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

III *. ELIMINATION OF HETERO-ALLENE MOLECULES FROM RHODIUM(I)-HETERO-ALLYLIC-PHOSPHINE COMPLEXES. THE FIRST COMPLEX WITH η^2-COORDINATED Ph_2PS^-

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Summary

Carbon monoxide causes elimination of the hetero-allene molecules *p*tolN=C=N*p*tol and Ph—N=C=O in $Rh(PPh_3)_2[Ph_2PC(N$*p*tol$)N$*p*tol$]$ and $Rh(PPh_3)_2[Ph_2PC(NPh)O]$, respectively. The resulting complex in both cases is $[Rh(CO)_2(PPh_3)(PPh_2)]_n$.

In the reaction of $RhCl(PPh_3)_3$ with $Ph_2P(S)C(N$*p*tol$)NH$*p*tol or $Ph_2P(S)$-$C(O)NHPh$ in the presence of a base, a similar elimination occurs yielding the liberated heterocumulene and $Rh(PPh_3)_2(SPPh_2)$. This complex is the first example of a species with a side-on coordinated Ph_2PS-moiety. We have also prepared this compound and other species, containing η^2-$SPPh_2$, via direct interaction of $RhCl(PPh_3)_3$ and $IrCl(PPh_3)_2(C_8H_{14})$ with $Ph_2P(S)H$. Upon reaction with CO, the chelating PPh_2 group is displaced by CO to give complexes with an end-on coordinated Ph_2PS^- ligand.

Finally, $Rh(PPh_3)_2(SPPh_2)$ incorporates three moles of PhNCS, one by insertion and two by disproportionation, to yield $Rh(PPh_3)(PhNC)(PhNCS_2)$-$[Ph_2P(S)C(S)NPh]$.

Introduction

Ph_2P^- and Ph_2PS^- can add to hetero-allene molecules X=C=Y (X, Y = S, NR, O) by nucleophilic attack at the central C atom to give a large number of hetero-allylic derivatives, as shown in Fig. 1.

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[*] For part II see ref. 2.

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TABLE 1

ANALYTICAL DATA

No.	Compound	Colour	Found (calcd.) (%)						Mol. weight
			C	H	O	Cl	P	S	
Id	$[Rh(PPh_2)(PPh_3)(CO)_2]_2 \cdot H_2O$	dark green	62.38	4.65	6.45	—	10.10	—	—
			(62.44)	(4.26)	(6.50)	—	(10.08)	—	—
IIIc	$Rh(SPPh_2)(PPh_3)_2$	orange brown	68.07	4.91	—	—	10.80	3.61	827 [a]
			(68.25)	(4.78)	—	—	(11.02)	(3.79)	(844)
IV	$RhCl(H)(PPh_3)_2(SPPh_2) \cdot C_6H_6$	yellow	68.59	5.19	—	3.69	9.52	3.24	469 [b]
			(67.61)	(4.94)	—	(3.70)	(9.70)	(3.34)	(479)
V	$IrCl(H)(PPh_3)_2(SPPh_2) \cdot C_6H_6$	yellow	62.49	4.69	—	3.31	8.15	3.02	577 [b]
			(61.80)	(4.52)	—	(3.29)	(8.88)	(3.05)	(574)
VI	$Rh(PPh_3)_2(CO)(SPPh_2)$	yellow	67.12	4.71	—	—	—	—	—
			(67.43)	(4.62)	—	—	—	—	—

[a] Mol. weight determined osmometrically in acetone. [b] Mol. weight determined osmometrically in CH_2Cl_2. $M/2$ calc.: 479 for IV, 574 for V.

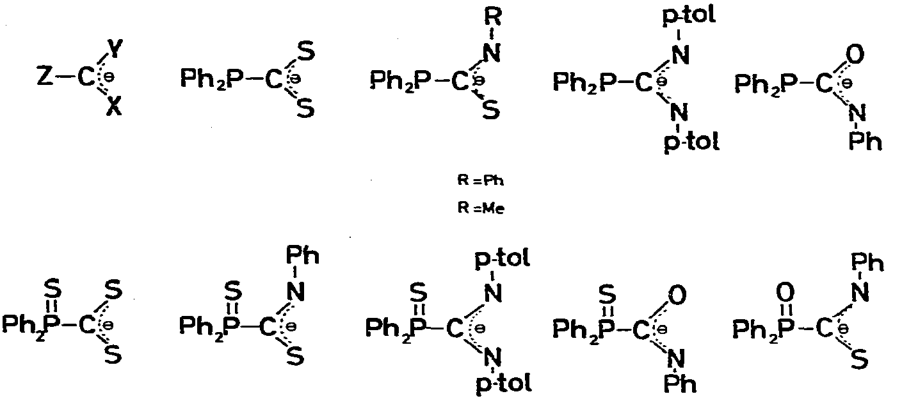


Fig. 1. The unsaturated hetero-allylic anions.

These anions, containing three hetero atoms with coordinating properties, are ambidentate. The complexation of a number of these chelates towards rhodium(I)- and iridium(I)-phosphine complexes are reported in previous papers [1—4]. Complexes of the type $M(PPh_3)_2[X—C(Z)—Y]$ and $M(PPh_3)(CO)[X—C(Z)—Y]$ (M = Rh, Ir) can be prepared in this way. However, in some cases the complexes are not sufficiently stable to be isolated, and a subsequent reaction occurs in which the heterocumulene is eliminated. In this paper the behaviour of a few of these complexes is discussed. In particular, attention is paid to one of the products, $Rh(PPh_3)_2(SPPh_2)$, resulting from the elimination.

In addition we have synthesized some $M(SPPh_2)$ complexes (M = Rh, Ir) and investigated their structures. In complexes of Ph_2PS^-, this ligand has previously been found to coordinate either end-on via sulfur [9], or to bridge two metal atoms via P and S [10—12]. In this paper we describe a different mode of bonding.

Experimental

IR spectra were measured on a Perkin Elmer 283 spectrophotometer (4000—200 cm^{-1}), mainly in CsI pellets.

$^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-1000 FT spectrometer at 40.5 MHz, using the deuterated solvent as internal look. Solutions for NMR measurements were prepared in a glove-box.

C, H and N analyses were carried out at the micro-analytical department of this university. Other elemental analysis and molecular weight determinations were performed by Prof. Dipl.-Ing. Dr. H. Malissa and G. Reuter, Analytische Laboratorien, Elbach über Engelskirchen, West-Germany. Analytical data are given in Table 1.

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

$RhCl(PPh_3)_3$ [5], $[IrCl(C_8H_{14})_2]_2$ [6], $Rh(PPh_3)_2[Ph_2PC(Np\text{-tol})Np\text{-tol}]$ and $Rh(PPh_3)_2[Ph_2PC(NPh)O]$ [2], $Ph_2P(S)H$ [7], and $Ph_2P(S)C(Np\text{-tol})NHp\text{-tol}$ and $Ph_2P(S)C(O)NHPh$ [8] were prepared according to literature procedures.

TABLE 2

IR AND $^{31}P\{^1H\}$ NMR DATA OF THE INTERMEDIATE COMPLEXES

Complex		δ(P-chelate) (ppm) [d]	$^1J(Rh—P_{chelate})$ (Hz)	ν(C≡O) (cm^{-1})	ν(C=E) (cm^{-1})
Ia	$Rh(PPh_3)_2]Ph_2PC(NPh)O]$ [b]				1624s (ν(C=O))
Ib	$Rh(PPh_3)(CO)[Ph_2PC(NPh)O]$ [c]	−3.3	108	1972vs	1640m(ν(C=O))
Ic	$Rh(PPh_3)(CO)_2(PPh_2)(PhNCO)$ [c]			1912vs 1987vs	1735m (ν(η^2-PhN=C=O))
Id	$[Rh(PPh_3)(CO)_2(PPh_2)]_n$ [b]	−46.5	155 (multiplet)	1900vs 1947vs	
IIa	$Rh(PPh_3)_2[Ph_2PC(N\textit{p}tol)N\textit{p}tol]$ [b]				1552vs (ν(C=N))
IIb	$Rh(PPh3)(CO)[Ph_2PC(N\textit{p}tol)N\textit{p}tol]$ [c]			1970vs	1569vs (ν(C=N))

[a] For PPh_3, see Table 3. [b] Measured in CsI pellets. [c] Measured in CH_2Cl_2 solution. [d] In ppm relative to $O=P(OMe)_3$ (TMP) internal reference, upfield shifts positive.

Preparation of $[Rh(PPh_2)(PPh_3)(CO)_2]_2 \cdot H_2O$ *(Id)*

On passing CO during 5 minutes through a solution of 0.3 mmol $Rh(PPh_3)_2[Ph_2PC(Np\text{-tol})Np\text{-tol}]$ or $Rh(PPh_3)_2[Ph_2PC(NPh)O]$ in 30 ml benzene the initial orange-yellow colour changed first to yellow and within an hour via brown to dark-green. After a few hours the green precipitate was filtered off, washed with benzene and diethyl ether, and dried in vacuo. Yield: 55%.

Preparation of $Rh(PPh_3)_2(SPPh_2)$ *(IIIc)*

a) 0.3 mmol of $Ph_2P(S)C(Np\text{-tol})NHp\text{-tol}$ was added to a solution of 0.3 mmol of $RhCl(PPh_3)_3$ in 30 ml anhydrous benzene. An equimolar quantity of n-BuLi was then injected. After stirring for 24 hours the mixture was filtered. After precipitation with n-hexane the complex was filtered off, washed with small portions of ethanol and diethyl ether, and dried in vacuo. Yield: 30%.

b) 0.3 mmol $Ph_2P(S)C(O)NHPh$ was added to a solution of 0.3 mmol $RhCl(PPh_3)_3$ in 30 ml benzene. After 20 minutes a small excess of Et_3N was added. After 24 hours the $Et_3N \cdot HCl$ was filtered off. The complex was precipitated with n-hexane, filtered off, washed with small portions of ethanol and diethyl ether, and dried in vacuo. Yield: 35%.

c) 0.3 mmol $Ph_2P(S)H$ was added to a solution of 0.3 mmol $RhCl(PPh_3)_3$ in 30 ml waterfree benzene. An equimolar quantity of n-BuLi was added. After two hours, the complex was precipitated with n-hexane, filtered off, washed with small portions of ethanol and diethyl ether, and dried in vacuo. Yield: 75%.

Preparation of $Rh(H)(Cl)(PPh_3)_2(SPPh_2) \cdot C_6H_6$ *(IV)*

0.3 mmol $Ph_2P(S)H$ was added to a solution of 0.3 mmol $RhCl(PPh_3)_3$ in 30 ml benzene. Within 15 minutes the colour changed from red to bright yellow. n-Hexane was added and the precipitate was filtered off, washed with small portions of benzene and diethyl ether and dried in vacuo. Yield: 90%.

Preparation of $Ir(H)(Cl)(PPh_3)_2(SPPh_2) \cdot C_6H_6$ *(V)*

0.3 mmol $Ph_2P(S)H$ was added to a solution of 0.15 mmol $[IrCl(C_8H_{14})_2]_2$ and 0.6 mmol PPh_3 in 30 ml benzene. In 20 minutes the colour changed from red to yellow. After addition of n-hexane the precipitate was filtered off, washed with small portions of benzene and diethyl ether, and dried in vacuo. Yield: 85%.

Preparation of $Rh(PPh_3)_2(CO)(SPPh_2)$ *(VI)*

CO was passed for 2 minutes through a solution of $Rh(H)(CI)(PPh_3)_2(SPPh)_2$ in 20 ml CH_2Cl_2, a yellow precipitate formed during about 30 minutes. After addition of n-hexane the complex was filtered off, washed with ethanol and diethylether, and dried in vacuo. Yield: 90%.

The reaction of $Rh(PPh_3)_2[Ph_2PC(NR)Y]$ ($Y = Np$-tol, $R = p$-tol; $Y = O$, $R = Ph$) with CO

We investigated the reaction between $Rh(PPh_3)_2[Ph_2PC(NPh)O]$ (Ia) and CO by means of IR and $^{31}P\{^1H\}$ NMR spectroscopy. Table 2 gives the relevant

TABLE 3

COMPLEXES AND INTERMEDIATES PRESENT AT DIFFERENT REACTION TIMES

Complex		0 h	0.5 h	2 h	20 h	45 h
Ia	$Rh(PPh_3)_2[Ph_2PC(NPh)O]$	++	+	—	—	—
Ib	$Rh(PPh_3)(CO)[Ph_2PC(NPh)O]$	—	++	++	+	+
Ic	$Rh(PPh_3)(CO)_2(PPh_2)(PhNCO)$	—	—	●	●	●
Id	$[Rh(PPh_3)(CO)_2(PPh_2)]_n$	—	—	~	+	++
	free PhNCO	—	—	—	+	++
Colour		yellow	yellow-orange	brown	green	green + precipitate of Id
$\delta(PPh_3)$ (ppm) (free and coordinated)			−11.0	−4.6	−2.0	−0.9

++ > 60%, + 20—60%, ~ 5—20%, ● present in very small quantity, — not present.

IR absorptions and the ^{31}P NMR parameters of the intermediate complexes present in the reaction mixture, and Table 3 shows the amounts of these intermediates as a function of time.

When less than one equivalent CO is introduced into a solution of $Rh(PPh_3)_2$-$[Ph_2PC(NPh)O]$ in benzene or dichloromethane the yellow-orange $Rh(PPh_3)$-$(CO)[Ph_2PC(NPh)O]$ (Ib) is formed by substitution of PPh_3 by CO. This complex is analogous to the complexes $Rh(PPh_3)(CO)[X—C(Z)—Y]$, described in our earlier papers [2,3]; $\nu(C\equiv O)$ at 1972vs cm^{-1} and $\nu(C=O)$ at 1640m cm^{-1} are consistent with the values usually found for this type of compound. The ^{31}P NMR spectrum indicates dynamic behaviour due to exchange of free and coordinated PPh_3. The PPh_3 resonance is broad and exhibits no $^1J(Rh—P)$ coupling. $^1J(Rh—P_{chelate})$ amounts to 108 Hz. Complex Ib defies isolation. It reacts with a second molecule of CO to give $Rh(PPh_3)(CO)_2[\overline{Ph_2PC(NPh})O]$; the colour changes slowly via brown to green. In the strained $\overline{Rh—P—C—N}$ four membered ring the P—C and Rh—N bonds are the weakest. By breaking these bonds, i.e. by elimination induced by the second CO molecule, a complex with a side-on coordinated PhN=C=O molecule can be generated (Ic). In the IR spectrum, recorded after two hours, a new absorption is observed at 1735 cm^{-1}, which we assign to $\nu(C=O)$ of the five coordinate intermediate $Rh(PPh_2)$-$(PPh_3)(CO)_2(\eta^2\text{-}PhN=C=O)$ (Ic). For the four-coordinate $Rh(Cl)(PCy_3)_2$-$(PhN=C=O)$ $\nu(C=O)$ was assigned at 1842s cm^{-1} by Van Gaal et al. [13]. These authors predict a substantial lowering of this frequency in five coordinate Rh complexes. The absorption at 1735 cm^{-1}, observed for Ic, is about 100 cm^{-1} higher than the reported value for $\nu(C=O)$ of a $[RNC(O)NR]^{2-}$ fragment, which may result from a coupling of two Ph—N=C=O entities [14—16], so that the formation of such derivatives can be excluded. Subsequently the η^2-coordinated hetero-allene molecule is eliminated from the coordination sphere, as is indicated in the IR spectrum by the formation of free PhN=C=O. Fig. 2 shows a possible reaction pathway, as discussed above.

The reaction between $Rh(PPh_3)_2[Ph_2PC(Np\text{-}tol)Np\text{-}tol]$ and CO in benzene proceeds similarly. *p*tolN=C=N*p*-tol is eliminated and the resulting Rh complex, formed in this reaction, is also Id.

The green compound Id analyses for $\{[Rh(CO)_2(PPh_2)(PPh_3)]_2 \cdot H_2O\}_n$. We

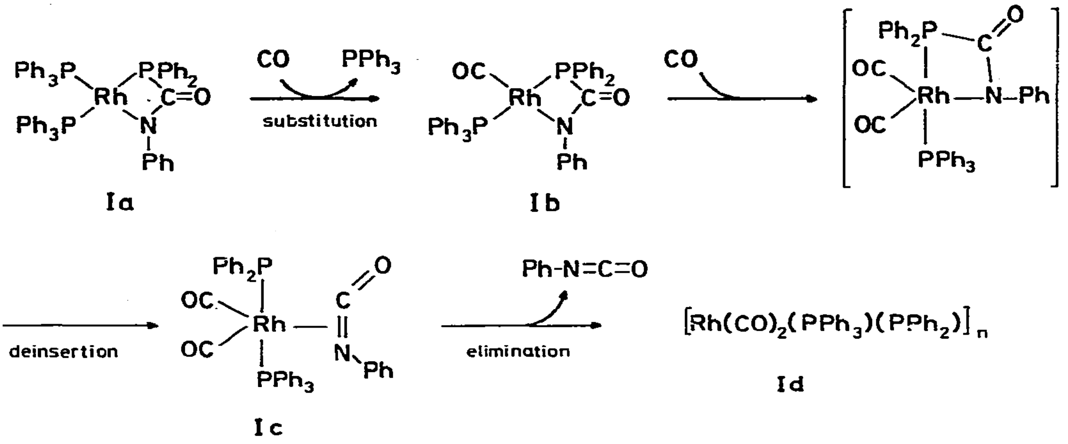
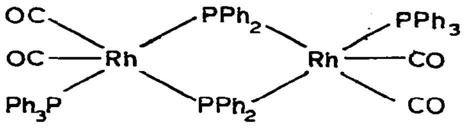


Fig. 2. The probable pathway for the reaction between $Rh(PPh_3)_2[Ph_2PC(NPh)O]$ and CO.

suggest a structure as given below, in which *n* equals 2, but we could not determine the molecular weight because it is insoluble in benzene and decomposes slowly in dichloromethane or chloroform to yield $RhCl(CO)(PPh_3)_2$ among other products. In Id the rhodium is five coordinate as indicated by $\nu(CO)$ at 1947 and 1900 cm^{-1}:



The reaction of $RhCl(PPh_3)_3$ with $Ph_2P(S)C(Y)NHR$ (Y = N*p*-tol, R = *p*-tol; Y = O, R = Ph) in the presence of a base

In earlier papers we reported that the reactions of $RhCl(PPh_3)_3$ with the molecules $Ph_2P(S)C(S)NHPh$ [2] and $Ph_2P(O)C(S)NHPh$ [3] in the presence of a base, e.g. Et_3N gave the stable complexes $Rh(PPh_3)_2[Ph_2P(S)C(S)NPh]$ and $Rh(PPh_3)_2[Ph_2P(O)C(S)NPh]$, respectively. The ligands are coordinated to Rh by S(P) and S and by O(P) and S in five membered chelate rings.

When $RhCl(PPh_3)_3$ is treated with $Ph_2P(S)C(Np\text{-tol})NHp\text{-tol}$ and an equimolar quantity n-BuLi or with $Ph_2P(S)C(O)NHPh$ in the presence of a small excess of Et_3N, the complexes $Rh(PPh_3)_2[Ph_2P(S)C(Np\text{-tol})Np\text{-tol}]$ (IIIa) and $Rh(PPh_3)_2[Ph_2P(S)C(NPh)O]$ (IIIb) are formed as a first intermediate, in which the hetero-allylic ligands coordinate through S(P) and N. After standing for a short time both complexes undergo fairly rapid elimination of the hetero-allene molecules *p*-tolN=C=N*p*-tol and Ph—N=C=O respectively, as observed by means of IR spectroscopy. The elimination is probably induced by the weak *N* coordination in the five membered ring and by the weak P—C bond of four coordinate three-valent phosphorus to the central atom of the X=C=Y fragment. We suppose the mechanism of these eliminations to be analogous to

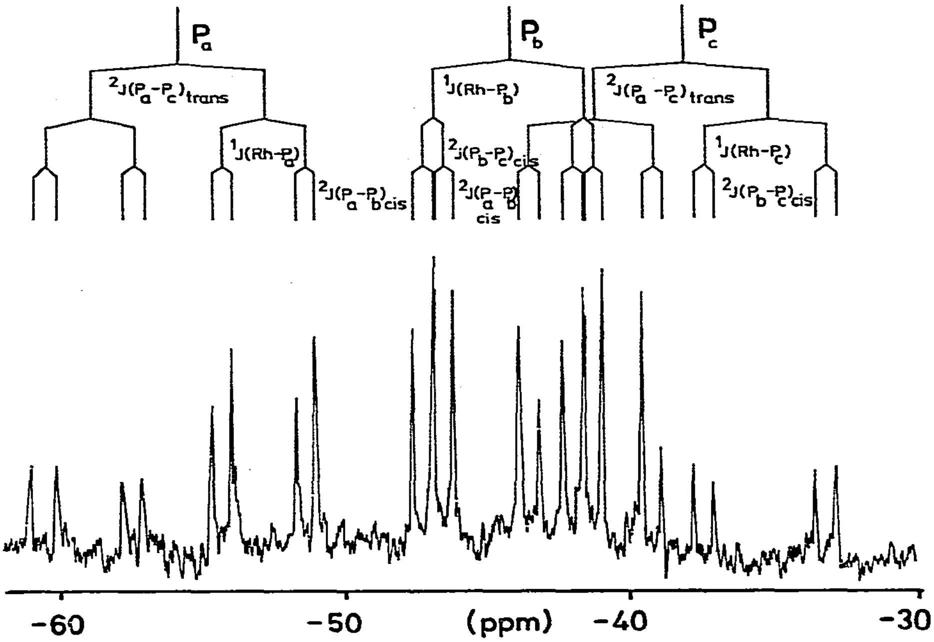


Fig. 3. The $^{31}[^1H]$NMR spectrum of $Rh(PPh_3)_2(SPPh_2)$.

those discussed in the previous section. The compound IIIc, which results from both reactions, analyses for $Rh(PPh_3)_2(SPPh_2)$. IIIc appears to be monomeric in acetone. The absorption at 513s cm^{-1} in the IR spectrum is assigned to ν(P=S), which agrees with an involvement of S in the coordination to the metal [2,11,17]. The $^{31}P\{^1H\}$ NMR spectrum (see Table 5 and Fig. 3) indicates three inequivalent phosphorus nuclei, which means that the P atom of the Ph_2PS^- moiety is coordinated to Rh. In particular the small value of $^1J(Rh—P_a)$ of 119 Hz demonstrates the incorporation of P_a into a three membered ring system. We conclude from these facts and from the requirement for four coordination for the Rh^I center, that the Ph_2PS^- ligand is coordinated side-on. Previously, R_2PS^- has been reported to complex with transition metals either end-on, through S [9], or by bridging two metal atoms through S and P [10—12], forming binuclear species. IIIc is the first example of a complex in which a

TABLE 4

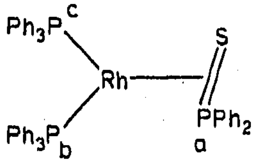
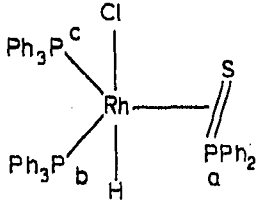
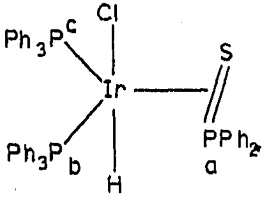
IR ABSORPTIONS IN cm^{-1}. SPECTRA MEASURED IN CsI PELLETS

Code	Complex	ν(C=E) [b]	ν(P=S)	ν(M—H)	ν(M—Cl)
IIIa	$Rh(PPh_3)_2[Ph_2P(S)C(Np\text{-tol})Np\text{-tol}]$ [a]	1546s (ν(C=N))	521m		
IIIb	$Rh(PPh_3)_2[Ph_2P(S)C(NPh)O]$	1618s (ν(C=O))	512m		
IIIc	$Rh(PPh_3)_2(SPPh_2)$		513s		
IV	$Rh(H)(Cl)(PPh_3)_2(SPPh_2) \cdot C_6H_6$		512s	2118m	262vw
V	$Ir(H)(Cl)(PPh_3)_2(SPPh_2) \cdot C_6H_6$		511s	2233m	263vw
VI	$Rh(CO)(PPh_3)_2(SPPh_2)$	1971 vs ν(C≡O)	516m		

[a] Measured in C_6H_6 solution. [b] E represents the exocyclic hetero atom.

TABLE 5

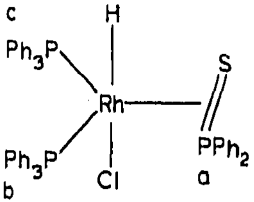
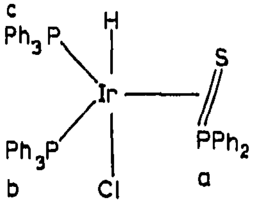
$^{31}H\{^{1}H\}$ NMR PARAMETERS

Complex	Code	δ(Pa)	^1J(Rh—Pa)	δ(Pb)	^1J(Rh—Pb)	δ(Pc)	^1J(Rh—Pc)	^2J(Pa—Pb)	^2J(Pa—Pc)	^2J(Pb—Pc)
	IIIc	−55.6	119	−44.1	210	−37.6	171	28 *cis*	246 *trans*	29 *cis*
	IV	−49.0	82	−39.6	160	−26.5	125	20 *cis*	347 *trans*	0 *cis*
			^2J(Pa—H) = 14		^2J(Pb—H) = 12		^2J(Pc—H) = 16			
	V	−17.5		−4.2		+2.0		18 *cis*	309 *trans*	0 *cis*
			no ^2J(P—H) coupling constants observed							

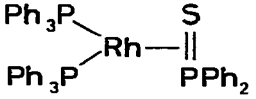
δ in ppm relative to O=P(OMe)$_3$ (TMP), internal reference; upfield shift positive; J in Hz, Solvent: CD_2Cl_2.

TABLE 6

^{1}H NMR SPECTROSCOPIC DATA

Complex	δ(M—H)	Intensity ratio	δ(H-arom)	$\frac{\text{Int M—H}}{\text{Int H-arom}}$	^1J(Rh—H)	$^2J(P_i$—H) (i = a, b, c)		
 (IV)	−17.6	quasi sextet 1 : 3 : 4 : 4 : 3 : 1	7.1—7.5 multiplet	0.020	9	12 (P_c)	10 (P_a)	10 (P_b)
 (V)	−21.3	quasi sextet 1 : 1 : 2 : 2 : 1 : 1	7.2—7.5 multiplet	0.021		16 (P_c)	16 (P_a)	12 (P_b)

δ in ppm relative to TMS. J in Hz. Spectra measured in CD_2Cl_2.



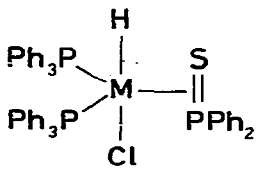


Fig. 4. The structure of Rh(PPh$_3$)$_2$(SPPh$_2$).

Fig. 5. The structure of M(H)(Cl)(PPh$_3$)$_2$(SPPh$_2$) (M = Rh, Ir).

coordinated R_2PS^- fragment is coordinated in an η^2-mode (see Fig. 4).

In order to support our conclusions we attempted an independent synthesis of Ph_2PS^- complexes by direct interaction of $RhCl(PPh_3)_3$ with $Ph_2P(S)H$ in benzene. From this reaction the complex Rh(H)(Cl)(PPh$_3$)$_2$(SPPh$_2$) (IV) can be easily obtained. We have also prepared the analogous Ir(H)(Cl)(PPh$_3$)$_2$(SPPh$_2$) (V) from $IrCl(PPh_3)_2(C_8H_{14})$ and $Ph_2P(S)H$. Molecular weight determinations point to monomeric IV and V. The IR spectra show ν(Rh—H) at 2118m cm^{-1} and ν(Ir—H) at 2233 m cm^{-1}, whereas the ν(M—Cl) absorptions are assigned at 262vw cm^{-1} for IV and 263vw cm^{-1} for V; ν(P=S) is observed at 512s cm^{-1} for IV and at 511s cm^{-1} for V. These values indicate again η^2-coordination of Ph_2PS^-. Tables 5 and 6 give the $^{31}P\{^1H\}$ NMR and ^1H NMR spectroscopic data. The ^{31}P NMR parameters of IV and V are in agreement with three inequivalent P atoms. The value of $^1J(Rh—P_a)$ of 82 Hz confirms the η^2-coordination of the Ph_2PS^- moiety. ^2J(PPh$_3$b—PPh$_3$c) of square planar *cis* Rh^I (PPh$_3$)$_2$[X—C-(Z)—Y] complexes varies from 35—50 Hz [2]. The value of ^2J(PPh$_3$b—PPh$_3$c) of Rh^I(PPh$_3$)$_2$(η^2-SPPh$_2$) is somewhat smaller. We ascribe this to the P—Rh—P angle which is larger than 90°. We draw a parallel with the P—Pt—P angle and ^2J(P—P) in Pt(PPh$_3$)$_2$(η^2-A=B) compounds, which have an angle of comparable size and also a small ^2J(P—P). A weaker M—η^2-ligand interaction is expected in the Rh^{III}(SPPh$_2$) complexes compared with the Rh^I(SPPh$_2$) compounds. This is accompanied with a larger PPh$_3$—Rh—PPh$_3$ aperture angle (called the "inter-ligand angle effect" by S. Otsuka [18]) and consequently a still smaller ^2J-(PPh$_3$b—PPh$_3$c) coupling constant. Actually in compounds IV and V ^2J(PPh$_3$b—PPh$_3$c) ≈ 0.

In the ^1H NMR spectra the hydride signals are observed at —17.6 ppm (Rh) and at —21.3 ppm (Ir) as quasi-sextets. The values of $^2J(P_i—H)$ (i = a, b, c) of IV, read from the ^1H NMR spectrum, are slightly smaller than the values from the ^{31}P NMR spectrum. The ^{31}P NMR spectrum of V does not show any $^2J(P_i—H)$ couplings, whereas the values from the ^1H NMR spectrum are larger than the values of $^2J(P_i—H)$ of the analogous Rh complex. The intensity ratio Int M—H/Int. H_{arom} indicates that about one molecule C_6H_6 must be present in the complexes.

Upon standing for a few days IV is converted into Rh(PPh$_3$)$_2$(SPPh$_2$) by loss of HCl. IIIc can also be prepared directly from $RhCl(PPh_3)_3$ and $LiP(S)Ph_2$. We were not able to obtain the good crystals required for an X-ray structure determination of either IV, V or IIIc. However, on the basis of the molecular weight determinations and the spectroscopic features the η^2-coordination of the Ph_2PS^- ligand in IIIc seems fairly reliable.

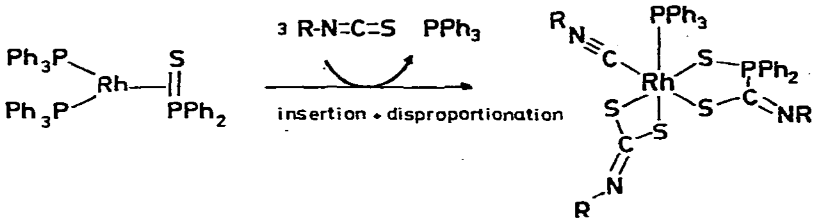


Fig. 6. The reaction at elevated temperature between $Rh(PPh_3)_2(SPPh_2)$ and PhNCS.

On passing CO through a solution of $Rh(H)Cl)(PPh_3)_2(SPPh_2)$, or $Rh(PPh_3)_2$-$(SPPh_2)$, the carbonyl complex $Rh(CO)(PPh_3)_2(SPPh_2)$ (VI) is formed, in which compound the Ph_2PS^- group is coordinated end-on via S to Rh. This compound was previously characterised and reported by Marsala et al. [9]. In the complexes $Rh(PPh_3)_2[Ph_2P\text{-}A]$, in which $[Ph_2P\text{-}A]$ represents a hetero-allylic ligand coordinating through P and the hetero atom A, the PPh_3 ligand *trans* to A, i.e. the phosphine which experiences the smallest *trans*-influence, is displaced by CO. In the present case on the contrary, $P_{chelate}$ is substituted, and CO is probably *trans* to Ph_2PS^-.

Insertion of Ph—N=C=S in the $Ph_2\overparen{PMS}$ system

$Rh(PPh_3)_2(SPPh_2)$ (IIIc) is formed from $Rh(PPh_3)_2[Ph_2P(S)C(N\textit{p}\text{-tol})N\textit{p}\text{-tol}]$ or $Rh(PPh_3)_2[Ph_2P(S)C(NPh)O]$ by elimination of *p*-tolN=C=N*p*-tol or PhN=C=O, respectively. We have already remarked that this tendency to elimination is probably connected with the weak *N* coordination of the hetero-allylic ligand. Since e.g. $Rh(PPh_3)_2[Ph_2P(S)C(S)NPh]$ is a stable complex, it should be possible to synthesize this complex from IIIc by insertion of Ph—N=C=S. We carried out this reaction by refluxing a mixture of IIIc and a large excess of Ph—N=C=S in benzene during two hours. From the resulting mixture $Rh(PPh_3)(PhNC)$-$(PhNCS_2)[Ph_2P(S)C(S)NPh]$ can be isolated as the main product (see Fig. 6). We previously prepared this compound by the reaction between $Rh(PPh_3)_2[Ph_2$-$P(S)C(S)NPh]$ and an excess of Ph—N=C=S, in which the hetero-allene molecules undergo a disproportionation [19]. In the present reaction insertion occurs together with disproportionation. Experiments with varying ratios of Ph—N=C=S/Rh revealed no preference for either insertion or disproportionation.

The overall reaction is the incorporation of three molecules of Ph—N=C=S. The reaction is well understood in view of the knowledge of the insertion and disproportionation properties of hetero-allenes.

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