

Lecture 5: The polymeric compounds of elements of groups I and II of periodic system.

The metal in main-group organometallic compounds can be any of the elements in the *s* block (i.e., groups 1 and 2) or any of the heavier elements in groups 13 through 15. (Groups 13–18 constitute the *p* block.) The elements at the borderline between the *d* block and *p* block—namely, zinc, cadmium, and mercury—will be discussed along with the *p*-block organometallics because of the similarity of their organometallic chemistry. In an internationally sanctioned system of nomenclature, the organic group is named first, followed by the metal, as in dimethylmercury. In writing the formula, this order is reversed, $\text{Hg}(\text{CH}_3)_2$. The organic groups, which are also called ligands, are named in the same way as for any organic compound. The number of carbon atoms on a group that are attached to the metal is indicated by the superscript in η^n . This convention is known as haptic nomenclature. A single point of attachment, η^1 , is usually not explicitly indicated, as in the above formula for dimethylmercury, a monohapto species. The compound with the common name *ferrocene* has the systematic name bis(η^5 -cyclopentadienyl)iron, where the number of cyclopentadienyl ligands (two) is indicated by the prefix *bis* and the number of sites of attachment (five) for each of these is indicated by η^5 . Ferrocene is thus called a pentahapto compound. The number of sites of attachment are also indicated in the formula $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$.

The stability and reactivity of organometallic compounds

The stability and reactivity of organometallic compounds are associated with the nature of the organic ligands and the metal to which they are attached. In each of the main groups of the periodic table (groups 1, 2, and 13–15), the thermal stability of a given type of organometallic compound generally decreases from the lightest to the heaviest element in a group. For example, in compounds containing group-1 metals, methyl lithium (LiCH_3) is much more stable than methyl potassium (KCH_3), and, in those with group-14 metals, tetramethylsilicon, $\text{Si}(\text{CH}_3)_4$, is stable in the absence of air at 500 °C (932 °F), whereas tetramethyllead, $\text{Pb}(\text{CH}_3)_4$, rapidly decomposes at that temperature. This trend in stability is a consequence in part of the decrease in M–C bond strength on going down within a group. The trend does not hold for the *d*-block elements (groups 3–12), where M–C bond strengths and stability often increase going down a group.

The reactivities of organometallic compounds with water and air vary widely. The highly active main-group metals such as lithium (Li), sodium (Na), magnesium (Mg), and aluminum (Al) form highly air- and water-sensitive organometallic compounds. For example, $\text{Al}_2(\text{CH}_3)_6$ undergoes immediate and violent reaction with water to liberate methane (CH_4) gas, and it bursts immediately into flame on contact with air. For the elements toward the right of the periodic

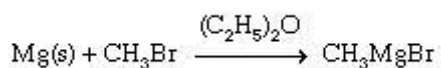
table (groups 14 and 15), the organometallic compounds are not water-sensitive; tetramethylsilicon, for example, does not react with water or air at room temperature.

The synthesis of *s*- and *p*-block organometallic compounds

Synthesis of *s*- and *p*-block organometallic compounds can often be accomplished by one of several general reaction types. The most important of these are outlined below.

FORMATION OF ALKYL LITHIUM AND GRIGNARD REAGENTS

The highly active metals combine with a halogen-substituted hydrocarbon to produce simple organometallic compounds. For example, methyllithium, an important reagent in organic synthesis, is produced commercially by following the reaction: $2\text{Li} + \text{CH}_3\text{Cl} \rightarrow \text{LiCH}_3 + \text{LiCl}$ With other active metals, such as magnesium, aluminum, and zinc, the reaction generally yields the organometallic halide. A common reaction of this type is the synthesis of a Grignard reagent, an alkylmagnesium halide that finds wide use in organic synthesis (the *s* indicates that the metal is in solid form).



DOUBLE DISPLACEMENT

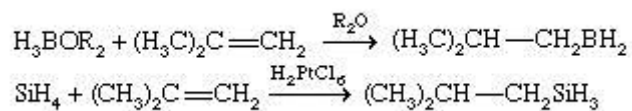
The synthesis of organometallic compounds by double displacement involves organometallic (MR) and binary halide (EX, where E is a metal or metalloid and X is a halogen) starting materials. It provides a convenient synthetic procedure that is widely used in the laboratory and to a lesser extent on a commercial scale. As the following examples illustrate, the organic group on the more active metal is transferred to the less active metal or metalloid. In this context the most common highly active metals are lithium, aluminum, and magnesium. $4\text{Li}(\text{CH}_3) + \text{SiCl}_4 \rightarrow 4\text{LiCl} + \text{Si}(\text{CH}_3)_4$ $\text{Al}_2(\text{CH}_3)_6 + 2\text{BF}_3 \rightarrow 2\text{AlF}_3 + 2\text{B}(\text{CH}_3)_3$

REDISTRIBUTION

Double displacements involving the same central element are often referred to as redistribution reactions. A commercially important example is the redistribution of silicon tetrachloride and tetramethylsilicon (also known as tetramethylsilane) at elevated temperatures. $\text{SiCl}_4 + (\text{CH}_3)_4\text{Si} \rightarrow \text{CH}_3\text{SiCl} + (\text{CH}_3)_2\text{SiCl}_2 + (\text{CH}_3)_3\text{SiH} + \dots$ The products from this reaction can be separated by distillation. This reaction is performed industrially where $(\text{CH}_3)_2\text{SiCl}_2$ is removed from the equilibrating mixture and then hydrolyzed to produce the intermediates for silicone polymers, which have the form $-(\text{Si}(\text{CH}_3)_2-\text{O})-n$ (For more information about the properties and synthesis of inorganic polymers, *see* inorganic polymer).

HYDROMETALLATION

The addition of a metal hydride to a multiple bond is called hydrometallation, and it leads to the formation of a metal-carbon bond. $M-H + H_2C=CH_2 \rightarrow MH_2C-CH_3$ This reaction is driven mainly by the high C-H bond strength relative to most E-H bond strengths. Two important hydrometallation reactions are hydroboration and hydrosilation, illustrated, respectively, by the following examples.

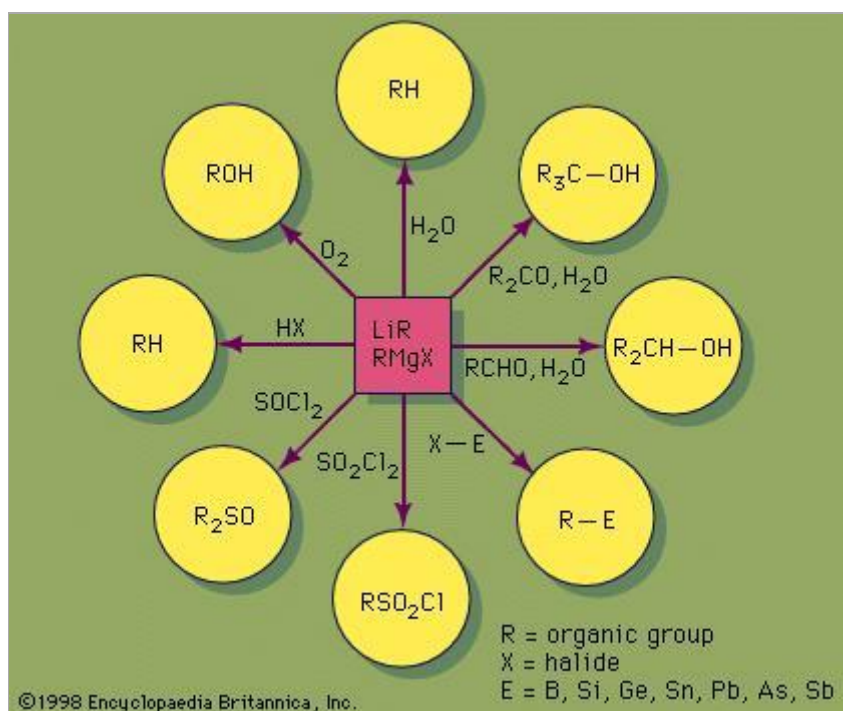


In the hydroboration and hydrosilation of an unsymmetrical alkene, the boron or silicon binds to the carbon atom that has less-bulky substituents, and the smaller hydrogen atom binds to the carbon atom that has bulky substituents— $(CH_3)_2C$ in the above equations. Hydroboration was discovered and developed in the United States by Herbert C. Brown, who shared the Nobel Prize for Chemistry in 1979 for this research. Both hydroboration and hydrosilation are widely used in the synthesis of complex organic molecules. In these applications, the B-C or Si-C bond is generally cleaved in a subsequent step to produce a product that is free of boron or silicon.

REDUCTION

All organometallic compounds are potential reducing agents, and those of the electropositive elements are very strong reducing agents because the metal gives up electrons to the carbon, resulting in a polar M-C bond with a partial positive charge on the metal and a negative charge on the carbon. Organometallic compounds of highly electropositive elements such as lithium, sodium, and aluminum ignite spontaneously and sometimes explode on contact with air or other oxidizing agents. The useful organometallic reagents $Li(CH_3)$, $Zn(CH_3)_2$, $B(CH_3)_3$, and $Al_2(CH_3)_6$ are spontaneously flammable in air (pyrophoric). Accordingly, techniques have been developed to handle these and other pyrophoric compounds. Glass reaction vessels sealed from the atmosphere and purged with nitrogen gas are commonly used for handling air-sensitive organometallic compounds in the laboratory. Large quantities of pyrophoric compounds such as $Al_2(C_2H_5)_6$ are routinely handled with ease in the chemical industry by using closed metal reactors for the production of these and other much less reactive compounds. Organometallic compounds have reduced reactivity when the metallic component is not highly electropositive and when the metal is completely surrounded by attached groups. For example, elevated temperatures are required to initiate combustion with $Si(CH_3)_4$ and $Sn(CH_3)_4$, and at room temperature they can be handled in air.

CARBANION CHARACTER



The partial negative charge of

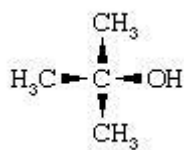
an organic group bonded to a highly active metal results in a distinctive pattern of reactivity that is frequently referred to as nucleophilic or carbanion character. Thus, organometallic compounds containing highly active (electropositive) metals, such as lithium, magnesium, aluminum, and zinc, react rapidly and completely with water, liberating a hydrocarbon in the process. For example, dimethylzinc liberates methane gas along with solid zinc hydroxide. $\text{Zn}(\text{CH}_3)_2 + 2\text{H}_2\text{O} \rightarrow \text{Zn}(\text{OH})_2 + 2\text{CH}_4$

The above hydrolysis of dimethylzinc can be viewed as a transfer of a slightly acidic H^+ from water to the strongly basic carbanion CH_3^- in dimethylzinc.

Alkyl lithium, alkyl aluminum, and alkyl magnesium compounds are the most common carbanion reagents in laboratory-scale synthetic chemistry; carbanion character is greatly diminished for the less metallic elements boron and silicon. The nucleophilic character of organometallic compounds of active metals has many synthetic applications. For example, the organic group in organometallic compounds of active metals attacks the carbonyl carbon of a ketone, and upon hydrolysis a tertiary alcohol results. Similarly, aldehydes can be converted to secondary alcohols by reaction with an organometallic reagent followed by hydrolysis. Double displacement reactions can be used to prepare sulfones (R_2SO_2) and sulfoxides (R_2SO) by treating thionyl chloride (SOCl_2) or sulfuryl dichloride (SO_2Cl_2) with an alkyl lithium or a Grignard reagent.

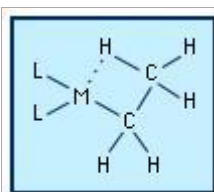
One consequence of the carbanion character of organometallic compounds containing active metals is the protolysis (proton-transfer) reaction that takes place with very weak protonic acids, including water. Alcohols react in a manner similar to the reaction of water, and this provides a convenient way of introducing an alkoxide (OR) substituent into an organometallic

compound. $(C_2H_5)_3Ga + HOCH_3 \rightarrow [(C_2H_5)_3GaOHCH_3] \rightarrow (C_2H_5)_2Ga(OCH_3) + C_2H_6$ The rate of reaction decreases with bulky organic groups on the alcohol. For example, *tert*-butyl alcohol,



reacts slowly with most active organometallics, and it is therefore employed in the laboratory to safely destroy reactive organometallic wastes.

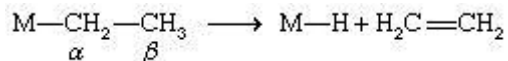
B-HYDROGEN ELIMINATION



The transition state thought to exist in the β -hydrogen elimination reaction and the addition of M-H across a C=C double bond. The hydrogen atom forms a bridge between the carbon and metal (M) atoms. L represents a ligand.

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This is a common organometallic reaction in which a hydrogen atom on a carbon atom that is one position removed from the metal (the β position) transfers to the metal with the liberation of an alkene. The following example shows the formation of ethylene, C_2H_4 .



This reaction is the reverse of the addition of an M-H bond to an alkene (*see above* Hydrometallation), and under some conditions significant equilibrium concentrations of both reactants and products are observed. The β -hydrogen elimination reaction is thought to proceed through the transition state, and as might be expected from this reaction mechanism, compounds with an accessible central metal atom tend to undergo β -hydrogen elimination readily. For example, it occurs with trialkylaluminum compounds but not with tetraalkylsilicon compounds, in which reaction of the silicon atom is hindered by the bulky substituents.

Reference:

<http://www.britannica.com/science/organometallic-compound#toc277970>