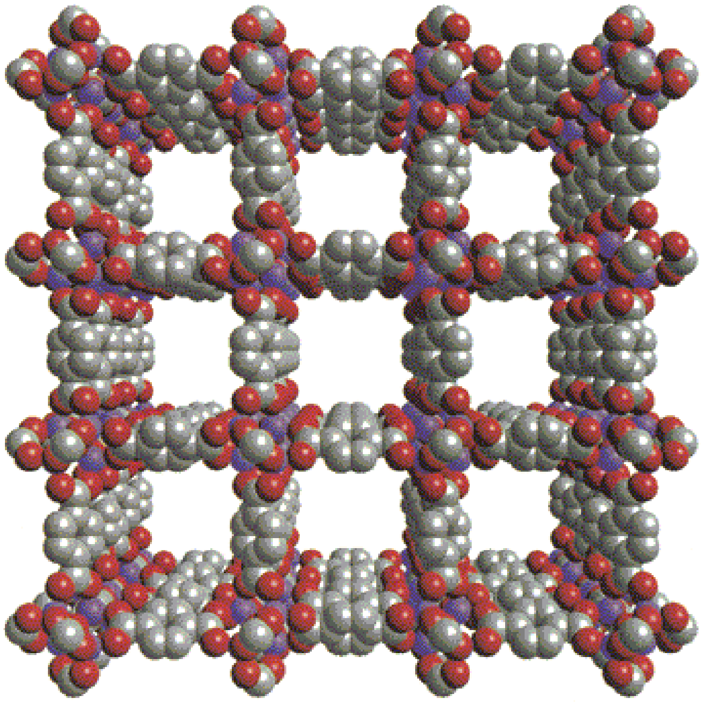
Polymeric Materials

Year 2
Option Module

Inorganic polymer chemistry

(RED)



Learning Objectives

By the end of this course you should:

i) understand the structural and electronic features of metal complexes that lead to polymerisation
ii) be able to describe the mechanism of metal-catalysed Ziegler-Natta and ring opening polymerisations of alkenes
iii) understand the terms atactic, isotactic and syndiotactic.
iv) understand basic relationships between polymer and metallocene complex structure for Ziegler-Natta catalysis
v) understand the possible polymer structures from ROMP
vi) understand the difference between enantiomorphic site control and chain end control for stereospecific polymerisation.
vii) understand the structures of common inorganic polymers, their preparation and applications.
viii) understand the concept of charge transfer complexes.
vix) describe the key structural and electronic features of charge transfer complexes that give rise to magnetic behaviour.
vx) understand how simple coordination polymer structures that can be built from combinations of metal ions and organic linkers
vxi) briefly describe uses of coordination polymers

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‘*Polymers*’, D. Walton and P. Lorimer, **2001**, Oxford Chemistry Primers
‘*Metallocenes-An introduction to sandwich complexes*’, N. J. Long, **1998**, Blackwell Science
‘*Advances in Non-Metallocene Olefin Polymerization Catalysis*’, V. C. Gibson and S. T. Spitzmesser, *Chem. Rev.* **2003**, 103, 283-315.
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‘Organometallic Magnets’ J. S. Miller and A. J. Epstein, *Coord. Chem. Rev.*, **2000**, 206-207, 651-660.
‘Metal-organic frameworks’, S. L. James, *Chem. Soc. Rev.*, **2003**, 32, 276-288
‘Engineering coordination polymers towards applications’, C. Janiak, *Dalton Trans.*, **2003**, 2781-2804.

Related Courses

Transition metals (AKDK)	year 1
Alkene and alkynes (RJKT)	year 1
Macromolecules (DKS)	year 1
Metal-ligand and metal-metal bonding (RED)	year 2
Organometallic chemistry (JML)	year 2
Inorganic reaction mechanisms (SBD)	year 2
Radicals in synthesis (AFP)	year 3
Supramolecular chemistry (DKS)	year 3
Inorganic materials chemistry (RED)	year 3
Solid state chemistry (KW)	year 3

Introduction

Polymers are ubiquitous; from the natural world (DNA, proteins, natural rubber, cellulose, silk) to man made (Nylon, polyethylene, polyvinylcholride, superglue etc.)

Metal complexes are of interest in polymerisation because:

1. They can catalyse polymerisation
2. Control polymer chain length and structure
3. Polymers containing metals can have useful properties (magnetic, electrical, optical, catalytic)

The topics this course will cover

1. The synthesis and mechanism of organic polymers using metal complex catalysts:

    Ziegler- Natta catalysis: used to prepare polyethylene and polypropylene. millions of tons a year.

    Ring opening polymerisation catalysis: used to prepare 'designer' functional polymers and polymers with high mechanical strength.

2. The synthesis and applications of polymers containing inorganic atoms:

    Main group containing polymers: polysiloxanes, polysilanes, polyphosphazenes.

    Transition metal containing polymers.

3. Organic-inorganic hybrid materials

    Organometallic magnets

    Metal coordination polymers (metal-organic frameworks)

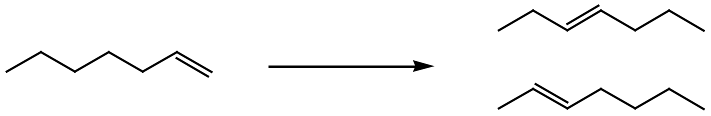
Metal Catalysed Reactions of Alkenes

Three main classes are **isomerisation**, **polymerisation** (including oligomerisation) and **metathesis**.

Here alkene polymerisation and ring opening metathesis polymerisation (ROMP) will be described.

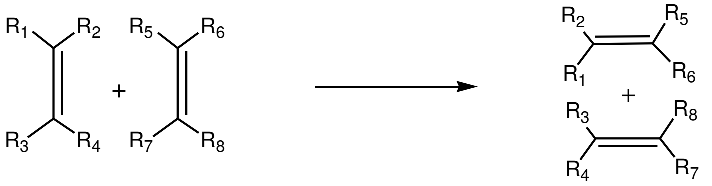
Driving force(s) for reaction

Isomerisation



Relative stability of alkenes and entropy

Metathesis

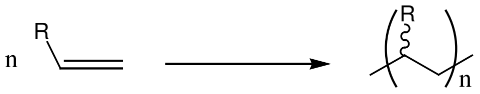


Relative stability of alkenes and entropy

Oligomerisation

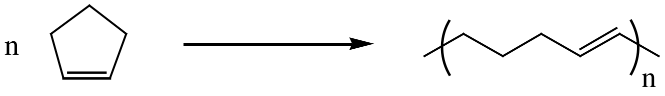
C-C σ-bond formation

Polymerisation



C-C σ-bond formation

Ring opening metathesis polymerisation (ROMP)



Relief of ring-strain

Polymerisation of alkenes

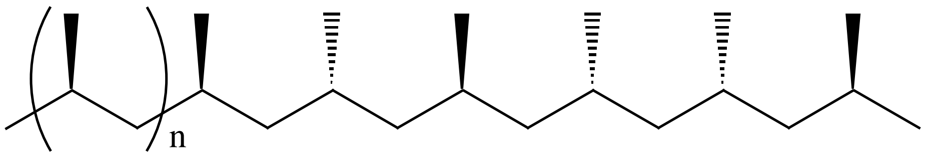
In 1955 Zeigler discovered that heterogeneous mixtures of $TiCl_4$ and $AlEt_3$ catalysed the polymerisation of ethene to linear polyethylene at room temperature and pressure.

Later Natta subsequently developed this and similar systems and demonstrated that propene could be polymerised stereospecifically to isotactic polypropylene.

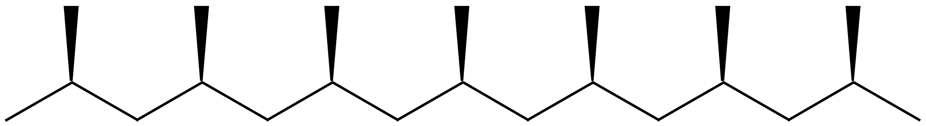
Aside: stereochemistry of polymers is described by the ***tacticity***

e.g. of propene

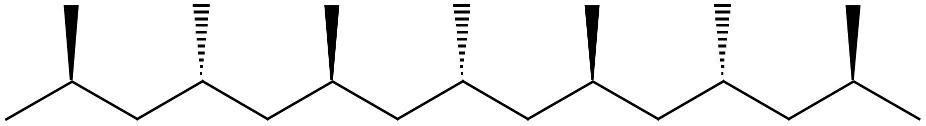
Atactic: adjacent stereocentres have random configuration



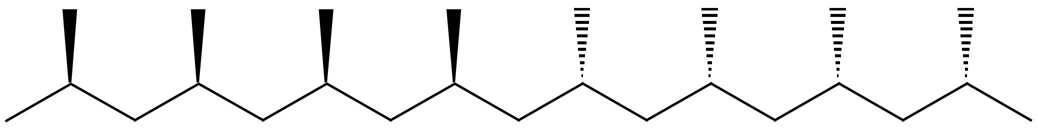
Isotactic: adjacent stereocentres have same configuration



Syndiotactic: adjacent stereocentres have opposite configuration



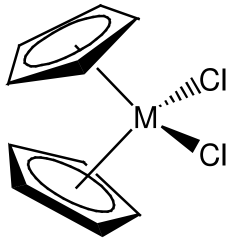
Stereoblock:



But using $TiCl_4/AlEt_3$ the tacticity is low and polydispersity is high.

Metallocenes

In the 1980's Kaminsky showed that early transition metal metallocene complexes in homogeneous solution could polymerise α-alkenes stereospecifically in the presence of a methyl aluminoxane (MAO) cocatalyst.

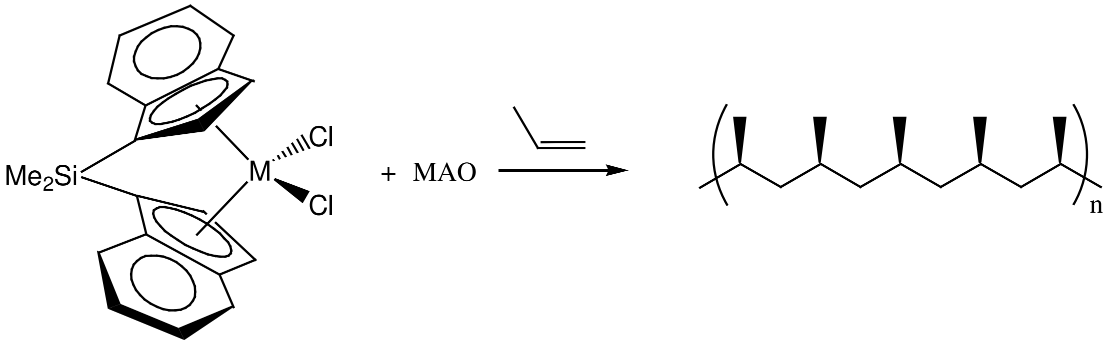


M = Ti, Zr, Hf

$AlMe_3 + H_2O \longrightarrow (MeAlO)_n$

methylaluminoxane
(MAO)

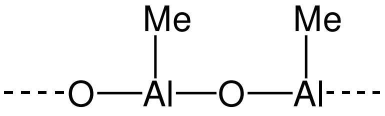
Later Britzinger showed that chiral metallocenes could rapidly polymerise α-alkenes with high stereospecificity (isotactic polymer) and low polydispersity.



M = Zr, Hf
ansa-bridge metallocene
*C*2 symmetric

Cocatalyst

MAO is made up of a complex mixture of clusters containing (MeAlO) moieties



$$\text{----O—}\overset{\text{Me}}{\text{Al}}\text{—O—}\overset{\text{Me}}{\text{Al}}\text{----}$$

MAO serves three key roles

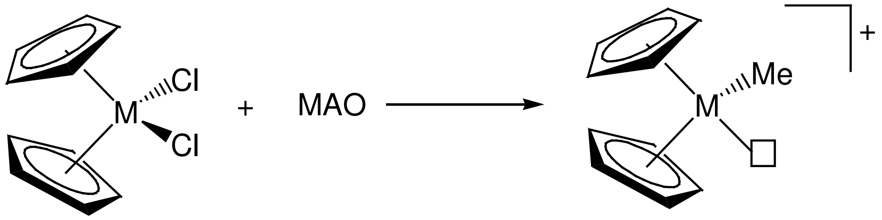
1. Alkylating agent for the formation of M-Me complexes

2. Lewis base, forming cationic metallocene. (cationic polymerisation)

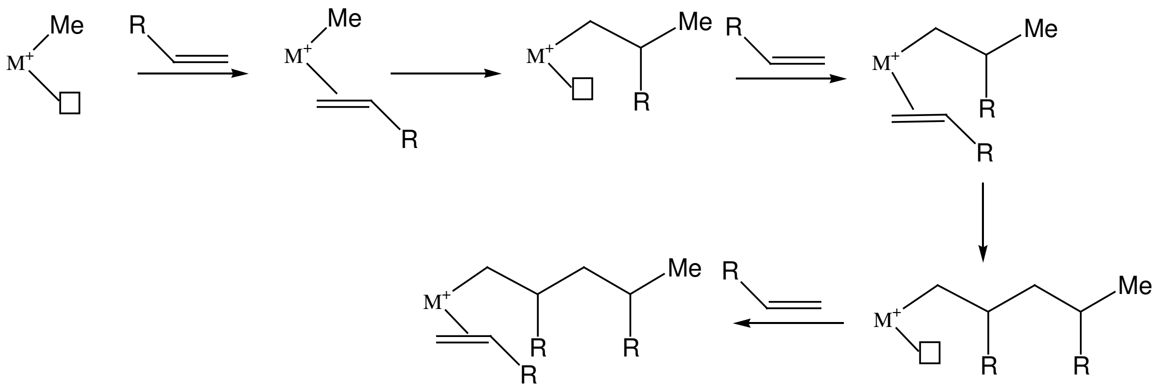
3. Removes water from the alkene feedstock. MAO: catalyst usually about 1000:1

Mechanism of alkene polymerisation

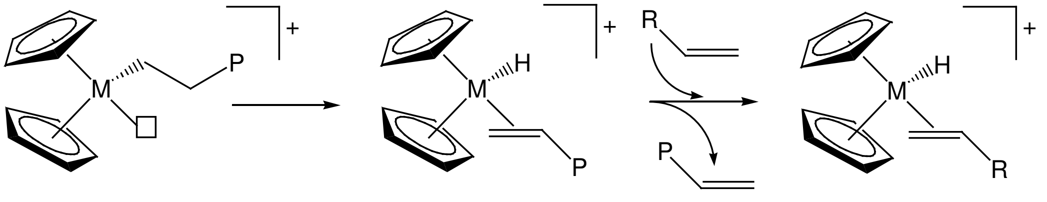
Initiation



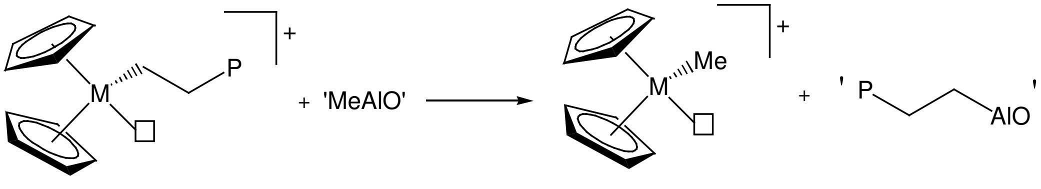
Basic propagation mechanism (essentially same for metallocenes and $TiCl_4/AlEt_3$)



Termination steps



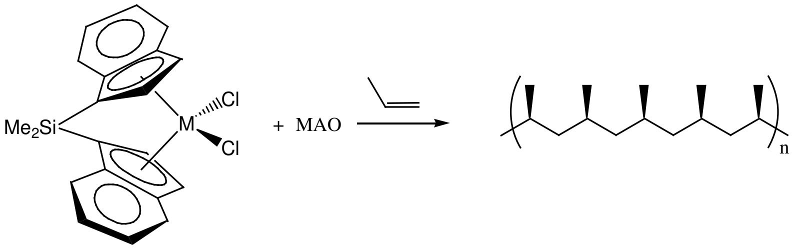
β-H elimination

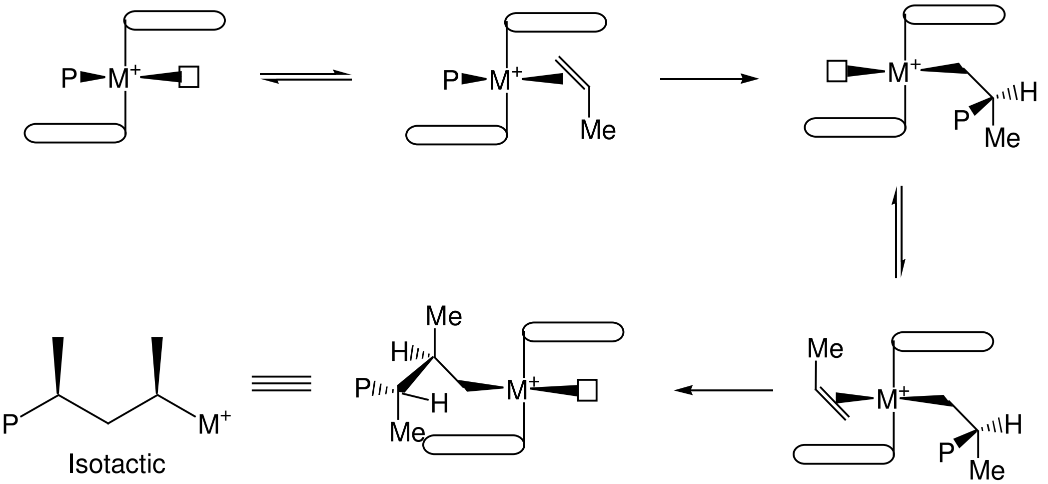


Chain transfer

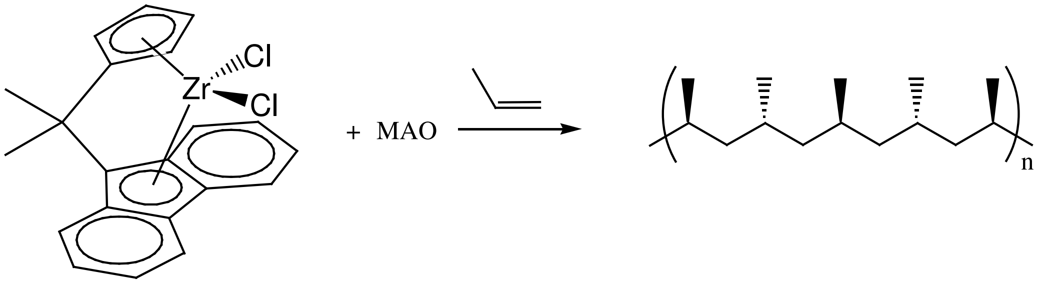
The relative rates of initiation (k_i), propagation (k_p) and termination (k_t) determine if polymerisation occurs and polymer dispersity.

Stereospecific Polymerisation





Syndiotactic polymers



C_s symmetric

These are examples of *enantiomorphic site control* where the stereochemistry is determined by the structure of the metal complex. In other polymerisations the growing polymer can determine polymer stereochemistry. This is called *Chain-end control* (we will see an example later).

Why early metal polymerisation catalysts work

1. Early metal complexes are electrophilic. Rapid binding of alkene increases k_p
2. Group 4 complexes are d^0. Back-bonding from metal to alkene is weak lowering the activation energy for insertion, k_p not reduced.

3. For metallocenes $k_p >>> k_t$ leads to every metallocene being catalytically active So called single-site catalysis leads to low polydispersity if k_i is $> k_p$

Many monomers can be polymerised by metallocenes but they are very sensitive to water (need lot of MAO) and are intolerant to some monomer polar functional groups.

Late-metal catalysts

Would be good because:

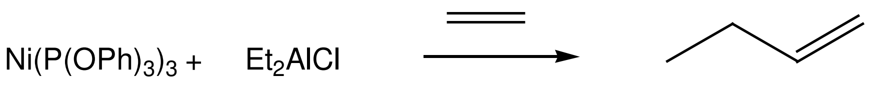
1. More kinetically stable to hydrolysis (stronger M-alkyl bond strength)
2. Would not need lots of MAO (bad for the environment)
3. Tolerant to polar monomers

But:

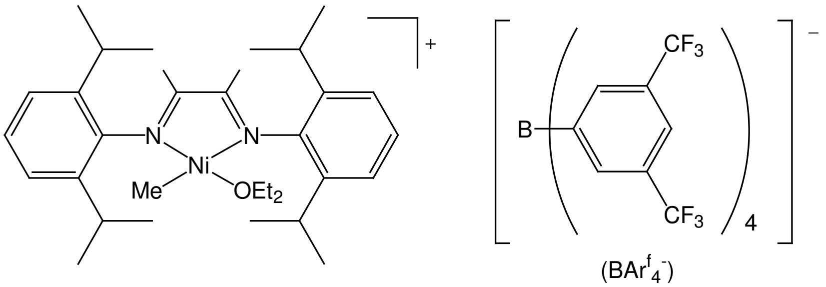
1. Late metals have strong metal-alkene back-bonding
2. Undergo rapid β-H elimination
3. Late metals are 'soft' and complexes are not usually electrophilic.

All lead to $k_p \approx k_t$. Late metals used in alkene dimerisation (oligomerisation).

e.g.



In 1996 Brookhart reported the polymerisation of ethene and α–alkenes using nickel and palladium di-imine complexes and a little MAO.



(BAr$^f_4{}^-$)

Why late metal polymerisation catalysts work

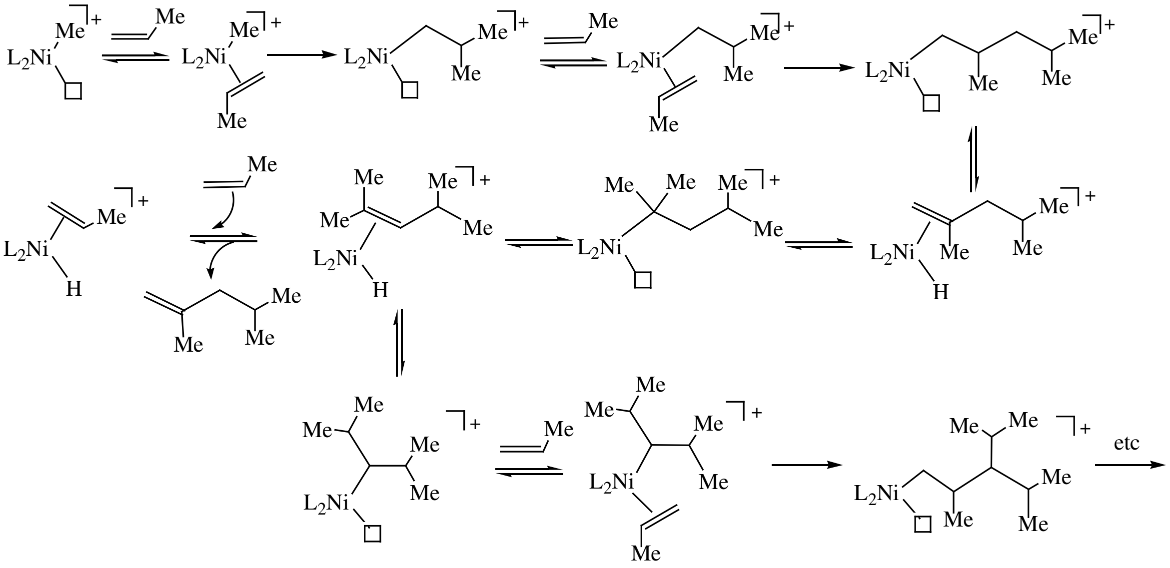
1. Imine ligands are hard donor ligands and the complex is charged. BAr^f anion is 'non-coordinating'. All these increase metal electrophilicity.

2. Bulky N-substituents prevent chain transfer.

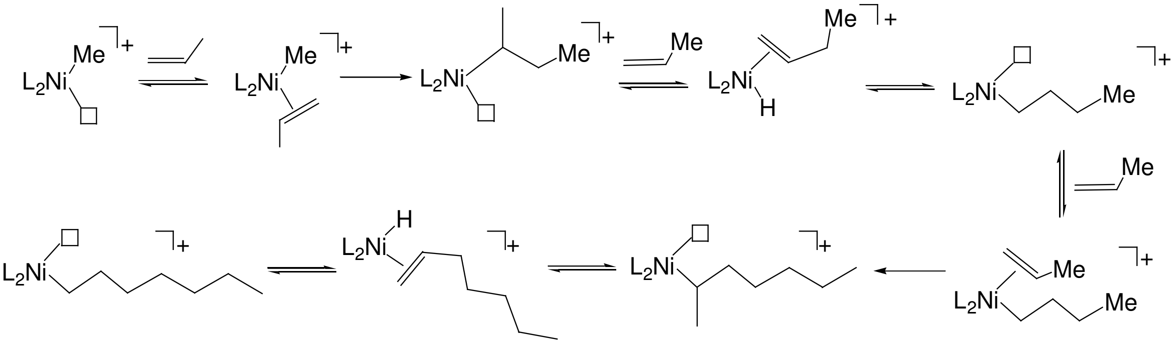
3. Chelating di-imine ligand forces *cis*-disposition of vacant site and growing polymer chain.

4. Ether is a weak ligand and can easily be substituted for an alkene to initiate polymerisation.

In contrast to group 4 using Ni and Pd catalysts the polymers are highly branched. Newer Co and Fe complexes give linear polyethylene.
Mechanism is basically the same except rate of isomerisation is competitive with rate of propagation, which leads to branching.



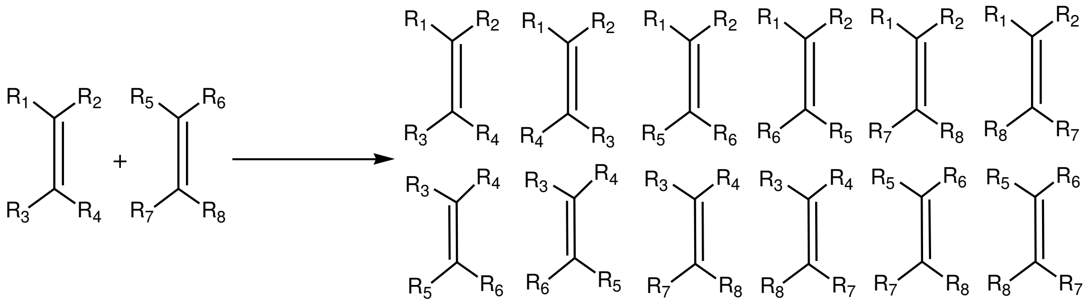
Isomerisation could be very useful for making polyethylene from propene



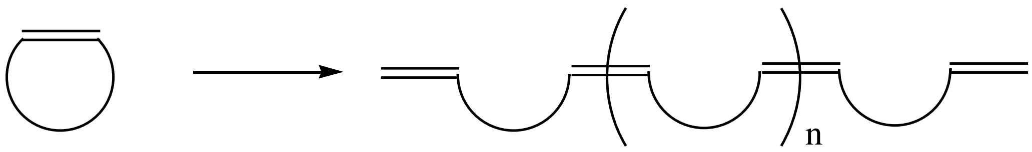
Ring Opening Metathesis Polymerisation (ROMP)

Metathesis: the result of exchange, substitution or exchange of atoms

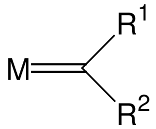
Olefin (alkene) metathesis



Ring opening metathesis polymerisation

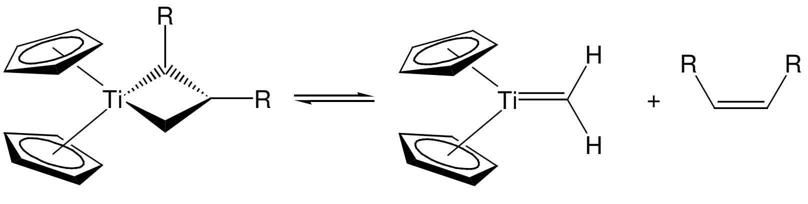


Metal alkylidene (carbene) complexes are central to all olefin metathesis processes.

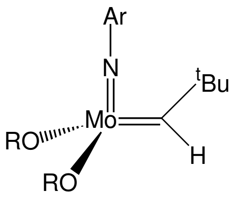


Schrock type carbene (R^1 and R^2 are C or H)

Precatalysts

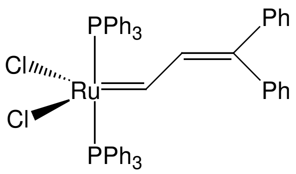


Goodyear



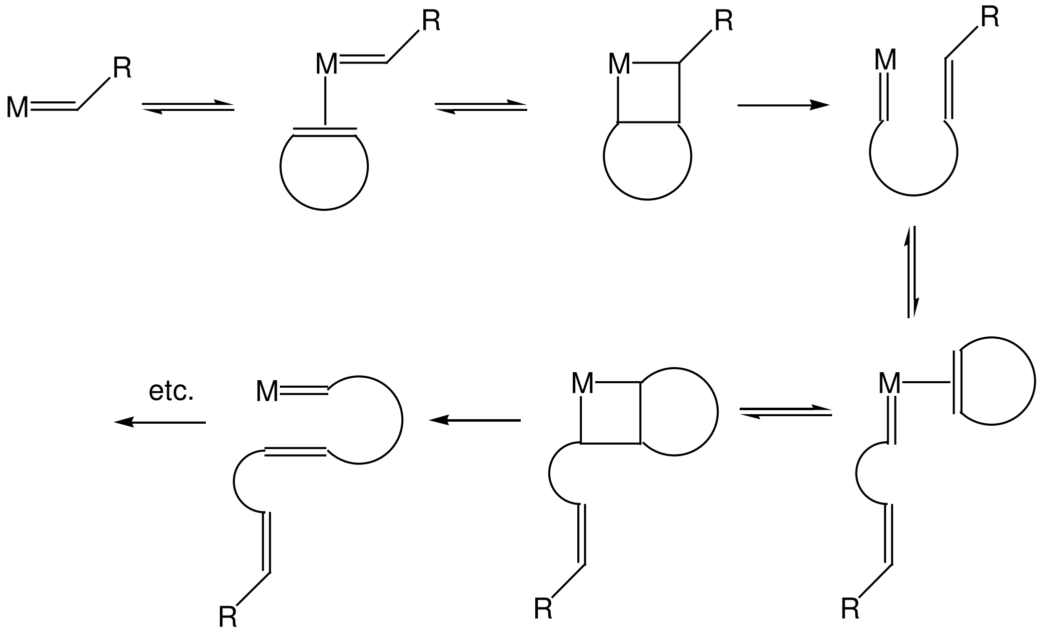
R = ^{t}Bu, $CMe(CF_3)_2$

Schrock

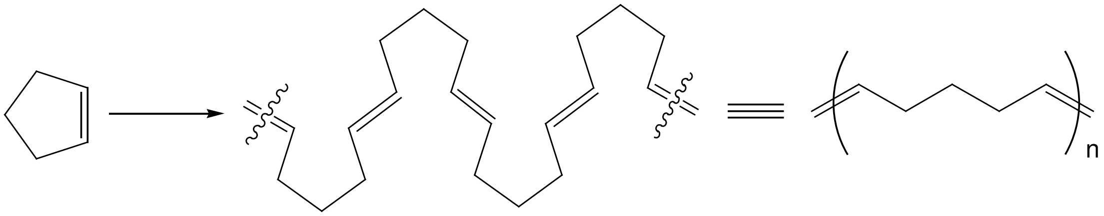


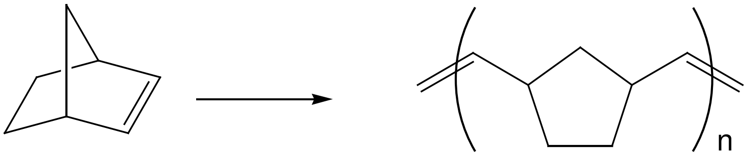
Grubbs

ROMP mechanism

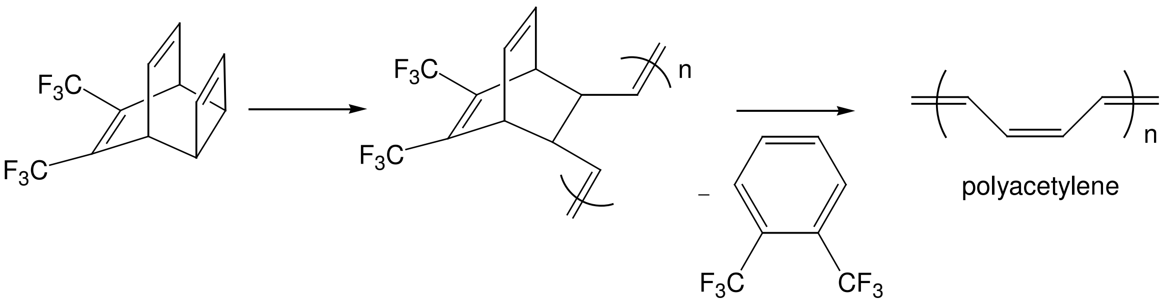


e.g.





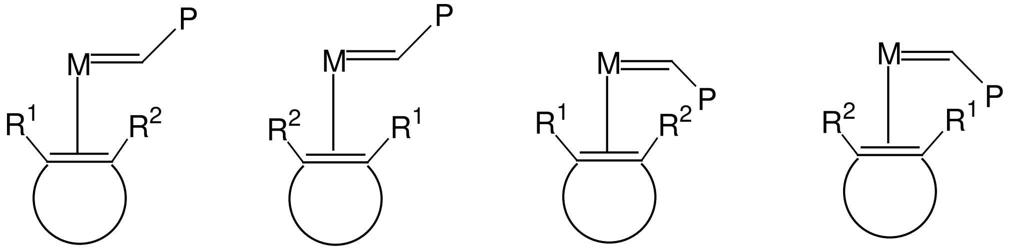
The polymers produced are very hard and have high mechanical strength. ROMP is also an easy method for the controlled formation of functionalised and conducting polymers.



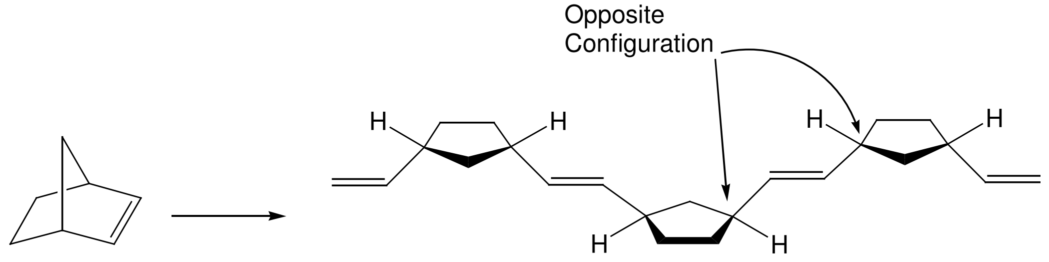
Also many cyclic diene monomers are used because they form a significant component of crude oil (i.e. they are cheap).

Stereochemistry of ROMP

Relative orientation of alkene and alkylidene determines stereochemistry



A closer look at norbornene

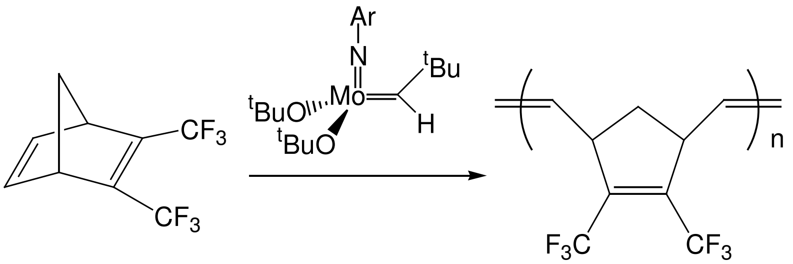


trans, isotactic polynorbornene

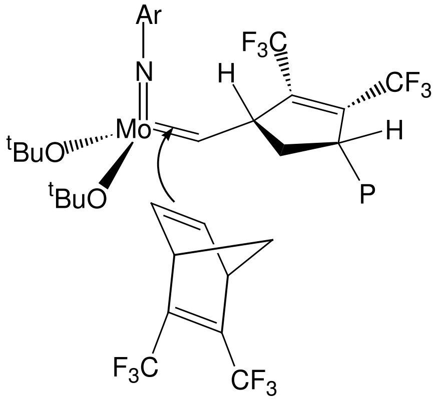
Trans isotactic polynorbornene is one of four possible stereoregular polymers. (cis and trans isotactic and cis and trans syndiotactic)

Stereochemistry is dependent on catalysts and/or monomer.

Can get enantiomorphic site or chain end control.
e.g. Chain end control. Incoming alkene is directed by polymer structure



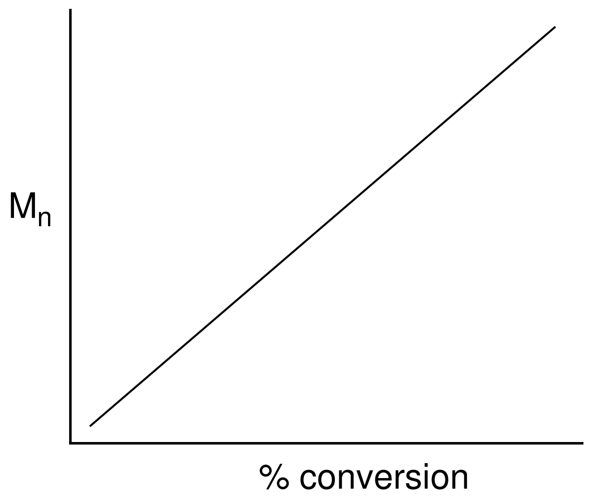
trans-isotactic



Mode of Ziegler-Natta and ROMP

Ziegler-Natta catalysis and ROMP are both examples of chain growth polymerisation.

Both are also living. k_i, k_p >>> k_t

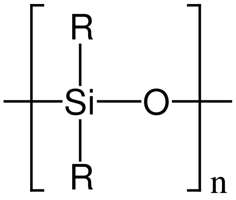


Inorganic Polymers

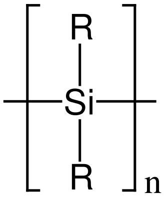
In addition to polymers that contain only carbon or other ‘organic’ atoms in the chain, polymers containing ‘inorganic’ atoms can also be formed.

These compounds are of interest because they offer the opportunity to develop new technological applications due to their reactivity, structure, and physical properties.

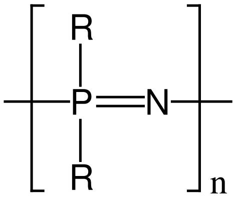
Many are now known. The most widely developed contain silicon as polysiloxanes and polysilanes. Another common class are the polyphosphazenes.



$$\left[-\overset{R}{\underset{R}{Si}}-O-\right]_n$$



$$\left[-\overset{R}{\underset{R}{Si}}-\right]_n$$



$$\left[-\overset{R}{\underset{R}{P}}=N-\right]_n$$

Polysiloxanes

Most important inorganic polymers with regard to commercial applications.
Medical: prosthetics, catheters, contact lenses, drug delivery capsules.
Non medical: e.g. elastomers, adhesives, lubricants, water repellents, molds, cosmetics.

Preparation

$$Si + 2\,RCl \longrightarrow R_2SiCl_2$$

$$R_2SiCl_2 + H_2O \xrightarrow{-HCl} (R_2SiO)_n$$

Ring opening polymersiation

$$(R_2SiO)_{3\text{ or }4} \xrightarrow{\text{cat.}} \left[-R_2SiO-\right]_n$$

cat. = acid or base

Chlorine free route

$$R_2Si(OAc)_2 + H_2O \xrightarrow{-AcOH} \left[-R_2SiO-\right]_n$$

PDMS (polydimethylsiloxane) is the most widely used

Polysilanes

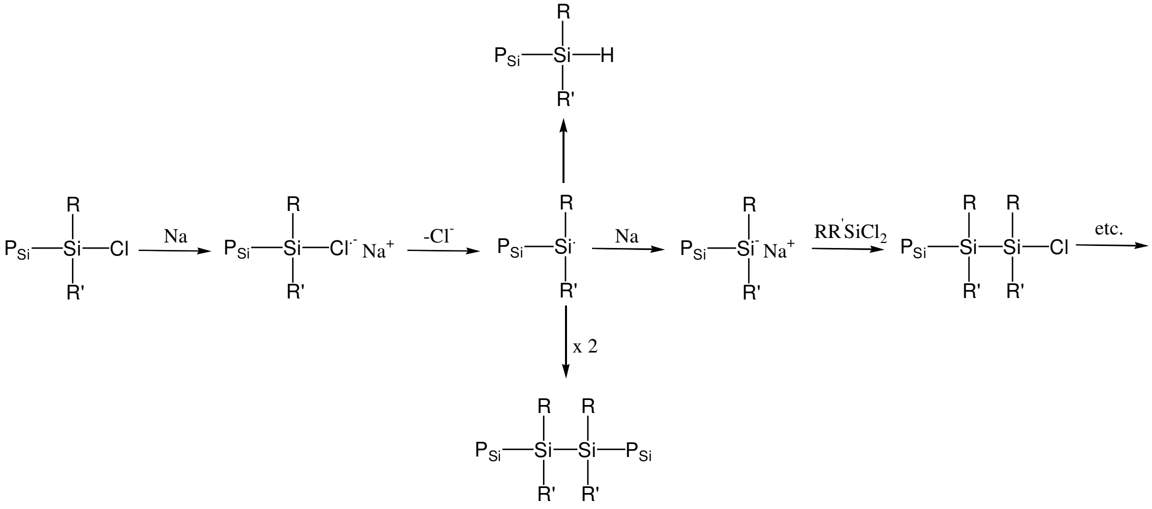
The polymer backbone contains only silicon atoms. A silicon chain allows electron delocalisation of sigma electrons. Many uses of polysilanes derive from the electron mobility.
Most uses are in the electronics industry as photoresists and precursors to silicon containing materials.

Preparation

Two general methods
Condensation of dichlorosilanes with alkali metals

$$RR'SiCl_2 \xrightarrow[> 100\ ^{o}C]{\text{Na, toluene}} (RR'Si)_n$$

Product distribution indicates radicals are important intermediates

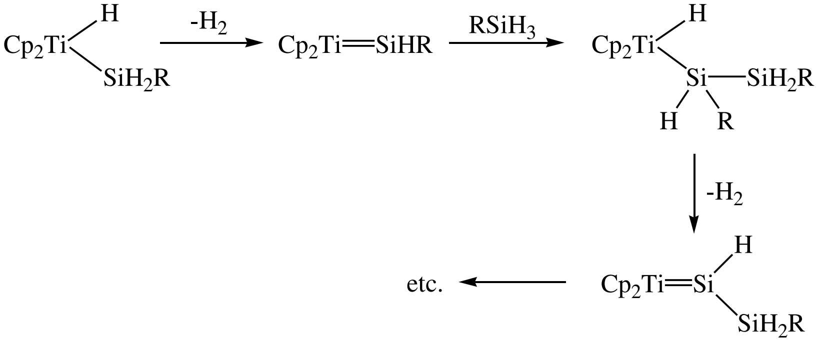


Dehydrogenative coupling of silanes

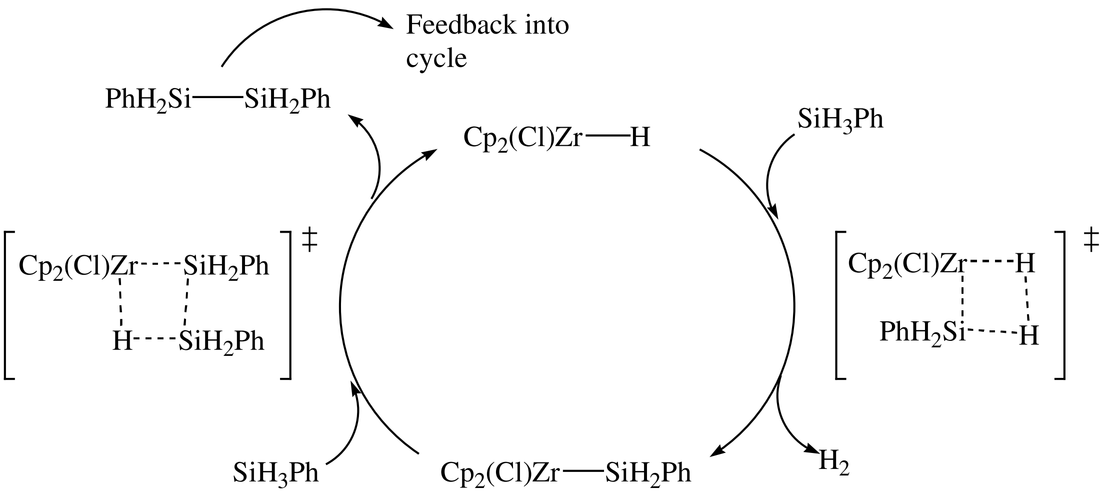
$$n\ RR'SiH_2 \xrightarrow{\text{catalyst}} H(SiRR')_nH \ + \ (n\text{-}1)\ H_2$$

Two proposed mechanisms

Via intermediate silylene



σ-bond metathesis

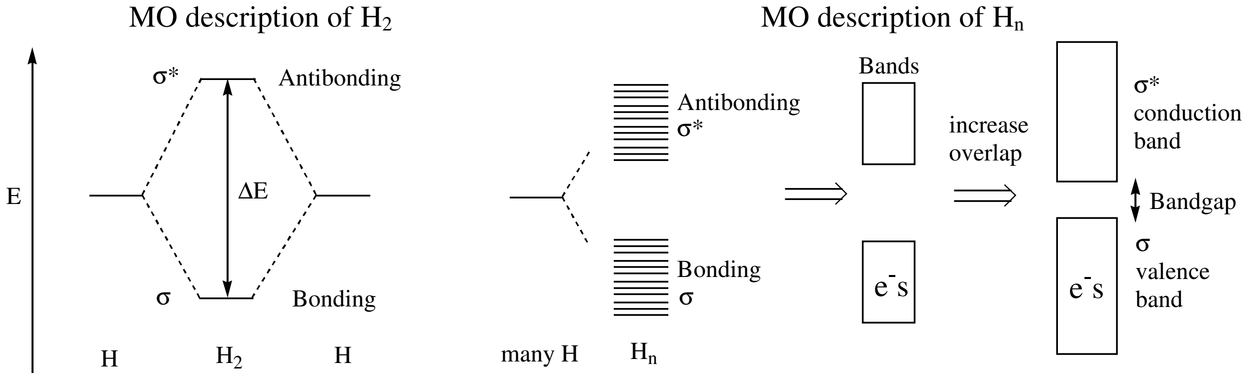


Properties

σ-electron delocalisation is present in polysilanes that contrasts organic polymers (e.g. polyacetylene) that have π-electron delocalisation.
Physcial properties arising from delocalisation including strong electronic absorption, conductivity, photoconductivity and photosensitivity.

σ-electron delocalisation occurs primarily because of the good overlap of Si-Si bonds and lower electronegativity of Si relative to carbon.

The electronic description of many atom materials can be described using band theory. You will study band theory in year 3, however briefly:



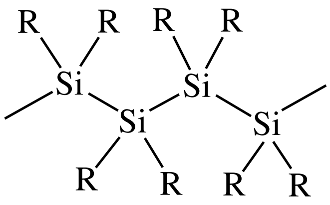
ΔE increases with greater overlap

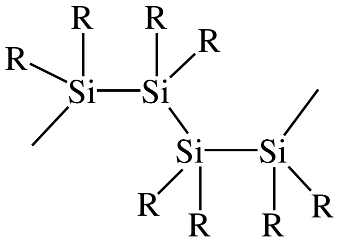
For conduction to occur a band must be partially filled. Can do this by:
1. Adding electrons to the conduction band by reaction with a reducing agent.
2. Removing electrons from the valence band by reaction with an oxidising agent.
3. Promoting electrons from the filled valence band to the empty conduction band using heat or light.

In polysilanes the band gap is such that 300-400nm light can excite electrons from valence band into conduction band.

The band gap is sensitive to:

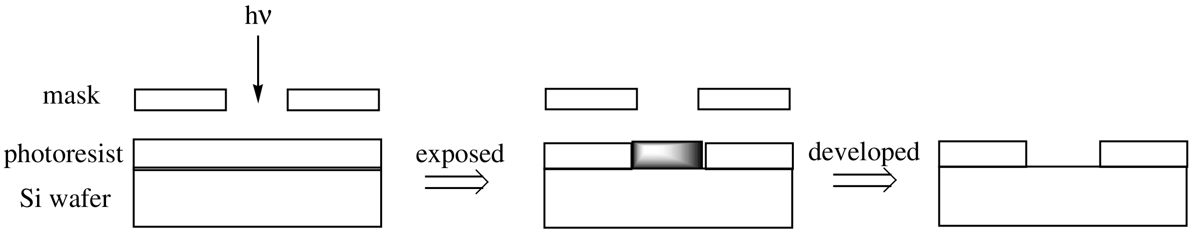
1. Chain length. Band gap decreases and absorption wavelength increases (lower energy). Reaches limit at ~ 30 Si atoms.
2. Conformation of polymer chain: trans conformation leads to absorption at lower wavelengths (better overlap).


all-trans


some-cis

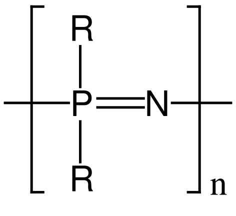
Conformation dependent on temperature that leads to strong theormochromism (colour change with temperature)

Polysilanes can be used as photoresists.



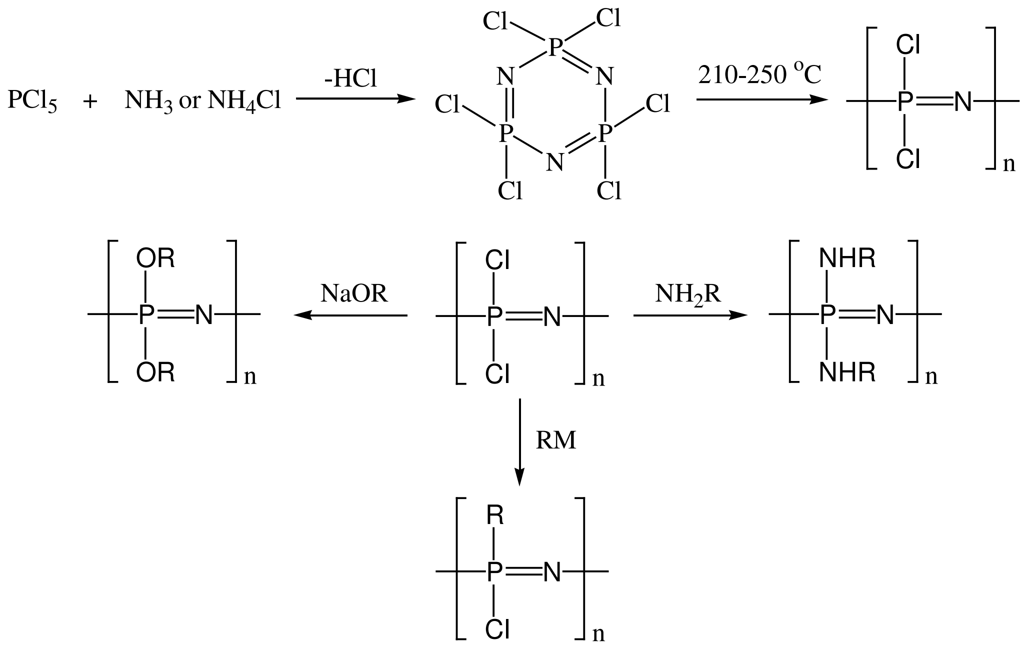
Polyphosphazenes

Largest class of inorganic polymers because of ease of side group modification.

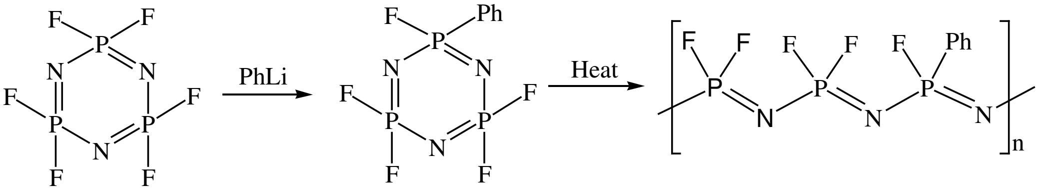

n > 15000

Backbone comprises alternate P and N atoms. Side groups (R) can be organic inorganic or organometallic. Method of synthesis allows modification of side groups.

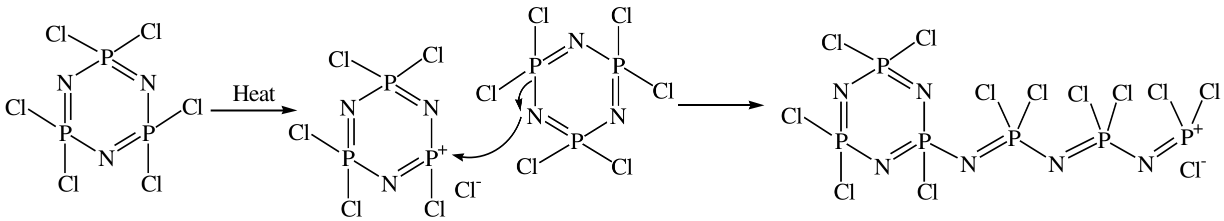
Uses include sold electrolytes (batteries), advanced elastomers (elastic at low temperature). Aerospace and automobile applications because of resistance to hydrocarbon solvents and oils, and flame resistance. Textiles.



Can also functionalise the P-N precursor prior to polymerisation.



Mechanism (ring opening polymerisation)



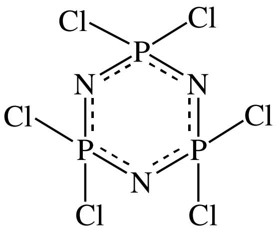
Cationic chain propagation.

Bonding in chain

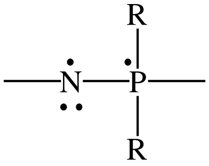
Cis and trans conformers exist and barrier to rotation about the P-N bond is very small. However, the bonding in phosphazenes is still not well understood although theories have been discussed since 1960.

Empirical observations:

Phosphazenes do not exhibit alternating bond lengths but the bond length is much less than a single P-N bond (multiple bond character). This means hypervalent P.



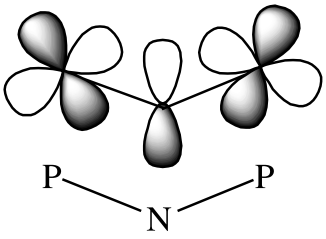
Polyphosphazenes are not coloured and do not conduct electricity that is characteristic of extensive conjugation.



σ-framework

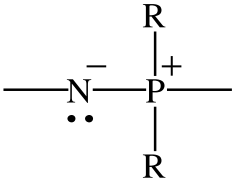
The problem is distribution of the remaining valence electrons.

Original Dewar proposed that Phosphorus-*3d* orbitals are involved in bonding to give P-N-P ‘islands’ where N $2p_z$ overlap P *3d* orbitals.



Rotation about P-N bond is low energy because N $2p_z$ can retain overlap with *3d* orbitals on rotation.

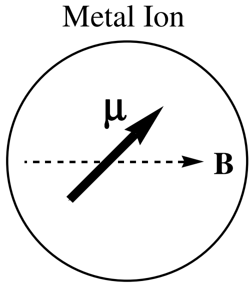
More recent calculations suggest ionic bonding appears to be dominant.



Organometallic (molecular) Magnets

Most magnets comprise of metals containing unpaired electrons in *d* and *f* based orbitals.

Microscopic magnetism



(**B** = magnetic field experienced by the ion)

Each metal ion has a magnetic moment μ the size of which depends on the spin and orbital angular moments.

These individual moments can interact (couple) with each other and behave collectively in a magnetic field.

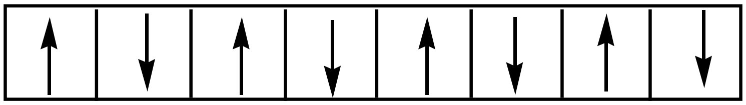
Types of BULK magnetism

Diamagnetism All solids exhibit diamagnetism. Atoms or molecules with closed shells of electrons are diamagnetic.

Paramagnetism is observed for compounds that contain unpaired electrons and *where the magnetic dipoles do not interact with each other*.

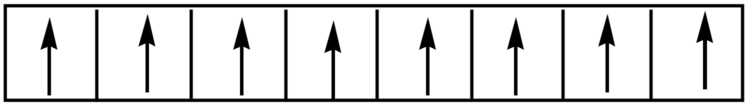
Antiferromagnetism **and** ***Ferromagnetism*** are observed for compounds that contain unpaired electrons and *where there is a strong interaction (coupling) between magnetic dipoles below a characteristic temperature*.

Antiferromagnets (moments antiparallel)



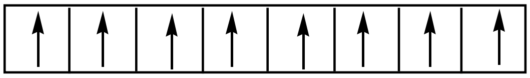
(arrows are the magnetic moments not individual electrons)

Ferromagnetism (moments parallel)

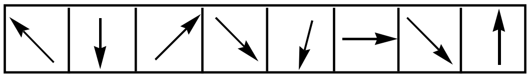


Most anti- and ferromagnets are comprised from condensed inorganic solids such as metal and metal oxides. This is because it is necessary that moments are close together to have a strong coupling. Organic based magnets were not initially considered likely because the moments would be too small and too dilute.

Above a critical temperature the thermal energy overcomes the coupling interaction between the moments and the material becomes paramagnetic.



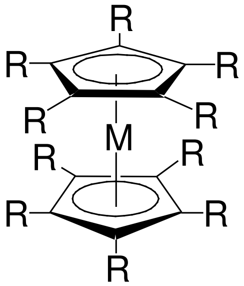
$T < T_C$



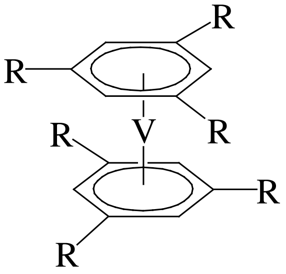
$T > T_C$

Organometallic magnets were first discovered in the 1980's.
They are described as *charge transfer complexes* because reaction usually occurs between a reducing organometallic reagent and an oxidizing organic compound.

Transition metal complexes include metallocenes.

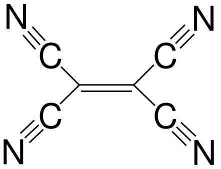


M = Cr, Mn, Fe

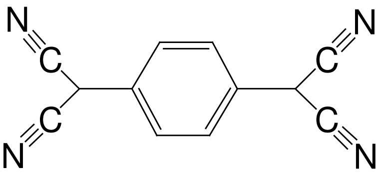


Important features of metallocenes are they are relatively small and can have S > 0 (high spin density) and ligands can be easily modified to allow structure-property relationships to be examined.

Organic compounds are usually planar and contain heteroatoms.



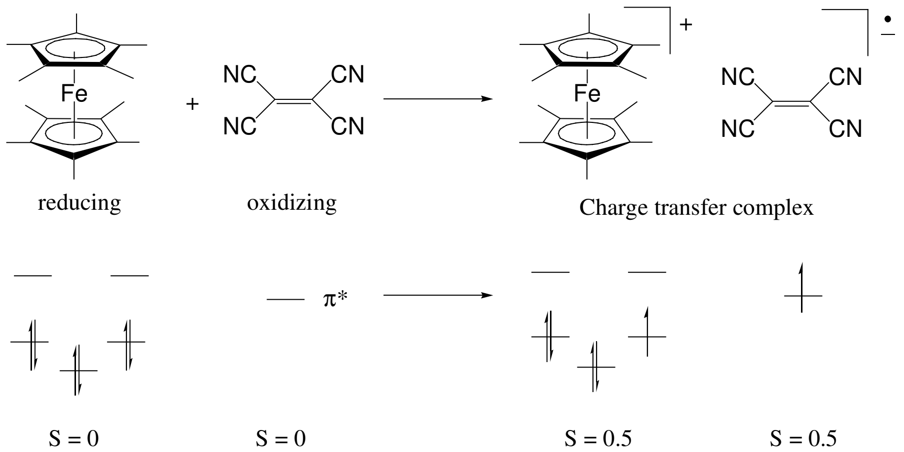
TCNE



TCNQ

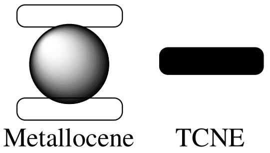
Important features of the organic molecules are that they are relatively small giving high spin density, oxidizing generating a radial anion, and flat allowing packing in the solid state the gives good coupling between the spins.

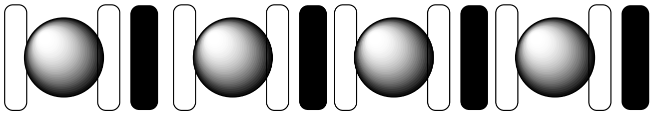
Charge transfer reaction



An electron is transferred from a metallocene 'd-orbital' to the organic π* orbital. Both cation and anion have unpaired electrons and can couple.

The solid state structure determines how the individual magnetic moments couple and what type of magnetic behaviour is observed. Linear chains are formed. Interchain coupling also very important to give a bulk ferromagnet.

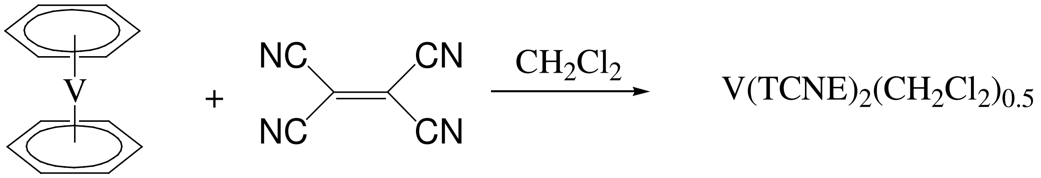




Chain structure of $[(C_5Me_5)_2Fe][TCNE]$

These compounds only give T_C below 5-10 K compared to 1073 K for iron metal. Main problem is coupling is still quite weak and moments dilute compared to al inorganic magnets.

However an organometallic magnet has been discovered with $T_C = 400$ K but its structure is unknown. A further disadvantage is that these materials decompose in air.



The general field of molecular magnetic materials is still at an early stage. There are many other metal-ligand combinations in addition to metallocene-based examples that continue to be investigated. The attraction is the opportunity to design materials from the bottom-up using molecules that can be modified and processed easily. There is also the opportunity to synthesise materials that exhibit combinations of properties that will form the basis of future technologies.

Metal Coordination Polymers

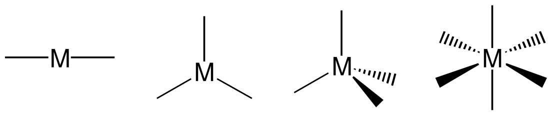
These polymers are prepared by linking metal ions or metal clusters with organic linking units.

Most studies are concerned with the formation of *porous* crystalline polymers.

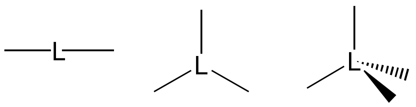
Porous solids can be used for catalysis, sensors, chromatography and sorption.
c.f. zeolites

Basic Idea

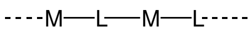
Modular approach



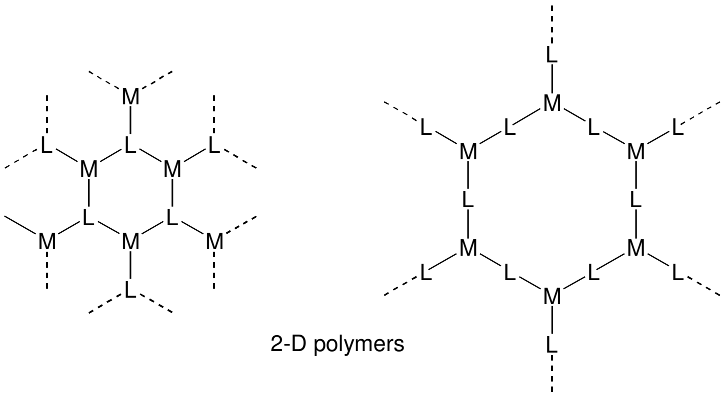
Metal ions



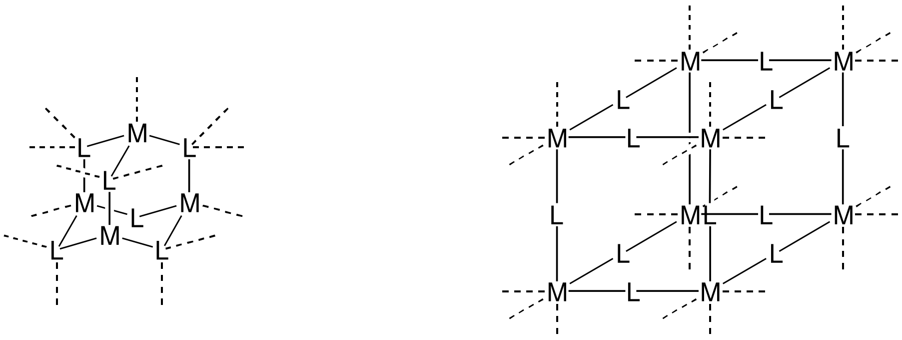
Organic linkers



1-D polymer



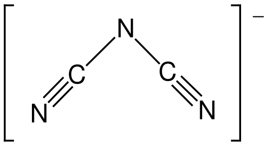
2-D polymers

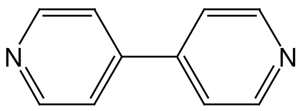


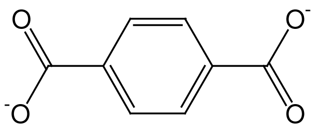
3-D polymers

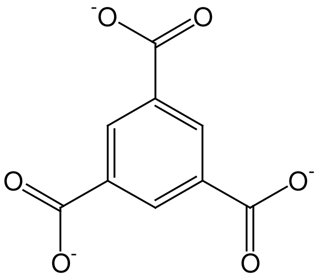
In principle a vast number of combinations of ‘M’ and ‘L’

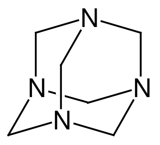
Examples of organic linkers

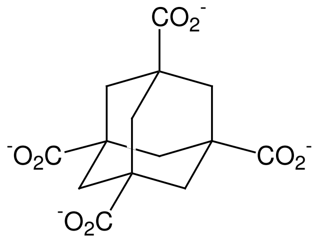




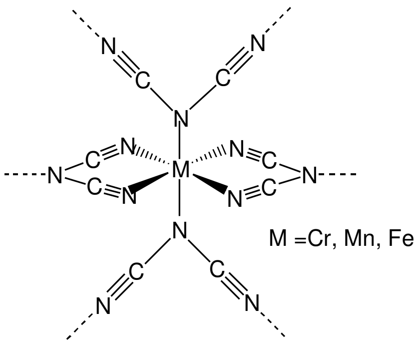




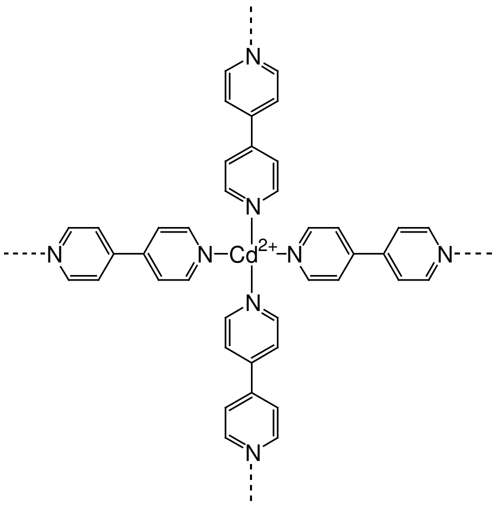


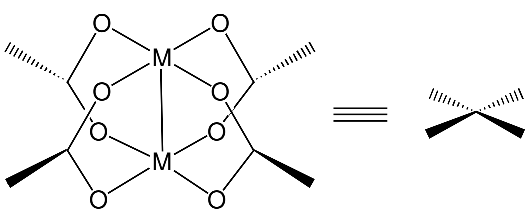


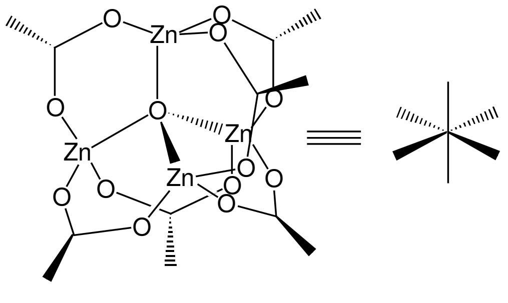
Examples of metal ions and clusters



M =Cr, Mn, Fe







Synthesis

Synthesis of 3-D porous coordination polymers is complex because the product is crystalline (and for characterisation single-crystals have to be > (25 µm)^3).

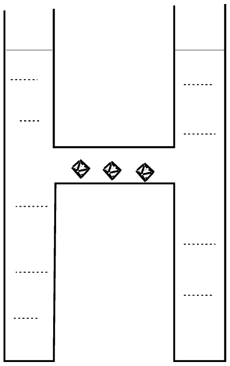
Every bond formed has to be consistent with crystal growth (must be a corrective mechanism for bond formation that is not consistent with crystal growth)

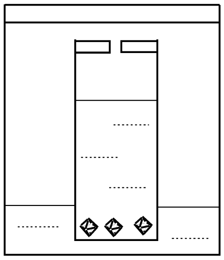
Two common methods

1. Controlled Diffusion

Add reactants into separate parts of vessel and wait.

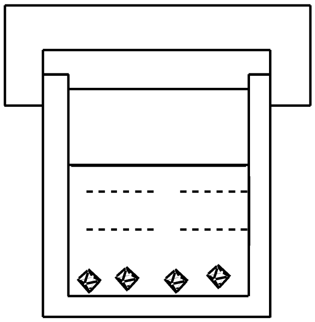
Good for large single crystal growth, but slow for large quantities and not always reproducible.

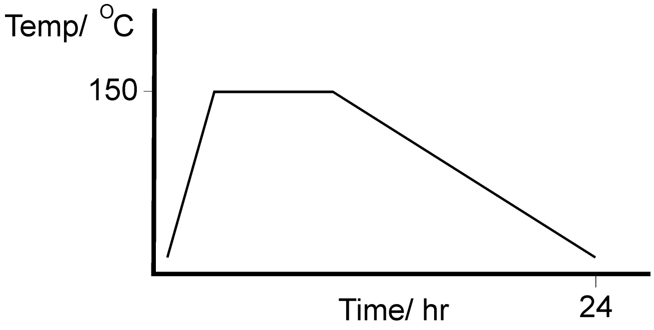




2. Hydrothermal Method

Add all reactants together into a hydrothermal bomb and heat and cool for a fixed period of time.

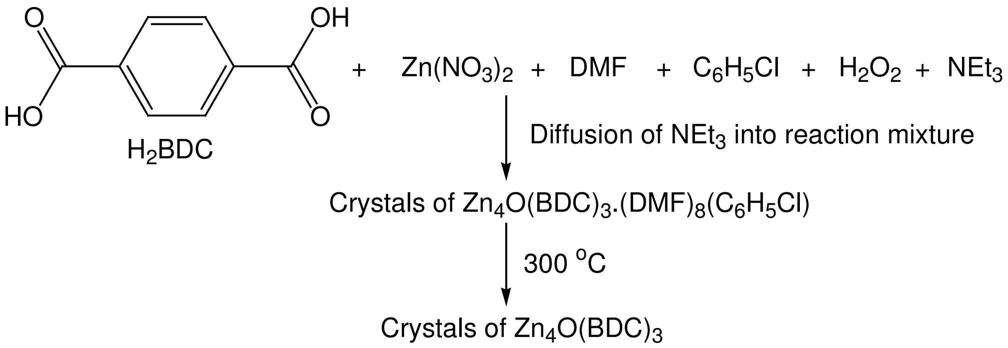


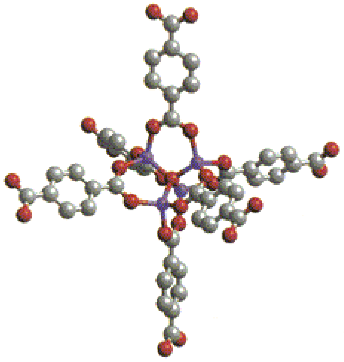


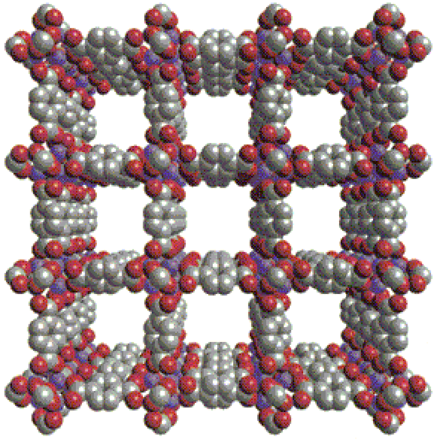
Not always large enough single crystals but good for large quantities and more reproducible.

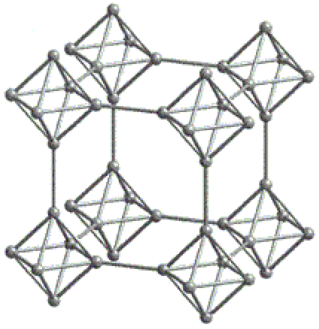
Compound usually crystallise with solvent in ‘pores’. The problem before 1999 was that all attempts to remove solvent of crystallisation resulted in collapse of the structure.

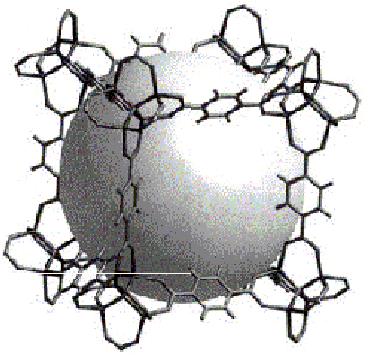
Example of a truly porous coordination polymer (there are now many)





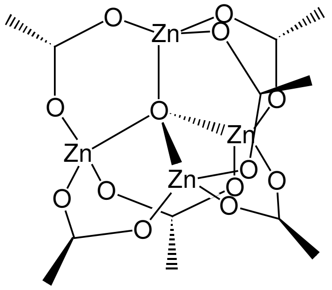




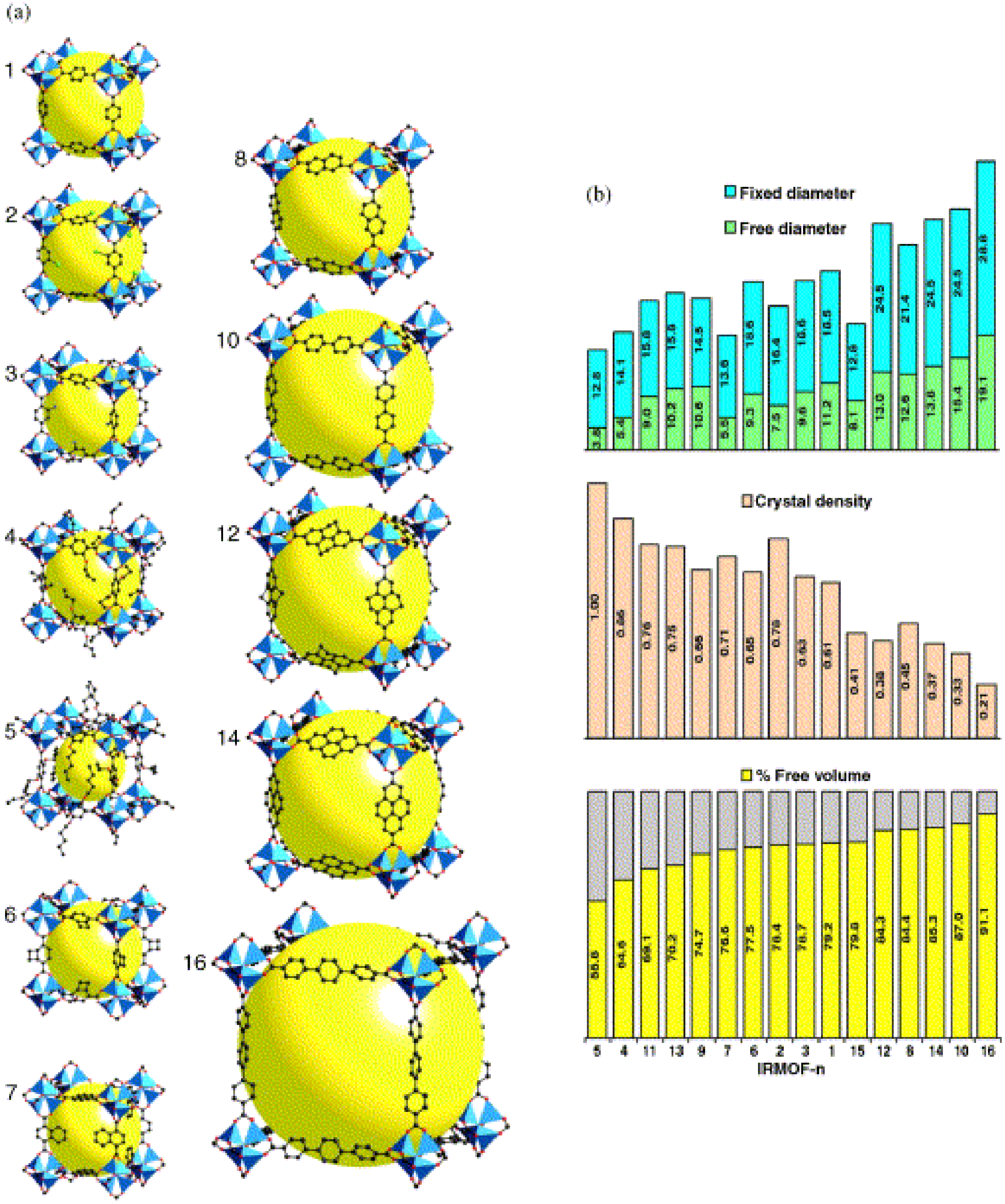


Pore sphere diameter 18.5 Å. (Big enough to accommodate molecules)

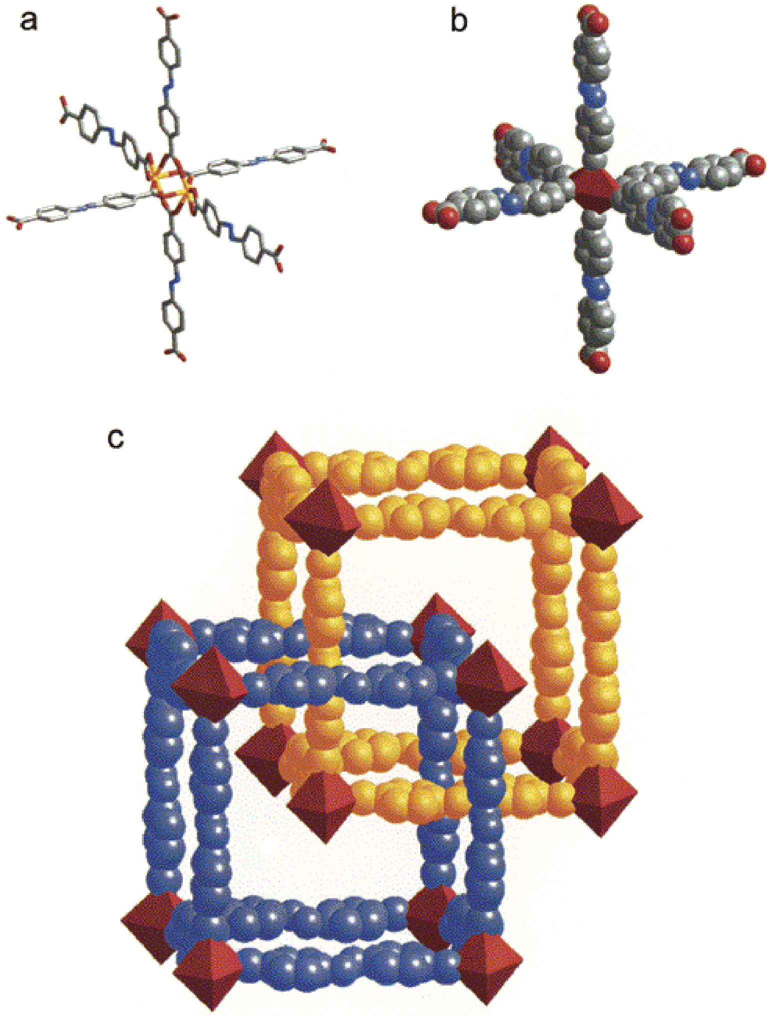
Metal moieties that are more complex than simple ions, such as the cluster Zn_4O are sometimes called secondary building units SBU's.



By changing the size of the inorganic linker it is possible to design a desired pore size. Note for structure 16 over 90% of the crystal volume is empty!



The formation of porous structures can be prevented by interpenetration of polymer frameworks.



Interpenetration is where individual frameworks link together with no covalent bonds between frameworks. These structures form due to non-covalent interactions during the crystal growing process and because porous solids are thermodynamically unstable with respect to condensed solids.

Properties of coordination polymers

Gas sorption

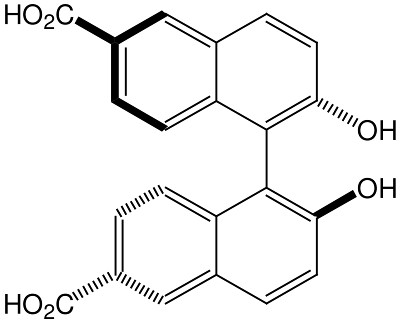
For application of 'clean' fuels gases such as H_2 and CH_4 require storage and access on demand. Heavy gas cylinders under large pressure are not efficient (or safe) and materials are required that can store large quantities of these gases and release them when needed. Coordination polymers are being investigated as storage media.

One of the Zn_4O(dicarboxylates) shown above (structure 6) is able to sorb methane effectively at 36 atm (safe compared to 205 for a cylinder).

Chirality-Asymmetric catalysis

Chiral organic linkers can be used to prepare chiral porous solids. These compounds are being investigated for asymmetric catalytic applications.

e.g.



Magnetism and sensors

In many complexes Fe(II) (d^6) exhibits spin crossover (i.e. a transition from high to low spin or vice versa). Fe(II) spin crossover is very sensitive to ligand environment. Fe(II) low spin is diamagnetic and Fe(II) high spin is paramagnetic. This change is usually accompanied by a dramatic colour change.

Fe(II) coordination polymers have recently been synthesised that change colour on absorption of small alcohols.