Handbook of Organometallic Compounds

HERBERT C. KAUFMAN

Senior Chemist
John B. Pierce Foundation
New Haven, Connecticut

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Preface

This book is dedicated to the chemists, past and present, who have collectively produced the sum total of knowledge recorded here, for the edification and inspiration of the chemists of the present and the future.

Whilst this comprehensive handbook covers the specific field of organometallic chemistry, its far-reaching importance extends into every applied branch of chemistry.

There is barely an area of commercial endeavor in which organometallics are not now used or being actively considered for potential use. Examples of these applications are: elastomers, plastics, paints, explosives, lubricants, fuels, pharmaceuticals, cement, pesticides, biochemistry, and photography. The author hopes that workers in these fields will find this handbook helpful wherein a choice of compounds through their physical properties are conveniently tabulated for a given use.

An extensive bibliography covering material of supplemental interest follows each element. The tables are conveniently arranged under each element within a periodic group—where individual compounds are easily found through their empirical formula. This avoids the problem of differences in nomenclature which are found among industries or nations.

To the basic researcher in this field, the availability of physical constants of all organometallics scattered throughout the literature and collated here will provide a point of departure for new and more sophisticated and exotic structures. Comparisons of physical constants of homologues within a given periodic group are readily made, thus providing predictable properties for compounds yet unmade.

I am most grateful to those friends, colleagues and associates who urged me on to a successful conclusion. The first portion of this work was undertaken as a matter of professional interest, and I am indebted to the John B. Pierce Foundation whose support assisted me in the completion of this work. I am particularly grateful to Mr. George B. Bailey, Dr. Lovic P. Herrington, Mr. George M. Rapp, and Miss Miriam Chernoff, of the John B. Pierce Foundation, for their aid and helpful suggestions.

Invitation is hereby extended to those readers who have pertinent physical property data to contribute these—with full credit for same—for inclusion in subsequent editions of this book.

HERBERT C. KAUFMAN

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New Haven, Connecticut

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Chapter 1

Introduction to Organometallic Chemistry

Background

Individual researchers since the 1840's have gradually built a discrete branch of chemistry out of two neglected appendages of classical organic and inorganic chemistry. Now that organometallic chemistry has gained such importance in science, each branch claims it for its own by various devices. Its nomenclature has not been developed at all consistently. Rather, some organometallics follow an organic style of nomenclature while others appear either inorganic or "colloquial" in design. As a consequence, its abstracts are generally scattered among the organic, inorganic and applied sections of the "abstract literature." For one hundred years, or until World War II, organometallic chemistry rémained unnoticed by most chemists. The urgency of war, however, prompted the reprinting of "Die Chemie der metallorganischen Verbindungen" by Krause and von Grosse, Borntraeger, Berlin (1937) in the United States.

Suddenly, the work of Frankland, Bunsen, Ehrlich, Kipping, Grignard, Kraus, Stock, Paneth, and Michaelis burst into clear view. The field was open and unlimited in scope. It was obvious to those in universities and industry alike that there would be an explosive increase in the findings of organometallic chemistry. The Dow-Corning Corporation was formed to investigate the organosilicons alone. Metal & Thermit expanded its organic chemistry division to investigate organotin compounds. National Lead and duPont researched organotitanium compounds, while universities under chemists like Gilman, Whitmore, Sommer, Burg, and Kosolapoff, tackled organolead, organoboron, and organophosphorus chemistry.

Scientists in other countries were active, too: Arbuzov, Nesmeyanov, and Andrianov in Russia; Eaborn, Emeleus and Wardlaw in England; van der Kerk and Luyten in Holland; Malatesta in Italy; and Wiberg, Fischer, Ziegler and Goehring in Germany; all have contributed heavily to the fundamental knowledge of organometallic chemistry.

In compiling this work one could not help but notice that the German workers are especially advanced in opening new vistas. Whereas the Americans and Russians are adept at preparing great numbers of homologues of known structures, the Germans are charting an exciting course in new and unusual chemical specie.

Occurrence

One of the obvious reasons for the rather late entry of organometallic compounds on the scene has been their absence in nature, except for substances such as hemoglobin and chlorophyll. Although Germany was the setting for the discovery of many new organometallics in the latter part of the nineteenth century, these developments long awaited industrial utilization.

An interesting case history in point was the development of the aryl silicates in 1885.

A paper by J. Hertkorn in "Berichte der Deutschen Chemischen Gesellschaft," **18**, 1679–99 (1885), contained a comprehensive study of the subject, the work having been performed at the University of Zurich (Switzerland). His studies indicated that the aryl silicates had a wide liquid range, were high boiling and possessed excellent thermal stability. These results went unnoticed and unused until 1938 when the Arthur D. Little Company found in it a basis for a useful heat transfer fluid. Subsequently this resulted in a patent being issued to Lotte Johnston of that company for this purpose—U. S. Patent #2,335,012 (1943). From this disclosure to the scientific world, work was begun and is still continuing at the John B. Pierce Foundation with emphasis on improved chemical structure, in order to improve physical properties and performance.

Nomenclature

Has confusion reigned where organometallic nomenclature is concerned? An attempt to please everyone would be welcomed, but to expect the results to be accepted would be futile. One has to compete with several acceptable national and international nomenclatures as well as those of common usage. In order to circumvent this hiatus, the universal empirical formula system is used as an index to the tables in Part II of this book. The author has chosen to name most of the organometallics as derivatives of the metallo or metalloidal hydride. Where two or more oxidation or quasi valence states appear, the suffix for the lowest oxidation state will end in -ine, the next higher state in -ene, and the highest in -ane. Thus, we have $(CH_3)(CH_3O)PCl$ as methyl methoxy chlorophosphine. The following examples further illustrate this system:

$(CH_3)_2PCl_3$	dimethyl trichlorophosphane
$(C_6H_5)_3As(O)$	triphenylarsane oxide
$(CH_3O)_3B$	trimethoxy borine
$(C_2H_5)_4NBH_4$	tetraethylammonium tetrahydroborane
SF_4	tetrafluoro sulfene
$SeCl_2$	dichloro selenine
TeF_6	hexafluoro tellurane
$(CH_3)_3PbOPb(CH_3)$	hexamethyl diplumboxane

In summation, the nomenclature is quite self-explanatory with the aid of the accompanying structural formulae as well as those easily recognizable compounds of a homologous nature.

Scope

The author has attempted to define organometallic compounds in the broadest sense. The classicist would insist on excluding all compounds except those having a C-M bond from the definition of an organometallic compound. This definition can have justification only when space for presentation is at a premium. The fact of the matter is that the number of compounds without C-M bonds, but with physical and chemical properties of organometallics, except the number of compounds *with* C-M bonds. As an example, one could cite tetraethoxy silane, tetraethylsilane, ethoxysodium, and ethylsodium. Of these, only the latter, an organometallic compound containing a C-M bond, is insoluble in organic solvents, ionic in character, and chemically and thermally unstable.

The blurring of the borders between organic and inorganic chemistry suggests that all compounds used in this study should contain features salient to both. Therefore, an organic radical may bond to the metal or metalloid via carbon, oxygen, sulfur, nitrogen, etc., and still result in compounds with similar physical properties and uses. Similarly, the metal or metalloid may be any element in the periodic table. In practice, most workers in organometallic chemistry are concerned with compounds of a covalent nature as opposed to ionic. That is, with materials whose melting and boiling points lie in the narrow range of −150°C to +400°C, versus those which fall between +300°C to 3500°C.

The tables also contain many compounds which are strictly inorganic or organic. These are presented where they are considered as useful intermediates or starting materials for the preparation of organometallic compounds. Examples of these are silicon tetrachloride, diborane, and arsenic trioxide. In addition, an abbreviated compilation of carbon, oxygen, sulfur, and nitrogen compounds is presented, so that the convenience of the researcher may be served. Thus, there is ready access for comparisons of physical constants of the homologues: hydrazine and diphosphine, diethyl oxide and diethyl selenium, and triphenyl chloromethane and triphenyl chlorogermane.

Compounds found in the tables are for the most part those which have been isolated. However, a few examples are given for those which exist only in organic or aqueous solution. Naturally, this limitation omits the thousands of Grignard organomagnesium halides which exist in solution alone and which are thoroughly covered in "Grignard Reactions of Nonmetallic Substances" by Kharasch and Reinmuth, Prentice-Hall, New York (1954).

Chapter 2

Preparation of Organometallic Compounds

TECHNIQUES

General preparative methods for organometallic compounds require much the same concern for experimental techniques as do those used in nonaqueous inorganic chemistry. With few exceptions, these compounds, as well as their intermediates, whether in solution or not, are extremely sensitive to water and/or oxygen. In addition, they are hazardous in that they may be pyrophoric, explosive and/or poisonous. Therefore, the use of an inert gas blanket of nitrogen, helium, or carbon dioxide (limited use) in addition to safety shields and/or glasses and a hood are indicated.

REACTIONS

General modes of preparation are outlined for each group of elements within the periodic table. Reactions recommended for one element in a group may be the poorest choice for another. The choice of a reaction is best made by consulting original sources for complete details relating to effectiveness, cost, and ease of preparation.

Group I-A

METAL-CARBON BONDS

(1) $RX + 2M \xrightarrow{\text{solvent}} RM + MX$
(2) $RH + M \rightarrow RM + \frac{1}{2}H_2$
(3) $R_2Hg(Zn) + 3M \rightarrow 2RM + (Zn)HgM$
(4) $R'H + RM \xrightarrow{\text{ether}} R'M + RH$
(5) $R{=}R + 2M \xrightarrow{\text{pol. org.}} MR{=}RM + H_2$

METAL-OXYGEN (SULFUR) (NITROGEN)-CARBON BONDS

(1) $R'OR' + RM \rightarrow R'OM + ROR'$
(2) $ROH + M \rightarrow ROM + \frac{1}{2}H_2$
(3) $NH_3 + M \rightarrow MNH_2 + \frac{1}{2}H_2$
(4) $R_2NH + MOH \rightarrow R_2NM + H_2O$

Group I-B

METAL-CARBON BONDS

(1) $RX + 2M \xrightarrow{\Delta} RM + MX$
(2) $RMgX + MX \xrightarrow{\text{ether}} RM + MgX_2$
(3) $3RLi + MX_3 \xrightarrow{\text{ether}} RMX_2 + R_2MX + 3LiX$
(4) $3RLi + RMX_2 + R_2MX \rightarrow 2R_3M + 3LiX$
(5) $R_4Pb(Sn) + MNO_3 \xrightarrow{\text{alcohol}} RM + R_3Pb(Sn)NO_3$
(6) $ArH + MX_3 \rightarrow ArMX_2 + HX$

METAL-OXYGEN (NITROGEN)-CARBON BONDS

(1) $RONa + MX \xrightarrow{\text{alcohol}} ROM + NaCl$
(2) $R_2NCN + MNO_3 \xrightarrow{2NH_4OH} M_2NCN + 2ROH + 2NH_4NO_3$
(3) $R_2C{=}NOH + M \xrightarrow{HNO_3} R_2C{=}NOM + NO_2$

Group II-A

METAL-CARBON BONDS

(1) $RX + M \xrightarrow[\Delta]{HgCl_2} RMX$
(2) $2RMgX + MX_2 \xrightarrow{\text{ether}} R_2M + 2MgX_2$
(3) $RMgX + MX_2 \xrightarrow{\text{ether}} RMX + MgX_2$
(4) $R_2Hg(Zn) + M \xrightarrow[\Delta]{\text{benzene}} R_2M + Hg(Zn)$
(5) $2RMX \xrightarrow{\Delta} R_2M + MX_2$

METAL-OXYGEN (NITROGEN)-CARBON BONDS

(1) $2RONa + MX_2 \xrightarrow{THF} (RO)_2M + 2NaX$
(2) $R_2NN(O) + R'MX \xrightarrow{\text{ether}} R_2NN(OMX)R'$
(3) $R_2NN(OMX)R' + R'MX \xrightarrow{\text{ether}} R_2NN(MX)R' + R'OMX$

Group II-B

METAL-CARBON BONDS

(1) $RX + M \xrightarrow[\text{benzene, ethylacetate}]{\text{Cu or Na}} RMX$

(2) $RMgX + MX_2 \xrightarrow{\text{ether}} RMX + MgX_2$

(3) $2RMX \xrightarrow{\Delta} R_2M + MX_2$

(4) $M(NO_3)_2[OAc]_2 + ArH \xrightarrow{\Delta} ArMNO_3[OAc]$

(5) $2RMX + 2Na \rightarrow R_2M + M + 2NaX$

(6) $MX_2 + CH_2N_2 \rightarrow XCH_2MX + N_2$

METAL-OXYGEN (SULFUR) (NITROGEN)-CARBON BONDS

(1) $2RMX + K_2S \rightarrow RMSMR + 2KX$

(2) $MO + 2RC(O)NH_2 \xrightarrow{\Delta} (RC(O)NH)_2M + H_2O$

(3) $M(OAc)_2 + NH_2C(O)RC(O)NH_2 \xrightarrow{\text{alcohol}} [(RC(O)N)_2]_2M$

(4) $MX_2 + 2RSNa \xrightarrow{\text{pol. org.}} M(SR)_2 + 2NaX$

Group III-A

METAL-CARBON BONDS

(1) $3C_5H_5Na + MX_3 \xrightarrow{\text{THF}} (C_5H_5)_3M + 3NaX$

Group III-B

METAL-CARBON BONDS

(1) $RMgX + MX_3 \xrightarrow{\text{ether}} MR_3 + 3MgX_2$

(2) $2R_2Zn(Hg) + MX_3 \rightarrow R_2MX + 2Hg(Zn)RX$

(3) $R_2MX + RMX_2 \rightarrow R_3M + MX_3$

(4) $2MH_3 + 3R{=}R \xrightarrow{\Delta} 2R_3M$

(5) $3RMgX + M(OR')_3 \rightarrow R_3M + 3MgXOR'$

(6) $HX + MR_3 \rightarrow R_2MX + RH$

(7) $HX + MR_3 \xrightarrow[\Delta]{AlCl_3} RMX_2 + RH$

(8) $3R_2Hg + 2M \rightarrow 2R_3M + 3Hg$

(9) $LiMH_4 + R_3M' \rightarrow LiMH_3R' + R_2MH$

(10) $RLi + R'_3M \rightarrow LiMR'_3R$

(11) $R_3M + MX_3 \xrightarrow{\Delta} RMX_2 + R_2MX$

(12) $3RX + 2M \rightarrow R_2MX + RMX_2$

(13) $3RLi + MX_3 \rightarrow R_3M + 3LiX$

METAL-OXYGEN (SULFUR) (NITROGEN)-CARBON BONDS

(1) $R_3M + R'C(O)H \xrightarrow{\text{ether}} R'CMR_2 + \frac{1}{2}R{=}R$

(2) $3H_3M + 3NH_3 \xrightarrow{300°} [MHNH]_3 + 6H_2$

(3) $3R_3M + 3R'NH_2 \xrightarrow{450°} [MRNR']_3 + 6RH$

(4) $LiMH_4 + R_2NH \cdot HX \rightarrow R_2NMH_2 + H_2 + LiX$

(5) $MX_3 + 3ROH \rightarrow M(OR)_3 + 3HX$

(6) $M(OR)_3 + R'MgX \rightarrow R'M(OR)_2 + R_2MOR$

(7) $MX_3 + 3RSH \rightarrow M(SR)_3 + 3HX$

(8) $M(OH)_3 + 3ROH \rightarrow M(OR)_3 + 3H_2O$

(9) $M_2S_3 + 6ROH \rightarrow 2M(OR)_3 + 3H_2S$

Group IV-A

METAL-CARBON BONDS

(1) $2C_5H_5MgX + MX_4 \xrightarrow{\text{ether}} (C_5H_5)_2MX_2 + MgX_2$

(2) $2C_5H_5Na + MX_4 \xrightarrow{\text{polyether}} (C_5H_5)_2MX_2 + 2NaX$

(3) $(C_5H_5)_2MX_2 + 2ArLi \rightarrow (C_5H_5)_2M(Ar)_2 + 2LiX$

METAL-OXYGEN-CARBON BONDS

(1) $4ROH + MX_4 \xrightarrow{\text{amine}} M(OR)_4 + 4\ \text{amine HX}$

Group IV-B

METAL-CARBON BONDS

(1) $4RMgX + MX_4 \xrightarrow{\text{ether}} R_4M + 2MgX_2$

(2) $2R_2Zn + MX_4 \rightarrow R_4M + 2ZnX_2$

(3) $R_2Hg + MX_4 \rightarrow RMX_3 + RHgX$

(4) $4RX + MX_4 + 4Na \rightarrow R_4M + 4NaX$

(5) $4RLi + MX_4 \rightarrow R_4M + 4LiX$

(6) $RI + MI_2 \rightarrow RMI_3$

(7) $R_2MX_2 + 2Na \xrightarrow{\text{ether}} R_2M + NaX_2$

(8) $4RX + M \xrightarrow{\text{Na(Cu)}} R_4M + 4NaX$

(9) $2ArN_2X + MX_4 \rightarrow Ar_2MX_2 + N_2 + MX_2$

(10) $MH_4 + 2R{=}R \xrightarrow{\Delta} R_4M$

(11) $KM(O)OK + RX \xrightarrow{\text{pol. org.}} RM(O)OK + KX$

(12) $MX_4 + R_4M \rightarrow RMX_3 + R_2MX_2 + R_3MX$

METAL-OXYGEN (SULFUR) (NITROGEN)-CARBON BONDS

(1) $R_2MX_2 + 2RNH_2 \rightarrow R_2M(NHR)_2 + 2HX$

(2) $MX_4 + 4ROH \xrightarrow{\text{amine}} M(OR)_4 + 4HCl\text{-amine}$

(3) $MX_4 + 4RSH \xrightarrow{\text{amine}} M(SR)_4 + 4HCl\text{-amine}$

(4) $MX_4 + 4RONa \xrightarrow{\text{pol. org.}} M(OR)_4 + 4NaX$

Group V-A

METAL-CARBON BONDS

(1) $2C_5H_5MgX + MX_4 \xrightarrow{THF} M(C_5H_5)_2 + 2MgX_2$

(2) $2C_5H_5Na + MX_5 \xrightarrow{THF} (C_5H_5)_2MX_3 + 2NaX$

METAL-OXYGEN-CARBON BONDS

(1) $M(O)X_3 + 3RONa \xrightarrow{pol.\ org.} (RO)_3M(O) + 3NaX$

(2) $MX_5 + 5ROH \xrightarrow{amine} (RO)_5M + 5HX\text{-amine}$

Group V-B

METAL-CARBON BONDS

(1) $4RC(O)OK + M_2O_3 \xrightarrow{\Delta} (R_2M)_2O$

(2) $3RMgX + MX_3 \xrightarrow{ether} R_3M + 3MgX_2$

(3) $ArN_2X + M(ONa)_3 \rightarrow ArM(O)(ONa)_2 + N_2 + NaX$

(4) $3RLi + MX_3 \rightarrow R_3M + 3LiX$

(5) $3RX + M_2O_3 \xrightarrow[\Delta]{NaOH} RM(O)(ONa)_2 + R_2M(O)ONa$

(6) $3RX + MX_3 + 3Na \rightarrow R_3M + 3NaX$

(7) $R_3MX_2 + 3RLi \rightarrow LiMR_6$

(8) $LiMR_6 + H_2O \rightarrow R_5M + RH + LiOH$

(9) $R_3M + 2HX \xrightarrow{\Delta} R_3MX_2 + H_2$

(10) $R_3M + RI \rightarrow R_4MI$

(11) $R_2MX + X_2 \rightarrow R_2MX_3$

(12) $MH_3 + RX \xrightarrow[\Delta]{press.} RMH_3X$

(13) $RMH_3X + NaOH \xrightarrow{H_2O} RMH_2 + NaX + H_2O$

(14) $MH_3 + ROH \xrightarrow[Al_2O_3/Ce_2O_3]{\Delta\ press.} RMH_2 + H_2O$

(15) $MH_3 + ArX \xrightarrow[Cu_2O/H_2O]{\Delta\ press.} ArMH_2 + CuX + H_2O$

(16) $NaMH_2 + RX \xrightarrow{\Delta} RMH_2 + NaX$

(17) $ArH + HOMH_2 \xrightarrow[\Delta]{AlCl_3} ArMH_2 + H_2O$

(18) $RM(O)_2 + 3H_2 \xrightarrow[\Delta]{Ni} RMH_2 + 2H_2O$

(19) $M + RX + NaOH \xrightarrow{H_2O} RMH_2$

(20) $3MH_3 + ROR \xrightarrow[press.]{\Delta} MR_3 + R_2MH + RMH_2$

(21) $RMH_2 + 3R'MgX \xrightarrow{ether} RMR'_2 + MgX_2 + R'H$

(22) $R_2Hg + MX_3 \xrightarrow{\Delta} RMX_2 + RHgX$

(23) $R_2MX_3 + SO_2 \xrightarrow{ligroin} R_2M(O)X + S(O)X_2$

(24) $RMX_2 + S \xrightarrow{CS_2} RM(S)X$

(25) $R_3M + RX \xrightarrow{pol.\ org.} R_4MX$

(26) $Ar_2MNa + Ar'I \rightarrow Ar_2MAr' + NaI$

METAL-OXYGEN (SULFUR) (NITROGEN)-CARBON BONDS

(1) $3ROH + MX_3 \xrightarrow{\Delta} ROMX_2 + (RO)_2MX$

(2) $3RSH + MX_3 \xrightarrow{amine} RSMX_2 + (RS)_2MX$

(3) $3RONa + MX_3 \xrightarrow{pol.\ org.} (RO)_3Na + 3NaX$

(4) $ROH + M(O)X_3 \rightarrow ROM(O)X_2 + (RO)_2M(O)X$

(5) $MX_3 + 2RNH_2 \xrightarrow{ligroin} RNHMX_2 + RNH_3X$

(6) $M(O)X_3 + 4RNH_2 \rightarrow (RNH)_2M(O)X + 2RNH_3X$

(7) $RNH_2 \cdot HX + MX_3 \xrightarrow{\Delta} RN{=}MX + 3HX$

(8) $6ROH + M_2O_3 \xrightarrow{\Delta} 2(RO)_3M + 3H_2O$

Group VI-A

METAL-CARBON BONDS

(1) $5ArMgX + MX_3 \xrightarrow{ether} Ar_5MX + 5MgX_2 + 3MX_2$

(2) $2(C_6H_6)_2MX + H_2 \rightarrow (C_6H_6)_2M + 2HX$

(3) $2C_5H_6 + M(CO)_6 \xrightarrow{\Delta} (C_5H_5)_2M$

(4) $(C_5H_5)_2M + 5(6)CO \xrightarrow{press.} (C_5H_5)_2M_2(CO)_{5(6)}$

(5) $C_5H_5MgX + MX_3 \xrightarrow{ether} (C_5H_5)_2M$

(6) $2Ar_4MX + H_2 \xrightarrow{alcohol} 2Ar_4M + 2HX$

(7) $M(CO)_6 + 2C_5H_6 \xrightarrow{300°C} (C_5H_5)_2M$

(8) $2C_5H_5Na + MX_5 \rightarrow (C_5H_5)_2MX_3 + (C_5H_5)_2MX_2$

METAL-OXYGEN-CARBON BONDS

(1) $M(O)X_3 + 3ROH \xrightarrow{amine} M(O)(OR)_3$

Group VI-B

METAL-CARBON BONDS

(1) $M + RX + NaOH \xrightarrow[NaOS(O)_2OH]{HC(O)H} MR_2$

(2) $RH + H_2MO_4 \xrightarrow{MO_3} RM(O)_2OH$

(3) $M + RMgX \xrightarrow[HCl]{ether} RMH \xrightarrow{NaOH} RMNa$

(4) $RMNa + RX \xrightarrow{pol.\ org.} R_2M + NaX$

(5) $M + 2RX \rightarrow R_2MX_2 \xrightarrow{\Delta} R_2M$
(6) $RMX + RLi \rightarrow R_2M + LiX$
(7) $2MX_4 + 3HgR_2 \rightarrow 2R_2M + 3HgX_2 + 2RX$
(8) $MNa + 2ROS(O)_2ONa \rightarrow R_2M$ $2Na_2SO_4$
(9) $MH_2 + R_2C(O) \xrightarrow{HX} R_2C(M) + H_2O$
(10) $2RMH + O_2 \rightarrow RMMR + H_2O$
(11) $2RMH + H_2SO_4 \rightarrow R_2M + H_2O$
(12) $RMMR + 4RX \xrightarrow{HgI} 2R_3MX$
(13) $2ArN_2X + Na_2M \rightarrow Ar_2M + 2NaX$
(14) $2RX + NaMMNa \rightarrow RMMR + 2NaX$
(15) $R_2M + H_2O_2 \xrightarrow{\text{acetone}} R_2M(O)$
(16) $R{=}R + MO_2 \rightarrow R_2M(O)_2$

METAL-OXYGEN (SULFUR) (NITROGEN)-CARBON BONDS

(1) $RM(O)ONa + XC(O)OR' \rightarrow RM(O)OR' + CO_2 + NaX$
(2) $RM(O)_2X + R'NH_2 \xrightarrow{NaOH} RM(O)_2NHR'$
(3) $RM(O)_2X + AgSR \rightarrow RM(O)_2SR'$
(4) $ArMX + NaOAr' \rightarrow ArMOAr' + NaX$
(5) $3RMH + HC(O)OH \rightarrow HC(MR)_3$
(6) $RC(O)X + R'MH \xrightarrow{\text{amine}} RC(O)MR'$
(7) $C(O)X_2 + 2RMH \rightarrow (RM)_2C(O)$
(8) $R_2NH + CM_2 + NaOH \rightarrow R_2NC(M)MNa$
(9) $R_2NC(M)MNa + R'X \xrightarrow{\text{alcohol}} R_2NC(M)MR'$
(10) $(HO)_2M(O)_2 + 2ROH \rightarrow (RO)_2M(O)_2 + H_2O$

Group VII-A

METAL-CARBON BONDS

(1) $RMgX + MX_3 \xrightarrow{\text{ether}} R_3M + MgX_2$
(2) $2C_5H_5Na + MX_5 \xrightarrow{THF} (C_5H_5)_2MH$
(3) $C_5H_5Na + MX_2 \xrightarrow{THF} (C_5H_5)_2M$
(4) $ArMgX + MX_2 \xrightarrow{\text{ether}} ArMX$

Group VII-B

METAL-CARBON BONDS

(1) $ROH + MH \xrightarrow{H_2SO_4} RM + H_2O$
(2) $ArMX_2 + Ar_2Hg \rightarrow Ar_2MX$
(3) $3ROH + PM_3 \rightarrow 3RM + P(OH)_3$
(4) $ROH + M_2S(O) \rightarrow RM + HM + SO_2$
(5) $3M_2 + CS_2 \xrightarrow{SbCl_5} M_4C$
(6) $3ROH + 3NaOM \xrightarrow{NaOH} M_3CH + 3HC(O)ONa$

(7) $R{=}R + 2HM \xrightarrow{\text{press.}} 2RM$
(8) $RM + X_2 \rightarrow RMX_2$
(9) $ArMX_2 + NaOH \rightarrow ArM(O) + NaX + HX$
(10) $ArMX_2 + NaOCl \rightarrow ArM(O)_2 + NaX + X_2$

Group VIII-A

METAL-CARBON BONDS

(1) $2C_5H_5MgX + MX_3 \xrightarrow{THF} (C_5H_5)_2M + 2MgX_2$
(2) $2C_5H_6 + N_2 + M \xrightarrow[K_2O/MoO_2Al_2O_3]{\Delta} (C_5H_5)_2Fe$
(3) $2C_5H_5MgX + M(O_2C_5H_7)_3 \xrightarrow{THF} (C_5H_5)_2M$
(4) $2C_5H_6 + MO \xrightarrow{\Delta} (C_5H_5)_2M + H_2O$
(5) $2C_5H_5Na + MX_3 \xrightarrow{THF} (C_5H_5)_2M + 2NaX$
(6) $2C_5H_6 + MX_2 \xrightarrow{\text{amine}} (C_5H_5)_2M + 2HX\text{-amine}$
(7) $C_{10}H_{10} + M(CO)_5 \xrightarrow{\Delta} (C_5H_5)_2M(CO)_2$

Group VIII-B

METAL-CARBON BONDS

(1) $6RMg + 3MX_2 \xrightarrow{\text{ether}} RMX_3 + R_2MX_2 + R_3MX$
(2) $2C_5H_5MgX + M(O_2C_5H_7)_3 \xrightarrow{\text{arom.}} (C_5H_5)_2Co$
(3) $C_5H_5Li + M(NH_3)_4(SCN)_2 \xrightarrow[-40°C]{NH_3} (C_5H_5)_2M \cdot 6NH_3$
(4) $2C_5H_6 + M(CO)_4 \xrightarrow{\Delta} (C_5H_5)_2M$
(5) $C_5H_5Na + MX_5 \xrightarrow{THF} (C_5H_5)_2MH$

Group VIII-C

METAL-CARBON BONDS

(1) $C_5H_5MgX + M(O_2C_5H_7)_2 \xrightarrow{THF} (C_5H_5)_2M$
(2) $C_5H_5Li + M(NH_3)_6(SCN)_2 \xrightarrow[-40°C]{NH_3} (C_5H_5)_2M \cdot 6NH_3$
(3) $3RMgX + MX_4 \xrightarrow{\text{arom.}} R_3MX + 3MgX_2$
(4) $R_3MX + RNa \xrightarrow{\text{arom.}} R_4M + NaX$
(5) $2R_3MX + K \rightarrow R_3MMR_3 + KX$
(6) $K_2MX_4 + 2R{=}R \xrightarrow[H_2O]{HCl} (R{=}R)_2MX_2 + 2KX$

LITHIUM

Li

Name	Lithium
Formula	Li
Molecular Weight	6.94
Characteristics	cubic - silvery
Solubility	d. H_2O, alc.
Specific Gravity	0.534
Melting Point	186
Boiling Point	1336
Reference	7

$LiCH_3$

Name	Methyl lithium
Formula	CH_3Li
Molecular Weight	21.96
Characteristics	solid
Melting Point	infus.
Addenda	spont. infl.
Reference	7

LiC_2H_5

Name	Ethyl lithium
Formula	C_2H_5Li
Molecular Weight	36.00
Characteristics	tablets - colorless
Solubility	s. org.
Melting Point	95
Boiling Point	Subl.
Vapor Pressure	$70^{0.00045}$
Reference	7

LiC_3H_7

Name	Propyl lithium
Formula	C_3H_7Li
Molecular Weight	50.04
Characteristics	liquid - colorless
Vapor Pressure	$50^{0.0005}$

LiC_4H_9

Name	Butyl lithium
Formula	C_4H_9Li
Molecular Weight	64.05
Characteristics	liquid - colorless
Solubility	s. org.
Vapor Pressure	$60^{0.00045}$ $70^{0.001}$
Heat of Sublimation	33 Kcal/mole
Dipole Moment	0.97 D

LiC_7H_7

Name	Benzyl lithium
Formula	$C_6H_5CH_2Li$
Molecular Weight	98.07
Characteristics	solid - yellow
Solubility	d. O_2; s. org.
Reference	3

LiH

Name	Lithium hydride
Formula	LiH
Molecular Weight	7.95
Characteristics	crystalline - gray-white
Solubility	d. H_2O, al.; v. sl. s. eth.
Specific Gravity	0.76-0.80 g/cc
Melting Point	680
Boiling Point	850 d.
Vapor Pressure	$500^{0.07}$; 680^{27}
Heat of Formation	21.34 Kcal/mole
Heat of Combustion	10.4 Kcal/g
Heat of Hydrolysis	(25) -31.76 kcal/mole (-26.59)
Entropy	5.9 cal/mole-deg
Specific Heat	8.3 cal/deg-mole
Reference	1, 8

LiHS

Name	Mercapto lithium
Formula	LiSH
Molecular Weight	40.01
Characteristics	solid - straw
Specific Gravity	(25) 1.38
Melting Point	d. 50^{VAC}
Heat of Formation	-60.0 Kcal/mole

LiH_2N

Name	Amino lithium
Formula	$LiNH_2$
Molecular Weight	22.96
Characteristics	cubic - colorless
Solubility	d. H_2O; s. pol. org., liq. NH_3
Specific Gravity	1.178
Melting Point	375
Boiling Point	430

LiH_4Al

Name	Lithium aluminum hydride
Formula	$LiAlH_4$
Molecular Weight	37.94
Characteristics	solid - white
Solubility	d. H_2O; s. eth.,THF
Melting Point	125 d.

LiH_4Ga

Name	Lithium gallium hydride
Formula	$LiGaH_4$
Molecular Weight	80.69
Characteristics	crystals - white
Solubility	d. H_2O; s. pol. org.

Li_2CH_2

Name	Methylene dilithium
Formula	$LiCH_2Li$
Molecular Weight	27.91
Characteristics	solid - brown
Solubility	d. H_2O, air; i. all
Addenda	spon. infl.

Li_2C_2

Name	Lithium carbide
Formula	Li_2C_2
Molecular Weight	37.90
Characteristics	solid - white
Solubility	d. H_2O; s. a.
Specific Gravity	(18) 1.65

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SODIUM

Na

Name	Sodium
Formula	Na
Molecular Weight	23.00
Characteristics	cubic - silver
Solubility	d. H_2O, alc.; i. org.
Specific Gravity	(20) 0.97
Melting Point	97.5
Boiling Point	880

$NaCH_3$

Name	Methyl sodium
Formula	CH_3Na
Molecular Weight	38.00
Characteristics	solid
Solubility	i. org.; d. air, H_2O
Melting Point	d. 200
Addenda	spont. infl.

NaC_2H

Name	Monosodium acetylide
Formula	$HC \equiv CNa$
Molecular Weight	48.03
Characteristics	crystals - white
Solubility	d. H_2O, a.; s. liq. NH_3
Melting Point	d. >210

$NaC_2H_3O_2$

Name	Acetoxy sodium
Formula	$CH_3C(O)ONa$
Molecular Weight	82.05
Characteristics	solid - white
Solubility	s. H_2O, pol. org.; i. org.
Specific Gravity	1.528
Melting Point	324

NaC_2H_4ON

Name	Sodium acetamide
Formula	$CH_3C(O)NHNa$
Molecular Weight	81.06
Characteristics	tablets - white
Solubility	d. H_2O, al.; sl. s. bz., liq. NH_3
Melting Point	300-50 d.

NaC_2H_5

Name	Ethyl sodium
Formula	C_2H_5Na
Molecular Weight	52.06
Characteristics	crystalline - white
Solubility	d. H_2O, al., eth., air; i. org.; s. diethyl zinc
Melting Point	d.
Addenda	spont. infl.
Reference	4

NaC_5H_5

Name	Cyclopentadienyl sodium
Formula	C_5H_5Na
Molecular Weight	88.09
Characteristics	solid
Solubility	d. H_2O, a., alk.; s. liq. NH_3, THF
Melting Point	infusible
Specific Conductivity	(-33) 1.22×10^{-3} (NH_3)

NaC_6H_5O

Name	Phenoxy sodium
Formula	$NaOC_6H_5$
Molecular Weight	116.15
Characteristics	solid - brown
Solubility	s. pol. org.

NaC_6H_6N

Name	Sodium anilide
Formula	C_6H_5NHNa
Molecular Weight	115.11
Characteristics	crystals - white
Solubility	d. H_2O, a., al.; s. liq. NH_3
Melting Point	d.
Addenda	hyg.

$NaC_6H_{12}O_7N$

Name	Sodium p-nitro-phenoxide
Formula	$NO_2C_6H_4ONa$ $4H_2O$
Molecular Weight	233.16
Characteristics	monoclinic yellow prisms
Solubility	s. H_2O (5.97^{25}); sl. s. alc.
Melting Point	36($-2H_2O$), 120($-4H_2O$)
Boiling Point	d.

$NaC_6H_{17}O_3$

Name	Sodium ethoxide-diethanol
Formula	C_2H_5ONa $2C_2H_5OH$
Molecular Weight	160.19
Characteristics	needles - white
Solubility	d. H_2O; i. NH_3; s. alc.
Melting Point	$-2C_2H_5OH$ (200)
Boiling Point	d.

NaC_7H_6ON

Name	Sodium benzamide
Formula	$C_6H_5C(O)NHNa$
Molecular Weight	143.12
Characteristics	powd. white
Solubility	d. H_2O, alc.; i. arom.
Melting Point	d.

$NaC_{10}H_7O$

Name	Sodium β-naphthoxide
Formula	$C_{10}H_7ONa$
Molecular Weight	166.15
Characteristics	powd. white
Solubility	s. H_2O, alc., eth.; i. lig.
Addenda	hyg.

$NaC_{12}H_9O$

Name	p-Biphenyloxy sodium
Formula	$NaOC_6H_4C_6H_5$
Molecular Weight	156.40
Characteristics	solid brown
Solubility	s. pol. org.

$NaC_{18}H_{15}B$

Name	Sodium triphenyl-borene
Formula	$NaB(C_6H_5)_3$
Molecular Weight	265.12
Characteristics	silky need. yellow-orange
Solubility	d. H_2O; s. eth. (0.08^{18})

$NaC_{19}H_{15}$

Name	Sodium triphenyl-methane
Formula	$NaC(C_6H_5)_3$
Molecular Weight	266.31
Characteristics	crystals - red
Solubility	d. H_2O; s. eth., arom., liq. NH_3
Dielectric Constant	(25) 7.11

$NaC_{19}H_{15}O$

Name	Triphenylmethoxy sodium
Formula	$(C_6H_5)_3CONa$

$NaC_{19}H_{15}O$ (Cont.)

Molecular Weight	282.31
Characteristics	solid
Dielectric Constant	(25) 1.62

NaH

Name	Sodium hydride
Formula	NaH
Molecular Weight	24.01
Characteristics	crystalline - white
Solubility	d. H_2O, alc.; i. liq. NH_3
Specific Gravity	1.396 g/cc
Melting Point	d.
Boiling Point	425 d.
Heat of Formation	13.8 Kcal/mole
Heat of Hydrolysis	(25) -30.63 Kcal/mole
Reference	7

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POTASSIUM

K

Name	Potassium
Formula	K
Molecular Weight	39.10
Characteristics	cubic - silver
Solubility	d. H_2O, alc.
Specific Gravity	(20) 0.86; (62) 0.83
Melting Point	62.3
Boiling Point	760

$KC_2H_3O_2$

Name	Acetoxy potassium
Formula	$CH_3C(O)OK$
Molecular Weight	98.16
Characteristics	solid - white
Solubility	s. H_2O, alc.; i. org.
Specific Gravity	1.810
Melting Point	292

$KC_6H_{15}Zn$

Name	Ethyl potassium-diethyl zinc adduct
Formula	$C_2H_5K\text{-}Zn(C_2H_5)_2$
Molecular Weight	191.66
Characteristics	solid
Solubility	s. org.; d. H_2O
Melting Point	68-71

KH

Name	Potassium hydride
Formula	KH
Molecular Weight	40.11
Characteristics	crystalline - white
Solubility	d. H_2O, alc.
Specific Gravity	1.43 g/cc
Melting Point	d.
Vapor Pressure	$\log p_{mm} = -5850/T + 11.2$
Heat of Formation	-14.5 Kcal/mole

KH_2N

Name	Amino potassium
Formula	KNH_2
Molecular Weight	55.13
Characteristics	solid - yellow
Solubility	d. H_2O, alc.
Melting Point	338
Boiling Point	400 Subl.

$K_xC_xO_x$

Name	Potassium carbonyl-polymer
Formula	$(KCO)_x$
Characteristics	crystalline - black
Solubility	d. alc., i. NH_3, org.
Melting Point	250 d.