

Advances in Astrobiology and Biogeophysics

Anna Neubeck
Sean McMahon *Editors*

Prebiotic Chemistry and the Origin of Life

 Springer

Advances in Astrobiology and Biogeophysics

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Anna Neubeck • Sean McMahon
Editors

Prebiotic Chemistry and the Origin of Life

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Editors

Anna Neubeck
Department of Earth Sciences
Uppsala University
Uppsala, Sweden

Sean McMahon
UK Centre for Astrobiology
University of Edinburgh
Edinburgh, United Kingdom

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Preface

This is a book about the beginnings of life on Earth from a geochemical and biochemical standpoint. It has been written by specialists working on the frontiers of several disciplines, and it is intended to provide a readable overview both for trained scientists and for advanced students in geobiology, astrobiology, and related fields. It is by no means a complete or comprehensive introduction to the field, but rather a work-in-progress report from some of its leading protagonists. We have tried to sidestep some well-worn arguments in favour of fresher perspectives and original insights. Nevertheless, the eleven peer-reviewed chapters assembled here outline many of the central questions that drive origins-of-life research today, suggest what the answers may be, and show how future work may settle them.

According to accepted common scientific understanding, life on Earth emerged through the self-organisation of lifeless matter far from thermodynamic equilibrium. Self-catalysing networks of chemical reactions gave rise to protocells: encapsulated, homeostatic units capable of reproducing themselves according to an internal genetic code. How this event or series of events unfolded is deeply unclear; the first half-billion years or so of life's history are missing from the record, and carbonaceous residues in the oldest known rocks have been heavily altered by heat, pressure, and the passage of time, destroying biochemical information. But if the origin of life cannot be observed, perhaps it can be reconstructed through painstaking, interdisciplinary scientific detective work. Clues are found in the chemistry of the elements, in the composition of meteoritic and primordial materials, in the biochemical and genetic makeup of viruses and cellular organisms alive today, in laboratory and computer simulations of prebiotic chemical reaction pathways, and in geochemical evidence from the early Earth. Cellular remains, when they finally appear in the rocks, tell us that life had already become surprisingly diverse, complex, and tolerant of environmental extremes when the fossil record began to be written. Taken together, these clues are beginning to tell a coherent story.

It is a story that begins in space. In **Chap. 1** of this volume, **Marco Fioroni** describes the synthesis of transition metals in supernovae and their chemical transformations in space and on the young, habitable Earth. He emphasises the importance of transition metals and minerals for organometallic chemistry on the

early Earth and also for the origin of life: today, almost 40% of all enzymatic reactions involve metalloenzymes. Several chemical pathways to form simple and complex building blocks and catalysts for life are thoroughly discussed, and the possible contribution of extraterrestrial organometallic/metallorganic compounds is emphasised.

In **Chap. 2**, **Robert M. Hazen and Shaunna M. Morrison** enlarge upon the mineralogical complement of the early Earth and its significance for prebiotic chemistry. They show that many biochemically central elements were supplied not in their rare and exotic mineral forms, but from the more common rock-forming minerals in which they occur as minor and trace elements. Thus, boron, molybdenum, phosphorus, and other elements would have been widely available at reactive surface sites of minerals such as olivine, pyroxene, feldspar, and magnetite, even though borate, molybdate, and phosphate minerals (and so on) were rare. This provides an elegant solution to a long-standing problem in origins-of-life chemistry.

Chapter 3, contributed by **Eva Stueeken and Nicholas Gardiner**, reconstructs the Hadean Earth as a complex, geologically dynamic world. The primordial crust, volcanic and hydrothermal systems, oceans, ice, the atmosphere, and the interfaces and transport pathways between these linked systems may all have played important roles in the operation of prebiotic chemical reaction networks. In this perspective, the major steps leading to the origin of life need not all have occurred in any single environmental setting or “crucible”. Rather, we can consider the early Earth as a global chemical reactor for the origin of life.

Chiral molecules—those that occur in left- and right-handed forms—are essential in the chemistry of life. In **Chap. 4**, **Axel Brandenburg** asks why biology prefers left-handed amino acids and right-handed carbohydrates, and whether this homochirality was a prerequisite for life or a consequence of it. We learn about biological and abiotic chiral dynamics and what drives the transition from racemic mixtures to homochirality. Brandenburg takes us through the fascinating story of the discovery of chiral molecules and how they might be used to find life on Mars. Homochirality may have emerged as a consequence of autocatalysis in the hypothetical RNA world, and in **Chap. 5**, **Frank Trixler** discusses the importance of mineral surfaces for concentration, selection, homochirality, and the synthesis of nucleotides in such a world. This chapter confronts the complexity of prebiotic nucleic acid synthesis and the multiple paradoxes that inevitably arise from this given the central role of nucleic acids in biology. Another seemingly indispensable feature of life is encapsulation: enclosure within semi-permeable boundaries is a prerequisite for homeostasis. In **Chap. 6**, **Augustin Lopez, Carolina Chieffo, and Michele Fiore** discuss the origins of these boundaries from a chemical perspective, including the synthesis of amphiphilic molecules and their self-assembly into protocellular boundaries on the early Earth. In **Chap. 7**, **Oliver Trapp** discusses the formation and self-modification of organic catalysts and their importance in the origin of chirality, nucleosides, and Darwinian life. Informed by the latest experimental results, he suggests several routes towards nucleic acid-based evolutionary systems and concludes that DNA and RNA may have arisen simultaneously on the early Earth.

The boundary between life and non-life is a debated question closely linked to our understanding of life's chemical and evolutionary origins. Ever since the discovery of bacteriophages in the 1910s, viruses have been central to these debates. **Donald Pan** considers multiple aspects on the role of viruses in the origin and definition of life in **Chap. 8**. Viruses may have played a crucial role in the onset of life and can serve as useful models of prebiotic replicators, although it remains unclear whether they predate the Last Universal Common Ancestor (LUCA) of cellular life. In **Chap. 9**, **Anthony Poole** examines efforts to reconstruct LUCA using the imperfect record of evolutionary history preserved in the genetic sequences of modern organisms. Time has blurred LUCA's traits, and the interpretation of features shared by its descendants is multifaceted. Horizontal gene transfer, gene displacement, and loss all obstruct the prospect of an unambiguous reconstruction of LUCA. Poole describes how these and other constraints limit the resolution at which LUCA can be reconstructed with commonly used methods and finally suggests a feasible procedure to reconstruct LUCA by focusing on general traits.

The first stages of biological evolution are not preserved in the rock record. Nevertheless, the oldest known fossils provide important insights into the nature of early life and its environment. In **Chap. 10**, **Barbara Cavalazzi and her colleagues** describe the cellular remains, fossil bio-sedimentary structures, and other chemical and mineralogical evidence of life present in some of Earth's oldest rocks, showing how these important but controversial materials can be critically interrogated and understood. The fossil record also contains key evidence for the timing of the origin of the eukaryotes. The nucleated cell and its organelles transformed the early biosphere and eventually permitted the emergence of complex, macroscopic, multicellular organisms like ourselves. Thus, in **Chap. 11**, **Heda Agic** concludes our volume by considering this momentous event (or a series of events) from a palaeontological perspective, presenting some recently described, remarkably well-preserved microfossils that record the early evolution of eukaryotes.

This book offers a partial snapshot of origins-of-life research in the early twenty-first century. Many of its chapters were written under strain in the midst of the global COVID-19 pandemic (another testament to the power of viruses), which caused some inevitable delays; we thank our contributors both for their perseverance and for their patience. We are also hugely grateful to the peer reviewers who provided expert critical feedback on the initial drafts of each chapter, and to Ramon Khanna and Christina Fehling at Springer Nature for their support and guidance. Despite all these efforts, we earnestly hope that this volume will *not* stand the test of time: progress in this field is not merely of academic interest but of fundamental importance to humankind. New data will come from many sources: increasingly sophisticated laboratory experiments, new computational approaches to prebiotic reaction pathways, and new discoveries in the rocks of the Earth, Mars, and other planetary bodies. But it will take many more years, much labour, and the skills and ideas of diverse people around the world to understand, finally, where we came from. We hope this book will inspire its readers to take part in this great adventure.

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Chapter 1

Transition Metal

Organometallic/Metallorganic

Chemistry: Its Role in Prebiotic

Chemistry and Life's Origin



Marco Fioroni

Abstract Without transition metals (TM) Life would not exist, at least not in the form we know. In fact, first row TM share an important ubiquitous presence in all Phyla where 30% of all proteins are ligated to a TM and 40% of enzymatic reactions are processed by a metallo-enzyme. Consequently it can be assumed that TM and their organometallic/metallorganic compounds played an important role in the prebiotic world as well as in the chemistry of Life's origin. In this chapter, I address the involvement of TM in prebiotic chemistry and the origin of Life, including the origin of both metabolism and genetics. I discuss both exogeneous (astrochemical) and endogenous synthesis and self-organization of organic building blocks, emphasizing the importance of TM mineral catalysts and inorganic-organic interactions. I highlight the presence of organic-inorganic conglomerates in meteorites, and argue that while the role of TM in endogenous synthesis is recognized and attracting much scientific interest, "organometallic-metallorganic astrochemistry" in exogenous synthesis requires further elaboration to understand its significance for prebiotic and origin-of-life chemistry.

1.1 Transition Metals: Elegance in Chemistry

The IUPAC (International Union of Pure and Applied Chemistry) defines a transition metal (TM) as:

An element whose atom has an incomplete d sub-shell, or which can give rise to cations with an incomplete d sub-shell (Hartshorn et al. 2015).

M. Fioroni (✉)

Smith Chemistry Building, The University of Memphis, Memphis, TN, USA

Department of Earth Sciences, Palaeobiology Uppsala University Geocentrum, Uppsala, Sweden
e-mail: mfioroni@memphis.edu

In such a short, simple sentence there is an opening towards a complex, elegant and unique chemical world!

In fact it can be well claimed that the importance of transition metals in the chemistry field is such that Life, industrial chemistry and technology; at least as we know them; would not exist.

In the history of Science TM have contributed to the understanding of the periodicity and relationship between the elements (Constable 2019) while in technology (Komskaa 2014), medicine (Lippard and Berg 1994) and industrial chemistry (Beller and Bolm 2004; Elschenaeroich 2006) their chemical-physical properties together with their catalytic abilities made them essential elements in the modern society and economy.

However when dealing with the prebiotic chemistry and Life's origin TM have, till now, attracted an oscillating interest due to the close relationship to the astrochemistry research field where TM have not been considered much yet.

In fact because of the increasing consensus between the researchers on the partial extraterrestrial origin of the Earth Life's building blocks (exogenous delivery), to understand how Life's building blocks have been synthesized means to unify astrochemistry and prebiotic chemistry within the special class of reactions resulting in the production of Life's chemical constituents *on Earth and in Space*.

As a consequence the "trio" astrochemistry-prebiotic chemistry-Life's origin, based on the actual knowledge piled up during the last decade, is increasingly entangled; though the "Life's origin" terms are, mainly, referred to the processes, evolution and flow of information organizing the chemical building blocks in a living system (Adami 2015; Seoane and Solé 2018).

Focusing on the exogenous delivery, organic and prebiotic molecules are proposed to be synthesized on extraterrestrial bodies from the interstellar medium (ISM), to circumstellar disks and planetary systems, as a consequence entering in the "classical" astrochemistry field.

However within the "classical" astrochemistry, TM have not played a consistent role though since the '80s there is an "underground" interest in their involvement in the astrochemistry reaction networks. *De facto* deleting TM from the modern astrochemistry knowledge would not make a huge difference, while in Life's chemistry, chemical industry and technology the impact would be enormous.

In synthesis "Earth" based chemistry recognizes the important role of TM while in more "celestial" matters TM seem not to be considered much.

When shifting the attention to the "endogenous delivery" hypothesis, stating the basic chemical constituents of Life's origin have been synthesized on Earth, TM do have some importance being presumably involved in ancient bio-synthetic pathways.

Hopefully, in a kind of "backfire" the prebiotic and Life's origin chemistry can help to rekindle interests toward TM in the astrochemistry field.

In the chapter development there will be a focus on a subset of the vast TM chemistry important to prebiotic and Life's origin chemistry. Such subset includes the CHNOPS elements as main constituents of the living matter and by definition the

TM-C(HNOPS) bonds will determine the organometallic (TM-C) and metallorganic (TM-X-C, X=H,N,O,P,S) chemistry of the astro-prebiotic-Life's origin chemistry.

Furthermore because "we are stardust", the link between exogenous delivery and endogenous synthesis applied only to TM related chemistry, will be better appreciated through knowledge of TM formation by stellar nucleo-synthesis (Sect. 1.2) and the condensation and formation of TM compounds after stellar explosions (Sect. 1.2.1).

Further paragraphs on TM-physical-chemistry Sect. 1.2.2, organometallic compounds Sect. 1.3, astro-organometallics Sect. 1.4 will be specially devoted to the description by molecular orbitals theory (MO) and some basic concepts to better understand TM related chemistry.

Finally a section referred to the TM organometallics and metallorganic chemistry applied to prebiotic and Life's origin chemistry classified by "metabolism first" or "genetic first" will follow Sect. 1.5.

1.2 TM Astro-Genesis

The Periodic Table starts with the Big Bang (^1H , ^3He , and ^4He) (Galli and Palla 2013). All the elements besides the ones produced during the Big Bang, apart from ^6Li , ^9Be , ^{10}B and ^{11}B continuously forming by *spallation* processes (Ramaty et al. 1997), are born during the stellar evolution and ejected in space during the stars life span or death.

The star type, i.e. giant, main sequence or dwarf, to mention only a few, and its correlated evolution is function of some initial parameters such as mass and metallicity (in astrophysics all elements but H and He are classified as "metals") well represented by the Hertzsprung-Russell temperature-luminosity diagram (Rose 1998).

Life of a star starts with the H fusion phase where He is produced by a proton-proton (pp) chain and/or by a CNO-cycle. When the H core is exhausted and enriched in He, H fusion continues in a shell enveloping the He core and the following gravitational contraction increases the core temperatures till igniting He [*Asymptotic Giant Branch* (AGB) stage]. Depending on the mass of the star this process can continue till the synthesis of ^{56}Fe in an *onion* layered structure (Limongi and Chieffi 2010), where a series of shells made of ^4He , ^{12}C , ^{20}Ne , ^{16}O and ^{28}Si are concentrically organized around a central $^{28}\text{Si}/^{56}\text{Fe}$ core (see Fig. 1.1).

The AGB stars are probably the main sources of C and N present in the actual Universe as well as of some of the heavier nuclides (Habing and Olofsson 2004; Herwig 2005). For example one AGB subclass *Thermal Pulsating Asymptotic Giant Branch* (TP-AGB) is characterized by a strong mix between the deep layers and the surface experiencing mass loss via strong stellar winds, thereby enriching the interstellar medium with the products of nucleosynthesis (Jordi and Iliadis 2011).

Elements heavier than ^{56}Fe are mainly produced in explosive nucleosynthesis classified as: r-process (rapid neutron capture) (Seeger et al. 1965); rp-process

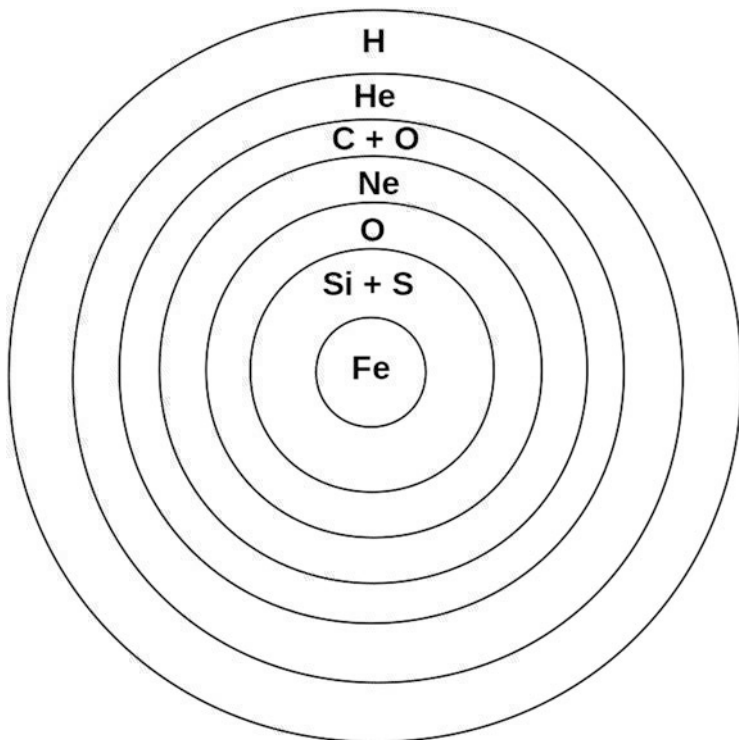


Fig. 1.1 The “onion like” structure of a massive star just prior to its death as “supernova” (type II, Ib, Ic). See ref. Nomoto et al. (2013)

(rapid proton capture) (Jordi and Iliadis 2011) and s-process (slow neutron capture), responsible for the nucleosynthesis in the stellar core (Arlandini et al. 1999; Busso et al. 1999) and the latter responsible for the synthesis of about half of the elements heavier than ^{56}Fe .

In particular, explosive nucleosynthesis, characterized by p-, ν -, νp -, α - and r-processes referring to core-collapse supernovae, (type II, Ib, Ic) are of outstanding importance being one the most prolific sources of Galactic elements (Nomoto et al. 2013). In general the complex phenomenon of explosive nucleosynthesis is predicted to be responsible of the majority of nuclides with $A > 12$.

TM are detected within supernova remnants with an overwhelming presence of Fe^{n+} , Ni^{n+} and Co^{n+} or in star atmospheres and envelopes forming molecules such as FeO (Furuya 2003), FeCN (Zack et al. 2011) and TiO/TiO₂ (Kamínski 2013).

The amounts of first row TM produced in a supernova explosion are “astronomical”. A total of $\sim 0.07 M_{\odot}$ (M_{\odot} = solar masses) of ^{56}Co in the ejecta (Leising and Share 1990) of the SN 1987A supernova were estimated, while an estimate for the ^{56}Ni masses deduced from 17 type Ia supernovae sets a range of 0.1–1.0 M_{\odot} (Stritzinger et al. 2006).

Fractional TM abundances such as Fe, Co, Ni are about $\sim 1-10^{-2/-3}$ as compared to Si (Cowley 1995). Higher atomic weight TM can be set with Si fractional abundances comprised between the Pb peak and the Fe peak at $10^{-5} < \text{TM} < 1$ (Cowley 1995).

It should be mentioned the relative TM abundances have been deduced by observational data as well as calculated on evolutionary models of stars/galaxies as refractory elements are not easy to be detected (Lodders 2003; Nomoto et al. 2013; Wood et al. 2019). In fact as reported in the next Sect. 1.2.1, all the heavy and refractory elements are depleted (Kuljeet and Piyush 2018; Thiabaud et al. 2014) and condensed into dust grains, resulting in an interesting mix of TM to develop a complex (organic) chemistry.

1.2.1 TM Condensation

Once dispersed in space, elements undergo a series of physical-chemical processes producing the “stardust”.

The TM abundances, physico-chemical state, evolution in time, location and distribution within the variety of astrophysical objects is still a work in progress and researchers are using a large variety of observational and theoretical tools (Ascasibar et al. 2015; Asplund 2005; Lodders 2003; Nomoto et al. 2013).

Low-mass AGB stars and *novae* are predicted to be the most prolific sources of dust in the Galaxy being characterized by dust forming episodes in the ejecta (Gehrz et al. 1998) posing the best conditions for gas/dust chemistry (Tielens 2013). Starting near the stellar photosphere, chemical species and dust condensates are produced in concentric shells characterized by a non-thermodynamic equilibrium due to steep temperature-density-radiation gradients (Schöier et al. 2011). As a consequence, circumstellar envelopes and disks can be well defined as *chemical factories* (Jones 2016; Li et al. 2020) also producing biologically relevant molecules (Bekaert et al. 2018). For example, in the C-rich shell of the AGB star IRC+10216 and VY Canis Majoris, over 70 different chemical compounds have been found (Tenenbaum et al. 2010a,b).

Most importantly, refractory-element-bearing species such as TM are predicted to be contained in mineral grains (Henning and Semenov 2013), as supported by condensation models (Lodders and Fegley 1999; Wood et al. 2019).

In fact, the difficulty in the detection of TM in their elemental and molecular forms (gas-phase) mainly derives from their inherent physical-chemical properties behaving as refractory elements easy to deplete and condense into dust grains (Schwander et al. 2014; Thiabaud 2014). For example, even if depleted the detected amount of Fe is 100 times less than what is expected justified by further condensation in silicate dust grains (Jenkins et al. 1986). As a consequence Fe together with its FeS derivative has been proposed to be included in interstellar silicates based on lithophile elements such as O, Si, Mg, Ca and Al (Savin et al.

2012) or included in interstellar silicates in the form of FeS (Köhler 2014; Wood et al. 2019) though by examining colder regions some evidence has been collected on the presence of iron in the ISM (Inter-Stellar Medium) in its neutral or ionic forms (Snow et al. 2002).

However refractory elements in circumstellar environments are not all contained in dust grains. Si containing molecules have been found in circumstellar shells together with molecules containing metals (Savin et al. 2012). In C-rich envelopes no-TM halides or cyanides (Pulliam et al. 2010) have been found, while in O-rich shells, oxides and hydroxides such as AlO and AlOH dominate with Al proposed to be condensed in Al₂O₃ (Tenenbaum and Ziurys 2010) where the presence of AlO and AlOH indicates that photospheric shocks are likely to disrupt grains.

Furthermore in C-rich shells, silicon is primarily present as SiC, when in O-rich objects in oxide condensates while P is probably present in the form of *schreibersite*, (Fe,Ni)₃P and Mg is contained in silicon and aluminum oxides (O-rich shells) and as MgS (C-rich shells).

The detection of silicate dust grains containing O, Si, Fe and Mg, as well as some Ca and Al, provides an important clue on dust chemical composition and evolution (Savin et al. 2012). For example to unveil the cooling history of the Solar Nebula, new kinetic condensation models have been applied to simulate the condensation of refractory metals based on the elemental analysis of Refractory Metal Nuggets (RMNs; i.e. submicrometer highly siderophile element rich metal alloys) in primitive meteorites (Mingen 2020).

Since all the heavy and refractory elements are condensed into dust grains (Kuljeet and Piyush 2018; Thiabaud et al. 2014), it is interesting to understand how TM can contribute to the development of a complex (organic) chemistry working as catalysts. In fact TM due to their bonding abilities with a vast set of organic and small inorganic molecules such as water or ammonia, open the possibility to be fixed not only in “dusty” inorganic particles condensates but also in organometallic or metallorganic compounds.

In the next Sect. 1.2.2 the physical-chemistry of TM is briefly reviewed.

1.2.2 *Physical-Chemistry of TM*

The TM physical-chemistry in the pure state or as part of chemical compounds is out of scope of the present study and there are excellent reviews and books dealing with it (Albright et al. 2013; Miessler et al. 2014; Vogiatzis et al. 2019). However it follows a short presentation on why TM have such a rich and flexible chemistry.

Basically the physical-chemical behaviour of TM is determined by their d shell electrons (d orbitals). In Fig. 1.2 a pictorial representation of the five d orbitals is shown.

In fact some TM properties like: (a) wide variety in the oxidation number, due to the relatively low energy gap between the different oxidation states; (b) magnetic properties such as paramagnetism due to the unpaired electrons; (c) color,

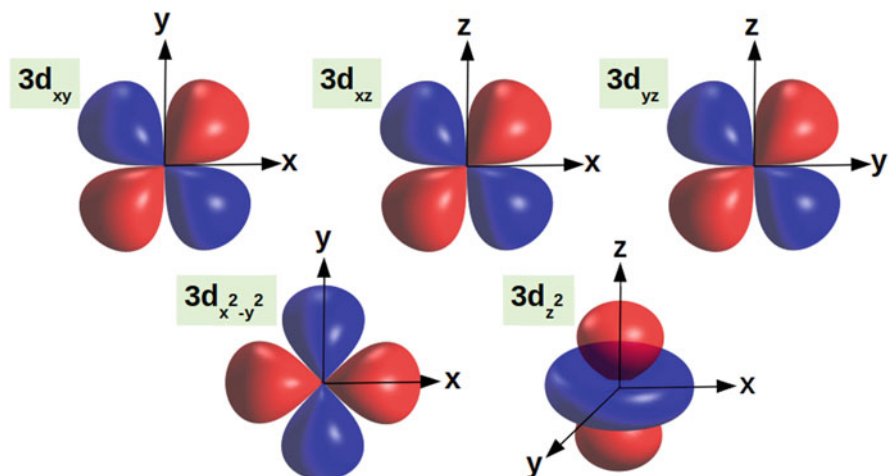


Fig. 1.2 Pictorial representation of the five d orbitals of a first row TM. Rendered by Avogadro Hanwell et al. (2012)

Table 1.1 Periodic table of the first row transition metals

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic Number	21	22	23	24	25	26	27	28	29	30
Electron configuration	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$

due to the *d-d* electronic transitions and most importantly for our analysis (d) catalytic abilities, due to the low energy difference between the oxidation states and involvement of the d orbitals (see Sect. 1.3).

The general electronic configuration of the d-block elements of which TM are part is: [Inert gas] $(n-1)d^{1-10} ns^{0-2}$. In Table 1.1 the electronic configuration of only the first row TM is reported.

The particular focus on first row TM is because in addition to Mo, Cd (both second row TM), W (third row TM) and some Lanthanides (f block) (Daumann 2019) many are essential to living organisms (Nielsen 1999).

A fast look at Table 1.1 tells us that Zn is not included in the TM family. In fact by definition a TM has a partially filled *d* shell while Zn has also in the oxidation state 2^+ a completely filled d shell. Furthermore with the exception of Cr and Cu where one s electron moves into the d shell once an electron is added during the *aufbau* process, the filling of the d orbitals follows the *Madelung* rule: [Inert gas] $ns^2 (n-1) d^{1-10}$ (not valid for the TM ions). It should be underlined that the *ns* and *np* orbitals contribute very little to TM chemical properties moving in a row from left to the right.

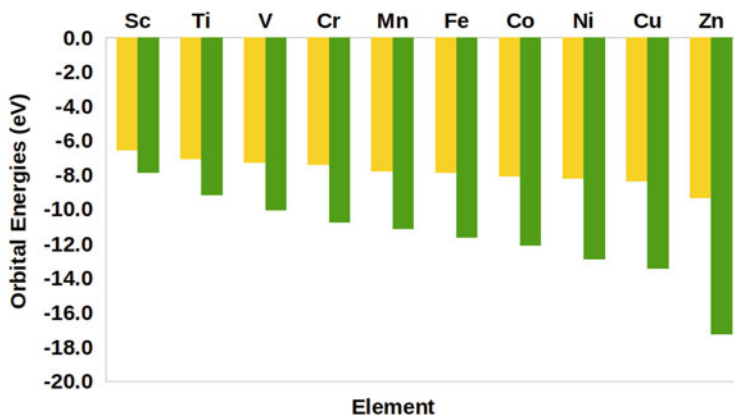


Fig. 1.3 Orbital energies of the first row TM. 4s orbitals = yellow; 3d orbitals = green. Data from ref. Mann et al. (2000)

This phenomenon is particularly important considering TM ions with charges $\geq 1+$. In fact TM ions with 1+/2+ or greater charges have no *s* electrons but only *d* electrons (Mann et al. 2000; Rich 1965) (see Fig. 1.3).

Furthermore and in particular in case of first row TM spin-forbidden reactions are easy to be accomplished. In fact the classical reaction scheme is based on a single determined Potential Energy Surface (PES) characterized by one spin. The jumping to a different PES (inter-system crossing) with a different spin is generally forbidden. However when TM are involved the inter-system crossing is easily allowed due to the strong spin-orbit coupling opening a new realm of reaction channels otherwise impossible to be reached (Miessler et al. 2014). Inter-system crossing is quite frequent for the first-row TM due to the large exchange constants between the 3d-orbitals, resulting in a large spin-orbit coupling.

To sum up, the ability to easily shuffle electrons between the *d* orbitals as well as their ability to mix with other donor/acceptor electron molecules (see Sect. 1.3) makes TM in both neutral and ionic forms “catalytic machines”.

1.3 Organometallic and Metal-Organic Compounds

The IUPAC definition of organometallic compounds (OC):

Classically compounds having bonds between one or more metal atoms and one or more carbon atoms of an organyl group. In addition to the traditional metals and semimetals, elements such as boron, silicon, arsenic, selenium and lithium are considered to form organometallic compounds (Moss et al. 1995).

In “common jargon” a metal-organic compound differs from an organometallic one because of the metal center bond to an organic molecule not by a C atom but by a hetero-atom. For example TM-alkoxides, TM-phosphinine, TM-alkylamides and

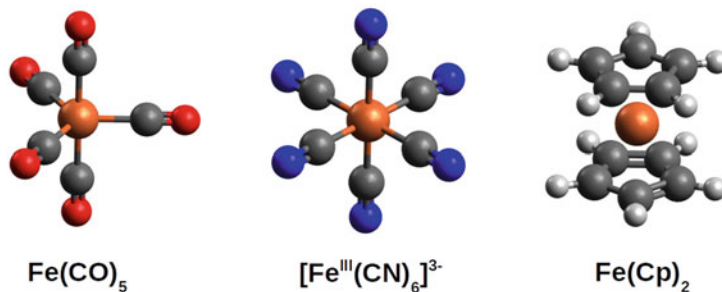


Fig. 1.4 “Classical” organometallic compounds: iron-pentacarbonyl; [iron(III) hexacyanide]³⁻; ferrocene. Rendered by Avogadro (Hanwell et al. 2012)

TM-NHC (NHC=N-heterocyclic carbene) are all metal-organic compounds where the organic molecule or ligand is bond to an O, P and N atom, respectively.

In the following explanation, if not directly cited, the OC term is used indifferently for the metal-organic compounds too.

In an OC the TM center is “surrounded” by ligand molecules (L) as in classical carbonyl compounds like $\text{Fe}(\text{CO})_5$, $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ or in a sandwich compound like ferrocene (see Fig. 1.4).

The importance of OC is due to their catalytic abilities. Especially in industrial processes (homogeneous phase) like hydrogenation, hydrosilylation, hydroformylation, hydrocyanation, olefin metathesis, alkene polymerization, alkene oligomerization, carbonylation and hydrocarboxylation would be impossible or extremely difficult to be performed if not for the OC (Cornils et al. 2017).

OC are not only used and studied in homogeneous catalysis but in the heterogeneous phase as well, where intermediates on metallic surfaces, metallic oxide and MOF (Metal-Organic Frameworks) are proposed to be similar to the homogeneous phase OC (Li and Liu 2014), one example is the Fischer-Tropsch process (van de Loosdrecht et al. 2013).

OC are also used in fine chemical or laboratory synthesis especially in cross-coupling reactions forming carbon-carbon bonds between complex substrates i.e. Suzuki-Miyaura coupling, Buchwald-Hartwig and Sonogashira coupling to cite only a few (de Meijere et al. 2013).

The chemistry of OC compounds is characterized by a series of important reactions such as gain or lose of one or several ligands, undergoing molecular rearrangement or the formation and breaking of bonds like TM-C, TM-X and TM-TM (Wilkins 2002). Here follows a list of the most typical reactions based on the scheme of Miessler et al. (2014). Details of the kinetics and reaction mechanisms can be studied in several books (Miessler et al. 2014; Wilkins 2002).

1. Reactions involving gain or loss of ligands

(a) Ligand dissociation and substitution

- one or more of the ligands is lost and substituted by a different one;

(b) Oxidative addition/Reductive elimination

- in the oxidative addition there is an increase in the oxidation state (formal) and coordination number of the metal
- the reductive elimination is the reciprocal of oxidative addition i.e. a decrease in both the oxidation and coordination number.

(c) Nucleophilic displacement

- some ligand displacement reactions can be considered as nucleophilic substitutions where ligands work as nucleophiles. Especially the negatively charged OC can be considered nucleophiles.

2. Reactions involving modifications of ligands

(a) Insertion

- insertion reactions are defined as formal insertions of one ligand (generally unsaturated) into another metal-ligand bond on the same complex;

(b) Hydride elimination

- transfer of a hydrogen atom from a ligand to the metal center;

(c) Abstraction

- defined as elimination reactions in which the coordination number of the metal does not change;

In a catalytic cycle where OC function as a catalyst many of the aforementioned single reactions are involved and each single reaction can be characterized by many reactions steps (Wilkins 2002).

Such an ensemble of reactions is possible due to the extreme flexibility of TM i.e. oxidation state, spin state, ligand geometry and the ability to accept/donate electrons to/from $\sigma - \pi$ donors/acceptors ligand molecules (Albright et al. 2013).

To illustrate the rationale behind single reactions based on a Molecular Orbital (MO) approach would be out of the scope of the present work and there exist excellent reviews (Albright 1982) as well as textbooks (Albright et al. 2013) on the argument.

However a short introduction to the MO theory of TM complexes on a “classical” octahedral complex made by six σ donor ligands (L) can give a hint on the complexity and elegance of TM compounds.

There are several steps needed to build an MO diagram such as is reported in Fig. 1.5 like: identify the symmetry group from the geometry, fix a reference axial system, determine the fragments, energy levels and symmetry of the fragment orbitals, combine fragment orbitals with same symmetry, electron insertion, check for MO mixing (Albright et al. 2013).

The amount of qualitative information to be obtained from such MO diagrams is quite detailed and gives a first impression on what properties the OC compounds examined has.

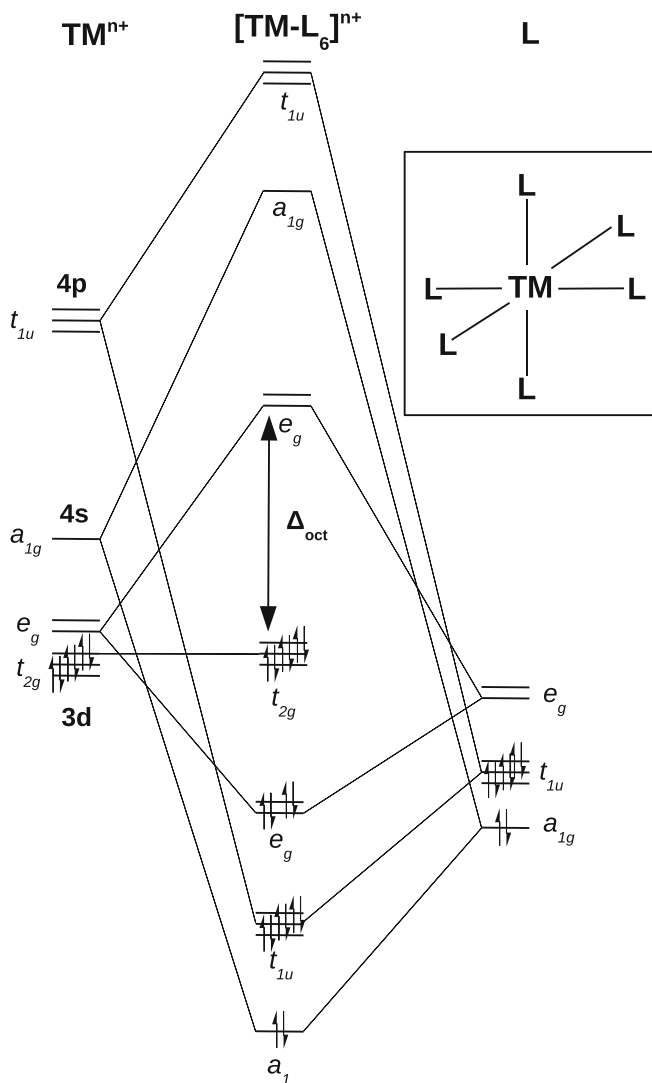


Fig. 1.5 Molecular orbitals of a generic octahedral TM-L_6 complex. $\text{L} = \sigma$ donor ligand

For example one important parameter is the octahedral splitting (Δ_{oct}) depending on the interaction strength between the ligands and the TM center.

As it can be seen in Fig. 1.5 the TM d-orbitals split energetically into two groups. The d_{xy} , d_{xz} and d_{yz} orbitals will be characterized by a lower energy compared to the d_{z^2} and $d_{x^2-y^2}$. This is due to the fact that the d_{xy} , d_{xz} and d_{yz} orbitals are subject to less repulsion compared to the d_{z^2} and $d_{x^2-y^2}$.

By definition when a ligand induces a large splitting of the d-orbitals (Δ) it is a “strong-field” ligand such as CN^- and CO while ligands like I^- or SCN^- are “weak-field” ligands inducing a small splitting.

It should be mentioned that the order of weak to strong field ligands is based on the “spectrochemical series” determined by experimental absorption spectra of cobalt complexes (Tsuchida 1938).

A MO diagram as reported in Fig. 1.5 can be built for each of the possible “fundamental” ligand geometries surrounding the TM such as square planar, pyramidal, tetrahedral, pentagonal and trigonal bi-pyramidal.

Focusing on some special ligands, the CO, CN^- and olefins ($\text{R}_1\text{-C}=\text{C-R}_2$) are of main interest and can be a representative ensemble in OC-astrochemistry.

In Fig. 1.6 a classical example of a CO molecule bond to a TM center is illustrated together with the correlated Molecular Orbital (MO) diagram (Albright et al. 2013).

By analyzing Fig. 1.6 the TM-CO bond is characterized by two main parts:

- (a) an electron donation from the CO lone pair mainly localized on the CO carbon into an empty TM d-orbital;
- (b) because of the electron donation the TM gets electron rich and in order to release the higher electron density a TM d-filled orbitals can interact with an unoccupied CO π^* orbital, defined as π -backbonding/backdonation.

The TM- CN^- case is very similar to the TM-CO as CO and CN^- are “isoelectronic” i.e. each molecule has two atoms and 10 valence electrons, where each single atom has five electrons as a lone-pair and a triple-bond.

Another example of great interest similar to the TM-CO/ CN^- bond is the TM-olefin bond described by the Dewar-Chatt-Duncanson model (Albright et al. 2013) and similar to the TM-CO bond/MO diagram (see Fig. 1.7).

Like in the previous CO-TM bond (see Fig. 1.6) there is a σ donation from the $\text{C}=\text{C}$ double bond π orbital of the olefin (ethylene in the example) together with a π -backbonding into an empty π^* orbital on ethylene.

1.4 Organometallic-Astrochemistry

In the previous sections a description of the TM properties with a particular emphasis on organometallic compounds was given.

There is no doubt that TM/OC chemistry determines an important *corpus* of chemical reactions in modern chemistry.

However by shifting the attention from “terrestrial” to more “celestial” problems the interest in TM within the astrophysicists/astrochemists community still occupies a light-weight place.

Citing Irikura et al. (1990):

Transition metals traditionally have been ignored in chemical models of interstellar clouds. Thermochemical considerations indicate that the formation of several important species can be catalyzed by transition metal ions. . .

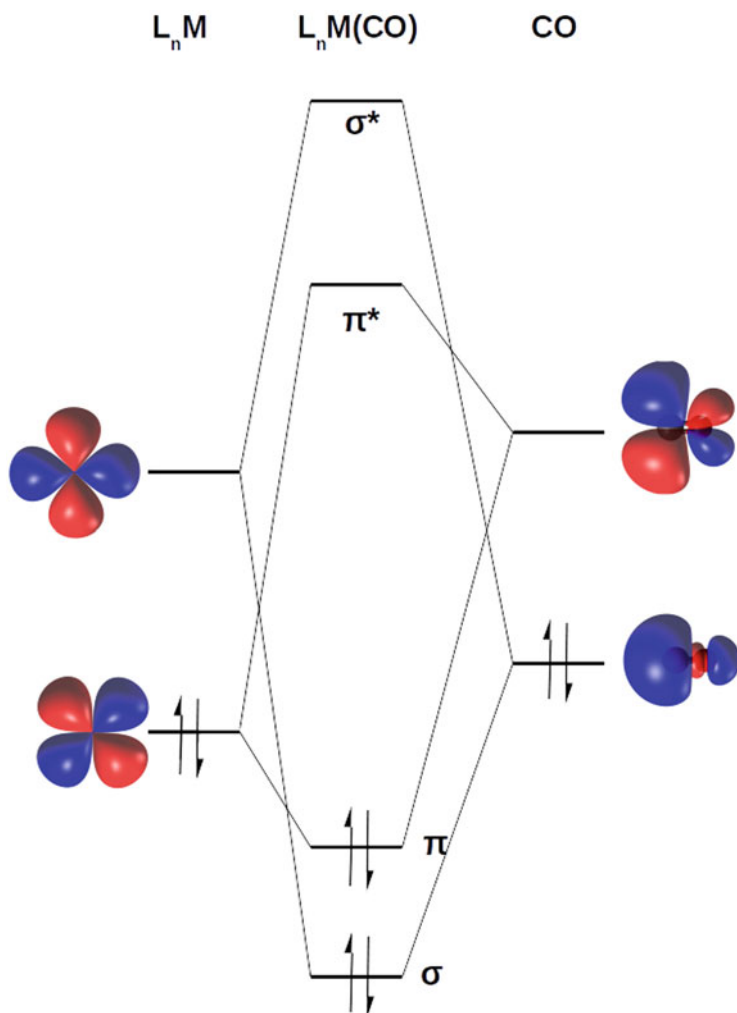


Fig. 1.6 MO diagram of the CO σ bond and π -backbonding with a TM center. Rendered by Avogadro Hanwell et al. (2012)

In fact seminal works considering the importance of TM in space date back to the 1980–1990s decades of the last century including the analysis of the formation of FeH^+ by radiative association in diffuse interstellar clouds (Irikura et al. 1990), the gas phase chemistry in interstellar clouds where Mg and Fe are included (Prasad et al. 1980), the PAH (Polycyclic Aromatic Hydrocarbons) and fullerene ions reactions in interstellar and circumstellar chemistry (Bohme 1992), the role of organometallic molecules in the interstellar and circumstellar chemistry (Klotz et al. 1994), the first analysis if organometallic reactions are efficient processes to be included into astrochemical reaction pathways (Serra et al. 1992), theoretical

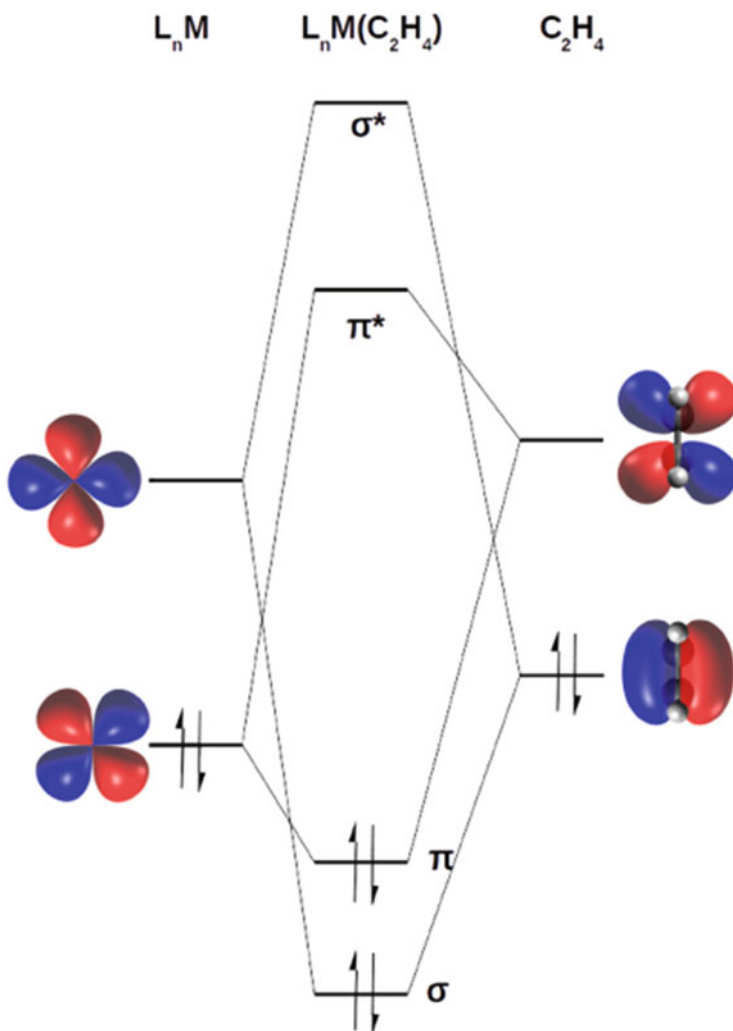


Fig. 1.7 MO diagram of an olefin double bond (C_2H_2) involved in a σ bond and π -backbonding with a TM center. Rendered by Avogadro Hanwell et al. (2012)

analysis of the coordination of Fe-PAH (Chaudret et al. 1991), experimental investigations on gas-phase reactions of $[Fe(CO)_n]^+$ with H and N (Mestdagh et al. 1992), the possible contribution of organometallic molecules in the solar system ices (Klotz et al. 1996), experimental investigations on PAH- $[TM]^+$ adducts in the gas phase (Boissel 1994) and photochemical reactions of the Fe oxide series (Fe, FeO, Fe_3O_4 , Fe_2O_3) (Duley 1980).

In the last decade there happened a slow growth of interest in TM and OC compounds as to explain iron depletion by iron-carbonyl species (Halfen and Ziurys

2007) or Fe-PAH (Szczepanski et al. 2006), Si-PAH π complexes (Joalland 2009), the 21 μm line by Ti-fullerene adducts (Kimura et al. 2005) and FeO (Li et al. 2013), the refractory components chemical evolution and condensation sequence in stars and disks (Schwander et al. 2014; Thiabaud et al. 2014), H₂ formation on Fe⁺ centers grafted on a silica surface (Fioroni and DeYonker 2016) and a consistent ensemble of laboratory based millimeter–submillimeter spectra of TM (Cr, Ni, Co) nitrides and carbides (Brewster and Ziurys 2001; Sheridan et al. 2002, 2003) whose detection would give further details on the AGB nucleosynthesis, dust-grain composition and gas-phase chemistry in circumstellar material.

Obviously once TM are introduced the correlated TM “organometallic chemistry” is implicitly proposed as some of the aforementioned compounds are organometallic in nature though in some pioneer studies the term “organometallic” or “coordination” was mentioned within the main title (Boissel 1994; Klotz et al. 1996, 1995, 1994; Marty et al. 1996; Serra et al. 1992).

More recently TM have been proposed to be players in the net of reactions involving the formation of organic/organometallic compounds in space by co-determining the homogeneous/heterogeneous chemistry represented by the gas/gas and gas/dust grain interactions function of the astrophysical object (Fioroni 2014, 2016).

Several classes of organometallic compounds based on the most abundant cosmic TM as Fe, Co and Ni and ligands such as CO, CN⁻, H₂O and PAH have been analyzed in their IR spectra to characterize the main features for a possible observational survey (Fioroni 2016).

Another class of OC analyzed are Fe-pseudocarbynes (Tarakeshwar et al. 2019). In fact, the presence of such compounds in circumstellar and interstellar environments can partially explain Fe depletion and they can act as catalysts to explain the composition gap between molecules containing nine or fewer carbon atoms and complex molecules.

Regarding Fe(CO)_n complexes, the interaction of Fe and CO at cryogenic conditions results in the formation of FeCO complex which in presence of an excess of CO ends up in the formation of CO₂ (Methikkalam et al. 2020).

The aforementioned list of literature shows a clear interest towards TM and their OC chemical derivatives but a main problem remains: no organometallic species could be observed within the inter-stellar medium with the exception of FeCN found in the dust envelope of the carbon star IRC+10216/CW *Leonis* (Zack et al. 2011).

TM containing molecules not organometallic are FeO, observed in the giant molecular cloud Sagittarius B2 (Furuya 2003) and TiO/TiO₂, observed in the red supergiant VY Canis Majoris (Kamínski 2013).

This is quite surprising since the ability of TM to bind to organic/inorganic molecules is a well established knowledge and this ability enables TM to produce stable chemical complexes with ligands such as the most abundant molecule in space i.e. CO; the organometallic “ligand prototype”; as well as other molecules/ligands like H₂O, CO or HCN/CN to mention few.

However main limitations exist in the *chemical analysis* of extraterrestrial bodies when such analysis is mainly (or only) based on the study of emission/absorption (UV/VIS/IR) and roto/vibrational transition spectra.

In fact, of the ≈ 204 molecules detected in space (interstellar and circumstellar medium), made of 16 different elements and ranging from a size of 2–70 atoms all have been detected across the electromagnetic spectrum i.e. MW to UV (McGuire 2018) in the gas-phase (Kwok 2016).

As a consequence there is an observational bias towards molecules that are easily detected by radio telescopes and thousands of observed molecular lines remain unassigned, due to the lack of laboratory data for comparison (Smith 2019).

In fact using only UV/VIS/IR/MW spectroscopical methods makes it extremely difficult to resolve and to obtain the complete data composition on a complex system especially if in the solid phase.

It is not by chance that the only discovery of organo-metallic molecule FeCN is based on the analysis of the 2 and 3 mm wavelength with the FeCN present in gas-phase (Zack et al. 2011).

It is important to note that the big step toward the assignment of detected lines as well as the modeling of possible complex inorganic/organic mixtures is based on the huge set of laboratory as well as theoretical/computational data that has been produced within the last 10 years (Ruf et al. 2018).

Comparison between the laboratory/theoretical data and the observational one made possible to partially elucidate the complex chemistry found in circumstellar/interstellar environments (Herbst et al. 2020).

However and most importantly the “breakthrough” in the understanding of the complex mixtures and interactions between the inorganic and the organic material is based on the in situ analysis of meteorites (Kebukawa et al. 2019; Schmitt-Kopplina et al. 2010; Smith et al. 2019).

The in situ analysis of meteorites is the link between OC astro-/pre-/Life’s origin chemistry.

In the next Sect. 1.5 the known OC compounds involved in the prebiotic and Life’s origin are listed, and future potentials of the topic will be developed.

1.5 OC in Pre-biotic and Life’s Origin

In 2010 Morowitz et al. published a paper with the title: *Ligand Field Theory and the Origin of Life as an Emergent Feature of the Periodic Table of Elements* (Morowitz et al. 2010). In summary the hypothesis is that by TM catalysis it is possible to build up the monomers that can be used to make more efficient and large protein catalyst. The title is a direct “hit” clearly pointing to the main contribution given by the TM and related OC to prebiotic reactions.

It should be underlined that not so rarely organometallic compounds characterized by a TM-C bond are confused with “metal organic compounds”, previously defined. For example the Fe-CN is an organometallic compound while Fe-NC is

a metal-organic compound. Furthermore in the term metal-organic compounds are contained where TM are not involved such as the “Grignard reagents” defined as R-Mg-X where R is an organic substituent, X is a halogen and Mg is an alkali-earth metal. For all of these reasons it has been decided to include some few interesting metal-organic compounds even though TM are not involved.

To unravel the contribution of TM, organometallic and metal-organic compounds in the synthesis of the Life’s building blocks it is helpful to split the synthetic chemical environments into two main locations: the “in Space” one responsible for the *exogenous delivery* and the “on Earth” responsible for the *endogenous synthesis* (Sandford et al. 2020).

As *exogenous delivery* one defines the delivery of organic building blocks by extraterrestrial objects like meteorites while *endogenous synthesis* is the synthesis of organics/prebiotic molecules on Earth due to shock waves (meteoric impacts), UV and electric discharge (Miller-Urey synthesis) and hydrothermal vents.

1.5.1 Exogenous Delivery

Space itself is an extremely heterogeneous chemical reactor where conditions like P, T, mass density, radiation and energetic particles vary to a great extent (Draine 2011) i.e. $10 \leq T(\text{K}) \leq 10^6$; $10^{-4} \leq n_H (\text{cm}^{-3}) \leq 10^6$.

Furthermore the matter is subject to a cycle from Star Formation→Planetary System→Stellar Outflows→Diffuse Interstellar Medium where chemistry can play a decisive role (Sandford et al. 2020).

Of particular interest are interstellar clouds and protostellar disks where presumably prebiotic astrochemistry occurs.

In interstellar clouds where $T \approx 20 \text{ K}$, dust particles with a siliceous core covered by ice of mixed composition like CO, H₂O, CO₂ CH₃OH are subject to a continuous bombardment of photons and/or energetic particles producing an extremely reactive mainly barrier-less radical chemistry (Boogert et al. 2015; Herbst 2013; Potapov et al. 2020).

Such ice processing produces an organic “milieux” that can be later incorporated into a planetary system (Solar system).

Once in the Solar system and during the proto-solar nebula stage due to the turbulent flow, the dust particles move near and far from the forming star experiencing a strongly variable range of T and radiation undergoing several cycles of $\approx 10^6$ years of irradiation-condensation-sublimation-condensation of the organic material ending up, by accretion, in asteroids that can deliver the organics to the planets by meteoritic bombardment (Bekaert et al. 2018; Chyba and Sagan 1992; Chyba et al. 1990; Ciesla and Sandford 2012).

The final product of such “cooking” phases is a mixed matrix of mineral-organic phases with interactions still under intensive investigation (Burton et al. 2012; Kebukawa et al. 2019; Le Guillou et al. 2014).