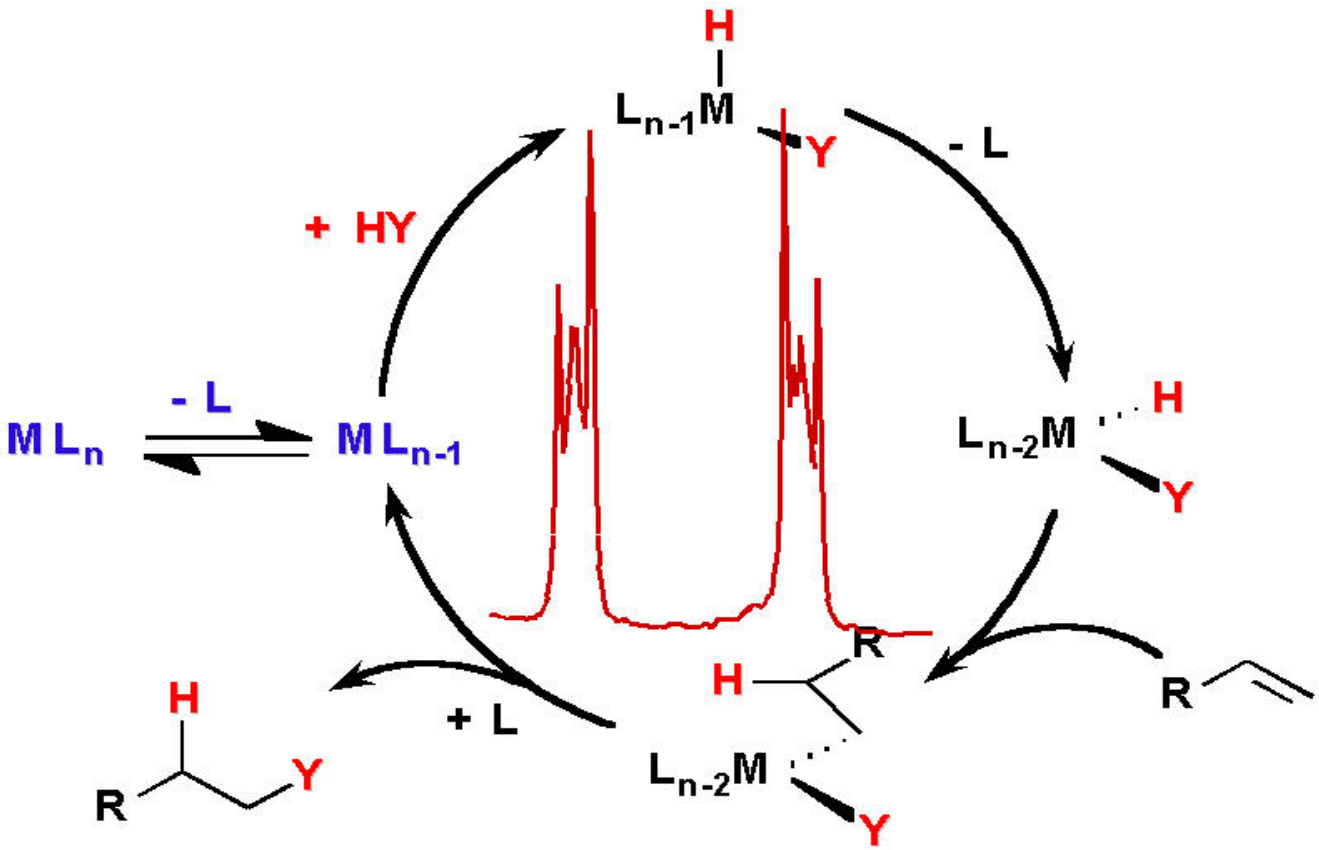
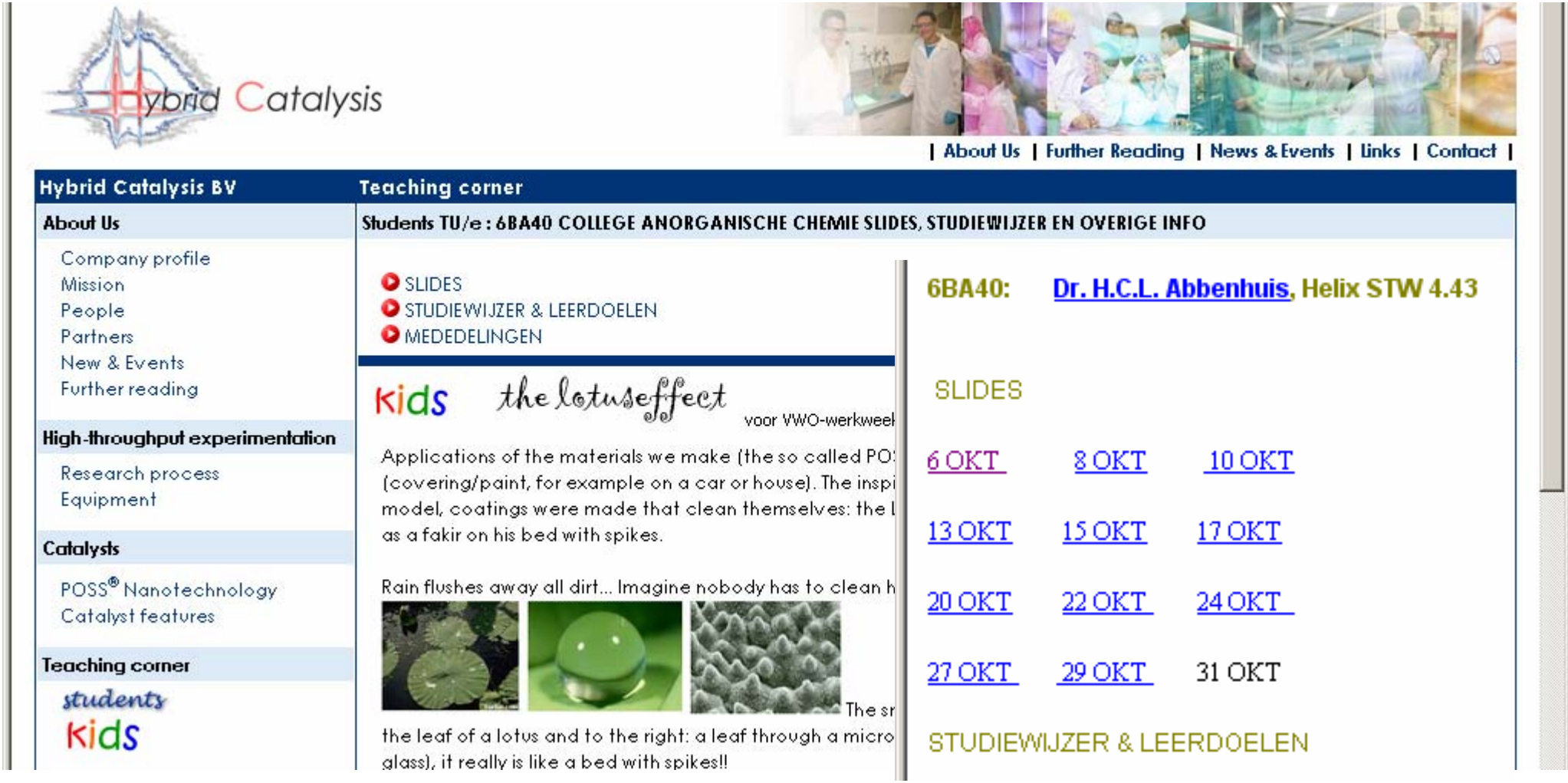
Inorganic Chemistry
6BA40



d-Metaal Chemie
Vri, 31-10-2008

Inorganic Chemistry 6BA40
Slides available:
http://www.hybridcatalysis.com/teachingcorner.htm



Gerealiseerde Leerdoelen

- de chemische binding van essentiële delen of van liganden in overgangsmetaal complexen en organometaalverbindingen beschrijven met behulp van kwalitatieve MO-diagrammen

- elektronenovergangen in overgangsmetaalcomplexen correleren met de eigenschappen van deze verbindingen

- de voornaamste reactiemechanismen in d-blok complexen weergeven

- voor d-blok organometaalverbindingen de basiseigenschappen en typerende chemische bindingen beschrijven

- kennis van chemische binding, reactie mechanismen en organometaalchemie

Nog te leren…

•eigenschappen van elementen en verbindingen daarvan aan de hand van de positie in het periodiek system uiteenzetten

•per d-blok metaal de meest optredende oxidatie toestanden noemen en typische verbindingen met hun reactiviteit

•Kennis toepassen op gecompliceerde (homogeen) katalytische systemen

Wetenschappelijke houding, het denken in overkoepelende termen, loslaten van het `hokjes denken', herkennen van de onderliggende principes

Inorganic Chemistry 6BA40
Leerdoelen

http://www.hybridcatalysis.com/teachingcorner.htm

- d-Metaal complexen, moleculaire vormen en isomerie, kristalveld- en Molecular Orbital Theorie (hoofdstuk 1.6-1.8; 2.8-9; 20, 21)
- Elektronen overgangen, magnetische eigenschappen en spectra in verbindingen van overgangsmetalen (hoofdstuk 21)
- Reactiemechanismen en kinetische aspecten (hoofdstuk 26)
- Organometaal verbindingen van de s-en p-blok elementen (hoofdstuk 19 / college slides)
- Organometaal verbindingen en hun voornaamste reacties (hoofdstuk 24 / college slides)
- Homogene Katalyse, basis kennis (hoofdstuk 27.1-27.6)

ZELFSTUDIE

- De eerste reeks overgangsmetalen (hoofdstuk 22)
- De tweede en derde reeks overgangsmetalen (hoofdstuk 23)

Hybrid Catalysis

www.hybridcatalysis,com

Erik Abbenhuis

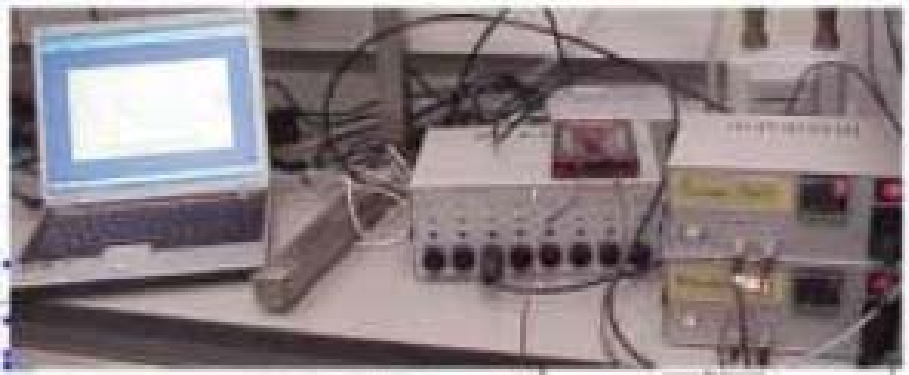
- B.V.; spin-off TU/e
- Productontwikkeling: katalysatoren uit nano-grondstof
- Dienst: R&D met robotische apparatuur / Custom Synthese

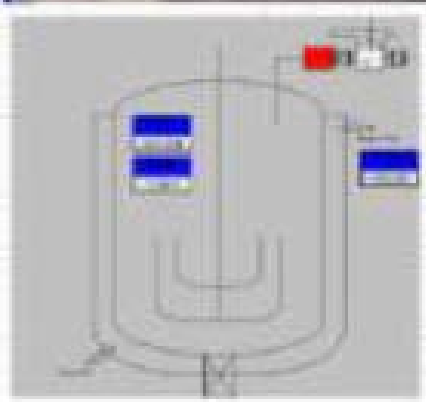
Hybrid Catalysis

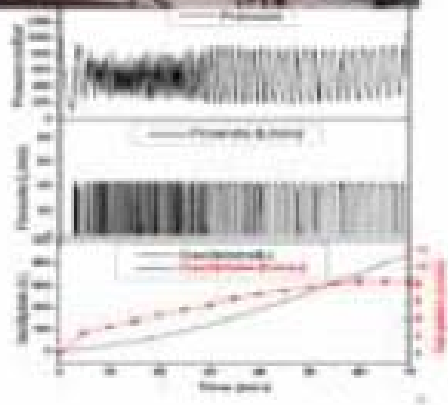
www.hybridcatalysis.com

Katalysator-screening

Miniplants door STW funding







Hybrid Catalysis

www.hybridcatalysis.com

Process intensification

Immobilized catalyst screening

Adaptable

Reactions can be heated and/or cooled on the same reactor.
Capable of integration into liquid handling equipment for full automation.

Scalable

Reactions can be easily scaled from mg to grams to kilos

Efficient

The high pressure / high temperature capability means many reactions progress to completion in minutes.
Reactions may be optimized "on the fly" to obtain optimum reaction conditions in minutes.

Safe

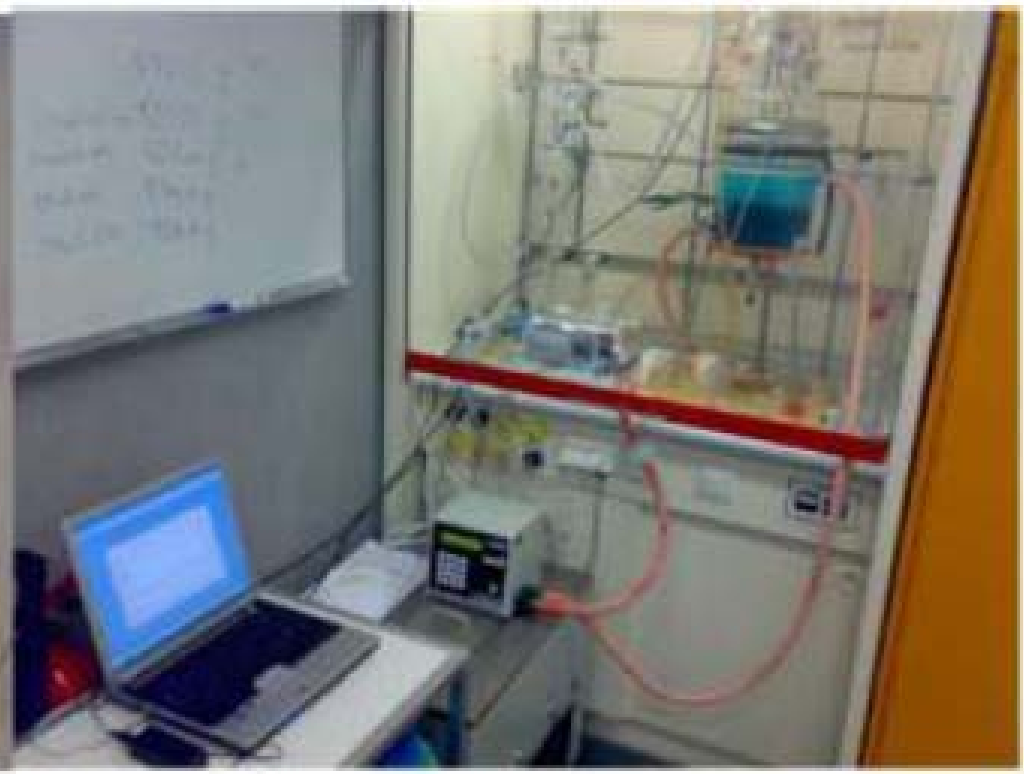
Low volume system with high temperature control meaning many volatile reactions can be safely and at high pressure.

Hybrid Catalysis

www.hybridcatalysis.com

Custom Synthesis

Kilo Lab door STW funding



- STW funding: ~k€ 15
- Opdrachten ter waarde van ~k€ 103

Hybrid Catalysis

www.hybridcatalysis.com

Project example
Propene dimerization

Figure 4 *The 4L double walled reactor with internal cooling*

Hybrid Catalysis

www.hybridcatalysis.com

Commercieel perspectief

Gebaseerd op huidige projecten

Binnen 3 jaar > 0.5 miljoen € omzet /jr in contractonderzoek

Exploitatie gebruiksrechten op eigen know-how

Klant A: 0.05 – 0.3 miljoen € omzet/jr vanaf nu

Omzet in productie nano-tech POSS katalysatoren

Klant B: kans op 1 tot 25 miljoen € omzet/jr over 1-10 jaar

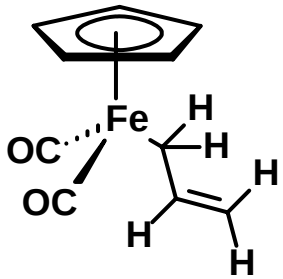
Klant C kans op 2 tot 10 miljoen € omzet/jr over 2-5 jaar

Investeringen Launching Customers:

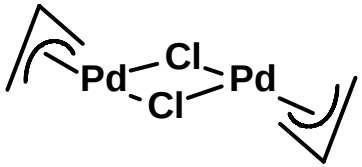
Klant B: k€ 188; Klant C k€ 120

Een eerste impressie van hoe Catalyst eruit zou kunnen gaan zien.

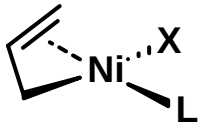
Metal Allyl Bonds
Bonding Modes



η^1- coordination

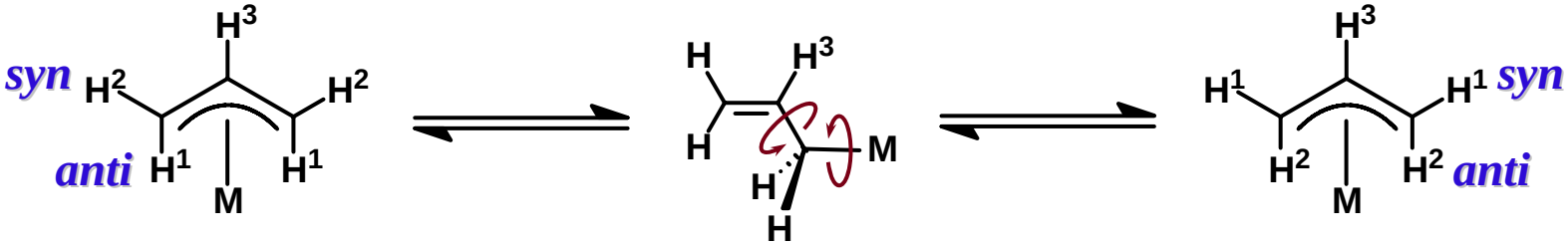


η^3- coordination



η^1- η^2- coordination

- ***Syn* and *anti* protons can be distinguished in ^{1}H-NMR spectrum**
- ***Dynamic behaviour (isomerization) on the NMR time-scale often leads to averaged signals***

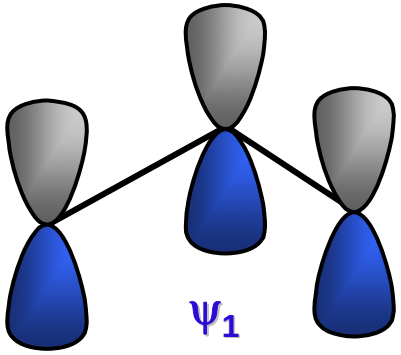


- **Allyl metal complexes are important intermediates and metal-precursors in catalytic reactions**

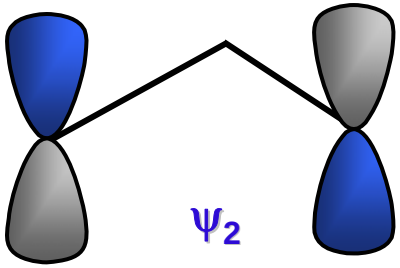
Metal Allyl Binding

σ-bonds | **π-bonds**

ligand A_2

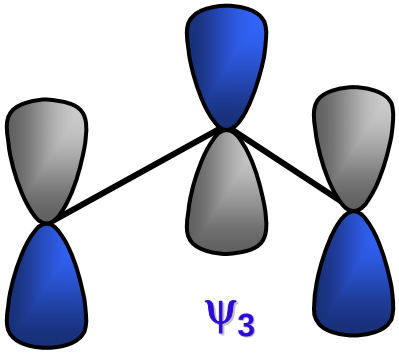


ψ_1



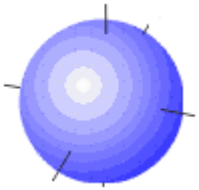
ψ_2

B_1

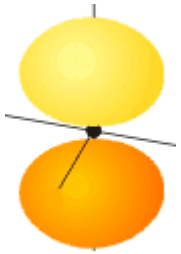


ψ_3

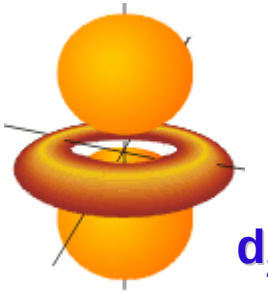
metal



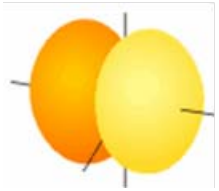
s



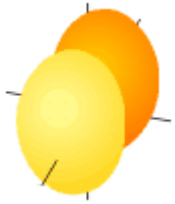
p_z



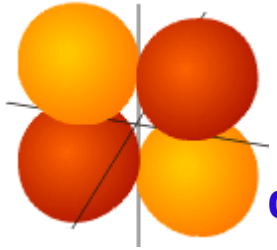
d_{z^2}



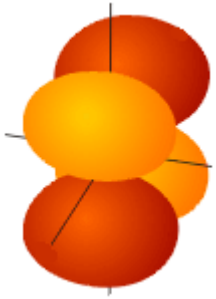
p_y



p_x



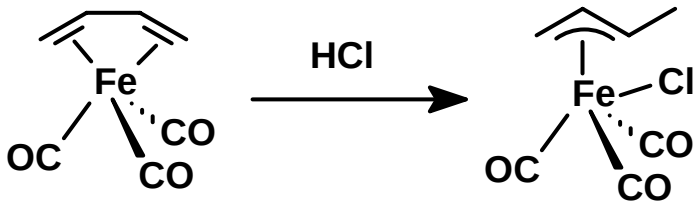
d_{yz}



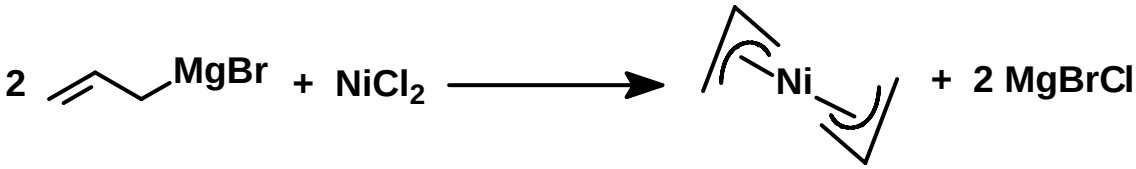
d_{xz}

Metal Allyl Bonds
Synthesis

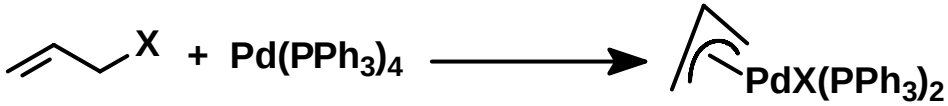
- **protonation of 1,3-diene complexes**



- **reaction of metal halides with an allyl-Grignard reagent**

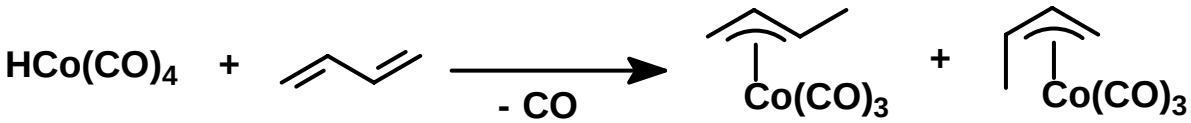


- **allylic substitution reactions**

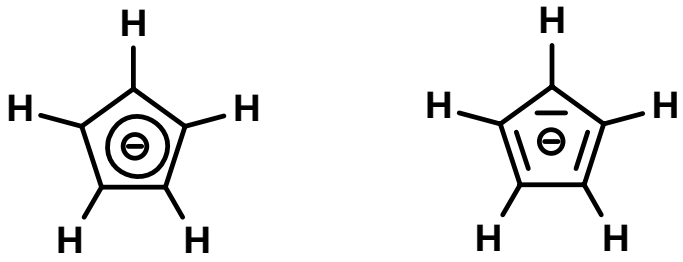


X = OAc, OC(=O)R

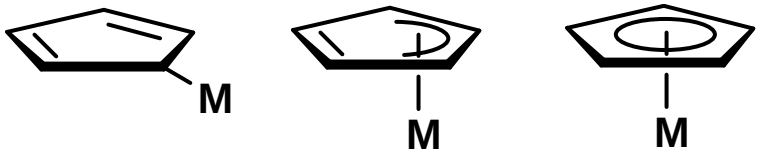
- **reaction of a metal-hydride with a 1,3-diene**



Cyclopentadienyl Metal Complexes
Metallocenes

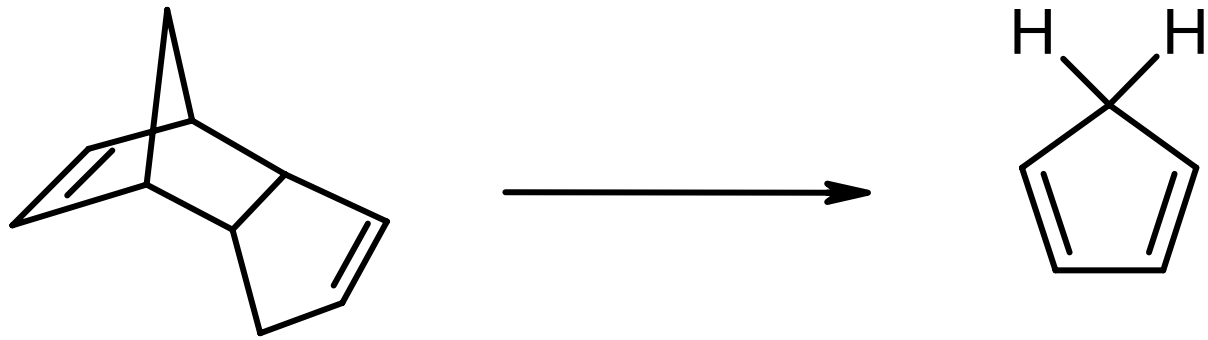


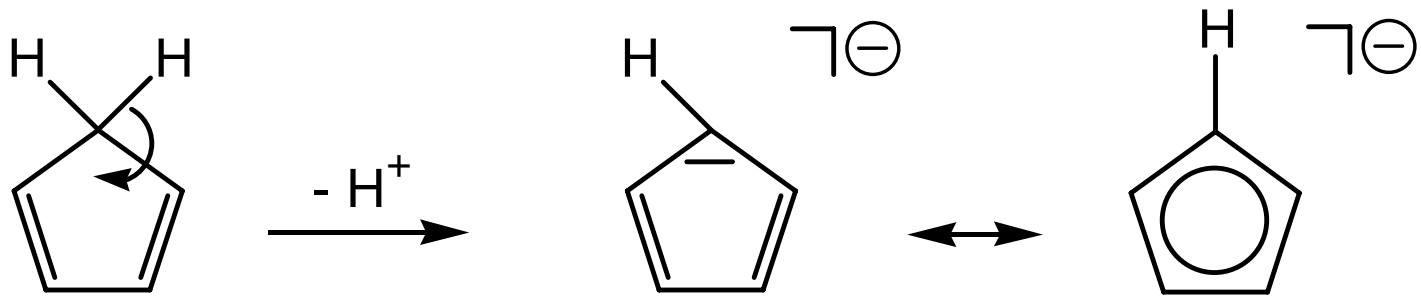
- **Important Ligand in Organometallic Chemistry**
- **Frequently used Ligand in Organometallic Chemistry: 1990: ~80% of Organometallic compounds contain the Cp Ligand**
- **Electron-Buffer Ligand: η^1; η^3; η^5 coordination common**



Cyclopentadienyl Metal Complexes

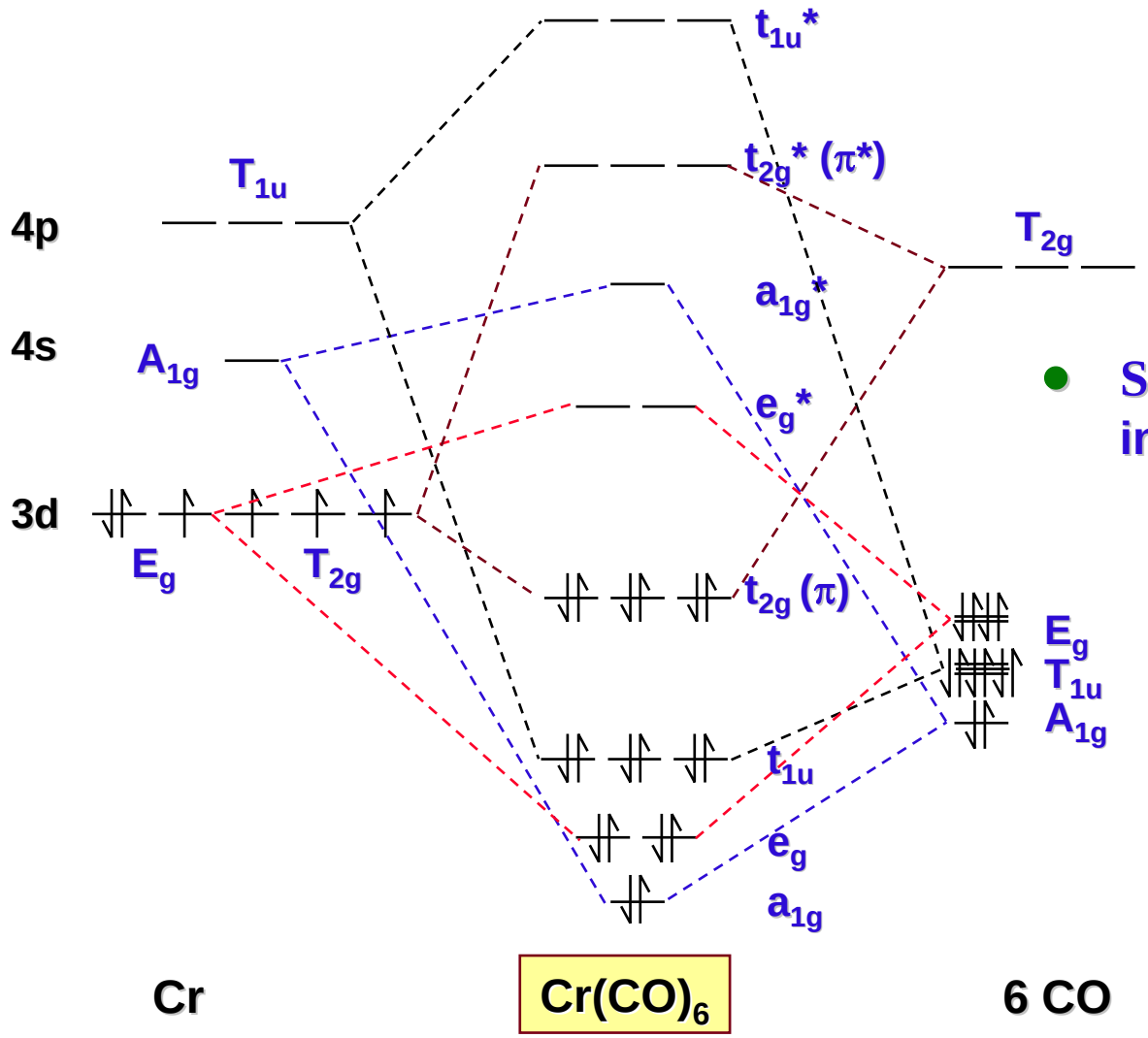
Metallocenes





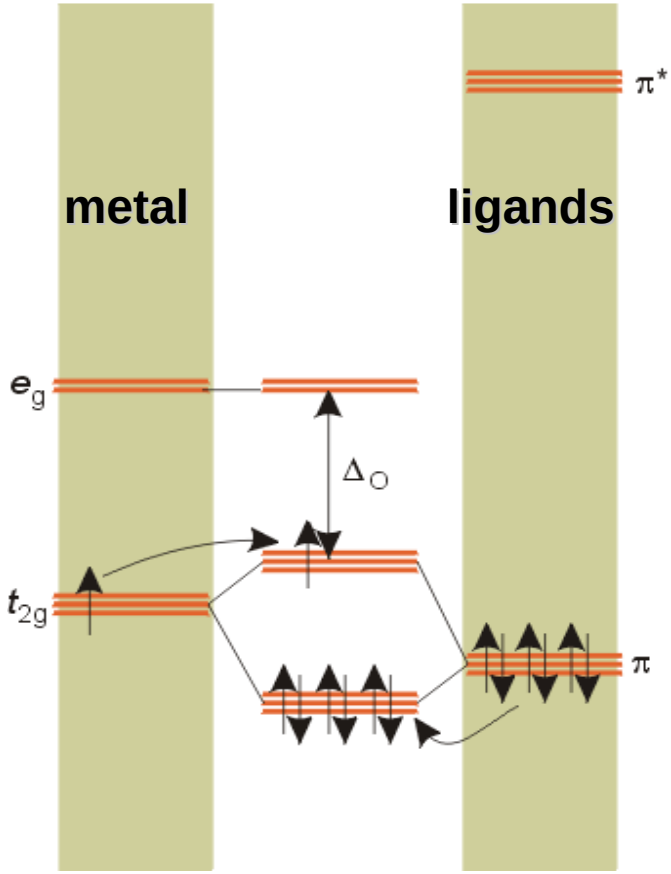
$$FeCl_2 + 2\ NaC_5H_5 \longrightarrow (C_5H_5)_2Fe + 2\ NaCl$$

18 Electron Rule
Octahedral Complex Including π-Bonding



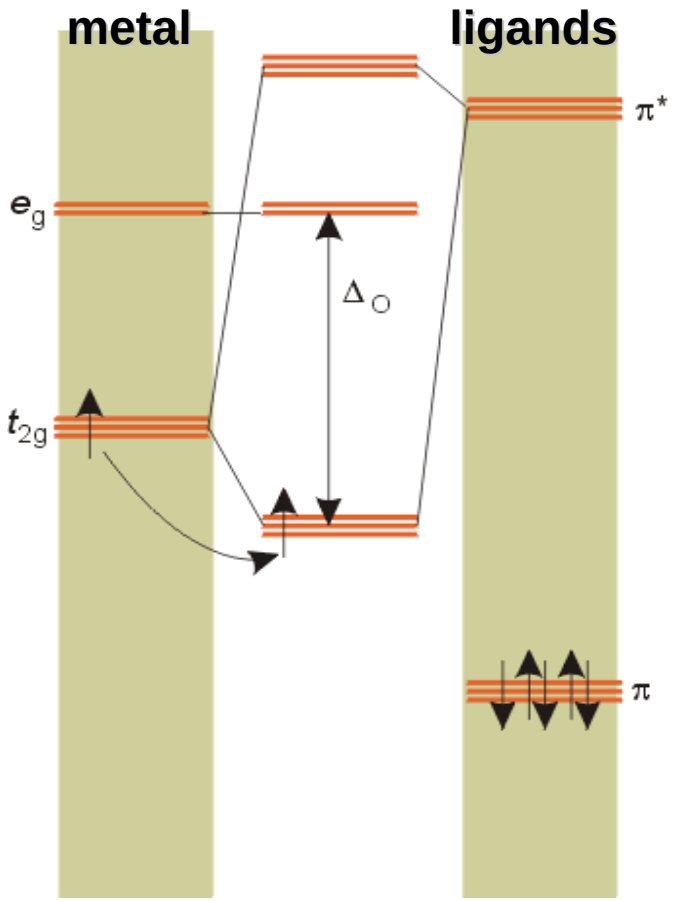
- Strong π-bonding interaction with CO

d-Metal Complexes
π-Bonding, Donor & Acceptor Ligands



π-donor ligands decrease Δ_O

π-acceptor ligands increase Δ_O

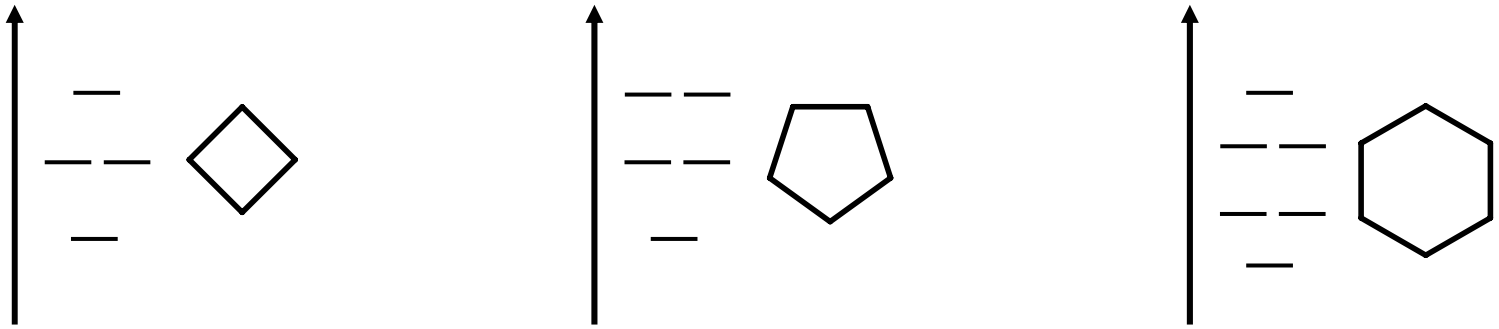


Cyclic Polyene Ligand Metal Complexes
The Perimeter Model

- How to find the right set of Ligand Group Orbitals (LGOs)?
- What about the relative order in energy?

- Symmetry provides an elegant way to determine a qualitative picture
  - draw the figure in a way that one corner points down
  - draw one line for a corresponding MO per corner on the same level

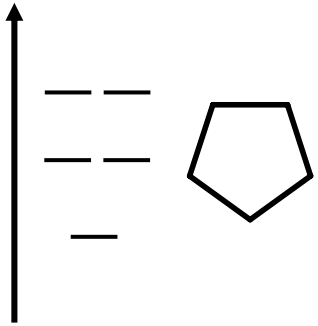
=> this gives a qualitative picture of the MO-scheme for the perimeter

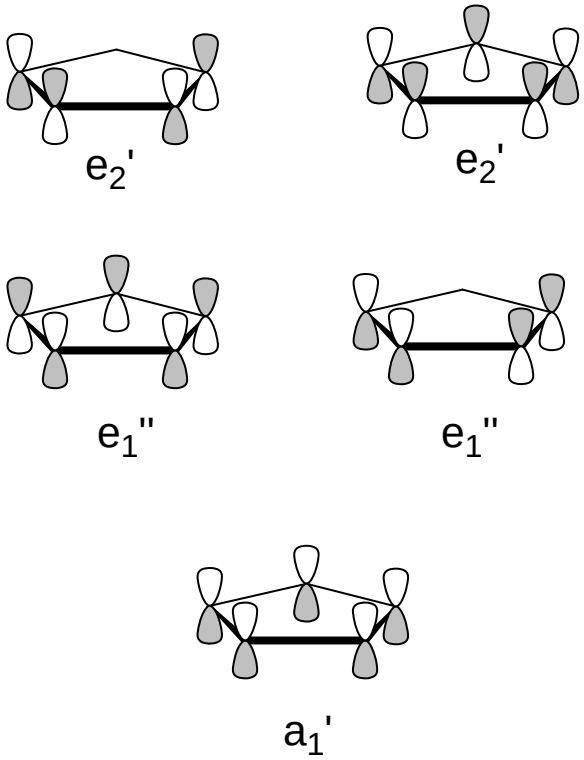


- Only the p_z orbitals contribute to the LGOs

=> The symmetry types can be found in the character tables

Cyclic Polyene Ligand Metal Complexes
The Perimeter Model

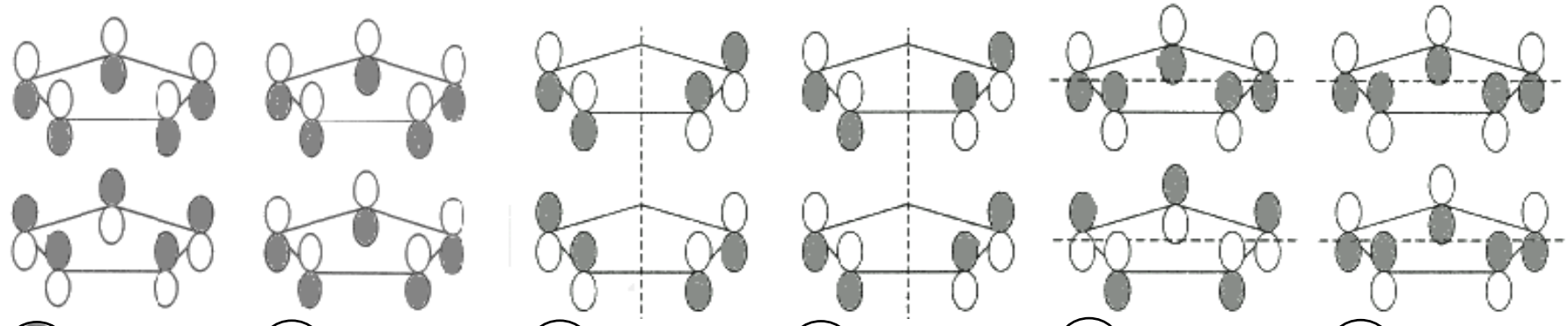




- **Only the p_z derived LGOs contribute to the binding with the metal**

Cyclopentadienyl Metal Complexes

Metallocenes



1 a'_1 — $3d_{z^2}$, 4s

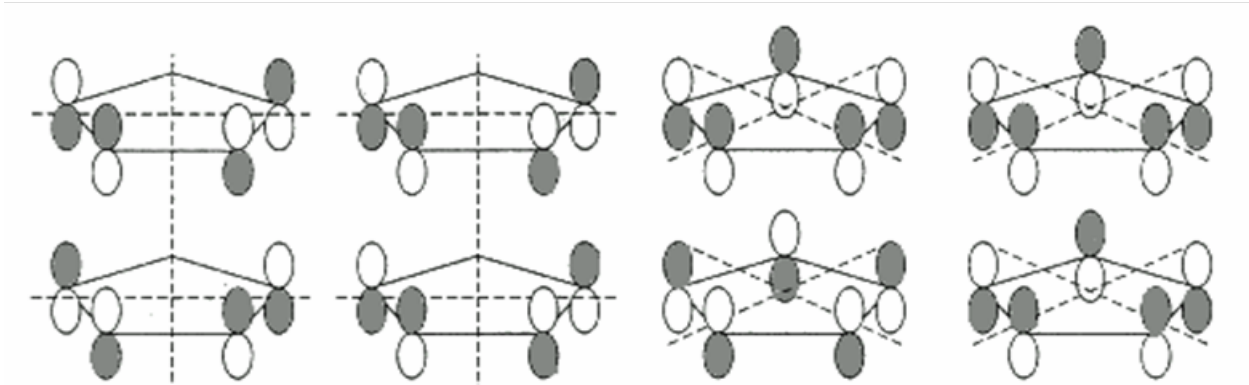
2 a''_2 — $4p_z$

3 e'_1 — $4p_x$

4 e''_1 — $3d_{yz}$

5 e'_1 — $4p_y$

6 e''_1 — $3d_{xz}$



7 e'_2 — $3d_{x^2-y^2}$

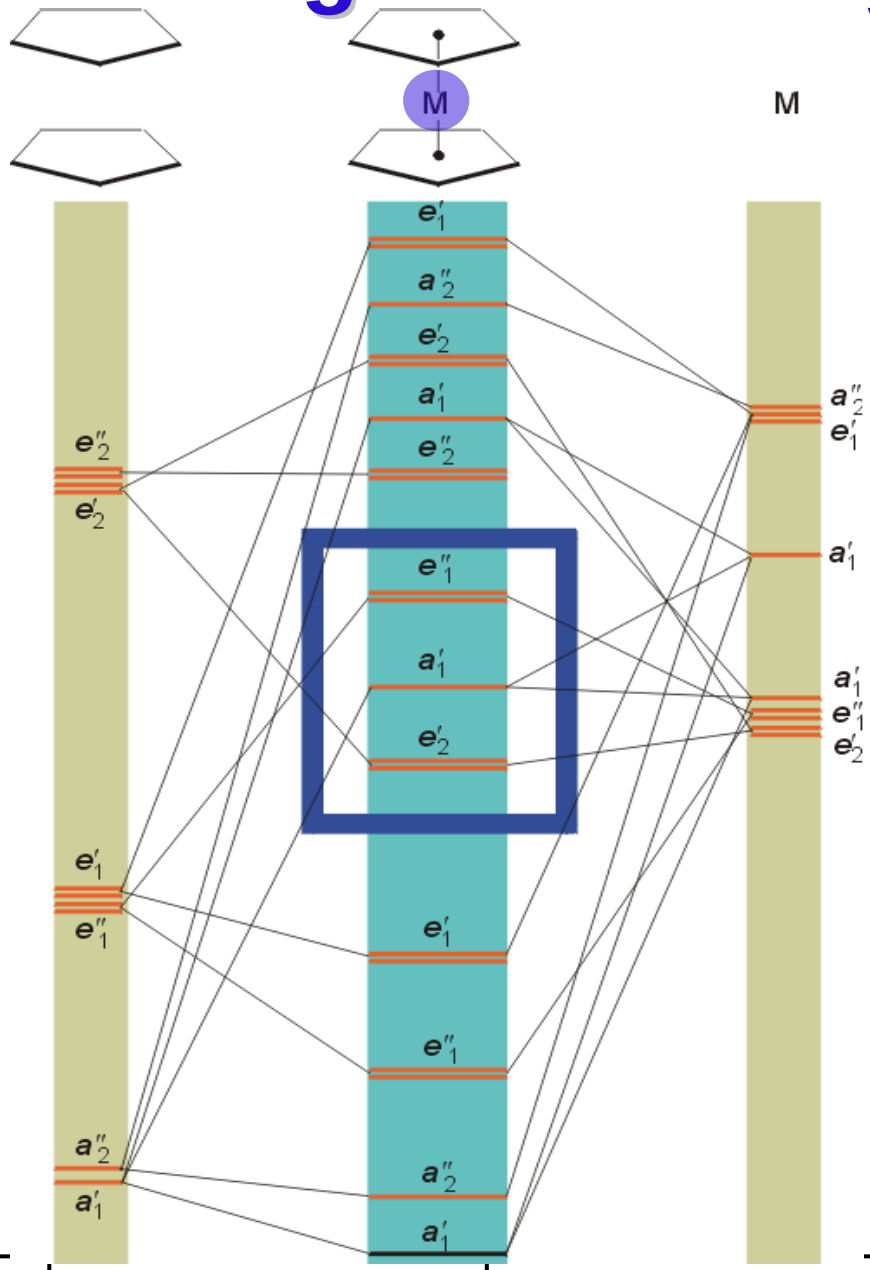
8 e''_2

9 e'_2 — $3d_{xy}$

10 e''_2

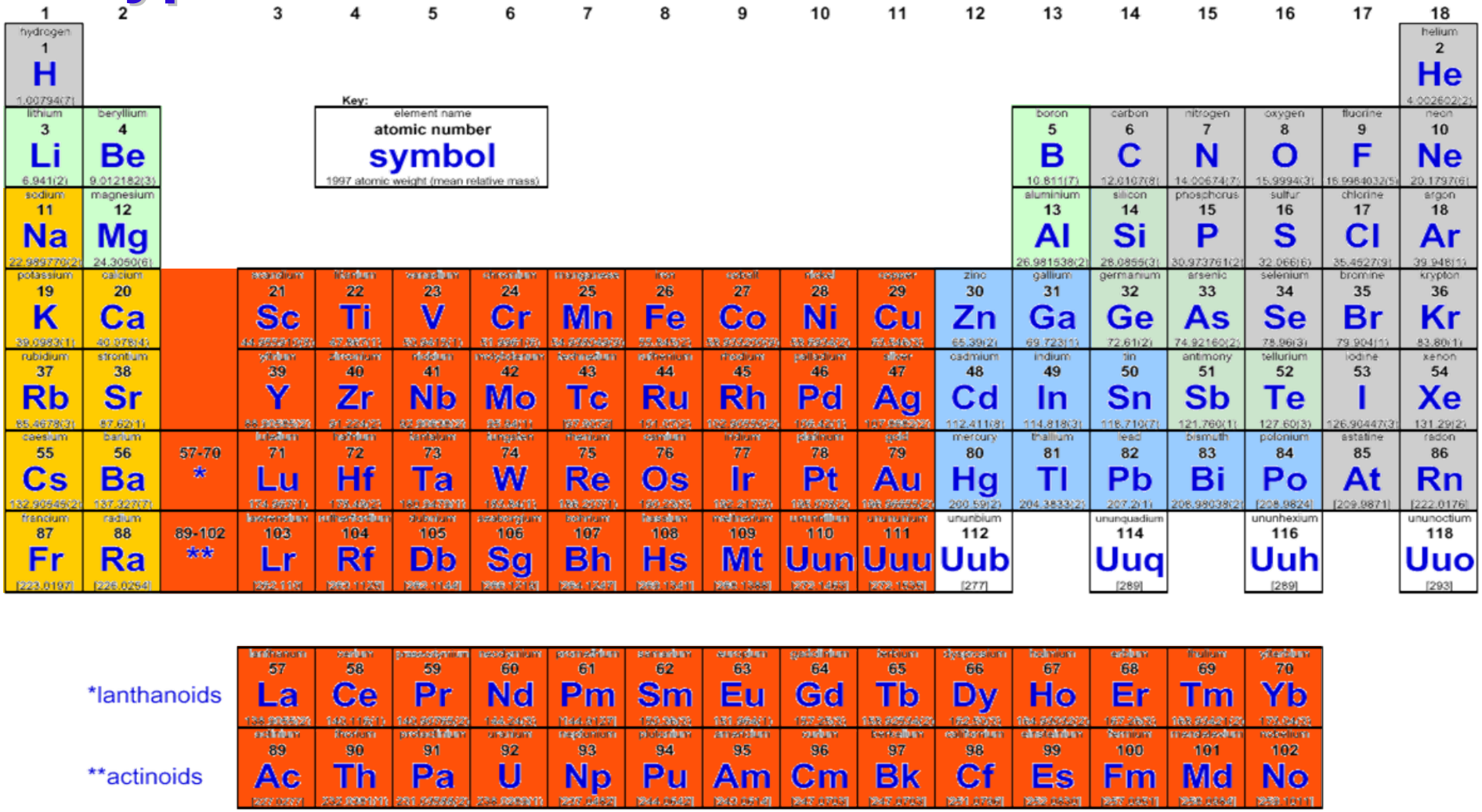
see also extra information
Ch24_ ferrocene

MO diagram for a D_{5h} Metallocene



- The 18 electrons of ferrocene will fill the orbitals up to the a'_1 orbital.
  - This is the most stable situation for a metallocene.
  - Cp^- provides a large ligand field splitting, comparable to CN^-.

Types of M-C Bonds in the Periodic Table



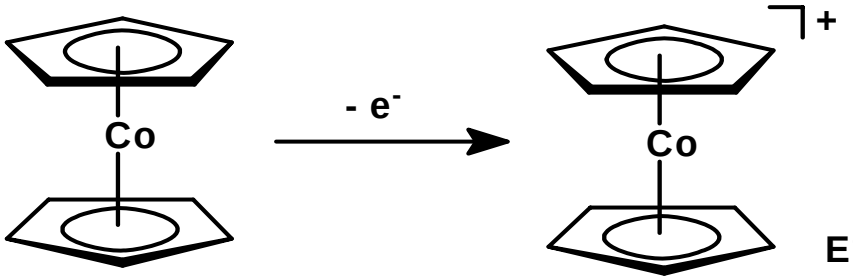
- electron deficiency compounds
- ionic compounds
- d-metals, M-C σ-bonding and π-bonding
- covalent M-C σ-bonding
- metalloids
- non-metals

Reactivity of Metallocenes

- Maximum stability for d^6 ($FeCp_2$ and $CoCp_2^+$)

	thermal decomp.
$FeCp_2$	> 450°C
$CoCp_2$	~ 150°C
$NiCp_2$	~ 100°C

- Reactivity of the electron-excess compounds d^n, n > 6

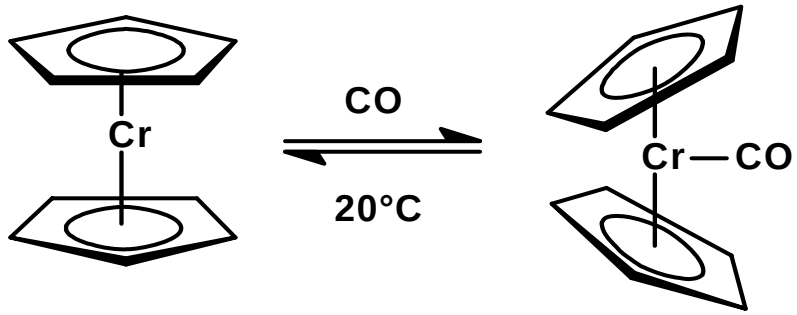


E° = - 0.7V

➔ Cobaltocene is a strong reducing agent, comparable to Zn!

Reactivity of Metallocenes

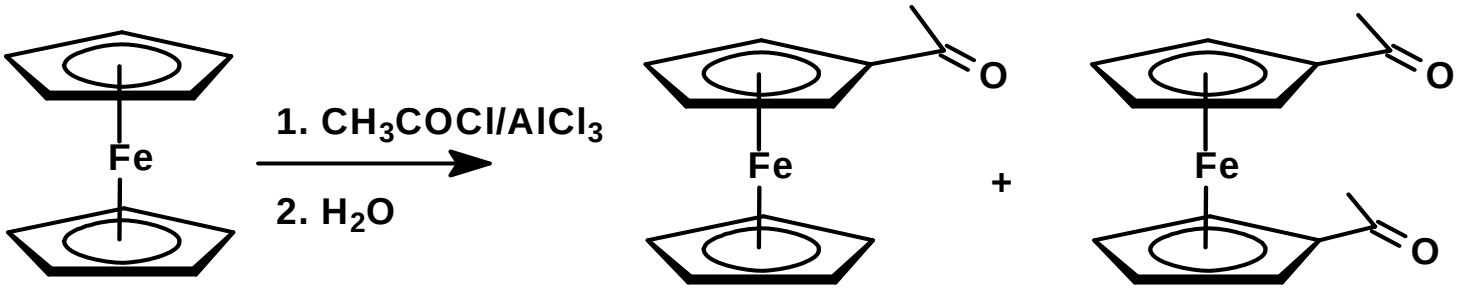
- **Reactivity of the electron-deficiency compounds d^n, n < 6**



***v* = 16** **v = 18**

moisture sensitive

- **Ligand reactivity**



~ 10^6 times more reactive than benzene

➔ **Ferrocene undergoes aromatic substitution, esp. Friedel-Crafts acylation. Also lithiation of the rings is possible.**

Trends and the Periodic Table
Groups 3-4

Sc	Ti	
Y	Zr	
La	Hf	
Ac		

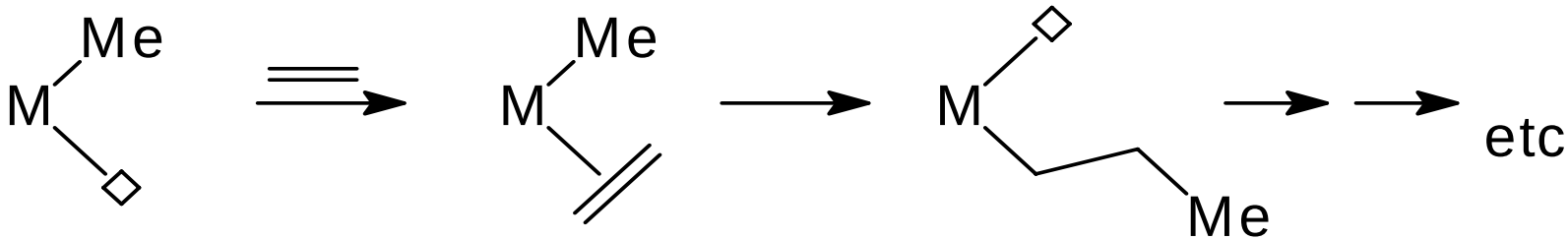
- **Strongly electrophilic and oxophilic**
- **Little redox chemistry (exception: Ti)**
- **Virtually always < 18*e* complexes**
- **Polar and very reactive M-C bonds**
- **Little *d*-electrons:**
  - **preference for "hard" s-donors**
  - **weak coordination to p-acceptors**

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

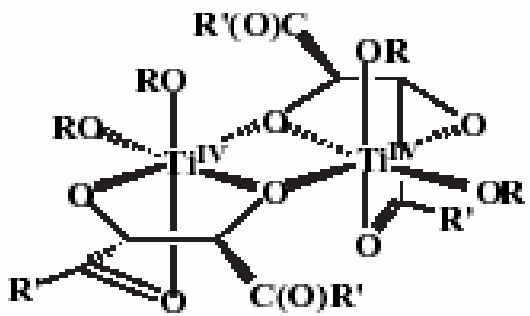
Early transition metals
Groups 3-4

Sc	Ti	
Y	Zr	
La	Hf	
Ac		

- **Typical catalysis: polymerization:**



Epoxidation:



Sharpless titanium-tartrate epoxidation catalyst

t-BuOOH, 4Å MS
CH_2Cl_2, -20°C

70-90% yield
94->98% *ee*

Sharpless *JACS* **1987** (109) 5765.

Middle transition metals
Groups 5-7

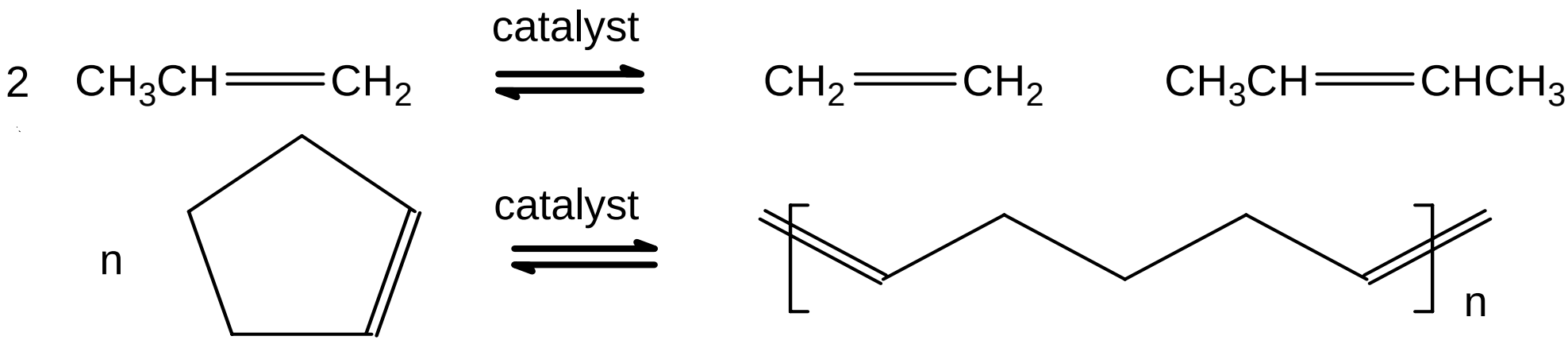
V	Cr	Mn
Nb	Mo	Tc
Ta	W	Re

- **Many oxidation states are accessible**
- **Mostly 18*e* complexes**
- **Ligands are strongly bound**
- **Strong, rather unreactive M-C bonds**
- **Preference for s-donor/p-acceptor combinations (CO!)**

Middle transition metals
Groups 5-7

V	Cr	Mn
Nb	Mo	Tc
Ta	W	Re

- **Typical catalysis: alkene and alkyne metathesis**



Late transition metals
Groups 8,9,10

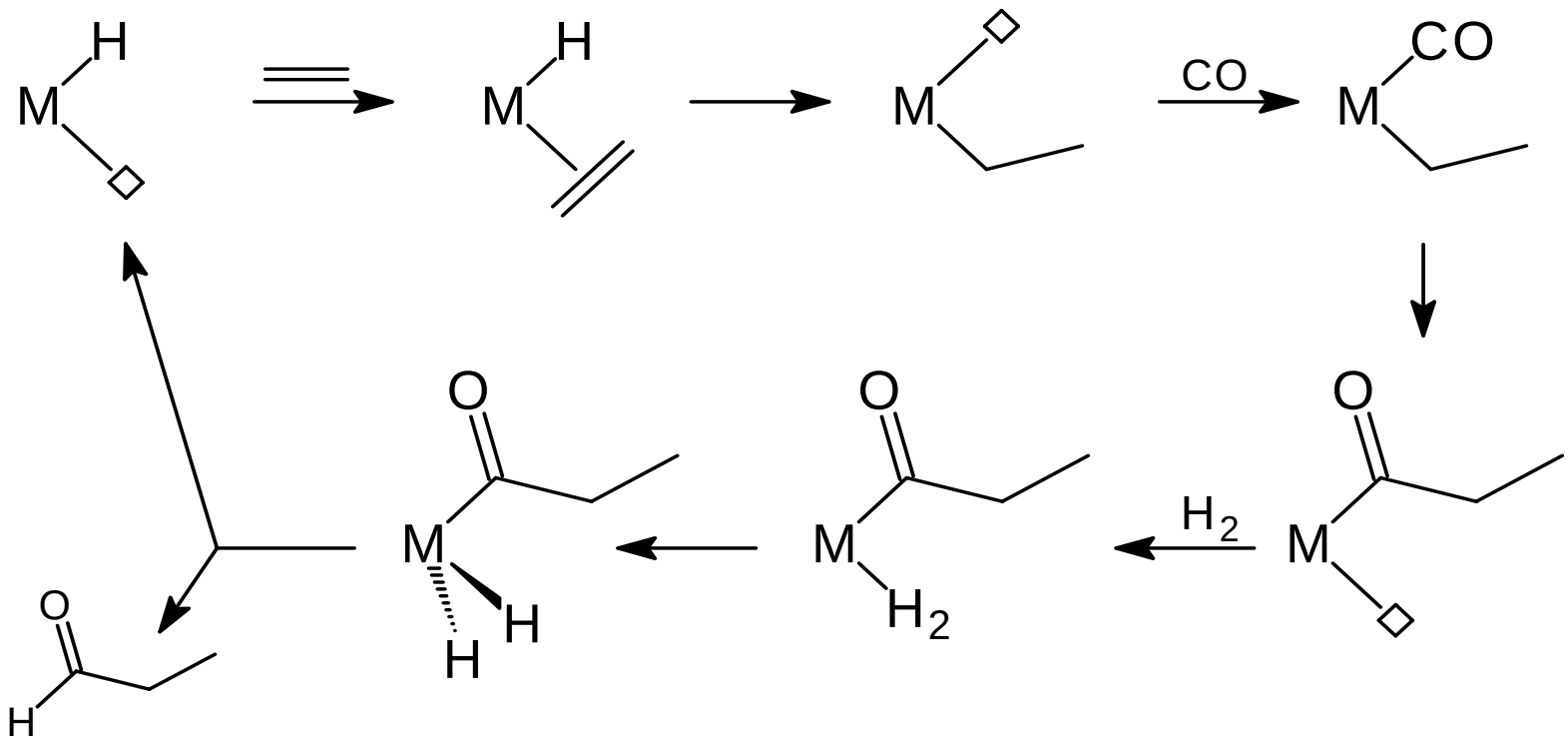
Fe	Co	Ni	Cu
Ru	Rh	Pd	Ag
Os	Ir	Pt	Au

- **Multiple oxidation states**
- **Mostly 18*e* of 16*e* complexes**
  - **16*e* typically square planar coordination**
- **Easy ligand association/dissociation**
- **Weak, not too reactive M-C bonds**
- **Even weaker, and reactive M-O/M-N bonds**
- **Preference for s-donor/(weak) p-acceptor bonding (Phosphines)**

Late transition metals
Groups 8,9,10

Fe	Co	Ni	Cu
Ru	Rh	Pd	Ag
Os	Ir	Pt	Au

- **Typical catalysis: hydroformylation (-silylation, -amination, -cyanation), hydrogenation, etc.**



Periodic trends

1st row:

- often unpaired electrons (paramagnetic)
- Several spin states accessible (HS/LS)
- Highest oxidation state less stable

$2^{nd}/3^{rd}$ row:

- "closed shell"
- Higher oxidation states relatively stable
- 2nd row often more reactive than 3rd

…Very bold generalizations for your research

- **Working with 1st row elements:**
  - difficult, you probably can't use NMR
- **Working with 2nd row elements**
  - You'll find exiting catalysts…
  - …they will be to active to be studied in detail
  - Nice for industry, less for academia
- **Working with 3rd row elements**
  - you'll make beautiful complexes and can study their reactivity in detail
  - Nice for academia, less for industry

Trends and Properties
Periodic Table

- **Oxidation State**

  - **As a rule of thumb: within one group: higher oxidation state is more stable**

  periodic table

  d-Elements

  - **Note: for main-group elements: lower oxidation state is more stable within one group (Tl^{+}, Pb^{2+}, Bi^{3+}): *"inert electron pair"***

Trends and Properties Periodic Table

- **Structural Properties**

  - **As a rule of thumb: within one group: higher coordination number possible:**

Group	3d	4d	5d
3	ScF_6^{3-}		
4	TiF_6^{2-}	ZrF_7^{3-}	HfF_7^{3-}
5	VF_6^{-}	$Nb(CN)_8^{5-}$	TaF_8^{3-}

Trends and Properties
Periodic Table

- **Atom (Ion) Radius**
  - ***r*** **decreases in going from the left to the right within one period**
  - ***r*** **increases in going from 1st to 2nd row element, but little change in going from 2nd to 3rd row element**

Ti: 1.47 Å	V: 1.34 Å	Cr: 1.17 Å
Zr: 1.60 Å	Nb: 1.46 Å	Mo: 1.39 Å
Hf: 1.58 Å	Ta: 1.46 Å	W: 1.39 Å

➢ ***Lanthanoide contraction: addition of f-Block elements:***

f-orbitals don't shield the nuclear charge efficiently: more "diffuse" and consequently Zeff increases which attracts all electrons!

LONG FORM OF PERIODIC TABLE

INDEX

Symbol

Atomic Mass → 1.008 | ← Atomic Number: 1

Electronegativity → 2.1 | ← Stable Oxidation State: ± 1

Melting Point (°C) → -259.2 | ← Atomic Radius (A°): 0.37

Full Name → HYDROGEN | ← Electronic Configuration: $1s^1$

H

SOLID ELEMENTS — GASEOUS ELEMENTS — LIQUID ELEMENTS

← s-Block Elements → *[ns^{1-2}]

Alkali Metals — Alkaline Earth Metals

Increasing Electronegativity →

← p - Block Elements (Except Helium) *[$ns^2 p^{1-6}$] →

Halogens — Noble Gases

Boron Family — Carbon Family — Pricogens — Chalcogens

GROUPS --- Vertical Columns

Decreasing Electronegativity ↓

PERIODS --- Horizontal Rows →

← d - Block Elements or Transition Elements *[$(n-1)d^{1-10} ns^{1-2}$] →

Period	IA (1)	IIA (2)	IIIB (3)	IVB (4)	VB (5)	VIB (6)	VIIB (7)	VIII (8)	VIII (9)	VIII (10)	IB (11)	IIB (12)	IIIA (13)	IVA (14)	VA (15)	VIA (16)	VIIA (17)	O (18)
1 [1s]	1.008 1 2.1 ± 1 -259.2 H 0.37 HYDROGEN $1s^1$																1.008 1 2.1 ± 1 -259.2 H 0.37 HYDROGEN $1s^1$	4.00 2 - -272.1 He 1.4 HELIUM $1s^2$
2 [2s 2p]	6.94 3 1.0 1 180 Li 1.34 LITHIUM [He] $2s^1$	9.01 4 1.5 2 1217 Be 1.1 BERYLLIUM [He] $2s^2$											10.81 5 2.0 3 2177 B 0.83 BORON [He] $2s^2 2p^1$	12.01 6 2.5 4 3727 C 0.77 CARBON [He] $2s^2 2p^2$	14.01 7 3.0 -3 -210 N 0.75 NITROGEN [He] $2s^2 2p^3$	15.99 8 3.5 -2 -219.8 O 0.73 OXYGEN [He] $2s^2 2p^4$	18.99 9 4.0 - 1 -218.6 F 0.72 FLUORINE [He] $2s^2 2p^5$	20.18 10 - -246.6 Ne 1.54 NEON [He] $2s^2 2p^6$
3 [3s 3p]	22.99 11 0.9 1 97.8 Na 1.54 SODIUM [Ne] $3s^1$	24.31 12 1.2 2 650 Mg 1.36 MAGNESIUM [Ne] $3s^2$											26.98 13 1.6 3 659 Al 1.18 ALUMINIUM [Ne] $3s^2 3p^1$	28.08 14 1.8 4 1410 Si 1.11 SILICON [Ne] $3s^2 3p^2$	30.97 15 2.1 5 44.1 P 1.06 PHOSPHORUS [Ne] $3s^2 3p^3$	32.06 16 2.6 6 119 S 1.09 SULPHUR [Ne] $3s^2 3p^4$	35.45 17 3.1 ±1 -101.0 Cl 0.99 CHLORINE [Ne] $3s^2 3p^5$	39.95 18 - -189.37 Ar 1.88 ARGON [Ne] $3s^2 3p^6$
4 [4s 3d 4p]	39.10 19 0.8 1 64 K 1.96 POTASSIUM [Ar] $4s^1$	40.08 20 1.0 2 850 Ca 1.97 CALCIUM [Ar] $4s^2$	44.96 21 1.3 3 1539 Sc 1.62 SCANDIUM [Ar] $3d^1 4s^2$	47.90 22 1.5 4 1660 Ti 1.47 TITANIUM [Ar] $3d^2 4s^2$	50.94 23 1.6 2-5 1917 V 1.34 VANADIUM [Ar] $3d^3 4s^2$	51.99 24 1.6 2,3,6 1857 Cr 1.17 CHROMIUM [Ar] $3d^5 4s^1$	54.94 25 1.6 2,4,7 1245 Mn 1.26 MANGANESE [Ar] $3d^5 4s^2$	55.85 26 1.8 2,3 1536 Fe 1.26 IRON [Ar] $3d^6 4s^2$	58.93 27 1.8 2,3 1495 Co 1.25 COBALT [Ar] $3d^7 4s^2$	58.69 28 1.8 2,3 1455 Ni 1.24 NICKEL [Ar] $3d^8 4s^2$	63.54 29 1.9 2 1083 Cu 1.27 COPPER [Ar] $3d^{10} 4s^1$	65.37 30 1.6 2 419.5 Zn 1.38 ZINC [Ar] $3d^{10} 4s^2$	69.72 31 1.8 3 29.8 Ga 1.26 GALLIUM [Ar] $3d^{10} 4s^2 4p^1$	72.59 32 1.9 4 940 Ge 1.22 GERMANIUM [Ar] $3d^{10} 4s^2 4p^2$	74.92 33 2.2 ± 3.5 817 As 1.19 ARSENIC [Ar] $3d^{10} 4s^2 4p^3$	78.96 34 2.6 2,4,6 221 Se 1.16 SELENIUM [Ar] $3d^{10} 4s^2 4p^4$	79.91 35 3.0 ± 1 -7.2 Br 1.14 BROMINE [Ar] $3d^{10} 4s^2 4p^5$	83.80 36 - -157.2 Kr 2.02 KRYPTON [Ar] $3d^{10} 4s^2 4p^6$
5 [5s 4d 5p]	85.47 37 0.8 1 39 Rb 2.11 RUBEDIUM [Kr] $5s^1$	87.62 38 1.0 2 768 Sr 1.92 STRONTIUM [Kr] $5s^2$	88.91 39 1.3 3 1530 Y 1.80 YTTRIUM [Kr] $4d^1 5s^2$	91.22 40 1.3 4 1852 Zr 1.60 ZIRCONIUM [Kr] $4d^2 5s^2$	92.91 41 1.6 5 2477 Nb 1.46 NIOBIUM [Kr] $4d^4 5s^1$	95.94 42 2.2 6 2610 Mo 1.39 MOLYBDENUM [Kr] $4d^5 5s^1$	98.91 43 2.1 7 2250 Tc 1.36 TECHNETIUM [Kr] $4d^5 5s^2$	101.07 44 2.2 3 2427 Ru 1.34 RUTHENIUM [Kr] $4d^7 5s^1$	102.91 45 2.2 3 1966 Rh 1.34 RHODIUM [Kr] $4d^8 5s^1$	106.40 46 2.2 2 1552 Pd 1.37 PALLADIUM [Kr] $4d^{10} 5s^0$	107.87 47 1.9 1 961.9 Ag 1.44 SILVER [Kr] $4d^{10} 5s^1$	112.40 48 1.7 2 321.1 Cd 1.49 CADMIUM [Kr] $4d^{10} 5s^2$	114.82 49 1.7 3 156.6 In 1.44 INDIUM [Kr] $4d^{10} 5s^2 5p^1$	118.69 50 2.0 4 231.8 Sn 1.41 TIN [Kr] $4d^{10} 5s^2 5p^2$	121.76 51 2.1 3 630.5 Sb 1.38 ANTIMONY [Kr] $4d^{10} 5s^2 5p^3$	127.60 52 2.1 4 449.5 Te 1.35 TELLURIUM [Kr] $4d^{10} 5s^2 5p^4$	126.90 53 2.6 + 1 113.9 I 1.33 IODINE [Kr] $4d^{10} 5s^2 5p^5$	131.30 54 2.6 0 -111.8 Xe 2.16 XENON [Kr] $4d^{10} 5s^2 5p^6$
6 [6s (4f) 5d 6p]	132.91 55 0.86 1 28.5 Cs 2.17 CESIUM [Xe] $6s^1$	137.34 56 0.9 2 725 Ba 2.17 BARIUM [Xe] $6s^2$	138.9 57 1.1 3 920 La 1.87 LANTHANUM [Xe] $5d^1 6s^2$	178.49 72 1.3 4 2222 Hf 1.58 HAFNIUM [Xe] $4f^{14} 5d^2 6s^2$	180.95 73 1.53 5 2986 Ta 1.46 TANTALUM [Xe] $4f^{14} 5d^3 6s^2$	183.85 74 1.7 6 3410 W 1.39 TUNGSTEN [Xe] $4f^{14} 5d^4 6s^2$	186.20 75 1.9 7 3180 Re 1.37 RHENIUM [Xe] $4f^{14} 5d^5 6s^2$	190.20 76 2.2 4 2700 Os 1.35 OSMIUM [Xe] $4f^{14} 5d^6 6s^2$	192.20 77 2.2 4 2454 Ir 1.36 IRIDIUM [Xe] $4f^{14} 5d^7 6s^2$	195.09 78 2.2 4 1772 Pt 1.38 PLATINUM [Xe] $4f^{14} 5d^9 6s^1$	196.97 79 2.4 3 1063 Au 1.44 GOLD [Xe] $4f^{14} 5d^{10} 6s^1$	200.59 80 1.9 2 -38.8 Hg 1.44 MERCURY [Xe] $4f^{14} 5d^{10} 6s^2$	204.37 81 1.8 1 303 Tl 1.48 THALLIUM [Xe] $4f^{14} 5d^{10} 6s^2 6p^1$	207.19 82 1.8 2 327.4 Pb 1.44 LEAD [Xe] $4f^{14} 5d^{10} 6s^2 6p^2$	208.98 83 1.9 3 271.4 Bi 1.54 BISMUTH [Xe] $4f^{14} 5d^{10} 6s^2 6p^3$	209.00 84 2.0 2 254 Po - POLONIUM [Xe] $4f^{14} 5d^{10} 6s^2 6p^4$	210.00 85 2.2 - 302 At ASTATINE [Xe] $4f^{14} 5d^{10} 6s^2 6p^5$	222 86 - 0 -71 Rn - RADON [Xe] $4f^{14} 5d^{10} 6s^2 6p^6$
7 [7s (5f) 6d]	223.00 87 0.7 1 - Fr - FRANCIUM [Rn] $7s^1$	226.00 88 0.9 2 700 Ra - RADIUM [Rn] $7s^2$	227.00 89 1.1 3 1050 Ac 1.878 ACTINIUM [Rn] $6d^1 7s^2$	261.118 104 Unq Rf** RUTHERFORDIUM [Rn] $5f^{14} 6d^2 7s^2$	262.12 105 Ha*** HAHNIUM	263.118 106 Sg Unh SEABORGIUM	262.12 107 Bh Uns BOHRIUM	265 108 Hs Uno HASSIUM	266 109 Mt Une MEITNEIUM	110 Uun UNNILENNIUM	111 Uuu	112 EXA-MERCURY Uub						

Metals — Non-Metals

Shaded are Metalloids

* → General Electronic Configuration

** → Rf (z=104) is also called as Kurchatovium (Ku)

*** → Ha (z=105) is also called as Neisbonium (Ns)

← f - Block Elements OR Inner Transition Elements *[$(n-2) f^{1-14} (n-1) d^{0-1} ns^2$] →

Rare Earths - I (4f - Series) Lanthanides *[$4f^{1-14} 5d^{0-1} 6s^2$]

Rare Earths - II (5f - Series) Actinides *[$5f^{1-14} 6d^{0-1} 7s^2$]

Period														
6	140.12 58 1.1 3 795 Ce 1.646 CERIUM [Xe] $4f^1 5d^1 6s^2$	140.91 59 1.1 3 919 Pr 1.828 PRASEODYMIUM [Xe] $4f^3 6s^2$	144.24 60 1.07 3 1020 Nd 1.821 NEODYMIUM [Xe] $4f^4 6s^2$	145.00 61 1.07 3 1080 Pm 1.810 PROMETHIUM [Xe] $4f^5 6s^2$	150.40 62 1.2 3 1070 Sm 1.802 SAMARIUM [Xe] $4f^6 6s^2$	151.96 63 1.01 3 826 Eu 2.04 EUROPIUM [Xe] $4f^7 6s^2$	157.6 64 1.1 3 1306 Gd 1.802 GADOLINIUM [Xe] $4f^7 5d^1 6s^2$	158.93 65 1.2 3 1356 Tb 1.782 TERBIUM [Xe] $4f^9 6s^2$	162.50 66 1.10 3 1500 Dy 1.773 DYSPROSIUM [Xe] $4f^{10} 6s^2$	164.93 67 1.2 3 1460 Ho 1.766 HOLMIUM [Xe] $4f^{11} 6s^2$	167.26 68 1.10 3 1497 Er 1.757 ERBIUM [Xe] $4f^{12} 6s^2$	168.93 69 1.2 3 1545 Tm 1.746 THULIUM [Xe] $4f^{13} 6s^2$	173.04 70 1.1 3 824 Yb 1.746 YTTERBIUM [Xe] $4f^{14} 6s^2$	174.97 71 1.2 3 1652 Lu 1.734 LUTETIUM [Xe] $4f^{14} 5d^1 6s^2$
7	232.04 90 1.3 4 1750 Th 1.798 THORIUM [Rn] $6d^2 7s^2$	231.00 91 1.14 5 1227 Pa 1.606 PROTOACTINIUM [Rn] $5f^2 6d^1 7s^2$	238.03 92 1.22 6 1130 U 1.53 URANIUM [Rn] $5f^3 6d^1 7s^2$	237.05 93 1.3 5 630 Np 1.31 NEPTUNIUM [Rn] $5f^4 6d^1 7s^2$	242.00 94 1.3 4 639.5 Pu 1.51 PLUTONIUM [Rn] $5f^6 7s^2$	243.00 95 1.3 3 994 Am 1.84 AMERICIUM [Rn] $5f^7 7s^2$	247.00 96 1.3 3 - Cm - CURIUM [Rn] $5f^7 6d^1 7s^2$	249.00 97 1.3 3 1285 Bk - BERKELIUM [Rn] $5f^9 6d^1 7s^2$	251.00 98 1.3 - - Cf - CALIFORNIUM [Rn] $5f^{10} 7s^2$	254.00 99 1.3 - - Es - EINSTENIUM [Rn] $5f^{11} 7s^2$	253.00 100 1.3 - - Fm - FERMIUM [Rn] $5f^{12} 7s^2$	256.00 101 1.3 - - Md - MENDELEVIUM [Rn] $5f^{13} 7s^2$	254.00 102 1.3 - - No 1.429 NOBELIUM [Rn] $5f^{14} 7s^2$	257.00 103 1.7 - - Lr - LAWRENCIUM [Rn] $5f^{14} 6d^1 7s^2$

Values are taken from Lange's Handbook of Chemistry
12th Edition, McGraw Hill Book Company, New York
Edited by: John A. Dean

Trends and Properties
Periodic Table

- **Relativistic Effects**

  - **Some phenomena of *heavy* elements can be explained by relativistic effects**

    - ***Very high ionization energy of 6s electrons***
    - ***Bond energies often increase down a group of d-block elements, whereas bond energies usually decrease down a group of p-block elements***
    - ***Colour of Gold (Au)***
    - ***Fluidity of Mercury (Hg)***
    - ***Difference of Pd and Pt in homogeneous catalysis with respect to oxidative addition and reductive elimination reactions***

Trends and Properties
Periodic Table

- **Relativistic Effects**

  - According to the theory of relativity , the mass *m* of a particle increases from its resting mass m_0 when its velocity *v* approaches the speed of light, *c*, and *m*, is then given by the equation:

$$m = \frac{m_0}{\sqrt{1-(v/c)^2}}$$

  - For the Bohr model *v* is given by:

$$v = \frac{Ze^2}{2\varepsilon_0 nh}$$

Z: atomic number
e: charge on the electron
ε_0: permittivity of a vacuum
h: Planck constant
n: main quantum number

Trends and Properties
Periodic Table

- **Relativistic Effects**

  - For n = 1 and Z = 1, v is only (1/137)c, but for Z = 80 (Hg), (v/c) is ~0.58c and consequently m = 1.2 m_0.

  - Radius r of the Bohr atom is given by:

$$r = \frac{Ze^2}{4\pi\varepsilon_0 m v^2}$$

  - Increase in m results in an approximately 20% contraction of the radius of the 1s (n = 1) orbital: relativistic contraction

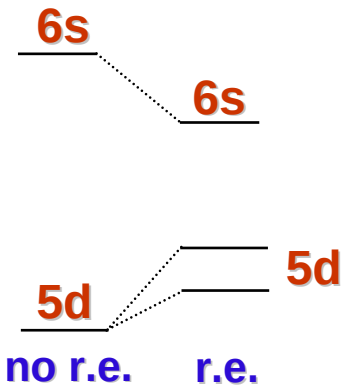
Trends and Properties Periodic Table

- **Relativistic Effects**

  - **Contraction of s- and p- orbitals (closer to the nucleus)**
  - **Expansion of the d-orbitals (Shielding of the nucleus charge)**

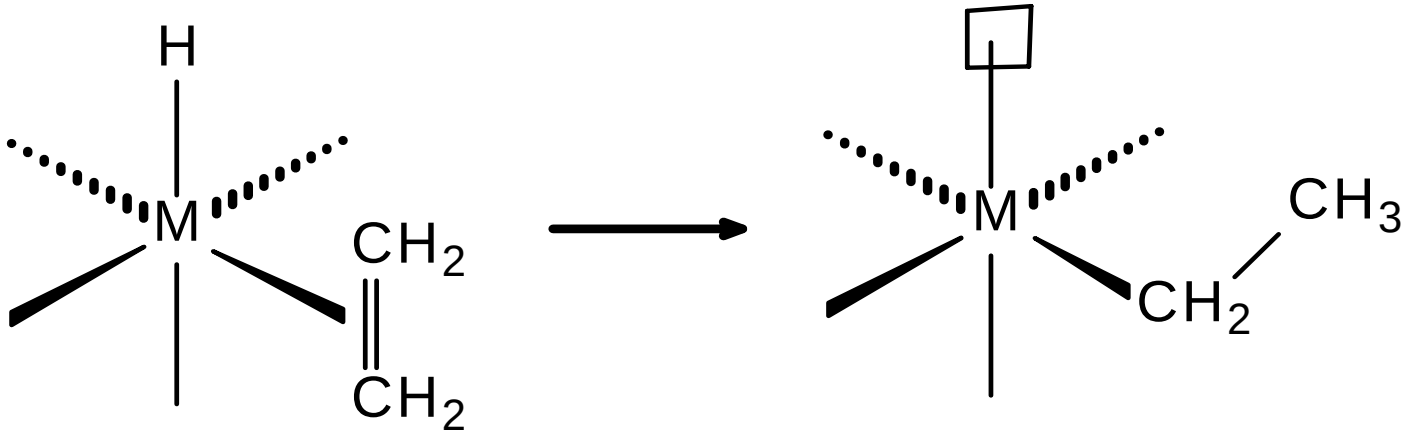
    - ***Very high ionization energy of 6s electrons: stabilization of Hg(0), Tl(I), Pb(II) and Bi(III) compared to Cd(0), In(I), Sn(II), Sb(III).***
      - **Inert electron pair!**

    - ***Lowering of 6s level and destabilizing of 5d level:***
      Gold: absorption at $h\nu$ = 2.4 eV (blue and violet): reflects yellow and red.

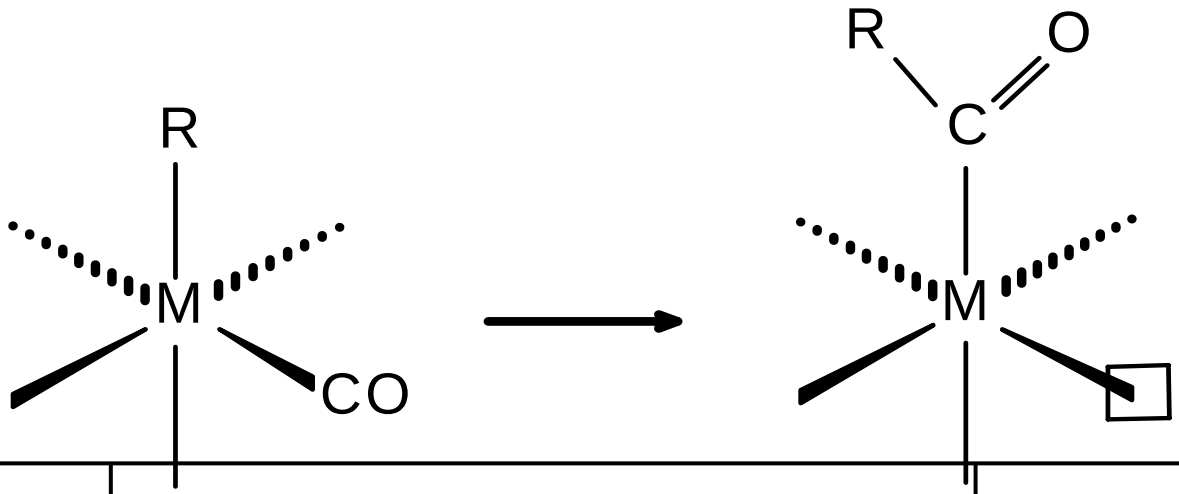


Elementary reactions

- **Insertions**



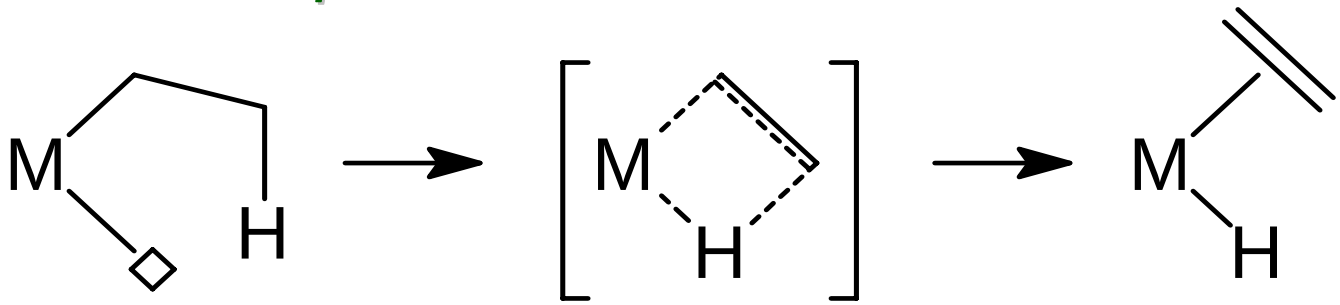
alkyl generation



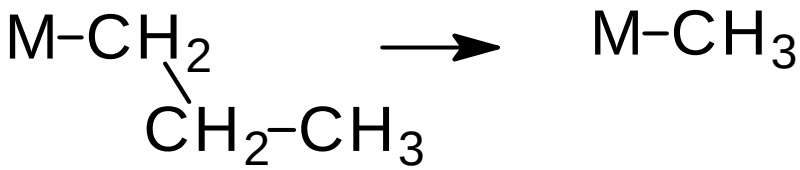
acyl formation

Elementary reactions

- **Most common: β-H elimination**



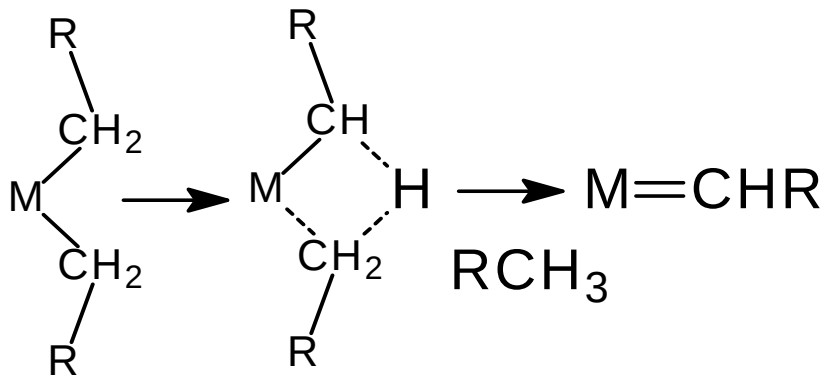
- **Other:**
  - **homolysis**
  - **α/γ/δ-eliminations**



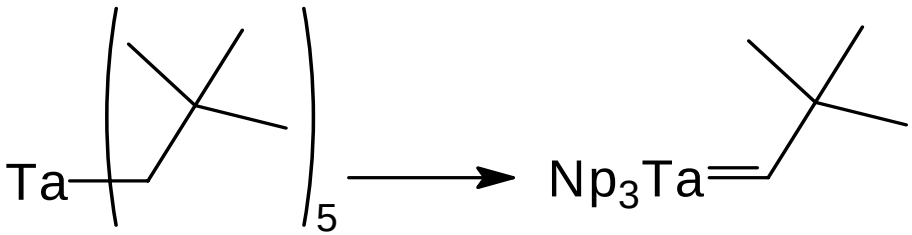
  - **reductive elimination (often with hydride or other alkyl)**
  - **Ligand Metallation (e.g. cyclometallation)**

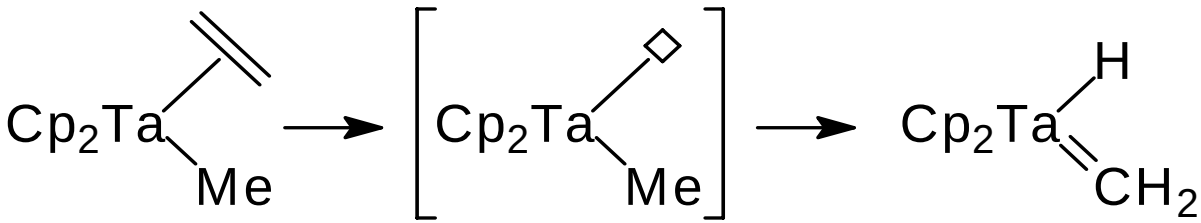
Synthesis of Schrock alkylidens

Decomposition of metal alkyls (α-eliminatie)

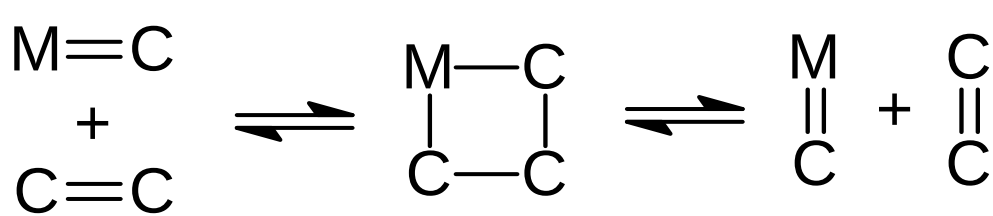


Examples:



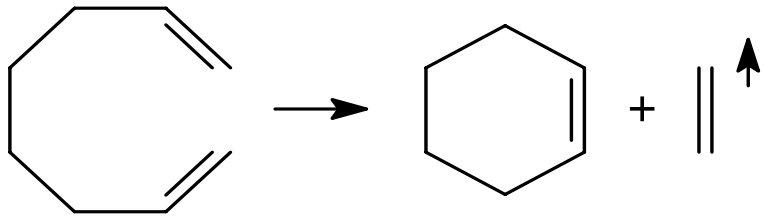


Catalytic Alkene Metathesis

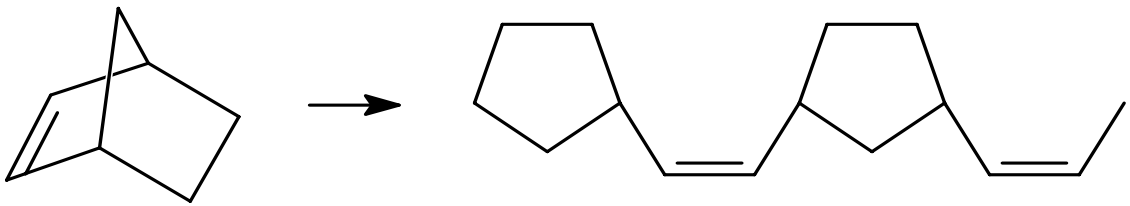


Driving forces:

- **Liberation of volatile reactants**



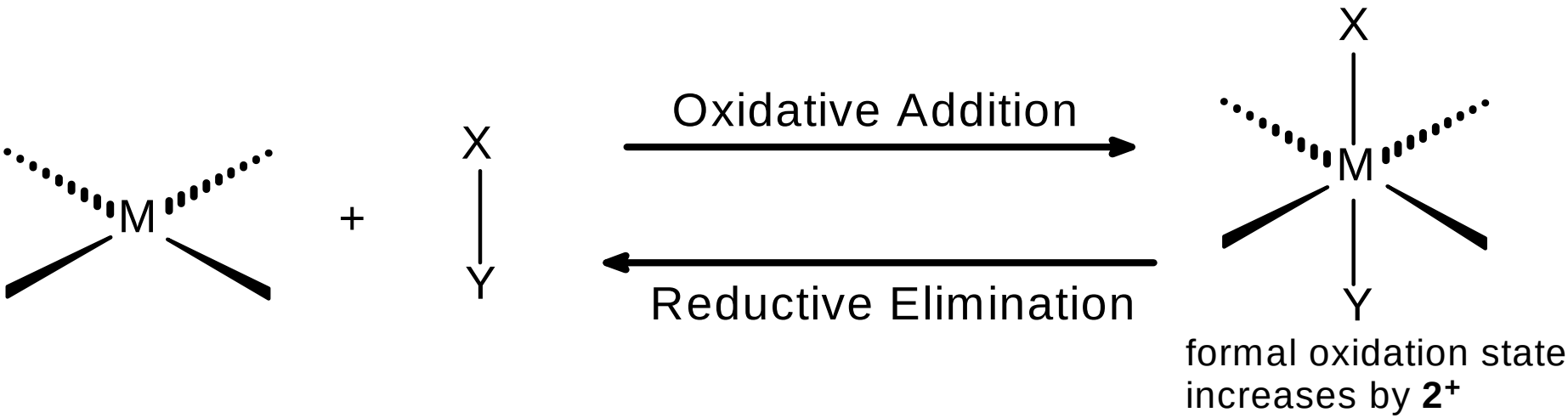
- **Reduction of Ring strain**

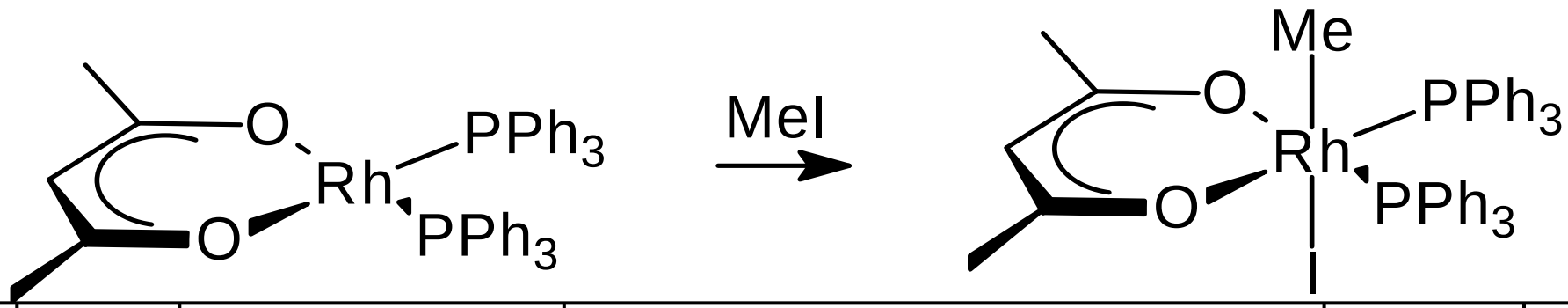


Olefin metathesis is key in the production of linear olefins at the Geismar, La., facilities of Shell Chemicals.

Elementary reactions

- **Oxidative Addition**





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kids *the lotuseffect* voor VWO-werkweek: hier klikken

Applications of the materials we make (the so called POSS-cubes) can be found in the addition to coatings (covering/paint, for example on a car or house). The inspiration comes from nature. With the leaves of the lotusplant as a model, coatings were made that clean themselves: the Lotus-effect. Dirt lays on the leaf as a fakir on his bed with spikes.

Rain flushes away all dirt... Imagine nobody has to clean his car ever again!

The small pictures show a raindrop on the leaf of a lotus and to the right: a leaf through a microscope (very good magnifying glass), it really is like a bed with spikes!!