Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

π-ALLYLIC COMPLEXES OF RHODIUM(III) AND PLATINUM(II)
I. PREPARATION, PROPERTIES AND STRUCTURE

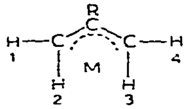
H. C. VOLGER AND K. VRIEZE
Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research N.V.), (The Netherlands)

(Received February 11th, 1967)

INTRODUCTION

Within the framework of our investigations into the behaviour of the allyl ligand in π-allyl–metal complexes, as governed by the nature of the other ligands, the electronic configuration of the metal and of the substituent groups in the allyl ligand, we recently reported in a preliminary communication[1] on the synthesis and properties of the complexes $[(Ph_3P)_2Pt(\pi\text{-}C_3H_5)]X$ and $(Ph_3P)_2Cl_2Rh(\pi\text{-}C_3H_4R)$ ($X = Cl$, Br and $R = H, CH_3$)*.

It was shown that in $CDCl_3$ solution the allyl ligand in both the platinum and the rhodium π-allyl complexes occurs in the so-called dynamic form at room temperature. The name "dynamic" was introduced by Wilke *et al.*[3] to indicate the magnetic equivalence of protons 1, 2, 3 and 4.



We interpreted this equivalence as being due to an intramolecular interconversion of proton 1 with 2 (and thus of 3 with 4) via a short-lived σ-allyl intermediate, analogous to the interpretation of the corresponding spectra of the systems $[(\pi\text{-}C_4H_7)PdCl]_2$–L ($L = Ph_3P, Ph_3As, Ph_3Sb$, etc.)[4].

This paper presents details on the preparation, configuration and properties of the above complexes, and of a number of analogous compounds, *viz.* $L_2Cl_2Rh(\pi\text{-}C_3H_4R)$ ($L = Ph_3As, Ph_3Sb$ and $[p\text{-}(CH_3)_2NC_6H_4]_3As$ and $R = H, CH_3$), $(Ph_3P)_2Cl_2Rh[\pi\text{-}(CH_3)_2C{=}CH{=}CH_2]$ and $\{(Ph_3P)_2Pt[\pi\text{-}(CH_3)_2C{=}CH{=}CH_2]\}Cl$.

Part II[5] will deal with the behaviour of the allyl ligand in the intramolecular interconversion process mentioned above, as a function of the electron-donating properties of the various ligands L.

PREPARATION AND PROPERTIES

Addition of L_3RhX to pure allyl halides at room temperature in a nitrogen atmosphere yielded the complexes $L_2X_2Rh(\pi\text{-}C_3H_4R)$:

---

* The synthesis of $(Ph_3P)_2Cl_2Rh(C_3H_5)$ from $(Ph_3P)_3RhCl$ and allyl chloride has recently been reported by Wilkinson and co-workers[2]. (See also note at the end of the paper.)

$$L_3RhX+CH_2{=}C(R){-}CH_2X \rightarrow L_2X_2Rh(\pi\text{-}C_3H_4R)+L$$

$$\begin{array}{lll} L=Ph_3P; & X=Cl, Br; & R=H, CH_3 \\ L=Ph_3As; & X=Cl; & R=H, CH_3 \\ L=Ph_3Sb; & X=Cl; & R=H, CH_3 \\ L=\{p\text{-}(CH_3)_2NC_6H_4\}_3As; & X=Cl; & R=CH_3 \end{array}$$

Likewise, use of $(CH_3)_2C{=}CH{-}CH_2Cl$ leads to the corresponding π-allylic complex. No π-allyl compounds could be prepared for $L=(C_2H_5)_2C_6H_5P$, $(n\text{-}C_4H_9)_3P$, $(CH_3)_2C_6H_5P$ and $P(OCH_2)_3CCH_3$.

Platinum(II) π-allyl compounds were prepared under similar conditions from $(Ph_3P)_4Pt$ and the allyl chloride:

$$(Ph_3P)_4Pt+R_2C{=}CH{-}CH_2X \rightleftarrows [(Ph_3P)_2Pt(\pi\text{-}C_3H_3R_2)]X+2\ Ph_3P$$

$$\begin{array}{ll} R=H; & X=Cl, Br \\ R=CH_3; & X=Cl \end{array}$$

TABLE 1

PHYSICAL PROPERTIES OF THE COMPLEXES L_2X_2Rh-allyl AND $[(Ph_3P)_2Pt\text{-allyl}]X$

Complex	*Colour*	*M.p. (°C)*	*Molar conductivity*[a] *(cm²·Ω⁻¹·mole⁻¹)*	*Mol. wt. at +37°*[b]	
				Found	*Calcd.*
$(Ph_3P)_2Cl_2RhC_3H_5$	yellow	144–146	3.6 (D) 15.4 (N)	730	739
$(Ph_3As)_2Cl_2RhC_3H_5$	yellow	188–189	0 (D) 0 (N)	(dec.)	
$(Ph_3Sb)_3Cl_2RhC_3H_5$	orange	190–205	0 (D) 0 (N)	870	921
$(Ph_3P)_2Br_2RhC_3H_5$	yellow	158–161	12 (D) 62 (N)	740	828
$(Ph_3P)_2Cl_2RhC_4H_7$	yellow	138–141	2.1 (D) 11.1 (N)	690	752
$(Ph_3As)_2Cl_2RhC_4H_7$	orange	175–180	0 (D) 0 (N)	770	841
$\{[p\text{-}(CH_3)_2N\text{-}C_6H_4]_3As\}_2Cl_2RhC_4H_7$	orange	250 dec.	0.8 (D) 5.6 (N)	1130	1105
$(Ph_3Sb)_2Cl_2RhC_4H_7$	orange	dec.	0 (D) 0 (N)	965	935
$(Ph_3P)_2Br_2RhC_4H_7$	reddish brown	151–153	10.4 (D) 36.0 (N)	780	842
$(Ph_3P)_2Cl_2Rh[CH_2{=}CH{=}C(CH_3)_2]$	orange	140–143	0.9 (D) 6.8 (N)	(dec.)	
$[(Ph_3P)_2PtC_3H_5]Cl$	white	195–200	32.0 (D) 75.9 (N)	710	795
$[(Ph_3P)_2PtC_3H_5]Br$	white	178–182	32.1 (D) 78.3 (N)	700	839
$\{(Ph_3P)_2Pt[CH_2{=}CH{=}C(CH_3)_2]\}Cl$	light yellow	107–114	13.1 (D) 57.8 (N)	(dec.)	

[a] In D (= 1,2-dichloroethane) uni-univalent electrolytes have generally a molar conductivity of ~30 cm²·Ω⁻¹·mole⁻¹. In N (= nitromethane) this value is about 80 cm²·Ω⁻¹·mole⁻¹. Conductivities were measured at room temperature with a concentration of the complex of about 1×10^{-3} *M*. [b] Measured with a Mechrolab vapour pressure osmometer model 201A and 1×10^{-2} *M* solutions at +37° in 1,2-$C_2H_4Cl_2$.

This reaction is reversible; addition of an excess of triphenylphosphine to a solution of the Pt π-allylic complexes in $CHCl_3$ yielded $(Ph_3P)_nPt$ ($n = 3, 4$), the corresponding allyl halide, and small amounts of the allyltriphenylphosphonium salt. Impure products were obtained in the reaction of $(Ph_3P)_4Pt$ with methallyl chloride.

Some physical properties of the complexes are recorded in Table 1.

The recorded molecular weights of the complexes clearly show that they are monomolecular. Furthermore, it appears from Table 1 that, in contrast to the compounds $L_2Cl_2Rh(\pi\text{-allyl})$, the bromide-containing complexes have an appreciable electric conductivity in solution due to dissociation of bromide ions.

The platinum allyl complexes show molecular conductivities characteristic of uni-univalent electrolytes. The fact that the experimental molecular weights are higher than half of the calculated value, might be attributed to the formation of ion pairs in the fairly highly concentrated solutions used for molecular weight measurements.

Addition of bromide and chloride ions (LiX) to the chloride and bromide rhodium compounds, respectively, leads to instantaneous exchange. Preference for coordination of either Br or Cl to Rh was not observed, as was shown by analysis.

STRUCTURE AND CONFIGURATION

The configuration of the complexes has been elucidated by means of (*a*) infrared, (*b*) proton magnetic resonance and (*c*) dipole moment measurements.

(*a*) *Infrared spectra*

For the compounds mentioned above no double-bond stretching frequencies were observed, which for σ-allyl metal complexes usually lie between 1600 and 1650 cm^{-1}. This is in agreement with the results obtained from NMR measurements, which are discussed in (*b*), and which show that the allyl group is π-bonded to the metal.

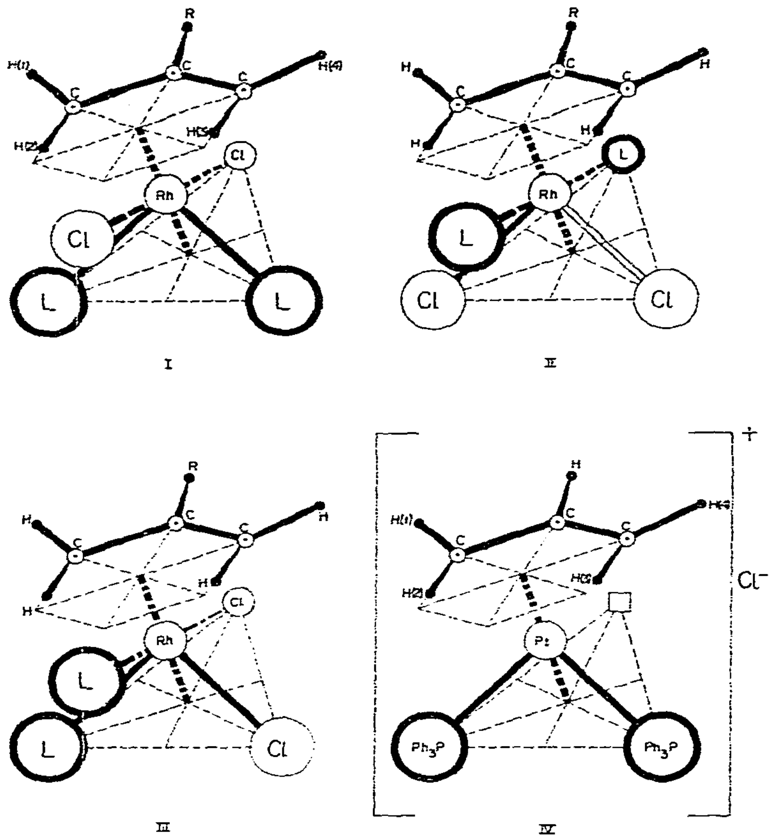
The three possible isomers of $L_2X_2Rh(\pi\text{-allyl})$ and the one of the uni-univalent electrolyte $(Ph_3P)_2Pt(\pi\text{-allyl})X$ are shown in Fig. 1.

(*b*) *Proton magnetic resonance*

Only the NMR data relevant to the determination of the configurations of the Rh–and Pt–allyl compounds are given here. The influence of the various ligands upon the temperature dependence of the allylic proton absorptions, in particular with respect to the process which makes the *syn*- and *anti*-protons magnetically equivalent, will be reported in Part II[5].

1. *Rhodium complexes*. The NMR data of the allylic rhodium complexes are summarized in Table 2. The phenyl proton absorptions have not been included. They are in all cases between 7.0 and 7.5 ppm from TMS (δ).

The allylic part of the NMR spectra of the arsine and stibine compounds (from $-60°$ to room temperature) consists of three signals in the intensity ratio 2:2:3, originating from protons (1,4) and (2,3) and the CH_3 group, respectively. This type of NMR pattern is usually observed for π-methallyl compounds, for which the molecule as a whole possesses a plane of symmetry perpendicular to the $C^1C^2C^3$-

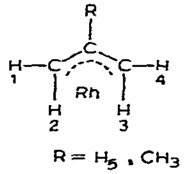


I II III IV

Fig. 1. The three possible configurations of $L_2Cl_2Rh(\pi\text{-}C_3H_4R)$ and the one of $[(Ph_3P)_2Pt(\pi\text{-}C_3H_5)]^+Cl^-$.

TABLE 2

CHEMICAL SHIFTS OF THE PROTONS 1 TO 4 AND OF THE R-SUBSTITUENT, IN PPM, FROM TMS (δ) OF $L_2X_2Rh(\pi\text{-}C_3H_4R)$ IN $CDCl_3$ AT ROOM TEMPERATURE AT 56.4 AND 100 Mc



Complex	*Protons* (1,4)	*Protons* (2,3)	*R = H or CH_3*
$(Ph_3P)_2Cl_2Rh(C_3H_5)$	2.90[b]		5.20 (R = H) (quintet)
$(Ph_3P)_2Cl_2Rh(C_4H_7)$[a]	3.75[c]		1.82 (R = CH_3)[d]
$(Ph_3P)_2Br_2Rh(C_4H_7)$	3.83		2.06
$(Ph_3As)_2Cl_2Rh(C_4H_7)$	4.10	3.74	1.80 (R = CH_3)[e]
$(Ph_3Sb)_2Cl_2Rh(C_4H_7)$	4.76	3.62	1.82 (R = CH_3)[e]
$\{[p\text{-}(CH_3)_2NC_6H_4]_3As\}_2Cl_2Rh(C_4H_7)$	4.07	3.72	1.85 (R = CH_3)[e]

[a] At −80° in CH_2Cl_2 three peaks are observed of intensity ratio 2:1:1 at 3.84, 3.60 and 3.50 ppm (δ), respectively. The weighted mean of these three peaks is 3.70 ppm, which agrees well with the chemical shift of the triplet (3.73 ppm) measured at room temperature in CH_2Cl_2. [b] Doublet; $J[(1,2,3,4)\text{-}5] = 9.0$ c/s. [c] Triplet; $J[(1,2,3,4)\text{-}P] = 2.0$ c/s. [d] Four peaks; $J(CH_3\text{-}P) = 1.2$ c/s and $J(CH_3\text{-}Rh) = 1.4$ c/s. [e] Doublet; $J(CH_3\text{-}Rh) = 1.6$ c/s.

plane of the allyl ligand, *viz.* $(\pi\text{-}C_4H_7PdCl)_2$[4], thus excluding structure (III) of Fig. 1. The substituted arsine compound $\{[p\text{-}(CH_3)_2NC_6H_4]_3As\}_2Cl_2Rh(C_4H_7)$ undoubtedly has the same structure as $(Ph_3As)_2Cl_2Rh(C_4H_7)$ in view of the almost identical chemical shifts of the allylic protons (Table 2).

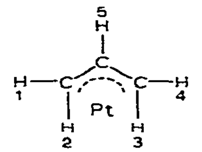
The allyl spectrum of the phosphine compound $(Ph_3P)_2Cl_2Rh(\pi\text{-}C_4H_7)$ shows at room temperature only two signals in the intensity ratio 4:3. The latter signal (1.82 ppm from TMS) is due to the CH_3 group, whereas the first signal (3.75 ppm in $CDCl_3$) originates from protons 1, 2, 3 and 4, which absorb at the same magnetic field (see Table 2). This spectrum is interpreted here in the same way as the corresponding spectra of $(\pi\text{-}C_4H_7)PdCl(L)$[5] (L = group-V donor ligand). The methallyl ligand appears to be π-bonded to the rhodium atom, the magnetic equivalence of protons 1, 2, 3 and 4 being caused by a process in which protons 1 and 2 (and thus 3 and 4) are interchanged. A sufficiently high rate of interchange results in the coalescence of the methylene proton absorptions. The phosphine compound has very probably the same symmetrical structure as the arsine and stibine compounds, since the methyl and methylene protons couple with two equivalent phosphorus nuclei and because of the similar dipole moments [see (c)]. (The methylene absorption at 3.75 ppm occurs as a triplet $\{J[(1,2,3,4)\text{–}P] = 2.0$ c/s$\}$, because of a coupling with two equivalent P-nuclei, while the CH_3 absorption appears as four lines through a combination of a coupling with the two P-nuclei (spin $\frac{1}{2}$) and one with the Rh-atom (spin $\frac{1}{2}$) (see Table 2).

From −80 to −50° the absorption at 3.75 ppm is split into three signals in the intensity ratio 2:1:1, instead of the two expected signals of equal intensity, as in the arsine and stibine compounds. The difference between the latter two signals, however, is very small (10 c/s at 100 Mc) and is very probably due to some slight asymmetry in the complex. The cause of this asymmetry is as yet unexplained. The three signals can then be assigned to protons (1,4), 2 and 3 (or 3 and 2), respectively.

A further interesting feature of the NMR spectra is the coupling of the Rh-spin with the methyl group of the methallyl ligand, while no perceptible coupling is found between the rhodium atom and the methylene protons (see Table 2)[1].

TABLE 3

CHEMICAL SHIFTS OF THE PROTONS 1 TO 5, IN PPM, FROM TMS (δ) OF THE COMPOUNDS $[(Ph_3P)_2Pt(\pi\text{-}C_3H_5)]X$ IN $CDCl_3$ AT ROOM TEMPERATURE (56.4 AND 100 Mc)



Complex	Protons 1,2,3,4	Proton 5
$[(Ph_3P)_2Pt(C_3H_5)]Cl$[a]	3.42 (four lines; $J[(1,2,3,4)\text{–}Pt] = 22$ c/s $J[(1,2,3,4)\text{–}5] = 11$ c/s)	5.69 (quintet)
$[(Ph_3P)_2Pt(C_3H_5)]Br$	3.56 (four lines; $J[(1,2,3,4)\text{–}Pt] = 22$ c/s $J[(1,2,3,4)\text{–}5] = 10$ c/s)	5.91 (quintet)

[a] At −50° two broad bands are observed at 3.79 and 2.94 ppm.

2. *Platinum complexes.* The NMR data of the phosphine platinum compounds are recorded in Table 3. The signal of the protons 1, 2, 3 and 4, which absorb at the

same magnetic field due to the interconversion of the *syn-* and *anti*-protons, is split into four lines in the intensity ratio 8:42:42:8 by a combination of a coupling with proton 5 and of one with the ^{195}Pt-isotope, which occurs in 33% natural abundance. The absence of coupling from the P-nuclei is explained by exchange of triphenylphosphine.

The NMR spectra (see Table 3) show at −50° the presence of two broad signals at 3.79 and 2.94 ppm from TMS, due to protons (1,4) and (2,3) respectively, which at room temperature coalesce to one absorption at 3.42 ppm. (We did not succeed in obtaining sharper signals for the absorptions at 3.79 and 2.94 ppm by lowering the temperature below −50°.)

The NMR evidence in combination with the uni-univalent character of the complexes strongly indicates a cationic species $[(Ph_3P)_2Pt(\pi\text{-}C_3H_5)]^{+}$*, analogous[6] to $[(Ph_3P)_2Pd\text{-allyl}]^{+}$, with a four-co-ordinate essentially planar structure, as usually found for four-co-ordinate compounds of Pd [and Pt(II)][7].

(*c*) *Dipole moments*

In order to distinguish, in the case of the compounds $L_2Cl_2Rh(\pi\text{-}C_4H_7)$, between the symmetrical structures (I) and (II), experimental and calculated dipole moments were compared. Dipole moments for the three configurations (I), (II) and (III) (Fig. 1) were calculated (see Table 4) from estimated partial bond moments of Rh→Cl and L→Rh and $\pi\text{-}C_4H_7\rightarrow Rh$, the arrows indicating the direction of the moment. Values derived for the bond moments of M→Cl and L→M in a whole series of complexes of the later transition elements are about 3.0±0.5 D and 4.3±0.5 D, respectively[8-13]. Since no values are known for π-methallyl→metal bond moments, we have used for the $\pi\text{-}C_4H_7\rightarrow Rh$ bond moment a number of values in the range of 2.0 to 6.0 D.

TABLE 4

CALCULATED DIPOLE MOMENTS (DEBYE) OF THE COMPOUNDS $L_2Cl_2Rh(\pi\text{-}C_4H_7)$

Assumed bond moment (D) for $\pi\text{-}C_4H_7\rightarrow Rh$	*Calculated dipole moments*[a] *for configuration*		
	(I)	*(II)*	*(III)*[b]
6.0	0.1	10.3	11.3
5.0	1.1	9.3	10.5
4.0	2.1	8.3	9.8
3.0	3.1	7.3	9.5
2.0	4.1	6.3	9.2

[a] The estimated values of the Rh→Cl and L→Rh bond moments are 3.0 and 4.3 D. [b] Configuration (III) already excluded on the basis of NMR.

The experimental values were found to be 3.5±0.2, 3.3±0.2 and 3.5±0.2 D for L = PPh_3, $AsPh_3$ and $SbPh_3$, respectively. These data can only be reconciled with structure (I), provided that a reasonable bond moment for the $\pi\text{-}C_4H_7\rightarrow Rh$

---

* Shaw and co-workers[6] seem to have obtained the same Pt-compound. No particulars, however, are given.

bond is used (Table 4) (*i.e.* about 2.0–3.0 D). For comparison the value 4.0 D of the π-$C_2H_4 \rightarrow Pt$ bond is recalled[14].

CONCLUSIONS

The methallyl complexes $L_2Cl_2Rh(\pi\text{-}C_4H_7)$ ($L = Ph_3P$, Ph_3As, Ph_3Sb) have configuration (I) with the ligands L trans to the allyl group[†]. The other compounds, which have similar properties, but for which no NMR or dipole moment measurements were carried out because of their instability in solution or because of poor solubility, have presumably the same configuration.

We have not been able to prepare π-allylrhodium compounds with alkylaryl-containing phosphorus ligands. This may be because of kinetic reasons or because of the intrinsic instability of these compounds.

Similarly, we have not been able to prepare the stable[*] π-allyl isomer $(Ph_3P)_2Cl_2Rh(\pi\text{-}C_4H_7)$, reported by Wilkinson and co-workers[2][**]. It would be interesting to investigate if this isomer has configuration (II) or (III) (Fig. 1).

In view of the uni-univalent character of the Pt-compounds $[(Ph_3P)_2Pt(allyl)]X$ only one configuration is possible, namely with both phosphines trans to the allyl group, which was confirmed by NMR.

The preparation of a series of iso-structural compounds of rhodium has enabled us to study the influence of various ligands on the behaviour of these complexes, in particular with respect to the process in which *syn*- and *anti*-protons change places.

These aspects will be treated in a subsequent paper (Part II)[5].

EXPERIMENTAL

All the preparations were carried out in an atmosphere of dry nitrogen (oxygen-free).

The elemental analyses were performed by means of the usual techniques, except for the metals and As, which were analysed by (radio-active) activation techniques.

Tris(triphenylphosphine)rhodium chloride

Triphenylphosphine (50 g) was added to a solution of 5.0 g $RhCl_3 \cdot 3\,H_2O$ in a mixture of 1800 ml of ethanol and 30 ml of water[15]. Refluxing the reaction mixture

---

[*] By stable is meant that no rearrangements of the allyl group occur.

[**] After this paper had been completed a publication appeared by Lawson *et al.*[20], who prepared $(Ph_3P)_2Cl_2Rh(C_3H_5)$ (two isomers, namely one with a stable σ-allyl and one with a stable π-allyl group), $(Ph_3P)_2Cl_2Rh(C_4H_7)$ (two isomers, apparently both with a dynamic allyl spectrum, called D and E, respectively) and $(Ph_3As)_2Cl_2Rh(\pi\text{-}C_4H_7)$ (one isomer) by refluxing L_3RhCl ($L = Ph_3As$, Ph_3Sb) with allyl halides. Comparison with the results obtained for our compounds (in particular with respect to the NMR spectra), which were prepared at room temperature, indicates that our allyl complex $(Ph_3P)_2Cl_2Rh(C_3H_5)$ is different from their two isomers, since it has a dynamic allyl group at room temperature. The isomer D of $(Ph_3P)_2Cl_2Rh(C_4H_7)$ has the same NMR spectrum as the complex in this publication, although it has a lower molecular weight. Isomer E has never been isolated by us. The Ph_3As compound seems to be the same as our arsine complex.

[†] Additional evidence is provided by the Rh–Cl stretching frequencies, which are about 315–340 cm^{-1}, characteristic for chlorine *trans* to chlorine[21].

for one hour resulted in the precipitation of dark red crystals, which were filtered off, washed with hot ethanol and dried. (Found: C, 70.0; H, 5.03; Cl, 3.86; P, 9.6; Rh, 11.2. $C_{54}H_{45}ClP_3Rh$ calcd.: C, 70.1; H, 4.9; Cl, 3.9; P, 10.1; Rh, 11.1%.)

Tris(triphenylphosphine)rhodium bromide. Similar procedure as described for the corresponding chloride (m.p. 118–123°). (Found: C, 66.4; H, 4.94; Br, 8.6; P, 9.3. $C_{54}H_{45}BrP_3Rh$ calcd.: C, 66.9; H, 4.6; Br, 8.3; P, 9.6%.)

Tris(triphenylarsine)rhodium chloride

A solution of 50 g triphenylarsine in 50 ml benzene was added to a suspension of 3.0 g μ-dichlorotetraethylenerhodium in 300 ml ethanol. The yellow precipitate was filtered off and washed with a small amount of methanol and finally with pentane. (Found: C, 64.5; H, 4.88; Cl, 2.63. $C_{54}H_{45}As_3ClRh$ calcd.: C, 61.4; H, 4.3; Cl 3.3%.)

Tris{tris[p-(dimethylamino)phenyl]arsine}rhodium chloride. Similar procedure as described for the unsubstituted arsine complex. (Found: C, 60.7; H, 6.49; N, 9.2. $C_{72}H_{90}As_3N_9ClRh$ calcd.: C, 59.5; H, 6.8; N, 8.7%.)

Tris(triphenylstibine)rhodium chloride. This bluish compound was prepared by the same method as described for the arsine compound. (Found: C, 56.0; H, 4.02; Cl, 2.20; Sb, 28.6. $C_{54}H_{45}ClRhSb_3$ calcd.: C, 54.1; H, 6.0; Cl, 2.9; Sb, 30.6%.)

Bis(triphenylphosphine)rhodium-π-allyl chloride

$(Ph_3P)_3RhCl$ (0.5 g) was slowly added to 100 ml of vigorously stirred pure allyl chloride. After 15 min the precipitate was filtered off and again added to 100 ml of a new portion of allyl chloride. The yellow precipitate was collected, washed with allyl chloride and dried. (Found: C, 62.6; H, 4.88; Cl, 10.6; P, 7.8; Rh, 13.5. $C_{39}H_{35}Cl_2P_2Rh$ calcd.: C, 63.3; H, 4.7; Cl, 9.6; P, 8.4; Rh, 14.0%.)

The following complexes were prepared by the same procedure.

Bis(triphenylphosphine)rhodium-π-methallyl chloride. Yellow-brown product. (Found: C, 62.9; H, 4.93; Cl, 9.5; P, 7.4; Rh, 13.9. $C_{40}H_{37}Cl_2P_2Rh$ calcd.: C, 63.7; H, 5.1; Cl, 9.3; P, 8.2; Rh, 13.7%.)

Bis(triphenylphosphine)rhodium-π-allyl bromide. Yellow crystals. (Found: C, 56.2; H, 4.45; Br, 21.2; P, 6.6; Rh, 10.4. $C_{39}H_{35}Br_2P_2Rh$ calcd.: C, 56.5; H, 4.2; Br, 19.3; P, 7.5; Rh, 12.2%.)

Bis(triphenylphosphine)rhodium-π-methallyl bromide. Brown compound. (Found: C, 57.5; H, 4.63; Br, 19.6; P, 6.9. $C_{40}H_{37}P_2RhBr_2$ calcd.: C, 57.0; H, 4.4; Br, 19.0; P, 7.4%.)

Bis(triphenylphosphine)rhodium-π-1,1-dimethylallyl chloride. Brown. (Found: C, 63.7; H, 5.20; Cl, 9.5; P, 7.7. $C_{41}H_{39}Cl_2P_2Rh$ calcd.: C, 64.1; H, 5.1; Cl, 9.3; P, 8.1%.)

Bis(triphenylarsine)rhodium-π-allyl chloride. Yellow. (Found: C, 57.4; H, 4.45; As, 18.9; Cl, 8.8; Rh, 12.8. $C_{39}H_{35}As_2Cl_2Rh$ calcd.: C, 56.6; H, 4.1; As, 20.0; Cl, 8.6; Rh, 13.7%.)

Bis(triphenylarsine)rhodium-π-methallyl chloride. Orange. (Found: C, 57.2; H, 4.59; As, 18.2; Cl, 8.0; Rh, 12.9. $C_{40}H_{37}As_2Cl_2Rh$ calcd.: C, 57.1; H, 4.4; As, 19.6; Cl, 8.4; Rh, 13.5%.)

Bis{[tris(p-dimethylamino)phenyl]arsine}rhodium-π-methallyl chloride. Yellow-orange. (Found: C, 59.1; H, 6.29; Cl, 5.8. $C_{52}H_{67}As_2Cl_2N_6Rh$ calcd.: C, 56.5; H, 6.6; Cl, 6.4%.)

Bis(triphenylstibine)rhodium-π-allyl chloride. (Found: C, 50.6; H, 3.86; Cl, 7.89; Rh, 11.9; Sb, 27.0. $C_{39}H_{35}Cl_2RhSb_2$ calcd.: C, 50.8; H, 3.8; Cl, 7.7; Rh, 11.2; Sb, 26.5%.)

Bis(triphenylstibine)rhodium-π-methallyl chloride. Orange. (Found: C, 50.1; H, 4.0; Cl, 7.6; Rh, 12.2; Sb, 26.3. $C_{40}H_{37}Cl_2RhSb_2$ calcd.: C, 50.8; H, 3.8; Cl, 7.7; Rh, 11.0; Sb, 26.1%.)

Tetrakis(triphenylphosphine)platinum

Prepared according to Malatesta and Carriello[16]; yellow, m.p. 78–86°.

Bis(triphenylphosphine)platinum-allyl chloride

Allyl chloride was added to a vigorously stirred concentrated solution of 5 g $(Ph_3P)_4Pt$ in 75 ml of benzene. The nearly colourless reaction mixture was poured into a large excess of pentane. The precipitate was filtered off and washed with benzene. The white complex was again washed with a large excess of pentane. (Found: C, 57.7; H, 4.41; Cl, 4.53; P, 7.4; Pt, 27.1. $C_{39}H_{35}Cl_2P_2Pt$ calcd.: C, 59.0; H, 4.1; Cl, 4.5; P, 7.8; Pt, 24.6%.)

By the same procedure the following complexes were prepared.

Bis(triphenylphosphine)platinum allyl bromide. Colourless. (Found: C, 57.1; H, 4.20; Br, 8.9; P, 7.7; Pt, 29.0. $C_{39}H_{35}Br_2P_2Pt$ calcd.: C, 55.9; H, 4.0; Br, 9.5; P, 7.3; Pt, 23.3%.)

Bis(triphenylphosphine)platinum-(1,1-*dimethylallyl*) *chloride.* Very pale-yellow. (Found: C, 59.9; H, 4.68; Cl, 4.45; P, 7.4; Pt, 26.3. $C_{41}H_{39}Cl_2P_2Pt$ calcd.: C, 59.8; H, 4.7; Cl, 4.3; P, 7.5; Pt, 23.7%.)

Dipole moment measurements

The dielectric constants of the solutions of $L_2Cl_2Rh(\pi\text{-}C_4H_7)$ in benzene were measured at 25° with a dipole meter as described by Hageman and Havinga[19].

The orientation polarizations were calculated from the dielectric constants

TABLE 5

DIPOLE MOMENT MEASUREMENTS OF $L_2Cl_2Rh(\pi\text{-}C_4H_7)$ AT +25° IN BENZENE

Complex	*Molar ratio (complex)* $\omega_2 \times 10^4$	ε	$\alpha = \frac{\Delta\varepsilon^a}{\omega}$	$\mu = 0.8468\sqrt{\alpha}$
$(Ph_3P)_2Cl_2Rh(\pi\text{-}C_4H_7)$	0	2.2751	17.2	3.51 D
	2.1052	2.2788		
	3.9856	2.2821		
	6.2118	2.2858		
$(Ph_3As)_2Cl_2Rh(\pi\text{-}C_4H_7)$	0	2.2752	15.2	3.30 D
	2.5505	2.2790		
	4.6911	2.2828		
	5.6299	2.2844		
$(Ph_3Sb)_2Cl_2Rh(\pi\text{-}C_4H_7)$	0	2.2753	16.7	3.46 D
	1.0228	2.2787		
	1.7747	2.2811		
	3.4014	2.2777		

[a] Calculated by method of least squares.

using the formula (compare ref. 13 and 18): $p_0 = \frac{3v_1}{(\varepsilon_1+2)^2}\alpha$ where v_1 = specific volume of benzene; ε_1 = dielectric constant of benzene; α is defined by the equation $\varepsilon = \varepsilon_1 + \alpha\omega_2$, where ω = molecular fraction of the solute.

Both the electron and the atom polarization are neglected in these calculations, which according to Jensen[13,18] gives a deviation of only a few percent.

The dipole moment can be calculated from the polarization p_0 using the formula $\mu = \frac{3}{2}\sqrt{kTMp_0/\pi N}$, where M is molecular weight of benzene, or $\mu^2 = 38.2\times 10^{-37}\,p_0$ or $\mu = 0.847\sqrt{\alpha}$ in Debye units. For the experimental data see Table 5.

SUMMARY

π-Allylic complexes $L_2X_2Rh(\pi\text{-}C_3H_4R)$ with L = Ph_3P, Ph_3As, $[p\text{-}(CH_3)_2\text{-}NC_6H_4]_3As$, Ph_3Sb; X = Cl, Br and R = H, CH_3 and the compound $(Ph_3P)_2Cl_2Rh\text{-}[\pi\text{-}(CH_3)_2C{=}CH{=}CH_2]$ have been obtained by reaction of the corresponding allyl halides with L_3RhX. Treatment of $(Ph_3P)_4Pt$ with allyl halides yielded uni-univalent complexes $[(Ph_3P)_2Pt(\pi\text{-}R_2C{=}CH{=}CH_2)]X$ with X = Cl, Br and R = H, CH_3.

The configuration of the compounds was determined by means of electrical conductivity measurements in solution, infrared, proton magnetic resonance and dipole moment measurements. It was shown that the Group V donor ligands L are both situated *trans* to the allyl ligand.

REFERENCES

1 H. C. Volger and K. Vrieze, *J. Organometal. Chem.*, 6 (1966) 297.
2 M. C. Baird, D. N. Lawson, J. T. Mague, J. A. Osborn and G. Wilkinson, (1966) 129.
3 G. Wilke, B. Bogdonavic, P. Hardt, P. Heimbach, W. Keim, M. Kröner, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Walter and P. Zimmermann, *Angew. Chem.*, 78 (1966) 157.
4 (a) K. Vrieze, C. MacLean, P. Cossee and C. W. Hilbers, *Rec. Trav. Chim.*, 85 (1966) 1077.
(b) K. Vrieze, P. Cossee, C. MacLean and C. W. Hilbers, *J. Organometal. Chem.*, 6 (1966) 672.
5 K. Vrieze and H. C. Volger, *J. Organometal. Chem.*, 9 (1967) 537.
6 J. M. Jenkins, M. S. Lupin, B. L. Shaw and A. C. Smithies, *9th I.C.C.C.*, St. Moritz-Bad, Switzerland, September 5-9, 1966, p. 346.
7 R. Mason and D. R. Russell, *Chem. Commun.*, (1965) 26.
8 M. Angoletta, *Gazz. Chim. Ital.*, 92 (1962) 811.
9 J. Chatt, R. S. Coffey and B. L. Shaw, *J. Chem. Soc.*, (1965) 7391.
10 J. Chatt and B. L. Shaw, *J. Chem. Soc.*, (1959) 705.
11 J. Chatt and F. A. Hart, *J. Chem. Soc.*, (1965) 812; (1960) 1378.
12 J. Chatt, N. P. Johnson and B. L. Shaw, *J. Chem. Soc.*, (1964) 2508.
13 K. A. Jensen and B. Nijgaard, *Acta Chem. Scand.*, 3 (1949) 474.
14 J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, (1953) 2939.
15 M. A. Bennett and P. A. Longstaff, *Chem. Ind. (London)*, (1965) 846.
16 L. Malatesta and C. Cariello, *J. Chem. Soc.*, (1958) 2323.
17 K. B. Everard, R. A. W. Hill and L. E. Sutton, *Trans. Faraday Soc.*, 46 (1950) 417.
18 K. A. Jensen, *Z. Anorg. Chem.*, 229 (1950) 249.
19 H. J. Hageman and E. Havinga, *Tetrahedron*, 22 (1966) 2271.
20 D. N. Lawson, J. A. Osborn and G. Wilkinson, *J. Chem. Soc. A*, (1966) 1733.
21 J. M. Jenkins, M. S. Lupin and B. L. Shaw, *J. Chem. Soc. A*, (1966) 1787.