Some studies on rhodium-group ivb complexes

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SOME STUDIES ON
RHODIUM-GROUP IVB COMPLEXES

by

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(Graduate Society)

A Thesis submitted in candidature
for the degree of Doctor of Philosophy
in the University of Durham.

September 1970

Summary

G.C. Hill

This thesis describes the preparation, properties and reactions of some rhodium-group IVb (Si, Ge, Sn) complexes. The main emphasis lies upon the preparation of compounds containing bonds between germanium and rhodium.

Compounds of the type $(Ph_3M)_2RhH(GeR_3)Cl$ (M = P, As; R = Me, Et) can be prepared by the reaction of $(Ph_3M)_3RhCl$ with an excess of trialkylgermane. The products dissociate readily in solution to give the free trialkylgermane and a rhodium(I) species.

$$(Ph_3M)_2RhH(GeR_3)Cl + \text{solvent} \rightleftharpoons (Ph_3M)_2RhCl(\text{solvent}) + R_3GeH$$

The reactions of $(Ph_3P)_2RhH(GeEt_3)Cl$ with CO, C_2H_4, HCl and Me_2PhP are reported. The reactions of R_3SnH and R_3SnCl (R = Me, n-Bu) with $(Ph_3P)_3RhCl$, and of R_3GeH (R = Me, Et) with a variety of rhodium(I)-phosphine complexes have also been studied.

In contrast to the analogous iridium complex, $(Ph_3P)_2Rh(CO)Cl$ did not react with trialkylgermanes to form a rhodium-germanium bond. A similar lack of reactivity was shown by $(Ph_3P)_3Rh(CO)H$ and $(Pr_3P)_2Rh(CO)Cl$. A five-coordinate complex, $(Ph_3P)_2Rh(CO)_2GeEt_3$ was prepared from the reaction between $(Ph_3P)_2Rh(CO)_2Na$ and triethylbromogermane.

The reaction of $(Ph_3P)_3RhCl$ with excess trichlorogermane gave the phosphonium salt of hexa(trichlorogermyl)rhodium(III), $[Ph_3PH]_3[Rh(GeCl_3)_6]$.

$$(Ph_3P)_3RhCl + 6HGeCl_3 \longrightarrow [Ph_3PH]_3[Rh(GeCl_3)_6] + H_2 + HCl$$

A similar salt was also formed when trichlorogermane was reacted with $(Ph_3P)_2Rh(CO)Cl$. Infrared spectral evidence has been obtained for the existence of a neutral rhodium(III) intermediate in this reaction. Rhodium(III) salts have also been prepared by the reaction of

trichlorogermane or trimethylammonium trichlorogermanite with rhodium trichloride. The rhodium(I) complexes $(Ph_3P)_2Rh(CO)GeCl_3$ and $[Me_3NH]_2[Rh(CO)(GeCl_3)_2Cl]$ have been prepared by the reaction of $(Ph_3P)_2Rh(CO)Cl$ with caesium- and trimethylammonium trichlorogermanite respectively.

The reaction of trichlorogermane with $[(C_8H_{12})RhCl]_2$ gave a mixture of $(C_8H_{12})RhH(GeCl_3)Cl$ and a cyclopentadienyl complex. A similar reaction with an excess of trichlorosilane yielded $(C_8H_{12})Rh(SiCl_3)_2Cl$. By contrast trichlorosilane reacted with π-$C_5H_5Rh(C_8H_{12})$ to give the complex π-$C_5H_5Rh(SiCl_3)_2 \cdot C_8H_{14}$.

The reaction of $[(PF_3)_4Rh]K$ with Et_3GeBr did not yield a stable triethylgermyl-rhodium(I) complex and an attempt to prepare a rhodium-molybdenum bonded compound was also inconclusive.

G. L. Hill

September 1970

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Note

The work described in this thesis was carried out at the University of Durham between September 1967 and September 1969, and at Queen's University, Belfast between September 1969 and September 1970. The work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

Part of the work described has been the subject of the following publication:

Rhodium-Germanium Complexes. J. Organometallic Chem., 1970, 22, C 48. (with F. Glockling).

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The reactions of $(Ph_3P)_3RhCl$:

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INTRODUCTION

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The introduction to this thesis is divided into two parts. The first is concerned mainly with the chemistry of rhodium(I) and (III) complexes although comparisons will be made when necessary to those of cobalt and iridium. Group IVb-transition metal complexes are the subject of the second part of the introduction and particular emphasis will be placed upon those of the cobalt group.

I THE CHEMISTRY OF RHODIUM

The importance of platinum metal complexes as homogeneous catalysts has stimulated research in this field over the past decade. Rhodium complexes have been found to be particularly effective catalysts and a great deal of effort has been devoted both to elucidating the mechanisms of the catalytic processes and in preparing new compounds. The oxidative addition reactions of rhodium(I) complexes have attracted particular interest and have led to a number of novel products. The general availability of modern spectral techniques such as infrared and nuclear magnetic resonance spectroscopy (where characterisation of complexes can be achieved using small quantities of material) has also contributed greatly to the expansion of interest in this field.

1. Comparative Chemistry of Cobalt, Rhodium and Iridium

TABLE I [1]

Element	Atomic Number	Atomic Weight	Configuration	Ionisation Potentials (e.v.) 1st	2nd	3rd	4th	5th	6th
Co	27	58.93	$3d^7 4s^2$	7.86	17.05	33.49	53	83.5	106
Rh	45	102.91	$4d^7 5s^2$	7.7	18.1	31.0	45.6	67	85
Ir	77	192.2	$5d^7 6s^2$	9.2	16	27	39	57	72

In its general chemistry, rhodium resembles iridium much more closely than cobalt although there are significant differences between them. This is a typical feature of transition metal chemistry in which the elements of a given group of the second and third transition series show similar chemical properties and exhibit definite differences from their counterparts in the first series. The cause of this is the lanthanide contraction. The filling of the 4f orbitals in the lanthanide series causes an increase in the effective nuclear charge experienced by the outer electrons, due to a lack of shielding. This causes a contraction of the 4f orbitals, thus resulting in a decrease in the atomic radii increase which would normally be expected in passing from the 2nd to the 3rd transition series. The net result of this is that rhodium and iridium have similar ionic and atomic radii whilst that of cobalt is significantly smaller.

Another general tendency is that the higher oxidation states are generally more stable for the 2nd and 3rd series of elements than for the 1st. This is reflected in the stability of Ir^{IV} and the relative unimportance of Rh^{II} and Ir^{II}.

Oxidation States VI, V and IV

For cobalt the higher oxidation states are difficult to obtain and of these the IV state is the only one which is found under normal conditions. The V and VI oxidation states are also rare for rhodium and iridium and are limited to the hexafluorides and salts of the MF_6^- ion. The IV state is of little importance for rhodium but iridium has a fairly extensive chemistry for the tetravalent state.

Oxidation State	Coord. No.	Geometry	Examples
VI, d^3	6	octahedral	RhF_6, IrF_6
V, d^4	6	octahedral	$Cs[RhF_6]$, $Cs[IrF_6]$
IV, d^5	6	octahedral	$[RhF_6]^{2-}$, $[IrCl_6]^{2-}$ $[CoF_6]^{2-}$

Oxidation State III

This is a common state and cationic and anionic complexes are known for all three metals. The simple Co^{III} ion is highly oxidising and will even oxidise water, but many complexes of the type $[Co(NH_3)_6]^{3+}$ are known. Rhodium and iridium differ from cobalt in forming octahedral complexes with halides such as $[IrCl_6]^{3-}$. They also form an extensive range of neutral complexes with π-bonding ligands such as phosphines and carbonyls. A large number of hydride species have been prepared.

Oxidation State	Coord. No.	Geometry	Examples
III, d^6	6	octahedral	$[RhCl_6]^{3-}$, $[IrCl_6]^{3-}$ $[Co(CN)_6]^{3-}$, $[Co(NH_3)_6]^{3+}$, $[Rh(NH_3)_5Cl]^{2+}$,

Oxidation State	Coord. No.	Geometry	Examples
III, d^6	6	octahedral	$[Ir(NH_3)_6]^{3+}$ $(R_3P)_3RhCl_3$, $(R_3P)_2Ir(CO)H_2Cl$
	5	trigonal bipyramidal	$(R_3P)_2IrH_3$, $(Ph_3P)_2RhHCl_2$

Oxidation State II

This is the characteristic state for cobalt in aqueous chemistry and a large number of tetrahedral and octahedral complexes are known. Rh^{II} and Ir^{II} complexes are rare and relatively unimportant.

Oxidation State	Coord. No.	Geometry	Examples
II, d^7	4	tetrahedral	$[CoCl_4]^{2-}$, $CoBr_2(PR_3)_2$
	5	Cu^{II} acetate structure	$[Rh(OCOR)_2]_2$
	6	octahedral	$[Co(NH_3)_6]^{2+}$

Oxidation State I

This oxidation state is known for all three elements in compounds stabilised by π-acceptor ligands. For cobalt the characteristic coordination number is five, whilst for rhodium and iridium both square planar and trigonal bipyramidal compounds are known. Co^{I} chemistry tends to centre around the tetracarbonyl compounds (i.e. $HCo(CO)_4$) whilst Rh^{I} and Ir^{I} are more effectively stabilised by phosphine ligands [i.e. $(Ph_3P)_2Ir(CO)Cl$, $(Ph_3P)_3RhCl$].

Oxidation State	Coord. No.	Geometry	Examples
I, d^8	4	planar	$[Rh(CO)_2Cl]_2$, $(Ph_3P)_2Ir(CO)Cl$

Oxidation State	Coord. No.	Geometry	Examples
I, d^8	5	trigonal bipyramidal	$[diphos]_2RhH$ $(Ph_3P)_3Ir(CO)H$ $HCo(CO)_4$

$[diphos] = Ph_2PC_2H_4PPh_2$

Oxidation States 0, -I

These are less important for rhodium and iridium than for cobalt as their carbonyl chemistry has been less extensively investigated. Examples of these compounds are:

0 $Co_2(CO)_8$, $Co_2(CO)_6(Ph_3P)_2$, $Co_4(CO)_{16}$
$Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, $Ir_4(CO)_{12}$, $Ir_6(CO)_{16}$
-I $[Co(CO)_4]^-$, $[Rh(CO)_4]^-$, $[Rh(PF_3)_4]^-$

2. Oxidative Addition Reactions of d^8 Complexes

The chemistry of d^8 rhodium(I) phosphine complexes is dominated by the oxidative addition reaction. This class of reactions has been recently reviewed[2] and so only the main features are presented below.

Oxidative addition is the term used to describe the reaction between a metal complex in the d^8 electronic configuration and a neutral covalent molecule to form a five or six-coordinate d^6 complex. The formal oxidation state of the metal atom is increased by two units. This type of reaction and its converse, reductive elimination, are extremely important as they are usually the key steps in homogeneous catalysis by d^8 transition metal complexes. A parallel can also be drawn between chemisorption of molecules on transition metal surfaces and the oxidative addition reaction.

Addition reactions to planar coordinatively unsaturated d^8

complexes appear to be one step processes and are often reversible. Examples of both _cis_ and _trans_ modes of addition,[3,4] and reaction with compounds with both polar and nonpolar bonds are known. (Fig. 1).

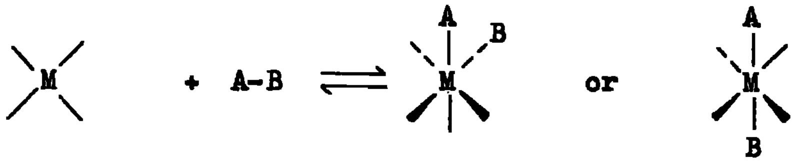


Fig. 1

(A-B) can be, for example, oxygen, olefins, acetylenes, hydrogen, nonmetal hydrides, hydrogen halides, protonic acids, alkyl halides, acyl halides, halogens or metal halides.

Five-coordinate d^8 complexes are coordinatively saturated and usually have the trigonal bipyramidal configuration. In contrast to the planar unsaturated complexes, they only appear to add polar or electrophilic molecules. Reaction can occur by two pathways. The first of these involves addition of a polar molecule to the five coordinate complex to form an intermediate salt which can often be isolated[5]. The salt can then irreversibly eliminate a neutral ligand (such as CO or Ph_3P) to form a product which is usually that resulting from overall _cis_ addition. (Fig. 2). The second pathway involves the prior dissociation of a ligand to give a more reactive four coordinate complex which then undergoes oxidative addition[6]. Reactions of this type are usually facilitated by heating or irradiation.

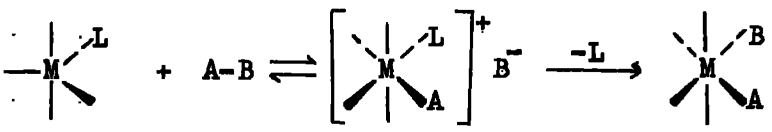


Fig. 2

(A-B) can be hydrogen halides, other strong acids, alkyl halides, mercuric halides, and perfluoroalkyl iodides.

The tendency for d^8 complexes to undergo oxidative addition depends upon the nature of the central metal ion and upon the ligands attached to it. Because the ligands strongly influence the reactivity of d^8 complexes it is only valid to make direct comparisons of reactivity between isostructural compounds within a single triad [e.g. $(Ph_3P)_2Rh(CO)Cl$ and $(Ph_3P)_2Ir(CO)Cl$]. It has been found[7] that ligands which increase electron density at the central metal atom increase the tendency for the metal to undergo oxidative addition. This tendency is also increased upon descending a triad or on passing from right to left within group VIII. (see Fig. 3).

An illustration of this is to be seen in the reaction of molecular hydrogen with the complexes $(Ph_3P)_2Ir(CO)Cl$, $(Ph_3P)_2Rh(CO)Cl$ and $(Ph_3P)_3RhCl$. The iridium complex $(Ph_3P)_2Ir(CO)Cl$ readily reacts with hydrogen at atmospheric pressure to give a stable dihydride[8], but the isostructural rhodium complex does not. When the carbonyl group is replaced by the less electron withdrawing triphenylphosphine ligand the complex $(Ph_3P)_3RhCl$ is formed which readily reacts with hydrogen at atmospheric pressure[9].

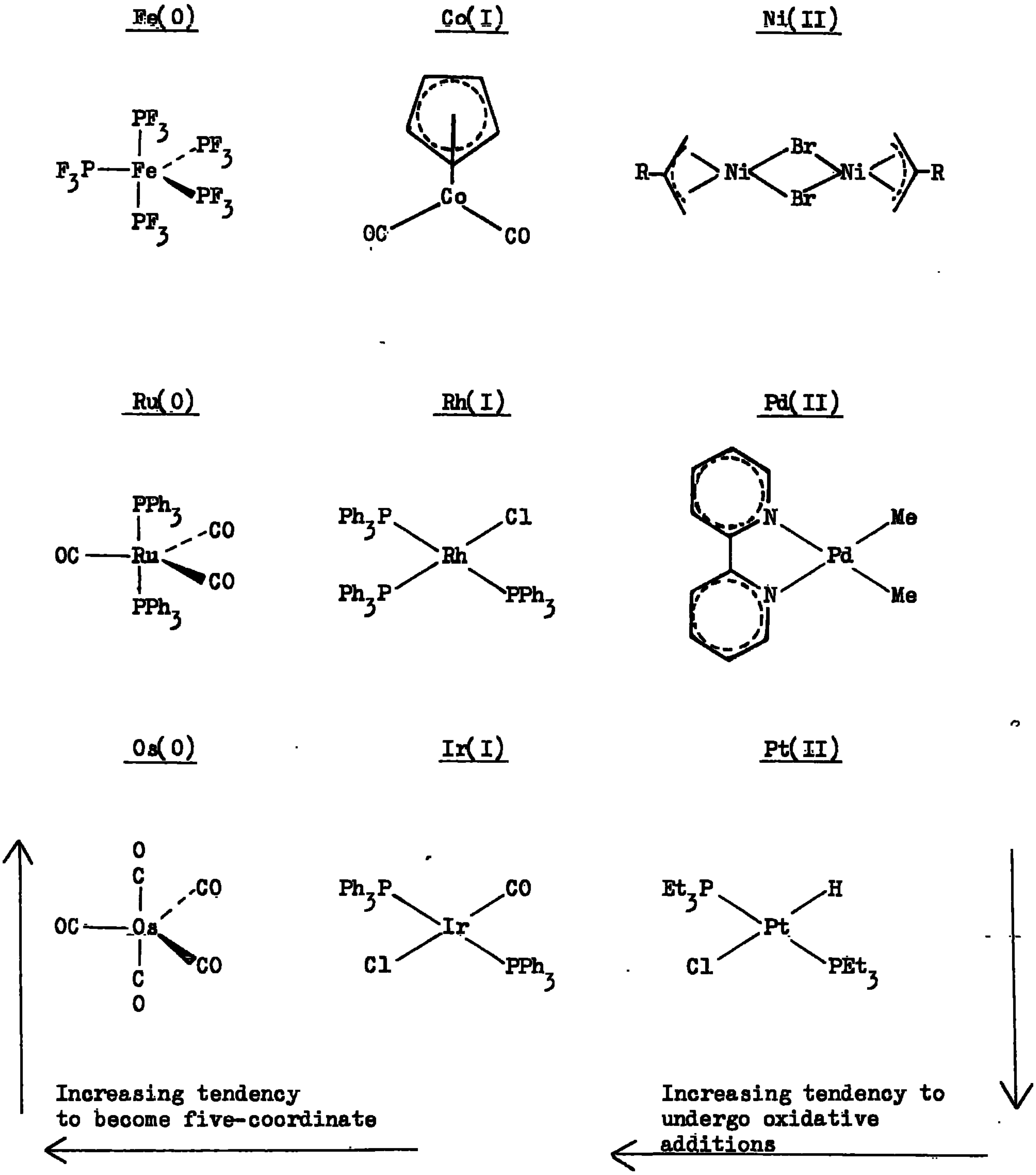


Fig. 3

Typical Group VIII complexes with d^8 configuration.

Fig. 3 also illustrates the tendency for an element having a

d^8 configuration to become five-coordinate as a triad is ascended or on passing from right to left along group VIII. In the extreme case this can be illustrated by the tendency of Fe(0) complexes to be five-coordinate whilst those of Pt(II) are four-coordinate.

3. Phosphine, Arsine and Stibine Complexes of Rhodium

(a) Complexes of the type $(Ph_3M)_3RhX$

One of the most extensively studied and important derivatives of rhodium(I) is the complex tris(triphenylphosphine)chlororhodium(I), $(Ph_3P)_3RhCl$. This compound was first reported in 1965 by two groups of workers[10,11] who prepared the compound independently. Subsequent work[12,13] soon showed the versatility of the complex which is often referred to as "Wilkinson's catalyst".

The compound is readily prepared by refluxing together rhodium trichloride trihydrate and a large excess of triphenylphosphine in ethanol. Reduction occurs and the dark burgundy-red crystals are obtained in essentially 100% yield. The corresponding bromide and iodide can also be made from ethanolic solutions of the trihalides. Reduction does not occur in the absence of an excess of triphenylphosphine and it appears likely that triphenylphosphine is the effective reducing agent.

$$RhCl_3 + \text{excess } Ph_3P + H_2O \longrightarrow (Ph_3P)_3RhCl + Ph_3PO + 2HCl$$

This reaction involving triphenylphosphine appears to be unique as other tertiary aryl alkyl-phosphines and -arsines react with ethanolic solutions of rhodium trichloride to give mononuclear rhodium(III) complexes $[(R_3M)_3RhCl_3]$[14,15], binuclear halogeno bridged complexes $[(R_3M)_4Rh_2Cl_6]$[14], and hydrido complexes $[(R_3M)_3RhHX_2]$[15]. Compounds of the type $(Ph_3L)_3RhCl$, (L = As, Sb) can be made from the bis-ethylene complex $[(C_2H_4)_2RhCl]_2$ and an excess of the ligand in the absence of air[16].

Tris(triphenylphosphine)chlororhodium(I) is air stable as a solid but solutions in benzene or dichloromethane rapidly absorb oxygen to give light brown crystals of $(Ph_3P)_2Rh(O_2)Cl\ (\frac{1}{2}CH_2Cl_2)$[12]. The infrared spectrum contains a band at ca. 900cm^{-1} due to coordinated oxygen but no bands attributable to ν(PO). The oxygen can be displaced by donor ligands, e.g. CO reacts to give $(Ph_3P)_2Rh(CO)Cl$.

In solution dissociation of a phosphine group occurs, e.g.

$$(Ph_3P)_3RhCl \underset{Ph_3P}{\overset{solvent}{\rightleftharpoons}} (Ph_3P)_2RhCl + Ph_3P$$

The dissociated species $(Ph_3P)_2RhCl$ has a vacant coordination site which can be occupied by a weakly bound solvent molecule (i.e. chloroform, benzene etc.) or by another ligand. The existence of this vacant site is essential to the catalytic activity of $(Ph_3P)_3RhCl$ and it also enables nucleophilic attack on rhodium to take place as well as the more usual electrophilic additions to d^8 complexes.

Molecular weight determinations[13] indicate that the dissociation is essentially complete in chloroform or benzene solution. ^{31}P n.m.r. studies[17] confirm that ligand exchange takes place by a dissociative mechanism but show that the complex is not completely dissociated in solution.

Donor solvents, such as pyridine, acetonitrile or dimethylsulphoxide, react with $(Ph_3P)_3RhCl$ to yield complexes of the type $(Ph_3P)_2RhCl(L)$.

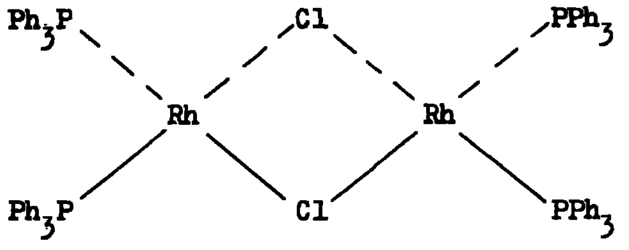


Fig. 4 Proposed structure of $[(Ph_3P)_2RhCl]_2$

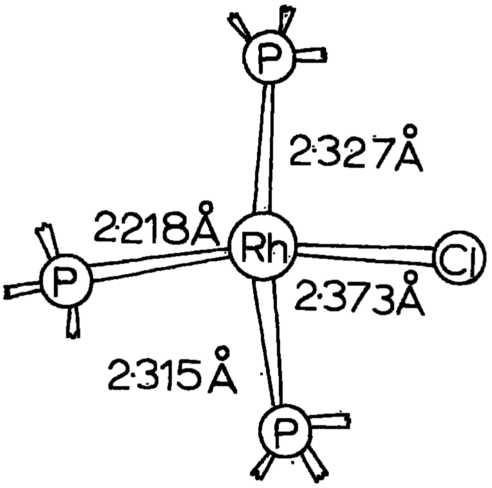


Fig. 5 Bond lengths in $(Ph_3P)_3RhCl$

In the absence of a donor solvent dimerisation may occur to give the orange-pink complex $[(Ph_3P)_2RhCl]_2$ which is halogen bridged (Fig. 4). The dimer readily takes up oxygen to give a product showing a strong band at 1150cm^{-1} in the i.r. spectrum which can be attributed to triphenylphosphine oxide.

The X-ray crystal structure of $(Ph_3P)_3RhCl$ shows that coordination to rhodium is not strictly planar but that the ligands are distorted slightly towards a tetrahedral arrangement (17a) (Fig. 5).

(b) Reactions of $(Ph_3M)_3RhX$

The ability of $(Ph_3P)_3RhCl$ to form adducts with donor molecules is shown particularly clearly in its affinity for carbon monoxide.

$$(Ph_3P)_3RhCl + CO \longrightarrow (Ph_3P)_2Rh(CO)Cl + Ph_3P$$

Saturation of benzene or chloroform solutions of the complex with carbon monoxide at room temperature gives an immediate reaction to yield the yellow complex chlorocarbonyl-bis(triphenylphosphine)rhodium(I). This reaction appears to be irreversible and has led to the use of $(Ph_3P)_3RhCl$ as a decarbonylating agent as carbon monoxide is readily abstracted from such compounds as aldehydes, acyl halides and aroyl halides[18-24]. The reactions become catalytic at higher temperatures.

$$ClC_6H_4CHO + (Ph_3P)_3RhCl \longrightarrow C_6H_5Cl + (Ph_3P)_2Rh(CO)Cl + Ph_3P$$

An analogous reaction is the abstraction of the thiocarbonyl group from carbon disulphide to give a deep red solution from which red crystals of bis(triphenylphosphine)(carbon disulphide)(π-carbon disulphide)chlororhodium(III) can be obtained. On boiling the complex in chloroform orange crystals of trans($Ph_3P)_2Rh(CS)Cl$ are obtained[25] which are analogous to $(Ph_3P)_2Rh(CO)Cl$.

An X-ray diffraction study[26] has shown that the complex has a square planar structure with trans phosphine groups. The Rh-C-S group is linear and the C-S distance is only slightly shorter than in carbon disulphide.

Ethylene, like carbon monoxide, reacts with solutions of $(Ph_3P)_3RhCl$ to give the bright yellow crystalline complex bis(triphenylphosphine)(ethylene)chlororhodium(I), $(Ph_3P)_2Rh(C_2H_4)Cl$[13].

$$(Ph_3P)_3RhCl + C_2H_4 \rightleftharpoons (Ph_3P)_2Rh(C_2H_4)Cl + Ph_3P$$

This is a reversible reaction and dissociation of the ethylene complex can be accelerated by sweeping the solution with nitrogen. Regeneration is quantitative on resaturating the solution with ethylene. The compound is stable in the solid state. The ethylene molecule is more firmly bound in the analogous arsine complex, $(Ph_3As)_2Rh(C_2H_4)Cl$[16], and the passage of nitrogen through solutions of the complex does not displace it so readily.

A similar but more stable complex is produced when solutions of $(Ph_3P)_3RhCl$ react with tetrafluoroethylene to yield pale yellow crystals of $(Ph_3P)_2Rh(C_2F_4)Cl$[27]. The complex does not dissociate in solution and treatment with triphenylphosphine does not displace tetrafluoroethylene. Treatment with carbon monoxide yields $(Ph_3P)_2Rh(CO)Cl$ however. An X-ray crystal structure determination of $(Ph_3P)_2Rh(C_2F_4)Cl$ shows that the C_2F_4 group occupies a position trans to chlorine[17a].

Both the phosphine and the arsine complexes, $(Ph_3M)_3RhCl$, react with diphenylacetylene to give a stable species $(Ph_3M)_2Rh(Ph_2C_2)Cl$, (M = P or As)[16].

A reversible addition reaction occurs with hydrogen to give a dihydride complex $(Ph_3P)_2RhH_2Cl$[13]. This is formally five-coordinate but can be isolated in a solvated form from chlorinated hydrocarbons i.e. $(Ph_3P)_2RhH_2Cl\ (\frac{1}{2}CH_2Cl_2)$.

It has been suggested that the dichloromethane is coordinated through chlorine and acts as a bridging ligand. A six-coordinate complex $(Ph_3P)_3RhH_2Cl$ has been isolated from solutions containing an excess of triphenylphosphine[15]. ^1H n.m.r. studies at 100 atmospheres pressure show that the hydrogen atoms are cis to one another (Fig. 6).

$$(Ph_3P)_2RhCl(S) + H_2 \rightleftharpoons (Ph_3P)_2RhH_2Cl(S)$$

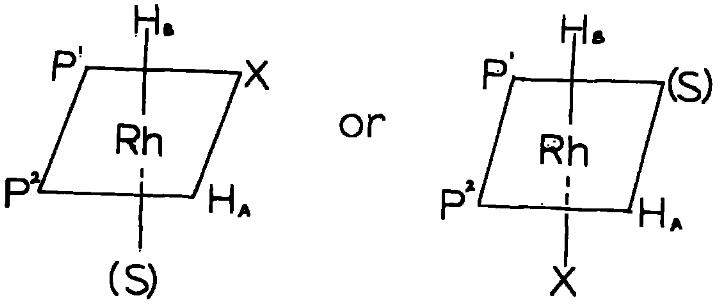


Fig. 6

A singlet (due to proton H_B) and a doublet (due to H_A) of equal integrated intensities are observed in the high-field ^1H n.m.r. spectrum. The doublet is caused by the H_A hydride resonance being split by coupling with the trans ^{31}P atom. The analogous triphenylarsine complex[16] shows only two lines of equal intensity in similar positions to those of the phosphine complex. The difference in the spectra provides good evidence for the existence of a solvated six-coordinate species in solution.

In contrast to $(Ph_3P)_2RhH_2Cl$, there is no appreciable dissociation of $(Ph_3As)_2RhH_2Cl$ in solution as the bound hydrogen is not displaced by a nitrogen stream.

Methyl iodide (but not methyl chloride or bromide) will also add to $(Ph_3P)_3RhCl$ to give a green solid which was formulated as $(Ph_3P)_2RhCl(Me)I.MeI$[28]. A crystallographic study[29] showed, however, that the compound had a square pyramidal structure (Fig. 7) when recrystallised from benzene and had the formula $(Ph_3P)_2Rh(Me)I_2.C_6H_6$. The benzene plays no part in the coordination about rhodium.

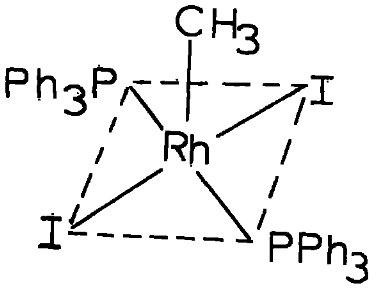


Fig. 7

The complex reacts with carbon monoxide to give $(Ph_3P)_2RhMe(CO)I_2$. Hydrogen chloride reacts readily with solutions of $(Ph_3P)_3RhCl$

in dichloromethane to give $(Ph_3P)_2RhHCl_2(\frac{1}{2}CH_2Cl_2)$[20,15]. The compound is unstable in the solid state to loss of both hydrogen chloride and dichloromethane. Solutions of the complex in cold solvents are stable however, and the equilibrium

$$(Ph_3P)_2RhCl(S) \underset{-HCl}{\overset{+HCl}{\rightleftharpoons}} (Ph_3P)_2RhHCl_2(S)$$

lies essentially completely to the right even for low concentrations of hydrogen chloride. ^1H n.m.r. studies show that the hydrogen atom is <u>cis</u> to two triphenylphosphine groups (see page 41).

This compound is particularly interesting as it undergoes hydrogen transfer reactions with ethylene, tetrafluoroethylene and acetylene to give rhodium(III) alkyl complexes[20].

$$\begin{aligned} (Ph_3P)_2RhHCl_2 \;+\; & C_2H_4 \longrightarrow (Ph_3P)_2Rh(Et)Cl_2 \\ +\; & C_2F_4 \longrightarrow (Ph_3P)_2Rh(C_2F_4H)Cl_2 \\ +\; & C_2H_2 \longrightarrow (Ph_3P)_2Rh(C_2H_3)Cl_2 \end{aligned}$$

These products are coordinatively unsaturated and the ethyl and vinyl complexes undergo further reaction with CO to give acyl and acryloyl complexes respectively. The acyl derivative is identical to that formed by the addition of propionyl chloride to $(Ph_3P)_3RhCl$. Intermediate species containing terminal carbonyl groups attached to rhodium have been detected at low temperature (-60°C) by infrared spectroscopy and the complex $(Ph_3P)_2Rh(CO)(C_2H_3)Cl_2$ has been isolated but is not very stable at room temperature. (Fig. 8).

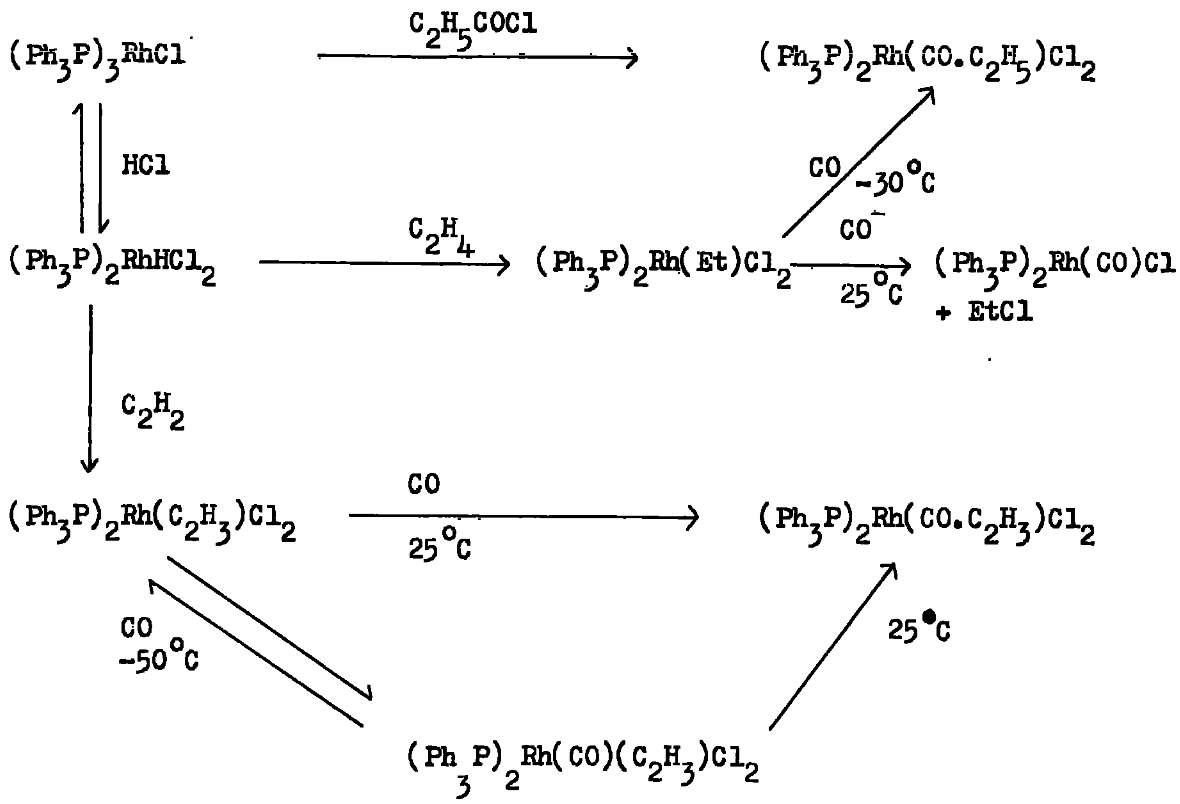
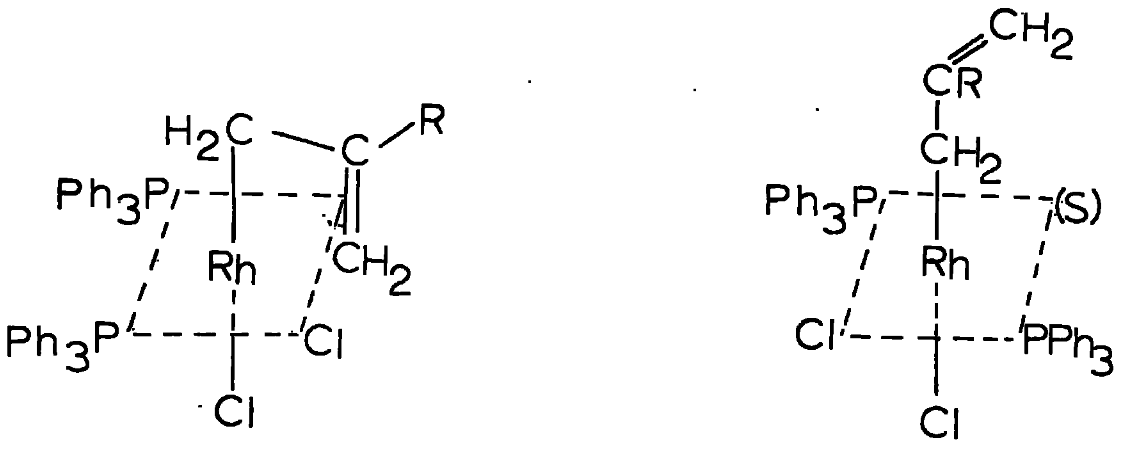


Fig. 8

Reactions of hydrido-dichloro-bis(triphenylphosphine)- and alkyl-rhodium complexes

Acyl and aroyl complexes have also been prepared by the direct addition of the acid halide to $(Ph_3P)_3RhCl$ in solution[20,21].

Reaction of $(Ph_3P)_3RhCl$ with allyl or 2-methylallyl chloride yields $(Ph_3P)_2Rh(RC_3H_4)Cl_2$, (R = H, Me)[28]. Each of the products is known in two forms in the solid state (Fig. 9). The ^1H n.m.r. spectra of the complexes suggest that in one case (A), the allyl group forms both a σ- and a π bond to rhodium whilst in the other it is fully π-bonded (C). One of the forms of $(Ph_3P)_2Rh(C_3H_5)Cl_2$ has structure (A) in the solid state but is thought to be a σ-allyl complex in solution(B). The carbonyl complex $(Ph_3P)_2Rh(CO)(C_3H_5)Cl_2$, which can be made by passing carbon monoxide into solutions of $(Ph_3P)_2Rh(C_3H_5)Cl_2$, also has this structure (B).

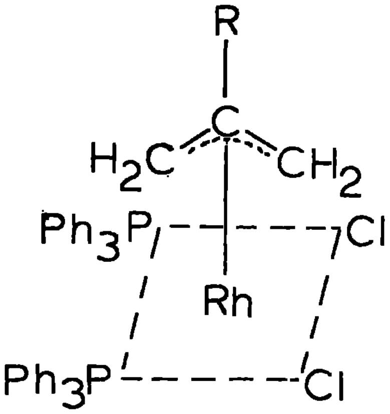


(A)

σ + π-allyl
(R = H or Me)

(B)

σ-allyl
(S = solvent or CO)

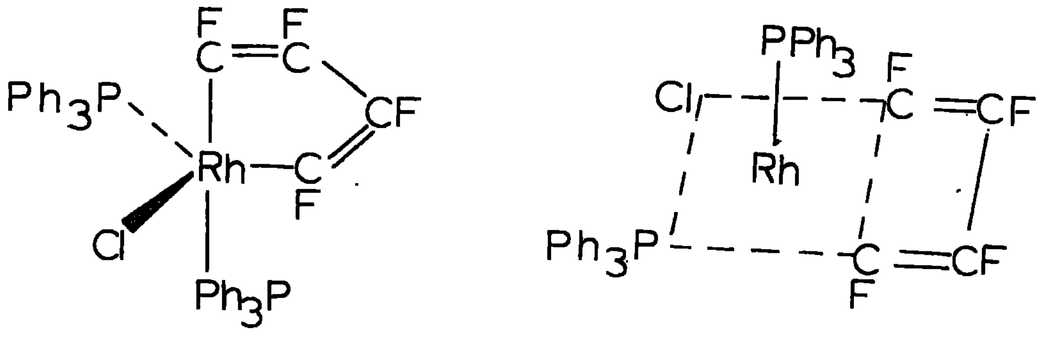


(C)

Fig. 9

Possible Structures of $(Ph_3P)_2Rh(RC_3H_4)Cl_2$-

Butadiene reacts with $(Ph_3P)_3RhCl$ to give a chelating diolefin complex of rhodium(I), $(Ph_3P)_2Rh(C_4H_6)Cl$[30]. In contrast to this hexafluorobutadiene reacts to give a complex of stoichiometry $(Ph_3P)_2Rh(C_4F_4)Cl$ with loss of fluorine. On the basis of i.r. and ^{19}F n.m.r. spectra the structures (A) or (B) (Fig. 10) have been suggested for this complex.



(A) (B)

Fig. 10

A reaction of the bridged dimer species, $[(Ph_3P)_2RhCl]_2$, with liquid sulphur dioxide to give the sulphur dioxide complex $(Ph_3P)_2Rh(SO_2)Cl$ has also been reported[31].

The reactions of $(Ph_3P)_3RhCl$ with hydrogen cyanide, hydrogen sulphide, and 4-methylbenzenethiol have been studied[32]. Oxidative addition reactions take place in each case to yield the products $(Ph_3P)_2Rh(HCN)_2Cl$, $(Ph_3P)_2RhH(SH)Cl$, and $(Ph_3P)_2RhH(SC_6H_4CH_3)Cl$ respectively.

(c) Catalytic activity of $(Ph_3P)_3RhCl$

In benzene or similar solvents $(Ph_3P)_3RhCl$ is a most efficient catalyst for homogeneous hydrogenation by molecular hydrogen at low temperature and pressure. The catalyst is specific for non-conjugated olefins (but not ethylene) and acetylenes. Other groups such as $C{=}O$ or NO_2 are unaffected. The hydrogenation is stereospecific for *cis*-addition and generally takes place without isomerisation of the olefin[13,33,34]. The catalytic activity is general for the range of complexes $(Ph_3P)_3RhX$ and increases in efficiency in the order Cl $<$ Br $<$ I, but the chloride is the most widely studied. The analogous arsine complex $(Ph_3As)_3RhCl$ is less efficient than $(Ph_3P)_3RhCl$ as are other tertiary phosphine complexes[35].

The mechanism of catalytic hydrogenation involves three steps: (a) hydrogen activation, (b) substrate activation and (c) hydrogen transfer. For the reaction to occur a delicate balance of equilibria must be maintained and the lability of the intermediates is critical. Because of this, even small changes in the ligands coordinated to rhodium greatly affect the catalytic activity. Thus for systems of the type $(Ph_3P)_2RhCl(L)$ hydrogen activation occurs readily if L is a poor π-acceptor (benzene, chloroform, pyridine etc.) but not if L is a good acceptor (ethylene, carbon monoxide, tetrafluoroethylene). Once the cis-dihydrido complex $(Ph_3P)_2RhH_2Cl(S)$ has been formed a competitive displacement of the weakly bonded solvent molecule (S) by the olefin must take place. This is the rate determining step[36]. The existence of the intermediate complex $(Ph_3P)_2RhH_2Cl$ (olefin) has not been proved directly but the evidence supports the existence of a vacant coordination site on the dihydride at which the olefin can be activated. As stereospecific cis reduction of the olefin occurs, this vacant site must be cis to the two metal hydrogen bonds.

The non-existence of a vacant site for olefin coordination in the iridium complex, $(Ph_3P)_2Ir(CO)Cl$, is presumably the main reason why it does not act as an efficient hydrogenation catalyst although it readily, and reversibly, activates molecular hydrogen[8].

The final hydrogen transfer step is thought to take place by the simultaneous transfer of both hydride ligands to the olefin as no alkyl intermediates have been detected in the reaction.

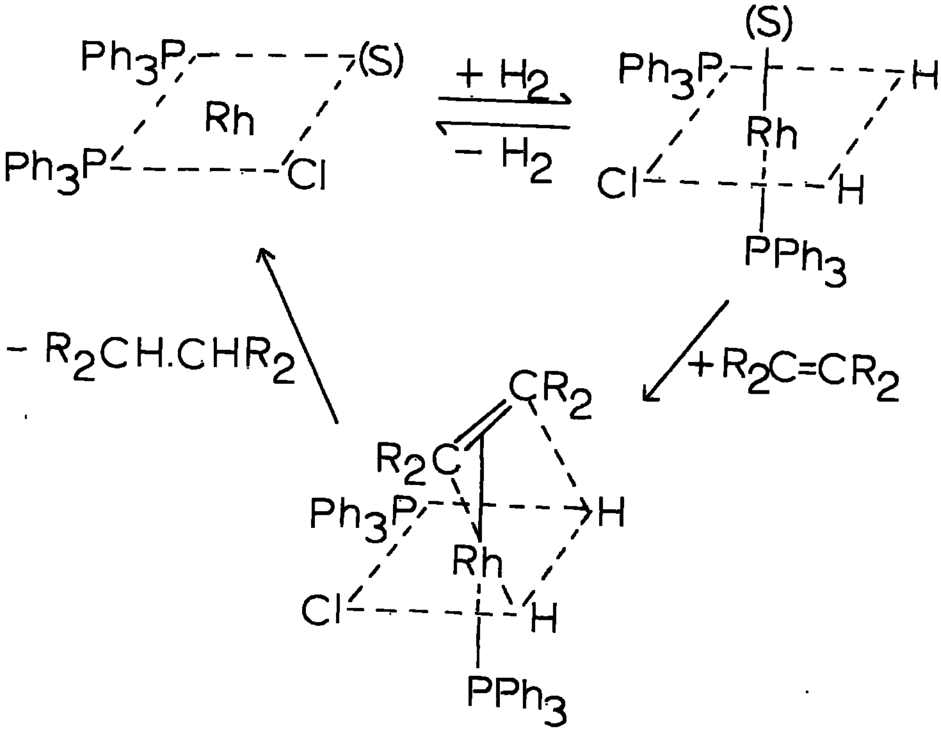


Fig. 11

Proposed Mechanism for the Homogeneous Hydrogenation of Olefins by $(Ph_3P)_3RhCl$.

$(Ph_3P)_3RhCl$ has also been used as a hydroformylation catalyst but $(Ph_3P)_2Rh(CO)Cl$ is probably the active species. The use of $(Ph_3P)_3RhCl$ as a decarbonylation catalyst[18-24] has already been briefly mentioned. Use has also been made of it as an oxidation catalyst in the conversion of cyclohexene to cyclohexene-1-one and cyclohexene-1-ol[37], and as an acetylene dimerisation catalyst[38].

(d) Comparison of $(Ph_3P)_3RhCl$ with $(Ph_3P)_3IrCl$

$(Ph_3P)_3IrCl$[39,39a] differs from the analogous rhodium complex in being only partly dissociated in organic solvents (molecular weight measurements). On heating solutions of the complex in organic solvents a hydrogen atom is lost from the ortho position of an aromatic ring on the ligand, with the formation of a metal carbon and a metal hydrogen bond.

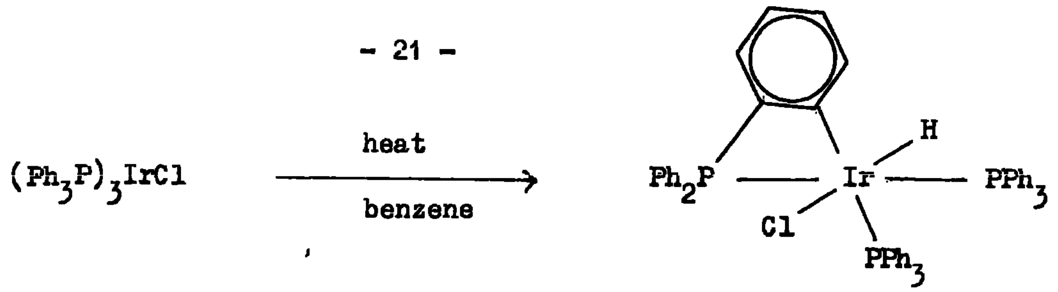


Fig. 12

The affinity of the complex for the formation of metal hydrogen bonds is also shown in its facile reactions with hydrogen chloride and hydrogen to yield $(Ph_3P)_3IrHCl_2$ and $(Ph_3P)_3IrH_2Cl$ respectively. The hydrogen addition reaction is irreversible, unlike that of its rhodium analogue. When $(Ph_3P)_3IrCl$ is heated in ethanol, hydrogen abstraction takes place to yield the dihydride and acetaldehyde.

The iridium complex reacts with CO and PF_3 in a similar manner to its rhodium analogue, one molecule of triphenylphosphine is displaced to give $(Ph_3P)_2Ir(CO)Cl$ and $(Ph_3P)_2Ir(PF_3)Cl$ respectively. By contrast however, no reaction occurs with ethylene.

(e) $(Ph_3P)_3RhH$ and $(Ph_3P)_4RhH$

These compounds have been reported by a number of workers[40-45]. The easiest method of preparation seems to be the reduction of $(Ph_3P)_3RhCl$ with ethanolic potassium hydroxide[44,45]. Both the tris(triphenylphosphine)- and the tetrakis(triphenylphosphine)rhodium(I) hydride can be formed depending upon the conditions of the reaction. $(Ph_3P)_4RhH$ dissociates in solution to $(Ph_3P)_3RhH$ and triphenylphosphine. Phosphine exchange occurs with the chelating phosphine $Ph_2PC_2H_4PPh_2$ to yield $(chel)_2RhH$. Oxidative addition reactions do not occur with iodine, methyl iodide, or mercuric chloride but cleavage of the rhodium hydrogen bond occurs. Addition of hydrogen chloride yields the known hydridodichloride complex, $(Ph_3P)_3RhHCl_2$, and treatment with nitric oxide in benzene gives purple crystals of the nitrosyl compound $(Ph_3P)_3RhNO$.

$$2(Ph_3P)_4RhH + I_2 \xrightarrow[\text{benzene}]{} 2(Ph_3P)_3RhI + H_2 + 2Ph_3P$$

$$(Ph_3P)_4RhH + CH_3I \longrightarrow (Ph_3P)_3RhI + CH_4 + Ph_3P$$

$$2(Ph_3P)_4RhH + HgCl_2 \longrightarrow 2(Ph_3P)_3RhCl + Hg + 2Ph_3P$$

$$(Ph_3P)_4RhH + 2HCl \longrightarrow (Ph_3P)_3RhHCl_2 + H_2 + Ph_3P$$

$$2(Ph_3P)_4RhH + 2NO \longrightarrow 2(Ph_3P)_3RhNO + 2Ph_3P + H_2$$

An X-ray diffraction study[46] on the tetrakis(triphenylphosphine)-rhodium(I) hydride showed that the arrangement of the phosphorus atoms around rhodium was tetrahedral. (Fig. 13). Although the hydride hydrogen atom was not observed it is suggested that it lies along the threefold axis through P(1) and the rhodium atom.

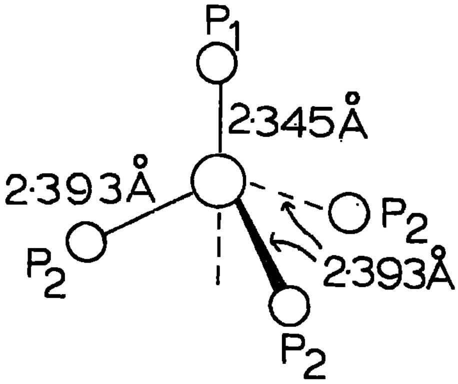


Fig. 13

$(Ph_3P)_4RhH$

(f) Other phosphine-Rh(I) complexes

Compounds of the type $[(dppe)_2M]X$, (dppe = $Ph_2PC_2H_4PPh_2$, M = Co or Ir, X = ClO_4, BPh_4, Cl, Br, I) are known to add hydrogen, hydrogen halides, carbon monoxide and sulphur dioxide to give five-or six-coordinate complexes[47,48]. The analogous rhodium complex $[(dppe)_2Rh]Cl$ shows none of these reactions. Its aliphatic analogue $[(dmpe)_2Rh]Cl$ (dmpe = $Me_2PC_2H_4PMe_2$) is very reactive however, and will activate hydrogen, carbon monoxide, hydrogen halides and halogens[49,50].

The hydrogen addition is reversible at room temperature. This illustrates the profound effect that a change of ligand can have upon the ability of the metal atom to undergo oxidative addition reactions. The less electronegative nature of dmpe apparently increases the electron density at the metal atom thus making it more reactive.

It is of interest that $[(dmpe)_2Rh(CO)]Cl$ does not activate hydrogen although $[(dmpe)_2Rh]Cl$ and $[(dppe)_2Ir(CO)]Cl$ do. It will, however, react with hydrogen halides and halogens to lose carbon monoxide and form compounds of the type <u>trans</u>-$[(dmpe)_2RhHX]Cl$.

$$\begin{array}{llll}
(Ph_3P)_3RhCl & + \ 2(dmpe) & \longrightarrow [(dmpe)_2Rh]Cl & \\
[(CO)_2RhCl]_2 & + \ 4(dppe) & \longrightarrow 2[(dppe)_2Rh]Cl & + \ 4CO \\
[(CO)_2RhCl]_2 & + \ 4(dmpe) & \longrightarrow 2[(dmpe)_2Rh(CO)]Cl & + \ 2CO \\
[(dmpe)_2Rh]Cl & & \overset{H_2}{\rightleftharpoons} [(dmpe)_2RhH_2]Cl & \\
[(dppe)_2Rh]Cl & + \ H_2 & \longrightarrow \text{no reaction} & \\
[(dmpe)_2Rh]Cl & + \ CO & \longrightarrow [(dmpe)_2Rh(CO)]Cl & \\
[(dppe)_2Rh]Cl & + \ CO & \longrightarrow \text{no reaction} & \\
[(dmpe)_2Rh(CO)]Cl & + \ HX & \longrightarrow [(dmpe)_2RhHX]Cl & + \ CO \\
[(dmpe)_2Rh]Cl & + \ HX & \longrightarrow [(dmpe)_2RhHX]Cl & \\
[(dmpe)_2Rh(CO)]Cl & + \ X_2 & \longrightarrow [(dmpe)_2RhX_2]Cl & + \ CO \\
[(dmpe)_2Rh]Cl & + \ X_2 & \longrightarrow [(dmpe)_2RhX_2]Cl &
\end{array}$$

<u>Fig. 14</u>

<u>The preparation and some reactions of $[(dmpe)_2Rh]Cl$ and $[(dmpe)_2Rh(CO)]Cl$</u>

Oxygen reacts with $[(dmpe)_2Rh]Cl$ to form the oxygen adduct $[(dmpe)_2RhO_2]Cl$[49,50]. Iridium complexes of the type $[(dppe)_2Ir]X$ (X = Cl, I and PF_6) form oxygen compounds readily[48,48a] but the corresponding rhodium adduct could only be isolated as the $[PF_6]^-$ salt, $[(dppe)_2RhO_2]PF_6$[48a]. $[(Ph_2AsCH = CHAsPh_2)_2Rh]Cl$[51] is also reported to undergo reactions with H_2, hydrogen halides, halogens, C_3H_5Cl, CH_3I, SO_2, NO_2, CO and PF_3 to give five- or six-coordinate adducts but not all of these products are well characterised.

Reduction of $[(dppe)_2Rh]X$ with $LiAlH_4$ or $NaBH_4$ yields $(dppe)_2RhH$ which is soluble in benzene[52]. This compound can also be obtained by phosphine exchange on $(Ph_3P)_4RhH$[42]. Oxidative addition occurs with hydrogen chloride and reactions also occur with perchloric acid and carbon tetrachloride.

$$\begin{array}{llcll} (dppe)_2RhH & + \; HCl & \longrightarrow & [(dppe)_2RhHCl]Cl & + \; H_2 \\ & + \; HClO_4 & \longrightarrow & [(dppe)_2Rh]ClO_4 & + \; H_2 \\ & + \; CCl_4 & \longrightarrow & [(dppe)_2Rh]Cl & + \; CHCl_3 \end{array}$$

Rhodium(I)-alkyl complexes of the type $(Ph_3P)_3RhR$, (R = alkyl) are known and can be prepared by the action of Grignard reagents on $(Ph_3P)_3RhCl$[53,54]. The rhodium-alkyl bond can be cleaved by hydrogen (600 p.s.i.g.) to yield $(Ph_3P)_3RhH$, or by phenol to give $(Ph_3P)_3Rh(OC_6H_5)$. Treatment of $(Ph_3P)_3RhC_6H_5$ with carbon monoxide yields $(Ph_3P)_2Rh(CO)C_6H_5$[55]. The action of heat on $(Ph_3P)_3RhMe$ liberates methane leaving an orange-yellow compound, shown to be $(Ph_3P)_2(Ph_2PC_6H_4)Rh$. The hydrogen is abstracted from the ortho position of one of the phenyl groups[54].

The compounds $(MePh_2P)_4RhH$[41], $(MePh_2P)_3RhCl$[41] and $(HPh_2P)_3RhCl$[56] have also been prepared but their reactions have not been reported.

Trifluorophosphine complexes of rhodium were first prepared by a high pressure synthesis on rhodium trichloride[57]. A more convenient low pressure synthesis from rhodium(I)-ethylene or -cyclooctene complexes has recently been described[58,59]. Treatment of the olefin complex $[(olefin)_2RhCl]_2$ with trifluorophosphine at 25° and

1 atmosphere pressure yields the red complex $[(PF_3)_2RhCl]_2$ which can be sublimed in vacuo. The reactions of this compound are summarised in Fig. 15.

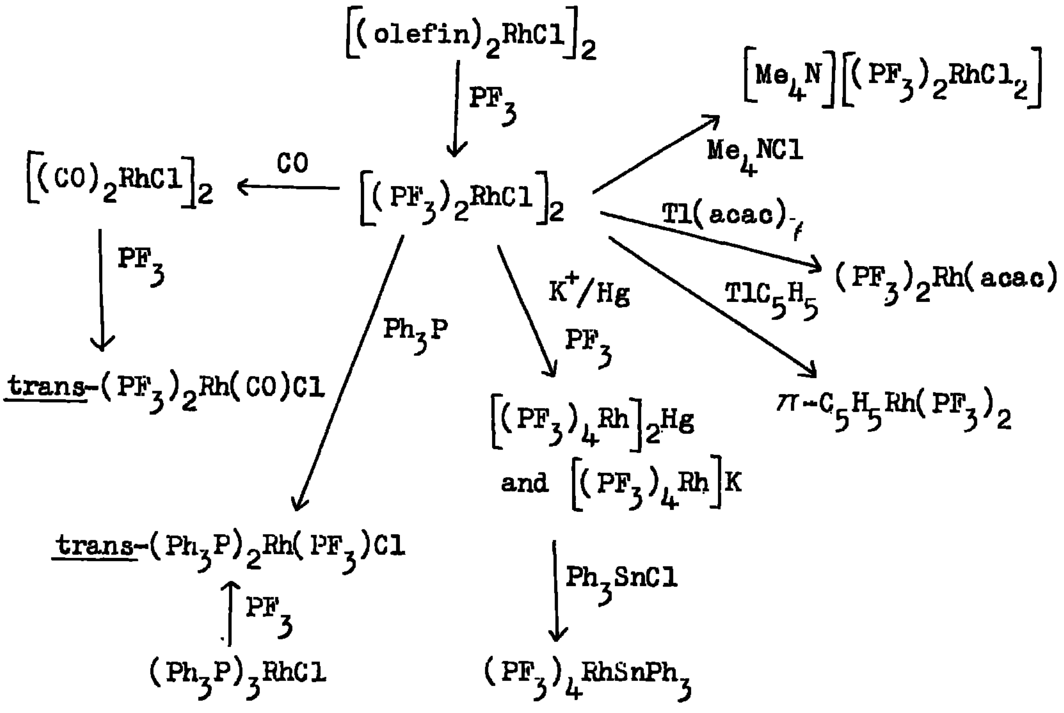


Fig. 15

Preparation and some reactions of $[(PF_3)_2RhCl]_2$.

Rhodium(I)-phosphite complexes of the type $[(PhO)_3P]_3RhCl$[60], $[(PhO)_3P]_2Rh(CO)Cl$[60], $[(PhO)_3P]_4RhH$[61] and $\{[(PhO)_3P]_4Rh\}_2$[62] are also known.

(g) Rhodium(III)-phosphine complexes

Many of these complexes are formed by oxidative addition reactions on Rh(I) compounds and have already been discussed. This section will concentrate on those compounds which are prepared directly from rhodium trichloride.

Addition of tertiary phosphines or tertiary arsines to hot alcoholic solutions of $RhCl_3$ has been reported to give complexes of the form mer-$(R_3M)_3RhX_3$, (X = halogen; M = As, P; R = alkyl or aryl) and small amounts of the isomeric complex fac-$(R_3M)_3RhX_3$ (Fig. 16) and of

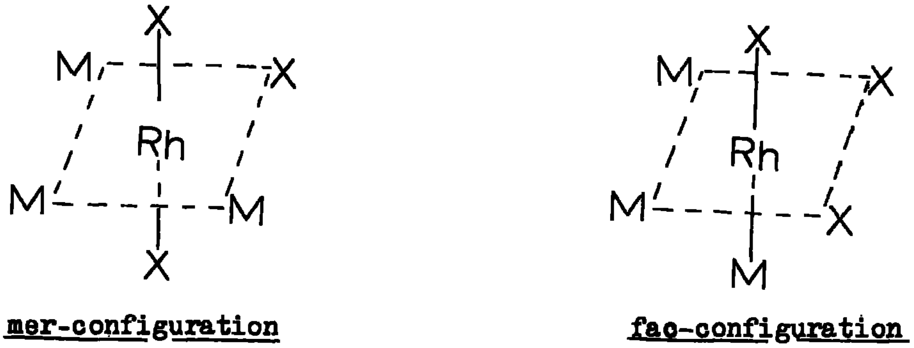


Fig. 16

$[Me_2PhPH][(Me_2PhP)_2RhCl_4]$[14,56,63]. The configurations of the isomers have been assigned on the basis of ^1H n.m.r., far i.r., and dipole moment studies (see page 41).

Attempts to replace the chloro-groups with alkyl or aryl groups failed, as also did attempts at reduction with $LiAlH_4$ or $NaBH_4$[14]. Because of their suitability for ^1H n.m.r. characterisation the dimethylphenylphosphine complexes have been the most extensively studied[63]. Metathetical replacement reactions on $(Me_2PhP)_3RhCl_3$ occur readily under mild conditions to give $(Me_2PhP)_3RhCl_2Y$ (Y = Br, I, NCO, NCS, NO_2 or N_3), and also $(Me_2PhP)_3RhY_3$ under more vigorous conditions. The chlorine in the trans-position to phosphorus in the compound mer-$(Me_2PhP)_3RhCl_3$ is the most readily substituted.

Binuclear complexes of the type $[(MR_3)_3Rh_2X_6]$ and $[(MR_3)_4Rh_2X_6]$ have also been prepared[14].

The effect of the basicity of the tertiary phosphine on the reaction with $RhCl_3$ has been studied by Sacco et al[15]. It was found that on addition of more basic phosphines (like trialkylphosphines) compounds of the type L_3RhX_3 were formed. With less basic phosphines (such as Et_2PhP) a hydride can easily be isolated. With triphenylphosphine reduction occurs to give a rhodium(I) complex.

$$RhX_3 \xrightarrow{+L} L_3RhX_3 \xrightarrow{+H,\ -Cl} L_3RhHX \underset{+HX}{\overset{-HX}{\rightleftharpoons}} L_3RhX$$

Treatment of $(EtPh_2P)_3RhCl_3$ with carbon monoxide gave the rhodium(I) complex $(EtPh_2P)_2Rh(CO)Cl$.

The complex $(EtPh_2P)_3RhHCl_2$ can also be prepared by the reduction of $(EtPh_2P)_3RhCl_3$ with hypophosphorous acid[15]. This reaction has also been used to prepare the analogous arsine complexes[64,65].

The complex $(Ph_2MeAs)_3RhHCl_2$ reacts with acrylonitrile to give a stable Rh(III)-alkyl bond, $(Ph_2MeAs)_3RhCl_2.CH(Me)CN$[66]. The hydrido complex also reacts with mercuric salts HgY_2 (Y = F, Cl Br, I, oAc) to give $(Ph_2MeAs)_3RhCl_2(HgY)$[67]. The species $(Et_2PhP)_3RhX_2(HgX)$ are also known[15].

Anionic complexes of the type $[(Ph_3P)_2RhX_4]^-$ have also been prepared by the reaction of $Ph_4AsCl.HCl$ with tris(triphenylphosphine) rhodium(I) chloride[68].

4. Carbonyl Compounds

(a) Rhodium(0) carbonyls

Rhodium(0) carbonyls were first made in 1943 by Hieber who reported the preparation of $HRh(CO)_4$, $Rh_2(CO)_8$, $[Rh(CO)_3]_n$ and $Rh_4(CO)_{11}$[69]. X-Ray diffraction studies have shown the last two compounds to be $Rh_4(CO)_{12}$[70] and $Rh_6(CO)_{16}$[71] respectively. Recent publications have reported improved syntheses for these two compounds[72-74] but so far it has not been possible to reproduce the preparations of $HRh(CO)_4$ and $Rh_2(CO)_8$.

Reduction of tetrahydrofuran solutions of $Rh_2(CO)_4Cl_2$ with alkali metals in the presence of CO yields the anion $[Rh(CO)_4]^-$ which is unstable in solution and very sensitive to hydrolysis or oxidation[75]. The anion has been isolated as the tetramethylammonium salt which is a white crystalline solid stable to 100°C. The anions $[Rh_{12}(CO)_{30}]^{2-}$, $[Rh_7(CO)_{16}]^{3-}$, $[Rh_6(CO)_{14}]^{4-}$ and $[Rh_3(CO)_{10}]^-$ have also been isolated recently[76,77].

$Rh_4(CO)_{12}$ reacts with triphenylphosphine to give the dimeric $Rh_2(CO)_4(Ph_3P)_4$. This compound will further react with oxygen to give a carbon dioxide complex, $Rh_2(CO)_2(CO_2)(Ph_3P)_3.C_6H_6$[78]. Other phosphine substituted carbonyl cluster compounds of rhodium have been reported[77,78a].

The most stable rhodium carbonyl derivatives are the cluster compounds. Comparison with the analogous cobalt derivatives shows that for cobalt these are the least stable. (Fig. 17)

Increasing Stability ←

$Na[Co(CO)_4]$	$Co_4(CO)_{12}$	$Co_6(CO)_{16}$
$Na[Rh(CO)_4]$	$Rh_4(CO)_{12}$	$Rh_6(CO)_{16}$

→ Increasing Stability

Fig. 17

The mixed cobalt-rhodium carbonyl complex $Co_2Rh_2(CO)_{12}$ has been prepared by treating $[Rh(CO)_2Cl]_2$ with one mole of $Zn[Co(CO)_4]_2$[79].

(b) Carbonyl halides

These are of the form $[Rh(CO)_2X]_2$ (X = Cl, Br, I), made by the action of carbon monoxide on rhodium trihalides[69,80,81], and $[Rh(CO)_2X_2]^-$ (X = Cl, Br, I), made from $[Rh(CO)_2X]_2$ and the halogen acid[82,83]. A binuclear species $[Rh_2(CO)_2X_4]^{2-}$ (X = Br, I) has also been reported[82] but recent work[83a] suggests that this should be formulated as $[Rh(CO)X_4]^-$. Compounds of the type $[Rh(CO)X_5]^{2-}$ have also been prepared[83a].

An X-ray crystal structure on $[Rh(CO)_2Cl]_2$ shows that two essentially planar $Rh(CO)_2Cl$ groups are joined by two chloride bridges, with the planes of the two groups inclined at an angle of 124° (Fig. 18). In the solid the dimers are held together in an infinite chain by weak metal-metal bonds. A bent metal-metal bond within the dimer has also been suggested[84].

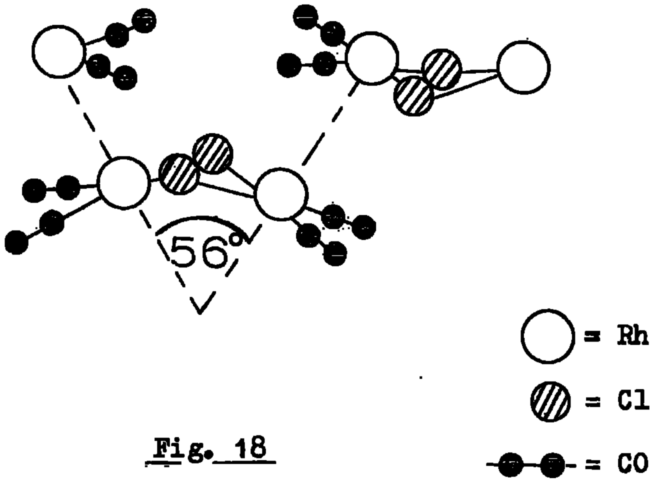


Fig. 18

Rhodium carbonyl chloride

Reactions of $[Rh(CO)_2Cl]_2$ are of four main types:

(a) bridge splitting reactions[85-87]

e.g. $[Rh(CO)_2Cl]_2 + 2C_5H_5N \longrightarrow 2Rh(CO)_2Cl.C_5H_5N$

$[Rh(CO)_2Cl]_2 + 4Ph_3P \longrightarrow 2(Ph_3P)_2Rh(CO)Cl + 2CO$

(b) bridge replacement[86]

$[Rh(CO)_2Cl]_2 + 2(CH_3COO)Ag \longrightarrow [Rh(CO)_2CH_3CO_2]_2 + 2AgCl$

(c) carbonyl replacement[52,88]

$$\left[Rh(CO)_2Cl\right]_2 + 2C_8H_{12} \longrightarrow \left[C_8H_{12}RhCl\right]_2 + 4CO$$

(d) adduct formation[89]

$$\left[Rh(CO)_2Cl\right]_2 + 2(\text{cyclohexa-1,3-diene}) \longrightarrow \left[Rh(CO)_2Cl\right]_2\cdot\text{diene}$$

A redistribution reaction with $\left[Rh(C_2H_4)_2Cl\right]_2$ has also been reported[81]

$$\left[Rh(CO)_2Cl\right]_2 + \left[Rh(C_2H_4)_2Cl\right]_2 \longrightarrow 2\left[Rh(CO)(C_2H_4)Cl\right]_2$$

(c) Carbonyl phosphine, arsine and stibine complexes

Complexes of the type trans-$(R_3M)_2Rh(CO)X$ (M = P, As; X = Cl, Br, I; R = alkyl or aryl) have been prepared by a variety of methods. The compounds were first made[85,87] by the action of R_3M on solutions of $\left[Rh(CO)_2Cl\right]_2$. Triarylphosphite complexes can also be prepared by this method[60].

$$\left[Rh(CO)_2Cl\right]_2 + 4R_3M \longrightarrow 2(R_3M)_2Rh(CO)Cl + 2CO$$

Reduction of $RhCl_3$ in boiling alcohol in the presence of carbon monoxide followed by the addition of tertiary phosphine or arsine is reported to give better yields in some cases[90]. An alternative method is to treat complexes of the type $(R_3P)_2Rh(CO)Cl_3$ with base (potassium hydroxide) in boiling ethanol[90].

$(Ph_3P)_2Rh(CO)Cl$ can be prepared readily by passing carbon monoxide through solutions of $(Ph_3P)_3RhCl$[13], or more conveniently by treatment with formaldehyde in boiling alcohol[91].

It has been reported that the complexes prepared from the reaction of triphenylstibine and $\left[Rh(CO)_2Cl\right]_2$ are better formulated as $\left[(Ph_3Sb)_3Rh(CO)Cl\right]\cdot C_6H_6$[92] than the previously reported $(Ph_3Sb)_2Rh(CO)Cl$ and $(Ph_3Sb)_3Rh(CO)_2Cl$[93].

All the ligands of $(Ph_3P)_2Rh(CO)Cl$ are very labile and it has been suggested that exchanges take place through a five-coordinate intermediate[94,95]. In spite of the kinetic lability the compound is thermodynamically very stable however.

Addition of solutions of sodium iodide to $(Et_2PhP)_2Rh(CO)Cl$ quickly led to the formation of $(Et_2PhP)_2Rh(CO)I$[90]. Attempts to alkylate the chloro-complex with Grignard reagents or organolithium compounds were unsuccessful and yielded only brown intractable products[90]. Similar attempts to prepare a Group IVb derivative by the reaction of triphenylsilyl-lithium with $(Ph_3P)_2Rh(CO)Cl$ also failed[96].

Compounds of the type $L_2Rh(CO)Cl$ (L = tertiary phosphine or arsine) have been shown to undergo oxidative addition reactions to give rhodium(III) complexes. Some typical addition reactions are shown in Fig. 19.

A comparison of these reactions with those of the analogous iridium complexes[102] or complexes of the type L_3RhCl (see pages 11-18) shows that oxidative addition occurs much less readily for $L_2Rh(CO)Cl$.

$(Ph_3P)_2Rh(CO)Cl + Cl_2 \longrightarrow (Ph_3P)_2Rh(CO)Cl_3$ 97,98

$(Bu_3P)_2Rh(CO)Cl + MeI \longrightarrow (Bu_3P)_2Rh(CO)(Me)ClI$ 98

$(Ph_3P)_2Rh(CO)Cl + HCl \longrightarrow (Ph_3P)_2Rh(CO)HCl_2$ 20

$(Ph_3P)_2Rh(CO)Cl + SO_2 \longrightarrow (Ph_3P)_2Rh(CO)(SO_2)Cl$ 99,100

$(Me_2PhP)_2Rh(CO)Cl + MeCOCl \longrightarrow (Me_2PhP)_2Rh(CO)(MeCO)Cl_2$ 101

$(Me_2PhP)_2Rh(CO)Cl + MeSO_2Cl \longrightarrow (Me_2PhP)_2Rh(CO)(MeSO_2)Cl_2$ 101

Fig. 19

Some oxidative addition reactions of $(Ph_3P)_2Rh(CO)Cl$

Where similar Rh(III) products exist those formed from $(Ph_3P)_2Rh(CO)Cl$ are less stable than those formed from the analogous iridium complex. $(Ph_3P)_2Rh(CO)Cl$ will not activate hydrogen and addition of hydrogen chloride gives $(Ph_3P)_2Rh(CO)HCl_2$ (always contaminated with starting material),[20] which is stable in the solid state but not in solution. $(Ph_3P)_2Ir(CO)Cl$ forms stable products with both these addends[8,103]. Similarly $(Ph_3P)_2Rh(CO)Cl$ will not react with mercuric chloride although the iridium complex gives $(Ph_3P)_2Ir(CO)(HgCl)Cl_2$[104].

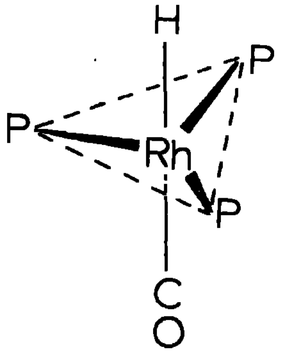
Alkyl halide additions to $L_2Rh(CO)X$ are known[98,105]. Reaction proceeds through an $L_2Rh(CO)MeX_2$ intermediate to give eventually an acyl product [e.g. $(Ph_3P)_2Rh(MeCO)I_2$]. These products can often also be made by addition of the acyl halide to $(Ph_3P)_3RhCl$[20] (see page 16). Compounds of the type $L_2Rh(CO)(RCO)Cl_2$ which are not very stable when $L = Ph_3P$ are more easily isolated when $L = Me_2PhP$[101]. The stereochemistry of the products formed by addition reactions to $(Me_2PhP)_2Rh(CO)Cl$ has been studied by an n.m.r. method[101] (see page 43) but no investigations have been made into whether cis- or trans-addition occurs.

The thiocarbonyl complex, $(Ph_3P)_2Rh(CS)Cl$, has already been mentioned (page 12). Oxidation by halogens gives Rh(III) complexes, $(Ph_3P)_2Rh(CS)X_3$.

$(Ph_3P)_2Rh(CO)Cl$ is an efficient hydroformylation catalyst[106] and is also probably the active species in catalytic decarbonylation reactions.

(d) $(Ph_3P)_3Rh(CO)H$

Hydridocarbonyl-tris(triphenylphosphine)rhodium(I) was first prepared by the reduction of $(Ph_3P)_2Rh(CO)Cl$ with hydrazine in the presence of an excess of triphenylphosphine[107]. An improved synthesis uses sodium borohydride as the reducing agent[108]. A crystal structure[109] shows that the compound has a trigonal bipyramidal structure with three phosphorus atoms in the trigonal plane and hydrogen and carbonyl groups in the axial positions. The rhodium atom is displaced 0.355Å below the equatorial plane towards the carbonyl group. (Fig. 20)



Rh-H = 1.72Å

Rh-P = 2.34Å

2.31Å

2.32Å

Rh-CO= 1.81Å

Fig. 20

$(Ph_3P)_3Rh(CO)H$

The complex dissociates in solution in two steps[108].

$$(Ph_3P)_3Rh(CO)H \underset{+Ph_3P}{\overset{-Ph_3P}{\rightleftharpoons}} (Ph_3P)_2Rh(CO)H \underset{+Ph_3P}{\overset{-Ph_3P}{\rightleftharpoons}} (Ph_3P)Rh(CO)H$$

At concentrations of 10^{-3}M it is suggested that $(Ph_3P)_2Rh(CO)H$ is the predominant species. The reaction of $(Ph_3P)_3Rh(CO)H$ with carbon monoxide involves a complex series of equilibria:

$$(Ph_3P)_3Rh(CO)H \rightleftharpoons (Ph_3P)_2Rh(CO)H \quad + \quad Ph_3P$$

$$(Ph_3P)_2Rh(CO)H \underset{H_2}{\overset{CO}{\rightleftharpoons}} (Ph_3P)_2Rh(CO)_2H$$

$$(Ph_3P)_2Rh(CO)_2H \underset{H_2}{\overset{CO}{\rightleftharpoons}} \left[(Ph_3P)_2Rh(CO)_2\right]_2 \quad + \quad H_2$$

$$\left[(Ph_3P)_2Rh(CO)_2\right]_2 \underset{CO}{\overset{N_2}{\rightleftharpoons}} \left[(Ph_3P)_2Rh(CO)(S)\right]_2 \quad + \quad 2CO$$

[S = solvent, e.g. benzene]

Solutions of $(Ph_3P)_3Rh(CO)H$ in dry, degassed benzene also undergo a slow spontaneous decomposition reaction to give a dimeric species, $[(Ph_3P)_2Rh(CO)]_2$[110].

$$2(Ph_3P)_3Rh(CO)H \longrightarrow [(Ph_3P)_2Rh(CO)]_2 + 2Ph_3P + H_2$$

$(Ph_3P)_3Rh(CO)H$ is an effective and highly selective catalyst for the homogeneous hydrogenation and hydroformylation of alk-1-enes[111]. Analogues, with less reactive metal-carbon bonds, of the species which are involved in the catalytic processes have recently been prepared, i.e. $(Ph_3P)_2Rh(CO)C_2F_4H$[112].

5. Organic Derivatives of Rhodium

Research in the field of organo-transition metal chemistry has flourished in the past twenty years and many new types of compound have been isolated. The chemistry of these compounds is well documented[113].

Rhodium forms a number of organic derivatives, especially with olefins, and only the more important complexes are mentioned below.

(a) Alkyl complexes

Several typical compounds have been discussed in other sections and will not be discussed further: $(Ph_3P)_2Rh(Me)ClI_2$ (page 14), $(Bu_3P)_2Rh(CO)(Me)ClI$ (page 31); $(Ph_3P)_2Rh(CO)(Me)Cl_2$ (page 16), $(Ph_3P)_2Rh(Et)Cl_2$ (page 15), $(Ph_3P)_2Rh(C_2F_4H)Cl_2$ (page 15), $(Ph_3P)_2Rh(CH = CH_2)Cl_2$ (page 15), $C_5H_5Rh(CO)CF_3I$ (page 37), $(Ph_3P)_3RhR$ (R = Me, Ph), (page 24), $(Ph_3P)_2Rh(CO)C_2F_4H$ (page 34).

(b) Olefin complexes

The field of transition metal-olefin complexes has recently been reviewed[114]. The passage of ethylene into aqueous methanol solutions of rhodium trichloride gives orange crystals of $[(C_2H_4)_2RhCl]_2$[115]:

$$2RhCl_3 + 2H_2O + 6C_2H_4 \longrightarrow [(C_2H_4)_2RhCl]_2 + 2CH_3CHO + 4HCl$$

The complex is a chloro-bridged dimer[116]. Other mono-olefin complexes can be prepared in a similar way (e.g. propylene[115], cyclo-octene[117]). Reaction of the ethylene complex with acetylacetone and cyclopentadienyl-sodium yield $(C_2H_4)_2Rh(acac)$ and π-$C_5H_5Rh(C_2H_4)_2$ respectively[118]. Tertiary phosphines and arsines completely displace the ethylene from $[(C_2H_4)_2RhCl]_2$ to give complexes of the type L_3RhCl (L = tertiary phosphine or arsine)[16]. Displacement of ethylene from $(C_2H_4)_2Rh(acac)$ by vinyl chloride or propylene to form complexes of the type $(olefin)_2Rh(acac)$ has been reported[119]. Both $[(C_2H_4)_2RhCl]_2$ and $(C_2H_4)_2Rh(acac)$ catalyse the dimerisation of ethylene[120].

Reaction of C_2H_4 and C_2F_4 with $(Ph_3P)_3RhCl$ to yield olefin complexes of the type $(Ph_3P)_2Rh(olefin)Cl$ has previously been discussed (see pages 12 and 13).

Diolefin complexes of rhodium[114,121] are well known and can be obtained by refluxing solutions of rhodium trichloride trihydrate with the diene. The complex formed with cyclo-1,5-diene is typical of this class of compound, $[(C_8H_{12})RhCl]_2$[122,123].

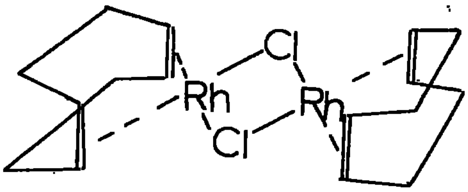


Fig. 21

$[C_8H_{12}RhCl]_2$

$[(C_8H_{12})RhCl]_2$ undergoes bridge splitting reactions to yield products such as π-$C_5H_5Rh(C_8H_{12})$, $(C_8H_{12})Rh(acac)$, $[(C_8H_{12})Rh(CH_3COO)]_2$[122] and $(C_8H_{12})RhCl(Ph_3P)$[124].

(c) Allyl complexes

The chemistry of allyl transition metal complexes has been extensively reviewed[125,126] and the structures of complexes of the type $(Ph_3P)_2Rh(RC_3H_4)Cl_2$ (R = H, Me) have previously been discussed (page 16). Some typical preparations are shown below.

$[Rh(CO)_2Cl]_2 + 6C_3H_5Cl + 4H_2O \longrightarrow [(C_3H_5)_2RhCl]_2 + 4CO_2 + 2C_3H_6 + 6HCl$ 127
$(Ph_3P)_3RhCl + C_3H_5Cl \longrightarrow (Ph_3P)_2Rh(C_3H_5)Cl_2 + Ph_3P$ 28
$RhCl_3 + 3C_3H_5MgCl \longrightarrow (C_3H_5)_3Rh + 3MgCl_2$ 127
$(Ph_3P)_3RhCl + C_3H_5MgCl \longrightarrow (Ph_3P)_3Rh(C_3H_5) + MgCl_2$ 128
$[(CO)_2RhCl]_2 + 2C_3H_5MgCl \longrightarrow 2(CO)_2Rh(C_3H_5) + 2MgCl_2$ 129
$[(C_3H_5)_2RhCl]_2 + 2TlC_5H_5 \longrightarrow 2(\pi\text{-}C_5H_5)Rh(C_3H_5)_2 + 2TlCl$ 127

Examples of pure π-allyl complexes, $(Ph_3P)_3Rh(\pi\text{-}C_3H_5)$; asymmetrically bonded π-complexes, $[(\pi\text{-}C_3H_5)_2RhCl]_2$; and compounds containing both π- and σ-allyl groups, $\pi\text{-}C_5H_5Rh(\sigma\text{-}C_3H_5)(\pi\text{-}C_3H_5)$, are known for rhodium.

Butadiene reacts with rhodium trichloride in methanol to give $C_4H_7RhCl_2(C_4H_6)RhCl_2C_4H_7$[130] which is believed to have a bridging butadiene group and two π-crotyl groups.

(d) Acetylene complexes

Only a few rhodium-acetylene complexes are known[131]. Two examples are shown below.

$(Ph_3P)_3RhCl + PhC{\equiv}CPh \longrightarrow (Ph_3P)_2Rh(PhC{\equiv}CPh)Cl + Ph_3P$ 16
$(Ph_3P)_2Rh(CO)Cl + HC{\equiv}CCO_2H \longrightarrow (Ph_3P)_2Rh(HC{\equiv}CCO_2H)Cl$ 132

The former has acetylene acting as a simple donor ligand (ν C≡C, 1900cm^{-1}), whilst the latter has the structure shown below (Fig. 22) (ν C=C, 1640cm^{-1}).

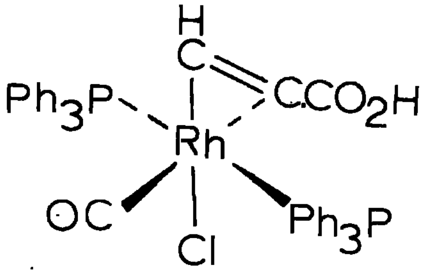


Fig. 22

(e) Cyclopentadienyl complexes

Reaction of sodium cyclopentadienide with $[Rh(CO)_2Cl]_2$ gives the orange liquid π-$C_5H_5Rh(CO)_2$[133]. Exposure of this compound to the air gives red crystals of the dimer $[\pi$-$C_5H_5Rh(CO)_2]_2$[134]. π-$C_5H_5Rh(CO)_2$ will undergo oxidative addition reactions with iodine to give π-$C_5H_5Rh(CO)I_2$[135], and with perfluoro-alkyl iodides to give π-$C_5H_5Rh(CO)_2RI$[136] (R = CF_3, C_2F_5, C_3F_7). The reaction with germanium and tin tetrahalides has been reported[137] to give compounds of the type π-$C_5H_5RhXMX_3$ although no details have been given. π-$C_5H_5Rh(Me_2PhP)(CO)$ has been prepared by the action of Me_2PhP on π-$C_5H_5Rh(CO)_2$[137] and its oxidative addition reactions with Cl_2, Br_2, CH_3COBr and CF_3COCl give isolable salts of the type $[\pi$-$C_5H_5Rh(CO)LX]^+X^-$. Alkyl halides react with π-$C_5H_5Rh(Me_2PhP)(CO)$ to form neutral acyl derivatives, π-$C_5H_5Rh(Me_2PhP)(COR)X$, probably via an ionic intermediate.

π-$C_5H_5Rh(C_2H_4)_2$[118] and π-$C_5H_5Rh(C_8H_{12})$[122] have similarly been prepared by the reaction of sodium cyclopentadienide with the corresponding chlorine-bridged olefin complex. π-$C_5H_5Rh(C_2H_4)_2$ reacts with sulphur dioxide to give π-$C_5H_5Rh(C_2H_4)_2(SO_2)$[138]. The mass spectra of some cyclopentadienyl rhodium olefin complexes have been reported[139].

Polymeric halide complexes, $[\pi\text{-}C_5H_5Rh(\text{halogen})_2]_x$[127,140] have also been prepared.

6. Determination of the Stereochemistry of Rhodium Compounds

An attempt has been made in this section to gather together some typical infrared data and to give a few illustrations of the uses of physical techniques in determining the structures of rhodium compounds.

The stereochemistry of many iridium complexes have been assigned by a combination of physical techniques and confirmed by X-ray studies. Generally a complete and unambiguous assignment of the stereochemistry of iridium complexes can be made on the basis of the ^1H n.m.r., infrared and far infrared spectra[142]. By contrast, apart from the work by Shaw et al[63,101], little effort has been made to determine the absolute stereochemistries of rhodium compounds. Two main reasons can be advanced for this: (a) the tendency for rhodium in the trivalent state to form five-coordinate as well as six-coordinate complexes, (b) the lack of reactivity of complexes of the type $L_2Rh(CO)X$ (L = tertiary phosphine or arsine, X = halogen) in the oxidative addition reaction compared to their iridium analogues. A number of X-ray studies have been made upon Rh(I) compounds but the information on Rh(III) complexes is negligible.

Infrared Spectra

(a) Near infrared spectra

Rhodium-hydrogen and carbonyl stretching frequencies are observed in the near infrared in a region clear of most other absorptions.

Some typical stretching frequency values are shown in Tables 2 and 3.

Table 2

Infrared data for hydrido complexes.

Compound	ν(Rh-H)cm^{-1}	trans ligand	reference
Rh(III)			
cis-$[(dmpe)_2RhH_2]Cl$	1900, 1870	P	50
trans-$[(dmpe)_2RhHCl]Cl$	2050	Cl	50
trans-$[(dmpe)_2RhHBr]Cl$	2030	Br	50
$(EtPh_2P)_3RhH_2Cl$	2059, 1915		15
$(Ph_3P)_3RhH_2Cl$	2082, 2012		15
$(Ph_3P)_2RhH_2Cl$, $0.5CH_2Cl_2$	2099, 2065		13
$(Ph_3P)_2RhH_2Br$, $0.5CH_2Cl_2$	2103, 2068		13
$(Ph_3As)_2RhH_2Cl$, $0.5CH_2Cl_2$	2051, 2030		16
$(Ph_3P)_2RhHCl_2$, $0.5CH_2Cl_2$	2105		20
$(Ph_3As)_2RhHCl_2$, $0.5CH_2Cl_2$	2069		16
$(Ph_3P)_3RhHCl_2$ α	2220		15
β	2120		15
$(EtPh_2P)_3RhHCl_2$ α	2120		15
β	1982		15
$(EtPh_2P)_3RhHBr_2$ α	2110		15
β	1964		15
$(Ph_3P)_2Rh(CO)HCl_2$	2122		20
trans-$[Rhen_2HCl]^+$	2100	Cl	141
cis-$[Rhen_2H_2]^+$	1969	N	141
Rh(I)			
$(dppe)_2RhH$	1902		52
$(Ph_3P)_3RhH$	2020		53
$(Ph_3P)_3Rh(CO)H$	2004		107

Table 3

Infrared data for carbonyl compounds

Compound	ν (CO)cm^{-1}	trans ligand	reference
Rh(I)			
$(Ph_3P)_2Rh(CO)Cl$	1965	Cl	105
$(Et_3P)_2Rh(CO)Cl$	1958	Cl	105
$(Me_2PhP)_2Rh(CO)Cl$	1970	Cl	101
Rh(III)			
$(Ph_3P)_2Rh(CO)HCl_2$	2049		20
$(Ph_3P)_2Rh(CO)(Me)Cl_2$	2062		20
$(Et_3P)_2Rh(CO)Cl_3$	2070		90
$(Me_2PhP)_2Rh(CO)(Me)Br_2$	2068,2053	Br	101
$(Me_2PhP)_2Rh(CO)(COMe)Cl_2$	2090,2067(1655)	Cl	101
$(Me_2PhP)_2Rh(CO)(C_4H_7)Cl_2$	2056	Cl	101

The position of the iridium-hydrogen absorption has been found to be dependent upon the *trans* ligand and the ranges quoted for ν(Ir-H) are 1750cm^{-1} (*trans* hydrogen), 2000-2100cm^{-1} (*trans* phosphine or carbonyl), 2180-2200cm^{-1} (*trans* chlorine)[142]. Rhodium would be expected to parallel this behaviour but as can be seen from Table 2 only a few cases are known where the *trans* ligand has been unambiguously identified. Most of the rhodium-hydrogen stretching frequencies so far assigned lie within the range 1900-2140cm^{-1}.

The frequency of terminal carbonyl groups for rhodium(III) compounds lie about 100cm^{-1} higher than the frequency range for rhodium(I) complexes (Table 3). The increase in frequency on going from Rh(I) to Rh(III) can be explained by a smaller back-donation of electrons from Rh(III) to the carbonyl ligand, due to the increased positive charge, leading to an increase in the CO bond order and stretching frequency. Carbonyl and rhodium-hydrogen stretching frequencies can be distinguished by spectroscopic comparison with the corresponding deuterides.

(b) Far infrared spectra

Shaw has shown that for complexes of Rh(III) with dimethylphenylphosphine and -arsine ligands, ν(Rh-Cl) falls into two ranges: 345-293cm^{-1} (two chlorines mutually trans), and 278-264cm^{-1} (chlorine trans to phosphine or arsine)[63]. (Table 4)

Other work[143] suggests that for square planar complexes ν(Rh-Cl) falls in the range 310-250cm^{-1} and for octahedral complexes ν(Rh-Cl) = 350-250cm^{-1}. Bridging metal chlorine stretching frequencies lie about 20-40cm^{-1} lower than the terminal vibrations. The ligand trans to the chlorine atom was found to influence ν(Rh-Cl) in the order:

$$\mathrm{Cl} > \mathrm{Br} > \mathrm{I} \sim \mathrm{CO} > \mathrm{CH_3} \sim \mathrm{PR_3} \sim \mathrm{AsR_3} > \mathrm{H}$$

$$\text{decreasing } \nu(\text{M-Cl}) \longrightarrow$$

Proton magnetic resonance spectroscopy

^{1}H n.m.r. spectroscopy is a valuable tool in structure determination. As well as indicating the presence and relative amounts of phosphine, organic and hydride groups attached to the transition metal it is often possible to deduce something about the stereochemistry.

It has been found for a number of octahedral hydride complexes that H-Rh-^{31}P coupling constants are of the order 80-150 Hz. for H trans to P, whilst the couplings for H cis to P are about 15 Hz. The τ values for H trans to P are also usually lower than those when H is trans to a halide[144].

In the high field ^{1}H n.m.r. spectrum of $(Ph_3P)_2RhHCl_2$, 0.5 CH_2Cl_2

Table 4

ν(Rh-Cl) for some rhodium-chlorine compounds.

Compound	ν(Rh-Cl)cm^{-1}	trans ligand	reference
Rh(I)			
$[Rh(CO)_2Cl]_2$	284, 274	CO	143
$[(C_2H_4)_2RhCl]_2$	273, 259, 250	C_2H_4	143
$[(C_8H_{12})RhCl]_2$	274, 254	C_8H_{12}	143
$(Ph_3P)_2Rh(CO)Cl$	309	CO	143
$(EtPh_2P)_2Rh(CO)Cl$	300	CO	143
$(Et_3P)_2Rh(CO)Cl$	302	CO	143
$(Ph_3P)_3RhCl$	296	Ph_3P	143
$[(Ph_3P)_2RhCl]_2$	303	Ph_3P	143
$[Bu_4N]\ [Rh(CO)_2Cl_2]$	320,290		20
Rh(III)			
$(Ph_3P)_2Rh(CO)Cl_3$	341, 316		143
$(Et_3P)_2Rh(CO)Cl_3$	335, 321, 270		143
cis$(Et_3P)_3RhCl_3$	305,292, 268-256 250,236	Et_3P	143
$(Ph_3P)_2Rh(CO)(Ph)Cl_2$	320, 283		20
$(Ph_3P)_2Rh(CO)(Me)Cl_2$	308, 297		20
$(Me_2PhP)_3RhCl_3$	339, 313	Cl	63
	273	Me_2PhP	
$(Me_2PhP)_3RhCl_2Br$	337, 311	Cl	63
$(Et_3P)_3RhCl_3$	339, 293	Cl	63
	264	Et_3P	
$(Et_2PhP)_3RhCl_3$	345, 323	Cl	63
	270	Et_2PhP	
$(Me_2PhAs)_3RhCl_3$	337, 306	Cl	63
	273	Me_2PhAs	

coupling is observed with ^{103}Rh (100%, I = ½) and further coupling with ^{31}P (100%, I = ½). The spectrum consists of an overlapping doublet of triplets centred on 26.1 τ with J(Rh-H) and J(P-Rh-H) = 17 Hz. The two phosphines must therefore be in equivalent or closely similar positions and the value of the coupling constant suggests that they are <u>cis</u> to the hydride. This has been interpreted in terms of the structures shown below (Fig. 23) although structures with the phosphines <u>trans</u> to each other cannot be ruled out on this evidence[20].

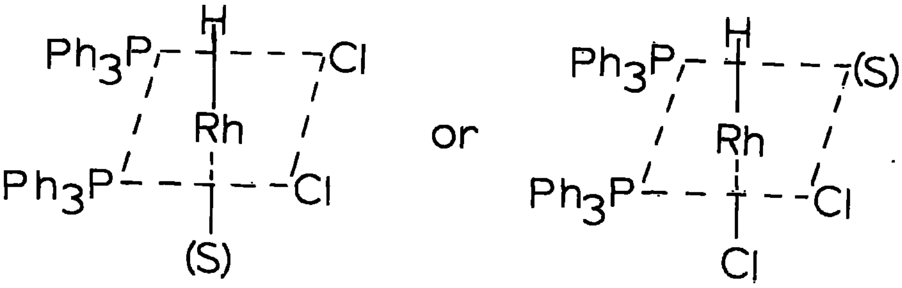
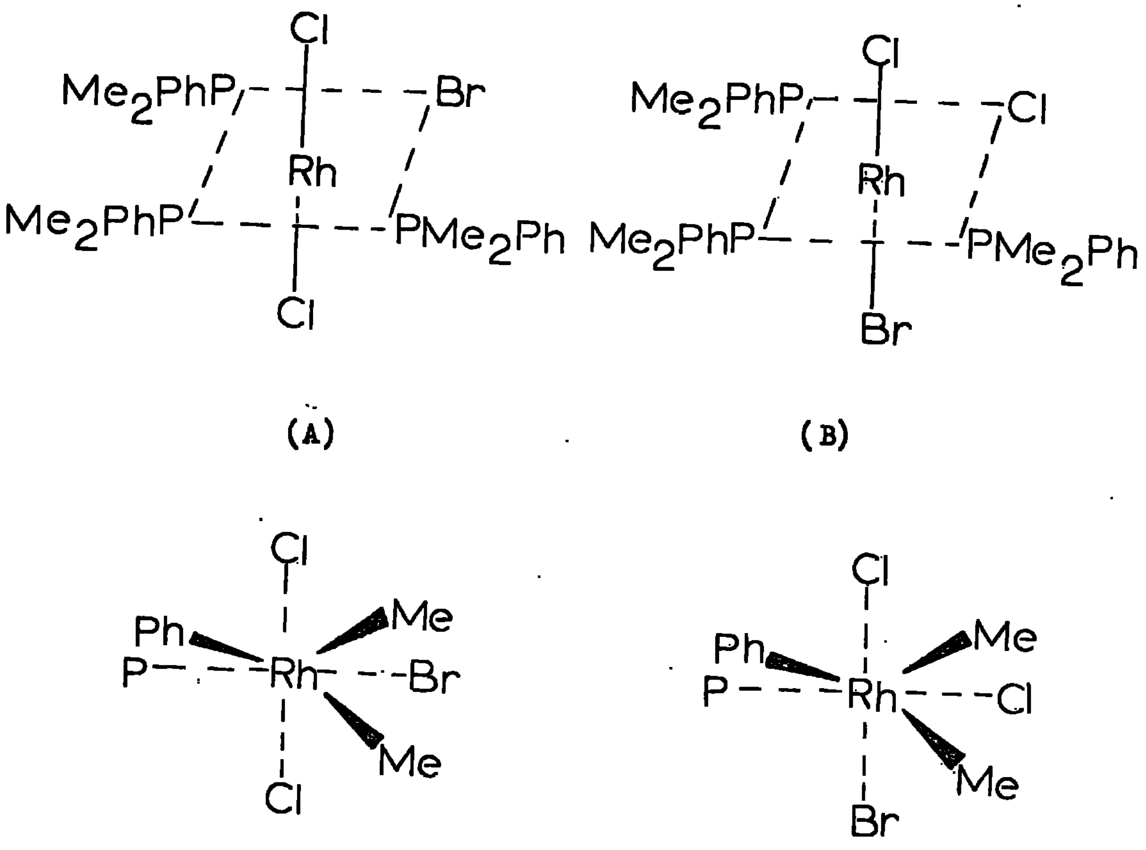


Fig. 23

This rather limited information can be supplemented if phosphines such as Me_2PhP, $MePh_2P$ or Et_3P are present in the molecule as it is then possible to determine whether the phosphines are <u>cis</u> or <u>trans</u> to one another[63]. The ^{1}H n.m.r. of free Me_2PhP shows a doublet in the methyl region due to spin-spin interaction ^{31}P (100%, I = ½). When two or more phosphines are coordinated to rhodium, a 1:1 doublet is still observed if the phosphines are <u>cis</u> to one another, but if they are mutually <u>trans</u> they exhibit a 1:2:1 triplet due to strong coupling between the two <u>trans</u> phosphorus atoms. Further, if there is no plane of symmetry along the P-Rh-P bond the methyl groups on the same phosphorus atoms experience slightly different magnetic environments and consequently resonate at different τ values to give two 1:2:1 triplets.



(A) (B)

View along the P-Rh-P axis

Fig. 24

This is illustrated in the ^1H n.m.r. spectrum of $(Me_2PhP)_3RhCl_2Br$. The spectrum consists of a well defined 1:2:1 triplet centred on 7.87 τ [J(P-C-H), 4.1 Hz.] and a 1:1 doublet centred on 8.74 τ [J(P-C-H), 11.5 Hz.] . The compound can therefore be unambiguously assigned the configuration (A), (Fig. 24) as this contains a plane of symmetry along the line P-Rh-P[63].

II TRANSITION METAL - GROUP IVB COMPOUNDS

Although relatively few compounds of this type were known in the early 1960's, compounds containing silicon, germanium, tin or lead bonded to most of the d-block transition elements have now been prepared. This and the fact that the topic has been the subject of four recent reviews[145-148] indicates the amount of effort that has been devoted to this field. Organogermanium-metal bonded complexes have also been the subject of a separate review[149]. This upsurge of activity is probably due to the intrinsic interest of compounds possessing both main group and transition metal characteristics, and also to the possible application of the compounds as catalysts.

1. Synthesis of Transition Metal-Group IVb Bonds

A number of methods have been used for the preparation of these compounds and the most important types are described below.

(a) Elimination of an alkali metal halide

This method can be further subdivided into two classes:

(i) those syntheses involving transition metal anions, and

(ii) those involving alkali metal derivatives of the group IVb element.

(i) $\pi\text{-}C_5H_5Mo(CO)_3Na + R_3GeCl \longrightarrow \pi\text{-}C_5H_5Mo(CO)_3(GeR_3) + NaCl$ 150

(R = Me, Et or Pr)

$(Ph_3P)Ir(CO)_3Na + Me_3SnCl \longrightarrow (Ph_3P)Ir(CO)_3(SnMe_3) + NaCl$ 151

(ii) $(Ph_2PC_2H_4PPh_2)PtCl_2 + 2(MePh_2SiLi) \longrightarrow (Ph_2PC_2H_4PPh_2)Pt(SiMePh_2)_2 + 2LiCl$ 152

$Ph_3PAuCl + Ph_3PGeLi \longrightarrow Ph_3PAuGePh_3 + LiCl$ 153

$(Et_3P)_2PtCl_2 + 2Ph_3GeLi \longrightarrow (Et_3P)_2Pt(GePh_3)_2 + 2LiCl$ 154

The main limitations upon the general use of these methods are the availability of the transition metal anion and the ease of preparation of the group IVb metal alkali derivative. Method (i) is particularly useful for the Cr, Mn, Fe and Co groups, and method (ii) for the Ti, Ni and Cu groups. Another drawback is that a competing side reaction involving halogen-metal exchange is sometimes involved.

(b) Elimination of neutral molecules

This heading covers a broad group of reactions involving the elimination of neutral molecules such as H_2, HCl, HNO_3, H_2O and Me_2NH. The elimination of H_2 provides a particularly clean reaction, whilst the presence of a base is sometimes necessary in the HCl eliminations to give complete reaction.

$Co_2(CO)_8 + 2Et_3SiH \longrightarrow 2Et_3SiCo(CO)_4 + H_2$ 155

$2Mn(CO)_5H + GeH_4 \longrightarrow H_2Ge[Mn(CO)_5]_2 + H_2$ 156

$C_5H_5Fe(CO)_2Cl + HGeCl_3 \longrightarrow C_5H_5Fe(CO)_2GeCl_3 + HCl$ 157

$(Ph_3P)_2Pt(H)Cl + Ph_3SnNO_3 \longrightarrow (Ph_3P)_2Pt(SnPh_3)Cl + HNO_3$ 158

$(Ph_3P)_2Pt(H)Cl + Me_3SnNMe_2 \longrightarrow (Ph_3P)_2Pt(SnMe_3)Cl + Me_2NH$ 159

$H_2Fe(CO)_4 + 2Ph_3PbOH \longrightarrow (Ph_3Pb)_2Fe(CO)_4 + 2H_2O$ 160

(c) Oxidative addition reactions

This method is restricted in its application but is particularly useful for the preparation of iridium and rhodium complexes. The transition metal increases its oxidation number by two units and its coordination number by either one or two units depending on whether or not a neutral ligand is eliminated.

$(Ph_3P)_2Ir(CO)Cl + 2Et_3GeH \longrightarrow (Ph_3P)_2Ir(CO)(GeEt_3)H_2 + Et_3GeCl$ 161

$(Ph_3P)_3RhCl + HSiCl_3 \longrightarrow (Ph_3P)_2RhH(SiCl_3)Cl + Ph_3P$ 162,163

$(Ph_3P)_3Ir(CO)H + Et_3SiH \longrightarrow (Ph_3P)_2Ir(CO)(SiEt_3)H_2 + Ph_3P$ 164

$Fe(CO)_5 + SnBr_4 \longrightarrow Br_3SnFe(CO)_4Br + CO$ 165

$2C_5H_5Co(CO)_2 + 2GeCl_4 \longrightarrow C_5H_5Co(CO)(GeCl_3)_2 + 3CO + CoCl_2 + (C_5H_5)$ 166

(d) Insertion reactions of divalent group IVb halides

Divalent group IVb halides (e.g. GeI_2) can often be inserted into transition metal-metal bonds and metal-halogen bonds to form new group IVb-transition metal bonds. The method has been extensively used but the main drawback is that GeI_2 and the divalent tin and lead halides are the only suitable group IVb metal halides available. Insertion into metal-halogen bonds requires a large excess of MX_2 to give complete reaction.

$Co_2(CO)_8 + GeI_2 \longrightarrow I_2Ge[Co(CO)_4]_2$ 167

$[C_5H_5Ni(CO)]_2 + SnCl_2 \longrightarrow Cl_2Sn[Ni(CO)C_5H_5]_2$ 167

$(Et_3P)_2PtHCl + SnCl_2 \longrightarrow (Et_3P)_2Pt(H)SnCl_3$ 168

(e) Reaction with metal-metal bonded complexes

Silyl- and germyl transition metal derivatives have been prepared from the reaction of bistrialkylsilyl- and bistrialkylgermylmercury with transition metal complexes. This method is particularly useful as it is difficult to prepare the corresponding trialkylsilyl- or germyl alkali metal complexes in good yield.

Hexamethylditin reacts with $(Ph_3P)_2Pt(C_2H_4)$ in an oxidative elimination reaction to yield $(Ph_3P)_2Pt(SnMe_3)_2$.

$(Et_3P)_2PtCl_2 + (Me_3Ge)_2Hg \longrightarrow (Et_3P)_2Pt(GeMe_3)Cl + Me_3GeCl + Hg$ 169

$[C_5H_5Mo(CO)_3]_2 + (Et_3Ge)_2Hg \longrightarrow 2C_5H_5Mo(CO)_3(GeEt_3) + Hg$ 170

$(Ph_3P)_2Pt(C_2H_4) + Me_6Sn_2 \longrightarrow (Ph_3P)_2Pt(SnMe_3)_2 + C_2H_4$ 171

2. Physical and Chemical Properties

Although there is obviously a great variation in their properties most of the transition metal-group IVb complexes exhibit a considerable degree of stability to oxidation or hydrolysis under normal conditions. Their thermal stability is generally greater than that of the analogous organo-transition metal complexes which suggests that the metal-metal bond is strengthened by π-bonding.

The stability of a particular complex depends upon the transition metal involved, the nature and number of the ligands bound to it, the group IVb metal, and the substituents attached to the group IVb metal. Although further work needs to be done to determine the effects of altering these variables some general trends are apparent and these are summarised below.

(a) Influence of the transition metal

In the platinum group, when the transition metal is the only variant, the stability of a series of compounds increases in the order $(Et_3P)_2Ni(GePh_3)_2$, (not isolated) $< (Et_3P)_2Pd(GePh_3)_2 < (Et_3P)_2Pt(GePh_3)_2$[153,172]. This parallels the increase in stability shown by organo-platinum complexes[173] as compared with those of palladium[174].

The tendency to form more stable group IVb transition metal complexes on descending a triad is also found in other groups. Iridium, for example, forms stable compounds of the type $(Ph_3P)_2Ir(CO)(SnMe_3)HCl$[175] and $(Ph_3P)_2Ir(CO)(GeMe_3)_2Cl$[161] but the analogous rhodium complexes have not been prepared. The trend is again apparent in the series $C_5H_5(CO)_3M\text{-}M'R_3$ (M = Cr, Mo, W; M' = Ge, Sn, Pb; R = CH_3, C_6H_5)[176] where the chromium compounds decompose even under an inert atmosphere after several weeks although the molybdenum and tungsten compounds are stable indefinitely.

(b) Influence of ligands bound to the transition metal

The effects of changes in the nature of the ligands upon the ability of transition metal complexes to undergo oxidative addition reactions has been discussed. Similarly the number and nature of the attached ligands has an effect upon the stability of the transition metal-group IVb complex. For example, the complex $Ph_3PAuGePh_3$ is very stable to oxidation or hydrolysis but the methyl analogue $Me_3PAuGePh_3$ decomposes almost immediately on exposure to air[177]. The copper and silver compounds, $Ph_3PMGePh_3$ which are sensitive to aerial oxidation and hydrolysis are more thermally stable and less reactive in the tetra-coordinate state, $(Ph_3P)_3M(GePh_3)$.

The addition of Me_3SiH to $(Ph_3P)_3RhCl$ yields $(Ph_3P)_2RhH(SiMe_3)Cl$ but no product can be obtained from reaction with $(Ph_3P)_2Rh(CO)Cl$[162]. Trimethylgermane reacts with $(Ph_3P)_2Ir(CO)Cl$ to give $(Ph_3P)_2Ir(CO)(GeMe_3)H_2$ but reaction with $(Et_3P)_2Ir(CO)Cl$ gives only the dihydride $(Et_3P)_2Ir(CO)H_2Cl$[161].

(c) Influence of the group IVb metal

Although much more work is needed before any firm conclusions can be drawn it appears, on the basis of decomposition temperatures and general chemical properties, that germanium and tin transition metal derivatives are probably more stable than those of silicon and lead. Care must be taken, however, not to draw conclusions about the metal-metal bond strength on the basis of decomposition temperatures alone as, for example, a weak carbon-lead bond could cause decomposition in spite of the presence of a strong M-Pb bond.

In the series of compounds $Ph_3M'Mn(CO)_5$, M' = Si, Ge, Sn, Pb, the tin derivative is thermally more stable than the lead compound and loses carbon monoxide only at 195°C. The melting points of the compounds are in the order Si(160-163°C) $\sim$ Ge(162-164°C) $>$ Sn(148-150°C) $\sim$ Pb(146-148°C), but the oxidative stability is in the reverse order Sn $>$ Pb $>$ Si[178].

A similar trend is found in the series of compounds $C_5H_5(CO)_3M-M'R_3$ (M = Cr, Mo, W; M' = Ge, Sn, Pb; R = CH_3, C_6H_5)[176] where the lead compounds have been found to be less stable towards aerial oxidation than their germanium and tin analogues. The corresponding silicon compounds could not be prepared from the transition metal anion and the silicon halide.

The greater reactivity of the silicon derivatives is also shown in the facile hydrolysis of $(Et_3P)_2Pt(SiMe_3)Cl$ although the analogous germanium compound is only slowly hydrolysed even in aqueous diglyme[169].

(d) Effect of substituents on the group IVb atom

In a series of compounds containing the grouping R_3M' (M' = group IVb atom) the order of stability of the complexes is found to be R = halogen > aryl > alkyl > hydride. This is particularly well exemplified by the series of complexes $(Ph_3P)_2RhH(SiCl_nR_{3-n})X$ (R = Me, Et; X = Cl, Br; n = 0, 1, 2, 3)[162]. The thermal stability of the complexes decreases markedly with the increase in the number of alkyl groups and a similar stability sequence is found in solution.

Table 5

Complex	decomposition temperature	stability in solution
$(Ph_3P)_2RhH(SiCl_3)Cl$	170°C	stable
$(Ph_3P)_2RhH(SiCl_2Me)Cl$	145°C	slowly decomposes
$(Ph_3P)_2RhH(SiClMe_2)Cl$	125°C	slowly decomposes
$(Ph_3P)_2RhH(SiMe_3)Cl$	95°C	dissociates instantly

Stability of the complexes $(Ph_3P)_2Rh(H)(SiCl_nMe_{3-n})Cl$

These variations in stability along the series may be caused mainly by the change in the effective electronegativity of the silyl group but $d\pi-d\pi$ bonding may also be involved.

Similarly $Cl_2Ge[Fe(CO)_2C_5H_5]_2$ is resistant to air, $Me_2Ge[Fe(CO)_2C_5H_5]_2$ is less so, and solutions of $H_2Ge[Fe(CO)_2C_5H_5]_2$ are rapidly decomposed.

3. Reactions of the Complexes

The reactions of the complexes are of three main types:

(a) those which cleave the metal-metal bond,

(b) replacement of ligands on the transition metal, and

(c) replacement of substituents on the main group metal.

With tin and lead derivatives the latter course is often preferred to cleavage of the metal-metal bond because of the relative weakness of tin-carbon and lead-carbon bonds.

(a) Halogens and hydrogen halides

With halogens attack generally occurs on the metal-metal bond to give both the transition metal and group IVb halide, e.g.

$$(Et_3P)_2Pt(GePh_3)_2 + 2I_2 \longrightarrow (Et_3P)_2PtI_2 + 2Ph_3GeI \qquad 154$$

Similarly the tungsten-germanium bond is cleaved by an excess of iodine to yield the tri-iodide.

$$C_5H_5(CO)_3WGeMe_3 + 2I_2 \longrightarrow C_5H_5(CO)_2WI_3 + Me_3GeI + CO \qquad 150$$

By contrast the reaction of $Ph_3SnMn(CO)_5$ with bromine in CCl_4 results in the cleavage of phenyl groups.

$$Ph_3SnMn(CO)_5 + 2Br_2 \longrightarrow Br_2PhSnMn(CO)_5 + 2PhBr$$

$$Ph_3SnMn(CO)_5 + 3Br_2 \longrightarrow Br_3SnMn(CO)_5 + 3PhBr \qquad 178$$

The behaviour of $Ph_3GeMn(CO)_5$ to attack by bromine is different. Both attack on the metal-metal bond and the germanium-carbon bond can occur under different conditions[179].

$$Ph_3GeMn(CO)_5 + Br_2 \xrightarrow[\text{2-3 hours}]{\text{R.T.}} BrMn(CO)_5 + Ph_3GeBr$$

$$Ph_3GeMn(CO)_5 \; + \; 3Br_2 \xrightarrow[130^\circ,\ 5\ \text{hours}]{\text{dibromoethane}} Br_3GeMn(CO)_5 \; + \; 3PhBr$$

Halogen acids generally cleave the metal-metal bond in a straightforward manner, but again some cleavages of carbon-group IVb metal bonds are known.

$C_5H_5(CO)_3MoGeMe_3 \; + \; HCl \longrightarrow C_5H_5(CO)_3MoH \; + \; Me_3GeCl$ 150

$(Et_3P)_2Pd(GePh_3)_2 \; + \; 2HCl \longrightarrow (Et_3P)_2PdCl_2 \; + \; 2Ph_3GeH$ 180

Cleavage of the analogous platinum complex, $(Et_3P)_2Pt(GePh_3)_2$, which exists in solution as a mixture of the <u>cis</u>- and <u>trans</u> isomers, is thought to proceed via an octahedral intermediate[154,181].

$$\begin{tikzcd}
 & \underline{\text{cis}}\text{-, }\underline{\text{trans}}\text{-}(Et_3P)_2Pt(GePh_3)_2 \arrow[d, "HCl"'] & \\
\underline{\text{cis}}\text{-}(Et_3P)_2Pt(Cl)GePh_3 \arrow[d, "HCl"'] & + & \underline{\text{trans}}\text{-}(Et_3P)_2Pt(Cl)GePh_3 \; + \; Ph_3GeH \arrow[d, "HCl"'] \\
\underline{\text{cis}}\text{- or }\underline{\text{trans}}\text{-}(Et_3P)_2PtCl_2 \; + \; Ph_3GeH & & \underline{\text{trans}}\text{-}(Et_3P)_2Pt(H)Cl \; + \; Ph_3GeCl
\end{tikzcd}$$

Hydrogen halides are milder and more selective reagents than halogens in their reactions with manganese compounds. Hydrogen chloride does not react with $Ph_3GeMn(CO)_5$ at temperatures up to 76°C[179] but the lead-manganese bond is cleaved at 25°C[178]. The tin analogue reacts at 0°C to give largely the dichlorotin derivative whilst at higher temperatures the trichlorotin compound can be obtained[178].

(b) <u>Reaction with organic and inorganic halides</u>

Cleavage of the metal-metal bond can be accomplished by a variety of organic halides including RI, $CHCl_3$, CCl_4 and $C_2H_4Br_2$. The cleavage of $Ph_3PAuGePh_3$ by $C_2H_4Br_2$ is believed to occur through a four-centre intermediate[153].

$Ph_3PAuGePh_3 \; + \; CCl_4 \longrightarrow Ph_3PAuCl \; + \; Ph_3GeCl$ 182

$$C_5H_5(CO)_3WGeMe_3 + C_2H_4Br_2 \longrightarrow C_5H_5(CO)_3WBr + C_2H_4 + Me_3GeBr \qquad 150$$

Inorganic halides such as $MgBr_2$ and $HgCl_2$ have also been used to cleave metal-metal bonds.

$$C_5H_5(CO)_3WGeEt_3 + HgCl_2 \longrightarrow C_5H_5(CO)_3WHgCl + Et_3GeCl \qquad 150$$

$$C_5H_5(CO)_3MoGeEt_3 + MgBr_2 \longrightarrow C_5H_5(CO)_3MoMgBr + Et_3GeBr \qquad 150$$

$$2H_3SiCo(CO)_4 + HgCl_2 \longrightarrow 2H_3SiCl + Hg[Co(CO)_4]_2 \qquad 183$$

(c) Hydrogenation

The hydrogenolysis of Ge-Pt and Si-Pt bonds is a reversible process, requiring a low activation energy and probably proceeding through an octahedral intermediate. The trans- compounds are more readily hydrogenated than their cis- analogues.

$$(Et_3P)_2Pt(GePh_3)_2 + H_2 \longrightarrow (Et_3P)_2Pt(H)GePh_3 + Ph_3GeH \qquad 154$$

$$\underline{\text{trans}}\text{-}(Et_3P)_2Pt(GeMe_3)GePh_3 + H_2 \longrightarrow \underline{\text{trans}}\text{-}(Et_3P)_2PtHGePh_3 + Me_3GeH \qquad 189$$

(d) Ligand exchange reactions

Ligand exchange reactions on the transition metal generally resemble those of comparable compounds without the metal-metal bond.

$$Ph_3GeMn(CO)_5 + Ph_3P \longrightarrow Ph_3GeMn(CO)_4PPh_3 + CO \qquad 179$$

$$C_5H_5(CO)_3WGeMe_3 + Et_2PH \longrightarrow C_5H_5(CO)_2(Et_2PH)WGeMe_3 + CO \qquad 150$$

$$(Et_3P)_2Pt(GeMe_3)Cl + Ph_2PC_2H_4PPh_2 \longrightarrow [(Ph_2PC_2H_4PPh_2)Pt(Et_3P)(GeMe_3)]Cl + Et_3P \qquad 169$$

$$(Et_3P)_2Pd(GePh_3)_2 + 2KCN \longrightarrow K_2[(CN)_2Pd(GePh_3)_2] + 2Et_3P \qquad 180$$

Some examples of the cleavage of carbon-group IVb bonds were discussed in section (a). The reverse process of alkylation of group IVb-halogen bonds has also been used to prepare new complexes. This method is particularly useful for preparing alkyl or aryl complexes from $SnCl_2$ and GeI_2 insertion products.

$[C_5H_5(CO)_2Fe]_2SnCl_2 + 2EtMgBr \longrightarrow [C_5H_5(CO)_2Fe]_2SnEt_2$ 184

$[C_5H_5(CO)_2Fe]_2GeI_2 + 2MeLi \longrightarrow [C_5H_5(CO)_2Fe]_2GeMe_2$ 185

$[C_5H_5(CO)_2Fe]_2GeI_2 + NaBH_4 \longrightarrow [C_5H_5(CO)_2Fe]_2GeH_2$ 185

$(Ph_2PC_2H_4PPh_2)Pt(SiBrPh_2)_2 + 2MeLi \longrightarrow (Ph_2PC_2H_4PPh_2)Pt(SiMe.Ph_2)_2$ 186

Redistribution reactions are also known:

$2(CO)_5MnSnPh_3 + (CO)_5MnSnCl_3 \longrightarrow 3(CO)_5MnSnPh_2Cl$ 178

Exchange reactions of the complete R_3M' moiety are known for platinum. These probably occur via a six-coordinate intermediate and the reaction can be thought of as an oxidative addition followed by a reductive elimination.

$(Et_3P)_2PtCl(SiH_2Cl) + ClGeH_3 \longrightarrow (Et_3P)_2PtCl(GeH_2Cl) + SiH_3Cl$ 187

$(Ph_2PC_2H_4PPh_2)PtCl(SiMe_3) + Me_3GeH \longrightarrow (Ph_2PC_2H_4PPh_2)PtCl(GeMe_3) + Me_3SiH$ 188

(e) Insertion into the metal-metal bond

Tin-manganese and germanium-manganese compounds have been found to react with fluoroolefins to give stable products containing the fluoroolefin inserted between the transition metal-group IVb bond.

$Me_3GeMn(CO)_5 + C_2F_4 \longrightarrow Me_3GeC_2F_4Mn(CO)_5$ 189

$Me_3SnMn(CO)_5 + C_2F_4 \longrightarrow Me_3SnC_2F_4Mn(CO)_5$ 190

Insertion products have also been found in the reaction of sulphur dioxide with complexes of the type $Me_3M'Fe(CO)_2C_5H_5$.

$Me_3GeFe(CO)_2C_5H_5 + SO_2 \longrightarrow Me_3Ge - S(O)_2 - Fe(CO)_2C_5H_5$ 191

When M' = Sn a polymer containing Sn-O-S(O)-Fe units was prepared.

4. The Nature of the Transition Metal-Group IVb Bond

The metal-metal bonds in transition metal-group IVb compounds consist of a σ-bond and $d\pi$-bond combination. This is analogous to the σ-donor π-acceptor system of phosphine and arsine complexes (R_3Ge^- and R_3As are isoelectronic). Further work is necessary to establish the extent of the $(d\rightarrow d)_\pi$ contribution to the bonding but the available evidence (X-ray, infrared and n.m.r. data)[146] suggests that it is secondary energetically to the σ bond.

Molecular structure data on a series of cobalt compounds of the type $R\text{-}Co(CO)_4$ (R = silyl or substituted silyl group) show a significant shortening in their metal-metal bond lengths compared with the theoretical bond lengths calculated from metallic covalent radii (Table 6). This has been interpreted in terms of partial $(d\rightarrow d)_\pi$ bonding in the cobalt-silicon bond[192]. In compounds of the type $R_3SnMn(CO)_5$ the observed Sn-Mn bond length is independent of R and about 0.1Å less than the sum of the covalent metal radii. Substitution of a carbonyl group by triphenylphosphine shortens the Sn-Mn bond still further, which is consistent with an increase in the multiple bond character of the metal-metal bond. As the phosphine has lower π-acceptor properties there is less competition by the phosphine

Table 6

Bond lengths for some transition metal-group IVb bonded complexes[192]

Compound	Exptl. length	Calcd. length	Contraction
$H_3SiCo(CO)_4$	2.38Å	2.49Å	0.11Å
$Cl_3SiCo(CO)_4$	2.25	2.48	0.23
$F_3SiCo(CO)_4$	2.23	2.48	0.25
$Me_3SnMn(CO)_5$	2.67	2.76	0.09
$Ph_3SnMn(CO)_5$	2.67	2.76	0.09
$Ph_3SnMn(CO)_4Ph_3P$	2.63	2.76	0.13

group for d electrons from manganese and these are therefore used to a greater extent in Sn-Mn bonding[146].

Far infrared studies on ν(Pt-Cl) show that in platinum complexes of the type $(R_3P)_2PtCl(L)$, R_3Si and R_3Ge have very strong inductive <u>trans</u> effects indicating a strong σ-bond[169]. Ph_3Sn and Ph_3Pb are comparable to the hydride ion whilst Cl_3Sn has a similar <u>trans</u> effect to Ph_3P[158]. Parshall[193] has used an n.m.r. method to estimate the relative σ and π contributions in a metal ligand bond in square planar complexes of platinum. Results show that the trichlorostannato ion is a weak σ-donor but a strong π-acceptor ligand.

5. Group IVb Derivatives of Cobalt, Rhodium and Iridium

The chemistry of group IVb derivatives of this group is of two types. The cobalt compounds are nearly all carbonyls with properties similar to those of the manganese and iron groups, whereas the rhodium and iridium compounds resemble more closely the analogous platinum, palladium and gold derivatives. Rhodium and iridium compounds are generally stabilised by tertiary phosphine, halogen and carbonyl ligands but no compounds having CO as the only neutral ligand are known, although it is possible that polynuclear rhodium carbonyl derivatives of group IVb may be prepared in the future.

A number of cobalt-group IVb derivatives of the general formula $RnM'[Co(CO)_4]_{4-n}$ (n = 1, 2, 3; R = alkyl, aryl, halogen; M = Si, Ge, Sn, Pb) have been prepared by the reaction between a group IVb organic halide and the tetracarbonyl-cobalt anion. This method has mainly been used for the preparation of the germanium and tin compounds.

$$3Co(CO)_4^- + SnCl_4 \longrightarrow ClSn[Co(CO)_4]_3 + 3Cl^- \qquad 194$$

$$Co(CO)_4^- + H_3SiI \longrightarrow H_3SiCo(CO)_4 + I^- \qquad 195$$

The reaction of group IVb hydrides with dicobalt octacarbonyl is particularly useful for the preparation of cobalt-silicon and cobalt-germanium bonds.

$2Me_3SiH + Co_2(CO)_8 \longrightarrow 2Me_3SiCo(CO)_4 + H_2$ 196

Diphenylgermane reacts with $Co_2(CO)_8$ to give a dicobalt heptacarbonyl which contains both bridging germanium and carbonyl ligands.

$Ph_2GeH_2 + Co_2(CO)_8 \longrightarrow Ph_2GeCo_2(CO)_7 + H_2 + CO$ 197

The heptacarbonyl reacts with CO under pressure to give $Ph_2Ge[Co(CO)_4]_2$.

Group IVb-cobalt compounds have also been prepared by the oxidative elimination reaction between a metal halide and $C_5H_5Co(CO)_2$.

$C_5H_5Co(CO)_2 + GeI_4 \longrightarrow C_5H_5Co(CO)IGeI_3 + CO$ 166

$2C_5H_5Co(CO)_2 + 2GeCl_4 \longrightarrow C_5H_5Co(CO)(GeCl_3)_2 + 3CO + CoCl_2 + (C_5H_5)$ 166

The reactions of the compounds have not been studied in detail but cleavage of the metal-metal bond, and carbonyl substitution reactions can occur.

$H_3SiCo(CO)_4 + HCl \longrightarrow H_3SiCl + HCo(CO)_4$ 183

$2H_3SiCo(CO)_4 + HgCl_2 \longrightarrow 2H_3SiCl + Hg[Co(CO)_4]_2$ 183

$Me_3SiCo(CO)_4 + Ph_3P \xrightarrow{uv} Me_3SiCo(CO)_3(Ph_3P) + CO$ 198

$Me_3SiCo(CO)_4 + Et_3P \longrightarrow [Me_3SiPEt_3]^+[Co(CO)_4]^-$ 198

$Me_3SiCo(CO)_4 + Me_3N \longrightarrow [Me_3SiNMe_3]^+[Co(CO)_4]^-$ 198

Rhodium and iridium derivatives have a formal oxidation level of I or III and the complexes can be 4-, 5- or 6-coordinate. Iridium shows a greater tendency to 6-coordination than rhodium. Although there are similarities between their group-IVb products the differences in stability and ease of preparation are very marked.

A series of rhodium-silicon complexes of the type $(Ph_3M)_2RhH(SiR_3)X$, (M = P, As, Sb; X = Cl, Br, I; R = Cl, OEt, Me, Et) has been prepared by the direct reaction at room temperature of $(Ph_3M)_3RhX$ with an excess of silane[162,163].

$$(Ph_3P)_3RhCl + Cl_3SiH \longrightarrow (Ph_3P)_2RhH(SiCl_3)Cl + Ph_3P$$

The stability of the phosphine complexes to thermal decomposition and to dissociation in solution varies widely from R = Cl, OEt (very stable) to R = alkyl or phenyl (completely dissociated in solution) (see page 50). The infrared spectra of the complexes show bands due to ν(Rh-H) in the region 2020-2130 cm^{-1} but no trends in the frequency values could be discerned. ^1H n.m.r. also indicates the presence of a direct Rh-H bond for some of the more stable complexes in the region 21-27 τ. The coupling with ^{31}P indicates that two phosphine ligands are <u>cis</u> to the hydride. Reactions with CO, PF_3 or C_2H_4 result in the loss of the silane and the formation of the known complexes $(Ph_3P)_2Rh(L)Cl$ (L = CO, PF_3, C_2H_4). Treatment with HCl yields $(Ph_3P)_2RhHCl_2$ and the silane.

Similar oxidative addition reactions occur with the iridium complex $(Ph_3P)_2Ir(CO)Cl$. The reaction with trialkylstannanes has been reported to give simple addition products of the type $(Ph_3P)_2Ir(CO)ClH(SnR_3)$[175].

$$(Ph_3P)_2Ir(CO)Cl + Me_3SnH \longrightarrow (Ph_3P)_2Ir(CO)ClH(SnMe_3)$$

In contrast to this the reaction of $(Ph_3P)_2Ir(CO)Cl$ with triethyl- or trimethylgermane yielded a dihydrido complex presumably by an addition, elimination, addition sequence[161].

$$(Ph_3P)_2Ir(CO)Cl + 2Et_3GeH \longrightarrow (Ph_3P)_2Ir(CO)(H)_2GeEt_3 + Et_3GeCl$$

The reaction with silanes was also thought to proceed by a simple reversible addition reaction but later studies[164] showed that the following sequence of reactions occurred.

$$\begin{array}{lcl}(Ph_3P)_2Ir(CO)Cl + R_3SiH & \rightleftharpoons & (Ph_3P)_2Ir(CO)ClH(SiR_3)\\ & & \downarrow \\ (Ph_3P)_3Ir(CO)H + R_3SiH & \rightleftharpoons & (Ph_3P)_2Ir(CO)(H)_2SiR_3\end{array}$$

The analogous rhodium complex, $(Ph_3P)_2Rh(CO)Cl$, will only react with trichlorosilane after a prolonged period of time (12 months) at 50°C to give a mixture of starting material and $(Ph_3P)_2Rh(CO)ClH(SiCl_3)$. Even in the solid state this product loses trichlorosilane[162].

The extent to which the ligands influence the course of the reaction is also shown in the reaction of $(Et_3P)_2Ir(CO)Cl$ with trimethylgermane, where a germanium-iridium bond is not formed.

$$(Et_3P)_2Ir(CO)Cl + 2Me_3GeH \longrightarrow (Et_3P)_2Ir(CO)ClH_2 + Me_6Ge_2$$

The reaction of triphenylgermane with $(Ph_3P)_2Ir(CO)Cl$ also proceeds by a different course to give the five-coordinate $(Ph_3P)Ir(CO)HCl(GePh_3)$. Attempts to prepare four-coordinate Rh(I) and Ir(I) compounds by the reaction of $(Ph_3P)_2M(CO)Cl$ with triphenylsilyl- or germyl-lithium reagents have failed[161,162].

The crystal structures of $(Ph_3P)_2RhCl(H)SiCl_3$[199] and $(Ph_3P)_2Ir(CO)(H)_2GeMe_3$[161] have been reported and are shown in Figs. 25 and 26.

Reactions of $(Ph_3P)_2Ir(CO)(H)_2GeR_3$, (R = Me or Et) with $HgCl_2$, HCl, I_2, H_2, O_2, C_2H_4, $C_2H_4Br_2$, Et_3P, and $Ph_2PC_2H_4PPh_2$ have also been reported.

$$(Ph_3P)_2Ir(CO)(H)_2GeEt_3 + I_2 \longrightarrow (Ph_3P)_2Ir(CO)(H)_2I + Et_3GeI$$

$$(Ph_3P)_2Ir(CO)(H)_2GeMe_3 + 2Et_3P \longrightarrow (Et_3P)_2Ir(CO)(H)_2GeMe_3 + 2Ph_3P$$

$$(Ph_3P)_2Ir(CO)(H)_2GeMe_3 + C_2H_4 \longrightarrow (Ph_3P)_2Ir(CO)GeMe_3 + C_2H_6$$

The reversible addition of the silicon hydrides $(Me)_n(EtO)_{3-n}SiH$ to $[(dppe)_2Ir]BPh_4$, (dppe = bis-1,2-diphenylphosphino-ethane) has also been studied[200]. The only stable product which could be isolated was that formed by the addition of triethoxysilane.

$$(EtO)_3SiH + [(dppe)_2Ir]BPh_4 \rightleftharpoons [(dppe)_2Ir(H)Si(OEt)_3]BPh_4$$

Anionic rhodium and iridium carbonyl complexes have been prepared

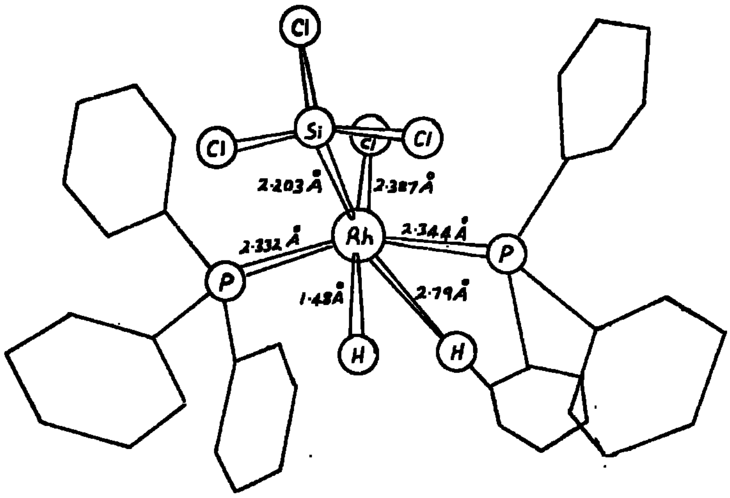


Fig. 25

Crystal structure of $(Ph_3P)_2RhH(SiCl_3)Cl$

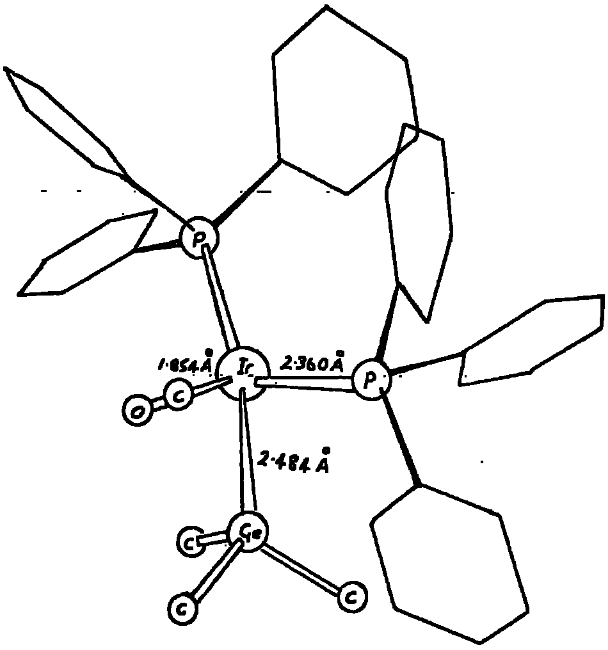


Fig. 26

Crystal structure of $(Ph_3P)_2Ir(CO)(H)_2GeMe_3$

by the reduction of $(Ph_3P)_2M(CO)Cl$ with sodium amalgam in a CO atmosphere. These have been used to prepare germanium and tin derivatives of iridium and a trimethylstannyl-rhodium complex[151].

$$[(Ph_3P)Ir(CO)_3]^{-}Na^{+} + Ph_3GeCl \longrightarrow (Ph_3P)Ir(CO)_3GePh_3 + NaCl$$
$$[(Ph_3P)_2Rh(CO)_2]^{-}Na^{+} + Me_3SnCl \longrightarrow (Ph_3P)_2Rh(CO)_2SnMe_3 + NaCl$$

A number of tin compounds of rhodium and iridium have also been prepared by the reaction of $SnCl_2$ with metal halides. These reactions have been extensively reviewed[146]. Although the rhodium-tin compounds are nearly all in the +1 oxidation state iridium has a far greater tendency to form compounds in the +3 state.

The reaction of $SnCl_2$ with $RhCl_3$ yields two different anionic species depending upon the reaction conditions. From solutions containing a low concentration of the trichlorostannite ion the binuclear anion $[Rh_2Cl_2(SnCl_3)_4]^{4-}$ has been precipitated by the addition of Me_4NCl[201], whereas tin rich solutions yield the ion $[Rh(SnCl_3)_4]^{3-}$. Under similar reaction conditions $[Ir_2Cl_6(SnCl_3)_4]^{4-}$ and $[IrCl_2(SnCl_3)_4]^{3-}$ have been isolated[201].

When alcoholic solutions of $RhCl_3$ and $SnCl_2$ are treated with triphenylphosphine the Rh(I) complex $(Ph_3P)_3RhSnCl_3$ is prepared[201]. Under similar conditions iridium salts yield $(Ph_3P)_3IrHCl(SnCl_3)$[202]. The rhodium complex dissociates in solution with loss of Ph_3P and $SnCl_2$.

The reaction of $SnCl_2$ with $[(CO)_2RhCl]_2$ can give a series of Rh(I) salts of general formula $[Rh(CO)(SnCl_3)_{3-n}Cl_n]^{2-}$, (n = 0, 1, 2) depending upon the relative Rh:Sn ratios used[203]. No Rh^{III}-Sn carbonyl complexes have been isolated but the reaction between Na_2IrCl_6 and $SnCl_2$ in the presence of carbon monoxide gives the Ir(III) complex $[Ir(CO)Cl_3(SnCl_3)_2]^{2-}$ and treatment of $(Ph_3P)_2Ir(CO)Cl$ with $SnCl_2$ in acetone gives $(Ph_3P)_2Ir(CO)HCl(SnCl_3)$[202]. A similar reaction of

$(Ph_3P)_2Rh(CO)Cl$ with $SnCl_2$ is reversible and gives a product which is probably $(Ph_3P)_2Rh(CO)SnCl_3$[146].

The addition of norbornadiene (NBD) to ethanolic solutions of $RhCl_3$ and $SnCl_2$ forms the tin compound $(NBD)_2RhSnCl_3$[201]. This will react with chlorine to form the insoluble Rh^{III} complex $(NBD)_2RhCl_2SnCl_3$. Iridium also forms diolefin complexes of the type $(cyclooctadiene)_2IrSnCl_3$[201].

DISCUSSION

Group IVb Derivatives of Rhodium

In recent years a great number of transition metal-group IVb complexes have been prepared and general methods for the preparation of these complexes are now well established. By comparison, until recently, relatively little effort had been devoted to studying the chemical reactions of these complexes.

At the outset of this work cobalt and iridium complexes with bonds to the group IVb elements silicon, germanium and tin were known, but much less was known about rhodium-group IVb metal complexes. For some time the only known rhodium compounds of this class were those formed by the insertion of $SnCl_2$ into rhodium-chlorine bonds[201-203]. Rhodium compounds such as $[(C_2H_4)_2RhCl]_2$ were known to be effective catalysts for the hydrosilation of olefins[164] and prior to the commencement of this work a brief report of the preparation of compounds of the type $(Ph_3P)_2RhH(SiR_3)Cl$ ($R = Cl_3$, Cl_2Me etc.) appeared in the literature[162]. During the course of these studies a more detailed description of these compounds has been given[162,163] and the preparation of the rhodium-tin complex $(Ph_3P)_2Rh(CO)_2SnMe_3$ has been reported[151].

Most of the work reported in this thesis concerns the reactions of complexes of rhodium with germanium compounds, although some reactions with organo-silanes and -stannanes have also been studied. These studies were undertaken in an attempt to provide additional information about the influence of a change in the transition metal or of the group IVb element upon the group IVb-transition metal bond. Work carried out in these laboratories showed that the addition of organogermanes to the iridium complex $(Ph_3P)_2Ir(CO)Cl$ yielded compounds of the type $(Ph_3P)_2Ir(CO)H_2(GeR_3)$ ($R = Me$, Et) whilst the corresponding reaction with organosilanes was, at that time, thought to give only a simple addition product of the type $(Ph_3P)_2Ir(CO)ClH(SiR_3)$, (R = OEt, Cl) in an equilibrium reaction. This suggested a marked increase in reactivity on going from silicon to germanium and it was of interest to see if this behaviour would also be shown in the rhodium series. It was also hoped that it would be possible to prepare rhodium-germanium complexes comparable to those of iridium so that a comparison could be made of their stability and of the reactivity of the metal-metal bond.

Tris(triphenylphosphine)rhodium(I) chloride is an air-stable solid and can be readily prepared by the reaction of rhodium trichloride with an excess of triphenylphosphine in boiling ethanol. The properties of this compound and its ability to add various molecules oxidatively have previously been discussed. The analogous arsine complex also undergoes oxidative addition reactions.

The reaction of trimethylgermane or triethylgermane with $(Ph_3P)_3RhCl$ or $(Ph_3As)_3RhCl$ gave a simple addition product of the type $(Ph_3M)_2RhH(GeR_3)Cl$ (M = P or As; R = Me or Et) with the loss of triphenylphosphine or triphenylarsine e.g.

$$(Ph_3P)_3RhCl + Et_3GeH \longrightarrow (Ph_3P)_2RhH(GeEt_3)Cl + Ph_3P$$

The products could only be isolated in the presence of a good excess of the trialkylgermane and it appeared that an equilibrium existed in the solution. Provided that only a small volume of solvent (benzene) was used the compounds could be prepared in a pure form, but if larger amounts of solvent were used the compounds could not be isolated. Presumably a rapid reaction occurs in the solvent and the product is then protected by precipitation. Attempted recrystallisation always led to the decomposition of the material. In a typical preparation triethylgermane (0.5ml, 3.1 mmole) was added to a suspension of

$(Ph_3As)_3RhCl$ (635mg., 0.6 mmole) to give a green solid, 492mg., (90%) after twelve hours at room temperature.

The trimethylgermane reactions were carried out in a breakseal apparatus which was separated into two parts by a glass sinter (por 3). This meant that the precipitated product could be filtered from the solution, washed with solvent and recovered in a pure form.

The rhodium-germanium compounds were, with the exception of $(Ph_3P)_2RhH(GeMe_3)Cl$, air-stable yellow or green complexes. The trimethylgermyl compound, $(Ph_3P)_2H(GeMe_3)Cl$ decomposed in air over a period of three months to give a light brown solid which showed a band at 1188 cm^{-1} which is characteristic of triphenylphosphine oxide. The analogous triethylgermyl-complex appeared to be stable indefinitely in air. The thermal stability of the complexes was moderately high and they all decomposed without melting in the range 90-120°C. The triethylgermyl-compounds were considerably more stable to thermal decomposition than their trimethylgermyl analogues but the replacement of Ph_3P by Ph_3As did not seem to affect the stability significantly (Table 7).

Dissociation of the complexes, with the loss of trialkylgermane, occurred in solution and the compounds could not be reprecipitated unchanged by the addition of light petroleum. This is in accord with the fact that the compounds cannot be isolated in the pure form except by crystallisation from solutions containing a good excess of the trialkylgermane.

$$(Ph_3P)_2RhH(GeR_3)Cl \ + \ \text{solvent} \ \rightleftharpoons \ (Ph_3P)_2RhCl(\text{solvent}) \ + \ R_3GeH$$

When (R = Me) the dissociation can be made complete by sweeping the solution of the complex with nitrogen. The ^1H n.m.r. data showed that free trialkylgermane was present in solutions of the complexes and also indicated the extent of the dissociation (see below).

In addition to the bands due to Ph_3M (M = P, As) and GeR_3 (R = Me, Et) the infrared spectra of the germyl-compounds showed bands in the region 2025-2114 cm^{-1}. (Table 7) which can be assigned to the Rh-H stretching mode. These bands were different from the Ge-H stretching frequencies of the free germanes and lay within the range observed for other hydrido complexes of rhodium(III) (see Table 2). Each compound showed two bands of similar intensity in this region. This may be due to a crystallographic effect or it could be due to the existence of isomers. A similar effect has been observed in the silyl-complexes[162,163]. The frequency values of the Rh-H stretching mode lie higher in each case for the triethylgermyl-complex than the trimethylgermyl-complex and this could indicate the presence of a stronger Rh-H bond in the triethylgermyl-compounds. The silyl-compounds were reported as exhibiting no regular trends in their frequency values. The far infrared spectra of the germyl-compounds also show two bands in the ν(Rh-Cl) region in each compound (Table 7).

Although ^1H n.m.r. studies on the complexes were restricted by extensive dissociation in solution signals characteristic of the trialkylgermyl group could be observed (Table 7). Two signals were generally found in this region, one could be attributed to the trialkylgermyl group bonded to rhodium and another to the free trialkylgermane. The integrated triphenylphosphine to total trialkylgermyl proton ratio corresponded to the presence of two triphenylphosphine ligands to one trialkylgermyl group. The relative intensities of these two signals indicated that the complexes were between 50 and 100% dissociated in dichloromethane solution. There was no indication that the triethylgermyl-complexes were less prone

Table 7

Physical Properties of the Compounds $(Ph_3P)_2RhH(GeR_3)Cl$

Compound	Colour	M. pt.	Infrared data (cm^{-1})^a	^1H n.m.r. data (τ)
$(Ph_3P)_2RhH(GeEt_3)Cl$	Yellow	117-119°C	ν(Rh-H) 2107, 2062(sh) ν(Rh-Cl) 306, 284	8.92^b 9.15 (Et_3GeH) 25.4 (Rh-H); J(Rh-H) = 19Hz; J(P-Rh-H) = 15Hz
$(Ph_3As)_2RhH(GeEt_3)Cl$	Green	118-121	ν(Rh-H) 2114, 2042 ν(Rh-Cl) 331, 318	8.98^c 9.30 (Et_3GeH)
$(Ph_3As)_2RhH(GeMe_3)Cl$	Green	90-95	ν(Rh-H) 2057, 2025(sh) ρ(MeGe) 815 ν(Rh-Cl) 334(sh), 322	9.92^c 9.67 (Me_3GeH)
$(Ph_3P)_2RhH(GeMe_3)Cl$	Yellow	90-94	ν(Rh-H) 2080, 2035 ρ(MeGe) 816 ν(Rh-Cl) 296, 290(sh)	
$(Ph_3P)_2RhH(GeCl_3)Cl$	Orange-yellow	148-152	ν(Rh-H) 2123(sh), 2098 ν(Ge-Cl) 372	

(a) all infrared data refers to the solid state, KBr or CsI

(b) in deuterobenzene

(c) in dichloromethane

to dissociation in solution than their trimethylgermyl-analogues or vice versa. The trialkylgermyl-derivatives of rhodium appear to be slightly more stable in solution than their trialkylsilyl-analogues as these are reported to dissociate instantly on dissolution[161,162].

A weak Rh-H signal was detected for the complex $(Ph_3P)_2RhH(GeEt_3)Cl$ in the high-field region, which is unique to hydride ligands. The signal was just detectable above the background noise but one would not expect to observe a strong signal because of (a) the extent of the dissociation of the compound in solution, and (b) the extent to which the signal of the single proton is split by coupling with ^{31}P and ^{103}Rh. The signal consisted of an overlapping doublet of triplets centred on 25.4τ, and coupling was observed with ^{103}Rh [100%, I = $\frac{1}{2}$. J(Rh-H) = 19Hz] and [^{31}P 100%, I = $\frac{1}{2}$, J(P-Rh-H) = 15Hz]. In order to obtain the required splitting the two phosphine ligands must therefore be in equivalent or closely similar positions. The value of the coupling constant also suggests that they are <u>cis</u> to the hydride ligand. Furthermore, the observed couplings demonstrated that the phosphine ligands do not dissociate in solution. Although no ^1H n.m.r. data have been reported for the analogous triethylsilyl-complex, due to a lack of stability in solution, the high field spectrum observed for the triethylgermyl-complex was similar to that reported for the triethoxy- and trichlorosilyl derivatives of rhodium which were more stable in solution [e.g. $(Ph_3P)_2RhH(SiCl_3)Cl$, τ(Rh-H) = 24.30, J(Rh-H) = 21Hz, J(P-Rh-H) = 14Hz].

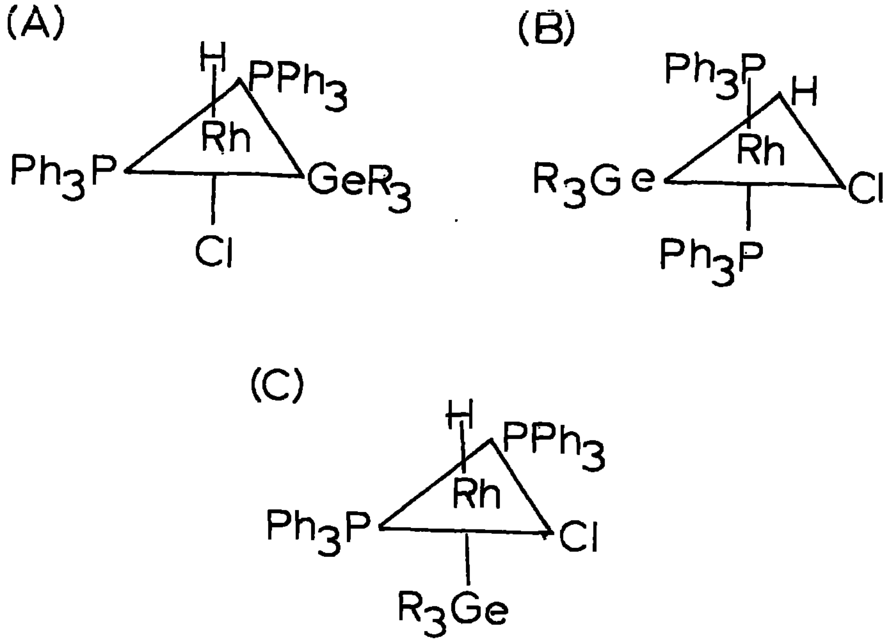


Fig. 27

Possible structures for $(Ph_3P)_2RhH(GeR_3)Cl$

It might be expected, on purely steric grounds, that the complexes of the type $(Ph_3P)_2RhH(GeR_3)Cl$ would adopt the regular trigonal bipyramidal configuration in which the phosphine and germyl ligands lay in the trigonal plane (Structure A, Fig. 27). On the basis of the ^1H n.m.r. evidence for the compound $(Ph_3P)_2RhH(GeEt_3)Cl$ any of these three structures A, B or C could be proposed. Care must be taken, however, in interpreting the ^1H n.m.r. data as the solution species need not necessarily have the same configuration as that found in the solid state. In solution a weakly bonded solvent molecule may occupy the sixth coordination site. The infrared spectra of the compounds does not help in distinguishing between the possible isomers. It is likely, however, that the compounds will adopt a similar configuration to that of $(Ph_3P)_2RhH(SiCl_3)Cl$. The structure of this compound has been determined by X-ray crystallography[199] (Fig. 25) and is described as being a highly distorted trigonal bipyramid with apical phosphines and H, Cl and $SiCl_3$ in the trigonal plane. Alternatively the structure can be described as a distorted tetragonal pyramid. One of the hydrogen atoms from the ortho position of a phenyl ring of one of the triphenylphosphine ligands also makes a close approach to the rhodium atom (2.79Å) thus blocking the sixth coordination site.

The reaction of the compound $(Ph_3P)_2RhH(GeEt_3)Cl$ with carbon monoxide in a benzene solution at room temperature resulted in the loss of triethylgermane and the formation of the known compound $(Ph_3P)_2Rh(CO)Cl$.

$$(Ph_3P)_2RhH(GeEt_3)Cl \;+\; CO \;\longrightarrow\; (Ph_3P)_2Rh(CO)Cl \;+\; Et_3GeH$$

The triethylgermane could be detected in a concentrate of the solvent by mass spectroscopy.

This behaviour is also shown by a number of other Rh(III) addition compounds and indicates the stability of the lower oxidation state when carbonyl ligands are attached to rhodium. Attempts were also made to react trialkylgermanes with $(Ph_3P)_2Rh(CO)Cl$ and these will be discussed later.

The reaction of carbon monoxide with the germyl-complex could occur by the attack of the π-bonding ligand on the formally 3-coordinate solution species formed by the dissociation of the germane (a), but it is possible that attack also occurs on the 5-coordinate complex itself to give an intermediate Rh^{III} carbonyl complex which immediately decomposes (b).

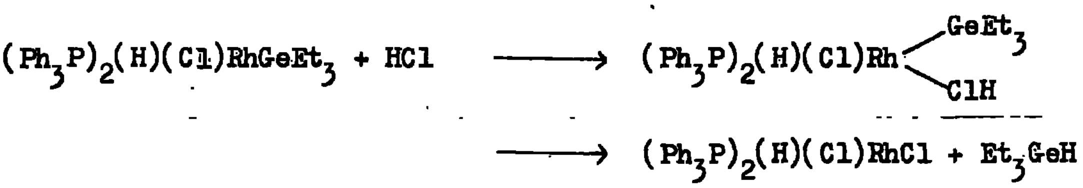
$$\begin{array}{lll}
(a) & (Ph_3P)_2RhH(GeEt_3)Cl + \text{solvent} \rightleftharpoons & (Ph_3P)_2RhCl(S) + Et_3GeH \\
 & (Ph_3P)_2RhCl(S) + CO \longrightarrow & (Ph_3P)_2Rh(CO)Cl + (S) \\
(b) & (Ph_3P)_2RhH(GeEt_3)Cl + CO \longrightarrow & [(Ph_3P)_2RhH(CO)(GeEt_3)Cl] \\
 & & \downarrow \\
 & (S = \text{solvent}) & (Ph_3P)_2Rh(CO)Cl + Et_3GeH
\end{array}$$

Rh^{III} carbonyl intermediates of this sort have been detected at low temperatures in the reaction of carbon monoxide with $(Ph_3P)_2Rh(Et)Cl_2$[20]. A small amount of $(Ph_3P)_2Rh(CO)ClH(SiCl_3)$ has also been found in the mixture formed by the prolonged reaction (50°C, twelve months) of trichlorosilane with $(Ph_3P)_2Rh(CO)Cl$[162].

The reaction with ethylene followed a similar course to that with carbon monoxide and the known compound $(Ph_3P)_2Rh(C_2H_4)Cl$ was isolated.

$$(Ph_3P)_2RhH(GeEt_3)Cl + C_2H_4 \longrightarrow (Ph_3P)_2Rh(C_2H_4)Cl + Et_3GeH$$

The reaction of the triethylgermyl-complex and anhydrous hydrogen chloride in dichloromethane resulted in a cleavage of the rhodium-germanium bond to form triethylchlorogermane and the known rhodium(III) compound $(Ph_3P)_2RhHCl_2$. The reaction differed from the analogous cleavage of $(Ph_3P)_2RhH[Si(OEt)_3]Cl$ which has been reported to give $(EtO)_3SiH$ rather than the chlorosilane, $(EtO)_3SiCl$. The mechanism proposed for the cleavage of the silyl-complex[162] may still apply for the germyl-compound and be followed by the reaction of triethylgermane with hydrogen chloride to give triethylchlorogermane.



$$(Ph_3P)_2(H)(Cl)RhGeEt_3 + HCl \longrightarrow (Ph_3P)_2(H)(Cl)Rh{<}\begin{smallmatrix}GeEt_3\\ ClH\end{smallmatrix}$$
$$\longrightarrow (Ph_3P)_2(H)(Cl)RhCl + Et_3GeH$$

Alternatively the bond may be cleaved in the opposite sense to give triethylchlorogermane and the unstable dihydride, $(Ph_3P)_2RhH_2Cl$, which could lose hydrogen and then oxidatively add a molecule of hydrogen chloride.

$$(Ph_3P)_2RhH(GeEt_3)Cl + HCl \longrightarrow (Ph_3P)_2RhH_2Cl + Et_3GeCl$$
$$(Ph_3P)_2RhH_2Cl + (S) \overset{-H_2}{\rightleftharpoons} (Ph_3P)_2RhCl(S) \overset{+HCl}{\rightleftharpoons} (Ph_3P)_2RhHCl_2$$

(S) = solvent

Phosphine exchange with dimethylphenylphosphine also occurs readily.

It was hoped that the product would be less dissociated in solution and that the stereochemistry of the complex could be determined by the splitting pattern of the methyl resonance of the dimethylphenylphosphine ligands. Neither the ^1H n.m.r. nor the infrared spectrum of the isolated solid indicated the presence of a rhodium-hydrogen bond however. The ^1H n.m.r. spectrum showed a broad resonance of low intensity centred on 9.0 τ which could be assigned to the triethylgermyl group but the spectrum could not be satisfactorily interpreted and it was obvious that the solid was not a pure compound. The ^1H n.m.r. data obtained for the compound together with the relative integrated intensities were as follows: phenyl protons 2.2, 2.7 τ (relative intensity 15); methyl protons 8.2 τ(2), 8.5τ (6), 8.7τ (6); ethyl protons, 9.0τ (4). The two resonances at 8.5τ and 8.7τ are of equal intensity and are probably a doublet due to the presence of two cis phosphine groups.

The reaction between an excess of trichlorogermane and $(Ph_3P)_3RhCl$ proceeds quite differently to those of the trialkylgermanes or of trichlorosilane. The addition of trichlorogermane to a benzene suspension of $(Ph_3P)_3RhCl$ gave an immediate reaction with the evolution of a gas to form a yellow tar. This was purified by extraction with benzene and ether and dried to give a solid product which analysed as the triphenylphosphonium salt $[Ph_3PH]_3[Rh(GeCl_3)_6]$. Hydrogen and hydrogen chloride were also found in the reaction products. The infrared spectra showed bands characteristic of the triphenylphosphonium ion and the trichlorogermyl group (Table 9). Further reactions of this type will be discussed later.

$$(Ph_3P)_3RhCl + 6HGeCl_3 \longrightarrow [Ph_3PH]_3[Rh(GeCl_3)_6] + H_2 + HCl$$

This product is best compared with the rhodium-tin compounds formed by the reaction of $SnCl_2$ with $RhCl_3$ in hydrochloric acid solution.

The ions $[Rh_2Cl_2(SnCl_3)_4]^{4-}$ and $[Rh(SnCl_3)_4]^{3-}$ have been prepared in this manner and contain rhodium in the +1 oxidation state[146,201]. Similar structures can be ruled out for the rhodium-germanium compound on the basis of its analysis and it appears to be in the +3 oxidation state. The tendency for the trichlorogermyl group to stabilise the upper oxidation state of the metal has also been noted for a series of platinum complexes[204]. A number of trichlorogermyl-platinum(IV) compounds have been prepared but the trichlorostannyl complexes are commonly found in the +2 oxidation state. Similarly it was found that hexa-coordinate trichlorogermyl-platinum compounds could be prepared although no analogous hexa-coordinate platinum-tin compounds were known.

The simple addition compound of trichlorogermane, $(Ph_3P)_2RhH(GeCl_3)Cl$ was prepared by the slow addition of an equimolar amount of trichlorogermane in benzene to a solution of $(Ph_3P)_3RhCl$, also in benzene. Concentration of the solution followed by the addition of petroleum ether precipitated a yellow-orange solid which was washed with benzene. The compound prepared in this manner was probably slightly contaminated by unreacted rhodium complex but showed infrared bands characteristic of the rhodium-hydrogen bond and the trichlorogermyl group (Table 7).

The compound was not as stable as its trichlorosilyl analogue and could not be recrystallised unchanged from solution. The presence of a direct rhodium-hydrogen bond could not be demonstrated by ^1H n.m.r. spectroscopy in deuterochloroform and presumably dissociation occurred in solution. The proton resonance for free $HGeCl_3$ in deuterochloroform has been measured and found to occur at 2.33 τ. Any signal due to dissociated $HGeCl_3$ would therefore be hidden by the broad resonances of the triphenylphosphine ligands of the complex (2.64 τ broad).

In contrast to the mild reaction of trimethylgermane with $(Ph_3P)_3RhCl$, trimethylstannane reacted extremely vigorously with this complex under similar conditions. The reaction was very exothermic and resulted in the complete decomposition of the rhodium compound to give rhodium metal, triphenylphosphine and hexamethyldistannane.

The reactions with tri(n-butyl)stannane and the silicon compound $(Me_3SiO)_2SiMeH$ proceeded in a similar manner to the trialkylgermane reactions with the formation of complexes of the type $(Ph_3P)_2RhH(MR_3)Cl$, $[M = Si, Sn; \; R = Bu, (Me_3SiO)_2SiMe]$. The infrared spectrum of the tin compound showed a rhodium-hydride stretching frequency at 2052 cm^{-1} and the butyl groups appeared in the ^1H n.m.r. spectrum as a series of broad resonances in region 8.0-9.4 τ. In addition to $\nu(Rh-H)$ at 2122 cm^{-1} the silyl compound showed bands characteristic of $\nu(SiO)$ at 1056, 1010 cm^{-1} and the ^1H n.m.r. spectrum in deuterochloroform showed two resonances due to methylsilyl groups at 10.0 τ and 10.35 τ (relative intensities 7:9). The corresponding infrared and ^1H n.m.r. data for the parent silane are: $\nu(Si-H)$ 2143 cm^{-1}; $\nu(SiO)$ 1020-1110 cm^{-1} (broad); MeSi - 9.9 τ.

The reactions of Bu_3SnCl and Me_3SnCl with $(Ph_3P)_3RhCl$ were also studied. In neither case could the product be positively identified but the infrared spectrum of each compound showed bands characteristic of the alkyl-tin group and two bands in the region where $\nu(Rh-Cl)$ and $\nu(Sn-Cl)$ would be expected. The product from the tri(n-butyl)chlorostannane reaction also showed the presence of butyl-tin groups in the ^1H n.m.r. spectrum as a broad series of resonances in the region 8.0-9.2 τ. The integrated proton ratio corresponded roughly to the presence of two triphenylphosphine ligands for each three butyl groups. Both of the compounds gave very low carbon analyses and it appears likely that cleavage of some of the alkyl groups from tin occurred in the reaction. The analyses could not definitely be assigned to any formula but they approach the empirical formula $(Ph_3P)_2RhR_3Cl_6Sn_3$ (R = Me, Bu).

The reactions of triethylgermane and trichlorosilane with tetrakis(triphenylphosphine)rhodium(I) hydride, $(Ph_3P)_4RhH$ are rather different to the analogous reactions with $(Ph_3P)_3RhCl$. In the reaction of triethylgermane with a suspension of $(Ph_3P)_4RhH$ in benzene most of the rhodium compound was recovered unchanged even after heating at a temperature of 50°C for ten days. This was rather surprising as it might have been expected that the greater electron releasing properties of the hydrido group relative to the chloro group would have encouraged an oxidative addition reaction. The difference in reactivity may be related to the presence of a fourth triphenylphosphine group in the hydride complex, although dissociation to $(Ph_3P)_3RhH$ takes place in solution, or it may be related to the instability of the dihydride complex which would be the result of an oxidative addition reaction. No evidence for the formation of a rhodium-germanium species was obtained but hydrogen and hexaethyldigermane were found amongst the reaction products. It is possible that a small amount of an intermediate rhodium-germanium bonded complex plays a part in the process leading to the formation of hexaethyldigermane. This could arise from the type of scheme proposed below.

$$\begin{tikzcd}
(Ph_3P)_4RhH \arrow[r, shift left, "\text{solution}"] & (Ph_3P)_3RhH + Ph_3P \arrow[l, shift left] \arrow[r, shift left, "+Et_3GeH"] & (Ph_3P)_2RhH_2GeEt_3 + Ph_3P \arrow[l, shift left] \arrow[d, shift left, "(S)"] \\
 & Et_6Ge_2 + (Ph_3P)_2Rh(H)(S) & (Ph_3P)_2RhGeEt_3(S) + H_2 \arrow[u, shift left] \arrow[l, "+Et_3GeH"']
\end{tikzcd}$$

(S = solvent)

The reaction of $(Ph_3P)_4RhH$ with trichlorosilane is complete within a matter of hours at room temperature, in the absence of solvent, to give $(Ph_3P)_2Rh(SiCl_3)_3$ and hydrogen. Difficulty was experienced in purifying the product because of its insolubility and the facile hydrolysis of the Si-Cl bond. The difference in reactivity between triethylgermane and trichlorosilane in this reaction may be solely related to the stability of the product (c.f. page 50) but may also be related to the more electropositive nature of the hydrogen atom in trichlorosilane. Rhodium(I) hydride complexes are known to react with acids with the loss of hydrogen in reactions of the type:

$$(Ph_3P)_4RhH + 2HCl \longrightarrow (Ph_3P)_3RhHCl_2 + H_2 + Ph_3P$$

$$(Ph_2PC_2H_4PPh_2)_2RhH + HClO_4 \longrightarrow [(Ph_2PC_2H_4PPh_2)_2Rh]^{+}ClO_4^{-} + H_2$$

Once the species $(Ph_3P)_nRhH_2(SiCl_3)$, ($n = 2$ or 3) was formed it would be expected to lose hydrogen readily and enable further attack by trichlorosilane to take place.

Trimethylgermane did not react with the complex $[(dppe)_2Rh]Cl$, ($dppe = Ph_2PC_2H_4PPh_2$) even at 60°C, although the analogous iridium complex underwent a reversible addition reaction with silanes and the triethoxysilyl complex, $[(dppe)_2IrH(Si[OEt]_3)]Cl$, has been isolated[200]. What was perhaps a little more surprising was the inability of the rhodium(I) phosphine complex $[(dmpe)_2Rh]Cl$, ($dmpe = Me_2PC_2H_4PMe_2$) to oxidatively add triethylgermane although it was known[50] to activate hydrogen in an equilibrium reaction. It was expected that the less electronegative aliphatic diphosphine might have stabilised the upper oxidation state sufficiently for a complex to be isolated.

The stability of the rhodium(III) complexes formed by the reaction of trialkylgermanes with $(Ph_3P)_3RhCl$ might also be expected to increase if a more basic ligand than triphenylphosphine was attached to rhodium.

An increase of electron density at the rhodium atom would be expected to stabilise the +3 oxidation state and hence to increase the tendency for oxidative addition reactions to take place. The reactions of trialkylgermanes with the complexes $(MePh_2P)_3RhCl$ and $(Me_2PhP)_3RhCl$ were therefore studied. These two compounds were chosen because of the usefulness of the methylphosphine ^1H n.m.r. pattern in establishing the stereochemistry of a complex. The compound $(Me_2PhP)_3RhCl$ could not be isolated in the solid form but was used as the red solution formed by the addition of dimethylphenylphosphine (3 mol. per Rh atom) in benzene to the ethylene complex $[(C_2H_4)_2RhCl]_2$. Both this solution and solutions of $(MePh_2P)_3RhCl$ were extremely air-sensitive.

The reaction of $(MePh_2P)_3RhCl$ with triethylgermane under the same conditions adopted for the preparation of $(Ph_3P)_2RhH(GeEt_3)Cl$ did not give the expected germyl-rhodium compound. The ^1H n.m.r. spectrum of the yellow solid showed the complete absence of the triethylgermyl group and the methylphosphine resonance appeared as a doublet at 8.45τ, $J(P-C-H) = 12.2Hz$. This indicated that the compound only contained two phosphine ligands and that these lay in the cis configuration. The infrared spectrum of the solid showed two small bands in the rhodium-hydrogen stretching region at 2080 and 1950 cm^{-1}. These disappeared on recrystallisation from benzene. The dihydrido-complexes $(Ph_3P)_3RhH_2Cl$ and $(EtPh_2P)_3RhH_2Cl$ are reported to have Rh-H vibrations at 2082, 2012 cm^{-1} and 2059, 1915 cm^{-1} respectively[15]. Both lose hydrogen readily in solution. The analysis of the compound did not distinguish between the two possible formulae $(MePh_2P)_2RhH_2Cl$ and $[(MePh_2P)_2RhCl]_2$ but the infrared evidence suggests that the dihydrido-complex was formed. A similar reaction has been reported to occur between trimethylgermane and $(Et_3P)_2Ir(CO)Cl$ to give $(Et_3P)_2Ir(CO)H_2Cl$ and hexamethyldigermane[161].

By contrast the reaction of $(MePh_2P)_3RhCl$ with trimethylgermane at $50^{\circ}C$ gave a mixture of polygermanium oxides and a yellow compound which contained the trimethylgermyl group bonded to rhodium. On the basis of the infrared and ^1H n.m.r. spectra this compound could best be formulated as $(MePh_2P)_2Rh(GeMe_3)_2Cl$ although the analytical data were not very satisfactory. The ^1H n.m.r. spectrum of the methylphosphine groups consisted of a doublet centred on 8.53τ, $J(P-C-H) = 12.5Hz$, which showed that the compound contained two cis phosphine ligands. The trimethylgermyl group appeared as a strong resonance at 9.55τ. The relative integrated intensities of the trimethylgermyl and methylphosphine protons (15:6) suggested the structure $(MePh_2P)_2Rh(GeMe_3)_2Cl$. Although the reaction was carried out in an evacuated sealed tube and the solvents were carefully degassed before seal off, the formation of polygermanium oxides indicated the presence of residual oxygen in the system.

A similar reaction carried out between $(Me_2PhP)_3RhCl$ and trimethylgermane gave only an intractable oxidation product of the rhodium complex.

In view of the relative stability of the compound $(Ph_3P)_2RhH(SiCl_2Me)Cl$ it might have been expected that $MeHSiCl_2$ would give a facile reaction with $(Me_2PhP)_3RhCl$ to form a fairly stable rhodium-silicon bond. In fact only the known compound mer-$(Me_2PhP)_3RhCl_3$ could be isolated from this reaction. The ^1H n.m.r. and far infrared spectra of the compound were identical to that reported by Shaw[63].

The reaction of $(Ph_3P)_2Rh(CO)Cl$ with sodium amalgam in the presence of carbon monoxide is reported to give a carbonylate anion from which the compound $(Ph_3P)_2Rh(CO)_2SnMe_3$ has been prepared[151]. We have used the reaction of the carbonylate ion with triethylbromogermane to prepare the germyl-rhodium(I) compound $(Ph_3P)_2Rh(CO)_2GeEt_3$, $[\nu(CO) = 1973, 1922\ cm^{-1}$; Et_3Ge, $8.76\tau]$. Evidence for the formation of $(Ph_3P)_2Rh(CO)_2GeMe_3$ from the reaction of the anion with trimethylbromogermane was also obtained but the compound could not be satisfactorily purified.

The compound $(Ph_3P)_2Rh(CO)_2GeEt_3$ decomposed, with loss of carbon monoxide, over a number of weeks under a nitrogen atmosphere. The decomposition could be followed by the decrease in intensity of the carbonyl band at 1922 cm^{-1}. The properties of the corresponding trimethylstannyl-rhodium compound have not been described but the germyl-iridium compound, $(Ph_3P)Ir(CO)_3GePh_3$, also decomposed over a period of weeks although the tin analogue was stable[151].
Attempts to precipitate further material from the $(Ph_3P)_2Rh(CO)_2GeEt_3$ reaction solution, by the addition of methanol, gave a mixture of yellow solids with a very different infrared spectrum to $(Ph_3P)_2Rh(CO)_2GeEt_3$. The intensity of the band at 1922 cm^{-1} had decreased relative to the broad band at 1973 cm^{-1}, and a new band had appeared at 2030 cm^{-1}. This new band was probably due to the formation of a rhodium hydride species such as $(Ph_3P)_2Rh(CO)_2H$. This could have been formed by the hydrolysis of the triethylgermyl-complex as hexaethyldigermoxane was found in a concentrate of the solvent. The infrared spectrum of $(Ph_3P)_2Rh(CO)_2H$ is variously reported to show bands at 2038 cm^{-1} $\nu(Rh\text{-}H)$, 1980, 1939 cm^{-1} $\nu(CO)$; and 2050 cm^{-1} $\nu(Rh\text{-}H)$, 1980, 1942 cm^{-1} $\nu(CO)$[108]. The hydride readily loses hydrogen and carbon monoxide to form the dimer $[(Ph_3P)_2Rh(CO)]_2$, $\nu(CO)$ 1965 cm^{-1}. A competing halogen-metal exchange reaction between the carbonylate anion and Et_3GeBr could also possibly occur to give $(Ph_3P)_2Rh(CO)Br$ and Et_3GeNa.

Unlike the analogous iridium complex $(Ph_3P)_2Rh(CO)Cl$ did not react with trimethyl- or triethylgermane to give compounds containing a rhodium-germanium bond. The reaction between $(Ph_3P)_2Ir(CO)Cl$

and trimethyl- or triethylgermane proceeded readily during twelve hours in refluxing benzene, or over a longer period at room temperature, to form the complex $(Ph_3P)_2Ir(CO)H_2GeR_3$ (R = Me or Et) and the chlorogermane, R_3GeCl[161]. Under similar conditions the rhodium compound was recovered unchanged.

Similarly $(Ph_3P)_3Rh(CO)H$ and $(Pr_3P)_2Rh(CO)Cl$ did not react with trimethyl- or triethylgermane to form a stable metal-metal bond although hexamethyl- or hexaethyldigermane could be detected in the reaction products. The difference in behaviour between rhodium and iridium in these reactions again illustrates the greater stability of the +3 oxidation state for iridium.

The complexes $(Ph_3P)_2M(CO)Cl$, (M = Rh, Ir) also behave differently in their reactions with trichlorogermane. The iridium compound reacts with an excess of trichlorogermane to give an immediate white precipitate of $(Ph_3P)_2Ir(CO)H_2GeCl_3$[161]. By contrast the addition of trichlorogermane to a solution of $(Ph_3P)_2Rh(CO)Cl$ in benzene gave an immediate reaction with the evolution of a gas and the separation of an orange-yellow tar. Attempts to recrystallise the compound from acetone or benzene also gave an orange tar. The compound was washed with benzene and ether and dried in vacuo to give an orange solid. The infrared spectrum (Table 9) showed that the compound was a triphenylphosphonium salt containing the trichlorogermyl group bound to rhodium. The presence of a strong carbonyl stretching band at 2099 cm^{-1} showed that rhodium was in the +3 oxidation state rather than the +1 state (see page 40). The compound could not be purified sufficiently to give a good analysis but probably has the formula $[Ph_3PH]_2[Rh(CO)(GeCl_3)_5]$ analogous to the known compounds of the anion $[Rh(CO)Cl_5]^{2-}$ [83a]. The only known rhodium-tin compounds of this type contain rhodium in the

+1 oxidation state, e.g. $[Rh(CO)(SnCl_3)_3]^{2-}$ 201, 203. The infrared data for these compounds are given in Table 8.

Table 8

Compound	Medium	ν(CO) cm^{-1}
$[Me_4N]_2[Rh(CO)Cl_5]$	Nujol	~2090 br.
$[Et_4N]_2[Rh(CO)Br_5]$	Nujol	2070
$[Et_4N]_2[Rh(CO)I_5]$	Nujol	~2040
$[Me_4N]_2[Rh(CO)Cl(SnCl_3)_2]$	-	2000

The difference in behaviour between rhodium and iridium in this reaction is probably due to the stability of the iridium dihydride and its poor solubility in benzene. Precipitation of the compound from solution may save it from further attack by trichlorogermane. If the rhodium compound had formed an analogous dihydride intermediate it would be expected to lose hydrogen readily and thus enable further attack to take place.

An attempt was made to see if it was possible to isolate any intermediate species by the controlled addition of 1:1 and 2:1 ratios of trichlorogermane to benzene solutions of $(Ph_3P)_2Rh(CO)Cl$. In each case a mixture containing unreacted $(Ph_3P)_2Rh(CO)Cl$ and a rhodium(III) species was formed but these could not be separated by fractional crystallisation. The mixture showed infrared bands characteristic of the trichlorogermyl group at 370 cm^{-1} and a band at 2090 cm^{-1} which could be assigned to the carbonyl group of a rhodium(III) species. No bands characteristic of the triphenylphosphonium ion or of a rhodium hydride were observed. On the basis of the infrared spectrum an intermediate such as $(Ph_3P)_2Rh(CO)(GeCl_3)_3$ or $(Ph_3P)_2Rh(CO)(GeCl_3)_2Cl$ may exist.

A similar addition of 1:1 and 2:1 ratios of trichlorogermane to benzene solutions of $(Ph_3P)_3Rh(CO)H$ also gave a mixture of products. Free triphenylphosphine was isolated from this mixture. The infrared spectrum of the solid suggested that it consisted of a mixture of the dimeric $[(Ph_3P)_2Rh(CO)]_2$, $[\nu(CO)\ 1990,\ 1970\ cm^{-1}]$; and a rhodium(III) carbonyl species $[\nu(CO)\ 2070\ cm^{-1}]$. The spectrum also showed the presence of trichlorogermyl groups $[\nu(Ge{-}Cl),\ 360\ cm^{-1}]$. No $(Ph_3P)_3Rh(CO)H$ was recovered unchanged and the infrared spectrum gave no indication of the presence of a rhodium-hydrogen bond or of the triphenylphosphonium ion.

Trichlorogermane is known to be highly polar and in some reactions it behaves like germanium(II) chloride[149].

$$HGeCl_3 \rightleftharpoons GeCl_2 + HCl$$

The compound can therefore be regarded as a source of $GeCl_2$ or of the $GeCl_3^-$ ion. In the two reactions which have previously been discussed the addition of excess trichlorogermane to the complexes $(Ph_3P)_3RhCl$ and $(Ph_3P)_2Rh(CO)Cl$ displaced the triphenylphosphine groups from rhodium with the formation of rhodium(III) triphenylphosphonium salts. The initial stages of these reactions may involve simple oxidative addition reactions but the displacement of Ph_3P must involve attack by the $GeCl_3^-$ ion. It is of interest to note that $GeCl_3^-$ is isoelectronic with Ph_3As.

Rhodium(III) trichlorogermyl-compounds were also prepared by the direct addition of trichlorogermane or trimethylammonium trichlorogermanite to rhodium trichloride trihydrate. This tendency for rhodium to form hexacoordinate trichlorogermyl-complexes and to adopt the

+3 oxidation state in these complexes, rather than the +1 state favoured for the trichlorostannyl-complexes, may be due to the smaller steric requirements of the trichlorogermyl ligand.

The addition of trimethylammonium trichlorogermanite to a solution of rhodium trichloride in hydrochloric acid gave an orange solution from which bright orange needles were obtained. These were air-stable and only decomposed at 255°C. The crystals analysed as $[Me_3NH]_3[Rh(GeCl_3)Cl_3]$ and showed a strong broad band in the far infrared spectrum at 360 cm^{-1}.

$$RhCl_3 + 3Me_3NHGeCl_3 \longrightarrow [Me_3NH]_3[Rh(GeCl_3)_3Cl_3]$$

The addition of trichlorogermane in hydrochloric acid (necessary to prevent hydrolysis) to an alcoholic solution of rhodium trichloride gave a red-orange solution. Addition of triphenylphosphine precipitated an air-stable yellow-orange solid which analysed as $[Ph_3PH]_3[Rh(GeCl_3)_2Cl_4]$, ν(Ge-Cl), 362 cm^{-1}.

$$RhCl_3 + 2HGeCl_3 + HCl + 3Ph_3P \longrightarrow [Ph_3PH]_3[Rh(GeCl_3)_2Cl_4]$$

Trichlorogermyl-complexes of rhodium(I) were also prepared by the reaction of caesium trichlorogermanite and trimethylammonium trichlorogermanite with $(Ph_3P)_2Rh(CO)Cl$. The reaction of the rhodium complex with caesium trichlorogermanite in tetrahydrofuran gave an orange solution from which a small amount of $(Ph_3P)_2Rh(CO)GeCl_3$ was isolated. The infrared spectrum of the compound showed the presence of a carbonyl group at 1978 cm^{-1} and of the trichlorogermyl group at 380 cm^{-1}. The compound could not be prepared entirely free of a small amount of $(Ph_3P)_2Rh(CO)Cl$ and it appears that some decomposition to $(Ph_3P)_2Rh(CO)Cl$ may occur in solution. The analogous tin compound could not be prepared in a pure condition either[146] and the equilibrium

$$(Ph_3P)_2Rh(CO)SnCl_3 \rightleftharpoons (Ph_3P)_2Rh(CO)Cl + SnCl_2$$

is known to occur in solution.

When solutions of $(Ph_3P)_2Rh(CO)Cl$ were refluxed in benzene with trimethylammonium trichlorogermanite a red precipitate was formed. This compound contained no triphenylphosphine ligands but a carbonyl stretching frequency was observed in the infrared spectrum at 1970 cm^{-1}. This is in the range expected for a rhodium(I) carbonyl compound. The infrared spectrum also showed the presence of the trichlorogermyl group, ν(Ge-Cl) 362 cm^{-1}. The compound could best be formulated as $[Me_3NH]_2[Rh(CO)(GeCl_3)_2Cl]$ on the basis of the infrared and analytical data. The reaction must involve attack at rhodium by the $GeCl_3^-$ ion with the displacement of triphenylphosphine.

$$(Ph_3P)_2Rh(CO)Cl + 2Me_3NHGeCl_3 \longrightarrow [Me_3NH]_2[Rh(CO)(GeCl_3)_2Cl] + 2Ph_3P$$

All of the compounds containing the trichlorogermyl group exhibit a strong broad band in the far infrared spectrum in the range 360-380 cm^{-1} (Table 9). This is possibly a combination band of the Rh-Cl and $GeCl_3$ stretching modes[205]. Similar bands have been observed in the spectra of trichlorogermylplatinum complexes[204]. Bands in the region of 2380 cm^{-1} ν(P-H), 900 cm^{-1} (P-H bend), and 1100, 720 cm^{-1} can be assigned to the triphenylphosphonium ion[204, 206, 207].

The addition of one equivalent of trichlorogermane to a tetrahydrofuran solution of the cyclooctadiene complex $[(C_8H_{12})RhCl]_2$ precipitated a small amount of orange-brown solid. The mass spectrum of this solid showed a molecular ion for the complex $(C_8H_{12})RhH(GeCl_3)Cl$ with the most abundant ion in the isotope abundance pattern at nominal mass 426. The isotope abundance pattern corresponded to that calculated by a computer program (written by A. Carrick and modified by A. McGregor) for the combination $C_8H_{13}RhGeCl_4$ (see Table 10). The infrared spectrum showed bands attributable to ν(Rh-H) at 2000 cm^{-1}

Table 9

Physical Properties of Trichlorogermyl-rhodium Complexes

Compound	Colour	M.pt.	ν(Ge-Cl)$^{(a)}$	ν(CO)$^{(b)}$	Bands attributable to $[Ph_3PH]^+$ $^{(b)}$
$[Ph_3PH]_3[Rh(GeCl_3)_6]$	yellow	138-141°C	370 cm^{-1}	- cm^{-1}	2389 ν(P-H), 1111, 881, 720 cm^{-1}
$[Ph_3PH]_2[Rh(CO)(GeCl_3)_5]$	orange-yellow	112-114	368	2099	2401 ν(P-H), 1114, 888, 723
$[Ph_3PH]_3[Rh(GeCl_3)_2Cl_4]$	orange-yellow	137-139	362	-	2382 ν(P-H), 1115, 885, 720
$[Me_3NH]_3[Rh(GeCl_3)_3Cl_3]$	orange	255 decomp.	360	-	-
$[Me_3NH]_2[Rh(CO)(GeCl_3)_2Cl]$	orange	200-204	362	1970	-
$(Ph_3P)_2Rh(CO)(GeCl_3)$	orange	196-200	380	1978	-

All infrared data refer to the solid state: (a) CsI; (b) KBr.

and to ν(Ge-Cl) at 370 cm^{-1}, but also indicated the presence of a cyclopentadienyl impurity in the compound ν(C-H), 3180 cm^{-1}. Attempted recrystallisation from THF led to the decomposition of $(C_8H_{12})RhH(GeCl_3)Cl$ and the recovery of $[(C_8H_{12})RhCl]_2$.

A cyclopentadienyl species was also reported to have been formed in the reaction of iodine with $[(C_8H_{12})RhCl]_2$ in ether at 0°C. In this case the only isolable product was π-$C_5H_5RhI_2$ [208]. The fate of the 3-carbon fragment in this curious reaction was not determined. A similar process possibly occurred in the reaction of trichlorogermane with $[(C_8H_{12})RhCl]_2$ to give the cyclopentadienyl impurity.

The addition of a good excess of trichlorosilane to a benzene solution of $[(C_8H_{12})RhCl]_2$ gave an orange solid which showed only the absorption bands characteristic of the cyclooctadiene and trichlorosilyl groups. The $SiCl_3$ absorption occurred as a series of unresolved bands in the range 480-550 cm^{-1}. No band attributable to a cyclopentadienyl species was observed. The mass spectrum showed the ion $(C_8H_{12})Rh(SiCl_3)_2^+$ at 479 m/e and the isotope abundance pattern corresponded to that predicted for $C_8H_{12}Cl_6RhSi_2^+$ by the computer program (Table 11). The analysis of the compound corresponded to its formulation as $(C_8H_{12})Rh(SiCl_3)_2Cl$. The compound was very moisture sensitive and after exposure to air the infrared spectrum contained bands characteristic of ν(SiO).

The addition of trichlorosilane to the cyclopentadienyl-cyclooctadienerhodium(I) complex, π-$C_5H_5RhC_8H_{12}$, gave an immediate reaction with the precipitation of a brown solid. Further reaction gave a yellow-orange solid. The reaction was carried out in a breakseal tube and work up yielded no hydrogen. As the solid was only sparingly soluble in all the common solvents it was purified

Table 10

Isotope combinations for the molecule/ion $C_8H_{13}RhGeCl_4$

Nominal Mass	Peak Mass	Relative Abundance
422	421.806223	24.000
423	422.809639	2.202
424	423.803478	63.110
425	424.805924	14.884
426	425.801739	100.000
427	426.803545	20.882
428	427.799889	88.731
429	428.801634	13.768
430	429.797845	43.693
431	430.800065	5.197
432	431.795715	11.961
433	432.798617	1.187
434	433.793574	1.710
435	434.796780	0.128

Table 11

Isotope combinations for the molecule/ion $C_8H_{12}RhSi_2Cl_6$

Nominal Mass	Peak Mass	Relative Abundance
477	476.765684	49.436
478	477.767069	9.568
479	478.762748	100.000
480	479.764124	19.083
481	480.759820	85.491
482	481.761183	16.005
483	482.756902	39.882
484	483.758249	7.269
485	484.754000	10.899
486	485.755322	1.894
487	486.751115	1.682
488	487.752393	0.219
489	488.748238	0.115

by extraction with benzene, and the solid recovered from the benzene extract was washed thoroughly with light petroleum. The infrared spectrum of the purified solid showed bands characteristic of the cyclopentadienyl group, ν(C-H) 3120 cm^{-1}; and to the trichlorosilyl group, ν(Si-Cl) 510, 478 cm^{-1}. The structure of the bands for the aliphatic C-H stretching modes [ν(C-H) 2925, 2855 cm^{-1}] differed from those of the cyclooctadiene-complex and now corresponded in shape to those of the cyclooctene-complex $[(C_8H_{14})RhCl]_2$.

The mass spectrum of the compound showed a molecular ion at 546 m/e (Table 12) which established the compound as π-$C_5H_5Rh(SiCl_3)_2C_8H_{14}$. The major ions in the spectrum were $C_5H_5Rh(SiCl_3)_2^+$ and $C_5H_5RhSiCl_2^+$. The other ions are shown in Fig. 26 together with a suggested breakdown pattern. The mass quoted in each case corresponds to the most abundant ion of the isotope abundance pattern.

The reaction of trichlorosilane with π-$C_5H_5Rh(C_2H_4)_2$ also yielded a similar brown solid. The mass spectrum showed a molecular ion for π-$C_5H_5Rh(SiCl_3)_2C_2H_4$, M = 464 (Table 13) and the suggested breakdown pattern is shown in Fig. 27. These reactions may involve an initial attack by trichlorosilane to give an allylic intermediate which then undergoes further reaction with trichlorosilane to give the mono-olefin complex i.e.

$$\begin{tikzcd}
\pi\text{-}C_5H_5RhC_8H_{12} \quad + \quad HSiCl_3 \arrow[r] & {[\pi\text{-}C_5H_5Rh(SiCl_3)(C_8H_{13})]} \arrow[d, "HSiCl_3"] \\
 & \pi\text{-}C_5H_5Rh(SiCl_3)_2(C_8H_{14})
\end{tikzcd}$$

A π-cyclooctenyl-complex of the type suggested as an intermediate has been isolated from the reaction of cycloocta-1,5-diene with pentamethylcyclopentadienyl-rhodium(III) dichloride[209].

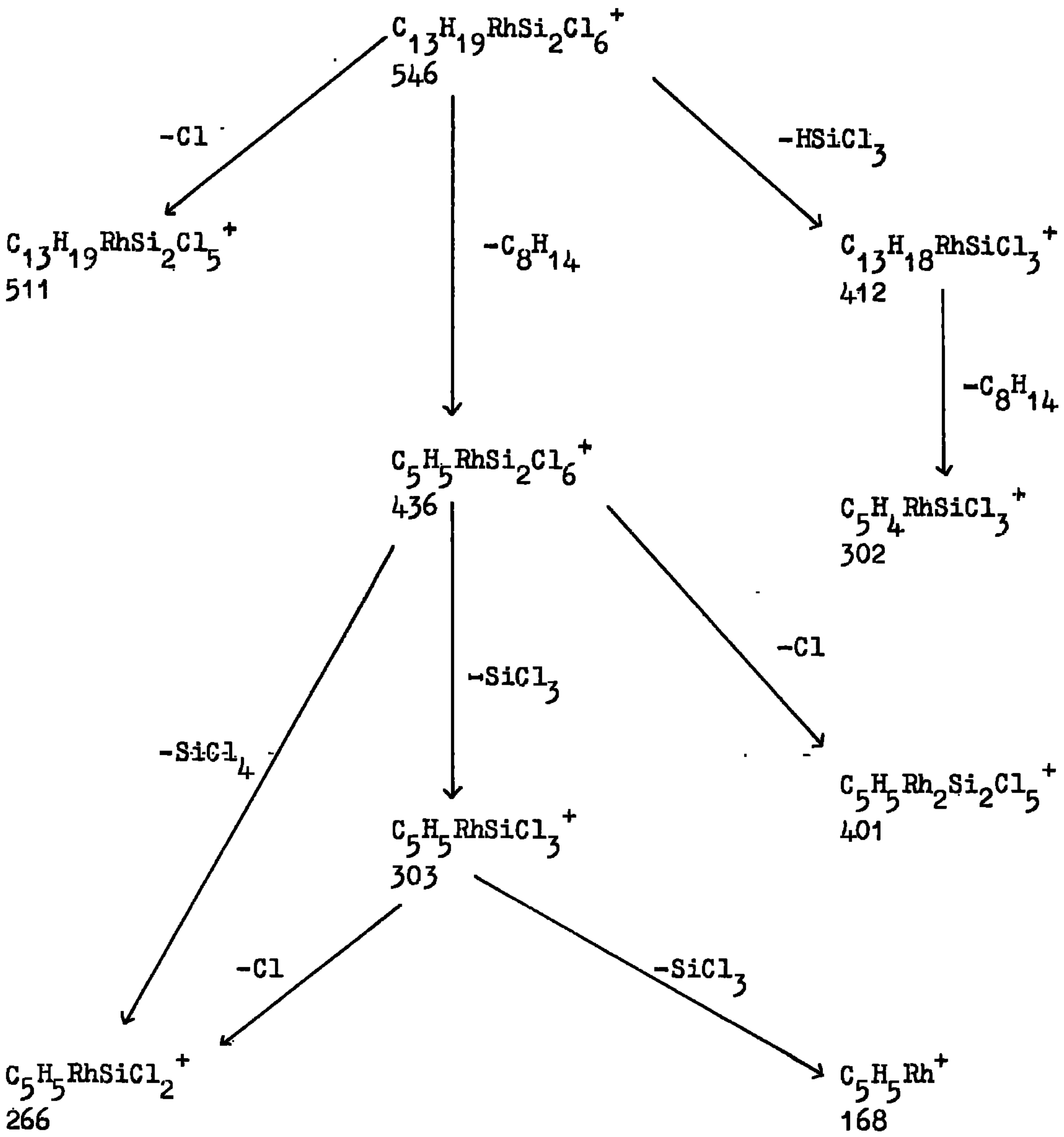
Table 12

Isotope combinations for the molecule/ion $C_{13}H_{19}RhSi_2Cl_6$

Nominal Mass	Peak Mass	Relative Abundance
544	543.820460	49.131
545	544.822307	12.318
546	545.817574	100.000
547	546.819371	24.654
548	547.814710	86.184
549	548.816443	20.774
550	549.811875	40.641
551	550.813525	9.496
552	551.809086	11.273
553	552.810620	2.494
554	553.806339	1.774
555	554.807708	0.290
556	555.803607	0.124

Fig. 26

Suggested fragmentation pattern of π-$C_5H_5Rh(SiCl_3)_2C_8H_{14}$



$SiCl_4^+$	170
$SiCl_3^+$	135

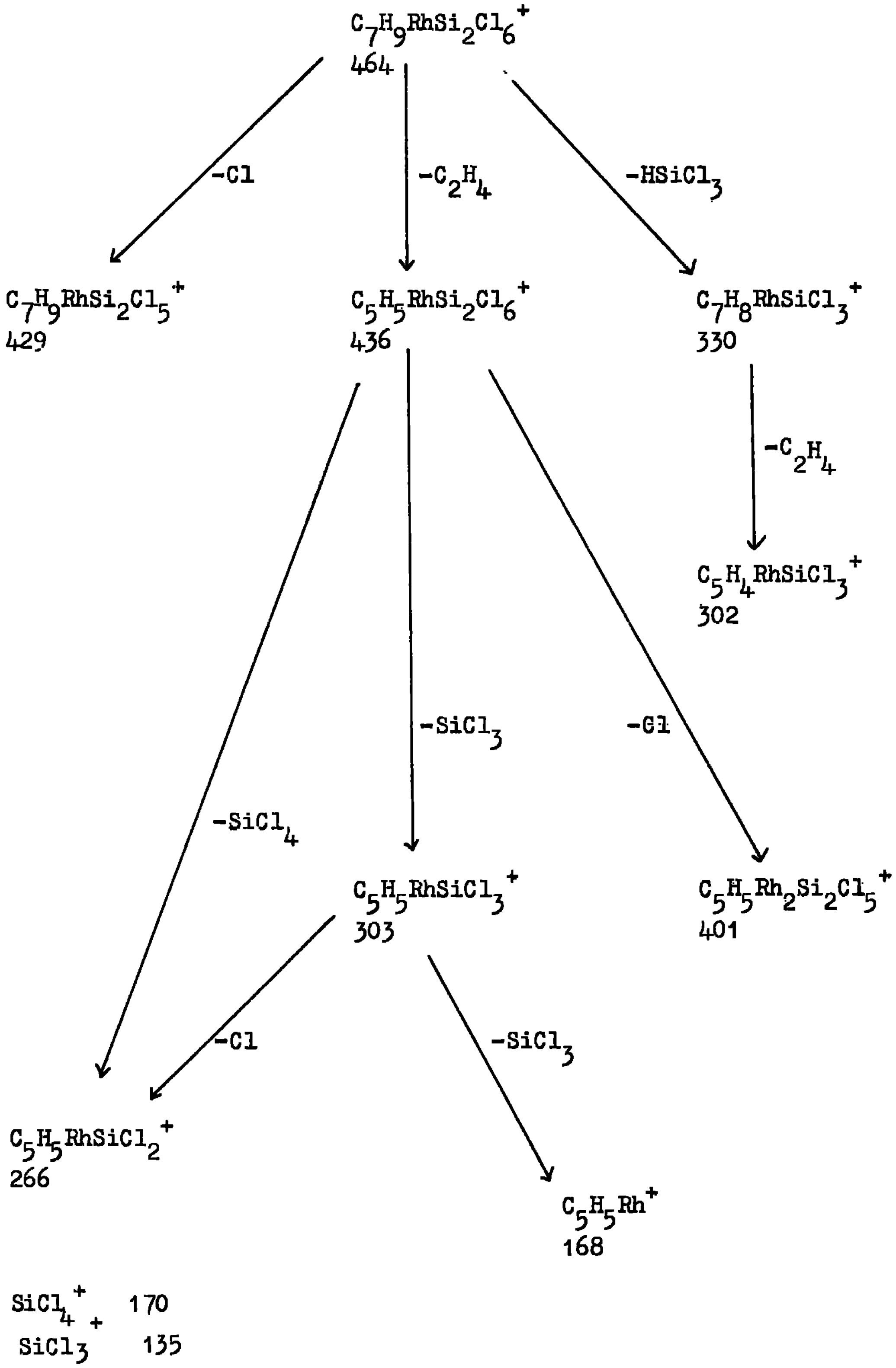
Table 13

Isotope combinations for the molecule/ion $C_7H_9RhSi_2Cl_6$

Nominal Mass	Peak Mass	Relative Abundance
462	461.742208	49.465
463	462.743459	8.996
464	463.739269	100.000
465	464.740514	17.931
466	465.736336	85.425
467	466.737573	15.027
468	467.733412	39.809
469	468.734635	6.771
470	469.730502	10.863
471	470.731700	1.728
472	471.727606	1.674
473	472.728761	0.195
474	473.724718	0.114

Fig. 27

Suggested fragmentation pattern of π-$C_5H_5Rh(SiCl_3)_2C_2H_4$



$$[\pi\text{-}C_5Me_5RhCl_2]_2 + 2C_8H_{12} \xrightarrow{EtOH/Na_2CO_3} 2[\pi\text{-}C_5Me_5RhCl(C_8H_{13})]$$

The addition of trimethylgermane to π-$C_5H_5RhC_8H_{12}$ only gave unreacted starting materials even after the reaction mixture had been heated for one month at 50°C. This difference in reactivity shown towards π-$C_5H_5RhC_8H_{12}$ by trichlorosilane and trimethylgermane could simply be interpreted in terms of metal-metal bond strengths but the more electropositive nature of the hydrogen atom in Cl_3SiH may also play a dominant role in the reaction course. The reaction could proceed by the oxidative addition of Cl_3SiH to π-$C_5H_5RhC_8H_{12}$ to give a rhodium(III) hydride which could then undergo hydrogen transfer to form a π-allylic complex. Unless a metal-olefin bond was first broken this route would involve a seven-coordinate rhodium intermediate. Alternatively, the reaction may proceed via a concerted electrophilic addition of trichlorosilane across a rhodium-olefin bond.

The reaction of trimethylgermane with π-$C_5H_5Rh(CO)Ph_3P$ did not result in the formation of a rhodium-germanium bond and only unreacted materials could be isolated from the reaction mixture.

Attempts were also made to form rhodium-silicon bonds by the reaction of bis(trimethylsilyl)mercury with the rhodium complexes $(Ph_3P)_2Rh(CO)Cl$ and $(Ph_3P)_3RhCl$. This type of reaction has been successfully utilised for the preparation of a number of platinum complexes (see page 47). When a solution of bis(trimethylsilyl)mercury was added at room temperature to a benzene solution of $(Ph_3P)_2Rh(CO)Cl$ in equimolar ratios a vivid dark red colouration was immediately produced in the solution. Only a small amount of mercury was precipitated. Removal of the solvent gave a red-brown solid which showed infrared bands characteristic of the trimethylsilyl group [ρ(Me), 798 cm^{-1}] and a carbonyl stretching frequency at 1970 cm^{-1}.

Attempts to recrystallise this material led to the recovery of $(Ph_3P)_2Rh(CO)Cl$ and eventually to an oxidised decomposition product.

The presence of a carbonyl band at 1970 cm^{-1} tended to suggest that the rhodium compound was not in the +3 oxidation state (see page 40) and should be regarded as an adduct of the type $(Ph_3P)_2Rh(CO)Cl.Hg(SiMe_3)_2$ rather than as $(Ph_3P)_2Rh(CO)(SiMe_3)(HgSiMe_3)Cl$. This interpretation of the reaction is in accord with the fact that red adducts of the type $[(C_8H_{12})RhCl]_2.2HgCl_2$ can be precipitated from methylene chloride solutions of $[(C_8H_{12})RhCl]_2$ by the addition of mercuric chloride[210]. These complexes dissociate readily in solution. It has also been found that $(Ph_3P)_2Rh(CO)Cl$ does not oxidatively add mercuric chloride although no details have been given and nor is any mention made of the formation of adducts[104]. The same paper reports that the iridium complex readily undergoes oxidative addition with $HgCl_2$ to form $(Ph_3P)_2Ir(CO)Cl_2(HgCl)$.

The analogous addition of $(Me_3Ge)_2Hg$ to $(Ph_3P)_2Ir(CO)Cl$ was also reported to give a red solution which faded on reflux. Unreacted $(Ph_3P)_2Ir(CO)Cl$ and a buff solid which was thought to be $(Ph_3P)_2Ir(CO)(HgGeMe_3)$ were isolated from the reaction mixture[161].

The only product which could be positively identified from the reaction of $(Ph_3P)_3RhCl$ with $(Me_3Si)_2Hg$ was the dimeric species $[(Ph_3P)_2RhCl]_2$. An oxidative addition to $(Ph_3P)_3RhCl$ may have occurred but if so the product was not stable enough for it to be isolated under the conditions of the reaction.

The reaction of the potassium salt $K[Rh(PF_3)_4]$ with triethylbromogermane was carried out in the hope that it would be possible to prepare a stable Rh(I)-germanium bonded complex. On the addition of triethylbromogermane to an ether solution of $K[Rh(PF_3)_4]$

a slight cloudiness was initially observed. The solution darkened on concentration (by the removal of solvent under vacuum) and only a brown intractable tar could be isolated. This material could not be purified by recrystallisation or by washing with other solvents.

An attempt to form a rhodium-molybdenum bond by the reaction of $[\pi\text{-}C_5H_5Mo(CO)_3]Na$ with $(Ph_3P)_2Rh(CO)Cl$ also gave inconclusive results. A brown solid could be isolated from the reaction mixture and this showed four strong carbonyl bands at 1967, 1876, 1777 and 1750 cm^{-1}. The band at 1967 cm^{-1} is probably associated with the rhodium atom and the others are in the region which would be expected for an anionic species such as $[\pi\text{-}C_5H_5Mo(CO)_3]^-$. The infrared spectrum also shows the presence of the cyclopentadienyl and triphenylphosphine groups. The solid was sparingly soluble in benzene and tetrahydrofuran but could not be properly purified.

No $(Ph_3P)_2Rh(CO)Cl$ could be crystallised from its solutions. If a metal-metal bond has been formed in this reaction the frequencies of the carbonyl groups associated with molybdenum tend to suggest that it has a very ionic nature.

EXPERIMENTAL

EXPERIMENTAL

1. The Preparation of Hydridochloro(triethylgermyl)bis(triphenylphosphine)rhodium(III), $(Ph_3P)_2RhH(GeEt_3)Cl$

Triethylgermane (0.5ml, 3.1 mmole) was added to a suspension of $(Ph_3P)_3RhCl$ (843 mg., 0.91 mmole) in benzene (5 ml) in a Schlenk tube. The suspension was stirred at room temperature and after thirty minutes the dark red solid began to turn yellow. Stirring was continued overnight and then the bright yellow solid was filtered from the orange solution. Free triphenylphosphine was found in the filtrate (identified by infrared spectroscopy). The solid was washed several times with light petroleum and dried in vacuo. This gave hydridochloro(triethylgermyl)bis(triphenylphosphine) rhodium(III), $(Ph_3P)_2RhH(GeEt_3)Cl$, m.p. 117-119 dec., 587 mg. (78%). [ν(Rh-H), (KBr), 2107, 2062 (sh) cm^{-1}; ν(Rh-Cl), (CsI), 306, 284 cm^{-1}. Found: C, 61.25; H, 5.50; Cl, 4.18; P, 7.82%. $C_{42}H_{46}ClGeP_2Rh$ requires C, 61.23; H, 5.59; Cl, 4.31; P, 7.53%].

2. The Preparation of Hydridochloro(trimethylgermyl)bis(triphenylphosphine)rhodium(III), $(Ph_3P)_2RhH(GeMe_3)Cl$

$(Ph_3P)_3RhCl$ (633mg., 0.69 mmole) was placed in a breakseal apparatus equipped with a glass sinter (por 3). Benzene (0.5 ml) and trimethylgermane (about 5 liquid ml) were condensed into the apparatus which was then sealed in vacuo. The apparatus was warmed to room temperature and the suspension stirred. Reaction was first noticeable after thirty minutes when the dark red solid began to lighten in colour. The suspension was stirred overnight to give a dark yellow solid which was filtered from the yellow solution. The apparatus was opened to a vacuum line and the volatile materials removed.

Fractionation of the volatiles yielded: hydrogen (2.44 N.cc., 0.11 mmole), unreacted trimethylgermane, and hexamethyldigermane (M, $Me_6{}^{146}Ge_2{}^+ = 236$). Triphenylphosphine was extracted from the solid residue with light petroleum and identified by infrared spectroscopy. The yellow filtered solid was washed with light petroleum to give hydridochloro(trimethylgermyl)bis(triphenylphosphine)rhodium(III), $(Ph_3P)_2RhH(GeMe_3)Cl$, m.p. 90-94°C dec., 511 mg. (96%).
[ν(Rh-H), (KBr), 2080, 2035 cm^{-1}; ν(Rh-Cl), CsI, 296, 290 (sh) cm^{-1}.
Found: C, 59.21; H, 4.95; Cl, 4.07%. $C_{39}H_{40}ClGeP_2Rh$ requires C, 59.91; H, 5.12; Cl, 4.31%.]

3. The Preparation of Hydridochloro(triethylgermyl)bis(triphenylarsine)rhodium(III), $(Ph_3As)_2RhH(GeEt_3)Cl$

Triethylgermane (0.5 ml, 3.1 mmole) was added to a suspension of $(Ph_3As)_3RhCl$ (635 mg., 0.6 mmole) in benzene (3 ml) in a Schlenk, The suspension was stirred at room temperature and the brown solid slowly turned yellow-green. Stirring was continued overnight and then the solid was filtered from the brown solution and washed several times with light petroleum. The compound was dried in vacuo yielding hydridochloro(triethylgermyl)bis(triphenylarsine)rhodium(III), $(Ph_3As)_2RhH(GeEt_3)Cl$, m.p. 118-121°C dec., 492 mg. (90%).
[ν(Rh-H), (KBr), 2114, 2042; ν(Rh-Cl), (CsI), 331, 318 (sh) cm^{-1}.
Found: C, 54.36; H, 4.59; Cl, 3.47%. $C_{42}H_{46}As_2ClGeRh$ required C, 55.31; H, 5.05; Cl, 3.90%].

4. The Preparation of Hydridochloro(trimethylgermyl)bis(triphenylarsine)rhodium(III), $(Ph_3As)_2RhH(GeMe_3)Cl$

$(Ph_3As)_3RhCl$ (1.06g., 1 mmole) was placed in a breakseal apparatus equipped with a sinter (por 3) and sealed to a vacuum line. Benzene (1 ml) and trimethylgermane (about 5 liquid ml) were condensed into the apparatus which was sealed and stirred magnetically. On warming to room temperature a gas was evolved and after a short time the brown solid began to lighten in colour. After one hour the solid, which was now completely olive green, was filtered and washed by back-distillation of solvent. The tube was broken open to the vacuum line to yield hydrogen (18.9 N.cc., 0.84 mmole). Fractionation of the volatiles gave unreacted trimethylgermane and a small amount of trimethylchlorogermane (M, $Me_2{}^{74}Ge^{35}Cl^+$ = 139). The green solid was dried in vacuo and was identified as hydridochloro(trimethylgermyl)-bis(triphenylarsine)rhodium(III), $(Ph_3As)_2RhH(GeMe_3)Cl$, m.p. 90-95°C dec., 720 mg. (82%).

[ν(Rh-H), (KBr), 2057 (m), 2025 (s) cm^{-1}; ν(Rh-Cl), (CsI), 334 (sh), 322 cm^{-1}. Found: C, 53.42; H, 4.45; Cl, 3.85%. Required for $C_{39}H_{40}As_2ClGeRh$: C, 53.84; H, 4.60; Cl, 4.08%].

5. The Reaction between $(Ph_3P)_3RhCl$ and an Excess of Trichlorogermane

Tris(triphenylphosphine)rhodium(I) chloride (351 mg., 0.38 mmole) was added to one arm of a two-limbed breakseal apparatus. Toluene (0.5 ml) and trichlorogermane (0.5 ml., 965 mg., 5.36 mmole) were added to the other limb under nitrogen. The solvent and reactant were degassed and the apparatus evacuated and sealed. The apparatus used was designed so that effective degassing of the reactants could be carried out without prior reaction.

On mixing the reactants an immediate reaction occurred. The solid did not all go into solution but formed a red tar from which bubbles of gas were evolved. After stirring for four hours the reaction was almost complete and the tarry solid was now completely yellow and the liquid colourless.

After a further twelve hours the tube was opened to a vacuum line to yield, after fractionation, hydrogen (8.38 N.cc., 0.374 mmole) (identified by mass spectroscopy) and hydrogen chloride (11.23 N.cc., 0.502 mmole) [infrared comparison, ν(H-Cl) P,R structure 2817, 2941 cm^{-1}]. The remaining volatiles were pumped off to give a yellow solid (727 mg.). The solid was completely insoluble in benzene, petrol and ether but tended to form a tarry substance on coming into contact with them. It was extremely soluble in tetrahydrofuran and acetone. Attempts to recrystallise the compound from these solvents failed and the solid was eventually thoroughly washed with benzene and ether and pumped to dryness.

The infrared spectrum of the solid showed absorptions attributable to the triphenylphosphonium ion at 2389 cm^{-1}, 1111 cm^{-1}, 881 cm^{-1} and 720 cm^{-1} (KBr) and to the trichlorogermyl group at 370 cm^{-1} (CsI). Band indicative of bridging rhodium chlorine groups were absent from the spectrum. No free triphenylphosphine was found in the benzene or ether washings. The data suggests that the compound should be formulated as $[Ph_3PH]_3[Rh^{III}(GeCl_3)_6]$, m.p. 138-141°C, yield 727 mg., (97%). [Found: C, 33.07; H, 2.73; Cl, 31.8; P, 4.72%. $C_{54}H_{48}Cl_{18}Ge_6P_3Rh$ requires C, 32.95; H, 2.44; Cl, 32.49; P, 4.73%].

6. The Reaction Between Equivalent Amounts of $(Ph_3P)_3RhCl$ and Trichlorogermane

Trichlorogermane (193 mg., 1.06 mmole) in benzene (20 ml) was added slowly to a solution of $(Ph_3P)_3RhCl$ (998 mg., 1.06 mmole) in benzene(20ml) to give an orange-brown solution. The solution was concentrated by the removal of benzene and an orange solid precipitated by the addition of petroleum ether. The solid was filtered, washed thoroughly with a small amount of benzene and petroleum ether and dried in vacuo. The infrared spectrum and analysis of the solid identified it as hydridochloro(trichlorogermyl)bis(triphenylphosphine) rhodium(III), $(Ph_3P)_2RhH(GeCl_3)Cl$, m.p. 148-152°C dec., 801 mg. (88%). [ν(Rh-H), (KBr), 2123 (sh), 2098 (m) cm^{-1}; ν(Ge-Cl), (CsI), 372 (s) cm^{-1}. Found: C, 48.32; H, 4.20; Cl, 17.34%. $C_{36}H_{31}Cl_4GeP_2Rh$ requires C, 51.2; H, 3.68; Cl, 16.85%].

7. The Reaction Between $(Ph_3P)_3RhCl$ and Trimethylstannane

Benzene (3 ml) and trimethylstannane ($\sim$2 ml) were condensed into a breakseal tube containing $(Ph_3P)_3RhCl$ (530 mg., 0.57 mmole). The tube was cooled to -196°C, evacuated and sealed. On allowing the tube to warm to room temperature an extremely vigorous reaction occurred. The solid all dissolved to give an orange-red solution with the evolution of gas. The reaction was very exothermic and had to be cooled when the benzene began to boil. After a few minutes the solution turned brown and a metallic mirror formed on the walls of the tube. The rhodium complex completely decomposed and work up yielded hydrogen (168 N.cc., 74.8 mmole), hexamethyldistannane (M, $Me_5{}^{240}Sn_2{}^{+}$ = 315), triphenylphosphine and rhodium metal.

8. The Reaction Between $(Ph_3P)_3RhCl$ and Tri(n-butyl)stannane

Tri(n-butyl)stannane (390 mg., 1.34 mmole) was added to a suspension of $(Ph_3P)_3RhCl$ (260 mg., 0.28 mmole) in benzene (3 ml). Over a period of two hours the solution turned orange and a few

orange-yellow crystals were deposited. After stirring overnight petroleum ether was added in small amounts to precipitate a yellow solid. This was filtered, washed thoroughly with petroleum ether and dried in vacuo. The infrared spectrum showed a band due to ν(Rh-H) and bands characteristic of the Bu_3Sn group. No band which could be assigned to ν(Sn-H) was observed. The ^1H n.m.r. spectrum also showed the presence of butyl groups. The compound is best formulated as hydridochloro(tri n-butylstannyl)bis(triphenylphosphine)rhodium(III), $(Ph_3P)_2RhH(Bu_3Sn)Cl$, m.p. 110°C dec., 248 mg. (92%).
[ν(Rh-H), (KBr), 2052 cm^{-1}; ν(Rh-Cl), (CsI), 310 cm^{-1}. Found: C, 55.36; H, 5.76%. $C_{48}H_{58}ClP_2RhSn$ requires C, 60.34; H, 6.08%].

9. The Preparation of Hydridochloro[bis(trimethylsiloxy)methylsilyl]-bis(triphenylphosphine)rhodium(III), $(Ph_3P)_2RhH[(Me_3SiO)_2SiMe]Cl$

$(Ph_3P)_3RhCl$ (594 mg.) was suspended in benzene (5 ml) and $(Me_3SiO)_2SiMeH$ (0.5 ml) was added. The rhodium complex reacted to give a clear orange solution. The solution was concentrated by removal of solvent and yellow crystals began to form. These were collected and identified by their infrared spectrum and analysis as $(Ph_3P)_2RhH[(Me_3SiO)_2SiMe]Cl$, m.p. 132-136°C dec., 368 mg. (65%). The ^1H n.m.r. spectrum in deuterochloroform showed two resonances in the range expected for methylsilyl compounds at 10.0 τ and 10.35 τ (relative intensity 7:9).
[ν(Rh-H), (KBr), 2122 cm^{-1}; ν(SiO), (KBr), 1056, 1010 cm^{-1}. Found: C, 58.65; H, 6.01; Cl, 4.26; P, 7.59%. $C_{43}H_{52}ClO_2P_2RhSi_3$ requires C, 58.40; H, 5.88; Cl, 4.01; P, 7.02%].

10. The Reaction of $(Ph_3P)_3RhCl$ with Tri(n-butyl)chlorostannane

Tri(n-butyl)chlorostannane (3 ml, 11.2 mmole) and benzene (0.5 ml) were added to $(Ph_3P)_3RhCl$ (257 mg., 0.28 mmole). On stirring some of the rhodium complex dissolved to give an orange solution but most of the solid did not react even after a number of hours. The mixture was heated to 80°C for fifteen minutes and all of the rhodium complex dissolved to give an orange solution. On cooling a sticky orange solid came out of the solution. The reaction was stirred for a further two weeks and petroleum ether (16 ml) added to precipitate a golden-yellow solid. The solid was filtered, extracted repeatedly with petroleum ether to remove the tri(n-butyl)chlorostannane and dried in vacuo, yield 465 mg. An attempt to recrystallise a portion of the solid from dichloromethane did not yield any crystals but the material could be recovered by the addition of ether.

The infrared spectrum of the solid showed the presence of aliphatic C-H groups. Two bands at 308 cm^{-1} and 325 cm^{-1} (CsI) were found in the far infrared spectrum and these could be due either to ν(Rh-Cl) or possibly to ν(Sn-Cl). The presence of aliphatic protons was also shown in the ^1H n.m.r. spectrum. The compound was not sufficiently soluble to give an accurate integration but the phosphine proton to butyl proton ratio appeared to be of the order 30:24. This corresponds roughly to the presence of three butyl groups for every two triphenylphosphine molecules in the compound. The solid analysed as C, 36.41, 36.45; H, 4.32, 3.89; Cl, 14.6%. This gives a C:H:Cl ratio of 14.77:20:2. No formula could be assigned to this analysis but $(Ph_3P)_2RhBu_3Sn_3Cl_6$, $C_{48}H_{57}Cl_6P_2RhSn_3$ requires C, 42.0; H, 4.16; Cl, 15.53%.

11. The Reaction of Trimethylchlorostannane with $(Ph_3P)_3RhCl$

Trimethylchlorostannane (975 mg., 4.89 mmole) and $(Ph_3P)_3RhCl$ (272 mg., 0.29 mmole) were stirred together in dichloromethane (0.5 ml) for one week. The addition of ether (8 ml) precipitated a yellow solid which was filtered and extracted with ether to remove triphenylphosphine and trimethylchlorostannane. The residual solid was dried in vacuo, yield 138 mg. Bands in the aliphatic C-H region (due to Me_3Sn^*) were observed in the infrared spectrum of the solid. The far infrared spectrum (CsI) showed two bands at 282 cm^{-1} and 320 cm^{-1} which could be due to ν(Rh-Cl) or ν(Sn-Cl). The solid analysed as C, 38.18, 38.29; H, 4.89, 4.98%. Although no formula could be assigned on this evidence $(Ph_3P)_2RhMe_3Sn_3Cl_6$, $C_{39}H_{39}Cl_6P_2RhSn_3$ requires C, 37.68; H, 3.14%. The compound was too insoluble to enable its ^1H n.m.r. spectrum to be examined.

12. The Reaction of $(Ph_3P)_2RhH(GeEt_3)Cl$ with Carbon Monoxide

Carbon monoxide was passed through a suspension of $(Ph_3P)_2RhH(GeEt_3)Cl$ (209 mg., 0.25 mmole) in benzene (5 ml). The solution gradually changed in colour from deep orange to yellow and all of the solid material went into the solution. Removal of the solvent yielded $(Ph_3P)_2Rh(CO)Cl$ (175 mg., 0.25 mmole) [ν(CO), (KBr), 1987, 1968 cm^{-1}; ν(CO), ($CHCl_3$), 1984 cm^{-1}]. A concentrate of the volatiles was shown to contain triethylgermane by mass spectroscopy (M, $Et_3{}^{74}Ge^+$ = 161).

13. The Reaction of $(Ph_3P)_2RhH(GeEt_3)Cl$ with ethylene

Ethylene was passed through a suspension of $(Ph_3P)_2RhH(GeEt_3)Cl$ (97 mg., 0.118 mmole) in chloroform (5 ml). The solid quickly dissolved to give a yellow solution. The addition of ether (3 ml) precipitated a yellow solid which was identified as the known compound $(Ph_3P)_2Rh(C_2H_4)Cl$ by infrared spectral comparison with an authentic specimum. Bands characteristic of $(Ph_3P)_2RhH(GeEt_3)Cl$ were absent from the spectrum. A concentrate of the volatiles was shown to contain hexaethyldigermoxane (M, $Et_5{}^{146}GeO^+ = 307$). This presumably arises from the hydrolysis or oxidation of triethylgermane.

14. The Reaction of $(Ph_3P)_2RhH(GeEt_3)Cl$ with Hydrogen Chloride

Hydrogen chloride gas was passed through a suspension of $(Ph_3P)_2RhH(GeEt_3)Cl$ (59 mg., 72 mmole) in dichloromethane (0.5 ml). The solid all dissolved to give a yellow-orange solution which was concentrated in a nitrogen stream and resaturated with hydrogen chloride. Addition of diethyl ether (1 ml) precipitated a bright yellow solid which was filtered and dried. The infrared spectrum of the solid showed it to be the known compound hydridodichloro-bis(triphenylphosphine) rhodium(III), 38 mg. (76%), ν(Rh-H), (KBr), 2105 cm^{-1}. The remaining solution was concentrated and shown to contain triethylchlorogermane by mass spectroscopy (M, $Et_3{}^{74}Ge^{35}Cl^+ = 196$).

15. The Reaction of $(Ph_3P)_2RhH(GeEt_3)Cl$ with Dimethylphenylphosphine

A solution of dimethylphenylphosphine (344 mg., 2.4 mmole) in benzene (3 ml) was added to $(Ph_3P)_2RhH(GeEt_3)Cl$ (197 mg., 0.24 mmole). An immediate reaction took place and most of the solid dissolved to give an orange-red solution. After stirring overnight the solvent was removed to give a red tar which was repeatedly extracted with petroleum ether to remove free phosphine.

The compound was then dissolved in a small amount of benzene and reprecipitated with petroleum ether to give an orange-red solid. The infrared spectrum of the solid showed that the compound contained dimethylphenylphosphine as a ligand but showed no rhodium hydride stretching frequency. The ^{1}H n.m.r. spectrum in deuterobenzene could not be satisfactorily resolved but the resonance at 9.0 τ can be assigned to the Et_3Ge moiety. [phenyl protons 2.2, 2.7 τ (relative intensity 15); other protons 8.2 τ (2); 8.5 τ (6); 8.7 τ (6); 9.0 τ (4)].

16. The Reaction of $(Ph_3P)_4RhH$ with Triethylgermane

Triethylgermane (0.4 ml, 2.49 mmole) and benzene (5 ml) were added to $(Ph_3P)_4RhH$ (534 mg., 0.51 mmole) in a breakseal tube. The tube was heated to 50-60°C for ten days before opening to a vacuum line. Hydrogen (6.62 N.cc., 0.30 mmole), unreacted triethylgermane and hexaethyldigermane (M, $Et_6{}^{146}Ge_2{}^+$ = 320) were found in the volatiles. The residual solid was extracted with petroleum ether to give unreacted starting material, 457 mg. [ν(Rh-H), 2142 cm^{-1} (KBr)].

The petroleum extract contained a small amount of soluble brown material. The infrared spectrum of this material showed no hydride band and contained only bands characteristic of triphenylphosphine and triphenylphosphine oxide.

17. The Reaction of $(Ph_3P)_4RhH$ with Trichlorosilane

$(Ph_3P)_4RhH$ (297 mg., 0.28 mmole) was placed in a breakseal apparatus equipped with a sinter and trichlorosilane (10 ml) was condensed into the apparatus from a vacuum line. The tube was evacuated and sealed. On warming to room temperature bubbles of gas were evolved from the suspension which was stirred magnetically. Reaction occurred over a period of a few hours and the suspended solid changed in colour from bright yellow to buff yellow. After one week the complex was filtered through the sinter and washed with trichlorosilane by back-distillation. The apparatus was opened to a vacuum line yielding hydrogen (22.2 N.cc., 0.99 mmole), unreacted trichlorosilane, triphenylphosphine, and the buff solid. The solid was only very sparingly soluble in the common solvents and an attempt to recrystallise a portion of it from a large volume of sodium-dried benzene yielded only the known complex $(Ph_3P)_2RhHCl_2$, [ν(Rh-H), 2142 cm^{-1} (KBr). Found: C, 61.89; H, 5.11; Cl, 12.92%. $C_{36}H_{31}Cl_2P_2Rh$ requires C, 61.80; H, 4.43; Cl, 10.15%]. This was presumably formed by hydrolysis of the trichlorosilyl complex by residual water in the solvent as the infrared of the solid residue showed strong bands in the region 1000-1100 cm^{-1} which could be assigned to ν(SiO).

The remainder of the solid was washed thoroughly with light petroleum and dried in vacuo. The infrared spectrum of the solid showed bands characteristic of coordinated triphenylphosphine and the trichlorosilyl group, ν (Rh-H) was absent. The analysis of the compound suggests that it should be formulated as tris(trichlorosilyl)-bis(triphenylphosphine)rhodium(III), $(Ph_3P)_2Rh(SiCl_3)_3$, 170°C dec., 243 mg. (91%).

[Found: C, 41.10; H, 3.86; Cl, 23.05%. $C_{36}H_{30}Cl_9P_2Si_3Rh$ requires C, 41.92; H, 2.91; Cl, 31.0%].

18. The Reaction of $[(Ph_2PC_2H_4PPh_2)_2Rh]Cl$ with Trimethylgermane

Trimethylgermane (0.5 liquid ml) and tetrahydrofuran (3 ml) were condensed onto $[(Ph_2PC_2H_4PPh_2)_2Rh]Cl$ (331 mg) in a breakseal tube. No reaction took place even after a number of weeks at 60°C and only unreacted $[(Ph_2PC_2H_4PPh_2)_2Rh]Cl$ was recovered (319 mg.).

19. The Reaction of $[(Me_2PC_2H_4PMe_2)Rh]Cl$ with Triethylgermane

Triethylgermane (0.2 ml) was added to a suspension of $[(Me_2PC_2H_4PMe_2)_2Rh]Cl$ (220 mg.) in benzene. The suspension was stirred for twenty hours, filtered and the yellow solid washed with hexane. The infrared spectrum of the dried solid showed it to be unreacted $[(Me_2PC_2H_4PMe_2)_2Rh]Cl$ (130 mg.).

20. The Reaction of $(MePh_2P)_3RhCl$ with Triethylgermane

Triethylgermane (0.3 ml, 1.87 mmole) was added to a suspension of $(MePh_2P)_3RhCl$ (380 mg., 0.51 mmole) in benzene (4 ml). After five hours the solid dissolved and the solution was stirred overnight. The solution was concentrated by the slow removal of solvent in a nitrogen stream to leave a solid residue which was washed with light petroleum and dried. The ^1H n.m.r. spectrum of the sample in deuterobenzene indicated the complete absence of the triethylgermyl group. A doublet centred on 8.45 τ, J(P-C-H) = 12.2 Hz, could be assigned to the presence of two cis methyldiphenylphosphine ligands. No high-field protons (to 30 τ) were observed in the ^1H n.m.r. spectrum but the infrared spectrum showed two bands at 2080 cm^{-1} and 1950 cm^{-1} (KBr) which were in the region expected for ν(Rh-H). On dissolution of the product in benzene and reprecipitation by the addition of petroleum ether these bands disappeared. Analysis of the yellow solid also tended to suggest that the compound should be formulated as $(MePh_2P)_2RhH_2Cl$ rather than as $[(MePh_2P)_2RhCl]_2$ but the differences involved were small.

[Found: C, 57.48; H, 5.26; Cl, 5.07%.

$C_{26}H_{28}ClP_2Rh$ requires C, 57.72; H, 5.18; Cl, 6.57%.

$C_{52}H_{52}Cl_2P_4Rh_2$ requires C, 57.94; H, 4.83; Cl, 6.59%.].

21. The Reaction of $(MePh_2P)_3RhCl$ with Trimethylgermane

Trimethylgermane(~1 liquid ml) and dry benzene (0.6 ml) were condensed onto $(MePh_2P)_3RhCl$ (302 mg., 0.41 mmole) in a breakseal tube. The system was degassed and sealed under vacuum. The tube was heated at 50°C for one week and the yellow solid darkened to give a brown solution. Work up yielded 97 N.cc. of non-condensible gas, unreacted trimethylgermane, a benzene solution of Me_6Ge_2 and polygermanium oxides, and a brown tar. The benzene solution was concentrated by distillation and was shown to contain Me_6Ge_2, Me_6Ge_2O and $Me_6Ge_3O_3$ by the presence of the ions $Me_5{}^{146}Ge_2{}^+$ (M = 221), $Me_5{}^{146}Ge_2O^+$ (M = 237), and $Me_5{}^{218}Ge_3O_3{}^+$ (M = 341) in the mass spectrum.

The brown tar was extracted with light petroleum to give a yellow-brown solid and an orange solution. The solution was concentrated to give a brown oil which was vacuum distilled in a microcup apparatus. The mass spectrum of the distillate showed that it consisted of a mixture of polygermanium oxides. The presence of the ions $Me_{13}{}^{436}Ge_6O^+$ (M = 647), $Me_{11}{}^{364}Ge_5O^+$ (M = 545), $Me_7{}^{290}Ge_4O_4{}^+$ (M = 459), $Me_5{}^{218}Ge_3O_3{}^+$ (M = 341) and $Me_5{}^{146}Ge_2O^+$ (M = 237) suggested that $Me_{14}Ge_6O$, $Me_8Ge_4O_4$, $Me_6Ge_3O_3$ and Me_6Ge_2O were present in the mixture.

The infrared spectrum of the yellow-brown solid showed that it contained bands characteristic of the Me_3Ge - group [ρ(Me), 810 cm^{-1}]

but no band due to ν(Rh-H) was present. The ^{1}H n.m.r. spectrum (deuterobenzene) showed resonances at 2.33 τ and 3.01 τ (phenyl groups); 8.53 τ doublet, J(P-C-H) = 12.5 Hz (methyl-phosphine); 9.55 τ (methyl-germane). The relative intensities of these resonances were 18.5: 6 : 15. The ^{1}H n.m.r. and analytical data suggested that the compound was best formulated as $(MePh_2P)_2Rh(GeMe_3)_2Cl$. [Found: C, 46.66; H, 4.98; Cl, 2.90%. $C_{32}H_{44}ClGe_2P_2Rh$ requires C, 49.63; H, 5.69; Cl, 4.59%].

22. Reaction between $(Me_2PhP)_3RhCl$ and Trimethylgermane

The complex $(Me_2PhP)_3RhCl$ was prepared in situ by the addition of dimethylphenylphosphine (688 mg., 4.98 mmole) and benzene (6 ml) under a nitrogen atmosphere to $[(C_2H_4)_2RhCl]_2$ (324 mg., 0.833 mmole). The solid dissolved to give a red solution with a vigorous evolution of ethylene. The breakseal tube was transferred to a vacuum line, evacuated and degassed, and trimethylgermane (117 N.cc., 5.22 mmole) condensed in. Over a period of three months the solution turned brown and work up gave a brown tar. The brown solid produced by crystallisation from cyclohexane showed no bands due to the Me_3Ge group either in the infrared or ^{1}H n.m.r. spectra. The presence of an infrared band at 1180 cm^{-1} suggested the presence of triphenylphosphine oxide.

A similar experiment between $(Me_2PhP)_3RhCl$ and triethylgermane gave identical results and no product could be isolated.

23. The Reaction of $(Me_2PhP)_3RhCl$ with Methyldichlorosilane

$(Me_2PhP)_3RhCl$ was prepared in situ by the addition of dimethylphenylphosphine (688 mg., 4.98 mmole) and benzene (6 ml) under a nitrogen atmosphere to $[(C_2H_4)_2RhCl]_2$ (325 mg., 0.833 mmole). Methyldichlorosilane (552 mg., 4.80 mmole) was added to the red solution and the reaction was stirred for one week before work up. The resultant yellow-brown solution was filtered and light petroleum was added to the filtrate to precipitate a yellow solid. The far infrared and ^{1}H n.m.r. spectrum of this solid were identical to that reported for mer-$(Me_2PhP)_3RhCl_3$. [ν (Rh-Cl), 339, 317, 273 cm^{-1}; triplet 8.11 τ, J(P-C-H) = 4.2 Hz; doublet 8.78 τ, J(P-C-H) = 11.4 Hz (in dichloromethane)].

24. The Preparation of $(Ph_3P)_2Rh(CO)_2GeEt_3$

A solution of $(Ph_3P)_2Rh(CO)Cl$ (1.04 mg., 1.51 mmole) in THF (90 ml) was added to 1% sodium amalgam (2 gm in 218 gm mercury) contained in a round bottomed flask fitted with a "Rotaflo" teflon tap. The whole system was evacuated and purged twice with carbon monoxide before being pressurised to 5 atm. with CO. The reaction was heated at 60°C and shaken overnight to give a pale yellow solution of the sodium salt of a phosphine-rhodium-carbonyl complex. [ν (CO) 1995 (sh), 1978, 1949 (sh), 1901, 1872 cm^{-1} (THF solution)].

The solution was filtered into a flask under nitrogen and triethylbromogermane (0.5 ml, 743 mg., 3.1 mmole) added to give an immediate cloudiness in the solution. This solution was filtered and concentrated, and the addition of a small amount of methanol gave a pale yellow microcrystalline solid. The infrared and ^{1}H n.m.r. spectrum of the solid showed bands characteristic of the triethylgermyl group and the compound was identified as $(Ph_3P)_2Rh(CO)_2GeEt_3$, m.p. 132°C dec., 415 mg. (33%) [ν (CO), (KBr), 1973, 1922 cm^{-1}; 2965-2840 (br), 1020-1005 (br), 800 (br) cm^{-1} (bands characteristic of Et_3Ge); 2.54 τ and 2.98 τ (intensity 2), (phenyl-phosphine groups); 8.76 τ (intensity 1), (triethylgermyl group). Found: C, 58.57; H, 4.49; P, 7.14%. $C_{44}H_{45}GeOP_2Rh$ requires C, 62.7; H, 5.34; P, 7.36%].

Attempts to recover more product by the removal of THF and the addition of methanol gave an impure compound which contained the Et_3Ge group but showed the band at 1922 cm^{-1} only as a shoulder of a much larger band at 1970 cm^{-1}. A small band at 2030 cm^{-1} was also observed in the spectrum. A third sample showed the complete absence of the Et_3Ge group but contained strong bands at 2053 cm^{-1} and 1968 cm^{-1}. A concentrate of the solvent showed the presence of Et_3GeBr and Et_6Ge_2O.

A similar reaction to the above using $(Ph_3P)_2Rh(CO)Cl$ (3.0 g., 4.39 mmole) and Me_3GeBr (1 ml, 7.79 mmole) gave an impure product, 1.89 g, which could not be satisfactorily purified. The infrared spectrum of the solid showed that it contained the trimethylgermyl group. [ν(CO) 1976, 1926 cm^{-1}; 817 cm^{-1} ρ(Me)].

25. The Reaction of $(Ph_3P)_2Rh(CO)Cl$ with Trimethylgermane

A good excess of trimethylgermane (3-4 liquid ml) was condensed onto $(Ph_3P)_2Rh(CO)Cl$ (362 mg., 0.52 mmole) in a breakseal tube and the tube evacuated and sealed. No visible signs of reaction were observed after one day at room temperature and so the tube was heated to 60°C. After two weeks at 60°C the solution was brown although not all of the yellow solid had dissolved. Work up yielded hydrogen (53.6 N.cc., 2.39 mmole), hexamethyldigermane (M, $Me_6{}^{146}Ge_2{}^+ = 236$) and a brownish solid. The solid was washed with a small amount of benzene to give a brown solution and unreacted $(Ph_3P)_2Rh(CO)Cl$, 305 mg. The solution was concentrated to give a small amount of sticky solid.

Mass spectroscopy showed that this contained polygermanium oxides. The mass spectra were confusing but the presence of the ions $Me_5{}^{146}Ge_2O^+$ (M = 237), $Me_5{}^{218}Ge_3O_3{}^+$ (M = 341), $Me_7{}^{290}Ge_4O_4{}^+$ (M = 459), $Me_9{}^{290}Ge_4O^+$ (M = 441), $Me_{11}{}^{364}Ge_5O^+$ (M = 545), $Me_{13}{}^{436}Ge_6O^+$ (M = 647) suggested that Me_6Ge_2O, $Me_6Ge_3O_3$, $Me_8Ge_4O_4$ and $Me_{14}Ge_6O$ were present in the mixture.

A repeat reaction in benzene solution in which the reactants were not heated for a prolonged period yielded only $(Ph_3P)_2Rh(CO)Cl$, hydrogen and hexamethyldigermane (M, $Me_6{}^{146}Ge_2{}^+$ = 236).

26. The Reaction of $(Ph_3P)_2Rh(CO)Cl$ with Triethylgermane

A mixture of triethylgermane (0.5 ml, 3.1 mmole) and $(Ph_3P)_2Rh(CO)Cl$ (498 mg., 0.72 mmole) in benzene (10 ml) was stirred under nitrogen at room temperature for one day and briefly refluxed (30 minutes) to give a brown solution. The solvent was removed and recrystallisation of the brown solution yielded only $(Ph_3P)_2Rh(CO)Cl$, 438 mg. A concentrate of the volatiles showed the presence of triethylgermane (M, $Et_3{}^{74}Ge^+$ = 161), hexaethyldigermane (M, $Et_6{}^{146}Ge_2{}^+$ = 320) and hexaethyldigermoxane (M, $Et_5{}^{146}Ge_2O^+$ = 307).

27. The Reaction of $(Ph_3P)_2Rh(CO)Cl$ with Hexamethyldigermane

Freshly distilled hexamethyldigermane (0.75 ml) and $(Ph_3P)_2Rh(CO)Cl$ (139 mg., 0.20 mmole) were heated together in benzene (2 ml) for two days. The yellow solution turned brown and removal of the volatiles left a brown solid from which only $(Ph_3P)_2Rh(CO)Cl$ was obtained. The volatiles were concentrated by removal of benzene and mass spectroscopy now showed the presence of Me_6Ge_2O (M, $Me_5{}^{146}Ge_2O^+$ = 237) in addition to Me_6Ge_2.

28. The Reaction of $(n\text{-}Pr_3P)_2Rh(CO)Cl$ with Trimethylgermane

Trimethylgermane (5-6 liquid ml) was condensed onto a degassed solution of $(n\text{-}Pr_3P)_2Rh(CO)Cl$ (760 mg., 0.20 mmole) in benzene (2 ml) and the tube was evacuated and sealed. After heating for three days at 80°C work up yielded hydrogen (15.18 N.cc., 0.68 mmole) and removal of the volatiles gave an oily yellow product. The infrared spectrum of the oil was identical to that of the starting material $\left[\nu(CO),\ 1960\ cm^{-1};\ \ \nu(Rh\text{-}Cl),\ 301\ cm^{-1}\right]$ and the ^1H n.m.r. spectrum showed no bands characteristic of the trimethylgermyl group. The mass spectrum of a concentrate of the volatiles showed the presence of hexamethyldigermane (M, $Me_6{}^{146}Ge_2{}^+ = 236$) and trimethylchlorogermane (M, $Me_2{}^{74}GeCl^+ = 139$).

29. The Reaction of $(Ph_3P)_3Rh(CO)H$ with Trimethylgermane

Trimethylgermane (2 liquid ml) was condensed onto $(Ph_3P)_3Rh(CO)H$ (706 mg., 0.77 mmole) in a breakseal tube. On warming to room temperature evolution of gas was observed as some of the solid went into solution. Work up, after six months at room temperature, yielded after fractionation: hydrogen (12.35 N.cc., 0.55 mmole), unreacted trimethylgermane, and hexamethyldigermane (M, $Me_6{}^{146}Ge_2{}^+ = 236$). The residual yellow solid (678 mg.) was shown to be a mixture of unreacted $(Ph_3P)_3Rh(CO)H$ and the known compound $\left[(Ph_3P)_2Rh(CO)\right]_2$ by infrared spectroscopy $\left[\nu(Rh\text{-}H),\ (KBr),\ 2040\ cm^{-1};\ \ \nu(CO),\ (KBr),\ 1971,\ 1928\ cm^{-1}\right]$.

30. The Reaction of $(Ph_3P)_3Rh(CO)H$ with Triethylgermane

Triethylgermane (0.1 ml, 0.62 mmole) was added to a solution of $(Ph_3P)_3Rh(CO)H$ (355 mg., 0.37 mmole) in benzene (8 ml). On heating to reflux temperature the orange-yellow solution turned red and heating was discontinued. The solution was concentrated and a small amount of petroleum ether was added to precipitate a yellow solid (306 mg.) which was identified by infrared spectroscopy as a mixture of unreacted $(Ph_3P)_3Rh(CO)H$ and the known compound $[(Ph_3P)_2Rh(CO)]_2$. $[\nu(Rh\text{-}H)$, (KBr), 2041, 2010 cm^{-1}; $\nu(CO)$, (KBr), 1974, 1927 $cm^{-1}]$. The band at 2041 cm^{-1} is absent in benzene solution.

31. The Reaction of $(Ph_3P)_3Rh(CO)H$ with Trimethylstannane

Trimethylstannane (2 liquid ml) was condensed from a vacuum line onto $(Ph_3P)_3Rh(CO)H$ (539 mg., 0.59 mmole) in a breakseal tube. On warming to room temperature a vigorous evolution of gas was observed and some of the yellow solid dissolved to give an orange-brown solution. Work up after four months at room temperature yielded hydrogen (129 N.cc., 5.8 mmole) and a sticky solid. The solid was washed repeatedly with petroleum ether to give an orange solution and a petrol insoluble yellow solid (170 mg.) which was shown to be unreacted $(Ph_3P)_3Rh(CO)H$ by its infrared spectrum. Removal of the solvent from the petroleum solution gave a tar which showed infrared bands due to the trimethylstannyl group and $\nu(CO)$, (KBr), at 1990 cm^{-1}. Attempts to recrystallise this material from benzene, petroleum ether, alcohol and diethyl ether yielded only very small amounts of a yellow solid. This also showed bands due to the trimethylstannyl group and a broad weak carbonyl band but did not contain triphenylphosphine. The solid gave a carbon analysis of only 15%. [Found: C, 15.38%; H, 4.30%].

32. The Reaction of $(Ph_3P)_2Rh(CO)Cl$ and an Excess of Trichlorogermane

Trichlorogermane (0.5 ml, 965 mg., 5.36 mmole) was added under

nitrogen to $(Ph_3P)_2Rh(CO)Cl$ (516 mg., 0.75 mmole) in benzene (2 ml). An immediate reaction took place at room temperature with the evolution of a gas. The mixture separated into a lower orange-yellow layer, which contained the rhodium complex, and a colourless upper layer. After stirring for one hour the volatile materials were removed under vacuum to leave a tar which on further pumping gave a yellow-orange solid. The solid was insoluble in petroleum ether, benzene or diethylether but became tarry when brought into contact with them. It was extremely soluble in acetone but attempts to recrystallise it from the solvent failed. Even the slow evaporation of solvent by a nitrogen stream yielded only a yellow tar. The compound was finally precipitated as a yellow tar by the addition of diethylether to the acetone solution. The tar was thoroughly washed with ether and pumped to dryness to give a yellow-orange solid (958 mg.) m.p. 112-114°C. No triphenylphosphine was found in the ether washings. The infrared spectrum of the solid showed bands characteristic of the triphenylphosphonium ion at 2401 cm^{-1}, 1114 cm^{-1}, 888 cm^{-1}, and 723 cm^{-1} (KBr), and to the trichlorogermyl group at 368 cm^{-1} (CsI). No bands indicative of bridged rhodium-chlorine bonds were observed. A strong band at 2099 cm^{-1} (KBr) could be assigned to $\nu(CO)$. Analysis did not distinguish between the possible formulae $[Ph_3PH]_2[Rh(CO)(GeCl_3)_5]$, $[Ph_3PH]_2[Rh(CO)(GeCl_3)_4Cl]$ and $[Ph_3PH][Ph_3PRh(CO)(GeCl_3)_4]$. All of these formulae would fit the spectral evidence although the former is perhaps the most likely. The possibility of solvation of the complex also exists. [Found: C, 33.44; H, 2.77; Cl, 29.46%.
$C_{37}H_{32}Cl_{15}Ge_5OP_2Rh$ requires C, 28.59; H, 2.06; Cl, 34.29%
$C_{37}H_{32}Cl_{13}Ge_4OP_2Rh$ requires C, 31.51; H, 2.27; Cl, 32.75%
$C_{37}H_{31}Cl_{12}Ge_4OP_2Rh$ requires C, 32.35; H, 2.25; Cl, 31.04%]

33. The Reaction of $(Ph_3P)_2Rh(CO)Cl$ with Trichlorogermane

(a) 1:1

Trichlorogermane (97 mg., 0.54 mmole) in benzene (40 ml) was added slowly to a solution of $(Ph_3P)_2Rh(CO)Cl$ (373 mg., 0.54 mmole) in benzene (60 ml). The solution was stirred for two hours before solvent was removed to give a yellow solid. This was shown to be a mixture of $(Ph_3P)_2Rh(CO)Cl$ and a rhodium(III) compound by its infrared spectrum and analysis. Attempted recrystallisation from benzene produced no separation of the two species. [ν(CO), (KBr), 1990, 1970 cm^{-1}, $(Ph_3P)_2Rh(CO)Cl$; ν(CO), (KBr), 2090 cm^{-1} (Rh^{III} species); ν(Ge-Cl), (CsI), 370 cm^{-1}; ν(Rh-Cl), (CsI), 308 cm^{-1}. Found: C, 54.46; H, 6.15; Cl, 11.0%. $(Ph_3P)_2Rh(CO)Cl$, $C_{37}H_{30}ClOP_2Rh$ requires C, 64.30; H, 4.34; Cl, 5.14%. $(Ph_3P)_2Rh(CO)HCl(GeCl_3)$, $C_{37}H_{31}Cl_4GeOP_2Rh$ requires C, 50.99; H, 3.56; Cl, 16.31%. $(Ph_3P)_2Rh(CO)Cl(GeCl_3)_2$, $C_{37}H_{30}Cl_7Ge_2OP_2Rh$ requires C, 42.34; H, 2.86; Cl, 23.7%.].

(b) 1:2

Trichlorogermane (193 mg., 1.08 mmole) in benzene (25 ml) was added dropwise to $(Ph_3P)_2Rh(CO)Cl$ in benzene (25 ml). The solution was filtered from a small amount of tar which had formed and was pumped to dryness. The infrared spectrum of the yellow solid showed that it was again a mixture of two products but that the concentration of the Rh^{III} species had increased. The infrared spectrum of the tar showed that it contained a phosphonium cation.

[yellow solid: ν(CO), (KBr), 1990, 1970 cm^{-1}, $(Ph_3P)_2Rh(CO)Cl$; ν(CO), (KBr), 2095 cm^{-1} (Rh^{III} species); ν(Ge-Cl), (CsI), 365 cm^{-1}; ν(Rh-Cl), (CsI), 308 cm^{-1}.

yellow tar: ν(CO), (KBr), 2100 cm^{-1}; ν(Ge-Cl), (CsI), 365 cm^{-1};

bands characteristic of $[Ph_3PH]^+$ 2395, 1110, 880, 720 cm^{-1}]

34. The Reaction between $(Ph_3P)_3Rh(CO)H$ and Trichlorogermane

(a) 1:1

Trichlorogermane (97 mg., 0.54 mmole) in benzene (25 ml) was added slowly to a solution of $(Ph_3P)_3Rh(CO)H$ (495 mg., 0.54 mmole) in benzene (25 ml). The solution was stirred for one hour, decanted from a small amount of orange tar which had formed and the solvent removed to give a yellow solid. Extraction of the solid with petrol gave triphenylphosphine (90 mg.). The infrared spectrum of the yellow solid suggested that it was a mixture. [ν(CO), (KBr), 1990, 1970 cm^{-1} (Rh^{I} species; ν(CO), (KBr), 2070 cm^{-1} (Rh^{III} species); ν(Ge-Cl), CsI), 360 cm^{-1}]. The infrared spectrum of the tar showed bands characteristic of the triphenylphosphonium ion.

(b) 1:2

Trichlorogermane (193 mg., 1.08 mmole) in benzene (25 ml) was added to $(Ph_3P)_3Rh(CO)H$ (495 mg., 0.54 mmole) in benzene (25 ml). Work up, as before, gave a similar mixture with an increase in the concentration of the Rh^{III} species.

35. The Reaction between Rhodium Trichloride and Trimethylammonium Trichlorogermanite

Trimethylammonium trichlorogermanite (3.32 gm., 13.9 mmole) was added to a solution of rhodium trichloride trihydrate (536 mg., 2.03 mmole) in a mixture of concentrated hydrochloric acid (50 ml) and distilled water (20 ml). The dark red solution turned orange on reflux. Reduction of the volume of the solution by distillation gave bright orange needles which were filtered, washed with ether and dried.

Analysis of the compound indicated the formula $[Me_3NH]_3[Rh(GeCl_3)_3Cl_3]$ which fits spectral observations, yield 1.52 g. (55%) m.p. 255°C dec., [ν(Ge-Cl), (CsI), 360 cm^{-1}. Found: C, 11.72; H, 3.01; Cl, 46.12; N, 4.78%. Required for $C_9H_{30}Cl_{12}Ge_3N_3Rh$: C, 11.65; H, 3.24; Cl, 45.96; N, 4.53%].

36. The Reaction of Rhodium Trichloride with Trichlorogermane and Triphenylphosphine

Trichlorogermane (309 mg., 1.72 mmole) in concentrated hydrochloric acid (6 ml) was added dropwise to a solution of rhodium trichloride trihydrate (411 mg., 1.56 mmole) in ethanol (6 ml). On the addition of trichlorogermane the original Burgundy red solution lightened in colour to red-orange. The solution was stirred at room temperature for thirty minutes and further diluted by the addition of ethanol (10 ml) and concentrated hydrochloric acid (10 ml). The addition of triphenylphosphine (1.23 g., 4.69 mmole) precipitated an orange-yellow solid. The suspension was stirred for a further two days and briefly refluxed before filtration. The solid was washed with conc. hydrochloric acid, ether, and petroleum ether. The infrared spectrum of the solid showed bands attributable to the triphenylphosphonium ion at 2382 cm^{-1}, 1115 cm^{-1}, 885 cm^{-1} and 720 cm^{-1} (KBr) and to the trichlorogermyl group at 362 cm^{-1} (CsI). Bands indicative of bridging Rh-Cl groups were absent from the spectrum. Spectral and analytical data indicated that the compound had the composition $[Ph_3PH]_3[Rh^{III}(GeCl_3)_2Cl_4]$, m.p. 137-139°C dec., 660 mg. (55%). [Found: C, 46.13; H, 3.69; Cl, 22.35%. Required for $C_{54}H_{48}Cl_{10}Ge_2Rh$: C, 46.55; H, 3.45; Cl, 25.48%].

37. The Reaction between $(Ph_3P)_2Rh(CO)Cl$ and Caesium Trichlorogermanite

(a) A solution of $(Ph_3P)_2Rh(CO)Cl$ (520 mg., 0.75 mmole) in benzene (40 ml) was refluxed for three days with caesium trichlorogermanite (4.72 mg., 1.51 mmole). The solution was filtered and the benzene removed to give unreacted $(Ph_3P)_2Rh(CO)Cl$, 490 mg. [ν(CO), (KBr), 1970 cm^{-1}].

(b) $(Ph_3P)_2Rh(CO)Cl$ (285 mg., 0.41 mmole) and caesium trichlorogermanite (503 mg., 1.61 mmole) were refluxed together in tetrahydrofuran (20 ml). The yellow solution turned orange after only five minutes. After refluxing for four hours the solvent was removed and the residual orange solid extracted with benzene. Addition of petroleum ether to the benzene extract gave trichlorogermyl(carbonyl)bis(triphenylphosphine)rhodium(I), $(Ph_3P)_2Rh(CO)GeCl_3$, 196-200°C dec., 116 mg. (34%). [ν(CO),(KBr), 1978 cm^{-1} (br); ν(Ge-Cl),(CsI), 385 cm^{-1}. Found: C, 50.29; H, 4.26; Cl, 12.4%. $C_{36}H_{30}Cl_3GeP_2Rh$ requires C, 53.23; H, 3.59; Cl, 12.7%]. The benzene-insoluble yellow solid also contained a rhodium complex as well as unreacted $CsGeCl_3$ but this could not be isolated.

38. The Reaction of $(Ph_3P)_2Rh(CO)Cl$ with Trimethylammonium Trichlorogermanite

$(Ph_3P)_2Rh(CO)Cl$ (304 mg., 0.44 mmole) and trimethylammonium trichlorogermanite, $Me_3NHGeCl_3$, (211 mg., 0.88 mmole) were refluxed together in benzene (30 ml) and after the first few minutes of reflux an orange species precipitated from the solution. The reaction was refluxed for a further four days and the orange solid filtered, thoroughly washed with benzene and dried in vacuo, yield 226 mg. The solvent was removed from the yellow solution to give unreacted $(Ph_3P)_2Rh(CO)Cl$.

The infrared spectrum of the orange solid showed the complete absence of bands due to triphenylphosphine ligands but bands due to the Me_3NH, CO, and $GeCl_3$ groups were present. The compound was insoluble or only sparingly soluble in most of the common solvents but could be reprecipitated as a yellow solid by the addition of ether to a nitromethane solution. The infrared and analytical data suggest the formulation $[Me_3NH]_2[Rh(CO)(GeCl_3)_2Cl]$, m.p. 200-204°C. [$\nu$(CO), KBr, 1970 cm^{-1}; ν(Ge-Cl), 362 cm^{-1}; ν(Rh-Cl), 310 cm^{-1}. Found: C, 15.17, 11.16; H, 3.81, 3.60; Cl, 36.06%. $C_7H_{20}Cl_7Ge_2N_2ORh$ requires C, 13.03; H, 3.10; Cl, 38.54].

39. The Reaction of $[(C_8H_{12})RhCl]_2$ with Trichlorogermane

Trichlorogermane (193 mg., 1.08 mmole) in benzene (10 ml) was added slowly to a solution of $[(C_8H_{12})RhCl]_2$ (381 mg., 0.77 mmole) in benzene (30 ml). After one hour the solution was filtered from the orange-brown crystals which had formed. Removal of solvent from the yellow filtrate gave a yellow solid (257 mg.) which was identified as unreacted $[(C_8H_{12})RhCl]_2$ by infrared spectroscopy. The infrared and mass spectra of the orange-brown solid (203 mg.) indicated that it contained $(C_8H_{12})RhH(GeCl_3)Cl$ although a cyclopentadienyl species was also present as an impurity. Attempted recrystallisation from THF resulted in the decomposition of the sample and only $[(C_8H_{12})RhCl]_2$ could be recovered from the solution.
[ν(Rh-H), KBr, 2000 cm^{-1}; ν(Ge-Cl), CsI, 370 cm^{-1}; M, $C_8H_{13}Cl_4GeRh^+$ = 426. Found: C, 25.71; H, 3.32%. Required for $C_8H_{13}Cl_4GeRh$: C, 22.50; H, 3.05%].

40. The Reaction of $[(C_8H_{12})RhCl]_2$ with Trichlorosilane

Trichlorosilane (1.34 g., 9.9 mmole) was added to a solution of $[(C_8H_{12})RhCl]_2$ (650 mg., 1.32 mmole) in benzene (30 ml). Removal of solvent after five hours gave a tarry solid which was washed with light petroleum to give a yellow solid (1.25 g.). The infrared spectrum showed no hydride stretching frequency but showed the characteristic absorption bands of the cyclooctadiene and trichlorosilyl groups. The mass spectrum did not show a molecular ion but the $(C_8H_{12})Rh(SiCl_3)_2^+$ ion was present M, $C_8H_{12}Cl_6RhSi_2^+$ = 479. The analysis suggested that the compound should be formulated as $(C_8H_{12})Rh(SiCl_3)_2Cl$. [Found: C, 18.45; H, 2.78; $C_8H_{12}Cl_7Si_2Rh$ requires C, 18.64; H, 2.33%].

41. The Reaction between π-$C_5H_5RhC_8H_{12}$ and Trichlorosilane

Trichlorosilane (5 ml) was condensed onto π-$C_5H_5RhC_8H_{12}$ (330 mg., 1.20 mmole) in a breakseal apparatus equipped with a glass sinter. On warming to room temperature the yellow crystals dissolved to give a yellow solution from which a dark brown solid quickly began to precipitate. Over a period of thirty minutes the colour of the solid lightened to give a yellow-orange precipitate and solution. The solution was filtered and the precipitate washed by back-distillation of trichlorosilane. Work up yielded no hydrogen. The precipitate was only very sparingly soluble in the common solvents and was extracted with benzene. The solvent was removed from the benzene extract and the brown solid was washed with light petroleum and dried in vacuo. The infrared spectrum of the solid contained no ν(Rh-H) band but showed bands characteristic of the C_5H_5, C_8H_{14} and $SiCl_3$ groups. The mass spectrum showed a molecular ion (M, $C_{13}H_{19}Cl_6Si_2Rh^+$ = 546) which identified the compound as bis(trichlorosilyl)cyclopentadienyl-cyclooctene rhodium (III), π-$C_5H_5Rh(SiCl_3)_2.C_8H_{14}$, darkens at 140°C. [Found: C, 26.09; H, 3.20%. $C_{13}H_{19}Cl_6Si_2Rh.\frac{1}{3}HSiCl_3$ requires C, 26.34; H, 3.21%].

42. The Reaction between π-$C_5H_5Rh(C_2H_4)_2$ and Trichlorosilane

The addition of trichlorosilane (4.02 g., 29.7 mmole) to π-$C_5H_5Rh(C_2H_4)_2$ (290 mg.,1.29 mmole) gave an immediate exothermic reaction with the evolution of a gas. Removal of trichlorosilane left a brown solid which was only sparingly soluble in organic solvents. The compound was purified by extraction with benzene. The infrared spectrum of the solid showed bands due to the trichlorosilyl group in addition to those due to coordinated ethylene and the cyclopentadienyl group. No rhodium-hydrogen stretching frequency was observed. The mass spectrum of the solid showed a molecular ion for π-$C_5H_5Rh(SiCl_3)_2C_2H_4$ (M, $C_7H_9Cl_6Si_2Rh^+$ = 464). The compound darkened without melting at 150°C.

43. The Reaction of π-$C_5H_5Rh(C_8H_{12})$ with Trimethylgermane

Trimethylgermane (0.5 liquid ml) and benzene (3 ml) were condensed onto π-$C_5H_5Rh(C_8H_{12})$ (376 mg., 1.36 mmole) in a breakseal tube. The tube was frozen to -196°C and evacuated before seal off. Heating at 50°C for one month produced no visible sign of reaction and work up yielded only hydrogen (1.33 N.cc., 0.06 mmole), unreacted trimethylgermane and π-$C_5H_5Rh(C_8H_{12})$ (344 mg.).

44. The Reaction between π-$C_5H_5Rh(CO)Ph_3P$ and Trimethylgermane

π-$C_5H_5Rh(CO)Ph_3P$ (344 mg., 0.75 mmole) was placed in a breakseal tube and benzene (3 ml) and trimethylgermane (0.5 liquid ml) were condensed into the tube. The tube was sealed and heated at 50°C for one month. Work up yielded only hydrogen (0.81 N.cc., 0.4 mmole), unreacted trimethylgermane and unreacted π-$C_5H_5Rh(CO)Ph_3P$ (328 mg., 95%).

45. The Reaction of $(Ph_3P)_2Rh(CO)Cl$ with bis-(trimethylsilyl)mercury

Bis-(trimethylsilyl)mercury (740 mg., 2.14 mmole) in benzene (10 ml) was dripped slowly into a solution of $(Ph_3P)_2Rh(CO)Cl$ (1.40 g., 2.03 mmole) in benzene (60 ml) at room temperature. A vivid dark red colouration formed immediately and the solution was stirred for three hours. The solution was filtered from the small amount of mercury which had been deposited and solvent was removed to give a red-brown solid. The infrared spectrum of this solid showed bands characteristic of the trimethylsilyl group and also a carbonyl band at 1970 cm^{-1} (KBr). Attempted recrystallisation from benzene gave a small amount of $(Ph_3P)_2Rh(CO)Cl$ and eventually led to the complete decomposition of the sample. The infrared spectrum of the residue showed a strong band at 1185 cm^{-1} which could be assigned to ν(PO) of triphenylphosphine oxide.

46. The Reaction of $(Ph_3P)_3RhCl$ with bis-(trimethylsilyl)mercury

Bis-(trimethylsilyl)mercury (410 mg., 1.2 mmole) in benzene (10 ml) was added slowly to a solution of $(Ph_3P)_3RhCl$ (840 mg., 0.91 mmole) in benzene (50 ml) without any noticeable colour change. The solution was stirred for three days at room temperature to give a red-brown solid which was filtered from the solution (330 mg.). The solid was contaminated by a small amount of mercury but the infrared spectrum showed that it was $\left[(Ph_3P)_2RhCl\right]_2$. On standing the solution yielded more orange-pink solid (120 mg.) which was also identified as $\left[(Ph_3P)_2RhCl\right]_2$ by analysis. [Found: C, 65.66; H, 5.08%. $C_{52}H_{60}Cl_2P_4Rh$ requires C, 65.4; H, 4.8%]. Removal of the solvent yielded a brown intractable solid which could not be purified. The infrared spectrum indicated that it did not contain the trimethylsilyl grouping.

47. Attempted Preparation of $(PF_3)_4RhGeEt_3$

A solution of $\left[(PF_3)_2RhCl\right]_2$ (810 mg., 1.3 mmole) in dried degassed diethyl ether (85 ml) was added under nitrogen to 1% potassium amalgam (1g. in 100g. mercury) in a flask equipped with "Rotaflo" taps. The system was frozen and evacuated. An excess of trifluorophosphine (600 N.cc., 26.8 mmole) was condensed into the flask which was sealed and shaken for three days to form the potassium salt $(PF_3)_4Rh^-K^+$.

The flask was opened under nitrogen and the yellow solution filtered from the potassium amalgam into a Schlenk. Triethylbromogermane (560 mg., 2.3 mmole) was added to the filtrate from a syringe. The colour of the solution did not change but a slight clouding of the solution was observed. Filtration followed by concentration of the solution under vacuum led to a darkening of the solution and cooling did not give any crystals. Removal of the solvent gave an intractable brown tarry material which could not be purified by recrystallisation or washing with other solvents. [Infrared data, (KBr): 2950 (m), 2920 (m), 2870 (m), 1330 (sh), 1320 (m), 1193 (m), 1142 (m), 800 (s,br), 525 (sh), 500 (s), 375 (m) cm^{-1}].

48. The Reaction of $[\pi\text{-}C_5H_5Mo(CO)_3]Na$ with $(Ph_3P)_2Rh(CO)Cl$

Freshly cracked cyclopentadiene (0.8g., 12 mmole) was added to a stirred suspension of sodium (0.24 g., 10 mmole) in tetrahydrofuran (THF) (20 ml). The suspension was stirred for 18 hours to give a pale pink solution of cyclopentadienylsodium. Molybdenum hexacarbonyl (2.63 g., 10 mmole) was added and the mixture refluxed for ten hours. Upon the addition of $Mo(CO)_6$ the solution turned yellow and the colour deepened on reflux.

A portion of the solution (2 ml, 1 mmole) was added under nitrogen to a solution of $(Ph_3P)_2Rh(CO)Cl$ (690 mg., 1 mmole) and an immediate colour change from yellow to orange-brown was apparent. After stirring for 14 hours the solvent was removed to give a red-brown solid. This material was completely insoluble in cyclohexane but could be extracted with benzene to give a brown solution. Concentration of the benzene solution did not give any crystals and the solvent was again removed to give a brown solid (672 mg.). The compound could not be properly recrystallised from benzene or THF and was recovered as a brown powder by the slow addition of ether to a THF solution.

The infrared spectrum of the solid showed four strong bands which could be assigned to $\nu(CO)$ at 1967, 1876, 1777, and 1750 cm^{-1}. In addition to these the spectrum also showed the presence of the cyclopentadienyl $[\gamma(C\text{-}H)$, 810 $cm^{-1}]$ and triphenylphosphine groups. The compound was too insoluble for ^1H n.m.r. characterisation and analysed as C, 62.26; H, 4.36%. $(Ph_3P)_2Rh(CO)Mo(\pi\text{-}C_5H_5)(CO)_3$, $C_{45}H_{35}MoO_4P_2Rh$ requires C, 60.0; H, 3.89%.

Experimental Methods

Nitrogen

All reactions and operations involving air-sensitive compounds were carried out in an atmosphere of dry, oxygen-free nitrogen. Commercial "white spot" nitrogen was further purified by passing the gas through copper turnings at 400°C, to remove oxygen, and then through a column of molecular sieve and a spiral trap at -196°C to remove water.

Solvents

Benzene, toluene, petroleum ether, diethyl ether and cyclohexane were redistilled from phosphorus pentoxide and dried by standing over sodium wire for one week. Methyl and ethyl alcohol were dried by treatment with magnesium activated with iodine. The dried solvents were distilled and stored over molecular sieve. Acetone was dried using molecular sieve. Tetrahydrofuran was distilled from lithium aluminium hydride immediately before use.

Analysis

Analyses were carried out in the microanalytical laboratories of Durham and Queen's Universities or by Drs. Weiler and Strauss, Banbury Road, Oxford.

Infrared Spectra

Spectra in the region 2.5-25μ were recorded on either a Grubb-Parson's Spectromaster, G.S.2A, or Perkin Elmer 457 spectrophotometer. Solids were examined as pressed discs in KBr or as Nujol Mulls. The region 20-50μ was recorded on either a Grubb-Parson's DM2 or DM4 spectrophotometer. The solids were generally examined as pressed discs in CsI.

^{1}H Nuclear Magnetic Resonance Spectra

The spectra were recorded on either a Perkin-Elmer R10 or a Varian H. A. 100 spectrometer.

Mass Spectra

These were recorded on an A.E.I. M. S. 9 instrument.

Preparation of Starting Materials

Most starting materials could be prepared by standard literature methods (see Table 14) or were available in the department.

Table 14

Compound	Ref.	Compound	Ref.
$(Ph_3P)_3RhCl$	9	$(Ph_3P)_2Rh(CO)Cl$	91
$(Ph_3As)_3RhCl$	16	$(Ph_3P)_3Rh(CO)H$	108
$(Ph_3P)_4RhH$	44	$[(C_8H_{12})RhCl]_2$	122
$(MePh_2P)_3RhCl$	41	$[(C_2H_4)_2RhCl]_2$	115
$(Pr_3P)_2Rh(CO)Cl$	90	$[(C_8H_{14})_2RhCl]_2$	117
$[(dmpe)_2Rh]Cl$	50	π-$C_5H_5Rh(C_8H_{12})$	122
π-$C_5H_5Rh(C_2H_4)_2$	118		

1. Bis(1,2-bisdiphenylphosphinoethane)rhodium(I) chloride

1,2-bisdiphenylphosphinoethane (1.33 g., 3.34 mmole) was added to a solution of $(Ph_3P)_3RhCl$ (790 mg., 0.854 mmole) in benzene (25 ml) and the solution refluxed. The yellow bis-chelate rhodium(I) complex precipitated from the solution and was filtered, washed with ether and dried in vacuo.

2. π-Cyclopentadienyl(triphenylphosphine)carbonyl rhodium(I)

A solution of cyclopentadienylsodium in tetrahydrofuran (3 ml., 0.50 molar) was added to a suspension of $(Ph_3P)_2Rh(CO)Cl$ in THF (20 ml) to give an orange solution. Orange crystals formed and these were collected and recrystallised from benzene to give $(Ph_3P)Rh(CO)(\pi$-$C_5H_5)$, 540 mg., 83%.

3. μ-Dichlorotetra(trifluorophosphine)dirhodium(I)[58,59]

Trifluorophosphine[211] (600 N.cc., 26.8 mmole) was condensed into a "Rotaflo" flask containing a suspension of $[(C_8H_{14})RhCl]_2$ (3.26g., 6.56 mmole) in diethylether (100 ml). An immediate reaction took place to give a red solution. Removal of the ether gave a red solid which was sublimed to give dark-red needles of $[(PF_3)_2RhCl]_2$, 2.10g., 51%.

4. Organogermanium compounds

These were all prepared by standard literature methods[149,212]. Tetraorganogermanes were prepared by reacting an excess of Grignard reagent with germanium tetrachloride. Trimethyl- and triethylbromogermane were prepared by refluxing bromine with the tetra-alkylgermane in n-propyl bromide. The trialkylgermanes, Me_3GeH and Et_3GeH, were prepared by reduction of the corresponding trialkylbromogermane with lithium aluminium hydride in dioxane or di-n-butyl ether.

5. Trichlorogermane

This was prepared by the method of Petrov et al[213]. A fast stream of dried hydrogen chloride was passed over a mixture of powdered germanium (50g.) and finely divided copper (10g.) heated in a silica tube to 450°C. Trichlorogermane was formed and was collected in a cooled receiver (-78°C). A fast flow of hydrogen chloride was essential for the reaction to occur at a reasonable rate. The yield of redistilled product was 98g. (80%).

6. Caesium Trichlorogermanite[214]

Germanium tetrachloride (9.4g., 5.1 ml.) was added to a stirred mixture of H_3PO_2(23.3g.) and 3M hydrochloric acid (60 ml). The solution was heated to 85°C for five hours, and then allowed to cool to 50°C before the addition of caesium iodide (11.9g.). A fluffy white precipitate formed and filtration gave white caesium trichlorogermanite (11.2g., 78%).

7. Trimethylammonium trichlorogermanite[215].

This was prepared in a similar manner to $CsGeCl_3$. Germanium tetrachloride (14g.) was reduced by hypophosphorous acid (35g.) in 3M hydrochloric acid (50 ml) and the complex precipitated by the addition of trimethylammonium chloride (6.23g.). The complex was filtered and dried in vacuo, yield 15.7g., 88%.

The compound is more soluble in benzene or tetrahydrofuran than its caesium analogue.

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