ORGANOGERMANIUM CHEMISTRY

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GERMANIUM, Mendeléeff's "eka-silicon", was discovered by Winkler in 1886 and the first organo-derivative, Et_4Ge, was reported in the following year. This compares with the preparation of Et_4Si by Friedel and Crafts in 1863, and ethyl derivatives of tin and lead by Löwig in 1852 and 1853. The rarity and high cost of germanium relative to silicon, tin, and lead have probably retarded development of its organic chemistry, and even today no significant chemical application has appeared for organogermanium compounds, although interest in organogermanium research is increasing greatly. Three reviews[1,2,2a] cover most of the literature up to 1962, whilst an excellent literature survey by Dub[3] extends to 1961. The object of this Review is to be critical without attempting a comprehensive coverage.

Germanium is closer to silicon in its organic chemistry than to tin and lead. This is reflected in the high thermal stability and relatively low reactivity of C–Si and C–Ge bonds, especially those involving alkyl rather than aryl or benzyl groups. The Si–Si and Ge–Ge bonds in compounds of the type $R_3M{\cdot}MR_3$ are also of much higher thermal stability and lower reactivity than the corresponding bonds in tin and lead compounds. Similarly metal–hydrogen bonds as in R_3MH and R_2MH_2 show a marked decrease in thermal stability and increased sensitivity to oxidation between germanium and tin; triorganoplumbanes, R_3PbH, are exceedingly unstable. The tendency to tetraco-ordination by the metal is extremely marked in all the organo-compounds, and monomers of the type R_2M are as yet unknown; reactions aimed at producing such compounds have invariably led to cyclic or linear oligomers, such as $(Ph_2Ge)_4$, in which association involves the formation of metal–metal bonds. Solvolysis reactions on organohalides such as R_3MX are far more rapid with silicon than the other metals, and decrease progressively to lead.[4]

All of the Group IV metals, Si to Pb, contrast markedly with carbon in not forming multiple p_π–p_π bonds, although there is strong evidence for d_π–p_π interaction between the metals and other atoms or groups.[5,6] Germanium, in common with the other metals of Group IV, can show a covalency of 5 and 6 especially in co-ordination compounds of the tetrahalides[7] [*e.g.*, $Me_3N{\cdot}GeF_4$ and $(Me_3N)_2GeF_4$].

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[1] O. H. Johnson, *Chem. Rev.*, 1951, **48**, 259.

[2] D. Quane and R. S. Bottei, *Chem. Rev.*, 1963, **63**, 403.

[2a] F. Rijkens, "Organogermanium Chemistry", Germanium Research Committee, 1964.

[3] M. Dub, "Organometallic Compounds", vol. 2, Springer Verlag, Berlin, 1961.

[4] A. L. Allred and E. G. Rochow, *J. Inorg. Nuclear Chem.*, 1958, **5**, 269.

[5] J. Chatt and A. A. Williams, *J. Chem. Soc.*, 1954, 4403.

[6] J. A. Bedford, J. R. Bolton, A. Carrington, and R. H. Prince, *Trans. Faraday Soc.*, 1963, **59**, 53.

[7] I. R. Beattie, *Quart. Rev.*, 1963, **17**, 382.

Formation of Germanium–Carbon Bonds

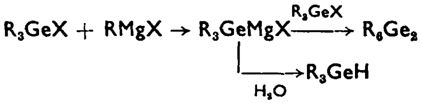
Grignard and Organolithium Reagents.—These are by far the most extensively used and versatile methods of establishing germanium–carbon bonds. When germanium tetrachloride is used, successive replacement of halogen by R groups occurs, but the reaction is difficult to control at the intermediate stages, and there are usually more satisfactory methods of preparing compounds of the types $RGeCl_3$, R_2GeCl_2, and R_3GeCl. Even with an excess of Grignard or organolithium reagent, yields of R_4Ge in excess of 80% are rare. One series of comparative experiments,[8] using C_8 to C_{18} Grignard reagents, gave yields of R_4Ge compounds in the range 5—47%. Clearly the reaction is frequently more complex than is indicated by (1).

$$GeCl_4 + 4RMgX \rightarrow R_4Ge \qquad (1)$$

These complexities are most apparent when sterically hindered organic groups are involved, resulting in incomplete substitution of halogen by R groups, and hence the formation of various types of oxides on subsequent hydrolysis:

$$R_2GeX_2 \rightarrow (R_2GeO)_n \qquad R_3GeX \rightarrow R_3GeOH + (R_3Ge)_2O$$

A further complication is the occurrence of halogen–metal exchange reactions which lead to such diverse products as di- and poly-germanes and organogermanium hydrides:



$$R_3GeX + RMgX \rightarrow R_3GeMgX \xrightarrow{R_3GeX} R_6Ge_2$$
$$R_3GeMgX \xrightarrow[H_2O]{} R_3GeH$$

An illustrative example is the reaction between an excess of isopropylmagnesium chloride and germanium tetrachloride, which has been reported[9,10] as giving, after hydrolysis, Pr^i_3GeH, Pr^i_3GeCl, and $(Pr^i_2GeO)_3$. A more recent investigation,[11] using vapour phase chromatography for the separation and identification of volatile products, revealed 10 major components. Sufficient of these have been identified to throw some light on the competing reaction paths involved. Even with a large excess of the Grignard reagent and a prolonged reaction time, hydrolysis gives the hydroxide, Pr^i_3GeOH, and the oxides $(Pr^i_3Ge)_2O$, $(Pr^i_2GeO)_3$, and $(Pr^i_2GeO)_4$. Chlorotri-isopropylgermane is also a major component together with the hydride, Pr^i_3GeH. The latter results from hydrolysis of an intermediate germyl-Grignard reagent, formed either by halogen–metal exchange or by direct reaction with excess of free magnesium:[12,13]

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[8] R. Fuchs, L. O. Moore, D. Miles, and H. Gilman, *J. Org. Chem.*, 1956, **21**, 1113.

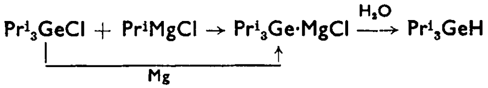
[9] H. H. Anderson, *J. Amer. Chem. Soc.*, 1953, **75**, 814.

[10] P. Mazerolles, Dissertation, Toulouse, 1959.

[11] A. Carrick and F. Glockling, *J. Chem. Soc.* (*A*)., 1966, in the press.

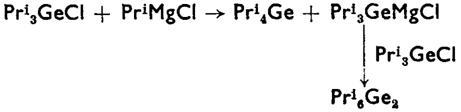
[12] F. Glockling and K. A. Hooton, *J. Chem. Soc.*, 1962, 3509.

[13] J. A. Semlyen, G. R. Walker, and C. S. G. Phillips, *J. Chem. Soc.*, 1965, 1197.



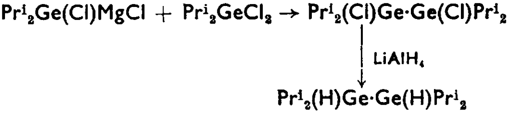
$$\begin{tikzcd}[column sep=small] \mathrm{Pr^i_3GeCl} \arrow[rr, bend right, "\mathrm{Mg}"'] & + \; \mathrm{Pr^iMgCl} \arrow[r] & \mathrm{Pr^i_3Ge{\cdot}MgCl} \arrow[r, "\mathrm{H_2O}"] & \mathrm{Pr^i_3GeH} \end{tikzcd}$$

Tetraisopropylgermane and hexaisopropyldigermane are also formed:



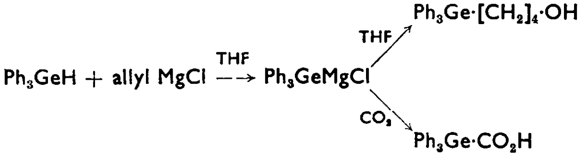
$$\begin{tikzcd} \mathrm{Pr^i_3GeCl} + \mathrm{Pr^iMgCl} \arrow[r] & \mathrm{Pr^i_4Ge} + \mathrm{Pr^i_3GeMgCl} \arrow[d, "\mathrm{Pr^i_3GeCl}"] \\ & \mathrm{Pr^i_6Ge_2} \end{tikzcd}$$

This reaction also provides evidence for intermediates of the type, $\mathrm{Pr^i_2Ge(Cl)MgCl}$:



$$\begin{tikzcd} \mathrm{Pr^i_2Ge(Cl)MgCl} + \mathrm{Pr^i_2GeCl_2} \arrow[r] & \mathrm{Pr^i_2(Cl)Ge{\cdot}Ge(Cl)Pr^i_2} \arrow[d, "\mathrm{LiAlH_4}"] \\ & \mathrm{Pr^i_2(H)Ge{\cdot}Ge(H)Pr^i_2} \end{tikzcd}$$

Polymeric isopropylgermanium oxides are also formed, probably by the hydrolysis and intermolecular dehydration of a whole range of organohalogenodi- and -poly-germanes such as $\mathrm{R_2(Cl)Ge{\cdot}(R)Ge(Cl){\cdot}Ge(Cl)R_2}$. Convincing evidence for the existence of germyl-Grignard reagents was first obtained by Gilman and Zuech.[14]



$$\begin{tikzcd} & & \mathrm{Ph_3Ge{\cdot}[CH_2]_4{\cdot}OH} \\ \mathrm{Ph_3GeH} + \text{allyl } \mathrm{MgCl} \arrow[r, "\mathrm{THF}"] & \mathrm{Ph_3GeMgCl} \arrow[ur, "\mathrm{THF}"] \arrow[dr, "\mathrm{CO_2}"'] & \\ & & \mathrm{Ph_3Ge{\cdot}CO_2H} \end{tikzcd}$$

Organolithium reagents appear rather less satisfactory for the preparation of symmetrical organogermanes.[15] For example, ethyl-lithium and germanium tetrachloride have given $\mathrm{Et_4Ge}$ (12%), $\mathrm{Et_6Ge_2}$ (9%), and much polymer. It is not clear whether the polymer was formed by the hydrolysis of intermediate ethylgermanium halides or by oxidation of lithiated intermediates.

Similar reactions have been used to prepare alkenyl and alkynyl germanes. Vinylmagnesium bromide and germanium tetrachloride react in tetrahydrofuran solution to give $\mathrm{(vinyl)_4Ge}$ (35%) and $\mathrm{(vinyl)_6Ge_2}$ (26%).[16] Alkynyls of the types $\mathrm{R_3GeC{:}CR'}$, $\mathrm{R_3GeC{:}CGeR_3}$, and $\mathrm{(PhC{:}C)_4Ge}$ have been obtained from reactions between the germanium halide and either the lithio- or Grignard alkynyls.[17,18] σ-Cyclopentadienyl and related derivatives of germanium have been reported, *e.g.*, $\mathrm{R_2Ge(C_5H_5)_2}$ and $\mathrm{R_3GeC_5H_5}$. The cyclopentadienyl group, which forms a normal Diels–Alder addition compound with maleic anhydride, can also be reduced

[14] H. Gilman and E. A. Zuech, *J. Org. Chem.*, 1961, **26**, 3035.

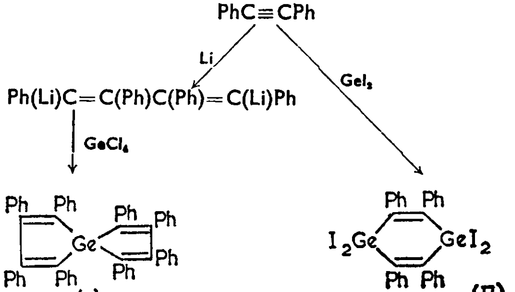
[15] H. Gilman, M. B. Hughes, and C. W. Gerow, *J. Org. Chem.*, 1959, **24**, 352.

[16] D. Seyferth, *J. Amer. Chem. Soc.*, 1957, **79**, 2738.

[17] K. H. Birr and D. Kraft, *Z. anorg. Chem.*, 1961, **311**, 235.

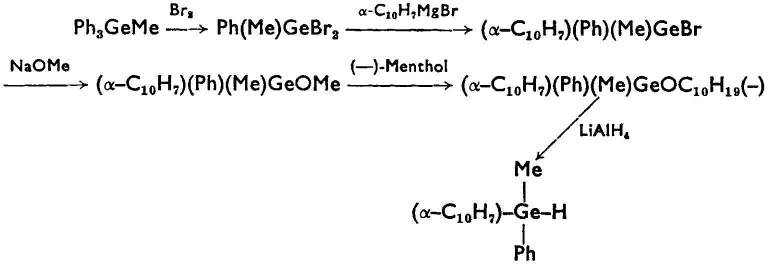
[18] C. Eaborn and D. R. M. Walton, *J. Organometallic Chem.*, 1964, **2**, 95.

with Raney nickel to the cyclopentyl derivative, $R_3GeC_5H_9$.[19,20] It has also been reported, though without detail, that the germanium–carbon bond in cyclopentylgermanium compounds is sufficiently robust to survive catalytic dehydrogenation at 600° to the cyclopentadienylgermanium compound.[21] A number of interesting compounds [*e.g.* (I)[22] and (II)[23,24]] are known in which germanium forms part of a cyclic system.



(I) (II)

Many artifices exist for the formation of unsymmetrical tetraorganogermanes; among the most important are differences in the reactivity of aryl and alkyl groups towards cleavage by various reagents. The illustration below includes the isolation and resolution of an asymmetric triorganogermane, $R_1R_2R_3GeH$. Substitution reactions of (III) occur with a considerable degree of stereospecificity,[25] and appear to parallel the more extensively studied behaviour of organosilanes.[26]



$$\mathrm{Ph_3GeMe} \xrightarrow{\mathrm{Br_2}} \mathrm{Ph(Me)GeBr_2} \xrightarrow{\alpha\text{-}\mathrm{C_{10}H_7MgBr}} (\alpha\text{-}\mathrm{C_{10}H_7})\mathrm{(Ph)(Me)GeBr}$$

$$\xrightarrow{\mathrm{NaOMe}} (\alpha\text{-}\mathrm{C_{10}H_7})\mathrm{(Ph)(Me)GeOMe} \xrightarrow{(-)\text{-Menthol}} (\alpha\text{-}\mathrm{C_{10}H_7})\mathrm{(Ph)(Me)GeOC_{10}H_{19}}(-)$$

$$\xrightarrow{\mathrm{LiAlH_4}} \begin{array}{c} \mathrm{Me} \\ | \\ (\alpha\text{-}\mathrm{C_{10}H_7})\text{-}\mathrm{Ge}\text{-}\mathrm{H} \\ | \\ \mathrm{Ph} \end{array}$$

(III) $[\alpha]_D + 26{\cdot}7°$

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[19] V. F. Mironov, T. K. Gar, and L. A. Leites, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1962, 1387.

[20] M. Lesbre, P. Mazerolles, and G. Manuel, *Compt. rend.*, 1962, **255**, 544.

[21] O. M. Nefedov and M. N. Manakov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1963, 769.

[22] F. C. Leavitt, T. A. Manuel, F. Johnson, L. V. Matternas, and D. S. Lehman, *J. Amer. Chem. Soc.*, 1960, **82**, 5099.

[23] M. E. Vol'pin, Yu. T. Struchkov, L. V. Vilkov, V. S. Mastryukov, V. G. Dulova, and D. N. Kursanov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1963, 2067.

[24] F. Johnson, R. S. Gohlke, and W. A. Nasutavicus, *J. Organometallic Chem.*, 1965, **3**, 233.

[25] R. G. Brook and G. J. D. Peddle, *J. Amer. Chem. Soc.*, 1963, **85**, 1869, 2338.

[26] L. H. Somer, *Angew. Chem., Internat. Edn.*, 1962, **1**, 143.

Addition of Ge–H to Alkenes and Alkynes.—The hydrosilation of olefins[27] has been known for some time, and analogous reactions, also of considerable synthetic value, have been carried out by use of R_3GeH and R_2GeH_2, usually with peroxide or chloroplatinic acid as catalyst,[28] although reactive vinyl monomers condense without added catalyst:[29,30,31]

$$\mathrm{Ph_3GeH + CH_3(CH_2)_5CH{:}CH_2 \xrightarrow{(PhCO)_2O_2} Ph_3Ge(CH_2)_7CH_3}$$

$$\mathrm{Et_3GeH + CH_2{:}CHCN \rightarrow Et_3GeCH_2CH_2CN}$$

Trichlorogermane is even more reactive in its addition to olefins, and will even add across the double bonds of one naphthalene ring.[32] Trialkylgermanes and monosubstituted acetylenes combine in the presence of a catalyst to give the alkenylgermane[33]

$$\mathrm{R_3GeH + R'C{:}CH \xrightarrow{H_2PtCl_6} R_3GeCH{:}CHR'}$$

Many alkenylgermanes of this type have been polymerised.[34]

The corresponding reactions of organotin hydrides probably proceed by a free radical mechanism.[34a,34b] The addition of simple olefins to organotin dihydrides requires no catalyst or solvent, but the reactions are accelerated by ultraviolet light. Both di- and tri- organotin hydrides often behave as reducing agents towards vinyl compounds having readily reducible groups:[35]

$$\mathrm{Ph_3SnH + CH_2{:}CH{\cdot}COR \rightarrow Ph_6Sn_2 + CH_2{:}CH{\cdot}CH(OH)R}$$

Other Methods.—Alkylation and arylation of germanium–halogen bonds have been carried out using organo-zinc,[36] -aluminium[37] and -mercury[38] compounds. Mercury diaryls and germanium(II) iodide give mainly Ar_2GeI_2.[39] Aluminium alkyls, some of which are commercially available, could provide the simplest and most effective method of converting germanium tetrachloride into its tetra-alkyls, especially in the presence of added sodium chloride.[40] High-temperature reactions, analogous to those used for preparing methylchlorosilanes, between alkyl chlorides and

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[27] A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, 1965, **87**, 16.

[28] R. Fuchs and H. Gilman, *J. Org. Chem.*, 1957, **22**, 1009.

[29] M. Lesbre and J. Satge, *Compt. rend.*, 1958, **247**, 471.

[30] M. C. Henry and M. F. Downey, *J. Org. Chem.*, 1961, **26**, 2299.

[31] J. Satge, *Ann. Chim.* (*France*), 1961, **6**, 519.

[32] S. P. Kalesnikov and O. M. Nefedov, *Angew. Chem., Internat. Edn.*, 1965, **4**, 352.

[33] P. Mazerolles, *Bull. Soc. chim. France*, 1960, 856.

[34] J. G. Noltes, H. A. Budding, and G. M. van der Kerk, *Rec. Trav. chim.*, 1960, **79**, 408.

[34a] W. P. Neumann and R. Sommer, *Annalen*, 1964, **675**, 10.

[34b] C. Barnetson, H. C. Clark, and J. T. Kwon, *Chem. and Ind.*, 1964, 458.

[35] R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, 1960, **60**, 459.

[36] J. H. Longle and V. H. Dibeler, *J. Amer. Chem. Soc.*, 1952, **74**, 2683.

[37] L. I. Zahkarkin and O. Yu. Okhlobystin, *Zhur. obshchei Khim.*, 1961, **31**, 3662.

[38] F. E. Brinkman and F. G. A. Stone, *J. Inorg. Nuclear Chem.*, 1959, **11**, 24.

[39] L. I. Emellyanova, V. N. Vinogradova, L. G. Makarova, and A. N. Nesmeyanov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1962, 53.

[40] K. Zeigler in "Organometallic Chemistry", ed. H. Zeiss, Reinhold, 1960.

germanium–copper mixtures give organochlorogermanes.[32] Trialkylgermanes react with certain diazonium compounds in the presence of a copper catalyst with the establishment of a Ge–C bond:[41]

$$R_3GeH + N_2CH{\cdot}COPh \rightarrow R_3Ge{\cdot}CH_2{\cdot}COPh + N_2$$

Similarly, organogermanium halides often yield the chloromethyl derivative with diazomethane:[42]

$$RGeCl_3 + CH_2N_2 \rightarrow RGe(Cl)_2CH_2Cl + N_2$$

Triorganogermyl–alkali-metal complexes (*e.g.*, Ph_3GeLi), which are used extensively in the preparation of R_3GeR' compounds, are discussed later.

Cleavage of Germanium–Carbon Bonds

Oxidation.—Germanium–carbon bonds are strikingly resistant to cleavage by oxidising agents. Complete degradation to GeO_2 occurs with aryl and higher alkylgermanes when fuming HNO_3–H_2SO_4 is used, preferably with the addition of ammonium persulphate, but the lower alkyls, especially triethylgermyl compounds, require fusion with perchlorate in a steel bomb. In contrast, phenylgermanium polymers inflame in nitric acid.[43] Chemical oxidation of aromatic side chains in arylgermanes is possible, but is evidently accompanied by moderate degradation:[44]

$$p\text{-}HOCH_2{\cdot}C_6H_4{\cdot}GePh_3 \xrightarrow{KMnO_4} p\text{-}HO_2C{\cdot}C_6H_4{\cdot}GePh_3 \quad 55\%$$

$$m\text{-}CH_3{\cdot}C_6H_4{\cdot}GePh_3 \xrightarrow{CrO_3} m\text{-}HO_2C{\cdot}C_6H_4{\cdot}GePh_3 \quad 10\%$$

Halogenation.—Aryl and benzyl-germanes are more readily brominated than alkylgermanes. For example Ph_4Ge is converted into Ph_3GeBr or Ph_2GeBr_2 by bromine in 1,2-dibromethane whereas tetraethylgermane resists bromination beyond the stage of Et_3GeBr by bromine in ethyl bromide.[1] Although tetrabenzylgermane is cleaved by bromine at room temperature,[45] free-radical bromination of $Ph_3Ge{\cdot}CH_2Ph$ with *N*-bromosuccinimide gives $Ph_3Ge{\cdot}C(Br)_2Ph$.[46] The addition of aluminium halides facilitates cleavage reactions; even iodine will cleave tetra-alkylgermanes in the presence of aluminium iodide.[47] Tetrakispentafluorophenylgermane, $(C_6F_5)_4Ge$, is stable to bromine in boiling 1,2-dibromethane.[48]

[41] J. Satge, *Ann. Chim.* (*France*), 1961, **6**, 519.
[42] D. Seyferth and E. G. Rochow, *J. Amer. Chem. Soc.*, 1955, **77**, 907.
[43] F. Glockling and K. A. Hooton, *J. Chem. Soc.*, 1963, 1849.
[44] R. A. Benkeser, C. E. de Boer, R. E. Robinson, and D. M. Sauve, *J. Amer. Chem. Soc.*, 1956, **78**, 682.
[45] R. J. Cross and F. Glockling, *J. Chem. Soc.*, 1964, 4125.
[46] A. G. Brook, M. A. Quigley, G. J. D. Peddle, N. V. Schwartz, and C. M. Warner, *J. Amer. Chem. Soc.*, 1960, **82**, 5102.
[47] M. Lesbre and P. Mazerolles, *Compt. rend.*, 1958, **246**, 1708.
[48] D. E. Fenton and A. G. Massey, *Chem. and Ind.*, 1964, 2100.

Solvolysis.—Aryl- and benzyl-type germanium groups undergo both acid-[49] and base-[50]catalysed solvolysis. Kinetic studies require that in the acid-catalysed cleavage the predominant mechanism involves attack by the electrophil on carbon, whereas alkaline cleavage primarily involves nucleophilic attack on the metal. Comparative studies on reactions of the type

$$p\text{-MeO}\cdot C_6H_4\cdot MR_3 + H_2O \rightarrow PhOMe + R_3MOH \quad (M = Si, Ge, Sn, Pb)$$

with use of aqueous methanolic perchloric acid show an enormous increase in rate in going from Ge to Sn (approximate relative reactivities: Si, 1; Ge, 3·6; Sn, 3·5 × 10^5; Pb, 2 × 10^8). This great change has been attributed, in part, to the decrease in M–C bond energy with increase in atomic weight of M, but also to the increasing availability of unoccupied *d*-orbitals with tin and lead, which introduces the possibility of a rapid initial co-ordination of solvent to the metal. In 80% methanol the base-catalysed cleavage of benzyl–Si occurs much more readily than that of benzyl–Ge, the approximate relative reactivities for $m\text{-Cl}\cdot C_6H_4\cdot CH_2\cdot MR_3$ being Ge, 0·001; Si, 1·0; Sn, 17. Studies on the acid solvolysis of $p\text{-}Me_3M\cdot CH_2C_6H_4\cdot SnMe_3$ (M = Si, Ge, Sn) have led to an order of electron release, $Me_3Sn > Me_3Ge > Me_3Si$.[51]

Cleavage of aryl–Ge bonds by sulphur trioxide is an electrophilic substitution and, as applied to the reaction

when one sulpho-group has been introduced the remaining Ge–aryl bond is deactivated, and no further cleavage occurs.[52]

Organogermanium–Alkali-metal Compounds.—This important class of derivative was originally obtained by the cleavage of Ph–Ge or Ge–Ge bonds by use of ammonia or amine solutions of an alkali metal, but the usefulness of these procedures is somewhat limited because of the reactivity of the solvent. More recently ethereal solvents such as tetrahydrofuran (THF) and ethylene glycol dimethyl ether (GDME) have been used:[15,45,53,54,55]

$$Ph_4Ge + 2Li \rightarrow Ph_3GeLi + PhLi$$
$$Ph_6Ge_2 + 2Li \rightarrow 2Ph_3GeLi$$
$$Ph_3GeX + 2Li \rightarrow Ph_3GeLi + LiX$$
$$Ph_3GeH + 2Li \rightarrow Ph_3GeLi + LiH$$

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[49] C. Eaborn and K. C. Pande, *J. Chem. Soc.*, 1960, 1566, 1961, 297, 5082.

[50] R. W. Bott, C. Eaborn, and T. W. Swaddle, *J. Chem. Soc.*, 1963, 2342.

[51] R. W. Bott, C. Eaborn, and D. R. M. Walton, *J. Organometallic Chem.*, 1964, **2**, 154.

[52] R. W. Bott, C. Eaborn, and T. Hashimoto, *J. Chem. Soc.*, 1963, 3906.

[53] H. Gilman and C. W. Gerow, *J. Amer. Chem. Soc.*, 1955, **77**, 4675, 5509, 1956, **78**, 5823.

[54] H. Gilman, F. K. Cartledge, and S. Y. Sim, *J. Organometallic Chem.*, 1963, **1**, 8.

[55] C. Tamborski, F. E. Ford, W. L. Lehn, G. J. Moore, and E. J. Soloski, *J. Org. Chem.*, 1962, **27**, 619.

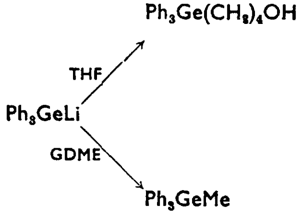
Phenyl-lithium formed in the first of the above reactions usually decomposes by reaction with the solvent and the second method is somewhat to be preferred. In certain cases cleavage of a Ge–H bond is an even more satisfactory method especially since it can be carried out in diethyl ether solution, thereby minimising subsequent reaction with the solvent.

$$Ph_3GeH + BuLi \rightarrow Ph_3GeLi + C_4H_{10} \quad (90\%)$$

These methods using ethereal solvents do not appear satisfactory for the formation of trialkylgermyl derivatives: $Pr^i_6Ge_2$ is unaffected by lithium in refluxing GDME,[11] whereas Et_3GeK is formed quantitatively in ethylamine solution:[56]

$$Et_6Ge_2 + K/EtNH_2 \rightarrow 2Et_3GeK$$

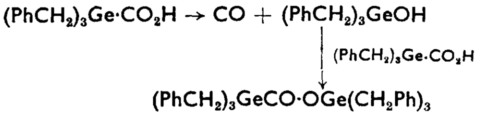
In ethereal solvents the reactions are rather temperamental: initiation periods vary from about 10 minutes to 10 hours, and an inert atmosphere must be rigorously maintained throughout.[57] Triphenylgermyl-lithium has never been isolated; its solutions which are orange-brown react slowly with solvent, but even after 5 days in refluxing tetrahydrofuran the Gilman Colour Test I remained positive:[14]



Oxidation of triphenylgermyl-lithium leads to the germanol, Ph_3GeOH, and hydrolysis to the hydride, Ph_3GeH, whilst bromination gives an 80% yield of hexaphenyldigermane. Carbonation of triphenylgermyl-lithium gives the acid, $Ph_3Ge{\cdot}CO_2H$, which decarbonylates at its melting point:[58]

$$Ph_3Ge{\cdot}CO_2H \rightarrow CO + Ph_3GeOH$$

The tribenzyl analogue is unstable at room temperature; loss of CO is accompanied by spontaneous esterification of the germanol.[45]



$$\begin{array}{l} (PhCH_2)_3Ge{\cdot}CO_2H \rightarrow CO + (PhCH_2)_3GeOH \\ \qquad\qquad\qquad\qquad \downarrow (PhCH_2)_3Ge{\cdot}CO_2H \\ \qquad\qquad (PhCH_2)_3GeCO{\cdot}OGe(CH_2Ph)_3 \end{array}$$

Lead analogues exist as an equilibrium mixture

$$R_3PbLi \rightleftharpoons R_2Pb + RLi$$

and, although there is no information on whether the deep red diaryl-

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[56] C. A. Kraus and E. A. Flood, *J. Amer. Chem. Soc.*, 1932, **54**, 1635.

[57] H. Gilman and C. W. Gerow, *J. Org. Chem.*, 1962, **27**, 1260.

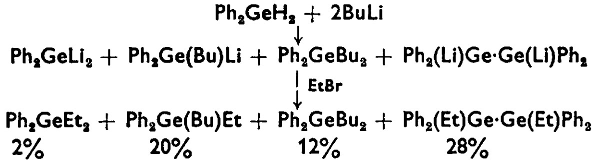
[58] A. G. Brook and H. Gilman, *J. Amer. Chem. Soc.*, 1954, **76**, 77.

lead compounds are associated, they are rapidly hydrolysed by water.[59,60] There is no evidence for a similar equilibrium involving triorganogermyllithium compounds; in ethereal solvents they are probably best regarded as solvated ion-pairs $[R_3Ge \cdots\cdot Li(ether)_n]$. The tetrahedral distribution of groups about the germanium must be preserved because of the high optical stability of the asymmetric lithio-derivative, $R_1R_2R_3GeLi$ (R_1 = Me, R_2 = Ph, R_3 = α-naphthyl), which undergoes a variety of substitution reactions without racemisation.[25] Triphenylgermylsodium, which is highly conducting in liquid ammonia solution, has been isolated as a benzene-soluble crystalline complex, $Ph_3GeNa(NH_3)_3$.[61]

Tetrabenzylgermane is readily cleaved by lithium, but in this case appreciable cleavage of a second benzyl group occurs, possibly by reaction of $(PhCH_2)_3GeLi$ with the benzyl-lithium formed in the cleavage of the first benzyl group.[45]

$$(PhCH_2)_4Ge \xrightarrow[0^\circ]{Li,GDME} (PhCH_2)_3GeLi + (PhCH_2)_2GeLi_2 + PhCH_2Li$$

The reaction between diphenylgermane and butyl-lithium has also provided evidence for the existence of a dilithio-derivative,[45] Ph_2GeLi_2:



$$\begin{array}{ccccccc} & & & Ph_2GeH_2 + 2BuLi & & & \\ & & & \downarrow & & & \\ Ph_2GeLi_2 & + & Ph_2Ge(Bu)Li & + \ Ph_2GeBu_2 \ + & Ph_2(Li)Ge{\cdot}Ge(Li)Ph_2 & & \\ & & & \downarrow{\scriptstyle EtBr} & & & \\ Ph_2GeEt_2 & + & Ph_2Ge(Bu)Et & + \ Ph_2GeBu_2 \ + & Ph_2(Et)Ge{\cdot}Ge(Et)Ph_2 & & \\ 2\% & & 20\% & 12\% & 28\% & & \end{array}$$

Examples of the reactions of R_3GeLi compounds, some of which are discussed in later sections, are summarised in Table 1.

TABLE 1. *Reactions of R_3GeLi*

Reactant	Products
O_2, H_2O	R_3GeOH
H_2O or ROH	R_3GeH
Br_2	R_6Ge_2
$R'X$	$R_3GeR' + (R_2' + R_6Ge_2)$
CO_2	$R_3Ge{\cdot}CO_2H$
$Ph_2C{:}CH_2$, H_2O	$R_3Ge{\cdot}CH_2{\cdot}CHPh_2$
Ph_2CO	$R_3Ge{\cdot}C(OH)Ph_2$
$R_3'SiBr$	$R_3Ge{\cdot}SiR_3' + (R_6Ge_2 + R_6'Si_2)$
GeI_2, H_2O	$(R_3Ge)_3GeH$
$GeCl_4$	$(R_3Ge)_4Ge$
$R_3'P{\cdot}AuCl$	$R_3Ge{\cdot}AuPR_3' + Li[Au(GePh_3)_2]$
$(R_3'P)_2Pt$ (or Pd) X_2	*cis* and *trans*-$(R_3Ge)_2Pt$ (or Pd) $(PR_3')_2$

Organogermanium Halides.—The following processes illustrate the main preparative methods for the three types: $RGeX_3$, R_2GeX_2, and R_3GeX.

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[59] H. Gilman, O. L. Marrs, W. J. Trepka, and J. W. Diehl, *J. Org. Chem.*, 1962, **27**, 1260.

[60] F. Glockling, K. A. Hooton, and D. Kingston, *J. Chem. Soc.*, 1961, 4405.

[61] C. A. Kraus and L. S. Foster, *J. Amer. Chem. Soc.*, 1927, **49**, 457.

$R_4Ge + X_2 \rightarrow R_3GeX + R_2GeX_2$ [1]
$R_4Ge + GeCl_4 \rightarrow$ all three types [62]
$GeI_2 + MeI \rightarrow MeGeI_3$ [63]

$$\left\{\begin{array}{l} R_3GeH + Br_2 \text{ (or } N\text{-bromosuccinimide)} \rightarrow R_3GeBr \text{ [64,65]} \\ RGeH_3 + Br_2 \rightarrow RGeBr_3 \text{ [66]} \end{array}\right.$$

$(R_3Ge)_2O + HX \rightarrow R_3GeX$ [1,3]
$(R_2GeO)_n + HX \rightarrow R_2GeX_2$

The choice of method depends on a variety of factors including the nature of the organic group R. Halide exchange reactions occur readily: for example, (n-hexyl)$_3$GeI can be obtained from the corresponding chloride by treatment with sodium iodide in acetone solution. The chloroethyl derivative, $Cl_3Ge{\cdot}CH_2{\cdot}CH_2Cl$ readily undergoes β-elimination of $GeCl_4$; in the presence of a base.[67] The thermal stability of organogermanium halides is considerable: $EtGeI_3$ decomposes about 350°. In the presence of a copper catalyst organogermanium halides react with diazomethane giving chloromethylene derivatives:

$$Ph_2GeCl_2 + CH_2N_2 \rightarrow Ph_2Ge(Cl){\cdot}CH_2Cl + N_2$$

$$PhGeCl_3 + CH_2N_2 \rightarrow PhGe(Cl)_2{\cdot}CH_2Cl + PhGe(Cl)(CH_2Cl)_2 + N_2$$

Although these reactions proceed by an ionic mechanism, Ph_3GeCl is evidently unreactive even in ether solution.[68]

In general, arylgermanium halides are more slowly hydrolysed than alkyl analogues, and always much more slowly than similar silicon compounds. Fluorides are more resistant to hydrolysis than other halides. Kinetic studies on the hydrolysis of triphenyl- and substituted triphenyl-germyl halides in aqueous dioxan and aqueous acetone are compatible with a pentaco-ordinate transition state rather than an S_N1 mechanism involving R_3Ge^+ intermediates.[69]

Various organogermanium halogenoids ($R_3Ge{\cdot}CN$, $R_3Ge{\cdot}NCS$, $R_3Ge{\cdot}NCO$) have been reported.[2] Infrared evidence suggests that trimethylcyanogermane consists of a mixture of isomers, Me_3GeCN and Me_3GeNC.[70] The silyl analogue is also considered to exist as an equilibrium mixture, $Me_3SiCN \rightleftharpoons Me_3SiNC$.[70a]

Oxygen Derivatives.—The immediate hydrolysis product of R_3GeX is the germanol, R_3GeOH but, with few exceptions (*e.g.*, R = Ph, $PhCH_2$, Pr^i) these undergo spontaneous intermolecular dehydration to the digermoxane $(R_3Ge)_2O$. The diols $R_2Ge(OH)_2$ formed by hydrolysis of the dihalides, R_2GeX_2, have not been isolated since they spontaneously de-

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[62] F. Rijkens and G. J. M. van der Kerk, *Rec. Trav. chim.*, 1964, **83**, 723.
[63] E. A. Flood, K. L. Godfrey, and L. S. Foster, *Inorg. Synth.*, 1950, **3**, 64.
[64] M. Lesbre and J. Satge, *Compt. rend.*, 1962, **254**, 4051.
[65] W. Gee, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 1964, 2845.
[66] E. H. Brooks, F. Glockling, and K. A. Hooton, *J. Chem. Soc.*, 1965, 4283.
[67] V. F. Mironov and N. G. Dzhurinskaya, *Izvest. Akad. Nauk. S.S.S.R., Otdel. khim. Nauk*, 1963, 75.
[68] K. Kramer and N. Wright, *Chem. Ber.*, 1963, **96**, 1877.
[69] O. H. Johnson and E. A. Schmall, *J. Amer. Chem. Soc.*, 1958, **80**, 2931.
[70] D. Seyferth and N. Kahlen, *J. Org. Chem.*, 1960, **25**, 809.
[70a] U. Wannagat and H. Seyffert, *Angew. Chem., Internat. Edn.*, 1965, **4**, 438.

hydrate to the oxides $(R_2GeO)_n$. The di-methyl-,[71] -phenyl-[72] and -iso-propyl-germanium oxides[9,11] exist as cyclic trimers, tetramers, and high polymers. The polymeric form of diphenylgermanium oxide rearranges to the cyclic trimer when heated above 200°. Germanium–oxygen bonds are cleaved by methyl-lithium[73] or by sodium in liquid ammonia:[1]

$$(Me_3Ge)_2O + MeLi \rightarrow Me_4Ge + Me_3Ge{\cdot}OLi$$

$$(Me_2GeO)_4 + 4MeLi \rightarrow 4Me_3Ge{\cdot}OLi$$

Thermal decomposition of Me_3GeOLi gives the digermoxane $(Me_3Ge)_2O$. The hydrolysis of dihalogenodimethylgermanes is of interest in relation to the well known behaviour of their silicon analogues. The available evidence[74] suggests that the hydrolysis may be reversible and, even in the presence of a weak base, gives only volatile (uncharacterised) germanium products. The tetramer $(Me_2GeO)_4$, formed by the action of aqueous sodium hydroxide on the dichloride, is freely water-soluble and, in dilute aqueous solution, cryoscopic molecular weight measurements correspond to monomeric Me_2GeO units, possibly present as the diol, $Me_2Ge(OH)_2$.

The existence of free germanoic acids, RGe(O)OH, formed by hydrolysis of the trihalides is uncertain; most probably these dehydrate spontaneously to polymeric germanoic anhydrides, $[(\text{-}RGe{\cdot}O\text{-})_2O]_n$, from which $RGeX_3$ can be regenerated with mineral acids. Ethylgermanoic anhydride is a white water-soluble solid which decomposes above 300° without melting.[1] It is conveniently prepared by the ammonolysis of $EtGeI_3$, followed by hydrolysis:

$$GeI_2 + EtI \rightarrow EtGeI_3 \xrightarrow{NH_3} (EtGeN)_n \xrightarrow{H_2O} [(EtGeO)_2O]_n$$

Alkoxides ranging from $(RO)_4Ge$ to R_3GeOR' are known, and can be prepared by the three general methods illustrated below:

$$R_3GeCl + NaOR' \rightarrow R_3Ge{\cdot}OR' + NaCl$$

$$R_3Ge{\cdot}NR'_2 + R'OH \rightarrow R_3Ge{\cdot}OR' + R'_2NH \;^{75}$$

$$R_2GeH_2 + R'OH \xrightarrow[100-150^\circ]{\text{Cu catalyst}} R_2Ge(OR')_2 \;^{76,77}$$

Alkoxides are readily hydrolysed like the alkoxysilanes and stannanes.

Organogermanium peroxides such as Ph_3GeO_2R' and $(Ph_3Ge)_2O_2$ have been obtained from the amine R_3GeNH_2 and a peroxide, *e.g.*,

$$Ph_3Ge{\cdot}NH_2 + H_2O_2 \rightarrow (Ph_3Ge)_2O_2$$

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[71] M. P. Brown and E. G. Rochow, *J. Amer. Chem. Soc.*, 1960, **82,** 4166.
[72] W. Metlesics and H. Zeiss, *J. Amer. Chem. Soc.*, 1960, **82,** 3321.
[73] I. Ruidisch and M. Schmidt, *Chem. Ber.*, 1963, **96,** 821.
[74] E. G. Rochow, *J. Amer. Chem. Soc.*, 1948, **70,** 1801.
[75] J. Satge, M. Lesbre, and M. Baudet, *Compt. rend.*, 1964, **259,** 4733.
[76] M. Lesbre and J. Satge, *Compt. rend.*, 1962, **254,** 4051.
[77] J. Satge, *Bull. Soc. chim. France*, 1964, 630.

They commonly decompose below 100° and are readily hydrolysed.

As might be expected, numerous esters of the type $R_3Ge{\cdot}OCOR'$ are known,[1,2] and usually have been prepared by heating together the organic acid and the organogermanium oxide:

$$(R_3Ge)_2O + 2R'CO_2H \rightarrow 2R_3Ge{\cdot}OCOR'$$

The esters undergo transesterification reactions readily, and are hydrolysed rapidly in alkaline solution.

Organogermanium Hydrides.—The types R_3GeH, R_2GeH_2, $RGeH_3$, $[R_2(H)Ge]_2$, and $R_2Ge(X)H$ are known. The most convenient preparative method is reduction ($LiAlH_4$ or $NaBH_4$) of the corresponding halide,[31] but they are also formed by the hydrolysis of R_3GeLi and R_3GeMgX. All types are stable to air at least for short periods, and they often show considerable thermal stability in the absence of oxygen. The dihydride Ph_2GeH_2 decomposes above 280°, and $(PhCH_2)_3GeH$ above 240°:

$$Ph_2GeH_2 \rightarrow Ge + H_2 + C_6H_6 + Ph_4Ge$$ [43]

$$(PhCh_2)_3GeH \rightarrow H_2 + PhCH_3 + (PhCH_2)_2 + \textit{trans}\text{-}PhCH{:}CHPh$$
$$+ \text{ a benzylgermanium polymer}$$ [45]

Pyrolysis of triphenylgermane at 300° gives a mixture of tetra- and diphenyl-germanes.[78]

The hydrides are moderately strong reducing agents. Solvolysis reactions require the presence of a copper catalyst:[57,76,77]

$$Et_3GeH + PhOH \xrightarrow{Cu} Et_3GePh + H_2$$

Metallation by reagents like butyl-lithium has already been mentioned, the selectivity of this reaction depending on the groups attached to germanium.[45] Bromination, either with bromine[64] or *N*-bromosuccinimide,[65] proceeds smoothly under mild conditions:

$$R_3GeH + Br_2 \rightarrow R_3GeBr + HBr$$

Organo-silanes, -germanes, and -stannanes react with diazomethane only in the presence of a chemical catalyst (Cu powder) or with photochemical activation. Triethylgermane is reported as giving Et_3GeMe in 9% yield, whilst diphenylgermane gives a mixture of Ph_2GeMe_2 and $Ph_2Ge(H)Me$.[79]

Nitrogen and Phosphorus Derivatives.—Ammonolysis of organogermanium halides occurs in liquid ammonia solution. Total exclusion of water is essential since germylamines of all types are highly sensitive to hydrolysis:

$$Ph_3GeBr + KNH_2/NH_3 \rightarrow Ph_3GeNH_2 \xrightarrow{H_2O} (Ph_3Ge)_2O$$

Primary germylamines show a marked tendency to decompose into the secondary and tertiary amines:

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[78] O. H. Johnson and D. M. Harris, *J. Amer. Chem. Soc.*, 1950, **72**, 5564.

[79] K. Kramer and A. Wright, *J. Chem. Soc.*, 1963, 3604.

$$R_3GeNH_2 \rightarrow (R_3Ge)_2NH \rightarrow (R_3Ge)_3N$$

Germylimines and nitrides, which are formed from the di- and tri-halides respectively, are associated to an unknown extent:

$$R_2GeX_2 \rightarrow (R_2GeNH)_n$$
$$RGeX_3 \rightarrow (RGeN)_n$$

The trimer, $(Me_2GeNMe)_3$, is formed from dichlorodimethylgermane and methylamine in ether solution.[79a] Secondary amines yield dialkylaminogermyl derivatives:

$$Et_2NH + GeCl_4 \xrightarrow{\text{pyridine}} (Et_2N)_4Ge$$

Lithium dialkylamides have been extensively used to establish Ge–N bonds.[75]

$$R_3GeCl + LiNR'_2 \rightarrow R_3GeNR'_2$$

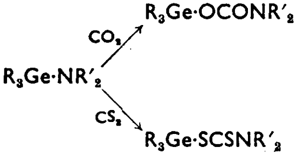
Dialkylaminogermanes are highly reactive towards alcohols, thiols, carboxylic acids, and, at elevated temperatures, even acetylenes cleave the Ge–N bond.

$$Et_3Ge{\cdot}OR' \xleftarrow{R'OH} Et_3Ge{\cdot}NR_2 \xrightarrow[150^\circ]{PhC{:}CH} Et_3Ge{\cdot}C{:}CPh + R_2NH$$

Transamination reactions occur readily:

$$Et_3Ge{\cdot}NMe_2 + PhNH_2 \rightarrow Et_3Ge{\cdot}NHPh$$

Of even greater interest are the aminogermylation reactions involving CO_2 and CS_2 which give carbamates and thiocarbamates



Similarly isocyanates and isothiocyanates give urea derivatives:

$$R_3Ge{\cdot}NR'_2 + PhNCO \rightarrow R_3Ge{\cdot}N(Ph)CONR'_2$$

A similar range of reactions has been reported for organotin–nitrogen compounds.[80]

The azides, Me_3GeN_3, $Me_2Ge(N_3)_2$,[81] and Ph_3GeN_3[82] have been described. Thermal decomposition of triphenylgermylazide at 200—400° liberates nitrogen with the formation of a polymeric gum, $(Ph_3GeN)_n$.

The phosphorus derivatives, $R_3Ge{\cdot}PPh_2$ and $R_2Ge(PPh_2)_2$ have been obtained from the appropriate germanium halides:[66]

[79a] I. Ruidisch and M. Schmidt, *Angew. Chem., Internat. Edn.*, 1964, **3**, 637.

[80] T. A. George, K. Jones, and M. F. Lappert, *J. Chem. Soc.*, 1965, 2157.

[81] O. J. Scherer and M. Schmidt, *J. Organometallic Chem.*, 1964, **1**, 490.

[82] W. T. Reichle, *Inorg. Chem.*, 1964, **3**, 402, 406.

$$Ph_2PLi + R_3GeCl \rightarrow R_3Ge{\cdot}PPh_2$$

The Ge–P bond, like Ge–N, is rapidly hydrolysed, especially when alkyl rather than phenyl groups are attached to germanium:

$$R_3Ge{\cdot}PPh_2 + H_2O \rightarrow (R_3Ge)_2O + Ph_2PH$$

Oxidation by air is also rapid:

$$R_3Ge{\cdot}PPh_2 + O_2 \rightarrow R_3GeO{\cdot}P(O)Ph_2$$

The Ge–P bond is also cleaved by bromine, methyl iodide, butyl-lithium and lithium aluminium hydride, but the phosphorus atom retains its donor character sufficiently to form the silver iodide complex $[Et_3Ge{\cdot}PPh_2{\cdot}AgI]_4$. The reaction between $GeCl_4$ and Ph_2PLi leads to tetraphenyldiphosphine and brown polymeric phosphinogermanes of variable composition, in contrast to the analogous reactions involving silicon[83] or tin,[84] both of which have given tetrakis-derivatives $(R_2P)_4M$.

Sulphur and Selenium Derivatives.—Organogermanium–sulphur compounds of the types R_3GeSR', $R_2Ge(SR')_2$, $(R_3Ge)S_2$, and $(R_2GeS)_3$ are known:[2,85]

$$Me_2GeCl_2 + H_2S \xrightarrow{H_2SO_4} (Me_2GeS)_3$$

$$Et_3GeH + BuSH \xrightarrow{Pt} Et_3Ge{\cdot}SBu$$

$$Ph_3GeX + RSH + Et_3N \rightarrow Ph_3GeSR + Et_3NHX$$

Organogermanium sulphides are evidently stable to air and only slowly hydrolysed by water. The thermal stability is also considerable as with the trialkylthiosilanes which, by contrast, are readily hydrolysed.[86,86a] Neither Si–S nor Ge–S compounds have yielded a sulphonium salt on treatment with methyl iodide; in all cases investigated cleavage of the M–S bond occurs:

$$Ph_3Ge{\cdot}SMe + 2MeI \rightarrow Ph_3GeI + (Me_3S)I$$

The trimeric selenium compound $(Me_2GeSe)_3$ has been described[87] as well as a mixed Sn–Se–Ge compound.[88]

$$Ph_3SnLi + Se \rightarrow Ph_3Sn{\cdot}SeLi \xrightarrow{Ph_3GeBr} Ph_3Sn{\cdot}Se{\cdot}GePh_3$$

Compounds Containing Ge–metal Bonds

Ge–Ge.—The formation of digermanes, R_6Ge_2, in the Grignard

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[83] G. Fritz and G. Poppenburg, *Angew. Chem.*, 1960, **72**, 208; *Internat. Edn.*, 1963, **2**, 262.

[84] H. Schumann, H. Kopf, and M. Schmidt, *J. Organometallic Chem.*, 1964, **1**, 366.

[85] W. E. Davidson, K. Hills, and M. C. Henry, *J. Organometallic Chem.*, 1965, **3**, 285.

[86] E. W. Abel, *J. Chem. Soc.*, 1960, 4406.

[86a] K. A. Hooton and A. L. Allred, *Inorg. Chem.*, 1965, **4**, 671.

[87] M. Schmidt and H. Ruf, *J. Inorg. Nuclear Chem.*, 1963, **25**, 557.

[88] H. Schumann, K. F. Thom, and M. Schmidt, *J. Organometallic Chem.*, 1964, **2**, 361.

synthesis of R_4Ge compounds can proceed by two routes, the second only being of importance when sterically hindered R groups such as *o*-tolyl are involved:[11,12]

$$\begin{tikzcd}
R_3GeX + Mg \arrow[r] & R_3GeMgX \arrow[r, "R_3GeX"] & R_6Ge_2 \\
 & R_3GeX + RMgX \rightleftharpoons & R_3GeMgX + RX \arrow[u, "R_3GeX"']
\end{tikzcd}$$

Trigermanes have also been suggested in similar reactions[13] which implies the formation of organohalogermyl Grignard reagents such as $R_2(X)Ge{\cdot}MgX$:[11]

$$R_2(X)Ge{\cdot}MgX \xrightarrow{R_3GeX} R_2(X)Ge{\cdot}GeR_3 \xrightarrow{Mg,R_3GeX} R_3Ge{\cdot}Ge(R)_2GeR_3$$

As preparative methods the reactions:

$$R_3GeLi + R_3GeCl \rightarrow R_6Ge_2 \leftarrow R_3GeX + Na$$

are of greater general utility.[1,2]

The Ge–Ge bond in R_6Ge_2 compounds is remarkably unreactive and of high thermal stability. Hexaphenyldigermane Ph_6Ge_2 melts without decomposition at 336° and is brominated slowly at room temperature[43] in 1,2-dibromethane, or rapidly at the b.p.:

$$Ph_6Ge_2 + Br_2 \rightarrow 2Ph_3GeBr$$

Some cleavage of Ge–phenyl also occurs giving Ph_2GeBr_2, in contrast to the bromination of Et_6Ge_2 which gives exclusively Et_3GeBr,[11] a reflection of the greater stability of alkyl–Ge towards brominative cleavage.

The strong tendency of germanium, in common with silicon[89] and tin,[90] to retain the co-ordination number 4 in its organo-derivatives by metal–metal bond formation is reflected in the formation of the cyclic oligomers $(Me_2Ge)_6$[91] and $(Ph_2Ge)_n$.[92] These colourless crystalline compounds have been obtained by Wurtz-type reactions:

$$Ph_2GeCl_2 + C_{10}H_8Na \rightarrow (Ph_2Ge)_5 + (Ph_2Ge)_6 + \text{polymeric } Ph_2Ge$$

$$Ph_2GeH_2 + Et_2Hg \rightarrow (Ph_2GeHg)_n \xrightarrow{\text{heat}} (Ph_2Ge)_4 + \text{polymeric } Ph_2Ge$$

$$Me_2GeCl_2 + Li \xrightarrow{\text{THF}} (Me_2Ge)_6 + \text{polymeric } Me_2Ge$$

When the last of these reactions is carried out in the presence of ethylene a small yield of dimethylgermanacyclopentane is obtained, which is perhaps indicative of a monomeric Me_2Ge intermediate:[93]

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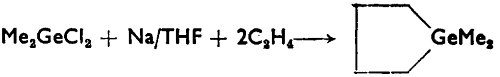
[89] H. Gilman and G. L. Schwebke, *J. Organometallic Chem.*, 1965, **3**, 382.

[90] W. V. Farrar and H. A. Skinner, *J. Organometallic Chem.*, 1964, **1**, 434.

[91] O. M. Nefedov, M. N. Manakov, and A. D. Petrov, *Doklady Akad. Nauk S.S.S.R.*, 1962, **147**, 1376.

[92] W. P. Neumann and K. Kühlein, *Annalen*, 1965, **683**, 1.

[93] O. M. Nefedov and M. N. Manakov, *Angew. Chem. Internat. Edn.*, 1964, **3**, 226.



The reaction between triphenylgermyl-lithium and germanium(II) iodide[43] provides another example of the tendency of germanium to tetra-co-ordination.

$$3Ph_3GeLi + GeI_2 \rightarrow (Ph_3Ge)_3GeLi \xrightarrow{H_2O} (Ph_3Ge)_3GeH$$

This type of reaction has been used to obtain the highly symmetrical and isomorphous tetrakistriphenylgermyl- (and stannyl-)stannanes.[94]

$$Ph_3GeLi + SnCl_2 \rightarrow (Ph_3Ge)_3SnLi \xrightarrow{Ph_3GeCl} (Ph_3Ge)_4Sn$$

$$Ph_3MLi + M'Cl_4 \rightarrow (Ph_3M)_4M'^{95}$$

$$M \text{ and } M' = Ge, Sn, Pb$$

Attempts to obtain diphenylgermanium by the reaction between germanium(II) iodide and phenyl-lithium have led to yellow air-sensitive polymers, intermediate in mean composition between PhGe and Ph_2Ge.[43] These amorphous polymers, which dissolve freely in benzene, were shown by controlled brominative degradation to contain Ph_3Ge, Ph_2Ge, PhGe and unphenylated germanium units.

Ge–Si, Ge–Sn.—Both types, *e.g.*, $Ph_3Ge{\cdot}SiPh_3$ and $Ph_3Ge{\cdot}SnMe_3$, are known:[1–3]

$$Ph_3GeLi + R_3MX \rightarrow Ph_3Ge{\cdot}MR_3 \ (M = Si \text{ or } Sn)$$

$$Ph_3SiK + Ph_3GeBr \rightarrow Ph_3Ge{\cdot}SiPh_3$$

Both methods of preparation give, in addition, the symmetrical products Ph_6Ge_2 and R_6M_2 formed by halogen–metal exchange and subsequent coupling. The mixed compounds have considerable thermal stability, but those involving germanium–tin bonds are more reactive than the digermanes. For example, in boiling xylene solution, oxygen cleaves with Ge–Sn bond in $Ph_3Ge{\cdot}SnPh_3$.[2] A Wurtz reaction with mixed halides also gives all three products which, in the example below, have been separated by vapour–phase chromatography:[95]

$$Et_3GeBr + Et_3SiBr + Na \xrightarrow{THF} Et_3Ge{\cdot}SiEt_3 + Et_6Si_2 + Et_6Ge_2$$

The low reactivity of the Ge–Ge bond in hexaethyldigermane is reflected in the observation that none of the mixed Ge–Si compound is formed when Et_6Ge_2 and Et_3SiBr are refluxed with sodium in tetrahydrofuran.[96]

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[94] H. Gilman and F. K. Cartledge, *Chem. and Ind.*, 1964, 1213.

[95] L. C. Willemsens and G. J. M. van der Kerk, *J. Organometallic Chem.*, 1964, **2**, 260.

[96] J. M. Shackelford, H. De Schmertzing, C. H. Heuther, and H. Podall, *J. Org. Chem.*, 1963, **28**, 1700.

Ge–B.—Evidence for the formation of an organogermaniumboron compound was first obtained from the reaction between BCl_3 and Ph_3GeNa in ether solution which produced a viscous oil, corresponding approximately to $(Ph_3Ge)_3B\cdot OEt_2$.[97] An anionic complex, $Me_4N[Ph_3Ge\cdot BPh_3]$ has been obtained from the reaction

$$Ph_3GeLi + Ph_3B \rightarrow Li[Ph_3Ge\cdot BPh_3]$$

It is readily hydrolysed but evidently resists solvolysis by methanol.[98]

Ge–Hg, Ge–Cd, Ge–Bi.—Triethylgermyl derivatives of mercury,[99] cadmium,[100] and bismuth[101] have been obtained by the reaction

$$Et_3GeH + Et_2M \rightarrow (Et_3Ge)_2M + 2C_2H_6 \qquad M = Hg \text{ or } Cd$$

$$Et_3GeH + Et_3Bi \rightarrow Et_3Ge\cdot BiEt_2 + (Et_3Ge)_2BiEt + C_2H_6$$

The compounds, which are readily oxidised, are also sensitive to light and decompose thermally above 100°:

$$(Et_3Ge)_2O + Hg \xleftarrow{O_2} (Et_3Ge)_2Hg \xrightarrow{h\nu} Et_6Ge_2 + Hg$$

The mercury–silicon compound $(Me_3Si)_2Hg$, which is readily prepared by shaking Me_3SiBr with sodium amalgam, is rather more stable,[102] decomposing between 100° and 160° to Me_6Si_2 and mercury. Thermal decomposition of the zinc–silicon complex $(Ph_3Si)_2Zn$ is surprising in that Si–Ph bonds are cleaved:[102]

$$(Ph_3Si)_2Zn \xrightarrow{>105^\circ} Zn + Ph_4Si + (Ph_2Si)_n$$

These thermal decompositions presumably proceed by a radical-chain mechanism, and abstraction rather than dimerisation processes evidently occur in some cases. The mixed germanium–silicon compound $Et_3Ge\cdot Hg\cdot SiEt_3$ gives appreciable yields of the mixed Ge–Si radical dimerisation product:[99]

$$\begin{tikzcd}
EtHg\cdot SiEt_3 + Et_3GeH \arrow[r] & C_2H_6 + Et_3Ge\cdot Hg\cdot SiEt_3 \arrow[d, "h\nu"] \\
& Et_3Ge\cdot SiEt_3 + Hg
\end{tikzcd}$$

The reaction of germanium–metal compounds with 1,2-dibromoethane is discussed under transition metal complexes, but it may be noted that the

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[97] F. B. Smith and C. A. Kraus, *J. Amer. Chem. Soc.*, 1952, **74**, 1418.

[98] S. O. Grim, G. Raab, and D. Seyferth, *J. Org. Chem.*, 1961, **26**, 3034.

[99] N. S. Vyazankin, G. A. Razuvaev, E. N. Gladyshev, and T. G. Gurikova, *Doklady Akad. Nauk S.S.S.R.*, 1964, **155**, 1108.

[100] N. S. Vyazankin, G. A. Razuvaev, and V. T. Bychkoo, *Doklady Akad. Nauk S.S.S.R.*, 1964, **158**, 382.

[101] O. A. Kruglaya, N. S. Vyazankin, and G. A. Razuvaev, *Zhur. obshchei Khim.*, 1965, **35**, 394.

[102] E. Wiberg, O. Strecher, H. J. Andrascheck, L. Kreuzbichler, and E. Straude, *Angew. Chem., Internat. Edn.*, 1963, **2**, 507.

mercury–germanium compound $(Et_3Ge)_2Hg$ is cleaved giving mercury and not mercuric bromide:

$$(Et_3Ge)_2Hg + C_2H_4Br_2 \rightarrow 2Et_3GeBr + Hg + C_2H_4$$

This contrasts with the behaviour of complexes involving germanium bonded to Cu, Ag, Au, Pt, and Pd, and possibly implies rapid thermal decomposition of the intermediate $Et_3Ge{\cdot}HgBr$. Hexaethyldilead is cleaved by 1,2-dibromoethane under mild conditions:[103]

$$Et_6Pb_2 + C_2H_4Br_2 \rightarrow 2Et_3PbBr + C_2H_4$$

Organogermanium–Transition Metal Complexes.—Organo-silicon, -germanium, -tin, and -lead complexes of transition metals are known, and some of their reactions are rather remarkable. Dicobaltoctacarbonyl and triorganosilanes interact at room temperature and, if an olefin is present, hydrocarbonylation reactions occur:[27]

$$R_3SiH + Co_2(CO)_8 \rightarrow R_3Si{\cdot}Co(CO)_4 + HCo(CO)_4$$

The hydrosilation of olefins using platinum(II) catalysts probably involve Pt^{IV} intermediates containing a Pt–Si bond,[27] and the low catalytic activity of Pd^{II} has been attributed to the relative instability of Pd^{IV}. Isomerisation of olefins[104] and the homogeneous hydrogenation[105,106] of alkenes and alkynes are among the reactions catalysed by platinum–tin complexes. The stability of the tin–manganese complex $Ph_3Sn{\cdot}Mn(CO)_5$ is remarkable; reagents such as chlorine and bromine cleave the tin–carbon bonds preferentially:[107]

$$Ph_3Sn{\cdot}Mn(CO)_5 + Br_2 \rightarrow 3PhBr + Br_3Sn{\cdot}Mn(CO)_5$$

The manganese and iron complexes $Ph_3Ge{\cdot}Mn(CO)_5$ and $Ph_3Ge{\cdot}Fe(CO)_2\pi\text{–}C_5H_5$ are stable in the solid state, but decompose in solution.[108] Triphenylgermyl complexes of copper, silver, and gold have been more closely studied:[109]

$$Ph_3GeLi + (R_3P)_nMCl \rightarrow Ph_3Ge{\cdot}M(PR_3)_n \quad M = Cu, Ag, Au; \quad n = 1 \text{ or } 3$$

The thermal stability and reactivity towards oxygen and water is greatly influenced by the structure and number of tertiary phosphine groups attached to the transition metal. Copper and silver gave isolable tetra-co-ordinate complexes only with triphenylphosphine as the π-bonding ligand, $(Ph_3P)_3M{\cdot}GePh_3$. Gold(I) forms a crystalline air- and water-stable

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[103] G. A. Razuvaev, Yu. I. Dergunov, and N. S. Vyazankin, *Zhur. obshchei Khim.*, 1961, **31**, 998.

[104] G. C. Bond and M. Hellier, *Chem. and Ind.*, 1965, 35.

[105] R. D. Cramer, R. V. Lindsey, C. J. Prewitt, and U. G. Stolberg, *J. Amer. Chem. Soc.*, 1965, **87**, 658.

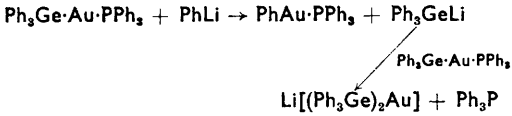
[106] R. D. Cramer, E. L. Jenner, R. V. Lindsey, and U. G. Stolberg, *J. Amer. Chem. Soc.*, 1963, **85**, 1691.

[107] R. D. Gorsich, *J. Amer. Chem. Soc.*, 1962, **84**, 2486.

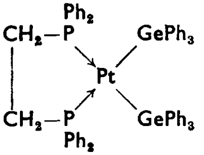
[108] D. Seyferth, H. P. Hofmann, R. Burton, and J. F. Helling, *Inorg. Chem.*, 1962, **1**, 227.

[109] F. Glockling and K. A. Hooton, *J. Chem. Soc.*, 1962, 2658.

complex $Ph_3Ge{\cdot}AuPPh_3$; the trimethylphosphine analogue is considerably more reactive. Gold has also provided the only example so far of a germanium–transition metal complex in which stabilisation by π-bonding ligands is not essential:



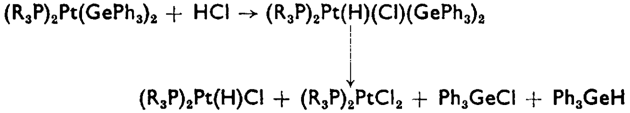
Square planar platinum(II) complexes[110,111] of the types $(R_3P)_2Pt(GePh_3)_2$ and $(R_3P)_2Pt(X)GePh_3$ (X = OR or I) are even more stable, and the former are unaffected by air, water, or caustic alkali. *trans*-Complexes are yellow whilst the *cis*-isomers are colourless, and there is evidence for cis–trans interconversion in solution. Ligand exchange reactions have been effected without cleavage of the Ge–Pt bonds giving complexes such as (IV) and (V). Many reagents (HCl, I_2, MgI_2, MeI, PhLi, $C_2H_4Br_2$, $LiAlH_4$) cleave the Ge–Pt bonds, but close examination of these reactions strongly suggests that some at least proceed *via* octahedral platinum(IV) intermediates:



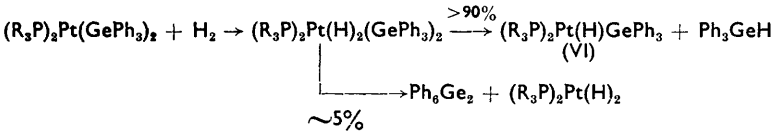
(IV)

$K_2[(CN)_2Pt(GePh_3)_2]$

(V)



The bistriphenylgermylplatinum complexes are remarkable for the extreme ease with which homogeneous hydrogenolysis of *one* of the Pt–Ge bonds occurs (0°/180 mm.H_2). The activation energy for this reaction is roughly 9 kcal./mole, which again suggests that the rate-determining step is conversion into a platinum(IV) intermediate:



Many hydridoplatinum complexes are surprisingly inert[112] and the complex(VI) is no exception, being stable to air, water, and alcoholic

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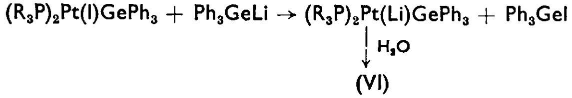
[110] R. J. Cross and F. Glockling, *J. Chem. Soc.*, 1965, 5422.
[111] R. J. Cross and F. Glockling, *J. Organometallic Chem.*, 1965, **3**, 253.
[112] J. Chatt, *Proc. Chem. Soc.*, 1962, 318.

alkali. The same compound can be obtained by the halogen–metal exchange reaction:



$$(R_3P)_2Pt(I)GePh_3 + Ph_3GeLi \rightarrow (R_3P)_2Pt(Li)GePh_3 + Ph_3GeI \quad \xrightarrow{H_2O} \text{(VI)}$$

Palladium–germanium complexes such as $(Et_3P)_2Pd(GePh_3)_2$ are of much lower thermal stability than their platinum analogues, but for the anionic cyanide complex $(Me_4N)_2[(CN)_2Pd(GePh_3)_2]$ the thermal stability is greatly enhanced.[113] Complexes involving germanium bonded to Cu, Ag, Au, Pd, and Pt all react quantitatively with 1,2-dibromoethane in what may well involve four-centred transition intermediates:

$$Ph_3P{\cdot}Au{\cdot}GePh_3 + C_2H_4Br_2 \rightarrow Ph_3P{\cdot}AuBr + Ph_3GeBr + C_2H_4$$

Spectroscopic properties

Infrared Spectra.—The Ge–H stretching frequency has been related to the Taft σ^* coefficients for a range of organogermanium hydrides.[114]

$$\nu(\text{GeH}) = 2008 + 16{\cdot}5\ \Sigma\sigma^*$$

Some of the most useful infrared bands found in organogermanes are listed in Table 2.[2,115,116,117] In some cases too few compounds have been examined to establish a frequency range.

TABLE 2. *Infrared spectra of organogermanes*

Frequency (cm.$^{-1}$)	Assignment	Frequency (cm.$^{-1}$)	Assignment
3651^a	νGeO–H[116]	700—670	νGe–OR
2063—1953	νGe–H	648—640	νGe–Bu trans
1473—1433	νGe–D	600—520	$\nu_{\text{asym.}}$Ge–C aliphatic
1427—1422	$\delta_{\text{asym.}}CH_3$	520—472	δGe–D
1259—1227	$\delta_{\text{sym.}}CH_3$	474^a	νGe–P
1093—1081	Characteristic Ph–Ge	425—362	νGe–Cl
		417	νGe–S[86a]
1040	νGe–OR[2]	351^a	νGe–Si
954^a	νGe–OP	335—312	Characteristic Ph–Ge
926—820	νGe–OGe	330—252	νGe–Br
719—710	δGe–H	303—268	Characteristic Ph–Ge
702	νGe–F[117]	283—263	νGe–I
		228	νGe–Ge

^{a}Single compound only

Raman Spectra.—Several studies have been made;[2] the Raman spectrum of Me_6Ge_2 has given ν(Ge–Ge) as 273 cm.$^{-1}$.

[113] E. H. Brooks and F. Glockling, *Chem. Comm.*, 1965, 510.
[114] R. Mathis, J. Satge, and F. Mathis, *Spectrochim. Acta*, 1962, **18**, 1463.
[115] R. J. Cross and F. Glockling, *J. Organometallic Chem.*, 1964, **3**, 146.
[116] R. West and R. H. Baney, *J. Phys. Chem.*, 1960, **64**, 822.
[117] T. N. Srivastava and M. Onyszchuk, *Proc. Chem. Soc.*, 1961, 205.

Ultraviolet Absorption Spectra.—Few studies have so far been reported,[2] but it is apparent that the ultraviolet spectra of organo-derivatives containing Group IV metal–metal bonds are of considerable interest.[118,118a] These commonly show a moderately strong absorption band between 200 and 300 mμ even in the absence of aromatic groups (Ph_6Ge_2,[119] λ_{max} 239; $Pr^i{}_6Ge_2$,[11] λ_{max} 210 mμ), due to the metal–metal bond chromophore. Silicon and germanium atoms directly attached to carbonyl and other chromophores such as the azide group produce a marked bathochromic effect on the long-wavelength transition of the chromophore.[120] In phenylpolysilanes of the type $Ph(Me_2Si)_nPh$ λ_{max} and ϵ increase as n increases.[120a,120b]

Proton Magnetic Resonance.—The proton resonances of a number of SiH, GeH, and SnH compounds have been examined;[45,121,122,123,124] these fall on the low-field side of tetramethylsilane, showing that a proton bonded to a non-transition metal atom does not have a large diamagnetic shielding.[125] Some examples are given in Table 3. The chemical shifts of methyl and ethyl protons in a number of alkylgermanium hydrides, halides, and alkoxides show an approximately linear relationship to the sum of the Taft σ^* coefficients.

TABLE 3. *Chemical shifts*[a]

	$\tau(CH_3)$	$\tau(CH_2)$		$\tau(GeH)$
Me_2GeEt_2	9·92	9·31	GeH_4	6·83
Et_3GeH		9·23	$MeGeH_3$	6·54
$EtGeBr_3$		7·70	Me_2GeH_2	6·24
Me_3GeCl	9·41		Me_3GeH	6·54
Me_2GeCl_2	8·86		Ph_2GeH_2	4·91
$MeGeCl_3$	8·42		Ph_3GeH	4·31

[a]Tetramethylsilane as internal standard

[118] W. Drenth, M. J. Janssen, G. J. M. van der Kerk, and J. A. Vliegenthart, *J. Organometallic Chem.*, 1964, **2**, 265.

[118a] D. N. Hague and R. H. Prince, *Chem. and Ind.*, 1964, 1492.

[119] D. N. Hague and R. H. Prince, *Proc. Chem. Soc.*, 1962, 300.

[120] R. West, *J. Organometallic Chem.*, 1965, **3**, 314.

[120a] H. Gilman, W. H. Atwell, and G. L. Schwelke, *J. Organometallic Chem.*, 1964, **2**, 369.

[120b] H. Gilman and W. H. Atwell, *J. Organometallic Chem.*, 1965, **4**, 176.

[121] P. E. Potter, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1964, 524.

[122] A. N. Egorochkin, M. L. Khidekel, V. A. Ponomarenko, G. Ya. Zueva, and G. A. Razuvaev, *Izvest. Akad. Nauk S.S.S.R., Ser. Khim.*, 1963, 1865; 1964, 373.

[123] H. Schmidbaur, *Chem. Ber.*, 1964, **97**, 1639.

[124] H. C. Clark, J. T. Kwon, L. W. Reeves, and E. J. Wells, *Inorg. Chem.*, 1964, **3**, 907.

[125] A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.*, 1964, 2747.