Chemical and mass spectrometric studies on organogermanes

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CHEMICAL and MASS SPECTROMETRIC STUDIES on ORGANOGERMANES

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CHEMICAL AND MASS SPECTROMETRIC STUDIES ON ORGANOGERMANES

by

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A Thesis in candidature for the Degree of Doctor of Philosophy
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for Patricia

ὁ ἀνεξεταστος βιος οὐ βιωτος ἀνθρωπῳ

Plato

The work described was carried out in the University of Durham between September 1964 and June 1967. It has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

A portion of this work has been the subject of two publications with F. Glockling.

"Isopropylgermanes", J. Chem. Soc., 1966, (A), 623.

"Mass and Abundance Data for Polyisotopic Elements", J. Chem. Soc., 1967, (A), 40.

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A.C., Durham,
June 1967.

CONTENTS

Page

Germanium Halides and Grignard Reagents

1.4. Experimental

1.4.1 Germanium (IV) iodide and isopropyl magnesium bromide

1.4.2 Germanium (IV) chloride and isopropylmagnesium chloride

PART 2 ORGANOGERMANIUM-TRANSITION METAL COMPLEXES

Introduction: Metal-metal bonds

2.1 Detection of metal-metal interaction

2.2. Compounds containing metal-metal bonds

Organogermanium-transition metal complexes

2.5 Experimental

2.5.2 Reactions of the complexes

Reactions of the tungsten mercury compound, $\pi C_5H_5(CO)_3WHgCl$

Reactions of mercuric chloride and platinum-germanium complexes

SUMMARY

The work described, which is concerned with various aspects of organogermanium chemistry, is presented in four parts.

Part 1. Germanium Halides and Grignard Reagents.

Grignard reagents provide one of the most versatile and widely used methods of forming germanium-carbon bonds, but in individual cases complications occur. The reactions between germanium tetrachloride and isopropylmagnesium chloride, and germanium tetraiodide and isopropylmagnesium bromide were examined with the object of obtaining a more detailed picture of the Grignard reaction for this sterically hindered case. Typically, an excess of the Grignard reagent gave some 25 volatile products, many of which were identified. The main features of the reaction are: (i) stepwise alkylation, giving di-, tri-, and tetra-substituted products

$$GeCl_4 + Pr^{i}MgCl \longrightarrow Pr^{i}_{2}GeCl_2 + Pr^{i}_{3}GeCl + Pr^{i}_{4}Ge;$$

(ii) isomerisation of isopropyl groups during the course of the reaction, leading to $Pr^{i}_{3}GePr^{n}$;

(iii) formation of germanium hydrides, probably via germyl Grignard reagents

$$Pr^{i}_{3}GeCl \longrightarrow Pr^{i}_{3}GeMgCl \xrightarrow{H_2O} Pr^{i}_{3}GeH;$$

(iv) formation of di- and oligo-germanes in small amount, possibly by a coupling reaction

$$Pr^{i}_{3}GeMgCl + Pr^{i}_{3}GeCl \longrightarrow Pr^{i}_{6}Ge_2 \quad \text{etc; and}$$

(v) the production, on hydrolysis of polymeric material containing Ge-O and Ge-H bonds.

Reaction mechanism requiring a dimeric form for the Grignard reagent are suggested, and infrared spectra of some isopropyl and n-propyl germanes are described.

Part 2. Organogermanium - Transition Metal Complexes.

A number of compounds have been described in which germanium is bonded to a transition metal, and some of these particularly those containing germanium bonded to platinum, have some unusual reactions. The present study examines the formation, stability and reactivity of representative compounds containing Ge-Mo and Ge-W bonds.

$$R_3GeX + \pi\text{-}C_5H_5(CO)_3MNa \longrightarrow \pi C_5H_5(CO)_3MGeR_3$$

$$M = Mo, W. \quad R = Me, Et, Pr^n$$

All these complexes are stable to water but undergo aerial oxidation as solids and in solution: all are thermally stable up to 200° and sublime readily in vacuo. The proton magnetic resonance spectra of the ethyl complexes indicate an effective electronegativity close to that of hydrogen for the germanium atom. Displacement of one carbonyl group occurs with "π-acid" reagents, Et_2PH reacts quantitatively, Me_3P and C_5H_5N incompletely, and Ph_3P gives an equilibrium from which the eight-coordinate molybdenum complex $\pi C_5H_5(CO)_3(PPh_3)MoGeR_3$ may be isolated. HCl, $C_2H_4Br_2$, and I_2 all cleave the metal-metal bond, and iodine reacts further, displacing a carbonyl group to give $\pi C_5H_5(CO)_2MI_3$. $MgBr_2$ and the tungsten complexes yield $\pi C_5H_5(CO)_3WMgBr.THF$ which, in benzene solution, probably contains a three coordinate magnesium atom. $HgCl_2$ gives $\pi C_5H_5(CO)_3WHgCl$, which may be used to establish W-M bonds by cleavage of further M-Ge units. This reaction is extended to other systems, including those involving Pt-Ge bonds, which yield $[(R_3P)_2Pt(GeR'_3)]_2$.

Part 3. Mass Spectra of Polyisotopic Molecules.

The fragmentation behaviour of polyisotopic molecules from the work in parts 1 and 2 under 70ν electron impact is described and discussed. Organo mono-, di-, tri-, and tetra-germanes give small parent ions which decompose to yield predominantly electron-pair bonded ions. The molybdenum- and tungsten-germanium compounds and their phosphine derivatives show much more complex breakdown patterns, involving considerable intraionic rearrangements, and the ease of rupture of the M-Ge bond is markedly dependent on the ligands surrounding it. In all cases, most of the ion current is carried by metal-containing species and those compounds which contained a metal-metal bond, other than the phosphine complexes, show intense ions containing these bonds intact. Ions are identified by high-resolution mass measurement and comparison of experimental and calculated isotope abundance patterns.

Part 4. Computational Techniques.

The characteristic isotope patterns produced in the mass spectra of molecules containing a number of polyisotopic elements cannot be obtained by the straightforward arithmetic involved in dealing with the mass spectra of organic compounds. Interpretation of the mass spectra of polyisotopic molecules is, however, greatly facilitated if precise masses and abundance values for the peaks in these patterns are readily available. Three computer programs are presented which produce mass and abundance data for both high and low resolution applications covering most requirements in the field of the mass spectrometry of organometallics. Precise data may be obtained for aggregates of any four elements (a,b,c,d) within the composition range $a_{1-10}\ b_{0-10}\ c_{0-10}\ d_{0-10}$ and low resolution data for a single element without limit to the number of atoms. Correction routines for the heavy isotopes of C,H,N, and O may be applied. Three further programs use information from the previous procedures to help in fitting chemical formula to measured masses, and one of these provides possible structural formulae directly from experimental masses.

PART 1

GERMANIUM HALIDES & GRIGNARD REAGENTS

THE numerous methods of establishing germanium-carbon bonds cover the whole range of techniques of synthetic organometallic chemistry. An understanding of the mechanisms of these reactions is of fundamental importance, yet in many cases these mechanisms are wholly mysterious: few preparations have been examined in detail; minor products which can be of considerable theoretical interest often completely escape attention. Even the exact nature of the initial reactants is sometimes in doubt, especially when these are generated and used in situ. Grignard reagents are perhaps the most important organometallic synthetic intermediates encountered in general chemical practice, but despite their familiarity, their reactions form prime examples of those whose detailed workings are almost entirely unknown. In the particular instance of their use with germanium halides yields of as low as 5% of the desired material have been obtained, with scarcely any comment. The deserved popularity of Grignard reagents, however, is apparent only in comparison with other available methods and it is here appropriate to review briefly the major synthetic routes applied to the formation of germanium-carbon bonds.

1.1. PRIMARY METHODS

Synthesis or organogermanes from unsubstituted germanium halides.

1.1.1. Preparation using organo- zinc, cadmium, and mercury compounds.

The action of diethylzinc on germanium tetrachloride was used by Winkler[8] in 1887 to prepare the first synthetic germanium compound, tetraethylgermane, in confirmation of Mendeleeff's predictions

$$GeCl_4 + 2R_2Zn \longrightarrow R_4Ge + 2ZnCl_2$$

Nowadays the inconvenience of making the extremely air-sensitive organozinc compound is usually sufficient to offset any advantages of a cleaner and less complex reaction than the Grignard synthesis. This method can be of value when small quantities of pure tetraorganogermanes are required and tetramethylgermane has been prepared[9] in quantitative yield in this way. A more useful compromise which has been employed successfully for all three tetratolylgermanes[10] is the addition of zinc chloride to the corresponding Grignard reagent, followed by germanium tetrachloride, the organozinc compound being used without isolation. In the case of the o-tolyl group, the Grignard reagent will not substitute more than three chlorines to any extent.[11]

The organo derivatives of cadmium and mercury are less reactive. No direct synthesis from a germanium halide using an organocadmium compound has been reported, but diethylcadmium reacts at 180° with triethylgermane to give bis(triethylgermyl)cadmium[12]

$$(C_2H_5)_2Cd + 2Et_3GeH \longrightarrow (Et_3Ge)_2Cd + 2C_2H_6$$

The mercury analogues of this compound, $(Me_3Si)_2Hg$, $(Me_3Ge)_2Hg$, bistrimethyl-silyl and germyl mercury, prepared from the organometallic halides and sodium amalgam have proved most useful synthetic intermediates in the production of germanium-transition metal bonds.[13]

Unsubstituted dialkyl- and diaryl-mercurys are only sufficiently reactive to effect monosubstitution of germanium tetrachloride

$$(CH_2{=}CH)_2Hg + GeCl_4 \xrightarrow{80^{\circ}} CH_2{=}CHGeCl_3 + CH_2{=}CHHgCl \quad [14]$$

$$Ph_2Hg + GeCl_4 \xrightarrow{140^{\circ}} PhGeCl_3 + PhHgCl \quad [15]$$

and only in moderate yields. A mixture of products is given with the diiodide

$Ar_2Hg + GeI_2 \longrightarrow ArGeI_3$, Ar_2GeI_2 (major product, 40-70%), Ar_3GeI. The halogen of $(m\text{-tolyl})_3GeI$ is not substituted by $(m\text{-tolyl})_2Hg$.[16] Functionally substituted dialkyl mercurys are, however, much more reactive towards germanium halides. They have been used in the preparation of unsymmetrical tetraorganogermanes[17,18] cleanly and in good yield. In these cases, both R-Hg units react

$$Bu^n_3GeI + (Pr^nOOCCH_2)_2Hg \longrightarrow Bu^n_3GeCH_2COOPr^n + HgI_2$$

The high toxicity of organomercury compounds is an obvious drawback to their routine use.

1.1.2. Organoaluminium Syntheses.

The alkylation of a number of metal halides by organoaluminium compounds has been studied at some length.[19] These reactions are often complicated; the equilibria set up with tin and silicon halides may be displaced by the addition of an alkali metal halide resulting in the precipitation of the stable complex salt $MAlX_4$. Descriptions of reactions of trimethyl-, triethyl-, triisobutyl- aluminium, and ethyl aluminium sesquibromide, $Et_3Al_2Br_3$, on germanium tetrachloride, sometimes with the addition of sodium chloride, report yields of up to 80%.[20,21] The reactions have been carried out in donor and hydrocarbon solvents, and without solvent; 78% of tetraethylgermane being isolated on heating Et_3Al and $GeCl_4$ together for six hours at 120-130°. Germanium tetrachloride, triethylaluminium and sodium chloride in refluxing hexane are reported[22] as giving 90% of tetraethylgermane according to the equation

$$3GeCl_4 + AEt_3Al + 4NaCl \longrightarrow 3Et_4Ge + 4NaAlCl_4$$

It is also claimed that ethylchlorogermanes may be prepared in this manner.

A recent and more detailed study[23] indicates that several equilibria are set up and that this class of reactions shows similar complications to the Grignard and organolithium syntheses. It was found that the rate of monoalkylation of germanium tetrachloride is slow compared to subsequent alkylation stages and consequently intermediate alkylchlorogermanes normally cannot be isolated, and that addition of sodium chloride to the Me_3Al-$GeCl_4$ system increases the rate of formation but not the yield of Me_4Ge. Ethereal solvents lead to undesirable complications, notably the production of solvent-cleavage materials and a reduction in yield of tetraorganogermane. In the case of methyl aluminium sesquichloride, refluxing with germanium tetrachloride in ether or diethyleneglycol dimethyl ether (diglyme) have only 10% of mixed alkylchlorogermanes. Addition of sodium chloride gave 65% of tetramethylgermane. This action of donor solvents contrasts with the case of tin tetrachloride and aluminium trialkyl reactions where their presence proved advantageous. In all cases with $GeCl_4$, di- and poly- germanes are produced the proportion increasing with the chain length of the aluminium alkyl. Reactive intermediates, of a type similar to the more firmly established germyl Grignards, containing Ge-Al bonds, are postulated,

$$R_3GeCl + R_3Al \longrightarrow R_3Ge\cdot AlR_2 \xrightarrow{R_3GeCl} R_6Ge_2 + \tfrac{1}{2}(R_2AlCl)_2 .$$

Increased temperatures lead to reduction of Ge-Cl bonds during the reaction with higher alkyls by intermediates formed by thermal decomposition

$$2Bu^{i}_3Al \longrightarrow (Bu^{i}_2AlH)_2 + 2C_4H_8$$

Germanium diiodide and trimethylaluminium yield a mixture of non-cyclic polymers containing $Me_{12}Ge_5$, $Me_{14}Ge_6$, and $Me_{16}Ge_7$, whereas triphenyl aluminium etherate and germanium diiodide have been described as giving phenyl-germanium polymers containing residual halogen.

A number of alkyl aluminiums are now available commercially and, despite its complications, the method is perhaps to be preferred for those cases in which the corresponding Grignard reaction gives poor yields or when the Grignard reagent itself is only difficultly accessible.

1.1.3. Syntheses using organo -lithium, -sodium, and -potassium compounds

Reactions of germanium tetrahalides with organo alkali metal compounds suffer from the drawbacks of greater difficulty of preparation of the starting material than the corresponding Grignard and the lower yields of the symmetrical tetra-organogermanes produced.[24] Detailed studies are lacking but, in the reaction of ethyl lithium with germanium tetrachloride,[25] side reactions predominate, much polymeric material being formed. Discounting aerial oxidation and reaction with solvent, several processes including halogen-metal exchange, and reduction to germanium (II), could take place.

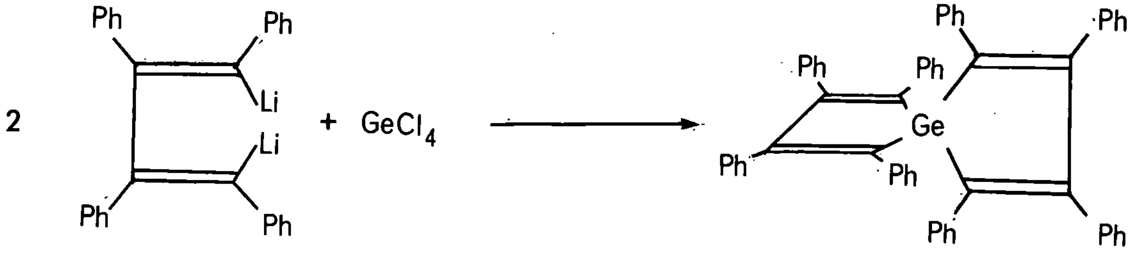
$$GeCl_4 \xrightarrow{RLi} R_3GeCl \xrightarrow{RLi} R_3GeLi \xrightarrow{R_nGeCl_{4-n}} R_3Ge{\cdot}GeR_nCl_{3-n} \longrightarrow \text{etc.}$$

$$GeCl_4 \xrightarrow{RLi} GeCl_2 \xrightarrow{RLi} \text{polymer}$$

One exception to this behaviour is phenyl lithium, 90% yields of tetraphenylgermane are reported from phenyl lithium and germanium tetrachloride. The perfluoro analogue is not quite so satisfactory[26,27]

$$4C_6F_5Li + GeCl_4 \xrightarrow{-65^o} (C_6F_5)_4Ge + (C_6F_5)_3GeCl$$

A single example of tetrasubstitution by an ethynyl lithium is reported, the preparation of $(C_6H_5C{\equiv}C)_4Ge$,[28] but a number of unsymmetrical olefinic and acetylenic germanes have been made from di- and tri- alkylhalogermanes and the corresponding organolithium.[29 - 32] Several interesting spirogermanes have been prepared using dilithio reagents, including



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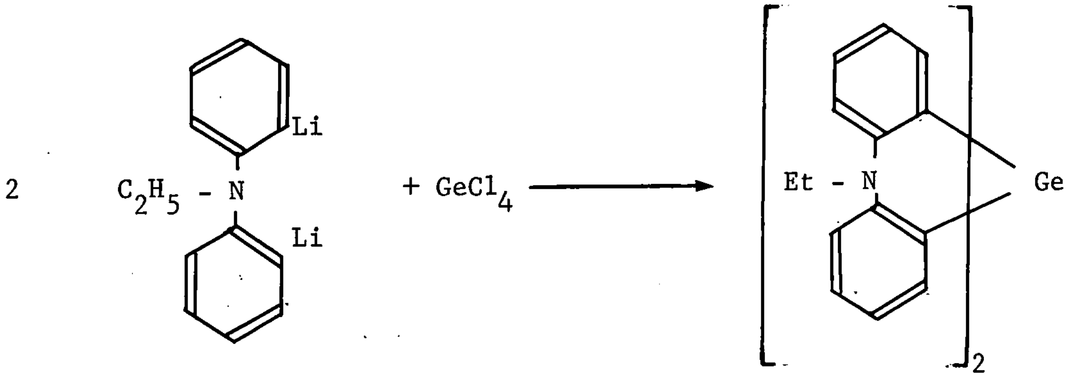

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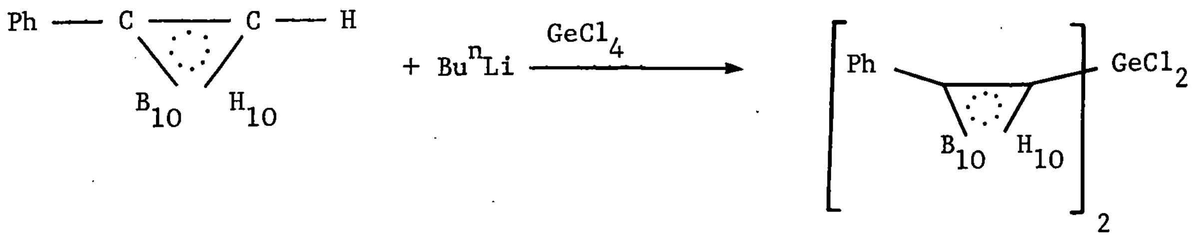
and a carborane compound via the lithium derivative[35]



The major use of organo lithium compounds is in the preparation of unsymmetrical organogermanes, especially in cases where substitution of a halogen is difficult. Arylation of the halides $(C_6H_{11})_3GeBr$, and (1-napthyl)$_3$GeBr by phenyl lithium and 1-napthyl lithium respectively occurs, when the reagent is used in excess, to give $(C_6H_{11})_3GePh$, (75%)[36]

and (1-napthyl)$_4$Ge (38%). No further substitution of these halides can be achieved using the corresponding Grignard reagents. Even isopropyl lithium, however, fails to give tricyclohexyl isopropylgermane.[37] In one reaction at least lithio derivatives are more selective than Grignard reagents, trimethylchlorogermane being produced from dimethyldichlorogermane in high purity[38]

$$Me_2GeCl_2 + CH_3Li \longrightarrow Me_3GeCl + LiCl$$

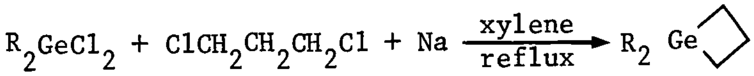
The corresponding Grignard reaction yield is only 12%.

No reactions are reported in which a sodium or potassium derivative has been prepared for use prior to reaction with an unsubstituted germanium halide, but a number of organo- sodium and potassium compounds with trialkylhalogermanes are useful e.g. the preparation of the germyl ferrocenes $[\pi\text{-}C_5H_4GePh_3]_2Fe$ and $\pi\text{-}C_5H_5Fe(\pi\text{-}C_5H_4GePh_3)$[39] and of acetylenic germanes.[40]

The closely allied Wurtz-Fittig reactions, although used early in the development of organogermanium chemistry have not achieved any great importance as primary reactions. Both tetraphenyl- and tetra p-tolyl germane were prepared by this method in 1927[41]

$$C_6H_5Br + GeCl_4 + Na \xrightarrow{Et_2O} (C_6H_5)_4Ge + NaCl$$

Preparation of spirogermanes is a more useful application of the Wurtz reaction, especially for four-membered rings, where diGrignard syntheses fail.[42]



The method is, however, most often applied to the formation of digermanes (see p.61) where good yields and straightforward reactions are reported. Complications and poor yields with germanium tetrahalides are almost certainly due, at least in part, to metal-metal bond formation of this type, eg.

$$GeCl_4 + PhCH{=}CHBr + Na \longrightarrow (PhCH{=}CH)_4Ge\ (17\%) + (PhCH{=}CH)_6Ge_2\ (5\%)$$ [43]

1.1.4. Direct Synthesis

The preparation of organohalogermanes from alkyl halides and germanium metal containing a small percentage of copper or, with a higher temperature, silver, parallels the commercially important method of producing organohalosilanes.

$$4RCl + Ge \xrightarrow[Ag/450^o]{Cu/300^o-400^o} R_nGeCl_{4-n} \quad (n = 0 - 4)$$

Germanium and methyl chloride react at 460° to give predominantly Me_2GeCl_2 and with copper present the reaction temperature may be lowered to 340°. Dimethyldichlorogermane is produced at this temperature, under optimum conditions in 56% yield, with some methyltrichlorogermane.[44] The proportion of this latter component increases with temperature (up to 550°) and amount of copper present. Ethyl chloride and methyl bromide react in a similar manner at 320° and 340° with copper present; chlorobenzene requires a higher temperature and a silver catalyst, diphenyldichlorogermane being the major product. A more detailed investigation[45] of the reaction with n-propyl chloride found that no isomerisation occurred at the temperatures involved (310°-330°), although it might be expected if free alkyl radicals were present. No isopropyl compounds were detected, but in contrast to the other preparations, the predominant product was the trihaloorganogermane.

The first unsaturated organogermanes - allytrichlorogermane and 2-methallyltrichlorogermane, were produced by direct synthesis.[46]

$$CH_2{=}CHCH_2Cl + Ge/Cu \xrightarrow{300^{o}} CH_2{=}CHCH_2GeCl_3$$

Methylene chloride and a germanium - copper mixture give a much more complex mixture of products[47]

$$CH_2Cl_2 + Ge/Cu \xrightarrow{370^\circ - 390^\circ} CH_3GeCl_3\ (27\%) + CH_2(GeCl_3)_2\ (28\%) +$$
$$\text{cyclo }(CH_2GeCl_2)_3\ \ 18\%$$

The method is suitable for the more simple aryl and alkyl halogermanes but is best applied on a large scale. It would undoubtedly be the industrial route to these compounds if they were ever required in quantity.

Closely related reactions include the uncatalyzed combination of alkyl halides with germanium dihalides to give alkyltrihalogermanes in good yield as typified by

$$MeI + GeI_2 \xrightarrow{\text{sealed tube}} MeGeI_3 \quad \cdots\cdots 48$$

and that of $GeCl_4$ or $GeBr_4$ with iodobenzene in the presence of copper catalyst to give phenyltri-iodogermane in 80% yield.[49] Caesium chloride and germanium dichloride form caesium trichlorogermanate which can react with organic halides to give organotrihalogermanes,[50]

$$GeCl_2 + CsCl \longrightarrow CsGeCl_3 \xrightarrow{EtI} EtGeCl_3$$

but the synthesis has not been developed.

1.1.5. The Grignard Reaction

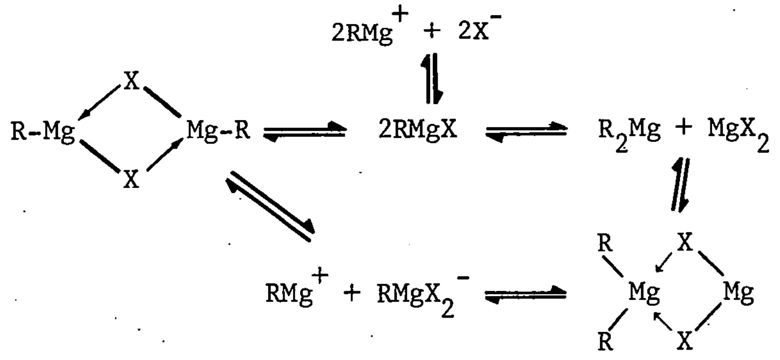
The earliest syntheses of organogermanes using this method were reported in 1925 when tetra-ethyl-, tetra-n-propyl-, tetraisoamyl-, and tetraphenylgermane were prepared.[41,51] Since that time the reaction has been increasingly and extensively used in organogermanium chemistry.

$$GeX_4 + 4RMgX \longrightarrow GeR_4 + 4MgX_2$$

$$R_nGeCl_{4-n} + (4-n)R'MgX \longrightarrow R_nGeR'_{4-n} + (4-n)MgX_2$$

The reagent is usually employed in excess (50-150%), the germanium halide often being added in benzene or toluene solution (the primary purpose of which is intended to be the raising of the boiling point of the reaction mixture, but see below), to the ethereal solution of the Grignard. The initial reaction is markedly exothermic and after this has subsided, reflux is often maintained for periods of up to 24 hours to ensure complete reaction. Work-up of tetraorganogermane preparations presents few difficulties as the unsubstituted organogermanes are stable towards air, dilute acids and alkalis, and hydrolysis of the mixture followed by ether extraction is usually convenient and efficient. Choice of the correct ether as solvent can be important from a preparative standpoint, especially when the major product has a boiling point close to a particular ether as has tetramethylgermane (to diethyl ether). It is usual to employ di-n-butyl ether for the Grignard preparation of this compound[52] which, being the most volatile product, may be distilled direct from the reaction, without hydrolysis. Vinyl and mesityl halides do not form Grignard reagents easily in di-ethyl ether and tetrahydrofuran (T.H.F.) is useful here. T.H.F. solutions of alkyl, aryl and alkenyl Grignards react with mono- and di-alkyl germanium hydrides upon long reflux (2-3 days), substitution of one of the hydrogen atoms occurring.[53] One report of the use of a hydrocarbon solvent[54] is that of the exothermic reaction between germanium tetrachloride, n-butyl chloride and magnesium in toluene or petroleum ether which gives, after two hours reflux, a 60% yield of tri-n-butylchlorogermane. Influence of solvent on yields from Grignard reactions with germanium halides has received no systemmatic attention at all. Differences in constitution of the reagents in different solvents is almost certainly at the root of corresponding variations both of mechanism and final product of the reaction.

The constitution of Grignard reagents, both in solution and crystalline form has been extensively investigated and there is now no doubt that for dilute solutions, prepared in di-ethyl ether from alkyl bromides and iodides the formulation as discrete monomers, $RMgX.2Et_2O$, is correct. At higher concentrations, and with chloride even at low (0.04 molar) concentrations, dimeric species preponderate, their general form being $[RMgX.So]_2$; both symmetrical and unsymmetrical halogen bridged structures are proposed. Higher polymeric forms are known and weakly donating solvents increase the tendency to association. All the three halogen types are monomers in T.H.F. Other species are present in solution and the present picture is one of extended series of equilibria, the concentrations of each species being determined by the factors mentioned



Two recent thorough reviews deal with these points in a detailed and critical manner.[55,56]

The mechanism of the reaction with metal halides has not been studied closely and many fundamental pieces of evidence are lacking. Certainly in these cases the nature of the reactions entity is unknown. Complete alkylation of a germanium tetrahalide is seldom achieved. The reaction often gives surprisingly poor yields and only a few examples of quantitative preparations are reported.[52,57,58] Discounting the possibility of difficulties in work-up or inadequate technique, low yields may be ascribed, in those cases which have been more thoroughly studied, to a number of remarkable complications. Substitution of the four halogens in the formation of R_4Ge compounds is clearly a stepwise process, the later stages being the slower. The slowing of the reaction is particularly marked with the more sterically bulky groups and has already been alluded to in the discussion on organo-lithium reagents (page 13) Rate of substitution is also a function of the halogen attached to germanium, reaction being slower for iodides than for bromides which are in turn slower than chlorides. Despite these differences and differences in rate of substitution of successive halogens it is not normally possible to isolate organohalogermanes merely by adjusting the stoichiometry. Some reactions with the higher alkyl Grignards have however achieved moderate success in this way.[53] More often than not organohalogermanes are undesirable by-products, e.g. phenylmagnesium bromide and germanium tetrachloride have been reported to give tribromophenylgermane in 19% yield.[60] When halides are prepared in this manner, they are almost invariably produced as a mixture of organo- mono-, di-, and tri-halogermanes which can be difficlut to separate as they often form azeotropic mixtures. Two general methods of separation have been employed; either reduction to the hydrides with $LiAlH_4$ or $NaBH_4$ or hydrolysis to the oxides with NaOH, both of which series of compounds are more easily separated by distillation

$$R_nGeCl_{4-n} + LiAlH_4 \longrightarrow R_nGeH_{4-n}$$

$$R_3GeCl + NaOH \longrightarrow R_3GeOH \longrightarrow (R_3Ge)_2O$$

$$R_2GeCl_2 + NaOH \longrightarrow R_2Ge(OH)_2 \longrightarrow (R_2GeO)_n, \; n = 3,4$$

$$RGeCl_3 + NaOH \longrightarrow (RGeOOH) \longrightarrow ((RGeO)_2O)_n, \; n \text{ large.}$$

Reconversion to halides is achieved by concentrated hydrohalogen acid for the oxides or elemental halogen on the hydrides.

One major accompaniment of low yields of R_4Ge compounds is the formation of di- and poly-germanes, and even in the case of tetraethylgermane, usually produced in over 80% yield, a small amount of hexaethyldigermane may be isolated.[26] This and other "side reactions" and mechanisms are discussed in more detail below. Some specific types of Grignard reagents and reactions peculiar to them are also considered.

1.1.5(a) Grignard reagents derived from unsaturated halides (alkenyl and alkynl Grignards)

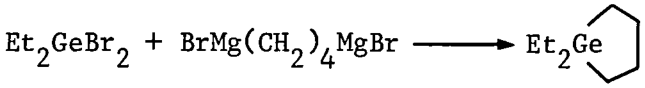
For the greater part, these reagents behave in exactly the same way as the alkyl Grignards. Vinyl magnesium bromide and germanium tetrachloride after a 20 hour reflux in T.H.F. give an appreciable yield of hexavinyldigermane (26%),[61] in addition to the tetravinyl compound (35%). Reaction of trialkylbromogermanes with acetylene monoGrignard requires 15 hours stirring in T.H.F.[2] The most common use of unsaturated Grignard reagents is the preparation unsymmetrical organogermanes of R_3GeR' type.

(b) DiGrignard reagents

Short chain or stereochemically rigid diGrignard reagents behave in the manner expected when reacting with R_3GeX compounds, e.g.

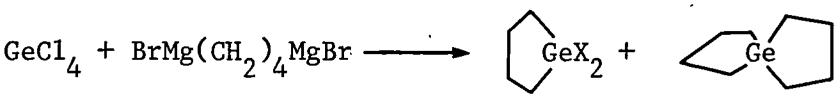
$$2Et_3GeBr + BrMgC{\equiv}CMgBr \longrightarrow Et_3GeC{\equiv}CGeEt_3 \quad \cdots 62$$

Polymeric materials might be anticipated from diorganodihalogermanes, but with 1,4-dibromobutane or 1,5-dibromopentane the germanacyclanes are produced in about 25% yield.



··· 58,63

This method does not produce the corresponding four-membered rings[43] however, for which the more reactive lithio derivatives must be used. Germanium tetrachloride and the four or five carbon atom di-Grignards give a mixture of the dihalogermanacyclane and the spiran



Separation is achieved by reduction of the halide with $LiAlH_4$ followed by distillation.

1,1-Ferrocenylene di-Grignard reacts with triphenylbromogermane in ether to give primarily the monosubstituted compound, $\pi\text{-}C_5H_5Fe\pi\text{-}C_5H_4GePh_3$ and a trace of the disubstituted material.[40]

(c) Halide exchange in Grignard syntheses

This process is particularly favoured when the Grignard reagent has a bulky organic group or the reaction with the germanium halide is slow. It is often advantageous to use a single halogen throughout a synthesis where possible - some interesting results have been observed -

$$Me_2GeCl_2 + MeMgBr \longrightarrow \underset{12\%}{Me_3GeCl} + \underset{25\%}{Me_2GeBr_2} \quad \cdots 64$$

$$Me_3GeCl + MeMgBr \longrightarrow \underset{22\%}{Me_3GeBr} + Me_4Ge \quad \cdots\cdots 65$$

$$Me(CH_2Cl)GeCl_2 + MeMgI \longrightarrow Me_3GeCH_2I \quad \cdots\cdots 64,65$$

$$Me_2Ge(OMe)_2 + MeMgI \longrightarrow Me_3GeI \quad \cdots\cdots 66$$

As the overall rate of a Grignard reaction and the amount of coupling to digermane and polygermanes are influenced by the nature of the halogen it is clear that complications such as the above should be avoided when seeking to produce the tetraorganogermane.

(d) β-Elimination in Grignard reactions

α or γ Chloroalkylhalogermanes and β-chloroalkenylhalogermanes react normally with Grignard reagents.

$$\mathrm{ClCH{=}CHGeCl_3 + CH_3MgBr \longrightarrow ClCH{=}CHGeCH_3}$$

β-Chloroalkylhalogermanes form the symmetrical tetragermane and the alkene

$$\mathrm{ClCH_2CH_2GeCl_3 + 4CH_3MgBr \longrightarrow C_2H_4 + (CH_3)_4Ge}$$

$$\mathrm{CH_3CH(Cl)CH_2GeCl_3 + 4CH_3MgBr \longrightarrow CH_3CH{=}CH_2 + (CH_3)_4Ge} \quad \cdots 78$$

This elimination reaction becomes more facile as group IV is descended, and has found application, in germanium chemistry, in the determination of the site of addition of trichlorogermane to unsymmetrical olefins. A unimolecular 5-coordinate transition state mechanism has been proposed.

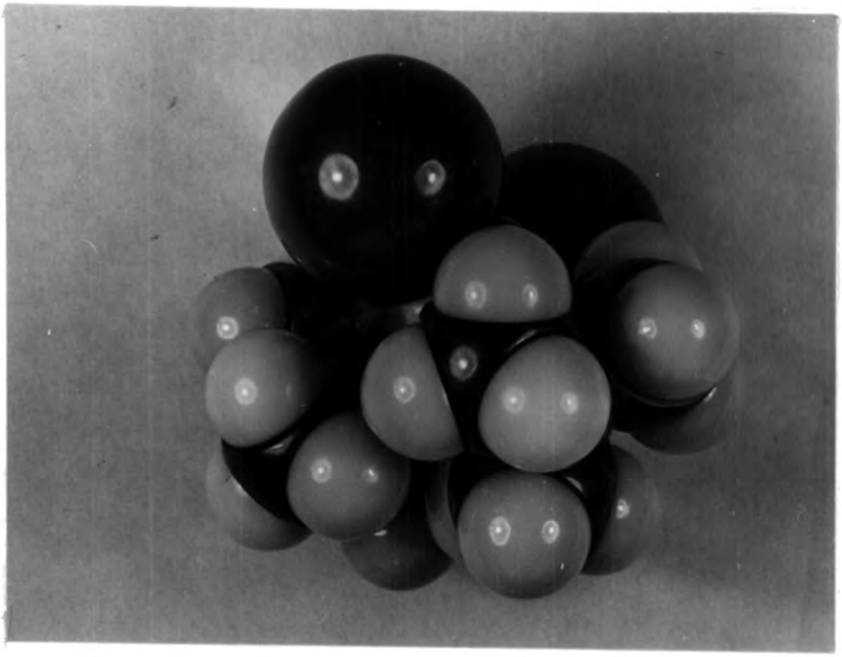
(e) Mixed Grignard Reagents

A recent study,[68] employing gas chromatographic methods of analysis, of the reaction between germanium tetrachloride and mixed Grignard reagents has shown that for the non "sterically hindered" cases, the tetraorganogermanes are produced in roughly statistical proportions. The method has been extended to conditions under which polygermanes are formed,[69] on addition of two alkyl halides and germanium tetrachloride to magnesium in diethyl ether. It is of interest to note that a small yield of trigermane was identified.

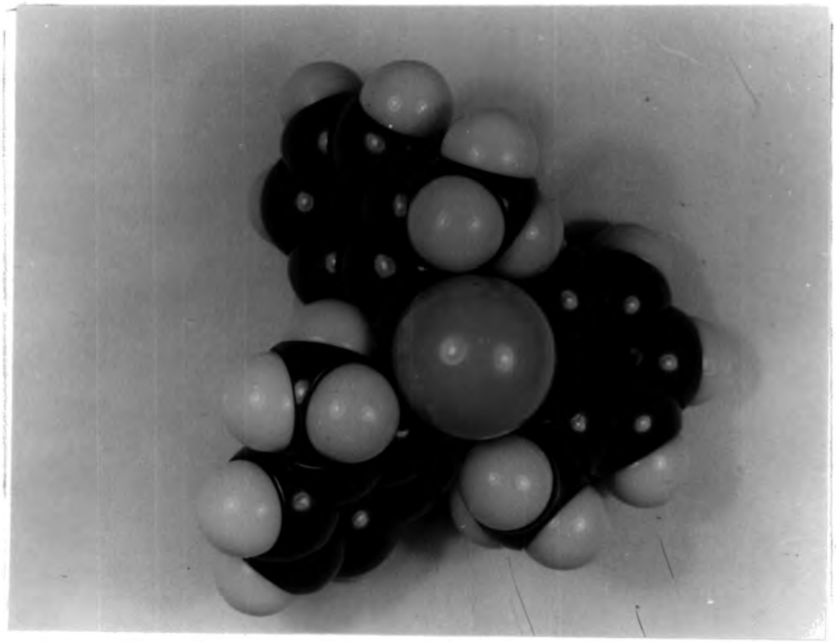
(f) Sterically hindered systems and germyl Grignard reagents

Grignard reactions involving bulky organic groups have thrown some light

PLATE 1



Pl.1.1 Di-t-butyldi-iodogermane



Pl.1.2 Tri-o-tolylbromogermane, showing almost maximum congestion about the halogen atom.

on the nature of the reactive intermediates and to a certain extent their mode of formation and action. The slow speed of these reactions especially in their later stages, gives opportunity for the build up of higher concentrations of intermediates which are not normally detected in the faster instances. A number of examples are known which, for all practical purposes, stop at the trisubstituted state; reference has already been made to the cyclohexyl[70] and 1-napthyl[38] cases where further substitution, even with a large excess of the Grignard and a long reaction time, does not occur. The ability of less bulky organic groups, e.g. methyl, ethyl, n-propyl, benzyl, in the form of Grignard reagents, to effect substitution of the final halogen[71] has been advanced in support of the hypothesis of steric crowding at the germanium atom. Although such tetrasubstituted germanes are undoubtedly rather cluttered, (see plates 1 and 2) these arguments must be viewed with some reserve as the corresponding lithio derivative does substitute tri-1-naphthylbromgermane and the organozinc compound reacts with tri-o-tolylbromgermane to give good yields of tetra-o-tolylgermane.[10] The only reported compound containing the even more bulky t-butyl group bonded to germanium is t-butyltrichlorogermane, prepared by direct synthesis.[72] t-Butyl magnesium bromide and germanium tetrachloride are reported to give only low yields of this compound, much polymeric material, and no other volatile organogermane. It is difficult to find steric reasons why at least the disubstituted compounds, (t-butyl)$_2$GeX$_2$, should not exist, but apparently none has ever been isolated ($\mathrm{Bu}^t_2\mathrm{GeI}_2$ is illustrated in pl.1). Considerable emphasis has been placed on the steric crowding of groups when bonded to germanium,[11,73] but the points just mentioned suggest that the major effect of bulky groups is not after the formation of the tetraorganogermane (i.e. in the physical impossibility of its stable existence) but rather during its formation. Thus these crowded organogermanes are only slowly produced (or not at all formed) because of "steric inhibition" of the mechanism. Multi-centre transition states and reactions at metal surfaces would both suffer from this effect.

One problem raised by the Grignard reaction, and sometimes accentuated in the slow sterically hindered cases, is that of the formation of di- and polygermanes. A coupling reaction involving a germyl Grignard reagent R_3GeMgX, fits the available evidence

$$R_3GeX + R_3GeMgX \longrightarrow R_3Ge.GeR_3 + MgX_2$$

No method has yet been devised for the isolation of such a compound, or even to produce one in good yield for subsequent reaction, but there is considerable strong evidence for their existance as intermediates in a number of systems. This type of intermediate was first postulated[61] to account for the formation of hexavinyldigermane from vinyl magnesium bromide and germanium tetrachloride. A reaction scheme involving reduction of the halide to a germanium (II) compound was proposed,

$$GeCl_4 + 2CH_2{=}CHMgBr \longrightarrow GeCl_2 + CH_2{=}CHCH{=}CH_2 + 2MgClBr$$

$$GeCl_2 + 2CH_2{=}CHMgBr \longrightarrow (CH_2{=}CH)_2Ge + 2MgClBr$$

$$(CH_2{=}CH)_2Ge + CH_2{=}CHMgBr \longrightarrow (CH_2{=}CH)_3GeMgBr$$

$$(CH_2{=}CH)_3GeMgBr + (CH_2{=}CH)_3GeCl \longrightarrow (CH_2{=}CH)_6Ge_2$$

Divinyl germane is unknown as such but is a possible reactive intermediate, and addition of an organometallic to a germanium (II) compound has been reported.[73] Reduction of a (transition) metal halide to a lower valence state was also cited as supporting evidence (the formation of bis-arene chromium(0) complexes from $CrCl_3$ and PhMgBr).

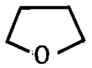
Subsequent attempts[73] to prepare trimethylgermyl magnesium chloride by reacting trimethylchlorogermane with metallic magnesium failed: similarly, reactions[74] based on analogy with the well-known action of an organolithium on a triorganogermane.

$$RLi + Ph_3GeH \longrightarrow RH + Ph_3GeLi$$

met with failure when the magnesium compounds were used. Allyl- and n-butyl magnesium halides were also investigated in this system (in diethyl ether) with no success. When, however, allyl magnesium chloride and triphenylgermane were refluxed in T.H.F. and the mixture carbonated and hydrolysed, triphenylgermyl carboxylic acid was isolated.

$$\begin{tikzcd}[column sep=small] Ph_3GeH + CH_2{=}CH{-}CH_2MgCl \arrow[r] & CH_2{=}CH{-}CH_3 + Ph_3GeMgCl \arrow[r, "CO_2"] & Ph_3GeCOOMgCl \arrow[d, "H_2O"] \\ & & Ph_3GeCOOH \end{tikzcd}$$

and some 4-hydroxybutyltriphenylgermane, formed presumably by a cleavage reaction.

$Ph_3GeMgCl$ +  $\longrightarrow Ph_3Ge(CH_2)_4OMgCl \xrightarrow{H_2O} Ph_3Ge(CH_2)_4OH$

Higher yields of this material were obtained on prolonged reflux, and phenyl magnesium bromide and triphenylgermane gave only the cleavage product and no $Ph_3GeCOOH$ on carbonation and hydrolysis. n-Butylmagnesium bromide was reported to have no reaction at all.

Closer examination of the system PhMgBr + $GeCl_4$,[11] yielded evidence for the production of the germyl Grignard Ph_3GeMgX by two routes; reaction of the trisubstituted halogermane and free metallic magnesium,

$$Ph_3GeCl + Mg \xrightarrow[\Delta]{} Ph_3GeMgCl$$

and a slower elimination reaction involving the Grignard itself

$$Ph_3GeCl + PhMgBr \longrightarrow PhCl + Ph_3GeMgBr$$

Evidence was obtained that the reactive finely divided magnesium sludge present after preparation of the Grignard was more effective than free magnesium in bulk. Separation from this sludge by filtration reduced recovery of hexaphenyldigermane (formed presumably by the coupling reaction mentioned above) from 69% with magnesium present to zero after filtration.

Examination of the reaction[11] of the three tolymagnesium bromides, both filtered and unfiltered, with germanium tetrachloride gave more evidence for the formation of the germyl Grignard; the production of significant yields of digermane, the isolation of the triorganogermane on hydrolysis and the triorganogermanium carboxylic acid on carbonation all supporting this view

$$\begin{tikzcd} & (CH_3C_6H_4)_3GeH \\ (CH_3C_6H_4)_3GeMgX \arrow[ur, "H_2O"] \arrow[dr, "CO_2{,}H_2O"'] & \\ & (CH_3C_6H_4)_3GeCOOH \end{tikzcd}$$

Isolation of the germane and carboxylic acid indicates that formation of the germyl Grignard is faster than its coupling to give digermane. Separate work[76] had established that the hydrides were not produced before hydrolysis or by the magnesium-acid reduction of the halides. The unfiltered organogermanium halides gave a much higher yield of digermane especially with the bulky, less reactive o-tolyl reagent, and it was suggested that the slow "halogen-metal exchange" could be an equilibrium, the RX species possibly being removed by Wurtz type reactions

$$(o\text{-tolyl})_3GeBr + (o\text{-tolyl})MgBr \rightleftharpoons (o\text{-tolyl})_3GeMgBr + o\text{-tolylBr}$$

this being largely responsible for the production of the significant (approx. 6%), amount of digermane formed in the absence of reactive magnesium sludge. In view of the difficulties encountered in removing colloidal metal from suspension and the well characterised production of magnesium in this form during the preparation of Grignard reagents to give solutions of varying degrees of clarity and colour, it is doubtful whether all free magnesium could be removed from these reactions by filtration alone. It is possible that these small amounts of free magnesium remaining, essentially in solution, could account for the small yields of digermane as large excesses of the Grignard were used. Separation of the reagents by crystallisation could provide a means of avoiding these complications.

A re-examination in 1959[77] of the reaction of isopropyl magnesium bromide and germanium tetrachloride, which earlier[78] had been reported as yielding after hydrolysis $Pr^{i}_{3}GeOH$, $(Pr^{i}_{2}GeO)_{3}$, and $(Pr^{i}Ge)_{n}$, showed that a considerable amount of $Pr^{i}_{3}GeH$ was also formed, thus demonstrating the likely existance of $Pr^{i}_{3}GeMgX$ in this system. The coupling reaction of this germyl Grignard and the triisopropylchlorogermane present was not observed and no hexaisopropyldigermane was isolated despite conditions being apparently favourable - 12% of $Pr^{i}_{3}GeOH$ (from $Pr^{i}_{3}GeX$) and 36% of $Pr^{i}_{3}GeH$, the major reaction product (from $Pr^{i}_{3}GeMgX$) were found after hydrolysis. Again emphasis was apparently placed on the steric factors operating in the, as then hypothetical, tetraorganogermane, rather than during the course of the reaction.

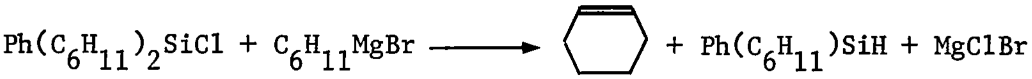
Analogous Grignard type intermediates have also been postulated in reactions of alkylhalosilanes, and as early as 1933[79] a mechanism involving a silyl Grignard reagent was invoked for the production of dicyclohexylphenylsilane from trichlorophenylsilane and cyclohexylmagnesium bromide

$$PhSiCl_3 + 2C_6H_{11}MgBr \longrightarrow Ph(C_6H_{11})_2SiCl$$

$$Ph(C_6H_{11})SiCl + C_6H_{11}MgBr \longrightarrow Ph(C_6H_{11})_2SiMgBr + C_6H_{11}Cl$$

$$Ph(C_6H_{11})SiMgBr \xrightarrow{H2O} Ph(C_6H_{11})SiH$$

Later work[80] showed that dicyclohexylphenylsilane was present before hydrolysis and the isolation of cyclohexane led to the proposal of a reductive mechanism for the formation of the organosilane, with an elimination process participating



Higher temperatures were reported to favour the production of silicon hydrides.

A study of the action of alkali metals and magnesium on triarylchlorosilanes in T.H.F.[81] showed that the silyl-metallic compounds were formed with the group I elements, but with magnesium present, Ph_3SiCl yielded hexaphenyl disilane. Again formation of a silyl Grignard was proposed

$$Ph_3SiCl + Ph_3SiMgCl \longrightarrow Ph_6Si_2 + MgCl_2$$

The action of a number of Grignard reagents on triphenylchlorosilane was examined. High yields of hexaphenyldisilane were obtained and with cyclohexylmagnesium bromide, cyclohexane and cyclohexene were also detected. In the same series of experiments, it was reported that mixtures of trimethylchlorosilane, triphenylchlorosilane and phenylmagnesium bromide under reflux gave 14% of 1,1,1-triphenyl 2,2,2-trimethyldisilane. Mechanisms advanced for all these reactions involved participation of silyl Grignard reagents and the authors suggested that, as no coupling (to give the disilane) was observed on refluxing Me_3SiCl and PhMgBr, aryl groups were required to stabilise the silyl Grignard. They also reported that experiments had ruled out participation of Ph_3SiH.

A brief re-examination of this reaction in connection with the tolylgermanium work previously mentioned showed a dependence on the presence of metallic magnesium - a more likely controlling factor.

The proposed formation of the germanium-magnesium intermediate in the vinyl reactions led to a suggestion that germanium had a higher electronegativity than silicon and that this was a decisive factor in the formation of the Ge-Mg bond. More frequent interpretation of silicon reactions subsequent to this in terms of silicon-magnesium intermediates positively discounted this argument.

Similar reactions with triorganohalostannanes and some other tin reactions (notably the cleavage of Ph_6Sn_2 by Mg) have also been[82] interpreted in terms of tin-magnesium intermediates of the R_2Mg and RMgX type and also reactions of Pb(II)aryls with Grignard reagents at low temperatures.

Drawing together major points, then, it would seem that there are fewer genuine examples of steric hinderance in simple organogermanes than was formerly thought to be the case. Steric influences can make themselves felt at three stages, in the substrate, reaction intermediates or activated complexes, and reaction products. Undue emphasis has been placed on the latter consideration in the past, and as most of the substrates do react fairly readily with some reagents (e.g. that with metallic magnesium) it would seem that steric control appears to exert its influence during the reaction, in the intermediates. Steric factors have not rightly been separated from other points which influence reactions of Grignards under normal circumstances.

Although never directly proven, the existence of germyl Grignard reagents R_3GeMgX, can be considered firmly established. It is certainly extremely difficult to formulate routes to many reaction products without their admission. The presence of reactive magnesium metal increases the yield of materials formed via germyl Grignard intermediates and is almost certainly responsible for the greater part of the formation of the germanium-magnesium bond. Evidence for their production by Grignard exchange is less soundly based, but cannot be entirely discounted.

Summary of the Grignard synthesis for organogermanes

The relative ease with which the Grignard reagents can be prepared, handled and used on the large scale undoubtedly plays the largest part in making them the most commonly used primary synthetic intermediate. Their added advantages include the moderate conditions required for reaction and, for the simple germanes and other special cases, their high yield of the tetrasubstituted material. The nature of the fully substituted germanes, apart from those containing functional groups in the organic portion - which would often be unsuitable for Grignard synthesis in any case - makes for an ease of separation with a miniumum of tedious work-up procedures. The availability of di-functional reagents can also be a particular advantage. Use of suitable secondary methods for substitution of the final halogen, or carefully controlled conditions can relieve difficulties in the "sterically hindered" systems, and complications from elimination and halogen exchange reactions can be obviated or minimised again by careful choice of reagents and conditions. The method is in general unsuitable for the preparation of organohalogermanes other than certain trisubstituted compounds, but can under controlled conditions furnish high yields of digermane.

Clearly much remains to be learned of the reaction of Grignard reagents with germanium halides. That these, like most other of the Grignard reactions are extremely complex is certain, and it seems likely that many factors are involved, some whose importance was not formerly apparent. It has, for example, only recently been fully appreciated that the donor solvent must be regarded as an integral part of the reagent and that an organomagnesium halide prepared in different solvents is essentially and fundamentally a different reagent in each case. Careful studies of organomagnesium halide-germanium halide systems could provide a key to better understanding of the whole field of Grignard reagent chemistry.

1.2. SECONDARY METHODS

Synthesis of organogermanes from compounds containing a germanium-carbon bond.

Although these methods play an exceedingly important part in the making of germanium-carbon bonds and germanium chemistry as a whole, they are in general irrelevant to our present purpose and so will be mentioned only very briefly for comparative purposes. The one exception - redistribution reactions - will be dealt with in slightly greater detail as it bears some relation to organoaluminium and organomagnesium reactions.

1.2.1. Synthesis from triorganogermanium-alkali metal compounds (R_3GeM)

This is a widely used, and important method, both for making germanium-carbon and germanium-metal bonds. Its major disadvantage is the restricted range of compounds of this type which can be prepared - M is usually Li, and R only C_6H_5-, C_2H_5- or $C_6H_5CH_2$- at present. Only triphenylgermyl-lithium and -sodium have been closely studied and much remains to be learned even about these compounds. None of this type of reagent has been isolated and all are generated and used in situ, in either diethyl ether or 1,2-dimethoxyethane (monoglyme) solution; triphenylgermyl sodium is more often used in liquid ammonia.

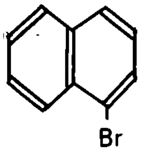
The points relevant to the role of the solvent in the Grignard reaction (page 29) apply equally to these reagents and perhaps more so as these compounds commonly react, over extended periods of time, with their solvent, forming in some cases appreciable percentages of cleavage products.

Reaction with organic halides is usually straightforward with monofunctional compounds

$$Ph_3GeLi + C_4H_{10}Cl \longrightarrow Ph_3GeC_4H_{10} + LiCl,$$

but complications can occur with di- and poly-halides, and aromatic halides in liquid ammonia - usually the production of di- and higher germanes [84]

$$HCCl_3 + Ph_3GeNa \xrightarrow{NH_3} Ph_6Ge_2 + (Ph_3Ge)_2CH_2$$



$$+ Ph_3GeNa \xrightarrow{NH_3} Ph_3GeNH_2 + C_{10}H_8 + NaBr$$

$$\downarrow H_2O$$

$$(Ph_3Ge)_2O$$

These reactions are of little general use because of the greater ease with which most unsymmetrical germanes can be prepared from the Grignard and the halogermane.

Aldehydes and ketones react with triorganogermanium-alkali metals in a manner analogous to their reaction with Grignards

$$Ph_3GeLi + CH_2O \longrightarrow Ph_3GeCH_2OLi \xrightarrow{H_2O} Ph_3GeCH_2OH \quad \cdots\cdots 88$$

$$Ph_3GeLi + Ph_2O \longrightarrow Ph_3GeC(OLi)Ph_2 \xrightarrow{H_2O} Ph_3GeC(OH)Ph_2 \quad \cdots 74$$

It is not certain whether the addition takes place exclusively one way - c.f. the silyl compounds where the reaction yields a silicon-oxygen bond. It is of interest that the optically active lithio derivative, Ph(Me)(1-naphthyl)GeLi, retains its configuration on reaction with benzophenone.[90] This and other reactions (e.g. carbonation) involving retention of configuration suggest a close ion-pair association, RR'R"Ge....Li, in solution.

Aromatic acyl halides at low temperatures give germyl ketones,

$$Ph_3GeLi + RCOCl \xrightarrow{-78\ \text{to}\ -23^{\circ}} Ph_3GeCOR + LiCl \qquad \cdots\cdots 91$$

but aliphatic acid chlorides react with two moles of lithiogermane to yield the bisgermyl-carbinol on hydrolysis. At higher temperatures addition to the more stable aryl germyl ketones also occurs

$$Ph_3GeLi + Ph_3GeCOPh \longrightarrow (Ph_3Ge)_2C(OH)Ph$$

Carbonation of the alkali metal reagents followed by hydrolysis leads to the corresponding germylcarboxyllic acid which decarbonylates on heating

$$Ph_3GeLi \xrightarrow{CO_2} Ph_3GeCOOLi \xrightarrow{H_2SO_4} Ph_3GeCOOH \xrightarrow{183^{\circ}} Ph_3GeOH + CO$$

The benzyl derivative spontaneously decarbonylates.[92]

1.2.2. Synthesis from organogermanium hydrides

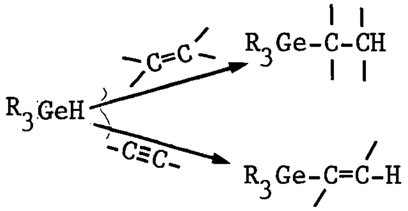
Two major reaction types may be distinguished here

1.-Elimination reactions involving organometallics- usually organolithium compounds and in certain cases elimination with organic halides

$$\begin{tikzcd}
 & R_3GeR' + LiH \\
R_3GeH \arrow[ur, "R'Li"] \arrow[dr, "R'X"'] & \\
 & R_3GeR' + HX
\end{tikzcd}$$

Both reactions are of considerable theoretical importance but little practical value.

2.-Addition reactions with carbon-carbon multiple bonds. A well characterised and extensively explored region, whose reactions show great versatility, allowing a wide range of organogermanes to be produced with relative ease



Reaction of triorganogermanes with alkali metal derivatives are often complex and markedly dependent on reaction conditions, - temperatures, solvent and the reagent present in excess all having significant effects. Two courses are open, and both are illustrated by the reaction of triphenylgermane and ethereal phenyllithium.[92-3]

$$\mathrm{PhLi(8\ fold\ excess)} \xrightarrow{\mathrm{Ph_3GeH}} \mathrm{Ph_4Ge} \qquad (70\%)$$

$$\mathrm{Ph_3GeH} \xrightarrow[\mathrm{PhLi}]{} \mathrm{Ph_6Ge_2} \qquad (55\text{-}60\%)$$

A number of examples of this competition of alkylation and "hydrogen-metal exchange" are known,[92] e.g.

$$\mathrm{Ph_2GeH_2} + \mathrm{2n\text{-}BuLi} \xrightarrow{1.4\mathrm{hr},\ -10^{\circ},\ 2,\mathrm{EtBr}} \mathrm{H_2} + \mathrm{Ph_2GeEt_2} \qquad (2\%)$$

$$\mathrm{Ph_2Ge(Et)(n\text{-}Bu)} \quad (20\%)$$

$$\mathrm{Ph_2Ge(n\text{-}Bu)_2},(12\%) + \mathrm{(Ph_2EtGe)_2},(28\%)$$

Griganrd reagents in diethyl ether have no reaction on germanium-hydrogen bonds, but in T.H.F. there is some evidence for hydrogen-metal exchange. Two isolated examples of alkylation are known[53]

$$\mathrm{(n\text{-}Bu)_2GeH_2} + \mathrm{CH_2{=}CHCH_2MgBr} \xrightarrow{\mathrm{THF}} \mathrm{(nBu)_2(CH_2{=}CHCH_2)GeH}$$

$$\mathrm{(n\text{-}C_7H_{15})GeH_3} + \mathrm{PhCH_2MgBr} \xrightarrow{\mathrm{THF}} \mathrm{(nC_7H_{15})(PhCH_2)_2GeH}$$

Both "hydrogen-halogen exchange" and alkylation reactions are possible with organogermanium hydrides and organic halides. The latter predominate in the case of unsaturated halides in ethereal solvents [94-5]

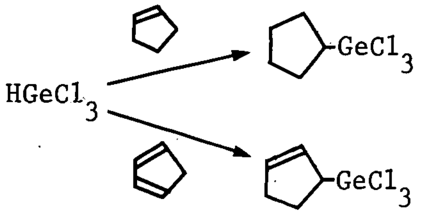
$$\mathrm{CH_2{=}CHCH_2Br} + \mathrm{HGeCl_3} \longrightarrow \mathrm{CH_2{=}CHCH_2GeCl_3}$$

The reaction of germanium hydrides and olefins closely parallels the more important hydrosilation processes. Many types of olefin react, usually under mild conditions which do not cause polymerisation, sometimes alone and exothermically but more often only with added catalyst. Both free radical and ionic initiators and catalysts are effective. Most studies have involved terminal double bonds and all have been interpreted in terms of terminal addition of the germanium entity. Little work has been done on the detailed course of reaction or isolation of minor products.

The addition of trichlorogermane to 1-hexane was the first reported reaction of this type[98]

$$HGeCl_3 + CH_2{=}CH(CH_2)_3CH_3 \xrightarrow{60^o} Cl_3Ge(CH_2)_5CH_3 \qquad (22\%)$$

and much further work as involved this substrate. The two five carbon cyclic olefins (few have been examined in this reaction) react rapidly with trichlorogermane[99]



The structure of this latter compound has not been unequivocally established. Chlorinated olefins react in the expected (addition) fashion[72]

$$ClCH{=}CHCH_3 + HGeCl_3 \xrightarrow{60^o\ 1\ hr} Cl_3GeCH(CH_3)CH_2Cl$$

as do more complex mono-olefins[67]

$$CH{=}C(Cl)SiCl_3 + HGeCl_3 \xrightarrow{H_2PtCl_6} Cl_3SiCH(Cl)CH(Cl)GeCl_3$$

Diolefins give mixtures of linear and cyclic compounds.

Alkylhalogermanes $RGe(H)X_2$ and $R_2Ge(H)X$ react readily and in good yield with olefins under mild conditions, and the method can be useful for preparation of symmetrical and unsymmetrial halogermanes[100]

$$CH_3Ge(H)Cl_2 + C_2H_4 \longrightarrow CH_3(C_2H_5)GeCl_2 \qquad (90\%)$$

In general, they show greater reactivity than the simple hydrides e.g. dibutyl chlorogermane adds to the double bond of allyl alcohol whereas tributyl germane fails to do so,[59] and also react easily with diolefins to give, in the case of diethylchlorogermane, good yields of the 1,4-addition product[101].

$$Et_2Ge(H)Cl + C_4H_8 \longrightarrow Et_2Ge(Cl)CH_2CH{=}CHCH_3$$

A great deal of work has been carried out on the systems of olefins and triaryl- and trialkyl- germanes.[102-3] This is by far the most widely used of the addition reactions, but yields are often no more than average, usually about 50%. In all cases terminal addition is postulated, but a different reaction, e.g. formation of Ge-O bonds from unsaturated alcohols can be achieved by the addition of copper powder.[104]

Some typical examples, from among many, include

$$(nPr)_3GeH + CH_2{=}CHCN \xrightarrow{\text{reflux}} (nPr)_3GeCH_2CH_2CN \qquad (42\%)$$

$$(nPr)_3GeH + CH_2{=}CHCOOCH_3 \longrightarrow (nPr)_3GeCH_2CH_2COOCH_3 \qquad (40\%)$$

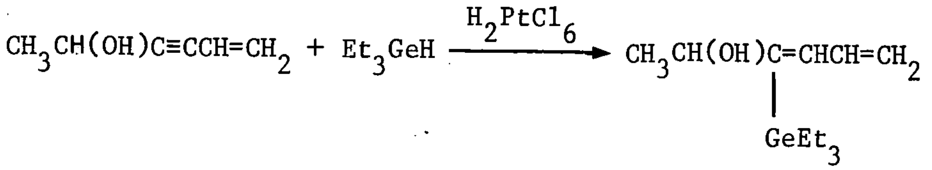
Dihydride and trihydride addition to olefins has also been studied but in less detail;[59] conditions can be adjusted to give simple trisubstituted and tetrasubstituted germanes as well as polymeric material.

Reaction of germanium hydrides with acetylenes proceeds in two stages; isolation of the intermediate organoalkenylgermane usually being possible as the second stage, further addition to these compounds, occurs only under more drastic conditions,

$$R'C\ CH + R_3GeH \longrightarrow R'CH{=}CHGeR_3 + R_3GeH \longrightarrow R_3GeC(R')HCH_2GeR_3$$

and this furnishes an important route to α-unsaturated germanes, often in high yields. Initial terminal additions is again proposed, second addition occurring at the adjacent atom.[105] Reaction temperatures vary in the range 50°-200°, and the addition of a catalyst, usually chloroplatinic acid increases yields, especially in the case of the R_3GeH compounds. Solvent again plays an important part, dilution usually aiding the isolation of the monosubstituted product, but in certain instances complicating the reaction e.g. $HGeCl_3$ and acetylene in ether yield monosubstituted, disubstituted and polymeric products. Polymeric material is also the major product with di- and tri- hydride, but conditions can be moderated to give successive substitution.

Compounds containing both double and triple bonds have also been examined and in all cases it is the triple bond which reacts with a deficiency of organogermane even when the double bond is terminal[106]



$$CH_3CH(OH)C{\equiv}CCH{=}CH_2 + Et_3GeH \xrightarrow{H_2PtCl_6} \underset{\displaystyle |\atop GeEt_3}{CH_3CH(OH)C}{=}CHCH{=}CH_2$$

(59%)

1.2.3. Redistribution reactions

In principle, the interchange of halogen atoms and alkyl radicals in the system

$$R_4Ge + GeCl_4 \longrightarrow R_{4-n}GeCl_2 + R_nGeCl_{4-n}$$

is efficient and, if it can be controlled to yield only one desired product attractive. The preparation of starting materials presents no difficulties but separation of a mixture of products could be tedious. A recent investigation of the reaction using a number of tetraalkyl and tetraaryl germanes[4] both in the presence and absence of anhydrous aluminium halides as catalysts, has shown that although not completely general or extremely easily controlled, the method does provide good yields of triorganochlorogermanes, certain diorganodichlorogermanes, and phenyltrichlorogermanes.

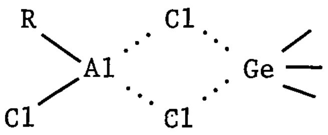
The reaction is usually carried out in a Carius Tube, the reactants being heated in the required proportions with 0.2 mole% of aluminium trichloride to 200° for the alkyl compounds, 100°-125° for the phenyl compounds although it is also reported to procede at these temperatures in vessels open to the atmosphere (with precautions against hydrolysis). Several catalysts were investigated including $ZnCl_2$, $BeCl_2$, BCl_3, PCl_3 $POCl_3$, PCL_5, but none of these was found to be effective at least for the reaction with Bu^n_4Ge. Typical results quoted include

$$\underset{(0.98)}{Et_4Ge} + \underset{(1.19)}{GeCl_4} \xrightarrow[200^\circ,\ 27\ hrs]{AlCl_3\ (0.2)} \underset{(2.11)}{Et_2GeCl_2} + \underset{(0.18)}{GeCl_4} + \text{other products}$$

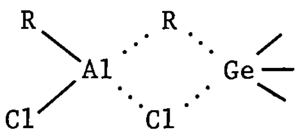
$$\underset{(1.00)}{Bu^n_4Ge} + \underset{(1.41)}{GeCl_4} \xrightarrow[220^\circ,\ 4\frac{1}{2}\ hrs]{AlCl_3\ (0.2)} \underset{(0.33)}{Bu^n_4GeCl} + \underset{(1.66)}{Bu^n_2GeCl_2}$$

(figures in parenthesis indicate mole %)

The reaction with tetra-n-propylgermane were also reported to procede satisfactorily to give dichlorodipropylgermane at 200° (but see p.48) Tentative suggestions which are almost entirely speculative, involve bridged intermediates in which germanium has increased its co-ordination number to five



(I)



(II)

It is argued that the electron releasing character of the R groups will tend to stabilise intermediates of type II by reducing the positive charge on germanium and thus weaken the bridging Ge-Cl bond, accordingly the alkyl group has a greater tendency to stay on the germanium when more organic groups are attached to it (i.e. susceptibility to alkylation increases in the series $GeCl_4 < RGeCl_3 \leq R_2GeCl_2$). The stability arguments apply in the opposite sense to intermediates of type I. This rather nebulous and simplified explanation is, however, in accord with the experimental facts. The analytical methods employed were not sensitive to small amounts of by-products and so considerable information on reaction mechanism could have been lost. No kinetic information was obtained. In one instance only were gaseous products examined.

1.3. GERMANIUM HALIDES AND GRIGNARD REAGENTS

FACTORS which have been cited as precluding good yields of tetrasubstituted organogermanes from the Grignard reaction include (a) low reactivity of the organomagnesium halide, (b) bulky organic groups and the presence of large halogen atoms, particularly iodine - steric interference -, and (c) unreactive intermediate organohalogermanes which resist further stepwise substitution. The usual outcome of the combined effect of these restraints is the production of digermanes and higher polymers via germylmagnesium intermediates, and, under suitable conditions, the amount of digermane produced can be high. Overall yields greater than 80% for complete substitution of germanium tetrachloride are rarely achieved. Aryl Grignard reagents are, in general, less reactive than their alkyl couterparts, and in controlled reactions give substantial amounts of digermane.[75] Coupling reactions in the alkyl series have rarely been reported; only a small amount of hexaethyldigermane can be isolated from the reaction of ethyl magnesium bromide and germanium tetrachloride. The isopropyl group, however, should provide sufficient steric hindrance to allow suitable conditions for coupling reactions to occur, and possibilities of varying the halogen attached to germanium could yield a means of directing the reaction course, if the reasons instanced are the controlling factors.

Accordingly, an investigation of the system Pr^iMgX-GeX'_4 was undertaken, with a view to obtaining a greater understanding of the mechanism of the reaction and a more detailed picture of the reaction products. Many of these products were expected to be sufficiently volatile for V.P.C. separation and characterisation. It was initially hoped that the system could be induced to yield significant amounts of digermane, $Pr^i_6Ge_2$ so that a study of the properties of this congested molecule could be made.

1.3.1. The system iso-propylmagnesium bromide-germanium tetraiodide, in diethyl ether.

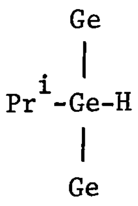
The reaction of iso-propylmagnesium bromide on germanium tetraiodide had hitherto not been reported. Experiments were carried out under the following conditions: (i) with excess Grignard reagent containing an excess of magnesium present from the preparation of the reagent, mostly in the form of a finely divided sludge, (ii) with an excess of filtered Grignard reagent, and (iii) with excess Grignard reagent and magnesium and the subsequent addition of tertiary-butyl chloride.

Acid hydrolysis of the mixture from the reaction with the filtered Grignard gave yields of between 9 and 11% of tri-isopropylgermane, whereas approximately twice this amount (21%) was formed in the reaction containing free magnesium sludge, even though reflux time was considerably reduced (by 75%). Again this indicates the extent of the more efficient attack on the trisubstituted halide in the presence of free magnesium to give the germyl Grignard reagent.

$$Pr^i_3GeCl \xrightarrow{Mg} Pr^i_3GeMgCl \xrightarrow{H_2O} Pr^i_3GeH$$

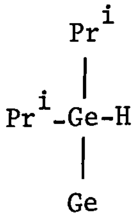
(although it does not <u>necessarily</u> imply attack by free magnesium). The filtered solution of the Grignard was a clear green colour and so probably contained colloidal or otherwise suspended magnesium and this, in the 2.5 fold overall excess of Grignard used, could have been responsible for the hydride isolated from the former reaction (if direct attack by magnesium does occur then the 'colloidal' magnesium would have to be present in 1/4 mole%).

Under all variations of experimental conditions listed, the major product (50-65%), was a yellow solid, involatile at temperatures up to 220° at 10^{-3}-10^{-4} mm. Chromatography of a solution of this solid in benzene (the material was readily soluble, cf. the description of $(Pr^iGe)_n$) on an alumina column yielded various fractions on elution with solvents of increasing stripping power, none of which could be characterised as a pure compound. Molecular weights, determined by vapour pressure osmometer, did not show consistency within individual samples but yielded 2,200 as a lower limit and a probable average value in the region of 4,000. Infrared spectra of the fractions showed broad ill-defined bands characteristic of νGe-O in polymeric oxides, each fraction differing qualitatively from the next in this respect in no systemmatic or readily assigned fashion. The most interesting of these materials was that eluted with a 1:1 benzene-ethanol mixture, a viscous yellow liquid, showing a medium intensity band in the infrared assigned to a Ge-H stretching frequency. That this band was due to Ge-H as an integral part of a polymeric structure (the material showed many features of the other polymeric oxides examined), was attested to by its absence in previous and subsequent eluates and the displacement of the peak from the "usual" range of 1990-2060 cm^{-1} to 1961 cm^{-1}. This value lies between that of the Ge-H stretching frequency in $(Ph_3Ge)_3GeH$ (1953 cm^{-1}) and Pr^i_3GeH (1988 cm^{-1}) and suggests that the Ge-H group is incorporated as



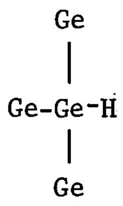
$$\text{Pr}^i\text{-}\underset{\underset{\text{Ge}}{|}}{\overset{\overset{\text{Ge}}{|}}{\text{Ge}}}\text{-H}$$

or



$$\text{Pr}^i\text{-}\underset{\underset{\text{Ge}}{|}}{\overset{\overset{\text{Pr}^i}{|}}{\text{Ge}}}\text{-H}$$

rather than



$$\text{Ge-}\underset{\underset{\text{Ge}}{|}}{\overset{\overset{\text{Ge}}{|}}{\text{Ge}}}\text{-H}$$

The presence of Ge-H bonds in a polymeric material further suggests that intermediates such as $Pr^i_2Ge(MgX)X$ or $Pr^iGe(MgX)X_2$ are present in the reaction mixture, indicating reaction of the germanium halide with magnesium (or some means of Ge-Mg bond formation) at an early stage of alkylation. Elemental analysis of this polymer indicated a mean isopropyl content per germanium atom of between 1 and 2. 30-50% of the solid chromatographed was strongly retained on the alumina column, and could only be removed by protracted (5 days) Soxhlet extraction with chloroform.

The remainder of the total reaction product (20-30%) consisted in each case, of material volatile below 200°C at 10^{-3}mm. In those reactions which had been hydrolysed with hydrochloric acid (5N), a small amount (2-4%) of triisopropylchlorogermane was identified. No other monohalide was isolated. No evidence was obtained for the presence of the digermoxane $(Pr^i_3Ge)_2O$, and molecular weight measurements (V.P. osmometer, in benzene) on the next most volatile material to the chloride indicated a dimeric form of Pr^i_2GeO, but this degree of association was not determined with absolute certainty. Only one band was observed in the Ge-O stretching frequency region of the infrared (at 851 cm^{-1}) which is consistent with a four membered ring structure. Two further components of the central fraction of the reaction product, $(Pr^i_2GeO)_3$, and, less satisfactorily, $(Pr^i_2GeO)_4$ were identified. This latter material was later shown to be a mixture of two compounds, probably $(Pr^i_2Ge)_4$ and $(Pr^i_2GeO)_4$, by vapour phase chromatography.

Treatment of a reaction performed with excess Grignard reagent and magnesium with D_2O, gave on careful extraction, avoiding contact with water and acids, Pr^i_3GeD in similar yield to the previous experiments. The infrared spectrum of the compound was recorded, characteristic bands being νGe-D, 1429 cm^{-1}, δGe-D, 504 cm^{-1}, ratio νGe-H/νGe-D. 1.399:1 Contact with dilute hydrochloric acid for four weeks at room temperature produced no significant change in the relative intensities of the Ge-H, Ge-D bands present in this material (the former from H_2O in the D_2O) indicating no significant D-H exchange between HCl and Pr^i_3GeD.

In none of the experiments was any hexaisopropyldigermane or tetraisopropylgermane detected. Examination of the volatile components of the reaction at a later date by vapour phase chromatography (V.P.C.) confirmed the absence of significant amounts of these materials.

An attempt to increase the yield of hydride or encourage the formation of digermane from the germyl Grignard present, by elimination reactions of the type

$$R_3GeMgX + Me_3CCl \longrightarrow Me_2C{=}CH_2 + MgX_2 + R_3GeH$$

$$2R_3GeMgX + 2Me_3CCl \longrightarrow 2Me_2C{=}CH_2 + 2MgX_2 + R_6Ge_2 + H_2$$

proved unsuccessful. Addition of t-butylchloride to the reaction mixture after an initial period of reflux, although appearing to proceed exothermically (perhaps dilution or other solvent effect) gave no overall change in the ratios of products as determined by the classical methods then employed, and no digermane. The mixture was not re-examined by V.P.C.

1.3.2. The system iso-propylmagnesium chloride-germanium tetrachloride in diethyl ether/benzene.

Previous work with isopropyl Grignard reagents and germanium tetrachloride had employed the organomagnesium bromide, and only three products, Pr^i_3GeOH, $(Pr^i_2GeO)_3$, and $(Pr^iGe)_n$, were characterised after alkaline hydrolysis of mild condition reactions. Later the presence of Pr^i_3GeH in this system was detected (see p.26). The present experiments were performed (i) with an excess of Grignard reagent containing the excess magnesium from its preparation, largely as finely divided sludge (ii) with excess Grignard from which the bulk magnesium had been filtered and (iii) with excess Grignard containing excess magnesium, and subsequent addition of lithium aluminium hydride. A separate Wurtz-Fittig type synthesis of hexaisopropyldigermane from tri-isopropylchlorogermane and sodium-potassium alloy was also studied.

The major proportion of the reaction product from each of the Grignard reactions was volatile, only 7-16% of involatile polymeric material, closely similar to the major product of the GeI_4-Pr^iMgBr reaction, being formed. Separation, analysis and characterisation of the components of these complex volatile mixtures was achieved by vapour phase chromatographic techniques (see p.186) and products from supporting syntheses were also characterised in this way. Extensive use was made of mass spectrometry to establish the exact elemental composition of some components; this is discussed more fully

Table 1

Vapour-phase chromatography[a] of reaction products

Component	Retention time (min.)[b]	Approximate % (relative area)[e] A	B	C	D	
1	1.58	2	$\sim\frac{3}{4}$	2	-	Isopropylbenzene
2	1.59		$\sim\frac{3}{4}$		-	n-Propylbenzene
3	2.12	10	35	39	d	$\mathrm{Pr}^{i}_{3}\mathrm{GeH}$
4	4.65	<1	<1	<1	16	$\mathrm{Pr}^{i}_{3}\mathrm{GeOH}$
5	5.65	47	31	8	3	$\mathrm{Pr}^{i}_{3}\mathrm{GeCl}$
6	6.75	12	4	10	3	$\mathrm{Pr}^{i}_{3}\mathrm{GePr}^{n}$
7	7.80	5	20	15	5	$\mathrm{Pr}^{i}_{4}\mathrm{Ge}$
	8-11	1	<1	<1	4	c, 3 peaks
	11.7	-	-	<1	8	c
	13.2	-	-	1	7	c
8	14.0	d	d	3	24	$(\mathrm{HPr}^{i}_{2}\mathrm{Ge})_2$
9	21.6	d	d	d	2	$\mathrm{Pr}^{i}_{6}\mathrm{Ge}_2$
10	26.6	d	d	d	7	$(\mathrm{Pr}^{i}_{3}\mathrm{Ge})_2\mathrm{O}$
11	42.0	6	<1	-	-	$(\mathrm{Pr}^{i}_{2}\mathrm{GeO})_3$
	32-39, 45-51	3	<1	-	-	c, oxides
12	56.9	<1	<1	4	-	$\mathrm{Pr}^{i}_{8}\mathrm{Ge}_4$
13	65.0	7	<1	-	-	$(\mathrm{Pr}^{i}_{2}\mathrm{GeO})_4$
Involatile residue		7	7	16	-	Polymeric oxides

A. From hydrolysis of $\mathrm{GeCl}_4 + \mathrm{Pr}^{i}\mathrm{MgCl}$ (b.p. up to $100^{\circ}/10^{-6}$ mm.).

B. From hydrolysis of $\mathrm{GeCl}_4 + \mathrm{Pr}^{i}\mathrm{MgCl} + \mathrm{Mg}$ (b.p. up to $100^{\circ}/10^{-6}$ mm.).

C. From hydrolysis of $\mathrm{GeCl}_4 + \mathrm{Pr}^{i}\mathrm{MgCl} + \mathrm{Mg} + \mathrm{LiAlH}_4$ (b.p. up to $70^{\circ}/10^{-5}$ mm.).

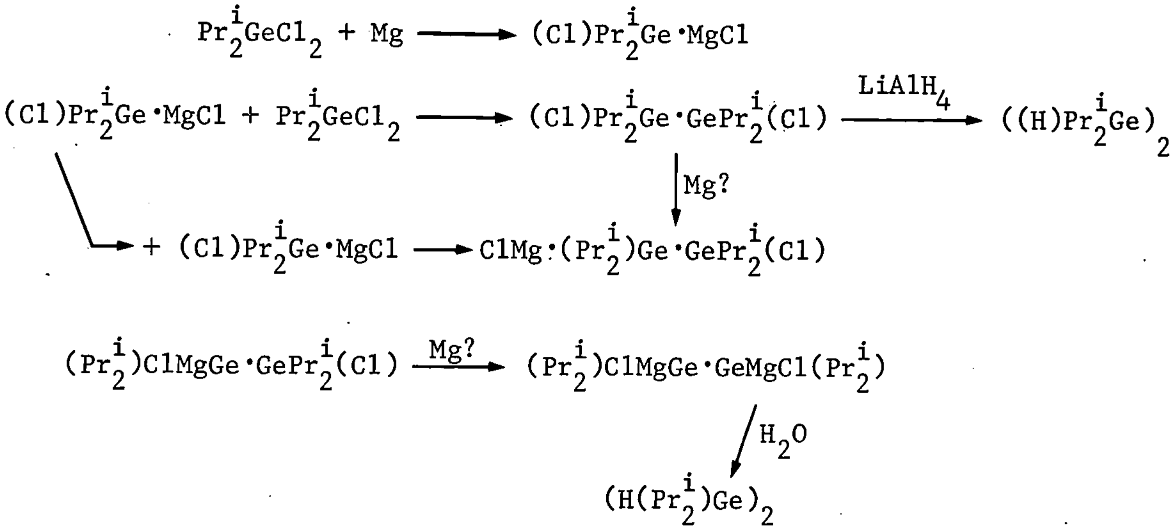
D. From $\mathrm{Pr}^{i}_{3}\mathrm{GeCl}$ + Na/K in toluene. Liquid product after filtration from $\mathrm{Pr}^{i}_{6}\mathrm{Ge}_2$ (b.p. up to $110^{\circ}/10^{-5}$ mm.).

[a] Pye 104, dual columns (5 ft., 4 mm. i.d.), dual flame ionisation detectors and Kent "Chromalog" integrator. Stationary phase 10% Apiezon L on 100-120 mesh Celite. N_2 carrier, flow 50 ml./min., temp. 160° for 12 min., 24°/min. rise to 200°. [b] Measured from injection as zero. [c] Unidentified. [d] Present, but not measured. [e] Areas measured on isothermal runs.

in part 3 (pp. 128-132)

Both filtered and unfiltered Grignard solutions, after hydrolysis (avoiding halogen acids) and work up by ether extraction and preliminary distillation, gave tri-isopropylgermane, (10-35%), the higher yield and more rapid rate of production from the reaction containing excess magnesium. Again coloured Grignard solutions were obtained after filtration and so these also probably contained some free magnesium. Nine other major components were detected which boiled between room temperature and 100° at 10^{-6}mm, and a total of 21 distinct peaks were seen in the chromatogram, although half of these were minor constituents representing 2-3% of the total product (table 1, columns A and B). In contrast to the previous system ($Pr^{i}MgBr$ —— GeI_4), the monohalide was present in large amounts at the end of the reaction; in the filtered Grignard experiments (A), it was the major product. Some small amount of hydrolysis occurred during work-up to give the corresponding germanol and digermoxane (components 4 and 10). The high recovery of this material indicates not only its low reactivity but also the fulfilment of one favourable condition for the production of the digermane. Again the dihalide (di-isopropyldichlorogermane) was not detected, only the tri- and tetrameric oxides derived from it by hydrolysis and dehydration (components 11 and 13). The dihalide almost certainly plays some part in polymer formation too. No material corresponding to the dimeric oxide mentioned above (1.3.1) was characterised.

Two of the components isolated provide further support for the idea that a germanium-magnesium bond can form in other than the last stage of the reaction. In this system evidence for the organogermyl Grignard derived from di-isopropyldichlorogermane, $ClPr^{i}_{2}Ge{\cdot}MgCl$, is provided by 1,1,2,2-tetra-isopropyldigermane (component 8), and octa-isopropylcyclotetragermane (component 12). The former compound was found in greatest proportion after lithium aluminium hydride reduction of the crude reaction mixture (table 1, column C, see also below) and is a major product from the Wurtz reaction discussed later. Reactions leading to its formation can be written



$$Pr^i_2GeCl_2 + Mg \longrightarrow (Cl)Pr^i_2Ge{\cdot}MgCl$$

$$(Cl)Pr^i_2Ge{\cdot}MgCl + Pr^i_2GeCl_2 \longrightarrow (Cl)Pr^i_2Ge{\cdot}GePr^i_2(Cl) \xrightarrow{LiAlH_4} ((H)Pr^i_2Ge)_2$$

$$(Cl)Pr^i_2Ge{\cdot}GePr^i_2(Cl) \xrightarrow{Mg?} ClMg{:}(Pr^i_2)Ge{\cdot}GePr^i_2(Cl)$$

$$+ (Cl)Pr^i_2Ge{\cdot}MgCl \longrightarrow ClMg{:}(Pr^i_2)Ge{\cdot}GePr^i_2(Cl)$$

$$(Pr^i_2)ClMgGe{\cdot}GePr^i_2(Cl) \xrightarrow{Mg?} (Pr^i_2)ClMgGe{\cdot}GeMgCl(Pr^i_2) \xrightarrow{H_2O} (H(Pr^i_2)Ge)_2$$

Comparison of the Ge-H stretching frequency of this material and the polymeric material containing Ge-H bonds from the Pr^iMgBr - GeI_4 experiments, 1966 and 1961 cm^{-1} respectively, again lends support to the presence of Pr^i_2GeH structures in the polymer and so at least some formation of germanium - magnesium bonds at a similar stage in the Pr^iMgBr-GeI_4 reaction. Octa-isopropylcyclotetragermane $(Pr^i_2Ge)_4$, was characterised by mass spectrometry and again could be derived from the germyl-Grignard intermediate $(Cl)Pr^i_2Ge{\cdot}MgCl$.

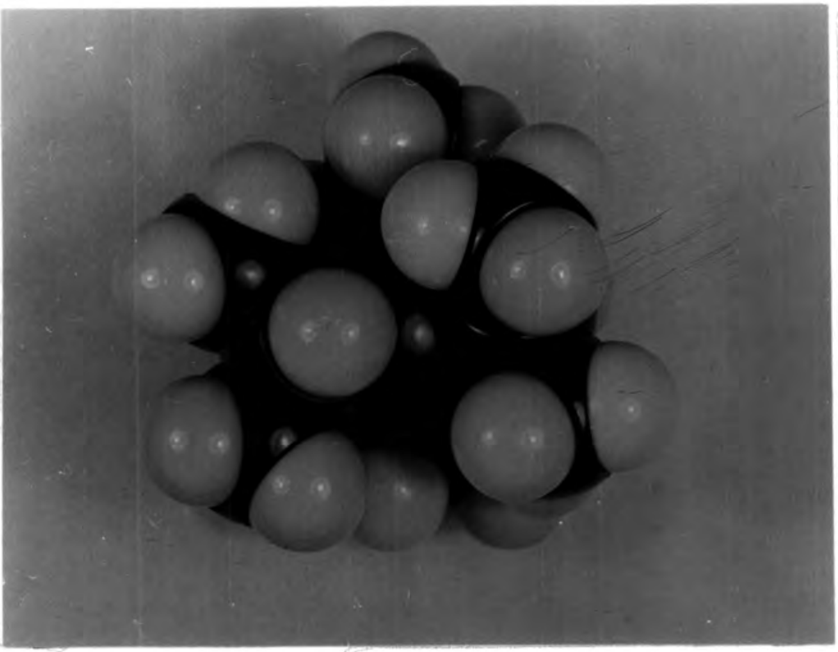
Components 6 and 7, tri-isopropyl-n-propylgermane and tetra-isopropyl germane respectively, were isolated by preparative scale V.P.C. and characterised beyond doubt as $C_{12}H_{28}Ge$ by high resolution mass measurements on their molecular ions. The identity of component 6 was established by synthesis of tri-isopropyl-n-propylgermane from tri-isopropylchlorogermane and n-propylmagnesium chloride, (note, in passing, that this Grignard reagent substitutes the final halogen of Pr^i_2GeCl relatively easily) and V.P.C. comparison of the two materials. The production of relatively large amounts of this compound suggests that some Grignard isomerisation takes place since the isopropylchloride used in the initial preparation of the Grignard reagent contained a maximum of 0.3 mole% of n-propylchloride, which could not account for the proportion of n-propyl groups recovered, even allowing for the tenfold excess of reagent used (10 fold excess for monosubstitution). Grignard reagent isomerisation catalysed by transition-metal halides is well known, and impurities in the magnesium (notably iron) may have been sufficient to effect the observed conversion. Alternatively, an equilibrium concentration of hydromagnesium halide could be involved,

$$xPr^iMgCl \rightleftharpoons [HMgX]_x + xC_3H_6 \rightleftharpoons xPr^nMgCl$$

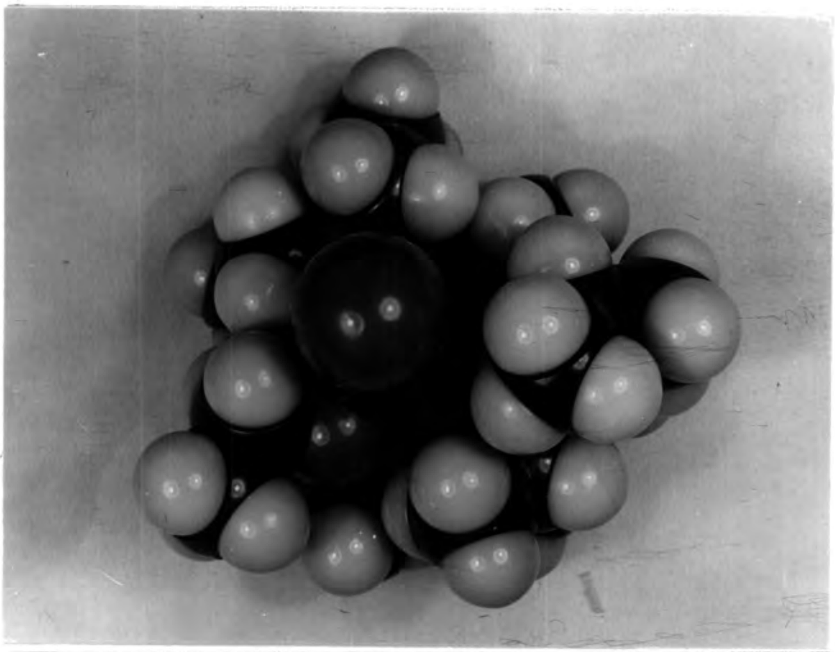
More likely the complex exchange equilibria which normally obtain in Grignard solutions (see p. 17) are involved in some way - this is borne out by the reduction in amount of tri-isopropyl-n-propylgermane recovered in the presence of excess magnesium; addition of more impurities from larger amounts of metal would be expected to favour increased production of this material; also the reduced reflux time and consequent lower tendency for loss of free C_3H_6 from the hydromagnesium equilibrium ought to favour an increase rather than decrease in isomerisation.

The formation isopropyl- and n-propyl-benzene does not necessarily imply the presence of transition-metal impurity having Friedel-Crafts activity, as it has been established that alkylation of aromatic-substrates by Grignard reagents does occur under certain conditions to give Friedel-Crafts type products, and that the reaction is catalysed by an active (nascent) form of

PLATE 2



Pl.2.1 Tetra-isopropylgermane



Pl.2.2 Tri-isopropylgermyl magnesium chloride di-ethyl etherate, monomeric form. Note the angular Ge-Mg-Cl skeleton and the "hemisphere" of organic groups round the germanium atom.

magnesium halide, the chloride being particularly active in this respect. Magnesium chloride is, of course, produced in bulk on reaction with germanium tetrachloride. Heating the magnesium chloride has been shown to reduce its activity as catalyst greatly, and hence alkylation reactions of this type are minimised by higher reaction temperatures. Control experiments in the present work showed that isopropyl- and n-propyl-benzene were produced in almost equal amounts when isopropylmagnesium chloride containing excess magnesium was refluxed with benzene for ten days. Here magnesium chloride could be produced in Wurtz type side reactions. A second batch of Grignard reagent under similar conditions contained not more than 5% of free n-propylmagnesium chloride (based on iodination of the solution and estimation of the isomeric propyl iodides by V.P.C.). The relatively high conversion of the small yet significant proportion of n-propylmagnesium chloride into tri-isopropyl-n-propylgermane clearly reflects the considerably lower steric requirement of the n-propyl group in comparison to that of the isopropyl radical during the course of the conversion.

The identity of component 7, tetra-isopropylgermane (pl. 2.1) was at first regarded with uncertainty in the light of the production of n-propyl substituted compounds, as it could have been any one of the four remaining isomeric tetrapropylgermanes. Three of these isomers (I, II, III) were accordingly synthesised for infrared and V.P.C. comparison studies. The routes employed may be summarised thus

$$GeCl_4 \xrightarrow{Pr^nMgBr} \underset{I.}{Pr_4^nGe} \xrightarrow{Br_2} Pr_3^nGeBr \xrightarrow{Pr^iMgBr} \underset{II.}{Pr_3^nGePr^i}$$

Table 2

Retention volumes of tetrapropylgermanes

	Relative retention volumes (V)*	
	Column A	Column B
Pr^n_4Ge	11.38	5.83
$Pr^n_3GePr^i$	11.53	5.63
$Pr^n_2GePr^i_2$	12.03	5.68
$Pr^nGePr^i_3$	13.36	6.50
Pr^i_4Ge	16.31	7.52

*$V = \dfrac{\text{retention time } Pr_4Ge}{\text{retention time } C_6H_6}$ referred to injection as zero

All values are the means of 5 injections.

Column A: 5 ft., 4 mm., 10% Apiezon L on 100-120 mesh Celite at 150° using 50 ml./min. N_2carrier at an initial column pressure of 20 lb./in. Flame ionisation detector.

Column B: 5 ft., 4 mm., 5% neopentyl glycol adipate on 100-120 mesh Celite at 110°. Flow,pressure and detector as for column A.

$$Ph_6Ge_2 \xrightarrow{Br_2} Ph_2GeBr_2 \xrightarrow{Pr^nMgBr} Ph_2GePr^n_2 \xrightarrow{Br_2} Pr^n_2GeBr_2 \longrightarrow Pr^n_2GePr^i_2$$

III.

Attempted dibromination of tetra-n-propylgermane gave only the monobromide and polybromo- derivatives, including $(C_3H_6Br)_4Ge$, even in the presence of aluminium bromide, and three attempts at the symmetrical redistibution reaction of equimolar amounts of tetra-n-propylgermane and germanium tetrachloride in the presence of aluminium trichloride failed to yield significant amounts of the dihalide and only the trisubstituted monohalide was produced at temperatures ranging from 150°-220° in sealed tubes (see 1.2.3.). All three isomers (I-III) showed different infrared spectra and retention volumes from components 6 and 7 and the latter was accordingly designated as tetra-isopropylgermane. The most striking feature of the retention volumes observed for the five tetrapropylgermanes on both polar (neopentyl glycol adipate) and non-polar (Apiezon L) columns is the increasing difference with successive substitution of isopropyl groups and the very large change between $Pr^i_3GePr^n$ and Pr^i_4Ge (table 2).

Addition of lithium aluminium hydride to the refluxing reaction in an attempt to reduce the range of products formed, produced some interesting variations in their proportions but the only significant removal was that of the higher oxides normally produced by hydrolysis of the dihalides. Clearly not all the Ge-Cl groups were reduced under the conditions employed and although 40% of tri-isopropylgermane, the expected major product, was recovered 8% of free tri-isopropylchlorogermane remained (table 1, column C) Relatively large amounts of tri-isopropyl-n-propylgermane were again isolated, an increased amount of the dihydrodigermane, and almost twice as much polymeric material. All these facts indicate a more active role for the $LiAlH_4$ than merely that of a reducing agent, but by this time the reaction mixture has become so complex that scarcely anything other than this can be said about it. These points, particularly the increased amount of polymer strongly suggest the formation of germanium-metal bonds other than in the germanium-magnesium intermediates.

The coupling reaction to yield digermane from the germyl Grignard occurred to only a very small extent (probably about 1%), despite the favourable conditions again, and the presence of hexa-isopropyldigermane was noted to about this extent in all three Grignard reactions. This compound was synthesised in good yield from tri-isopropylchlorogermane and a 1:1 sodium-potassium alloy in refluxing toluene. The composition of the liquid product from the reaction, after hydrolysis, extraction, distillation and filtration from the crystalline digermane, is given in table 1, column D. The digermane is a colourless, well crystalline solid, subliming at 125° at atmospheric pressure(MPt 235°-240° sealed tube) and showing a single strong absorption band at 209.5mμ. This Wurtz reaction producing the digermane is interesting in its co-production of tri-isopropylgermane and large amounts of tetraisopropyldigermane, which implies that in refluxing toluene, isopropyl groups are cleaved by the alkali metals in preference to the germanium-germanium bond

$$\begin{tikzcd}
\mathrm{Pr}^{i}_{3}\mathrm{GeCl} + \mathrm{Na/K} \arrow[r] & \mathrm{Pr}^{i}_{6}\mathrm{Ge}_{2} + & \mathrm{Pr}^{i}_{3}\mathrm{GeK} + \arrow[d, "H_2O"] & (\mathrm{KPr}^{i}_{2}\mathrm{Ge})_{2} \arrow[d, "H_2O"] \\
 & & \mathrm{Pr}^{i}_{3}\mathrm{GeH} & (\mathrm{HPr}^{i}_{2}\mathrm{Ge})_{2}
\end{tikzcd}$$

The small amount of tri-isopropylgermane recovered indicates that formation of the germyl-alkali metal compound is relatively slow (a significant amount of unreacted Pr^i_3GeCl was recovered; also Pr^i_3GeOH presumably from hydrolysis of this halide under strongly basic conditions during work-up), and that, once formed, its conversion to digermane is relatively rapid. This contrasts with the Grignard experiments where the formation of the necessary germanium-magnesium intermediate is more rapid than its conversion to the digermane. A separate experiment established that the germanium-germanium bond of hexa-isopropyldigermane is resistant to cleavage by lithium metal in refluxing 1,2-dimethoxyethane.

The polymeric material produced in each Grignard experiment (including that involving lithium aluminium hydride) was similar to the polymer formed in the Pr^iMgBr-GeI_4 reaction, and partial separation into distinct fractions could be achieved by precipitation from mixed solvents. Each fraction showed strong Ge-O absorption in the infrared, but no Ge-H bands were detected. Molecular weight measurements again indicated a range of 2000-4000 and analytical data a mean isopropyl to germanium ratio of between one and two.

In conclusion, the following points emerge: (i) both hexa-isopropyldigermane and tetra-isopropylgermane are capable of existence and are very stable compounds, and so steric interactions between the isopropyl groups in these materials cannot be very great. Interaction is certainly not great enough to render them significantly more unstable than the non-hindered organogermanes, and this is further supported by the preferential cleavage of the Ge-C bonds, rather than the Ge-Ge bond, of the digermane by alkali metals.

(ii) Despite the fulfillment of the conditions which are normally quoted as being favourable for the production of digermane in a Grignard reaction, viz. survival of R_3GeX in the presence of R_3GeMgX, very little digermane is produced in either of the systems examined.

(iii) Formation of germanium-magnesium bonds can occur at the disubstituted stage (from R_2GeX_2) and possibly earlier.

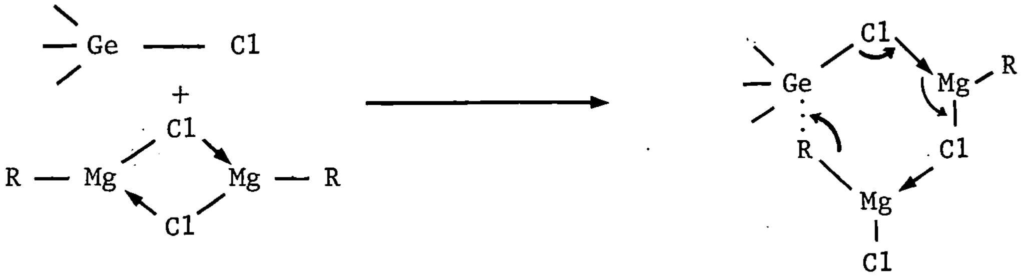
(iv) Formation of germanium-magnesium intermediates is faster in the presence of free metallic magnesium; also, more Pr^i_4Ge is produced from the reaction containing excess magnesium.

(v) Polymer production indicates the survival of at least a dihalide or dihalide-metallic derivative, and probably a trihalide too. (Cyclic oxide formation confirms the presence of dihalides at the hydrolysis stage).

(vi) Slow isomerisation of the Grignard occurs, both when heated alone and during the reaction.

(vii) Little or no Pr^i_4Ge is produced in the $Pr^iMgBr-GeI_4$ system.

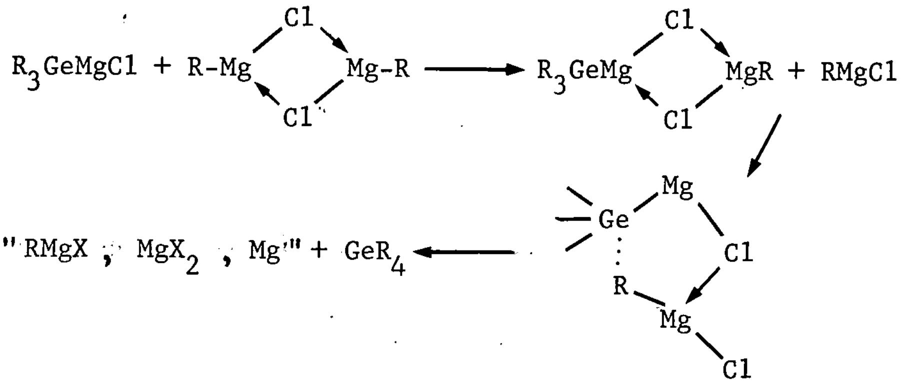
This latter point is perhaps the most striking from the point of view of a possible reaction scheme. The alkyl magnesium bromides are known to be largely monomeric in diethyl ether, whereas the corresponding chlorides exist as dimers in similar solutions. Even at the relatively high concentrations ($\simeq 1$ mole/litre) of "RMgX" employed this can be taken to be essentially the situation, especially as the chloride was used in ether/benzene solution. As the final alkylation stage only took place with the alkyl magnesium chloride, cyclic intermediates involving a dimeric Grignard immediately spring to mind for this transfer



(I)

This type of intermediate, although probably attractive for the early stages of alkylation does not account for the increased substitution of the final halogen in the presence of free magnesium. In this case five membered rings, derived from a germyl Grignard - alkyl magnesium halide dimer, could provide a closer, less cluttered approach to the "underside" of the germanium atom for the alkyl group

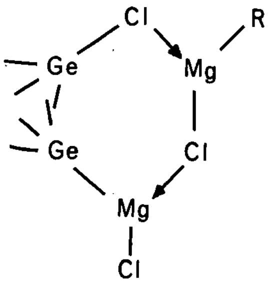
$$R_3GeCl + Mg \longrightarrow R_3GeMgCl$$



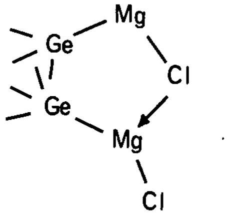
(II)

Whether these intermediates play any part in the reaction or not, it seems extremely likely that the nature of the halogen present, from the point of view of its bridging ability, is a major consideration, and that conditions which favour Grignard dimerisation (i.e. halogen bridging) also favour production of Pr^i_4Ge. The isomerisation observed can also be interpreted in favour of cyclic transition states such as I and II as it is well known that the n-propyl group has much better bridging capabilities than the isopropyl group. Conversion from iso- to n-propyl under the bridging conditions of both I and II, involving shift of just one hydrogen atom, would seem to be possible if not favourable. In the experiments "without" magnesium (type I intermediates predominantly?) high conversion to $Pr^i_3GePr^n$ (on the final stage of substitution?) is in line with this explanation. Isomerisation in the Grignard alone could take place during the (similar) rapid transfer processes of groups between magnesium atoms, a small proportion of which lead to the production of the better bridging group. If this is so then isomerisation should proceed steadily in increasing amount rather than being an equilibrium process.

In the production of the digermane, both type I and type II intermediates (from R_3GeCl + $R_3GeMgCl$, and $R_3GeMgCl$ dimer respectively) would surely encounter grave hindrance, both the alkyl "sides" of the germanium fragments "facing" each other,



Ia.



IIa

and one is led to postulate a simple Wurtz type coupling of R_3GeCl and monomeric R_3GeMgX, where hindrance to close approach of the germanium atoms after co-ordination of the chlorine to the magnesium is perhaps not as great. This is in line with the production of the hindered (o-tolyl)$_6$Ge$_2$ from the o-tolyl-MgBr reagent in the presence of magnesium, but not with the $Pr^{i}MgBr$-GeI_4 results. Perhaps the extreme size of the iodine atom has some controlling effect here (the tetrahedral Mg atom is in a very hindered environment in $Pr^{i}_3GeMgX.2Et_2O$, see pl.2). Clearly more work is required to put these hypotheses on a sounder footing. Kinetic experiments, to establish rate of Pr^{i}_4Ge production with respect to Grignard, could be reasonably straightforward using V.P.C. techniques for analysis, and so could experiments to check the dependence of digermane production on halogen and degree of association of Grignard reagent. In any event, it seems extremely likely that further examination of the system Pr^iMgX-GeX_4-ethers could provide much more very valuable information on the nature and modes of reaction of Grignard reagents as a whole.

1.3.3. Infrared Spectra

The main spectroscopic problem has been distinguishing n-propyl- from isopropyl-germanes. All the isopropylgermanes examined showed a doublet with peaks of roughly equal, medium intensity in the ranges 1387-1380 and 1370-1360 cm^{-1} which is absent from the spectra of n-propylgermanes, although not easily distinguished in $Pr^n_3GePr^i$. A sharp, medium intensity band at 879-877 cm^{-1} was also present in isopropyl- and absent in n-propyl-germanes. Considerably more bands enable n-propyl- to be distinguished from isopropyl-germanes. These occur at 1420-1416m, 1375-1373m, 1333-1326m, 1072-1069s, 725-714m, 692-677s, 642-635m cm^{-1}. In diphenyldi-n-propylgermane the last three bands were insufficiently clear for diagnostic purposes, whilst in tri-n-propylbromogermane the band at 643 cm^{-1} was extremely weak and the 725-714 band was shifted to 731 cm^{-1}. It is probable, by analogy with the spectra of n-butylgermanes, that the 642-635 band is associated with the trans conformation of the n-propyl group.

Differences in the carbon-hydrogen stretching region (2960-2862 cm^{-1}) were also of some use in differentiating between the isomeric propylgermanes. Tetra-n-propylgermane showed four bands (2955s, 2925s, 2898m,sh, 2863m), whilst in $Pr^n_3GePr^i$ and $Pr^n_2GePr^i_2$ an additional band at 2940 cm^{-1} was just discernible. In both $\mathrm{Pr}^i_4\mathrm{Ge}$ and $\mathrm{Pr}^i_3\mathrm{GePr}^n$ this band was strong and clearly defined at 2938 cm^{-1}. The 2955 band was constant throughout the series of isomers except for $\mathrm{Pr}^i_4\mathrm{Ge}$ where it appeared at 2960 cm^{-1}. The 2925 band, which was strong and well defined in $\mathrm{Pr}^n_4\mathrm{Ge}$, $\mathrm{Pr}^n_3\mathrm{GePr}^i$ and $\mathrm{Pr}^n_2\mathrm{GePh}_2$, was weaker in $\mathrm{Pr}^n_2\mathrm{GePr}^i_2$ and appeared as a shoulder at 2817 cm^{-1} in the other two isomers. The 2898 band in $\mathrm{Pr}^n_4\mathrm{Ge}$ was shifted to 2885-2883 cm^{-1} in the other two isomers and was intensified. The 2863 band, which was relatively weak in $\mathrm{Pr}^n_4\mathrm{Ge}$ intensified progressively as isopropyl groups were substituted for n-propyl, until in $\mathrm{Pr}^i_4\mathrm{Ge}$ it was the strongest of the CH absorptions.

Medial values for the infrared bands common to all the isopropylgermanes examined (other than CH stretching vibrations) are as follows: 1463m, 1383m, 1368m, 1224m-s, 1156w, 1080w, 1010m, 1000m, 917w-m, 877m-s, 804w-s cm^{-1}. The band at 1224 cm^{-1} was shifted to 1256 in the cyclic oxides $(\mathrm{Pr}^i_2\mathrm{GeO})_{3\text{ and }4}$ and in the digermane $(\mathrm{Pr}^i_2\mathrm{GeH})_2$. Additional bands present in individual compounds are listed below, together with some probable assignments

$\mathrm{Pr}^i_3\mathrm{GeH}$	1998s(νGeH), 710(δGeH), 565m(ν asym., GeC), 556sh,m(ν sym.,GeC), 522w, 420s, 313s, 239w.
$\mathrm{Pr}^i_3\mathrm{GeD}$	1433s(νGeD), 564(ν asym., GeC), 542(ν sym., GeC), 508s(δGeD), 420s, 311s.
$\mathrm{Pr}^i_3\mathrm{GeCl}$	1025m, 562s(ν asym.,GeC), 521w(ν sym., GeC), 419m, 370s(νGeCl), 323w.
$\mathrm{Pr}^i_4\mathrm{Ge}$	559m(ν asym.,GeC), 549m.
$\mathrm{Pr}^i_6\mathrm{Ge}_2$	992sh,m, 543s(ν asym.,GeC), 536m(ν sym., GeC), 505w, 415s, 318m, 304m.
$(\mathrm{Pr}^i_2\mathrm{GeH})_2$	1966(νGeH), 971s, 799s(δGeH), 709w, 685m, 540(νGeC).

$(Pr^i_2GeO)_3$ 976m, 952s, 844s(νGeO), 583m(νGeC).

$(Pr^i_2GeO)_4$ 975m, 956s, 844s(νGeO), 583m(νGeC), 552m.

Tetra-n-propylgermane had absorption bands at 1460s, 1420m, 1375m, 1330m, 1214w, 1196w, 1070s, 1028w, 1004m, 888w, 805w, 725m, 692s, 639 (νGeC trans), 567m(ν asym., GeC), 552w(ν sym., GeC), 321m. The mixed n-propyl-isopropylgermanes showed the expected bands with some overlapping, and only the germanium-carbon stretching frequencies are given below.

$Pr^n_3GePr^i$ 642m(νGeC trans), 560w, 344w(νGeC, including νGeC gauche for Pr^nGe).

$Pr^n_2GePr^i_2$ 642m, 555m, 544m.

$Pr^nGePr^i_3$ 636m, 555m, 521w.

Mass Spectra of compounds from this work, including the isomeric tetrapropylgermanes, hexaisopropyldigermane, and the trimeric and tetrameric cyclic oxides are discussed in part 3.

1.4 EXPERIMENTAL

For details of V.P.C. and other experimental techniques, see appendix.

1.4.1. (a) Germanium (IV) Iodide and Isopropylmagnesium Bromide. Germanium (IV) iodide (27.5 gm., 47 mmole) was added cautiously (as solid) to 500 ml. of clear green ethereal solution of isopropylmagnesium bromide, being half of a solution resulting from the reaction of 123 gm. of isopropylbromide and 26 gm. of magnesium in 1 litre of diethyl ether which had been filtered through a No.4 sinter. The mixture was heated under reflux for 16.1/4 hours and yielded, after hydrolysis using first water then dilute acid, extraction of the ethereal layer, and removal of the ether, 8.32 gm. of a yellow viscous liquid. This material distilled in vacuo (10^{-3}mm) with receivers cooled to -35° gave three major fractions. The first distilling below 60°C 1.02gm, $Pr^{i}_{3}GeH$, had b.p. $176^{\circ}/740$ mm (lit 176°). Its ^{1}H n.m.r. spectrum (tetramethylsilane as standard) showed GeH at τ 6.36 and the methyl proton doublets at τ 8.8 with the CH multiplets overlapping these on the low field side. The germanium-hydrogen to alkyl-hydrogen ratio was 1:23.7. The remainder of the volatile material, a colourless very viscous liquid distilling between 60° and 220°C, 2.46 gm, yielded on redistillation at atmospheric pressure in a "micro-cup" apparatus, at 200° a centre cut showing one major GeO band in the infrared (844s, 826sh cm^{-1}). Elemental analysis (found C, 36.3; H, 6.89%) gave no clear indication of constitution ($(Pr^{i}_{2}GeO)_{n}$ requires C 41.5, H 8.1%; $((Pr^{i}GeO)_{2}O)_{n}$ requires C 25.4, H 5.03%), and a later brief examination by V.P.C. showed the material as a mixture of at least four compounds, probably containing $(Pr^{i}_{2}GeO)_{3}$ and $(Pr^{i}_{2}GeO)_{4}$. The residue from the initial distillation, 4.86 gm. of a yellow solid, was taken up in 15 ml. of benzene (in which it was easily though slowly soluble) and chromatographed on a 35 x 2.5 cm. alumina column using 250 ml. portions of 1:1 benzene-40°-60° petroleum ether; benzene, 1:1 benzene-ethanol; ethanol; acetone and chloroform for elution. The infrared spectra of fractions eluted (0.52 gm. of a yellow viscous liquid with the first solvent, 0.07 gm. of a clear viscous liquid with benzene, insignificant amounts for the others except benzene-ethanol) showed the features expected for polymeric oxide, with slight qualitative differences in intensities of bands between fractions, but that of the material eluted with benzene-ethanol (1.47 gm. markedly yellow viscous liquid) contained in addition bands at1961w-m(νGe-H), 734m(δGe-H?), 697m, 678s, 673m,sh, cm^{-1}. Analysis of this material gave C 34.2, H 6.26% ($(Pr^{i}Ge)_{n}$ requires C 31.2, H 6.1% and see values for oxides above). The rest of the polymer was strongly retained on the alumina of the column, some 50-60% of this residue being removed by Soxhelet extraction with chloroform over 5 days.

(b) A similar experiment using (24.2 gm. 41.5 m mole) of GeI_4 and 500 ml. (approx. 0.5 mole) of an ethereal solution of isopropylmagnesium bromide which contained the residual magnesium from the preparation of the Grignard described above gave after stirring for 46 hours at room temperature and 4.3/4 hours at reflux temperature, hydrolysis, extraction and distillation, 6.75 gm. of yellow viscous liquid. This was separated into 2.13 gm. Pr^i_3GeH, characterised by infrared comparison with material from above experiment; 1.40 gm. of mixed oxides distilling in the range 175^o-220^o at 10^{-2}mm, C 37.7% H 7.3%, average molecular weight 710, a degree of association for Pr^i_2GeO of 4.06; and 3.22 gm. of involatile yellow solid, which was chromatographed in the manner described yielding 0.53 gm. from 1:1 benzene-petroleum containing Ge-H bands as above, no significant amount with benzene, 0.57 gm. with benzene-ethanol and 0.18 gm. with ethanol whose infrared spectra corresponded with the equivalent fractions from the previous experiment. 1.94 gm. of material remained on the column and extraction with chloroform removed 1.03 gm. (yellow) viscous liquid, qualitatively different infrared spectrum from the other fractions).

(c) A further experiment with excess magnesium present, hydrolysed with 8 ml. (0.44 mole, 100% excess) D_2O, followed by decantation of the ethereal layer, which was then washed quickly with water, dried and carefully distilled, gave 0.9 gm. Pr^i_3GeD (found C 51.4, H 10.8%, $C_9H_{21}DGe$ requires C 53.02, H 10.8%), with infrared spectrum as recorded above. 1.53 gm. of mixed oxides, and 4.96 gm. of involatile yellow polymer were recovered.

(d) Germanium (IV) Iodide, Isopropylmagnesium Bromide, and excess Magnesium, with the addition of t-Butyl Chloride. - 29.0 gm. (50 m mole) of GeI_4 and 250 ml. (approx. 0.25 mole) of isopropylmagnesium bromide containing excess magnesium (10%) were refluxed for 24 hrs., 13.89 gm. (0.15 mole) of Bu^tCl were added and reflux continued for a further 48 hours. Work up as above gave 9.58 gm. of yellow viscous material which on distillation gave 0.83 gm. Pr^i_3GeH, 0.12 gm. mixture of Pr^i_3GeH and Pr^i_3GeCl, 0.17 gm. Pr^i_3GeCl, and approximately 1.5 gm. of the less volatile distillate. The remaining material was not examined.

1.4.2. (a) Germanium (IV) Chloride and Isopropylmagnesium Chloride. - Germanium (IV) chloride (15 gm.·07mole) in benzene (150 ml.) was added slowly to a filtered ethereal solution of isopropylmagnesium chloride, prepared from isopropyl chloride (39.3 gm.) and magnesium (13 gm.) in ether (300 ml.). Hydrolysis after 66 hr. under reflux followed by ether extraction, and distillation gave a pale yellow liquid (12.8 gm.). Removal of traces of solvent from this material in vacuo via a trap cooled to -23^{o}, gave in this trap a colourless condensate (1.33 gm.) containing components 1-7 (Table 1, column A). The yellow liquid separated into the following fractions: b.p. $50-80^{o}/10^{-4}$mm (2.8 gm.) (components 1-7); b.p. $80-95^{o}/10^{-4}$mm (5.1 gm.) (components 3-7); b.p. $95-100^{o}/10^{-5}$mm (1.31 gm.) (components 3-12); b.p. $95-100^{o}/10^{-6}$mm (1.3 gm.) (components 8-13). Samples of the major components were isolated by preparative scale V.P.C.

Component 3, Pr^i_3GeH had b.pt. 176^{o} and infrared spectrum as the material from 1.4.1. Components 4 and 5 were characterised by comparison of their infrared spectra and retention times with authentic specimens. Component 6 tri-isopropyl-n-propylgermane, a colourless air stable liquid (found: C, 59.0;

H, 11.8; $C_{12}H_{28}Ge$ requires C, 58.8; H, 11.4%) and component 7, tetraisopropylgermane were characterised as described in the text. Component 11, trimeric di-isopropylgermanium oxide, was a colourless liquid (found: C, 41.0; H, 8.1%, M (mass spectrum) 524 for $^{218}(Ge)_3$ Calc. for $C_{18}H_{42}Ge_3O_3$: C, 41.0; H, 8.1%; M, 524). Component 13 tetrameric di-isopropylgermanium oxide, was also a colourless liquid (found: C, 44.7; H, 9.0; $C_{24}H_{56}Ge_4O_4$ requires C, 41.0; H, 8.1%). The highest mass observed with certainty in its mass spectrum corresponded to loss of one isopropyl group ie.$Pr^i_7Ge_4O_4$, with the calculated Ge_4 isotope pattern. A very small ion set occurred in the region of the expected molecular ion but the isotope pattern was not distinct.

The dark yellow semi-solid residue from the distillation (0.86 gm.) was freely soluble in benzene (found: C, 34.2; H, 6.2%; M (vapour pressure osmometer) 2000-4000, varying with sample, age, and concentration). On long exposure to air the colour faded and viscosity diminished, but the material remained involatile. Both the original and "aged" polymers showed strong broad absorption centred on 833 cm^{-1} characteristic of ν(Ge-O) in polymeric oxides.

(b) A similar experiment in which an excess of magnesium was present throughout, gave after hydrolysis and work up as above, a volatile mixture (10.34 gm.) and an involatile residue of mixed polymeric oxides (0.8 gm.) V.P.C. of the volatile mixture showed products identical with those discussed but in different proportions (Table 1, column B).

1.4.3. Germanium (IV) Chloride, Isopropylmagnesium Chloride and Lithium Aluminium Hydride. - Germanium (IV) chloride (15 gm.) in benzene was added slowly to isopropylmagnesium chloride (0.5 mole) in ether (200 ml.) containing an excess of magnesium (10%). After 20 hr. under reflux lithium aluminium hydride (6.0 gm.) was added as a slurry in ether, and refluxing continued for a further 19 hr. Acid hydrolysis gave an ether soluble mixture (10.3 gm.) which was separated into three fractions: b.p. 175^{o}-$180^{o}/760$ mm (6.0 gm.) (components 1-7 of Table 1, column C); b.p. 40-$45^{o}/10^{-3}$mm (0.94 gm.) (components 3-7); b.p. 50-$70^{o}/10^{-5}$mm (3.34 gm) (components 3-10). Component 8, 1,1,2,2;tetra-isopropyldigermane, was a colourless liquid (found: C, 45.9; H, 9.1%; M, 320.0689. $C_{12}H_{30}Ge_2$ requires C, 44.2; H, 9.4%; M, 320.0778 for $^{146}Ge_2$). The identity of component 12, cyclo-octaisopropyltetragermane is based entirely on its mass spectrum which showed a well defined characteristic Ge_4 isotope pattern for the molecular ions of which masses 634 and 636 were the most abundant (found: M, 634.1243 and 636.1246, $C_{24}H_{56}Ge_4$ (i.e. $Pr^{i}_{8}Ge_4$) requires 634.1266 and 636.1255 for the two central peaks of the Ge_4 isotope combinations (see part 3). The orange semi-solid residue 1.67 gm. showed strong broad Ge-O absorption (810-890 cm^{-1}). The colour of this material faded and its viscosity diminished standing in air, but no volatile material was produced.

1.4.4. <u>Wurtz Reaction on Chlorotri-isopropylgermane</u>.- Chlorotri-isopropylgermane (4.7 g.) in toluene (150 ml.) was refluxed for 7 days with sodium (8 gm.) and potassium (8 gm.). The solution darkened progressively to a deep red. Hydrolysis, with propanol in benzene, and then with aqueous ethanol, discharged the colour, giving a liquid mixture (3.29 gm.) from which hexa-isopropyldigermane (0.5 gm.) separated as colourless needles. After recrystallisation from propan-2-ol and sublimation at $125^{o}/740$ mm, it had m.p. 235-240^{o} (sealed tube) (found: C, 53.0; H, 10.5%; M (v.p. osmometer) 407. $C_{18}H_{42}Ge_2$ requires C, 53.7; H, 10.7%, M, 403). It showed a single, sharp band at 209.5 mμ ($\log_{10}\epsilon$ 3.81). The mother-liquids contained components 3-10 (Table 1, column D)

1.4.5. Tri-n-propylisopropylgermane. - Bromotri-n-propylgermane (14.1 gm.) in ether (20 c.c.) was heated under reflux for 24 hr. with a filtered ethereal solution of isopropylmagnesium bromide, from isopropylbromide (8.8 gm.) and magnesium (2.0 gm.). Hydrolysis ether extraction and distillation gave tri-n-propylisopropylgermane, b.p. 227-228°/758 mm (8.0 gm. 65%) (found: M, 246.1405 for ^{74}Ge, $C_{12}H_{28}Ge$ requires M, 246.1403).

1.4.6. Di-n-propyldi-isopropylgermane. - Hexaphenyldigermane (20 gm.), bromine (16.5 gm.) and 1,2-dibromoethane were heated under reflux for 45 min. Distillation gave crude dibromodiphenylgermane, b.p. 80-120°/10^{-4}mm (9.1 gm.) which was heated under reflux for 15 hr. with an excess of n-propylmagnesium bromide, from magnesium (4 gm.) and n-propylbromide (16.2 gm.). Hydrolysis, ether extraction and distillation gave crude diphenyldi-n-propylgermane, b.p. 110-112°/10^{-2} mm (4.8 gm.) which without further purification (found: C, 24.9; H, 4.3%) was refluxed for 3 days with an excess of ethereal isopropylmagnesium bromide. Hydrolysis, extraction, distillation and V.P.C. separation of the main component on a 5% neopentyl glycol adipate-celite column gave di-n-propyldi-isopropylgermane (found: M, 246.1403 for ^{74}Ge, $C_{12}H_{28}Ge$ requires M, 246.1403).

1.4.7. Attempted Cleavage of Hexaisopropyldigermane. - Stirring hexisopropyldigermane (0.25 gm.) with lithium shot (1/2 gm.) as a paste in 0.3 ml. dry monoglyme gave no sign of colour after 36 hours. Addition of a further 10 ml. monoglyme and heating to reflux temperatures caused black specks to appear and after approximately 4 hours a faint yellow orange colour developed on the surface of the lithium. Continued reflux for a further 48 hours produced no further change. Hydrolysis and ether extraction yielded 0.37 gm. of a colourless viscous liquid which on removal of remaining solvent-traces gave 0.11 gm. of a white waxy solid with infrared spectrum similar to the polymers described above, and 0.09 gm. of unchanged digermane. V.P.C. examination of the viscous liquid showed no material of retention time below that of the digermane and only a very minor peak at a greater retention time. V.P.C. of the final solvent fraction showed the presence of trace quantities ($<0.5\%$) of tri-isopropylgermane.

PART 2

ORGANOGERMANIUM - TRANSITION METAL COMPLEXES

AT first sight the growth of interest in compounds containing metal-metal bonds over the last five years is remarkable. In the context of possible industrial applications as highly specific catalysts, their potentialities as synthetic intermediates in the laboratory, and their undoubted challenge to the bonding theorists, this interest is perhaps not so surprising. Indeed it seems that these compounds will soon occupy as prominent and useful a position in modern chemistry as the more familar materials containing metal-carbon bonds. Not very long ago, discrete compounds containing metal-metal-bonds were uncommon and considered exceptional; at the present time at least one example is known for every member of the d-block transition elements, and in some cases, especially the heavier metals in low formal oxidation states, the tendency to form these links becomes a governing factor in their chemistry.

Metal-metal interaction varies from weak coupling of electron spins, as in the metal carboxylates, e.g. $Cu_2(O_2CCH_3)_4(H_2O)_2$, to the very strong "multiple bonds" in species such as $Re_2Cl_8^{2-}$, and it is in general no easy task to set out well defined reliable criteria which may be applied to any compound to test for the presence of a metal-metal bond. In some instances, definition of metal-metal bonding or decisions between interaction and no interaction seem quite arbitrary. This is, however, not an uncommon situation in a field which is under very active investigation and from which only a relatively small amount of data suitable for making generalised deductions, has emerged. Of necessity then, the area embraces a number of apparently arbitrary definitions. For example, the concepts of oxidation state and electron configuration, so useful in the aqueous and organometallic chemistry of the d-block elements, if persued to any length in connection with metal-metal bonded compounds soon not only take on an arbitrary form but often become virtually meaningless. The definition of oxidation state for metal atoms in these compounds due to Lewis[89] is perhaps the most helpful; "the formal charge left on an atom when all the ligands are removed in their closed-shell configuration and any element-element bonds are broken homolytically". Similarly the formal electron configuration of a metal atom may be defined as the configuration before metal-metal bonding is considered to occur. In $Mn_2(CO)_{10}$ and Hg_2Cl_2, for example, the electron configuration of the manganese atom is d^7, and of the mercury $d^{10}s^1$, and the corresponding oxidation states are Mn(0) and Hg(I). For compounds containing dissimilar metals bonded together, even these definitions can be ambiguous.

It is possible to survey the field of metal-metal bonding from a number of angles but one of the more profitable frameworks for discussion, and that employed here, is first to deal with methods used in the detection of such linkages, and then follow with an examination of some of the examples of compounds containing metal-metal bonds. The bulk metals and metallic alloys, which contain one extreme kind of metallic interaction, will not be considered. The discrete compounds fall into two categories, those with two-centre metal-metal bonds, and those, the cluster compounds, which contain multi-centre interactions. Parallels may be drawn with the normal two-centre localised bonding, and electron deficient, multi-centre bonding encountered in the more familiar areas of chemistry. The former category can be further subdivided into compounds containing bonds between identical and different metal atoms. Preparative methods for metal-metal bonds have received scarcely any systematic attention, and these will be discussed only very briefly.

2.1. DETECTION OF METAL-METAL INTERACTION

The major techniques used to detect the presence of metal-metal bonds include X-ray analysis, magnetic and spectroscopic methods.

2.1.1. X-ray Structural Analysis

Although undoubtedly the surest and most direct way of indicating the presence of metal-metal bonds within a molecule, the method is not without its pitfalls. In those cases where two metal atoms are adjacent with no bridging groups between them such as in $Mn_2(CO)_{10}$ or $Re_2Cl_8^{2-}$, the existence of a metal-metal bond is self evident. In general, short metal-metal distances are indicative of bonding even in the presence of bridging groups, but considerable difficulty can arise as to the maximum distance between two atoms consistant with some degree of bonding still being present. Reference is often cited to the interatomic distances in pure metals, and bonding radii have been compiled using these data.[43] But in certain instances, bonds between metal atoms may be considerably longer than those indicated on this basis, and yet still involve direct metal-metal interaction. For example, in $[\pi C_5H_5(CO)_3Mo]_2$, there is necessarily a metal-metal bond as the dimer contains adjacent Mo atoms with no bridging groups, and this is the only linkage between the two halves of the quite stable molecule; the Mo-Mo distance is 3.22Å.[107] In MoO_2, where Mo-Mo bonding is again postulated, the Mo atoms lie in chains bridged by pairs of oxygen atoms, with alternate Mo-Mo distances of 2.50 and 3.10Å.[108] The shorter distance is considered to indicate a bond, and the longer not. Yet this "long" distance is shorter than the bonding distance in $[\pi C_5H_5(CO)_3Mo]_2$. Other similar ambiguities exist. Complexes of Cu(I), Ag(I), and Au(I) are known where metal-metal distances are relatively short, e.g. in the polymeric complexes, $(MC{\equiv}CR)_n$.[109] Normally it is not considered that metal-metal bonding would occur between atoms of d^{10} configuration, but if the distance between the atoms is taken as indicative of bonding then metal-metal interaction must be present in these compounds. As the complexes are diamagnetic, it seems necessary, moreover, to assume some degree of multiple bonding. The related thiocarbamate complexes of copper, $[Cu(S_2CNR_2)]_n$, contain in some cases nearly regular tetrahedra of Cu atoms, with dimensions small enough for significant metal-metal interaction, thus making them cluster compounds.[110]

Clearly the length of a bond of any given multiplicity between two metal atoms is a sensitive function of the nature of the ligands present in the compound, its stereochemistry, the oxidation state of the metal and probably other factors. Equally clearly the criterion of interatomic distance for the presence of metal-metal bonds in compounds must be used with considerable caution.

2.1.2. Magnetic Measurements

As the magnetic properties of metallic complexes are easily measured, evidence based on these measurements is frequently adduced to indicate the presence of metal-metal bonds. The lowering of the magnetic moment of a metal atom in a compound compared to the value expected for the isolated ion is often quoted in support of a metal-metal bonded structure, and this lowering, sometimes to a value close to zero, is thus assumed to be due to pairing of spins in the metal-metal interactions. In fact this can be far from the truth, and extreme caution must be exercised in the interpretation of magnetic data, for a number of reasons.

(a) For systems containing an even number of electrons on the metal atom, spin pairing can arise from irregularities in the environment of the isolated ion, or some other stereochemical requirement, which split orbitals which would otherwise be degenerate, rather than from metal-metal bonding. The interpretation of the structure of $[ReCl_4]^-$ as a tetrahedral monomer (rather than as a dimer with square prism geometry) is a striking example of the reversal of this reasoning.[111] This possibility of the reduction of the paramagnetism of isolated units is particularly relevant to the heavier transition elements, where intraionic spin pairing becomes relatively easy.

(b) Magnetic interaction between metal atoms can occur via bridging groups. The spin paired binuclear complexes $[(EtOCS_2)MoO]_2O$ and $[(RuCl_5)_2O]^{4-}$ are classical examples of this, both containing linear M-O-M groupings.[112-3] More extreme examples may be chosen from among the simple metal oxide and halide systems, many of which are antiferromagnetic, e.g. RuO_2. Here each Ru^{IV} ion is in the centre of a regular octahedron of oxide ions, each of which is shared with two other ruthenium ions. There are no localised two-centre metal-metal bonds, and the long Ru-Ru distances preclude any other form of direct interaction, yet despite the octahedrally co-ordinated d^4 ions, the compound is diamagnetic. Explanations in terms of extended molecular orbitals-energy bands - involving both metal and oxygen orbitals fit the observed facts best.[114] The MoO_2 structure, on the other hand, as already noted does contain Mo-Mo bonds, and is diamagnetic. The dangers of drawing immediate inferences on bonding from comparison of magnetic data are obvious.

(c) The heavier transition elements often have high values for spin-orbit coupling constants, and this can lead to lowered magnetic susceptibilities in the absence of metal-metal bonds, e.g. Os^{IV} has a λ value $\sim 3600\ cm^{-1}$, giving an effective magnetic moment for its t_{2g}^{4} (octahedral) configuration of 1.2BM (Bohr magnetons) which, taken at its face value, would not immediately suggest the presence of two unpaired electrons. Cr^{II}, on the other hand, with $\lambda \sim 90\ cm^{-1}$, gives in the same configuration a "normal" moment of 3.6BM, fairly easily correlated with the expected moment for two electrons (2.83BM).

There are however a large number of genuine cases where magnetic data have proved useful. The diamagnetism of iron enneacarbonyl, coupled with an observed short iron-iron distance[115] was used to indicate (correctly) the presence of an Fe-Fe bond in this complex. Some of the most interesting systems from a magnetic point of view, those in which complete spin pairing has not occurred e.g. the dimeric metal carboxylates, contain metal-metal bonds which bear the major part of the magnetic interaction. Rhodium acetate monohydrate has a remarkably short metal-metal distance[116] and this and the analogous chromium complex are virtually diamagnetic.[117] A multiplicity greater than one can be assigned to these bonds.

2.1.3. Spectroscopic Methods

Little systematic investigation of the visible and ultraviolet spectroscopic properties of metal-metal systems has been undertaken, but work on polarised spectra in this region has revealed the presence of metal-metal interaction in such complexes as the nickel dimethylglyoximato group.[118] The absorption spectra of similar d^8-donor systems have also been interpreted in terms of metal-metal bonding.[119]

Infrared and Raman studies on intermetallic complexes have as yet not been widely undertaken, since the metal-metal stretching vibrations normally occur at low frequencies, $< 200 \text{ cm}^{-1}$, but with the improvement of apparatus and techniques in the far infrared region, particularly better resolution and reliability from both grating and interferometric spectrometers, this method will undoubtedly find a more extensive use in the future. Some instances of its use have been recorded, notably the Raman spectra of mercurous nitrate solutions, where the Hg-Hg stretch at 160 cm^{-1} directly confirmed the presence of the metal-metal bond.[120] More recently the same technique has been used to show the presence of Cd_2^{2+} in the $Cd_2(AlCl_4)_2$ system.[121]

The most widely used region of the spectrum is the near infrared, where metal-ligand and ligand vibrations occur. Spectra from this region can give an indirect but useful indication of the presence of a metal-metal link. For example, the infrared spectrum of dicobalt octacarbonyl exhibits a marked solvent dependence. In the solid phase, its spectrum shows the presence of bridging carbonyl groups, and other data indicate that a metal-metal link is also present; in solution some of the vibrations due to the bridging carbonyls disappear, and isomerisation to a solely metal-metal bonded dimeric form in equilibrium with the bridged structure is postulated (the non bridged form has staggered trigonal bipyramidal geometry with the Co-Co bond axial).[122] It is clear that detection of structural changes of this sort is extremely important, especially in explaining the reactivity of these compounds.

Finally the mass spectrometric methods outlined in parts 3 and 4 give a direct indication of the number of metal atoms present in a molecule in the vapour phase. Although this does not necessarily indicate the existence of a metal-metal bond in a compound, the exact elemental composition of the remainder of the molecule could preclude the presence of bridging groups. Taken in conjunction with, for example, infrared spectroscopic evidence, the method does represent a powerful addition to available techniques.

A number of authors have examined and discussed the factors which influence the formation of metal-metal bonds,[123-5] particularly between atoms of the same metal, in efforts to make some deductions of predictive value, but with little success. Correlations with sublimation energy, orbital sizes and types, and repulsion effects between filled orbitals and ionic charges have all proved more or less unsatisfactory. At this stage it would seem that more experimental data are required, particularly limits of stability of compounds in terms of position of the metal atoms in the periodic table, the nature of the ligands and the oxidation state of the metal (despite the elusive quality of this parameter), before theory can rise from an ad hoc basis to a predictive scope.

2.2. COMPOUNDS CONTAINING METAL-METAL BONDS

2.2.1. Bonds between identical atoms

For the earlier transition elements, metal-metal bonding occurs readily, even in the high oxidation levels, whereas for the later transition elements it seems to be restricted to the lower states. Data are still limited but it seems that the tendency for metal-metal bonding in all oxidation states reaches a maximum in the centre of the periodic table. A representative of nearly all the common oxidation levels is known for molybdenum: Mo(V), $[Mo(OC_6H_5)_3Cl_2]_2$, (IV) $[MoO_2]_x$, (III) $[Mo_2Cl_9]^{3-}$, (II) $[MoCl_2]_x$, (I) $[\pi C_5H_5Mo(CO)_3]_2$, (-I) $[Mo_2(CO)_{10}]^{2-}$, and there seems to be no reason why the remaining gaps (Mo(-II), (0), (VI), for the commonly occurring levels) should not be filled, although there are as yet no examples of bonding for the d^6 configuration (Mo(0)). This may be associated with the ready formation of octahedral spin-paired complexes for metals with this configuration and its relatively high stability. The series of molybdenum compounds illustrates a number of the various sub classes of materials which contain M-M bonds. Some further examples are now discussed.

(a) Organometallic compounds and metal carbonyls

The metal-metal bonds of compounds such as the polygermanes and -stannanes are among the oldest known examples of M-M interaction in discrete compounds, but the nature of the elements with their filled sub-shells and electron pair bonding gives the resulting localised linkages more of the character of the catenation observed in sulphur and (particularly) carbon compounds rather than the characteristics associated with the transition-metal interactions. The bonds observed for germanium and tin vary very little in length from compound to compound, are always spin paired and always of unit multiplicity. One feature of interest in this area is the extent, if any, to which electronic effects can be transmitted through these bonds.

Virtually all the polynuclear carbonyls and their derivatives contain metal-metal bonds, both in the presence and absence of bridging groups, and these compounds fall into two structural categories along these lines. Examples of non-bridged structures, held together solely by M-M links, include $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$, and of bridged structures, $Fe_2(CO)_9$, and (in the solid phase) $Co_2(CO)_8$. There seem to be no simple qualitative reasons why bridged structures should be more or less stable than non-bridged ones, e.g. a $(CO)_4Mn(CO)_2Mn(CO)_4$ unit rather than $(CO)_5Mn\text{-}Mn(CO)_5$, and reference has already been made to the isomerisation of $Co_2(CO)_8$, from a bridged to a non-bridged structure, in solution. It seems probable that other interconversions could be induced to occur on substitution of the carbonyl ligands; the compounds $Co_2(CO)_7(PPh_3)$ and $Co_2(CO)_6(PPh_3)_2$ contain no bridging groups.[126-7]

The metal carbonyls and their derivatives form as a whole a very important group of M-M bonded materials and are also among the earliest known compounds in which this link was well characterised.

(b) Carboxylate salts

These have already been mentioned in connection with their magnetic properties. There is still considerable discussion on the degree of bonding which exists between the metal atoms for the Cr^{II}, Rh^{II}, and Mo^{II} acetates, where four, three, and four electrons respectively from each metal atom become completely paired. The intermetallic distances in these compounds are either nearly the same as or less than the estimates of bonding radii due to Pauling, Cr^{II} 2.46Å, (estimated, 2.36), Rh^{II} 2.45Å, (2.50), Mo^{II} 2.11, (2.60),[89] and in the case of molybdenum at least it seems fairly certain that the bond has some multiple character. It is possible however, that a considerable amount of the spin pairing in the Cr^{II} and Rh^{II} complexes is of a fairly weak nature, similar to that in the Cu^{II} compound. It is interesting to note that the Mo complex is isoelectronic and isosteric with the $[Re_2Cl_8]^{2-}$ ion, where multiple bonding is recognised.

(c) The $[Re_2X_8]^{2-}$ ion and its derivatives.

This small but important group of compounds has recently been the focus of much attention. Members which are at present characterised include $[Re_2X_8]^{2-}$ X = Cl, Br, SCN, $[Tc_2Cl_8]^{2-}$, and some $Re_2X_6H_2$ species.[128-32] The major and very unusual features of the structure are exceedingly short M-M distances, Re 2.24Å, Tc 2.13Å, (Pauling estimates 2.75, 2.72Å respectively) and an eclipsed rotomeric configuration. These two points and the observed diamagnetism of the compound are best explained in terms of a quadruple bond between the metal atoms, and this is considered to be made up of a σ bond, two π bonds and a δ bond.[133]

(d) Crystalline halides and oxides

There exists a large number of compounds with pairs of metal atoms close enough to be considered bonded together, but having also two or three bridging halide or chalcogenide atoms. The majority of the compounds contain metal atoms in octahedra of oxide or halide ions which in many cases form infinite close packed or distorted close packed arrays, although sometimes the octahedra are joined only into small groups or bands. When metal-metal bonding occurs, the metal atoms move away from the centre of their octahedra and approach each other across a face or edge. Compounds containing these bonds across faces and edges of octahedra respectively, include $[W_2Cl_9]^{3-}$ and NbI_4.[134-5] When analogous compounds are formed by the lightest and heaviest metals of a group, the heavier one usually shows much greater metal-metal interaction. For example, in the diamagnetic $[W_2Cl_9]^{3-}$ (W-W distance 2.41Å), there is distinct metal-metal bonding, but in $[Cr_2Cl_9]^{3-}$, the metal atoms remain at the centres of their octahedra and have normal magnetic moments. A similar comparison exists between CrO_2 and MoO_2. These facts have been used to demonstrate the greater "homophilicity" - the tendency for an element to form bonds to itself - for the heavier transition metals.[136]

(e) Other types

Mention has already been made of the spectroscopic evidence for M-M bonding in complexes such as Ni(dimethylglyoxime)$_2$ and $[Pt(NH_3)_4][PtBr_4]$, and the classical example of the Hg_2^{2+} ion. Many other isolated examples could be cited, such as the Mo^V complexes $[Mo(OC_6H_5)_3Cl_2]_2$ and $[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2+}$, and $MoCl_2$, all of which are structurally interesting and important. The Mo^V phenoxide, directly related to $[MoCl_5]_2$, (dimeric, with chlorine bridges, Mo-Mo 3.84Å, paramagnetic)[137] shows the effect of a reduction of formal charge on the metal atom in bringing into play direct M-M interactions (Mo-Mo distance in the phenoxide 2.8Å, chlorine bridges again present).[138] The complex is also diamagnetic. Very recently the extremely interesting complex $[(Ph_3P)_2IPt]_2$ has been prepared.[201]

2.2.2. Bonds between dissimilar metal atoms.

These are conveniently divided into compounds containing transition metals bonded together and transition elements bonded to main group elements. At present only a relatively small number of these complexes is known, but there can be no doubt that a very great variety is capable of existence.

(a) Transition metal-transition metal bonds. A number of mixed carbonyls are known both with bridging groups, e.g. $\pi C_5H_5Fe(CO)_2Co(CO)_4$, and without bridges, e.g. $(CO)_5Mn\text{-}Re(CO)_5$, $\pi C_5H_5(CO)_2Fe\text{-}Mo(CO)_3\pi C_5H_5$. The properties of these compounds are similar to their homonuclear analogues. Mixed d^8-donor complexes of the type $[M(NH_3)_4][M'X_4]$, which have metal-metal interactions in the solid state have been prepared for palladium and platinum,[119] and the binuclear compound $(Ph_3P)_2IPt\text{-}NiI(PPh_3)_2$ has recently been characterised.[201]

One of the most fruitful preparative areas has involved metals with $d^{10}s'$ configuration - complexes of Cu, Ag, and particularly, Au and Hg. A large number of adducts of phosphine gold halides and mercury halides has been prepared and these two metallic units behave in many ways as pseudo halogens. Some of the more interesting examples include $Ph_3PAu\text{-}M(CO)_3\pi C_5H_5$, (M = Mo, W), $Ph_3PAu\text{-}V(CO)_6$, $(Ph_3P)_2XPt\text{-}AuPPh_3$, (X = Br, Cl), $(Ph_3P)_2XPtHgX$, (X = Cl, I),[201,139] (CO)ClXIrHgX, (X = Cl, Br, I, CH_3COO),[152] $(Ph_2AsMe)_3Cl_2Rh\text{-}HgX$, (X = F, Cl, Br, I, CH_3COO). Analogous compounds of copper and silver are known e.g.[139] $(Ph_3P)_2ClPtCu(PPh_3)_3$, (triarsine) $Ag\text{-}Mn(CO)_5$, (triarsine $M)_2Fe(CO)_4$, (M = Cu,Ag). Very little work has been done on the reactivities of these compounds but deductions have been made from infrared data on the relative electronegativities of some of the metallic units. The Hg-Fe stretching frequency (196 cm^{-1}) in the compounds $(XHg)_2Fe(CO)_4$ has been determined,[140] and the compound $\pi C_5H_5(CO)_2FeHgCo(CO)_4$ was the earliest example of three metal atoms covalently bound together.

(b) Transition-metal - main group metal bonds. These are more limited in number, and at present include only the lower members of groups III and IV. Germanium-transition-metal bonds, in $Ph_3Ge\text{-}Mn(CO)_5$ and $Ph_3GeFe(CO)_2\pi C_5H_5$[39,141] formed the earliest members of this class. Analogous tin compounds are now known,[142] and in addition, the di-, tri-, and tetra-substituted structures[143-5] $[(CO)_5Mn]SnMe_2[W(CO)_3\pi C_5H_5]$, $PhSn[Re(CO)_5]_3$, and $[\pi C_5H_5Fe(CO)_2]_2Sn[Mo(CO)_3\pi C_5H_5]_2$. The chemistry of germanium bonded to platinum and palladium incompounds such as $(R_3P)_2M(GeR'_3)_2$ and $(R_3P)_2XMGeR'_3$, (M = Pt, Pd; R' = Ph, Me; R = Ph, Pr^n, Et; X = Br, Cl, I, NCS, OR) represents virtually the only area which has been at all extensively studied. Again analogous tin derivatives have been prepared. A number of complexes containing cobalt bonded to Ga, In and Tl are known,[146-7] including $BrIn[Co(CO)_4]_2.THF$, $X_2GaCo(CO)_4.THF$, $Tl[Co(CO)_4]_3$, acac $Ga[Co(CO)_4]_2$ etc. Very little is known about the reactivity of these complexes.

The area is important in that it represents the borderline of the discipline, having affinities with both metal-organic and intermetallic chemistry, and much of value on relative stabilities of various bond types under controlled conditions, and reaction mechanisms should emerge.

2.2.3. Metal Atom Cluster Compounds.

These are compounds containing a number of metal atoms each of which is bound to all or most of the others. A small number of compounds of this type has been known for some years but most of the members of the class have been discovered or recognised (rather than prepared) only recently, and research in this area is currently very much in vogue. A formal definition of a cluster compound as one "containing a finite group of metal atoms which are held together mainly or to a significant extent by bonds directly between the metal atoms, even though some non-metal atoms may be intimately associated with the cluster", has been suggested,[148] and this is broad enough to include binuclear complexes. This point has led to the drawing of a parallel between clusters and homologous series of carbon compounds, with the clusters as the main body of the series and the binuclear complexes as the first number, atypical in much the same way as methane is an atypical paraffin. The analogy has much to recommend it, if only that it emphasises the widespread and far from unusual nature of metal-metal bonds. Two classes of metal atom cluster compounds can be distinguished in the presently known examples: (i) the lower halides, and to a lesser extent, oxides, and (ii) polynuclear metal carbonyls and related systems involving NO, organic π-systems and "π-acid" ligands.

For the lower halides only triangular M_3 and octahedral M_6 groupings have so far been found, but in several variations corresponding to the number and arrangement of the bound halide ions. These include structures typified by[149] Nb_3Cl_8, $Re_3Cl_{12}^{3-}$, $Mo_6X_8^{4+}$ and $Nb_6Cl_{12}^{2+}$. The metal carbonyls contain examples of trinuclear, $Os_3(CO)_{12}$, tetranuclear, $Co_4(CO)_{12}$, pentanuclear, $Fe_5(CO)_{15}C$ (a square based pyramid with a carbon atom embedded in the base) and hexanuclear, $Rh_6(CO)_{16}$, clusters. Several derivatives of these structures are known, e.g. $(\pi C_5H_5)_3Ni_3(CO)_2$, and there are other likely candidates such as $Fe_3(CO)_{11}^{2-}$, $Ni_4(CO)_9^{2-}$, where complete proof of metal-metal bonding is as yet lacking.

Considerable effort has gone into the description of the electronic structure of these complexes, both in valence bond terms[150] and by molecular orbital methods, and in general the latter system seems to be the more useful.[133] A pure valence bond approach would require very "bent bonds" for many of the metal-metal links, and as in such cases as $Nb_6X_{12}^{2+}$, there is not an integral number of electron pairs per metal-metal bond, resonance between canonical forms would have to be postulated. In the Nb_3Cl_8 structure, for example, the metal atoms are all equivalent and a fractional oxidation number of 8/3 must be assigned to these atoms, which is not easily reconciled with conventional two-centre bonds. Simple M.O. theory has accounted, in a qualitative way, for the magnetic properties, bond lengths and structures of the complexes, but as yet a number of parameters have not been well enough evaluated to enable quantitative predictions, e.g. on electronic spectra, to be made. The success of the method in predicting bond orders (and thus approximate bond lengths) and the magnetic properties of the complexes has been demonstrated for several cases.[149] The $M_6X_{12}^{2+}$ species has 16 electrons from the M_6 group, and MO theory predicts exactly 8 bonding orbitals, thus leaving no unpaired electrons, and giving a bonding order of 8/12. $Mo_6X_8^{4+}$ has 24 electrons, 12 bonding orbitals, is thus diamagnetic and has a M-M bond order 12/12: Re_3Cl_9 ($Re^{III}Cl_3$) bond order 6/3, diamagnetic. The related Re_3Cl_{12} ($Re^{IV}Cl_4$) should withdraw 3 electrons from the Re_3 cluster, leaving a single unpaired electron, in accord with its observed paramagnetism; similar predictions for the paramagnetism of the "$MX_{2.5}$" compounds ($[M_6X_{12}]^{3+}$), one unpaired electron, are confirmed by experiment.

2.3. PREPARATION AND PROPERTIES OF METAL-METAL BONDED COMPOUNDS

Very little systematic work has been carried out in these fields. Preparation of the bi- and tri-nuclear complexes (as distinct from the tri-nuclear clusters) is often remarkably straightforward, M-M and M-M' bonds resulting from simple metatheses or additon reactions. Representative reactions include, for the addition reactions[201,152]

$$(Ph_3P)_4Pt \quad + \quad Ph_3PAuCl \longrightarrow (Ph_3P)_2ClPt\text{-}AuPPh_3$$

$$(Ph_3P)_2Ir(CO)_2 \quad + \quad HgCl_2 \longrightarrow (Ph_3P)_2(CO)Cl_2Ir\text{-}HgCl$$

$$(Ph_3P)_4Pt \quad + \quad (Ph_3P)_2PtCl_2 \longrightarrow (Ph_3P)_2ClPt\text{-}PtCl(PPh_3)_2$$

The very widely used metathetical reaction is a development of that originally used to prepare σ-bonded organic derivatives of Cr, Mo, and W, viz.

$$\pi C_5H_5M(CO)_3Na + RX \longrightarrow \pi C_5H_5(CO)_3M\text{-}R + NaX \quad \cdots\cdots 153$$

Many examples of this extremely general reaction are known

$$Na_2Fe(CO)_4 + 2Ph_3PAuCl \longrightarrow (Ph_3PAu)_2Fe(CO)_4 + 2NaCl \quad \cdots\cdots 154$$

$$NaMn(CO)_5 + (\text{triarsine})CuBr \longrightarrow (\text{triarsine})Cu\text{-}Mn(CO)_5 + NaBr \quad 155$$

$$Br_2PhSnRe(CO)_5 + 2NaRe(CO)_5 \longrightarrow PhSn[Re(CO)_5]_3 + 2NaBr \quad \cdots\cdots 144$$

and, reversing the roles of the transition metal and the main group element

$$(R_3P)_2MCl_2 + 2Ph_3GeLi \longrightarrow (R_3P)_2M(GePh_3)_2 + 2LiCl \quad (M{=}Pt,Pd)^{86\cdot 7}$$

$$(Ph_3P)_nMCl + Ph_3GeLi \longrightarrow (Ph_3P)_nMGePh_3 + LiCl \quad (M{=}Cu,Ag,Au;\ n{=}1,3) \quad 85$$

The insertion of lower valent main group halides into metal-metal bonds already present in a molecule has proved an interesting and useful synthetic route.

$$[\pi C_5H_5Fe(CO)_2]_2 + MX_2 \longrightarrow [\pi C_5H_5Fe(CO)_2]_2MX_2 \quad (M{=}Ge,Sn;\ X{=}I,Cl)^{156}$$

$$InBr + Co_2(CO)_8 \xrightarrow{THF} [Co(CO)_4]_2InBr.THF \quad \cdots\cdots 146\cdot 7$$

and the reaction of metallic mercury with the mixed Fe-Co complex is related,

$$Hg + \pi C_5H_5(CO)_2Fe\text{-}Co(CO)_4 \longrightarrow \pi C_5H_5(CO)_2Fe\text{-}Hg\text{-}Co(CO)_4 \quad \cdots\cdots 145$$

An elimination reaction,

$$GeH_4 + HMn(CO)_5 \xrightarrow{20^o} H_2Ge[Mn(CO)_5]_2 + H_2 \quad \cdots\cdots 157$$

has been employed, and the useful synthetic route

$$(R_3P)_2PtCl_2 + (Me_3Ge)_2Hg \longrightarrow (R_3P)_2ClPtGeR_3 + ClHgGeR_3 \quad 13$$

could also be classed as an elimination. Some use has been made of thermal decompositions to prepare heteronuclear complexes.

$$[Re(CO)_6][Co(CO)_4] \longrightarrow (CO)_5ReCo(CO)_4 + CO \qquad \cdots 158$$

There is as yet no specific instance of a reaction deliberately designed to produce cluster compounds from mononuclear starting materials and all such complexes have been prepared by chance or as "undesirable" by-products. Development of rational syntheses for these compounds represents a considerable challenge.

The common physical properties of the metal-metal bonded materials are in the main well documented, apart from certain of the clusters where spectroscopic measurements are inadequate. All are more or less stable to air, at least for short periods of time, and most of the M-M linkages seem remarkably resistant to attack except under certain highly specific conditions, e.g.

$$(R_3P)_2Pt(GePh_3)_2 + H_2 \xrightarrow{20mm} (R_3P)_2Pt(H)GePh_3 + Ph_3GeH \qquad \cdots 86$$

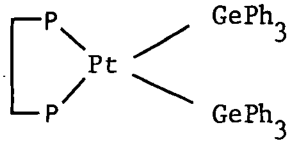
Some of the metal cluster structures are retained throughout chemical reactions and are only broken up under extremely forcing conditions. Three major classes of reaction of compounds containing metal-metal bonds may be distinguished: ligand exchange and redox reactions, in which the metallic skeleton remains intact, and degradation processes, in which it is broken up. Many instances of both neutral and ionic ligand exchange reactions are known

$$(Ph_3P)_3Re_3Cl_9 \xrightarrow{Me_2SO} (Me_2SO)_3Re_3Cl_9 \qquad \cdots 132$$

$$(Et_3P)_2Pt(OH)GePh_3 \xrightarrow{EtOH} (Et_3P)_2Pt(OEt)GePh_3$$

86

$$(Et_3P)_2Pt(GePh_3)_2 \xrightarrow{Ph_2PC_2H_4PPh_2}$$



Redox reactions such as

$$[M_6X_{12}]^{2+} \longrightarrow [M_6X_{12}]^{4+} + 2e \quad (M = Nb,Ta) \qquad 159$$

have been reported for the cluster compounds and seem feasible for the simpler complexes. Degradation of the metal-metal structures or cleavage of isolated bonds occurs on severe oxidation, base hydrolysis, and, for carbonyl types, on pyrolysis. Main group-transition metal bonds have been cleaved by halogens, and halogen containing compounds e.g. $C_2H_4Br_2$

$$Ph_3GeAuPPh_3 + C_2H_4Br_2 \longrightarrow Ph_3GeBr + BrAuPPh_3 + C_2H_4 \qquad 85$$

and RX,

$$(Et_3P)_2Pt(GeR'_3) + HCl \longrightarrow (Et_3P)_2Pt(H)GeR'_3 + R'_3GeCl \qquad 86$$

with one striking exception,

$$Ph_3SnM(CO)_5 + 2Br_2 \longrightarrow PhBr_2SnM(CO)_5 + 2PhBr \quad (M = Mn, Re) \qquad 144$$

2.4. ORGANOGERMANIUM-TRANSITION ELEMENT COMPLEXES

BONDS between transition elements and the metals of the fourth main group have an important role in the chemistry of metal-metal bonded complexes. Not only do they represent a connecting link between the areas of metal-organic and intermetallic chemistry, and for this reason provide useful reference points for comparisons between fairly familiar and very novel compounds, but also the relatively straightforward nature of their bonding should provide growing points for the examination of the bonding properties and reaction mechanisms in the more complicated cases. This study of a few organogeramnium complexes of molybdenum and tungsten and some of their derivatives was undertaken with a view to increasing our understanding of this type of compound and their reactions and also to clarify the relationship which exists between the

TABLE 2.1

Physical Properties and Analytical Data for the Complexes

	compound	M.Pt.	colour	yield[a]	calculated,%		found,%		νCO cm^{-1}	τ_{cp}	τ_R
					C	H	C	H			
I	$\pi C_5H_5(CO)_3MoGeMe_3$	87-88°	v.pale pink	65%	36.3	3.89	36.7	3.67	1999 1929, 1905 [b]	5.42	9.39[b]
II	$\pi C_5H_5(CO)_3MoGeEt_3$	26.5°	pink	45%	41.5	4.95	41.5	4.81	1994 1926, 1907 [c]	5.35	8.82[b][e]
III	$\pi C_5H_5(CO)_3MoGePr^n_3$	<25° ?	brick red	~10%	mass spectrometric						
IV	$\pi C_5H_5(CO)_3WGeMe_3$	106-107°	buff	50%	29.3	3.13	29.6	3.33	2010 1931, 1908 [c]	4.70	9.37[d]
V	$\pi C_5H_5(CO)_3WGeEt_3$	36°	yellow-orange	48%	34.1	4.09	34.2	4.25	2006 1923, 1905 [c]	5.37	8.84[b][e]

(a) overall, based on $M(CO)_6$

(b) in benzene solution

(c) in cyclohexane solution

(d) in deuterochloroform solution

(e) to centre of complex resonance

organometallic and intermetallic compounds.

Germanium was selected as the main group element rather than tin because of the relative instability of the tin-carbon bond which could complicate the reactions of an Sn-M bond and their study considerably. No gross differences were found between the properties of molybdenum-germanium and tungsten-germanium complexes, and all the reactions tried on both metallic systems worked as far as could be ascertained, in the same way. If anything the tungsten complexes were more stable (less reactive towards a number of reagents) than their molybdenum analogues, a point in parallel with the reactivities of their σ-bonded organic compounds. The complexes will thus be discussed as a whole, in terms of the reactions of the M-Ge bond or the ligands which surround it.

2.4.1. Preparation and Properties

The general metathetical reaction mentioned earlier was used to prepare the complexes, which were isolated in crystalline form in reasonable yields

$$M(CO)_6 + NaC_5H_5 \xrightarrow{\text{THF, } Bu^n_2O} Na[M(CO)_3\pi C_5H_5] + 3CO \;\ldots\ldots\; 2i$$

$$[\pi C_5H_5(CO)_3M]Na = R_3GeBr \longrightarrow \pi C_5H_5(CO)_3MGeR_3 + NaBr \;\ldots\ldots\; 2ii$$

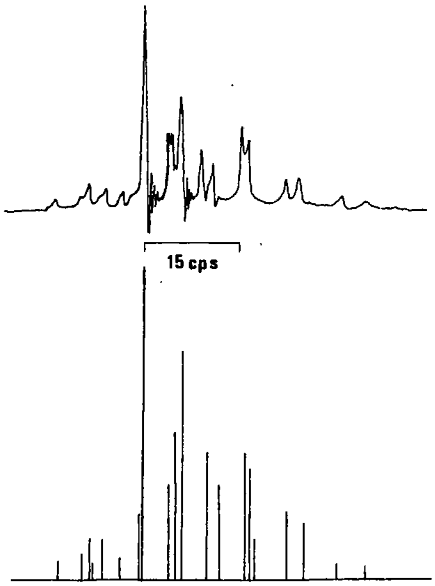
$M = Mo, W;\ R = Me, Et$ (and Pr^n for Mo only)

The main physical properties of the complexes are listed in table 2.1. Overall yields from the reaction were not perhaps as high as they might be, and in the tungsten case this is almost certainly due to the higher temperatures required to substitute the three CO groups of $W(CO)_6$ by $C_5H_5^-$, and the generally increased difficulty of this stage (2,i) compared with the molybdenum compound. Dimethyl formamide (D.M.F.) is often recommended as a solvent for this reaction, but it was found that this did not give improved yields and actively complicated the second stage. A long reflux at stage 2i using di-n-butyl ether proved more satsifactory as the sodium cyclopentadienide could be prepared in situ in this solvent, although it was considerably less soluble in this liquid than in tetrahydrofuran (T.H.F.) or D.M.F. The complexes were all soluble in the common organic solvents and, surprisingly, were not attacked by some of the highly halogenated ones (CCl_4, $CHCl_3$) at least over a period of one day. All crystallised readily from cooled pentane or pentane-ether solution and could be sublimed at low pressures at temperatures up to and above their melting points. Their infrared spectra in solution in the carbonyl stretching region was in accord with expectations for compounds with C_S symmetry and having essentially the same geometry as the analogous σ-bonded organic derivatives, see illustration, page 89a, fig. 2.2.

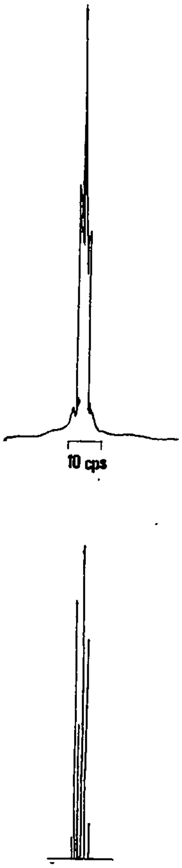
2.4.2. Proton magnetic resonance spectra

Proton magnetic resonance spectra of the ethyl complexes (II and V) were interesting from a number of points of view. Both these compounds showed very "collapsed" ethyl resonances; in the tungsten complex the methyl and methylene proton resonances overlapped so much as to give virtually a single line - five peaks could just be distinguished, with separations of 1-2 cps. In the molybdenum complex, eight somewhat more definite peaks with slightly larger separations could be detected. This not only indicates free rotation about the M-Ge bond, at room temperature, i.e. equivalence of all the Et radicals despite the possibility of hindrance from the carbonyl groups and the cyclopentadienyl ring, but also, taking the straightforward Dailey-Shoolery interpretation of the methyl-methylene coupling constant-chemical shift ratio,[163] an environment which gives the germanium atom an effective electronegativity close to that of hydrogen. Comparing the spectra of these compounds with those of

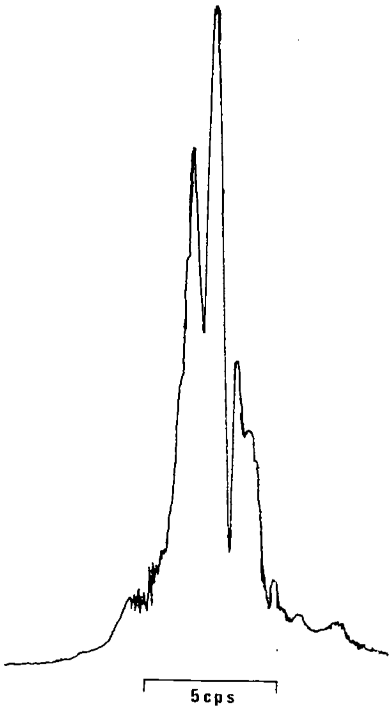
Fig. 2.1 Proton Magnetic Resonance Spectra



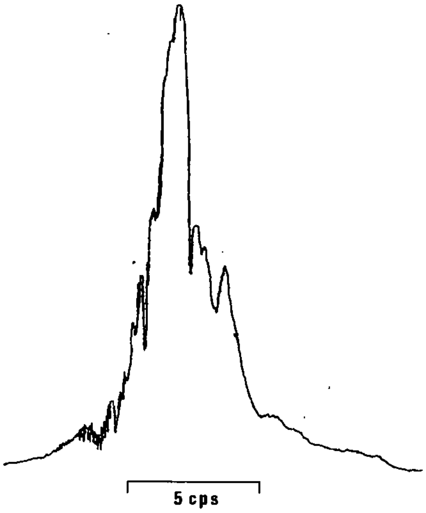
(a) Experimental (top) & theoretical p.m.r. spectrum of Et_4Ge. (ref. 160)



(b) Experimental & theoretical spectrum of Et_3GeCl. (ref. 161)



(c) Ethyl resonance of π-$C_5H_5(CO)_3MoGeEt_3$



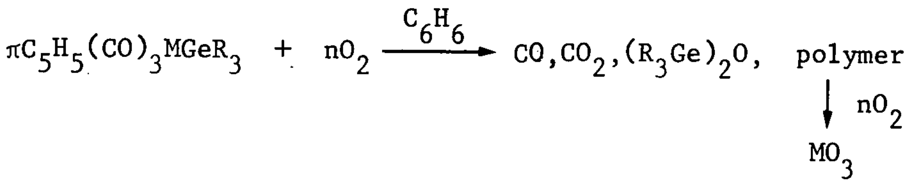
(d) Ethyl resonance of π-$C_5H_5(CO)_3WGeEt_3$

Et_4Ge and Et_3GeCl (illustrated opposite), it would seem that the germanium has increased its effective electronegativity (i.e. supplied electron density to the more electronegative transition metal), and slightly more so in the tungsten compound, where the lines of the ethyl structure are closer together, than in the molybdenum case. It is thus interesting to note, and it is perhaps not completely fortuitous, that the mean of the Pauling electronegativities (Xp) for tungsten and germanium, 2.19 (Xp, W = 2.36, Xp, Ge = 2.01) is closer to the electronegativity of hydrogen, 2.20, than the mean of the Mo-Ge values, 2.09. This is, of course, a very simplified interpretation and undoubtedly terms from the magnetic anisotropy of the M-Ge system and other interactions have some bearing on the chemical shift-coupling constant ratio.

The p.m.r. spectra of the methyl complexes showed the expected peaks from the C_5H_5 and $-CH_3$ groups.

2.4.3. Oxidation

The three molybdenum complexes were completely oxidised in solution within 18 hours to give CO, CO_2, $(R_3Ge)_2O$ and a deep blue ill defined molybdenum containing material which in the early stages of reaction retained much carbonyl and hydrocarbon.



$$\pi C_5H_5(CO)_3MGeR_3 + nO_2 \xrightarrow{C_6H_6} CO, CO_2, (R_3Ge)_2O, \text{ polymer} \xrightarrow{nO_2} MO_3$$

The stretching frequencies for the residual carbonyl in this undoubtedly polymeric material were shifted to lower energy (by 20-40 cm^{-1}) from the values observed on the original complex, and the number of separate bands increased. In no case was the final fate of the C_5H_5 ring determined. A trace of material of lower retention time than benzene was detected in the v.p.c. of the reaction mixture, but this could not be satisfactorily correlated with any reasonable hydrocarbon species. It seems feasible that at least some of the cyclopentadiene could become attached to germanium, c.f. the thermal decomposition processes. On further contact with oxygen, the blue material lost its infrared structure and was converted to one of the blue forms of molybdenum trioxide. When formed in solution, this oxide could not be removed either by filtration or prolonged centrifuging and exhibited a marked Tyndall cone. During the oxidation process, the colour of solutions of complexes I and II changed from light pink, through deep red, clear yellow green, finally to deep blue. Mass spectrometric examination of the incompletely oxidised material gave evidence for the presence of $(R_3Ge)_3COH$ species under low resolution, but satisfactory high resolution mass measurements were not obtained. A maximum of 15% oxidation of the crystalline complexes (I and II) occurred over three months at 20^o, with the formation of a red-brown surface layer. The methyl complex, II, was explosively oxidised by nitric acid.

Both of the tungsten compounds, IV and V, were much more stable towards oxygen, the methyl complex particularly so. 81% of this compound was recovered unchanged after contact in benzene solution with excess oxygen for 40 days at room temperature. Again the products detected were CO, CO_2, $(R_3Ge)_2O$, and WO_3 - this latter being deep yellow. No very striking colour changes were observed during the reaction. The ratio of CO_2 to CO found in all three experiments was approximately 1:3.

2.4.4. Hydrolysis

All the complexes I-V were unaffected by air-free water over a period of two days, at room temperature.

2.4.5. Thermal Decomposition

The thermal stability of these complexes is striking. Very slow decomposition of the molybdenum - ethyl compound (II) occurred at 150°-200° with partial loss of CO and the production of a small amount of $C_5H_5GeEt_3$, paralleling the rearrangement and decomposition processes which occur under electron impact. Much unchanged material (approx.90%) persisted even after two days at 200°. The tungsten - methyl complex (IV) was even more resistant to thermal breakdown, and after five days at 190° 91% of unchanged material was recovered, leaving a small amount of red crystalline $[\pi C_5H_5(CO)_3W]_2$, and a little green black (polymeric) material soluble in acetone. 9.0 mole% of CO was recovered

$$\pi C_5H_5(CO)_3MGeR_3 \xrightarrow[2\text{-}5\ \text{days}]{200^{\circ}} CO, C_5H_5GeR_3, [\pi C_5H_5(CO)_3M]_2,\ \text{polymer 10\% overall.}$$

All the complexes sublimed readily at 60°-80° under 10^{-2} - 10^{-4} mm.

2.4.6. Ligand Exchange Reactions

The reactions of the complexes with a number of nitrogen and phosphorus compounds were investigated.

Displacement of one carbonyl group from all the complexes occurred readily with an excess of di-ethylphosphine, in which they were also easily soluble.

$$\pi C_5H_5(CO)_3MGeR_3 + Et_2PH \longrightarrow \pi C_5H_5(CO)_2(Et_2PH)MGeR_3 + CO, \quad (100\%)$$

In all the cases the reaction was complete and quantitative after 14 days at 20°, and was probably essentially so in a much shorter time. No further reaction could be induced with the excess phosphine present. All these phosphine complexes were very air sensitive and either pale yellow or yellow green, π-cyclopentadienyltriethylgermyldiethylphosphinodicarbonyl molybdenum formed low melting crystals and the corresponding complex from the tungsten-methyl compound (IV) was an oil.

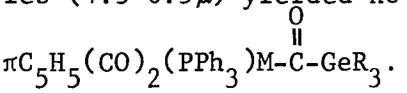
The reaction of the complexes with triphenylphosphine was more complicated

After 1-4 hours at 60° solutions of triphenylphosphine and the complexes (in benzene and cyclohexane) began to deposit a light brown flocculent material, and roughly the same amount of this material remained throughout the period of heating. Opening the reaction vessels ("break-seal" tubes) after 14 days at 60°-80° yielded CO equivalent to 10-50% reaction, depending on the complex and the ratio of phosphine to starting material. In no case, even after prolonged heating (20 days) was 100% reaction (in terms of liberated CO) detected. Work up of the solutions under nitrogen gave in all cases complexes corresponding to loss of one carbonyl group.

$$\pi C_5H_5(CO)_3MGeR_3 + PPh_3 \longrightarrow \pi C_5H_5(CO)_2(PPh_3)MGeR_3 + CO$$

A reaction in an essentially open system (under nitrogen) gave a good yield. 70%, of the corresponding phosphine complex from the molybdenum-ethyl compound (II), within 24 hours.

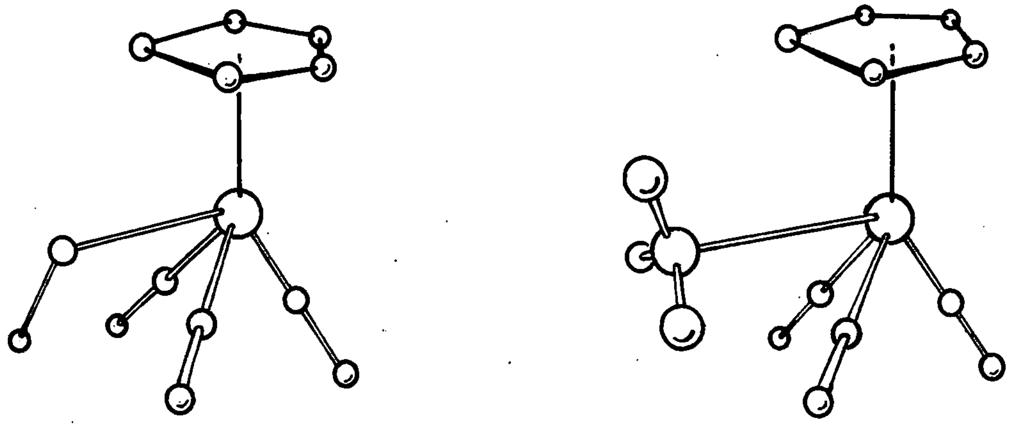
The observations suggested an equilibrium process, and shaking of a benzene solution of the dicarbonyl-triphenylphosphine complex $\pi C_5H_5(CO)_2(PPh_3)WGeMe_3$, (VI) in an atmosphere of CO for 14 days at 18°C, gave infrared and mass spectrometric evidence for the presence of the tricarbonyl complex (IV), and demonstrated the reversibility of the reaction. On bubbling a slow stream of carbon monoxide through a solution of $\pi C_5H_5(CO)_2(PPh_3)WGeMe_3$ in refluxing benzene for 18 hours, the tricarbonyl complex was regenerated in >50% yield.

Mass spectrometry of the brown precipitate formed early in the molybdenum reactions showed in a low resolution trace, ions due to $\pi C_5H_5(CO)_3(PPh_3)MoGeEt_3$, with a well defined MoGe isotope pattern, but although the low resolution spectrum was completely reproducible and obtained under low source pressure conditions, satisfactory precise masses could not be obtained for these ions, probably due to the small amount of sample available. The infrared spectrum of this material, and of the crude product from the tungsten reactions examined, both as solids and in solution, in the region of the carbonyl stretching frequencies (4.5-6.5μ) yielded no evidence for the formation of a germyl ketone,  $\pi C_5H_5(CO)_2(PPh_3)M\text{-}\overset{\overset{O}{\|}}{C}\text{-}GeR_3$. Solutions taken directly from the reaction vessel and examined with the minimum of delay showed the same result. The fragmentation pattern of the molybdenum tricarbonyl-phosphine complex was similar to that of the starting materials, i.e. was more likely to contain an Mo-Ge bond rather than an Mo-CO-Ge unit. Furthermore the reaction mixture and products were unaffected over a period of five days by air-free water dissolved in acetone. A germyl ketone would normally be expected to undergo rapid hydrolysis.

Similar intermediates ($\pi C_5H_5(CO)_3(PPh_3)WGeR_3$) could not be isolated from the tungsten reactions. Examination of the reaction mixtures and crude reaction products for the tungsten complexes did, however, reveal three distinct C-H stretching frequencies in the region expected for the C-H stretch of the protons in the C_5H_5 ring, and this prompted an attempt to follow the proton magnetic resonance spectrum of this structure during the reaction.

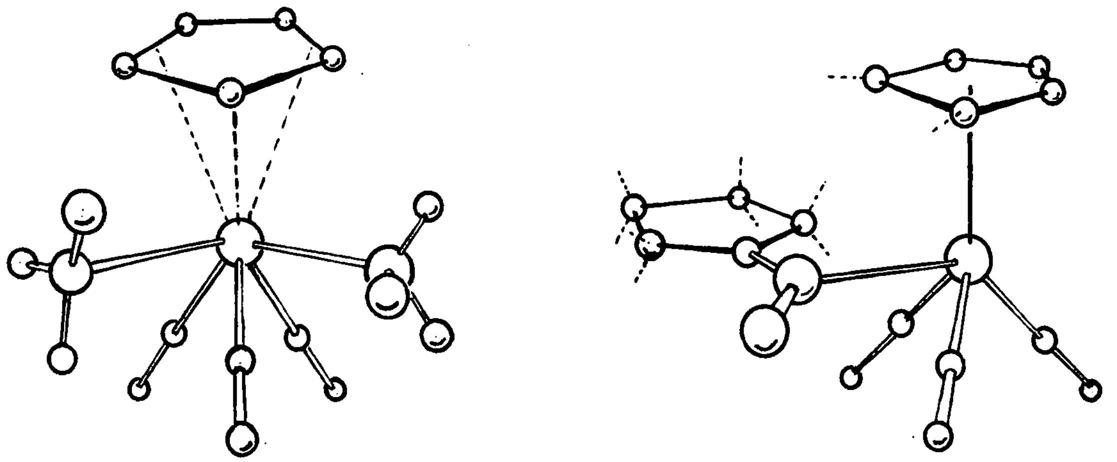
Previous experiments had shown that both the dicarbonyl-phosphine and tricarbonyl complexes were unaffected by air-free chloroform over a period of at least six weeks, and so deuterochloroform was used as a solvent for the reaction, which was carried out in an n.m.r. tube joined to a thin-walled bulb to contain the carbon monoxide. The lollipop-shaped tube was designed to fit into the spectrometer and spin in the usual manner so that the reaction could be followed continuously. A solution containing about 0.1 m mole of the dicarbonyl-phosphine complex in 0.4 cc of solvent was used, the bulb holding,

FIGURE 2.2



(a) The molecular structure of π-$C_5H_5(CO)_3MoC_2H_5$. (ref. 164)

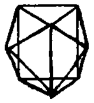
(b) Possible structure, based on (a), for π-$C_5H_5(CO)_3MoGe(CH_3)_3$ etc..



(c) Suggested ψ-undecahedral geometry for the intermediates, π-$C_5H_5(CO)_3(PPh_3)MGeR_3$.

(d) Possible structure of π-$C_5H_5(CO)_3WMgBr.THF$, showing crowding round the Mg atom.

The undecahedral form is



at one atmosphere, roughly a ten-fold excess of CO. About one hour from the start of the reaction, i.e. after sealing CO in the tube and allowing the solution to warm from -196° to 35°, the resonance due to the C_5H_5 protons of the tricarbonyl complex could just be detected. After ten hours, a second resonance, a single line lying between those of the C_5H_5 protons of the dicarbonyl-phosphine and the tricarbonyl complex, was detected, and this rose to a maximum peak height about 20 hours from the start of the reaction, and then began to diminish. The resonance from the tricarbonyl complex grew steadily. Integration of the peaks proved unreliable at the small sample concentration used, but a plot of the peak heights of starting material and product against time gave an approximate half-life for the reaction of about 30 hours. The resonance lying between the two large peaks was attributed to the intermediate $\pi C_5H_5(CO)_3(PPh_3)WGeMe_3$, the single line indicating a π-bonded ring similar in character to those in the stable complexes. This line could no longer be detected after about 60 hours reaction time, and at its maximum, the amount present in terms of peak heights was about 20% of the total C_5H_5 resonance. No other changes in the spectrum were detected during the reaction: the phenyl resonance remained complex, and as the difference in chemical shift between the methyl group resonances in authentic starting material and product is only 3 c.p.s., little could be gained from examination of this part of the spectrum. The position of the C_5H_5 resonances, $\pi C_5H_5(CO)_2(PPh_3)WGeMe_3$, -302 c.p.s., $\pi C_5H_5(CO)_3(PPh_3)WGeMe_3$, -314c.p.s., $\pi C_5H_5(CO)_3WGeMe_3$ -323 c.p.s. (relative to TMS) can perhaps to correlated with deshielding effects which might be expected to occur due to the increased acceptance of electron density from the metal atom by the incoming carbonyl group, in accordance with its higher degree of π acidity than the phosphine: less electron density need be distributed to the C_5H_5 ring by the transition metal when more carbonyl groups are present. The problem of the geometry and bonding in the intermediate remains. Assuming a planar terdentate cyclopentadiene ring donating six electrons to the transition metal, which is in formal oxidation stateII, and "normal" bonding for the rest of the ligands (i.e. discounting a ketonic carbonyl, as discussed above) then these intermediates have not only an eight co-ordinate metal atom, unusual in itself, but also 20 electrons available for bonding, rather than the "preferred" rare gas configuration of 18. It is remarkable that a complex such as this should be stable enough to be isolated and to yield a mass spectrum showing a molecular ion of reasonable intensity in the molybdenum case ($\pi C_5H_5(CO)_3(PPh_3)MoGeEt_3$). The geometry of such a molecule fits a pseudo-undecahedral arrangement of groups well. This, has two sets of three equivalent positions, and two other (single) positions. The two sets of three sites could be occupied by the three carbonyl groups and the cyclopentadiene ring leaving the two equatorial sites for the germanium and phosphorus fragments, as illustrated on page 89a.

The reaction between triphenyl phosphine and the tricarbonyl complexes is thus shown to be reversible and to proceed through an intermediate 1:1 adduct, which in favourable cases may be isolated.

$$\pi C_5H_5(CO)_3MGeR_3 \overset{PPh_3}{\rightleftharpoons} [\pi C_5H_5(CO)_3(PPh_3)MGeR_3] \underset{\substack{CO \\ \text{1 atom } 20^{o}}}{\rightleftharpoons} \pi C_5H_5(CO)_2(PPh_3)MGeR_3$$

The yellow-orange crystalline dicarbonyl-phosphine complexes were all stable to air over a period of several days.

This reaction is in direct contrast to that recently reported[165] between triphenyl-phosphine and the molybdenum and tungsten σ-bonded carbon compounds,

($\pi C_5H_5(CO)_3MCH_3$), which yields the substitution product, $\pi C_5H_5(CO)_2(PPh_3)MCH_3$, only with difficulty and proceeds via the acetyl complex $\pi C_5H_5(CO)_2(PPh_3)MCOCH_3$, which was isolated in the molybdenum case. Like the reactions between $\pi C_5H_5(CO)_2FeCH_3$ and phosphines (which give under similar conditions solely the acetyl derivatives and no substitution product),[166] a marked dependence on reaction medium was noted, and the authors stressed the need for donor solvents, finding that no reaction occurred in hydrocarbons. No mention was made of reversibility for the reaction, but the "smooth decarbonylation" of the phosphine-acetyl derivative of molybdenum in refluxing THF was observed.

A propionyl derivative of molybdenum, $\pi C_5H_5(CO)_3MOCOC_2H_5$ has been prepared by the direct action of carbon monoxide on $\pi C_5H_5(CO)_3MoEt$ at 100 atmospheres and 80^o; thermal decomposition of this very air sensitive compound gave $[\pi C_5H_5(CO)_3Mo]_2$ as the only identified product.[162] The ketonic carbonyl stretching frequencies quoted are, for $\pi C_5H_5(CO)_3MoCOEt$, 1675 cm^{-1}, and for $\pi C_5H_5(PPh_3)(CO)_2MoCOMe$, 1605 cm^{-1}, an unusually low value.

Trimethyl phosphine in slightly more than 1:1 molar ratio appeared to react in the same way with compound III, giving over 46 days at room temperature CO equivalent to 31% reaction. Work up in the usual fashion yielded the dicarbonyl-phosphine complex, $\pi C_5H_5(CO)_2(Me_3P)WGeMe_3$.

The molybdenum-ethyl complex, (II) was only sparingly soluble in di-n-propylamine, and formed in part a heavy invincible oil in this liquid. Less than 1% displacement of CO occurred over two months at room temperature.

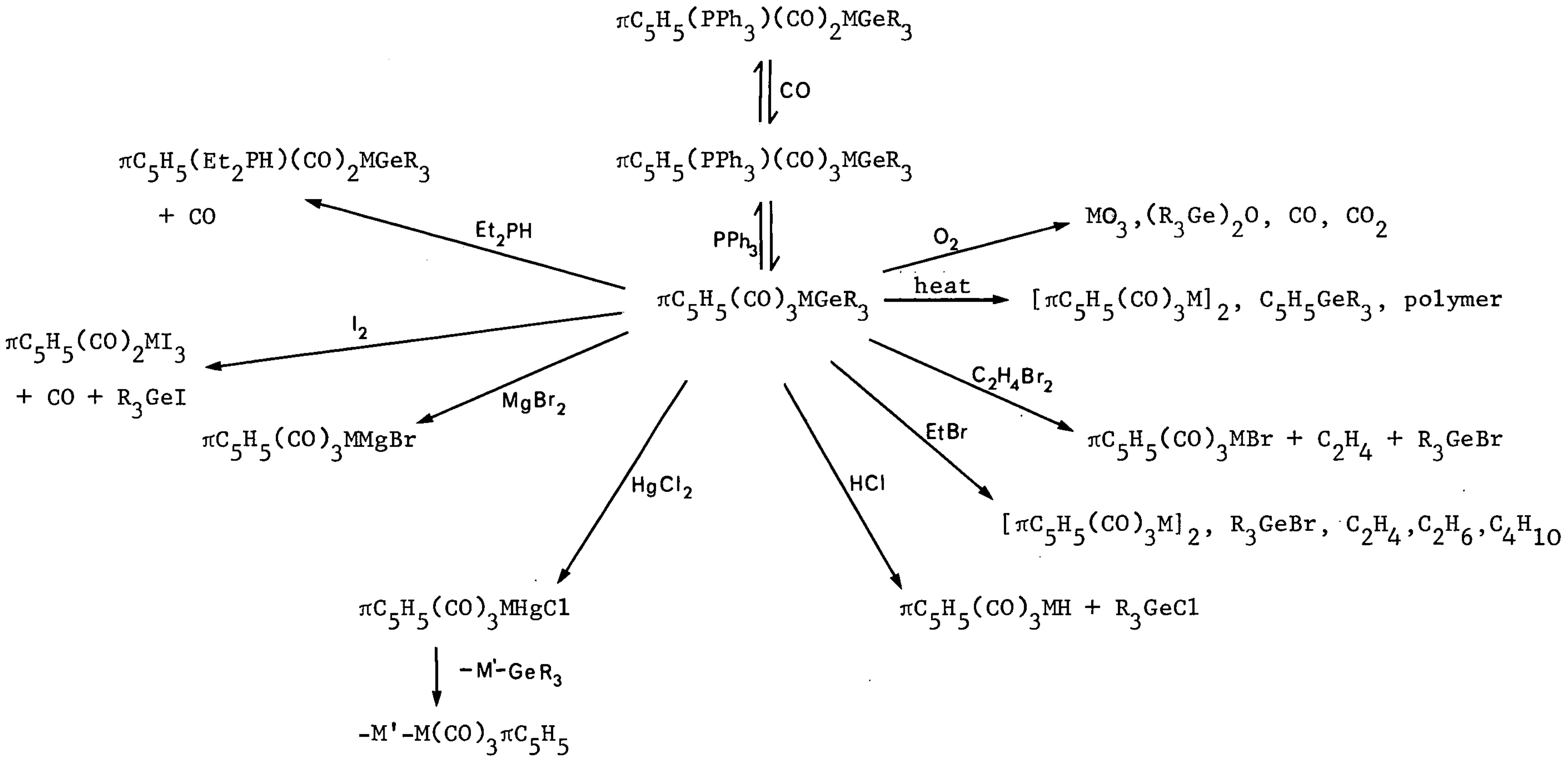
With pyridine and the tungsten-methyl complex , (IV) 4.6% reaction occurred in ten days. On work up, a definite colour change was observed in the residual solid, (after removal of the amine in vacuo) on admitting nitrogen to the reaction tube. This was the first contact the reaction product had with nitrogen, as the reactants were sealed in the tube in vacuo. Elemental analysis of the solid at this stage showed a nitrogen content of approximately 1%, although no pyridine could be detected in the mass spectrum of the material. High resolution mass measurements on the groups of peaks at mass 450 (i.e. molecular ions $\pi C_5H_5(CO)_3WGeMe_3$, and, if present of $\pi C_5H_5(CO)_2N_2WGeMe_3$) gave values lying between those expected for the tricarbonyl and dicarbonyl-nitrogen complexes, and could thus be interpreted as evidence for the solid being a mixture of these two compounds. The rather tenuous evidence suggests the possibility of the existence of an N_2 complex and its formation in a manner analogous to the reverse phosphine reaction, i.e. displacement of the nitrogen ligand by molecular nitrogen. If the pyridine carbonyl displacement reaction could be induced to give better yields of the pyridine complex, perhaps under more forcing conditions in a system where displaced CO could escape, this hypothesis could more easily be tested. Reflux of a benzene solution of the dicarbonyl-phosphine complex under a steady flow of nitrogen showed after ten days no significant change in its infrared spectrum in the region of the carbonyl stretching frequencies.

The action of the various donor molecules in displacing CO from the tricarbonyl complexes can be rationalised on consideration of their π-acceptor properties. The order of increasing π-acidity of the ligands gives the order of ease of displacement of CO

$$Pr^n_2NH < C_5H_5N < Me_3P \sim PPh_3 < Et_2PH$$

It would be interesting to extend this series to include other ligands such as NO, a very good π acceptor and also a three-electron donor (could this result in complexes of the type $\pi C_5H_5(NO)_2(L)MGeR_3$, L = CO, PX_3, RNC etc. with the

FIGURE 2.3. Some Reactions of the Complexes



same electronic configuration as the 8-co-ordinate intermediates but seven-co-ordinate geometry?). Arsenic- and sulphur- containing ligands, which have roughly the same π-acidity as the trialkyl and tri-aryl phosphines, could give interesting, easily reversible reactions with the tricarbonyl complexes.

2.4.7. Cleavage of the Metal-Metal Bond

In contrast to the facile reaction of hydrogen at low partial pressures with one Pt-Ge bond of the complexes $(R_3P)_2Pt(GeR'_3)_2$, hydrogenolysis of the molybdenum-germanium bond in complexes I and II did not occur even after 5 days at 50° and 300 atmospheres of hydrogen. Trimethylsilane and phenyl acetylene were also unreactive towards the molybdenum-germanium compounds.

The stability of all the complexes and their triphenyl phosphine derivatives towards the highly halogenated solvents chloroform and carbon tetrachloride has already been mentioned. With ethylene dibromide however, the expected cleavage reaction occurred, yielding after 2-4 days at 60^o-80^o the quantitative amount of ethylene and the corresponding transition metal- and germanium-bromides.

$$\pi C_5H_5(CO)_3MGeR_3 + C_2H_4Br_2 \longrightarrow \pi C_5H_5(CO)_3MBr + BrGeR_3 + C_2H_4$$

Some small amount of permanent gas, probably CO, was isolated from the reactions and it seems likely that on prolonged heating, the transition metal halide reacts further, either with free halogen formed during the major reaction, or with the excess ethylene dibromide, in a manner similar to the iodine reaction described below.

Ethyl bromide also cleaves the metal-metal bond in a reaction whose products indicate at some stage the presence of alkyl radicals. The reaction was slow at room temperature, but after heating for nine days at 70°, the tungsten-methyl complex and ethyl bromide gave approximately 52% of ethylene containing some ethane. Butane was detected by V.P.C. of the ethyl bromide used as solvent, and the other major products were trimethylbromogermane and π-cyclopentadienyltricarbonyl tungsten dimer. The molybdenum compounds gave analogous products.

$$\pi C_5H_5(CO)_3MGeR_3 + C_2H_5Br \longrightarrow R_3GeBr + [\pi C_5H_5(CO)_3M]_2 + C_2H_4 + C_2H_6 + C_4H_{10}$$

None of the corresponding transition metal- or germanium-hydrides or the hexa-alkyl digermanes was detected. The presence of some small amount of the transition metal halide, which implies the formation of a tetraalkyl germane or hexa-alkyl digermane, was not satisfactorily confirmed but could not be ruled out.

All the tricarbonyl complexes (I-V) were readily soluble in the halogen compounds mentioned.

Reaction of the complexes with ethereal hydrogen chloride gave only two products.

$$\pi C_5H_5(CO)_3MGeR_3 + HCl \xrightarrow{Et_2O,\ 20^o} \pi C_5H_5(CO)_3MH + R_3GeCl$$

The mass spectrum of the molybdenum-containing material from this reaction on the ethyl complex (II) showed intense molecular ions due to the metal hydride, and no trace of the molybdenum halide. V.P.C. examination of the germanium-containing portion similarly showed no trace of germanium hydride.

Excess iodine in benzene solution cleaved the metal-metal bond and went on to displace one carbonyl group giving an interesting tri-halo compound.

$$\pi C_5H_5(CO)_3MGeR_3 + 2I_2 \longrightarrow \pi C_5H_5(CO)_2MI_3 + R_3GeI + CO$$

The molybdenum-halogen compounds of this type were reported at almost the same time as this reaction was performed.[167] They are diamagnetic and non-electrolytes and the authors suggested a high oxidation level for the transition element to account for the high CO stretching frequencies, and also a possible eight-co-ordinate structure. The molybdenum trihalogen complexes containing bromine and chlorine decompose with the liberation of carbon monoxide. An 18-electron, seven co-ordinate structure, however, could be proposed, if the presence of an X_2 unit donating two electrons is allowed, and such an X_2X formulation could account for the loss of CO in the decomposition of these compounds. Attempts to indicate the presence of an I_2 unit in $\pi C_5H_5(CO)_2WI_3$ in the present work by examining its visible/near U.V. spectrum in benzene solution for charge-transfer bands, (by analogy with the the well known I_2-benzene complex) proved inconclusive.

Perhaps the most interesting cleavage reactions occurred with metal halides. These were carried out only on the tungsten complexes but there seems to be no reason why the molybdenum compounds should not react in the same way.

Freshly sublimed mercuric chloride readily cleaved the W-Ge bond of complexes IV and V in THF solution to give the bright lemon yellow tungsten mercury chloride almost quantitatively

$$\pi C_5H_5(CO)_3WGeR_3 + HgCl_2 \xrightarrow[\text{THF}]{\text{room temp.12 hrs.}} \pi C_5H_5(CO)_3WHgCl + R_3GeCl \qquad 75\%$$

This metal-metal bonded compound is air stable in solid form over a few days but is light sensitive giving a black deposit of mercury metal within 1 hour on exposure to sunlight. (c.f. the germanium silicon mercury compounds $(Me_3Ge)_2Hg$ and $(Me_3Si)_2Hg$). The -HgCl unit was capable of further reaction with another M-Ge bond as described below.

The tungsten complexes also reacted with freshly prepared anhydrous magnesium bromide in T.H.F. to yield the extremely interesting pink tungsten-magnesium compound - the first compound containing an M-M bond to a group II element to be isolated. Elemental analysis indicated one molecule of co-ordinated tetrahydrofuran on the solid state, and the p.m.r. spectrum of a saturated solution in benzene conformed this, indicating a 1:1 ratio of C_5H_5 to C_4H_8O

$$\pi C_5H_5(CO)_3WGeR_3 \ + \ MgBr_2 \xrightarrow[5\ \text{days}]{\text{THF},\ 20^o} \pi C_5H_5(CO)_3WMgBr.THF \ + \ BrGeR_3$$

Molecular weight measurements in freezing benzene, were rather restricted by low solubility but indicated a monomeric unit for the compound in this solution. The magnesium atom in the monomer must then be three co-ordinate, one of the few examples of magnesium in this unusual configuration.[168] If the geometry of this compound conforms roughly to that suggested for the trialkylgermyl derivatives, then steric reasons for the inability of the unit to dimerise could readily by justified from the nearness of the carbonyl and cyclopentadiene groups to the bulky T.H.F. ring and bromine atom attached to a trigonal magnesium atom. This is illustrated on page 89a, fig. 2.2.

2.4.8. Reactions of the tungsten-mercury compound and other M-Ge derivatives

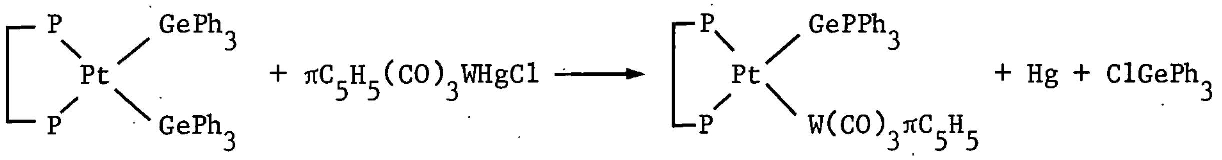
The presence of the potentially reatice -HgCl unit in the tungsten-mercury complex, $\pi C_5H_5(CO)_3WHgCl$, prompted an examination of the action of this compound on other germanium-metal bonds in the hope of producing perhaps a linear W-Hg-M' grouping which might then be induced to yield a W-M' bond.

Addition of a solution of the tungsten-mercury compound to a benzene-T.H.F. solution of the germanium-gold complex, $PPh_3AuGePh_3$, resulted in an immediate precipitation of mercury and the decomposition of a very thin almost transparent, red film of gold on the walls of the reaction vessel. The pale yellow tungsten-gold complex $\pi C_5H_5(CO)_3WAuPPh_3$ was isolated in good yield (approx.70%) after only ten minutes stirring of the reaction mixture.

$$PPh_3AuGePh_3 + \pi C_5H_5(CO)_3WHgCl \longrightarrow \pi C_5H_5(CO)_3WAuPPh_3 + Hg + ClGePh_3$$

The amount of decomposition to metallic gold was very small indeed.

Similarly the reaction of the tungsten-mercury compound in 1:1 molar ratio with the platinum complex $(Ph_2PC_2H_4PPh_2)Pt(GePh_3)_2$ in THF yielded an immediate precipitate of mercury and the buff platinum-tungsten-germanium complex.

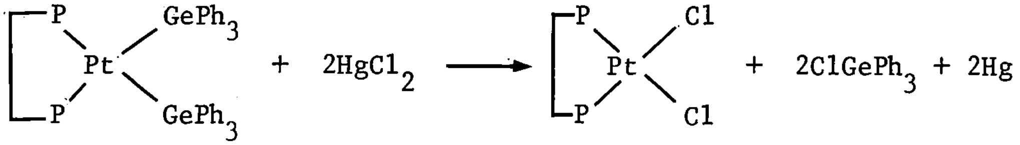


This reaction was also rapid. In this cases the metallic mercury is assumed to come from the decomposition of $R_3GeHgCl$, and elimination of this compound from an octahedral Pt complex intermediate, by analogy with the Ir-Hg [152] complexes, seems feasible. The platinum-tungsten-germanium complex was not easy to purify because of solubility difficulties but infrared, elemental analysis and mass spectrometry indicated that the major product of the reaction was this compound.

The reaction of the tungsten-mercury compound with the more soluble $(Et_3P)_2(I)PtGeMe_3$ was, in contrast, more complicated and the major product, a dark red crystalline solid, was probably the tungsten dimer $[\pi C_5H_5(CO)_3W]_2$, although it was not completely characterised. The fate of the platinum and germanium containing portion of the reactants was not easy to ascertain. These facts could lend rather dubious support to an octahedral addition intermediate with all possible elimination reactions occurring. Metallic mercury was again deposited almost immediately.

In an attempt to further establish the generality of the cleavage of M-Ge bonds and to extend the synthetic method for metal-metal bonds which was begining to emerge, the reaction of mercuric chloride on the two platinum complexes,

$(Ph_2PC_2H_4PPh_2)Pt(GePh_3)_2$ and $(Et_3P)_2Pt(GePh_3)_2$, was investigated. The former in 2:1 molar ratio with a THF solution of mercuric chloride gave after long stirring only the chelating phosphine platinum dichloride and unreacted starting material as the major platinum containing products.



Presumably the small solubility of these compounds allowed the cleavage of both Pt-Ge complexes to proceed to completion before any further other reaction could take place.

The soluble platinum complex however, reacted in a more interesting manner. Slow dropwise addition of a solution of mercuric chloride in THF to a THF solution of $(Et_3P)_2Pt(GePh_3)_2$ (overall molar ratio Pt complex:$HgCl_2$::2:1) resulted in an immediate precipitation of mercury, and a golden solution remained on allowing the mercury to settle out. This solution turned first orange, then brown over some 45 minutes, depositing a brown film (presumably metallic Pt) on the walls of the reaction vessel, in a manner reminiscent of the tungsten-mercury-gold complex reaction. Filtration yielded a brown solution from which light brown crystals were precipitated. The elemental analysis, infrared spectrum and mass spectra of this material all indicated the formation of a dimeric platinum germanium complex, presumably containing a Pt-Pt bond.

$$2(Et_3P)_2Pt(GePh_3)_2 + HgCl_2 \longrightarrow (Et_3P)_2(Ph_3Ge)Pt\text{-}Pt(GePh_3)(PEt_3)_2 + ClGePh_3 + (ClHgGePh_3)$$

It seems likely that the light brown colour of the compound is not genuine but is due to the precipitation of a fine film of Pt metal. Very soon after this, the report of the preparation of the $(PPh_3)_2XPt\text{-}PtX(PPh_3)_2$ and $(PPh_3)_2ClPtHgCl$ complex by an addition reaction appeared. This more direct confirmation of the stability of the Pt-Hg bond lends support to a Pt-Hg-Cl intermediate for the above reaction which then attacks a Pt-Ge bond in another molecule, possibly forming an octahedral (addition) intermediate before decomposing to the Pt-Pt complex.

The cleavage of M'-Ge bonds by M-Hg-Cl units is thus a general process which, in the simpler cases studied, yields the M-M' bond directly, and could thus become an extremely useful method of synthesis of previously unattainable metal-metal bonded complex, particularly polynuclear compounds.

An attempt to prepare a σ-bonded aryl tungsten compound using the "tungsten Grignard reagent" and bromobenzene

$$\pi C_5H_5(CO)_3WMgBr + BrPh \xrightarrow{THF} \pi C_5H_5(CO)_3W\sigma C_6H_5 + MgBr_2$$

yielded only the tungsten hydride on work up. Accidental hydrolysis over the extended period of the small scale reaction could not be ruled out

$$\pi C_5H_5(CO)_3WMgBr \xrightarrow{H_2O} \pi C_5H_5(CO)_3WH$$

It is interesting to note that earlier attempts to prepare the phenyl-tungsten compound and similar complexes using the conventional Grignard reagent on the tungsten halide also failed[153]

$$\pi C_5H_5(CO)_3WBr + ArMgBr \longrightarrow \text{tarry material}$$

and the σ bonded aryl tungsten complexes remain unknown.

2.5. EXPERIMENTAL

2.5.1. Preparation of the complexes

π-Cyclopentadienyltrimethylgermyltricarbonyl molybdenum(I). - Freshly cracked cyclopentadiene (4.0 gm., 0.062 mole) was added slowly to a stirred suspension of sodium (1.2 gm., 0.048 mole) in freshly distilled tetrahydrofuran (T.H.F., 120 ml.) and the pink solution was refluxed for two hours to ensure complete reaction. The solution was allowed to cool and molybdenum hexacarbonyl (12.6 gm., 0.0476 mole) was added and the mixture refluxed, with stirring, for 15 hours. Vigorous effervescence occurred during the first hour of reflux and the colour of the solution slowly changed to a clear orange. Trimethylbromogermane (9.5 gm., 0.048 mole) in THF (50 ml.) was added slowly to the stirred solution at room temperature, and the solution turned yellow with the formation of a thick white precipitate. After reflux for a further three hours, the colour changed to an orange-red. The solution was filtered (under nitrogen), the THF removed in vacuo, replaced by degassed pentane (40 ml.) and the solution again filtered to remove sodium bromide which had been dissolved in the THF. Lustrous, platy crystals were deposited from the solution at -10^{o}. The mother liquors were decanted and the crystals were washed with pentane at -78^{o}, redissolved, filtered and recrystallised to give very pale pink crystals of the methyl complex (11.5 gm., 65%) with analytical data as shown in table 2.1. Sublimation at 50^{o}-55^{o} and 10^{-4} mm gave the methyl complex as virtually colourless plates.

π-Cyclopentadienyltri-ethylgermyltricarbonyl molybdenum (II) was prepared in an analogous manner from sodium cyclopentadienide (0.074 mole) molybdenum hexacarbonyl (16.3 gm., 0.062 mole) and tri-ethylbromogermane (15 gm., 0.062

mole). The complex crystallised as pink needles from pentane at -60^{o} (9.6 gm., 46%, analytical data as in table 2.1.). Its ultra violet/visible spectrum in ethanol showed three main bands λ_{max} 207 mμ, log ϵ 3.44; λ_{max} 263 mμ, log ϵ 3.00; λ_{max} 320 mμ log ϵ 2.40.

Similarly, tri-n-propylbromogermane (12 gm., 0.043 mole) and the dosium salt of π-cyclopentadienyltricarbonyl molybdenum in THF (0.043 mole) yielded the brick-red complex π-cyclopentadienyltri-n-propylgermyltricarbonyl molybdenum(III). Some difficulty was experienced in the isolation of this material because of its great solubility in all the common solvents, and it was crystallised from pentane at -78^{o} with considerable loss. Its low melting point (approx. 25^{o}) added to the difficulties and only mass spectrometric and infrared (i.r.) characterisation were obtained.

The tungsten complexes π-cyclopentadienyltrimethylgermyltricarbonyl tungsten (IV) and the tri-ethylgermyl analogue (V) wereprepared in a similar fashion, but using di-n-butyl ether as a reaction medium. The sodium"shot" for the reactions was prepared in situ in this solvent and refluxed for 12 hours to ensure complete reaction with the added cyclopentadiene. White crystals of sodium cyclopentadienide formed on cooling the solution, and after addition of the tungsten carbonyl, the mixture was refluxed for 36 hours before adding the germanium halide. Addition of 20-30% (by volume) of THF was advantageous because of the increased solubility of the reactants in this material. The tungsten-germanium-methyl complex (IV) was prepared on an 0.025 molar scale (yield 5.8 gm., 50%) and the tungsten-germanium ethyl complex on an 0.013 molar scale (yield 3.2 gm., 48%).

All the complexes had characteristic, sweetish, nauseating odours. Infrared and analytical data are given in table 2.1.

2.5.2. Reactions of the complexes

(i) Oxidation. The molybdenum-methyl complex (I) (91 mg., 0.25 mmole) was dissolved in benzene (2.5 ml.) in a "break-seal" tube, which was then filled with dry oxygen (25 ml.) sealed and shaken for 20 days. Over the first 17 hours of shaking the colour of the solution changed as described in the text. Fractional condensation of the volatile products gave CO (9.07 ccs at S.T.P. (Nccs), identified by its infrared and mass spectrum and estimated by combustion) CO_2 (2.18 Nccs i.r. and m.s. identification), ratio of complex to CO and CO_2 1:1.61:0.57 mole, respectively. Examination of the benzene solvent by vapour phase chromatography (V.P.C.) on Apiezon L. (A.P.L.) and neopentylglycol adipate (N.G.A.) stationary phases confirmed the presence of hexamethyl digermane. The crude blue residue showed considerable infrared structure (table 2.) and the mass spectrum of this material showed peaks due to $(Me_3Ge)_2O$ and others which could be ascribed to a compound of the formula $(Me_3Ge)_3COH$. Mass spectrometry on other blue residues from similar experiments showed peaks which could be ascribed to this latter compound under low resolution but high resolution confirmation of this formulation could not be obtained. No significant amount of material could be soxhelet extracted with benzene from the blue powder, which on further exposure to air lost all its i.r. bands othern than a very broad metal-oxygen vibration centred on 12 μ, and failed to yield any mass spectrum from a direct insertion probe.

The molybdenum-ethyl complex (II) sealed in oxygen gave after standing at room temperature for 3 months, a small amount of CO and CO_2 (<1 Ncc, identified by mass spectrumetry) and, in part, a brown-black solid [Found: C, 35.4; H,4.42%; stoichiometry $C_{14}H_{20}O_7MoGe$, i.e. $C_5H_5(CO)_3(O_4)MoGeEt_3$ requires C,35.8; H,4.26%] which showed four distinct vibrations in the carbonyl stretching region of the infrared (1961, 1946, 1916, 1883 cm^{-1}, in KBr). This material was non-melting at temperatures up to 350° and was slightly soluble in benzene and methanol to give orange-red solutions which turned blue on exposure (6-12 hours) to air. Starting material was also recovered.

After 40 days in contact with 410 Nccs (18.3 mmole) of oxygen, a benzene solution of the tungsten-methyl complex (0.436 gm., 0.966 mmole, in 10 ml. benzene) gave on soxhelet extraction of the solid residue with benzene 87.7% (by wt.) of unchanged material (i.r. characterisation). Roughly 6.5 Ncc (0.3 mmole equiv.) of CO_2 and 27 Ncc of CO (1.2 mmole equiv. estimated by combustion) were collected, a total of approx. 1.5 mmole equiv. for CO removed from the complex and putting the limits of oxidation for the material at 12 and 50%. The lower value is the more reliable. V.P.C. examination showed the presence of $(Me_3Ge)_2O$ in the solvent.

(ii) Hydrolysis. A solution of the molybdenum-ethyl complex (0.20 gm.) in a mixture of carefully degassed acetone (8 ml.) and D_2O gave no permanent gas after standing for two days at room temperature. Careful examination of the solvent by v.p.c. gave no evidence for any volatile metal-containing compound or hydrocarbon species. The i.r. spectrum of the solid material recovered by benzene extraction (under N_2) was identical with that of starting material. A similar experiment with the molybdenum-methyl complex (I) gave the same result, and during the course of the reactions of the tungsten complexes, sensitivity to water was not observed.

(iii) Pyrolysis. The molybdenum-ethyl complex (II), (0.21 gm. 0.51 mmole) was heated in a vacuum apparatus for 6 days at 150°-160°. Carbon monoxide (0.40 Nccs, 0.017 mmole equiv.) was collected from above the fused solid after cooling, and further heating at 200° for two days produced only a very small additional amount of gas (< 0.05 Nccs). Sublimation of the solid in vacuo gave 0.185 gm. (89%) of starting material (i.r. characterisation) and about 10 mg . of a red solid [Found: C,40.3; H,4.23%] part of which slowly sublimed at 60^{o}-70^{o} and 10^{-5} mm to give scarlet crystals. The initial red material was slightly soluble in benzene and molecular weight measurements in this solvent (V.P. osmometer) gave values in the range 615-740.

Complex I behaved in a similar manner, with little decomposition occurring below 200^{o}.

A small quantity of the molybdenum-ethyl complex was heated to 200^{o} for 15 minutes in the hot inlet system of the mass spectrometer and after this time the volatile products were allowed to enter the ionisation chamber. $C_5H_5GeEt_3$ was detected (and characterised) in good amount, together with peaks at higher masses which could be ascribed to ion fragments from the unaltered complex.

Heating the tungsten-methyl complex (0.138 gm., 0.307 mmole) in a small volume (6 ml.) break seal tube for 5 days at 180-190^{o} gave 0.614 Ncc of CO (0.0896 mmole equiv.). Sublimation of the residual solid from the tube gave 91.1% (by wt.) of unchanged starting material (i.r. characterisation) and a few milligrams of light red crystals identified (by i.r.) as $[\pi C_5H_5W(CO)_3]_2$ A very small amount (~ 1 mg.) of a green-black, involatile, acetone soluble material remained in the reaction vessel after the sublimation.

(iv) Reactions wirh Di-ethylphosphine. The molybdenum-ethyl complex, II, (0.17 gm., 0.42 mmole) was sealed with 3 ml. of freshly distilled di-ethylphosphine in an evacuated break seal tube. After standing for 28 days at room temperature, the solution yielded 8.65 Nccs (92 mole%) of carbon monoxide. Removal of the excess phosphine in vacuo and recrystallisation of the residue from pentane at -20^{o}, gave the pale yellow, air sensitive, low melting crystalline complex π-cyclopentadienyltri-ethylgermyldi-ethylphosphinodicarbonyl molybdenum (ν P-H 2286 cm^{-1}, ν CO 1942s, 1910 m,sh, 1848s cm^{-1}, ν CH of C_5H_5 3106 cm^{-1}; M ^{170}(MoGe) 468). No further characterisation of this material was obtained.

A similar reaction between 0.161 gm. (0.358 mmole) of the tungsten-methyl complex, (IV) and 2.5 ml. of di-ethylphosphine gave 7.98 Nccs (100 mole%) of CO after 14 days at room temperature. All efforts to recrystallise the residual material from methylcyclohexane and $40^{\circ}/60^{\circ}$ petroleum failed to give a solid and π-cyclopentadienyltrimethylgermyldi-ethylphosphinodicarbonyl tungsten was obtained as a golden yellow air sensitive liquid [Found: C,32.6; H,4.90%, M^{256}(WGe) 512. $C_{15}H_{25}O_2$ P WGe, i.e. $C_5H_5(CO)_2(Et_2PH)WGeMe_3$ requires C,32.8; H,4.91%; M ^{256}(WGe) 512]. ν CO 1941s, 1861s, cm^{-1} (in CCl_4) ν P-H 2286 cm^{-1}.

(v) Triphenylphosphine reactions.

(a) In sealed systems: The molybdenum-methyl complex (I) (0.325 gm., 0.895 mmole) and triphenylphosphine (0.62 gm., 2.4 mmole) were dissolved in 5 ml. of benzene and heated in a break seal tube for 24 days at 65°. After this time 6.53 Nccs (31.8 mole%) of carbon monoxide were collected from above the solution. The yellow-brown material (25.3 mg.) which was formed during the first 4 hours of heating was removed from the solution by filtration and the i.r. spectra of this solid and the solution were examined in the region 4.5-6.5 μ as soon after removal from the apparatus as possible. Three major bands occurred in this range (1818s, 1894m, 2016m, cm^{-1}, in KBr) none of which could be ascribed to a ketonic configuration for a C-O unit. The mass spectrum of the solid showed under unit resolution rather ill-defined ions corresponding to $C_5H_5(CO)_3(PPh_3)MoGeMe_3$. An 0.5% solution of water in acetone (2 ml.) had no effect on the appearance of the remainder of the benzene solution of the crude product and gave no additional gas. The i.r. spectrum of the material after removal of the acetone, water and benzene remained unchanged and was identical with the i.r. of similar reactions (without addition of water) at the same stage. Replacement of the benzene by methylcyclohexane gave, at -20° to -40° pale yellow crystals of π-cyclopentadienyltrimethylgermyltriphenylphosphinodicarbonyl molybdenum MPt 215°-216° (sealed tube). [Found: C,57.24, H,5.06; P,5.93, $C_{28}H_{29}O_{2}GeMoP$, i.e. $C_5H_5(PPh_3)(CO)_2MoGeMe_3$ requires C,56.33; H,4.90; P,5.14%]. ν CO ($\frac{1}{2}$ mg./cc in $CDCl_3$) 1911s, 1894m,sh, 1831s, cm^{-1}. The proton magnetic resonance spectrum of this material (50 mg./cc in $CDCl_3$) showed resonance corresponding to πC_5H_5, τ 5.18, C_6H_5, τ 2.53, and CH_3, τ 9.42 in the ratio 5.2:15.0:9.7.

A tube containing 0.324 gm. (0.898 mmole) of the molybdenum-methyl complex and 0.24 gm. (0.91 mmole) of triphenyl phosphine dissolved in 1 ml. benzene gave, after heating for 24 hrs. at 65°, 4.7 Nccs of CO (24 mole%) and on immediate removal of benzene and washing the resultant solid with 4 x 6 ml. of $40^{\circ}/60^{\circ}$ petroleum, a buff powder (MPt 100°-200° dec; Found: C,52.3; H,4.64; P, 5.7%) whose mass spectrum under low source pressure conditions showed ions ascribed to $C_5H_5(CO)_3(PPh_3)MoGeMe_3$. A tube containing 0.322 gm. (0.898 mmole) of the methyl complex and 0.546 gm. (2.09 mmole) of PPh_3 in 5 ml. benzene gave 2.44 Nccs (12 mole%) of CO after 24 days at room temperature, and 34.8 mg. of the yellow-brown intermediate (present from about 12 hours after the start of the reaction). Again the dicarbonyl-phosphine complex was the major product, crystallising from a sherry-coloured solution in methylcyclohexane.

Similarly the ethyl complex with both an excess of and 1:1 molar ratio of triphenylphosphine in methylcyclohexane yield, after heating 65°-70° for 1-7 days 25-31 mole% of CO and buff crystals of π-cyclopentadienyltri-ethylgermyltriphosphinodicarbonylmolybdenum (25%) MPt 165°-170° dec (open tube) ν CO, 1937s; 1898w,; 1858s, cm^{-1}. [Found: C,58.3; H,4.35; P,6.85; M ^{170}(MoGe), 612: $C_{32}H_{35}GeMoO_2$, i.e. $C_5H_5(CO)_2(PPh_3)MoGeEt_3$ requires C,57.6; H,5.29; P,4.6%]. The initial light brown precipitate gave a reproducible mass spectrum under low pressure conditions, showing ions corresponding to $C_5H_5(CO)_3(PPh_3)MoGeEt_3$ with the required MoGe isotope pattern easily distinguishable, but satisfactory high resolution mass measurements were again not obtained. In all experiments unchanged starting materials were recovered, and careful V.p.c. examination of the solvents under a wide range of condtions showed no trace of volatile metal-containing compounds.

Similar experiments with the tungsten-methyl complex, IV, gave from 1.06 mmole (0.478 gm.) of (IV) and 1.23 mole (0.326 gm.) of PPh_3 in 5 ml. of methylcyclohexane, 22.5 mole% (5.29 Nccs) of CO, after heating for 30 days at 65°. A further 2.5 mole% (0.59 Nccs) was removed from above the mixture four hours later, during which time the reaction tube was left attached to the vacuum apparatus at room temperature. Work up in the usual fashion under nitrogen gave π-cyclopentadienyltrimethylgermyltriphenylphosphinodicarbonyltungsten (0.243 gm., 34%) [Found: C,52.8; H,3.87; P,6.35; M ^{256}(WGe) 684 $C_{28}H_{29}O_2GePW$, i.e. $C_5H_5(CO)_2(PPh_3)WGeMe_3$ requires C,49.1; H 4.27; P,4.52%]. From a reaction of IV with a 3 fold excess of the phosphine at 65°, 17 mole% of CO was isolated Reproducible mass spectra on the brown solid present during these reactions were not obtained; the i.r. of the crude reaction products showed in addition to the usual 3 ν CO bands, 3 ν C-H bands for the C_5H_5 unit at 3135,3125,3096 cm^{-1}.

(b) in an open system. To the molybdenum-ethyl complex (II) (approx. 3.6 gm. 0.086 mole) in pentane (8 ml.) in a double shlenk tube, was added a benzene-pentane (5.30 ml.) solution of triphenyl phosphine (2.4 gm., 0.092 mole) Over the first 15 minutes of stirring, a small amount of buff material appeared. The sherry coloured solution was stirred at room temperature overnight, filtered, and the solvent removed in vacuo to give an orange-yellow solid which did not give crystals from pentane at -78°. After allowing the solution to stand under nitrogen for a further five days the pentane was replaced by methylcyclohexane, and work up in the usual fashion gave the phosphine-dicarbonyl complex (ca. 4gm. ~75%).

(vi) Reaction of the tungsten phosphine-dicarbonyl complexes with carbon monoxide

(a) Sealed system. The tungsten-phosphine-dicarbonyl complex (π-$C_5H_5(CO)_2(PPh_3)WGeMe_3$), (0.048 gm.) dissolved in 1:1 benzene-acetone (6 ml.) was sealed in a 120 ml. flask filled with CO at atmospheric pressure and was shaken for 14 days at 18°. The i.r. spectrum of the recovered material (38 mg. of solid) showed three major carbonyl stretching frequencies, and the mass spectrum of this material showed unequivocally the presence of the tricarbonyl complex ($\pi C_5H_5(CO)_3WGeMe_3$). Exposure of the crude reaction product (as a semi-solid before recrystallisation gave large Ph_3PO^+ and $Ph_3PO_2^+$ ions its mass spectrum which were not normally observed in the spectra of the dicarbonyl-phosphine complexes (which are reasonably air stable) and these ions were attributed to oxidation of the tricarbonyl-phosphine intermediate.

(b) open system. A slow current of carbon monoxide was passed through a refluxing solution of the dicarbonyl-phosphine complex (33 mg.) in benzene (5 ml.). After 18 hours reflux was stopped and the i.r. of the solution then showed three major carbonyl stretching frequencies (2026s, 1929s, 1835s, cm^{-1}, of the tricarbonyl compound). The benzene solvent was then allowed to evaporate under a current of CO and the mass spectrum of the solid residue (33 mg.) was determined without further treatment. This showed ions due to π-$C_5H_5(CO)_3WGeMe_3$ (mol. ion intensity 1.2) and $\pi C_5H_5(CO)_2(PPh_3)WGeMe_3$, (mol. ion intensity 1.0 but none due to a tricarbonyl-phosphine complex ($\pi C_5H_5(CO)_3(PPh_3)WGeMe_3$). The i.r. spectrum of the solid corresponded to a mixture of the dicarbonyl-phosphine and tricarbonyl complexes in the ratio indicated by the mass spectrum.

(c) N.M.R. experiment. A solution of approc. 0.1 mmole (50-60 mg.) of the tungsten dicarbonyl-phosphine ($\pi C_5H_5(CO)_2(PPh_3)WGeMe_3$) in 0.4 ml. $CDCl_3$ containing T.M.S., was made up in an NMR tube (ca. 4 mm I/D, 138 mm long) attached to a spherical thin walled bulb (40 mm I/D, total volume of apparatus, 18.9 cc), by distilling the liquids onto the solid in the tube from a vacuum apparatus. The tube was filled with CO at atmospheric pressure, with the solution cooled to -193^{o} and sealed. The experiment and its results are described in the text,

(vii) Reaction with trimethylphosphine. The tungsten-methyl complex, (IV), (0.439 gm., 0.974 mmole) was dissolved in benzene (5 ml.) in a break seal tube and trimethylphosphine (27.0 Nccs, 1.20 mmole) was condensed onto the solution. After two days at room temperature, a few long, light-green needle shaped crystals were noted in the dull yellow green solution and these remained until the tube was opened 44 days later. On opening the tube 6.91 Ncc (31.6 mole%) of CO were obtained. Work up of the solution in the usual fashion (under N_2) yielded, from a brilliant golden-yellow solution in methylcyclohexane yellow crystals of π-cyclopentadienyltrimethylgermyltrimethylphosphinodicarbonyl tungsten MPt 80^{o} ν CO 1887s, 1799s, cm^{-1} (in KBr) [Found: C,31.55; H,4.57; M ^{256}(WGe) 588, $C_{13}H_{23}O_2PGeW$ i.e. $C_5H_5(CO)_2(PMe_3)WGeMe_3$ requires C,31.3; H,4.65%]. The complex smelled strongly of trimethylphosphine.

(viii) <u>Reaction with di-n-propylamine</u>. The molybdenum-ethyl complex, (II), (0.193 gm. 0.474 mmole) dissolved in freshly distilled di-n-propylamine (6 ml.) gave only a very small amount of permanent gas (0.1 Ncc, 1% reaction) after standing for two months at room temperature. A heavy red-orange oil formed over the first 3 hours, and this yielded after removal of the excess amine, in vacuo, 0.083 gm. of unreacted starting material (i.r. and m.s. characterisation).

(ix) <u>Reaction with pyridine</u>. The tungsten-methyl complex, (IV), (0.369 gm. 0.822 mmole) dissolved in 2 ml. redistilled pyridine gave after 10 days at room temperature 0.85 Ncc (4.6 mole%) of CO. The light pink solid remaining after removal of excess amine in vacuo turned dark red over 5 minutes on admitting nitrogen to the system and the mass spectrum of the material gave for the ion set centred at 450 the masses 447.96926,448.96800, 449.96771, 450.9710, 451.96778, 452.96941. $C_{11}H_{14}O_3WGe$ i.e. cp $(CO)_3WGeMe_3$ requires 447.966362, 448.966187, 449.966899, 450.966394, 451.967229, 452.969975. $C_{10}H_{14}O_2N_2WGe$ i.e. cp $(CO)_2N_2WGeMe_3$ requires 447.97797, 448.97742, 449.97841, 450.97788, 451.97890, 450.97788, 451.97890, 452.98121. One of the pyridine complex was isolated on work up.

(x) <u>Cleavage by 1,2-dibromoethane</u>. The molybdenum-methyl complex, (I), (0.376 gm., 1.03 mmole) dissolved in 1,2-dibromoethane, (5.1 gm.), gave after heating for four days at 70°-78°, ethylene (21.7 Nccs, 94.1 mole%) and lustrous dark red crystals (from pentane ay -10° to -20°) of π-cyclopentadienyltricarbonyl molybdenum bromide. [Found: C,29.53; H,1.88; Br,23.8; $C_8H_5O_3BrMo$ requires C,29.56; H,1.55; Br,24.6%]. The 1,2-dibromoethane recovered was shown by V.p.c. measurements (comparison with authentic material) to contain 9.4-11.0 wt.% of Me_3GeBr in 2.7 gm. of solution (i.e. 90-100 mole% of Me_3GeBr, τ_{Me} 3.47 in $C_2H_4Br_2$). A similar experiment, with heating for four days at 90° gave in addition to 100 mole% ethylene, 3.9 Nccs (17 mole%) of permanent gas (probably CO) and a small amount of red brown powder, shown by mass spectrometry to be a molybdenum polybromide containing C_5H_5 and probably 2 CO groups.

(xi) Cleavage by ethyl bromide. The molybdenum-ethyl complex, II, (0.145 gm., 0.349 mmole) and redistilled ethyl bromide (5 ml.) were allowed to stand for 4 months at room temperature, the solution slowly turning deep red. Fractional condensation of the volatile products yielded no permanent gas, and 5.10 Nccs of a gas which passed through a trap held at -78° and which was shown by i.r. and mass spectrum to be a mixture of ethylene and ethane. V.p.c. examination of the excess ethyl bromide showed, on comparison with authentic materials, the presence of triethylbromogermane, no tetraethylgermane or hexa-ethyldigermane, and some butane. The residual red solid was separated by fractional crystallisation from benzene/pentane into starting material (i.r. characterisation) and bis(π-cyclopentadienyl-tricarbonyl molybdenum), (characterised by i.r. and elemental analysis).

A similar experiment in which the tungsten-methyl complex (IV) (0.368 gm., 0.819 mmole) and ethyl bromide (5 ml.) were heated for 9 days at 65° gave a dark red solution containing very dark red crystals and 9.57 Nccs (52.4 mole%) of ethane/ethylene mixture, and other products analogous to the molybdenum reaction. ($C_4H_{10}Me_3GeBr$, starting material, and $[\pi C_5H_5W(CO)_3]_2$, 74 mg.). In this reaction about 1.3 Nccs of CO were also obtained and polybromo tungsten compound (approx. 10 mg.) similar in character to that that from the reaction of ethylene dibromide on the molybdenum complex. No other products were identified.

(xii) Cleavage by hydrogen chloride. The molybdenum-methyl complex (0.332 gm. 0.915mmole) and about 5 ml. of dry diethylether saturated with hydrogen chloride were stirred magnetically in a vacuum apparatus at room temperature for four days. The clear solution turned slowly light orange and deposited orange-yellow crystals. After removal of solvent and excess HCl, the residue was heated to 60^{o}-70^{o} at 10^{-3}mm (closed system) and over $1\frac{1}{2}$ hours yielded well formed pale yellow crystals of π-cyclopentadienyltricarbonyl molybdenum hydride (ν Mo-M 1786 cm^{-1}, in CS_2; M ^{98}Mo 248). The mass spectrum of this hydride showed intense molecular ions with a clean Mo isotope pattern and no trace of the halide $C_5H_5(CO)_3MoCl$ (M, ^{133}(MoCl), 282). V.p.c. examination of the ether showed trimethylchlorogermane and no trace of trimethylgermane.

Dry hydrogen chloride gas bubbled through a benzene solution of the molybdenum ethyl complex also yielded the molybdenum hydride and triethylchlorogermane.

(xiii) Cleavage by iodine. The tungsten-methyl complex, (0.393 gm. 0.872 mmole), iodine (0.634 gm., 2.50 mmole) and benzene (15 ml.) were allowed to stand for 76 days at room temperature, and after this time yielded 19.33 Nccs (98.9 mole%) of CO. The greater part of the excess iodine was removed from the residual red-brown solid by sublimation at 45^{o} and 10^{-6} mm, and the brown powder left was washed 4 x 5 ml. benzene: it did not crystallise from pentane or benzene, but was characterised as π-cyclopentadienyldicarbonyltri-iodo-tungsten (0.439 gm., 73.4%), ν CO 2062s, 2020s, 2004s,sh cm^{-1}. [Found: C,12.17; H,1.22; I,56.7; $C_7H_5O_2I_3W$ i.e. $C_5H_5(CO)_2WI_3$ requires C,12.26; H, 0.74; I,55.5%]. The compound proved too insoluble for n.m.r. in benzene and at a source temperature of 180^{o}-200^{o} yielded a mass spectrum showing large I_2^+ and $[C_5H_5(CO)_2IW]_2^+$ ions. The presence of Me_3GeI in the benzene solvent was confirmed by mass spectrometry.

(xiv) Cleavage by mercuric chloride. To a solution of the tungsten-methyl complex (IV) (0.487 gm., 1.08 mmole) in freshly distilled THF (2 ml.) was added a solution of freshly sublimed mercuric chloride (0.296 gm., 1.09 mmole) in THF (3 ml.). After some 10-15 minutes the pale yellow solution became noticeably cloudy and on stirring at room temperature overnight and removal of solvent gave the bright lemon yellow solid, π-cyclopentadienyltricarbonyltungsten mercury chloride (0.181 gm., 31.8%) (MPt 196°-197°, dec. [Found: C,17.07; H,1.13; $C_8H_5O_3$, i.e. $\pi C_5H_5(CO)_3WHgCl$ requires C,16.89, H,0.89%] νCO 1923, 2015 cm^{-1}, in C_6H_6. The compound had a low temperature coefficient of solubility in the common solvents, but came down as bright yellow crystals on slow evaporation of a THF solution. It was found to the air stable over a period of 2-3 days, but darkened rapidly in sunlight (15-30 minutes) depositing metallic mercury.

A similar experiment with 0.940 gm. (1.91 mmole) of the tungsten-ethyl complex (V) and 0.520 (1.92 mmole) of mercuric chloride in a total of 15 ml. THF gave after 2 hours stirring at room temperature 0.733 gm. (67.4%) of the tungsten-mercury compound. At a source temperature of 190°, the molecular ions from this compound were not visible on its mass spectrum but large Hg^+ and $\pi C_5H_5(CO)_3W^+$ ions were found.

(xv) Cleavage by magnesium bromide. Anhydrous magnesium bromide was prepared in one limb of a doubled shlenk tube from magnesium turnings (0.52 gm. and 1,2-dibromoethane (1.0 gm.) in freshly distilled (from $LiAlH_4$) THF (12 ml.). After the initial vigorous reaction had subsided, the mixture was heated to 45° for 4 hrs. with stirring and filtered hot (70°) through the central disc of the shlenk into the other limb. To this solution was added a solution of the tungsten-ethyl complex (V), 0.795 gm., 1.62 mmole) in THF (8 ml.) and the mixture was stirred at room temperature for 4 days, during which time the pink colour lightened somewhat. The THF was then removed in vacuo and the residual pink solid extracted with benzene, to give an orange red solution. The benzene was removed from this solution and the extraction repeated. Replacement of the benzene by pentane did not yield crystals at -70^{o} but removal of the pentane and washing with 3 x 5 ml. of this solvent gave the pink solid π-cyclopentadienyltricarbonyltungstenmagnesium bromide tetrahydrofuranate (approximately 0.4 gm.) ν CO 1916s, 2025s, 2044w, cm^{-1} in C_6H_6 [Found: C,25.5; H,2.85; $C_{12}H_{13}O_4WMgBr$, i.e. $C_5H_5(CO)_3WMgBr$. C_4H_8O requires C,28.3; H,2.57%, $C_5H_5(CO)_3WMgBr$ requires, C,22.0; H,1.15; $C_5H_5(CO)_3WMgBr.2THF$ requires C,33.1; H,3.64%] The p.m.r. spectrum of a saturated solution of the compound in benzene showed the C_5H_5 singlet at τ 5.44, the THF "triplet" resonance at τ 6.00, and the THF high field resonance centred on τ 8.58, with relative intensities 15:12:13 respectively.

Molecular weight measurements in freezing benzene (under N_2) gave values of 546 (0.109 gm. cpd, 10 ml. benzene, (K = 5.5) Δ =0.125°) and 393 (0.069 gm. cpd, 10 ml. benzene, Δ 0.110^{o}), $\pi C_5H_5(CO)_3WMgBr.THF$ requires 509. The compound redissolved in benzene slowly and with difficulty, even on warming.

Reactions of the tungsten-mercury compound $\pi C_5H_5(CO)_3WHgCl$ (xvi) with triphenylgermyltriphenylphosphine gold. The gold complex, $PPh_3AuGePh_3$ (0.0620 gm. 0.0815 mmole) was dissolved in a 1:1 mixture (6 ml.) of THF/benzene to give a clear solution. Addition of the tungsten-mercury compound (0.0512 gm. 0.0914 mmole) in THF (3 ml.) caused an immediate blackening of the solution with the deposition of metallic mercury and a thin red film of gold on the walls of the limb of the shlenk tube. The mixture was stirred for 15 minutes, and filtered to give a light yellow solution from which a buff powder π-cyclopentadienyltricarbonyl tungsten-gold triphenylphosphine (0.0442 gm., 68.5%) was obtained [Found: C,41.6; H,3.06; P, 3.48, $C_{26}H_{20}O_3PWAu$ i.e. $\pi C_5H_5(CO)_3WAuPPh_3$, requires C,39.4; H,2.54, P,3.91%].

(xvii) with 1,2-bis(diphenylphosphine)ethanebistriphenylgermylplatinum. To a suspension of the platinum complex (0.125 gm., 0.104 mmole) in THF (15 ml.) was added a THF solution (5 ml.) of the tungsten-mercury compound (0.0653 gm., 0.115 mmole). A precipitate of metallic mercury formed, the platinum complex slowly went into solution and the yellow colour of the liquid deepened on stirring overnight. The solution was filtered and on removal of solvent in vacuo and washing with pentane yielded 1,2-bis(diphenylphosphine)ethanetriphenylgermylπ-cyclopentadienyl tungsten platinum (0.0841 gm., 68.4%) as a light yellow solid. (MPt 200° dec., [Found: C,47.38; H,3.97; P,3.66; $C_{54}H_{44}O_3P_2PtWGe$, i.e. $(Ph_2PCH_2)_2Pt(GePh_3)W(CO)_3\pi C_5H_5$, requires C,50.76; H,3.60; P,5.03%]. The mass spectrum of this compound at a source temperature of 180°-200° showed the ions Ph_3Ge^+ and $C_5H_5(CO)_3W^+$ and other ions with a PtWGe isotope pattern up to mass 990. Weak ions in the region of the molecular ions (mass 1230) could be detected but their isotope pattern could not be distinguished clearly. The compound was slightly air sensitive showing marked darkening after 10 days exposure.

(xviii) with bis(tri-ethylphosphine)trimethylgermyliodoplatinum. To the platinum complex (0.120 gm., 0.177 mmole) in THF (2 ml.) was added a THF solution (3 ml.) of the tungsten-mercury compiund (0.095 gm., 0.167 mmole). An immediate precipitate of mercury was thrown down, leaving, after stirring for 15 minutes, and filtration a clear orange solution from which dark red crystals (33 mg.) were obtained. The i.r. of these crystals was consistent with their formulation as $\pi C_5H_5(CO)_3W(I)Pt(PEt_3)_2$, but their elemental analysis [Found: C,24.3; H,1.68; P,1.23; I,1.32%) was not ($C_{20}H_{35}O_3P_2IPtW$, requires C,26.95; H,3.96; P,6.95; I,14.24%. $[\pi C_5H_5(CO)_3W]_2$, i.e. $C_{16}H_{10}O_6W_2$ requires

C,27.8; H,1.51%) Time did not allow further pursuit of the reaction.

Reactions of mercuric chloride and platinum-germanium complexes.

(xix) Mercuric chloride and $(Ph_2PCH_2)_2Pt(GePh_3)_2$. To a suspension of the platinum complex (0.651 gm., 0.542 mmole) in THF (15 ml.) was added a THF solution (1.5 ml.) of freshly sublimed mercuric chloride (0.147 gm., 0.272 mmole). A precipitate of mercury slowly formed during two days stirring at room temperature. The mother liquors were decanted and after removal of solvent in vacuo the residual white solid was separated into Ph_3GeCl (i.r. characterisation; the most soluble portion) and $(Ph_2PCH_2)_2PtCl_2$ (i.r. and m.s. characterisation). The insoluble white solid remaining after removal of mercury by sublimation at 80^o and 10^{-6} mm was unreacted starting material. No other products were detected.

(xx) Mercuric chloride and $(Et_3P)_2Pt(GePh_3)_2$. A THF solution (1 ml.) of mercuric chloride (0.0388 gm., 0.143 mmole) was added dropwise over 15 minutes to a stirred solution of the platinum complex (0.295 gm., 0.283 mmole) in THF (5 ml.). Mercury was precipitated during the addition and on allowing the solution to stand for 30 mins., its colour changed from light yellow, through orange to a dull yellow-brown. The solution was then filtered and reduced to a small volume. Slow addition of $40^o/60^o$ petroleum (5 ml.) gave a light brown, microcrystalline solid, bis(triphenylgermylbis(triethylphosphine) platinum), [Found: C,50.94; H,5.78; P,7.45; $C_{60}H_{90}P_4Pt_2Ge$, i.e. $[(Et_3P)_2PtGePh_3]_2$ requires C,49.00; H,6.17; P,8.42%]. MPt. 151-152^o (hot stage). The i.r. of this material was closely similar to that of $(Et_3P)_2Pt(GePh_3)_2$, showing only intensity differences in the bands due to the $GePh_3$ unit. The mass spectrum of this material at a source temperature of 190^o showed a number of differences from the mononuclear platinum complex at high masses and ions with Pt_2Ge_2

isotope patterns were observed at masses from 950 to 1500.

(xxi) Attempted preparation of π-cyclopentadienylσ-phenyltricarbonyltungsten. To a solution of π-cyclopentadienyltricarbonyltungsten magnesium bromide (0.1 gm.) in THF (10 ml.) was added an excess (0.5 ml.) of freshly distilled bromobenzene The mixture was stirred at room temperature for 4 days, during which time the colour lightened and a white precipitate was formed. After filtration, removal of solvent, benzene extraction of the solid, and recrystallisation from $40^{o}/60^{o}$ petrol at -50^{o} the solution yielded pale yellow crystals (ca.10 mg. [Found: C,26.9; H,2.23%]) whose i.r. spectrum indicated the absence of a phenyl group and showed a close similarity to that of $\pi C_5H_5(CO)_3WH$ ($C_8H_6O_3W$ requires C,28.9; H,1.81%. νCO 2020, 1929 cm^{-1}.)

PART 3

MASS SPECTROMETRY OF POLYISOTOPIC MOLECULES

THE forty years since the classical work of Aston, Bainbridge and Dempster have seen the field of positive ion in analysis widen continuously. Present applications of mass spectrometry range from automatic control of industrial production plant to complete analysis of microgram quantities of rare poisons, and the rate of diversification shows no sign of slowing. Mass spectrometers first began to be familar pieces of laboratory equipment about fifteen years ago in response to the petroleum industry's need for an accurate and fast method of quantitative analysis of mixtures of closely similar organic compounds. Not unnaturally, the growth of the discipline has continued largely within the realm of carbon chemistry, and this growth has often been rapid and with far-reaching consequences. The recent advent of commercially produced high-resolution mass spectrometers has brought a new dimension - or rather several dimensions - to the subject. Not only are these instruments capable of measuring ion masses, in some cases up to 1000 mass units (m.u.) with a precision of a few parts per million, but they can also give ion abundance values to a high degree of accuracy, thus at once disposing of previous distinctions between mass spectrographs and mass spectrometers. Above all, these instruments are able to provide, at least in theory, data which can lead to the exact elemental composition of every ion in a spectrum, a situation which has been likened to the comparison of a colour photograph (a complete high resolution spectrum) with the "black and white" picture of the unit mass resolution spectra of earlier machines.

In contrast to the already widespread and still growing applications of mass spectrometry to organic molecules, only a few investigations of inorganic compounds have been reported. Most of these studies have involved anisotopic elements or elements containing one dominant isotope (e.g. iron). Studies of compounds containing two or more metallic elements are rare and those of molecules with a metal-metal bond even less common. All the work on polymetallic compounds, including some in which high resolution facilities have been available,[169] has so far ignored the fundamental problem of calculation of the apparent masses of peaks from metallic aggregates, and so has been without direct confirmation of the elemental composition of ions in the spectra obtained. In the majority of cases, the molecules examined have been sufficiently simple for low resolution identification to be adequate, there have been few instances, for example, where doublets arising from loss of fragments such as C_2H_4 and CO have been encountered, or even possible. In one or two cases, however, it is apparent that some information has been lost because of this lack of the facility for unambiguous confirmation of the composition of ions.

The present study of a number of more complex organometallic and intermetallic compounds has made considerable use of high resolution mass measurement, based on data specifically produced for each polyisotopic unit considered. This need for continuous use of mass measurement has arisen for a number of reasons. First, the molecules are complicated enough for multiplet peaks to be commonplace; loss of fragments such as C_2H_5, C_2H_4 HCO and CO all of which occur in the breakdown of the intermetallic carbonyls studied, results in ions whose isotope patterns overlap or superpose. Similar difficulties occur with alkyl-alkenyl, and H_2-H loss in the alkylgermanes. Secondly, all the isotope patterns for the compounds containing more than one atom of one or more polyisotopic element, which form such a characteristic feature of their spectra, are sufficiently different from the patterns due to each individual element to require complete elucidation if they are not to lead to considerable uncertainty in assignments. For example, for ions containing a Ge_2 unit, the largest peak does not occur at a mass corresponding to the sum of the masses of the most abundant isotopes for two separate germanium atoms (i.e. 2 x 74 = 148) but at mass 146. Similarly in the MoGe pattern, the largest peak is 170, which is not the sum of the most abundant isotopes for the separate metals (98 and 74). Clearly if the nature of this "mass contraction" were not appreciated, some difficulties in interpretation would result. Finally, the mass spreads of the isotope patterns can be troublesome. These are often as large as 30 mu, spreads of 15-20 mu are common, and even if the nature of a molecule is such as to preclude formation of actual doublets, differences between ions of as much as a CH_3 or CO unit can still react in ion sets whose extremities overlap sufficiently to grossly distort their abundance patterns. Under low resolution conditions, where abundance values (pattern recognition) and accurate determination of mass spreads are all important, this could lead to problems of interpretation impossibly difficult to solve.

Methods of calculating abundance patterns and mass values are presented in Part 4, and the fundamental nature of these data is again emphasised here, without them assigments of formulae to ions in these spectra would be extremely uncertain. It is clear that as more complex molecules are analysed, increasing reliance must be placed on accurate mass measurements for elucidation of fragmentation patterns (and so molecular structure), and that in turn reliance must be placed on calculations such as those outlined later.

Previous work on metallic compounds has been almost entirely with the transition metal cyclopentadienyls, carbonyls and their derivatives. Some isolated studies on other structural types have been undertaken. An early comparison of the fragmentation of the alkyls of the group IV metals [170] showed that the molecular ions of these compounds are usually of low intensity. Careful measurement of the abundance of the germanium isotopes gave valuable additional data for calculation of the atomic weight of germanium.[171] More recent studies[172-4] have confirmed the high probability of decomposition for the molecular ions of these compounds and have brought to light a number of interesting fragmentation routes, for example alkene elimination, as discussed for the germanium compounds in the present work, has been found to be a dominant process. One particularly unusual elimination,[173]

$$Et_3M^+ \longrightarrow MeMEt_2^+ + CH_2^{\bullet} \qquad M = Ge,Sn,Pb.$$

$$Ph_2SnEt^+ \longrightarrow Ph_2SnMe^+ + CH_2^{\bullet}$$

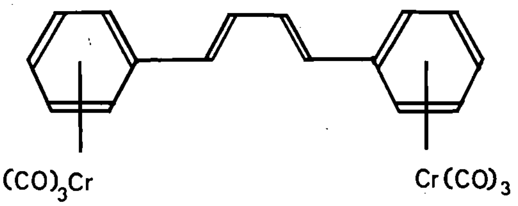
has been observed giving low abundance ions. Interesting correlations and differences in breakdown patterns betwen the mixed aryl-alkyl group IV organometallics and the homo-substituted compounds have emerged from these studies.

A number of mercury alkyls have been investigated[175] and show marked differences from the group IV alkyls. Hydrocarbon fragments, which constitute only a minor part of the total ion current from the latter molecules, made up the principal part of the spectrum of the mercury compounds. A study of the silanes SiH_4, Si_2H_6, and Si_3H_8 is of interest in that it provides some comparison with the corresponding alkanes and metalloid and metallic hydrides.[176] The ions formed by loss of an even number of hydrogen atoms were more abundant than those formed by losing an odd number. Moreover, compared with the corresponding hydrocarbons, the silanes show a greater facility for fission of both Si-H and Si-Si bonds. The formation of the three ions C^+, C_2^+, and C_3^+ constitute between 0.04 and 0.36% of the total hydrocarbon spectrum as compared with 10.4-32.9% for the corresponding silanes.

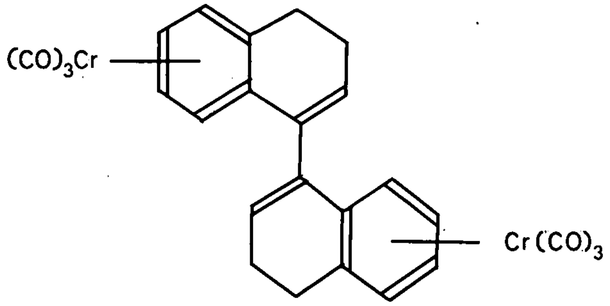
A series of studies[177,178] on both mononuclear and polynuclear (M-M, M'-M, and M'-M_2 type) hydrides of some some group IV and V elements employed isotopically pure ^{74}Ge and ^{120}Sn in compounds including $^{74}Ge_2H_6$, $^{74}Ge_3H_8$, $^{74}Ge_2SiH_8$, $Si^{74}GeH_6$, and $^{120}Sn_2H_6$; and interesting and undoubtedly expensive way of avoiding calculation of precise masses and abundance patterns for polyisotopic aggregates and of simplifying otherwise rather congested spectra.

The more plentiful studies on simple mononuclear metal carbonyls have led to some important results. The clastograms (plots of ion abundance against ionising beam energy) for the group VI compounds ($Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$[178-9] suggest that the major decomposition route is single ionisation of the molecule followed by successive stepwise loss of neutral CO fragments. Careful measurements indicated that the appearance potential of the molecule-ions rose with the atomic numbers of the central metal atom, which is the same trend shown by the ionisation potentials of the (isolated) metal atoms, and so it was concluded that the electron loss on ionisation of these compounds is entirely from the metal atom, rather than from the organic portion of the molecule. In all cases ions of the type MC^+ and MC_2O^+ were observed, thus confirming (with the tacit assumption that no rearrangement had occurred!) that the bonding to CO groups in these ions is through the carbon atom rather than through the oxygen; ions of the type $M(CO)_nC^+$ occur more commonly for the heavier metal atoms.[169] Under mass spectrometric conditions usually employed, however, there seems to be little evidence for the reversal of the normal M-C bonding pattern in the carbonyls, despite the large amounts of energy available (70 ev = 1614 K cals/mole). A number of other first row transition metal carbonyls have also been studied, including the binuclear carbonyls of cobalt and manganese.[179] Again stepwise loss of CO fragments occurred and for the Mn compound M-M bond fission. More recent work[169] on the manganese compound has revealed some interesting comparison with its rhenium analogue. In the spectrum of Re_2CO_{10}, about 96% of the ion current is carried bt fragments containing two metal atoms whereas for the Mn compound this is reduced to 59%. This would seem to give further confirmation of the tendency for the heavier metals to form stronger M-M bonds, as discussed in Part 2. A number of multiply charged ions were identified for $Re_2(CO)_{10}$, but none in the spectrum of $Mn_2(CO)_{10}$ and this again suggests a greater ability of the heavier metal to maintain metal-metal bonding in higher acid-ation levels. The phosphine substituted carbonyls $(R_3PMn(CO)_4)_2$ showed [169] extremely interesting variations in the intensity of the di-metallic fragments of which the $(R_3P)_2Mn_2(CO)_8$, $(R_3P)_2Mn_2(CO)_4$ and $(R_3P)_2Mn_2$ types were the major ions. Metastable transitions for the loss of four carbonyl groups at once were recorded. It was also noted that substitution of a phosphine for carbonyl in these dimetallic compounds drastically reduced the number of M-M containing fragments, in keeping with the reported tendency of the phosphine derivatives, particularly aryl phosphines, to give paramagnetic monomeric species when prepared by heating of the parent carbonyl with the phosphine.

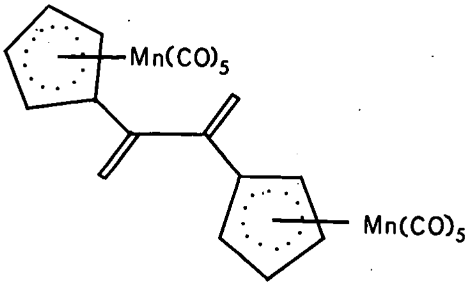
Removal of large numbers of carbonyl groups all at once has been noted for other dimetallic compounds, particularly for diene-carbonyl derivatives, and this process seems to be a sensitive function of structure. The compound

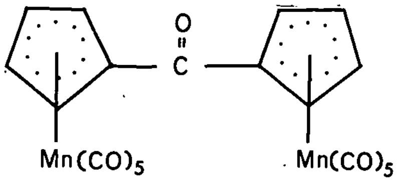


is reported to lose its CO groups in a stepwise fashion,[180] i.e. species corresponding to the basic skeleton with losses of all possible numbers of CO groups were observed, whereas the related compound

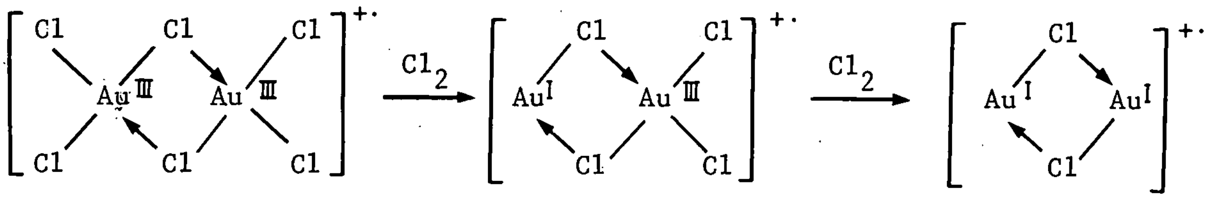


exhibits peaks due to loss of 3, 4 and 6 carbonyls only. Simultaneous loss of three carbonyl groups (metastable confirmed) occurs in the Mn compounds

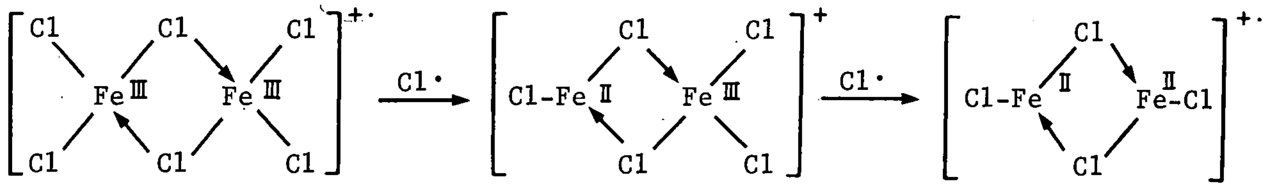




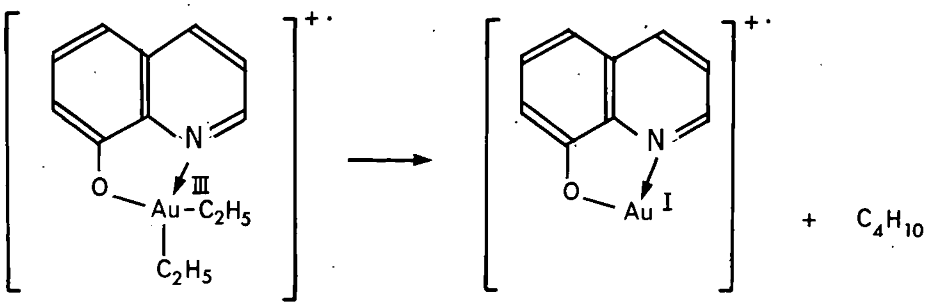
and this concerted elimination was suggested to have changes of valence state (correctly oxidation number) as its driving force.[180] Interpretation of concerted or single radical loss in terms of oxidation level ("valence") changes was first propounded to explain the differences between the mass spectra of AuCl$_3$ and FeCl$_3$,[181] both of which molecules have similar dimeric structures in the vapour phase. The former compound readily loses neutral Cl$_2$ molecules, whereas the iron compound decomposes with loss of Cl atoms, and this behaviour was rationalised in terms of the preferred oxidation levels of the metals, the loss of Cl_2 representing $Au^{III} \rightarrow Au^{I}$ transition, and of Cl· an $Fe^{III} \rightarrow Fe^{II}$ change;



and,



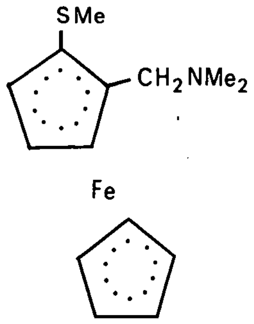
The influence of the $Au^{III} \rightarrow Au^{I}$ change was also demonstrated in the spectrum of diethyl auric oxinate where an unusual elimination occurs,

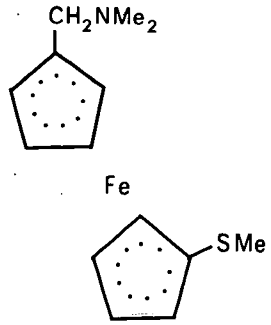


A detailed study of a number of metal acetylacetonates made effective use of these factors in the rationalisation of their spectra.[182] It has also been noted[174] that the greater part of the odd electron ions of the tetraorganostannes and -germanes decompose by loss of neutral odd electron fragments, and that ions containing an even number of electrons lose even -electron fragments, thus retaining as far as possible electron pair bonding throughout the remaining ion, and indicating the importance of this type of bond for these main group elements.

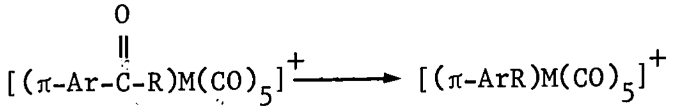
Cyclopentadienyl metal compounds have been fairly widely investigated, including the biscyclopentadienyls of vanadium, chromium, iron, cobalt, nickel, rhodium, ruthenium and manganese, and the cyclopentadienides of sodium and magnesium.[184-7] It was concluded that the variations in stability of these complexes in the mass spectrometer were directly related to the nature of the central metal atom.[187] Only rarely has the fragmentation of the cyclopentadienyl ring itself been studied. This unit is normally very stable under electron impact when π-bonded to a metal and often produces quite complex areas of low intensity peaks when it does begin to fragment. Both C_2H_2 and C_2H_4 loss have been recorded from $(\pi C_5H_5)_2ReH$, and C_5H_5 breakdown ions included $C_8H_8Re^+$, $C_8H_6Re^+$, and $C_6H_4Re^+$, although this pattern may not be typical, because of the presence of the extra hydrogen atom.[183]

Considerable lability has been reported for substituents attached to the $-C_5H_5$ rings of some metal cyclopentadienyls, the compounds





for example give almost identical mass spectra.[187] Related rearrangements and eliminations include



$$[(\pi\text{-Ar-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-R})M(CO)_5]^+ \longrightarrow [(\pi\text{-ArR})M(CO)_5]^+ ,$$ (metastable confirmed, M=Mn,Re)

and $$[(\pi\text{-}(C_5H_4COR)Fe\pi C_5H_5]^+ \longrightarrow [RFe\pi C_5H_5]^+$$

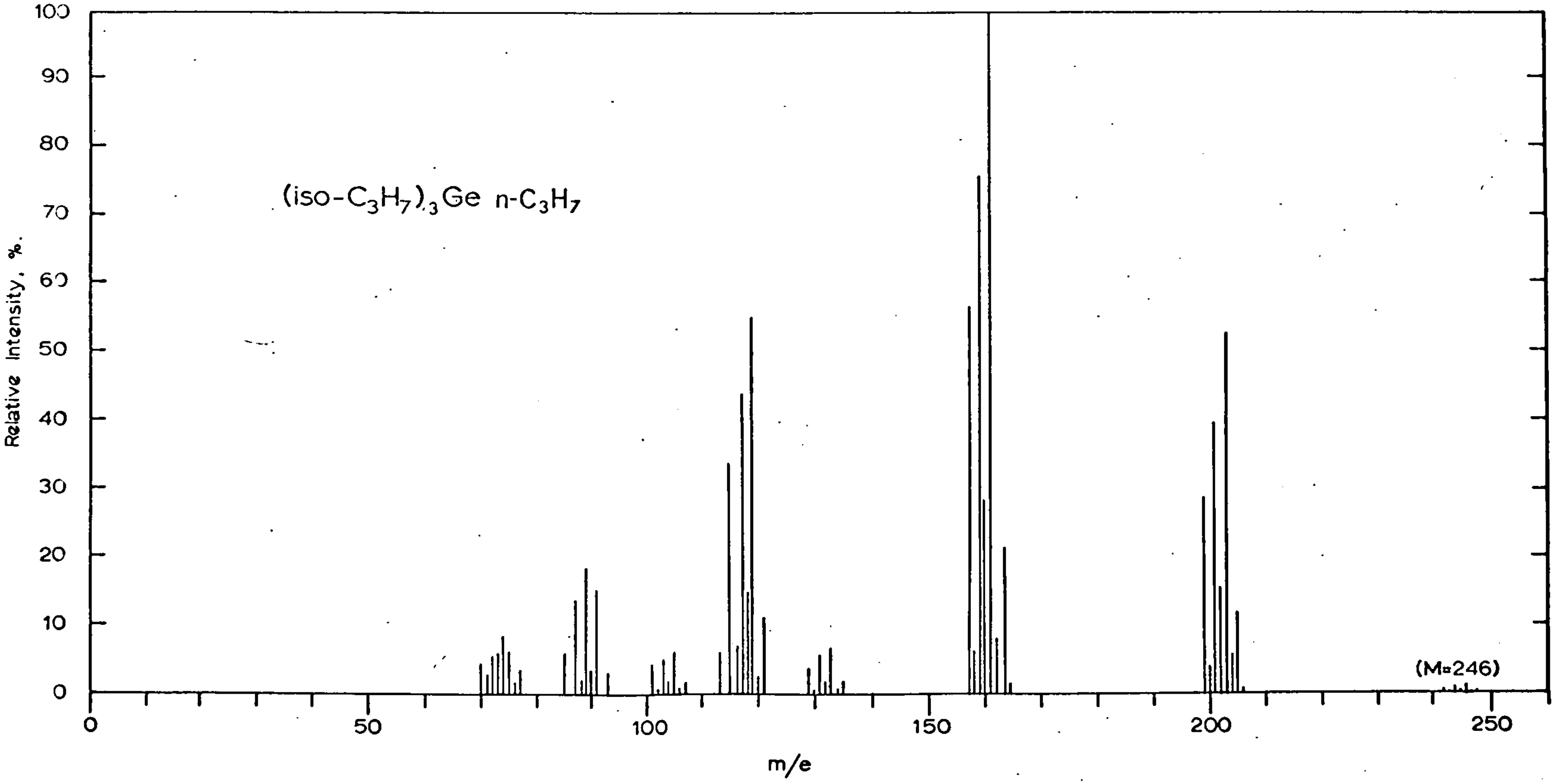
$$C_5H_5\text{-}C_5H_4^+ \longrightarrow C_5H_4\text{-}C_5H_4^+$$ 186

Intramolecular transfer of a C_5H_5 ring from one metal to another has been observed for $[(\pi C_5H_5)Fe(CO)_2]_2$ giving $(C_5H_5)_2Fe^+$ and exchange of C_5H_5 and C_6H_5 in the compound $\pi C_5H_5Fe(CO)_2SnPh_3$. No intermetallic transfer of CO groups has been reported, however, and this fact together with the absence of $Fe(CO)_5^+$ in the spectrum of $Fe_3(CO)_{12}$ were interpreted[169] as evidence in favour of the recently proposed cyclic structure (a triangle of iron atoms) for this compound, which would not then contain a $Fe(CO)_5$ unit.

Some other trimetallic compounds have been rather briefly examined, including $Ru_3(CO)_{12}$, $Hg[Fe(CO)_2\pi C_5H_5]_2$ and $Cl_2Sn[Fe(CO)_2\pi C_5H_5]_2$.[169]

In all cases these early studies have shown that a great deal can be learned about the stability and structure of organometallic and intermetallic compounds from their mass spectra, providing that interpretation is thorough and cautious. In particular the field of the metal-metal bonded molecules whose mass spectrometric study is very much in its infancy should add considerably to our understanding of this important class of compounds.

The main purpose of this study of the mass spectra of some polyisotopic organometallic molecules has been analytical - that is, has been concerned primarily with the identification of compounds. Because of this, some detail, particularly for the more complex molecules is lacking, and the transition metal complexes have not been given the attention they undoubtedly deserve:


(iso-C$_3$H$_7$)$_3$Ge n-C$_3$H$_7$
Relative Intensity, %.
0
10
20
30
40
50
60
70
80
90
100
m/e
0
50
100
150
200
250
(M=246)

the major trends and the more interesting decomposition of these molecules have been elucidated and these give some impression of the variety of reactions which occur in a mass spectrometer. Two classes of molecule can be distinguished: the homonuclear polyisotopics, in this case organogermanium compounds (including some organomonogermanes), and the heteronuclear compounds, organogermanium-transition metal complexes and some derivatives. These will be dealt with in turn. In all cases high resolution (approx. 1:10,000) mass measurement was used to establish the identity of the ions, and representative examples of results are given in Tables 3.1 and 3.2.

MASS SPECTROMETRY OF POLYISOTOPIC MOLECULES

3.1. Homonuclear compounds

(a) The tetrapropylgermanes.

The major features of the spectra of these molecules are summarised in the illustrations, the fragmentation diagram, and the table of mass measurements. All five tetrapropylgermanes gave closely similar spectra, the only sifferences being in the ratios of the intensities of hydride containing fragments, particularly $PrGeH_2^+$ to Pr_3Ge^+. This was smallest for Pr^i_4Ge, (1:1.23) has its largest increase between Pr^i_4Ge and $Pr^i_3GePr^n$, the value in the latter case being (1.06:1) and remained at about (1.1:1) for the other molecules. This is certainly connected with the ability of the Pr_3Ge^+ and Pr_2GeH^+ fragments to eliminate C_3H_6 effectively and could be interpreted as evidence in favour of a five-membered ring system for the transfer of a hydrogen atom from the $-CH_3$ of $n-C_3H_7$ to the germanium atom.

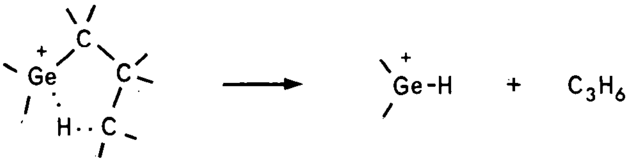
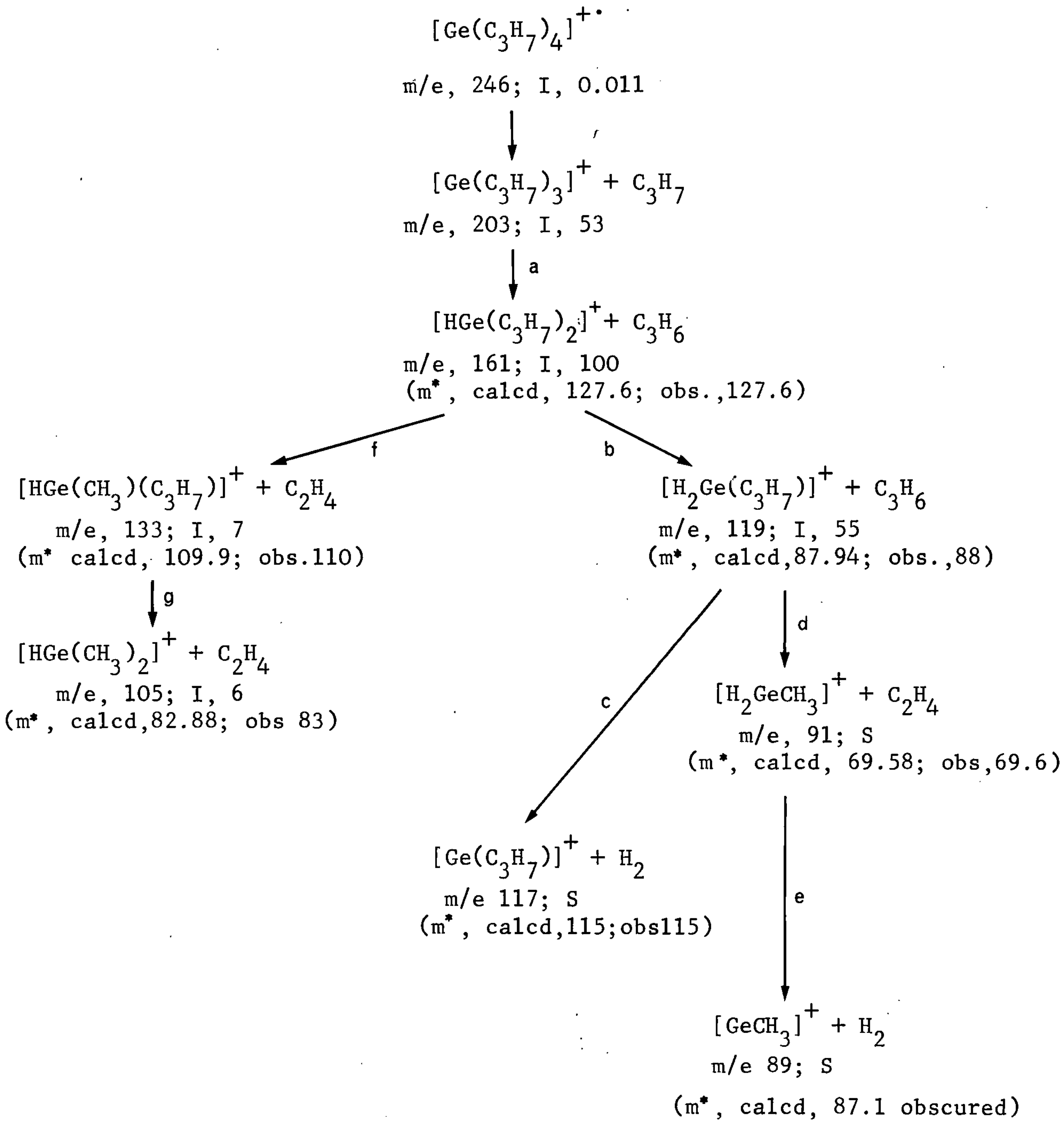


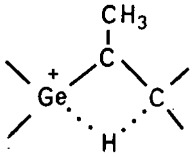
Fig.3.1. Fragmentation of Tetraisopropylgermane

m^* = mass of metastable ion I = relative intensity

s = superimposed pattern



A situation which cannot obtain for the iso-C_3H_7 group, unless isomerisation occurs. Presumably a corresponding four-membered ring transition state for the Pr^i unit is less geometrically and energetically favourable and requires more energy for the transfer

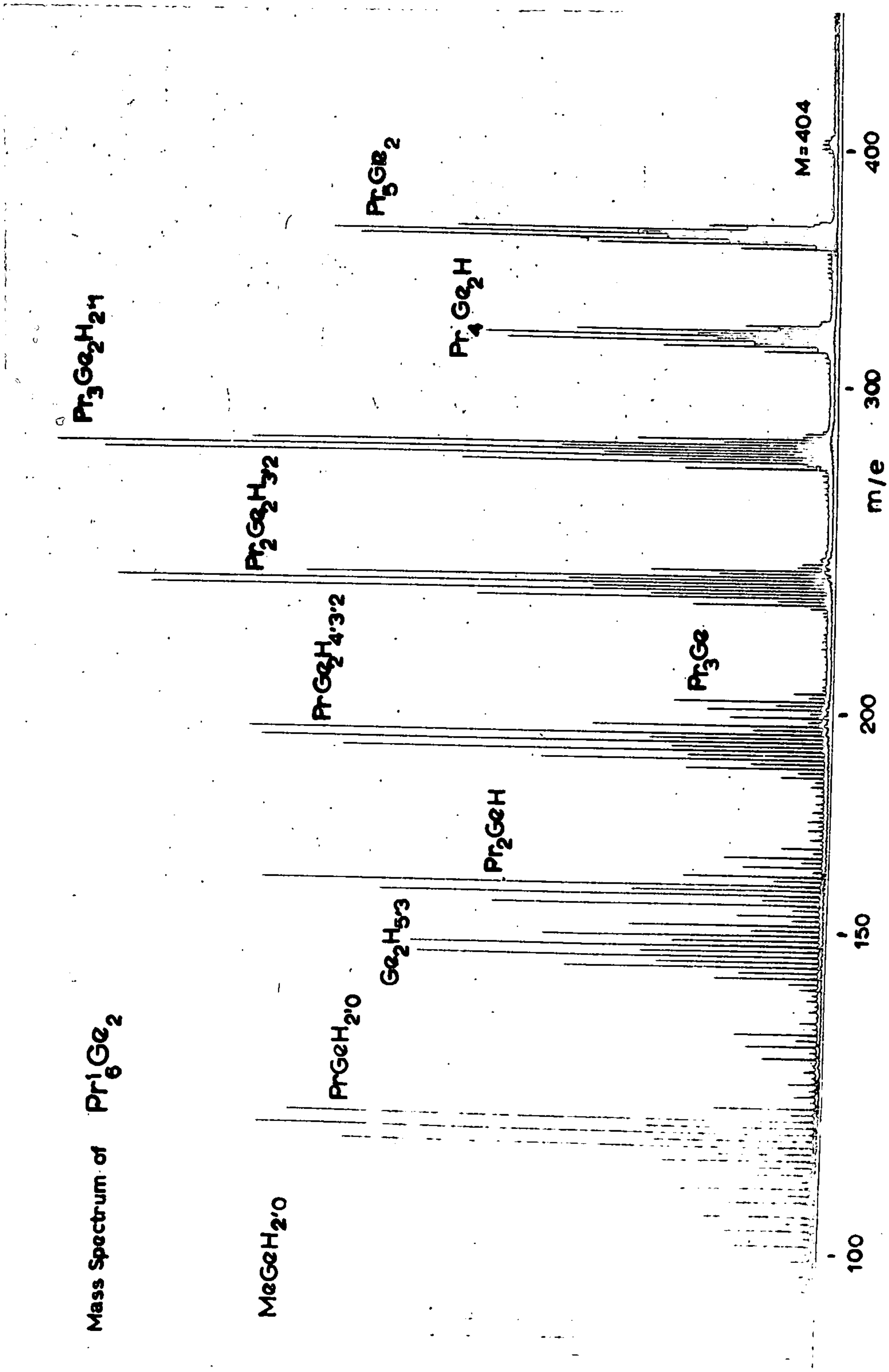


Labelling studies might provide valuable information on this process.

The molecular ions are of low intensity, compared with the most abundant species, Pr_2GeH, (1:90 for Pr^i_4Ge) and the eight major fragments are produced by molecular elimination reactions following ionisation rather than by direct cleavage of parts of the alkyl groups, appropriate metastable ions being clearly visible. All the major ions contain an even number of electrons and may be formulated with electron pair bonds. No metastable was recorded for direct decomposition of the (odd-electron) molecular ions, bit it seems likely that Pr_3Ge^+ is produced by expulsion of a C_3H_7 fragment from the molecular ion rather than by direct cleavage of a Ge-C bond on ionisation. Decomposition of Pr_3Ge^+ occurs by loss of propene [reactions (a) and (b), Fig.3.2], followed by ethylene [reactions (d), (f), and (g)] and hydrogen [reactions (c) and (e)]. Transition (e) could not be confirmed directly as the region of the expected metastable set (80-87 mu) is occupied by metastable peaks derived from transitions (b) and (g) both of which are intense.

(b) Hexa-isopropyldigermane

Although its spectrum contains comparatively few major groups of peaks, in common with the major characteristic of most gpIV organometallic compounds, Mass Spectrum of $Pr^i_6Ge_2$



the detailed fragmentation of the molecule is remarkably complex. One striking feature is the large number of ions in which the Ge-Ge bond remains intact, these accounting for approximately 75% of the total ion current. The base peak is, a dimetallic (even-electron) fragment containing, presumably, both three- and four-coordinate germanium, $\mathrm{Pr}^i_3\mathrm{Ge}_2\mathrm{H}_2$, and the molecular ions are only 1% as abundant as this species. Eliminations of successive molecules of propene dominate the fragmentation behaviour, and the digermanium hydrides $(\mathrm{Ge}_2\mathrm{H}_5)^+$, $(\mathrm{Ge}_2\mathrm{H}_3)^+$ and $(\mathrm{Ge}_2\mathrm{H})^+$ are the final products of this process. Large metastable peaks with well defined Ge_2 isotope patterns resulted from these reactions in the higher mass region of the spectrum but at lower masses, with so many overlapping patterns some of the metastables could not be assigned unambiguously. For example, the strong transitions which occur over the range 192-205 mu probably result from three parallel processes

$$(\mathrm{Pr}^i_3\mathrm{Ge}_2\mathrm{H}_2)^+ \longrightarrow (\mathrm{Pr}^i_2\mathrm{Ge}_2\mathrm{H}_3)^+ + \mathrm{C}_3\mathrm{H}_6 \qquad m^* \ 199.5$$

$$(\mathrm{Pr}^i_3\mathrm{Ge}_2\mathrm{H})^+ \longrightarrow (\mathrm{Pr}^i_2\mathrm{Ge}_2\mathrm{H}_2)^+ + \mathrm{C}_3\mathrm{H}_6 \qquad m^* \ 198.5$$

$$(\mathrm{Pr}^i_3\mathrm{Ge}_2)^+ \longrightarrow (\mathrm{Pr}^i_2\mathrm{Ge}_2\mathrm{H})^+ + \mathrm{C}_3\mathrm{H}_6 \qquad m^* \ 197.8$$

High resolution mass measurements on selected ions provide evidence for the following reaction paths, involving loss of propene or hydrogen

$$(\mathrm{Pr}^i_5\mathrm{Ge}_2)^+ \longrightarrow (\mathrm{Pr}^i_4\mathrm{Ge}_2\mathrm{H})^+ \longrightarrow (\mathrm{Pr}^i_3\mathrm{Ge}_2\mathrm{H}_2)^+ \longrightarrow$$
$$(\mathrm{Pr}^i_2\mathrm{Ge}_2\mathrm{H}_3)^+ \longrightarrow (\mathrm{Pr}^i\mathrm{Ge}_2\mathrm{H}_4)^+ \longrightarrow (\mathrm{Ge}_2\mathrm{H}_5)^+ \longrightarrow (\mathrm{Ge}_2\mathrm{H}_3)^+$$

$$(\mathrm{Pr}^i_4\mathrm{Ge}_2)^+ \longrightarrow (\mathrm{Pr}^i_3\mathrm{Ge}_2\mathrm{H})^+ \longrightarrow (\mathrm{Pr}^i_2\mathrm{Ge}_2\mathrm{H}_2)^+ \longrightarrow (\mathrm{Pr}^i\mathrm{Ge}_2\mathrm{H}_3)^+ \longrightarrow$$
$$\longrightarrow (\mathrm{Ge}_2\mathrm{H}_4)^+$$

$$(\mathrm{Pr}^i_3\mathrm{Ge}_2)^+ \longrightarrow (\mathrm{Pr}^i_2\mathrm{Ge}_2\mathrm{H})^+ \longrightarrow (\mathrm{Pr}^i\mathrm{Ge}_2\mathrm{H}_2)^+ \longrightarrow (\mathrm{Ge}_2\mathrm{H}_3)^+$$

Table 3.3 Mass Spectrum of $\mathrm{Pr^i_6Ge_3O_3}$

Principal fragments, 530 - 117 mu.

"Group" masses represent the most abundant peak for a given combination of germanium isotopes.

Group at mass	Abundance	Probable assignment
524	0.37	$(\mathrm{Pr^i_6Ge_3O_3})^+$
509	0.31	$(\mathrm{Pr^i_5Ge_3O_3CHCH_3})^+$
481	100	$(\mathrm{Pr^i_5Ge_3O_3})^+$
455	6.9	$(\mathrm{Pr^i_4\ Ge_3O_3(H_2)CH_3})^+$
439	24	$(\mathrm{Pr^i_4Ge_3O_3})^+$
423	1.9	$(\mathrm{Pr^i_3Ge_3O_3CHCH_3})^+$
409	19	$(\mathrm{Pr^i_2Ge_3O_3CHCH_3})^+$
395	12	$(\mathrm{Pr^i_3Ge_3O_3})^+$
379	26	$(\mathrm{Pr^i_3Ge_3O_2})^+$
351	19	$(\mathrm{Pr^i_3Ge_2O_3CHCH_3})^+$
335	7.9	$(\mathrm{Pr^i_3Ge_2O_2CHCH_3})^+$
291	16	$(\mathrm{Pr^i_3Ge_2O})^+$
265	21	$(\mathrm{Pr^iGe_2O_3CHCH_3})^+$
249	8.1	$(\mathrm{Pr^iGe_2O_2CHCH_3})^+$
204.5	0.1	$(\mathrm{Pr^i_2Ge_3O_3(CHCH_3)_2})^{++}$
203	38	$(\mathrm{Pr^i_3Ge})^+$
167.5	0.2	$(\mathrm{Pr^i_3Ge_2O_2CHCH_3})^{++}$
161	71	$(\mathrm{Pr^iGeOCHCH_3})^+$
133	25	$(\mathrm{Pr^iGeO})^+$
117	33	$(\mathrm{Pr^iGe})^+$

Two very small ion sets corrpesonding to loss of both 16 and 15 mu (CH_4 and CH_3) from the ions $(Pr^i_5Ge_2)^+$ and $(Pr^i_2GeH_3)^+$ were observed in the low resolution spectrum (intensity about 1% of each of the ions from which they were derived) but apart from this no evidence for processes other than loss of propene was obtained. The stage at which fission of the Ge-Ge bond occurs was not unambiguously determined, but it must be from an ion containing at least three propyl groups, because of the appearance of $Pr^i_3Ge^+$. These three groups need not necessarily be attached to the same germanium atom before the Ge-Ge bond breaks, however, since transfer of alkyl radicals from one atom to another has been noted in the breakdown of compounds of the type $R'_3M\text{-}M'R_3$ (e.g. $Me_3SiGe(CH_2C_6H_5)_3$), and this could occur immediately prior to or during the bond fission.

Decomposition of $Pr^i_3Ge^+$ followed the same routes discussed for the tetrapropyl germanes. No doubly charged ions were observed.

(c) Trimeric di-isopropyl germanium oxide, $(Pr^i_2GeO)_3$.

The molecular ions for this compound were very weak compared to those due to loss of one isopropyl group (ratio 1:273) and $Pr^i_5Ge_3O_3$ formed the base peak of the spectrum. This extremely high decomposition probability is also observed for the simpler oxides $(R_3M)_2O$ M = Ge,Si, where in some cases the molecular ion is difficult to detect: the first fragment is also intense for these molecules. Reaction processes involving rearrangement of ions were much less apparent than with the compounds previously discissed and were not clearly evident until the cyclic system had degraded to fragments containing only one germanium atom. A number of losses of odd-electron units, particularly $CH_3\cdot$ and $C_3H_7\cdot$ were noticeable, and the C_2H_4 ($-CHCH_3$?) radical was observed in a

Table 3.1. **Some High-Resolution Mass Measurements**

Organogermanium Compounds

m/e	deviation (p.p.m)	assignment
	$Pr^{i}_{4}Ge$	
246.1405	+1	$Pr^{i}_{4}Ge^{+}$
203.0853	+1	$Pr^{i}_{3}Ge^{+}$
161.0386	0	$Pr^{i}_{2}GeH^{+}$
118.9914	-2	$Pr^{i}GeH_{2}^{+}$
90.9603	0	$MeGeH_{2}^{+}$
	$Pr^{i}_{6}Ge_{3}O_{3}$	
477.0274	0	$Pr^{i}_{5}{}^{214}Ge_{3}O_{3}$
478.0291	+2	$Pr^{i}_{5}{}^{215}Ge_{3}O_{3}$
479.0263	+1	$Pr^{i}_{5}{}^{216}Ge_{3}O_{3}$
480.0281	+3	$Pr^{i}_{5}{}^{217}Ge_{3}O_{3}$
481.0249	+1	$Pr^{i}_{5}{}^{218}Ge_{3}O_{3}$
482.0245	-2	$Pr^{i}_{5}{}^{219}Ge_{3}O_{3}$
483.0245	+2	$Pr^{i}_{5}{}^{220}Ge_{3}O_{3}$
484.0259	+3	$Pr^{i}_{5}{}^{221}Ge_{3}O_{3}$
	$Pr^{i}_{6}Ge_{2}$	
361.1174	+3	$Pr^{i}_{5}{}^{146}Ge_{2}^{+}$
318.0730	+4	$Pr^{i}_{4}{}^{145}Ge_{2}H^{+}$
275.0245	+1	$Pr^{i}_{3}{}^{144}Ge_{2}H_{2}^{+}$
231.9798	-2	$Pr^{i}_{2}{}^{143}Ge_{2}H_{3}^{+}$
231.9524	-1	$Pr^{i}_{2}{}^{146}Ge_{2}^{+}$
203.0857	+4	$Pr^{i}_{3}{}^{74}Ge^{+}$
192.9287	-3	$Pr^{i}{}^{146}Ge_{2}H_{4}^{+}$
190.9130	-3	$Pr^{i}{}^{146}Ge_{2}H_{2}^{+}$
146.8855	+3	${}^{142}Ge_{2}H_{5}^{+}$
146.8674	-5	${}^{144}Ge_{2}H_{3}^{+}$
146.8516	+3	${}^{146}Ge_{2}H^{+}$

number of ions. One interesting ion set with central mass 455 corresponded to $C_{13}H_{33}Ge_3O_3$ i.e. $Pr^i_4(CH_3Ge_3O_3H_2$, and gave evidence both for the normal alkene loss and for an open structure for the ring at this stage. It is of interest that loss of oxygen occurs only after loss of three isopropyl groups (395-379 sets). Two doubly charged ions were identified, $(Pr^i_3Ge_2O_2CHCH_3)^{2+}$ and $(Pr^i_2Ge_3O_3CHCH_3)^{2+}$. There was no evidence for the production of the ion set at mass 203 ($Pr^i_3Ge^+$) by process involving metastable transitions but, as mentioned earlier, transfer of alkyl groups in gp IV metal organic ions has been observed. Metastable peaks corresponding to reaction (a) (Fig.3.2.) were observed. The major mass groupings and their probable assignments are listed in Table 3.3.

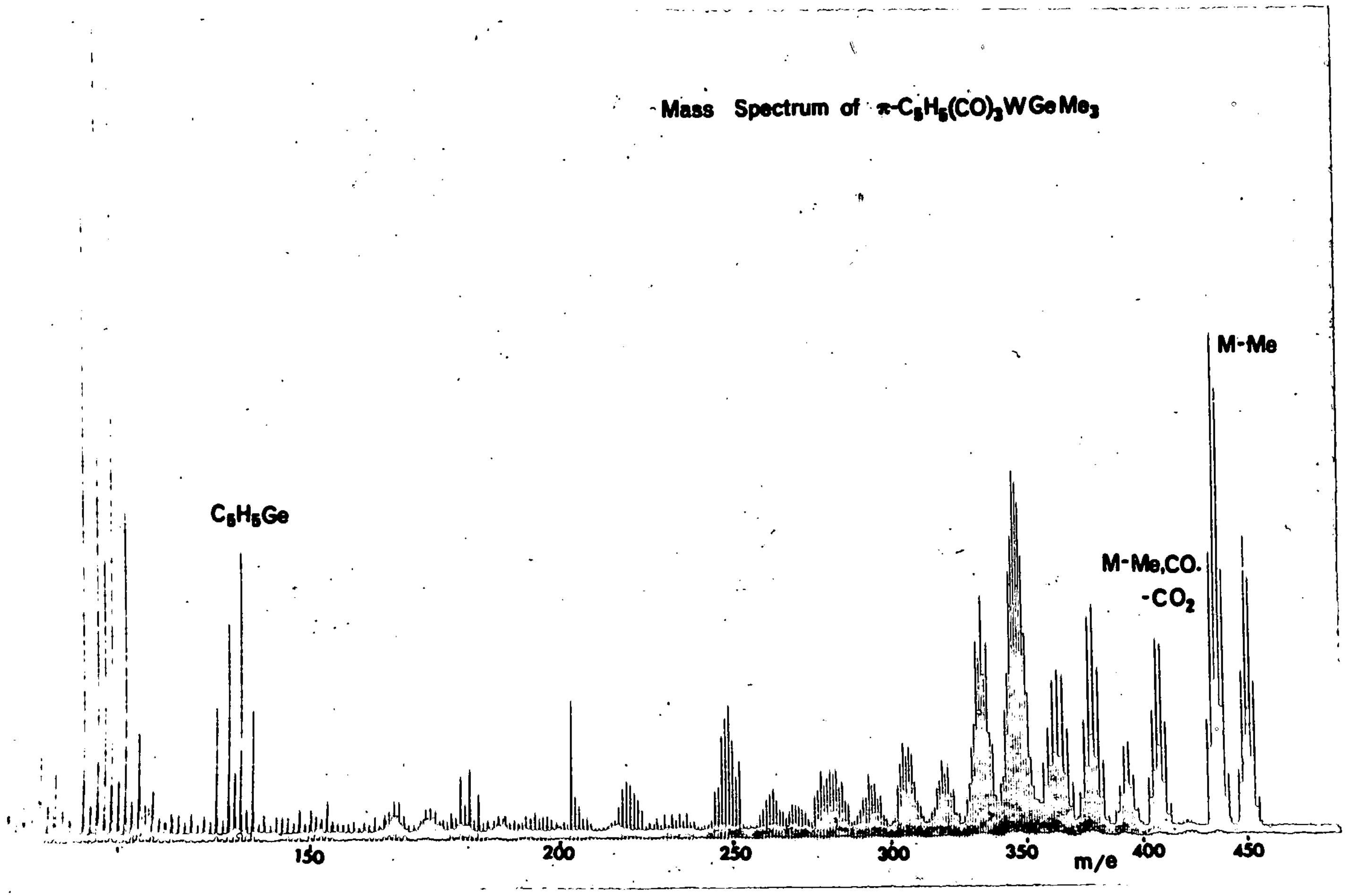
The mass spectrum of octaisopropylcyclotetragermane was not examined in detail, but two ion sets, of the same intensity formed by loss of C_2H_5 and C_2H_4, and C_3H_6 and C_3H_7 from the molecular ion were noted. Again a considerable amount of the ion current was carried by species containing four germanium atoms. $Pr^i_3Ge^+$ was also present to a small extent.

3.2. Heteronuclear Compounds.

(a) The tricarbonyl organogermanium transition metal complexes, $\pi C_5H_5(CO)_3MGeR_3$

All the compounds of this type (M= Mo,W, R = Me; and Et and Pr^n for Mo only) showed intense molecular ions and the greater part of their spectra was made up of ions containing the metal-metal bond intact, (over 75% of the ion current for $\pi C_5H_5(CO)_3MoGeEt_3$ was carried by MoGe species). The most abundant fragment of highest mass was invariably that corresponding to loss of R from the molecular ion.

$$C_5H_5(CO)_3MGeR_3^{+\cdot} \longrightarrow C_5H_5(CO)_3MGeR_2^{+} + R\cdot \qquad \text{------------} \quad (i)$$



Mass Spectrum of π-$C_5H_5(CO)_3WGeMe_3$

and for the higher alkyl groups, R = Et and Pr^n this was the only decomposition route of any significance for this ion. The trimethyl germyl molybdenum compound, however, showed ions of intensity comparable to those formed by transition (i), from initial loss of a carbonyl group

$$C_5H_5(CO)_3MoGeMe_3^{+\cdot} \longrightarrow C_5H_5(CO)_2MoGeMe_3^{+\cdot} + CO \quad \text{--------} \quad (ii)$$

giving an ion containing an odd number of electrons, and in the subsequent breakdown of the compound, this decomposition route was always in competition with the loss of alkyl radicals.

The trimethyl germyl tungsten compound showed intense ions due to an inital loss of CO_2

$$C_5H_5(CO)_3WGeMe_3^{+\cdot} \longrightarrow C_5H_5(CO)CWGeMe_3^{+\cdot} + CO_2 \quad \text{--------} \quad (iii)$$

although the question of whether the CO_2 was eliminated as a molecule, from a concerted rearrangement, or by successive (or simultaneous) emission of CO and O could not be resolved directly as the area of the expected metastable peaks was covered by the extremities of two large metastable sets from other reactions. There was, however, no large metastable present for loss of a CO_2 molecule. Any ions from this compound due to initial loss of CO from the molecular ion were, if present at all, smaller than the metstable set for the transition corresponding to (i), and could not be detected

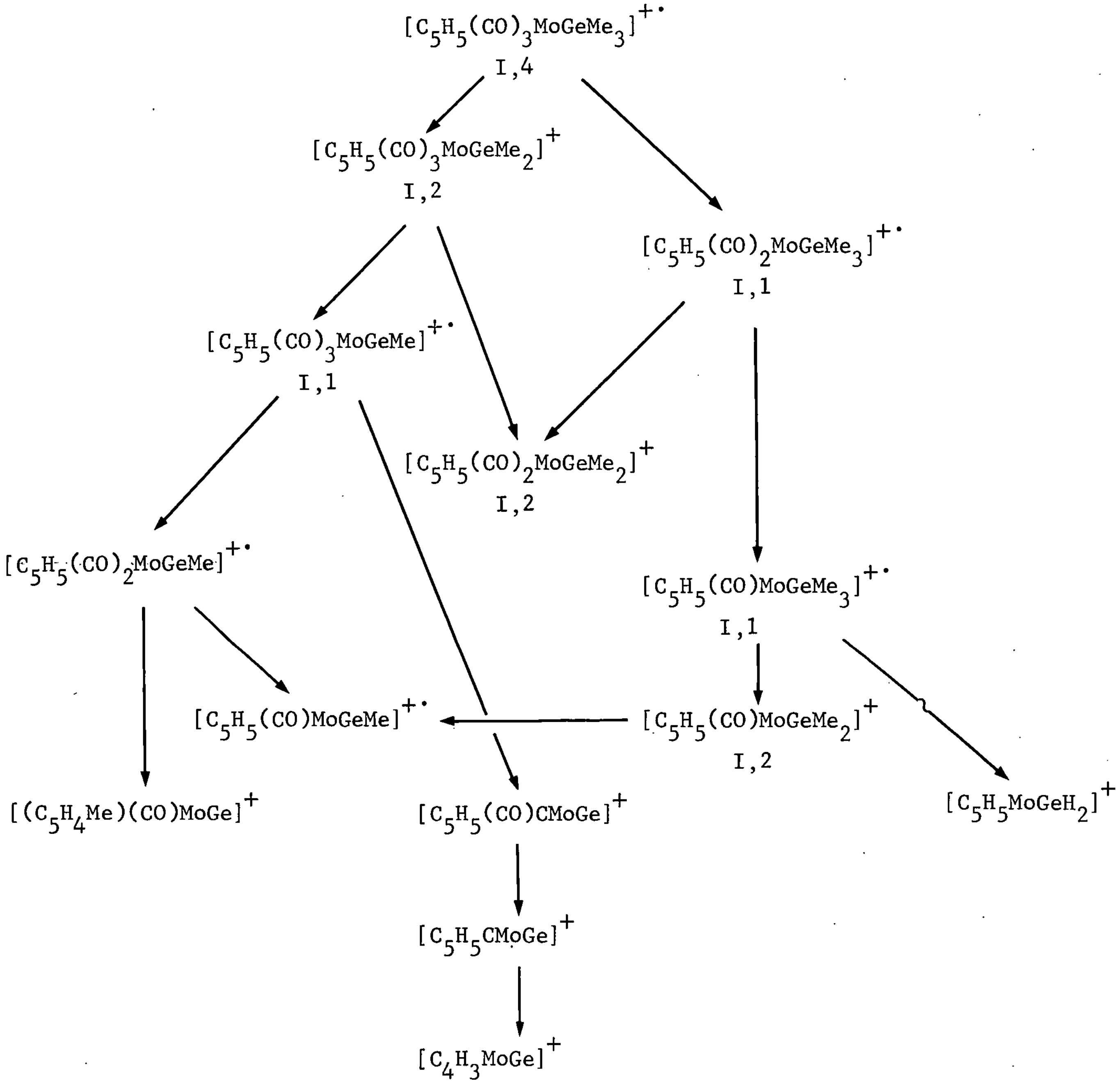
$$C_5H_5(CO)_3WGeMe_3^{+\cdot} \longrightarrow C_5H_5(CO)_3WGeMe_2^{+} + Me\cdot \qquad m^* \ 421$$

$$C_5H_5(CO)_2WGeMe_3 \ = \ 422$$

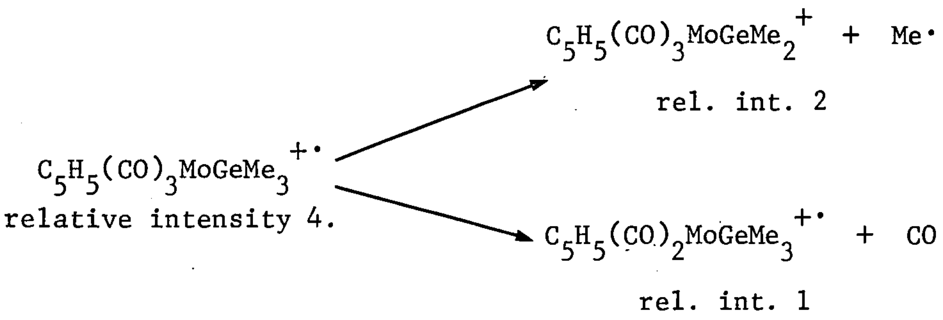
These differences in initial fragmentation behaviour for the three types of molecule, the methyl-molybdenum, methyl-tungsten and higher alkyl molybdenum

Fig.3.2 Some Fragmentation Paths of π-$C_5H_5(CO)_3MoGeMe_3$

I = relative intensity.



complexes, seem to be fairly typical of the differences throughout their spectra. The molybdenum-methyl complex showed ions due to loss of both CO and Me units, those resulting from the alkyl radical loss being somewhat more intense than those from the carbonyl loss



$$C_5H_5(CO)_3MoGeMe_3^{+\cdot} \longrightarrow C_5H_5(CO)_3MoGeMe_2^{+} + Me\cdot$$

relative intensity 4. rel. int. 2

$$C_5H_5(CO)_3MoGeMe_3^{+\cdot} \longrightarrow C_5H_5(CO)_2MoGeMe_3^{+\cdot} + CO$$

rel. int. 1

The molybdenum-ethyl and -propyl compounds showed much more complex breakdowns, following all possible competing paths and no particularly dominant process, alkene elimination and loss of alkyl radicals and carbonyl groups (including HCO & H_2CO loss) all giving relatively intense ions.

$$C_5H_5(CO)_3MoGeEt_2^{+} \longrightarrow C_5H_5(CO)_3MoGeEt(H)^{+} + C_2H_4$$

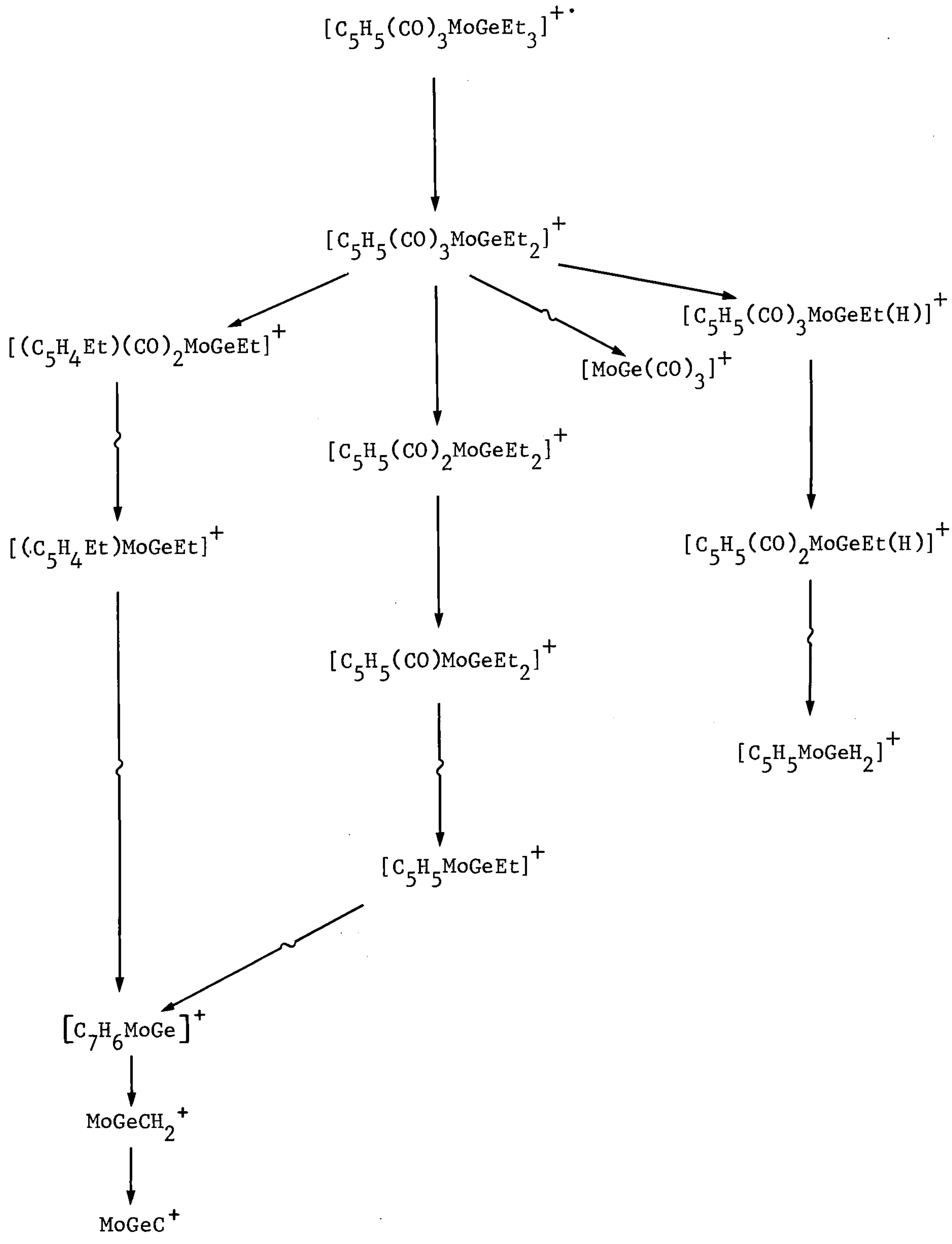
$$C_5H_5(CO)_3MoGeEt^{+} \longrightarrow C_5H_5(CO)_3MoGe^{+} + Et^{\cdot}$$

$$C_5H_5(CO)_3MoGeEt_2^{+} \longrightarrow C_5H_5(CO)_2MoGeEt_2^{+} + CO$$

There was some tendency, as shown in these compounds, to retain an even electron configuration for many of the ions.

The tungsten methyl complex showed peaks from cleavage of C-O bonds from the earliest stages of breakdown (this process was noted for the molybdenum analogue only after loss of two Me units) and provided a different pattern of ions from that of the molybdenum compound, showing losses of 15,16,28,29,30 and 44 mu fragments (probably CH_3, O, CO, HCO, H_2CO and CO_2 although loss of CH_4 and C_2H_4 from $-GeMe_3$ or $-GeMe_2$ cannot be ruled out: the latter reaction certainly does occur at some stage).

Fig.3.3 Some Fragmentation Paths of π-$C_5H_5(CO)_3MoGeEt_3$

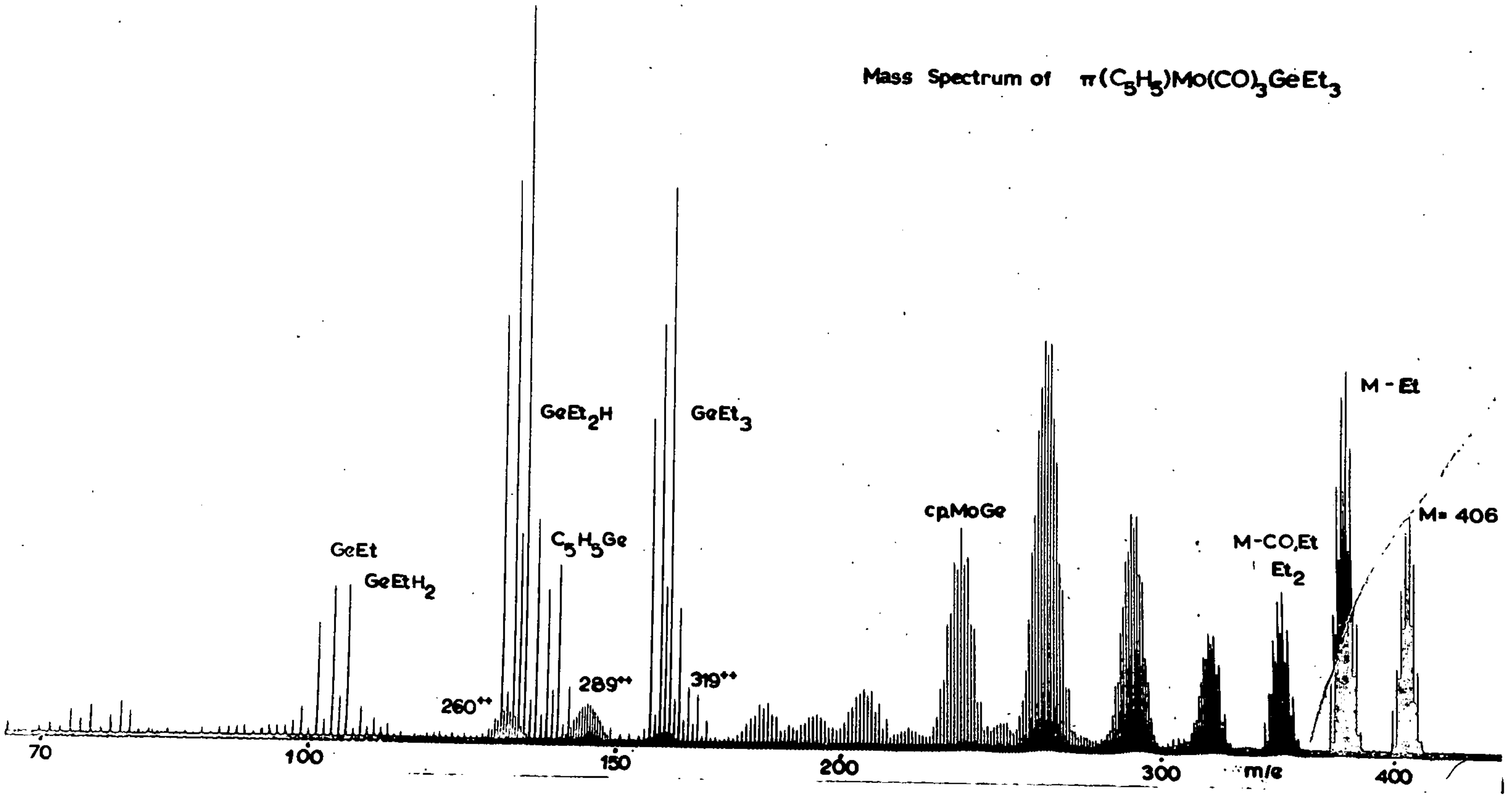


The metal-germanium bond reamined intact for the greater proportion of the ions until all six initially surrounding groups (CO and R) were removed, leaving as in the case of the simple alkyl germanes, hydride fragments, $C_5H_5MGeH_2^+$. The presence of such hydride ions implies loss of either $CH_2\cdot$ or C_2H_4 from the methyl complexes. Some rupture of the M-Ge link occurred at an early stage, however, as the GeR_3^+ ion was seen in all the spectra, $GeMe_3^+$ forming the base peak of the methyl compounds, and the corresponding major breakdown fragment of GeR_3^+ for the higher alkyl units (i.e. R_2GeH^+) appearing as the largest set in the spectra of the propyl and ethyl complexes.

No fragments containing solely molybdenum or tungsten were detected, although the regions of the spectra in which they would occur was in all cases very complex, being occupied by numerous doublet and triplet ion sets with no clearly defined isotope patterns.

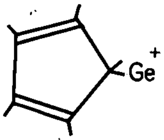
Those ions which retained the metal-metal bond intact and a C_5H_5 unit could always be formulated with the cyclopentadiene ring as C_5H_5. In some cases, however, notably, after loss of HCO had occurred, this procedure (of retaining a C_5H_5 unit in the formulation of the ion) left a C_2H_4 or a CH_2 unit to be accommodated in the remainder of the ion. The apparent presence of these entities, which are not favoured in the breakdown of the simple alkyl germanes, is perhaps better explained in terms of transfer of C_2H_5 or CH_3 groups to the C_5 ring (which remains π-bonded to the transition metal) to give $C_5H_4C_2H_5$, and $C_5H_4CH_3$ units, the hydrogen removed in the HCO group thus coming from the cyclopentadiene rather than the alkyl group. There is, of course, no means of distinguishing between isomeric ions such as $(C_5H_4Et)MoGeEt_2^+$, $C_5H_5MoGeEt_2(C_2H_4)^+$, and $C_5H_4MoGeEt_3^+$, and the rearrangement

Mass Spectrum of $\pi(C_5H_5)Mo(CO)_3GeEt_3$



must remain speculative. No other fragments containing C_5H_4Et, similar units or their breakdown products were detected.

The production of the fairly intense $C_5H_5Ge^+$ ion in all the spectra is probably analogous to the ions produced by the migration of alkyl groups in molecules such as $R_3Si\text{-}GeR'_3$ menioned earlier. Two processes are possible (a) the transfer of the germanium atom and its attached alkyl groups to the C_5 ring which is at that time still π bonded to the transition metal - i.e. a process involving initial metal-metal bond breaking or (b) transfer of the C_5 ring to germanium with the metal-metal bond intact followed by subsequent M-M rupture (variations could include synchronous transfer and bond breaking). The former process could occur from an early stage, i.e. when the germanium retained two or three alkyl groups, the latter process would be expected to occur at a later stage, after considerable breakdown of the GeR_3 unit had taken place. In no case was an intense ion corresponding to $C_5H_5GeR_{2\text{ or }3}^+$ seen, and inly in the spectrum of the methyl-molybdenum complex was there a suggestion of the ion $C_5H_5GeCH_3^+$, so it would seem more likely that $C_5H_5Ge^+$ production occurred at a late stage in the breakdown of these compounds, by the second process, (b). $C_5H_5Ge^+$ can also be formulated as $C_5H_4GeH^+$, although C_5H_5 could be σ bonded to germanium as



The fragmentation of the cyclopentaiene ring attached to the M-Ge skeleton which only occurred after loss of the six other radicals produced complex multiplet ions with group centres 13 and 26 mu apart, by loss of, presumably, CH, C_2H_2, H_2 and H units.

Table 3.2. Some High-Resolution Mass Measurements

Organgermanium-Transition Metal Complexes.

m/e	deviation (p.p.m)	assignment
	$\pi C_5H_5(CO)_3MoGeEt_3$	
406.9715	+5	$\mathrm{cp(CO)_3{}^{171}(MoGe)Et_3^+}$
405.9690	0	$\mathrm{cp(CO)_3{}^{170}(MoGe)Et_3^+}$
404.9705	-4	$\mathrm{cp(CO)_3{}^{168}(MoGe)Et_3^+}$
403.9704	-4	$\mathrm{cp(CO)_3{}^{168}(MoGe)Et_3^+}$
376.9297	0	$\mathrm{cp(CO)_3{}^{170}(MoGe)Et_2^+}$
348.9351	+1	$\mathrm{cp(CO)_2{}^{170}(MoGe)Et_2^+}$
348.8992	+2	$\mathrm{cp(CO)_3{}^{170}(MoGe)Et(H)^+}$
318.9025	-4	$\mathrm{cp(CO)_2{}^{170}(MoGe)Et^+}$
259.9063	+2	$\mathrm{cp\ \ {}^{166}(MoGe)Et^+}$
181.8431	-1	$\mathrm{{}^{168}(MoGe)CH_2^+}$
181.8349	0	$\mathrm{{}^{169}(MoGe)CH^+}$
181.8266	-4	$\mathrm{{}^{170}(MoGe)C^+}$
144.44933		$\mathrm{cpCO\ \ {}^{170}(MoGe)C_2H_4^{++}}$
144.47682		$\mathrm{cp\ \ {}^{165}(MoGe)Et_2H^{++}}$
	$\pi C_5H_5(CO)_3WGeMe_3$	
448.9665	+1	$\mathrm{cp(CO)_3{}^{255}(WGe)Me_3^+}$
447.9663	0	$\mathrm{cp(CO)_3{}^{254}(WGe)Me_3^+}$
407.9822	+9	$\mathrm{cp(CO)C^{257}(WGe)Me_3^+}$
407.9472	0	$\mathrm{cp(CO)\ {}^{256}(WGe)Me_2^+}$
406.9783	+4	$\mathrm{cp(CO)C^{256}(WGe)Me_3^+}$
406.9467	-4	$\mathrm{cp(CO)_2{}^{255}(WGe)Me_2^+}$
	$\pi C_5H_5(CO)_2(PPh_3)MoGeEt_3$	
480.0339	-4	$\mathrm{cp(CO)_2{}^{96}Mo(PPh_3)(H)^+}$
452.0246	-4	$\mathrm{cp(CO)\ {}^{98}MoPPh_2C_6H_4^+}$
425.0340	+3	$\mathrm{{}^{13}CC_4H_5{}^{98}MoPPh_2C_6H_4^+}$
239.9920	0	$\mathrm{C_5H_5{}^{98}MoC_6H_6^+}$

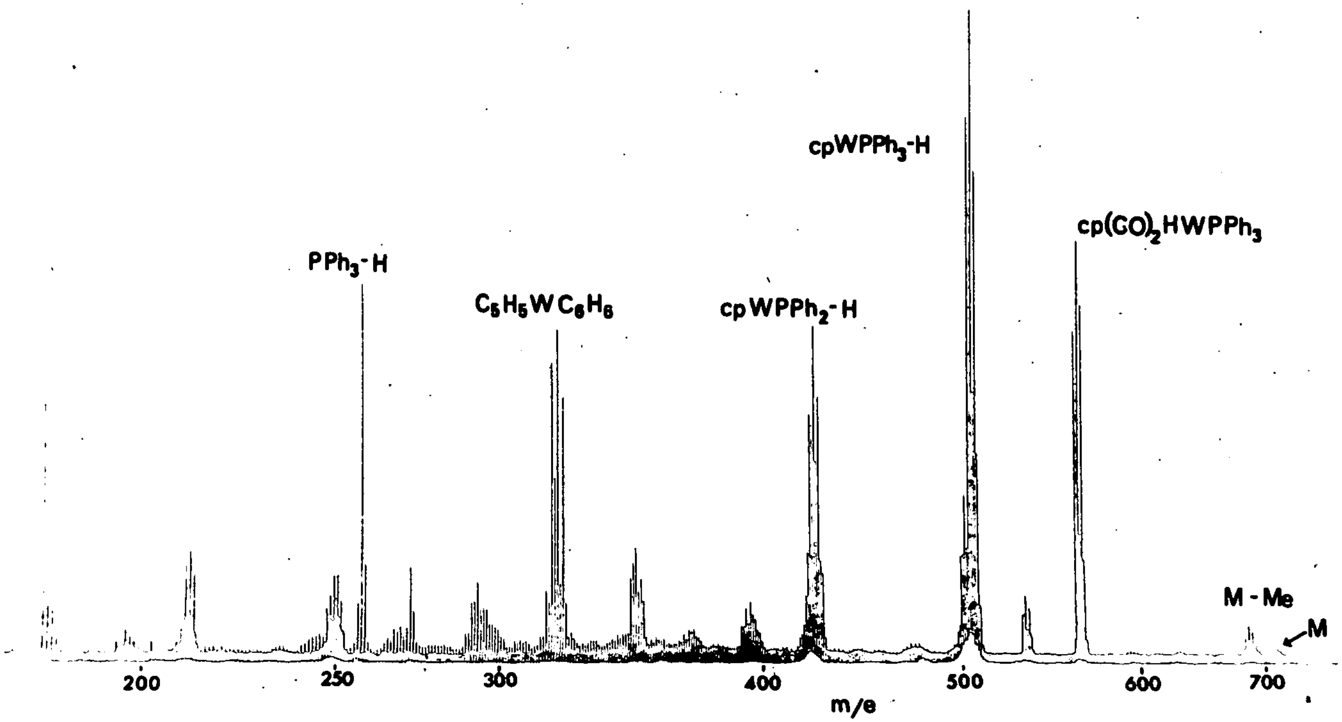
A number of doubly charged ions were clearly visible in the spectra. For the tungsten methyl compound, these corresponded to all the major M-M containing fragments, i.e. $C_5H_5(CO)_nWGeR_m^{++}$ m = 0-2, n = 0-3, indicating again the high stability of the metal-metal link in higher oxidation levels for the heavier transition metals. It is interesting to note that the intensities of the ion groups, as seen at unit mass resolution differed in the doubly charged state from those of the singly charged ions. The doubly charged ions from the tungsten-methyl compound increased uniformly in intensity from high to los mass, while their singly charged couterparts alternated in intensity as described above, indicating perhaps that any stabilising effect of the carbonyl groups and the loss of CH_3 units was not so effective for the ions with the greater charge. For the molybdenum-ethyl complex, which showed ions corresponding to $C_5H_5(CO)_3MoGe^{++}$, $C_5H_5(CO)_2MoGe^{++}$ and $C_5H_5(CO)MoGe^{++}$, the reverse was apparently true, the group $C_5H_5(CO)_2MoGe^{++}$ and its isobars being the most intense. In the same molybdenum compound, two small ions corresponding to $C_5H_5MoGe^{++}$ and Et_3Ge^{++} were observed in the low resolution trace. Doubly charged ions in the spectrum of the molybdenum methyl complex were very much less intense and could not be assigned unambiguously from the low resolution spectrum.

The reactions discussed are summarised in the partial fragmentation diagrams.

(b) The dicarbonyl-phosphine complexes, $\pi C_5H_5(CO)_2(PPh_3)MGeR_3$.

In these compounds, $\pi C_5H_5(CO)_2(PPh_3)MGeR_3$, R = Me, Et for Mo, and Me for M=W, the number of ions containing the M-M link was virtually limited to those at high mass in which complete loss of the alkyl groups from the germanium had not yet occured. These were much less intense than the corresponding ions in

Mass Spectrum of π-$C_5H_5(CO)_2(Ph_3P)WGeMe_3$



the tricarbonyl complexes, in agreement with the trends found on substitution of phosphines for CO groups in $Mn_2(CO)_{10}$. The molecular ions were still easily detected however. Rupture of the M-Ge bond occurred in all cases before that of the M-P bond, leaving a number of large ions containing the transition element as the sole metal. The M-Ge bond could just be detected as remaining until the $[(C_5H_5(PPh_3)MGe]^+$ stage. One of the major M-M bond fission processes was the strange elimination of a neutral germanium hydride fragment, best seen in the molybdenum ethyl complex

$$[C_5H_5(CO)_2(Ph_3P)MoGeH_2]^+ \longrightarrow [C_5H_5(CO)_2(PPh_3)MoH]^+ + GeH \quad \ldots\ldots. \text{(i)}$$

$$555 \longrightarrow 482 + 75, \quad m^* = 419$$

the apparent discrepancies in mass arising from the "mass contraction" for the MoGe combination, as mentioned previously. The metastable set from this transition has a different isotope pattern from any of the metallic fragments, but occupies the region calculated by considering transitions occurring from each of the largest individual isotope combinations, e.g. $^{172}(Mo\ Ge)^+ \longrightarrow {}^{98}(Mo)^+ + {}^{74}Ge$ etc. Two other interesting reactions among the ions containing just the transition element were noted,

$$[C_5H_5(CO)_2MH(PPh_3)]^+ \longrightarrow [C_5H_5(CO)M(PPh_2C_6H_4)]^+ + H_2CO \quad \ldots\ldots \text{(ii)}$$

and

$$[C_5H_5M(PPh_2C_6H_4)]^+ \longrightarrow [C_5H_5MC_6H_6]^+ + P(C_6H_4)_2 \quad \ldots\ldots \text{(iii)}$$

both of these processes being confirmed by high resolution mass measurement and the presence of the appropriate metastable peaks. Transition (ii) is formulated with loss of hydrogen from the phosphine rather than the cyclopentadiene ring in the basis of the subsequent rearrangement to the "sandwich" ion, with elimination of the presumably very stable "phosphonium" unit. The ion $[C_5H_5MoC_6H_6]^+$, isoelectronic with (neutral) chromocene, forms the base peak of the spectrum of the molybdenum-ethyl compound. Transition iii and its associated ions were present in the spectrum of the molybdenum- and tungsten-methyl phosphine compounds, $\pi C_5H_5(CO)_2PPh_3MGeMe_3$, but to a lesser extent than for the ethyl compound. Transitions (i) and (ii) occurred to an even smaller extent, presumably because of the difficulties in producing a Ge-H species from the $GeMe_3$ grouping. The ions $[C_5H_5(CO)MPPh_2C_6H_4]^+$ can of course be formed by routes other than via the germanium hydride. Two large doubly charged ions corresponding to $C_5H_5MP(C_6H_4)_2$ and $C_5H_5MPPh_3$ were observed. Transfer of germanium to cyclopentadienyl did not occur to any appreciable extent, and ions corresponding to, and derived from, the GeR_3 fragment were very small.

For the diethyl phosphine analogous of these compounds $\pi C_5H_5(CO)_2(Et_2PH)MGeR_3$ the largest ion was that due to cleavage of M-M bond, $[\pi C_5H_5(CO)_2(Et_2PH)M]^+$, but fragments containing metal-metal bonds were more abundant in these spectra (M = Mo, R = Et, Me = W, R = Me) than for the triphenyl phosphine complexes. The rearrangement of the transition metal phosphine containing ion to either $\pi C_5H_5MC_2H_5$ or $\pi C_5H_5MC_2H_4$ was not confirmed but could not be ruled out from the low resolution spectrum.

PART 4

COMPUTATIONAL TECHNIQUES

THE intensity patterns of the groups of peaks making up each ion are one of the most striking features of the mass spectra of organometallic compounds containing polyisotopic elements. For ions with only a single atom of such an element, the number and intensity of the major peaks in these groups correspond to the number of naturally occurring isotopes of the element and their relative abundance. The ion set Me_3Ge^+, for example, consists of five major peaks corresponding to $(Me_3Ge^{70})^+$, 21%, $(Me_3Ge^{72})^+$, 27%, $(Me_3Ge^{73})^+$, 8% $(Me_3Ge^{74})^+$, 36%, and $(Me_3Ge^{76})^+$, 8%, and similar much less intense sets from ions with the same metal isotopes but increasing numbers of C^{13} atoms. The characteristic patterns formed by ions containing more than one atom of one or more polyisotopic element often cover a large mass spread, between the peak from the combination of all the isotopes of lowest mass number to that containing all the isotopes of highest mass number, (for Ge_2, mass 140, $Ge^{70}Ge^{70}$, to mass 152, $Ge^{76}Ge^{76}$) and in calculating these isotope patterns, i.e. of the abundance of each nominal mass as seen under low resolution conditions, the intensity contribution of each isotope combination to each integral mass must be considered. For example, mass 166 in the MoGe pattern has contributions from Mo^{96} Ge^{70}, $Mo^{94}Ge^{72}$, and $Mo^{92}Ge^{74}$. For groupings containing more than one atom of the same element, these contributions are not immediately additive, as allowance must be made for the increased probability of occurrence of combinations containing varying numbers of dissimilar nuclides, which, being proportional to the number of different permutations of the isotopes present and the product of their abundances, results in a binomial relationship. General expressions for the abundance of a peak at a particular mass within an isotope pattern formed from a given number of atoms of a single polyisotopic element have been derived[188] and may be evaluated directly, for the simpler cases, by conventional means. Solution of these or similar expressions for abundances cannot be avoided, even if only the nominal mass of the most intense peak of an isotope pattern is required, since this does not, in general, correspond to the sum of the nominal masses of the most abundant isotopes of the separate elements. This point is absolutely fundamental to the mass spectrometry of polyisotopic molecules and is in direct contrast with the situation obtaining for organic compounds.

The precise masses of the isotope combinations contributing to any particular integral mass usually have a spread of less than 50 p.p.m. (parts per million) and with a maximum spectrometer resolution of 1:20,000, appear, at the relatively high mass at which they are normally measured, as a single peak with a precise mass corresponding to the weighted arithmetic mean of the exact mass of each of the contributing combinations, and a relative abundance which is the sum of the relative probabilities of occurrence of these combinations. If all the data which may be obtained from the examination of isotope patterns under high resolution are to be used, the value for the precise mass of each peak in the pattern must be calculated, as well as its abundance. Provision of exact mass values not only increases the order of magnitude of the task but also requires a different approach to the solution of the general expression for abundances. The binomial relationships encountered soon increase the labour of a manual calculation for the larger patterns to overwhelming proportions, and they then become much better suited to the higher speeds and greater reliabilities of electronic digital computers.

This section deals with computer-based methods of handling the arithmetic required for the elucidation of the mass and abundance values characteristic of isotope patterns. These form the basic data for studies of the mass spectra of polyisotopic organometallic compounds and without them the elemental composition of fragments within the spectrum of such a compound cannot be determined unequivocally. Methods are also considered for tackling the inverse problem of fitting elemental compositions to experimentally measured values of masses and abundances. Here again, for the polyisotopic organometallics, vast amounts of arithmetic result for exhaustive coverage of all possibilities and the repetitive nature of the process is well suited to computer methods.

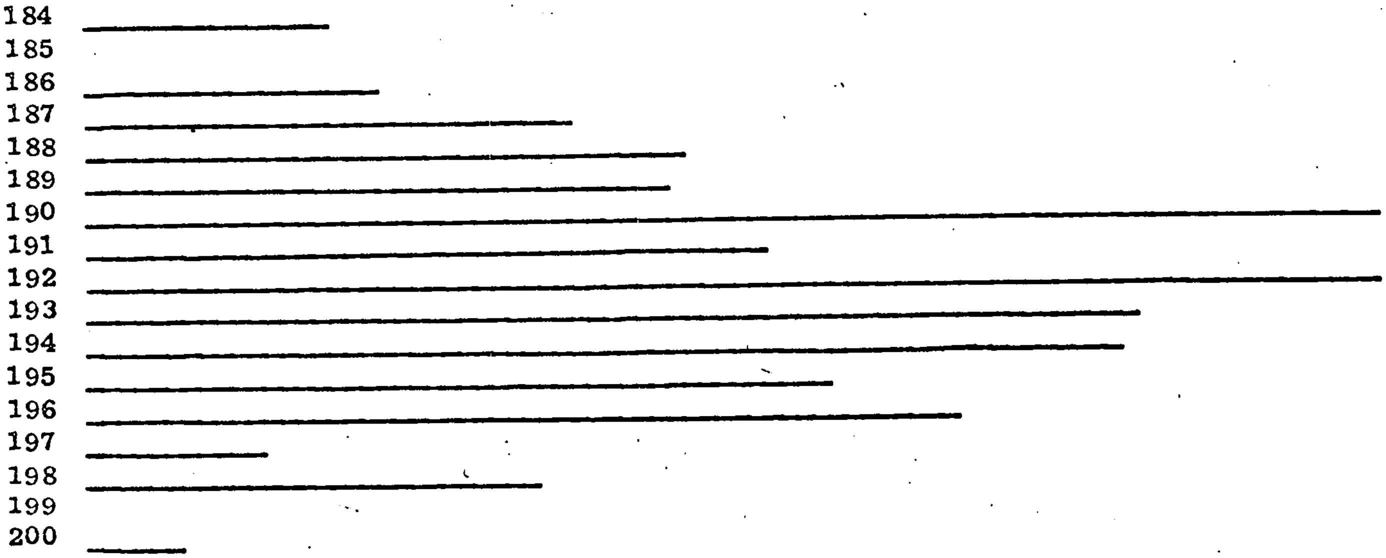
The two fields, of synthesis of isotope patterns and analysis and interpretation of experimental measurements from spectra containing these patterns, will be considered separately. Six computer programs are presented, three in each category, and these will be dealt with in turn, first in general, explaining their purpose and relevance in chemical terms, and then as a full specification giving all details of their working methods and requirements. This latter section presupposes a familiarity with general computing terminology, of the capabilities and mode of operation of the computer for which the program was written and a working knowledge of the programming language.[198-200] These specifications also include the program text. Examples of output are given and results relevant to the work described in part 3 are collected in Appendix 1.

There has been no previous work on the problem of calculating the apparent precise mass of peaks resulting from the combination of groups of metallic isotopes, and only a small amount on the provision of abundance values for aggregates of polyisotopic atoms; patterns for all combinations of bromine and chlorine up to a total of eight atoms, (i.e. $Br_{0-8}\ Cl_{8-Br}$) and for up to eight sulphur atoms have been evaluated[188]. The relatively recent advent of commercially produced high resolution mass spectrometers is perhaps at the root of this apparent lack of interest. Considerable use has been made of electronic computers in the mass spectrometry of organic compounds. They have been employed in the production of mass and abundance tables[189-90], in the solution of algorithms for the derivation of empirical formulae from a precisely measured ion mass[191], here often in conjunction with some method of checking the answer against a probable composition of the parent compound[192], and recently in two sophisticated routines for the wholly automatic recording and interpretation of complete high resolution spectra. These latter methods involve direct coupling of a computer to mass spectrometer, and have been used to produce the now well known "element maps"[193] and complete sequence determinations for amino acids in various types of protein[194-5]; in both cases precise mass was used as a sufficient criterion of elemental composition. Methods for automatic quantitative analysis of mixtures of similar compounds by computer, using abundance measurements from the spectrum of the mixture have been in use for some time in the petroleum industry[196].

The three programs dealing with conversion of experimental data to elemental composition and formulae, owe something to the methods just mentioned, in basic concept if not in detail. It must be emphasised, however, that any analysis of spectra of polyisotopic molecules depends fundamentally on the basic data of the pattern synthesis, and the degree of success achieved in analysis is directly related to that attained in

ABUNDANCES output

```
Isotope abundance pattern for two molybdenum atoms

      Nominal    Relative
       Mass      Abundance
        184       19.2408
        185        0.0000
        186       22.1281
        187       38.0933
        188       46.3966
        189       44.8336
        190       99.5008
        191       52.8153
        192      100.0000
        193       80.8979
        194       80.2035
        195       57.4411
        196       67.4294
        197       13.9076
        198       34.9530
        199        0.0000
        200        7.0789
```



End

the calculation of the isotope pattern.

4.1. COMPUTATIONAL TECHNIQUES FOR MOLECULES CONTAINING POLYISOTOPIC ELEMENTS

4.1.1. Basic Data - Masses and Abundances for Peak Patterns.

(i) ABUNDANCES.

This program provides abundance values for each nominal mass in the pattern resulting from the combination of any number of atoms of a single polyisotopic element. The Diophantine expression for the intensity of a peak within an isotope pattern given by Beynon is evaluated directly for each mass and the final answers are displayed in parallel columns under the headings Nominal Mass and Relative Abundance, this latter value being normalised to the most intense peak as 100. A pictorial version of the abundance values is also output, which gives a more quickly comprehensible idea of what the pattern would look like in a conventional low resolution trace of a mass spectrum. For most purposes the routine is superseded by ISOCOMB-4, but it remains useful for polymeric materials containing more than ten atoms of a particular polyisotopic element; e.g. small silicone molecules, some boron-containing compounds, and some germanium polymers, which are outside the present scope of ISOCOMB-4.

It is perhaps interesting to note that the Diophantine expressions to which the program gives a solution, are a classical mathematical problem which as their name suggests were first studied by the ancient Greek philosophers.

(ii) ISOCOMB-4

By effecting a complete synthesis from basic principles of an isotope pattern formed by the combination of up to ten atoms each of up to four

ISOCOMB-4 output

```
Isotope Abundance Patterns.
Peak Patterns in Mass Spectra of Compounds containing one atom of tungsten
and three of bromine.

Isotope , Combination          Mass             Abundance
 ( mass numbers )                                Product
   180  79  79  79         416.702024          8.25220
   182  79  79  79         418.703313          1359.03
   183  79  79  79         419.705332          738.572
   184  79  79  79         420.705234          1582.36
   186  79  79  79         422.709382          1469.41
   180  81  79  79         418.700020          24.2470
   182  81  79  79         420.701307          3993.17
   183  81  79  79         421.703328          2170.10
   184  81  79  79         422.703228          4649.36
   186  81  79  79         424.707378          4317.48
   180  81  81  79         420.698014          23.7478
   182  81  81  79         422.699307          3910.97
   183  81  81  79         423.701326          2125.43
   184  81  81  79         424.701224          4553.65
   186  81  81  79         426.705376          4228.60
   180  81  81  81         422.696010          7.75299
   182  81  81  81         424.697301          1276.82
   183  81  81  81         425.699321          693.892
   184  81  81  81         426.699218          1486.64
   186  81  81  81         428.703372          1380.52

Number of combinations:-  20


Nominal    multiplicity    spread     Peak  Mass     Relative
 Mass                      (ppm.)     (wtd mean)     Abundance

  417      singlet                    416.702024       0.0813
  418      no combination
  419        2              7.9       418.703253      13.6312
  420      singlet                    419.705332       7.2780
  421        3              17        420.702404      55.1765
  422      singlet                    421.703328      21.3847
  423        4              32        422.702596      98.9116
  424      singlet                    423.701326      20.9444
  425        3              24        424.703349     100.0000
  426      singlet                    425.699321       6.8378
  427        2              14        426.703776      56.3191
  428      no combination
  429      singlet                    428.703372      13.6039
```

different polyisotopic elements, this program produces all the information necessary for the examination of these patterns in a mass spectrometer at both high and low resolution.

The routine generates a pattern by setting up each isotope combination in turn and from these calculating the two parameters needed for the calculation of the weighted mean peaks. These parameters, a precise mass and an "abundance product", the latter formed from the product of the isotopic abundances of the nuclides present and the total number of atoms in the combination and divided by the factorial of the total numbers of each different isotope present, are listed in the first part of the program's output, alongside their respective isotope combination in columns headed mass and abundance product. All the individual precise masses and abundance products are then combined to give the final pattern, which is tabulated under the headings of nominal mass (integral mass number of the peak), multiplicity (number of isotope combinations having the same nominal mass), spread (difference between extreme masses of the contributing combinations, in p.p.m.), peak mass, (weighted arithmetic mean of contributions to multiplet masses) and relative abundance (sum of abundance products of individual combinations normalised to the most abundant peak in the final pattern as 100).

For most purposes, only the data in the last two columns are used, but under optimum conditions, the peaks from the individual isotope combinations can be observed; for example the $Mo^{97}Ge^{76}$ - $Mo^{100}Ge^{73}$ doublet (mass spread 22 p.p.m.) could be seen as two peaks at mass 173 with a resolution of 1:20,000 but at higher mass this fine structure disappears, and in the molecular ions of $\pi C_5H_5(CO)_3MoGeEt_3$, the peak collapses to a singlet at the weighted mean mass under this resolution. In the cases where the fine structure is resolved, the mass data from the first part of the output can be used.

The calculations and output are for the bare metallic skeleton only. Production of masses and abundances corresponding directly to those observed for ions containing the organic elements is the function of the next program, and ISOCOMB-4 produces a data tape for these calculations which can be read without further preparation directly into this program.

(iii) PEAK PATTERN.

This is a relatively simple and straightforward routine which gives the abundance for each nominal mass number of any isotope pattern derived from the combination of polyisotopic atoms and atoms of the organic elements, a pictorial version of these abundances, and precise masses for a number of peaks in the pattern and the (separate) organic portion of the ion. The program is unusual in that it produces an accurate pictorial print-out of the abundance values using the normal punched tape-controlled electrical typewriter. Corrections to the basic isotope pattern produced by ISOCOMB-4 for the presence of the heavy isotopes C^{13}, H^{2}, N^{15}, O^{17} and O^{18} are made in an appropriate fashion which is sufficiently accurate for virtually all purposes. If necessary the mass values for the final ion, both the nominal values printed alongside each abundance and the precise masses, can include any number of phosphorus atoms, and one other monoisotopic element e.g. fluorine or iodine, which can be specified by the user. A picture of each actual ion required is thus produced. Apart from the data, tape from ISOCOMB-4 or some other suitably prepared tape, the only information by the program is the formula of the ion in question. The mass data stored in

MASS 250

C	H	Ge	N	O	mass	m-3	m-2	m-1	m+1	m+2
9	10	1	3	1	0.000432	6.040	73.352	28.708	10.911	21.371
11	12	1	0	2	0.004754	6.603	73.191	29.368	11.979	21.581
5	12	1	4	3	0.007963	3.979	73.937	26.106	7.258	21.601
7	14	1	1	4	0.012286	4.557	73.772	26.791	8.344	21.778
10	12	1	2	1	0.013987	6.425	73.242	29.180	11.614	21.403
6	14	1	3	3	0.021519	4.372	73.825	26.593	7.969	21.610
9	12	1	4	0	0.023221	6.246	73.294	28.992	11.247	21.225
8	16	1	0	4	0.025840	4.948	73.661	27.273	9.051	21.793
11	14	1	1	1	0.027544	6.809	73.133	29.650	12.314	21.439
7	16	1	2	3	0.035074	4.764	73.714	27.077	8.678	21.623
10	14	1	3	0	0.036777	6.632	73.184	29.464	11.949	21.259
12	16	1	0	1	0.041098	7.191	73.025	30.116	13.012	21.479
6	16	1	4	2	0.044307	4.580	73.766	26.881	8.303	21.453
8	18	1	1	3	0.048630	5.155	73.603	27.558	9.385	21.640
11	16	1	2	0	0.050332	7.015	73.075	29.932	12.649	21.298
7	18	1	3	2	0.057864	4.972	73.655	27.364	9.012	21.469
9	20	1	0	3	0.062185	5.543	73.492	28.037	10.090	21.662
12	18	1	1	0	0.063888	7.396	72.967	30.397	13.347	21.340
8	20	1	2	2	0.071418	5.362	73.544	27.844	9.720	21.489
13	20	1	0	0	0.077443	7.776	72.859	30.860	14.042	21.387
7	20	1	4	1	0.080652	5.179	73.597	27.650	9.347	21.316
9	22	1	1	2	0.084975	5.750	73.434	28.321	10.425	21.513
8	22	1	3	1	0.094208	5.569	73.486	28.130	10.055	21.338
10	24	1	0	2	0.098529	6.136	73.324	28.795	11.128	21.541
9	24	1	2	1	0.107763	5.956	73.376	28.606	10.760	21.365
8	24	1	4	0	0.116996	5.776	73.427	28.415	10.390	21.189
0	1	3	0	2	0.763557	13.400	80.372	26.807	27.958	86.373
0	3	3	1	1	0.786347	13.574	80.377	27.097	28.295	86.330
1	5	3	0	1	0.799901	13.891	80.317	27.630	28.968	86.364
0	5	3	2	0	0.809135	13.749	80.381	27.387	28.632	86.287
1	7	3	1	0	0.822691	14.066	80.321	27.919	29.305	86.322
2	1	2	0	5	0.825740	13.291	93.560	19.963	25.989	74.436
1	1	2	2	4	0.834974	13.308	93.741	19.654	25.666	74.339
2	9	3	0	0	0.836246	14.381	80.261	28.449	29.975	86.360
6	1	2	0	2	0.840998	13.442	93.781	23.746	29.960	74.743
0	1	2	4	3	0.844207	13.325	93.921	19.342	25.342	74.243
2	3	2	1	4	0.848530	13.323	93.706	20.310	26.354	74.419
5	1	2	2	1	0.850232	13.462	93.974	23.448	29.650	74.643
1	3	2	3	3	0.857764	13.341	93.888	20.001	26.032	74.322
4	1	2	4	0	0.859465	13.481	94.167	23.148	29.338	74.543
3	5	2	0	4	0.862085	13.338	93.667	20.964	27.040	74.500
6	3	2	1	1	0.863788	13.473	93.913	24.094	30.327	74.731
2	5	2	2	3	0.871318	13.356	93.851	20.657	26.720	74.402
5	3	2	3	0	0.873022	13.492	94.108	23.797	30.017	74.630
7	5	2	0	1	0.877343	13.484	93.849	24.737	31.001	74.820
1	5	2	4	2	0.880552	13.373	94.035	20.349	26.399	74.304
3	7	2	1	3	0.884875	13.370	93.810	21.311	27.406	74.484
6	5	2	2	0	0.886576	13.503	94.045	24.443	30.694	74.719
2	7	2	3	2	0.894108	13.388	93.995	21.005	27.087	74.386
4	9	2	0	3	0.898429	13.384	93.764	21.963	28.089	74.567

the program are on the C^{12} scale[197] and the values used for relative abundances of the organic element heavy isotopes are those given by Beynon[188].

4.1.2. Interpretative Methods.

Programs concerned with the production of chemical formulae from experimental values of masses and abundances.

(i) MASS TABLE

Quite early, in the work on organogermanes described in part 1, interpretation of their mass spectra became lengthy and tedious, in terms of checking measured masses against proposed constitutions of various ions. A tabulation of all masses for all chemically possible ions was clearly desirable, but equally clearly a complete tabulation involving all the germanium isotopes for a number of germanium groupings and all the commonly encountered elements was out of the question. A compromise sacrificing completeness over a restricted range to wider limits and more manageable proportions was adopted, by listing masses for the most abundant isotope peaks of the groupings Ge, Ge_2, Ge_3 and Ge_4 taken in combination with all chemically possible numbers, in terms of valence saturation, of the organic elements within certain limits. No lower limit, other than zero, was placed on these elements: upper limits were nine carbon atoms per free germanium valence, four nitrogen and six oxygen atoms and hydrogen to valence saturation. The program also calculated and printed values of the intensity of peaks surrounding the one under consideration, for pure species corresponding to each particular formulation of the peak, providing three on the low mass side (M-3, M-2, M-1) and two on the high mass side (M+1, M+2). The abundance values assumed unit resolution of peaks only, and so the

FORMULATOR

```
Possible mass fomulations.
Ions in spectrum of pi-cyclopentadienyltri-ethylgermyltricarbonylmolybdenum

Allowed error  ± 10 p.p.m.


 Ion Mass    metal      C   C*     H   H*    N    O    calc. mass    dev
348.966845
              162      10    0    19    0    0    3    348.969701    8.2
              165      10    1    17    1    0    2    348.963476   -9.7
              166      11    0    19    0    0    2    348.967546    2.0
              166      11    0    17    1    0    2    348.969093    6.4
              170      11    1    18    0    0    1    348.967298    1.3
              170      11    1    16    1    0    1    348.968846    5.7
              170      12    0    17    1    0    1    348.964374   -7.1
              172       8    1    18    1    0    3    348.963496   -9.6
              173       8    1    19    0    0    3    348.967873    2.9
              173       8    1    17    1    0    3    348.969421    7.4
              173       9    0    20    0    0    3    348.963401   -9.9
              173       9    0    18    1    0    3    348.964951   -5.4


 Ion Mass    metal      C   C*     H   H*    N    O    calc. mass    dev
348.935104
              162      12    1    14    0    0    1    348.931820   -9.4
              162      12    1    12    1    0    1    348.933370   -5.0
              165       9    1    15    0    0    3    348.934834   -.77
              165       9    1    13    1    0    3    348.936382    3.7
              165      10    0    14    1    0    3    348.931911   -9.1
              167      13    1    13    0    0    0    348.936886    5.1
              167      13    1    11    1    0    0    348.938434    9.5
              167      14    0    14    0    0    0    348.932416   -7.7
              167      14    0    12    1    0    0    348.933964   -3.3
              169      10    1    15    0    0    2    348.932476   -7.5
              169      10    1    13    1    0    2    348.934024   -3.1
              170      11    0    15    0    0    2    348.935734    1.8
              170      11    0    13    1    0    2    348.937281    6.2
              174      11    1    14    0    0    1    348.934307   -2.3
              174      11    1    12    1    0    1    348.935853    2.2


 Ion Mass    metal      C   C*     H   H*    N    O    calc. mass    dev
318.979069
              167      10    1    19    0    0    0    318.977863   -3.8
              167      10    1    17    1    0    0    318.979413    1.1
              168      11    0    19    0    0    0    318.981797    8.6
              170       7    1    20    0    0    2    318.981181    6.6
              170       8    0    19    1    0    2    318.978258   -2.5
              174       8    1    18    1    0    1    318.976832   -7.0
```

tabulation accommodated the needs of both high and low resolution measurements. A mass range of 74-400 was covered, resulting in a 740 page output, the whole of which was sorted automatically into order of increasing mass to make it more easy to use. Unfortunately concentration on the major isotope masses was not always sufficient to characterise a complex pattern, and smaller compilations over restricted mass ranges and composition limits including all Ge isotopes and some C^{13} atoms, would have proved useful. The program could be adapted to produce these but the other formulation routines described below were developed and in general proved more useful.

(ii) FORMULATOR.

This program provides a straightforward method of dealing with mass values which are otherwise difficult to formulate. The routine checks the experimental mass in question against all the chemically possible formulations for the constituent atoms of the particular compound, including those containing C^{13} and H^{2}. Each formula whose mass lies within a specified range of the experimental value, conveniently the expected error in measurement, is printed out. Provision is made for dealing with up to four different isotope patterns in one spectrum e.g. $PtGe_2$, PtGe, Pt and Ge in the spectrum of $(Et_3P)_2Pt(GePh_3)_2$, as well as those purely organic fragments which could result from the compound studied e.g. biphenyl in the above case. All the possibilities for each measured mass are printed under headings showing the metal isotope peak present, the formulation, including separately any C^{13} or H^{2}, the calculated mass for the particular formulation, and the deviation in p.p.m. of the measured value from that calculated. The method was designed so that every possibility would be checked, thus at the very least giving an indication that if no formulation was found for an ion,

FORMGROUP

```
Possible mass formulations.
Ions in spectrum of pi-cyclopentadienyltrimethylgermyltriphenylphosphino-
 dicarbonyltungsten

Allowed error, + 5.0 p.p.m.


 Ion Mass   metal     C  C*    H  H*   N   O   P   calc. mass   dev
325.032049
             74      12   2   18   0   0   2   1   325.032302  -.77
                                                                  4H Me CO CO cp Bzn
             74      12   2   16   1   0   2   1   325.030752   4.0
                                                                  3H Me CO CO cp Bzn
                                                                  4H CO CO cp Ph Me
            182      11   0    9   1   0   0   0   325.032799  -2.3
                                                                  cp Ph
            183       6   2   13   0   0   0   1   325.032488  -1.3
                                                                  cp Me Me My
                                                                  2H Ph Me Me
            183       6   2   11   1   0   0   1   325.030939   3.4
                                                                  1H Ph Me Me
            184       6   2   11   0   0   2   0   325.033600  -4.8
                                                                  3H Me CO CO cp
            184       6   2    9   1   0   2   0   325.032054  -.02
                                                                  2H Me CO CO cp
            184       8   0   12   1   0   0   1   325.032757  -2.2
                                                                  cp Me Me My
                                                                  2H Ph Me Me
            186       3   2   12   1   0   2   1   325.032643  -1.8
                                                                  3H Me Me Me CO HCO
                                                                  4H Me Me CO CO Me

 Ion Mass   metal     C  C*    H  H*   N   O   P   calc. mass   dev
326.036797
             72      15   2   17   0   0   0   1   326.035238   4.8
                                                                  1H cp Ph Bzn
             73      15   2   15   0   0   2   0   326.037274  -1.5
                                                                  no grouping
             73      15   2   13   1   0   2   0   326.035726   3.3
                                                                  no grouping
            182      10   1   11   0   0   0   0   326.037700  -2.8
                                                                  cp Bzn
            182      10   1    9   1   0   0   0   326.036154   2.0
                                                                  cp Ph
            183      11   0   11   0   0   0   0   326.036365   1.3
                                                                  cp Bzn
            184       7   1   14   0   0   0   1   326.037659  -2.6
                                                                  cp Me Me Me
                                                                  3H Ph Me Me
            184       7   1   12   1   0   0   1   326.036111   2.1
                                                                  cp Me Me My
                                                                  2H Ph Me Me
            186       8   0   12   0   0   2   0   326.038071  -3.9
                                                                  4H Me CO CO cp
```

one definitely did not exist within the error limits and composition range allowed. This simple but effective routine has proved helpful in assigning masses from the congested areas of the spectra of the organogermanium transition metal complexes, particularly multiplet peaks.

(iii) FORM GROUP

This program provides a way of dealing with the translation of empirical formulae found for ions into possible groupings of structural entities present in the original compound or which could be derived from them by known fragmentation processes. It is thus an approach to a truly automatic interpretation routine. It consists of two separate sections, an extended FORMULATOR routine, similar to that described above, but with some modifications to increase its scope and speed, and a self contained sub-program which performs the grouping operation on the formulae found for each ion mass. It was the intention to provide a routine which followed the methods one "intuitively" employs to deduce the probable structure of an ion from its formula, and by applying this to all the results found for each experimental mass, to relieve the user of the labour of checking all but the likely candidates found by the method. The final algorithm used was a relatively simple multistage addition and subtraction process which was both fast and exhaustive.

The basis of the method is the tendency for the organometallic compounds studied to fragment in certain well defined ways, e.g. the prevailing alkene loss from the alkylgermanes, and the great stability of other groups e.g. phenyl, cyclopentadienyl, carbonyl etc. under electron impact, thus making it possible to include a substantial number of fragmentation routes within a relatively small amount of stored data. Fragmentation routes and data for 27 groups are contained in the routine, including the alkyl, alkenyl and alkynyl radicals up to C_4, the common aromatic radicals, and a number of heteroatom groups. These are listed in full in the specification. The procedure can easily be expanded to accommodate more or alternative routes, the basic control statements, described in the specification and logic flow chart, being designed with this in mind.

Special provision is made for the inclusion of fluorine in the grouping routine so that fluorocarbon peaks e.g. from the mass standard, can be processed at the same time as hydrocarbon fragments. Provision is also made in the formulation routine, for the inclusion of phosphorus and one other monoisotopic element, at the user's discretion. The output format is similar to that of FORMULATOR described above, with the addition of the structural formula for each empirical formulation which is printed out next to the value of the deviation, or if more than one possibility exists they are printed out one below the other in this position. An example of output is given on page 149a.

4.2. PROGRAM SPECIFICATIONS.

The routines described above are all written in the dialect of Algol 60 appropriate to the machine with which they were used (either an Elliott 803, E.E.L.M. KDF9, or I.C.T. Atlas). Algol 60 has the advantage of being one of the major internationally recognised programming languages, as well as having a wide practical acceptance in this country. By virtue of its powerful logical facilities, it is also particularly appropriate to the solution of the present problems.[199]

4.2.1. ABUNDANCES.

Language: Elliott 8 hole Algol (for 803 implementation)

Method: Consider an element with a number of isotopes whose masses

M, M + 1, M + 2, M + 3, etc. have relative abundances a_o, a_1, a_2, a_3, etc. Values are required for the relative probabilities of occurrence of polyatomic aggregates (ions) containing r atoms of the element and which have masses rM, rM + 1, rM + 2, etc.

For the mass rM, this value is a_o^r,

for the mass rM + 1, $ra_o^{r-1}a_1$, $= a_o^r\left[\frac{r!}{(r-1)!}\cdot\frac{a_1}{a_o}\right]$,

for the mass rM + 2, $\left(ra_o^{r-1}a_2 + \frac{r.r-1}{2}\, a_o^{r-2}a_1^2\right)$,

$$= a_o^r\left[\frac{ra_2}{a_o} + \frac{r!}{(r-2)!2!}\cdot\left(\frac{a_1}{a_o}\right)^2\right],$$

and for mass rM + 3

$$\left(ra_o^{r-1}a_3 + r.r-1.a_o^{r-2}a_1a_2 + \frac{r.r-1.r-2}{3!}\cdot a_o^{r-3}.a_1^3\right),$$

$$= a_o^r\left[\frac{ra_3}{a_o} + \frac{a_1a_3}{a_o^2}\cdot\frac{r!}{(r-2)!} + \frac{r!}{(r-3)!3!}\cdot\left(\frac{a_1}{a_o}\right)^3\right]$$

$$= a_o^r r!\left[\frac{b_3}{(r-1)!} + \frac{b_1b_2}{(r-2)!} + \frac{b_1^3}{(r-3)!3!}\right] = a_o^r r!\ P_3 \quad \ldots\ldots\ldots\ldots\ 4.i$$

where $b_x = a_x/a_o$.

Generalising this, the probability of occurrence of the mass (rM + S) is $a_o^r r! P_S$ where

$$P_S = \sum \frac{b_1^{i1}.b_2^{i2}.b_3^{i3}\ldots\ldots.b_n^{in}}{i_1!i_2!i_3!\ldots\ldots i_n!(r-i_1-i_2-i_3\ldots\ i_n)!}, \quad \ldots\ldots\ldots\ 4.ii$$

the sum being taken over all partitions of S such that

$$i_1 + 2i_2 + 3i_3 + \ldots\ldots + ni_n = S \qquad \ldots\ldots\ldots\ 4.iii$$

(note 1)

The program sets up and stores in the two dimensional (triangular) array X, products of successive "b factors" (i.e. the b_1 b_2, $b_1b_2b_3$,...... terms of 4.i)

```
Abundances ;

begin
     integer b,j,n,p,q,u,h,t,w,z,r,g,k,in,st,ab;
     real I,v,sum,ans,abmax;
     integer array title[1:15];

     in:= 1;  instring(title,in);  in:= 1;
     read  st,r,z,g;
     print ££1?Isotope abundance pattern for ?;  outstring(title,in);
     print ££12S6?Nominal£S4?Relative£ls8?Mass£s5?Abundance?;

  begin  integer array A,C,IM,M[1:r],F[0:z];
         real array D,E[1:r],X[1:r,0:z],AB[0:g];
         switch  SS:= S1,S2,S3,S4,S5,S6,S7,S8;

   read I; for h:= 1 step 1 until r do read IM[h],E[h];
   for h:= 1 step 1 until r do begin D[h]:= E[h]/I; M[h]:= IM[h]-st;
            C[h]:= g div h; if z < C[h] then C[h]:= z end;
   for h:= 1 step 1 until r do
            begin X[h,0]:= 1;  for t:= 1 step 1 until C[h] do X[h,t]:= D[h]*X[h,t-1]
            end;

  F[0]:= 1;  for h:= 1 step 1 until z do F[h]:= h*F[h-1];   n:= 0;

  S8:  b:= n;  p:= r; sum:= 0; for h:= 1 step 1 until r do A[h]:= 0;

  S1:  A[p]:= b div M[p];  b:= b-M[p]*A[p];

  S2:  if b=0 then goto S3 else begin if p=1 then goto S7 else p:= p-1; goto S1  end;

  S3:  w:= z;  for h:= 1 step 1 until r do w:= w-A[h];  if w < 0 then goto S7;

   v:= 1;  for h:= 1 step 1 until r do v:= v*X[h,A[h]]/F[A[h]];  v:= v/F[w];
   sum:= sum+v;  if n=0 then goto S6;

  S7:  if p=1 then begin b:= b+A[1]*M[1];  A[1]:= 0; goto S4 end else goto S5;

  S4:  p:= p+1;  if p=r+1 then goto S6;  if A[p]=0 then goto S4 else goto S5;

  S5:  A[p]:= A[p]-1;  b:= b+M[p];  goto S2;

  S6:  ans:= I*F[z]*sum;  AB[n]:= ans;  n:= n+1;  if n ≤ g then goto S8;

  abmax:= 0;  for h:= 0 step 1 until g do abmax:= if AB[h]>abmax then AB[h] else abmax;

    for h:= 0 step 1 until g do AB[h]:= (AB[h]/abmax)*100;
    for h:= 0 step 1 until g do print ££LS8??,sameline,digits(3),z*st+h,££S4??,
      aligned(3,4),AB[h];
    print ££L4??;  for h:= 0 step 1 until g do begin ab:= AB[h]*0.8; print digits(3),
      z*st+h,£ ?;  for p:= 1 step 1 until ab do elliott(7,4,64,0,7,4,126)  end;

    end;
 end of program;
```

Values for the exponentiated products for each term in the P_S summation (i.e. the numerators of 4.ii) are obtained from this array by multiplying together elements selected using the indexing array A (equivalent to the i values of 4.ii), which in turn is set up from the values of the maximum mass excess (over that of the "basic peak" at rM) to be considered, and the current value of the mass excess (n, equivalent to S) via the identifiers "b" and "p". These are used to generate the "partitions" required for satisfaction of expression 4.iii. Each term of the P summation is temporarily stored in location "V" (overwritten by each fresh value) and the whole summation is generated and stored in the location "sum". The final value for the probability of occurrence of a peak at mass number n is stored in location "ans" and transferred to the array AB for later use in the normalisation routine. Factorials are set up and held in the array F (note 2) and initial "b factor" values in array D. Array C stores index values for the triangular array X (n factors in 4.iii) and arrays IM and E hold the values of isotope masses and abundances (for nuclides other than that of the lowest mass), read in as data. The final values for the abundances are normalised to the largest as 100 (lines 29-30) and are output in tabular form. Finally instructions of lines 33-34 produce a pictorial version of these values (reduced by a factor of 0.8 to fit on the normal width flexowriter carriage) each line representing an abundance being labelled with its corresponding mass number. The instruction pair in the Elliott procedure of line 34 produces the characters "space" and "underline" (on channel one) more efficiently than the conventional "print" statement.

Notes:

1. The partitions of S are given by taking the coefficient the power of x^s in the expansion of

$$\frac{1}{(1-f_1x)(1-f_2x^2)(1-f_3x^3)\ \ldots\ (1-f_sx^s)} = (1+f_1x+f_1^2x^2+\ \ldots\ )\ (1+f_2x^2+f_2^2x^4+\ \ldots\ )$$

$$\ldots\ (1+f_sx^s+f_s^{2s}x^{2s}+\ \ldots\ ),$$

and the number of such partitions is given by

$$\frac{1}{2\pi i}\oint\frac{dz}{(1-z)(1-z^2)(1-z^3)\ \ldots\ (1-z^s).z^{s+1}}$$

2. The array F storing the required factorials is of type integer and it must be noted that 13! > 536870911, the maximum integer capacity of the 803, so that if the program is required for use in calculations involving more than 13 atoms, this array must be removed and redeclared as type real (where capacity ≈ 5.8×10^{76}, ≃ 57!). This is the only likely cause of failure in the present programe. Little error is introduced by this approximation (i.e. real rather than integrer factorials): note that the factorials of ISOCOMB-4 are stored as real numbers.

Requirements:

8192 word configuration for translation with Elliott library program A.304 (Elliott 8 hole Algol). 4096 configuration is sufficient for running a pre-compiled version, ABUNDANCES occupying 2233 location in A.304 translation.

Time:

1. Translation, using A.304, 6 minutes 30 seconds.

2. Running. Variable: 5 seconds per combination (see p.156a) is a reasonable guide.

4.2.2. ISOCOMB-4

Language: Elliott 8 hole Algol. Primarily for the 803. May be used directly with the Atlas Elliott compiler.

Method: For any ion set from a molecule containing atoms of elements with several abundant isotopes, the probability of occurrence of a particular isotope combination, P_i, is directly proportional to the product of the natural abundance of each isotope and the number of possible permutations of the isotopes forming the combination, i.e.

$$P_i \quad \alpha \quad \frac{a_1.a_2.a_3. \;\ldots\ldots\; a_n.n!}{i_1!i_2!i_3! \;\ldots\ldots\; i_n!}$$

where a_x is the relative abundance of the xth isotope, n the number of atoms in the combination, and i_x the number of atoms of the xth isotope present in the combination.

The probability of occurrence of a peak at a particular mass number A_m, is proportional to the sum of the probability of occurrence of each of the contributing isotope combinations, and, if relative probabilities are concerned, constants of proportionality may be neglected, giving as the relation for the relative abundance (probability) of a peak at A_m as

$$A_m = \sum_{1}^{c=z} \frac{a_{c1}.a_{c2}.a_{c3}. \;\ldots\ldots\; a_{cn}.n!}{i_{c1}!i_{c2}!i_{c3}! \;\ldots\ldots\; i_{cn}!}$$

where the summation is taken over all possible (z) combinations (c) of the same nominal mass number (m). The precise mass at which a peak of particular nominal mass occurs corresponds to the weighted arithmetic mean of the precise masses of the combinations which have that nominal mass. This assumes, however, a spectrometer resolution incapable of separating the individual combination masses at the measured mass, which as explained above, is normally the case.

The recursive procedure "isoset" forms the isotope combination for the required number of atoms of each element in turn. The combinations are stored in the three-dimensional array IC as the corresponding integral mass numbers, the subscripts of this array being the index number of the element concerned, the index number of the atom of the combination, and the index number of the combination itself respectively. The precise mass, the sum of the isotope exact masses, of the combination, is stored in the array MC, indexed by element and combination number. An abundance product, indexed in the same manner, and formed from the product of the relative abundance of each isotope divided by the product of the factorial of the numbers of different isotopes present, is stored in the array AP, the searching routine of lines 48 to 52 providing these numbers in the array "index". Control variables "b", "d" and "B" ensure entry at the required loop of "isoset" and "d" delays entry into the calculation routines until the innermost loop is reached. The for statement routine of lines 80-87 forms the final isotope combination, FIC for all atoms of all the elements present (this is over-written by each combination after print out), the final mass of the combination, FM, and the final abundance product FAP. These latter arrays are retained for subsequent sorting into order of ascending mass, which is achieved by the minimal storage method of lines 97-113. A straightforward sort-by-exchange routine is used with modifications which allow the sort to begin where the first, and end where the last, exchange occurred on the previous pass. An exit occurs when the last exchange orders the set and no further exchange would take place on the next pass. These points effect considerable time economies. Faster methods such as the "Shellsort" or "Stringsort" routines are not used because of their high work space requirements.[198]

The ordered precise masses are converted to integral values (note 1) and stored in the array IFM. A single pass through this list groups the masses of the same nominal value together (line 121) and computes the weighted arithmetic mean of their precise masses [i.e. $\Sigma(m.a.)/\Sigma a$] and the relative abundance (Σa) for the peak. Values for the multiplicity and spread (in p.p.m.) of the peak are obtained at the same time (note 2). The final print statement produces the information in tabular form, the relative abundances being normalised to the largest as 100 and a data tape suitable for direct input to the PEAK PATTERN program (described later) is output on a second channel. These data consist of the title string (in quotes), number of peaks in the pattern, nominal mass values and abundances for each peak, and five precise masses, two on the high mass, and two on the low mass side of the largest peak and this peak itself, or if this is impossible, five peaks which include the largest (note 3).

Format and position of column headings are maintained by the procedure "space".

Notes:

1. The present program uses the "entier" value for the real to integer conversion, thus assuming that the mass defect for all peaks of the same nominal value is either always positive or always negative. The program will fail if peaks of the same nominal value lie both above and below the integral value (e.g. 123.999 and 124.001 would be regarded as 123 and 124 respectively, thus grouping them with the wrong nominal mass number). The same problem arises with the "rounded off" real-integer conversion, at the half integral value (e.g. 123.499 and 123.501 being regarded as 123 and 124). With combinations of large mass defect elements, the latter problem, i.e. a defect approaching 0.5 mass units, is more likely to occur, and the "entier" procedure (with storage of the values to obviate unnecessary re-calculation) is adopted, without further complicating the program to allow for both possibilities. This point should, however, be borne in mind as a possible cause of failure or incorrect results. Reprogramming for the "rounding" conversion merely requires removal of the "entier" procedure call.

2. The values for the multiplicity and spread of a peak are most useful when the individual combinations can be resolved, as described above, as an aid to the location and fuller description of the peak. It must be remembered that the multiplicity (or number of contributing combinations) is a "fine structure" parameter and nothing to do with other ions of the same nominal mass. The spread quoted is a maximum figure and gives equal weight to small peaks at

```
ISOCOMB - 4;
begin
     integer N,nmax,h,j,in,SN,SP,SPU,SPL,ICL,FML;
     integer array na,ni,w[1:4],title[1:15];
     real array M,A[1:4,1:10],F[0:45];

     in:=1;  instring(title,in);   in:=1;
     print ££R30L?Isotope Abundance Patterns.£L?Peak Patterns in Mass Spectra of?,
          £ Compounds containing ?;    outstring(title,in);

     read N;  for h:=1 step 1 until N do read  na[h],  ni[h];
     if buffer(1,£;?) then read  ICL,  FML  else begin  ICL:= 210; FML:= 420  end;
     for h:=1 step 1 until N do for j:=1 step 1 until ni[h] do read M[h,j],A[h,j];

     SN:=0;  for h:=1 step 1 until N do SN:=SN+na[h];

     nmax:=0; for h:=1 step 1 until N do nmax:= if na[h]>nmax then na[h] else nmax;

     F[0]:=1;  for h:=1 step 1 until SN do F[h]:=h*F[h-1];

     SPU:= SPL:= 0;    for h:= 1 step 1 until N do
     begin  SPU:= SPU+M[h,ni[h]]*na[h];    SPL:= SPL+M[h,1]*na[h]   end;
     SP:= SPU-SPL+1;

     for h:= 1 step 1 until N do w[h]:= 0;

 begin real array IC[1:N,1:nmax,1:ICL],MC,AP[1:N,1:FML],FM,FAP[1:FML],I[1:10];
      integer Y;
      integer array st,index,interstore[1:10];

   procedure  isoset(a,b,c,d);
     value a,b,c,d;
     integer a,b,c,d;

        begin integer B,isointer,t,x,z;
              real AA,FF;
              switch SS:=S1,S2,S3,S4,S5,S6,S7,S8;

        B:= if b > 5 and b=d then b-5 else if b > 5 then 5 else b;

     if b > d then z:= 0 else
     if b=d and b > 5 and b ≠ 10 then begin z:= 5; st[b+1]:= 1; goto SS[B] end else
     if b=d and b = 10 then begin z:= 5; Y:= 1 end else
     if b=d and b < 5 then begin z:= 0; st[B+1]:= 1; goto SS[B] end else
     begin z:= 0; Y:= 1 end;

 S5:    for st[5+z]:= Y step 1 until c do
         begin I[5+z]:= M[a,st[5+z]];
 S4:      for st[4+z]:= st[5+z] step 1 until c do
           begin I[4+z]:= M[a,st[4+z]];
 S3:        for st[3+z]:= st[4+z] step 1 until c do
             begin I[3+z]:= M[a,st[3+z]];
 S2:          for st[2+z]:= st[3+z] step 1 until c do
               begin I[2+z]:= M[a,st[2+z]];
 S1:            for st[1+z]:= st[2+z] step 1 until c do
                 begin I[1+z]:= M[a,st[1+z]];
```

```
        if b > 5 and d≠1 then begin Y:= st[1+z]; isoset(a,b,c,1) end;

        if d ≤ 5 then
     begin    w[a]:= w[a]+1;  MC[a,w[a]]:= 0;

        for h:= 1 step 1 until b do
        begin  MC[a,w[a]]:= MC[a,w[a]]+I[h];  IC[a,h,w[a]]:= I[h] end;

        if b=1 then goto S6;

        interstore[1]:= I[1];  x:= 1;  index[1]:= 1;
        for h:= 2 step 1 until b do
     begin  isointer:= I[h]; if isointer=interstore[x] then index[x]:= index[x]+1
       else  begin  x:= x+1;  interstore[x]:= I[h];  index[x]:= 1  end
     end;

     FF:= 1;  for h:= 1 step 1 until x do FF:= FF*F[index[h]];
     AA:= 1;  for h:= 1 step 1 until b do AA:= AA*A[a,st[h]];

        AP[a,w[a]]:= AA/FF;

     end;   goto S7;

  S6:    AP[a,w[a]]:= A[a,st[1]];

  S7:             end; if B=1 then goto S8;
                end; if B=2 then goto S8;
              end; if B=3 then goto S8;
            end; if B=4 then goto S8;
          end;

  S8:  end isoset ;

  procedure space(a);
      value a;   integer a;
      begin integer J,K;    K:= 2*abs(SN-5);
      if a=1 and SN > 5 then begin for J:=1 step 1 until K do print ££s?? end else
      if a > 1 and a < 5 then begin for J:=1 step 1 until K do print ££s?? end
  end space ;

begin integer k,f,p,q,r,s,t,R,V,n;
      real ULSP,LLSP,AN;
      integer array FIC[1:SN],nm,Q[1:SP],ST[1:4],IFM[1:FML];
      real array AB,sumM,sumA,spread,meanmass[1:SP],mainmass[1:5];
      switch  S:= S9;

        print ££L2??; space(1); print £Isotope  Combination£s8??; space(1);
        print £Mass£s10?Abundance£l??; space(1);
        print ££s2?( mass numbers )£s??; space(1); print ££s24?Product£l??;

    for f:=1 step 1 until N do isoset(f,na[f],ni[f],na[f]);

    n:=0;  if N < 4 then for h:= N+1 step 1 until 4 do w[h]:= 1;
```

```
    for ST[4]:= 1 step 1 until w[4] do
    for ST[3]:= 1 step 1 until w[3] do
    for ST[2]:= 1 step 1 until w[2] do
    for ST[1]:= 1 step 1 until w[1] do
     begin    n:= n+1;    s:= 0;
       for j:= 1 step 1 until N do
       for k:= 1 step 1 until na[j] do
       begin    s:= s+1; FIC[s]:= IC[j,k,ST[j]]   end;

       FM[n]:= 0;    FAP[n]:= 1;
         for t:= 1 step 1 until N do
         begin  FM[n]:= FM[n]+MC[t,ST[t]];   FAP[n]:= FAP[n]*AP[t,ST[t]]  end;

       FAP[n]:= FAP[n]*F[SN];

      space(SN);  for h:=1 step 1 until SN do print sameline,digits(3), FIC[h];
      space(SN);  print ££S4??, sameline,aligned(3,6),FM[n],££S7??,freepoint(6),
      FAP[n],££L??;

     end;

     r:= 1;   s:= n-2;

  begin  real inter;  boolean anychange;
        for q:=1,q+1 while anychange do
     begin  anychange:=false;
        for p:= r step 1 until s do
        if FM[p+1] < FM[p] then
        begin if not anychange then r:= p-1;
              inter:= FM[p+1];
              FM[p+1]:= FM[p];
              FM[p]:= inter;
              inter:= FAP[p+1];
              FAP[p+1]:= FAP[p];
              FAP[p]:= inter;
              anychange:= true
        end;
        s:= s-1;  if r=s then goto S9
     end
  end;

 S9:  for h:=1 step 1 until SP do begin sumA[h]:= sumM[h]:= 0;  Q[h]:=0  end;
      for h:=1 step 1 until n do IFM[h]:= entier(FM[h]);

 R:= IFM[n+1]:= 0;

for h:=1,V+1 while h ≤ n do
     begin  V:=h;  R:=R+1;
        if IFM[h+1] = IFM[h] then
          begin  LLSP:=FM[h];
             for k:=h,k+1 while IFM[k] = IFM[k-1] do
```

```
               begin V:=k;  Q[R]:= Q[R]+1;
                 sumM[R]:= sumM[R]+ FM[k]*FAP[k];
                 sumA[R]:= sumA[R]+ FAP[k];
                 ULSP:= FM[k]
               end;
               meanmass[R]:= summ[R]/sumA[R];
               spread[R]:= ((ULSP-LLSP)/meanmass[R])*₁₀6
          end else
          begin  Q[R]:=1;  meanmass[R]:=FM[h];
                   sumA[R]:= FAP[h];   spread[R]:=0
          end
      end;

      AN:=0;   for h:=1 step 1 until R do
      begin AN:= if sumA[h] > AN then sumA[h] else AN; nm[h]:=meanmass[h]  end;

   k:=0;

  print ££L2?Number of combinations:-?,sameline,digits(3),n,££R80L5?Nominal£S4??,
  £multiplicity£S4?spread£S5?Peak  Mass£S5?Relative£ls?Mass£S22?(ppm.)£S5??,
  £(wtd mean)£S5?Abundance£L??;
  for h:=1 step 1 until R do
  begin k:=k+1;  print ££ls??,sameline,digits(3),nm[h];  if Q[h]=1 then print ££S6??,
     £singlet? else print sameline,digits(2),££S7??,Q[h],££S3??;
     if spread[h]=0 then print ££s15??  else print sameline,££S10??,freepoint(2),
     spread[h],££s??;   AB[k]:= (sumA[h]/AN)*100;
     if abs((sumA[h]/AN)*100-100)<₁₀-6 then begin if R-h < 2 then s:= 2-R+h else
     if h<3 then s:= h-3 else s:=0;  for j:=1 step 1 until 5 do
     mainmass[j]:= meanmass[h-(3+s)+j]   end;
     print ££s4??,sameline,aligned(3,6),meanmass[h],££s4??,aligned(3,4),(sumA[h]/AN)
     *100; if h < R and nm[h+1] ⊨ nm[h]+1 then begin k:=k+1;  print ££ls??,sameline,
     digits(3),nm[h]+1,££S6?no combination?;  AB[k]:= 0 end
  end;

  print ££s2r80??,punch(2),££r80L2Q??;
      in:=1;  punch(2);     outstring(title,in);
  print ££ul??,digits(2),k,££s212??;
  for h:=1 step 1 until k do print digits(3),nm[1]-1+h,££s7??,sameline,aligned(3,4),
     AB[h],££S2??; for h:=1 step 1 until 5 do print aligned(3,6),mainmass[h],££S2??;

  end of main block ;

  end of procedure block ;

end;
```

NUMBER OF COMBINATIONS

for a given number of atoms of a single
element with a given number of isotopes

No. of atoms	Number of isotopes →								
1	2	3	4	5	6	7	8	9	10
2	3	6	10	15	21	28	36	45	55
3	4	10	20	35	56	84	120	165	220
4	5	15	35	70	126	210	330	495	715
5	6	21	56	126	252	462	792	1287	2002
6	7	28	84	210	462	924	1716	3003	5005
7	8	36	120	330	792	1716	3432	6435	11440
8	9	45	165	495	1287	3003	6435	12870	24310
9	10	55	220	715	2002	5005	11440	24310	48620
10	11	66	286	1001	3003	8008	19448	43758	92378

Read number of combinations at intersection of row containing number of atoms and column containing number of isotopes.

Note that numbers (including top row) form Pascal's Triangle with apex in top left corner.

extreme mass values which make minor contributions to the overall nominal peak envelope.

3. If the peak pattern has less than five peaks with non-zero abundance values, failure will occur. Thus values for 2 or 3 atoms of a single di-isotopic element (see appended table) could not be calculated without a subscript overflow. These cases are trivial.

Requirements:

8192 configuration, with magnetic film backing store for translation if the Elliott library program A.304 (Elliott 8 hole Algol) is used. ISOCOMB-4 occupies 3737 locations.

Time:

1. Translation: using A.304 and backing store on the 803, 17 minutes 10 seconds.
2. Running: 10-14 seconds per combination, depending on the number of atoms and total number of combinations.

On the Chilton Atlas, calculation of the Ge_7 pattern (330 combinations) used 3099 Instruction Interrupts (approx. 20 seconds) and 40/113 blocks of store (execute/compile). Compilation required 2102 Instructions.

Failure:

For possible causes see notes 1 and 3 and the note on the Data Format.

Data Format:

```
£ title string, maximum 71 printable characters?

N

na[1]     ni[1]
na[2]     ni[2]
  :         :

M[1,1]    A[1,1]
M[1,2]    A[1,2]
  :         :

M[2,1]    A[2,1]
M[2,2]    A[2,2]
  :         :
```

N = number of different elements present (type integer)

na[1] = number of atoms of element 1 present (integer), and so on for element 2, etc.

ni[1] = number of isotopes of element 1, (integer).

M[1,1] = precise mass of isotope 1 of element 1 (real). Note that the "element" subscript increases more slowly, i.e. data should give all isotopes of element 1 first, then all isotopes of element 2, etc.

A[1,1] = Abundance of isotope 1 of element 1, subscripted as above (real). Conveniently, abundances for each isotope are punched normalised to the sum total for each element as 10 (i.e.ΣA(for element n)= 10). No scaling factors are incorporated in the program but no inaccuracy has been detected with abundance products up to 10^7.

Note:

*The number of combinations for a given number of atoms of a single element with a given number of isotopes is determined by the coefficients of Pascal's Triangle i.e. the binomial expansion, see table. The total number of combinations with several elements present is obtained from the product of the combinations for the separate elements. The limits set on the arrays IC, FM, FAP, MC, AP, and IFM, are 210 for ICL and 420 for FML, which are suitable for 2 x combinations for six atoms of a penta-isotopic element. A facility for altering these array limits to suit the particular problem is incorporated, being a "buffer" controlled read statement. Insertion of a ";" character immediately following the last digit of the last isotope number causes the next two numbers (integer) to be read as values for ICL (the maximum number of combinations for the largest number of atoms of the element with the largest number of isotopes present) and FML (total number of combinations). The values already present in the program should be adequate for most needs. However, note that a value of 330 for FML and ICL, i.e. for 7 atoms of a penta-isotopic element, produces "space overflow" on an 803 in 8192 configuration. No other character is necessary on the data tape, and if no ";" is present, the read instruction is ignored.

4.2.3. PEAK PATTERN

Language: Elliott 8 hole Algol.

Method: The straightforward method of correcting each peak of the basic hetero atom pattern (which is generated by ISOCOMB-4 and read in as data) in the manner of Beynon, is used, i.e. the ratio of the probabilities of occurrence of a peak at mass number m + 1 due to the presence of heavy isotopes of carbon, hydrogen, oxygen and nitrogen is given by

$$\frac{P_{m+1}}{P_m} = w\left[\frac{c}{100-c}\right] + x\left[\frac{h}{100-h}\right] + y\left[\frac{n}{100-n}\right] + z\left[\frac{o_1}{100-o_1-o_2}\right]$$

where w,x,y, and z are the numbers of carbon, hydrogen, nitrogen and oxygen atoms respectively in the ion and c,h,n,o_1 and o_2 the natural abundance (probability of occurrence) of C^{13}, H^2, N^{15}, O^{17} and O^{18}. Similarly for the m + 2 peak the ratio is

$$\begin{aligned}\frac{P_{m+2}}{P_m} = {} & z\left[\frac{o_2}{100-o_1-o_2}\right] + \frac{w(w-1)}{2} : \left[\frac{c}{100-c}\right]^2 + \frac{x(x-1)}{2} \cdot : \left[\frac{h}{100-h}\right]^2 + \\ & y\left[\frac{(y-1)}{2}\right]\cdot\left[\frac{n}{100-n}\right]^2 + \frac{z(z-1)}{2}\left[\frac{o_1}{100-o_1-o_2}\right] + wx.\left[\frac{c}{100-c}\right]\cdot\left[\frac{h}{100-h}\right] + \\ & wy\left[\frac{c}{100-c}\right]\cdot\left[\frac{n}{100-n}\right] + wz.\left[\frac{c}{100-c}\right]\cdot\left[\frac{o_1}{100-o_1-o_2}\right] + xy\left[\frac{h}{100-h}\right]\cdot\left[\frac{n}{100-n}\right] + \\ & xz.\left[\frac{h}{100-h}\right]\cdot\left[\frac{o_1}{100-o_1-o_2}\right] + yz\left[\frac{n}{100-n}\right]\cdot\left[\frac{o_1}{100-o_1-o_2}\right]\end{aligned}$$

This latter value is usually small (because of the square terms of quantities already of the order of 10^{-2}) except for ions with very large amounts of "organic" material. Although corrections may be applied by extension of the procedure to the m + 3 and higher peaks, the process is curtailed at this point (m + 2). Experimental justification for this under normal working conditions is adequate. Each ion pattern is normalised to the largest peak as 100 and the pictorial representation, i.e. line representing each nominal mass peak, is correct to ± 0.5, the length being the value of the abundance rounded

```
PEAK PATTERN ;

begin  real ORGM,CF1,CF2,HF1,HF2,NF1,NF2,OF1,OF2,OF21,CABN,NFC,massX,abcor1,abcor2;
       integer ab,cab,in,h,j,k,C,H,N,On,P,CM,noX,head,nobase,inn;
       array AB[1:50],mainmass[1:5],CAB[1:52];
       integer array title[1:15],elem[1:5],nm[1:50];
       switch  SS:= repeat,exit;

in:= 1;  instring(title,in);  in:= 1;

print ££l?Isotopic Abundance Patterns.£l2?Peak Patterns in Mass Spectra of ?,
      £Compounds containing ?;     outstring(title,in);     in:= 1;

read k;

for h:= 1 step 1 until k do  read  nm[h],  AB[h];
for h:= 1 step 1 until 5 do  read  mainmass[h];

wait;
read  nobase,  head;     if nobase = 1 then goto repeat;

print ££l3?Basic Heteroatom Pattern.£l2?Nominal£s6?Relative£ls?Mass£s8?Abundance?;
for h:= 1 step 1 until k do
   begin print ££ls??,sameline,digits(3),nm[h];  ab:= AB[h]; if AB[h] > ₁₀-5 then
          print sameline,££S7??,aligned(3,4),AB[h],££S12??;
          for j:= 1 step 1 until ab do elliott(7,4,64,0,7,4,126)
    end;

  if buffer(1,£;?) then goto exit ;

repeat:    wait;

     read  noX;   if noX ≠ 0 then begin inn:= 1;  instring(elem,inn); inn:= 1;
     read  massX   end;

     read C,H,N,On,P;

  print ££r10016?Basic Pattern ?; if head = 1 then begin print £(?; in:= 1;
   outstring(title,in);  print  £)?  end;
  print  £, corrected for light elements.£l2?Number of atoms present:-?;

   if C ≠ 0 then print £  C?,sameline,digits(2),C;
   if H ≠ 0 then print £  H?,sameline,digits(2),H;
   if N ≠ 0 then print £  N?,sameline,digits(2),N;
   if On ≠0 then print £  O?,sameline,digits(2),On;
   if P ≠ 0 then print £  P?,sameline,digits(2),P;
```

```
      if noX ≠ 0 then begin print ££s2??; outstring(elem,inn); print sameline,
       digits(2),noX   end;    print  ££12s?Nominal£s6?Relative£ls2?Mass£s8?Abundance?;

      CF1:= C*1.0806₁₀-2;      CF2:= (CF1*(C-1)*1.0806₁₀-2)/2;
      HF1:= H*1.6003₁₀-4;      HF2:= (HF1*(H-1)*1.6003₁₀-4)/2;
      NF1:= N*3.8145₁₀-3;      NF2:= (NF1*(N-1)*3.8145₁₀-3)/2;
      OF1:= On*3.9093₁₀-4;     OF2:= On*2.0048₁₀-3;     OF21:= (OF1*(On-1)*3.9093₁₀-4)/2;

      abcor1:= CF1+HF1+NF1+OF1;
      abcor2:= CF2+HF2+NF2+OF2+OF21+CF1*HF1+CF1*OF1+CF1*NF1+HF1*NF1+NF1*OF1+HF1*OF1;

      for h:= 1 step 1 until k+2 do CAB[h]:= 0;
      for h:= 1 step 1 until k do
      begin CAB[h]:= CAB[h]+AB[h];
            CAB[h+1]:= CAB[h+1]+AB[h]*abcor1;
            CAB[h+2]:= CAB[h+2]+AB[h]*abcor2
      end;

CABN:= 0;  for h:= 1 step 1 until k+2 do CABN:= if CAB[h] > CABN then CAB[h] else CABN;

CM:= C*12+N*14+On*16+H+P*31+nm[1]+noX*massX;
ORGM:= C*12+H*1.00782522+N*14.00307438+On*15.99491415+P*30.9737634+noX*massX;

for h:= 1 step 1 until k+2 do
    begin print ££ls??,sameline,digits(4),CM+h-1;  cab:= (CAB[h]/CABN)*100;
      if CAB[h] > ₁₀-5 then print ££s7??,sameline,aligned(3,4),(CAB[h]/CABN)*100,££S12??;
      for j:= 1 step 1 until cab do elliott(7,4,64,0,7,4,126)
    end;

print ££L2?Major heteroatom peak masses for this ion:-£s??;
  for h:= 1 step 1 until 5 do print sameline,aligned(4,5),mainmass[h]+ORGM,££S2??;
  print ££L2?Mass of organic residue:-?,sameline,aligned(4,5),ORGM;

   if not buffer(1,£;?) then goto repeat;

exit:

end of program  mod. 4;
```

to the nearest integer in units 2.1 mm. long. Masses of the "organic" elements are incorporated in the program on the scale C^{12} = 12 mass units exactly, and precise values for the five central peaks (or five peaks containing the most abundant ion), are calculated together with the mass of the "organic" portion which allows values other than those given to be obtained by simple addition. Provision is made for the presence of phosphprus (monoisotopic) and one other monoisotopic element (unspecified) in the ion. The relevant data, number of atoms, chemical symbol or name, and mass being read in by making use of a controlled read procedure (see Data Format). Thus the masses given for an ion correspond with a complete rather than partial formulation, by including atoms which make no contribution other than mass.

Various "buffer"- and variable-controlled read statements (detailed under Data Format and illustrated in the examples), allow (i) omission of the print out for the basic heteroatom pattern (the variable "nobase"), (ii) the inclusion, or otherwise, of the title string enclosed in parentheses, in each pattern heading (the variable "head"), and (iii) stopping after printing the basic pattern (buffer ";", after "head"). Entry to the calculation routine, for the same basic heteroatom pattern, recurs automatically after each set of data until a ";" is encountered.

Values for the relative abundances of C^{13}, H^{2}, N^{15}, O^{17} and O^{18} are taken from Beynon.

Requirements:

8192 word configuration for translation by Elliott library A.304, 4096 configuration is sufficient for running, PEAK PATTERN occupying 2474 locations. Note: the output is designed specifically for reproduction by Friden "Flexowriter" working in the Elliott 8 channel telecode. It must also have a carriage at least 134 characters (11.5") wide.

Time:

1. Translation: using A.304. 6 minutes 40 seconds.

2. Running: 1-2 minutes per pattern (20 peaks).

Data Format:

1. Data tape produced by ISOCOMB-4

£ title string: maximum 71 printable characters?

K

```
nm[1]     AB[1]
nm[2]     AB[2]
  :         :

mainmass[1]
    .
    .
    .
mainmass[5]
```

K = number of peaks in pattern (including "gaps"); (integer).

nm[1] = nominal mass 1,2--etc., (integer).

AB[1] = relative abundance of peak at nominal mass 1,2--. Normalised to largest as 100, (real).

mainmass[1] = precise mass value 1, - 2, etc. subject to restrictions mentioned, (real).

2. Further data required

nobase head *

noX **

C H N O P *

noX **

C H N O P *

:

nobase, head; are control variables which must have the value 0 or 1.

nobase = 0 causes the basic heteroatom pattern to be printed

nobase = 1 causes this printing to be omitted.

head = 0 omits heading (title string, in parentheses) from each subsequent pattern.

head = 1 prints this heading.

noX = number of atoms of additional monoisotopic element present. This value must be zero with the format presented above (see **).

C, H, N, O, P = number of atoms of carbon, hydrogen, nitrogen, oxygen and phosphorus present. A value for each of these must be present on tape.

All the above identifiers are of type integer.

*The character ";" inserted here (immediately after the last digit) causes the program to stop.

** For values other than 0, the following data immediately are required:

£ element name or symbol, max. 21 characters?

massX

massX = precise mass of monoisotopic element introduced (real).

Note: A "data wait" occurs after reading in the first portion of the data and on each entry into the calculation routine for each ion produced.

4.2.4. MASS TABLE

Language: KDF9 Algol

Method: Precise mass values for formulae corresponding to a particular nominal mass are obtained by a cyclic process which sets up all possible combinations for the elements C, Ge, N and O, within certain careful controlled composition limits. If the exact mass of a chemically possible formulation falls between the integral mass under consideration and the next integral mass, the theoretical abundance values for the m - 3, m - 2, m - 1, m + 1, and m + 2 peaks of this ion set are calculated and, together with formula, and decimal part of the exact mass, are stored prior to sorting. Print out occurs, after sorting, at the end of the process for the particular mass unit interval, and is arranged to give blocks of 55 lines (approximately quarto size) and to include any necessary repetition of headings.

The for statements of lines 28, 35-37, set up the values of the element numbers (C, Ge, N, and O), the limit for the carbon number being found by the calculation of lines 33 and 34. A lower value of 1, an upper value of nine per free germanium valence (i.e. assuming polygermanes to have -Ge-Ge- links rather than Ge-C-Ge) or an intermediate limit equivalent to the number of carbon atoms making up the whole of the remainder of the mass after subtraction of the germanium mass, are all possible, the smallest appropriate value being chosen. Numbers of hydrogen atoms present are calculated by either line 41 or 42. Two possibilities must be considered, because of the rounding real to integer conversion and the large mass defect of the metal isotope; the rounding conversion can give rise to a formula with one hydrogen too few and lead to the loss of a valid possibility from the table, unless the "entier" value (line 42) is used to check an element number set if no possibility is found from the "rounding" routine for hydrogen number. If a formula fulfills the constitutional requirements of line 43, and its mass is within the range of one mass unit considered at that time the abundance calculation of lines 46-56 is entered. Note that line 43 merely requires that the formula must be possible from the normal valence requirements and that ions containing little or no hydrogen are not excluded. The correction factors employed in the abundance calculation are set up at the head of the program to obviate unnecessary recalculation, and for a single atom of a heavy isotope (i.e. for corrections to the p + 1 peak) are stored in the arrays Cf1, HF1, NF1, and OF1, for each organic element, respectively, Simiarly the arrays CF2, HF2, NF2, and OF21, hold the corrections for p + 2 peak from two atoms of a single heavy isotope. Oxygen, with two heavy isotopes also has the array OF2 which stores corrections to the p + 2 peak from a single atom of O^{18}. The required factor corresponding to the number of atoms of each organic element present is selected from these arrays, and the new values for the germanium isotope pattern peaks are re-normalised to the largest, i.e. that corresponding to the nominal mass being considered, as 100. The two dimensional integer array "stack" hold the formulae which are indexed by element and formula number, and the similar real array "store", holds the decimal portion of the exact mass (in store [1]) and the abundances of peaks m-3 to m+2 (in store [2-6]), the second subscript again being formula number. Sorting of these eleven arrays into order corresponding to that of increasing mass is achieved by a relative indexing method, using the auxiliary array "sort", and the familar sort-by-exchange routine of lines. Only the vector containing the mass values is actually sorted, together with the row index vector sort [2]. On exit from the routine this contains the final values of the formula number indices required to keep each row vector of the storage matrix (the ten arrays other than store [1]) with the correct value of the mass. The <u>for</u> ststament controlled <u>print</u> routine outputs the results in tabular form (with the aid of the index vector) and also prints the column headings and maintains the 55 line block format. The whole of the program forms

```
Mass Table ;

begin library A0,A6;
      integer a,b,h,j,k,n,C,F1,F2,F3,F4,G,Ge,H,M,N,On,count,lim,Clim;
      real ABN,mass,mGe,CF1,CF2,HF1,HF2,NF1,NF2,OF1,OF2,OF21;
      integer array nab[1:4],stack[1:5,1:400];
      real array AB[1:14],abGe[1:4,1:10],sort[1:2,1:400],store[1:6,1:400]
         CF1,CF2[0:50],HF1,HF2[0:99],NF1,NF2[0:4],OF1,OF2,OF21[0:6];

            open(20);    open(30);

        a:= read(20);    b:= read(20);

        for h:= 1 step 1 until 4 do nab[h]:= read(20);
        for h:= 1 step 1 until 4 do
              for j:= 1 step 1 until nab[h] do abGe[h,j]:= read(20);

      close(20);    count:= 0;

      F1:= format([ssnd]);
      F2:= format([4sd.dddddd]);
      F3:= format([ssnnd.ddd]);
      F4:= format([sndd]);

      for h:= 0 step 1 until 50 do
        begin CF1[h]:=h*1.0806₁₀-2; CF2[h]:=(CF1[h]*(h-1)*1.0806₁₀-2)/2; end;
      for h:= 0 step 1 until 99 do
        begin HF1[h]:=h*1.6003₁₀-4; HF2[h]:=(HF1[h]*(h-1)*1.6003₁₀-2)/2; end;
      for h:= 0 step 1 until 4 do
        begin NF1[h]:=h*3.8145₁₀-3; NF2[h]:=(NF1[h]*(h-1)*3.8145₁₀-3)/2; end;
      for h:= 0 step 1 until 6 do
        begin OF1[h]:=h*3.9093₁₀-4; OF2[h]:=h*2.0048₁₀-3;
          OF21[h]:=(OF1[h]*(h-1)*3.9093₁₀-4)/2;   end;

for M:= a step 1 until b do
    begin count:= count+3;    n:= 0;
  if count < 51 then goto S1 else goto S2;

  S1:    write text(30,[[3cs]MASS***]);  write(30,F4,M);  goto S3;

  S2:    count:= 3;  write text(30,[[p]]);  goto S1;

  S3:   for Ge:= 1 step 1 until 4 do
           begin if Ge=1 then mGe:=  73.921150 else
                 if Ge=2 then mGe:= 145.843356 else
                 if Ge=3 then mGe:= 217.765914 else
                 if Ge=4 then mGe:= 290;

           lim:= (M-mGe)/12;  if lim < 1 then lim:= 1;
           Clim:= if lim < 18*Ge+18 then lim else 18*Ge+18;
```

```
          for C:= 0 step 1 until Clim do
            for On:= 0 step 1 until 6 do
              for N:= 0 step 1 until 4 do
         begin
            if Ge=4 and C < 15 then mGe:= 289.688432 else
            if Ge=4 and C ≥ 15 then mGe:= 291.687278;

            H:= M-C*12-N*14-On*16-mGe; G:= 1; goto S10;

 S9:        H:= M-C*12-N*14-On*16-entier(mGe); G:= 0;

 S10:       mass:= mGe+C*12+H*1.00782522+N*14.00307438+On*15.99491494;
       if mass < M+1 and mass ≥ M and H ≤ 2*C+2*Ge+N+2 and H ≥ 0 then goto S4
       else if G=1 then goto S9 else goto S5;

 S4:     n:= n+1;  for h:= 1 step 1 until nab[Ge]+2 do AB[h]:= 0;
         for h:= 1 step 1 until nab[Ge] do
         begin AB[h]:= AB[h]+abGe[Ge,h];
               AB[h+1]:= AB[h+1]+abGe[Ge,h]*(CF1[C]+HF1[H]+NF1[N]+OF1[On]);
               AB[h+2]:= AB[h+2]+abGe[Ge,h]*(CF2[C]+HF2[H]+NF2[N]+OF21[On]+
         OF2[On]+CF1[C]*HF1[H] CF1[C]*OF1[On]+CF1[C]*NF1[N]+HF1[H]*OF1[On]+
         HF1[H]*NF1[N]+NF1[N]*OF1[On];    end;

ABN:=0; for h:=1 step 1 until nab[Ge]+2 do
begin if AB[h] > ABN then begin ABN:= AB[h]; k:= h; end end;

stack[1,n]:= C; stack[2,n]:= H; stack[3,n]:= Ge;
stack[4,n]:= N; stack[5,n]:= On; store[1,n]:= mass-M;
store[2,n]:= (AB[k-3]/ABN)*100;
store[3,n]:= (AB[k-2]/ABN)*100;
store[4,n]:= (AB[k-1]/ABN)*100
store[5,n]:= (AB[k+1]/ABN)*100;
store[6,n]:= (AB[k+2]/ABN)*100;

if G=1 then goto S9;

S5:    end
    end;

if n=0 then goto S12 else if n=1 then begin
write text(30,[[c3s]C***H**Ge***N***O[6s]MASS[6s]M-3[6s]M-2[6s]M-1[6S]M+1[6s]M+2[c]]);
for h:= 1 step 1 until 5 do write(30,F1,stack[h,1]);
write(30,F2,store[1,1]);
for h:= 2 step 1 until 6 do write(30,F3,store[h,1]);
count:= count+2;
end;

if n=1 then goto S12;

for h:=1 step 1 until n do sort[1,h]:= store[1,h];
for h:= 1 step 1 until n do sort[2,h]:= h;
```

```
begin integer p,q;
    real inter;
    boolean anychange;
    for q:= 1,q+1 while anychange do
      begin anychange:= false;
          for p:= 1 step 1 until n-1 do
          if sort[1,p+1] < sort[1,p] then
           begin inter:= sort[1,p+1];
                 sort[1,p+1]:= sort[1,p];
                 sort[1,p]:=  inter;
                 inter:= sort[2,p+1];
                 sort[2,p+1]:= sort[2,p];
                 sort[2,p]:= inter;
                 anychange:= true;
           end
      end
end;

for h:= 1 step 1 until n do
begin  if h=1 then goto S6 else goto S7;
S6:
write text(30,[[c3s]C***H**Ge***N***O[6s]MASS[6s]M-3[6s]M-2[6S]M-1[6s]M+1[6s]M+2[c]]);

count:=count+1;

S7:       write text(30,[[c]]);
          for j:= 1 step 1 until 5 do write(30,F1,stack[j,sort[2,h]]);
         write(30,F2,store[1,sort[2,h]]);
         for j:= 2 step 1 until 6 do write(30,F3,store[j,sort[2,h]]);
         count:= count+1;
         if count=55 then goto S8 else goto S13;

S8:     write text(30,[[p3c]*Mass***]);
        write(30,F4,M);
        write text(30,[[3s]continued]);
       h:= h+1; count:= 3; goto S6;

S13:    end;

S12:    end;

       close(30);

end
```

the scope of a *for* statement which steps the value of the nominal mass, the upper and lower limits of which are read as data. Provision is made for those cases in which the 292 peak of the Ge_4 pattern becomes larger than that at 290, i.e. for formulations with $C > 15$. In these instances, renormalisation to the corrected 292 metal peak occurs. Correction factors for up to and including 50 carbon, 99 hydrogen, 4 nitrogen and 6 oxygen atoms are stored.

Time:

For binary program from magnetic tape after usual Walgol/Kalgol translation, compilation and establishment, 200 mins. 27 secs., to cover mass range 74-400 in three runs.

Data Format:

a b

nab[1]

nab[4]

abGe[1,1]
abGe[1,2]

abGe[2,1]
abGe[2,2]

a = lower (inclusive) mass limit (*type integer*)

b = upper (inclusive) mass limit (*integer*)

nab[1] = number of peaks (abundances) of first metallic unit (here Ge) considered, then for Ge_2, Ge_3, Ge_4 (*integer*)

abGe[1,1] = abundance of peak 1 for metallic unit 1 etc. element subscript (first) increases more slowly (*real*)

```
Formulator ;

begin integer  V,X,IM,E,h,j,in,noX,UC,UH,UN,UOn,C,H,N,On,C1,H1,HH,CC;
     real AE,massX,PM,inter,interH,dev;
     real array I[1:4],M[0:4,0:40];
     integer array title[1:15],elem[1:5];
     switch SS:= S1,S2,S3,exit;

   in:= 1;   instring(title,in);   in:= 1;
   read E;   for h:= 1 step 1 until E do read I[h];
   read AE;   if buffer(1,£;?) then begin instring(elem,in);  in:= 1;
              read noX, massX, V end else begin noX:= V:= 0; massX:= 0 end;
   read UC, UH, UN, UOn;
   for h:= 1 step 1 until E do for j:= 0 step 1 until I[h] do read M[h,j];

   print ££L?Possible mass fomulations.£l?Ions in spectrum of ?;
   outstring(title,in);  in:= 1;  print ££l2?Allowed error  ±?,sameline,
   freepoint(2),AE,£p.p.m.?;  if noX ≠ 0 then begin print ££s3?X = ?;
   outstring(elem,in) end;       M[0,0]:= 0;

 S1:  read PM;   h:= j:= 0;
      print ££L4S2?Ion Mass£s4?metal£S5?C  C*£S4?H  H*£s3?N£S3?O?;
      if noX ≠ 0 then print ££S3?X?; print ££S3?calc. mass   dev?,aligned(3,6),
       PM;   goto S2;

 S3:     for h:= 1 step 1 until E do
          for j:= 1 step 1 until I[h] do
        begin if PM < M[h,j] then goto exit;
 S2:       for C:= 0 step 1 until UC do
            for N:= 0 step 1 until UN do
             for On:= 0 step 1 until UOn do
              for C1:= 0 step 1 until 1 do
               for H1:= 0 step 1 until 1 do
                for X:= 0 step 1 until noX do

   begin  inter:= PM- M[h,j] - C*12 - C1*13.0033543 - H1*2.01410219 - N*14.00307438
                  - On*15.99491415 - X*massX;

     H:= inter;   HH:= H+H1;   CC:= C+C1;   IM:= M[h,j];
   if HH ≤ UH and H ≥ 0 and HH ≤ 2*CC+M[h,0]+N+V+2 then
    begin   interH:= inter - H*1.00782522;
            dev:= (interH/PM)*₁₀6;
        if abs(dev) ≤ AE then
     begin if  IM = 0 then print ££LS16?HC? else print ££LS14??,
       sameline,digits(3),IM;
       print sameline,digits(2),££s4??,C,££S2??,digits(1),C1,££s2??,digits(2),
         H,££s2??,digits(1),H1,££s2??,N,££s2??,On;
       if X ≠ 0 then print sameline,££s2??,digits(1),X;
       print ££s2??,sameline,aligned(3,6),PM-interH,££s2??,freepoint(2),dev;
     end;
    end;
   end;
  exit:   if h=0 then goto S3;
 end;    if not buffer(1,£;?) then goto S1;

end of program;
```

4.2.5. FORMULATOR

Language: Elliott 8-hole Algol

Method: A simple cyclic routine is used to set up all chemically possible combinations of the atoms of the elements present in the compound under investigation. Each experimental mass is considered individually and is read at the beginning of the program. The nested for statements of lines 20-20 set up the numbers of C, N, O, C^{13} and D atoms between the limits read as data and 0 for the major isotopes and 0 and 1 for the heavy isotopes. Line 28 allows the inclusion of one other polyisotopic element e.g. fluorine or phosphorus in the formulation, and the switched statements of lines 20-21 pick out each metal isotope peak considered in turn. Up to four sets of up to 40 peaks are allowed, and provision is made for those cases in which the experimental mass does not contain a metal (e.g. C_6H_5-C_6H_5 or PPh_3). The hydrogen content corresponding to a particular combination of the "hetero" and "organic" atoms required to make up the experimental mass is determined in lines 29-31 and chemically impossible formulae are rejected in line 32. Experimental and calculated masses are compared in lines 33-35 and if the difference between the two (deviation, observed-calculated mass) is less than or equal to the allowed error the formulation together with the calculated mass and deviation is output in tabular form by the statements of lines 36-41. Reentry of the formulation loops occurs until the for statements are exhausted whereupon another experimental mass is read and reentry of the main body of the program occurs. A ";" character after mass value stops the program.

The routine is recommended only for those cases requiring absolutely complete coverage of all possible formulations since it is rather uneconomical, all these possibilities being calculated for each mass considered. This is remedied in the extended formulator routine of FORMGROUP.

Requirements

8192 word configuration for translation, 4096 configuration is sufficient for running. FORMULATOR occupies

Time:

Translation: (using A.304)

Running: about 20 minutes per experimental mass for the limits C = 14, H = 20, O = 3, X = N = 0

Data Format:

```
£ title, maximum 71 characters?

E

I[1]


AE

UC   UH   UN   UOn

M[1,1]
M[1,2]


M[2,1]
M[2,2]



PM
.
.
PM';
```

E = number of polyisotopic aggregates (metallic units) maximum 4 (type integer)

I[1] = number of peaks of polyisotopic unit 1,2 .... (integer)

AE = allowed error, p.p.m. (real)

UC, UH, UN, UOn = upper limits of numbers of carbon, hydrogen, nitrogen and oxygen considered (conveniently the molecular formula of the compound in whose spectrum the peaks appear, or some lower values, integer)

M[1,1] = exact mass of peak 1 of polyisotopic unit 1, etc. Element subscript (first) increases more slowly (real).

PM --- PM' = experimental masses, terminated by ";" (real)

Additional data for optional extra monoisotopic element are inserted here after a ";" character (immediately after the last digit of AE). Data required:

£ element name?

noX massX V

noX = maximum number of atoms of element required (integer)

massX = exact mass of element (real)

V = valence in excess of 2 (negative values included, i.e. for fluorine, V = -1 (integer)

4.2.6. FORM GROUP

Language: Elliott 8-hole Algol. Primarily for Atlas implementation

Method: The main working section is a "formulator" routine similar to that just described, with the addition of a loop for the element phosphorus in the main for statement set and an increase in the upper limit of the number of C^{13} atoms (to 2). All the experimental masses are read in at the beginning of the routine, with the proviso that the smallest is read first and the largest last, and as each chemically possible formulation lying in this range is found all the experimental masses are checked against it. Valid formulations are stored in a manner similar to that employed in MASS TABLE

INDEX NUMBERS of groups

Index (GT[2,h])	Name or abbreviation, as output	Chemical Formula
1	cp	C_5H_5
2	Ph	C_6H_5
3	Bzn	C_6H_6
4	Phy	C_6H_4
5	BT	C_7H_7
6	Me	CH_3
7	Et	C_2H_5
8	Ety	C_2H_3
9	Pr	C_3H_7
10	Al	C_3H_6
11	Pry	C_3H_5
12	Bu	C_4H_9
13	CO	
14	O	
15	OO	
16	H	
17	NN	
18	N	
19	NH	
20	NHH	
21	HCO	
	My	CH_2
	Etl	C_2H_4
	Act	C_2H
	MAl	C_4H_8
	Buy	C_4H_7
	cpy	C_5H_4

After completion of the formulation, the formula store matrix is sorted by relative indexing into order of increasing experimental mass using the auxillary row vector "sort[j]", and are output with the aid of this indexing vector in a format similar to that described for FORMULATOR. The grouping routine is entered after each formula is printed.

This routine consists of two procedures. The first "name", stores and prints the chemical symbols or abbreviations for the structural groups considered, and is a simple switch controlled series of print statements. "name" must be declared and evaluated before "group".

The procedure "group" deals with the translation of the empirical formula presented to it as its actual parameters (values for numbers of C,H,N and O atoms) into the structural units present in the original compound, or known breakdown fragments of these units. The basic logic is a multi-stage switched addition and subtraction routine, working on a "snakes and ladders" principal A steering vector, flo[q], is set up prior to entry of the procedure (line and this holds the index numbers of the structural units present in the compound considered, e.g. for $\pi C_5H_5(CO)_3MoGeEt_3$ values of flo[q] would be 1,($\equiv C_5H_5$), 7($\equiv C_2H_5$),7,13($\equiv$ CO),13,13. (a number must be present for each group considered - see appended table. The vector is conveniently ordered in terms of decreasing carbon number but not necessarily so). The for statements which control the main body of the procedure select values from this array in turn (in a cyclic fashion, as every unit must be considered as a leading set) and the formula corresponding to this unit is then subtracted, in the statement labelled "forward" from the current values of cc, hh, nn, and oo (the working storage of the CHN and O values, the original figures are preserved in CC, HH, NN and OO for use on further cycles). The main decision

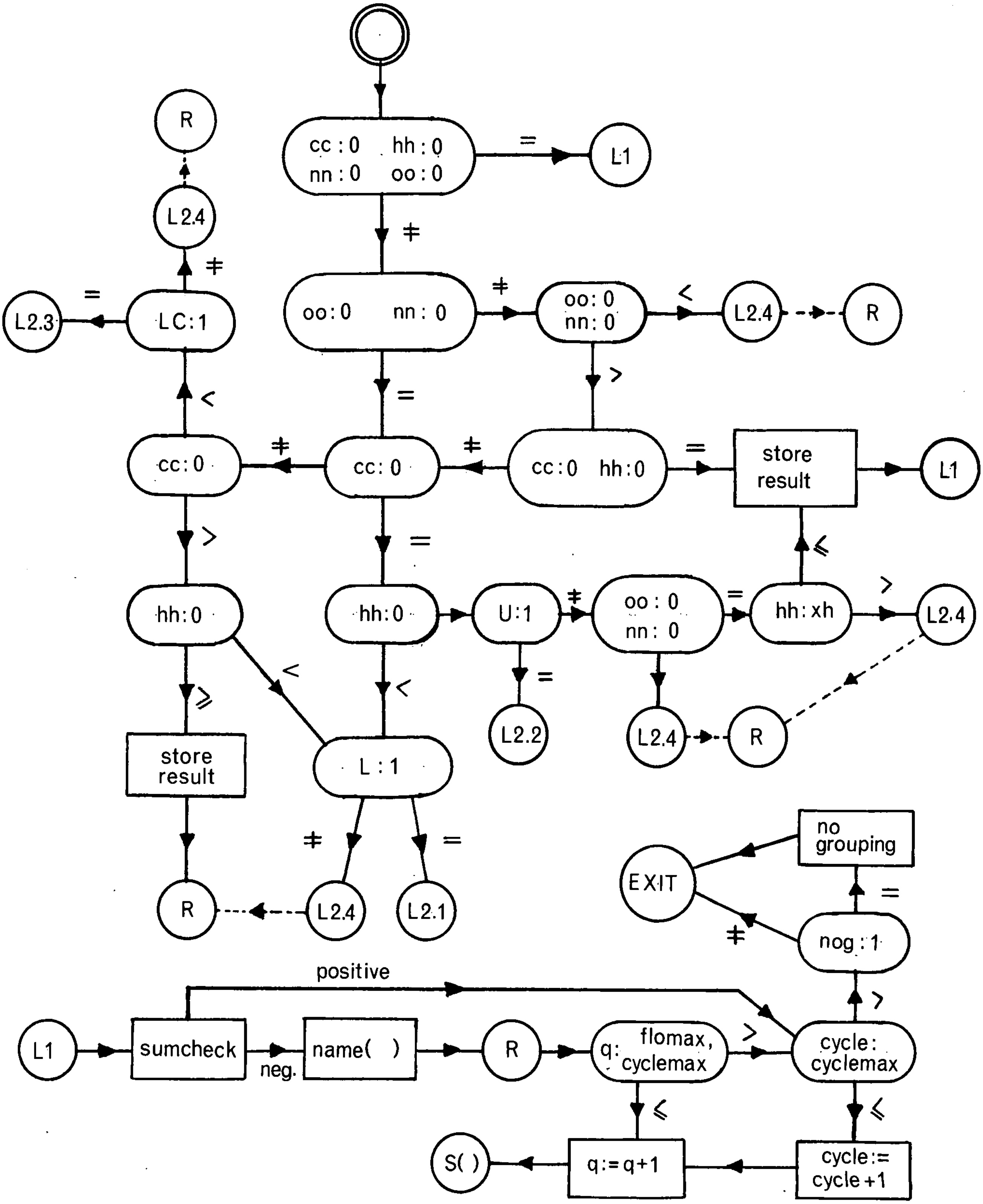


Fig. 4.1 FORMGROUP subroutine decision loop logic.

loop (see flow chart, opposite) is then entered, and depending on the values of the element numbers, either the subtraction routine is continued, using the next group selected from the "flo" vector or if any element number is negative, the "backward" loop is entered followed by the appropriate inner or outer loop (from the switch bank "move") depending on the fragmentation characteristics of the unit considered. These are described by the steering variables L,LC, and U. The grouping routine is regarded as successful when values of 0 are found for all the elements and the "check" loop is then entered. If the grouping has not been found previously (the cyclic process can give duplicates) it is then output using the procedure "name". Reentry occurs until all the structural units have been considered, and if no grouping is found, a message to this effect is output.

The formula data for 27 structural groups are stored in the labelled statements of lines 49 – 77, as assigments of the integers c1, h1,n1 and o1, and in addition five steering variables are also assigned. The integer n holds values of the actual parameter of the procedure "name" (which corresponds to the symbol of each unit) and the identifiers L, LC, and U (which have values 0 or 1) signify the type of fragmentation path which can be followed. L=1 indicates that a route involving fewer hydrogen atoms (for the same or a similar number of carbon atoms) is available, LC=1 that a path with fewer carbon atoms is open, and U=1 that a route with more hydrogen atoms may be taken. For example the C_2H_5 unit which can fragment by loss of CH_3 or C_2H_4 (to a group with fewer carbon atoms) or loss of hydrogen atoms has both L and LC = 1 (switch unit S7)

In statements labelled D4, provision is made for the presence of "extra"

```
Formgroup ;

begin integer C,H,N,On,P,UC,UH,UN,UOn,UP,C1,H1,V,noX,X,E,G,NG,GF,TM,R,in,flomax,HL,
              h,j,p,r,s,lm,hm;
     real intermass,massX,AE,dev;
     integer array stack[1:9,1:400],GT[1:2,1:25],sort[1:400],flo[1:25],
                   elem[1:5],title[1:50];
     real array store[1:3,1:400],I[1:6],M[0:6,0:40],PM[1:50];
     switch SS:= SS1,SS2,SS3,SS4,SS5,SS6;

  procedure name(GN);
     value GN;  integer GN;
   begin switch P:= P1,P2,P3,P4,P5,P6,P7,P8,P9,P10,P11,P12,P13,P14,P15,P16,P17,
                    P18,P19,P20,P21,P22,P23,P24,P25,P26,P27,EE;
    goto P[GN];

  P1: print £cp ?; goto EE; P2: print £cpy ?; goto EE; P3: print £Bzn ?; goto EE;
  P4: print £Ph ?; goto EE; P5: print £Phy ?; goto EE; P6: print £BT ?; goto EE;
  P7: print £Me ?; goto EE; P8: print £My ?; goto EE; P9: print £Et ?; goto EE;
  P10: print £Etl ?; goto EE; P11: print £Ety ?; goto EE; P12: print £Act ?; goto EE;
  P13: print £Pr ?; goto EE; P14: print £Al ?; goto EE; P15: print £Pry ?; goto EE;
  P16: print £Bu ?; goto EE; P17: print £MAl ?; goto EE; P18: print £Buy ?; goto EE;
  P19: print £CO ?; goto EE; P20: print £HCO ?; goto EE; P21: print £H ?; goto EE;
  P22: print £OO ?; goto EE; P23: print £O ?; goto EE; P24: print £NHH ?; goto EE;
  P25: print £NH ?; goto EE; P26: print £N ?; goto EE; P27: print £NN ?; goto EE;
  EE:
   end name;

  procedure group(CC,HH,NN,OO);
    value CC,HH,NN,OO;  integer CC,HH,NN,OO;
    begin integer cc,hh,nn,oo,Q,q,n,L,U,LC,c1,h1,n1,o1,eh,t,way,ment,sum,nog,
                  cycle,count;
          integer array hold,SCS[1:25],CS[1:27];
          switch S:= S1,S2,S3,S4,S5,S6,S7,S8,S9,S10,S11,S12,S13,S14,S15,S16,
                      S17,S18,S19,S20,S21;
          switch SL:= SL1,SL2,SL3,SL4,SL5,SL6,SL7,SL8,SL9,SL10,SL11,SL12;
          switch SU:= SU1,SU2,SU3,SU4,SU5;
          switch SC:= SC1,SC2,SC3,SC4,SC5,SC6;
          switch SD:= D1,D2,D3,D4,decide,forward,backward,out,check;
          switch move:= inn,inup,down,next;


   CS[1]:= 101; CS[2]:= 102; CS[3]:= 103; CS[4]:= 104; CS[5]:= 105; CS[6]:= 106;
   CS[7]:= 2001; CS[8]:= 2002; CS[9]:= 2003; CS[10]:= 2004; CS[11]:= 2005;
   CS[12]:= 2006; CS[13]:= 2007; CS[14]:= 2008; CS[15]:= 2009; CS[16]:= 2010;
   CS[17]:= 2011; CS[18]:= 2012; CS[19]:= 30001; CS[20]:= 30002; CS[21]:= 30003;
   CS[22]:= 30004; CS[23]:= 30005; CS[24]:= 30006; CS[25]:= 30007; CS[26]:= 30008;
   CS[27]:= 30009;

          nog:= 1;
   for cycle:= 1 step 1 until flomax do
    begin   cc:= CC; hh:= HH; nn:= NN; oo:= OO;   count:= r:= 0;
     for q:= cycle step 1 until flomax, 1 step 1 until cycle-1 do
      begin
```

```
        goto S[flo[q]];

 S1:  c1:= 5; h1:= 5; n1:= o1:= 0; L:= Q:= n:= 1; LC:= U:= 0; goto forward;
SC1: ;SU1: ;SL3: ;
 S2:  c1:=6; h1:=5; n1:= o1:= 0; L:=1; U:=1; LC:=0; Q:=2; n:=4; goto forward;
SU2: ;S3:  c1:=6; h1:=6; n1:= o1:= 0; L:=1; U:=0; LC:=0; Q:=3; n:=3; goto forward;
SL2: ;S4: c1:=6; h1:=4; n1:= o1:= 0; L:=0; U:=1; Q:=1; LC:=0; n:=5; goto forward;
 S5:  c1:=7; h1:=7; n1:= o1:= 0; L:= U:= 0; LC:= Q:= 1; n:=6; goto forward;
SC4: ;S6: c1:=1; h1:=3; n1:= o1:= 0; L:=1; U:= LC:= 0; Q:=7; n:=7; goto forward;
SC5: ;S7: c1:=2; h1:=5; n1:= o1:= 0; L:=1; U:=0; LC:=1; Q:=4; n:=9; goto forward;
SL11: ;S8: c1:=2; h1:=3; n1:=o1:=0; L:=1; U:= LC:= 0; Q:=8; n:=11; goto forward;
SC6: ;S9: c1:=3; h1:=7; n1:=o1:=0; L:=1; U:=0; LC:=1; Q:=5; n:=13; goto forward;
SL5: ;S10: c1:=3; h1:=6; n1:=o1:=0; L:=1; U:=LC:=0; Q:=9; n:=14; goto forward;
SL9: ;S11: c1:=3; h1:=5; n1:=o1:=0; L:=U:=LC:=Q:= 0; n:= 15; goto forward;
 S12: c1:=4; h1:=9; n1:= o1:= 0; L:=1; U:=0; LC:=1; Q:=6; n:=16; goto forward;
SL10: ;S13: c1:=1; h1:= n1:= 0; o1:=1; L:=0; U:=1; LC:=0; Q:=3; n:=19; goto forward;
 S14: c1:= h1:= n1:= 0; o1:=1; L:= U:= LC:= Q:=0; n:=23; goto forward;
 S15: c1:= h1:=n1:=0; o1:=2; L:= U:= LC:= Q:=0; n:=22; goto forward;
 S16: c1:=0; h1:=1; n1:= o1:=0; L:= U:= LC:= Q:=0; n:=21; goto forward;
 S17: c1:= h1:=0; n1:=2; o1:=0; L:= U:= LC:=Q:= 0; n:=27; goto forward;
 S18: c1:= h1:=0; n1:=1; o1:= 0; L:= 0; U:=1; LC:=0; Q:=4; n:=26; goto forward;
SU4: ;S19: c1:=0; h1:= n1:= 1; o1:=0; L:=0; U:=1; LC:=0; Q:=5; n:=25; goto forward;
SU5: ;S20: c1:=0; h1:=2; n1:=1; o1:=0; L:= U:= LC:= Q:=0; n:= 24; goto forward;
SU3: ;S21: c1:=1; h1:=1; n1:=0; o1:=1; L:=1; U:=LC:=0; Q:=10; n:=20; goto forward;
 SL1: c1:=5; h1:=4; n1:= o1:= 0; L:= U:= LC:= Q:=0; n:=2; goto forward;
 SL4: c1:=2; h1:=4; n1:= o1:=0; L:=1; U:= LC:=0; Q:=11; n:=10; goto forward;
 SL6: c1:=4; h1:=8; n1:= o1:=0; L:=1; U:= LC:=0; Q:=12; n:=17; goto forward;
 SL7: c1:=1; h1:=2; n1:= o1:=0; L:= U:= LC:= Q:= 0; n:=8; goto forward;
 SL8: c1:=2; h1:=1; n1:= o1:=0; L:= U:= LC:= Q:= 0; n:=12; goto forward;
 SL12: c1:=4; h1:=7; n1:= o1:=0; L:= U:= LC:= Q:=0; n:=18;
SC2: ;SC3: ; comment labels not used ;

 forward: count:= count+1; cc:= cc-c1; hh:= hh-h1; nn:= nn-n1; oo:= oo-o1;
          hold[count]:= n;   goto decide;

 backward: cc:= cc+c1; hh:= hh+h1; nn:= nn+n1; oo:= oo+o1;
           count:= count-1;   goto move[ment];

   inn: goto SL[Q];  inup: goto SU[Q];  down: goto SC[Q];

  decide: if cc=0 and hh=0 and nn=0 and oo=0 then goto check else
          if oo=0 and nn=0 then goto D1 else if oo<0 or nn<0 then
          begin ment:=4; goto backward; end else goto D2;

  D1: if cc=0 then begin if hh<0 then goto D3 else goto D4; end else
      if cc<0 then begin if LC=1 then begin ment:=3; goto backward; end else
      begin ment:=4; goto backward; end; end else begin if hh<0 then
      goto D3 else goto next; end;

  D2: if cc=0 and hh=0 then goto next else goto D1;

  D3: if L=1 then begin ment:=1; goto backward; end else begin ment:=4;
      goto backward; end;

  D4: if U=1 then begin ment:=2; goto backward; end else begin if hh ≤ 4 then
```

```
     begin r:=1; eh:= hh; hh:= 0; end else goto out; if oo=0 and nn=0 then goto check
     else goto next; end;

  check: sum:= 0; for t:= 1 step 1 until count do sum:= sum+CS[hold[t]];
         SCS[cycle]:= sum;  for t:= 1 step 1 until cycle-1 do
         if sum=SCS[t] then goto out; if r=1 then print ££1s68??,sameline,
         digits(1),eh,£H ? else print ££1s69??; for t:= 1 step 1 until count
         do name(hold[t]);  nog:= 0;  goto out;

  next:  end;

  out:  end;  if nog=1 then print ££1s69?no grouping?;

 end group;

    in:= 1;  instring(title,in);  in:= 1;  GF:= G:= 0;
    read E;  for h:= 1 step 1 until E do read I[h];
    for h:= 1 step 1 until E do for j:= 0 step 1 until I[h] do read M[h,j];
    read AE; if buffer(1,£;?) then begin instring(elem,in); in:=1; read noX,
            massX, V, GF; end else begin noX:= V:= GF:= 0; massX:= 0; end;
    read UC,UH,UN,UOn,UP;
    if not buffer(1,£;?) then begin G:= 1; read NG; for h:= 1 step 1 until
       NG do read GT[1,h], GT[2,h]; end;
    for h:= 1,h+1 while not buffer(1,£;?) do begin read PM[h]; TM:= h; end;

   p:= 0; for h:= 1 step 1 until NG do for j:= 1 step 1 until GT[1,h] do
   begin p:= p+1;  flo[p]:= GT[2,h]; end;   flomax:= p;
   lm:= entier(PM[1]);   hm:= PM[TM]+1;

  print ££1?Possible mass formulations.£1?Ions in spectrum of ?;
  outstring(title,in); in:= 1; print ££12?Allowed error, ±?,sameline,freepoint(2),
  AE,£ p.p.m.?; if noX≠0 then begin print ££s5?X= ?; outstring(elem,in); end;
  if GF=1 and G=1 then print ££12?** N.B. In grouping routine,flourine and hydrogen?,
  £ considered as one element?;

  M[0,0]:= 0;  R:= h:= j:= 0;  goto SS3;
 SS2:  for h:= 1 step 1 until E do
        for j:= 1 step 1 until I[h] do
 begin SS3: for C:= 0 step 1 until UC do
   for N:= 0 step 1 until UN do
    for On:= 0 step 1 until UOn do
     for X:= 0 step1 until noX do
      for P:= 0 step 1 until UP do
       for C1:= 0 step 1 until 2 do
        for H1:= 0 step 1 until 1 do
   begin  HL:= 2*(C+C1)+M[h,0]+N+P+X*V+2-H1;  HL:= if HL<UH then HL else UH;
         for H:= 0 step 1 until HL do
    begin  intermass:= M[h,j]+C*12+C1*13.0033543+H1*2.01410219+N*14.00307438
             +On*15.99491415+H*1.00782522+P*30.9737634+X*massX;
     if intermass ≥ lm and intermass ≤ hm then begin
     for r:= 1 step 1 until TM do
      begin dev:= ((PM[r]-intermass)/PM[r])*₁₀6;
        if abs(dev) ≤ AE then
       begin  R:= R+1;
```

```
   store[1,R]:= PM[r]; store[2,R]:= intermass; store[3,R]:= dev;
   stack[1,R]:= M[h,j]; stack[2,R]:= C; stack[3,R]:= C1;
   stack[4,R]:= H; stack[5,R]:= H1; stack[6,R]:= N;
   stack[7,R]:= On; stack[8,R]:= X; stack[9,R]:= P;
   sort[R]:= R;
    end;
  end;         end;
end;
end; if h=0 then goto SS2;
end;

  r:= 1; s:= R-1;
  begin real inter; boolean anychange;
   for h:= 1,h+1 while anychange do
   begin anychange:= false;
    for j:= r step 1 until s do
     if store[1,j+1]<store[1,j] then
     begin if (not anychange) and j ≠ 1 then r:= j-1;
      inter:= store[1,j+1];
       tore[1,j+1]:= store[1,j];
      store[1,j]:= inter;
      inter:= sort[j+1];
       ort[j+1]:= sort[j];
      sort[j]:= inter;
      anychange:= true;
     end;
    s:= s-1;
    end;
   end;

SS1:  for h:= 1 step 1 until R do
 begin if h=1 then goto SS4 else goto SS5;
SS4:  print ££14s2?Ion Mass£s4?metal£s5?C  C*   H  H*   N   O?;
 if UP≠0 then print ££s3?P ; if noX≠0 then print ££s4?X?;
 print ££s3?calc. mass  dev?;  goto SS6;

SS5: if store[1,h]-store[1,h-1]>⏨-6 then begin  goto SS4;   SS6: print
     aligned(3,6),store[1,h]; end; if stack[1,sort[h]]=0 then print ££ls16?HC? else
     print ££ls14??,sameline,digits(3),stack[1,sort[h]];
 print sameline,digits(2),££s4??,stack[2,sort[h]],££s2??,digits(1),stack[3,sort[h]],
 ££s2??,digits(2),stack[4,sort[h]],££s2??,digits(1),stack[5,sort[h]],££s2??,
 stack[6,sort[h]],££s2??,stack[7,sort[h]];
  if UP≠0 then print sameline,££s2 ?,digits(1),stack[9,sort[h]];
  if noX≠0 then print sameline,££s2??,digits(2),stack[8,sort[h]];
 print ££s2??,sameline,aligned(3,6),store[2,sort[h]],££s2 ?,freepoint(2),
 store[3,sort[h]];       if G=1 and GF=0 then
          group(stack[2,sort[h]]+stack[3,sort[h]],stack[4,sort[h]]+
              stack[5,sort[h]],stack[6,sort[h]],stack[7,sort[h]])

 else if G=1 and GF=1 then
         group(stack[2,sort[h]]+stack[3,sort[h]],stack[4,sort[h]]+stack[5,sort[h]]+
             stack[8,sort[h]],stack[6,sort[h]],stack[7,sort[h]]);

 end;

end of program ;
```

hydrogen atoms in a structure e.g. from breakdown of the alkyl groups attached to metals by alkene loss and this value should be adjusted for individual cases. No attempt has been made to correlate numbers of structural units with a valence value for the metallic unit present, since this would involve at least one extra array whose indexing would be complex, (thus slowing down the routine) but this is clearly desirable.

Note: For flow charting conventions, see ref. 198. In the diagram, L2 represents the switch bank "move", L2.1-4 being equivalent to inn, inap, down and out, S() represents the entry point of the main data list, and R and "imaginary" entry point controlled by the initial for statements of lines 42-44.

Time: for six masses of Atlas, with limits C=14, H=20, O=3, N=P=0, about 6 minutes including compilation. Time for the formulator routine increases directly with the limits used, and it is not recommended for analysis of a full spectrum. The grouping routine, however, is fast.

Data Format:

A list of structural group index numbers is appended. Data symbols as for FORMULATOR.

```
£ title?

E
I[h]

M[h,j]

AE (; E element? noX  massX  V  GF)

UC  UH  UN  UOn  UP(;)*

GT[1,h]  GT[2,h]


PM
:
:
PM;
```

GF = steering variable for inclusion of fluorine (or other element) in grouping routine. GF = 1 adds H F and takes this as equivalent to H for grouping purposes.

GF = 0 omits this.

UP = maximum number of phosphorus atoms

GT[1,h] = number of structural units of type h to be considered

GT[2,h] = index number of unit h

*A ";" character here omits the grouping routine and the program reverts to a purely "formulator" mode.

APPENDIX 1

ISOTOPE PATTERNS

Isotope Abundance Patterns.

Peak Patterns in Mass Spectra of Compounds containing two germanium atoms

Isotope Combination (mass numbers)		Mass	Abundance Product
70	70	139.848554	4.22714
72	70	141.846017	11.2751
73	70	142.847637	3.20325
74	70	143.845427	14.9965
76	70	145.845637	3.19091
72	72	143.843480	7.51856
73	72	144.845099	4.27204
74	72	145.842890	20.0001
76	72	147.843099	4.25558
73	73	145.846720	.606841
74	73	146.844510	5.68203
76	73	148.844720	1.20901
74	74	147.842300	13.3006
76	74	149.842509	5.66014
76	76	151.842719	.602176

Number of combinations:- 15

Nominal Mass	multiplicity	spread (ppm.)	Peak Mass (wtd mean)	Relative Abundance
140	singlet		139.848554	17.7626
141	no combination			
142	singlet		141.846017	47.3786
143	singlet		142.847637	13.4602
144	2	14	143.844777	94.6093
145	singlet		144.845099	17.9513
146	3	26	145.843357	100.0000
147	singlet		146.844510	23.8762
148	2	5.4	147.842494	73.7720
149	singlet		148.844720	5.0803
150	singlet		149.842509	23.7842
151	no combination			
152	singlet		151.842719	2.5304

Isotope Abundance Patterns.
Peak Patterns in Mass Spectra of Compounds containing three germanium atoms

Isotope Combination (mass numbers)			Mass	Abundance Product
70	70	70	209.772831	8.69099
72	70	70	211.770294	34.7724
73	70	70	212.771914	9.87882
74	70	70	213.769703	46.2491
76	70	70	215.769913	9.84077
72	72	70	213.767756	46.3745
73	72	70	214.769377	26.3499
74	72	70	215.767167	123.361
76	72	70	217.767377	26.2484
73	73	70	215.770996	3.74300
74	73	70	216.768787	35.0467
76	73	70	218.768997	7.45716
74	74	70	217.766577	82.0382
76	74	70	219.766787	34.9118
76	76	70	221.766997	3.71422
72	72	72	215.765219	20.6159
73	72	72	216.766840	17.5709
74	72	72	217.764629	82.2606
76	72	72	219.764840	17.5032
73	73	72	217.768460	4.99187
74	73	72	218.766249	46.7403
76	73	72	220.766461	9.94530
74	74	72	219.764040	109.411
76	74	72	221.764250	46.5603
76	76	72	223.764460	4.95350
73	73	73	218.770080	.472729
74	73	73	219.767870	6.63945
76	73	73	221.768080	1.41273
74	74	73	220.765661	31.0835
76	74	73	222.765870	13.2278
76	76	73	224.766080	1.40729
74	74	74	221.763450	48.5073
76	74	74	223.763659	30.9638
76	76	74	225.763871	6.58841
76	76	76	227.764080	.467289

Number of combinations:- 35

Ge_3

Nominal Mass	multiplicity	spread (ppm.)	Peak Mass (wtd mean)	Relative Abundance
210	singlet		209.772831	4.4446
211	no combination			
212	singlet		211.770294	17.7828
213	singlet		212.771914	5.0521
214	2	9.1	213.768729	47.3683
215	singlet		214.769377	13.4755
216	4	27	215.767174	80.5775
217	2	9.0	216.768137	26.9090
218	4	18	217.765914	100.0000
219	3	18	218.766658	27.9587
220	4	17	219.764842	86.1543
221	2	3.6	220.765854	20.9824
222	4	21	221.764017	51.2402
223	singlet		222.765870	6.7648
224	2	3.6	223.763770	18.3684
225	singlet		224.766080	0.7197
226	singlet		225.763871	3.3694
227	no combination			
228	singlet		227.764080	0.2390

Ge_4

280	singlet		279.697106	1.1381
281	no combination			
282	singlet		281.694570	6.0714
283	singlet		282.696188	1.7249
284	2	6.9	283.692812	20.2211
285	singlet		284.693652	6.9012
286	4	20	285.691167	45.8066
287	2	6.8	286.692089	18.3829
288	5	20	287.689726	77.6657
289	4	20	288.690475	30.7756
290	6	20	289.688437	100.0000
291	4	13	290.689227	38.1479
292	8	26	291.687281	98.4648
293	4	13	292.688119	32.5566
294	6	16	293.686327	73.0355
295	4	16	294.687339	19.6986
296	5	16	295.685573	39.3927
297	2	2.7	296.687129	7.1285
298	4	16	297.685166	14.5771
299	singlet		298.687228	1.3076
300	2	2.7	299.685097	3.3873
301	singlet		300.687439	0.0927
302	singlet		301.685228	0.4342
303	no combination			
304	singlet		303.685437	0.0231

Isotope abundance pattern, one atom each of tungsten & germanium

Isotope Combination (mass numbers)		Mass	Abundance Product
180	70	249.871257	.065792
182	70	251.872548	10.8351
183	70	252.874567	5.88838
184	70	253.875266	12.6156
186	70	255.878617	11.7151
180	72	251.868720	.087744
182	72	253.870009	14.4503
183	72	254.872029	7.85309
184	72	255.872729	16.8249
186	72	257.876079	15.6239
180	73	252.870339	.024928
182	73	254.871630	4.10533
183	73	255.873649	2.23106
184	73	256.874350	4.77994
186	73	258.877699	4.43874
180	74	253.868128	.116704
182	74	255.869421	19.2197
183	74	256.871439	10.4450
184	74	257.872139	22.3780
186	74	259.875490	20.7806
180	76	255.868339	.024832
182	76	257.869628	4.08952
183	76	258.871649	2.22246
184	76	259.872350	4.76154
186	76	261.875699	4.42165

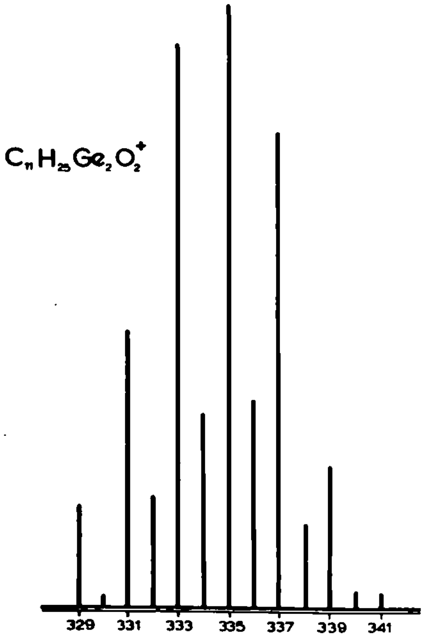
Number of combinations:- 25

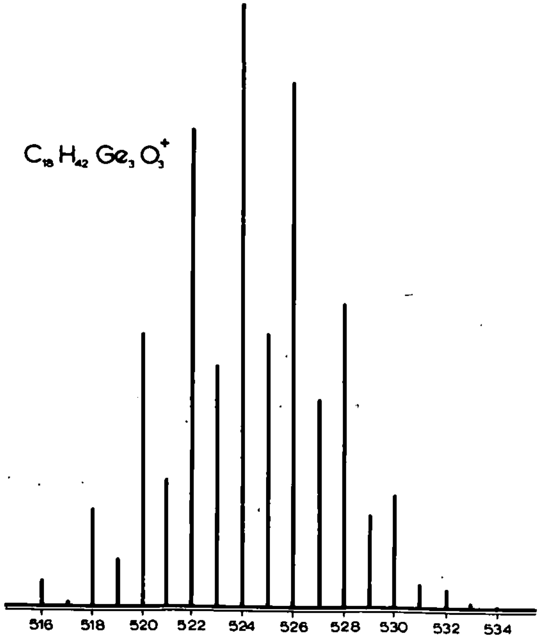
Nominal Mass	multiplicity	spread (ppm.)	Peak Mass (wtd mean)	Relative Abundance
250	singlet		249.871257	0.1315
251	no combination			
252	2	15	251.872518	21.8389
253	2	17	252.874549	11.8229
254	3	28	253.872442	54.3484
255	2	1.6	254.871893	23.9094
256	5	40	255.872876	100.0000
257	2	11	256.872353	30.4404
258	3	25	257.873359	84.1566
259	2	23	258.875680	13.3183
260	2	12	259.874905	51.0684
261	no combination			
262	singlet		261.875699	8.8405

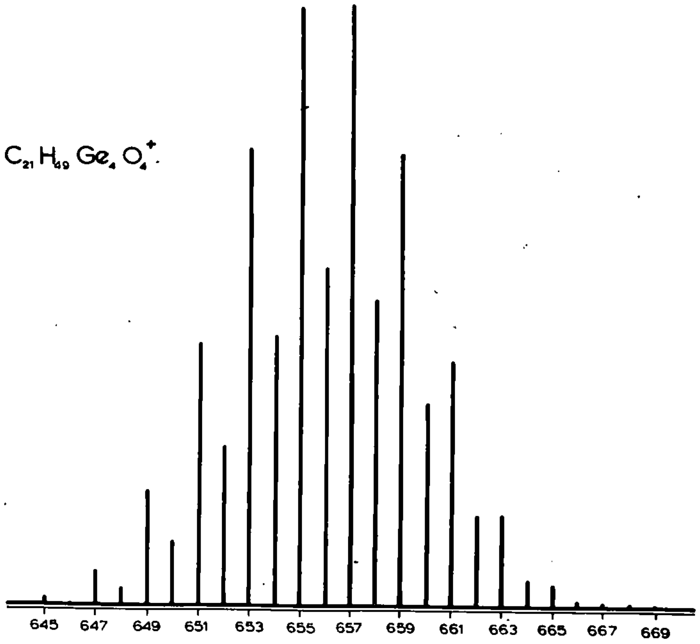
MoGe

Isotope Combination (mass numbers)		Mass	Abundance Product
92	70	161.830567	6.52163
94	70	163.829018	3.75014
95	70	164.829997	6.45584
96	70	165.828827	6.78480
97	70	166.830027	3.88584
98	70	167.829787	9.76600
100	70	169.831847	3.95574
92	72	163.828029	8.69762
94	72	165.826480	5.00141
95	72	166.827460	8.60988
96	72	167.826290	9.04860
97	72	168.827490	5.18238
98	72	169.827250	13.0245
100	72	171.829310	5.27561
92	73	164.829650	2.47099
94	73	166.828101	1.42090
95	73	167.829080	2.44606
96	73	168.827910	2.57070
97	73	169.829110	1.47231
98	73	170.828871	3.70025
100	73	172.830930	1.49880
92	74	165.827439	11.5683
94	74	167.825890	6.65213
95	74	168.826870	11.4516
96	74	169.825700	12.0351
97	74	170.826900	6.89283
98	74	171.826660	17.3233
100	74	173.828720	7.01683
92	76	167.827649	2.46147
94	76	169.826100	1.41542
95	76	170.827080	2.43664
96	76	171.825909	2.56080
97	76	172.827110	1.46664
98	76	173.826871	3.68600
100	76	175.828930	1.49302

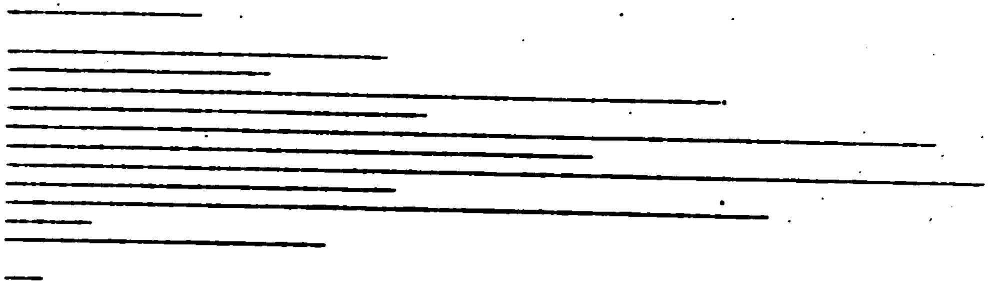
Nominal Mass	multiplicity	spread (ppm.)	Peak Mass (wtd mean)	Relative Abundance
162	singlet		161.830567	20.4420
163	no combination			
164	2	6.0	163.828327	39.0175
165	2	2.1	164.829900	27.9811
166	3	14	165.827637	73.2045
167	3	15	166.828242	43.6215
168	5	23	167.827662	95.2079
169	3	6.2	168.827174	60.1969
170	5	36	169.827270	100.0000
171	3	12	170.827492	40.8416
172	3	20	171.827140	78.8628
173	2	22	172.829041	9.2951
174	2	11	173.828082	33.5479
175	no combination			
176	singlet		175.828930	4.6799


$C_{11}H_{25}Ge_2O_2^+$
329
331
333
335
337
339
341

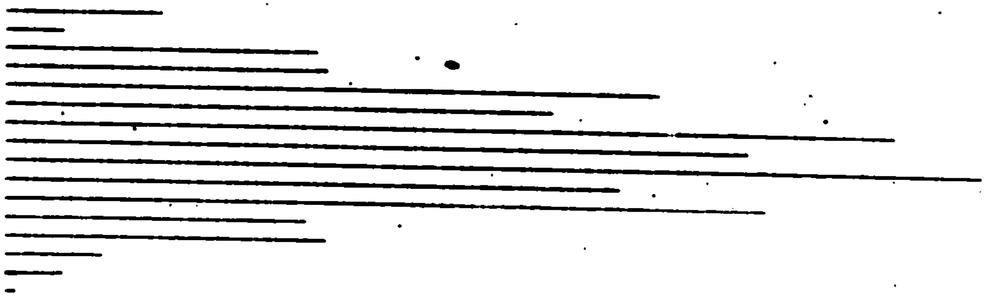

$C_{18}H_{42}Ge_3O_3^+$
516
518
520
522
524
526
528
530
532
534


$C_{21}H_{49}Ge_4O_4^+$
645
647
649
651
653
655
657
659
661
663
665
667
669

```
Isotopic Abundance Patterns.
Peak Patterns in Compounds containing one atom each of molybdenum and germanium.


Basic Heteroatom Pattern.
Nominal        Relative
 Mass          Abundance
  162          20.4420
  163
  164          39.0775
  165          27.9811
  166          73.2048
  167          43.6218
  168          95.2079
  169          60.1969
  170         100.0000
  171          40.8416
  172          78.8628
  173           9.2951
  174          33.5479
  175
  176           4.6799
```



```
Basic Pattern (one atom each of molybdenum and germanium.), corrected for light elements.

Number of atoms present:-  C 32  H 35  O  3  P  1

Nominal        Relative
 Mass          Abundance
  660          16.0285
  661           5.6811
  662          31.6861
  663          32.7261
  664          67.1629
  665          55.8951
  666          90.5165
  667          75.7876
  668         100.0000
  669          62.7875
  670          78.3248
  671          31.2126
  672          32.9739
  673           9.7574
  674           5.4134
  675           1.2937
  676           0.2433

Major heteroatom peak masses for this ion:-  666.060193   667.060637   668.059661   669.060214   670.059530

Mass of organic residue:- 498.232386
```

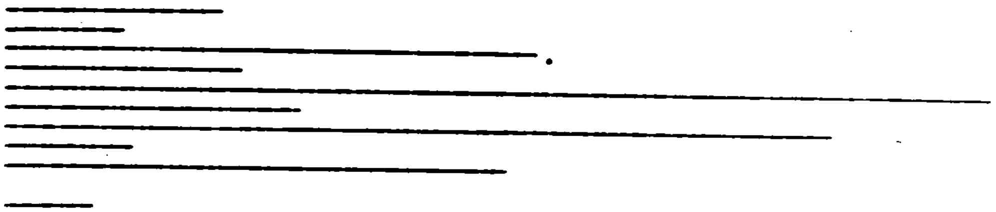


Isotopic Abundance Patterns.

Peak Patterns in Mass Spectra of Compounds containing one atom each of tungsten and germanium.

Basic Heteroatom Pattern.

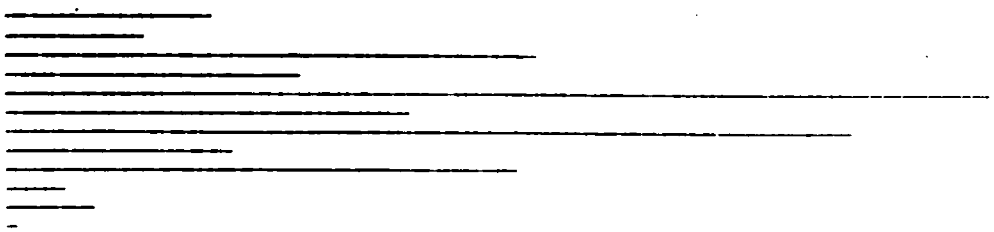
Nominal Mass	Relative Abundance
250	0.1318
251	
252	21.8389
253	11.8229
254	54.3484
255	23.9094
256	100.0000
257	30.4404
258	84.1566
259	13.3183
260	51.0684
261	
262	8.8406



Basic Pattern (one atom each of tungsten and germanium.), corrected for light elements.

Number of atoms present:- C 11 H 14 O 3

Nominal Mass	Relative Abundance
444	0.1269
445	0.0155
446	21.0772
447	13.9868
448	54.1147
449	29.6337
450	100.0000
451	41.4734
452	86.0471
453	23.1611
454	51.8985
455	6.1915
456	9.1647
457	1.0432
458	0.1096



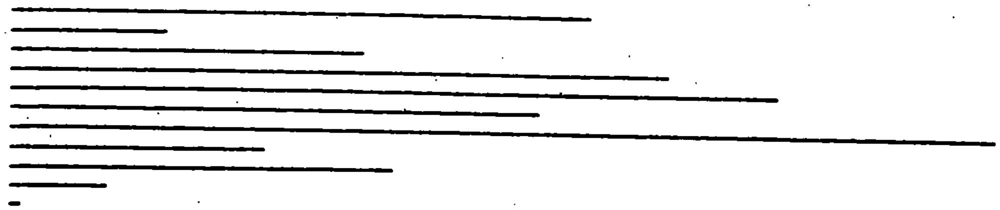
Major heteroatom peak masses for this ion:- 447.966362 448.966187 449.966899 450.966394 451.967229

Mass of organic residue:- 194.094295

Basic Pattern (one molybdenum atom), corrected for light elements.

Number of atoms present:- C 25 H 21 O 2 P 1

Nominal Mass	Relative Abundance
476	58.7302
477	16.1092
478	36.1308
479	67.4011
480	78.4035
481	54.0883
482	100.0000
483	25.5289
484	39.1589
485	9.7712
486	1.4309



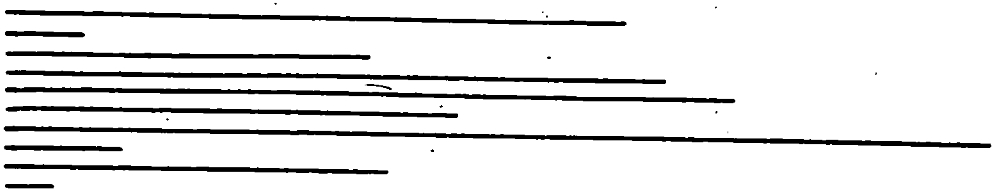
Major heteroatom peak masses for this ion:- 479.035419 480.032469 481.033669 482.033429 484.035489

Mass of organic residue:- 384.127920

Basic Pattern (one molybdenum atom), corrected for light elements.

Number of atoms present:- C 11 H 11

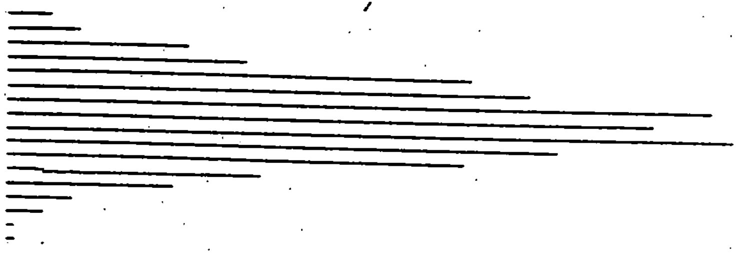
Nominal Mass	Relative Abundance
235	63.4416
236	7.6527
237	36.9017
238	67.2022
239	73.8192
240	46.1791
241	100.0000
242	11.7105
243	39.1112
244	4.0418
245	0.2552



Major heteroatom peak masses for this ion:- 237.993677 238.990626 239.991827 240.991588 242.993646

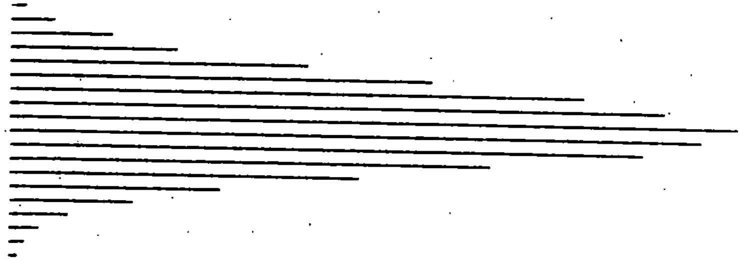
Mass of organic residue:- 143.086077

```
Basic Pattern (one atom of platinum and two of germanium), corrected for light elements.

Number of atoms present:-  C 48  H 60  P  2

 Nominal      Relative
  Mass        Abundance
  1028          0.0023
  1029          0.0012
  1030          0.1469
  1031          0.0792
  1032          6.3354
  1033          9.5345
  1034         25.3498
  1035         33.8803
  1036         64.3092
  1037         71.5320
  1038         96.8567
  1039         89.4034
  1040        100.0000
  1041         76.5205
  1042         62.9699
  1043         34.8383
  1044         23.1191
  1045          9.3855
  1046          4.7177
  1047          1.4273
  1048          0.5102
  1049          0.0975
  1050          0.0252
```



```
Major heteroatom peak masses for this ion:-  1036.22606   1037.22663   1038.22518   1039.22539   1040.22476

Mass of organic residue:-  698.41704
```

```
Basic Pattern (two atoms each of platinum and germanium), corrected for light elements.

Number of atoms present:-  C 60  H 90  P  4

 Nominal      Relative
  Mass        Abundance
  1454
  1455
  1456          0.0001
  1457          0.0000
  1458          0.0026
  1459          0.0033
  1460          0.0989
  1461          0.1634
  1462          2.2931
  1463          5.6765
  1464         13.9192
  1465         23.3266
  1466         41.3948
  1467         58.1613
  1468         79.3655
  1469         89.7528
  1470        100.0000
  1471         95.1358
  1472         86.6880
  1473         65.8201
  1474         48.0761
  1475         29.1613
  1476         17.4587
  1477          8.3163
  1478          4.1578
  1479          1.5361
  1480          0.6296
  1481          0.1709
  1482          0.0582
  1483          0.0085
  1484          0.0028
```



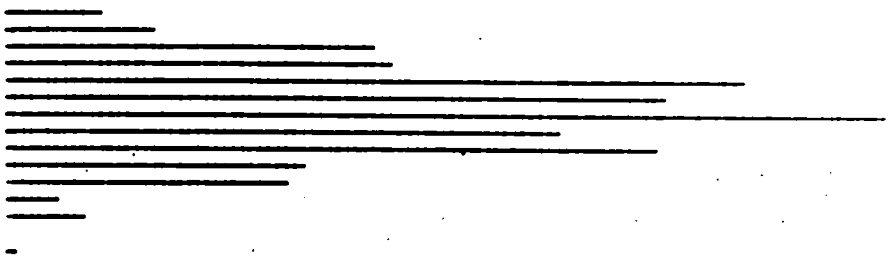
```
Major heteroatom peak masses for this ion:-  1468.37216   1469.37221   1470.37171   1471.37192   1472.37160

Mass of organic residue:-  934.59933
```

Isotopic Abundance Patterns.

Peak Patterns in Mass Spectra of Compounds containing one atom each of platinum,tungsten and germanium

Basic Heteroatom Pattern.

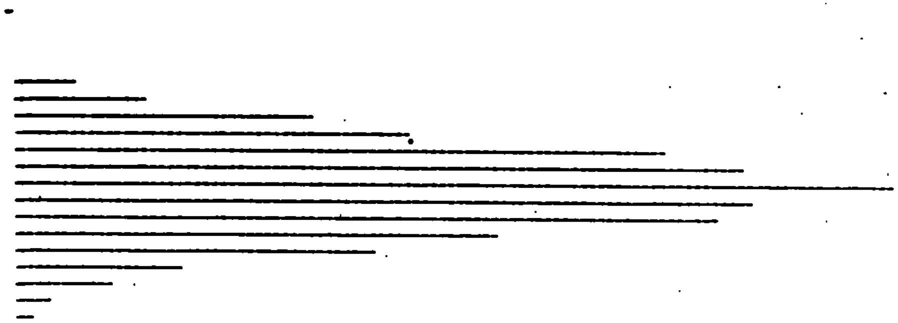
Nominal Mass	Relative Abundance
440	
441	
442	0,0086
443	0,0022
444	0,3368
445	0,2070
446	11,3432
447	16,9844
448	41,7888
449	43,6469
450	84,3322
451	75,2828
452	100,0000
453	62,8686
454	72,7506
455	33,7949
456	32,3466
457	5,8469
458	8,7423
459	
460	0,9419



Basic Pattern (one atom each of platinum,tungsten and germanium), corrected for light elements.

Number of atoms present:- C 82 H 44 O 3 P 2

Nominal Mass	Relative Abundance
1218	
1219	
1220	0,0036
1221	0,0034
1222	0,2097
1223	0,2810
1224	7,3407
1225	14,9715
1226	33,9896
1227	44,7943
1228	74,0280
1229	83,2362
1230	100,0000
1231	84,1642
1232	80,3003
1233	64,9472
1234	40,6832
1235	19,0487
1236	11,1106
1237	3,7942
1238	1,5228
1239	0,3423
1240	0,0994



Major heteroatom peak masses for this ion:- 1228,11268 1229,11352 1230,11341 1231,[illegible] 1232,[illegible]

[illegible] residue: 778,2765

APPENDIX 2

EXPERIMENTAL METHODS

1. Nitrogen Supply and Glove Box

All reactions and operations involving air sensitive compounds or intermediates were carried out in an atmosphere of pure, dry, oxygen-free nitrogen. Further purification of commercial "white spot" nitrogen was achieved by passing the gas through a tower containing B.T.S. catalyst (an active form of copper on a zeolite support) at 170° and through a column of molecular sieve and a long spiral trap cooled to -198° to remove traces of moisture.

The perspex evacuable glove box (by Mecaplex of Grenchen, Switzerland) was mounted on a wheeled trolley (approx. 4' x 2' 6" x 3') with all its ancillary equipment housed on a lower decking below the working surface. All control valves and switches were mounted on a vertical front panel of the trolley, between the upper and lower decking. Two copper furnaces were used in the recycle circuit to remove oxygen, one, specially built in stainless steel, contained 2 kg of copper and was run at 450°, the other, in series with the first was of glass containing B.T.S. catalyst, the black-light grey colour change of which indicating when regeneration of the two units was required. The usual recycle pump was mounted outside the main glove chamber in a specially made gas-tight perspex box, equipped with serum caps so that the pump bearings could be oiled without shutting down the system. Two large liquid nitrogen-cooled traps were incorporated in the recycle circuit and a mercury manometer activating a relay provided a low pressure cut-out for the recycle pump, to avoid damage caused by inadvertant partial evacuation of the main chamber by this pump if a blockage in the nitrogen traps occurred (icing up). The main chamber of the box could be evacuated (normally only necessary on initial start up or after removing the domed top of the chamber), the gloves being protected by port covers. A slight modification was made to these consisting of a rotable disc, mounted co-axially with the main disc, which could be moved to cover gaps required to hold the discs in place, and thus give the gloves additional support against the atmospheric pressure.

The transfer port was routinely evacuated, a mercury manometer and "vasustat" connected to the main pumping line giving pressure indications. The chamber could be let down either to nitrogen from the box or from the main laboratory supply line, a mercury float valve non-return blow off preventing accidental ingress of air if the latter method was chosen. A pressure of 0.1-1 mm was normally achieved in the transfer tube and a purge of 3-5 minutes was usually allowed after letting it down to nitrogen. The normal time for entry to box via the transfer tube was 10-15 minutes in total, compared with 20-45 minutes for the conventional "purge only" boxes. The present unit could of course be used in this mode also.

2. Infrared Spectra

The region 2.5-25 u was recorded on either a Grubb-Parsons G.S.2A or "Spectromaster" spectrophotometer. Solids were examined as pressed discs in KBr or KI, or as mulls in nujol or perfluorokerosene. Liquids were examined as thim films between KBr or KI plates. Carbonyl compounds were examined in solution over the range 4.5-6.0 μ using either an unreactive solvent transparent in this region, e.g. CCl_4, $CHCl_3$ or CS_2, or, in the case of benzene or thick films of cyclohexane, by carefully cancelling out solvent absorptions using a variable path-length cell filled with solvent in the reference beam. The wavelength scale for these spectra was calibrated against the bands of known frequency in polystyrene. The region 20-50 μ was recorded on a Grubb-Parsons D.M.2/D.B.3 instrument, solids being examined as nujol mulls between ceasium iodide plates.

3. Nuclear Magnetic Resonance Spectra.

Proton magnetic resonance spectra were recorded on a Perkin-Elmer R.10 instrument using a 60 mc/s R.F. field at a temperature of 33°. Measurements relate to tetramethyl silane (τ = 10) as internal standard.

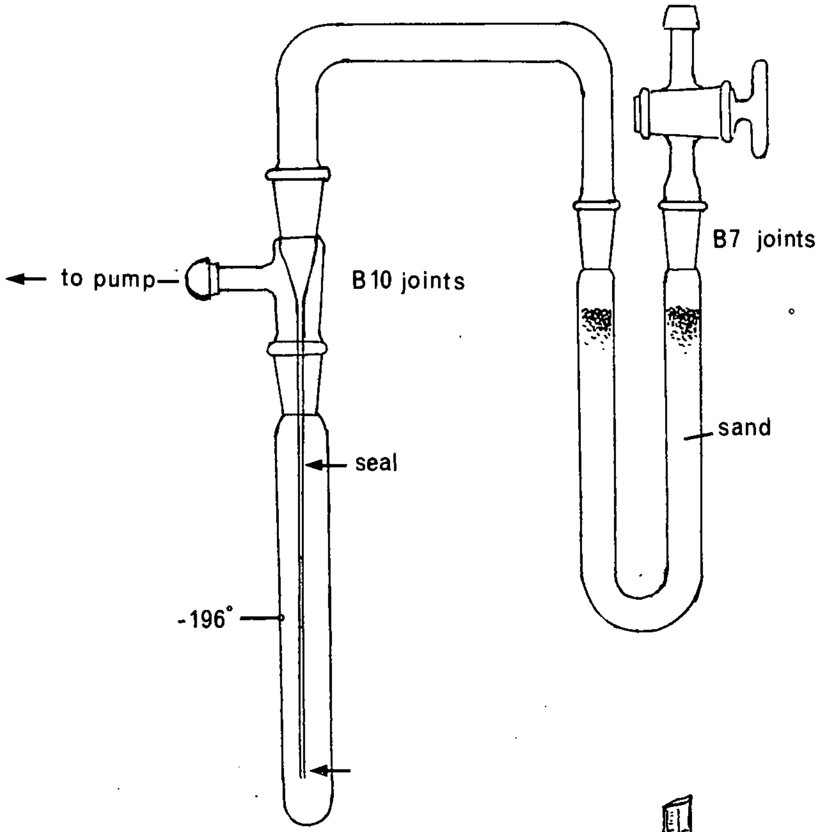
4. Mass Spectra

Mass spectra were studied on an A.E.I. M.S.9 instrument using a 70 ev 100 μA ionising beam and 8 kv accelerating potential. Ionisation chamber temperatures were varied according to the compound under examination in the range 65°-250°. Volatile liquids were introduced through a gallium cell or hot inlet, and solids by a direct insertion probe. All mass measurements were by the peak switching method using perfluorotri-n-butylamine as comparison standard, and relate to $^{12}C=12$ mu exactly.

5. Vapour-Phase Chromatography

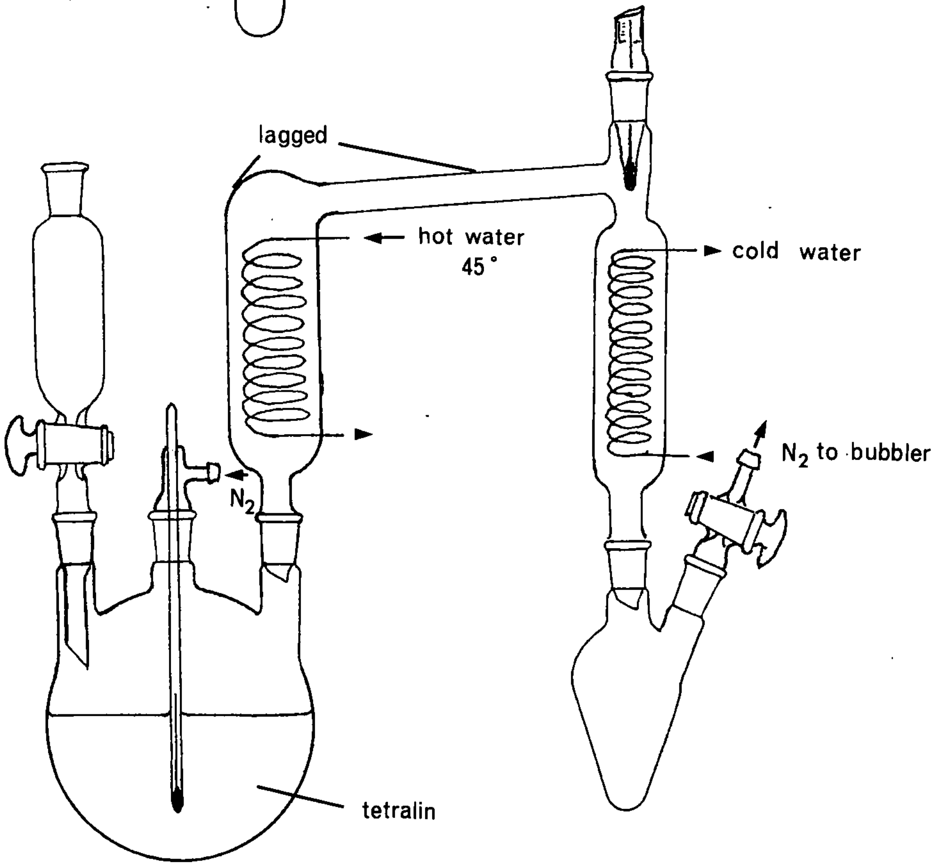
For the greater part of the analytical work described, Pye 104 single and dual column machines equipped with flame ionisation detectors were used with a number of stationary phases: 10% Apiezon L on 100-120 mesh "celite" (approx. 400 plates per foot, 4 mm column) was found to be the most generally useful for organogermanes. It was also found that unless the ratio of hydrogen to oxygen (in the air) used in the detector was greater than that normally employed for organic compounds, pronounced non linearity of response occurred leading to "double-peaking". A Kent "Chromalog" integrator was connected in parallel with the (Honeywell-Brown) recorder.

A Perkin-Elmer 451 chromatograph was used for some early work, but with a



Vacuum Distillation Apparatus

for V.P.C. samples collected on sand



Dicyclopentadiene Cracker, after ref. 202

silicone elastomer stationary phase (column 'O') at 200° marked anti-Langmuir absorption occurred for the higher germanes, particularly for $Pr^i_6Ge_2$.

Small "preparative scale" separations for mass spectrometry were carried out on a Pye "Panchromatograph" using a Hamilton fraction collector. The U-tubes of the collector were fitted with B7 sockets and filled with carefully cleaned large grained quartz sand. The commercially produced serum caps fitted the B7 joints snugly and held high vacuum (10^{-4} mm) for short periods. Volatile organogermanes were collected with the tubes cooled in liquid air and were removed from the sand by vacuum distillation into a capillary tube, using the apparatus shown opposite. The organogermane solidified in the collecting capillary, the long tube surrounding it being held at -196°. After carefully letting down the apparatus to dry nitrogen and allowing it to warm to room temperature, the capillary was sealed above and below the drop of liquid collected, which could then be stored in this form, or transferred directly into the mass spectrometer through the gallium or hot flask inlet from the capillary.

Larger amounts of components of mixtures were collected using an Aerograph "Autoprep".

6. Solution Molecular Weights

Molecular weights of air stable materials were determined in benzene at 37° using a Mechrolab Vapour Pressure Osmometer at concentrations ranging from 0.003M to 0.1M using resublimed triphenylphosphine for calibration. Solution molecular weights of air sensitive compounds were measured by the wellknown cryoscopic method in benzene (see e.g. ref. 203.)

7. A conventional mercury float valve vacuum line[203] was used for measurement of permanent gas and fractionation of volatile products from reactions in break-seal tubes. All solvents (B.D.H. analar grade) were dried by standing over sodium wire, or in the case of 1,2-dimethoxyethane and tetrahydrofuran, were distilled from lithium aluminium hydride immediately before use.

Xylene and di-n-butyl ether used to prepare sodium sand were distilled from sodium immediately prior to use. All the solvents used for the organo-germanium -molybdenum and tungsten compounds were de-oxygenated by repeated pumping and letting down to nitrogen.

Cyclopentadiene was obtained by cracking dry ($MgSO_4$) commercial dicyclopentadiene in the apparatus illustrated on p. 187a. The 1 litre flask containing tetralin is held at reflux temperature (210°) and the dicyclopentadiene is allowed to drip in slowly. Depolymerisation is almost immediate and quantitative (dicyclopentadiene begins to crack at about 125°) and the cyclopentadiene vapour, BPt 42°, passes up the hot water condenser, which returns the tetralin to the boiler, and is condensed by the cold water spiral and collected in the small flask. Pure cyclopentadiene can be produced quickly and in quantity in this way, and the method is much less troublesome than the normal fractional distillation processes. A slow current of dry nitrogen helps the passage of the cyclopentadiene through the double condenser system which was constructed in one piece, without intermediate ground joints, to prevent loss of the vapour.

Other starting materials were prepared by the usual methods available in the literature.[202-4]

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