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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.

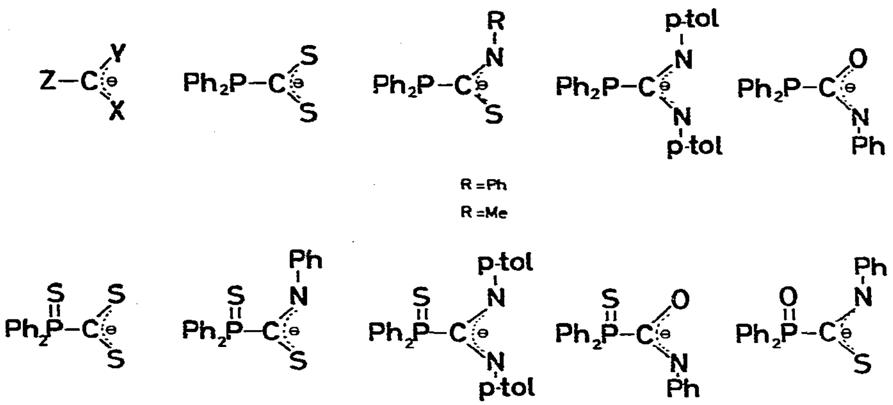


Fig. 1. The unsaturated hetero-allylic anions.

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 $Rh(H)(Cl)(PPh_3)_2(SPPh)_2$ 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 $Rh(PPh_3)_2[Ph_2PC(NR)Y]$ ($Y = Np\text{-tol}$, $R = p\text{-tol}$; $Y = O$, $R = Ph$) 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(PPh₃)(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 $Rh(PPh_3)(CO)_2[Ph_2PC(NPh)O]$; the colour changes slowly via brown to green. In the strained 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 $Rh(PPh_3)_2[Ph_2PC(N\textit{p}\text{-tol})N\textit{p}\text{-tol}]$ 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

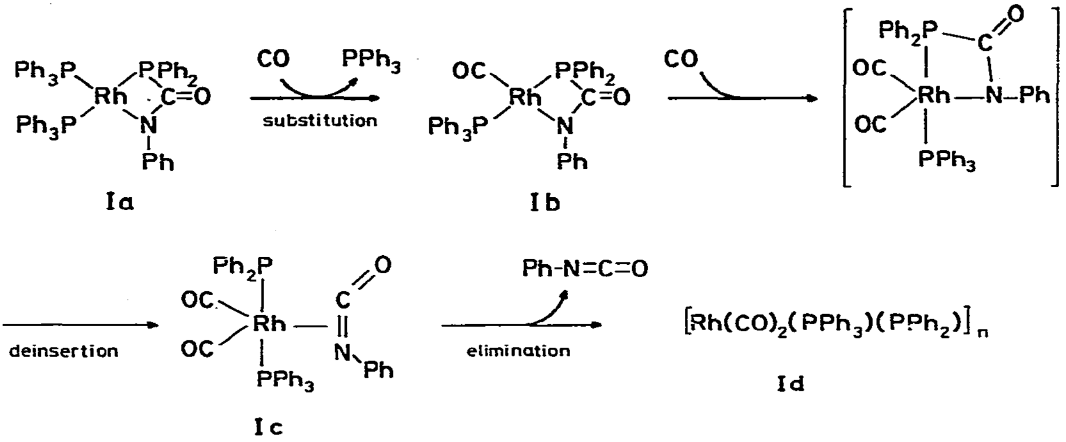
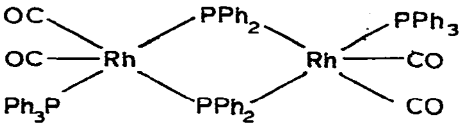


Fig. 2. The probable pathway for the reaction between $Rh(PPh_3)_2[Ph_2PC(NPh)O]$ and CO.

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 ν(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 $Ph_2P(S)C(N$*p*-tol)NH*p*-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 $Rh(PPh_3)_2[Ph_2P(S)C(N$*p*-tol)N*p*-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

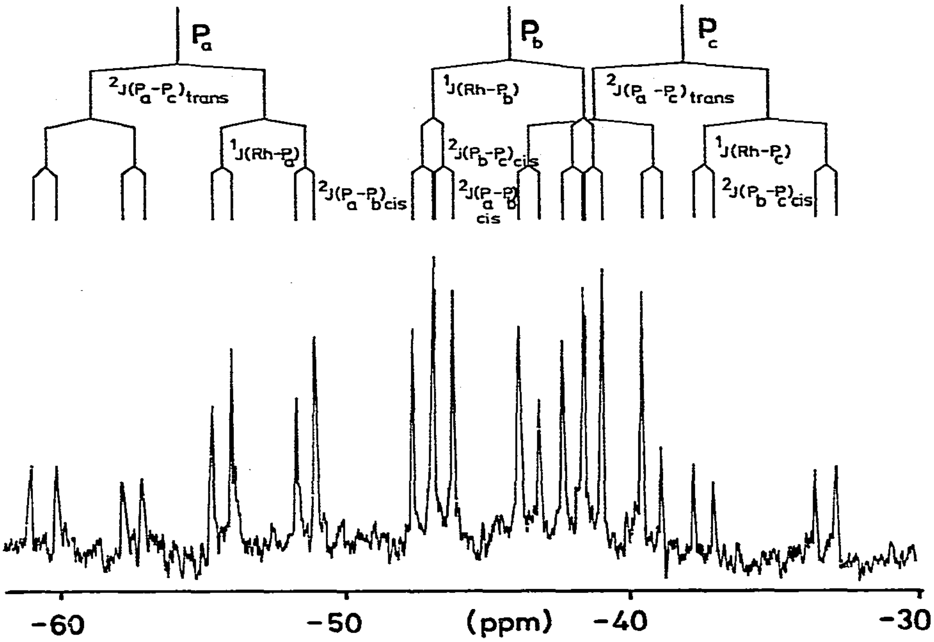


Fig. 3. The ^{31}[^{1}H]NMR spectrum of Rh(PPh$_3$)$_2$(SPPh$_2$).

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{^{1}H} NMR spectrum (see Table 5 and Fig. 3) indicates three inequivalent phosphorus nuclei, which means that the P atom of the Ph$_2$PS$^-$ moiety is coordinated to Rh. In particular the small value of ^{1}J(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$_2$PS$^-$ ligand is coordinated side-on. Previously, R$_2$PS$^-$ 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

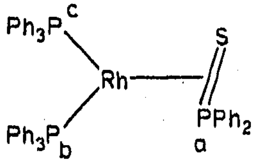
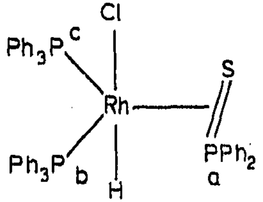
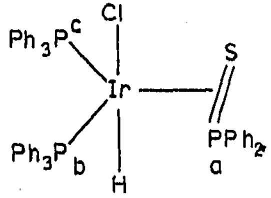
IR ABSORPTIONS IN cm^{-1}. SPECTRA MEASURED IN CsI PELLETS

Code	Complex	ν(C=E) [b]	ν(P=S)	ν(M—H)	ν(M—Cl)
IIIa	Rh(PPh$_3$)$_2$[Ph$_2$P(S)C(N*p*-tol)N*p*-tol] [a]	1546s (ν(C=N))	521m		
IIIb	Rh(PPh$_3$)$_2$[Ph$_2$P(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$_2$) · C$_6$H$_6$		512s	2118m	262vw
V	Ir(H)(Cl)(PPh$_3$)$_2$(SPPh$_2$) · C$_6$H$_6$		511s	2233m	263vw
VI	Rh(CO)(PPh$_3$)$_2$(SPPh$_2$)	1971 vs ν(C≡O)	516m		

[a] Measured in C$_6$H$_6$ solution. [b] E represents the exocyclic hetero atom.

TABLE 5

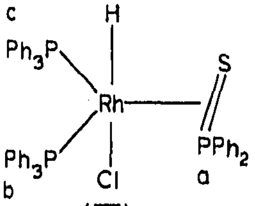
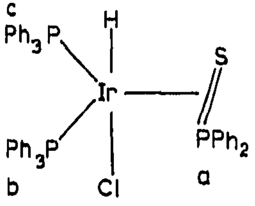
$^{31}H\{^{1}H\}$ NMR PARAMETERS

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							

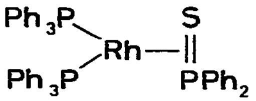
δ in ppm relative to O=P(OMe)$_3$ (TMP), internal reference; upfield shift positive; J in Hz, Solvent: CD_2Cl_2.

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.



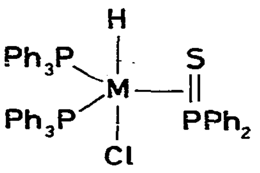


Fig. 4. The structure of $Rh(PPh_3)_2(SPPh_2)$.

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. $^2J(PPh_3b—PPh_3c)$ of square planar *cis* Rh^I $(PPh_3)_2[X—C-(Z)—Y]$ complexes varies from 35—50 Hz [2]. The value of $^2J(PPh_3b—PPh_3c)$ of $Rh^I(PPh_3)_2(\eta^2\text{-}SPPh_2)$ 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 $Pt(PPh_3)_2(\eta^2\text{-}A{=}B)$ 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 "interligand angle effect" by S. Otsuka [18]) and consequently a still smaller $^2J(PPh_3b—PPh_3c)$ coupling constant. Actually in compounds IV and V $^2J(PPh_3b—PPh_3c) \approx 0$.

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.

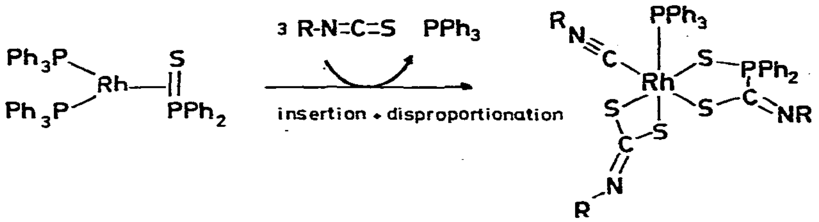


Fig. 6. The reaction at elevated temperature between $Rh(PPh_3)_2(SPPh_2)$ and PhNCS.

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 $Ph_2\overline{PMS}$ system

$Rh(PPh_3)_2(SPPh_2)$ (IIIc) is formed from $Rh(PPh_3)_2[Ph_2P(S)C(N$*p*-tol)N*p*-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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