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

II *. RHODIUM(I)- AND IRIDIUM(I)-PHOSPHINE COMPLEXES OF HETERO-ALLYLIC LIGANDS OF THE TYPE $[Ph_2PC(X)NR]^-$ (X = S, NR, O) AND $[Ph_2P(Q)C(S)NR]^-$ (Q = S, O). SYNTHESIS AND ^{31}P-NMR

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Summary

Some known and new hetero-allylic derivatives $[Ph_2PC(X)NR]^-$ (X = S, NR, O) and $[Ph_2P(Q)C(S)NR]^-$ (Q = S, O) have been shown to react with rhodium(I)- and iridium(I)-phosphine compounds to give stable complexes $M(PPh_3)_2[Ph_2PC(X)NR]$ (A) and $M(PPh_3)_2[Ph_2P(Q)C(X)NR]$ (B) (M = Rh, Ir) in which the ligands are bidentate. P, S(P) and O(P) are always coordinated and the coordination preference of the other atoms is: S > NR > O.

A and B react with carbon monoxide to give $M(PPh_3)(CO)[Ph_2PC(X)NR]$ and $M(PPh_3)(CO)[Ph_2P(Q)C(S)NR]$, respectively, in which CO is preferentially found *trans* to the chelate donor atom with the lowest *trans*-influence.

A correlation between $\sqrt{^1J(Rh{-}P_1) \times {}^1J(Rh{-}P_2)}$ and $^2J(P_1{-}P_2)_{cis}$ of 0.946 was found; an even better correlation with $r = 0.988$ gave the equation: $^2J(P_1{-}P_2)_{cis} = 0.43\sqrt{^1J(Rh{-}P_1) \times {}^1J(Rh{-}P_2)} - 0.072\,|{}^1J(Rh{-}P_1) - {}^1J(Rh{-}P_2)| - 30.8$ Hz. A similar correlation was shown by a number of asymmetric *cis*-Pt^0-bis-phosphine (η^2-ligand) complexes and *trans*- and *cis*-WLL′-$(CO)_4$ complexes reported in the literature.

Introduction

By addition of $Ph_2P{-}H$ or $Ph_2P(Q){-}H$ (Q = S, O) to the hetero-allene molecules S=C=NR (R = Ph, Me), *p*-tolN=C=N*p*-tol and O=C=NPh, hetero-allylic

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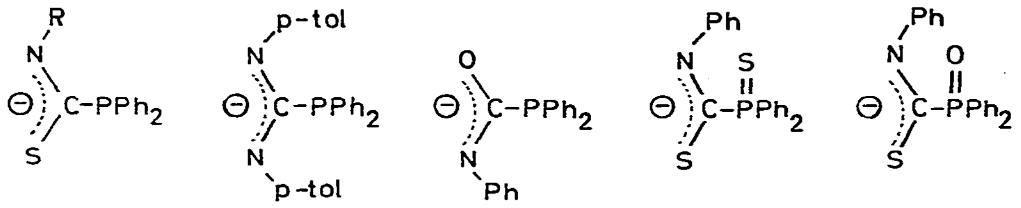


LI R=Ph LIII LIV LV LVI
LII R=Me

Fig. 1. The ambidentate hetero-allylic chelating ligands $[X—C(Z)—Y]^-$, used in this paper; LI, *P,P*-diphenyl-*N*-phenyl-phosphinothioformamido; LII, *P,P*-diphenyl-*N*-methyl-phosphinothioformamido; LIII, *P,P*-diphenyl-*N,N'*-di-*p*-tolyl-phosphinoformamidinato; LIV, *P,P*-diphenyl-*N*-phenyl-phosphinoformamido; LV, *P,P*-diphenyl-*N*-phenyl-thiophosphinylthioformamido: LVI, *P,P*-diphenyl-*N*-phenyl-phosphinylthioformamido.

derivatives result with the general formula $Ph_2PC(X)NHR$ (X = S, NR, O) and $Ph_2P(Q)C(S)NHR$ (Q = S, O). The synthesised ligands are shown in Fig. 1 in their deprotonated forms.

These ligands are ambidentate, because of the presence of three hetero atoms with coordinating properties. The mode of coordination of the ambidentate ligands can be determined by means of IR and ^{31}P NMR spectral parameters.

Gal et al. [2,3] reported the complexes $Rh(PPh_3)_2(LI)$ and $Rh(PPh_3)_2(LVI)$. LI was found to coordinate to rhodium through P and S, giving a four-membered chelate ring complex, whereas LVI coordinated through O(P) and S, resulting in a five-membered chelate ring complex.

Experimental

IR spectra were measured on a Perkin-Elmer 283 spectrophotometer (4000—200 cm^{-1}), 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 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. Analytical data are given in Table 1.

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

$RhCl(PPh_3)_3$ [4], $[IrCl(C_8H_{14})_2]_2$ [5], $Ph_2PC(S)NHR$ (R = Ph, Me) [6], $Ph_2PC(Np\text{-tol})NHp\text{-tol}$ [7], $Ph_2PC(O)NHPh$ [8], $Ph_2P(S)C(S)NHPh$ and $Ph_2P(O)C(S)NHPh$ [9] were prepared according to literature procedures.

$Rh(PPh_3)_2[X\text{-}C(Z)\text{-}Y]$ (IIa, IVa, Va)

0.3 mmol of the protonated ligand was added to a solution of 0.3 mmol $RhCl(PPh_3)_3$ in 20 ml benzene. After 20 minutes a small excess of Et_3N was added and after 12 hours the $Et_2N \cdot HCl$ was filtered off. The complex was precipitated with n-hexane, filtered off, washed with ethanol and diethyl ether, and dried in vacuo. [^1H NMR IIa: $\tau(Me)$ 7.00 ppm (s), 7.23 ppm (s)].

$Rh(PPh_3)_2[Ph_2PC(Np\text{-}tol)Np\text{-}tol]$ *(IIIa)*

The initial red solution from 0.3 mmol $RhCl(PPh_3)_3$ and 0.3 mmol Ph_2PC-(N*p*-tol)NH*p*-tol in 20 ml benzene changed to orange-red upon addition of an equimolar amount n-BuLi. The complex was precipitated with n-hexane, filtered off, washed with ethanol and diethylether and dried in vacuo. [^{1}H NMR: τ(Me) 8.16 ppm (s), 8.22 ppm (s)].

$Ir(PPh_3)_2[X\text{-}C(Z)\text{-}Y]$ *(VIIa, IXa, Xa, XIa)*

To a solution of 0.15 mmol $[IrCl(C_8H_{14})_2]_2$ and 0.6 mmol PPh_3 in 30 ml benzene 0.3 mmole of the protonated ligand was added. After 20 minutes a small excess Et_3N was added. The initial red colour changed in three hours to yellow. After removal $Et_3N \cdot HCl$ by filtration the complex was precipitated with n-hexane, filtered off, washed with small amounts ethanol and diethylether, and dried in vacuo.

$Ir(PPh_3)_2[Ph_2PC(Np\text{-}tol)Np\text{-}tol]$ *(VIIIa)*

This complex could not be isolated. On addition of an equimolar amount n-BuLi to a solution of 0.15 mmol $[IrCl(C_8H_{14})_2]_2$, 0.6 mmol PPh_3 and 0.3 mmol Ph_2PC(N*p*-tol)NH*p*-tol in 30 ml benzene, VIIIa was formed, as could be proved by IR measurements of the reaction-mixture. However, VIIIa was not stable and a subsequent elimination of *p*-tolN=C=N*p*-tol occurred, as will be described elsewhere [10].

TABLE 1

ANALYTICAL DATA

(Theoretical values in parentheses)

No.	Compound	colour	Found (calcd.) (%)			yield (%)
			C	H	N	
IIa	$Rh(PPh_3)_2[Ph_2PC(S)NMe]$	yellow	67.9 (67.4)	5.2 (5.0)	1.7 (1.6)	75
IIIa	$Rh(PPh_3)_2[Ph_2PC(Np\text{-}tol)Np\text{-}tol]$	yellow-orange	72.1 (73.1)	5.4 (5.3)	2.5 (2.7)	70
IVa	$Rh(PPh_3)_2[Ph_2PC(NPh)O]$	yellow-orange	69.0 (68.5)	5.2 (5.3)	1.5 (1.6)	70
Va	$Rh(PPh_3)_2[Ph_2P(S)C(S)NPh]$	yellow	68.2 (67.4)	5.0 (4.6)	1.3 (1.4)	70
Vb	$Rh(PPh_3)(CO)[Ph_2P(S)C(S)NPh]$	orange	60.4 (61.2)	4.1 (4.1)	2.0 (1.9)	85
VIIa	$Ir(PPh_3)_2[Ph_2PC(S)NPh]$	yellow-brown	64.0 (63.7)	4.7 (4.4)	1.3 (1.4)	70
VIIb	$Ir(PPh_3)(CO)[Ph_2PC(S)NPh]$	orange	55.7 (56.9)	4.1 (3.8)	1.8 (1.7)	75
IXa	$Ir(PPh_3)_2[Ph_2PC(NPh)O]$	yellow-brown	62.1 (64.7)	4.9 (4.4)	1.5 (1.4)	45
Xa	$Ir(PPh_3)_2[Ph_2P(S)C(S)NPh]$	yellow-orange	60.2 (61.8)	4.5 (4.2)	1.4 (1.3)	40
Xb	$Ir(PPh_3)(CO)[Ph_2P(S)C(S)NPh]$	yellow	57.0 (54.7)	3.9 (3.6)	1.5 (1.7)	35
XIa	$Ir(PPh_3)_2[Ph_2P(O)C(S)NPh]$	yellow	62.6 (62.7)	4.3 (4.3)	1.2 (1.3)	40
XIb	$Ir(PPh_3)(CO)[Ph_2P(O)C(S)NPh]$	yellow	56.0 (55.7)	4.0 (3.7)	1.5 (1.7)	35

M(PPh$_3$)(CO)[X—C(Z)—Y] (Vb, VIIb, Xb, XIb)

On passing CO through a solution of 0.3 mmol M(PPh$_3$)$_2$[X—C(Z)—Y] in 30 ml benzene the colour of the reaction mixture rapidly changed from yellow to orange-yellow. Dilution with n-hexane and cooling gave an orange or yellow precipitate.

The analogous complexes IIIb, IVb, VIIIb and IXb could not be prepared. IIIa, IVa and IXa reacted differently with CO [10]. Yields are given in Table 1. The Ir complexes were more difficult to obtain and were much less stable than the Rh analogs.

Results and discussion

Reactions and products

The Rh^I and Ir^I complexes M(PPh$_3$)$_2$[X—C(Z)—Y] can be prepared either by a metathetical substitution using the Li salts of the ligands or by means of a N—H bond breaking reaction activated by a base, e.g. Et$_3$N.

The complex Ir^{III}(H)(Cl)(PPh$_3$)$_2$[Ph$_2$PC(S)NPh] is one of the products of the reaction between [IrCl(C$_8$H$_{14}$)$_2$]$_2$, PPh$_3$ and Ph$_2$PC(S)NHPh without addition of Et$_3$N. This indicates that the N—H bond breaking is an oxidative addition reaction. The N—H bond breaking does not occur with Ph$_2$PC(N*p*-tol)NH*p*-tol. Probably this ligand is not sufficiently acidic to give a facile N—H bond breaking. [IrCl(C$_8$H$_{14}$)$_2$]$_2$ reacts with [Ph$_2$PC(N*p*-tol)N*p*-tol]$^-$Li$^+$ to give the intermediate {Ir(PPh$_3$)$_2$[Ph$_2$PC(N*p*-tol)N*p*-tol]}, as can be observed from the IR spectrum of the reaction mixture. A subsequent elimination reaction occurs, and this will be discussed later [10].

The carbonyl complexes of the type M(PPh$_3$)(CO)[X—C(Z)—Y] can be prepared by passing CO through a solution of M(PPh$_3$)$_2$[X—C(Z)—Y] one phosphine being replaced by CO. In the case of Rh(PPh$_3$)$_2$[Ph$_2$PC(N*p*-tol)N*p*-tol] and M(PPh$_3$)$_2$[Ph$_2$PC(O)NPh], however, a second reaction takes place [10]. This subsequent elimination also occurs to some extent in the reaction of Ir(PPh$_3$)$_2$-[Ph$_2$P(S)C(S)NPh] and Ir(PPh$_3$)$_2$[Ph$_2$P(O)C(S)NPh] with CO. The occurrence of this second reaction may explain the fairly low yields in the syntheses of both Ir complexes.

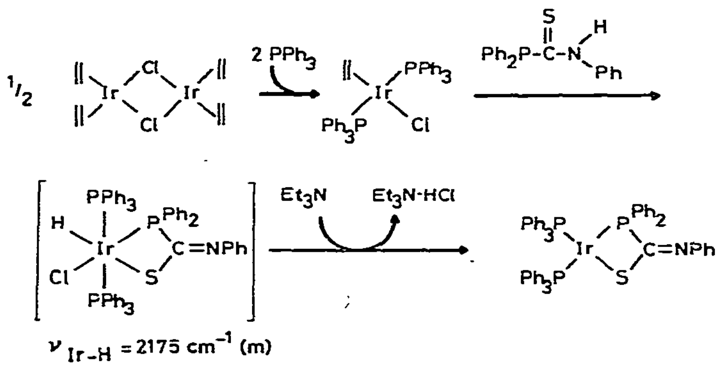


Fig. 2. Formation of Ir(PPh$_3$)$_2$[Ph$_2$PC(S)NPh] from IrCl(PPh$_3$)$_2$(C$_8$H$_{14}$) and Ph$_2$PC(S)NHPh via an oxidative addition reaction.

IR spectra and mode of coordination

Table 2 shows the relevant absorptions in the IR spectra between 2000 and 500 cm^{-1}. In these complexes a strong absorption can be attributed to a normal mode having $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{E})$ of the exocyclic C=E band as the main component [11—14]. Two regions are found for this absorption: 1500—1575 cm^{-1}, attributed to $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$, and 1620—1640 cm^{-1}, assigned to $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$. This establishes for all complexes the mode of bidentate coordination of the ambidentate ligands.

Coordination by P and S is observed for the complexes of $[\mathrm{Ph_2PC(S)NR}]^-$ (R = Ph, Me). The ligand $[\mathrm{Ph_2PC(N}p\text{-tol)N}p\text{-tol}]^-$ is obviously coordinated by P and N. For the complexes of $[\mathrm{Ph_2PC(X)NR}]^-$ (X = S, NR) $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ is found in the region 1547—1575 cm^{-1}, whereas the complexes of $[\mathrm{Ph_2PC(NPh)O}]^-$ have $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{E})$ at about 1620 cm^{-1}, which is assigned to $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$. Therefore $[\mathrm{Ph_2PC(NPh)O}]^-$ is coordinated by P and N.

The ligands $[\mathrm{Ph_2P(Q)C(S)NPh}]^-$ (Q = S, O) have $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ in the region 1509—1533 cm^{-1} and form five-membered chelate rings as is also indicated by the values of ν(P=Q). In the spectra of $\mathrm{M(PPh_3)(L)[Ph_2P(S)C(S)NPh]}$ (M = Rh, Ir L = PPh_3, CO) new absorptions of medium intensity are observed in the region 602—625 cm^{-1} and of strong intensity between 512—520 cm^{-1}. These absorptions are assigned to ν(P=S). For complexes of the ligand $\mathrm{R_2P(S)CSS^-}$ ν(P=S) was reported in the range 580—610 cm^{-1}; for $\mathrm{Pd[Ph_2P(S)C(S)S]_2}$ ν(P=S) was assigned at 601 cm^{-1} [15], and $\mathrm{Zn[Cy_2P(S)C(S)S]_2}$ at 597 cm^{-1} [16]. In complexes of the ligand $\mathrm{R_2PS^-}$ and $\mathrm{R_2PHS}$ ν(P=S) was assigned at 520 cm^{-1} for $\mathrm{[Mn(CO)_4(\mu\text{-}Me_2PS)]_2}$ [22], and at 495 cm^{-1} for $\mathrm{Mo(CO)_5(SPHMe_2)}$ [23]. ν(P=O) decreases 45—50 cm^{-1} on complexation. The mode of coordination to form a five membered chelate ring complex was already established for $[\mathrm{Ph_2P(O)C(S)NPh}]^-$ [2].

ν(PCS) is observed from 920—930 cm^{-1} for the four ring complexes, whereas the five ring compounds exhibit ν(PCS) in the region 952—970 cm^{-1}.

In the carbonyl complexes the C≡O absorptions are observed from 1950—1987 cm^{-1}, which is normal for four coordinate Rh and Ir complexes. The value of ν(CO) is somewhat higher for the Rh complex than for the analogous Ir compound.

Summarising, we have found that P, S(P) and O(P) are always coordinated and that the coordination preference of the other groups is S > NR > O.

^{31}P NMR spectra and correlation between coupling constants

The measured $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR parameters are given in Table 3. The values are not corrected for higher order effects. The spectra of $\mathrm{Rh(PPh_3)_2[Ph_2PC(N}p\text{-tol)N}p\text{-tol]}$ and $\mathrm{Rh(PPh_3)_2[Ph_2P(S)C(S)NPh]}$ are shown in Figs. 3 and 4, respectively.

Assignments are as given in Table 3. All the complexes contain two PPh_3 ligands *cis* to each other. As observed by Gal et al. for five of the complexes [2], the PPh_3 group with the highest value of ^1J(Rh—P), i.e. the phosphine *trans* to the hetero atom with the lowest *trans*-influence, is displaced by a π-acceptor ligand such as CO. In the four-membered chelate ring complexes the phosphine *trans* to the hetero atom S or NR is displaced by CO, whereas in Va and VIa the

TABLE 2

IR ABSORPTIONS (cm^{-1})

No.	Complex	$\nu(C\equiv O)$	$\nu(C=E)$	$\nu(P=Z)$		$\nu(P-C-S)$	$\nu(N-Ph)$
Ia	$Rh(PPh_3)_2[Ph_2PC(S)NPh]$		1547vs ($\nu(C=N)$)			925w	803w
Ib	$Rh(PPh_3)(CO)[Ph_2PC(S)NPh]$	1975vs	1572s ($\nu(C=N)$)			930m	803w
IIa	$Rh(PPh_3)_2[Ph_2PC(S)NMe]$		1575vs ($\nu(C=N)$)			927m	
IIIa	$Rh(PPh_3)_2[Ph_2PC(Np\text{-}tol)Np\text{-}tol]$		1552vs ($\nu(C=N)$)				
IVa	$Rh(PPh_3)_2[Ph_2PC(NPh)O]$		1624vs ($\nu(C=O)$)				808w
Va	$Rh(PPh_3)_2[Ph_2P(S)C(S)NPh]$		1520s ($\nu(C=N)$)	625m ($\nu(P=S)$)	520s ($\nu(P=S)$)	960m	798w
Vb	$Rh(PPh_3)(CO)[Ph_2P(S)C(S)NPh]$	1987vs	1524s ($\nu(C=N)$)	612m ($\nu(P=S)$)	515s ($\nu(P=S)$)	952m	800w
VIa	$Rh(PPh_3)_2[Ph_2P(O)C(S)NPh]$		1511s ($\nu(C=N)$)		1135s ($\nu(P=O)$)	968m	802m
VIb	$Rh(PPh_3)(CO)[Ph_2P(O)C(S)NPh]$	1980vs	1533s ($\nu(C=N)$)		1130s ($\nu(P=O)$)	968m	802w
VIIa	$Ir(PPh_3)_2[Ph_2PC(S)NPh]$		1552vs ($\nu(C=N)$)			922m	801m
VIIb	$Ir(PPh_3)(CO)[Ph_2PC(S)NPh]$	1955vs	1555vs ($\nu(C=N)$)			920m	804w
VIIIa	$Ir(PPh_3)_2[Ph_2PC(Np\text{-}tol)Np\text{-}tol]$ [a]		1562vs ($\nu(C=N)$)				
IXa	$Ir(PPh_3)_2[Ph_2PC(NPh)O]$		1621vs ($\nu(C=O)$)				806w
Xa	$Ir(PPh_3)_2[Ph_2P(S)C(S)NPh]$		1509s ($\nu(C=N)$)	610m ($\nu(P=S)$)	515s ($\nu(P=S)$)	957m	795w
Xb	$Ir(PPh_3)(CO)[Ph_2P(S)C(S)NPh]$	1951vs	1529s ($\nu(C=N)$)	602m ($\nu(P=S)$)	512s ($\nu(P=S)$)	951m	800w
XIa	$Ir(PPh_3)_2[Ph_2P(O)C(S)NPh]$		1512s ($\nu(C=N)$)		1132s ($\nu(P=O)$)	970m	802m
XIb	$Ir(PPh_3)(CO)[Ph_2P(O)C(S)NPh]$	1947vs	1517s ($\nu(C=N)$)		1140s ($\nu(P=O)$)	965m	803w

Spectra measured in CsI pellets ([a] measured in benzene solution).

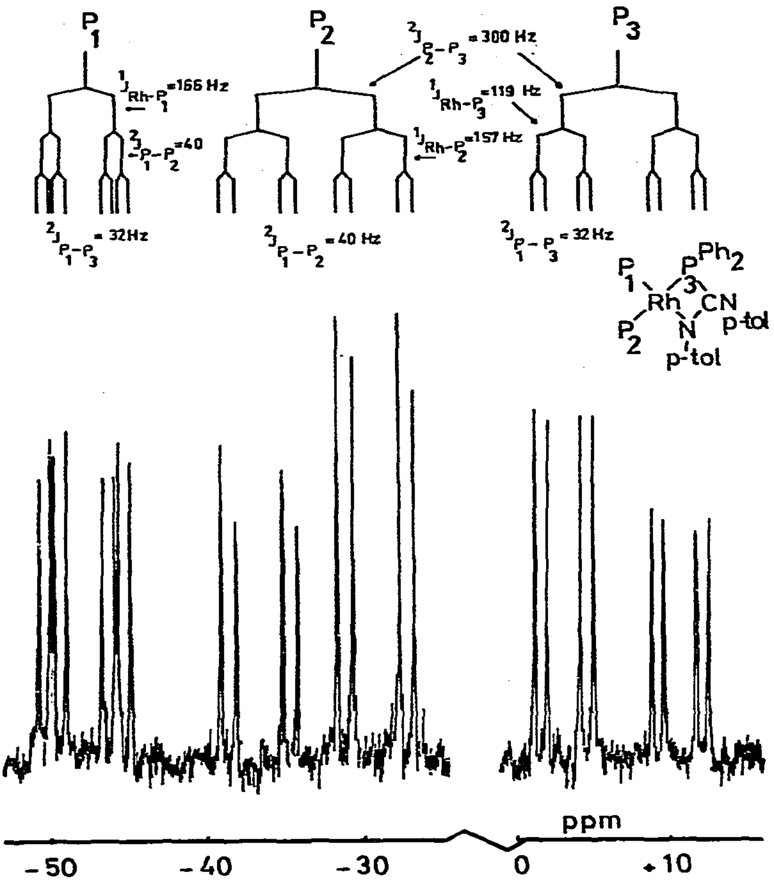


Fig. 3. The ^{31}P $\{^1H\}$ NMR spectrum of $Rh(PPh_3)_2[Ph_2PC(Np\text{-}tol)Np\text{-}tol]$.

PPh_3 ligand *trans* to S(P) and O(P) is replaced. It is noteworthy that the spectrum of Va differs slightly from that of VIa. The $^2J(Rh—Q—P_3)$ coupling is 3 Hz in VIa and unobserved in Va, whereas the $^3J(P_1—Rh—Q—P_3)$ coupling is unobserved in VIa and 3 Hz in Va.

Summarised, $^1J(Rh—P_i)$ ($i = 1, 2$) is observed in the range 164—202 Hz for the PPh_3 ligand that is substituted by CO, and 148—170 Hz for the phosphine which is not displaced, while $^1J(Rh—P_3)$ for the ligand PPh_2-group lies in the range 102—124 Hz. $^2J(P_1—P_2)_{cis}$ varies from 35 to 47 Hz in the Rh complexes and from 14 to 22 in the Ir analogues, whereas $^2J(P_2—P_3)_{cis}$ is observed from 24 to 36 Hz. $^2J(P_2—P_3)_{trans}$ in the four membered chelate ring complexes is found from 300—333 Hz for the Rh complexes and amounts to 340 Hz for $Ir(PPh_3)_2[Ph_2PC(S)NPh]$.

There is an approximate linear relationship between $^1J(Rh—P_i)$ and $\delta(P_i)$, the correlation coefficient being 0.844. Gal et al. have attributed such a relationship to the *trans*-influence of the various hetero atoms.

It has been mentioned that variations in $^1J(M—P)$ and $^2J(P—P)$ are expected to parallel each other [17—19]. Indeed $^1J(Rh—P_i)$ and $^2J(P_1—P_2)_{cis}$ exhibit similar

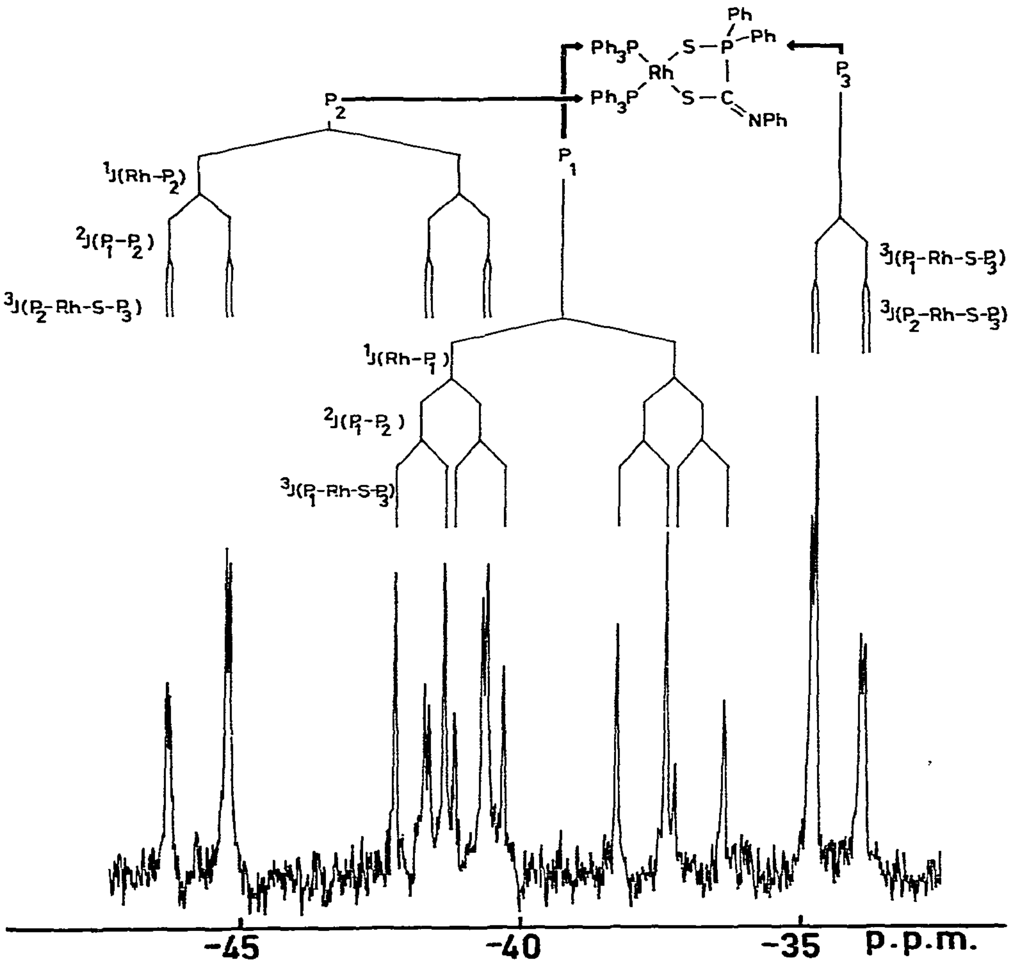
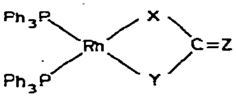


Fig. 4. The ^{31}P $\{^1$H$\}$ NMR spectrum of Rh(PPh$_3$)$_2$[Ph$_2$P(S)C(S)NPh].

trends. Therefore, we have examined the correlations for the set of asymmetric complexes of the type Rh(PPh$_3$)$_2$[X—C(Z)—Y] (X $\neq$ Y) described in this paper and the related compounds reported by Gal et al. [2], assuming the same sign for all complexes (positive).



^1J(Rh—P$_1$) and ^2J(P$_1$—P$_2$)$_{cis}$ gave a low correlation coefficient of 0.45. However, the correlation between the geometric mean $\sqrt{^1J(\mathrm{Rh—P_1}) \times {}^1J(\mathrm{Rh—P_2})}$ and ^2J(P$_1$—P$_2$)$_{cis}$ was 0.946, implying that ^2J(P$_1$—P$_2$) is related to both of the ^1J coupling constants. The relationship between ^2J(P$_1$—P$_2$)$_{cis}$ and $\sqrt{^1J(\mathrm{Rh—P_1} \times {}^1J(\mathrm{Rh—P_2})}$ is plotted in figure 5 [x]. The plot reveals that ^2J(P$_1$—P$_2$)$_{cis}$ is also a

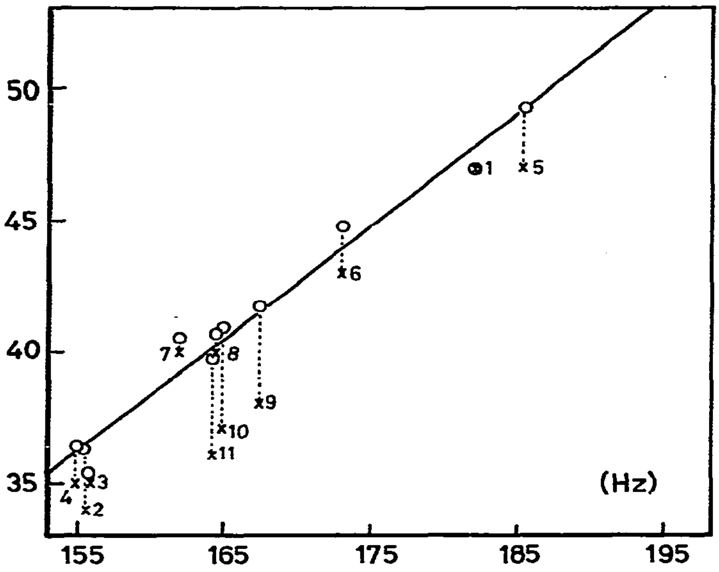


Fig. 5. Plot of $^2J(P_1{-}P_2)_{cis}$ versus $\sqrt{^1J(Rh{-}P_1) \times {}^1J(Rh{-}P_2)}$ [X] and of $^2J(P_1{-}P_2)_{cis} + 0.072|^1J(Rh{-}P_1) - {}^1J(Rh{-}P_2)|$ versus $\sqrt{^1J(Rh{-}P_1) \times {}^1J(Rh{-}P_2)}$ [o]. Solid line calculated, using equation 1 in the form:

$$^2J(P_1{-}P_2)_{cis} + \frac{b}{\mu}|^1J(Rh{-}P_1) - {}^1J(Rh{-}P_2)| = \frac{a}{\mu}\sqrt{^1J(Rh{-}P_1) + {}^1J(Rh{-}P_2)} - c$$

with $\frac{a}{\mu} = 0{\cdot}43$, $\frac{b}{\mu} = 0.072$ and $c = 30.8$ Hz. Complexes: 1, $Rh(PPh_3)_2[Me_2NC(S)NPh]$; 2, $Rh(PPh_3)_2[Ph_2PC(S)S]$; 3, $Rh(PPh_3)_2[Ph_2PC(S)NPh]$; 4, $Rh(PPh_3)_2[Ph_2PC(S)NMe]$; 5, $Rh(PPh_3)_2[Ph_2P(O)C(S)NPh]$; 6, $Rh(PPh_3)_2[Ph_2P(S)C(S)NPh]$; 7, $Rh(PPh_3)_2[Ph_2PC(N$*p*-tol$)N$*p*-tol$]$; 8, $Rh(PPh_3)_2[Ph_2PC(NPh)O]$; 9, $RhCl(PPh_3)_3$ [24]; 10, $RhBr(PPh_3)_3$ [24]; 11, $RhI(PPh_3)_3$ [24].

function of the absolute value of the difference of the two coupling constants $^1J(Rh{-}P_1)$ and $^1J(Rh{-}P_2)$, which is a measure of the asymmetry within the complex, so that an empirical relation between $^1J(M{-}P_1)$, $^1J(M{-}P_2)$ and $^2J(P_1{-}P_2)$ may be given:

$$^2J(P_1{-}P_2)_{cis} = \frac{1}{\mu}[a\sqrt{^1J(M{-}P_1) \times {}^1J(M{-}P_2)} - b|^1J(M{-}P_1) - {}^1J(M{-}P_2)|] - c \qquad (1)$$

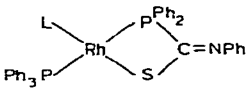
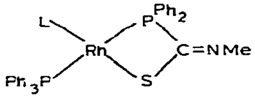
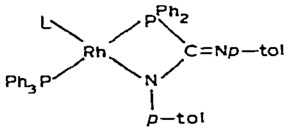
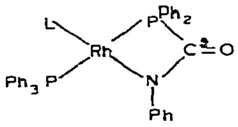
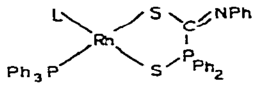
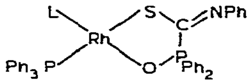
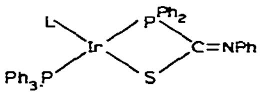
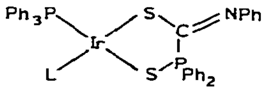
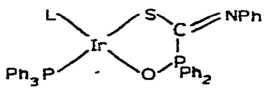
μ represents the nuclear magnetic moment of the metal in nuclear magnetons; a, b and c are empirical constants. For the set of asymmetric *cis*-Rh^I-bisphosphine complexes we computed: $a/\mu = 0.43$ $b/\mu = 0.072$ and $c = 30.8$ Hz, with a correlation-coefficient $r = 0.988$.

, The existence of such a correlation is confirmed by the similar behaviour of ten iso-structural asymmetric *cis*-Pt^0-bisphosphine-(η^2-ligand) complexes, the NMR parameters of which are reported by Meij et al. [20—21]. In Fig. 6 the plot of $^2J(P_1{-}P_2)_{cis}$ versus $\sqrt{^1J(Pt{-}P_1) \times {}^1J(Pt{-}P_2)}$ is shown. Again signs are taken as positive, except $^2J(P_1{-}P_2)_{cis}$ of compounds 3 and 4. If the signs for $^2J(P_1{-}P_2)_{cis}$ of compounds 3 and 4 are not taken as negative, no acceptable correlation results.

The correlation between $^2J(P_1{-}P_2)_{cis}$ and $^1J(Pt{-}P_i)$ ($i = 1, 2$) has a correlation coefficient of 0.46; the value for the correlation between $^2J(P_1{-}P_2)_{cis}$ and

TABLE 3

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

Complex	Number	L	δ_1	$^1J(Rh-P_1)$	group *trans*	δ_2
	Ia	PPh_3	−41.5	164	S	−32.6
	Ib	CO				−31.2
	IIa	PPh_3	−41.5	164	S	−33.6
	IIIa	PPh_3	−48.0	166	N	−32.7
	IVa	PPh_3	−47.7	169	N	−32.4
	Va	PPh_3	−43.4	186	S(P)	−39.3
	Vb	CO				−41.4
	VIa	PPh_3	−54.8	202	O(P)	−40.9
	VIb	CO				−35.6
	VIIa	PPh_3	−19.4		S	−21.3
 [a]	Xa	PPh_3	−33.1		S(P)	−19.7
	XIa	PPh_3	−38.4		O(P)	−24.2

In ppm relative to $O{=}P(OMe)_3$ (TMP), internal reference; upfield = +; *J* in Hz. Measured in CD_2Cl_2 solution.

[a] Decomposes slowly in CD_2Cl_2.

$\sqrt{^1J(Pt-P_1) \times {}^1J(Pt-P_2)}$ is 0.949. Using expression 1 we calculated a correlation coefficient of 0.990 with $a/\mu = 0.077$ $b/\mu = 0.0097$ and $c = 285$ Hz.

Although no theoretical interpretation is available a relationship such as expressed in equation 1 may have a fundamental basis.

The term $\sqrt{^1J(M-P_1) \times {}^1J(M-P_2)}$ is a measure for the contribution of the *s*

$^1J(\mathrm{Rh{-}P_2})$	group *trans*	δ_3	$^1J(\mathrm{Rh{-}P_3})$	group *trans*	$^nJ(\mathrm{P_1{-}P_2})$	$^nJ(\mathrm{P_1{-}P_3})$	$^nJ(\mathrm{P_2{-}P_3})$
148	$-\mathrm{PPh_2}$	+6.0	119	$\mathrm{PPh_3}$	35 *cis*	24 *cis*	330 *trans*
136	$-\mathrm{PPh_2}$	+7.8	102	$\mathrm{PPh_3}$			332 *trans*
147	$-\mathrm{PPh_2}$	+8.2	120	$\mathrm{PPh_3}$	35 *cis*	25 *cis*	333 *trans*
158	$-\mathrm{PPh_2}$	+6.6	119	$\mathrm{PPh_3}$	40 *cis*	32 *cis*	300 *trans*
160	$-\mathrm{PPh_2}$	+0.8	124	$\mathrm{PPh_3}$	40 *cis*	36 *cis*	302 *trans*
161	S	−34.4	0	$\mathrm{PPh_3}$	43 *cis*	3 *trans*	36 *cis*
175	S	−40.7	5	$\mathrm{PPh_3}$			24 *cis*
170	S	−28.6	3	$\mathrm{PPh_3}$	47 *cis*	0 *trans*	18 *cis*
152	S	−33.1	4	CO			17 *cis*
	$-\mathrm{PPh_2}$	+11.1		$\mathrm{PPh_3}$	20 *cis*	20 *cis*	342 *trans*
	S	−17.4		$\mathrm{PPh_3}$	30 *cis*	6 *trans*	26 *cis*
	S	−27.6		$\mathrm{PPh_3}$	19 *cis*		12 *cis*

orbitals to the two metal—ligand bonds, as $^1J(\mathrm{M{-}P_1})$ and $^1J(\mathrm{M{-}P_2})$ are mainly determined by the *s* character of the M—P bonds [25—27]. $^2J(\mathrm{P_1{-}P_2})_{cis}$ is determined by the metal *s* and *d* character of the M—P bonds in the case of $\mathrm{Rh^I}$ and by the *s*, *p* and *d* character in the case of $\mathrm{Pt^0}$, because this coupling takes place via the metal-centre. The metal *s*- and *d*-orbitals have opposite contributions to

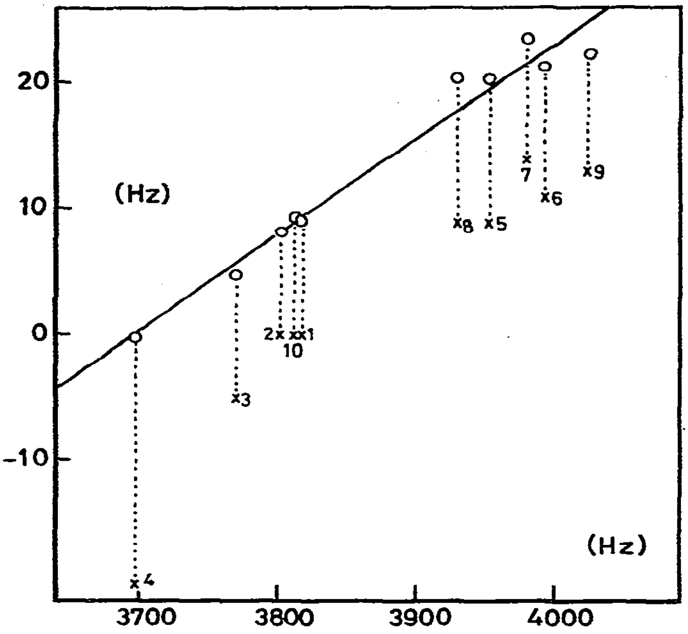


Fig. 6. Plot of $^2J(P_1—P_2)_{cis}$ versus $\sqrt{^1J(Pt—P_1) \times {}^1J(Pt—P_2)}$ [X] and of $^2J(P_1—P_2)_{cis} + 0.0097\,|^1J(Pt—P_1) - {}^1J(Pt—P_2)|$ versus $\sqrt{^1J(Pt—P_1) \times {}^1J(Pt—P_2)}$ [o]. Solid line calculated, using equation 1 in the form:

$$^2J(P_1—P_2)_{cis} + \frac{b}{\mu}|^1J(Pt—P_1) - {}^1J(Pt—P_2)| = \frac{a}{\mu}\sqrt{^1J(Pt—P_1) \times {}^1J(Pt—P_2)} - c$$

with $\frac{a}{\mu} = 0.077$, $\frac{b}{\mu} = 0.0097$ and $c = 285$ Hz. Complexes: 1, $Pt(PPh_3)_2$(*p*-tolN=S=N*p*-tol); 2, $Pt(PPh_3)_2$-(*p*-Cl-phenylN=S=N*p*-Cl-phenyl); 3, $Pt(PPh_3)_2$(3,5-xylylN=S=N-3,5-xylyl); 4, $Pt(PPh_3)_2CS_2$); 5, $Pt(PPh_3)_2$-(PhN=S=O); 6, $Pt(PPh_3)_2$(*p*-tolN=S=O); 7, $Pt(PPh_3)_2$(*o*-tolN=S=O); 8, $Pt(PPh_3)_2$(3,5-xylylN=S=O); 9, $Pt(PPh_3)_2$(2,4,6-mesitylN=S=O); 10, $Pt(PPh_3)_2$(PhN=S=NPh) [20—21].

$^2J(P_1—P_2)_{cis}$, because of the node of the *d*-orbital (i.e. the *d*-orbital changes sign over 90°).

The values of *a* (0.038) and *b* (0.0064) of the Rh^I series are comparable with the values of *a* (0.047) and *b* (0.0059) of the Pt^0 series; the difference between *a*(Rh) and *a*(Pt) can be related to the different coordination number, which is four for Rh^I and three for Pt^0.

That $^2J(P_1—P_2)_{cis}$ is close to zero indicates that the *s* and *d* contributions cancel each other. Such a cancelling is obviously less present in the *trans*-coupling, which is determined by the difference between the contribution of the metal p_σ-orbital and the metal *s*- and d_σ-orbitals. The number of compounds in our set is too small to allow a statistical treatment of the $^2J(P_i—P_j)_{trans}$ data.

Dr. W.A. Schenk of the University of Würzburg has kindly provided us with the coupling constant data for the complexes *cis*- and *trans*-LL′W(CO)$_4$ (L,L′ = tertiary phosphine, aminophosphine or phosphite) [28]. In these complexes the substituents on phosphorus were varied but not those on the other ligands on the metal. Nonetheless, for the 17 *trans*-complexes an expression for $^2J(P_1—P_2)$ $P_2)_{trans}$ similar to equation 1 gives a good fit with a correlation coefficient *r* of 0.990 and $a_{trans}/\mu_W = 0.759$, $b_{trans}/\mu_W = 0.067$ and $c = 152$ Hz. Clearly, similar rules govern the $^1J(\text{M—P})$ and $^2J(\text{P}_1\text{—P}_2)$ relationship in *cis* and *trans* complexes.

For the 10 *cis* LL′W(CO)$_4$ complexes, the correlation according to equation 1 is poorer. These complexes are found in groups which are apparently determined by the number of alkoxy groups present on the phosphorus. The statistical constants are: $a_{cis}/\mu_W = 0.039$, $b_{cis}/\mu_W = 0.0057$ and $c = -2.4$ Hz, with a correlation coefficient of 0.912. The *a* values of the tungsten complexes cannot be compared with the values of the rhodium and platinum complexes because different phosphines are involved.

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