric *trans*-structure of the $RhCl(alkyne)(PCy_3)_2$ complexes.

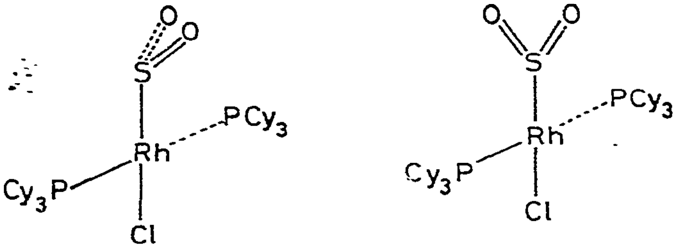
The acetylenes are expected to be situated perpendicular to the coordination plane (V).



(V)

R = Ph, H, Et

Sulfur dioxide reacts quickly with $RhCl(PCy_3)_2$ to form $RhCl(PCy_3)_2(SO_2)$. This complex does not form a sulfate with oxygen. Conversely, the dioxygen compound $RhCl(PCy_3)_2(O_2)$ does not react with SO_2. According to MO calculations, one expects for a square planar d^8-complex a non-planar M—SO_2-moiety [37], but the IR frequencies of the SO stretching vibrations at 1266 cm^{-1} (ν_{as}) and 1121, 1111 cm^{-1} (ν_{sym}) agree better with a planar Rh—SO_2 group [23] (VI).

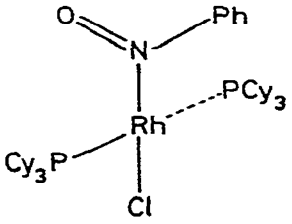


(VI)

Possible structures of $RhCl(PCy_3)_2(SO_2)$

We attribute the presence of two absorption bands at the position of the symmetric stretch (near 1120 cm^{-1}) to Fermi resonance doubling, caused by the overtone of the δSO_2 at 570 cm^{-1}.

A clean reaction between PhNO and $RhCl(PCy_3)_2$ could only be obtained if cyclooctene was removed from the reaction mixture. The resulting product $RhCl(PCy_3)_2(PhNO)$ shows ν(NO) at 1357 cm^{-1}, indicative of N-bonded h^1-coordination [39]. The ^1J(Rh—P) value of 153.1 Hz agrees with this h^1-coordination (VII). PhNO as a ligand is mostly N-bonded [38], but with low-valent metals iron (0) [39] and palladium (0) [40] side-on coordination to a first metal by N and O with simultaneous bridging to a second metal by N has been found.



(VII)

^{31}P *NMR spectra*

In Table 2 are collected the ^{31}P NMR data of the four-coordinated addition complexes of $RhCl(PCy_3)_2$. All spectra are characterised by a doublet, caused by coupling with Rh ($I = \frac{1}{2}$), and consequently all complexes possess two equivalent phosphorus nuclei, proving the *trans*-structure for the complexes. We consider the groups of h^2- and of h^1-ligand containing complexes separately.

The chemical shifts show not many regularities, although it may be noticed that for the complexes with h^2-ligands the range of shift-values is smaller (between —14 and —24 ppm) than is the range for the complexes with h^1-ligands (from —9 to —30 ppm).

The ^1J(Rh—P) coupling constant contains more information. The group of h^1-ligand containing complexes has on the average a higher coupling constant than the group of h^2-ligand containing complexes. The ^1J(Rh—P) value varies regularly with the *cis*-ligand, indicative of a strong *cis*-influence on this value. There is a correlation between the π-acceptor strength of the *cis*-ligand and the coupling constant; the coupling constant decreases with increasing π-acceptor strength of the *cis*-ligand, going from PhNO to N_2 to CO to SO_2 for the h^1-ligands, and going from C_2H_4 and acetylenes to RNCX and SCX for the h^2-ligands. Even in fine detail this correlation is present: the coupling constant decreases going from diethylacetylene to acetylene to diphenylacetylene, and going from allylNCS and MeNCS to TolNCS and PhNCS.

It is likely that changes in coupling constants may be related to changes in the percentage *s*-character of the rhodium hybride orbital used in the rhodium—phosphorus bond [41]. Various explanations of the observed trends are possible: *(i)* The larger orbital contraction for more positive rhodium centers may have a direct influence on the Rh—P bond and diminish the *s*(Rh)-character of this bond; *(ii)* The synergic effect, operating both in the rhodium-to-π-acid bond and the rhodium-to-phosphorus bond may be evoked for an explanation of the observed *cis*-influence: the coordination of a strong π-acid may weaken the Rh—P π-bond and by synergism the Rh—P σ-bond; and/or a strong π-bond between rhodium and the *cis*-ligand may strengthen the σ-bond between rhodium and the π-acid, and by competition weaken the Rh—P σ-bond. At least the second part of this argument seems unlikely to us, considering the results we obtained on metal—alkyne complexes, which show that the more strongly π-bonding h^2-ligand tends to be the more weakly σ-bonding h^2-ligand [29]. The first part of argument *(ii)* has been critisized by Venanzi [41], who argued that the metal—phosphorus π-bond is too weak to cause by an indirect mechanism such changes in the σ-bond.

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