



ELEMENTS OF ORGANO- METALLIC CHEMISTRY

F. R. Hartley

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Elements of Organometallic Chemistry

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Monographs for Teachers

This is another publication in the series of Monographs for Teachers which was launched in 1959 by the Royal Institute of Chemistry. The initial aim of the series was to present concise and authoritative accounts of selected well-defined topics in chemistry for those who teach the subject at GCE Advanced level and above. This scope has now been widened to cover accounts of newer areas of chemistry or of interdisciplinary fields that make use of chemistry. Though intended primarily for teachers of chemistry, the monographs will doubtless be of value also to a wider readership, including students in further and higher education.

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Preface

The idea of this monograph arose during a one-day symposium for schoolteachers on 'Organometallic Chemistry' that was held in Southampton in October 1971. A number of schoolteachers approached me and pointed out that whilst what the speakers had been saying was very interesting there were two major stumbling blocks to introducing organometallic chemistry into school teaching. The first was the lack of a suitably simple textbook and the second was the lack of any suitable experiments. Over the past three years, with a great amount of help from schoolteachers in the Southampton area and colleagues in the university, especially Dr C. Burgess, I have attempted to remedy this situation by offering this monograph, in which I have included a number of experiments that may be used to illustrate some of the principles of practical organometallic chemistry.

Many organometallic experiments use sophisticated equipment to overcome the inherent instability of organometallic compounds, and are thus difficult to carry out in schools. The experiments given here have all been extensively modified from the original literature and in this I am indebted to Mrs G. Temple-Nidd of the Southampton College for Girls, Mr T. G. B. Hackston of Barton Peveril College (Eastleigh), Dr A. W. Shaw of the South Wilts Grammar School for Girls (Salisbury) and Dr R. P. Smith of Richard Taunton College (Southampton) all of whom have devoted a considerable amount of their free time to developing these experiments. I am also indebted to the Goldsmiths' Company who generously gave us some financial help for this work from their John Perryn charity bequest.

Organometallic chemistry is a relatively recent subject. Although the first organometallic compound was reported in 1830 and the foundations of non-transition metal organometallic chemistry were laid towards the end of the nineteenth and at the beginning of the twentieth century by Grignard and others, transition metal organometallic chemistry did not really get under way until the 1950s when it was spurred on by the discovery of ferrocene. Recently it has received further recognition through the award of the 1973 Nobel Prize for Chemistry to two of the leading organometallic chemists, namely Professors G. Wilkinson and E. O. Fischer. Whilst Grignard reagents have long been a part of university undergraduate courses, transition metal organometallic chemistry has only been taught widely in the past eight years. Hence there are many schoolteachers who have never been formally taught anything about the subject and some of these may well ask, 'why teach organometallic chemistry in schools?' My answer is, firstly organometallic chemistry has

recently become a very important part of the armoury of the industrial chemist and is thus not a further branch of chemistry of purely academic interest, and secondly it lies on the boundaries of organic and inorganic chemistry and thus utilizes the concepts of both, helping to fuse the subject together and break down the traditional barriers which it was so fashionable to build a few years ago. Throughout this monograph and especially in chapter 5 I have, where possible, emphasized the applications of organometallic chemistry.

Whilst it would be impertinent of a university chemist to tell schoolteachers how to teach their subject, some suggestions as to how organometallic chemistry could be introduced into a curriculum may be in order. In the first place students taking the Nuffield scheme undertake a two-stage preparation around the end of their first year. Some of the experiments described in Chapter 7 could well be used here. Looking further to the future, organometallic chemistry could well join chemical engineering, biochemistry and food science as one of the areas of the subject for further specialization.

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1. Introduction

What is an organometallic compound?

For the purposes of this monograph an organometallic compound is considered to be any compound containing a direct bond between a metal atom and one or more carbon atoms. However, metal-carbonyls ($M-CO$), metal cyanides ($M-CN$) and metal carbides (*e.g.* CaC_2) are not considered in this monograph because their properties are closely related to those of many other compounds usually considered in inorganic chemistry.

Types of organometallic compounds

The first useful subdivision of organometallic compounds is by metal which gives five types of organometallic compound: ionic, covalent, electron deficient, transition metal and others.

Ionic

Ionic organometallic compounds are generally only formed by the most electropositive elements, namely sodium, potassium, rubidium, caesium and francium. However, slightly less electropositive metals such as magnesium can occasionally form ionic compounds when the negative charge on the organic moiety can be delocalized over several carbon atoms. Thus sodium forms ionic butylsodium whereas the less electropositive magnesium forms a covalent butyl compound. Magnesium, however, forms an ionic cyclopentadienide ($Mg^{2+}\{C_5H_5\}_2$) where the negative charge can be delocalized over the five carbon atoms of the cyclopentadienide ring.

Ionic organometallic compounds are typical ionic compounds and are consequently insoluble in hydrocarbon solvents and crystalline solids when obtained pure. This, however, is not easy as they are readily hydrolysed and sensitive to oxygen.

Covalent

Volatile, covalent organometallic compounds are formed by zinc, cadmium and mercury and the non-transition metals of groups III (other than aluminium), IV and V. They are the simplest type of organometallic compound known involving an electron-pair bond to which the metal and the organic group each contribute a single electron. Their properties resemble those of typical organic compounds in that they are volatile, soluble in organic solvents and insoluble in water. They include, of course, compounds such as tetraethyllead the famous (or infamous!) antiknock additive in petrol.

Electron deficient

The organometallic compounds of lithium, beryllium, magnesium and aluminium all form electron deficient structures, in which there are insufficient valence electrons to allow all the atoms to be linked by traditional two-electron two-centre bonds. All four metals form very strongly polarizing cations, that is they have a very high 'charge to radius' ratio, which enables the cations to 'pull electron density away from an anion' (*i.e.* polarize that anion). As a result the charge separation in the potentially ionic methyl compound



decreases and a covalent, but polar, structure results.



It is apparent that such a highly polar structure will associate strongly so that we may expect the overall structure to be polymeric. This is just what does happen. Additionally, there is an interesting gradation in properties in that aluminium alkyls form dimers, beryllium and magnesium alkyls form linear chains and lithium alkyls form 3-dimensional polymers. These different structures are reflected in the volatilities of these compounds which increase sharply from methyl lithium through dimethylberyllium to trimethylaluminium (Table 1) in spite of an increase in the molecular weight of the monomer.

Table 1. Properties of electron deficient compounds.

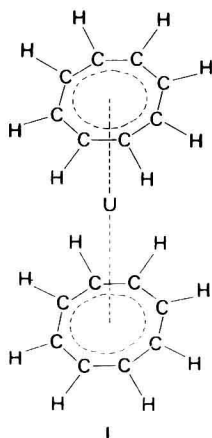
Compound	Molecular weight of monomer	Structure	Volatility
LiMe	21.96	3d-polymer	Infusible
BeMe ₂	39.08	Linear chain	Sublimes at 200 °C
AlMe ₃	72.09	Dimer	Melts at 15.4 °C

Transition metal

The most important difference between transition metals and non-transition metals is the ability of the former to bond to more than one carbon atom. This ability, which stems from the symmetry properties of the *d*-orbitals present in the valence shells of transition metals, enables transition metals to form such a wide range of complexes that it is more convenient to classify them in terms of the organic ligand (p 3) than in terms of the metal.

The lanthanide and actinide metals, although their organometallic chemistry has not been studied in such detail as the transition metals,

appear to resemble the latter in their ability to bond to more than one carbon atom of an organic ligand, *e.g.* $[\text{U}(\text{C}_8\text{H}_8)_2]$ (I)



Others

The organometallic compounds of calcium, strontium, barium and radium have not been widely investigated, possibly because the metals are relatively inaccessible and their alkyls show no significant advantages over those of magnesium and lithium reagents. In general their properties appear to be intermediate between those of magnesium alkyls and the alkali metal alkyls.

Classification of ligands

Whilst non-transition metals form organometallic compounds with only a narrow range of ligands such as alkyl, aryl and σ -cyclopentadienyl groups, transition metals form complexes with a very wide range of organic groups. Accordingly it is valuable to classify these compounds according to ligand type rather than metal. The most important difference between transition and non-transition metals is the ability of the former to bond to more than one carbon atom of an organic ligand and it is convenient to classify ligands according to the number of their carbon atoms which are involved in bonding to the metal.*

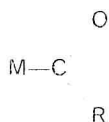
* The classification obtained here from the number of carbon atoms bound to the metal is essentially the same as that developed by Green (in *Organometallic compounds*, Vol. 2 — see Suggested Reading), on the basis of the number of electrons donated by the ligand. The present classification is offered not simply to be different but in the hope that it may be conceptually simpler to grasp. Furthermore, it enables us to retain the concept of the formal oxidation state (pp 7–8) that has been of great value in inorganic chemistry.

One-carbon-bonded ligands

One-carbon-bonded ligands are ligands in which only one carbon atom of the ligand is bound directly to the metal. Such ligands can be further subdivided into three groups, namely hydrocarbon, acyl and carbene ligands.

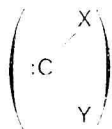
Hydrocarbon ligands include alkyl ($-\text{CH}_3$), aryl ($-\text{C}_6\text{H}_5$), alkenyl ($-\text{CH}=\text{CH}-\text{CH}_2$), σ -cyclopentadienyl ($-\text{C}_5\text{H}_5$), and alkynyl ($-\text{C}\equiv\text{CH}$) groups. All these groups form compounds with both transition and non-transition metals.

Acyl ligands involve the direct bonding of the carbon atom of an acyl group to a metal:



Such complexes are formed by transition but not by non-transition metals.

Carbene ligands involve the coordination of the carbon atom of a carbene



to a metal. The metal is generally a transition metal and the groups X and Y are often groups such as $-\text{OR}$ and $-\text{NR}_2$.

Two-carbon-bonded ligands

Alkenes and alkynes act as two-carbon-bonded ligands because the carbon atoms at each end of the multiple bond are both involved in bonding to the metal atom.

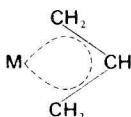


It should be noted that the two carbon atoms need not be equidistant from the metal atom, and indeed in many, if not all, complexes of unsymmetrically substituted alkenes and alkynes such as $\text{RCH}=\text{CH}_2$, the two metal-carbon bond lengths are slightly different. As already

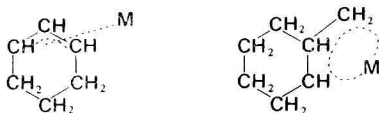
noted alkenes and alkynes only form complexes with transition metals.*

Three-carbon-bonded ligands

Complexes in which 3-carbon atoms are bound directly to a transition metal are known as π -allyl or π -enyl complexes. The simplest of these ligands is the π -allyl (π -C₃H₅) group but all the carbon atoms may bear substituents, or the three carbon atoms may be part of a ring. The complexes are normally represented schematically by



and should be distinguished from the σ -allyl complexes in which the allyl group is bound as a one-carbon-bonded ligand ($M-CH_2-CH=CH_2$). Further examples of π -allylic ligands are:



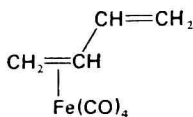
Four-carbon-bonded ligands

There are two major types of four-carbon-bonded ligands, (a) acyclic ligands such as butadiene and (b) cyclic ligands such as cyclobutadiene.

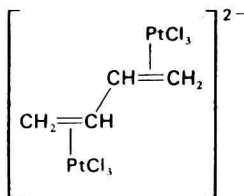


Whilst cyclobutadiene always acts as a four-carbon-bonded ligand butadiene does not always do so. Occasionally it prefers to act as a two-carbon-bonded ligand to one (II) or two (III) metal atoms.

* These complexes are known as π -complexes a label that results from their bonding (p 40). They should be distinguished from the σ -complexes ($M-CR=CR_2$ and $M-C\equiv CR$) formed by alkenes and alkynes that have lost one hydrogen atom from the carbon atom adjacent to the metal. These latter are, of course, classified above under hydrocarbon ligands.



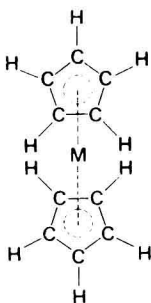
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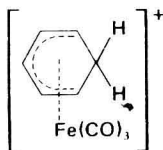
III

Five-carbon-bonded ligands

Ligands in which five or more carbon atoms are directly bound to a transition metal are generally cyclic ligands. Five-carbon-bonded ligands are known as 'di-enyl' ligands and although typified by the 5-membered ring ligand ' π -cyclopentadienyl' are also formed by 6- and 7-membered hydrocarbon ligands. The π -cyclopentadienyl group gives rise to the famous metallocene series of complexes — for example, ferrocene, nickelocene and ruthenocene — in which a divalent transition metal is sandwiched between two planar cyclopentadienyl rings (IV). $[(\pi\text{-C}_6\text{H}_7)\text{Fe}(\text{CO})_3]\text{BF}_4$ (V) is an example of a five-carbon-bonded complex formed by the 6-membered cyclohexadienyl ring.



IV



V

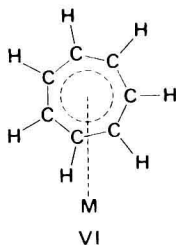
Six-carbon-bonded ligands

Although benzene is undoubtedly the most important six-carbon-bonded ligand other ligands such as cycloheptatriene and cyclooctatetraene also form complexes in which only six of their carbon atoms are bound directly to the metal. Heterocyclic ligands such as pyridine and thiophene also form complexes which are electronically and structurally analogous to benzene complexes.

Seven-carbon-bonded ligands

π -Cycloheptatrienyl complexes, (VI), in which seven carbon atoms

are bound to the transition metal are formed by vanadium, chromium, manganese, iron, cobalt, molybdenum, tungsten and rhodium.

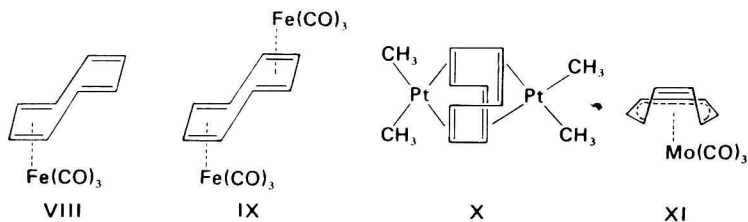


Eight-carbon-bonded ligands

Cyclooctatetraene (VII) forms a number of complexes particularly



with the actinides in which it is planar with all eight carbon atoms equidistant from the metal (*e.g.* $\text{U}(\text{C}_8\text{H}_8)_2$ — *see* p 3). However, cyclooctatetraene also forms complexes in which it acts as a 4- (VIII), 2×4 - (IX), 4×2 - (X) and a 6-carbon-bonded ligand (XI).

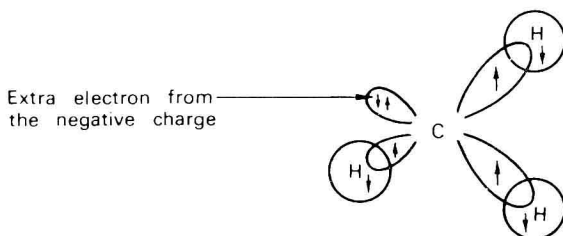


Oxidation state

Although the oxidation state of an element is only a formalism that is obtained by applying a set of rules and thus has no absolute meaning it has nevertheless become a very useful formalism. The oxidation state of a metal is defined as 'the charge remaining on that metal after all the ligands have been removed in their closed shell conditions (*e.g.* chlorine as Cl^-) and any metal-metal bonds have been cleaved homolytically — *i.e.* the presence of a metal-metal bond does not alter the oxidation state of the metal'. Thus magnesium in MgCl_2 is Mg^{2+} after removing chlorine as Cl^- and so magnesium is said to be in the +2 oxidation state which is written as magnesium(II). Similarly in $[(\text{PPh}_3)_2\text{PtCl}_2]$ after removing Cl as Cl^- and

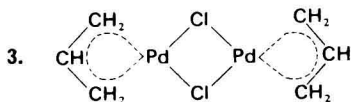
triphenylphosphine as the neutral PPh_3 ligand $+2$ is left as the oxidation state of platinum — *i.e.* platinum(II).

How do these rules apply to organometallic compounds? The even-carbon-bonded ligands such as ethene, butadiene and benzene are all neutral in their closed shell configurations and so do not influence the oxidation state of the metal. By contrast the odd-carbon-bonded ligands are all formally negatively charged in their closed shell configuration and so contribute one unit to the oxidation state of the metal. Thus to get eight electrons in the sp^3 orbitals around the carbon of methyl we require four electrons from the carbon valence orbitals, three from the hydrogen atoms and one more from the negative charge. Thus methyl is formally CH_3^- .

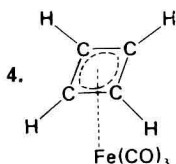


Applying these rules to a number of organometallic compounds.

1. MeMn(CO)_5 Carbon monoxide is neutral.
Methyl carries formal $1-$ charge.
 \therefore Manganese is in $+1$ oxidation state.
2. $\text{K}^+[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$ Ethene is neutral.
Chlorine carries formal $1-$ charge.
Complex ion carries overall $1-$ charge.
 \therefore Platinum is in $+2$ oxidation state.



π -Allyl is an odd-carbon-bonded ligand and therefore carries a formal $1-$ charge. Chlorine carries a formal $1-$ charge. Thus two palladium atoms share a formal $4+$ charge and so palladium is in $+2$ oxidation state.

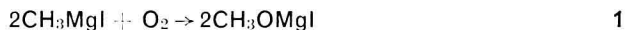


Cyclobutadiene is an even-carbon-bonded ligand and is therefore formally neutral.
Carbon monoxide is neutral.
 \therefore Iron is in zero oxidation state.

As a further help in assigning the formal charge on ligands it may be noted that ligands whose name ends in -ene are even-carbon-bonded ligands and formally neutral (*e.g.* ethene, benzene *etc.*), whereas ligands whose name ends in -yl are odd-carbon-bonded ligands and formally uninegative (*e.g.* methyl, π -allyl, π -cycloheptatrienyl *etc.*).

Stability

In order to describe a compound as 'stable' it is important to specify what the compound is stable to, for example, is it stable to heat, air oxidation or hydrolysis? Consider a Grignard reagent such as methylmagnesium iodide. It is clearly stable at around room temperature with respect to decomposition to magnesium and methyl iodide, after all it is formed by the interaction of these two, but it is very sensitive to oxidation and hydrolysis (reactions 1 and 2),

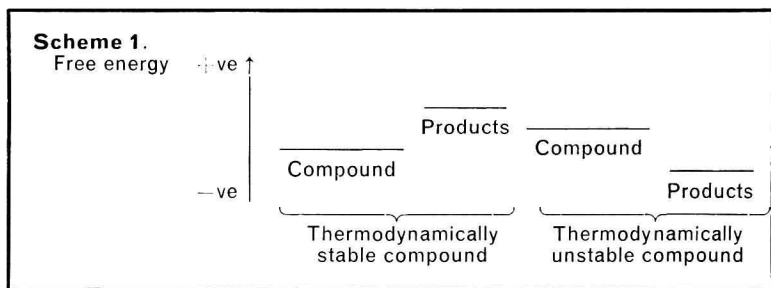


so that it is necessary to exclude air and moisture during its preparation and subsequent storage. Clearly then to describe such a compound as 'stable' without further qualification is meaningless.

There are basically two types of stability, namely thermodynamic and kinetic.

Thermodynamic stability

A compound is thermodynamically stable if 'its free energy is lower (*i.e.* more negative) than the sum of the free energies of the products formed when it reacts' (Scheme 1). Unfortunately there is not a lot of



free energy data available for organometallic compounds although there is rather more enthalpy data — generally obtained from measuring heats of combustion. If this is to be used then allowance must be made for the entropy term in the equation

$$\Delta G = \Delta H - T\Delta S$$

Table 2. Estimates of the thermodynamic stabilities of selected organometallic compounds.

Compound	Type of stability to be considered	Enthalpy data (ΔH_f° , kJ mol ⁻¹)	Net enthalpy change	Estimate of entropy	Conclusion
Me ₂ Cd	Thermal stability, decomposition assumed to occur by $\text{Me}_2\text{Cd} \rightarrow \text{Cd} + \text{C}_2\text{H}_6$	Me ₂ Cd(l) C ₂ H ₆ (g) Cd(cryst) 70.0 -84.5 0	154.5 kJ mol ⁻¹ , i.e. favours decomposition	Will favour decomposition since a gas is formed	Thermodynamically unstable to heat
EtLi	Thermal stability, decomposition assumed to occur by $\text{EtLi} \rightarrow \text{LiH} + \text{CH}_2 = \text{CH}_2$	EtLi(cryst) C ₂ H ₄ (g) LiH(cryst) -58.55 52.40 -90.45	20.50 kJ mol ⁻¹ , i.e. favours stability	Will favour decomposition because the entropy of gaseous ethene is high (65.4 kJ mol ⁻¹) at room temperature compared to the entropies of crystalline solids (e.g. entropy of formation of LiH = 7.55 kJ mol ⁻¹ at room temperature)	Thermodynamically unstable to heat
Cr(C ₆ H ₅) ₂	Thermal stability, decomposition assumed to give Cr metal and benzene	Cr(C ₆ H ₅) ₂ (cryst) Cr(cryst) C ₆ H ₆ (l) 150.8 0 -49.05	52.7 kJ mol ⁻¹ , i.e. favours decomposition	Will favour decomposition since a liquid (or gas, above its boiling point) is formed	Thermodynamically unstable to heat