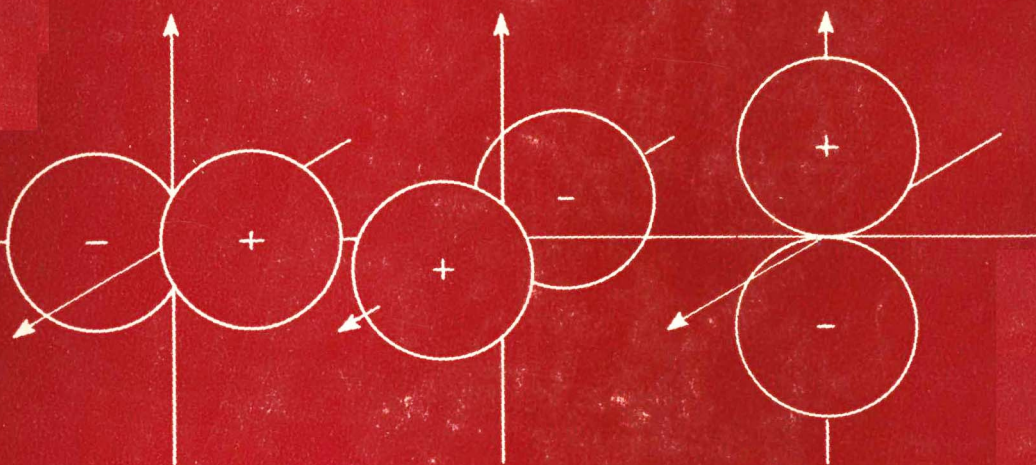


THE CHEMISTRY OF ORGANOMETALLIC COMPOUNDS



ROCHOW

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HURD

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LEWIS

A comprehensive, unified coverage of the theoretical, factual, and practical aspects of organometallic compounds.

John Wiley & Sons, Inc., publishers

The Chemistry of Organometallic Compounds

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--- Preface

Even in the days when the line between organic and inorganic chemistry was quite sharply drawn, chemists of either variety had to know something about the preparation and utilization of organometallic compounds. The application of organometallic substances like the Grignard reagents to the synthesis of organic compounds is so vital as to occupy a prominent place even in introductory courses, and the role of similar reagents in expanding our knowledge of elements like silicon, tin, and lead is equally respected in systematic courses on inorganic chemistry. Nevertheless, the treatment in either course is usually functional (if not perfunctory) in its approach and empirical in its details. There are, of course, some good reference works like Krause and von Grosse's *Die Chemie der metallorganischen Verbindungen* (1937) and the Goddard and Goddard volumes in *Friend's Textbook on Inorganic Chemistry* (1930), but these by their very completeness are large and formidable to the student and usually remain library references. We have seen a need for a comprehensive and integral treatment of the subject in a rather brief and readable form, and we have tried to meet that need with this volume.

In the middle 1940's we were associates in the General Electric Research Laboratory. Since that time, two of us have taught graduate courses in the chemistry of organometallic compounds at Harvard University and at the University of Delaware, and in our individual researches all of us have been intimately concerned with the preparation and utilization of organometallic compounds. We have tried to bring our differing trainings and experiences to bear on a general approach to this subject within the confines of a small book that must be short in order to be available to its intended audience. We have tried

to present the theoretical, factual, and practical aspects of organometallic compounds in a form that will be useful to the student and to the more general reader with a background in college chemistry. We have not written a compendium (which would have had to be truly immense *), but instead have tried to be selective and critical in our choice of topics and examples.

The subject matter has been organized on the basis of the general properties of the carbon-metal bond; electronegativity and bond polarity have been used freely as indicative of the type of organometallic compound to be expected in a given instance. Considerable use has been made of the classical studies of Gilman in this field, including his valuable reactivity series, and we are grateful to him for the guidance thus offered. While the general plan of the book is described in more detail in the introduction, we should like to emphasize the preference we have shown for considering the broad governing principles of the subject before taking up any of the descriptive material.

It would have been easy to write at greater length about our own research interests and to include a great deal of information about Grignard reagents and their usefulness in the laboratory and in industrial practice. However, since there have appeared a number of books devoted exclusively to Grignard reagents, and since more such books apparently are in prospect, we have felt justified in assigning to organomagnesium compounds only the amount of importance due them as interesting examples of their type of substance.

It is our hope that this volume will find some usefulness among graduate students in chemistry as well as among research workers who are inclined (or would like to incline) toward the field that we find so interesting. We should appreciate comments concerning the organization and coverage of the book, and, of course, we shall be indebted to any of our readers who find errors of fact or statement and bring them to our attention.

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February, 1957

* As one measure of the necessary length, consider the excellent work by M. S. Kharasch and Otto Reinmuth on *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, New York, 1954, which devoted 1384 pages to this one area of the subject in order to be complete.

Contents

	Introduction	1
Chapter 1	General Considerations	5
2	Theory of the Carbon-Metal Bond	15
3	Preparative Methods	42
4	Compounds of the Alkali Metals	65
5	Compounds of the Group II Elements	77
6	Compounds of the Group III Elements	124
7	Compounds of the Group IV Elements	142
8	Compounds of the Group V Elements	198
9	Compounds of the Group VI and VII Elements	224
10	Compounds of the Transition Metals	231
11	Organometallic Compounds in Organic Synthesis	275
12	Special Types of Organometallic Compounds	310
	Author Index	321
	Subject Index	335

Introduction

The history of organometallic compounds is commonly supposed to have begun with the famous researches of Robert Bunsen on cacodyl, $(\text{CH}_3)_4\text{As}_2$, in 1841, although unrecognized organic derivatives of metals must surely have been encountered long before. Bunsen considered that he had found a good example of an organic "element" (which we would now call a radical) in the methyl group which formed so interesting a compound with arsenic, and so made a considerable contribution to the theory of chemical constitution. Many more such significant contributions were to come during the next thirty years, for newly discovered organic compounds of mercury, cadmium, zinc, tin, lead, silicon, and many other metals added much to our understanding of these elements. For one thing, the assignment of the first accurate atomic weights of these metals was facilitated by the study of their alkyl compounds. One must remember that a century ago, when the perfection of gravimetric methods of analysis allowed the accurate determination of relative combining weights, there was still confusion between combining weights and atomic weights because the principal or "characteristic" valences of the elements were not known. These confusions could not be resolved by inorganic procedures if the element in question formed two or more chlorides or oxides, as so many elements did. However, each metallic element was found to form only one volatile compound with ethyl or methyl groups, if it formed any at all, and this one ethyl or methyl derivative could be purified to any desired degree by distillation. Analysis for carbon and hydrogen by the well-established procedures of combustion analysis then provided unequivocal evidence about the number of "normal" valencies the metal ex-

hibited, and hence led to a clear choice of atomic weight. With unequivocal weights and valencies, a periodic system of the elements became possible.¹

After a period of decreased activity from 1875 to 1895, organo-metallic chemistry erupted at the turn of the century with a series of brilliant discoveries in the areas of chemotherapy and organic synthesis. We need only mention the names of Ehrlich, Grignard, and Schlenk to call to mind this golden age and the mark it has left on organic, inorganic, and physiological chemistry. Again to cite but one example of effect, and that taken from what was an obscure corner of chemistry at the time, Kipping's application of Grignard's methods to the synthesis of organic compounds of silicon opened up a whole new area of organosilicon chemistry, and this led ultimately to a new industry concerned with silicone polymers. One might turn equally well to the influence of Schlenk's work on the development of the synthetic rubber industry, or the influence of mercurials and arsenicals on medical practice of the day. Further impetus came a short time later from an entirely unexpected source, the fuel requirements of the internal-combustion engine. A series of striking deductions led Thomas Midgley to the conclusion that the phenomenon of "knocking" in such engines is related to the molecular structure of the fuel rather than to the design of the electrical ignition system, as had been thought. A long series of tests showed further that organic compounds of lead and tellurium were highly effective in altering the chemical course of the combustion, and so began the industrial production of tetraethyllead as a gasoline additive. In 1920 it would have been hard to think of a chemical less likely to achieve commercial importance, but by 1936 some twenty thousand tons a year of tetraethyllead were being produced by the sodium alloy method developed by Kraus. The annual production is now enormously greater, and has reached such proportions as to endanger our natural resources of lead (which is a decidedly scarce element anyway). Not the least important result

¹ We now take a different view of matters, and recognize it as a characteristic peculiarity of chemical bonding that lead exhibits only its group valence in forming a volatile "normal" alkyl such as tetraethyllead, $(C_2H_5)_4Pb$, whereas lead in most of its inorganic compounds separates the 6s electrons as an inert pair and acts like a divalent element. However, a century ago the bare conclusion without its explanation was none the less useful on this account. Indeed, we are still learning more about the role of the s electrons in the chemical bonding of the heavier elements through the distinctions between (for example) the volatile, colorless, monomeric tetramethyltin, $(CH_3)_4Sn$, and the less well-known yellow, polymeric, nonvolatile dimethyltin, $[(CH_3)_2Sn]_n$.

of this development has been to bring organometallic chemistry very much into public view, and so to illustrate how effective small proportions of such metallic derivatives can be when they function as catalysts. The effectiveness of dibutyltin dilaurate in preventing discoloration or degradation of polyvinyl chloride plastics provides another good example, and incidentally points out another young industry growing out of fundamental knowledge about organometallic compounds.

It should not be assumed from these rather random remarks that fundamental or theoretical organometallic chemistry (as distinct from commercial developments) has been coasting along on the discoveries of fifty or one hundred years ago. On the contrary, it now appears as though another discovery has opened up an entirely new area of organometallic chemistry and has doubled its scope. This is the preparation of biscyclopentadienyliron, or *ferrocene*, by Kealy and Pauson,² and by Miller, Tebboth, and Tremaine.³ The substance itself is remarkable for its stability and its aromatic behavior, but what is far more important is that Wilkinson, Fischer, and others have expanded the original breakthrough into a comprehensive organic chemistry of almost all of the transition metals and even most of the rare earths. These metals, comprising more than half of those in the periodic system, seemed by nature incapable of forming "normal" alkyls like those of the A-subgroup metals. Now they have a distinct organometallic chemistry of their own, the theory and practice of which is considered in later chapters.

If we were to attempt a more complete historical survey of the subject, it would be necessary to bring in at this point most of the factual material in the succeeding chapters in order to understand the nature and importance of each succeeding development. The historical approach has seemed less compact, less well organized, and less useful than a systematic survey by groups, and so the group system is followed in Chapters 4 through 10 of this book. The rest of the book is organized around this core. The types of organometallic compounds, and the general characteristics of each type, are described in Chapter 1; the theory of the carbon-metal bond in its various aspects (including the bonds to transition metals) is then discussed separately in Chapter 2. The third chapter, on methods of preparation, covers those general methods that have served for most of the substances described in

² T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951).

³ S. A. Miller, J. A. Tebboth, and J. F. Tremaine, *J. Chem. Soc.*, **1952**, 632.

Chapters 4 through 10, making unnecessary any repetition in those chapters. After a consideration of compounds of the metals by major groups (not in complete handbook listing but with critical regard for common characteristics), there follows a brief survey of the reactions of organometallic substances with organic compounds, and finally a chapter on the relation of hydrides, carbonyls, and carbides to the general subject of organometallic compounds.

There has been considerable inconsistency in the naming of organometallic compounds. In 1931 the International Union of Chemistry adopted a set of rules for the nomenclature of organic compounds.⁴ Rule 48, covering most organometallic compounds, reads as follows: "Organometallic compounds will be designated by the names of the organic radicals united to the metal which they contain, followed by the name of the metal. Examples: dimethylzinc, tetraethyllead, methylmagnesium chloride. However, if the metal is united in a complex manner it may be considered as a substituent. Example: $\text{ClHgC}_6\text{H}_4\text{COOH}$, chloromercuribenzoic acid."

We have adhered to this rule for all organometallic compounds except those of silicon, germanium, arsenic, and antimony. A special system of nomenclature has been adopted for silicon compounds,⁵ and many compounds of germanium are named as derivatives of germane, GeH_4 , by analogy with the silanes. Compounds of arsenic and antimony are named according to IUC rule 34, which considers them as derivatives of arsine and stibine. Rule 34 might be applied also to organobismuth compounds, but it is current practice to apply rule 48; for instance, $(\text{C}_6\text{H}_5)_3\text{Bi}$ is triphenylbismuth, not triphenylbismuthine.⁶

The terms *alkyl* and *aryl*, used as nouns, are general terms denoting compounds in which the metal is attached only to organic radicals. Except where it is desired to differentiate alkyl from aryl derivatives, the term *alkyl* is used as the inclusive term for R_xM compounds. Thus, diphenylzinc may be referred to as an alkyl.

No systematic nomenclature has been adopted for organometallic complexes. Two possible systems are illustrated by the names for $\text{Li}(\text{CH}_3)_4\text{B}$: lithium tetramethylboron and lithium tetramethanoborate. A third system, used in Germany, is illustrated by the term lithium tetramethylborate.

⁴ A. M. Patterson, L. T. Capell, and M. A. Magill, *Chem. Abstr.*, **39**, 5935 (1945); A. M. Patterson, *J. Am. Chem. Soc.*, **55**, 3905 (1933).

⁵ R. O. Sauer, *J. Chem. Educ.*, **21**, 303 (1944); *Chem. Eng. News*, **24**, 1233 (1946).

⁶ See for instance H. Gilman and H. L. Yale, *Chem. Revs.*, **30**, 281 (1942).

CHAPTER 1

General Considerations

SCOPE

For the present purposes *organometallic* compounds may be defined as those having carbon-metal bonds, the word *bond* being taken to include all types of chemical combination or linkage that do not involve an intermediate atom. This definition excludes salts of organic acids, chelate compounds, organosubstituted metal amines or amides, and esters or ethers of the amphoteric elements, for in all these carbon is bonded to the metal through a third element. It seems appropriate, however, to broaden the definition to the extent of including as metals all the metalloids and the elements having any metallic behavior whatever, for these add interesting examples and applications without deviating radically from the general pattern.

The formation of organic derivatives is a very general phenomenon among the chemical elements. With the exception of the inert gases, most of the elements are known to form compounds of one sort or another with hydrocarbon groups; that is, compounds in which chemical bonds are established between the element and carbon. With some elements, such organic compounds may be stable to rather high temperatures or may be quite inert chemically. With others, the organic compounds may be very unstable or highly reactive. There are a few elements for which no organic compounds have been isolated as yet, but there appears to be no theoretical reason why such elements should not form organic derivatives under some conditions, and with continued research the number of elements in this category is dwindling.

Classifying the very large number of known organometallic compounds into a few distinct types is not a simple matter. For example,

we observe that most of them are predominantly covalent, volatile, and soluble in organic solvents, whether the particular element is metallic or metalloid. The more electropositive elements form organometallic compounds that are nonvolatile, insoluble solids of considerable ionic character, and a few elements form compounds that are intermediate in nature, being solid and polymeric although more covalent than ionic; but in general we do not observe marked discontinuities in physical properties on considering the compounds of successive

H																		He
Li Be												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	
Fr Ra		Ac**																
* Rare earth metals		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
** Uranium metals		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf								

Fig. 1. Types of Organometallic Compounds

elements across a given period or down a given group of the Periodic Table. Hence, it is more appropriate to discuss organometallic compounds as a group (with emphasis on their interrelationships) than to attempt a rigid classification into types and subtypes.

To orient the reader in the field of organometallic chemistry, the Periodic Table of the elements (Fig. 1) has been marked to indicate the principal types of organometallic derivatives. It should be emphasized that in general the dividing lines do not represent sharp differentiations in physical properties or major differences in the nature of the chemical bonds between the various elements and carbon, but are drawn merely to indicate general areas. Although the figure is largely self-explanatory, a few points of interest may be mentioned. The light elements lithium, beryllium, and magnesium form organometallic compounds of intermediate character, less ionic than those of the remaining elements of Groups I and II. The transition metals are notable for the variety of their organic derivatives; ionic, covalent, and special *d*-orbital-bonded compounds are known in which a single

organic group (the cyclopentadienyl) participates. Some ionic behavior is found among the predominantly covalent compounds of the elements enclosed in solid lines, especially the heavier ones. The non-metals are not enclosed by the solid line, even though they form covalent compounds with organic radicals, simply because they are outside the scope of this book. The inert gases are the only elements that cannot conceivably form direct bonds to carbon.

FACTORS GOVERNING THE PROPERTIES OF ORGANOMETALLIC COMPOUNDS

The properties of an organometallic compound depend both on the nature of the central atom, or "parent element," and on the nature of the organic group or groups attached to that atom. Thus in considering the chemical behavior and the physical properties of an organometallic compound we will want to focus particular attention on the chemical bond between the parent element and carbon. The nature of this bond, that is, its strength and degree of polarity, is considered at length in Chapter 2. Although a knowledge of the behavior of the carbon-metal bond is essential to understanding the chemistry of organometallic compounds, other factors also are of importance.

As an example, the formation of the coordinate link in complexes between boron alkyls and amines is governed by the steric properties of the alkyl groups. Reactions are known in which groups other than organic groups attached to the central atom react without affecting the bond between the central atom and the attached organic groups; an example of this type of reaction is the hydrolysis of a methylsilicon halide to form a methylsilicon oxide or silicone. Organic groups, particularly when substituted, often can undergo characteristic organic reactions without affecting the bond between the group and the parent element. Again, the size of the attached organic groups in an organometallic compound may play an important part in determining the chemical and physical properties of the compound quite independently of the nature of the carbon-metal bond in the compound.

In comparing the properties of the various compounds, three kinds of trend will be of particular interest: (a) the effect of the organic groups, that is, the variations in properties between compounds of the same parent element with different types of attached organic groups; (b) the variations in properties between compounds having the same type of organic groups attached to successive elements within a given group of the Periodic Table; and (c) the variations in properties be-

tween compounds having the same type of organic groups attached to successive elements across a given period. These will now be considered in sequence.

The effect of the organic group

The differences in physical properties that are observed as we consider the different organic derivatives of a particular element can generally be explained quite sufficiently on the basis of the sizes, shapes and polarities of the organic groups. For example, the boiling points of the normal alkyls of silicon increase in regular fashion with the size of the organic groups:

$(\text{CH}_3)_4\text{Si}$	b.p. 26.5°	
$(\text{C}_2\text{H}_5)_4\text{Si}$	153	
$(n\text{-C}_3\text{H}_7)_4\text{Si}$	212	
$(n\text{-C}_4\text{H}_9)_4\text{Si}$	275	est. from lower pressures
$(n\text{-C}_8\text{H}_{17})_4\text{Si}$	318	

This same sort of behavior may be observed with the compounds of any of the elements in Groups III through VII (excluding the transition elements in the A-subgroups) and with compounds of the Group IIB elements zinc, cadmium, and mercury. The solid, polar compounds of the more strongly electropositive elements of Groups I and II are not volatile, so they cannot be compared in this fashion. With lithium and beryllium, however, the effect of the nature of the organic group on the properties of the compound becomes quite pronounced. With the alkyls of beryllium, for example, the dimethyl derivative differs considerably from the higher normal alkyls:

$(\text{CH}_3)_2\text{Be}$	solid, sublimes at over 200°
$(\text{C}_2\text{H}_5)_2\text{Be}$	liquid, b.p. 195° est.
$(\text{C}_3\text{H}_7)_2\text{Be}$	liquid, b.p. 245
$(\text{C}_4\text{H}_9)_2\text{Be}$	liquid, b.p. 293 est.

Similarly, methyl lithium, CH_3Li , is a nonvolatile solid whereas some of the higher normal alkyls of lithium have measurable volatility at elevated temperatures. These differences are due, in part at least, to the greater electronegativity of the methyl group as compared with that of the higher alkyl groups and appear to be most pronounced with lithium and beryllium, with which carbon-metal bonds are intermediate in polarity, but it would be a considerable oversimplification to explain the effect solely on this basis. It is known that certain derivatives of these elements are considerably associated or polymerized.

Differences in molecular symmetry may cause anomalies in the volatilities of certain substituted organometallic compounds, as in the series of methylchlorosilanes where a maximum boiling point is reached:

$(\text{CH}_3)_4\text{Si}$	b.p. 26.5°	mol. wt. 88
$(\text{CH}_3)_3\text{SiCl}$	57.3	108.6
$(\text{CH}_3)_2\text{SiCl}_2$	70.0	129
CH_3SiCl_3	65.7	149.5
SiCl_4	57.6	170

The densities of the normal alkyls of a metal vary in regular and logical fashion. With most elements, the densities of the alkyls decrease as the size of the alkyl groups is increased. With some of the lighter elements, including boron and silicon, the densities of the alkyls *increase* with increasing size of alkyl group.

The substitution of branched-chain hydrocarbon groups for straight-chain, or normal, hydrocarbon groups generally increases the volatility of an organometallic compound:

Di- <i>n</i> -butylmercury, $(n\text{-C}_4\text{H}_9)_2\text{Hg}$	b.p. 105° at 10 mm
Diisobutylmercury, $(i\text{-C}_4\text{H}_9)_2\text{Hg}$	86 at 10 mm
Tetra- <i>n</i> -amylsilane, $(n\text{-C}_5\text{H}_{11})_4\text{Si}$	318 at 760 mm
Tetraisoamylsilane, $(i\text{-C}_5\text{H}_{11})_4\text{Si}$	275 at 760 mm

In general, the replacement of hydrogen in an organic group by a heavier atom decreases the volatility of the organometallic compound. An exception to this is the complete replacement of hydrogen by fluorine; the perfluoroalkyls of the various elements may have boiling points lower than those of the normal alkyls.

Transitions within a given group

With but few exceptions, the different elements in a given group all form the same general type of organic derivatives. In any homologous series, therefore, the weights and sizes of the parent elements will be important in determining differences in physical properties. If we confine our attention to the methyl derivatives of the various elements within a given group, we observe a substantial increase in normal boiling point with molecular weight:

$(\text{CH}_3)_3\text{N}$	b.p. 3.5°	$(\text{CH}_3)_4\text{C}$	b.p. 9.5°
$(\text{CH}_3)_3\text{P}$	42	$(\text{CH}_3)_4\text{Si}$	26.5
$(\text{CH}_3)_3\text{As}$	52.8	$(\text{CH}_3)_4\text{Ge}$	43.4
$(\text{CH}_3)_3\text{Sb}$	80.6	$(\text{CH}_3)_4\text{Sn}$	78
$(\text{CH}_3)_3\text{Bi}$	110	$(\text{CH}_3)_4\text{Pb}$	110

This same general behavior is observed in similar series with other organic radicals. In Groups I and II the effect of carbon-metal bond polarity on the properties of the organo derivatives becomes apparent, and only certain compounds of the lightest elements, lithium in Group I and beryllium in Group II, exhibit any appreciable volatility.

As far as is known, within a given group both the densities and the refractive indices of compounds within a series of analogous organic derivatives increase with the weight of the parent element.

Transitions across a period

The accompanying table shows melting points and boiling points for the methyl, ethyl, and normal propyl derivatives of the first period elements and for the methyl derivatives of the B elements in the fourth period.*

	CH_3Li	$(\text{CH}_3)_2\text{Be}$	$(\text{CH}_3)_3\text{B}$	$(\text{CH}_3)_4\text{C}$	$(\text{CH}_3)_3\text{N}$	$(\text{CH}_3)_2\text{O}$	CH_3F
m.p.	dec.	dec.	-161.5	-19.5	-124	-138	-141.8
b.p.	dec.	200° subl.	-20.2	9.4	3.5	-25	-78.6
	$\text{C}_2\text{H}_5\text{Li}$	$(\text{C}_2\text{H}_5)_2\text{Be}$	$(\text{C}_2\text{H}_5)_3\text{B}$	$(\text{C}_2\text{H}_5)_4\text{C}$	$(\text{C}_2\text{H}_5)_3\text{N}$	$(\text{C}_2\text{H}_5)_2\text{O}$	$\text{C}_2\text{H}_5\text{F}$
m.p.	95	-12	-92.9	-41	-114.7	-120 ca	-143.2
b.p.	subl. 70° vac	195	95	139.2	89.4	34.6	-37.7
	$\text{C}_3\text{H}_7\text{Li}$	$(\text{C}_3\text{H}_7)_2\text{Be}$	$(\text{C}_3\text{H}_7)_3\text{B}$	$(\text{C}_3\text{H}_7)_4\text{C}$	$(\text{C}_3\text{H}_7)_3\text{N}$	$(\text{C}_3\text{H}_7)_2\text{O}$	$\text{C}_3\text{H}_7\text{F}$
m.p.	liq. r.t.	liq. r.t.			-93.5	-122	-159
b.p.		246	156	177	156.5	90.1	-3.2
	CH_3Ag	$(\text{CH}_3)_2\text{Cd}$	$(\text{CH}_3)_3\text{In}$	$(\text{CH}_3)_4\text{Sn}$	$(\text{CH}_3)_3\text{Sb}$	$(\text{CH}_3)_2\text{Te}$	CH_3I
m.p.	solid	-4.5	88.4				-66.5
b.p.	-40 dec.	106	135.8	78	80.6	82	42.5

Several points of interest are apparent. The physical properties are determined, not only by the polarity of the bond between the parent element and carbon, but also by the molecular weight and symmetry of the compound. Also, with the exception of the large differences between the properties of dimethylberyllium and trimethylboron, the changes in physical properties are gradual rather than abrupt. The table also illustrates the effect of increasing the size of the organic group, particularly in the physical properties of the lithium and beryllium alkyls.

Figure 2 illustrates in graphic form the rather regular transitions in boiling point among the normal ethyl derivatives of a number of elements as a function of the position of the parent element in the Periodic Table. As in the previous table, some of the data in this figure

* Some of the data in the table have been extrapolated from vapor-pressure data at lower temperatures.

are extrapolated values. The anomalous positions of the beryllium and aluminum compounds are consequences of polymerization.

With but few exceptions, the *molecular volumes* of the normal alkyls vary in regular fashion across a given period, the minimum in any

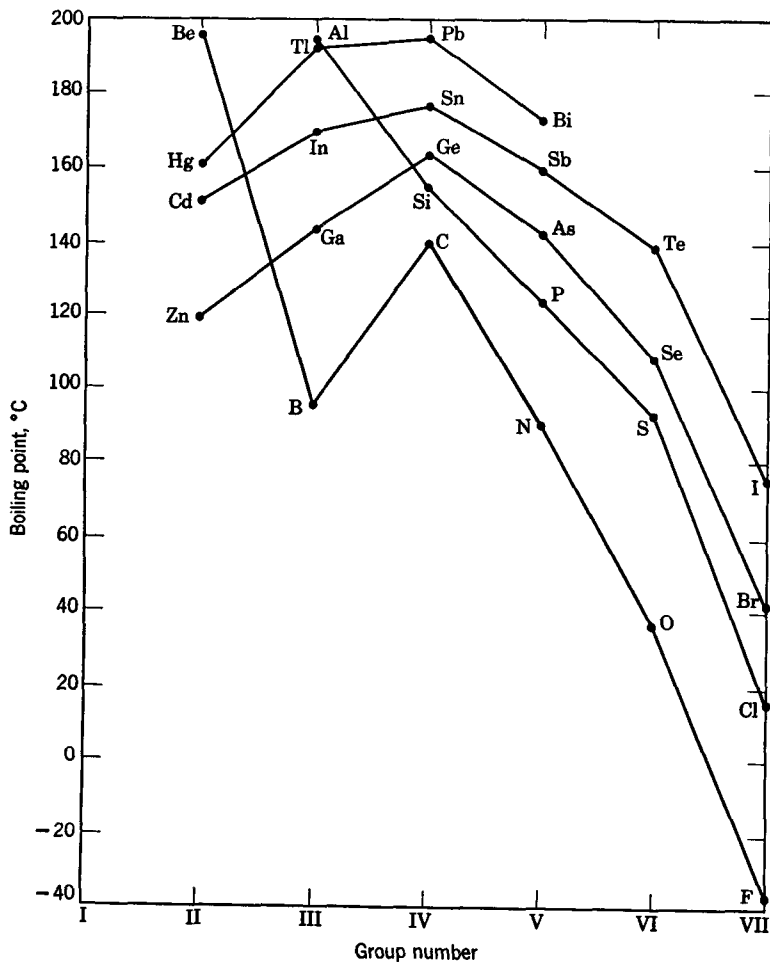


Fig. 2. Boiling Points of Ethyl Compounds

given period occurring with the Group IV element. Within a given group, the molecular volumes in a particular series of compounds decrease with increasing weight of the parent element.

In many cases, the boiling points of unknown compounds may be

estimated from data on existing compounds by the method of Kinney¹ as elaborated by Lewis and Newkirk.²

GENERAL TRENDS IN CHEMICAL PROPERTIES

A few broad generalizations can similarly be made concerning the trends in chemical behavior of organometallic compounds.

THERMAL STABILITY. It is observed that in any one group the compounds of the heavier elements are less stable toward thermal decomposition than those of the light elements. For example, the alkyls of lead readily decompose at temperatures at which the alkyls of silicon are quite stable. Also, it is observed that thermal stability is higher in the compounds of the more electronegative elements in a given period than in compounds of the more electropositive elements in the same period: tetramethyltin can be distilled without decomposition at 78°, whereas methylsilver decomposes at temperatures above -40°. From what is known of them, it appears that the covalent alkyl derivatives of the transition elements are less stable than the compounds of their counterpart elements in the same period. There is, however, no direct correlation between the thermal instability of organometallic compounds and their chemical reactivities.

The thermal stabilities of the compounds of a particular element depend largely on the nature of the attached organic groups, and in a number of cases may be greatly enhanced by the substitution of more electronegative units (such as halogen) for some of the organic groups, as in the organometallic halides of gold, thallium, and titanium.

SPONTANEOUS INFLAMMABILITY. Ignition upon exposure to air is observed with a large number of organometallic compounds, particularly the lower alkyl derivatives of the electron acceptor elements in Group III (B, Al, Ga, In, Tl) and Group II (Be, Mg, Zn, Cd), the alkyls of the alkali metals and alkaline earth metals in Groups I and II (Li, Na, K, Rb, Cs, Ca, Sr, Ba), and with some compounds of the electron donor elements in Group V (P, As, Sb, Bi). Alkyl derivatives of many other metals also are known to oxidize readily on exposure to air, but they may not ignite. The tendency to spontaneous ignition, which is in reality the consequence of a rapid and exothermal reaction with atmospheric oxygen, possibly catalyzed by water vapor, is considerably reduced in the higher alkyl and aryl derivatives. For exam-

¹ C. R. Kinney, *J. Am. Chem. Soc.*, **60**, 3032 (1938); *Ind. Eng. Chem.*, **32**, 559 (1940); **33**, 791 (1941); *J. Org. Chem.*, **6**, 220, 224 (1941); **7**, 111 (1942).

² R. N. Lewis and A. E. Newkirk, *J. Am. Chem. Soc.*, **69**, 701 (1947).