Main Group Organometallics:

Since the synthesis of diethyl zinc by E.C. Frankland in 1849 and the synthesis of organo magnesium compounds by Grignard some fifty years later compounds having a metal atom to a carbon atom bond have been the subject of exhaustive experimentation and use.

An organometallic compound is defined as one have an M-C bond and includes the metalloids such as Boron and silicon.

Comparison with hydrogen compounds:

E-C are quite similar in strength and polarity to E-H bonds and there are many structural and chemical similarities between alkyl compounds and their hydrogen analogues.

This can be shown as follows:

Like the hydrides the alkyls can be ionic or molecular however the general tendency is for the alkyls to be more covalent than the hydrides yet largely ionic substances such as sodium naphtalide Na [C₆H₄] and the Grignard reagents RMgX are well characterized.

The heavier alkali metals, being of a soft nature tend to have more covalent nature and these tend to crystallize in the Nickel arsenide structure.

The M-C bonds always remain considerably polar, especially those of the s-block, except for beryllium, but this polarity is lost in the metalloids.

There is a great diversity in structure, so much so that it blurs any attempt at general classification.
MO theory provides quite a straightforward explanation of bonding even for unusual compounds.

For example [LiCH₃]₄ can be readily visualized as a 4 center 2 electron bond where a face of three lithium atoms can combine with one carbon orbital:

Zinc hydride, ZnH₂ is an ionic solid, yet the dimethyl compounds of Zn, Cd and Hg are simple linear molecules which are not associated in gas, solid, liquid or solution form. These have 4 valence electrons, two from the metal and two from the alkyl group and do not complete their valence shells like Be and Mg by bridging.

\[ \text{CH}_3 - M - \text{CH}_3 \]

In the Be and Mg case the metal electrons hybridize to form tetrahedral \(sp^3\) orbitals which have the correct geometry for bridging whilst for the heavier metals we get \(p\) and \(d\) mixing which could lead to a linear hybrid.

Trimethyl boron exists as a discrete monomer whilst BH₃ dimerises to B₂H₆. It is likely that a bridge of two methyl groups attached to a B would encounter steric hindrance.

Tetramethyl silane and trimethyl arsine are electron precise compounds and their shape can be accounted for by simple VSEPR theory. However the bond angles of the heavier elemental compounds cannot be readily explained.
SYNTHESIS:

There are 4 general methods to form the M-C bond.

1) Reaction of metals with haloalkanes and haloarenes:

\[ 2 \text{M} + \text{RX} \rightarrow \text{M-R} + \text{MX} \]

Methyl lithium and the Grignard Reagents are produced in this manner.

2) Transmetallation:

This is the replacement of a weakly electropositive metal (typically mercury) with a more electropositive one.

\[ 2 \text{Ga} + 3 \text{Hg(CH}_3)_2 \rightarrow 3 \text{Hg} + 2 \text{Ga(CH}_3)_2 \]

Such reactions are usually carried out in a sealed glass tube and the mixture gently heated. The mercury can be then easily removed.

3) Metathesis:

This is a double replacement reaction:

\[ \text{MR} + \text{EX} \rightarrow \text{MX} + \text{ER} \]

This is a very effective way of preparing many organometallics:

\[ \text{Li}_4(\text{CH}_3)_4 + \text{SiCl}_4 \rightarrow \text{Si(CH}_3)_4 + 4 \text{LiCl} \]

In general it can be considered as follows:

\[ \text{MR} + \text{EX} \rightarrow \text{ER} + \text{MX} \]

M is usually Li, Mg, Al and Zn whilst E is typically Si, B, As and P. R is a carbanion and X is a halide.

The alkyl or aryl group tends to migrate from the less to the more electronegative element.

\[ 2 \text{Al}_2(\text{CH}_3)_6 + 3 \text{GeCl}_4 \rightarrow 3 \text{Ge(CH}_3)_4 + 4 \text{AlCl}_3 \]

Sometimes methathesis is carried out with the same central element and this is referred to as redistribution.

\[ \text{SiCl}_4 + \text{Si(CH}_3)_4 \rightarrow \text{Si(CH}_3)_3\text{Cl} \]

\[ \rightarrow \text{Si(CH}_3)_2\text{Cl}_2 \text{ etc.} \]

Main group Organometallics
4) Hydrometallation:
Addition of E-H across a multiple bond.

\[ E-H + CH_2=CH_2 \rightarrow EH_2C-CH_3. \]

The most important of these reactions are hydroboration and hydrosilation.

\[ R_2O.BH_3 + CH_2=CHR' \rightarrow R_2O + H_2B-CH_2-CH_2R' \]

This route is particularly useful in forming boron to carbon and silicon to carbon bonds.

**Stability:**

There is quite a similarity with the hydrides. The heavy metal alkanes are very susceptible to homolytic cleavage. Tetraethyl lead cleaves at the Pb-C bond to give methyl radicals. Dimethylcadmium can decompose explosively. Because of this inert atmosphere techniques are necessary as these compounds will react with oxygen, moisture and even carbon dioxide.

**Reactions:**

They are all potentially reducing agents and those with electropositive elements are in fact strong reducing agents. The compounds of the more electropositive elements ignite spontaneously in air as those that can dissociate and leave vacant or unfilled orbitals.. combustion takes place by radical chain processes.

Their reactions can be considered as of a nucleophilic carbanion nature:
The carbanion character is greatly reduced for the less metallic elements. As may be inferred these compounds have many synthetic applications.

**Lewis Acidity:**

Electron deficient organometallics are by their nature Lewis acids on account of the unoccupied orbitals on the metal:

\[ \text{B(C}_6\text{H}_5)_3 + \text{Li(C}_6\text{H}_5) \rightarrow \text{Li[B(C}_6\text{H}_5]_4} \]

Even organometallics which utilize bridges to obtain more electrons have the bridges cleaved:

\[ \text{Al}_2(\text{CH}_3)_6 + 2\text{N(C}_2\text{H}_5)_3 \rightarrow 2(\text{CH}_3)_3\text{AlN(C}_2\text{H}_5)_3. \]

**β hydrogen elimination:**
This is the reversal of the addition across a double bond.

\[ \text{M CH}_3, \text{CH}_2 \rightarrow \text{MH + CH}_2=\text{CH}_2. \]

Under some conditions an equilibrium of both product and reactants are observed.

It is believed that β hydrogen bridges to an open coordination site on the metal is formed.

![Diagram](image)

If this is the real case it can be expected that atoms with low coordination are likely to undergo such reactions.

Heating aluminum *hexa iso* butane is therefore expected to decompose:

\[ \text{Al}_2^*(\text{but})_6 \rightarrow 2 \text{Al}^*(\text{but})_3 \rightarrow \text{Al}^*(\text{but})_2\text{H} + \text{iso-C}_4\text{H}_8. \]
Alkaline earth metals:

Organoberyllium and organomagnesium compounds have significant covalent character whilst the heavier ones are more ionic. The Be and Mg compounds have a strong tendency towards 4 coordination, but for Be 3 coordination is also common.

The Be compounds may be formed by metathesis with magnesium Grignard reagents or transmetallation with mercury compounds.

\[ \text{BeCl}_2 + 2 \text{RMgX} \rightarrow \text{BeR}_2 + 2 \text{MgXCl} \]

Very often the solvent is adducted;

\[ \text{Be} + \text{Hg(CH}_3)_2 \rightarrow \text{Be(CH}_3)_2 + \text{Hg.} \]

Beryllium cyclopentadienide is obtained by heating BeCl₂ with sodium cyclopentadieneide and has different structure in the solid and gas phase.

Simple organoberyllium compounds will react with water, oxygen and weak Bronsted acids, but as all Be compounds are highly toxic there is little interest in using them commercially.
Grignard reagents on the other hand are vastly used in organic synthesis.

These reagents undergo an equilibrium reaction in ether known as the Schlenk equilibrium:

\[ 2R\text{MgX} \leftrightarrow R_2\text{Mg} + \text{MgX}_2 \]

The compounds \( R_2\text{Mg} \) are likely to form adducts with the ether solvent and various structures have been identified. With dioxane a tetramer has been isolated.

If the ether solvent forms unwanted Lewis complexes than alkylaluminum or alkylolithium compounds are used as these are soluble in hydrocarbons.

**Zinc and cadmium compounds:**

These can be formed by transmetallation from the aluminum analogues.

\[ \text{ZnCl}_2 + \text{Al}_2(\text{CH}_3)_6 \rightarrow \text{Zn}(\text{CH}_3)_2 + [(\text{CH}_3)_2\text{AlCl}]_2. \]

Alkylzinc compounds are pyrophoric whilst the cadmium ones react more slowly in air. They form stable complexes especially with chelating amine and the C-Zn bond has greater carbanion nature than the C-C bond. Hence the reaction:

\[ \text{Zn}(\text{CH}_3)_2 + (\text{CH}_3)_2\text{C}=\text{O} \rightarrow (\text{CH}_3)_3\text{C} = \text{O-ZnCH}_3 \] proceeds easily the analogous reaction with cadmium does not occur.

Various interesting structures with mixed cyclopentadienyl groups are known.
Organomercury compounds:

Again methathesis, especially with Grignard reagents is a favourite method of formation:

\[ \text{HgX}_2 + 2\text{RMgX} \rightarrow \text{HgR}_2 + 2\text{MgX}_2 \]

They are useful for transmetallation with more electropositive elements by are poisonous. However whilst dimethyl zinc is pyrophoric, dimethyl mercury survives exposure to air.

Brain damage discovered in Minmata in Japan has been caused by certain types of bacteria capable of methylating mercury and that Hg(CH₃)₂ and Hg(CH₃)⁺ enter the food chain because they rapidly penetrate cell wall.

Hg has a high affinity (soft to soft) for the sulphhydryl atoms in enzymes and this makes it highly poisonous.

Organoboron compounds:

\[ \text{BF}_3 + 3\text{RMgX} \rightarrow \text{BR}_3 + 3\text{MgFX}. \]

The trialkyls are mild Lewis acids and form the \([\text{BR}_4]^-\) anions of which the tetraphenylborate is well known.

The tetraphenylborate anion is quite large and will in fact for an insoluble potassium salt which is an example of how large equasl sized counter ions tend towards insolubility. This can be used as a gravimetric analysis of a potassium / sodium ion mixtures.

Organohaloboranes - \(\text{R-B-X}\) are more reactive than the simple trialkyl boranes and many be obtained as follows:

\[ 3\text{BCl}_3 + 6\text{AlR}_3 \rightarrow 3\text{R}_2\text{BCl} + 6\text{AlR}_2\text{Cl}. \]

The chemistry of carboranes is of course very vast.
**Organoaluminium compounds:**

Alkylaluminium compounds exist as bridged dimers in which the $sp^3$ orbital of a CH$_3$ group is isolobal with a 2 s orbital. The Al-C-Al bridging angle is approximately 75° which is smaller than that of a bridging halogen.

The dimers tend to dissociate in the pure liquids and the extent of dissociation depends very much on the bulk of the alkyl group.

Triphenyl aluminium also exists as a dimer.

Alkylaluminium compounds have been extensively investigated on account of their use as catalysts to polymerize alkenes and as chemical intermediates.

They are relatively inexpensive carbanion intermediates

**Gallium, indium and thallium organometallic compounds.**

Trimethyl boron is a monomer, trimethyl aluminium is a dimer whilst the trimethyl compounds of Ga, In and Th are monomers.

The carbanion character is greatest for the aluminium compounds and is reduced as follows:

$$\text{Al}_2\text{R}_6 \rightarrow \text{GaR}_3 > \text{InR}_3 > \text{TlR}_3 > \text{BR}_3.$$  

A typical synthesis of these compounds is:

$$3 \text{Li}_4\text{(C}_2\text{H}_5\text{)}_4 + 4 \text{GaCl}_3 \rightarrow 12 \text{LiCl} + 4 \text{Ga(C}_2\text{H}_5\text{)}_3$$
Organosilicon compounds

For the s block elements, except for beryllium, the M-C bond is very polarized. This polarization is greatly reduced in the C-Si bond. However we still obtain the

\[ \text{Si}^{5+} - \text{C}^{6-} \] situation.

The bond disassociation energy of Si - C is lower than that of the C - C bond but appreciably high at between 250 and 335 kJmol\(^{-1}\).

In its reactions with carbon, silicon remains tetravalent and the compounds such as the tetralkys and tetrarylks are thermally stable and the Si - C bonds is not easily hydrolyzed or oxidized by air. Tetraphenylsilicon boils at 530°C.

In general the bond lengths of silicon with counter atoms are appreciably longer than the bonds lengths of carbon with the same counter atoms. With oxygen the bond length is 25% longer.

- **Reactions:**
  The reactivity of organosilicon compounds is considered as arising from the following:
  a) the polarity of the Si - C bond allows nucleophilic attack on the Si and electrophilic attack on the carbon. This polarity is greater than that found in C - C bonds and hence organosilicon compounds are more reactive than their organic analogues.
  
  b) Silicon also posses d orbitals and these may be utilized to form transition species thereby facilitating displacement reactions at the silicon site.

- **Nucleophilic substitutions:**
  The substitution mechanism for silicon is usually Sn2 and not Sn1. A five-co ordinate transition pathway is normally followed and this is extremely fast. Depending on the nature of the leaving or attacking groups the stereochemistry may be retained or an inversion takes place.
Stabilization of $\beta$-carbocations and $\alpha$-carbon - metal bonds.

During reactions of organosilicon compounds it is commonplace that the carbon atom which is $\beta$ to the silicon behaves like a carbocation and the carbon atom $\alpha$ to the silicon behave like a carbanion.

$$\text{Si} - C^{\delta^-} - C^{\delta^+} -$$

This is thought to be caused by overlap between vacant $p$ orbitals on the $\beta$ carbon and the $\sigma$ orbital between the silicon atom and the $\alpha$ carbon atom.

Silicon also has the ability to stabilize $\alpha$ carbanions for the following reasons:
1. Overlap of the $\alpha$ C-M bond with an Silicon $d$-orbital and;
2. Overlap of the $\alpha$ C-M bond with the $\sigma$ orbital of an adjacent Si-C bond. The C-Si $\sigma$ orbital has a higher coefficient on the Silicon orbital.

The stability of carbanions $\alpha$ to silicon facilitates nucleophilic attack on vinylsilanes.

Organosilicon compounds
Preparation

The simplest laboratory preparation of Si - C bonds is via Grignard reagents, organolithium or organoaluminium compounds. Typical reactions are:

a) $\text{RMgX + SiCl}_4 \rightarrow \text{RSiCl}_3 + \text{MgXCl}$;

b) $\text{Li}_4(\text{R})_4 + \text{SiCl}_4 \rightarrow \text{Si}(\text{R})_4 + 4 \text{LiCl}$

c) 

in b) above R is CH₃. However the reaction is generic but the organolithium compound would not necessarily be a tetramer.

However the compounds used are expensive and not economically viable on an industrial scale.

In industry the action of alkyl or aryl halides on silicon alloyed with copper, or Sodium or magnesium is preferred. The simplest reaction is:

$$2 \text{MeCl} + \text{Si} \rightarrow \text{Me}_2\text{SiCl}_2$$

However other products are formed which include MeSiCl₃, Me₃SiCl, SiCl₄ and various disilanes. All these products can be separated by fractional distillation and are useful starting materials for other silicon products.

Methylchlorosilanes are rapidly hydrolyzed to form an Si - O bond.

$$\text{Me}_3\text{SiCl} + \text{H}_2\text{O} \rightarrow \text{Me}_3\text{SiOH} + \text{H}_3\text{O}^+ + \text{Cl}^-$$

These can then easily dimerise as follows:

$$2 \text{Me}_3\text{SiOH} \rightarrow \text{Me}_3\text{SiOSiMe}_3 + \text{H}_2\text{O}$$

The hydrolysis of dimethylchlorosilane is much more complex and finally yields a mixture of cyclic and linear oligomers. These contain the group (Me₂SiO)ₙ.

Siloxanes

These are compounds with the general formula $\text{R}_n\text{SiO}_m\text{SiR}_n$ and the simplest is therefore $\text{Me}_3\text{SiO}_1\text{SiO}_1\text{SiMe}_3$. 

Organosilicon compounds
The bond angle is substantially wide at 148° and the short Si - O bond (1.47Å) is again suggestive of extensive p-d π bonding between the oxygen and silicon. The phenyl equivalent is actually linear.

In these compounds the Si-O-Si bridge may easily bend and the oxygen shows very little Lewis basicity. This is because the lone pairs on the oxygen overlap with the empty d orbitals on the adjacent silicon. The lone pairs become delocalised and are therefore no longer available. The delocalisation also renders the structures more flexible and hence siloxanes behave like elastomers such as rubber.

Similar overlap is observed in compounds where the oxygen is replaced with nitrogen. These amines are only very weakly basic.

**Polysiloxanes** have very important applications in solid-state electrolytes especially in lithium hydride batteries.

The linear polymers may be stabilized by blocking the end groups by Me₃Si groups. This is achieved by introducing varying amount of (Me₃Si)₂O into the hydrolysis mixture. There is no specific polymer chain length but a Gaussian distribution about a mean.

The relatively short polymers (Si₈) are too volatile and not useful. They are distilled away. Other methyl silicones are oils and have a low temperature coefficient of viscosity (10% f that of normal carbon oils). This is attributed to:

a) free rotation of the Me groups coupled with the flexibility of the chain leading to larger intermolecular distances and smaller intermolecular forces;

b) a tendency to form helical coils.

**Silicone Oils:**

Silicone oils exhibit remarkable surface effects due to the presence of the polar Si-O bond and the non-polar hydrocarbon group in the same polymer. Hence textiles treated with these oils become water repellent and resistant to water borne stains. Within the fiber the polymers orient themselves to project a hydrocarbon surface.
Closely related are non-stick surfaces. Treated paper can be easily peeled away from an adhesive surface. Nearly all vehicle tires are made in molds that have been treated with silicone oils to give an easy release.

Silicone oils are also used as lubricant for wax. It is physically difficult to rub wax on to a surface. If however between 4 and 10% of a silicone oil is added waxing (floors, cars, boats etc.) becomes simpler.

**Silicone Rubbers:**

Natural rubber is obtained from palm trees, which grow in particular areas of the world, notably the Far East such as in Malaysia. The Japanese occupied these areas during the last world war and there was frantic research carried out in the USA to produce synthetic rubber.

Rubbers, in general are long chain polymers in which occasional cross-links are present. This results in a high degree of reformation under stress but without any flow. Increasing the cross links will result in greater rigidity and eventually into hard resinous materials.

Silicone rubber, like silicone oils is a polymer of the type \((R_2SiO)_n\) but of longer chain lengths. Hence very strict control is necessary in the addition of chain ending materials, which need to be highly purified.

Chain lengths are about 6000 to 7000 units. These polymers are in fact ‘gums’ which are then mixed with a filler and finely divided silica or carbon. Cross-linking is obtained by heating the mixture after it has been formed.

Silicone rubbers are unique as they retain their flexibility even at -80°C and up to +250°C. These make them useful for the aviation industry. Moreover they are chemically inert and used in cosmetic surgery.

**Silicone Resins:**

These are rigid polymers with extensive cross-linking. They are obtained by the hydrolysis of \(R_2SiCl_2\) mixed with a substantial amount of \(RSiCl_3\). They
are used for making electrically insulating materials and because of their water repellent properties they are using in masonry and baking.

Resins can also be obtained by using phenylchlorosilanes as the starting materials.

$$\text{HSiCl}_3 + \text{C}_6\text{H}_6 \rightarrow \text{PhSiCl}_3$$

The phenylchlorosilanes is then hydrolyzed with a mixture of water and toluene and a low molecular weight oligomers soluble in toluene is obtained. The toluene is evaporated and further polymerization is obtained by heating under pressure. The product is used to make ‘glass cloth’.

**Silylcarbinol**s:
These have the general formula $\text{R}_3\text{Si}-\text{C(OH)}\text{R}^1\text{R}^2$. On treatment with a base or a metal as a catalyst the silyl group migrates from the carbon to the oxygen.

![Silylcarbinol Reaction](image)

**Friedl Craft alkylation of organosilicon compounds:**

Typical reactions are:

$$\text{PhSiMe}_3 + \text{RCOCl} \rightarrow \text{PhCOR} + \text{Me}_3\text{SiCl}$$

![Friedl Craft Alkylation](image)

These new aromatic type materials may prove useful in the development of new silicone products.

**Polyacarbosilanes:**

Starting from linear polymers of the type $[-\text{RR'}\text{SiC}_2\text{H}_2^-]_n$ and treating these with metallic sodium will yield polymers $[-\text{RR'}\text{SiO}^-]_n$. These can be used as precursors for silicon carbide products.
**Silsesquioxanes**

Silsesquioxanes refer to all structures with an empirical formula of $\text{R}_{\text{SiO}}_{3/2}$. R can be H, alkyl, akenyl, aryl group.

A typical structure is cubane with the silicon atoms at the vertices of the cube. An oxygen atom bridges the silicons at the edges and there is one R group on each silicon atom.

However they can also have partial cage type, ladder type and random type. These compounds find application in protective, electrical insulating and adhesive materials.