The crystal structures of some inorganic complexes containing metal-hydrogen and metal-germanium bonds

M. L. Schneider

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THE CRYSTAL STRUCTURES OF SOME INORGANIC COMPLEXES CONTAINING METAL-HYDROGEN AND METAL-GERMANIUM BONDS

by

M.L. SCHNEIDER

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PREFACE

I wish to express my sincere thanks to Dr. H.M.M. Shearer, under whose supervision this work was conducted, for his invaluable encouragement and guidance. I would also like to thank Professor G.E. Coates and Professor F. Glockling for the interest they have taken in this work. In addition, I would like to thank Dr. N.A. Bell for the preparation of the beryllium compound, and to Professor Glockling's co-workers for the preparation of the transition metal compounds, especially Mr. A. McGregor for providing a sample of the nickel complex.

MEMORANDUM

The work described in this thesis was carried out in the University of Durham between October 1966 and July 1969. This is the original work of the author, except where acknowledged by reference, and has not been submitted for any other degree.

Part of this work has been the subject of a paper presented at the Fourth International Conference on Organometallic Chemistry, Bristol, 1969.

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$(Ph_3P)Ni(C_5H_5)GeCl_3 \cdot \frac{1}{2}C_6H_6$

$HBe[N(Me)CH_2CH_2NMe_2]$

SUMMARY

X-ray diffraction techniques have been used to examine the structural chemistry of four compounds containing metal-hydrogen and metal-germanium bonds. Three of the structures were solved by the heavy atom method, and one by the symbolic addition method. The parameters were refined with three-dimensional data by the method of least squares. With the exception of the palladium compound, the data was collected on a four-circle diffractometer.

$(Et_3P)_2Pd(H)Cl$ is the first complex containing a Pd-H bond to be isolated. The compound crystallises in the space group $P2_1/c$ with the cell dimensions a = 9·07, b = 13·82, c = 14·48Å, β = 92.9°. The palladium coordination is square planar with the chlorine trans to the hydrogen (not observed in the X-ray study) and the two phosphines situated in the two remaining sites. The Pd-Cl bond length (2·427 ± 0·005Å) can be compared to the Pt-Cl bond length of 2·422Å in trans-$(Ph_2EtP)_2Pt(H)Cl$, and the Pd-Cl distance of 2·299Å in the $PdCl_4^{2-}$ ion. This is indicative of the strong trans influence of the hydride.

$(Ph_3P)_2Ir(CO)(H)_2GeMe_3$ crystallises in the space group $P2_1/c$ with the cell dimensions a = 13·63, b = 11·04, c = 26·07Å, β = 92·5°. The iridium coordination is octahedral with the two phosphine groups cis to each other; one is trans to a hydrogen, and the other trans to the germyl

group, in agreement with the proposed structure. The Ir-Ge bond length is 2·484 ± 0·002Å. With two cis triphenylphosphines, and a relatively unoccupied hydride region, a distortion of the angle at iridium is observed.

$(C_5H_5)Ni(Ph_3P)GeCl_3$ crystallises in the space group C2/c, with the unit cell dimensions a = 15·08, b = 11·89, c = 29·11Å, and β = 93·38°. This is the first compound containing a Ni-Ge bond which has been isolated. There are indications that the cyclopentadienyl ligand contains localised bonding, thus the coordination at nickel can be postulated to be tetrahedral, with the ring occupying two sites. The Ni-Ge bond length is 2·248 ± 0·001Å.

$HBe[N(Me)CH_2CH_2NMe_2]$ is dimeric in the solid state. The space group is considered to be $P\bar{1}$, with one dimer in the unit cell, having the dimensions a = 7·44, b = 6·05, c = 8·24Å, α = 104·0, β = 95·7, γ = 97·0°. The structure was solved by the symbolic addition method, and the present value of the R factor is 0·106. The molecular configuration is similar to that found in the analogous zinc compound.

Chapter 1

Direct Methods in the Solution of the Phase Problem

From the intensity data collected in a crystallographic study, only the magnitudes of the structure factors are known. The phase problem is the elucidation of these phases, either by direct or indirect methods. In early work, trial-and-error methods were employed, which involved postulating an atomic arrangement, then checking to see if it was correct. This meant that any information about the structure was used and required a large amount of experience (Lipson and Cochran, 1953a). Following from previous work (Zernike and Prins, 1927), Patterson (1934, 1935) developed a Fourier method in which the vectors between atoms in the unit cell are obtained. Harker (1936) pointed out that, in certain planes of the Patterson function, information can be obtained from the vectors between atoms related by the symmetry elements of the space group. Later, based on previous work (Wrinch, 1939), a number of workers independently developed superposition methods. These methods, in general, require some previous knowledge of the structure.

It was found that a heavy atom in the structure, the position of which could be deduced from the Patterson function, would phase those structure factors to which it contributed (Robertson and Woodward, 1937). Lipson and Cochran (1953b) pointed out that the method works best when the squares of the atomic numbers of the light atom is about equal to those of the heavy atoms. If it is impossible to incorporate a heavy atom into the molecule, then the previous or other Fourier techniques must be used. For simple structures this may be feasible, but for more complex ones it can be difficult or impossible. Because of this problem researchers have attempted to develop direct methods in order to obtain the phases directly from the structure factors, or related quantities.

The first attempt at the direct solution of the phase problem, which has led to the present techniques, was the development of the Harker-Kasper inequalities (Harker and Kasper, 1948). For this work, a unitary structure factor, U_H, was defined by

$$U_H = F_H \Big/ \sum_{j=1}^{N} f_j(H) \qquad (1.1)$$

H defines the indices hkl

N is the number of atoms in the unit cell and

f_{Hj} is the scattering factor for the j^{th} atom.

Inequalities were derived for all 230 space groups, so it is impossible to discuss them in any detail. The method of application was to derive a consistent set of phases for the structure factors. For example in the space groups with the symmetry element $\bar{1}$, the following relationships can be derived,

$$U_H^2 \leq \tfrac{1}{2}(1 + U_{2H}) \qquad (1.2)$$

and for the sum of two unitary structure factors U_H and U_K

$$(U_H + U_K)^2 \leqslant \{1 + s(H)s(K)s(\overset{H}{\cancel{K}} + K)|U_{H - K}|\}\ \{1 + s(H)s(K)s(H - K)|U_{H - K}$$

where (1.3)

s(H) is the sign of the structure factor F_H

Later workers expanded the range of inequalities, with the final extension to the Karl-Hauptmann inequalities (Karle and Hauptmann, 1950) which was used as a basis for their later work.

The step from inequalities to equalities came with the work of Sayre (1952), which was interpreted and expanded by Cochran (1952) and Zachariasen (1952). The method was based on an analysis of the expression

$$f_s = \int_{u=-\infty}^{\infty} \rho_u \cos 2uS(du) = (\rho o/2)\exp(-\tfrac{1}{2}\pi S^2)$$

where ρ_o = is the electron density at the atomic centre,

ρ_u = is the electron density at a distance u from the centre,

assuming a Gaussian distribution

$$\rho_u = \rho_o \exp(-2\pi u^2)$$

and $S = 2\sin\theta/\lambda$

The basic formula developed was

$$s_{H+K} = s_H\, s_K \qquad (1.4)$$

The method as used by Zachariasen (1952) is in many ways similar to the technique used in the symbolic addition method. He made use of the strongest set of reflections, and employed symbols to represent the signs of structure factors. In this way he was able to determine the signs of 168 U's, and thus effect a solution of the structure of Metaboric acid.

In an examination of the relationships between strong structure factors, Karle and Hauptmann arrived at a method similar to Zachariasen's. Their method was to examine the joint probability distributions (Karle and Hauptmann, 1953). Rather than using unitary structure factors, they employed the normalised structure factor, E,

$$|E_H|^2 = \frac{|F_H|^2}{\epsilon \sum f_{\underline{i}}^2(H)} \qquad (1.5)$$

where ϵ is a factor which takes into account the space group extinctions.

This type of structure factor has a number of properties, among them a distribution which is indicative of the centric, or acentric space groups. From their work the following distributions are found:

	centric	acentric
$<\|E\|>$	0·798	0·886
$<\|E\|^2>$	1·000	1·000
$<\|E^2-1\|>$	0·968	0·736
$\|E\|>3$	0·3%	0·01%
$\|E\|>2$	5·0%	1·8%
$\|E\|>1$	32·0%	37·0%

The centric space groups form the simplest case. For these space groups the structure factor reduces to the form

$$F_{hkl} = 2\sum_{j=1}^{N/2} f_j \cos 2\pi(hx_j + ky_j + lz_j) \qquad (1.6)$$

If the origin is shifted to one of the eight centres of symmetry in the unit cell, say to $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ the position of an atom at x,y,z is, in the new system, $x-\frac{1}{2}$, $y-\frac{1}{2}$, $z-\frac{1}{2}$. The structure factor (1.6) now becomes:

$$\begin{aligned}
(F_{hkl})_{\frac{1}{2},\frac{1}{2},\frac{1}{2}} &= 2\sum f_j \cos 2\pi[h(x_j-\tfrac{1}{2}) + k(y_j-\tfrac{1}{2}) + l(z_j-\tfrac{1}{2})] \\
&= 2\sum f_j \cos 2\pi[hx_j + ky_j + lz_j - \tfrac{1}{2}(h + k + l)] \\
&= 2\sum f_j [\cos 2\pi(hx_j + ky_j + lz_j)\cos\pi(h + k + l) + \\
&\qquad \sin 2\pi(hx_j + ky_j + lz_j)\sin\pi(h + k + l)] \\
&= 2\sum f_j \cos 2\pi(hx_j + ky_j + lz_j)\cos\pi(h + k + l)
\end{aligned}$$

$$(F_{hkl})_{\frac{1}{2},\frac{1}{2},\frac{1}{2}} = (F_{hkl})_{ooo}(-1)^{h+k+l} \qquad (1.7)$$

This analysis can be carried out for each centre, and the result is that in all cases in centric space groups structure factors with h = 2n, k = 2n l = 2n are invariant to change in origin. For this reason, they are called structure invariants. Other structure factors are effected by a change of origin, and have been called structure semi-invariants. In centred cells, there are sets of origins, and, depending upon centering conditions, there may be other invariants. For example in C-centred cells, the structure factor F_{uug} is an invariant, where u is an odd number and g is an even number.

Based on these studies, it is possible to choose an origin from the structure semi-invariants. The choice is limited by the space group, but in general it will follow these rules:

1. In Euclidian space of N dimensions, there are a maximum of N linearly independent vectors which make up the basis set for that space.
2. If in a group of two or more reflections one of them is linearly dependent modulo 2, then all the reflections in that parity group are determined by the structure.

Linearly independent modulo 2 requires that

$$\mathrm{mod}|2|(H_1 + H_2 + H_3) \neq 0 \qquad (1.8)$$

The first rule is derived from vector analysis, and the second is a direct result of the studies of structure invariants and semi-invariants.

For example in the primitive cells in the triclinic, monoclinic, and orthorhombic systems, three vectors are needed to specify the origin. If, after examining the strongest normalised structure factors, a reflection in the ugg group is taken, a second reflection with gug may be chosen as the second vector. At this point, any reflection in the parity groups ugg, gug, ggg, uug, is not allowed, so a reflection in the group guu is employed. Thus the set is

u g g (1)
g u g (2)
g u u (3)

Thus the full set of groups will come from these three as is seen below: ggg (by definition), ugg (1), gug (2), ggu (2+3), uuu (1+3), guu (3), ugu (1+2+3), uug (1+2).

In centred cells, the number of parity groups becomes smaller, as in the case of a C centred cell with the groups ggg, ggu, uuu, uug. In this case there are only two possible groups which can be used to determine the origin. Karle and Hauptmann (Hauptmann and Karle, 1959) have derived the possible parity groups which can be used in these non-primitive space groups.

It was mentioned that the structure factors must have large E values. This is justified by the fact that the origin determining reflections must enter into enough strong interactions in order to phase the rest of the planes. The probability that an interaction is correct is

$$P(H)_{+} \approx \tfrac{1}{2} + \tfrac{1}{2}\tanh(\sigma_3\sigma_2^{-3/2}|E_H| \sum_{K}|E_K E_{H-K}|) \qquad (1.9)$$

which was first suggested by Woolfson (1954) and Cochran and Woolfson (1955). The values for σ_n are defined as

$$\sigma_n = \sum_{j=1}^{N} z_j^n$$

In their original work, a number of relationships were derived, but experience has shown that the best two were $\sum_1$ and $\sum_2$. $\sum_1$ gives the relationships between E_H and E_{2H}. In the space group $P\bar{1}$, this takes the form

$$sE_{2H} \approx E_H^2 - 1 \tag{1.10}$$

In higher systems, this relationship will have more than one term, but if there is anything in the structure which may cause the higher relationships to fail, the simpler (1.10) should be used. At the present time, this relationship may give indications, when symbols are used, in the assignment of signs. It has been pointed out by Woolson (1961) that this relationship is nothing more than an origin removed, sharpened Patterson.

The most powerful sign relationship is $\sum_2$. This is similar to the Sayre sign formula (1.4). It is expressed in the form:

$$sE_H \approx s\sum_K E_K E_{H-K} \tag{1.11}$$

This, when used with (1.9), can give most of the signs.

The method as it is now employed goes as follows.

1. The data is put on an absolute scale, then converted to normalised structure factors using (1.5).
2. The origin determining signs are fixed, as was explained earlier.
3. These signs are placed in (1.11) until no further additional signs are found (keeping $P(H)_+$ high i.e. about 0·99).
4. Employing additional symbols as needed, while altering the probability level as the determination proceeds.
5. Finding relationships between the symbols, and possibly using additional relationships to give one choice.
6. Computing an E map, and solving the structure in the normal way.

If the space group has no change of signs amongst symmetry related structure factors then one symbol, if it is assigned, must be negative. On the E map, parts of the molecule may be seen, but not the entire structure. If this is the case, only part of the signs are determined correctly and a different set of signs should be assigned to the symbols. If all the E maps are examined, the existence of homometric structures may be found.

In the acentric case, the problem becomes more complex. In this case, the structure factor has the form

$$F_{hkl} = \sum_{j=1}^{N} f_j \exp(2\pi i(hx_j + ky_j + lz_j))$$

As in the centric case, the origin is changed. Now it is moved to x_o, y_o, z_o and the structure factor becomes

$$(F_{hkl})_{x_oy_oz_o} = \sum f_j \exp(2\pi i(h(x_j-x_o) + k(y_j-y_o) + l(z_j-z_o)))$$

$$= \sum f_j \exp(2\pi i(hx_j + ky_j + lz_j)) \exp(-2\pi i(hx_o + ky_o + lz_o))$$

$$(F_{hkl})_{x_oy_oz_o} = (F_{hkl})_{ooo} \exp(-2\pi i(hx_o + ky_o + lz_o)) \quad (1.12a)$$

$$\text{or} \quad (\phi)_{x_oy_oz_o} = (\phi)_{ooo} - 2\pi(hx_o + ky_o + lz_o) \quad (1.12b)$$

Thus as in the case of the centric space groups, there are relationships between the F_H sets. The primitive space groups can be broken into three types, and thirteen classes. A complete analysis of the choice of the origin planes has been determined (Karle and Hauptmann, 1961; Hauptmann and Karle, 1956). For example in the case of P1, the only invariant is the plane F_{ooo}, whereas in higher space groups, F_{ggg} planes are invariant.

Following from the Karle-Hauptmann inequalities (Karle and Hauptmann, 1950) it is possible to derive the condition (Karle and Hauptmann, 1956; 1966)

$$\phi_H = \langle \phi_K + \phi_{H-K} \rangle_K \qquad (1.13)$$

which can be related to

$$\tan\phi_H = \frac{\sum_K |E_K E_{H-K}| \sin(\phi_K + \phi_{H-K})}{\sum_K' |E_K E_{H-K}| \cos(\phi_K + \phi_{H-K})} \qquad (1.14)$$

A third formula which completes those necessary for the application of the method is

$$\phi_H = \frac{\sum_K |E_K E_{H-K}| (\phi_K + \phi_{H-K})}{\sum_K |E_K E_{H-K}|} \qquad (1.15)$$

With these formulae and the rules for the assignment of the origin and the enantiomorph (Hauptmann and Karle, 1956; Karle and Hauptmann, 1961) it is possible to determine the phases in an acentric space group.

Employing the method of Karle (Karle and Karle, 1966a),the structure factors are converted to normalised factors in the way mentioned for the centric case. The origin and an enantiomorph are chosen according to the criteria mentioned elsewhere. As in the centric case, symbols can be assigned, and the use of (1.13) will give additional phases based upon the phases and symbols. After a number of planes have been given a phase, 157 in the case of Panamine (Karle and Karle, 1966b), they are refined employing (1.14), and new planes are added using the relationship (1.15). The refinement of the phases can be followed by an examination of the R index which is defined as

$$R = \frac{\sum_{K_r} \left| |E_H|_{obs} - |E_H|_{calc} \right|}{\sum_{K_r} |E_H|_{obs}} \qquad (1.16)$$

and employing rejection criteria (Karle and Karle, 1966a). The average phase deviation appears to be about 20° to 25°.

A second method for the earlier assignment of signs has been proposed (Hauptmann, Fisher, Hancock and Norton, 1969) employing earlier studies of strong structure invariants (Karle and Hauptmann, 1957; Hauptmann, 1962). The invariant

$$\cos(\phi_1 + \phi_2 + \phi_3) \quad \text{when } H_1 + H_2 + H_3 = 0 \qquad (1.17)$$

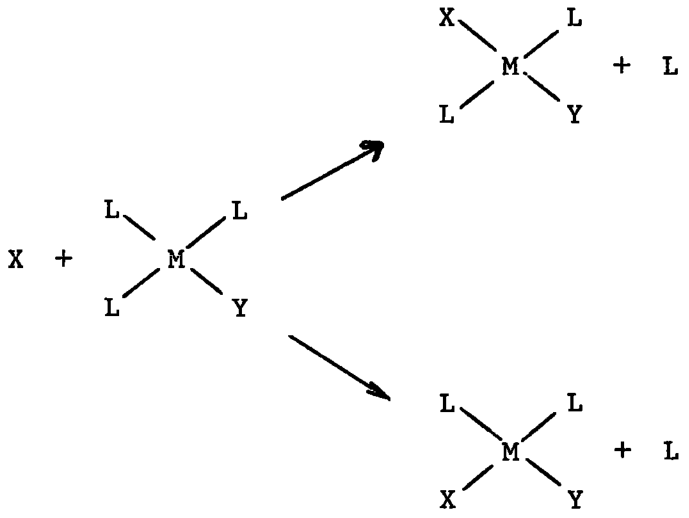
can be minimised using least squares techniques. The first set of signs is found, then refinement proceeds as above. This method has been used in the solution of Estriol (Cooper, Norton and Hauptmann, 1969).

These are but two of the ways the acentric formulae have been applied. In some cases it has been necessary to compute E maps, find parts of the molecule, get the phases of some of the stronger structure factors, add additional planes (using 1.15) then refining them. The first method has worked in a number of structure determinations, although the method described above was needed in some cases. The second method, although it is more suitable for use in a computer programme, has only been reported for the solution of two structures. The future will bring better methods of application of these formulae, and may well find new relationships which will give a truly fool-proof, one step method of phase determination.

Chapter 2

The Trans Effect

With square planar compounds of the type ML_3Y, two possible isomers result from the reaction



The trans effect is the ease in which the group L is replaced by X. This subject has been reviewed (Basolo and Pearson, 1962) and is defined as:

> "The trans effect is the effect of a co-ordinated group Y upon the rate of substitution reactions of the group L opposite to Y."

For platinum(II) compounds this effect has been studied in detail, with the result that a number of series have been resolved. Basolo (1965) gives a qualitative order:

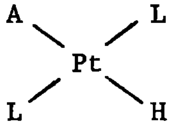
C_2H_4, NO, CO, CN > R_3P, H^-, $SC(NH_2)_2$ > CH_3^- > $C_6H_5^-$ > SCN^- > NO_2^- > I^-
Br^- > Cl^- > NH_3 > OH^- > H_2O

With a number of infrared series studied, it became apparent that there were two effects. Zundahl and Drago (1968) referred to two separate effects: the trans effect, i.e. the kinetic effect,and the trans influence, the physical effect. This study, employing an extended Huckel treatment, indicated that the two series arising from these effects were similar for σ-bonded ligands, and that there was a cis influence comparable in magnitude to the trans influence. The investigation gave a trans influence series based upon the overlap populations in the $PtCl_2(L)(NH_3)$ series of complexes. A more detailed examination of the crystallographic and infrared evidence supports his primary conclusion that there are two effects, but does not support his two secondary conclusions: the relative magnitudes of the cis versus trans influence, and the orders of the trans effect with respect to the trans influence.

Infrared Studies

From a review on sigma-bonded platinum compounds (Cross, 1967) a series of ν(Pt-H) and ν(Pt-C) can be constructed and are listed in Tables 2a, 2b, and 2c. Further information (Adams and Chandler, 1969; Adams, Chatt, Gerratt and Westland, 1964) about ν(Pt-Cl) and ν(Pd-Cl) is listed in Tables 2d, 2e, and 2f. From these values two series can be deduced: a trans influence series and a cis influence series.

Table 2a



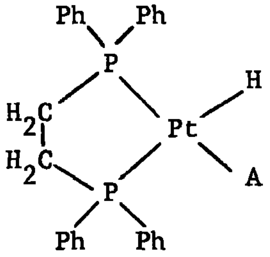
L	A	ν-(Pt-H) cm^{-1}	
Pr_3P	$GePh_3$	1975	
PP	$GeMe_3$	1998(Nujol)	
Et_3P	C=CPh	2020	
Et_3P	$GeMe_3$	2041	
Et_3P	CN	2041	
PP *	Cl	2043	2020(KBr)
Me_3P	$GePh_3$	2051	2024(KBr)
Ph_3P	$SnCl_3$	2100	
Et_3P	$SnCl_3$	2105	
Et_3As	SCN	2108	
Et_3P	SCN	2112	
Et_3As	I	2139	
Et_3P	NO_2	2150	2193(Nujol)
Et_3P	I	2155	
Et_3As	Br	2167	
Et_3As	Cl	2174	
Et_3P	Br	2178	
$PhEt_2P$	I	2179	
Me_3P	Cl	2182	
Et_3P	Cl	2183	
Ph_3P	I	2186	
Ph_2EtP	I	2189	
$PhEt_2P$	Cl	2199	

contd./

Table 2a

Ph_2EtP	Cl	2206
Ph_3P	Cl	2220
Et_3P	CNO	2229
Et_3P	NO_3	2242

x PP forms



(Cross, 1967)

Table 2b

L_2PtAH

ν-(Pt-H) cm^{-1}

X	Et_3As	Me_3P	Et_3P	Pr_3P	$PhEt_2P$	Ph_2EtP	Ph_3P
SCN	2108		2112				
I	2139		2155		2179	2189	2186
Br	2167		2178				
Cl	2174	2182	2183	2183	2199	2206	2220
Ph_3Ge		2051		1975			

(Cross, 1967).

Table 2c

L_2PtRA

ν(Pt-C) cm^{-1}

		R=Me		R=Et	
	A	Me_3P	Et_3P	Me_3P	Et_3P
cis	Et	-	-	511,500	516,496
cis	Me	525,508	526,506	-	-
cis	Cl	529	527	-	-
trans	I	538	540	-	522
trans	Br	546	548	-	-
trans	Cl	551	551	-	538
trans	SCN	558	556	-	-
trans	NO_3	567	566	-	-

$(Et_2PCH_2CH_2PEt_2)PtMe_2$	521,512
$(EtCH_2CH_2SEt)PtMe_2$	555,548

(Cross, 1967).

L_2PtCl_2

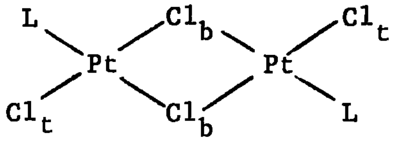
Table 2d

	L	ν-(Pt-Cl) cm^{-1}		ref.
trans	$AsEt_3$	346		A
trans	PPh_3	343		A
cis	$SeEt_2$	333	316·6	B
cis	SEt_2	330	318·2	B
cis	PPh_3	330	293	A
cis	NH_3	326·0		B
cis	$AsEt_3$	315	288	A
cis	$AsPr_3$	309		B
cis	PPr_3	307	277	B
cis	PEt_3	303·2	280·8	B

A Adams and Chandler, 1969.

B Adams, Chatt, Gerratt and Westland, 1964.

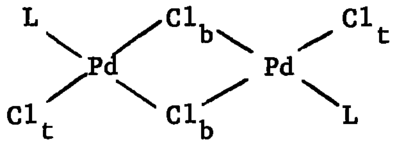
Table 2e



L	ν-(Pt-Cl)$_b$ cm^{-1}	ν-(Pt-Cl)$_t$ cm^{-1}
C_2H_4	318 (311)sh	360
$AsPr_3$	320	357
C_3H_6	320	361
$AsEt_3$	324	350
$P(OEt)_3$	325	361
PPr_3^n	325 (317)sh	357
PEt_3	325 (314)sh	353
PCl_3	328 (319)sh	365

(Adams and Chandler, 1969)

Table 2f



L	ν-(Pd-Cl)$_b$ cm^{-1}	ν-(Pd-Cl)$_t$ cm^{-1}
PEt_3	300 (261)sh	355
PPr_3^n	301 (255)sh	356
$AsEt_3$	301 (264)sh	354
$AsPr_3^n$	302 (261)sh	358
$P(OEt)_3$	305 (266)sh	364

(Adams and Chandler, 1969)

Trans Influence

ν(Pt-H)

Pp > R_3P > C=CPh > $GeMe_3$, CN^- > $GePh_3$ > $SnCl_3$ > SCN^- > NO_2^- > I^- > Br^- > Cl^- > CNO^- > NO_3^-

ν(Pt-Cl)

$P(OEt)_3$, AsR_3, PR_3 > PCl_3, C_2H_4, C_3H_6, p-tolidine, R_2Te, Cl^-

Cis Influence

ν(Pt-H)

PPh_3 > $PEtPh_2$ > PEt_2Ph > PR_3 > $AsEt_3$

The largest difference in frequency within the trans effect series for ν(Pt-H) is 367 cm^{-1}, whereas in the cis series it is 54 cm^{-1}, which corresponds to the difference between the trans influences of SCN^- and Cl^-. The small differences of the ν(Pt-H) in the cis series may not be significant if the criterion of Murrell (1969) is used, as the greatest change is about 1·5% of its total frequency. A second point of interest is, for the phosphine ligands, the magnitude of the cis influence increases with the number of phenyl groups attached to phosphorus.

X-ray Studies

A number of compounds which exhibit, or would be expected to exhibit, the trans influence have been studied by X-ray structural methods. Most of this work has centred on the platinum(II) complexes in which are observed the most significant changes. In conjunction with information available about Pd(II), Ir(III),Ni(II), and Pt(IV) compounds, it is possible to get a broad picture of the trans influence from the Tables 2g to 2j.

The most noticeable deviation from the kinetic series is the position of the double bond as measured by the Pt-N bond length in $C_2H_4Pt(NMe_3)Cl_2$ (Alderman, Owston and Rowe, 1960). This length is, within experimental error, the same as in an unperturbed bond. This would indicate that ethylene, under these conditions, has a small trans influence, whereas it has one of the largest trans effects. This inconsistency has been observed in other complexes containing chlorine trans to a double bond (Baenziger, Richards and Doyle, 1965; Mason and Robertson, 1969).

Palladium(II) complexes have been studied, but not to the same degree as have been the platinum(II) series. It becomes noticeable that these complexes exhibit bond lengths similar to those found in platinum(II) compounds, although the substitution of Pd for Pt in a compound exhibiting a strong trans influence has yet to be studied. In general, the series derived from bond lengths is very similar to that obtained from infrared studies, and similar series are obtained for both the Pt(II) and the Pd(II) compounds.

Theories

It has been shown in the proceeding sections that there are two

Table 2g

Pt-Cl and Pt-Br bond lengths

Compound	Trans Ligand	Pt-X (Å)	Reference
$[Pt(acac)_2Cl]^-$	O	2•28(1)	Mason, Pauling and Venanzi, 1969
t-$(PEt_3)_2PtCl_2$	Cl	2•30(1)	Messmer and Amma, 1965
t-$Pt(C_2H_4)NHMe_2Cl_2$	Cl	2•31(4)	Alderman, Owston and Rowe, 1960
$(C_{12}H_{17})_2Pt_2Cl_2$	C=C	2•31(1)	Mason, Robertson and Whimp, 1968
α-$[Pt_2(SCN)_2Cl_2(PPr_3)_2]$	SCN	2•37	Owston and Rowe, 1960
c-$(PMe_3)_2PtCl_2$	P	2•37(1)	Messmer, Amma and Ibers, 1967
$(C_2H_4)PtCl_3^-$	C=C	2•41	Wunderlich and Mellor, 1954; 1955
t-$(PPh_2Et)_2Pt(H)Cl$	H	2•42(1)	Eisenberg and Ibers, 1965
$[Pt^{IV}(etn)_4Br_2]^-$	Br	2•44	Graven and Hall, 1966
t-$(PPhMe_2)_2(SiPh_2Me)PtCl$	Si	2•45(1)	Harrison, 1968
t-$(PEt_3)_2Pt(H)Br$	H	2•56	Owston, Partridge and Rowe, 1960

Table 2h

Pt-N and Pt-P bond lengths

Bond	Compound	Trans ligand	Pt-X (Å)	Reference
Pt-N	$t\text{-}(C_2H_4)NHMe_2PtCl_2$	C=C	2·02(19)	Alderman, Owston and Rowe, 1960
	$Pt_2(SCN)_2Cl_2(PPr_3)_2$	PPr_3	2·05	Owston and Rowe, 1960
	$Pt(NH_3)^{2+}_4$	NH_3	2·06	Atoji, Richardson and Rundle, 1957
Pt-P	$Pt_2(SCN)_2Cl_2(PPr_3)_2$	SCN	2·16	Owston and Rowe, 1960
	$t\text{-}(PEt_3)_2Pt(H)Br$	PEt_3	2·26	Owston, Partridge and Rowe, 1960
	$t\text{-}(PPh_2Et)_2Pt(H)Cl$	PPh_2Et	2·267(8)	Eisenberg and Ibers, 1965

Table 2i

Pd-Cl bond lengths

Compound	Trans Ligand	Pd-Cl (Å)	Reference
t-$(DMSO)_2PdCl_2$	Cl	2·287(2)	Bennett, et al, 1967
$PdCl_4^{2-}$	Cl	2·299(4)	Bell, Hall and Waters, 1966
$PdCl_6^{2-}$	Cl	2·300(7)	Bell, Hall and Waters, 1966
$(C_7H_8)PdCl_2$	C=C	2·316(1)	Baenziger et al, 1961; 1965
$[(C_2H_4)PdCl_2]_2$	Cl	2·32[b]	Dempsey and Baenziger, 1958
$(C_3H_5)PdCl_2$	$H_2C{=}C(H)CH_2$	2·41[b]	Smith, 1965; Oberhansli, 1965
$[(C_2H_4)PdCl_2]_2$	C=C	2·42[b]	Dempsey and Baenziger, 1958

[b] Pd-Cl distance in the Pd-Cl-Pd bridge

TABLE 2j

Ir-CO bond lengths

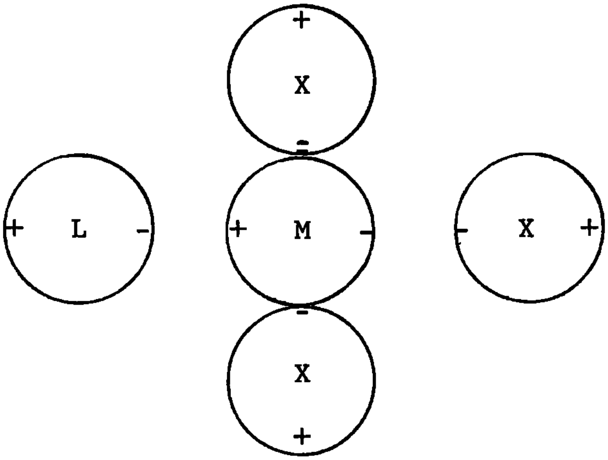
Compound	trans ligand	bond length	Ref.
$IrCl(CO)NO(PPh_3)_2$	Cl	$1{\cdot}70(5)^{*}$	Derek, Hodgson and Ibers (1969)
$IrI_2(bpy)C_2H_3O_2$	N	$1{\cdot}80(2)$	Albano, Bellon and Sansoni (1969)
$(Ph_3P)_2Ir(CO)(H)_2GeMe_3$	H	$1{\cdot}855(16)$	Present work
$IrI(CO)NO(PPh_3)_2$	I	$1{\cdot}86(1)^{*}$	Hodgson and Ibers (1968)
$IrIO_2(CO)(Ph_3P)_2{\cdot}CH_2Cl_2$	O_2	$1{\cdot}83\text{-}1{\cdot}88^{d}$	McGinnety, Doedeng and Ibers (1967)
$IrClSO_2CO(Ph_3P)_2$	Cl	$1{\cdot}96(4)^{*}$	Placa and Ibers (1966)
$Ir(H)CO(FUMN)(Ph_3P)_2$	H	$1{\cdot}98(2)^{d}$	Manojlovic-Muir, Muir and Ibers (1969)

d disordered

* five co-ordinate

different effects, and, as would be expected, no single theory will explain both. In the case of the trans influence, a theory must be based upon the ground state of the molecule, whereas the kinetic effect must examine the activated complex.

Grinsberg (1935), based on the work done for an electrostatic theory (Chernyav, 1927; Nekrosav, 1937), developed the polarisation theory. This theory, employing induced dipoles in the metal atom and a polarised ligand, explains the weakening of the trans ligand in the manner described below. If the ligand L of the complex MLX_3 can be more easily polarised than the ligand X, then orientation of the induced dipole in the metal atom will be



This induced dipole will weaken the M-X bond trans to L.

This explains the dipole moment observed in the series trans-$[PtClR(PEt_3)_2]$ where the order of R was H > Me > C_6H_5 > Cl (Basolo, Chatt, Gray, Pearson and Shaw, 1961).

The theory applies only to σ-bonding ligands such as H^- and CH_3^- (Chatt and Shaw, 1962) where it is impossible for π-bonding to take place. It must still be realised that, although it explains a number of observed phenomen~~on~~a, this is an electrostatic interaction.

Consistent with extensions of the polarisation theory, which stated that only the valence electrons be considered (Batsanov, 1957; 1959), Syrkin (1948) proposed a modification of the theory. His theory is based on the fact that even though the metal in Pt(II), Pd(II) and Ni(II) complexes is sp^2d hybridised, it is possible to consider it as having s + d, s - d, and two p orbitals. The ligand which is able to form the stronger covalent bonds will use the s + d hybrid orbital. Since the s - d orbital is directed at an angle of 90^o to the s + d, the ligand in the trans position must use one of the p orbitals, which is of higher energy. In the case of third row transition elements, the order of orbital stabilities is:

$$5d \sim 6s > 6p$$

It follows from this theory, that the trans influenced ligand would have a longer bond length, or a lower stretching frequency. In most cases this is observed, but not in the case of an amine trans to ethylene. In general, this theory predicts most observations of the trans influence.

Following the work of Gray and Langford (1966), McWenny, Mason and Towl (1969) expanded the theory that the magnitude of the M-L and M-X σ overlap integrals can be a guide to the trans influence. They suggest that if the σ-orbital of the ligand L has a greater overlap with the metal p-σ orbital than does the orbital on the ligand X, the M-L bond is strengthened at the expense of the M-X bond. Overlap integrals were calculated for a number of atoms; for Pt(II) compounds, the following series was found:

$$\text{Si, H, C, P} > \text{Cl} > \text{N} > \text{O} > \text{F}$$

In the same work, the Pt-Cl bond length was plotted as a function of the Pauling electronegativity of the trans influencing ligand. The result is a smooth curve, assuming that C=C has the same electronegativity as a single trigonal carbon atom.

There have been theories employing the use of π-bonds formed between the metal and the ligand, thus stabilizing a five co-ordinate activated complex (Chatt, Duncanson and Venanzi, 1955; Orgel, 1956). These may explain the kinetic effect, but do not seem a probable explanation for the trans influence.

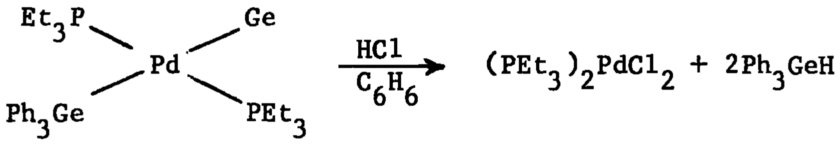
A number of workers have explained the bonding with ligands, such as ethylene and carbon monoxide, in transition metal complexes as containing π bonds due to back bonding from the metal. In comparing the normal Pt-N bond length in trans-[Pt(C_2H_4)NH(Me_2)Cl_2] to other metal ligand bonds in ethylene complexes, the workers state that there was no observed trans effect [i.e. trans influence] since the nitrogen did not have any orbitals with which to interact with the π orbitals that were used to bond with the ethylene.

Chapter 3

The Crystal Structure of $(Et_3P)_2Pd(H)Cl$

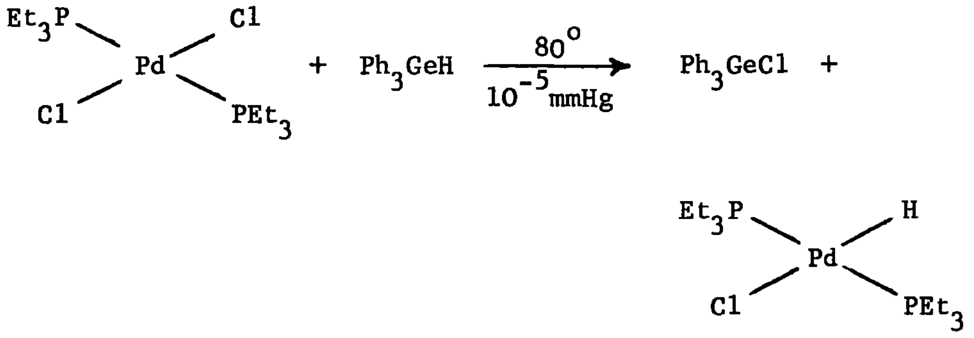
INTRODUCTION

When the reaction



was carried out, the yellow solid mixture of products had bands in the infrared due to ν(Ge-H) and ν(Pd-Cl), but not ν(Ge-Cl). Since the two compounds had similar solubilities, vacuum sublimation was employed to separate them. The mixture became black as palladium was formed; an i.r. spectrum of the white sublimate showed ν(Ge-H), but there was a small additional band in the hydride region of the spectra, which was attributed to ν(Pd-H).

These observations suggested that the products reacted in the following manner:



This was not a reasonable method for the preparation of $(Et_3P)_2Pd(H)Cl$, but the use of the compound Me_3GeH allowed the removal of the other products in the reaction.

$$\text{trans-}[(Et_3P)_2PdCl_2] + Me_3GeH \longrightarrow \text{trans-}[(Et_3P)_2Pd(H)Cl] + Me_3GeCl$$

The reaction can be carried out at room temperature, and over a week the complex crystallises <u>in situ</u>. The time can be shortened if the reaction is carried out at a higher temperature, or if palladium black is added, but the quality of the crystals is inferior.

An examination of the infrared spectra showed a ν(Pd-H) at 2035 cm^{-1}. Together with the fact that the starting material was in the trans configuration, this fixed the stereochemistry as the trans isomer (Brooks and Glockling, 1966; 1967). It was inferred from the infrared spectra that there was a strong trans influence. A structural investigation was therefore carried out in order to provide additional information about the strength of the trans influence.

EXPERIMENTAL

The compound crystallises in rectangular thick plates with the greatest elongation in the $\{100\}$ direction and well developed $\{010\}$ and $\{001\}$ faces. When kept in a water - and oxygen - free atmosphere, the crystals remain clear, but upon exposure to air, they decompose to black chunks. Because of this sensitivity, the crystal used in the study was mounted in a thin-walled capillary tube.

Although the related compound $(Et_3P)_2Pt(H)Br$ (Owston, Partridge and Rowe, 1960) is stable to air, it decomposes when placed in an X-ray beam. The palladium complex is less stable than the platinum compound, thus its decomposition on exposure to X-radiation was expected to be at least as great. In order to minimise the exposure time, a large crystal (1·2 mm x 0·4 mm x 0·3 mm) was used.

After about 20 minutes exposure to X-radiation, the crystal turned a glowing red. This corresponded to the first stages of decomposition observed in crystals which were exposed to sunlight in a glove-box. The room was kept dark for the remainder of the data collection.

It was observed after a few days that the colour seemed to reside mainly on the surface of the crystal. After the data was collected, other crystals were exposed to light. Some of these turned red in a few hours, whereas others over a period of weeks. This decomposition was probably caused by small amounts of oxygen or water in the tube, and the reaction initiated by the action of light.

The data was collected by the precession method, the nets hnl, n = 0-5, and hkn, n = 0-6, being recorded. The observed reflections obeyed the following conditions:

h0l   l = 2n
0k0   k = 2n

These conditions are unique to the space group $P2_1/c$ in the monoclinic system. The unit cell dimensions were calculated from measurements on the h0l and hk0 nets. The e.s.d. calculated from the measurements on the films were smaller than seemed justified by the experimental method; the values were increased to those shown below.*

$a = 9{\cdot}07(2)\text{Å}$ $b = 13{\cdot}82(2)\text{Å}$ $c = 14{\cdot}48(2)\text{Å}$

$\beta = 92{\cdot}89(10)^\circ$ $V = 1812\text{Å}^3$ $Z = 4$

$D_o = 1{\cdot}37\ \text{g/cm}^3$ $D_c = 1{\cdot}39\ \text{g/cm}^3$

The intensities were corrected for Lorentz and polarisation factors, but not for absorption ($\mu = 13{\cdot}04\ \text{cm}^{-1}$ for Mo K_α). The structure factors were placed on a common scale using the method of least squares (Monahan, Shiffer and Shiffer, 1967). A total of 1816 independent planes was obtained.

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* The figure in brackets refers to the least significant figures of the measurement. This method will be used in the remainder of the work.

SOLUTION

The structure was solved using the heavy atom method. In the Patterson function an examination of the Harker line $(0,v,\frac{1}{2})$ and the Harker section $(u,\frac{1}{2},w)$ gave the position of the palladium atom, which was confirmed by the peak at $(2x,2y,2z)$ arising from the vector between two atoms related by the centre of symmetry. The ratio of the heights of the double weight to the single weight peak was as expected. The position of the palladium atom at this stage was

$$x/a = 0{\cdot}243 \qquad y/b = -0{\cdot}062 \qquad z/c = -0{\cdot}115$$

Two F_o synthes~~i~~es were calculated. The first was based upon the palladium position with an R index of 0·37

where $$R = \frac{\sum \big|\,|F_o| - |F_c|\,\big|}{\sum |F_o|}$$

and yielded positions for the two phosphorus atoms and the chlorine atom. The second was calculated from the heavy atom positions (R = 0·24), and gave the positions of the six methylene carbon atoms and two possible positions for the methyl carbon atoms. These last two atoms were in different phosphine groups and, due to the large number of spurious peaks, were not included in the subsequent least squares calculation (R = 0·21). A difference map was computed, which revealed the positions of the six methyl carbon atoms.

REFINEMENT

The refinement was carried out employing the method of least squares with the block diagonal approximation. The scattering factors for carbon (McWeeny, 1951), phosphorous (Tomii and Stam, 1958), chlorine (Dawson, 1960), and palladium (Thomas and Umeda, 1957) were used. In the case of palladium, the real part of the dispersion correction was applied, using the values of Dauber (1955).

Three cycles of refinement were carried out with all atoms having isotropic temperature factors ($R = 0{\cdot}14$). For the next two cycles the heavy atoms were treated as anisotropic ($R = 0{\cdot}09$). At this stage, the remaining atoms were given anisotropic thermal parameters and refined for two additional cycles. The last four cycles were calculated employing the following weighting scheme:

$$\sqrt{w} = {}^{1}/(P_1 + |F_o| + P_2\,|F_o|^2)^{\frac{1}{2}}$$

An analysis of the final parameters can be seen in Table 3c. When the refinement was terminated, the shift in any parameter was less than one third of its e.s.d. The final atomic coordinates are given in Table 3a, and the thermal parameters in Table 3b.

A difference map calculated after the final cycle gave one peak larger than $0{\cdot}6$ e.A^{-3} at ($0{\cdot}650$, $0{\cdot}425$, $0{\cdot}410$) with a peak height of $1{\cdot}04$ e.A^{-3}. This is related to the palladium position by the relationship

Table 3a.

	$^{x}/a$	$^{y}/b$	$^{z}/c$	B_{iso} ($\AA^2$) ж
Pd	0•24360(11)	-0•06361(8)	-0•14762(6)	3•66
Cl	0•23838(64)	-0•21562(33)	-0•23148(28)	6•86
P(1)	0•22960(42)	0•03268(31)	-0•27811(23)	4•23
P(2)	0•25128(38)	-0•13327(26)	-0•00278(22)	3•51
C(1)	0•29422(239)	0•16023(138)	-0•27016(124)	6•25
C(2)	0•04095(209)	0•05192(190)	-0•32641(148)	7•09
C(3)	0•32694(247)	-0•01462(176)	-0•37789(124)	8•16
C(4)	0•23340(246)	0•22372(141)	-0•20329(158)	9•52
C(5)	-0•04470(234)	-0•03447(194)	-0•34776(185)	9•34
C(6)	0•49520(194)	-0•02917(192)	-0•35391(146)	8•16
C(7)	0•12468(207)	-0•23894(162)	0•00237(151)	8•56
C(8)	0•19822(255)	-0•05941(152)	0•09659(125)	6•42
C(9)	0•42205(211)	-0•18940(209)	0•03987(123)	7•03
C(10)	-0•02667(173)	-0•21528(147)	-0•02671(128)	7•17
C(11)	0•30006(261)	0•03140(157)	0•10955(130)	7•37
C(12)	0•49667(195)	-0•25290(146)	-0•03050(121)	5•94

ж Values obtained from the last cycle of isotropic refinement.

Final value of the atomic coordinates and their standard deviations (x 10^5)

Table 3b

Final values of the Temperature Parameters* and their standard deviations (x 10^5)

	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Pd	0·01661(13)	0·00461(5)	0·00348(4)	0·00027(12)	0·00201(11)	-0·00055(17)
Cl	0·04191(118)	0·00585(26)	0·00483(19)	-0·00226(48)	0·00352(78)	-0·00183(86)
P(1)	0·017337(54)	0·00567(21)	0·00391(15)	0·00101(42)	0·00136(46)	0·00030(57)
P(2)	0·01516(48)	0·00461(19)	0·00340(13)	0·00050(36)	0·00274(41)	0·00013(49)
C(1)	0·03832(415)	0·00649(109)	0·00760(107)	-0·00255(232)	0·01696(351)	-0·00323(368)
C(2)	0·02003(295)	0·01645(235)	0·00976(135)	0·00392(332)	-0·00365(316)	-0·00273(429)
C(3)	0·03436(411)	0·01157(175)	0·00644(98)	0·00274(271)	0·00877(336)	0·00177(453)
C(4)	0·03669(461)	0·00630(116)	0·01099(151)	0·00555(253)	-0·00344(421)	0·00109(353)
C(5)	0·02345(350)	0·01420(213)	0·01476(206)	0·00091(400)	-0·00912(429)	-0·01205(447)
C(6)	0·01642(250)	0·01700(219)	0·00996(134)	-0·00012(337)	0·00488(292)	0·01074(387)
C(7)	0·02211(301)	0·01060(156)	0·01156(153)	0·00691(309)	-0·00167(345)	-0·00805(356)
C(8)	0·03812(437)	0·00916(145)	0·00640(96)	-0·00127(242)	0·01029(340)	-0·00629(413)
C(9)	0·02393(320)	0·02060(264)	0·00695(101)	0·00608(314)	0·00661(289)	0·02468(499)
C(10)	0·01661(248)	0·01069(151)	0·00900(115)	-0·00361(254)	0·00288(270)	-0·00712(297)
C(11)	0·04032(461)	0·00831(130)	0·00668(102)	-0·00484(260)	-0·00602(359)	-0·00537(421)
C(12)	0·02308(281)	0·00975(138)	0·00742(98)	-0·00045(244)	0·00623(274)	0·01349(342)

* B_{ij} refers to the expression $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2klB_{23} + 2lhB_{13})]$

Table 3c

Final analysis of the weighting factor

$$\sqrt{w} = 1/(15{\cdot}07 + |F_o| + 0{\cdot}007|F_o|^2)^{\frac{1}{2}}$$

F_{obs} Ranges	N	$\left(\sum w\Delta^2\right)/N$
0-12	102	0•26
12-15	224	0•23
15-17	198	0•21
17-20	163	0•17
20-22	118	0•18
22-25	126	0•11
25-27	102	0•09
27-30	78	0•15
30-35	121	0•17
35-40	105	0•12
40-45	81	0•18
45-55	122	0•15
55-75	133	0•19
75-	134	0•27

$$P_i' - P_i \approx \tfrac{1}{2}$$

where P_i' is the x,y,z coordinate found above, and P_i is for the correct position of the palladium atom. There were a few peaks larger than 0·4 e.Å^{-3} but it was impossible to assign them to any hydrogen position. In the region where the hydride would be expected, there was no peak higher than 0·35 e.Å^{-3} within a distance of 2·5Å. A smeared peak with a height of 0·55 e.Å^{-3} was found at the position 0·300, 0·075, 0·050 at a distance of about 3·5Å from the palladium atom.

DESCRIPTION

As was expected , the palladium coordination was approximately square planar. The hydrogen, which was not observed, is located trans to the chlorine, and the two phosphine groups are situated in the remaining sites.

There is a small distortion from planarity in the central portion of the molecule, as can be seen in Table 3g. The mean plane was calculated employing weights based upon the e.s.d.'s of the individual atoms. The large value of χ^2 indicates that the deviation from planarity is significant. The two phosphorus atoms are situated out of the plane with the chlorine and the palladium located close to, or on the plane. This distortion has been found in platinum hydrides, but is not found in $(Et_3P)_2PtCl_2$.

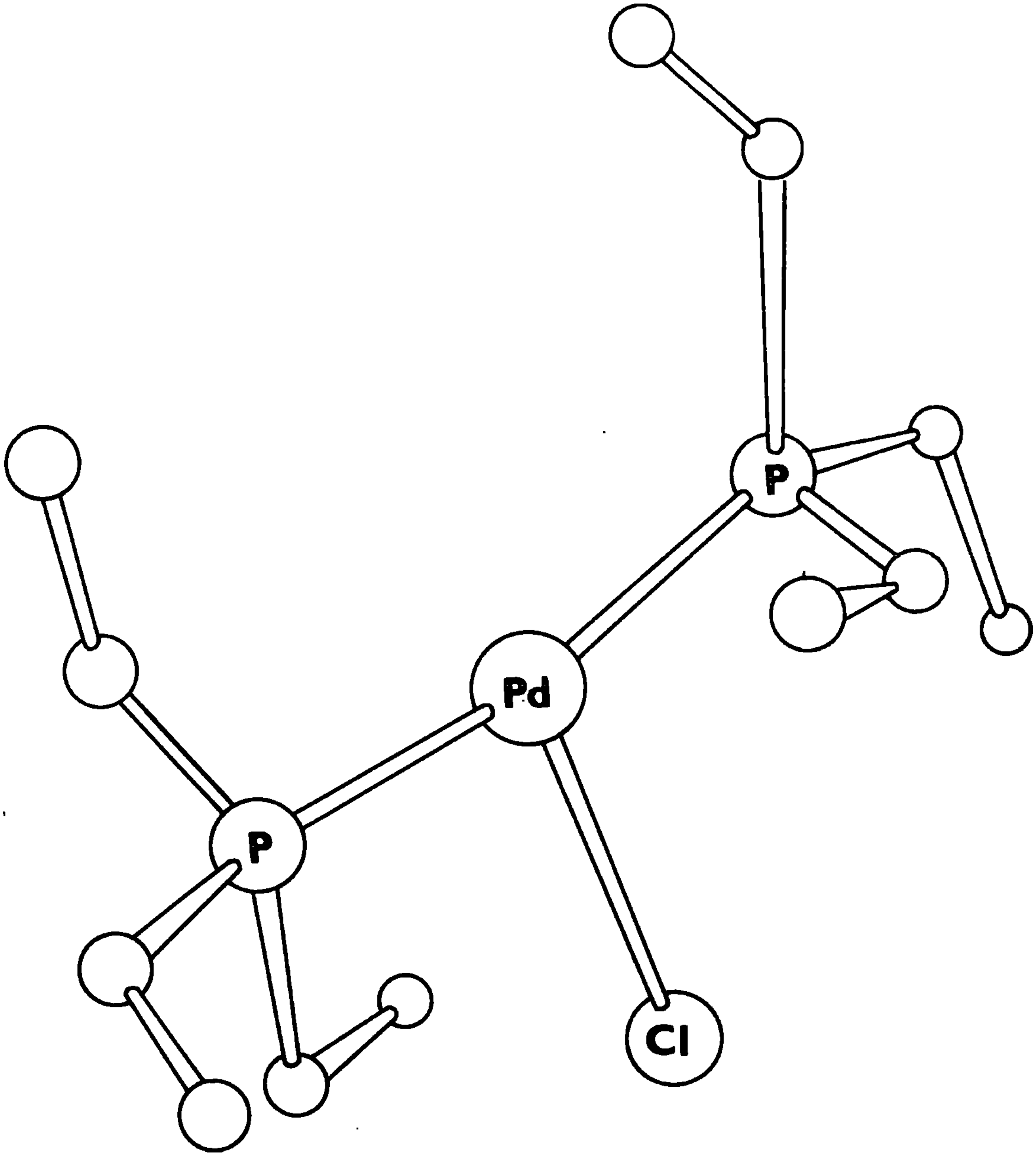

Fig.3A

Perspective Drawing

Table 3g

Best Plane for the central atoms

	X	Y	Z	P
Pd	2•3148	-0•8798	-2•1348	-0•0044(10)
Cl	2•3287	-2•9821	-3•3475	0•0085(58)
P(1)	2•2832	0•4520	-4•0219	0•0301(38)
P(2)	2•2786	-1•8431	-0•0402	0•0241(34)

χ^2 = 134•0057

Sum of P(1) = 0•0583

$$-0{\cdot}9999X - 0{\cdot}0084Y - 0{\cdot}0075Z + 2{\cdot}2868 = 0$$

The chlorine atom is located 2•427(5)Å from the palladium atom. This is longer than the sum of the covalent radii (2•30Å), or the distance found in the $PdCl_4^{2-}$ ion with a value of 2•300Å (Bell, Hall and Waters, 1966). It is in very good agreement with the Pt-Cl bond length of 2•42(1)Å found in $(Ph_2EtP)_2Pt(H)Cl$, in fact they are the same at the 99•5% confidence level. This suggests that the trans influence is as strong as that found in Pt(II) complexes.

With a value of 169•35°, the P-Pd-P angle is distorted from 180°. This distortion increases the separation of the phosphorus atoms from the chlorine, with a mean P-Pd-Cl angle of 95·26°. The two values obtained from the structure are the same at the 99·9% confidence level.

The two phosphine groups are chemically equivalent, with the two Pd-P bond lengths having a mean value of 2·308Å, at the 99·5% confidence level. This distance is shorter than the sum of the covalent radii (2·41Å), yet is longer than values of about 2·26Å found in Pt(II) complexes (Owston, Partridge, Rowe, 1960; Eisenberg and Ibers, 1965). The ethyl groups on both phosphorus atoms are in a helical formation. The carbon atoms are related by an approximate centre of symmetry located midway between the two phosphorus atoms.

The C-P-C angle (101·76°) [×] and the Pd-P-C angle (116·3°) represents distortions from the theoretical value of 109·47°. This increases the Pd-P separations, but gives rise to larger C-C steric interactions in the phosphine group. This type of distortion is found in other phosphine groups when acting as ligands. Following the work by Gillespie (1963) it can be explained in terms of some multiple bonding with the palladium atoms. Other workers (Pidcock, Richards and Venanzi, 1966), in an analysis of the Fermi contact from N.M.R., state that the bond between the phosphorus and the metal is strongly sigma in character. The P-C bond length of 1·844Å is also in good agreement with values found in phosphines in similar environments.

[×] In all cases, unless otherwise stated, the values given are the averages for all equivalent lengths or angles.

The C-C bond length of 1•500Å is shorter than the value in diamond of 1•5445Å. This value may arise from the thermal motion of the methyl carbon atoms, which have B_{iso} values within a range between 7•17Å^2 and 9•52Å^2. An analysis of this motion, and a correction based upon it, would give somewhat longer values for the bond length.

The P-C-C angle of 114•3° is larger than the tetrahedral value. A similar effect has been observed in aliphatic hydrocarbons, where it has been attributed to steric interactions.

The non-bonding contacts which are of interest are those which involve a contact with chlorine. The closest contacts within the molecule are with C(7), having a value of 3•603(22)Å, and both phosphorus atoms with an average value of 3•50Å. Both of these values are somewhat shorter than the calculated values 3•80Å and 3•70Å respectively. The closest intermolecular contact is 3•998Å with C(8) at the position $(x,\frac{1}{2}-y,\frac{1}{2}+z)$. The methylene carbon atoms are separated by an average value of 2•86Å, and the methyl by values larger than 4Å.

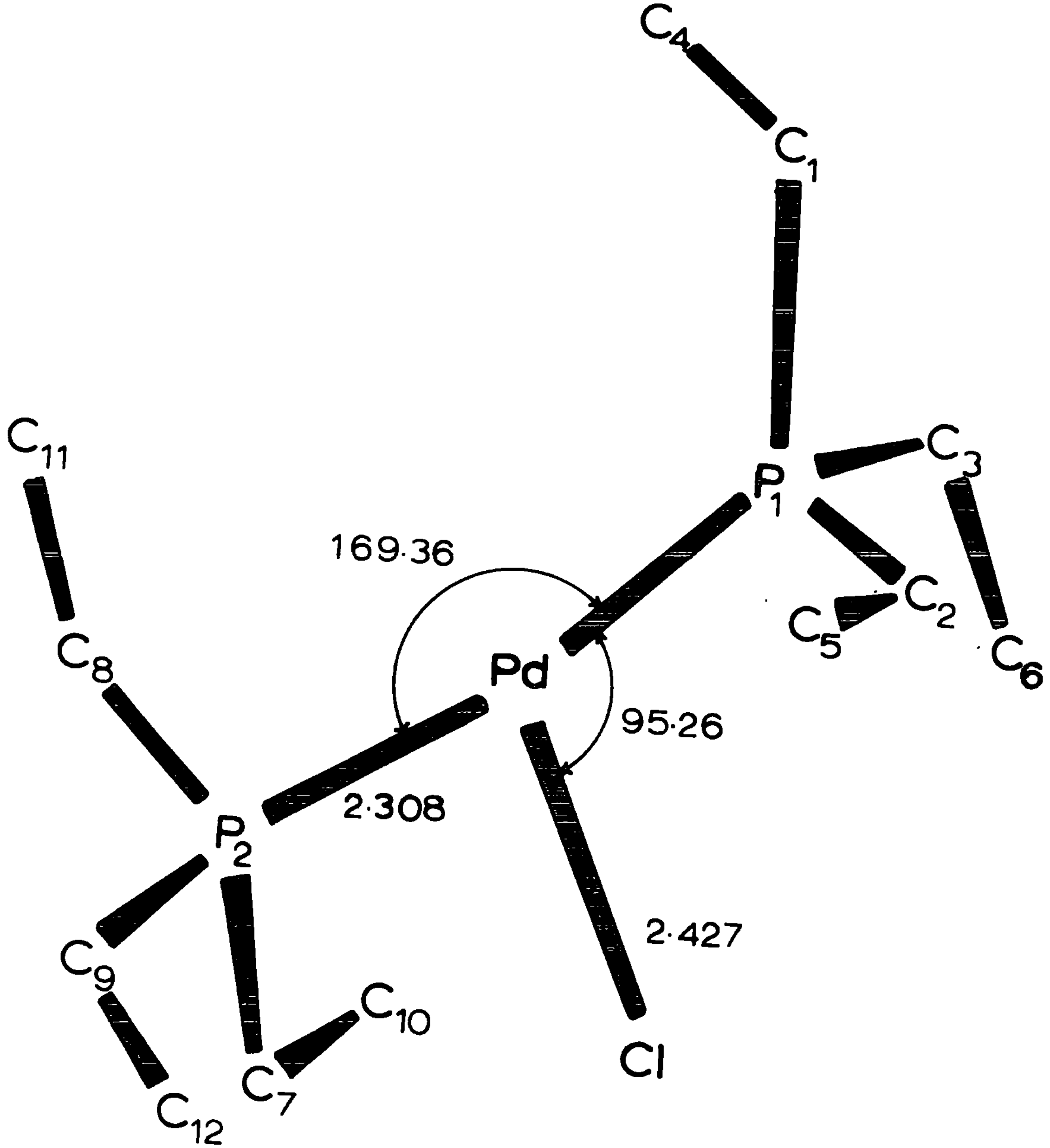

Fig.3B

Some Bond Lengths and Angles

Table 3d

Bond lengths (Å) and their standard deviations (Å x 10^3)

Pd-Cl	2•427(5)
Pd-P(1)	2•310(4)
Pd-P(2)	2•306(3)
P(1)-C(1)	1•860(20)
P(1)-C(2)	1•833(20)
P(1)-C(3)	1•850(20)
P(2)-C(7)	1•862(21)
P(2)-C(8)	1•848(20)
P(2)-C(9)	1•811(21)
C(1)-C(4)	1•437(29)
C(2)-C(5)	1•450(35)
C(3)-C(6)	1•559(29)
C(7)-C(10)	1•451(25)
C(8)-C(11)	1•564(31)
C(9)-C(12)	1•528(29)

Average Values

Pd-P	2•308
P-C	1•844
C-C	1•500

Table 3e

Angles and their standard deviations (x 10^2)

Cl-Pd-P(1)	95·24(15)°
Cl-Pd-P(2)	95·28(15)
P(1)-Pd-P(2)	169·35(14)
Pd-P(1)-C(1)	119·47(63)
Pd-P(1)-C(2)	114·04(72)
Pd-P(1)-C(3)	115·23(70)
Pd-P(2)-C(7)	111·96(67)
Pd-P(2)-C(8)	118·70(67)
Pd-P(2)-C(9)	118·37(73)
C(1)-P(1)-C(2)	99·81(94)
C(1)-P(1)-C(3)	102·87(92)
C(2)-P(1)-C(3)	103·03(99)
C(7)-P(2)-C(8)	102·58(93)
C(7)-P(2)-C(9)	99·63(98)
C(8)-P(2)-C(9)	102·87(98)
P(1)-C(1)-C(4)	119·39(148)
P(1)-C(2)-C(5)	116·14(168)
P(1)-C(3)-C(6)	111·78(147)
P(2)-C(7)-C(10)	112·73(144)
P(2)-C(8)-C(11)	111·24(141)
P(2)-C(9)-C(12)	114·70(149)

Average Values

Cl-Pd-P	95·26
Pd-P-C	116·30
C-P-C	101·76
P-C-C	114·33

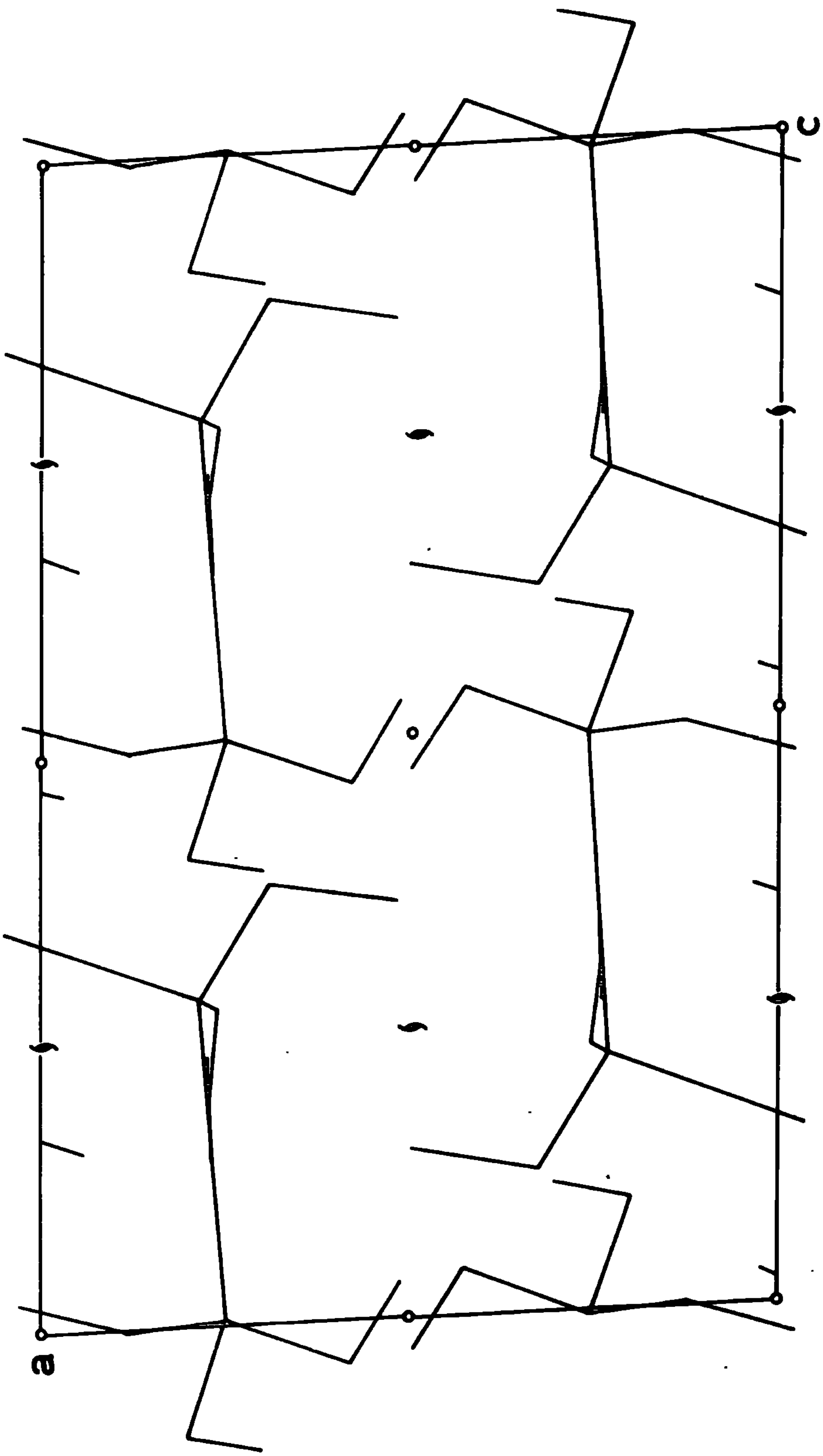

Fig.3C

Projection on the 010 Plane

Table 3f

Non-Bonding Contacts

Atom A	Atom B	Equivalent Position	A - B
Cl	P(1)	1	3·500 Å
Cl	P(2)	1	3·498
Cl	C(3)	1	3·61
Cl	C(5)	1	3·91
Cl	C(6)	1	3·95
Cl	C(7)	1	3·60
Cl	C(10)	1	3·91
Cl	C(12)	1	3·68
Cl	C(7)	4	3·99
Cl	C(8)	4	3·99
P(1)	P(2)	1	4·60
C(1)	C(2)	1	2·83
C(1)	C(3)	1	2·90
C(2)	C(3)	1	2·88
C(7)	C(8)	1	2·90
C(7)	C(9)	1	2·80
C(8)	C(9)	1	2·86
C(4)	C(9)	2	3·85
C(4)	C(10)	2	3·90
C(4)	C(5)	3	3·84
C(6)	C(11)	2	3·91
C(6)	C(12)	4	3·95
C(10)	C(2)	3	3·86
C(10)	C(11)	2	3·71
C(11)	C(12)	2	3·78
C(m)	C(m')	1	2·86 ⁎

⁎ Average for the six CH_2 CH_2 contacts listed above

Equivalent position

1	x, y, z	3	$\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$
2	$\bar{x}, \bar{y}, \bar{z}$	4	$x, \frac{1}{2}-y, \frac{1}{2}+z$

TABLE 3h

Final Values of the Observed and Calculated Structure Factors

H	K	L	|FO|	FC
3	0	0	29	-28
4	0	0	200	216
5	0	0	34	26
6	0	0	67	-71
7	0	0	31	-27
8	0	0	45	52
9	0	0	16	17
10	0	0	23	-21
11	0	0	13	-10
-11	0	2	14	14
-9	0	2	28	-30
-7	0	2	62	68
-5	0	2	96	-98
-4	0	2	29	-34
-3	0	2	134	171
-2	0	2	97	92
-1	0	2	113	-124
1	0	2	73	80
2	0	2	172	151
3	0	2	112	-108
4	0	2	70	-70
5	0	2	51	53
6	0	2	31	33
7	0	2	20	-25
8	0	2	12	-10
9	0	2	36	11
-7	0	4	14	-11
-6	0	4	19	17
-5	0	4	42	40
-4	0	4	31	-35
-3	0	4	57	-65
-2	0	4	10	71
-1	0	4	119	106
0	0	4	14	-9
1	0	4	100	-88
2	0	4	25	17
3	0	4	36	37
4	0	4	22	-14
5	0	4	36	-33
7	0	4	22	25
-9	0	6	18	16
-8	0	6	26	27
-7	0	6	34	-35
-6	0	6	29	-28
-5	0	6	55	57
-4	0	6	62	57
-3	0	6	59	-54
-2	0	6	29	-25
-1	0	6	81	82
0	0	6	107	102
1	0	6	95	-98
2	0	6	61	-52
3	0	6	53	43
4	0	6	71	79
5	0	6	51	-51
6	0	6	54	-57
7	0	6	20	20
8	0	6	30	32
10	0	6	19	-17
-8	0	8	36	39
-7	0	8	32	31
-6	0	8	46	-47
-5	0	8	61	-60
-4	0	8	80	76
-3	0	8	100	98
-2	0	8	109	-105
-1	0	8	106	-112
0	0	8	112	109
1	0	8	103	104
2	0	8	74	-75
3	0	8	76	-92
4	0	8	36	39
5	0	8	47	50
6	0	8	16	-15
7	0	8	29	-34
9	0	8	17	17
-8	0	10	18	-17
-7	0	10	16	15
-6	0	10	29	28
-5	0	10	17	-15
-4	0	10	44	-44
-3	0	10	20	19
-2	0	10	41	34
0	0	10	61	-59
2	0	10	44	43
4	0	10	34	-38
6	0	10	19	19
-7	0	12	19	-20
-5	0	12	38	36
-3	0	12	91	-51
-2	0	12	17	-15
-1	0	12	71	71
0	0	12	17	15
1	0	12	56	-53
2	0	12	18	-20
3	0	12	38	42
4	0	12	18	12
5	0	12	30	-30
6	0	12	18	-12
7	0	12	17	15
-8	0	14	28	24
-6	0	14	37	-38
-4	0	14	52	54
-2	0	14	69	-65
-1	0	14	19	-21

H	K	L	|FO|	FC
0	0	14	66	62
1	0	14	25	27
2	0	14	66	-60
3	0	14	71	-26
4	0	14	38	40
5	0	14	18	17
6	0	14	24	-26
-7	0	16	19	20
-5	0	16	32	-27
-4	0	16	19	-17
-3	0	16	36	33
-2	0	16	22	21
-1	0	16	30	-30
0	0	16	76	-26
1	0	16	26	25
2	0	16	17	19
3	0	16	16	-14
4	0	16	18	-17
6	0	16	8	10
-3	0	18	15	-14
-1	0	18	17	15
1	0	18	16	-13
3	0	18	12	12
2	1	0	15	9
3	1	0	70	-77
4	1	0	35	-33
5	1	0	43	46
6	1	0	10	-4
7	1	0	36	-36
9	1	0	14	13
-10	1	1	21	-21
-9	1	1	15	-15
-8	1	1	42	-40
-7	1	1	35	40
-6	1	1	77	-73
-5	1	1	67	-66
-4	1	1	76	89
-3	1	1	131	120
-2	1	1	159	-147
-1	1	1	158	-171
1	1	1	168	192
2	1	1	126	-127
3	1	1	138	-147
4	1	1	45	47
5	1	1	95	91
6	1	1	29	-26
7	1	1	45	-41
9	1	1	26	25
-8	1	2	17	-14
-7	1	2	14	15
-6	1	2	36	34
-4	1	2	50	-47
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-1	1	2	45	-38
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3	1	2	10	10
4	1	2	51	-49
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8	1	2	13	-13
-10	1	3	13	11
-9	1	3	15	-13
-8	1	3	21	-20
-7	1	3	14	11
-6	1	3	46	46
-5	1	3	21	-17
-4	1	3	58	-54
-3	1	3	22	18
-2	1	3	129	131
-1	1	3	43	37
0	1	3	18	-24
1	1	3	25	-23
2	1	3	110	103
3	1	3	11	17
4	1	3	36	-34
5	1	3	10	-8
6	1	3	28	29
8	1	3	16	-15
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-5	1	4	19	-16
-4	1	4	18	21
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-1	1	4	15	-17
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-2	1	5	16	14
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3	1	5	68	71
5	1	5	59	-58
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-6	1	6	11	-11

H	K	L	|FO|	FC
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-1	1	6	46	-51
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1	1	6	35	37
2	1	6	14	-18
3	1	6	36	-33
5	1	6	25	24
6	1	6	20	-17
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-2	1	7	141	-151
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1	1	7	18	23
2	1	7	126	-129
3	1	7	30	-27
4	1	7	81	88
5	1	7	27	27
6	1	7	54	-56
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-1	1	8	63	-67
0	1	8	22	-16
1	1	8	53	48
2	1	8	15	17
3	1	8	38	-35
4	1	8	21	-23
5	1	8	19	21
7	1	8	12	-11
8	1	8	14	-9
-9	1	9	25	-23
-7	1	9	38	38
-6	1	9	12	9
-5	1	9	53	-55
-4	1	9	13	-15
-3	1	9	88	80
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-1	1	9	84	-81
0	1	9	35	-34
1	1	9	80	82
2	1	9	42	41
3	1	9	49	-52
4	1	9	31	-31
5	1	9	23	23
6	1	9	14	20
7	1	9	13	-14
8	1	9	15	-13
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-5	1	10	15	13
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0	1	10	39	-37
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4	1	12	19	19
5	1	12	14	14
6	1	12	14	-12
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-7	1	13	14	-13
-6	1	13	14	-20
-5	1	13	24	21
-4	1	13	25	29

H	K	L	|FO|	FC
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-1	1	13	37	37
0	1	13	43	41
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3	1	13	23	24
4	1	13	35	33
6	1	13	25	-23
8	1	13	19	14
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-5	1	14	22	-20
-4	1	14	24	-19
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-2	1	14	19	19
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2	1	14	23	20
3	1	14	18	-17
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5	1	15	26	26
7	1	15	12	-15
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-6	1	17	12	15
-4	1	17	21	-20
-2	1	17	26	25
0	1	17	24	-23
2	1	17	17	16
4	1	17	13	-11
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3	2	0	8	7
4	2	0	78	75
5	2	0	13	14
6	2	0	39	-40
7	2	0	24	-23
8	2	0	20	19
9	2	0	12	8
10	2	0	13	-11
-11	2	1	12	10
-9	2	1	21	-19
-8	2	1	14	-15
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-6	2	1	24	24
-5	2	1	63	-66
-4	2	1	48	-40
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-2	2	1	69	58
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1	2	1	150	137
2	2	1	81	78
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4	2	1	76	-68
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7	2	1	24	-27
8	2	1	24	-22
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3	2	2	28	-28
4	2	2	38	-34
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6	2	2	23	20
7	2	2	19	-19
8	2	2	13	-14
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1	2	3	81	-73
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4	2	3	23	-28
5	2	3	37	-37
7	2	3	14	18
-8	2	4	18	-22
-6	2	4	20	18
-5	2	4	15	12

H	K	L	|FO|	FC
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-3	2	4	14	-19
-2	2	4	70	77
-1	2	4	11	0
2	2	4	76	75
3	2	4	19	20
4	2	4	49	-61
6	2	4	26	29
7	2	4	13	12
8	2	4	14	-16
-8	2	5	17	21
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-4	2	5	58	56
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4	2	5	61	61
5	2	5	23	30
6	2	5	34	-35
7	2	5	18	-17
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-7	2	6	34	-35
-5	2	6	56	55
-4	2	6	23	25
-3	2	6	93	-81
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-1	2	6	91	86
0	2	6	51	59
1	2	6	86	-81
2	2	6	67	-71
3	2	6	76	78
4	2	6	65	64
5	2	6	42	-41
6	2	6	39	-38
7	2	6	20	17
8	2	6	18	19
-9	2	7	23	-21
-7	2	7	45	41
-5	2	7	53	-57
-4	2	7	11	-13
-3	2	7	76	75
-2	2	7	17	16
-1	2	7	84	-86
0	2	7	14	-13
1	2	7	14	11
2	2	7	30	24
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4	2	7	17	-14
5	2	7	47	45
7	2	7	27	-26
9	2	7	14	14
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Chapter 4

The Crystal Structure of $(Ph_3P)_2Ir(CO)(H)_2GeMe_3 \cdot \frac{1}{2}C_6H_6$

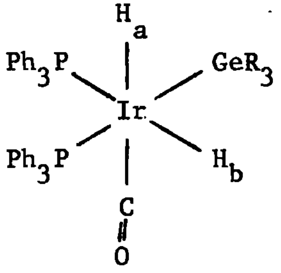
INTRODUCTION

When trans-$(Ph_3P)_2Ir(CO)Cl$ is reacted with R_3GeH, instead of forming the expected addition compound $(Ph_3P)_2(GeR_3)(CO)Ir(H)Cl$, the product $(Ph_3P)_2Ir(CO)(H)_2GeR_3$ was obtained by the reaction

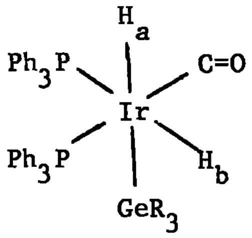
$$\text{trans-}(Ph_3P)_2Ir(CO)Cl + 2GeR_3H \longrightarrow R_3GeCl + \text{trans-}(Ph_3P)_2Ir(CO)(H)_2GeR_3$$

The reaction takes place over a number of weeks at 20°C, but at the reflux temperature of benzene requires only 12 hours. This compound can be crystallised from benzene, and, in one case, crystals formed in the reaction tube when it was left to cool slowly. The compound is stable to the air.

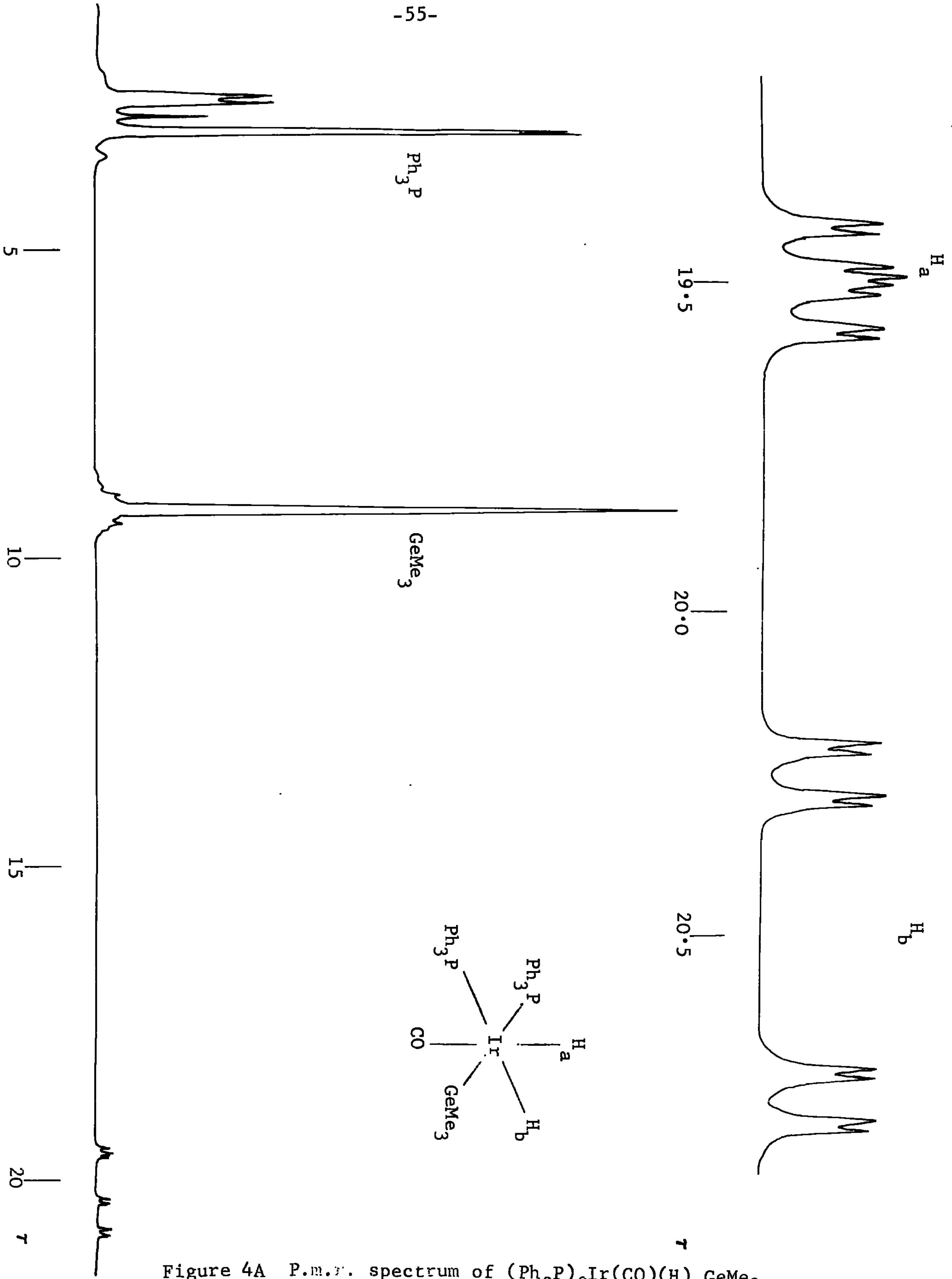
A 220 MHz N.P.R. study (Fig.4A) indicated that the two hydrogen atoms were cis to one another, with one cis to both phosphorus atoms, and one cis to one and trans to the other. This would yield two possible structures



(I)



(II)



<u>Figure 4A</u> P.m.r. spectrum of $(Ph_3P)_2Ir(CO)(H)_2GeMe_3$

From the absence of the long range ^{1}H-Ir-GeCH$_3$ coupling it was concluded that the correct structure was (I) (Glockling and Wilbey, 1969).

Later work on the compound yielded the rather interesting reaction

$$\text{trans-}(Ph_3P)_2Ir(CO)(H)_2GeR_3 + C_2H_4 \longrightarrow (Ph_3P)_2Ir(CO)GeR_3 + C_2H_6$$

which can be followed by

$$(Ph_3P)_2Ir(CO)GeR_3 + H_2 \longrightarrow (Ph_3P)_2Ir(CO)(H)_2GeR_3$$

In order to determine the correct stereochemistry of the compound with R = Me, it was decided to examine the crystal structure. If it was (I), then it was hoped that the length of the Ir-C bond length in the CO group would give further insight into the trans influence in Ir(III) compounds.

EXPERIMENTAL

The crystal employed in the study was recrystallised from benzene and mounted on a thin glass fibre. This crystal was cleaved from a larger crystal elongated in the 010 direction and cut to the dimensions 0·4 mm x 0·5 mm x 0·09 mm, thus being a rather thin, square plate with well developed $\{001\}$ faces.

Precession photographs were taken with the crystal mounted about b*, and, from the 0kl and hk0 nets, unit cell dimensions were calculated. When the crystal was placed on a four-circle diffractometer is was offset from the b axis in order to reduce the values of χ for the 0k0 reflections. The unit cell parameters and orientation matrix were refined employing the method of least squares (Busing and Levy, 1967) on the reflections

-3 0 26	14 0 6	-10 -8 0
9 1 16	4 1 26	0 12 0 *
0 -8 -22 *	0 -8 22	-9 0 -18

* included in refinement of the unit cell parameters only.

A 0·5mm diffracted beam collimater was employed in order to resolve the reflections due to the Mo Kα_1 and Mo Kα_2 radiation. The values for these reflections ranged from 19·19° (9 1 16) to 23·25° (0 -8 ± 22) for Mo Kα_1. The unit cell parameters were obtained as

$a = 13{\cdot}629(10)$Å $b = 11{\cdot}044(5)$Å $c = 26{\cdot}069(11)$Å

$\beta = 92{\cdot}52(3)^{\circ}$ $D_o = 1{\cdot}52$ g/cm^3 $D_c = 1{\cdot}54$ g/cm^3

$V = 3919{\cdot}9$Å^3 $Z = 4$ units of $(Ph_3P)_2IrCO(H)_2GeMe_3{\cdot}\frac{1}{2}C_6H_6$

The space group was determined from the precession photographs, and confirmed from measurements made on the diffractometer. The absences corresponded to the space group $P2_1/c$, which has been discussed in the previous chapter.

The data was collected employing a $\theta - 2\theta$ scan of 60 steps (0·01°/step) for 1·5 sec. per step. The backgrounds were measured at each side of the reflection for 15 sec. each. Three standard reflections (0 0 4; 0 1 5;

3 1 3) were measured every fifty reflections, and a drive to datum was carried out at the same interval. A 3·5 mm diffracted beam collimater was employed in order to minimise the background, and still have a margin for error in the calculation of the position of the reflection. Two shells of data were collected: 0° to 15°, measuring one half of the sphere of reflection, and 15° to 20°, measuring one quarter of the sphere. An attempt to collect a shell from 20° to 23° failed when the intensity of the standard reflections dropped suddenly, thus only part of the third shell was collected. A total of 5763 reflections were measured.

The counts for the equivalent reflections, $hk\bar{l}$ and $\bar{h}kl$, were averaged before correcting for Lorentz and polarization factors. A reflection was considered to be observed if the net measured intensity was greater than twice the e.s.d. calculated from counting statistics. The e.s.d. (σ_N) is defined as:

$$\sigma_N = \sqrt{(r_b\bar{B} + \bar{P})/n}$$

with

$$\bar{P} = \sum_{i}^{n} P_i/n$$

$$\bar{B} = \sum_{i}^{n} \bar{B}_i/n$$

where

r_b is defined as t_p/t_b

and t_p = total counting time for the peak

t_b = total counting time for both backgrounds

n = the number of times the peak was measured

There were 3560 observed reflections which were used in the refinement of the structure. For the solution of the structure, 2065 reflections with net counts larger than 500 were used.

SOLUTION

The structure was solved by the heavy atom method. The four heavy atoms were located from an unsharpened Patterson function. From an examination of the Harker line and the Harker section, the position of the iridium atom was deduced, which was confirmed by the presence of a peak at (2x,2y,2z). Based upon this position, the germanium atom and the two phosphorus atoms were found by examination of the vectors between them and iridium. At this stage the positions of the atoms were:

atom	x/a	y/b	z/c
Ir	0•205	0•125	0•1175
Ge	0•3075	-0•0375	0•0825
P(1)	0•0508	0•192	0•137
P(2)	0•300	0•1875	0•1738

Two cycles of least squares refinement were calculated (R = 0•25), and a difference map was computed. From this it was possible to arrive at the positions for all the phenyl carbon atoms. The remaining atoms were located from a second difference map calculated after refining the coordinates of the atoms already found for a further two cycles (R = 0•14). There were three peaks remaining with heights greater than 3 e.$\mathring{A}^{-3}$ located around the centre of symmetry at ($\frac{1}{2}$,$\frac{1}{2}$,0). These were later identified as half of a benzene molecule.

REFINEMENT

As in the case of the palladium hydride, the block diagonal approximation to the method of least squares was employed. The scattering factors for the heavy atoms were corrected for anomalous scattering, both the terms $\Delta f'$ and $\Delta f''$ being employed.

The heavy atoms were given anisotropic temperature factors, and two cycles of refinement gave R = 0•067. The full set of data was then employed (3560 planes) at this stage, and three cycles of refinement led to an R index of 0•062. After one cycle of refinement with all atoms having anisotropic temperature parameters the weighting function

$$\sqrt{w} = 1/(p_1 + |F_o| + p_2|F_o|^2 + p_3|F_o|^3)^{\frac{1}{2}}$$

was employed, where before unit weights were used. The weighting scheme was examined at the end of each cycle, and corrected as required. After four cycles, the R index became 0•052, and the shift of any parameter was less than one third of its e.s.d. The final coordinates are listed in Table 4a, the thermal parameters in Table 4b, and the final weighting

TABLE 4a

Final Atomic Coordinates and their Standard Deviations (x 10^5)

Atom	x/a	y/b	z/c	B_{iso} *
Ir	0·20424(4)	0·12455(5)	0·11673(2)	2·76
Ge	0·31056(13)	-0·03637(17)	0·08249(8)	4·71
O	0·23247(86)	0·28541(128)	0·02525(45)	6·02
P(1)	0·04857(29)	0·19411(38)	0·13902(16)	3·95
P(2)	0·32228(27)	0·21147(35)	0·17498(15)	5·20
C(1)	0·22254(110)	0·22724(159)	0·06170(61)	4·37
C(2)	0·42346(135)	-0·09831(144)	0·12587(94)	6·62
C(3)	0·22990(149)	-0·18535(169)	0·06791(90)	6·61
C(4)	0·36492(143)	0·00693(215)	0·01565(83)	7·14
C(5)	0·02211(100)	0·22065(133)	0·20607(57)	3·31
C(6)	-0·04749(120)	0·30851(154)	0·22022(73)	5·16
C(7)	-0·06531(140)	0·32417(158)	0·27320(76)	5·61
C(8)	-0·01351(122)	0·25486(152)	0·31054(66)	4·74
C(9)	0·05606(117)	0·16942(153)	0·29521(60)	4·49
C(10)	0·07482(111)	0·15436(148)	0·24336(61)	4·50
C(11)	-0·04577(105)	0·08010(149)	0·11996(64)	4·35
C(12)	-0·05516(132)	0·04866(233)	0·06840(70)	6·71
C(13)	-0·12297(143)	-0·04485(252)	0·05331(87)	7·92
C(14)	-0·17879(137)	-0·10024(198)	0·09023(86)	6·71
C(15)	-0·17031(122)	-0·06547(156)	0·14050(74)	4·98
C(16)	-0·10509(116)	0·02772(150)	0·15715(68)	4·81
C(17)	0·00172(118)	0·33015(164)	0·10678(60)	4·61
C(18)	0·06644(130)	0·42800(149)	0·09909(58)	4·41
C(19)	0·03520(171)	0·53457(189)	0·07529(71)	6·65
C(20)	-0·06215(183)	0·54800(221)	0·05794(89)	8·11
C(21)	-0·12637(154)	0·45764(237)	0·06499(90)	8·13
C(22)	-0·09744(141)	0·34191(219)	0·08808(86)	7·54
C(23)	0·31162(100)	0·37596(138)	0·18521(56)	3·66
C(24)	0·22490(115)	0·41951(133)	0·20584(61)	3·89
C(25)	0·20982(120)	0·54413(158)	0·21137(67)	4·99
C(26)	0·28105(134)	0·62708(159)	0·19766(67)	5·26
C(27)	0·36958(137)	0·58242(158)	0·17772(80)	5·56
C(28)	0·38483(121)	0·45683(154)	0·17256(66)	4·91
C(29)	0·45008(98)	0·19999(125)	0·15565(58)	3·65
C(30)	0·52525(113)	0·15605(146)	0·18984(69)	4·79

contd./

Table 4a contd.

Atom	x/a	y/b	z/c	B_{iso}[*]
C(31)	0·62050(117)	0·14432(150)	0·17123(66)	4·56
C(32)	0·64061(115)	0·17627(152)	0·12154(62)	4·22
C(33)	0·56746(111)	0·22399(161)	0·08738(65)	4·40
C(34)	0·47011(112)	0·23545(136)	0·10603(60)	3·90
C(35)	0·32926(103)	0·15092(148)	0·23979(58)	4·07
C(36)	0·31402(117)	0·02516(149)	0·24779(65)	4·82
C(37)	0·32168(131)	-0·02210(192)	0·29742(72)	6·08
C(38)	0·34312(124)	0·05135(194)	0·33959(70)	5·46
C(39)	0·35957(121)	0·17520(187)	0·33167(62)	5·18
C(40)	0·35327(108)	0·22373(167)	0·28189(56)	4·31
C(41)	0·42511(166)	0·42069(230)	-0·01692(89)	8·32
C(42)	0·52425(197)	0·41750(222)	-0·03741(86)	8·48
C(43)	0·59646(170)	0·49856(210)	-0·01809(81)	7·46

[*] From the last cycle when B_{iso} was refined.

TABLE 4b

Final Thermal Parameters[a] and their Standard Deviations (x 10^5)

	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Ir	0·00291(3)	0·00629(5)	0·00147(1)	-0·00041(4)	0·00048(3)	-0·00024(8)
Ge	0·00474(12)	0·00891(18)	0·00299(4)	-0·00352(15)	0·00050(11)	0·00127(24)
P(1)	0·00356(24)	0·00793(39)	0·00165(7)	-0·00009(27)	0·00084(21)	-0·00093(52)
P(2)	0·00336(23)	0·00625(34)	0·00149(6)	0·00015(23)	0·00025(20)	0·00094(48)
O	0·00706(88)	0·01726(170)	0·00211(23)	0·00348(104)	0·00085(73)	-0·00278(202)
C(1)	0·00370(100)	0·01197(185)	0·00182(30)	-0·00056(123)	-0·00086(87)	0·00235(231)
C(2)	0·00646(131)	0·00465(156)	0·00511(64)	-0·00213(151)	-0·00242(144)	0·00429(228)
C(3)	0·00874(156)	0·00801(181)	0·00420(57)	-0·00546(171)	-0·00031(147)	-0·00412(283)
C(4)	0·00705(143)	0·01914(299)	0·00311(46)	-0·00536(196)	0·00429(132)	0·00432(339)
C(5)	0·00307(89)	0·00723(139)	0·00189(29)	0·00109(105)	0·00171(81)	-0·00424(195)
C(6)	0·00484(111)	0·00831(170)	0·0304(41)	-0·00144(138)	0·00241(108)	0·00034(232)
C(7)	0·00798(141)	0·00797(165)	0·00306(43)	-0·00167(140)	0·00451(127)	-0·00319(261)
C(8)	0·00601(117)	0·00965(179)	0·00215(33)	-0·00120(123)	0·00179(100)	-0·00730(237)
C(9)	0.00540(111)	0·01042(177)	0·00169(29)	-0·00073(114)	0·00056(90)	-0·00525(231)
C(10)	0·00425(102)	0·00985(178)	0·00188(29)	-0·00016(114)	-0·00072(88)	-0·00366(218)
C(11)	0·00299(92)	0·00958(166)	0·00226(33)	-0·00016(120)	-0·00026(89)	-0·00226(207)
C(12)	0·00572(128)	0·02575(348)	0·00185(34)	-0·00473(182)	0·00042(103)	-0·01051(352)
C(13)	0·00567(136)	0·02683(389)	0·00318(50)	-0·00637(234)	0·00111(130)	-0·01072(386)
C(14)	0·00592(130)	0·01505(261)	0·00349(49)	-0·00312(183)	0·00057(128)	-0·00261(302)
C(15)	0·00525(117)	0·00818(166)	0·00300(42)	-0·00006(139)	0·00042(110)	-0·00079(238)
C(16)	0·00470(108)	0·00808(159)	0·00261(37)	0·00033(128)	0·00072(101)	-0·00057(226)
C(17)	0·00522(112)	0·01282(198)	0·00156(28)	0·00103(120)	0·00018(91)	0·00287(244)
C(18)	0·00873(136)	0·00858(162)	0·00137(27)	0·00094(109)	0·00121(97)	0·00425(248)
C(19)	0·01415(206)	0·01243(227)	0·00184(34)	-0·00060(146)	-0·00004(132)	0·00921(361)

contd./

Table 4b contd.

	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
C(20)	0·01344(214)	0·01566(282)	0·00308(51)	0·00300(199)	0·00291(168)	0·00921(410)
C(21)	0·00781(158)	0·02365(350)	0·00351(54)	0·00644(228)	-0·00064(146)	0·01940(405)
C(22)	0·00563(134)	0·02053(318)	0·00337(50)	0·00602(203)	0·00029(131)	0·00697(339)
C(23)	0·00331(90)	0·00703(134)	0·00165(27)	0·00027(113)	0·00023(80)	0·00066(204)
C(24)	0·00552(110)	0·00592(136)	0·00201(31)	-0·00124(104)	0·00109(93)	0·00125(203)
C(25)	0·00546(114)	0·00991(180)	0·00221(33)	-0·00080(130)	-0·00108(98)	-0·00085(243)
C(26)	0·00828(136)	0·00830(161)	0·00224(34)	-0·00154(135)	0·00077(109)	0·00013(270)
C(27)	0·00742(134)	0·00750(169)	0·00329(45)	-0·00005(139)	0·00157(125)	-0·00270(249)
C(28)	0·00574(118)	0·00906(173)	0·00227(34)	0·00206(128)	0·00189(101)	-0·00033(238)
C(29)	0·00266(88)	0·00544(134)	0·00209(30)	0·00000(102)	0·00120(81)	-0·00125(179)
C(30)	0·00384(101)	0·00851(171)	0·00272(37)	-0·00017(123)	0·00069(98)	0·00479(213)
C(31)	0·00509(109)	0·00898(176)	0·00234(34)	-0·00143(125)	0·00031(97)	0·00071(228)
C(32)	0·00465(107)	0·00979(168)	0·00191(30)	-0·00153(117)	0·00102(91)	-0·00236(226)
C(33)	0·00367(100)	0·01113(183)	0·00219(33)	-0·00057(129)	0·00131(92)	0·00008(231)
C(34)	0·00500(108)	0·00692(145)	0·00186(29)	-0·00021(106)	0·00123(89)	-0·00024(208)
C(35)	0·000306(92)	0·01085(184)	0·00168(27)	0·00007(112)	0·00041(80)	-0·00070(210)
C(36)	0·00502(109)	0·00902(167)	0·00229(33)	0·00404(127)	0·00115(97)	0·00230(231)
C(37)	0·00615(127)	0·01549(243)	0·00246(38)	0·00275(160)	0·00214(112)	-0·00141(294)
C(38)	0·00489(115)	0·01766(256)	0·00224(36)	0·00525(162)	0·00153(103)	0·00464(289)
C(39)	0·00494(112)	0·01740(248)	0·00159(29)	0·00090(137)	0·00078(93)	0·00481(275)
C(40)	0·00364(97)	0·01425(203)	0·00133(26)	0·00177(121)	-0·00009(81)	0·00064(238)
C(41)	0·01010(177)	0·01985(326)	0·00272(46)	0·00259(196)	-0·00007(144)	-0·00609(394)
C(42)	0·01609(237)	0·01588(293)	0·00246(45)	0·00106(183)	0·00087(165)	-0·00089(431)
C(43)	0·01179(189)	0·01586(270)	0·00250(42)	0·00089(175)	0·00244(144)	0·00001(376)

a where B_{ij} refers to the expression

$$\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2klB_{23} + 2hlB_{13})]$$

TABLE 4c

Final Analysis of the Weighting Function

$$\sqrt{w} = 1/(300{\cdot}0 + |F_o| + 0{\cdot}003\ |F_o|^2 + 0{\cdot}0003\,|F_o|^3)^{\frac{1}{2}}$$

F_o Range	Number	$\Sigma(w\Delta^2)/N$
0-30	469	0•11
30-40	473	0•06
40-50	409	0•04
50-60	394	0•04
60-70	289	0•05
70-80	286	0•03
80-100	424	0•03
100-140	469	0•04
140-500	347	0•04

analysis in Table 4c.

A difference map calculated after the refinement had been completed did not reveal any other features in the structure. The two peaks which were found in the map, larger than 1 $e.\mathring{A}^{-3}$, did not correspond to any chemically reasonable unit. An examination for the hydrogen atoms was not attempted since, with two such heavy atoms in the structure, the chance of finding them was considered remote.

DESCRIPTION

The crystallographic study confirmed the structure deduced from the N.M.R. spectra, with (I) having the correct stereochemistry. The unit cell contains, in addition to the complex, two molecules of benzene, the solvent from which the crystals were grown. Thus in the crystalline state, the correct formula is $(Ph_3P)_2Ir(CO)(H)_2GeMe_3.\frac{1}{2}C_6H_6$.

With a regular octahedral complex, there are three planes, mutually perpendicular, each passing through the central atom and four of the attached atoms in the coordination sphere. In the present case, two of the attached atoms are hydrogen and their positions were not determined. The equations of these mean planes are given in Table 4f. In the case of the central atoms, the equations were calculated using (a) unit weights for all atoms, (b) weights based upon the standard deviations of the atoms, (c) the positions of the three coordinated atoms alone and (d) the positions of two coordinated atoms and the iridium atom.

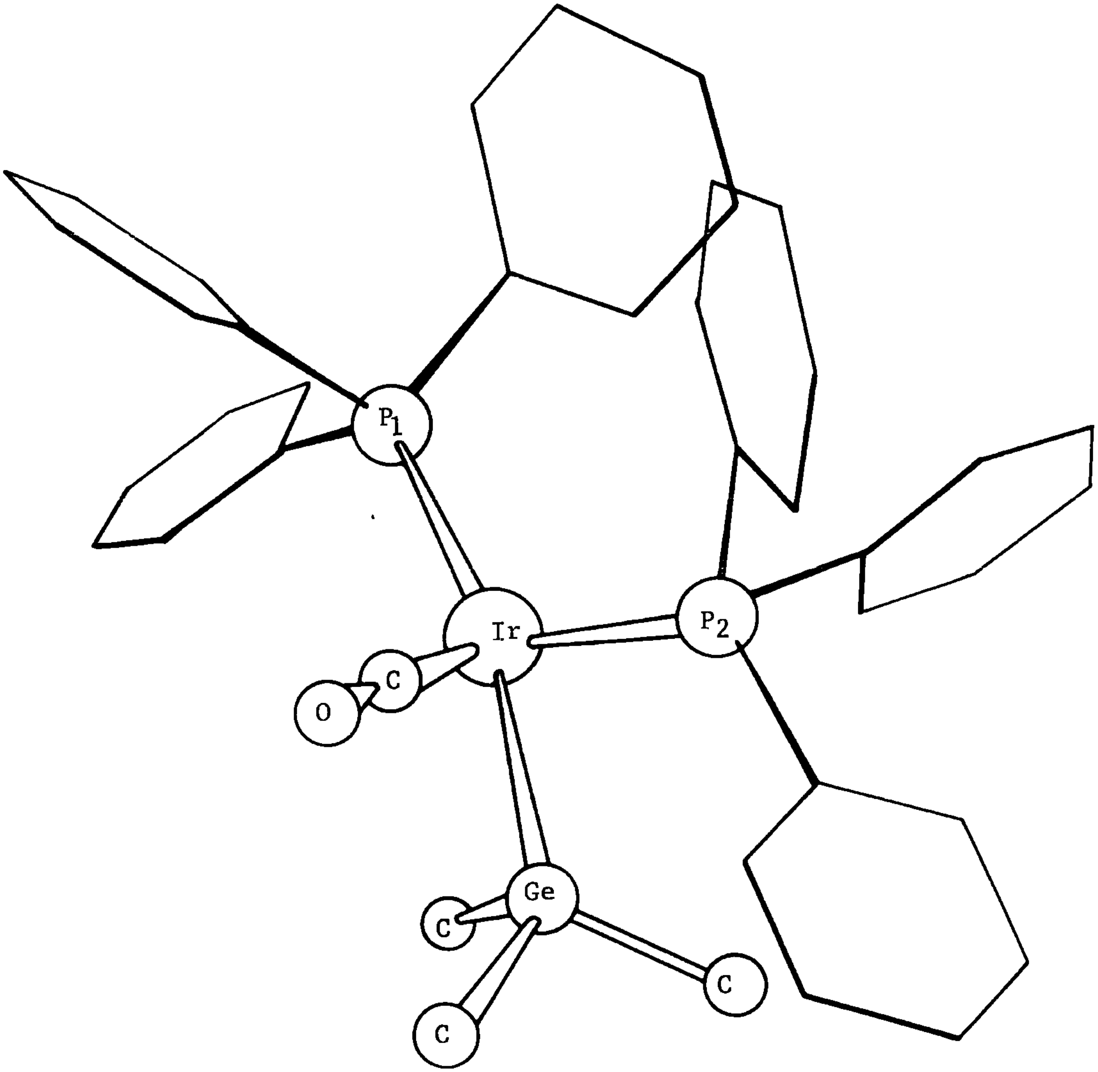


Fig.4B

Perspective Drawing

Plane I involved the atoms P(1), P(2), Ge, Ir. Good agreement was found between the equation (a) of this plane and that of the plane through the coordinated atoms. Both of these planes differed from the weighted plane, for which χ^2 = 15;327 confirming that the deviations from this plane are large.

Plane II includes the atoms P(1), Ge, C(1), and Ir and involves even larger deviations. In the case of the weighted plane, χ^2 = 10,754, but the carbon atom was located 1·62Å from the mean plane. If unit weights are used, the distance from the plane of the carbon atom is lessened, but χ^2 becomes larger. The Table below gives the dihedral angles, in each case, between the plane with unit weights and the other two planes.

Plane	Weighted	Three coordinated atoms
I	12·66°	2·14°
II	52·00°	7·38°

The iridium atom is displaced 0·26Å from plane Ic in the direction of the carbonyl group and also 0·48Å from plane IIc in the direction of P(2). This shows that the iridium atom does not lie at the intersection of the two planes, and is thus displaced from the expected centre of the coordination sphere. This effect is also observed in the dihedral angles within the central region as shown in the Table below.

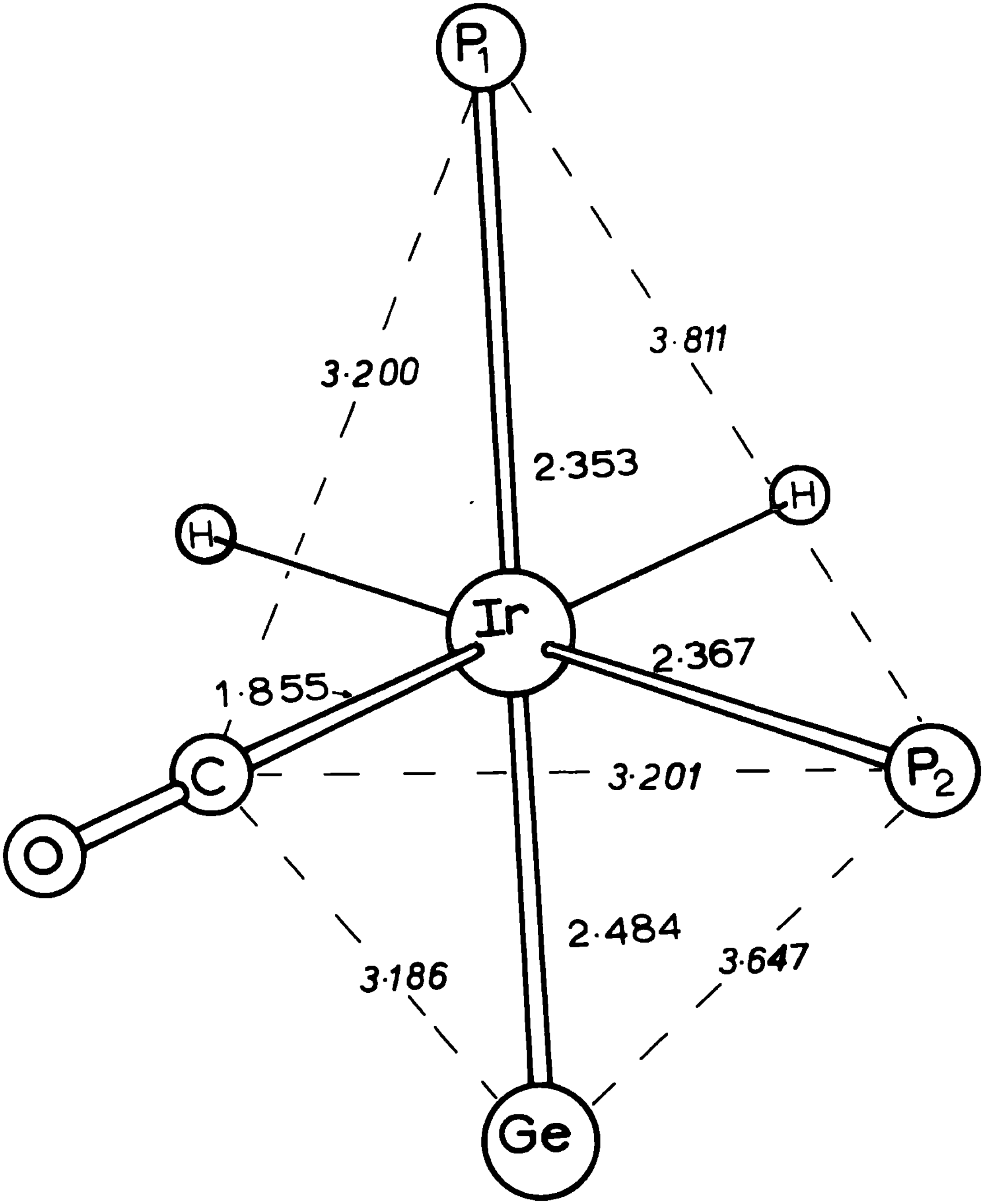


Fig.4C

Some Bond Lengths (Schematic Representation)

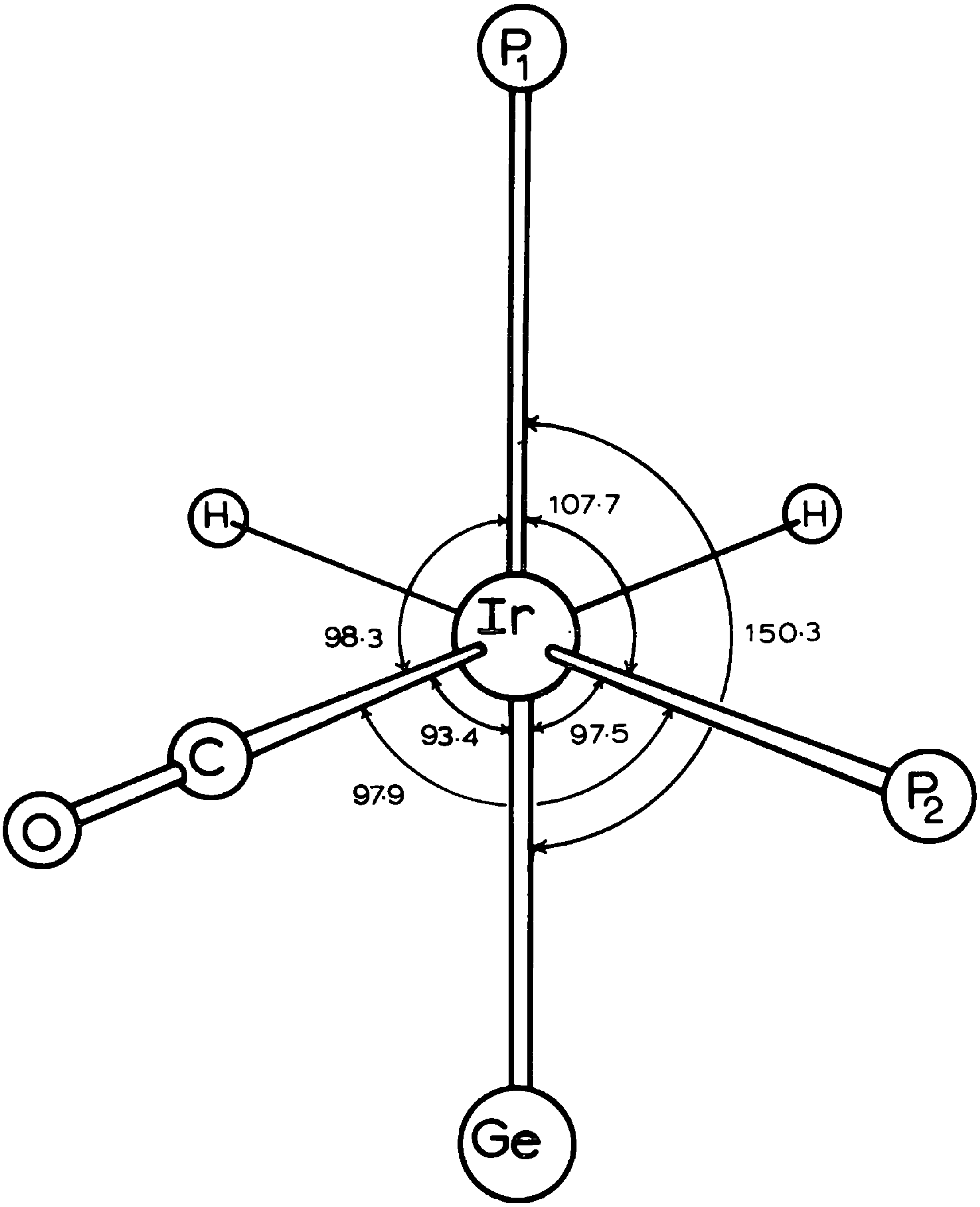


Fig.4D

Some Bond Angles (Schematic Representation)

Table 4j

Plane A	Plane B	Weighted	Unit weight	Three coordinated atoms
1	II	100·49°	109·91°	119·34°
I	III(d)	81·67°	69·41°	69·34°
II	III(d)	76·14°	91·12°	91·07°

The distortion can also be observed in the angles at iridium, where all the angles involving cis non-hydrogen atoms are greater than 90°. The P(1)-Ir-P(2) angle of 107·7(1)° is greater than the value of 101·2(4)° found in a square planar Pt(II) compound (Kashiwagi et al., 1969), but less than the value of 114·1(1)° found in a pseudo-octahedral compound (Manojlovic-Muir, Muir and Ibers, 1969). This value arises from the presence of additional steric factors, other than those due to the phosphine ligands, which were not found in either of the other two examples.

The P(1)-Ir-Ge angle would ideally be 180°, but is 150·3(1)°. This is explained when the P(2)-Ir-Ge angle of 97·5(1)° is considered. The $GeMe_3$ group has a number of contacts with the phenyl groups attached to P(2), which forces it to open the angle at the same time as the angle between the two phosphorus atoms is increased. These four atoms lie roughly in the same plane, thus an approximation of the two distortions gives an increase of 25·2°, a value close to the 30° difference found in the P(1)-Ir-Ge angle, where it is bent toward the hydride region.

From this information given, it is possible to arrive at some conclusions regarding the additional steric factors involved in this compound. There are three large groups in this molecule: the two phosphine ligands and the germyl group. Cis to these three groups, there is the carbonyl group, which forms close contacts with these ligands. There are two cis hydrogens, resulting in a relatively unoccupied region which the three larger groups can use to relieve the stresses applied by their close contacts. For this reason, it is possible to think of this molecule as being approximately one sided, in the general form of a "V". It is important to remember that the more the molecule becomes deformed, the more strain is put on the bonds' angles, and additional steric interactions can occur.

The Ir-C(1)-O angle has a value of 175•70(1•44)°. The Student t value for this, in comparison to an angle of 180° is 2•99, thus the oxygen can be considered colinear with the iridium atom and carbon(1) at the 0•2% probability level. The C-O bond length of 1•16(2)Å has one of the longest values found in iridium carbonyl complexes which range from 1•05Å (McGinnety, Doesens and Ibers, 1966) to 1•165Å (Manojlovic-Muir, Muir and Ibers, 1969). The Ir-C(1)bond length of 1•854(16)Å is one of the shortest values found, as can be seen from an examination of Table 2j. This, together with the long C-O bond, indicates that there may be strong back donation from the iridium atom to the carbonyl group.

The two P-Ir-C angles are in good agreement with each other, with an average value of 98·1°. This is larger than the C(1)-Ir-Ge angle of 93·4(5)°. Yet the carbonyl group has three equal intra-molecular contacts of 3·200(16)Å, 3·201(16)Å, and 3·186(17)Å between C(1) and P(1), P(2) and Ge respectively. The contacts involving the oxygen atom are normal, the closest contact being between it and one of the carbon atoms in the benzene molecule (3·25Å).

All the Ge-C bond lengths in the GeMe$_3$ group agree very well, with an average value of 1·993(6)Å ($\chi^2 = 0{\cdot}73$). This is in good agreement with other values obtained for the Ge-C bond length, such as the value of 1·98Å in GeMe$_4$ (Glockling, 1969). The C-Ge-C angles have an average value of 104·6(6)°, with good agreement between all values ($\chi^2 = 4{\cdot}7$). This angle is smaller than the tetrahedral value; this deviation will be discussed later.

Although a mean value for the Ir-Ge-C angle can be calculated (115·84°), it is apparent that the three angles are not equal. These angles range between 109·4° and 119·4° for C(3) and C(2) respectively. This variation can be explained in terms of the steric interactions for each of the carbon atoms. The atom C(2) has contacts of less than 4Å with four carbons in phenyl (V), as well as the normal contacts within the germyl group. C(3), on the other hand, only has contacts with carbon atoms within the group. The third carbon atom in the ligand, C(4), has a number of intermolecular contacts of less than 4Å, including one with itself in the symmetry related position ($\bar{x},\bar{y},\bar{z}$) at a distance of 3•80Å.

It is interesting to note that the internal relationships within the $GeMe_3$ group are consistent, but the steric interactions move the entire unit in relation to the iridium atom. This same effect is found in the phosphine groups, as will be noted later.

The Ge-Ir bond length of 2•484(2)Å can only be compared to the sum of the covalent radii, 2•56Å. This is consistent with the germanium iridium bond having some partial double bonding arising from (d_π-d_π) interactions.

Within the seven benzene rings, all the C-C distances have an average value of 1•406(3)Å with χ^2 = 22•5. This is within,experimental error, the same value found by electron diffraction of 1•397(1)Å. The average C-C-C angle of 119•97(22)°, with χ^2 = 44•21 agrees with the expected value of 120°. The r.m.s. deviations for the bond length is 0•023Å, and for the angle is 1•80°. This is in good agreement with average e.s.d.'s calculated by the least squares programme of 0•026Å and 1•65° for the bond lengths and angles respectively. Mean planes for the phenyl groups (unit weights) gave the values listed in Table 4g. The χ^2values ranged from 1•34 to 4•06, with four of them having values around 2•25, indicating that the rings are planar within experimental error. The distance from the plane to the bonded phosphorus atom varied between 0•023(2)Å and 0•131(4)Å. These deviations are probably caused by the steric interactions of the phenyl groups.

The mean value of the six C-P-C angles is 102•3(3)°, with χ^2 = 9•35, This is less than the tetrahedral value, but is in good agreement with values found in other phosphines. The average P-C bond length is 1•833(5)Å, with good agreement amongst the six values measured (χ^2 = 3•81). It also agrees with other measured values. A comparison of these lengths and angles with those in the PEt_3 ligand, as measured in the palladium compound reveals that there is no significant difference in going from an alkyl to an aryl phosphine in these cases.

The two Ir-P bonds have an average length of 2•360(3)Å. The individual values are 2•353(4)A and 2•367(4)A involving P(1) and P(2) respectively. The value of the Student t function is 2•54, so that the difference in lengths is not significant at the 1% probability level. From these two measurements, the order in the trans influence series appears to be

$$H \sim Ge$$

As in the germyl group, there is a large range of Ir-P-C angles, varying between 109•5(5)° and 120•5(5)°, and having an average value of 115•8°. The χ^2 value of 246 employing five degrees of freedom, indicates that the values are not the same, even at the 0•01% confidence level. This variation is caused by the non-bonding contacts within the structure, thus giving rise to large steric effects.

Phenyl(I) has the largest Ir-P-C angle, with a value of 120•5(5)°. This is caused by the crowding of phenyl (I) by phenyl (II), phenyl (IV) and phenyl (VI). Two of these groups, phenyl (II) and phenyl (IV), have ortho hydrogens which give close contacts, forcing phenyl (I) to conform to an angle where it is able to relieve this strain.

Phenyl (II) has the smallest angle, 109·5(5)°. Most of its contacts are with phenyl (III) and the symmetry related position of phenyl (V) at $(x, \frac{1}{2}+y, \frac{1}{2}-z)$.

Phenyl (III) with an angle of 117·1(6)° has relatively few interactions with other phenyl groups. One interesting point is the position of the ortho hydrogen bonded to C(18), which is directed toward the coordination sphere of the iridium. It is unlikely that it is engaged in bonding with the metal, since the distance from the iridium atom to the hydrogen would be greater than 3Å.

Phenyl (IV) has few contacts, and thus a fairly normal angle of 115·9(5)°. The few contacts are long ones with phenyl (V), phenyl (VI), and phenyl (I), the latter interacting with one of the ortho hydrogens.

Phenyl (V) as has been mentioned before, has an interaction with the germyl group. This is its only important contact, thus there is little distortion in the Ir-P-C angle of 114·9(5)°. One of its ortho hydrogens points towards the oxygen, but the distance involved would make any bonding impossible.

Phenyl (VI), like the other phenyl groups of this phosphine, has a relatively undistorted angle of 117·1(5)°. As before, it is possible to find an ortho-hydrogen bonded to C(36), which is directed toward the coordination sphere of the iridium.

The benzene of crystallisation is located within a hole formed by the ligands phenyl (IV), $GeMe_3$, CO, phenyl (II), and phenyl (III), with the latter located at the position $(\bar{x},\bar{y},\bar{z})$. As is expected, this molecule has a large thermal motion, when compared with the phenyl groups attached to the phosphorus atoms. The closest contacts are between the oxygen and C(41) and C(43'), with distances of 3·25(2)Å and 3·35(3)Å respectively. These contacts with the oxygen may explain why the solvent molecule is not disordered, since there is a possibility of weak interactions between the hydrogens and the oxygen. These interactions will take place at either end of the molecule, since it is situated about a centre of inversion at $(\frac{1}{2},\frac{1}{2},0)$.

The molecular arrangement in this compound is strongly influenced by the large number of steric interactions. At the present time the chemistry of the complex is being studied, as was noted earlier, and these steric factors may well play an important part of its chemistry.

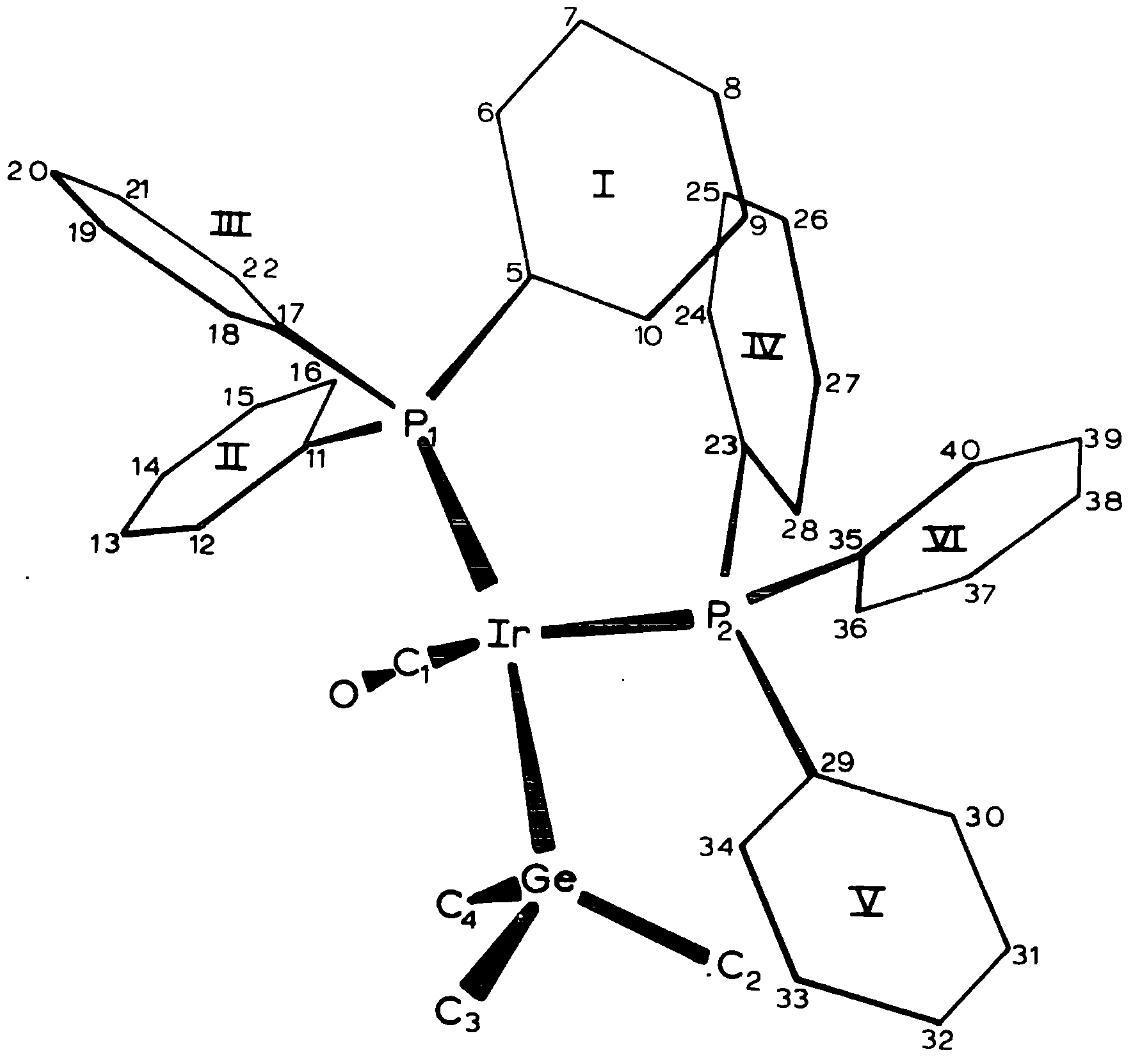


Fig.4E

Numbering of Atoms

TABLE 4d

Final Bond Lengths and their Standard Deviations [a]

Central coordination sphere	Ir-Ge	2·484(2)Å
	Ir-P(1)	2·353(4)
	Ir-P(2)	2·367(4)
	Ir-C(1)	1·854(16)
$GeMe_3$ and CO ligands	Ge-C(2)	1·990(20)
	Ge-C(3)	2·006(19)
	Ge-C(4)	1·982(22)
	C(1)-O	1·160(21)
Phosphine Groups	P(1)-C(5)	1·824(15)
	P(1)-C(11)	1·852(16)
	P(1)-C(17)	1·823(18)
	P(2)-C(23)	1·843(16)
	P(2)-C(29)	1·839(14)
	P(2)-C(35)	1·816(16)
Phenyl (I)	C(5)-C(6)	1·42(2)
	C(6)-C(7)	1·42(3)
	C(7)-C(8)	1·40(3)
	C(8)-C(9)	1·41(2)
	C(9)-C(10)	1·40(2)
	C(10)-C(5)	1·39(2)
Phenyl (II)	C(11)-C(12)	1·39(3)
	C(12)-C(13)	1·43(3)
	C(13)-C(14)	1·39(3)
	C(14)-C(15)	1·37(3)
	C(15)-C(16)	1·41(2)
	C(16)-C(11)	1·42(2)
Phenyl (III)	C(17)-C(18)	1·42(2)
	C(18)-C(19)	1·39(3)
	C(19)-C(20)	1·39(3)
	C(20)-C(21)	1·34(3)
	C(21)-C(22)	1·46(3)
	C(22)-C(17)	1·42(3)

Phenyl (IV)	C(23)-C(24)	1·40(2)
	C(24)-C(25)	1·40(3)
	C(25)-C(26)	1·39(2)
	C(26)-C(27)	1·42(3)
	C(27)-C(28)	1·41(2)
	C(28)-C(23)	1·39(2)
Phenyl (V)	C(29)-C(30)	1·41(2)
	C(30)-C(31)	1·41(2)
	C(31)-C(32)	1·38(2)
	C(32)-C(33)	1·40(2)
	C(33)-C(34)	1·44(2)
	C(34)-C(29)	1·39(2)
Phenyl (VI)	C(35)-C(36)	1·42(2)
	C(36)-C(37)	1·40(3)
	C(37)-C(38)	1·39(3)
	C(38)-C(39)	1·40(3)
	C(39)-C(40)	1·40(2)
	C(40)-C(35)	1·39(2)
Benzene	C(41)-C(42)	1·48(3)
	C(42)-C(43)	1·41(3)
	C(43)-C(41)	1·32(3)

a (x 10^3) for all bonds except carbon-carbon

(x 10^2) for carbon-carbon bonds

TABLE 4e

Final Angles and their Standard Deviations [*]

Central coordination sphere	Ge-Ir-P(1)	150·33(11)°
	Ge-Ir-P(2)	97·47(10)
	Ge-Ir-C(1)	93·39(50)
	P(1)-Ir-P(2)	107·70(14)
	P(1)-Ir-C(1)	98·33(51)
	P(2)-Ir-C(1)	97·91(51)
GeMe$_3$ and CO ligands	C(2)-Ge-C(3)	103·26(83)
	C(2)-Ge-C(4)	105·84(86)
	C(3)-Ge-C(4)	104·74(87)
	Ir-Ge-C(2)	119·36(58)
	Ir-Ge-C(3)	109·36(60)
	Ir-Ge-C(4)	112·95(63)
	Ir-C(1)-O	175·70(1·44)
Phosphine Groups	C(5)-P(1)-C(11)	101·67(70)
	C(5)-P(1)-C(17)	103·26(72)
	C(11)-P(1)-C(17)	102·22(74)
	C(23)-P(2)-C(29)	100·91(66)
	C(23)-P(2)-C(35)	103·28(68)
	C(29)-P(2)-C(35)	102·60(68)
	Ir-P(1)-C(5)	120·50(50)
	Ir-P(1)-C(11)	109·55(52)
	Ir-P(1)-C(17)	117·15(56)
	Ir-P(2)-C(23)	115·91(48)
	Ir-P(2)-C(29)	114·94(47)
	Ir-P(2)-C(35)	117·00(51)
Phenyl (I)	P(1)-C(5)-C(6)	121·5(1·2)
	P(1)-C(5)-C(10)	117·9(1·1)
	C(10)-C(5)-C(6)	120·6(1·4)
	C(5)-C(6)-C(7)	118·7(1·5)
	C(6)-C(7)-C(8)	120·3(1·6)
	C(7)-C(8)-C(9)	119·5(1·6)
	C(8)-C(9)-C(10)	120·6(1·5)
	C(9)-C(10)-C(5)	120·2(1·4)

contd./

Table 4e (contd.)

Phenyl (II)	P(1)-C(11)-C(12)	117·6(1·3)
	P(1)-C(11)-C(16)	120·4(1·2)
	C(16)-C(11)-C(12)	122·0(1·6)
	C(11)-C(12)-C(13)	118·6(1·8)
	C(12)-C(13)-C(14)	119·5(2·0)
	C(13)-C(14)-C(15)	120·8(2·0)
	C(14)-C(15)-C(16)	121·7(1·7)
	C(15)-C(16)-C(11)	117·2(1·5)
Phenyl (III)	P(1)-C(17)-C(18)	119·1(1·2)
	P(1)-C(17)-C(22)	122·8(1·4)
	C(22)-C(17)-C(18)	118·1(1·6)
	C(17)-C(18)-C(19)	122·0(1·6)
	C(18)-C(19)-C(20)	120·3(1·9)
	C(19)-C(20)-C(21)	119·6(2·2)
	C(20)-C(21)-C(22)	122·7(2·2)
	C(21)-C(22)-C(17)	117·2(1·9)
Phenyl (IV)	P(2)-C(23)-C(24)	117·8(1·1)
	P(2)-C(23)-C(28)	122·5(1·2)
	C(28)-C(23)-C(24)	119·7(1·4)
	C(23)-C(24)-C(25)	120·4(1·4)
	C(24)-C(25)-C(26)	120·9(1·6)
	C(25)-C(26)-C(27)	118·5(1·6)
	C(26)-C(27)-C(28)	120·4(1·7)
	C(27)-C(28)-C(23)	120·0(1·5)
Phenyl (V)	P(2)-C(29)-C(30)	121·3(1·1)
	P(2)-C(29)-C(34)	117·6(1·1)
	C(34)-C(29)-C(30)	121·1(1·4)
	C(29)-C(30)-C(31)	117·8(1·5)
	C(30)-C(31)-C(32)	121·5(1·5)
	C(31)-C(32)-C(33)	121·6(1·5)
	C(32)-C(33)-C(34)	117·2(1·5)

contd./

Table 4e contd.

Phenyl (VI)	P(2)-C(35)-C(36)	119•6(1•2)
	P(2)-C(35)-C(40)	121•6(1•2)
	C(40)-C(35)-C(36)	118•8(1•4)
	C(35)-C(36)-C(37)	119•8(1•5)
	C(36)-C(37)-C(38)	121•4(1•7)
	C(37)-C(38)-C(39)	118•9(1•7)
	C(38)-C(39)-C(40)	120•3(1•6)
	C(39)-C(40)-C(35)	120•8(1•5)
Benzene	C(43')-C(41)-C(42)	120•2(2•2)
	C(41)-C(42)-C(43)	119•5(2•1)
	C(42)-C(43)-C(41')	120•3(2•2)

* (x 10^2) for all angles except X-C-X

(x 10^0) for angles about carbon

TABLE 4f

Mean Planes within the Coordination Sphere

Plane	A	B	C	D	χ^2	Ir	Ge	P(1)	P(2)	C(1)	O
Ia	0·1647	0·6575	-0·7353	-1·0879	107936	0·193	-0·074	-0·082	-0·037	(2·044)	-
Ib	0·2266	0·6250	-0·7470	-0·8312	15327	0·020	-0·087	-0·420	-0·163	(1·870)	-
Ic	0·1548	0·6510	-0·7431	-1·2174	0	(0·264)	0·0	0·0	0·0	(2·115)	-
IIa	-0·5000	-0·3925	-0·7218	-3·8928	375789	-0·352	0·141	0·152	(-2·703)	0·059	(0·391)
IIb	-0·1815	0·3054	-0·9348	-2·8975	10754	-0·005	0·016	0·076	(-1·410)	1·624	(2·676)
IIc	-0·5571	-0·3638	-0·7465	-3·7628	0	(-0·483)	0·0	0·0	(-2·824)	0·0	(0·376)
IIId	0·7124	-0·6175	-0·3334	-0·0249	0	0·0	2·455	-2·198	0·0	0·0	0·046
Standard Deviations						0·001	0·002	0·004	0·004	0·016	0·013

Plane I involves Ir, P(1), P(2), and Ge

Plane II involves Ir, P(1), Ge, C(1)

Plane III " Ir, C(1), and P(2)

$AX' + BY + CZ' - D = 0$ X', Y, Z' refer to the orthogonal coordinates in Å

() Atoms not included in the plane

TABLE 4g

Mean Planes* of the Phenyl Groups

Phenyl Group	A	B	C	D	2	distance of the P from the plane	Ir-P-C
I	-0·7093	-0·7020	-0·0647	-2·1182	2·07	0·023(4)Å	120·5(5)°
II	-0·7063	0·6881	-0·1662	0·6498	4·06	-0·131(4)	109·5(5)
III	0·2645	-0·3733	-0·8892	0·6323	2·14	-0·038(4)	117·2(6)
IV	-0·3729	0·0456	-0·9267	-5·8025	2·54	0·123(4)	115·9(5)
V	-0·2000	-0·9279	-0·3146	-4·5318	2·55	0·093(4)	114·9(5)
VI	0·9790	-0·1763	-0·1021	3·2028	1·36	0·024(4)	117·0(5)

* $AX' + BY + CZ' - D = 0$ X', Y, Z' refer to the orthogonal coordinates in Å

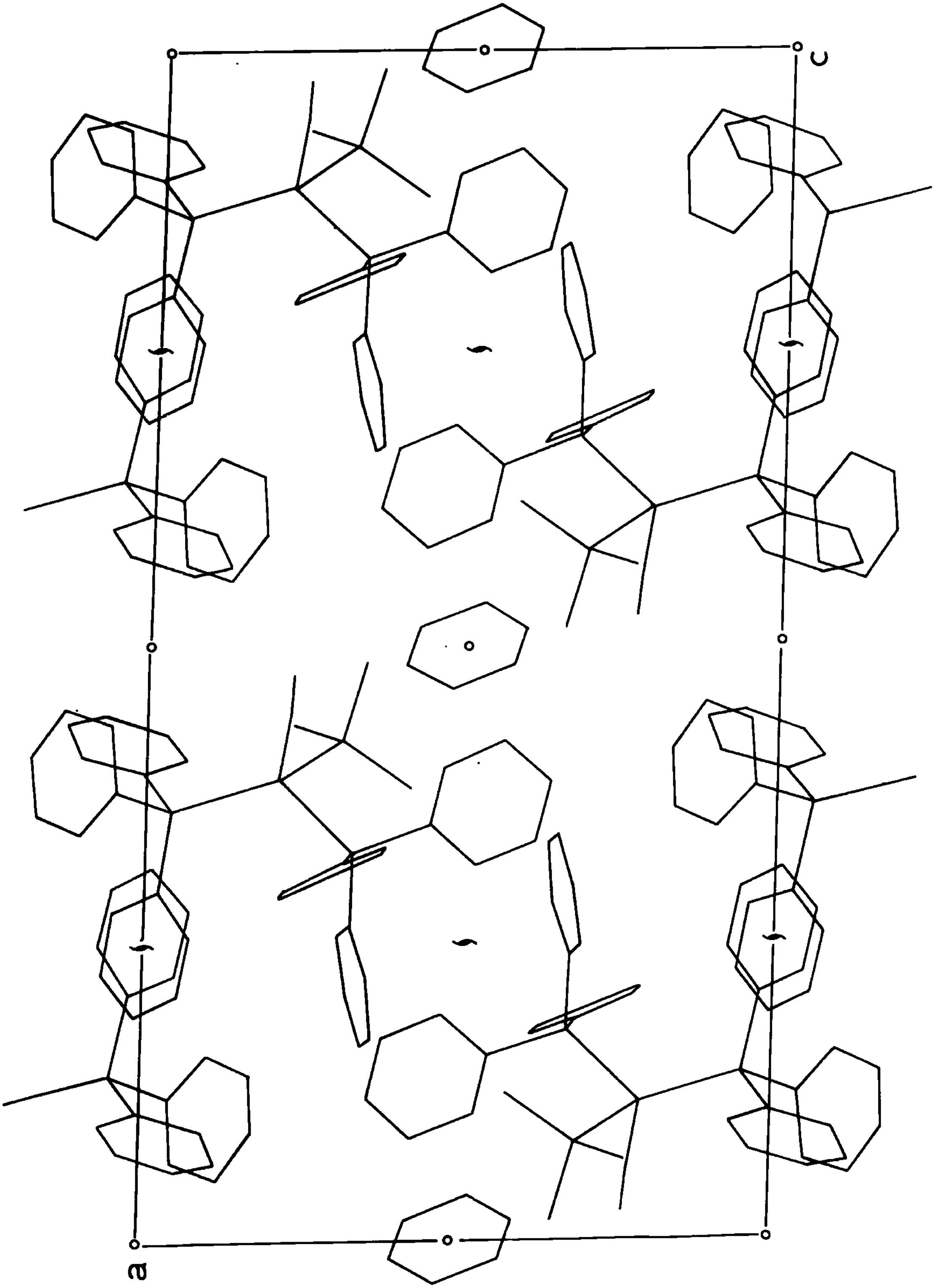


Fig.4F.

Projection on the 010 Plane

TABLE 4h

Some Non-bonding Contacts within the Molecule *

	Atom A	Atom B	A-B (Å)
Central atoms and Oxygen	Ir	O	3·01
		C(2)	3·87
		C(3)	3·67
		C(4)	3·73
		C(11)	3·45
		C(17)	3·57
		C(23)	3·58
		C(29)	3·56
		C(35)	3·58
		C(10)	3·82
		C(12)	3·79
		C(18)	3·86
		C(34)	3·85
		C(36)	3·83
	Ge	C(29)	3·71
		C(34)	3·74
	P(1)	P(2)	3·81
		C(24)	3·83
	P(2)	Ge	3·65
		C(2)	3·92
		C(10)	3·93
	O	Ge	3·98
		C(4)	3·58
		C(18)	3·42
		C(34)	3·82
		C(41)	3·25
		C(43)	3·35

* Contacts within a phenyl group are not given

Standard deviations range from 0·02 to 0·03Å for carbon-carbon lengths and 0·01 to 0·02Å for heavy atom-carbon lengths.

Table 4h contd.

	Atom A	Atom B	A-B (Å)
	C(1)	Ge	3·19
		P(1)	3·20
		P(2)	3·20
		C(4)	3·37
		C(17)	3·47
		C(18)	3·25
		C(34)	3·52
Phosphine groups	C(5)	C(11)	2·85
		C(17)	2·86
	C(11)	C(17)	2·86
	C(23)	C(29)	2·84
		C(35)	2·87
	C(29)	C(35)	2·85
$GeMe_3$ group	C(2)	C(3)	3·13
		C(4)	3·17
		C(29)	3·40
		C(30)	3·52
		C(31)	3·94
		C(29)	3·40
		C(30)	3·52
		C(31)	3·94
		C(34)	3·78
		C(36)	3·82
	C(3)	C(4)	3·16
	C(4)	C(34)	3·70
Phenyl (I)	C(5)	C(16)	3·00
		C(18)	3·68
		C(22)	3·67
		C(24)	3·53
	C(6)	C(16)	3·58
		C(22)	3·50
	C(10)	C(16)	3·54
		C(24)	3·73
		C(35)	3·47
		C(36)	3·56

contd./

Table 4h contd.

	Atom A	Atom B	A-B (Å)
Phenyl (II)	C(11)	C(6)	3·63
		C(10)	3·65
		C(22)	3·08
	C(12)	C(22)	3·33
Phenyl (III)	C(17)	C(6)	3·07
		C(12)	3·35
Phenyl (IV)	C(23)	C(34)	3·42
		C(40)	3·06
	C(24)	C(10)	3·73
		C(18)	3·45
		C(40)	3·37
	C(25)	C(18)	3·68
	C(28)	C(34)	3·24
Phenyl (V)	C(29)	C(28)	3·01
		C(36)	3·65
		C(40)	3·61
	C(30)	C(28)	3·85
		C(36)	3·61
		C(40)	3·51
Phenyl (VI)	C(35)	C(24)	3·39
		C(30)	3·02
	C(40)	C(23)	3·06
		C(24)	3·37
		C(30)	3·51
Benzene	C(41)	C(33)	3·93
		C(34)	3·83
		C(38)b	3·87
	C(42)	C(33)	3·92
		C(27) a	3·99
		C(38) b	3·98
	C(43)	C(1) a	3·35
		C(34) a	3·81

a located at the position $\bar{x},\bar{y},\bar{z}$

b located at the position $x,\frac{1}{2}-y,\frac{1}{2}+z$

TABLE 4i

Intermolecular Contacts

Atom A	Atom B	Position	A-B (Å)
O	C(43)	2	3·35
	C(13)	2	3·64
	C(14)	2	3·67
	C(20)	2	3·61
C(1)	C(13)	2	3·81
C(2)	C(27)	1	3·86
C(4)	C(13)	2	3·71
	C(14)	2	3·81
	C(4)	2	3·81
	C(33)	2	3·84
C(7)	C(25)	3	3·70
	C(26)	3	3·76
	C(16)	3	3·66
	C(10)	3	3·67
C(8)	C(19)	3	3·86
	C(25)	3	3·57
	C(15)	3	3·40
	C(16)	3	3·50
C(9)	C(15)	3	3·68
	C(25)	3	3·88
C(10)	C(7)	3	3·67
C(15)	C(31)	1	3·79
	C(32)	1	3·73
C(16)	C(25)	3	3·78
C(19)	C(20)	2	3·62
C(20)	C(20)	2	3·68
C(26)	C(30)	3	3·87
	C(31)	3	3·62

contd./

TABLE 4i contd.

Atom A	Atom B	Position	A-B (Å)
C(27)	C(30)	3	3·77
	C(39)	3	3·85
	C(38)	3	3·88
C(31)	C(37)	3	3·85
C(38)	C(41)	4	3·87

Position		Position	
1.	$x,y,z,$	2.	$\bar{x},\bar{y},\bar{z},$
3.	$\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$	4.	$x,\frac{1}{2}-y,\frac{1}{2}+z$

TABLE 4k

Final Values of the Observed and Calculated Structure Factors

H	K	L	|FO|	FC
0	0	2	44	-66
0	0	4	188	-177
0	0	6	142	-145
0	0	8	68	70
0	0	10	183	178
0	0	12	65	-71
0	0	14	101	-111
0	0	16	102	111
0	0	18	75	80
0	0	20	97	-100
0	0	22	103	-101
0	0	24	52	43
0	0	26	51	51
1	0	0	132	127
1	0	2	512	-503
1	0	-2	470	470
1	0	4	207	-214
1	0	-4	31	-30
1	0	6	60	-52
1	0	-6	352	-364
1	0	8	226	254
1	0	-8	76	-70
1	0	10	135	-146
1	0	-10	144	150
1	0	12	284	-324
1	0	-12	16	27
1	0	14	134	142
1	0	-14	16	-43
1	0	16	133	147
1	0	-16	39	-42
1	0	18	97	-105
1	0	-18	146	153
1	0	20	55	-37
1	0	-20	87	83
1	0	-22	33	-46
1	0	24	66	67
1	0	-24	70	-71
1	0	-26	40	30
1	0	28	52	-45
1	0	-28	68	50
2	0	0	267	-248
2	0	2	50	-55
2	0	-2	28	-31
2	0	4	283	276
2	0	-4	101	108
2	0	6	246	305
2	0	-6	100	-33
2	0	8	31	-45
2	0	-8	183	-173
2	0	10	147	-159
2	0	-10	131	124
2	0	12	21	21
2	0	-12	118	125
2	0	14	202	224
2	0	16	18	-25
2	0	-16	160	-168
2	0	18	104	-106
2	0	-18	67	-71
2	0	-20	153	164
2	0	22	91	97
2	0	-22	67	71
2	0	-24	104	-97
2	0	26	67	-60
2	0	-26	57	-54
2	0	-28	41	41
3	0	0	150	151
3	0	2	147	146
3	0	-2	561	-542
3	0	4	323	307
3	0	-4	74	52
3	0	6	66	48
3	0	-6	70	70
3	0	8	188	-186
3	0	-8	119	-113
3	0	10	24	15
3	0	-10	88	-87
3	0	12	297	317
3	0	-12	139	152
3	0	-14	137	137
3	0	16	119	-129
3	0	18	42	-44
3	0	-18	178	-180
3	0	20	95	98
3	0	-20	64	-73
3	0	22	43	36
3	0	-22	148	145
3	0	24	63	-60
3	0	-24	68	67
3	0	26	44	-43
3	0	-26	96	-92
3	0	-28	33	-28
4	0	0	87	81
4	0	2	217	182
4	0	-2	158	-128
4	0	4	91	-76
4	0	-4	123	-117
4	0	6	303	-298
4	0	-6	100	96
4	0	8	42	46
4	0	-8	117	110
4	0	10	377	393
4	0	-10	198	-192
4	0	12	50	-56
4	0	-12	260	-254
4	0	14	212	-223
4	0	-14	173	165
4	0	16	92	-90
4	0	-16	174	200
4	0	18	51	50
4	0	-18	36	-23
4	0	20	172	169
4	0	-20	147	-142
4	0	22	76	-78
4	0	-22	27	-15
4	0	24	103	-97
4	0	-24	112	101
4	0	26	46	48
4	0	-26	37	29
5	0	0	137	187
5	0	2	97	-95
5	0	-2	221	[illegible]
5	0	4	224	-217
5	0	-4	241	-264
5	0	6	115	105
5	0	-6	38	-35
5	0	8	251	251
5	0	-8	346	325
5	0	-10	232	230
5	0	12	265	-254
5	0	-12	104	-100
5	0	14	67	-65
5	0	-14	148	-150
5	0	16	78	72
5	0	-16	116	114
5	0	18	147	155
5	0	-18	114	115
5	0	20	64	-66
5	0	-20	47	-41
5	0	22	114	-107
5	0	-22	111	-105
5	0	24	66	63
5	0	-24	56	47
6	0	0	125	128
6	0	2	263	-276
6	0	-2	152	157
6	0	4	115	-119
6	0	-4	61	-62
6	0	6	172	171
6	0	-6	232	-216
6	0	-8	54	-58
6	0	10	174	-174
6	0	-10	101	103
6	0	12	60	-53
6	0	-12	128	127
6	0	14	108	107
6	0	-14	220	-213
6	0	16	92	94
6	0	-16	62	-58
6	0	18	46	-48
6	0	-18	96	90
6	0	20	107	-112
6	0	-20	78	68
6	0	22	70	76
6	0	-22	51	-46
7	0	0	300	-287
7	0	2	184	-183
7	0	-2	277	263
7	0	4	130	127
7	0	-4	223	224
7	0	6	143	134
7	0	-6	100	-18
7	0	8	133	-137
7	0	-8	253	-254
7	0	10	38	-47
7	0	-10	64	-64
7	0	12	125	122
7	0	-12	137	145
7	0	14	90	80
7	0	-14	41	61
7	0	16	42	-41
7	0	-16	140	-134
7	0	18	143	-141
7	0	-18	87	-81
7	0	20	40	44
7	0	-20	71	67
7	0	22	95	100
7	0	-22	64	59
7	0	-24	37	-42
8	0	0	304	-306
8	0	2	145	147
8	0	-2	144	-144
8	0	4	251	252
8	0	-4	124	127
8	0	-6	257	261
8	0	8	164	-166
8	0	-8	48	-49
8	0	10	51	49
8	0	-10	212	-202
8	0	12	97	100
8	0	-12	55	-52
8	0	14	35	-35
8	0	-14	112	103
8	0	16	148	-142
8	0	-16	58	-53
8	0	18	48	49
8	0	-18	79	-82
8	0	20	108	108
8	0	-20	35	-36
8	0	-22	62	57
9	0	0	157	157
9	0	2	240	250
9	0	-2	210	-221
9	0	4	37	-39
9	0	-4	135	-134
9	0	6	172	-175
9	0	-6	102	99
9	0	8	67	-69
9	0	-8	141	148
9	0	10	114	119
9	0	12	41	43
9	0	-12	96	-96
9	0	14	127	-123
9	0	-14	24	-15
9	0	16	46	-43
9	0	-16	126	133
10	0	0	165	171
10	0	2	77	-79
10	0	-2	164	166
10	0	4	146	-152
10	0	-4	158	-167
10	0	6	46	-12
10	0	-6	115	-121
10	0	8	109	116
10	0	-8	55	63
10	0	10	118	115
10	0	-10	106	108
10	0	12	62	-60
10	0	-12	40	-38
10	0	14	78	-74
10	0	-14	124	-133
10	0	-16	63	66
11	0	0	38	-37
11	0	2	187	-200
11	0	-2	175	167
11	0	4	54	-53
11	0	-4	53	62
11	0	6	147	151
11	0	-6	106	-100
11	0	8	115	121
11	0	-8	64	-64
11	0	10	72	-71
11	0	-10	105	112
11	0	12	91	-90
11	0	-12	71	73
11	0	-14	114	-117
12	0	0	161	-166
12	0	-2	56	-60
12	0	4	167	172
12	0	-4	125	131
12	0	6	67	69
12	0	8	104	-101
12	0	-8	111	-116
13	0	0	33	-34
13	0	2	32	36
13	0	-2	88	-77
13	0	-4	53	51
0	1	1	272	265
0	1	2	464	-444
0	1	3	137	-149
0	1	4	16	4
0	1	5	461	-447
0	1	6	244	246
0	1	7	97	105
0	1	8	45	37
0	1	9	165	177
0	1	10	153	-174
0	1	11	35	-37
0	1	12	116	-121
0	1	13	45	-56
0	1	14	93	100
0	1	15	120	122
0	1	17	107	113
0	1	18	83	-88
0	1	19	35	-35
0	1	20	72	-72
0	1	21	66	-67
0	1	24	56	44
0	1	25	76	64
0	1	27	36	30
0	1	28	14	-25
1	1	0	363	-354
1	1	1	167	-153
1	1	-1	250	229
1	1	2	52	-49
1	1	-2	133	122
1	1	3	131	-131
1	1	-3	223	213
1	1	4	91	94
1	1	-4	216	242
1	1	5	41	46
1	1	-5	84	79
1	1	6	66	69
1	1	-6	140	-141
1	1	7	372	411
1	1	-7	133	-139
1	1	8	145	-151
1	1	-8	196	-198
1	1	9	16	-7
1	1	-9	31	36
1	1	10	155	-167
1	1	-10	92	87
1	1	11	126	-141
1	1	12	110	130
1	1	-12	80	74
1	1	13	72	-82
1	1	-13	33	-38
1	1	14	141	154
1	1	-14	64	56
1	1	15	92	81
1	1	-15	82	-89
1	1	16	87	-89
1	1	-16	71	-74
1	1	17	31	24
1	1	-17	56	63
1	1	18	97	-99
1	1	-18	87	-95
1	1	19	60	-60
1	1	-19	48	49
1	1	20	45	38
1	1	-20	67	73
1	1	21	25	-30
1	1	22	77	72
1	1	-22	60	60
1	1	23	64	61
1	1	-23	95	-87
1	1	25	28	30
1	1	26	55	-27
1	1	27	40	-38
1	1	-27	66	53
2	1	0	138	-126
2	1	1	281	-258
2	1	-1	308	-283
2	1	2	25	-28
2	1	-2	172	-164
2	1	-3	46	-44
2	1	4	212	206
2	1	-4	164	167
2	1	5	402	404
2	1	-5	223	216
2	1	6	25	19
2	1	-6	138	134
2	1	7	27	31
2	1	-7	37	-33
2	1	8	107	-116
2	1	-8	154	-155
2	1	9	167	-170
2	1	-9	75	-73
2	1	10	55	60
2	1	-10	174	-179
2	1	11	144	-154
2	1	-11	80	93
2	1	12	[illegible]	221
2	1	13	93	77
2	1	-13	32	34
2	1	14	71	-74
2	1	-14	120	121
2	1	15	145	153
2	1	-15	100	-135
2	1	16	150	-169
2	1	-16	57	55
2	1	17	67	-70
2	1	-17	30	-34
2	1	18	74	86
2	1	-18	91	-89
2	1	19	53	-54
2	1	-19	70	73
2	1	20	80	74
2	1	-20	72	-76
2	1	21	54	51
2	1	-21	60	65
2	1	-22	71	77
2	1	23	34	31
2	1	-23	28	-10
2	1	24	63	-67
2	1	-24	46	43
2	1	-25	67	-63
2	1	-26	38	-40
2	1	27	46	-37
2	1	28	51	-41
2	1	-28	30	-27
3	1	0	177	166
3	1	1	28	34
3	1	-1	175	-164
3	1	2	183	177
3	1	-2	46	-77
3	1	3	431	-422
3	1	-3	73	-36
3	1	4	51	-37
3	1	-4	193	-185
3	1	5	13	-21
3	1	-5	137	120
3	1	6	156	-163
3	1	-6	42	40
3	1	7	255	-250
3	1	8	23	-20
3	1	-8	184	180
3	1	9	103	-105
3	1	-9	82	-83
3	1	10	158	163
3	1	11	77	70
3	1	-12	140	-153
3	1	13	175	170
3	1	-13	126	124
3	1	14	146	-152
3	1	-14	31	-32
3	1	15	67	-71
3	1	-15	73	65
3	1	-16	35	29
3	1	17	101	-107
3	1	-17	100	-101
3	1	18	84	87
3	1	-18	54	50
3	1	-19	122	-125
3	1	-20	126	-131
3	1	21	46	51
3	1	-21	50	53
3	1	22	51	-60
3	1	-23	91	88
3	1	24	55	-46
3	1	-24	75	77
3	1	25	51	-47
3	1	26	57	47
3	1	-26	33	27
3	1	-27	69	-52
3	1	-28	60	-54
4	1	0	145	135
4	1	1	33	32
4	1	-1	74	87
4	1	2	15	-3
4	1	-2	251	251
4	1	3	77	68
4	1	-3	205	-206
4	1	4	181	-177
4	1	-4	185	-165
4	1	5	277	-260
4	1	-5	106	107
4	1	6	47	-44
4	1	-6	205	-176
4	1	7	90	-90
4	1	-7	170	167
4	1	8	176	187
4	1	-8	143	138
4	1	9	143	144
4	1	-9	77	-71
4	1	-10	244	224
4	1	11	170	176
4	1	-11	177	-172
4	1	12	134	-141
4	1	-12	88	-87
4	1	13	78	-80
4	1	-13	18	-10
4	1	14	18	-22
4	1	-14	73	-76
4	1	15	161	-161
4	1	-15	174	177
4	1	16	140	66
4	1	17	31	24
4	1	-17	40	88
4	1	18	69	72
4	1	-18	96	96
4	1	19	19	104
4	1	-19	118	-115
4	1	20	71	-75
4	1	-21	81	-74
4	1	22	74	-72
4	1	-22	95	-38
4	1	23	57	-51
4	1	-23	46	40
4	1	24	36	31
4	1	-25	61	51
4	1	25	[illegible]	[illegible]
4	1	-26	77	63
4	1	27	14	[illegible]
5	1	0	21	-29
5	1	1	6	[illegible]
5	1	-1	56	37
5	1	2	[illegible]	[illegible]
5	1	-2	[illegible]	[illegible]
5	1	3	101	-121
5	1	-3	116	-129
5	1	4	[illegible]	[illegible]
5	1	-4	[illegible]	[illegible]
5	1	5	60	-67
5	1	-5	224	-237
5	1	6	[illegible]	135
5	1	-6	[illegible]	-152
5	1	7	167	152
5	1	-7	132	124
5	1	8	[illegible]	[illegible]
5	1	-8	174	-176
5	1	9	82	43
5	1	-9	234	221
5	1	10	[illegible]	[illegible]
5	1	-10	174	154
5	1	11	76	-131
5	1	-11	58	-62
5	1	12	129	122
5	1	13	152	-155
5	1	-13	242	-235
5	1	14	73	75
5	1	-14	116	[illegible]
5	1	15	37	45
5	1	-15	21	-13
5	1	16	45	44
5	1	-16	66	-64
5	1	17	114	116
5	1	-17	117	112
5	1	-18	60	35
5	1	19	27	23
5	1	-19	50	51
5	1	20	37	-35
5	1	-20	62	62
5	1	21	66	-60
5	1	-21	65	-62
5	1	22	45	43
5	1	-22	27	-10
5	1	23	46	-41
5	1	-23	24	-27
5	1	24	74	65
5	1	-24	67	-57
5	1	25	41	37
5	1	-27	36	29
6	1	0	245	-243
6	1	1	42	40
6	1	-1	156	152
6	1	2	65	-61
6	1	3	46	-45
6	1	-3	76	74
6	1	4	227	223
6	1	-4	127	127
6	1	5	65	31
6	1	-5	131	-135
6	1	6	81	37
6	1	-6	60	33
6	1	7	47	55
6	1	-7	136	-133
6	1	8	125	-131
6	1	-8	163	-134
6	1	9	46	-52
6	1	-9	167	178
6	1	10	84	-81
6	1	-10	62	-53
6	1	11	111	-111
6	1	-11	216	211
6	1	12	77	81
6	1	-12	172	165
6	1	13	52	51
6	1	-13	43	-44
6	1	14	63	67
6	1	15	123	113
6	1	-15	143	-133
6	1	-16	115	-139
6	1	17	27	17
6	1	-17	33	-32
6	1	18	61	-60
6	1	19	96	-35
6	1	-19	66	69
6	1	-20	52	47
6	1	21	48	-40
6	1	-21	33	30
6	1	22	41	54
6	1	-22	41	52
6	1	-23	37	-34
6	1	25	44	35
6	1	-25	32	-25
6	1	-26	34	-37
7	1	0	156	-153
7	1	1	211	-215
7	1	-1	53	50
7	1	2	226	225
7	1	-2	127	-131
7	1	3	17	-18
7	1	-3	136	131
7	1	4	170	174
7	1	-4	84	81
7	1	5	120	120
7	1	-5	88	85
7	1	6	175	-179
7	1	-6	124	127
7	1	7	41	-44
7	1	-7	168	-161
7	1	8	34	-32
7	1	-8	27	-27
7	1	9	114	-111
7	1	-9	162	-153
7	1	10	110	110
7	1	-10	136	-134
7	1	11	27	29
7	1	-11	54	61
7	1	12	66	67
7	1	-12	41	-42
7	1	13	47	[illegible]
7	1	-13	146	147
7	1	14	40	-44
7	1	-14	142	138
7	1	-15	26	-27
7	1	16	67	-63
7	1	17	106	-101
7	1	-17	110	-110
7	1	18	27	19
7	1	-18	147	-103
7	1	20	60	[illegible]
7	1	-20	27	-27
7	1	21	50	51
7	1	-21	61	62
7	1	-22	16	10
7	1	23	61	63
7	1	24	51	-48
7	1	-24	40	42
7	1	-25	16	-14
8	1	0	155	153
8	1	1	67	-60
8	1	-1	242	-241
8	1	2	131	129
8	1	-2	135	-138
8	1	3	187	182
8	1	4	117	-122
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6	9	-1	64	77
6	9	-2	26	-25
6	9	3	35	[illegible]
6	9	-3	21	16
6	9	4	93	41
6	9	-4	72	45
6	9	5	67	-47
6	9	6	63	55
6	9	7	73	70
6	9	-7	67	-71
6	9	8	50	-51
6	9	10	81	-79
6	9	11	70	-68
6	9	-11	67	66
6	9	-12	37	30
6	9	14	43	54
6	9	15	36	35
6	9	-15	51	-55
6	9	-16	47	-39
7	9	1	80	-88
7	9	-1	14	-29
7	9	2	46	77
7	9	-2	59	-64
7	9	-3	63	59
7	9	-4	31	-16
7	9	5	84	87
7	9	-5	30	32
7	9	6	41	-41
7	9	-6	54	56
7	9	-7	32	-30
7	9	8	74	-76
7	9	9	64	-64
7	9	-9	46	-35
7	9	-10	40	-37
7	9	-11	30	31
7	9	12	73	67
7	9	13	62	35
7	9	-13	45	49
7	9	-14	64	65
0	10	1	87	-80
0	10	2	27	[illegible]
0	10	3	61	-56
0	10	5	44	63
0	10	6	36	44
0	10	7	73	45
0	10	9	27	18
0	10	11	93	-18
0	10	15	46	65
1	10	1	103	-111
1	10	-1	36	-33
1	10	3	[illegible]	41
1	10	-3	105	133
1	10	-4	[illegible]	-42
1	10	5	64	72
1	10	-5	61	55
1	10	-7	72	-75
1	10	-8	65	-47
1	10	9	83	-43
1	10	-9	41	-132
1	10	-11	43	-42
1	10	13	102	154
1	10	-13	33	44
1	10	-15	24	[illegible]
2	10	-1	125	-124
2	10	3	75	78
2	10	-5	128	127
2	10	-6	33	-25
2	10	7	52	-50
2	10	-7	67	74
2	10	8	30	31
2	10	-9	57	[illegible]
2	10	11	76	77
2	10	-11	64	-79
2	10	-13	52	51
2	10	14	26	20
2	10	15	85	-82
2	10	-15	71	75
3	10	1	116	116
3	10	2	33	-18
3	10	3	52	47
3	10	-3	150	-134
3	10	5	83	-81
3	10	6	41	18
3	10	7	54	-50
3	10	-7	117	115
3	10	9	59	58
3	10	-9	37	37
3	10	11	33	37
3	10	-11	72	-76
3	10	-12	24	-20
3	10	13	71	-70
3	10	-13	38	-38
3	10	15	43	-47
3	10	-15	47	48
4	10	1	54	52
4	10	-1	124	127
4	10	3	83	-84
4	10	-4	31	-30
4	10	5	91	-86
4	10	-5	124	-119
4	10	7	67	59
4	10	-8	34	33
4	10	9	85	75
4	10	-9	80	76
4	10	11	56	-54
4	10	-11	42	23
4	10	13	41	-45
4	10	-13	71	-67
5	10	1	33	-35
5	10	-1	54	51
5	10	-2	24	31
5	10	3	43	-35
5	10	-3	121	117
5	10	5	[illegible]	[illegible]
5	10	-6	[illegible]	[illegible]
5	10	7	114	103
5	10	-7	75	-76
5	10	9	13	-24
5	10	-10	70	20
5	10	11	75	-73
5	10	-11	74	77
5	10	-13	31	-11
6	10	1	[illegible]	-38
6	10	-1	82	-81
6	10	3	54	55
6	10	-3	34	45
6	10	5	116	117
6	10	-5	77	75
6	10	9	97	-97
6	10	-9	67	-62
7	10	1	37	35
7	10	-1	76	-77
7	10	3	111	105
7	10	-3	40	-33
7	10	4	42	-43
7	10	-4	28	-27
7	10	-5	45	42
7	10	7	97	-95
7	10	-7	37	42
7	10	8	34	-31
7	10	-9	47	-48
0	11	1	56	-56
0	11	2	64	-77
0	11	3	36	38
0	11	5	48	62
0	11	6	51	64
0	11	10	40	-56
0	11	11	34	-24
1	11	0	56	-64
1	11	1	54	53
1	11	-1	46	-52
1	11	3	68	78
1	11	-3	55	-59
1	11	4	64	62
1	11	-4	62	66
1	11	-5	28	23
1	11	7	70	-71
1	11	-7	59	61
1	11	8	46	-49
1	11	-8	63	-60
1	11	10	45	-42
1	11	11	56	53
1	11	-11	37	-37
1	11	12	56	47
1	11	-12	39	39
2	11	1	64	62
2	11	-1	48	45
2	11	-2	67	-74
2	11	-3	57	-57
2	11	4	49	41
2	11	5	85	-84
2	11	-5	46	-45
2	11	-6	61	70
2	11	-7	48	45
2	11	8	45	-48
2	11	9	54	54
2	11	-10	57	-58
2	11	-11	35	-37
3	11	0	36	36
3	11	-1	66	66
3	11	2	46	31
3	11	-2	41	-43
3	11	3	60	-67
3	11	-4	71	-81
3	11	-5	53	-59
3	11	6	60	-67
3	11	-6	33	37
3	11	7	74	75
3	11	-8	65	70
3	11	9	34	35
3	11	-9	46	52
3	11	10	58	57
4	11	0	64	58
4	11	1	39	-46
4	11	-2	46	45
4	11	-3	42	40
4	11	-4	43	-37
4	11	5	64	55
4	11	-6	67	-72
4	11	7	37	34
4	11	-7	37	-40
4	11	8	52	43
4	11	-8	31	32
4	11	9	81	-81
5	11	1	38	-42
5	11	2	72	-70
5	11	-2	60	57
5	11	-3	37	32
5	11	-4	48	51
5	11	5	41	23
5	11	6	60	59
5	11	-6	58	-53
5	11	-8	43	-43
6	11	0	54	-66
6	11	-1	37	-30
6	11	2	34	-27
6	11	3	46	48
6	11	-4	45	43
0	12	0	76	-103
0	12	4	76	42
1	12	1	32	-6
1	12	-1	34	20
1	12	2	88	85
1	12	-2	104	-111
1	12	4	38	14
2	12	0	84	92

Chapter 5

The Crystal Structure of $(Ph_3P)Ni(C_5H_5)GeCl_3 \cdot \frac{1}{2}C_6H_6$

INTRODUCTION

The compound $(Ph_3P)Ni(C_5H_5)GeCl_3$ was prepared by the reaction

$$(Ph_3P)Ni(C_5H_5)Cl + CsGeCl_3 \longrightarrow (Ph_3P)Ni(C_5H_5)GeCl_3 + CsCl$$

At the present time little of its chemistry is known, although the N.P.R. and the infrared spectra indicated the presence of the Ge-Ni bond. In order to gain additional information about metal-germanium bonding, the structure was studied by X-ray diffraction techniques.

EXPERIMENTAL

The compound was prepared by the method described above. A number of attempts were made to crystallise the light green powder, which was accomplished by dissolving the complex in benzene in a sealed tube, then cooling slowly over a long period. The crystals were a dark green with ill-defined faces. Since only about six crystals were available for the crystallographic study, and the chemistry was not known, the density was not determined. The crystals were mounted in thin-walled capillary tubes under an atmosphere of nitrogen, although there were indications that the compound was stable to the air.

Preliminary photographic data was obtained by the precession method. Examination of the h0l, 0kl, and 1kl showed the reflections were present when h0l h = 2n, l = 2n

0kl k = 2n

1kl k = 2n + 1

and the condition h + k was inferred. There are two space groups which satisfy these conditions, Cc and C2/c. A reasonable value of the density would be obtained if there were eight molecules in the unit cell. Based upon this, the space group was thought most likely to be the latter, an assignment which has proved correct.

The crystal, with the dimensions 0·3 mm x 0·2 mm x 0·2 mm, was mounted on the diffractometer in some general orientation, and aligned as described for the iridium compound. The reflections

0	12	11	1	9	18	0	-10	-22
-15	-1	-5	-14	0	4	0	-12	-15
-13	-1	-12	-14	0	-8	0	4	27

were employed in the calculation of the orientation matrix and the unit cell parameters using the method of least squares. Values of θ varied from $19{\cdot}30^{\circ}$ (-14 0 4) to $23{\cdot}71^{\circ}$ (0 -12 -15). The parameters obtained were

$a = 15{\cdot}080(3)\text{Å}$ $b = 11{\cdot}889(5)\text{Å}$ $c = 29{\cdot}113(11)\text{Å}$

$\beta = 93{\cdot}383(10)^{\circ}$ $V = 5210\text{Å}^{3}$ $D_c = 1{\cdot}54\ \text{g./cm}^{3}$

Z = 8 units of $(C_5H_5)(C_6H_5)_3PNiGeCl_3{\cdot}\frac{1}{2}C_6H_6$

$\mu = 25{\cdot}89\ \text{cm}^{-1}$ for Mo Kα

A θ- 2θ scan was carried out, consisting of 60 steps (0·01°/step) with a counting time of two seconds per step. The background was measured at each side of the scan for a time of twenty seconds each. Three standard reflections, 0 -4 0, 0 0 8, 2 0 0, were measured every fifty reflections, when a drive to datum was carried out. One quarter of the sphere of reflection was measured within the range $\theta = 0^{\circ}$ to $\theta = 26^{\circ}$, employing Mo Kα radiation. A total of 5380 reflections was measured, of which 2862 had net counts greater than three e.s.d.'s. The data was corrected for Lorentz and polarisation factors.

SOLUTION

The structure was solved by the heavy atom method, with six heavy atom positions being found from the Patterson function. The centrosymmetric space group C2/c was consistent with the vectors observed in the function, and the successful refinement has shown this to be the correct choice. The solution was complicated by the fact one peak occurred at the intersection of the Harker line $(0,v,\frac{1}{2})$ and the Harker section $(u,0,w)$ and that a number of Ge-Ni vectors occurred on this section, having the same peak height as the Ni-Ni and Ge-Ge double weight vectors. It was further discovered that the x/a and z/c coordinates of the nickel and germanium atoms were similar, so that overlapping occurred on the Harker section and the positions of these atoms were obtained from the body of the Patterson function. After these positions were found, an inspection of the Ni-Cl, Ni-P, Ge-Cl and Ge-P vectors yielded the remaining heavy atom positions. At this stage, the atomic coordinates were

Atom	x/a	y/b	z/c
Ni	0•0175	0•01125	0•11025
Ge	0•0475	0•1925	0•11575
P	0•1520	-0•06375	0•1205
Cl(1)	0•1926	0•270	0•1924
Cl(2)	-0•0046	0•2875	0•0588
Cl(3)	-0•0114	0•3075	0•1747

Three cycles of least squares refinement led to an R factor of 0•26. A difference map was computed and allowed the remaining carbon atoms to be located. In addition four peaks, two of which were situated of the two-fold axis at 0,y,$\frac{1}{4}$, were assigned as carbon atoms, which comprised one half of a benzene molecule.

REFINEMENT

The refinement was carried out as described in the previous chapters, with the Ni, Ge, P and Cl atomic scattering factors corrected for the effects of anomalous scattering, both of the terms $\Delta f'$ and $\Delta f''$ being employed.

A further three cycles of least squares refinement of the atomic coordinates reduced the R factor to 0•10. The six heavy atoms were given anisotropic thermal parameters, and refined for four cycles (R = 0•068). The light atoms were then given anisotropic temperature factors, and the R index became 0•057. In the last three cycles, the weighting function

$$\sqrt{w} = 1/(p_1 + |F_o| + p_2|F_o|^2 + p_3|F_o|^3)^{\frac{1}{2}}$$

was employed.

The positions of the twenty-four hydrogen atoms were calculated, assuming D_{6h} symmetry for the benzene rings and D_{5h} for the cyclopentadienyl ring. Three cycles of least squares refinement with the hydrogen atom positions included in the structure factor calculation only, lowered the R factor to 0·052. There were still shifts in the carbon atom positions, and an investigation of the C-H bond lengths showed that they were longer than the original value (1·08Å) by differences of 0·01Å to 0·05Å. The hydrogen atom positions were recalculated and an additional two cycles of refinement were carried out to a final R factor of 0·0507. With the exception of the four carbons in the benzene molecule, where some shifts in the coordinates or the temperature parameters oscillated in the last two cycles, the shift in the parameters for the atoms was less than one third of an e.s.d.

A difference map calculated at the end of the refinement failed to exhibit any peak height greater than 0·5 e.Å^{-3}. The final atomic coordinates are listed in Table 5a, the thermal parameters in Table 5b, and an analysis of the weighting function in Table 5c.

The changes in the R index caused by the use of anisotropic thermal parameters for both the heavy and light atoms, and the inclusion of the

TABLE 5a

Final Atomic Coordinates and their Standard Deviations (x 10^5)

Atom	x/a	y/b	z/c	B_{iso}
Ni	0·01796(6)	0·00954(9)	0·10811(3)	3·13
P	0·14797(13)	-0·06164(17)	0·12250(7)	2·94
Ge	0·04772(6)	0·19362(8)	0·11777(3)	3·80
Cl(1)	0·17962(16)	0·26618(21)	0·12929(11)	5·43
Cl(2)	-0·00334(22)	0·29639(25)	0·05925(10)	6·36
Cl(3)	-0·01657(20)	0·27504(27)	0·17458(11)	6·42
C(1)	-0·05012(63)	-0·09598(98)	0·05992(37)	6·07
C(2)	-0·08349(64)	0·01159(99)	0·05432(34)	5·73
C(3)	-0·11549(59)	0·04312(95)	0·09872(40)	5·89
C(4)	-0·10726(61)	-0·04827(101)	0·12615(38)	5·80
C(5)	-0·06276(63)	-0·13203(90)	0·10603(39)	5·81
C(6)	0·15229(46)	-0·20885(65)	0·10635(25)	3·07
C(7)	0·12499(55)	-0·29227(68)	0·13571(27)	3·71
C(8)	0·12099(58)	-0·40415(76)	0·12227(30)	4·32
C(9)	0·14363(60)	-0·43363(74)	0·07867(36)	4·91
C(10)	0·17019(64)	-0·35229(79)	0·04814(34)	4·88
C(11)	0·17576(56)	-0·24070(75)	0·06203(29)	4·01
C(12)	0·23281(46)	0·00466(62)	0·08914(25)	3·07
C(13)	0·32226(54)	0·00495(85)	0·10366(34)	4·85
C(14)	0·38225(59)	0·05547(97)	0·07561(39)	5·81
C(15)	0·35620(71)	0·10570(88)	0·03448(36)	5·74
C(16)	0·26730(68)	0·10395(80)	0·02050(31)	4·82
C(17)	0·20620(56)	0·05533(70)	0·04748(27)	4·00
C(18)	0·18982(53)	-0·05727(68)	0·18265(25)	3·58
C(19)	0·25602(56)	-0·13152(76)	0·19882(29)	4·10
C(20)	0·28830(64)	-0·12324(82)	0·24481(31)	4·90
C(21)	0·25672(67)	-0·04316(88)	0·27280(30)	5·05
C(22)	0·19195(72)	0·03085(84)	0·25704(30)	5·29
C(23)	0·15812(60)	0·02371(74)	0·21131(26)	4·20
C(24)	0·00000	-0·20435(181)	0·25000	10·11
C(25)	-0·06552(94)	-0·25875(151)	0·22949(57)	9·55
C(26)	-0·06747(92)	-0·37328(152)	0·22786(53)	9·24
C(27)	0·00000	-0·43010(147)	0·25000	9·56
H(1)	-0·01952	-0·14275	0·03333	12·30
H(2)	-0·08083	0·06172	0·02341	11·40
H(3)	-0·14551	0·12263	0·10679	11·90
H(4)	-0·12721	-0·05136	0·16306	11·60

TABLE 5a contd.

Atom	x/a	y/b	z/c	B_{iso}
H(5)	-0·04406	-0·21243	0·12088	11·60
H(7)	0·10713	-0·26917	0·16988	7·40
H(8)	0·09954	-0·46768	0·14575	8·60
H(9)	0·14042	-0·52040	0·06784	10·00
H(10)	0·18781	-0·37557	0·01396	9·60
H(11)	0·19710	-0·17649	0·0348	8·00
H(13)	0·34367	-0·03353	0·13606	9·60
H(14)	0·45181	0·05512	0·08725	11·60
H(15)	0·18521	-0·03443	0·11022	11·40
H(16)	0·24547	0·14223	-0·01191	9·60
H(17)	0·13611	0·05546	0·03589	8·00
H(19)	0·28114	-0·19460	0·17619	8·20
H(20)	0·33911	-0·18057	0·25794	9·60
H(21)	0·28291	-0·03784	0·30805	10·00
H(22)	0·16699	0·09383	0·27968	10·5
H(23)	0·10721	0·08116	0·19824	8·3
H(24)	0·00000	-0·11346	0·25000	20·0
H(25)	-0·11916	-0·21211	0·21203	19·0
H(26)	-0·12093	-0·42020	0·21055	19·0
H(27)	0·00000	-0·52117	0·25000	19·0

TABLE 5b

Final Thermal Parameters^a and their Standard Deviations (x 10^5)

Atom	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Ni	0·00669(4)	0·00310(8)	0·00098(1)	-0·00026(5)	-0·00055(4)	0·00020(10)
P	0·00045(9)	0·00547(15)	0·00085(2)	-0·00038(10)	-0·00038(8)	0·00026(19)
Ge	0·00446(4)	0·00627(7)	0·00123(1)	-0·00057(5)	-0·00033(4)	0·00167(10)
Cl(1)	0·00531(13)	0·00756(21)	0·00252(5)	-0·00233(16)	-0·00049(13)	-0·00232(26)
Cl(2)	0·00948(20)	0·00955(25)	0·00200(5)	0·00265(17)	-0·00185(15)	0·00093(36)
Cl(3)	0·00777(17)	0·01277(31)	0·00211(5)	-0·00390(19)	0·00121(15)	0·00495(37)
C(1)	0·00423(49)	0·01337(114)	0·00205(18)	-0·00386(74)	-0·00188(47)	-0·00150(118)
C(2)	0·00554(52)	0·01383(116)	0·00154(14)	0·00061(67)	-0·00329(45)	-0·00250(132)
C(3)	0·00334(44)	0·01195(109)	0·00260(21)	-0·00144(77)	-0·00094(48)	0·00131(111)
C(4)	0·00405(49)	0·01473(125)	0·00207(18)	-0·00003(78)	0·00164(47)	-0·00385(127)
C(5)	0·00447(50)	0·01024(102)	0·00236(19)	0·00016(70)	-0·00101(49)	-0·00348(114)
C(6)	0·00300(34)	0·00593(63)	0·00100(10)	-0·00041(40)	-0·00033(30)	0·00065(74)
C(7)	0·00489(43)	0·00581(66)	0·00110(11)	0·00013(43)	-0·00065(35)	-0·00112(88)
C(8)	0·00469(46)	0·00765(75)	0·00132(12)	0·00059(50)	-0·00126(39)	-0·00049(94)
C(9)	0·00490(48)	0·00591(72)	0·00212(17)	-0·00115(56)	-0·00090(46)	0·00023(95)
C(10)	0·00605(55)	0·00751(78)	0·00161(14)	-0·00259(55)	0·00055(45)	0·00124(107)
C(11)	0·00480(44)	0·00723(73)	0·00120(12)	-0·00085(48)	0·00020(36)	0·00012(94)
C(12)	0·00337(34)	0·00482(58)	0·00106(10)	-0·00091(41)	0·00067(30)	-0·00052(75)
C(13)	0·00341(40)	0·01003(91)	0·00186(15)	-0·00017(63)	-0·00012(39)	-0·00052(102)
C(14)	0·00320(43)	0·01322(114)	0·00240(19)	-0·00189(77)	0·00060(46)	-0·00240(114)
C(15)	0·00711(63)	0·00877(88)	0·00188(17)	-0·00206(65)	0·00212(52)	-0·00441(122)
C(16)	0·00734(62)	0·00719(75)	0·00135(13)	-0·00046(53)	0·00113(46)	-0·00350(112)
C(17)	0·00519(46)	0·00633(67)	0·00101(11)	-0·00023(44)	0·00015(36)	-0·00042(90)
C(18)	0·00446(42)	0·00668(66)	0·00086(10)	0·00050(41)	-0·00131(32)	-0·00255(87)

TABLE 5b contd.

Atom	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
C(19)	0·00446(44)	0·00870(82)	0·00111(11)	0·00058(48)	-0·00082(36)	0·00092(97)
C(20)	0·00621(55)	0·00926(92)	0·00125(13)	0·00113(54)	-0·00143(43)	-0·00237(112)
C(21)	0·00706(59)	0·01098(97)	0·00097(11)	0·00048(54)	-0·00166(41)	-0·00399(123)
C(22)	0·00904(69)	0·00884(89)	0·00101(12)	-0·00038(52)	-0·00092(47)	-0·00168(127)
C(23)	0·00639(52)	0·00756(75)	0·00079(10)	-0·00024(44)	-0·00027(36)	0·00162(102)
C(24)	0·01508(171)	0·01209(219)	0·00535(60)		0·01149(167)	
C(25)	0·00902(94)	0·02512(218)	0·00355(34)	0·01148(145)	0·00442(92)	0·00964(233)
C(26)	0·00801(90)	0·02641(230)	0·00276(27)	0·00210(129)	-0·00058(78)	-0·01313(233)
C(27)	0·01262(153)	0·00757(159)	0·00425(49)		0·00233(137)	

[a] where B_{ij} refers to the expression

$$\exp[-(h^2B_{11} + k^2B_{22} + 1^2B_{33} + 2hkB_{12} + 2k1B_{23} + 2h1B_{13})]$$

TABLE 5c

Analysis of the Weighting Function

$$\sqrt{w} = 1/(600 + |F_o| + 0{\cdot}0005|F_o|^2 + 0{\cdot}00002|F_o|^3)^{\frac{1}{2}}$$

$\|F_o\|$ range	N	$\Sigma(w\Delta^2)/N$
0-30	320	0•05
30-50	295	0•04
35-40	284	0•03
40-45	251	0•03
45-50	177	0•02
50-60	315	0•02
60-70	248	0•02
70-80	178	0•02
80-100	235	0•02
100-130	228	0•02
130-140	322	0•04

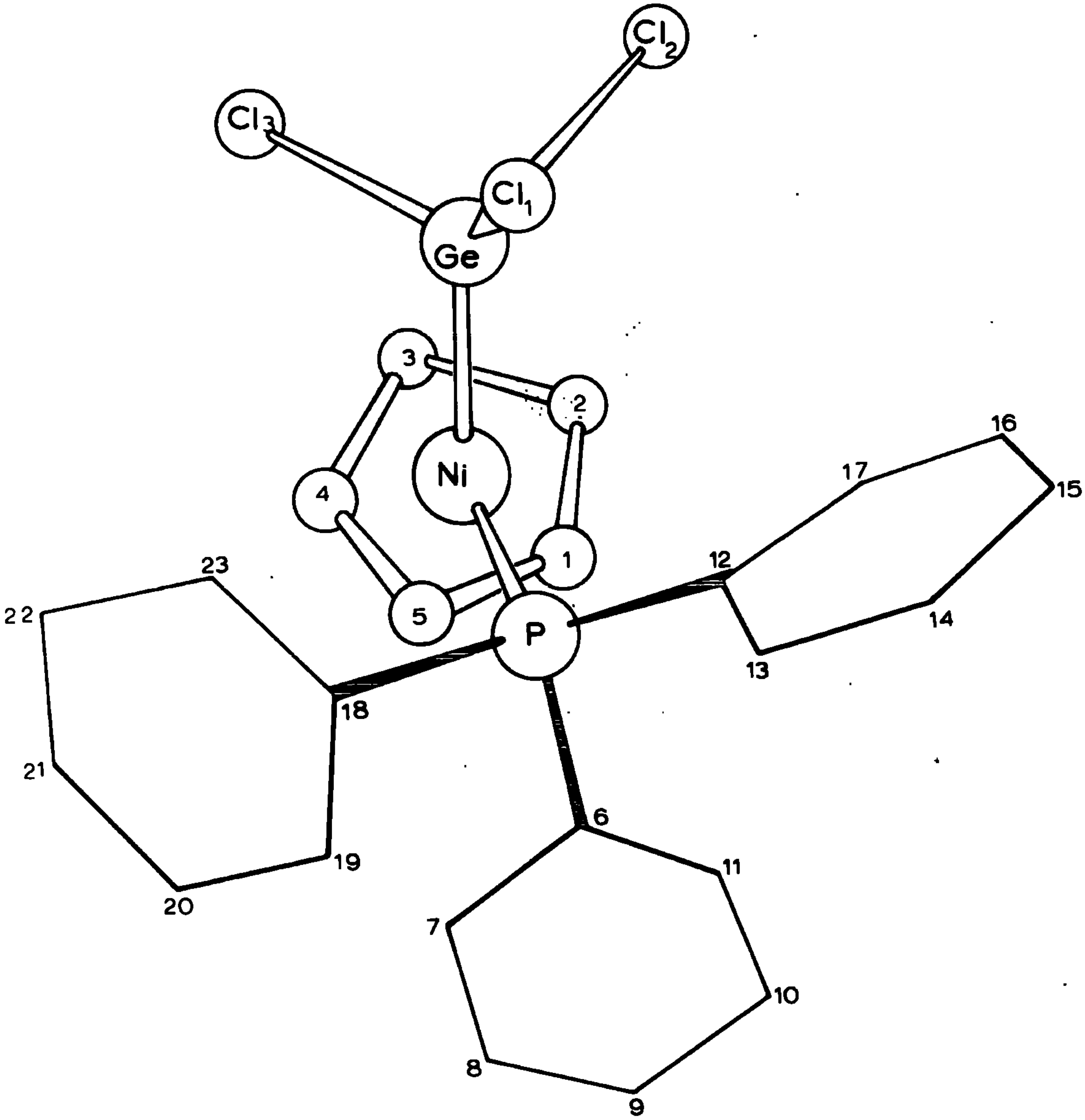

Fig.5A

Perspective Drawing

hydrogen atoms is significant at the highest listed probability level of 99•5% (Hamilton, 1965).

DESCRIPTION

The coordination about the nickel was as expected, with phosphorus, nickel and germanium atoms located in a plane approximately perpendicular to that of the cyclopentadienyl ring. The nickel can be considered four or five coordinate if the cyclopentadienyl groups fills two or three coordination sites. The latter is unlikely, but some workers have proposed a mixture of both (Churchill and O'Brian, 1968). In this compound, there is a significant distortion of the cyclopentadienyl ring, implying that the nickel is four coordinate.

The cyclopentadienyl moiety is expected to planar, but a calculation of the mean plane derived from all five carbon atoms in the ring resulted in a value for χ^2 of 31•7, which indicates that the ring is non-planar. From an examination of the deviations from planarity, two additional planes were calculated: one including C(1), C(2), C(3), and C(5) (χ^2 = 1•6) and the other passing through C(3), C(4) and C(5). These planes form a dihedral angle of 161•39°, a difference of 18•6° from coplanarity.

There were two sets of C-C bond lengths. The first includes C(1)-C(5) and C(2)-C(3), having a mean value of 1•444Å. The second set consists of C(1)-C(2), C(3)-C(4), and C(4)-C(5) bonds, with an average length of 1•382Å. The average of all five bond lengths is 1•407Å (χ^2 = ~~2•05~~ 20·5),

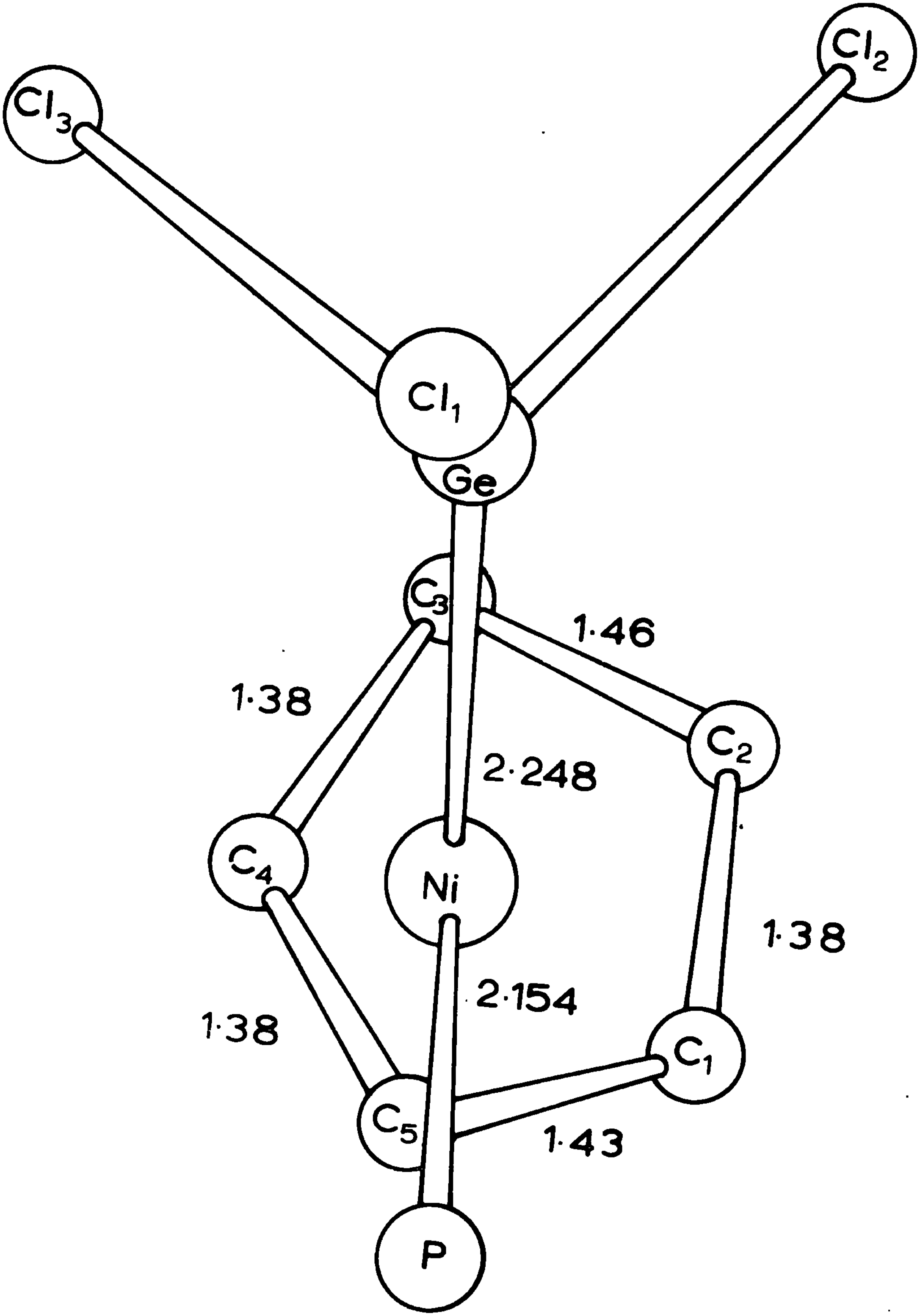

Fig.5B

View in the Nickel, Phosphorus, Germanium Plane and Some Bond Lengths which can be compared to that obtained by taking the average of C-C bond length, 1·149Å, in twenty-three structures containing a π-cyclopentadienyl ring (Wheatly, 1967). The C-C-C angles are equal within experimental error, having a mean value of 107·92°. This is the same as found in two related compounds, with values of 107·9° and 108·0° (Churchill and O'Brian, 1968; 1969).

The distance from the nickel atom to the mean plane calculated from all five atoms in the ring is 1·721Å. This is shorter than the values found in $Cp(PPh_3)NiC_6X_5$ (X = H, F) of 1·776Å and 1·769Å respectively (Churchill and O'Brian, 1968; 1969). As would be expected, the Ni-C distances are also shorter, with a mean value of 2·096Å, in comparison to 2·144Å and 2·139Å in the two previously mentioned compounds. These Ni-C distances appear to differ amongst themselves, and form two sets of values. The first is the distance to C(1), C(2), and C(4), where the mean value is 2·117Å. The second group consists of C(3) and C(5), having the average distance of 2·065Å. The five C-Ni-C angles, formed by adjacent carbon atoms in the ring, have an average value of 39·19°. The value of χ^2 is 31·2, thus indicating that the difference between the individual values is significant. Again there are two types of angles, with those located along the longer C-C bonds in the ring being the larger (40·40°). The smaller angles have a mean value of 38·39° (χ^2 = 0·92). The mean angle is similar to those measured in other compounds.

TABLE 5d

Final Bond Lengths and their Standard Deviations (x 10^3 Å)

	Bond	Length (Å)
	Ni-Ge	2·248(1)
	Ni-P	2·154(2)
	Ni-C(1)	2·104(11)
	Ni-C(2)	2·124(10)
	Ni-C(3)	2·054(9)
	Ni-C(4)	2·123(10)
	Ni-C(5)	2·076(10)
	Ge-Cl(1)	2·176(3)
	Ge-Cl(2)	2·199(3)
	Ge-Cl(3)	2·191(3)
cyclopentadienyl ring		
	C(1)-C(2)	1·380(16)
	C(2)-C(3)	1·455(15)
	C(3)-C(4)	1·385(16)
	C(4)-C(5)	1·381(15)
	C(5)-C(1)	1·433(16)
Phosphine		
	P-C(6)	1·814(8)
	P-C(12)	1·830(7)
	P-C(18)	1·827(8)
Phenyl I		
	C(6)-C(7)	1·388(11)
	C(7)-C(8)	1·387(12)
	C(8)-C(9)	1·379(14)
	C(9)-C(10)	1·388(14)
	C(10)-C(11)	1·388(13)
	C(11)-C(6)	1·410(11)
Phenyl II		
	C(12)-C(13)	1·390(11)
	C(13)-C(14)	1·390(14)
	C(14)-C(15)	1·375(15)
	C(15)-C(16)	1·378(15)

contd./

TABLE 5d contd.

	Bond	Length (Å)
Phenyl II		
	C(16)-C(17)	1·373(13)
	C(17)-C(12)	1·392(11)
Phenyl III		
	C(18)-C(19)	1·394(12)
	C(19)-C(20)	1·401(12)
	C(20)-C(21)	1·358(14)
	C(21)-C(22)	1·373(14)
	C(22)-C(23)	1·400(12)
	C(23)-C(18)	1·378(12)
Benzene		
	C(24)-C(25)	1·297(19)
	C(25)-C(26)	1·363(26)
	C(26)-C(27)	1·353(18)

TABLE 5e

Final Angles and their Standard Deviations (x 10^2)

Coordination Sphere		
	P-Ni-Ge	100·69(7)°
	P-Ni-Cp	134·41(36)
	Ge-Ni-Cp	124·70(36)
	C(1)-Ni-C(2)	38·11(41)
	C(2)-Ni-C(3)	40·73(41)
	C(3)-Ni-C(4)	38·67(42)
	C(4)-Ni-C(5)	38·38(41)
	C(5)-Ni-C(1)	40·08(41)
$GeCl_3$		
	Cl(1)-Ge-Cl(2)	100·04(11)
	Cl(2)-Ge-Cl(3)	100·90(12)
	Cl(3)-Ge-Cl(1)	98·61(12)
	Cl(1)-Ge-Ni	125·39(9)
	Cl(2)-Ge-Ni	112·69(9)
	Cl(3)-Ge-Ni	115·50(9)
cyclopentadienyl		
	C(5)-C(1)-C(2)	108·67(93)
	C(1)-C(2)-C(3)	105·75(91)
	C(2)-C(3)-C(4)	108·97(93)
	C(3)-C(4)-C(5)	107·79(96)
	C(4)-C(5)-C(1)	108·44(93)
phosphine		
	C(6)-P-C(12)	103·95(34)
	C(12)-P-C(18)	106·48(35)
	C(18)-P-C(6)	105·08(35)
	C(6)-P-Ni	112·01(25)
	C(12)-P-Ni	112·61(25)
	C(18)-P-Ni	115·74(27)
Phenyl I		
	C(7)-C(6)-C(11)	118·13(71)
	C(8)-C(7)-C(6)	121·42(75)
	C(9)-C(8)-C(7)	119·63(82)
	C(10)-C(9)-C(8)	120·57(87)
	C(11)-C(10)-C(9)	119·61(87)
	C(6)-C(11)-C(10)	120·71(79)

contd./

TABLE 5e contd.

Phenyl II		
	C(13)-C(12)-C(17)	119·26(73)
	C(14)-C(13)-C(12)	118·42(85)
	C(15)-C(14)-C(13)	122·47(97)
	C(16)-C(15)-C(14)	118·28(96)
	C(17)-C(16)-C(15)	120·75(89)
	C(12)-C(17)-C(16)	120·79(77)
Phenyl III		
	C(19)-C(18)-C(23)	120·35(75)
	C(20)-C(19)-C(18)	118·68(79)
	C(21)-C(20)-C(19)	120·57(87)
	C(22)-C(21)-C(20)	121·10(92)
	C(23)-C(22)-C(21)	119·41(89)
	C(18)-C(23)-C(22)	119·88(80)
Benzene		
	C(24)-C(25)-C(26)	121·92(1·50)
	C(25)-C(26)-C(27)	117·93(1·40)
	C(26)-C(27)-C(26')	120·08(1·21)

The plane passing through the nickel, phosphorus and germanium atoms forms a dihedral angle of 88·32° with the mean plane of all five atoms in the cyclopentadienyl ring. The same plane forms dihedral angles of 83·45° and 101·93° with the planes calculated from the four carbon atoms and the three carbon atoms in the ring respectively. The carbon atoms, C(3) and C(5), which have the shortest Ni-C distances lie near the plane formed by the three central atoms, at distances of 0·19Å and 0·36Å. The centre of mass of the ring lies 0·11Å from this plane. Cl(1) is located 0·22Å from the plane, whereas Cl(2) and Cl(3) lie on either side of the plane at distances of 1·56Å and 1·78Å respectively. If a plane is calculated including the three atoms and the centre of mass of the cyclopentadienyl ring (Cp), the value of χ^2 becomes 1954.

The P-Ni-Ge angle of 100·69° is smaller than the Ge-Ni-Cp angle of 124·7(4)° or the P-Ni-Cp angle of 134·4(4)°. These angles may arise through steric interactions within the molecule. The smallest angle involves interactions between the phosphine and the germyl group, which is limited by Cl(1) contacts with phenyl II and phenyl III. Cl(2) and Cl(3) have interactions with the cyclopentadienyl ring, thus giving the larger value. The phosphine group is the largest ligand, and thus causes the largest angle. A second factor which will influence the angles is the coordination of the nickel atom. This will be discussed later.

The Ge-Cl bonds have an average length of 2·189Å, but with a rather large χ^2 value of 51·7. Two of the bond lengths, Ge-Cl(2) and Ge-Cl(3), are experimentally the same with a mean value of 2·195(2)Å. The other bond, Ge-Cl(1), is shorter with a value of 2·176(3)Å. All three lengths are greater than the value of 2·1139(10)Å found in $HGeCl_3$ by microwave studies (Venkateswarlu, Mockler and Gordy, 1953). The angles at germanium are distorted as can be seen by an examination of the Cl-Ge-Cl angles (100·04°, 98·61°, 100·90°, with e.s.d.'s of 0·11°) and the Ni-Ge-Cl angles (125·36°, 112·69°, 115·50°, with e.s.d.'s of 0·09°). In all cases, the length and angles involving Cl(1) appear to deviate the most. It is intersting to note that Cl(1) is almost coplanar with the phosphorus, germanium and nickel atoms, and is located opposite to the cyclopentadienyl ring.

Both Cl(2) and Cl(3) have no close contacts with phenyl groups in the same molecule, but have some with phenyl groups in other molecules. The chlorine-chlorine contacts within the group are very similar, with values of 3·35Å, 3·31Å and 3·38Å.

The Ni-Ge bond length of 2·248(1)Å can be compared to the sum of the covalent radii (2·61Å). The short bond length, and the small Cl-Ge-Cl angles suggest that there is some $(d_\pi - d_\pi)$ bonding between the germanium and the nickel. This will be discussed later.

The three phenyl groups are planar, within experimental error, as shown in Table 5f. As was found for the triphenylphosphine ligands in the

TABLE 5f

Some Mean Planes

Plane I Atoms in plane C(1), C(2), C(3), C(4), C(5)

Equation of plane $-0{\cdot}8768X' - 0{\cdot}3660Y - 0{\cdot}3119Z' - 0{\cdot}6250 = 0$

$\chi^2 = 31$

Distance of atoms from plane (Å)

C(1)	0·002	C(2)	0·018	C(3)	-0·032	C(4)	0·034	C(5)	-0·034

Plane II Atoms in plane C(1), C(2), C(3), C(5)

Equation of plane $-0{\cdot}885X' - 0{\cdot}3664Y - 0{\cdot}2862Z' - 0{\cdot}6874 = 0$

$\chi^2 = 1{\cdot}5$

Plane III Atoms in plane C(3), C(4), C(5)

Equation of plane $-0{\cdot}8512X' - 0{\cdot}3950Y - 0{\cdot}3445Z' - 0{\cdot}3445 = 0$

Plane IV Atoms in plane Ni, Ge, P

Equation of plane $0{\cdot}2423X' + 0{\cdot}0762Y - 0{\cdot}9672Z' + 3{\cdot}0096 = 0$

Distance of atoms from plane (Å)

Cl(1)	0·219	Cl(2)	1·586	Cl(3)	-1·782	C(3)	-0·189
C(5)	-0·364	Cp	0·112				

Plane V Atoms in the plane Phenyl I

Equation of plane $-0{\cdot}9298X' + 0{\cdot}1336Y - 0{\cdot}3430Z' + 3{,}3581 = 0$

$\chi^2 = 2{\cdot}5$

contd./

TABLE 5f contd.

Plane VI Atoms in the plane Phenyl II

Equation of plane $0\cdot1502X' - 0\cdot8702Y - 0\cdot4692Z' + 0\cdot7607 = 0$

$\chi^2 = 1\cdot0$

Plane VII Atoms in the plane Phenyl III

Equation of plane $0\cdot7211X' + 0\cdot6363Y - 0\cdot2741Z' + 0\cdot0466 = 0$

$\chi^2 = 0\cdot8$

X', Y, Z' are orthogonal coordinates in Angstroms iridium compound, the phosphorus atom lies out of the planes of the phenyl groups by a significant amount. None of the carbon atoms differ significantly from coplanarity.

The C-P-C angles have an average value of 105•2°. The value of χ^2 (9•8) indicates that they are the same at the 0•8% confidence level. The mean P-C bond length of 1•824(1)Å (χ^2 = 0•8) is in agreement with the value found in the iridium compound, thus indicating that the phosphine is normal. The Ni-P-C angles reflect the distortion of the phosphine with respect to the nickel. These angles have a mean value of 113•4°, but span the range 112•0° to 115•7°. This is a smaller difference than found in the iridium complex, indicating that the molecule is relatively free from steric interactions causing distortion of the molecule.

Within the three phenyl groups, the agreement between the individual bond lengths and angles is good. The average C-C distance is 1•386(3)Å, with χ^2 = 16. The mean C-C-C angle is 120•1(2)°, with χ^2 = 31•9. A comparison of the individual bond lengths and angles with the mean values resulted in r.m.s. deviations of 0•011Å and 1•09°. The value for the bond lengths is smaller than the average value calculated from the least squares sums, but the value for the angles is slightly larger.

Phenyl(I) has contacts with both phenyl(II) and phenyl(III). For interactions involving the ortho-hydrogen atoms, the minimum distance of 2•65Å is between H(11) and C(12). The intermolecular contacts are similar

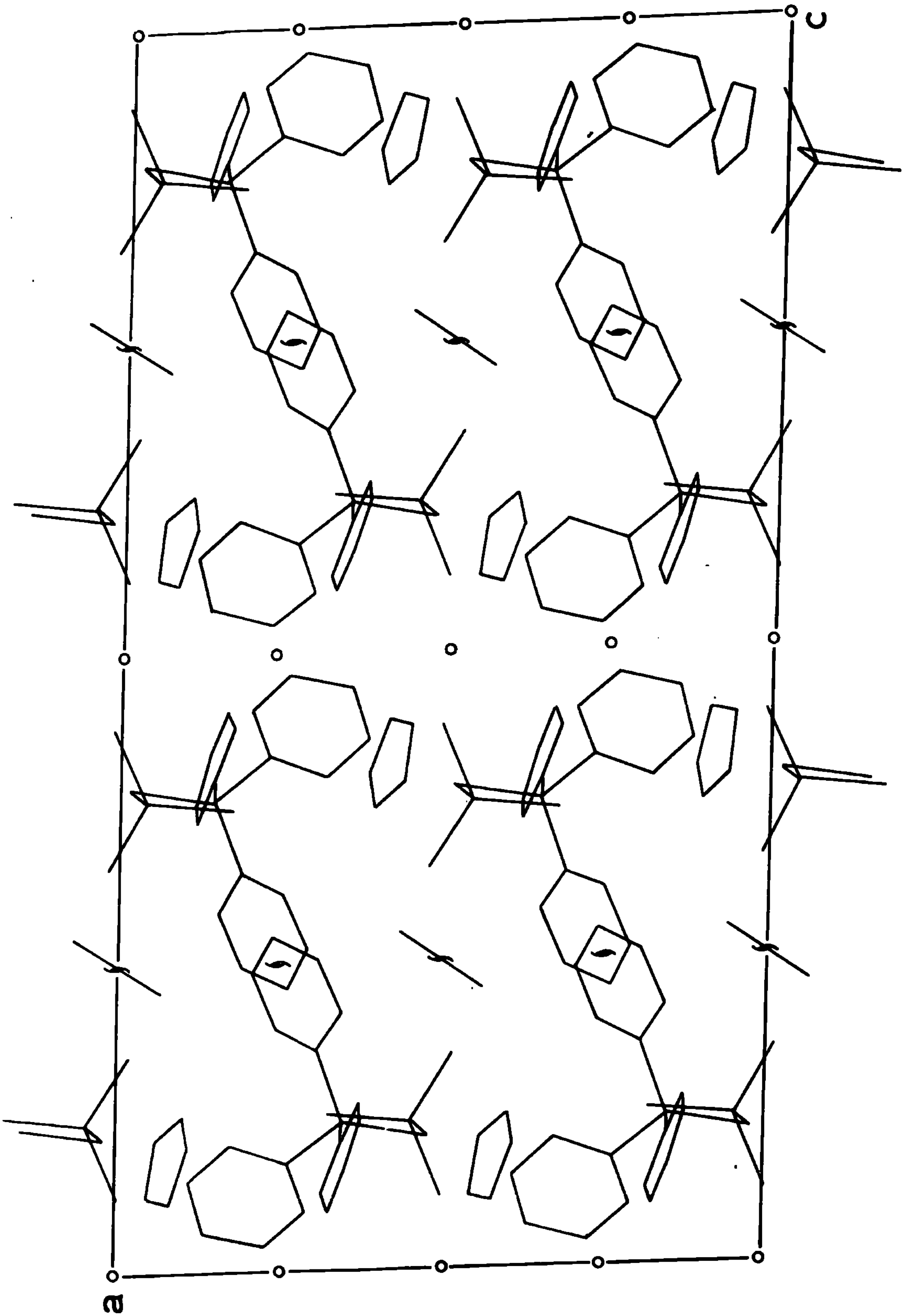

Fig.5C

Projection on the 010 Plane

TABLE 5g

Some Intramolecular Contacts

Atom A	Atom B	A-B (Å)
Ni	Cl(1)	3·93
	Cl(2)	3·70
	Cl(3)	3·76
Ge	P	3·39
	C(2)	3·40
	C(3)	3·07
	C(4)	3·73
	C(17)	3·63
	H(3)	3·03
Cl(1)	Cl(2)	3·35
	Cl(3)	3·31
	C(12)	3·43
	C(17)	3·50
Cl(2)	Cl(3)	3·38
	C(2)	3·59
Cl(3)	H(23)	3·02
P	C(1)	3·43
	C(5)	3·29
C(5)	C(6)	3·37
	C(7)	3·48
C(6)	C(12)	2·87
	C(13)	3·61
	C(18)	2·89
	C(19)	3·17
C(7)	C(18)	3·24
	C(19)	3·24
	H(19)	2·82

TABLE 5g contd.

Atom A	Atom B	A-B (Å)
C(11)	C(12)	3·13
	C(13)	3·82
	C(17)	3·58
C(12)	C(18)	2·93
	C(19)	3·58
	C(23)	3·80
	H(11)	2·65
	H(19)	2·51
C(13)	C(19)	3·41
C(17)	H(11)	2·77
C(18)	H(7)	2·83
	H(13)	2·77
C(19)	H(7)	2·86
	H(13)	2·59
C(24)	C(18)	3·97
	C(23)	3·82
	H(4)	3·58
	H(5)	3·78
	H(7)	3·02
C(25)	C(4)	3·89
	C(5)	3·90
	H(4)	3·24
	H(5)	3·24
	H(7)	3·21
C(26)	H(5)	3·69
	H(7)	3·44
	H(8)	3·74
C(27)	H(7)	3·49
	H(8)	3·49
H(1)	H(11)	2·29
H(13)	H(19)	2·46
	H(5)	3·78
	H(7)	3·01

TABLE 5g contd.

Atom A	Atom B	A-B (Å)
H(24)	H(4)	3·17
	H(5)	3·96
	H(7)	3·45
	H(22)	3·59
	H(23)	3·24
H(25)	H(4)	2·38
	H(5)	2·95
	H(7)	3·76
H(26)	H(5)	3·82
	H(8)	3·96
H(27)	H(8)	3·52

TABLE 5h

Intermolecular Contacts

Atom A	Atom B	Position	A-B (Å)
Cl(1)	C(21)	7	3·72
Cl(2)	C(13)	5	3·89
	C(14)	5	3·59
Cl(3)	C(19)	5	3·71
	C(20)	5	3·87
C(1)	C(17)	2	3·83
C(2)	C(16)	2	3·69
	C(17)	2	3·49
C(3)	C(9)	5	3·66
	C(10)	5	3·69
C(4)	C(21)	3	3·76
	C(22)	3	3·76
C(5)	C(14)	5	3·89
C(8)	C(14)	5	3·80
	C(21)	7	3·85
C(9)	C(16)	6	3·83
C(10)	C(16)	6	3·75
C(16)	C(16)	6	3·70
	H(10)	6	2·99
C(20)	H(26)	5	2·98
C(21)	H(4)	3	2·78
	H(25)	3	2·78
C(22)	H(4)	3	2·76
C(24)	C(18)	3	3·97
	C(23)	3	3·82
C(25)	C(19)	3	3·95
	C(20)	3	3·84
	C(21)	3	3·86
	C(22)	3	3·97

TABLE 5h contd.

Atom A	Atom B	Position	A-B (Å)
C(26)	C(20)	5	3·73
	C(21)	5	3·64
	C(22)	5	3·94
	H(7)	3	3·31
	H(8)	5	3·48
	H(21)	5	3·87
C(27)	C(20)	5	3·93
	C(20)	7	3·93
	C(21)	5	4·00
	C(21)	7	4·00
	H(20)	5	3·86
	H(21)	5	3·98
H(1)	H(2)	2	2·50
H(2)	H(17)	2	2·33
H(4)	H(21)	3	2·54
	H(22)	3	2·50
H(8)	H(21)	7	2·32
H(10)	H(11)	6	2·46
H(26)	H(13)	5	2·58

Position	Position
1. $x,y,z,$	2. $\bar{x},\bar{y},\bar{z},$
3. $\bar{x},y,\frac{1}{2}-z$	4. $x,\bar{y},\frac{1}{2}+z$
5. $\frac{1}{2}+x,\frac{1}{2}+y,z$	6. $\frac{1}{2}-x,\frac{1}{2}-y,\bar{x}$
7. $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$	8. $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$

with the shortest value of 2·23Å between H(9) and H(21) in the equivalent position $\frac{1}{2}$-x, $\frac{1}{2}$+y, $\frac{1}{2}$-z.

Phenyl(II) is involved in contacts with the $GeCl_3$ ligand. This involves contacts between H(17) and Cl(1) which tilts the ring to some extent. The intermolecular contacts are with the cyclopentadienyl ring and with the $GeCl_3$ group, both at positions related by the C-centering of the cell.

Phenyl(III) also has contacts with the $GeCl_3$ ligand. In this case, H(23) has a contact with Cl(1). The net result is that the ring is moved down slightly. The intermolecular contacts are with the benzene molecule.

The benzene molecule lies on the two-fold axis located at 0,y,$\frac{1}{4}$. The surrounding groups are phenyl(III) and the cyclopentadienyl ring. Other long contacts involve phenyl(I). There was no evidence for disordering of the molecule. There was a large amount of thermal motion, and the refinement of the atomic parameters was slow, which could explain the rather short C(24)-C(25) bond length of 1·30(2)Å.

DISCUSSION

The original interest in this compound lay in the Ni-Ge bond length, and in the geometry of the $GeCl_3$ group, which will be discussed in Chapter 7. A close examination of the π-cyclopentadienyl group has indicated that it was not planar. This distortion, which has been described earlier, indicates that there is a possibility of some localised bonding in the ring. This can be deduced from the two slightly different bond lengths in the ring, which is reflected in the different C-Ni-C angles, and also from the non-planarity of the ring, similar to that found in cyclopentadiene molecules (Mason and Wilkinson, 1964).

In addition, an examination of the position of the nickel atom in relation to the centre of mass of the ring, indicates that the bonding may not be symmetrical. Nickel(II) complexes have two types of four-coordination: square planar and tetrahedral. It was observed that the Ge-Ni-P angle was $100{\cdot}7^{\circ}$, a value midway between the angles associated with these two coordination symmetries. The partially localised bonding in the ring is so located that the nickel could have a tetrahedral type configuration. The carbon atoms C(3), C(4) and C(5) could be considered as a π-allyl system, and the rather short C(1)-C(2) bond as a double bond. It must be mentioned that the degree of localised bonding is small, and, in general, the π-cyclopentadienyl moiety is bonding in the normal manner.

There are two possible explanations for this small amount of localised bonding in the ring. The first is that the molecule as a whole is an unsymmetric π-bonded system. An examination of a number of structures (Bennett et al., 1964) led to the postulation of localised π-bonding in cyclopentadienyl ligands for unsymmetric molecules. In all compounds (Bailey, Gerloch and Mason, 1964; Bennett et al., 1962; Bennett and Mason, 1963; Churchill and Mason, 1963; Dahl and Wei, 1963; Gerloch and Mason, 1965)

the differences

were small, with an average value of 0·025Å. Although in each molecule the differences in bond lengths were not normally significant, an overall examination gave indications that partially localised bonding was taking place. In no case was a significant deviation from planarity mentioned, as was found for the ring for this compound.

A second factor which may give rise to this effect is the preference of Ni(II) to form tetrahedral systems in order to relieve steric crowding. In this complex the somewhat localised bonds are positioned so as to complete a distorted tetrahedran about the nickel. The combination of these two possible factors may contribute to the effect observed in the bond lengths and angles in the cyclopentadienyl group, and its relationship to the nickel.

The concept of localised bonding in cyclopentadienyl ligands has been used (Carrick and Glockling, 1968) to explain the bonding in certain molecules. In addition the compound $(C_5H_5)Ni(C_5H_7)$ has been reported (Green, Pratt and Wilkinson, 1958), where a delocalised π-allyl type bond in the (C_5H_7) group has been proposed.

TABLE 5i

Final Values of the Observed and Calculated Structure Factors

H	K	L	|FO|	FC
0	0	2	95	77
0	0	4	626	-632
0	0	6	540	-513
0	0	8	367	357
0	0	10	115	111
0	0	12	352	-347
0	0	14	326	-315
0	0	16	285	274
0	0	18	262	250
0	0	20	78	-76
0	0	22	125	-122
0	0	26	23	11
0	0	30	50	-51
0	0	34	23	28
2	0	0	326	291
2	0	2	293	-287
2	0	-2	428	421
2	0	4	374	-363
2	0	-4	355	-352
2	0	6	216	203
2	0	-6	447	-448
2	0	8	99	97
2	0	-8	63	62
2	0	10	110	-112
2	0	-10	314	313
2	0	12	149	-148
2	0	14	58	41
2	0	-14	462	-440
2	0	16	127	128
2	0	-16	54	51
2	0	18	175	171
2	0	-18	357	350
2	0	20	84	-80
2	0	-20	64	64
2	0	22	42	-40
2	0	-22	146	-142
2	0	24	26	-26
2	0	-24	93	-98
2	0	-26	81	81
2	0	-28	105	102
2	0	-30	23	-35
2	0	-32	67	-61
2	0	-34	30	29
4	0	0	189	188
4	0	2	72	67
4	0	-2	211	-191
4	0	4	94	90
4	0	-4	70	70
4	0	6	218	196
4	0	-6	318	-303
4	0	8	41	46
4	0	-8	144	-142
4	0	10	52	-55
4	0	-10	194	201
4	0	12	122	-121
4	0	-12	267	277
4	0	14	194	-199
4	0	-14	170	-166
4	0	16	95	91
4	0	-16	63	-68
4	0	18	139	140
4	0	-18	123	126
4	0	-20	135	140
4	0	22	77	-79
4	0	-22	38	-39
4	0	24	24	26
4	0	-24	193	-193
4	0	-28	73	67
4	0	30	30	-37
4	0	-32	62	-60
4	0	34	29	19
6	0	0	335	334
6	0	2	138	-135
6	0	-2	260	253
6	0	4	346	-336
6	0	-4	79	-74
6	0	6	134	137
6	0	-6	258	-251
6	0	8	129	130
6	0	-8	63	-67
6	0	10	109	-107
6	0	-10	114	122
6	0	12	204	-209
6	0	-12	75	77
6	0	14	25	-22
6	0	-14	212	-222
6	0	16	182	185
6	0	18	101	102
6	0	-18	67	80
6	0	20	65	-66
6	0	-20	76	77
6	0	22	44	-42
6	0	-22	30	-36
6	0	24	31	31
6	0	-24	67	-65
6	0	-26	38	-37
6	0	-28	102	101
8	0	0	43	41
8	0	2	247	-250
8	0	-2	311	306
8	0	4	98	-100
8	0	-4	90	88
8	0	6	225	226
8	0	-6	237	-241
8	0	8	84	77
8	0	-8	223	-227
8	0	10	159	-164
8	0	-10	270	266
8	0	12	47	-48
8	0	-12	167	169
8	0	14	126	129
8	0	-14	116	-124
8	0	16	38	36
8	0	-16	119	-125
8	0	18	46	-48
8	0	-18	37	39
8	0	20	83	-82
8	0	-20	109	110
8	0	24	38	38
8	0	-24	75	-42
8	0	-28	56	43
8	0	-30	29	30
10	0	0	82	-79
10	0	2	71	-70
10	0	-2	55	59
10	0	4	26	27
10	0	-4	151	148
10	0	6	131	128
10	0	-6	85	-87
10	0	-8	231	-228
10	0	10	146	-150
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10	0	-12	118	117
10	0	16	46	43
10	0	-16	93	-98
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10	0	-20	91	99
10	0	-22	75	78
10	0	-24	59	-71
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10	0	-28	36	52
10	0	-30	34	36
12	0	4	37	36
12	0	-4	74	73
12	0	8	53	-62
12	0	-8	74	-67
12	0	-12	45	47
12	0	-14	34	32
12	0	-16	50	-47
12	0	18	41	48
12	0	-18	41	-44
12	0	-20	37	38
12	0	22	38	-41
12	0	-22	61	71
12	0	24	37	-33
12	0	-26	53	-68
14	0	2	25	-17
14	0	-2	27	24
14	0	-4	64	89
14	0	-6	25	-19
14	0	8	47	48
14	0	-8	89	-84
14	0	-12	36	33
14	0	14	38	-39
14	0	-16	24	-28
14	0	18	47	47
14	0	-18	40	-40
14	0	22	36	-37
14	0	-22	36	32
16	0	-8	37	-41
16	0	12	35	-33
18	0	4	27	-11
1	1	0	352	335
1	1	1	172	-158
1	1	-1	102	102
1	1	2	108	-104
1	1	-2	220	232
1	1	3	208	-195
1	1	-3	171	208
1	1	4	366	-340
1	1	-4	312	-331
1	1	5	223	211
1	1	-5	155	-154
1	1	6	146	-130
1	1	-6	106	-111
1	1	7	125	-117
1	1	-7	84	-78
1	1	8	264	256
1	1	-8	200	197
1	1	9	100	-94
1	1	-9	148	-132
1	1	10	167	163
1	1	-10	255	254
1	1	-11	143	142
1	1	12	330	-305
1	1	-12	37	-36
1	1	13	32	36
1	1	14	149	-147
1	1	-14	247	-237
1	1	15	177	173
1	1	-15	189	-172
1	1	16	60	55
1	1	-16	43	42
1	1	18	160	158
1	1	-18	145	148
1	1	19	108	-108
1	1	-19	152	148
1	1	-20	63	59
1	1	-21	50	56
1	1	22	58	-57
1	1	-22	119	-110
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1	1	-23	64	-64
1	1	-24	46	-46
1	1	-26	56	48
1	1	27	33	-32
1	1	-28	44	43
1	1	31	31	31
1	1	-31	36	-24
1	1	-32	39	-40
1	1	33	36	27
3	1	0	150	129
3	1	1	274	-255
3	1	-1	88	84
3	1	2	235	217
3	1	-2	143	130
3	1	3	254	-242
3	1	-3	420	409
3	1	4	107	-93
3	1	-4	288	-268
3	1	5	96	96
3	1	-5	51	56
3	1	6	56	-47
3	1	-6	206	-204
3	1	7	35	-36
3	1	-7	173	172
3	1	8	221	204
3	1	-8	22	26
3	1	9	87	-79
3	1	-9	196	-219
3	1	10	28	28
3	1	-10	179	235
3	1	-11	79	86
3	1	12	35	-40
3	1	13	112	107
3	1	-13	82	80
3	1	14	124	-126
3	1	-14	117	-122
3	1	15	155	154
3	1	-15	148	-143
3	1	16	23	24
3	1	-16	115	-114
3	1	17	52	-43
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3	1	-20	104	104
3	1	-21	72	67
3	1	22	35	-40
3	1	-22	92	-87
3	1	23	66	66
3	1	24	31	-26
3	1	-24	173	-172
3	1	25	32	-34
3	1	-25	67	-70
3	1	26	53	67
3	1	27	35	-35
3	1	28	33	31
3	1	-28	66	79
3	1	-29	31	34
3	1	31	46	40
3	1	32	51	-53
3	1	-33	48	-36
5	1	0	110	107
5	1	1	455	-430
5	1	2	100	-76
5	1	-2	103	93
5	1	3	27	-28
5	1	-3	161	157
5	1	4	153	-149
5	1	-4	49	-55
5	1	5	310	299
5	1	-5	166	159
5	1	6	39	34
5	1	-6	185	-177
5	1	-7	43	-40
5	1	8	136	142
5	1	-8	27	-20
5	1	9	261	-254
5	1	-9	185	-180
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5	1	-10	106	111
5	1	11	95	93
5	1	-11	63	62
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5	1	-12	65	69
5	1	13	173	175
5	1	-13	61	71
5	1	14	118	-120
5	1	-14	48	-65
5	1	15	71	74
5	1	-15	46	-59
5	1	-16	46	-58
5	1	17	160	-157
5	1	-17	105	-107
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5	1	-18	33	37
5	1	19	68	-69
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5	1	21	88	91
5	1	-21	48	46
5	1	22	64	-69
5	1	23	31	34
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5	1	30	50	-45
5	1	32	34	-29
5	1	-32	30	-26
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7	1	-1	126	-128
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7	1	-3	65	60
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7	1	-4	67	-68
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7	1	-5	238	276
7	1	6	161	159
7	1	-6	202	-192
7	1	7	246	-252
7	1	-7	32	31
7	1	8	257	262
7	1	-8	61	53
7	1	9	96	-100
7	1	-9	273	-266
7	1	-10	244	242
7	1	11	183	186
7	1	12	161	-167
7	1	-12	44	50
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7	1	15	96	-100
7	1	16	106	108
7	1	-16	116	-119
7	1	17	26	-25
7	1	-17	60	-67
7	1	18	35	38
7	1	-18	46	58
7	1	20	72	-72
7	1	-20	54	68
7	1	21	27	38
7	1	-21	32	41
7	1	22	62	-60
7	1	-22	37	-43
7	1	23	53	-55
7	1	-23	53	63
7	1	-24	39	-41
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7	1	-28	36	33
7	1	29	30	38
9	1	1	47	48
9	1	2	124	-130
9	1	-2	195	192
9	1	3	20	-17
9	1	-3	124	-120
9	1	4	90	-71
9	1	5	123	-125
9	1	-5	146	142
9	1	6	90	96
9	1	-6	156	-155
9	1	7	104	-107
9	1	-7	142	140
9	1	8	63	71
9	1	-8	63	-62
9	1	9	68	68
9	1	-9	109	-103
9	1	10	51	-51
9	1	-10	136	135
9	1	11	115	119
9	1	-11	112	-107
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9	1	-16	112	-116
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9	1	-19	44	-49
9	1	-20	91	109
9	1	23	31	-33
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9	1	-24	52	-67
9	1	-27	29	-44
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11	1	2	56	-60
11	1	-2	32	33
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11	1	22	48	-44
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13	1	2	50	-45
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13	1	3	39	35
13	1	-3	60	-56
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13	1	5	47	-44
13	1	-5	34	34
13	1	-6	56	-51
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13	1	11	74	79
13	1	-11	67	-69
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15	1	-21	29	-22
17	1	0	34	-31
17	1	-1	35	36
17	1	2	35	-31
17	1	-2	28	23
17	1	3	37	-40
17	1	-4	30	30
17	1	-5	29	-31
17	1	6	32	21
17	1	7	34	30
17	1	-12	47	45
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0	2	5	68	-61
0	2	6	262	-250
0	2	7	74	75
0	2	8	46	44
0	2	9	97	-87
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0	2	11	148	-141
0	2	12	51	49
0	2	14	85	-83
0	2	15	17	-14
0	2	16	154	-149
0	2	17	46	43
0	2	18	18	-16
0	2	20	103	99
0	2	23	40	38
0	2	24	40	-38
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0	2	29	39	-37
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0	2	34	32	-28
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2	2	-3	54	-53
2	2	4	40	39
2	2	-4	262	-254
2	2	5	247	233
2	2	-5	65	-75
2	2	6	208	-187
2	2	-6	117	121
2	2	7	214	204
2	2	-7	242	-257
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2	2	9	23	-25
2	2	-9	27	27
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2	2	11	133	-131
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2	2	-13	25	30
2	2	14	73	-76
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2	2	15	47	52
2	2	-15	110	-107
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2	2	-16	68	-71
2	2	17	50	-46
2	2	-18	36	-26
2	2	19	66	-66
2	2	20	98	98
2	2	-20	100	98
2	2	-22	52	-48
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2	2	-23	43	-46
2	2	24	77	-74
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2	2	-25	38	-39
2	2	27	39	-44
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2	2	-30	42	40
2	2	32	32	-31
2	2	-32	41	-38
2	2	34	45	-50
2	2	-34	30	-31
4	2	0	117	-105
4	2	1	86	-91
4	2	-1	266	-255
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4	2	3	124	114
4	2	-3	176	170
4	2	4	18	15
4	2	-4	27	-32
4	2	5	326	313
4	2	-5	35	36
4	2	6	54	-65
4	2	-6	105	-191
4	2	-7	255	-268
4	2	8	162	154
4	2	-8	146	148
4	2	9	220	-211
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4	2	10	127	131
4	2	-10	93	84
4	2	11	113	-116
4	2	-11	115	123
4	2	12	26	21
4	2	13	118	115
4	2	-13	136	135
4	2	14	160	-161
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4	2	15	25	24
4	2	-15	51	-54
4	2	16	105	-109
4	2	-16	111	-120
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4	2	-17	94	-99
4	2	18	54	51
4	2	19	31	-29
4	2	-19	52	56
4	2	20	114	111
4	2	-20	66	66
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4	2	-21	81	82
4	2	22	70	-69
4	2	-22	59	61
4	2	23	51	49
4	2	24	103	-99
4	2	-24	55	-56
4	2	-25	47	-35
4	2	26	68	66
4	2	-26	32	-35
4	2	27	40	-40
4	2	28	112	109
4	2	-29	28	32
4	2	-30	56	50
4	2	32	86	-86
4	2	-34	52	-44
6	2	0	26	-17
6	2	1	111	-106
6	2	-1	195	-183
6	2	2	73	-65
6	2	-2	32	-35
6	2	3	102	100
6	2	4	70	-74
6	2	-4	80	-82
6	2	5	88	86
6	2	-5	198	188
6	2	6	144	-148
6	2	-6	13	15
6	2	7	27	-27
6	2	8	185	186
6	2	-8	165	152
6	2	9	44	-43
6	2	-9	106	-100
6	2	10	297	305
6	2	-10	38	45
6	2	11	24	29
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3	11	-3	88	80
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3	11	-4	57	-53
3	11	5	61	58
3	11	-5	36	27
3	11	-6	45	-46
3	11	-7	44	-42
3	11	8	49	46
3	11	9	56	-57
3	11	-9	31	-31
3	11	-10	67	66
3	11	-11	34	35
3	11	12	51	-54
3	11	-13	51	50
3	11	14	45	-38
3	11	-14	89	-92
3	11	15	31	24
3	11	16	33	36
3	11	-17	63	-63
3	11	18	54	48
3	11	-18	52	49
3	11	-21	50	48
5	11	0	56	56
5	11	1	54	-53
5	11	2	54	-56
5	11	-2	56	53
5	11	-3	41	45
5	11	4	77	-77
5	11	-4	33	-35
5	11	5	30	28
5	11	-5	51	51
5	11	6	50	49
5	11	-6	71	-71
5	11	-7	42	-33
5	11	8	65	81
5	11	9	33	-32
5	11	-9	50	-51
5	11	-10	73	72
5	11	12	63	-60
5	11	-13	35	37
5	11	-14	57	-51
5	11	15	42	40
5	11	16	35	35
5	11	-17	30	-32
5	11	-18	45	39
5	11	19	32	-23
5	11	-20	29	24
7	11	1	55	-54
7	11	2	55	-53
7	11	-2	54	58
7	11	-3	54	55
7	11	-5	61	43
7	11	6	72	77

H	K	L	|FO|	FC
7	11	-6	55	-59
7	11	-8	43	-40
7	11	9	40	-23
7	11	-9	43	-49
7	11	10	52	-46
7	11	-10	61	56
7	11	-12	36	35
7	11	13	54	50
7	11	-13	36	30
7	11	-14	51	-52
7	11	-16	40	-31
7	11	-17	40	-36
7	11	-20	51	37
9	11	-1	44	-48
9	11	2	32	-28
9	11	3	34	30
9	11	-4	33	31
9	11	-5	64	47
9	11	7	29	-30
9	11	-8	42	-40
9	11	9	28	-17
9	11	-9	52	-51
9	11	11	43	43
9	11	-12	42	41
9	11	-13	46	-43
11	11	-7	50	41
11	11	-11	52	-47
0	12	1	101	-97
0	12	3	80	-78
0	12	5	77	77
0	12	7	86	81
0	12	9	41	-40
0	12	11	104	-103
0	12	15	76	72
0	12	19	55	-51
2	12	1	63	-66
2	12	-2	30	-24
2	12	-3	36	35
2	12	5	76	74
2	12	-7	75	-72
2	12	9	80	-58
2	12	-9	53	-57
2	12	10	37	32
2	12	-11	66	61
2	12	13	30	25
2	12	-13	92	57
2	12	14	17	-16
2	12	15	44	16
2	12	-15	70	-68
2	12	-17	70	-69
4	12	1	35	-36
4	12	4	40	-38
4	12	-4	30	-35
4	12	5	39	33
4	12	8	43	40
4	12	-9	46	-45
4	12	10	48	45
4	12	-10	30	26
4	12	-13	57	56
4	12	14	30	-32
4	12	15	31	23
6	12	1	61	-61
6	12	2	26	-10
6	12	-3	41	39
6	12	5	70	70
6	12	7	28	18
6	12	-7	30	-32
6	12	8	32	34
6	12	-8	31	24
6	12	9	42	-45
6	12	11	32	-33
6	12	13	29	27
6	12	15	31	26
8	12	-1	56	-54
8	12	3	46	40
8	12	5	42	37
8	12	-5	52	55
8	12	7	42	-41
8	12	-8	32	30
8	12	9	48	-47
8	12	-9	60	-58
8	12	10	33	30
8	12	-13	50	52
10	12	-1	31	-31
10	12	4	40	-37
10	12	-5	40	40
10	12	-7	31	27
1	13	1	44	-46
1	13	-1	46	40
1	13	7	31	28
1	13	-7	42	-48
1	13	-8	41	-34
1	13	11	35	-28
1	13	-11	37	30
1	13	12	31	22
1	13	14	28	-6
1	13	-14	31	26
1	13	16	30	-17
3	13	2	32	30
3	13	-5	28	20
3	13	6	34	-33
5	13	2	31	28
5	13	-5	26	-28
5	13	6	44	-45
5	13	7	40	37
5	13	10	40	40
7	13	1	43	-36
7	13	2	39	36
7	13	-3	42	30
7	13	4	32	-28
7	13	-4	39	-34
7	13	6	41	-38
7	13	-7	39	-38
7	13	-8	38	31
0	14	0	35	34
0	14	4	31	-31
2	14	5	30	-25

Chapter 6

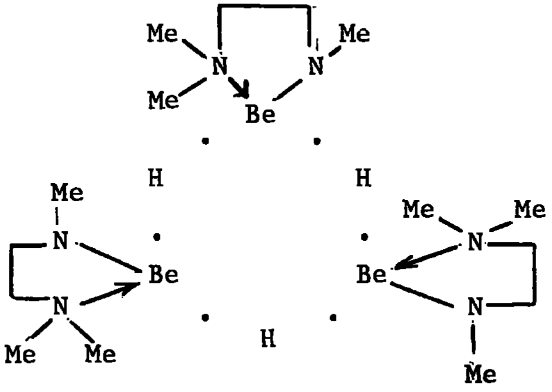
The Crystal Structure of $HBe[N(Me)CH_2CH_2NMe_2]_2$

INTRODUCTION

The compound $HBe(MeNCH_2CH_2NMe_2)$ was prepared by the reaction

$$BeH_2 + Me_2NCH_2CH_2N(Me)H \longrightarrow HBe(MeNCH_2CH_2NMe_2) + H_2$$

The reaction is carried out in a sealed tube at room temperature, using toluene as the solvent, and the compound crystallised from a mixture of toluene and hexane. In solution, the compound is a trimer, unlike the analogous zinc compound which was dimeric (Bell and Coates, 1968). Based upon the infrared spectra, the workers proposed the structure as:



EXPERIMENTAL

The crystal used in the study was mounted in a thin-walled capillary tube, since the compound is reactive to both air and water. In this way, the crystal exhibited no signs of decomposition over a period of three years.

The crystal had the dimensions 0·4 mm x 0·3 mm x 0·2 mm and showed well-developed faces.

Two sets of data were collected, pnotographic and diffractometer. In both cases the same crystal was employed. The space group was determined from the photographic data, which showed no systematic absences. The unit cell was triclinic with the dimensions:

$a = 7{\cdot}51\text{Å}$ $b = 6{\cdot}04\text{Å}$ $x = 8{\cdot}27\text{Å}$

$\alpha = 109{\cdot}12^{\circ}$ $\beta = 96{\cdot}83^{\circ}$ $\gamma = 94{\cdot}70^{\circ}$

$V = 358{\cdot}02\text{Å}^{3}$ $Z = 2$

$\mu = 0{\cdot}67\ \text{cm}^{-1}$ for Mo Kα

$D_c = 1{\cdot}04\ \text{g./cm}^3$ $D_o = 1{\cdot}05\ \text{g./cm}^3$

The reduced cell parameters were calculated (Delaunay, 1933), but no higher symmetry was indicated.

For the photographic data, the nets nkl, n = 0,2, and hkn, n = 0,2, were recorded employing the precession method with Mo Kα radiation, as well the nets hnl, n = 0,5, using the equi-inclination Wissenberg technique and Cu Kα radiation. The data was corrected for Lorentz and polarisation factors, then scaled employing the method as described for the palladium compound. These three sets of data were averaged, yielding a total of 1002 observed reflections.

A second set of data was later collected on a four-circle diffractometer using MoKα radiation. The crystal was aligned in the usual manner, and the orientation matrix and the unit cell parameters were calculated from the reflections

-2 4 7	1 -3 -8	10 -3 1
1 6 3	5 -5 6	1 2 -10
2 -4 -7	-3 3 -9	7 5 -1
-9 -1 3		

The unit cell dimensions calculated from these reflections are

$a = 7{\cdot}440(3)\text{Å}$ $b = 6{\cdot}047(3)\text{Å}$ $c = 8{\cdot}240(3)\text{Å}$

$\alpha = 103{\cdot}97(2)^\circ$ $\beta = 95{\cdot}75(2)^\circ$ $\gamma = 97{\cdot}02(2)^\circ$

The difference between the two sets of parameters obtained are appreciable. In the case of the film data, the reciprocal lengths were obtained by a least squares method, yet the errors in the real cell dimensions involve the errors in all six of the measured quantities. For the diffractometer data, the ten reflections used in the least squares calculation had values of θ ranging from 24·91° (5 -5 6) to 29·665° (10 -3 1). By using a proper least squares method in the triclinic system good dimensions can be obtained.

The data was collected as described previously, with 80 steps (0·01°/step), and counting for 1·5 seconds per step. The backgrounds were measured at each side of the scan with a stationary counter for twenty seconds. The standard reflections 1 1 2, 2 -1 -1, -1 -1 -1, were measured every fifty reflections, when a drive to datum was executed. The data was collected from the full sphere of reflection with $0^{\circ} < \theta \leqslant 30^{\circ}$. A total of 3161 independent reflections were measured. A reflection was considered to be observed if its net count was greater than three times its e.s.d. At a later stage, it was noted that the counts had been scaled by a factor of 0•3765 so that the data chosen had net counts greater than 4•889 times the e.s.d. In this way, 959 reflections were selected. The data was corrected for Lorentz and polarisation factors.

SOLUTION

The symbolic addition method, discussed in Chapter 1, together with the photographic data, was used for the solution of the structure. The reflections were placed on an absolute scale employing the method of Wilson (1942), with K = 0•5139 and B = 2•92. The normalised structure factors were calculated using (1•5). The distribution of the normalised structure factors is given in Table 6a. From this distribution the space group appears to be the centrosymmetric $P\bar{1}$.

A total of 197 normalised structure factors, each with a magnitude greater than 1•5, were used in the solution. Two attempts were made to solve the structure. The first was carried out by hand, determining the signs of 127 reflections, and the second, employing a computer programme (see Appendix I).

The first attempt was done by hand. The values of B and K were calculated, then used to obtain the normalised structure factors. This was

TABLE 6a

Distribution of the normalised structure factors

	observed	centric	acentric
$<\|E\|>$	0•844	0•798	0•886
$<\|E\|^2>$	1•102	1•000	1•000
$<\|E\|^2 - 1>$	1•020	0•980	0•736
$\|E\| > 3$	0•61%	0•3%	0•01%
$\|E\| > 2$	4•92%	5•0%	1•8%
$\|E\| > 1$	34•51%	32•0%	37•0%

followed by the computation of a sigma two listing. The reflections given in Table 6b were used as the starting set of signs and symbols. From the origin determining reflections, and the symbols q,r,s, and t, it was possible to derive the signs or symbols for 63 structure factors. At that stage, the plane -2 2 3 was assigned a symbol, and thus a set of 127 phased structure factors were obtained. Toward the end of this process, a few inconsistencies were observed. E maps based upon the derived phases, were calculated, but no chemically reasonable structure was found. A comparison of the normalised structure factors employed in this attempt with those of the second showed some of them to have larger values. The

TABLE 6b

reflection	|E|	sign or symbol
-4 5 -8	2•66[a]	+
1 1 4	2•72	+
-1 1 -3	2•66	-
2 0 5	2•60	q
2 3 -5	2•60[b]	r
1 1 2	2•51	s
6 0 -1	2•53	t
-2 2 3	2•27	u

a later found to be 1•13
b later found to be 1•72

result of this error meant that relationships of apparently high probability were not reliable. This was probably caused by the lower values of B and K employed. In this case, the values of the unobserved reflections were included on a somewhat crude basis.

In the second attempt, the unobserved reflections were one half the minimum intensity in a net, corrected for Lorentz and polarisation factors, then scaled as for the observed. A series of six programmes developed by F.R. Ahmed and S.R. Hall were employed to implement the symbolic addition method. The scale and temperature factors obtained are those quoted earlier.

There is a choice of sigma two listings available from the programmes. The full search, listing all triple product interactions for each normalised structure factor greater than 1•5, was used in order that the maximum amount of information about the symbols could be obtained. This is important in the space group $P\overline{1}$, where the equivalent structure factors F_{hkl} and $F_{\overline{h}\overline{k}\overline{l}}$ always have the same sign, and thus the trivial solution, where all the signs are positive, will always occur. In order to obtain a sufficient amount of information about the symbols, the largest number of interactions for each plane is necessary.

Four assignments of the origin determining signs and the subsequently defined symbols were employed in order to give an unambiguous set of signs. These are summarised in Table 6c.

The first assignment was carried out by the programme, for both the origin determining signs and the symbols. This will be called the basic solution, since the information obtained from the other assignments was used to give signs to the symbols. The only definite fact that was obtained was that b was equal to c , and some indications that they were both positive.

In the second assignment, the same origin was chosen by giving positive signs to structure factors, the signs of which were obtained in the eighth cycle of assignment I. This showed that different interactions produced similar results, but since there were few strong cross interactions, no definite assignment of signs could be made.

TABLE 6c

Comparison of Origins and Symbols

	I			II				III				IV		
Plane	|E|	Sign	Plane	|E|	S	S_b	Plane	|E|	S	S_b	Plane	|E|	S	S_b
$\bar{3}$ 3 3	3•25	+	6 0 $\bar{1}$	3•82	+	+	$\bar{3}$ 3 3	3•25	+	+	$\bar{3}$ 3 3	3•25	+	+
2 0 5	2•93	+	1 6 5	3•26	+	+	$\bar{2}$ 2 3	2•53	+	b	2 0 5	2•93	+	+
1 6 5	3•26	+	1 $\bar{7}$ 3	2•51	+	c	1 6 3	3•27	+	ac	1 6 5	3•26	+	+
1 1 4	2•86	a	$\bar{3}$ 3 3	3•25	d	+	6 0 $\bar{1}$	3•82	g	+	1 1 4	2•86	j	a
1 1 5	2•63	b	2 0 5	2•93	e	+	2 0 5	2•93	h	+	1 1 5	2•63	k	b
1 1 2	2•57	c	1 1 4	2•86	f	a	1 1 4	2•86	i	a				
	a = - b = + c = +			d = + e = + f = -				g = + h = + i = -				j = - k = +		

Strongest Structure Factor in each Parity Group not Defined as an Origin or by a Symbol

Plane	Parity Group	|E|	I	II	III	IV
$\bar{2}$ 4 8	eee	3•28	+	+	+	+
6 6 $\bar{1}$	eeo	3•05	+	+	+	+
2 5 6	eoe	2•66	-	-	+	-
10 $\bar{3}$ 1	eoo	3•28	+	+	-	+
$\bar{3}$ 4 2	oee	2•31	-	-	+	-
1 $\bar{2}$ 9	oeo	2•84	-	-	+	-
5 $\bar{5}$ 6	ooe	2•53	-	-	-	-
7 5 $\bar{1}$	ooo	2•83	+	+	+	+

o is defined as odd;   e is defined as even;

S_b is the symbol or sign in the basic solution

For the third investigation, a different origin was chosen by selecting as an origin determining reflection a plane which had indications in the basic solution, of a negative sign. There were a large of strong cross interactions, thus a possible assignment of signs could be made. The only self-consistent set of signs in both this and the basic solution was

$$a = -$$
$$b = c = +$$

In order to check this, a fourth examination was carried out in which the programme was able only to employ two symbols, rather than the three needed in the original solution. This verified the assignment b = c, and contained a number of strong indications that the sign of b was positive. Thus the number of symbols could be reduced to one, a, which must be negative.

An E map was computed from the 197 phased E's derived from the previously assigned symbols. The map yielded the structure shown in Figure 6A. Subsequent isotropic and anisotropic least squares refinement gave an R index of 0•1628 after neglecting those planes with large ΔF. At this stage, the diffractometer data became available, and similar refinement lowered the R factor to 0•1268. A difference map calculated did not exhibit any large peaks, but it was possible to find the positions of six hydrogen atoms. Inclusion of these atoms with isotropic temperature factors in the refinement led to a final R factor of 0•1062. Two planes

TABLE 6d

Atomic Coordinates and their Standard Deviations (x 10^5)

Atom	x/a	y/b	z/c	B_{iso}[a]
Be	-0·13870(92)	0·04182(126)	0·44455(82)	2·68
N(1)	0·06769(58)	0·01473(81)	0·36127(52)	2·67
N(2)	-0·27110(61)	-0·19595(88)	0·28422(57)	3·18
C(1)	0·04028(78)	-0·19790(104)	0·22203(66)	3·10
C(2)	-0·13185(80)	-0·34972(103)	0·23523(72)	3·38
C(3)	0·16561(89)	0·20367(123)	0·31080(76)	3·81
C(4)	-0·33103(97)	-0·09344(142)	0·14597(78)	4·51
C(5)	-0·43328(86)	-0·33165(138)	0·32326(91)	4·50
H(1)	0·13906(751)	-0·30177(946)	0·22451(676)	0·71(1·05)
H(2)	0·03328(694)	-0·14907(898)	0·11145(630)	0·33(0·98)
H(3)	-0·18027(898)	-0·48496(1160)	0·12831(822)	2·46(1·45)
H(4)	0·17562(872)	0·37874(1111)	0·38732(799)	1·84(1·42)
H(5)	0·10158(759	0·24588(963)	0·19850(708)	1·16(1·14)
H(6)	-0·37250(1032)	-0·22792(1315)	0·06261(951)	2·92(1·74)

[a] Based upon the last cycle of refinement

e.s.d. are quoted for the hydrogen atoms which were refined with isotropic parameters only.

TABLE 6e

Final Thermal Parameters* and their Standard Deviations (x 10^5)

	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Be	0·01251(117)	0·02323(225)	0·00984(96)	0·00595(228)	0·00366(168)	0·00364(253)
N(1)	0·01237(77)	0·02521(146)	0·00919(62)	0·00187(152)	0·00472(108)	0·00429(168)
N(2)	0·01210(82)	0·03360(185)	0·01146(71)	0·00273(182)	0·00027(118)	0·00641(197)
C(1)	0·01031(106)	0·02859(202)	0·01031(79)	0·00023(197)	0·00614(146)	0·01092(230)
C(2)	0·01614(111)	0·02445(190)	0·01363(96)	-0·00392(213)	0·00394(162)	0·00578(231)
C(3)	0·01881(124)	0·03744(249)	0·01233(91)	0·00886(242)	0·00770(174)	0·00148(281)
C(4)	0·02330(158)	0·05379(330)	0·01115(93)	0·00405(278)	-0·00728(193)	0·02657(370)
C(5)	0·01357(118)	0·04759(302)	0·01885(125)	0·00858(311)	0·00335(192)	-0·01158(294)

* where B_{ij} refers to the expression

$$\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2klB_{23} + 2hlB_{13})]$$

with $(|\Delta F|/|F_o|) > 3{\cdot}0$ were excluded from the least squares totals. There were no shifts greater than one third of an e.s.d. in the last cycle of refinement. Other light atom structures have lead to much lower R values, and work on this structure is still proceeding. The final atomic coordinates are listed in Table 6d, and the thermal parameters in Table 6e.

DESCRIPTION

Since the refinement of the structure is not complete, only a description of the structure will be given. The basic molecular configuration is the same as those observed for two trimethylethylenediamine complexes, namely HZnTriMED (Moseley, Shearer and Spencer, 1969) and MeMgTriMED (Magnuson and Stucky, 1969). Both of these complexes are dimeric, with one half related by a centre of symmetry to the other. The molecules possess a four-membered ring containing the two metal atoms bridged by nitrogen. Each TriMED moiety acts as a bidentate ligand, with one nitrogen located in the bridge, and the other bonded to a metal atom, thus forming a five-membered ring. In this way, the metal atom achieves four-coordination, although the position of the hydridic hydrogen was not determined.

The Be-N(1) distance, 1·753(8)Å, is shorter than the Be-N(2) bond length of 1·805(9)Å, the same effect as is observed in the two previously mentioned structures. The Be-N(1) distance is the same as that found, within experimental error, in $[Be(NMe_2)_2]_3$ (Atwood and Stucky, 1967),

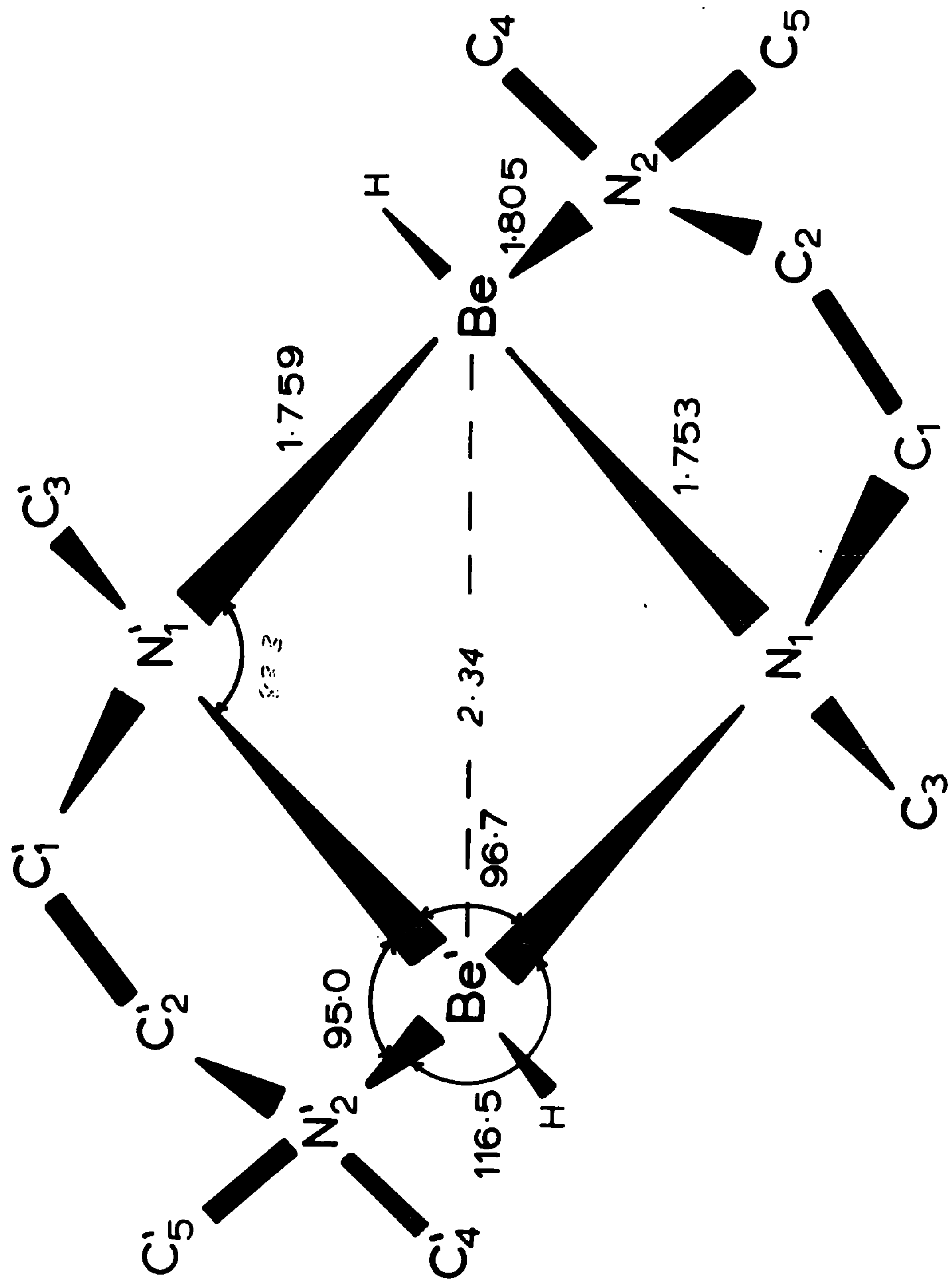


Fig.6A

Some Bond Lengths and Angles (Schematic Representation)

TABLE 6f

A Comparison of the Bond Lengths and their Standard Deviations ($\times 10^3$) HMTriMED, where M = Be, Zn

	M = Be	M = Zn
M-N(1)	1·753(8) Å	2·060(10) Å
M-N(1')	1·759(8)	2·062(11)
M-N(2)	1·805(9)	2·186(11)
N(1)-C(1)	1·479(7)	1·479(16)
N(1)-C(3)	1·447(9)	1·455(21)
N(2)-C(2)	1·496(8)	1·488(18)
N(2)-C(4)	1·479(9)	1·488(22)
N(2)-C(5)	1·482(9)	1·507(22)
C(1)-C(2)	1·511(9)	1·514(23)

TABLE 6g

A Comparison of the Angles and their Standard Deviations in HMTriMED, where M = Be, Zn

	M = Be	M = Zn
N(1)-M-N(1')	96·69(40)°	92·0(4)°
N(1)-M-N(2)	95·00(40)	84·1(4)
N(2)-M-N(1')	116·52(44)	110·6(5)
C(1)-N(1)-C(3)	110·04(46)	110·2(1·1)
M -N(1)-C(3)	120·94(45)	119·1(9)
M'-N(1)-C(3)	120·29(45)	117·1(9)
M -N(1)-C(1)	108·58(42)	109·9(7)
M'-N(1)-C(1)	111·06(42)	110·7(9)
M -N(1)-M'	83·31(38)	88·0(4)
C(2)-N(2)-C(4)	111·25(48)	112·5(1·2)
C(2)-N(2)-C(5)	109·54(48)	109·6(1·3)
C(2)-N(2)-M	102·38(42)	102·2(8)
C(4)-N(2)-C(5)	108·27(51)	109·9(1·2)
C(4)-N(2)-M	104·79(46)	102·6(1·0)
C(5)-N(2)-M	120·41(47)	119·8(9)
N(1)-C(1)-C(2)	108·96(47)	111·5(1·0)
N(2)-C(2)-C(1)	107·40(47)	110·6(1·4)

TABLE 6h

A Comparison of the Intramolecular Contacts in HMTriMED, where M = Be and Zn

Atom A	Atom B	A-B (Be)Å	A-B (Zn)Å
M	M	2·335	2·864
M	C(1')	2·674	2·932
M	C(2')	3·182	3·372
M	C(3)	2·789	3·046
M	C(3')	2·785	3·016
M	C(4)	2·609	2·901
M	C(5)	2·856	3·213
M	N(2')	3·478	3·902
N(1)	N(1')	2·624	2·964
N(1)	N(2)	2·623	2·845
C(1)	C(4)	2·948	2·978
C(3)	C(5')	3·309	3·662

Covalent radii of the atoms

Zn = 1·31Å

Be = 1·06Å

TABLE 6i

Intermolecular contacts less than 4Å

C(2)-C(3)	3·816(10)
C(3)-C(5)	3·815(10)

where the central bridging Be-N bond length is 1·76Å.

The Be-N(1)-Be' angle of 83·31(38)° does not differ from the angle of 82·4° found in the dimethylamine complex. The N(1)-Be-N(1') angle of 96·69(40)° can be compared with the values found in the previously mentioned compound, where the three coordinate beryllium has an angle of 103·9°, and the four coordinate a value of 93·30°.

The trimethylethylenediamine moeity has bond lengths and angles similar to those found in the analogous zinc hydride. The C(1)-C(2) bond length of 1·511(9)Å is the same, within experimental error, as the corresponding value of 1·514(23)Å. The average C-N bond length is 1·479Å, compared with the value of 1·48Å. This length can also be compared with the distance of 1·47Å in triethylamine (Allen and Sutton, 1950) and 1·48Å in the TMED moeity in AlH_3TMED (Palenik, 1964). There is no deviation from tetrahedral coordination within the C-N-C and the N-C-C angles, which have a mean value of 109·84°.

The Be-Be' non-bonding contact of 2·335(38)Å, where Be' refers to the atom related by the centre of symmetry, is greater than both the distances found in $[Be(NMe_2)_2]_3$, 2·18A, and in $Na_2(Et_4Be_2H_2)$, 2·20A (Adamson and Shearer, 1965). In the second compound, the two beryllium atoms are bridged by hydrogens.

A comparison of the intramolecular contacts in the beryllium and the zinc hydrides are given in Table 6h. When the difference of 0·25Å in the covalent radii is taken into account, the assignment is quite good.

There are only two intermolecular contacts less than 4Å. These are C(2)-C(3), 3·816(10)Å, and C(3)-C(5), 3·815(10)Å. This is unlike the zinc hydride, where the two intermolecular contacts were 3·891Å for C(3)-C(4), and 3·643Å for C(3)-C(5). Thus the beryllium compound shows close contacts between methyl and methylene carbon atoms unlike the zinc analogue. There are no non-hydrogen intermolecular contacts with the beryllium at a distance less than 4Å.

In light of the relatively large R factor, the refinement is not considered to have been completed. There are still some hydrogen atom positions to be found, among them the hydride. At the present time further work on this structure is in progress.

TABLE 6j

Observed and Calculated Structure Factors

H	K	L	|FO|	FC
1	0	0	21.3	27.6
3	0	0	4.1	-1.6
4	0	0	3.9	-5.9
5	0	0	4.9	-4.4
7	0	0	3.4	4.2
9	0	0	1.5	-1.8
10	0	0	2.5	-2.9
0	0	1	17.4	-13.5
1	0	1	9.4	7.0
-1	0	1	26.0	-24.1
2	0	1	24.8	-25.2
-2	0	1	21.0	21.0
-3	0	1	17.7	17.9
4	0	1	3.0	-2.5
-4	0	1	7.6	6.4
5	0	1	1.2	-1.5
-5	0	1	3.2	3.3
6	0	1	5.6	-6.4
-6	0	1	10.8	11.7
7	0	1	4.9	-5.1
-7	0	1	2.3	2.4
0	0	2	40.9	-40.7
-1	0	2	19.2	-20.5
2	0	2	6.7	8.3
-2	0	2	7.6	-6.3
3	0	2	1.7	2.1
-3	0	2	2.1	-2.5
4	0	2	3.6	4.0
-4	0	2	8.0	-7.6
5	0	2	1.4	-2.2
-5	0	2	6.2	5.5
6	0	2	3.8	4.6
-6	0	2	1.3	-1.9
-7	0	2	4.7	-4.5
-8	0	2	2.9	2.7
-9	0	2	2.5	2.6
-10	0	2	2.4	2.5
0	0	3	10.0	10.0
1	0	3	3.2	-4.3
-1	0	3	1.2	3.0
-2	0	3	2.2	1.2
3	0	3	2.0	-2.3
-3	0	3	6.4	-7.8
-4	0	3	3.6	4.2
5	0	3	2.3	-2.5
-5	0	3	3.6	4.7
6	0	3	2.0	-2.3
-6	0	3	7.8	-7.7
7	0	3	3.4	3.4
-7	0	3	2.3	-2.4
8	0	3	2.1	-1.9
-8	0	3	2.7	-3.2
-9	0	3	2.5	-2.3
-1	0	4	6.6	5.0
2	0	4	10.9	-11.5
-2	0	4	5.2	6.6
3	0	4	4.6	-5.3
-3	0	4	1.9	-1.9
4	0	4	2.3	2.3
5	0	4	6.9	7.4
-5	0	4	4.3	-4.4
7	0	4	2.5	2.4
-7	0	4	4.6	4.8
8	0	4	3.0	3.3
-8	0	4	2.4	2.8
0	0	5	2.6	-3.3
1	0	5	9.9	10.7
-1	0	5	1.4	2.1
2	0	5	16.6	16.1
-2	0	5	3.4	-4.5
3	0	5	2.3	2.7
4	0	5	1.6	-1.7
-4	0	5	2.3	-2.6
-6	0	5	2.6	2.5
7	0	5	3.8	-4.0
0	0	6	1.5	1.4
1	0	6	9.7	-9.7
-1	0	6	2.7	2.7
-2	0	6	1.4	1.2
-3	0	6	3.1	3.3
4	0	6	5.1	-5.3
-4	0	6	5.7	6.0
5	0	6	2.6	-2.5
-5	0	6	6.2	6.0
-8	0	6	1.6	-1.6
1	0	7	5.4	-5.4
-1	0	7	4.9	-4.6
2	0	7	6.7	-8.6
-2	0	7	5.5	-5.2
3	0	7	2.1	1.8
-3	0	7	3.0	-3.1
-5	0	7	3.2	-3.1
-7	0	7	2.5	2.5
-8	0	7	1.8	1.8
1	0	8	3.9	4.0
-2	0	8	2.4	2.2
3	0	8	1.7	2.1
-3	0	8	3.4	3.3
4	0	8	3.9	4.2
-4	0	8	4.1	-4.1
-5	0	8	5.2	-5.0
-6	0	8	3.4	-3.3
-7	0	8	3.7	-3.2
0	0	9	7.8	2.5
1	0	9	3.7	3.9
-1	0	9	2.0	1.7
2	0	9	2.3	2.2
-2	0	9	2.6	2.5
3	0	9	2.5	-2.5
4	0	9	2.3	-2.1
5	0	9	1.6	-1.6
-5	0	9	4.3	4.1
-6	0	9	1.6	1.8
-3	0	10	2.2	-1.9
-4	0	10	2.1	2.1
-5	0	10	2.3	1.9
0	1	0	24.3	24.1
1	1	0	16.7	-16.2
1	-1	0	44.2	44.0
2	1	0	2.5	3.2
2	-1	0	6.0	-2.9
3	1	0	10.8	10.5
3	-1	0	9.8	8.0
4	1	0	5.3	5.5
4	-1	0	3.3	-5.2
5	1	0	1.6	-2.3
5	-1	0	6.3	-6.8
6	1	0	5.9	5.8
6	-1	0	6.6	-6.4
7	-1	0	3.1	-3.6
8	1	0	1.8	-1.8
0	1	1	23.9	22.1
0	1	-1	9.0	-38.8
1	1	1	15.3	-12.8
-1	1	-1	6.6	-6.8
1	-1	1	15.3	-16.5
-1	1	1	15.2	-15.3
2	1	1	9.4	-9.6
2	1	-1	9.2	10.9
2	-1	1	25.0	-21.6
-2	1	1	15.6	11.6
3	1	-1	12.4	9.1
3	-1	1	18.0	-17.6
-3	1	1	26.4	26.8
4	1	1	3.6	4.1
4	1	-1	3.9	-4.0
-4	1	1	8.4	8.6
5	1	-1	10.5	10.8
6	1	1	3.4	-3.5
6	1	-1	5.2	5.8
6	-1	1	2.7	2.4
7	1	1	2.3	2.6
7	1	-1	1.9	-1.5
7	-1	1	3.5	-4.1
-7	1	1	2.4	3.0
8	-1	1	2.1	-2.2
9	-1	1	1.9	1.7
0	1	2	7.6	7.6
0	1	-2	7.6	-8.4
1	1	2	33.7	29.6
1	-1	2	23.5	-23.3
-1	1	2	15.1	-12.5
2	1	-2	12.6	8.6
2	-1	2	1.9	-2.7
3	1	2	2.6	-2.4
3	1	-2	20.2	-16.5
3	-1	2	3.7	2.9
-3	1	2	12.5	-11.4
4	1	2	6.3	-6.5
4	1	-2	10.6	-11.4
4	-1	2	7.7	8.3
-4	1	2	10.7	-10.7
5	1	-2	6.3	-6.1
5	-1	2	4.0	4.0
6	1	-2	11.2	-11.2
6	-1	2	4.1	4.1
-6	1	2	9.4	9.5
7	-1	2	6.2	6.8
-7	1	2	1.7	1.8
8	1	-2	3.8	3.5
-8	1	2	1.7	1.7
9	1	-2	3.4	3.7
-9	1	2	2.2	2.2
0	1	3	12.6	-11.5
0	1	-3	13.8	15.5
1	1	3	3.7	-1.5
1	1	-3	2.1	4.0
1	-1	3	32.7	29.7
-1	1	3	7.9	7.5
2	1	3	2.8	1.8
2	1	-3	5.8	-4.2
2	-1	3	6.5	6.4
-2	1	3	1.8	1.7
3	1	3	1.5	-1.1
3	1	-3	4.3	-5.0
-3	1	3	1.9	-2.8
4	1	-3	10.4	9.9
4	-1	3	1.6	-2.3
5	1	3	6.0	-6.4
5	1	-3	2.4	-2.6
5	-1	3	3.7	-3.8
-5	1	3	8.6	9.8
6	-1	3	6.6	-6.9
7	1	3	3.1	-3.9
7	1	-3	1.6	-1.6
-7	1	3	3.6	-3.6
8	1	3	2.4	-2.5
8	1	-3	3.2	-3.0
8	-1	3	3.4	3.5
9	1	-3	3.7	-3.6
-9	1	3	2.1	-2.2
0	1	4	7.5	-7.6
0	1	-4	8.3	-7.6
1	1	4	15.6	-16.4
1	1	-4	6.2	6.3
-1	1	4	4.9	-5.8
2	1	4	5.8	-6.3
3	1	-4	5.4	4.2
3	-1	4	10.8	-11.2
4	1	4	5.7	6.6
-4	1	4	3.0	3.2
5	1	4	3.3	3.3
5	1	-4	3.0	3.8
5	-1	4	4.3	5.2
6	1	-4	6.8	6.9
6	-1	4	1.7	1.6
-6	1	4	6.2	-7.7
7	1	4	4.2	4.1
7	1	-4	3.7	3.2
7	-1	4	2.6	-3.0
-8	1	4	1.9	2.1
0	1	5	3.9	4.2
0	1	-5	4.1	-4.3
1	1	5	12.1	12.6
1	-1	5	11.1	-11.0
2	1	5	6.2	6.5
2	-1	5	10.5	9.9
-2	1	5	1.4	-1.6
3	1	5	2.1	1.7
3	1	-5	3.2	-2.7
3	-1	5	5.7	5.7
-3	1	5	2.8	-2.8
4	1	-5	1.6	-1.7
4	-1	5	1.5	-1.6
5	1	5	3.8	4.0
-5	1	5	5.1	-5.5
7	-1	5	2.9	-2.8
8	-1	5	2.7	-2.5
-8	1	5	3.1	-3.0
9	1	-5	2.5	2.1
0	1	6	3.1	2.7
0	1	-6	1.5	2.0
1	-1	6	7.2	-6.5
-1	1	6	11.3	12.0
2	-1	6	7.6	-7.2
-2	1	6	5.3	5.2
3	1	6	5.0	-5.2
3	1	-6	4.8	4.3
3	-1	6	3.7	3.6
-3	1	6	3.1	3.2
4	1	6	4.7	-5.5
4	1	-6	6.8	6.9
4	-1	6	3.1	-3.1
5	1	-6	2.7	-3.0
5	-1	6	2.3	-2.5
-5	1	6	1.7	2.2
6	1	-6	3.4	-3.6
-6	1	6	3.6	3.6
7	1	6	2.4	-2.6
7	1	-6	3.2	-3.3
0	1	-7	4.6	4.3
1	1	7	6.9	-7.3
1	1	-7	3.0	-3.1
1	-1	7	5.9	5.8
-1	1	7	4.0	-4.2
2	1	-7	6.3	-6.9
2	-1	7	4.6	-4.0
-2	1	7	5.9	-6.1
3	1	7	2.4	2.3
3	1	-7	2.9	-2.9
3	-1	7	3.0	-2.8
-3	1	7	2.3	-2.3
4	1	-7	6.3	-6.2
5	1	7	2.3	-2.3
5	1	-7	1.8	-1.6
-5	1	7	3.0	3.0
6	1	-7	3.9	3.6
6	-1	7	2.9	2.9
-6	1	7	2.1	2.0
7	1	-7	2.6	2.3
7	-1	7	2.2	2.5
-7	1	7	3.6	3.5
-8	1	7	2.6	2.5
1	-1	8	3.8	3.3
-1	1	8	5.3	-5.4
2	1	8	1.7	-1.8
2	1	-8	5.1	5.1
2	-1	8	5.1	4.5
3	1	8	3.9	4.0
3	-1	8	2.5	2.4
-3	1	8	1.9	2.1
4	1	-8	3.7	-3.1
4	-1	8	3.4	3.6
-5	1	8	3.3	-1.6
-6	1	8	3.1	-3.3
-7	1	8	3.0	-3.1
-8	1	8	2.1	-1.8
1	1	9	2.6	3.0
2	1	9	2.0	-2.1
2	1	-9	3.6	3.5
-2	1	9	2.3	2.1
3	1	9	2.6	-2.9
4	1	-9	5.1	4.7
4	-1	9	1.7	-1.5
-4	1	9	2.5	-2.7
5	1	-9	3.6	2.7
5	-1	9	2.0	-1.9
0	1	-10	3.1	-2.6
1	1	-10	2.2	-2.0
2	1	-10	3.8	-3.6
-2	1	10	1.8	1.8
1	1	-11	1.9	1.9
4	1	-11	3.7	-3.2
0	2	0	10.8	-11.0
1	-2	0	5.4	6.8
2	2	0	13.7	10.6
2	-2	0	2.8	-4.0
3	2	0	12.6	11.3
3	-2	0	11.3	-10.1
4	2	0	9.1	-8.0
5	-2	0	3.7	-3.6
7	2	0	3.6	-3.1
7	-2	0	2.9	-3.5
0	2	1	6.6	-6.4
1	2	1	13.1	-13.4
1	2	-1	11.6	-7.8
1	-2	1	3.2	-6.3
-1	2	1	7.6	-5.9
2	2	1	1.8	-0.9
2	2	-1	2.0	-1.9
2	-2	1	3.7	-1.1
-2	2	1	19.8	-18.6
3	2	1	8.2	9.1
3	2	-1	17.6	-13.7
3	-2	1	12.5	-12.3
-3	2	1	13.6	13.9
4	2	1	6.9	7.0
4	-2	1	9.3	-9.3
-4	2	1	14.2	12.3
5	2	1	2.5	-2.9
5	2	-1	9.4	9.2
5	-2	1	4.5	-4.9
-5	2	1	4.4	4.1
6	2	1	3.4	3.5
7	-2	1	5.7	6.1
-7	2	1	4.2	-4.0
-8	2	1	1.6	-1.4
9	-2	1	2.3	2.3
10	-2	1	1.9	2.3
0	2	2	24.9	25.6
1	2	2	10.9	10.1
1	2	-2	4.0	6.7
1	-2	2	10.0	11.1
-1	2	2	2.2	-1.8
2	2	2	2.8	-2.0
2	2	-2	9.0	-7.8
2	-2	2	4.5	-4.0
-2	2	2	4.0	4.2
3	2	2	2.6	-3.4
3	2	-2	17.6	-16.8
3	-2	2	6.9	6.8
-3	2	2	5.3	2.5
4	2	2	3.2	4.2
4	2	-2	2.6	-3.4
4	-2	2	8.9	9.3
-4	2	2	10.4	-10.1
5	2	2	4.2	4.6
5	2	-2	9.5	-9.1
5	-2	2	6.0	6.1
-5	2	2	6.4	-6.3
6	2	-2	2.6	-1.8
6	-2	2	1.8	0.9
7	2	2	2.6	3.0
7	2	-2	2.0	1.9
7	-2	2	4.2	4.4
-7	2	2	3.7	3.3
8	2	-2	2.9	2.9
8	-2	2	1.9	1.6
9	-2	2	2.4	-2.5
0	2	3	1.6	-1.4
0	2	-3	5.0	-5.9
1	2	3	7.9	7.4
1	2	-3	3.6	4.1
1	-2	3	16.8	14.2
-1	2	3	6.4	5.4
2	2	3	2.8	-2.7
2	2	-3	2.9	2.9
2	-2	3	15.6	16.2
-2	2	3	18.3	18.8
3	2	3	1.7	-2.2
3	2	-3	17.5	15.7
-3	2	3	3.2	4.0
4	2	3	5.1	-5.7
4	2	-3	6.0	5.7
4	-2	3	3.4	3.6
5	2	3	2.3	-2.1
5	2	-3	1.6	1.1
5	-2	3	2.4	-2.4
6	2	3	3.3	-3.7
6	-2	3	7.8	-8.0
-6	2	3	3.8	4.2
7	2	3	3.2	-3.4
7	2	-3	1.8	-2.0
7	-2	3	6.7	-6.1
8	2	-3	3.1	-2.6
8	-2	3	1.7	1.4
9	2	-3	3.1	-3.1
0	2	4	12.3	-12.1
0	2	-4	10.7	-9.7
1	2	4	5.4	-5.1
1	2	-4	2.7	-2.2
1	-2	4	17.2	-17.6
-1	2	4	3.7	-3.1
2	2	-4	3.8	4.5
2	-2	4	2.5	0.9
-2	2	4	7.3	-7.7
3	2	4	2.5	-2.2
3	2	-4	4.0	4.3
3	-2	4	8.9	-8.3
-3	2	4	5.4	-5.7
4	2	-4	4.9	4.6
4	-2	4	7.1	-7.5
5	2	4	4.0	-4.2
5	2	-4	6.1	6.3
5	-2	4	3.7	4.1
-5	2	4	5.2	5.6
6	2	4	2.0	1.9
6	2	-4	1.8	0.8
6	-2	4	2.9	3.0
7	2	4	2.0	2.0
-8	2	4	4.3	4.5
9	2	-4	2.6	2.8
0	2	5	2.7	2.1
0	2	-5	7.1	6.6
1	2	-5	4.6	4.4
1	-2	5	7.6	-5.0
-1	2	5	4.8	-5.4
2	2	5	4.8	5.3
2	2	-5	6.7	-7.1
2	-2	5	4.0	-4.0
-2	2	5	7.2	-7.9
3	2	5	2.6	2.8
3	2	-5	11.2	-11.7
3	-2	5	5.6	5.5
-3	2	5	4.4	-4.7
4	2	5	5.1	5.4
4	2	-5	4.9	-4.6
4	-2	5	3.0	-3.6
5	2	5	2.0	1.8
5	2	-5	5.9	-5.5
6	2	5	2.2	-2.0
6	-2	5	3.0	3.4
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8	2	-5	2.5	2.0
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0	2	-6	3.1	2.6
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2	-2	6	2.9	-2.9
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3	2	6	2.2	-2.5
3	2	-6	8.0	8.0
3	-2	6	2.8	-3.3
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4	-2	6	3.1	3.5
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5	2	6	4.7	4.4
5	2	-6	3.8	-3.5

H	K	L	|FO|	FC
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1	2	7	1.1	-1.6
1	2	-7	6.1	-6.7
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4	2	7	2.6	-1.0
4	2	-7	1.9	-1.6
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6	2	-7	3.4	2.7
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0	2	8	3.6	4.0
1	2	-8	2.6	2.5
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3	2	-8	1.8	-1.4
3	-2	8	2.8	2.1
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0	2	-10	2.7	-2.2
1	2	-10	4.4	-4.3
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2	-2	10	2.5	2.0
3	2	-10	1.8	-1.4
0	2	-11	2.0	1.6
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3	2	-11	1.9	-1.6
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4	3	1	6.4	-6.1
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4	3	2	8.1	8.6
4	3	-2	1.7	-2.0
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0	3	3	4.4	2.1
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6	3	3	3.3	-3.7
6	-3	3	3.6	-1.4
7	-3	3	4.7	-4.7
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0	3	-4	3.5	-5.6
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2	3	-4	1.8	-2.0
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4	3	4	5.6	-5.0
4	3	-4	5.3	4.5
4	-3	4	8.4	-8.4
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6	3	-4	2.2	2.6
6	-3	4	2.7	2.7
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6	-3	5	2.4	2.6
7	-3	5	2.3	2.0
8	-3	5	1.8	1.5
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1	3	6	2.0	-1.4
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2	3	-7	4.4	4.4
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3	3	-8	2.6	-2.2
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1	3	-9	1.8	1.3
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1	3	-10	3.1	-2.7
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3	-3	10	7.2	1.8
1	3	-11	2.0	2.4
0	4	0	3.4	2.6
1	4	0	7.8	6.8
1	-4	0	2.1	2.2
2	4	0	2.6	2.7
3	4	0	5.6	-4.8
3	-4	0	6.1	6.8
4	-4	0	4.3	4.5
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6	4	0	2.5	-2.1
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9	-4	0	2.2	-2.0
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4	4	2	1.9	-1.6
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7	4	-2	2.1	1.6
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1	4	3	3.7	4.2
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4	4	-4	2.3	2.3
4	-4	4	3.6	3.4
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1	4	-5	3.4	-5.0
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3	-4	5	2.8	2.6
4	4	-5	2.1	-2.1
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6	-4	8	2.8	-2.3
2	4	-9	1.8	1.7
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0	4	-11	2.3	1.4
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6	5	0	2.8	-2.5
7	-5	0	3.4	-3.3
0	5	1	7.0	-7.1
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2	5	1	2.9	-2.6
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3	5	1	2.8	-7.0
3	5	-1	2.3	1.7
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6	-5	1	4.1	-4.0
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1	5	-2	2.3	-1.2
2	5	2	3.0	2.5
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3	5	-2	3.0	-2.8
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4	5	2	1.9	-1.6
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2	5	-3	4.2	-4.5
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7	5	-3	1.9	-1.3
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4	5	-5	2.2	-1.8
5	5	-5	2.0	-1.8
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0	6	-1	2.2	-1.8
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7	-6	1	2.1	-1.7
1	6	2	3.2	2.7
2	6	2	3.3	3.2
2	6	-2	1.6	-1.0
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3	-6	2	3.2	3.2
4	-6	2	3.3	2.9
5	-6	2	2.6	2.3
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3	6	-5	1.7	-1.5
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4	6	-6	2.5	1.8
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6	-6	6	2.6	-1.7
2	-6	7	2.0	-2.1
3	-6	7	2.8	-2.0
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2	-6	8	2.4	2.1
4	6	-8	1.7	-1.2
0	7	0	2.4	-1.9
3	-7	1	1.8	-1.2
4	-7	1	2.5	-1.9
0	7	2	2.6	2.5
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4	-7	2	2.1	1.9
5	-7	2	2.3	1.6
6	-7	2	2.1	1.6
-1	7	4	1.9	-1.8
4	7	-4	1.9	1.3
0	8	-1	2.1	1.4

Chapter 7

Some Aspects of the Bonding in The Three Transition Metal Compounds

TRANS-INFLUENCE

In both the palladium and the iridium compounds there were bonds whose length could be explained in terms of the trans-influence.

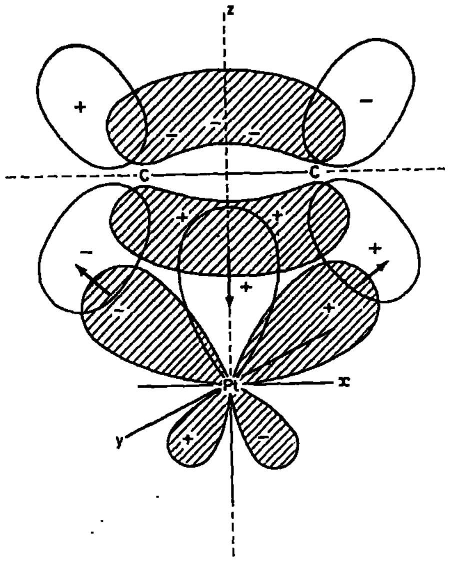
In the palladium compound, the Pd-Cl bond length of 0•13Å is greater than in the unperturbed system of $PdCl_4^{2-}$ due to the large trans-influence of the hydride. As was mentioned before, the same metal-chlorine distance is found in a platinum hydride. This has the direct implication that the magnitude of the trans-influence in the palladium series is very similar to that found in the platinum. This conclusion is in good agreement with both the relative overlap integrals computed for the metal-chlorine bond trans to a hydrogen (McWeeny, Mason and Towl, 1969) and the Pauling electronegativities for platinum and palladium. These values are listed below.

	Pt	Pd	
Covalent Radii	1•31Å	1•31Å	Pauling (1960)
Overlap integrals	0•50	0•51	McWeeney et al (1969)
Electronegativity	2•2	2•2	Pauling (1960)

From these values, it is only reasonable that the same magnitude of the influence would be observed with both metals.

This, a sigma complex, agrees with most trans influence theories, which have been described earlier. Yet, an examination of other compounds where one of the ligands has the ability to enter into back-bonding with the metal, such as the carbonyl in the iridium compound, indicates that the ligands fail to exhibit the same effect suggested by the kinetic series. These cases require a reexamination of the trans-influence.

Most of the theories which have been proposed have examined only one ligand, sigma bonding ones in general. It is necessary to look at the amount of back-bonding which can take place between the metal and either of the ligands in question. For example in the compound $C_2H_4PtNH_3Cl_2$, where the trans influence of the ethylene group is not observed, the competition for the s±d orbitals described by Syrkin, must be evaluated. In this case the trans influencing ligand, (C_2H_4), is able to enter into strong back-bonding with the platinum, thus the competition for the stronger sigma bonding orbitals will be lessened. This is shown in the drawing below.



In the case of the iridium compound, there is a carbonyl ligand trans to a hydrogen. From the lengths of the Ir-C and C-O bonds, it is apparent that strong back-bonding takes place. Thus there is little competition for the stronger sigma bonding orbitals. Consequently, in compounds where back-bonding between one of the ligands and the metal atom is possible, the ligand in the trans position is able to form stronger bonds, if possible, utilizing the s±d orbitals. Because of this, the trans-influence of the hydride is small.

In cases where the metal atom has few orbitals which are free to enter into back-bonding, the trans-influence will be observed, but will vary with the ability of the metal atom to enter into back-donation. Should the metal atom orbitals have a smaller s character, for example in octahedral complexes, a smaller amount of partial rehybridisation will take place, as in the case of Pt(IV) and Ir(III) complexes. Thus the trans-influence will vary greatly depending upon the amount of rehybridisation taking place.

One of the cases which a molecular orbital approach (McWeeny et al, 1969) was unable to explain, is the stronger trans-influence of the trialkylphosphines in relation to the triarylphosphines. The bonding of the phosphorus to the metal has been discussed previously, where it was apparent that there is some degree of back-bonding. This may be small, as in the case where there are a number of ligands which are able to enter into this type of bonding, but can be large when there are fewer ligands which are able to enter back-donation, or where when there are a large number of orbitals available for back-bonding on the metal. In the former case, the amount of back-donation would be about the same for both the triaryl and the trialkylphosphines. For the latter case, it would be expected that the triarylphosphines would have a greater amount of back-bonding, and thus would show a smaller trans-influence. This is confirmed by the relative ν(Pt-Cl) with the chlorine trans to the phosphine in cis-$(R_3P)_2PtCl_2$, where R is Et, $Pr^{\underline{n}}$, and Ph. The difference between the alkyls and the phenyl phosphines is shown in Table 2d, and amounts to 25 cm^{-1}, a 9% change.

Of the two transition metal hydrides studied, the palladium compound is an example of an almost pure σ-bonding between the metal and the two ligands, hydrogen and chlorine. In this case, a large trans-influence is observed as would be expected.

The iridium compound, on the other hand, is a more complex case. The carbonyl is trans to one hydrogen, but a large trans-influence of this hydride is not observed. This is an example of a pure σ-bonding ligand trans to a π-bonding one. The two phosphorus-metal distances had the same value (2·360Å), thus confirming that hydrogen and germanium have the same trans-influence. A value was found with two PPh_3 in the apical positions of a shorter trigonal bypyramidal complex (2·39Å). The order is the same as

$$Ge \sim H > PR_3$$

Within this molecule, there are four ligands which appear to have some degree of back-bonding with the metal. In this case, the phosphine groups form weaker acceptor bonds, since the carbonyl appears to have a very strong one. The amount of back-bonding between the metal and the phosphines and the germyl groups is enough to distort the angles in the ligands, but not enough to change the observation of the trans influence.

GROUP IVB-METAL BONDS

Group IVB elements bond to transition metals, and a number of crystal structures have been reported. The group IVB atoms have been shown not to change the coordination of the transition metal, as was observed in the iridium and nickel complexes. Thus, the discussion in compounds of this type must centre upon the type of bonding taking place. There are two basic types of compounds which have been studied: R_3EM and R_2EM_2, where E is the group IVB metal, and M is the transition metal. Some examples of these compounds are shown in Table 7a.

The short Ni-Ge and Ir-Ge bond lengths of 2·248Å and 2·484Å respectively, indicate that there is a strong possibility of $(d_\pi - d_\pi)$ bonding. The Ge-C bond lengths are close to the values found in $GeMe_4$, whereas the Ge-Cl bonds are longer than those in $HGeCl_3$, but are in better agreement with the sum of the covalent radii. From this observation, it can be postulated that the germanium prefers $(d_\pi - d_\pi)$

TABLE 7a

Some Compounds containing Group IVB-Transition Metal Bonds

Compound	M-E	Contraction	X-E-X[a]	M-E-X
$Cl_3Si\text{-}Co(CO)_4$	2·254(3)Å	0·015Å	105°	113°
$Ph_3Ge\text{-}Mn(CO)_5$	2·54(2)	0·05	-	-
	2·60	0·01	-	-
$Cl_2Ge[Fe(CO)_2Cp]_2$	2·36(1)	0·10	96	128
$Cl_3Ge\text{-}Ni(Ph_3P)Cp$	2·248(1)	0·22	99	117
$Me_3Ge\text{-}Ir(CO)(H)_2(Ph_3P)_2$	2·484(2)	0·10	104	116
$Me_3Sn\text{-}Mn(CO)_5$	2·674(3)	0·10	107	112
$Ph_3Sn\text{-}Mn(CO)_5$	2·674(4)	0·10	106	113
$Ph_3Sn\text{-}Mn(CO)_4(Ph_3P)$	2·627(1)	0·14	105	115
$Ph_2Sn[Mn(CO)_5]_2$	2·70(1)	0·07	100	117
$Ph_3Sn\text{-}Fe(CO)_2Cp$	2·536(3)	0·10	105	113
$Cl_2Sn[Fe(CO)_2Cp]_2$	2·49	0·15	94	128
$Sn[Fe(CO)_4]_4$	2·54(1)	0·10	-	69,133
$Cl_3Sn\text{-}Ir(COD)_2$	2·642(2)	0·12	-	113,124

[a] X is Cl, C.

(Young, 1968)

bonding with the metal to $(d_\pi - p_\pi)$ bonding with the chlorine atoms. In $R_3SnMn(CO)_5$ there is little difference in the Mn-Sn bond length between the methyl and phenyl derivatives. No definite conclusions can be reached about the relative strengths of the group IVB-metal bonds until a complete series of compounds consisting of R_3EM, where R = Cl,Ph,Me, and E = Si,Ge,Sn and Pb has been investigated.

The C-Ge-C angles in the iridium compound and the Cl-Ge-Cl angles in the nickel compound are significantly less than the tetrahedral value. Based upon the analysis of π-bonding (Gillespie and Nyholm, 1957), it can be deduced that there is some multiple bonding between the germanium and the transition metal atom. In the $GeCl_3$ group, these angular distortions become more apparent. From Table 7a, it can be observed that the Cl-E-Cl angle becomes smaller the metal progresses from Si to Sn. This may be due to the stronger back-donation from the transition metal.

A comparison of the apparent contractions in the metal-germanium bonds for the nickel (0•22Å) and the iridium (0•10Å) compounds with those in Table 7a indicates strong π-bonding, in fact the nickel compound shows the largest in the table. To rely on these values as a comparison of the amount of $(d_\pi - d_\pi)$ bonding between metals can be misleading. As an example, the Co-Si bond is contracted by a value of 0•015Å based upon the authors criteria (Young, 1968) yet a different choice of metallic radii derived from metal-metal distances reported in International Tables (1962) gives a contraction as large as 0·18Å. A number of structures of manganese are also listed, yet the contractions can be 0·04Å less if a different radius is chosen. In all cases, there is observed a shortening of the M-E bonds, and a contraction of the X-E-X angles, in agreement with the premise that there is some (d_π-d_π) bonding between the group IVB metal and the transition metal, but a comparison may not be unambiguous.

Only one Ni-Ni distance is listed, thus only one nickel-germanium bond length can be calculated. On this basis, there appears to be a contraction in the bond. The same is true for the Ir-Ge bond.

The distortion observed in the $GeCl_3$ ligand is similar to that found in the $SnCl_3$ moiety when bonded to iron (Corey and Head, 1969). A satisfactory explanation for this effect cannot be given, but it may be due to stronger (p_π-d_π) bonding between Cl(1) and the germanium. This may be related to the observation that this atom lies close to the plane formed by nickel, germanium and phosphorus.

APPENDIX I

Computer Programmes

Calculations were performed primarily on the IBM 360/67, the Northumbrian ~~Northern~~ Universities Multiple Access Computer. The IBM 1130, and the Elliott 803, located at the University of Durham, were used for minor calculations. I would like to thank the staff at both installations for assistance.

The series of programmes was written by F.R. Ahmed, S.R. Hall, M.E. Pippy and C.P. Saunderson at the Divisions of Pure Physics and Pure Chemistry of the National Research Council of Canada (Ottawa), and modified by H.P. Stadler at Newcastle University. I am indebted to them for making these programmes available to me.

I am grateful to Mr. J. Twiss for his programmes for Lorentz and polarisation corrections, as well as the programme for the printing of the structure factors.

A number of programmes were written in collaboration with Mr. Twiss to handle sundry needs.

Symbolic Addition Programmes

Two sets of programmes were used for the symbolic addition procedure. The first was a sigma two listing programme written by Dr. J. Daly, and was employed in the first attempt using this method.

The second set was written by S.R. Hall, and revised by F.R. Ahmed. This set of programmes of five sections: calculations of the values of B and K, computing and sorting the normalised structure factors, listing the sigma two relationships, deriving signs and symbols for the stronger E's, and giving a final set of signed normalised structure factors. The fourth stage allows the choice of either automatic or manual selection of origin determining planes. The selection of symbols is automatic, but the probability level at which they are introduced can be controlled.

APPENDIX II

Derivation of the standard deviation for a reflection when the background counting time is unequal to the peak scanning time.

The Net count, N, is defined as

$$N = P - B \qquad \text{II.1}$$

where

$$B = r(b_1 + b_2) \qquad \text{II.2}$$

and

$$r = \frac{t_P}{t_{b_1} + t_{b_2}}$$

if $t_{b_1} = t_{b_2}$

then

$$N = P - r(b_1 + b_2)$$

The e.s.d. is

$$\sigma_N^2 = \left(\frac{\partial N}{\partial P}\right)^2 \sigma_P^2 + \left(\frac{\partial N}{\partial b_1}\right)^2 \sigma_{b_1}^2 + \left(\frac{\partial N}{\partial b_2}\right)^2 \sigma_{b_2}^2 \qquad \text{II.3}$$

$$= \sigma_P^2 + r^2 \sigma_{b_1}^2 + r^2 \sigma_{b_2}^2$$

$$= \sigma_P^2 + r^2 (\sigma_{b_1}^2 + \sigma_{b_2}^2)$$

by counting statistics

$$\sigma_P^2 = P$$

$$\therefore \quad \sigma_N^2 = P + r^2(b_1 + b_2)$$

substituting the expression for B

$$\sigma_N^2 = P + rB \qquad \text{II.4}$$

$$\sigma_N = \sqrt{P + rB} \qquad \text{II.5}$$

for n measurements

$$\overline{P} = \frac{\Sigma P_i}{n}$$

and

$$\overline{B} = \frac{\Sigma B_i}{n}$$

$$\overline{N} = \overline{P} - \overline{B}$$

for n observations

$$\sigma_{\overline{N}}^2 = \sigma_{\overline{P}}^2 + r^2 \sigma_{\overline{b}}^2$$

but

$$\overline{P} = \frac{1}{n}(P_1 + P_2 + \ldots\ldots P_n)$$

$$\sigma_{\overline{P}}^2 = \left(\frac{1}{n}\right)^2 \sigma_{P_1}^2 + \left(\frac{1}{n}\right)^2 \sigma_{P_2}^2 + \left(\frac{1}{n}\right)^2 \sigma_{P_3}^2 + \ldots \left(\frac{1}{n}\right)^2 \sigma_{P_n}^2 \qquad \text{II.6}$$

$$= \left(\frac{1}{n}\right)^2 n\,\overline{P}$$

$$= \left(\frac{1}{n}\right)\overline{P}$$

the same holds true for σ_b^2

$$\therefore \qquad \sigma_N^2 = \frac{1}{n} (\overline{P} + r^2\overline{b})$$

$$\sigma_N = \sqrt{\frac{1}{n} (\overline{P} + r\,\overline{B})} \qquad \text{II.7}$$

where P is the total peak counts for a reflection b_1 and b_2 are the counts for each background and $b = b_1 + b_2$

t_P is the total time for the scan

t_{b_1} and t_{b_2} are the times for each background

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