# COMPREHENSIVE ORGANOMETALLIC CHEMISTRY

The Synthesis, Reactions and Structures
of Organometallic Compounds

*Editor*
SIR GEOFFREY WILKINSON, FRS

*Deputy Editor*
F. GORDON A. STONE, FRS

*Executive Editor*
EDWARD W. ABEL

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# COMPREHENSIVE ORGANOMETALLIC CHEMISTRY

## The Synthesis, Reactions and Structures of Organometallic Compounds

### Volume 1

EDITOR

### Sir Geoffrey Wilkinson, FRS

*Imperial College of Science & Technology*
*University of London*

DEPUTY EDITOR

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*University of Bristol*

EXECUTIVE EDITOR

### Edward W. Abel

*University of Exeter*

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# COMPREHENSIVE
# ORGANOMETALLIC CHEMISTRY

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Chemistry

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# Preface

Although the discovery of the platinum complex that we now know to be the first $\pi$-alkene complex, $K[PtCl_3(C_2H_4)]$, by Zeise in 1827 preceded Frankland's discovery (1849) of diethylzinc, it was the latter that initiated the rapidly developing interest during the latter half of the nineteenth century in compounds with organic groups bound to the elements. This era may be considered to have reached its apex in the discovery by Grignard of the magnesium reagents which occupy a special place because of their ease of synthesis and reactivity. With the exception of trimethyl-platinum chloride discovered by Pope, Peachy and Gibson in 1907 by use of the Grignard reagent, attempts to make stable transition metal alkyls and aryls corresponding to those of main group elements met with little success, although it is worth recalling that even in 1919 Hein and his co-workers were describing the 'polyphenylchromium' compounds now known to be arene complexes.

The other major area of organometallic compounds, namely metal compounds of carbon monoxide, originated in the work starting in 1868 of Schützenberger and later of Mond and his co-workers and was subsequently developed especially by Hieber and his students. During the first half of this century, aided by the use of magnesium and, later, lithium reagents the development of main group organo chemistry was quite rapid, while from about 1920 metal carbonyl chemistry and catalytic reactions of carbon monoxide began to assume importance.

In 1937 Krause and von Grosse published their classic book 'Die Chemie der Metallorganischen Verbindungen'. Almost 1000 pages in length, it listed scores of compounds, mostly involving metals of the main groups of the periodic table. Compounds of the transition elements could be dismissed in 40 pages. Indeed, even in 1956 the stimulating 197-page monograph 'Organometallic Compounds' by Coates adequately reviewed organo transition metal complexes within 27 pages.

Although exceedingly important industrial processes in which transition metals were used for catalysis of organic reactions were developed in the 1930s, mainly in Germany by Reppe, Koch, Roelen, Fischer and Tropsch and others, the most dramatic growth in our knowledge of organometallic chemistry, particularly of transition metals, has stemmed from discoveries made in the middle years of this century. The introduction in the same period of physical methods of structure determination (infrared, nuclear magnetic resonance, and especially single-crystal X-ray diffraction) as routine techniques to be used by preparative chemists allowed increasingly sophisticated exploitation of discoveries. Following the recognition of the structure of ferrocene, other major advances quickly followed, including the isolation of a host of related $\pi$-complexes, the synthesis of a plethora of organometallic compounds containing metal–metal bonds, the characterization of low-valent metal species in which hydrocarbons are the only ligands, and the recognition from dynamic NMR spectra that ligand site exchange and tautomerism were common features in organometallic and metal carbonyl chemistry. The discovery of alkene polymerization using aluminium alkyl–titanium chloride systems by Ziegler and Natta and of the Wacker palladium–copper catalysed ethylene oxidation led to enormous developments in these areas.

In the last two decades, organometallic chemistry has grown more rapidly in scope than have the classical divisions of chemistry, leading to publications in journals of all national chemical societies, the appearance of primary journals specifically concerned with the topic, and the growth of annual review volumes designed to assist researchers to keep abreast of accelerating developments.

Organometallic chemistry has become a mature area of science which will obviously continue to grow. We believe that this is an appropriate time to produce a comprehensive review of the subject, treating organo derivatives in the widest sense of both main group and transition elements. Although advances in transition metal chemistry have appeared to dominate progress in recent years, spectacular progress has, nevertheless, also been made in our knowledge of organo compounds of main group elements such as aluminium, boron, lithium and silicon.

In these Volumes we have assembled a compendium of knowledge covering contemporary organometallic and carbon monoxide chemistry. In addition to reviewing the chemistry of the ele-

ments individually, two Volumes survey the use of organometallic species in organic synthesis and in catalysis, especially of industrial utility. Within the other Volumes are sections devoted to such diverse topics as the nature of carbon–metal bonds, the dynamic behaviour of organometallic compounds in solution, heteronuclear metal–metal bonded compounds, and the impact of organometallic compounds on the environment. The Volumes provide a unique record, especially of the intensive studies conducted during the past 25 years. The last Volume of indexes of various kinds will assist readers seeking information on the properties and synthesis of compounds and on earlier reviews.

As Editors, we are deeply indebted to all those who have given their time and effort to this project. Our Contributors are among the most active research workers in those areas of the subject that they have reviewed and they have well justified international reputations for their scholarship. We thank them sincerely for their cooperation.

Finally, we believe that 'Comprehensive Organometallic Chemistry', as well as providing a lasting source of information, will provide the stimulus for many new discoveries since we do not believe it possible to read any of the articles without generating ideas for further research.

E. W. ABEL                                                                     F. G. A. STONE
*Exeter*                                                                       *Bristol*

G. WILKINSON
*London*

# Contributors to Volume 1

Dr N. A. Bell
Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB, UK

Professor J. J. Eisch
Department of Chemistry, State University of New York at Binghamton,
Binghamton, NY 13901, USA

Professor R. N. Grimes
Department of Chemistry, University of Virginia, Charlottesville, VA 22901, USA

Professor G. E. Herberich
Institute für Anorganische Chemie der Technischen Hochschule Aachen,
Templergraben 55, D-5100 Aachen, Federal Republic of Germany

Dr H. Kurosawa
Department of Petroleum Chemistry, Osaka University, Yamadakami, Suita, Osaka, Japan

Dr W. E. Lindsell
Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh EH14 4AS, UK

Dr J. H. Morris
Department of Pure and Applied Chemistry, University of Strathclyde,
Thomas Graham Building, 295 Cathedral Street, Glasgow G1 1XL, UK

Professor J. D. Odom
Department of Chemistry, University of South Carolina, Columbia, SC 29208, USA

Professor T. Onak
Department of Chemistry, California State University, 5151 State University Drive,
Los Angeles, CA 90032, USA

Dr M. E. O'Neill
Chemistry Department, Durham University Science Laboratories, South Road,
Durham DH1 3LE, UK

Professor L. J. Todd
Department of Chemistry, Indiana University, Chemistry Building,          .
Bloomington, IN 47401, USA

Professor D. G. Tuck
Department of Chemistry, University of Windsor, Windsor, Ontario N9B 3P4, Canada

Dr K. Wade
Chemistry Department, Durham University Science Laboratories, South Road,
Durham DH1 3LE, UK

Dr J. L. Wardell
Department of Chemistry, University of Aberdeen, Meston Walk,
Old Aberdeen AB9 2UE, UK

# Contents of Other Volumes

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# Contents

# 1

# Structural and Bonding Relationships among Main Group Organometallic Compounds

M. E. O'NEILL and K. WADE

*University of Durham*

## 1.1 INTRODUCTION

### 1.1.1 General Considerations

Although this series of volumes, as the adjective 'comprehensive' in the title implies, is intended to provide a reasonably full account of organometallic chemistry, the purpose of this introductory chapter is to indicate the salient structural and bonding features of main group organometallic compounds by use of illustrative examples rather than by a comprehensive coverage. It is hoped that this will convey some feeling not only for the reasons why certain organometallic compounds have rather peculiar structures, but also for the relative stabilities and reactivities of the various types of compound, characteristics relevant to some of the chapters of Volumes 7 and 8 as well as to the other chapters in the present volume and Volume 2, to which the reader is referred for further details of specific systems.

The definition of organometallic compound used here is that which is most commonly used:[1-8] we shall be concerned with compounds in which the organic groups or residues are attached to metal atoms by metal–carbon bonds. Also in conformity with common practice, we shall include in our discussion some systems that strictly should be described as 'organometalloidal', for example organo-boron, -silicon, -germanium and -arsenic systems. By doing so, we shall be considering together as one family the organo derivatives of elements more electropositive than carbon. Like metal–carbon bonds, metalloid–carbon bonds in general have a polarity $M^{\delta+}$—$C^{\delta-}$, which is one of the characteristic features that distinguish organometallic compounds from other types of organic compound, in which carbon is found at the positive end of bonds to nonmetallic elements like nitrogen, oxygen, fluorine, chlorine or bromine.

This bond polarity makes the organic groups R in metal alkyls or aryls, $MR_n$, carbanionic in character, susceptible to attack by electrophiles, while the metal atoms themselves are susceptible to nucleophilic attack, not only on account of their positive charges, but also because they generally have vacant orbitals that can accommodate electronic charge from nucleophiles. This in turn is because most (though not all) metal atoms have more valence shell orbitals than electrons, so when the electrons are paired off in bonds to alkyl or aryl groups, the surplus orbitals remain empty, or else find limited use in multicentre metal–carbon bonding, one pair of electrons being associated with two or more metal atoms as well as one carbon atom, instead of being shared between just one metal and one carbon atom.

These characteristics of organometallic systems, which are discussed in more detail below, may be contrasted with those of other types of organic compound in which the atoms of non-metallic elements like nitrogen, oxygen or the halogens (which have more valence shell electrons than orbitals) generally possess lone pairs of electrons and function as the sites for attack by electrophiles.

In the following sections we outline the manner in which organometallic compounds can be broadly classified according to their structural types, and consider some thermochemical aspects of organometallic chemistry relevant to the synthesis, stability and reactivity of organometallic compounds. Attention is then focused on the various types of structural unit that are found among main group organometallic systems, and the special bonding problems they pose: organometallic chemistry has provided a rich territory for theoreticians in search of stimulating problems.

### 1.1.2 The Main Structural Types

Although, as indicated above, a bond polarity $M^{\delta+}$—$C^{\delta-}$ is a general characteristic of organometallic systems, the degree of this polarity, and the tendency of systems to adopt associated structures involving multicentre metal–carbon bonding, are characteristics that vary markedly with the metal. Since they are reflected in the bulk properties of metal alkyls and aryls, they form a convenient basis for the classification of organometallic compounds, as illustrated in Figure 1.[5,7]

For example, the metal–carbon bonds in alkyl derivatives of the less electropositive metals and metalloids like boron, silicon, germanium and arsenic are only slightly polar. Such derivatives are typically 'organic' in their bulk properties: low melting, volatile, soluble in non-polar solvents. The boiling temperatures of the methyl derivatives given in Table 1[5] show, for instance, that these derivatives are much more volatile than most other derivatives of these elements. Thus trimethylborane, $BMe_3$ (b.p. $-22\,°C$), has a volatility similar to that of the comparable alkane isobutane, $CHMe_3$ (b.p. $-12\,°C$), while the boiling points of the tetramethyls, $MMe_4$, of the Group IV elements (M = C, Si, Ge, Sn and Pb) show only a slight increase with molecular mass down the

Li Be → metals with a strong tendency to form alkyl- or aryl-bridged species → B C N O F Ne

Na* Mg / Al Si P S Cl Ar

K Ca* Sc* Ti V Cr Mn Fe Co Ni Cu* Zn Ga* Ge As Se Br Kr

Rb Sr Y* Zr Nb Mo Tc Ru Rh Pd Ag Cd In* Sn Sb Te I Xe

Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl* Pb Bi Po At Rn

metals that form ionic derivatives

transition metals; $\pi$-complexes tend to predominate

metals and metalloids that form volatile, covalent organo derivatives

non-metals

*metals that also participate in alkyl- or aryl-bridging

**Figure 1** Types of organometallic compound

**Table 1** The Boiling Temperatures (°C) of the Methyl Derivatives $MMe_n$ of Some Metals and Metalloids

| MMe$_2$ | | MMe$_3$ | | MMe$_4$ | | MMe$_3$ | |
|---|---|---|---|---|---|---|---|
| Be | 220[a,b] | B | −22 | C | 10 | N | 3 |
| Mg | —[b] | Al | 126[c] | Si | 27 | P | 40 |
| Zn | 44 | Ga | 56 | Ge | 43 | As | 52 |
| Cd | 106 | In | 136 | Sn | 77 | Sb | 79 |
| Mg | 93 | Tl | 147[a] | Pb | 110 | Bi | 110 |

[a] Extrapolated boiling temperature. [b] Unlike their Group II congeners, which have discrete molecular structures $MMe_2$, the dimethyl derivatives of beryllium and magnesium have associated polymeric structures $(MMe_2)_n$ in the solid phase. The volatility of $(MgMe_2)_n$ is too low to allow a meaningful boiling/sublimation temperature to be quoted. [c] Trimethylaluminium crystallizes and vaporizes as the dimer $Al_2Me_6$.

group. Some representative structures of these molecular methyl derivatives are shown in Figure 2a. Note that the trimethyl derivatives of the Group V metals arsenic, antimony and bismuth are unusual among main group metal alkyls in possessing lone pair electrons on their metal atoms.

In contrast to these systems, organo derivatives of the most electropositive metals like sodium or potassium are essentially ionic, $M^+R^-$. These exceedingly reactive substances have salt-like properties such as high melting temperatures, low volatilities, and low or negligible solubilities in non-polar, noncoordinating solvents like pentane or hexane. Between these two extremes are systems with highly polar but nevertheless essentially covalent metal–carbon bonds, the polarity of which acts as a source of reactivity; these systems include such useful reagents as lithium alkyls, magnesium alkyls and aryls (Grignard reagents), and aluminium alkyls. It is these same metals that show the most marked tendency to indulge in multicentre bonding: their alkyls and aryls adopt associated structures (Figure 2b) in which the bonding power of pairs of electrons is spread over more than just two atoms. Since the study of such systems has done much to clarify our understanding of chemical bonding in general as well as metal–carbon bonding in particular, and since these associated structures serve as models for the intermediates or transition states in many organic reactions, particular attention will be focused on them in the present survey.

A third category of structure (Figure 2c) found occasionally among main group organometallic compounds, though much more often among transition metal derivatives (see Volumes 3–6), is that of metal–hydrocarbon $\pi$-complexes. In these the metal atom or ion is located above the plane of a set of carbon atoms in an unsaturated organic ligand like an alkene or alkyne, a cyclopentadienyl ring, or a benzyl residue, making use of the $\pi$-bonding electrons of the ligand to bond strongly to two or more of the ligand carbon atoms.

These various structural types can conveniently be distinguished by indicating the number of carbon atoms through which a particular ligand coordinates to a metal (the *hapticity* of the ligand, designated either by $h^n$ or $\eta^n$ in the formula), and the number of metal atoms to which that ligand bonds. For example, when a monovalent organic residue like an alkyl or aryl group bonds terminally to a single metal atom through just one of its carbon atoms, its mode of attachment is referred
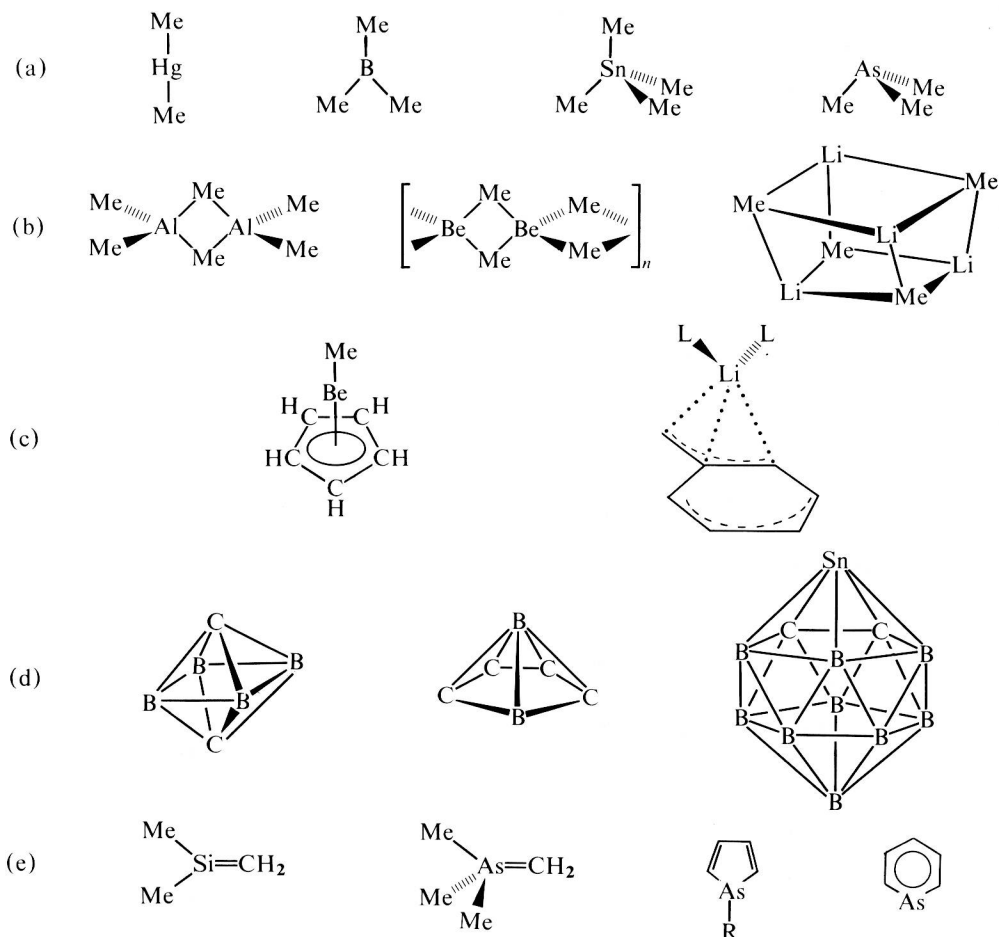
**Figure 2** Some representative structures of main group organometallic compounds. (a) Molecular structures of the monomeric metal methyls $HgMe_2$, $BMe_3$, $SnMe_4$ and $AsMe_3$. (b) The associated structures of $(AlMe_3)_2$, $(BeMe_2)_n$ and $(LiMe)_4$, *i.e.* $Al_2Me_4(\mu_2\text{-}Me)_2$, $[Be(\mu_2\text{-}Me)_2]_n$ and $[Li(\mu_3\text{-}Me)]_4$. (c) The metal–hydrocarbon $\pi$-complexes $BeMe(\eta^5\text{-}C_5H_5)$ and $Li(\eta^3\text{-}CH_2C_6H_5)\cdot N(CH_2CH_2)_3N$. (d) The carboranes and metallacarboranes $C_2B_4H_6$, $C_4B_2H_6$ and $Sn(\eta^5\text{-}C_2B_9H_{11})$; each carbon and boron atom has one terminal hydrogen atom attached (not shown). (e) Species containing metal–carbon multiple bonds

to as monohapto ($h^1$ or $\eta^1$) or $\sigma$-bonded. When a similar monovalent group bridges two metal atoms, as do two of the six methyl groups of hexamethyldialuminium, $Al_2Me_6$ (Figure 2b), its mode of bonding is referred to as $\mu_2$. The methyl ligands of tetrameric methyllithium, $(LiMe)_4$, bridge three metal atoms (Figure 2b) and so are referred to as $\mu_3$-bonded. The cyclopentadienyl residue in cyclopentadienyl(methyl)beryllium, $MeBe(C_5H_5)$ (Figure 2c), is $h^5$ (or $\eta^5$) bonded.

Examples of a fourth category of structure among main group organometallic compounds are shown in Figure 2d. These are carboranes[9] and metallacarboranes,[10] mixed cluster systems containing carbon and boron atoms or carbon, boron and metal atoms in their polyhedral molecular skeletons. The development of our understanding of how their molecular skeletons are held together by relatively few electrons (like bridged metal alkyls, they are electron deficient[11] in the sense that they contain fewer bond pairs than bonding atom contacts) has provided a welcome stimulus to bonding theories and allowed us to recognize the family relationships that link metal–hydrocarbon $\pi$-complexes with boron hydride and metal carbonyl clusters on the one hand, and carbocations and small ring hydrocarbon systems on the other.[12] These points will be illustrated in Section 1.6 below.

One further category of compound that is little represented in main group organometallic chemistry, though of increasing importance in transition metal chemistry, is that of species containing metal–carbon multiple bonds (Figure 2e). Carbene complexes, $L_nM{=}CR_2$, or carbyne complexes, $L_nM{\equiv}CR$, where M is a main group metal of Groups I–IV, are generally unstable to association, *e.g.* equation (1). Evidently their multiple bonds represent a less strong bonding arrangement than the greater number of single bonds that form when they oligomerize or poly-

$$2Me_2Si=CH_2 \longrightarrow Me_2Si\diagdown_{CH_2}^{CH_2}\diagup SiMe_2 \qquad (1)$$
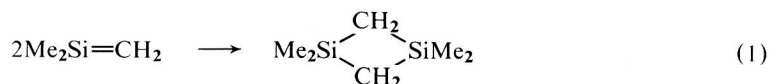
merize. The monomers are known only as highly reactive short-lived intermediates in certain reactions. Monomeric arsenic, antimony and bismuth ylides, $R_3MCR'_2$, analogues of Wittig reagents $R_3PCR'_2$, are known, however, and these same metal atoms have been incorporated adjacent to carbon atoms in unsaturated ring systems like arsabenzene (*cf.* pyridine, see Figure 2e) and arsoles (*cf.* pyrroles), though the aromaticity of these ring systems is markedly less than that of their nitrogen analogues. The metal-carbon bonds in the ylides are perhaps better represented by the canonical form $L_n\overset{+}{M}-\overset{-}{C}R_2$ rather than $L_nM=CR_2$.

Further elaboration of these structural and bonding aspects will be found below after a brief survey of thermochemical aspects of main group organometallic chemistry in Section 1.2.

## 1.2 THERMOCHEMICAL ASPECTS

### 1.2.1 General Considerations

The usefulness of many organometallic compounds as reagents, and their reactivity towards oxidizing agents, acids, water and assorted multiply-bonded compounds, reflects the relative weakness of metal-carbon bonds compared with metal-nitrogen, -oxygen or -halogen bonds. Most metal alkyls and aryls, $MR_n$, are thermodynamically (though not necessarily kinetically) unstable to hydrolysis to metal hydroxide, $M(OH)_n$, and hydrocarbon, RH, and also, like organic compounds in general, are unstable to oxidation to metal oxide, carbon dioxide and water. Many are also thermodynamically unstable with respect to their constituent elements (M, C and $H_2$) or to the mixture of hydrogen, hydrocarbons and metal that normal thermal decomposition would afford. Some, like the simpler alkyls and aryls of lithium, magnesium, zinc, boron and aluminium, are so reactive to oxygen and/or moisture as to need protection from the atmosphere. Such compounds need to be prepared, characterized, stored and used under controlled atmosphere conditions, *e.g.* in apparatus filled with dry nitrogen or argon, or under vacuum. Others, although thermodynamically unstable with respect to oxidation and hydrolysis, nevertheless survive exposure to air and moisture only because there is no easy route by which such reactions can proceed. In order to appreciate the category into which specific compounds fall, it is helpful to consider some of the considerable body of thermochemical data now available on organometallic compounds.[6,13,14]

### 1.2.2 Enthalpies of Formation and Bond Enthalpies

The standard molar enthalpies of formation ($\Delta H_f^\circ$) and metal-carbon average molar bond enthalpies ($E_m(M-C)$) of some gaseous metal methyls, $MMe_n$, of main group metals M are given in Table 2. The group trends in $\Delta H_f^\circ$ are illustrated in Figure 3. From Table 2 and Figure 3 it is apparent that decomposition of these compounds into the metal or metalloid M, carbon and hydrogen would be an exothermic process for such heavy metal alkyls as $HgMe_2$, $PbMe_4$ and $BiMe_3$ (*i.e.* $-\Delta H_f^\circ$ is negative), and also for $ZnMe_2$, $CdMe_2$ and $InMe_3$. However, for such compounds as $BMe_3$, $AlMe_3$, $SiMe_4$ and $GeMe_4$, the process would be endothermic ($-\Delta H_f^\circ$ is positive).

The metal-carbon average molar bond enthalpies (or bond enthalpy terms), $E(M-C)$ in Table 2, represent the average enthalpy terms associated with the metal-carbon bonds of $MMe_n$, such that the enthalpy change for the disruption of these compounds into metal atoms and methyl

**Table 2** Standard Molar Enthalpies of Formation ($\Delta H_f^\circ$/kJ mol$^{-1}$) and Metal-Carbon Average Molar Bond Enthalpies ($E_m(M-C)$/kJ mol$^{-1}$) of Some Gaseous Metal Methyls $MMe_n$

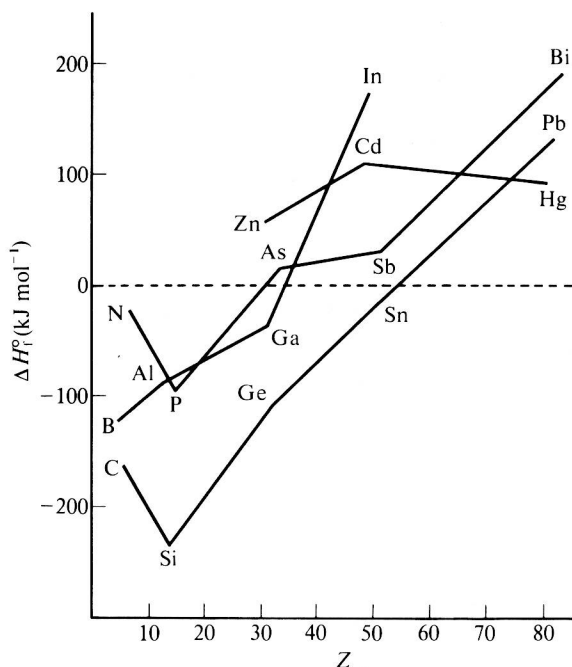| *Group II*, $MMe_2$ | | | *Group III*, $MMe_3$ | | | *Group IV*, $MMe_4$ | | | *Group V*, $MMe_3$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| M | $\Delta H_f^\circ$ | $E_m$ | M | $\Delta H_f^\circ$ | $E_m$ | M | $\Delta H_f^\circ$ | $E_m$ | M | $\Delta H_f^\circ$ | $E_m$ |
| — | — | — | B | −123 | 365 | C | −167 | 358 | N | −24 | 314 |
| — | — | — | Al | −81 | 274 | Si | −245 | 311 | P | −101 | 276 |
| Zn | 50 | 177 | Ga | −42 | 247 | Ge | −71 | 249 | As | 13 | 229 |
| Cd | 106 | 139 | In | −173 | 160 | Sn | −19 | 217 | Sb | 32 | 214 |
| Hg | 94 | 121 | Tl | — | — | Pb | 136 | 152 | Bi | 194 | 141 |

**Figure 3**   Group trends in the standard molar enthalpies of formation, $\Delta H_f^\circ$, of some gaseous metal methyls

radicals is equal to $nE(\text{M—C})$. The manner in which they vary with M is worth noting. Boron–carbon bonds are slighly stronger than carbon–carbon bonds, but the larger Group III metals form M—C bonds that get progressively weaker as the group is descended. Similar group trends are to be seen in Groups II, IV and V: within each group, the metal–carbon bonds get weaker as they get longer.
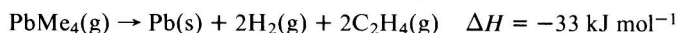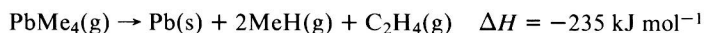
### 1.2.3 Thermal Stability

The above thermochemical data provide a rough guide to the thermodynamic stability of these metal alkyls, in the absence of free energy data for specific reactions, but have to be used with caution if an indication of thermal stability is required. Generally, metal alkyls decompose, when heated, into assorted hydrocarbons, some hydrogen and the metal (or metal hydride), rather than into the constituent elements, so the enthalpies of formation of the hydrocarbon products must be taken into account.

As an example of how the identities of the hydrocarbons produced can influence the enthalpy change associated with the decomposition of a metal alkyl, one can consider different possible modes of decomposition of tetramethyllead, $PbMe_4$, which normally generates ethane *via* methyl radicals:[15]

$$PbMe_4(g) \rightarrow Pb(s) + 2C_2H_6(g)$$
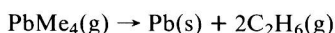
Since the standard molar enthalpy of formation of ethane, $\Delta H_f^\circ$, is $-85 \text{ kJ mol}^{-1}$,[6] the enthalpy change for this decomposition reaction is $-307 \text{ kJ mol}^{-1}$. The reaction is thus highly exothermic, some $170 \text{ kJ mol}^{-1}$ more so than the hypothetical decomposition into the elements in their standard states. Moreover, since the reaction generates more gaseous molecules than it consumes, it would be expected to be accompanied by an increase in entropy. With $T\Delta S$ positive and $\Delta H$ negative, $\Delta G (= \Delta H - T\Delta S)$ would also be negative, implying that $PbMe_4$ is thermodynamically very unstable with respect to these products.

Other possible decomposition reactions are as follows:

$$PbMe_4(g) \rightarrow Pb(s) + 2MeH(g) + C_2H_4(g) \quad \Delta H = -235 \text{ kJ mol}^{-1}$$
$$PbMe_4(g) \rightarrow Pb(s) + 2H_2(g) + 2C_2H_4(g) \quad \Delta H = -33 \text{ kJ mol}^{-1}$$

These are clearly thermodynamically less likely reactions, and in practice hydrogen, methane and ethylene feature only as minor decomposition products.