ORGANOMETALLIC CHEMISTRY

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Course organization and recommended texts

- 14 weeks, 13 classes (1 week is public holiday)
- Course will contain exercises & examples
- Content will be available on Moodle (CH-223 Organometallics)
- Written exam

Basic and easy reading:

- "Organometallics 1" and "Organometallics 2" by M. Bochmann (Oxford Chemistry Primers 1994).

Others (more general, but each contains relevant sections):

- "Inorganic Chemistry" by P. Atkins, T. Overton, J. Rouke, M. Weller, and F. Armstrong (Oxford University Press 2006).
- "Inorganic Chemistry" by C. Housecroft and A. Sharpe (Pearson Prentice Hall 2005).
- Also very useful: Rob Toreki's Organometallic Hypertextbook - http://www.ilpi.com/organomet/ (contains online tests).

The course and exercises suffice for the exam. I recommend also looking for courses online for comparisons.

Slides from past course will also be accessible on moodle.

Course Outline

1) **Introduction and the Basics** types of organometallic complex; formal oxidation state; d^n electron count; coordinative unsaturation and saturation; bonding; Pauling electroneutrality principle; kinetic and thermodynamic stability the 18 (and 16) electron rule; how to electron count.

2) **Principal Reaction Types:** salt elimination; protonolysis; oxidative addition; reductive elimination; oxidative coupling; reductive cleavage; migratory insertions; elimination reactions; σ-bond metathesis.

3) **Metal–Carbon σ-Bonds:** bonding modes; metal compounds containing alkyls, hydrides, carbenes, carbynes, and carbonyls

4) **Metal–Carbon π-Bonds:** structure and bonding in metal compounds containing alkenes, alkynes, allyls, dienes, cyclopentadienyls, arenes

5) **Homogeneous Catalysis:** introduction to homogeneous catalysis; survey of some important catalytic cycles.

Definition and Context:

"An organometallic complex is one which contains, by definition, at least one metal–carbon bond (ionic or covalent, localized or delocalized) between one or more carbon atoms of an organic group or molecule and a main group, transition, lanthanide, or actinide metal atom (or atoms)."

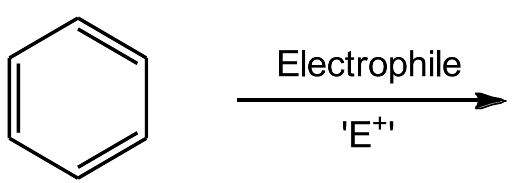
Organometallic chemistry is typically regarded as a subset of Inorganic Coordination Chemistry (See Course Wendy Queen), although it is really a major discipline in its own right and it is at the interface of organic and materials chemistries.

Why the interest?

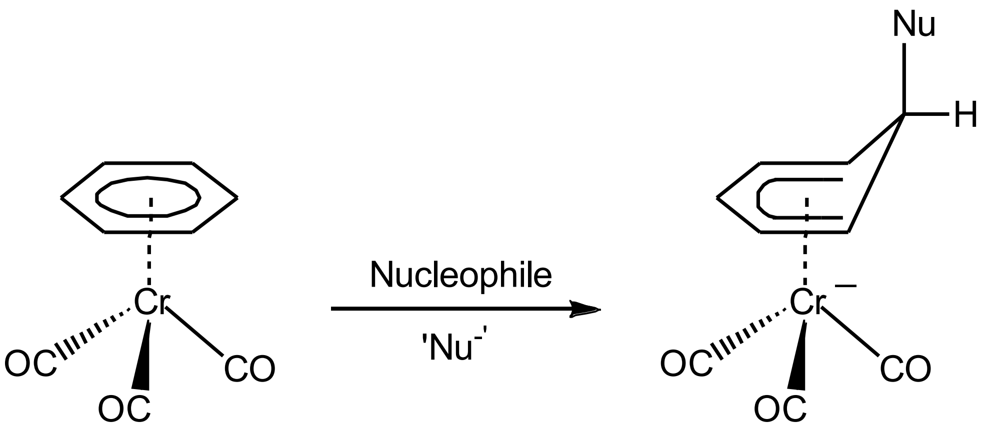
- Chemical - new compounds adjusting bonding and reaction theories, trapping organic intermediates, inverting reactivity.
- Commercial - catalysts for industrial processes
- Biological - vitamin B_{12} coenzyme has a Co–alkyl bond, bio-sensors, artificial metalloenzymes, bio-nanotechnology, enantioselective catalysis

Why are OM compounds interesting?

They are used to modify classic organic reactivity:

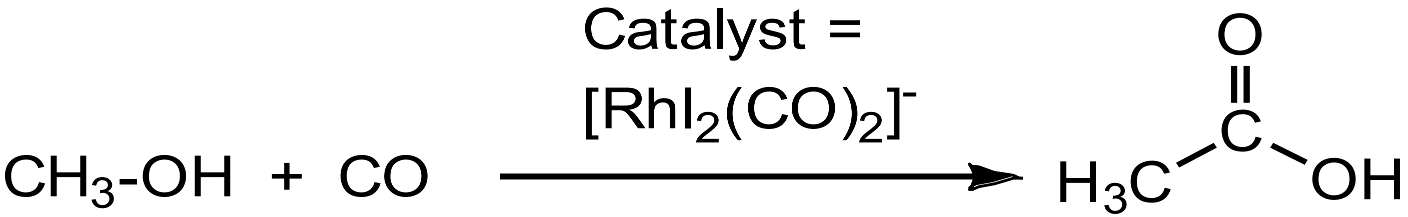


Electrophilic substitution

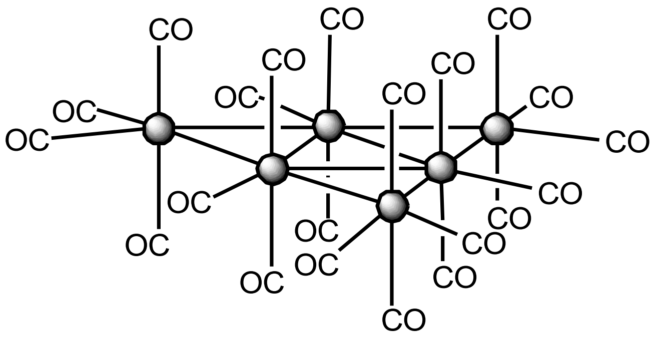


Nucleophilic addition

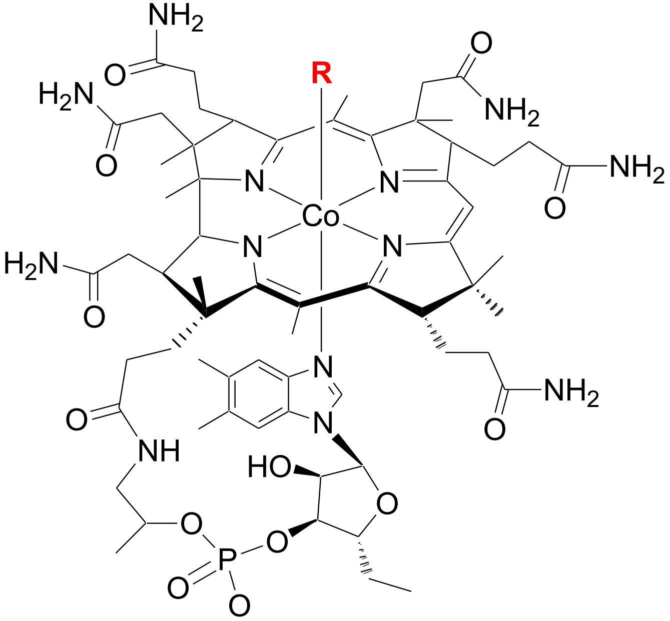
They can be used as catalysts. For example: The catalytic conversion of methanol and CO to acetic acid – the Monsanto process



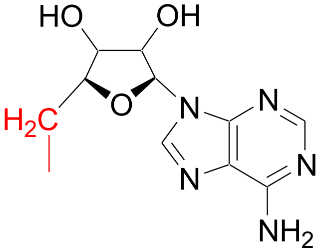
They can serve as model for heterogeneous catalysts that are not easy to characterize owing to their non soluble properties.



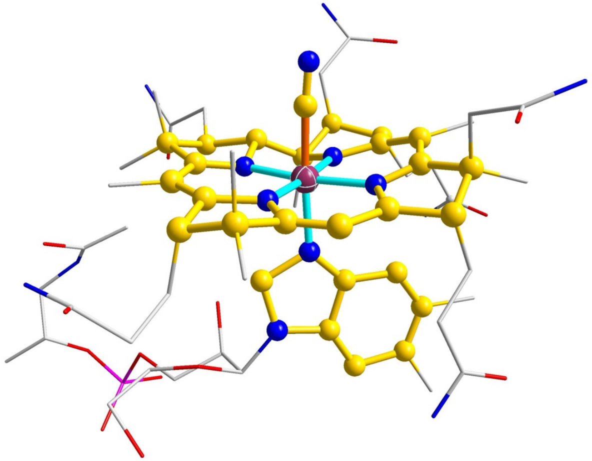
There are examples of OM complexes originating in nature. Example: Vitamin B12

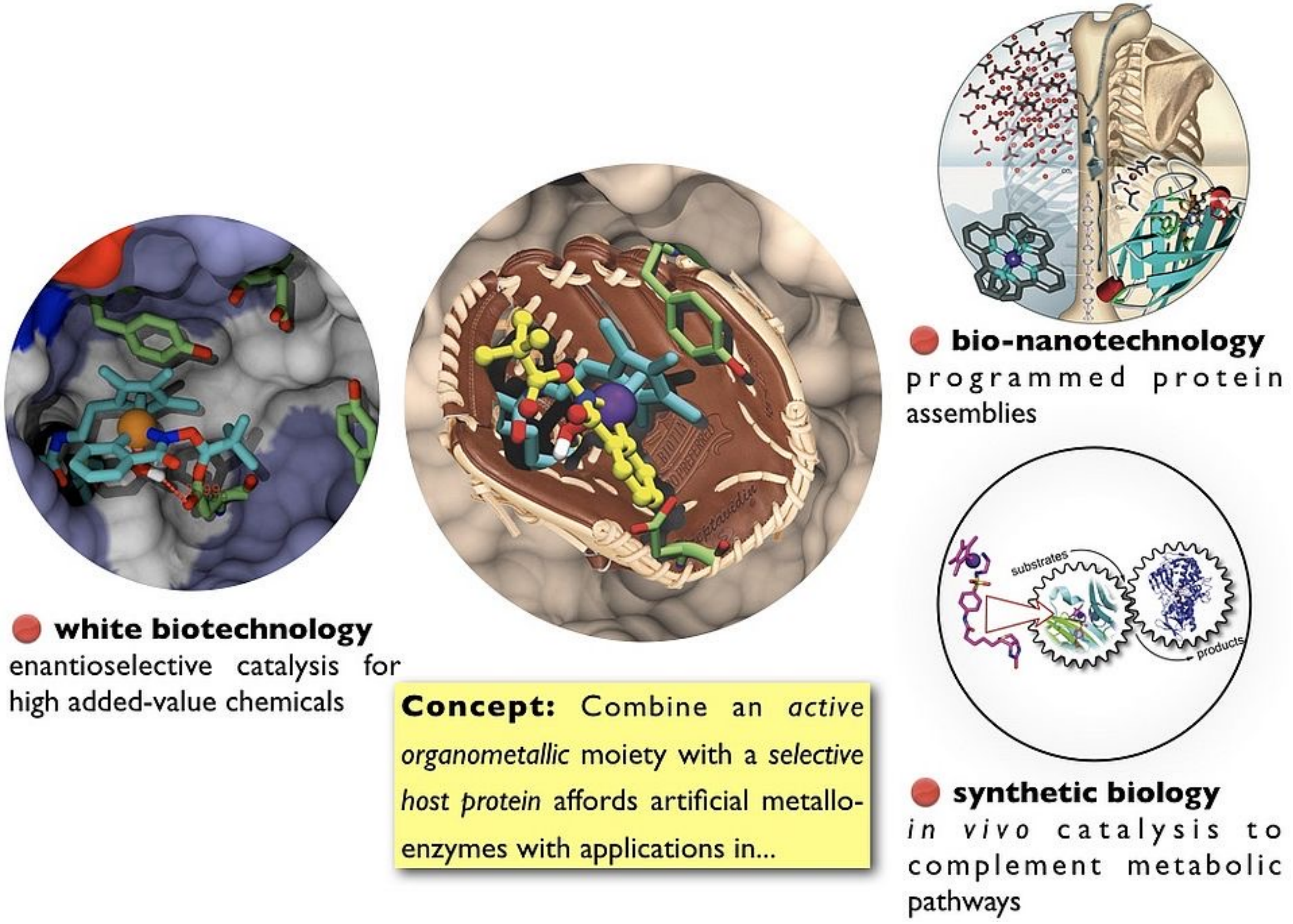


R = CN (Vitamin B_{12})
R = CH_3 (Methylcobalamin)
R = 5'-Desoxyadenosyl (Coenzyme B_{12})



5'-Desoxydenosyl:





white biotechnology
enantioselective catalysis for high added-value chemicals

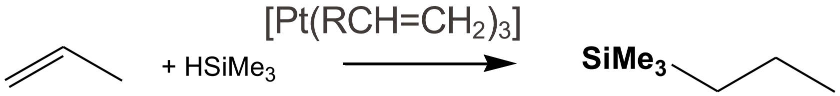
Concept: Combine an *active organometallic* moiety with a *selective host protein* affords artificial metallo-enzymes with applications in...

bio-nanotechnology
programmed protein assemblies

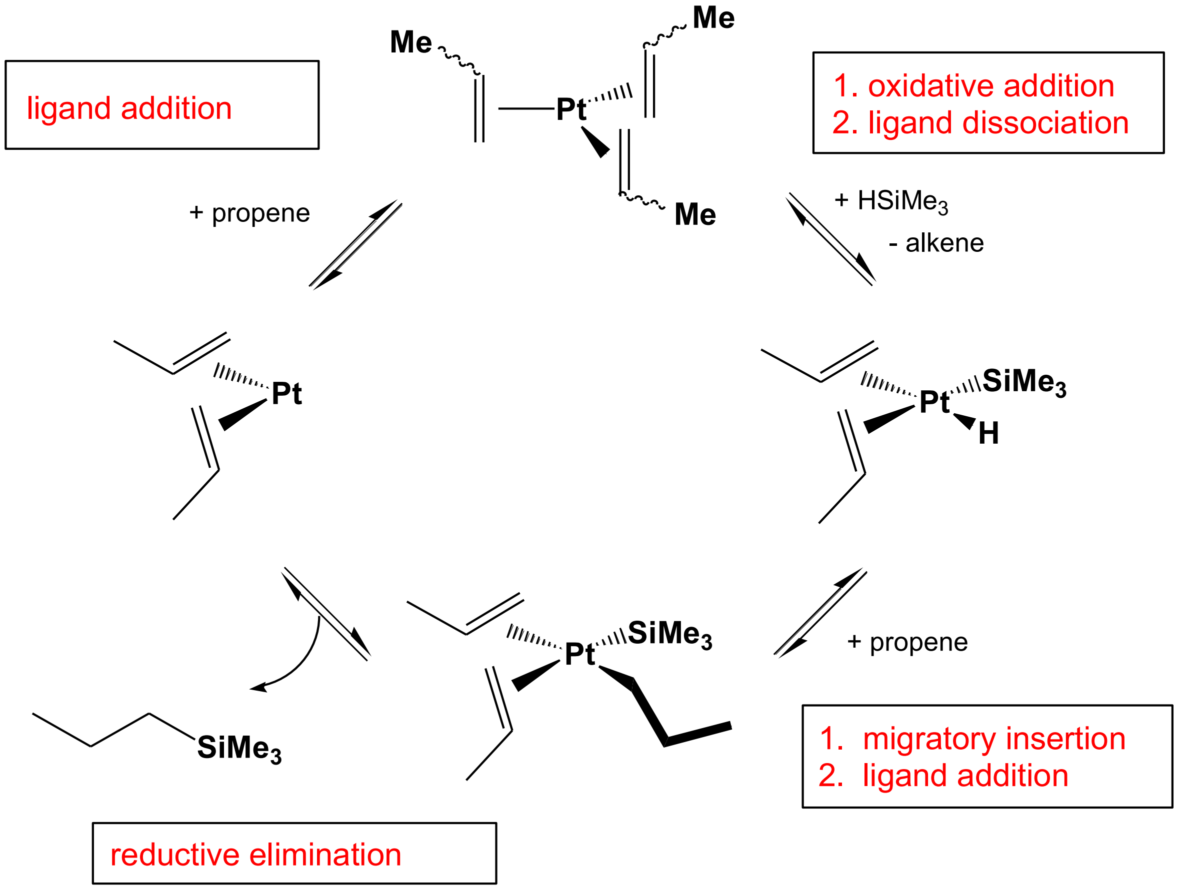
synthetic biology
in vivo catalysis to complement metabolic pathways

- Taken from T.Ward research website

An example of a Pt-catalyzed reaction



Hydrosilylation



ligand addition

1. oxidative addition
2. ligand dissociation

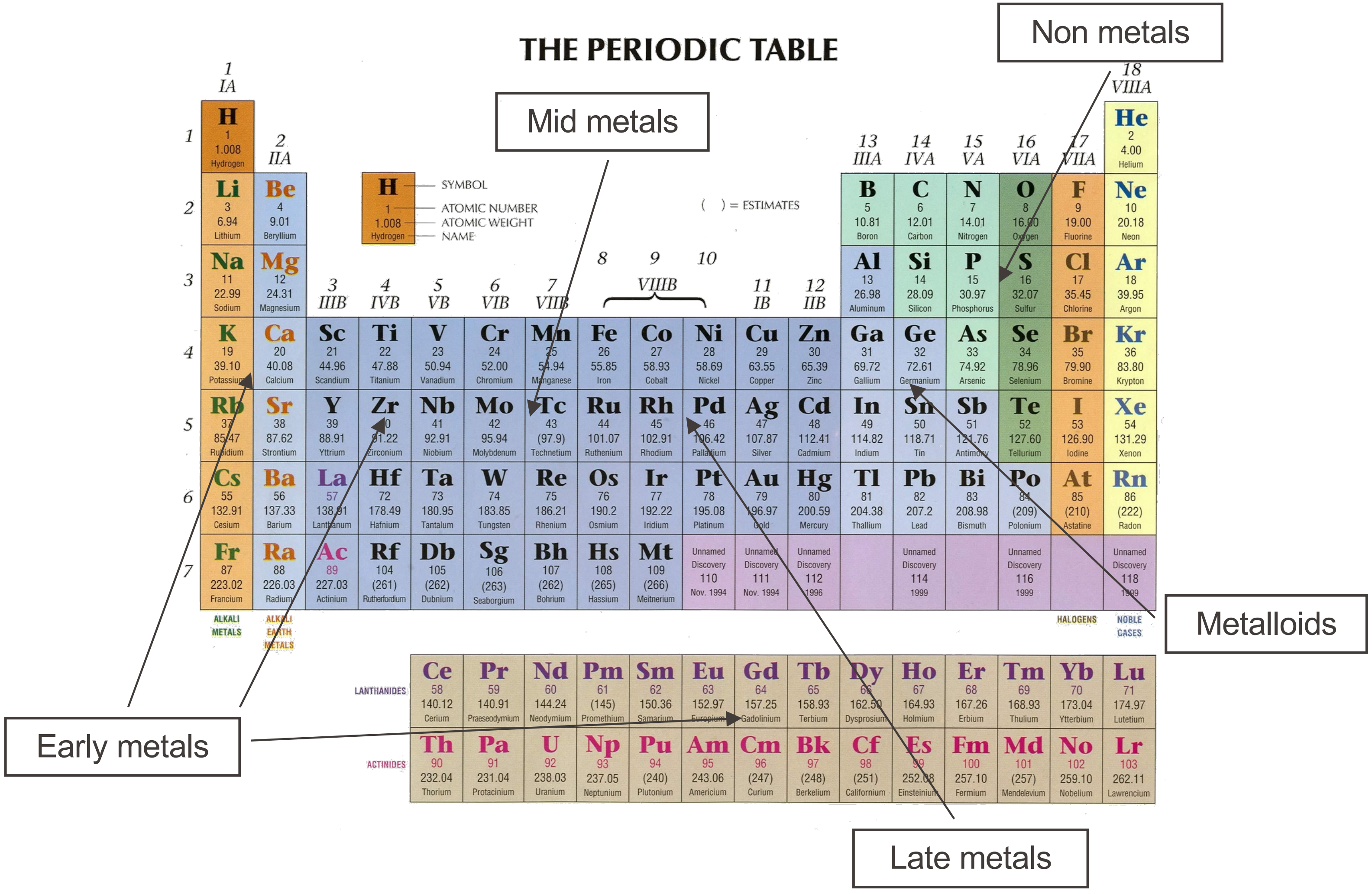
1. migratory insertion
2. ligand addition

reductive elimination

Note that there are different numbers of ligands on the metal. Too many is bad, too few is bad. How can you tell how many to use??

Electron counting is the key, which is presented later in this chapter.

Nomenclature:



Non metals

Mid metals

Metalloids

Early metals

Late metals

THE PERIODIC TABLE

H — SYMBOL
1 — ATOMIC NUMBER
1.008 — ATOMIC WEIGHT
Hydrogen — NAME

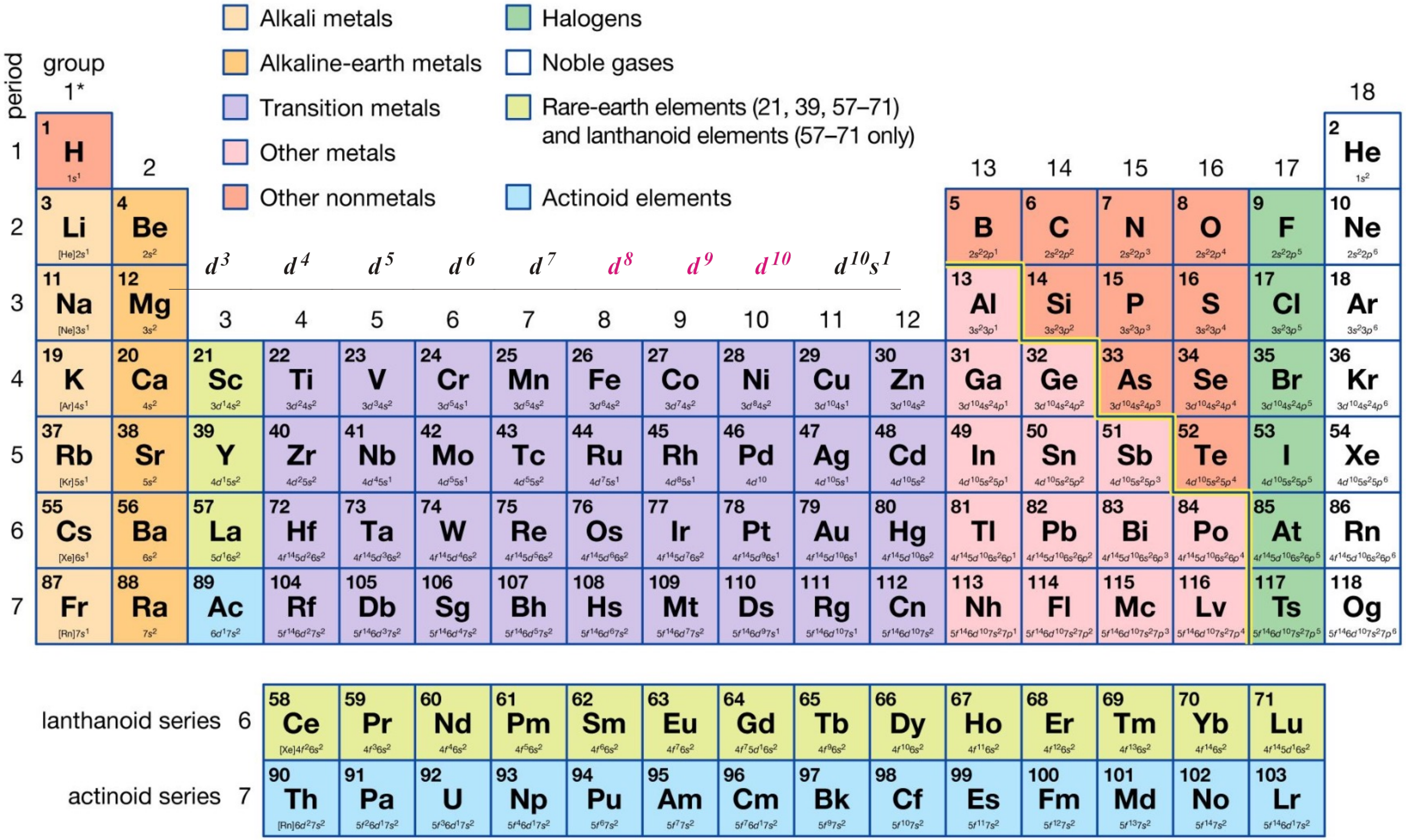
( ) = ESTIMATES

	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	H 1 1.008 Hydrogen																	He 2 4.00 Helium
2	Li 3 6.94 Lithium	Be 4 9.01 Beryllium											B 5 10.81 Boron	C 6 12.01 Carbon	N 7 14.01 Nitrogen	O 8 16.00 Oxygen	F 9 19.00 Fluorine	Ne 10 20.18 Neon
3	Na 11 22.99 Sodium	Mg 12 24.31 Magnesium											Al 13 26.98 Aluminum	Si 14 28.09 Silicon	P 15 30.97 Phosphorus	S 16 32.07 Sulfur	Cl 17 35.45 Chlorine	Ar 18 39.95 Argon
4	K 19 39.10 Potassium	Ca 20 40.08 Calcium	Sc 21 44.96 Scandium	Ti 22 47.88 Titanium	V 23 50.94 Vanadium	Cr 24 52.00 Chromium	Mn 25 54.94 Manganese	Fe 26 55.85 Iron	Co 27 58.93 Cobalt	Ni 28 58.69 Nickel	Cu 29 63.55 Copper	Zn 30 65.39 Zinc	Ga 31 69.72 Gallium	Ge 32 72.61 Germanium	As 33 74.92 Arsenic	Se 34 78.96 Selenium	Br 35 79.90 Bromine	Kr 36 83.80 Krypton
5	Rb 37 85.47 Rubidium	Sr 38 87.62 Strontium	Y 39 88.91 Yttrium	Zr 40 91.22 Zirconium	Nb 41 92.91 Niobium	Mo 42 95.94 Molybdenum	Tc 43 (97.9) Technetium	Ru 44 101.07 Ruthenium	Rh 45 102.91 Rhodium	Pd 46 106.42 Palladium	Ag 47 107.87 Silver	Cd 48 112.41 Cadmium	In 49 114.82 Indium	Sn 50 118.71 Tin	Sb 51 121.76 Antimony	Te 52 127.60 Tellurium	I 53 126.90 Iodine	Xe 54 131.29 Xenon
6	Cs 55 132.91 Cesium	Ba 56 137.33 Barium	La 57 138.91 Lanthanum	Hf 72 178.49 Hafnium	Ta 73 180.95 Tantalum	W 74 183.85 Tungsten	Re 75 186.21 Rhenium	Os 76 190.2 Osmium	Ir 77 192.22 Iridium	Pt 78 195.08 Platinum	Au 79 196.97 Gold	Hg 80 200.59 Mercury	Tl 81 204.38 Thallium	Pb 82 207.2 Lead	Bi 83 208.98 Bismuth	Po 84 (209) Polonium	At 85 (210) Astatine	Rn 86 (222) Radon
7	Fr 87 223.02 Francium	Ra 88 226.03 Radium	Ac 89 227.03 Actinium	Rf 104 (261) Rutherfordium	Db 105 (262) Dubnium	Sg 106 (263) Seaborgium	Bh 107 (262) Bohrium	Hs 108 (265) Hassium	Mt 109 (266) Meitnerium	Unnamed Discovery 110 Nov. 1994	Unnamed Discovery 111 Nov. 1994	Unnamed Discovery 112 1996		Unnamed Discovery 114 1999		Unnamed Discovery 116 1999		Unnamed Discovery 118 1999
	ALKALI METALS	ALKALI EARTH METALS															HALOGENS	NOBLE GASES

LANTHANIDES	Ce 58 140.12 Cerium	Pr 59 140.91 Praseodymium	Nd 60 144.24 Neodymium	Pm 61 (145) Promethium	Sm 62 150.36 Samarium	Eu 63 152.97 Europium	Gd 64 157.25 Gadolinium	Tb 65 158.93 Terbium	Dy 66 162.50 Dysprosium	Ho 67 164.93 Holmium	Er 68 167.26 Erbium	Tm 69 168.93 Thulium	Yb 70 173.04 Ytterbium	Lu 71 174.97 Lutetium
ACTINIDES	Th 90 232.04 Thorium	Pa 91 231.04 Protactinium	U 92 238.03 Uranium	Np 93 237.05 Neptunium	Pu 94 (240) Plutonium	Am 95 243.06 Americium	Cm 96 (247) Curium	Bk 97 (248) Berkelium	Cf 98 (251) Californium	Es 99 252.08 Einsteinium	Fm 100 257.10 Fermium	Md 101 (257) Mendelevium	No 102 259.10 Nobelium	Lr 103 262.11 Lawrencium

← Electropositive   Electronegative →

Periodic table with atomic number, symbol, and electron configuration



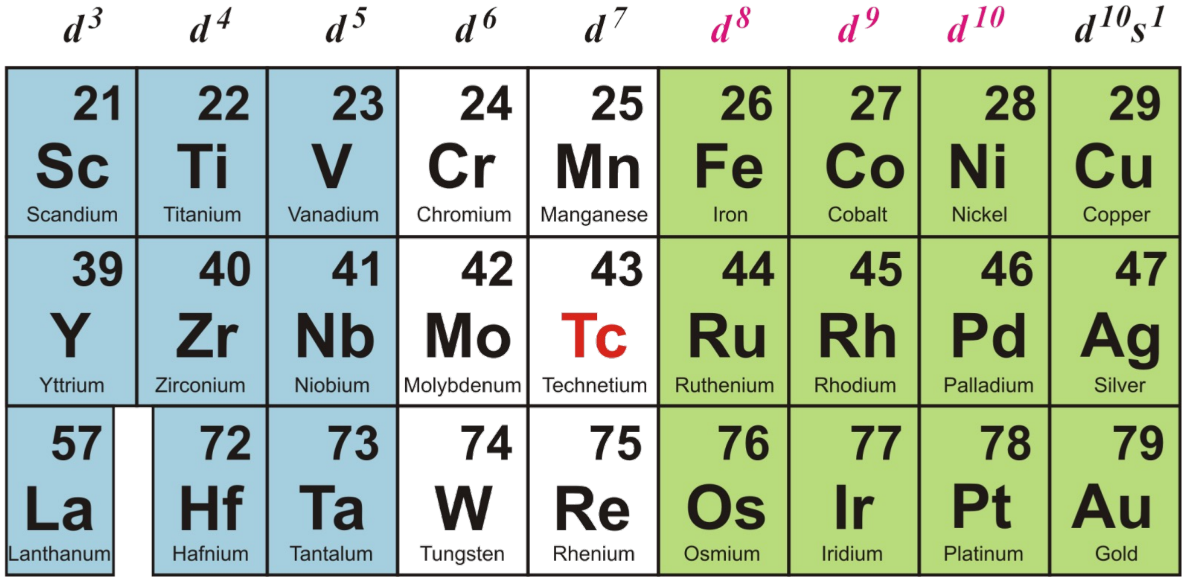
■ Alkali metals
■ Alkaline-earth metals
■ Transition metals
■ Other metals
■ Other nonmetals
■ Halogens
□ Noble gases
■ Rare-earth elements (21, 39, 57–71) and lanthanoid elements (57–71 only)
■ Actinoid elements

period \ group	1*	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
			d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}	$d^{10}s^1$							
1	1 **H** $1s^1$																	2 **He** $1s^2$
2	3 **Li** $[He]2s^1$	4 **Be** $2s^2$											5 **B** $2s^22p^1$	6 **C** $2s^22p^2$	7 **N** $2s^22p^3$	8 **O** $2s^22p^4$	9 **F** $2s^22p^5$	10 **Ne** $2s^22p^6$
3	11 **Na** $[Ne]3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^23p^1$	14 **Si** $3s^23p^2$	15 **P** $3s^23p^3$	16 **S** $3s^23p^4$	17 **Cl** $3s^23p^5$	18 **Ar** $3s^23p^6$
4	19 **K** $[Ar]4s^1$	20 **Ca** $4s^2$	21 **Sc** $3d^14s^2$	22 **Ti** $3d^24s^2$	23 **V** $3d^34s^2$	24 **Cr** $3d^54s^1$	25 **Mn** $3d^54s^2$	26 **Fe** $3d^64s^2$	27 **Co** $3d^74s^2$	28 **Ni** $3d^84s^2$	29 **Cu** $3d^{10}4s^1$	30 **Zn** $3d^{10}4s^2$	31 **Ga** $3d^{10}4s^24p^1$	32 **Ge** $3d^{10}4s^24p^2$	33 **As** $3d^{10}4s^24p^3$	34 **Se** $3d^{10}4s^24p^4$	35 **Br** $3d^{10}4s^24p^5$	36 **Kr** $3d^{10}4s^24p^6$
5	37 **Rb** $[Kr]5s^1$	38 **Sr** $5s^2$	39 **Y** $4d^15s^2$	40 **Zr** $4d^25s^2$	41 **Nb** $4d^45s^1$	42 **Mo** $4d^55s^1$	43 **Tc** $4d^55s^2$	44 **Ru** $4d^75s^1$	45 **Rh** $4d^85s^1$	46 **Pd** $4d^{10}$	47 **Ag** $4d^{10}5s^1$	48 **Cd** $4d^{10}5s^2$	49 **In** $4d^{10}5s^25p^1$	50 **Sn** $4d^{10}5s^25p^2$	51 **Sb** $4d^{10}5s^25p^3$	52 **Te** $4d^{10}5s^25p^4$	53 **I** $4d^{10}5s^25p^5$	54 **Xe** $4d^{10}5s^25p^6$
6	55 **Cs** $[Xe]6s^1$	56 **Ba** $6s^2$	57 **La** $5d^16s^2$	72 **Hf** $4f^{14}5d^26s^2$	73 **Ta** $4f^{14}5d^36s^2$	74 **W** $4f^{14}5d^46s^2$	75 **Re** $4f^{14}5d^56s^2$	76 **Os** $4f^{14}5d^66s^2$	77 **Ir** $4f^{14}5d^76s^2$	78 **Pt** $4f^{14}5d^96s^1$	79 **Au** $4f^{14}5d^{10}6s^1$	80 **Hg** $4f^{14}5d^{10}6s^2$	81 **Tl** $4f^{14}5d^{10}6s^26p^1$	82 **Pb** $4f^{14}5d^{10}6s^26p^2$	83 **Bi** $4f^{14}5d^{10}6s^26p^3$	84 **Po** $4f^{14}5d^{10}6s^26p^4$	85 **At** $4f^{14}5d^{10}6s^26p^5$	86 **Rn** $4f^{14}5d^{10}6s^26p^6$
7	87 **Fr** $[Rn]7s^1$	88 **Ra** $7s^2$	89 **Ac** $6d^17s^2$	104 **Rf** $5f^{14}6d^27s^2$	105 **Db** $5f^{14}6d^37s^2$	106 **Sg** $5f^{14}6d^47s^2$	107 **Bh** $5f^{14}6d^57s^2$	108 **Hs** $5f^{14}6d^67s^2$	109 **Mt** $5f^{14}6d^77s^2$	110 **Ds** $5f^{14}6d^97s^1$	111 **Rg** $5f^{14}6d^{10}7s^1$	112 **Cn** $5f^{14}6d^{10}7s^2$	113 **Nh** $5f^{14}6d^{10}7s^27p^1$	114 **Fl** $5f^{14}6d^{10}7s^27p^2$	115 **Mc** $5f^{14}6d^{10}7s^27p^3$	116 **Lv** $5f^{14}6d^{10}7s^27p^4$	117 **Ts** $5f^{14}6d^{10}7s^27p^5$	118 **Og** $5f^{14}6d^{10}7s^27p^6$

lanthanoid series 6	58 **Ce** $[Xe]4f^26s^2$	59 **Pr** $4f^36s^2$	60 **Nd** $4f^46s^2$	61 **Pm** $4f^56s^2$	62 **Sm** $4f^66s^2$	63 **Eu** $4f^76s^2$	64 **Gd** $4f^75d^16s^2$	65 **Tb** $4f^96s^2$	66 **Dy** $4f^{10}6s^2$	67 **Ho** $4f^{11}6s^2$	68 **Er** $4f^{12}6s^2$	69 **Tm** $4f^{13}6s^2$	70 **Yb** $4f^{14}6s^2$	71 **Lu** $4f^{14}5d^16s^2$
actinoid series 7	90 **Th** $[Rn]6d^27s^2$	91 **Pa** $5f^26d^17s^2$	92 **U** $5f^36d^17s^2$	93 **Np** $5f^46d^17s^2$	94 **Pu** $5f^67s^2$	95 **Am** $5f^77s^2$	96 **Cm** $5f^76d^17s^2$	97 **Bk** $5f^97s^2$	98 **Cf** $5f^{10}7s^2$	99 **Es** $5f^{11}7s^2$	100 **Fm** $5f^{12}7s^2$	101 **Md** $5f^{13}7s^2$	102 **No** $5f^{14}7s^2$	103 **Lr** $5f^{14}6d^17s^2$

- Please print this table and use it for the exercices

General Trends for the Transition Metals



d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}	$d^{10}s^1$
21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper
39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver
57 La Lanthanum	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold

Early Transition Metals

low electronegativities

higher oxidation states

“harder” metal centers

Late Transition Metals

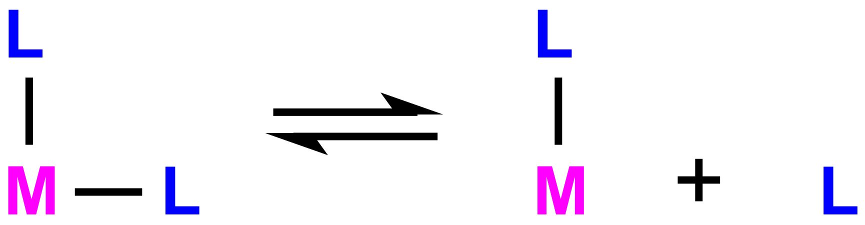
higher electronegativities

lower oxidation states

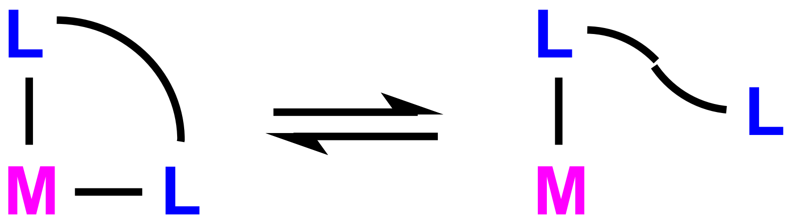
“softer” metal centers

Some Important Ligand Nomenclature

Chelate Effect (See Queen Course): “chelate” is from the Greek meaning “claw” or to grab on to. Since most metal-ligand bonds are relatively weak compared to C-C bonds, M-L bonds can often be broken rather easily, leading to dissociation of the ligand from the metal. Higher stability conferred by polydentate ligands.



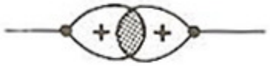
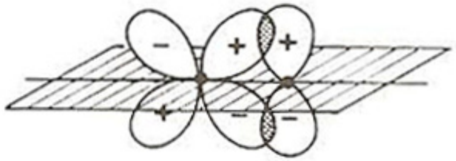
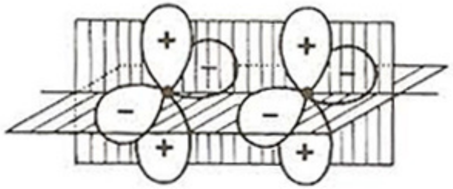
From a ***kinetic viewpoint***, if one of the ligands dissociates, it will remain close enough to the metal center to have a high probability of re-coordinating before another ligand can get in and bind.

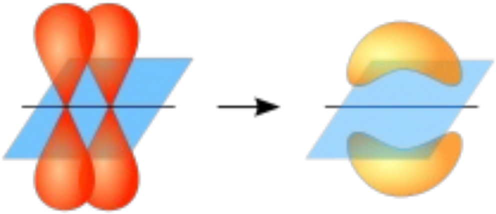


From a *thermodynamic viewpoint*, by tethering two donor ligands together, one removes most of the entropic driving force for dissociating a ligand and thus making more particles in solution (more disorder).

Some Important Ligand Nomenclature

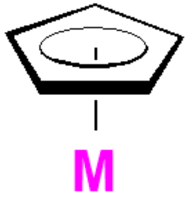
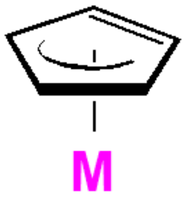
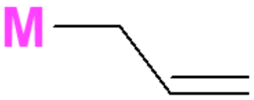
The designations σ, π, and δ bond are defined as follows:

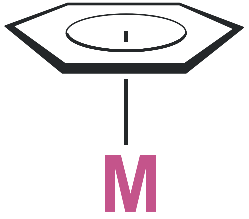
Overlap	Number of nodal planes including the bond axis	Bond type	Example
	0	σ	$>B-CH_3$
	1	π	$(CO)_5Cr=CR_2$
	2	δ	$[R_4Re≣ReR_4]^{2-}$



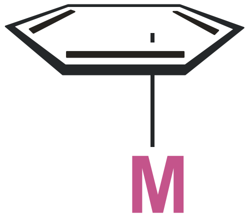
η^x "eta-*x*" was originally developed to indicate how many *contiguous* donor atoms of a π-system were coordinated to a metal center. **Hapticity** is another word used to describe the bonding mode of a ligand to a metal center. An η^5-cyclopentadienyl ligand, for example, has all five carbons of the ring bonding to the transition metal center.

η^x values for all-carbon based ligands where the x value is odd usually indicate *anionic* carbon ligands (e.g., η^5-Cp, η^1-CH_3, η^1-allyl or η^3-allyl, η^1-$CH{=}CH_2$). The # of electrons donated (ionic method of electron counting) by the ligand is usually equal to $x + 1$. Even η^x values usually indicate *neutral* carbon π-system ligands (e.g., η^6-C_6H_6, η^2-$CH_2{=}CH_2$, η^4-butadiene, η^4-cyclooctadiene). The # of electrons donated by the ligand in the even (*neutral*) case is usually just equal to x.

			
η^5-Cp	η^3-Cp	η^3-allyl	η^1-allyl



η^6-C_6H_6



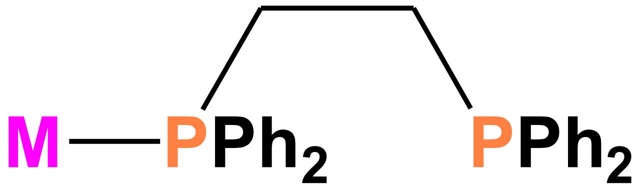
η^4-C_6H_6

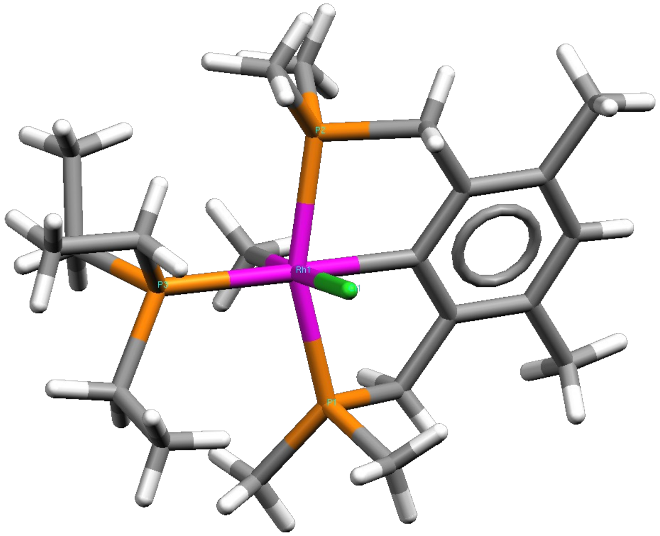
κ^x

“kappa-*x*” was developed to indicate how many *non*-*contiguous* donor atoms of a ligand system were coordinated to a metal center.

This usually refers to non-carbon donor atoms, but can include carbons.

A κ^1-dppe ($Ph_2PCH_2CH_2PPh_2$) ligand, for example, has only one of the two phosphorus donors bonded to the transition metal center.



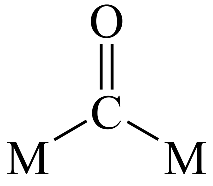


The bis-chelating (tridentate) ligand shown to the left almost always coordinates in a κ^3-fashion. Because this is the normal coordination mode, most authors would not use the κ^3-designation.

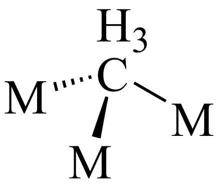
μ_x “mu-*x*” is the nomenclature used to indicate the presence of a **bridging ligand** between two or more metal centers. The *x* refers to the number of metal centers being bridged by the ligand. Usually most authors omit $x = 2$ and just use μ to indicate that the ligand is bridging the simplest case of two metals.

There are 3 different general classes of bridging ligands:

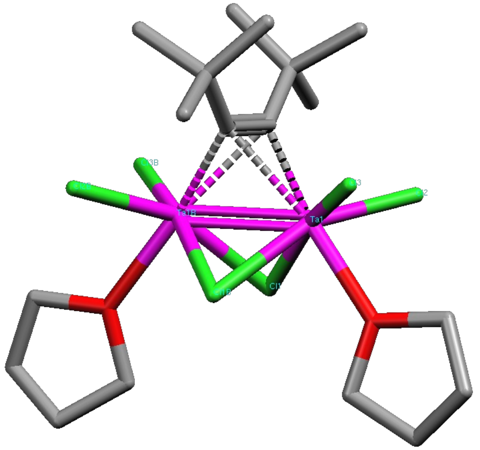
1) Single atom bridges
2) Two donor atoms separated by a bridging group (typically organic)
3) Two donor atoms bonded to one another (alkynes, O_2^{x-}, S_2^{x-}, allyl$^-$, etc)



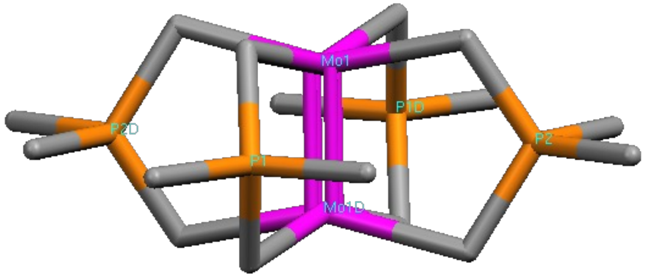
μ



μ_3



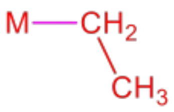
Ta$_2$(μ-*t*-Bu-C≡C-*t*-Bu)(μ-Cl)$_2$Cl$_4$(THF)$_2$



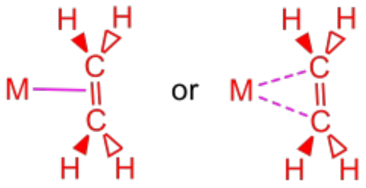
Mo$_2$[μ-CH$_2$P(Me)$_2$CH$_2$]$_4$

Problem: Use eta and mu in the following examples

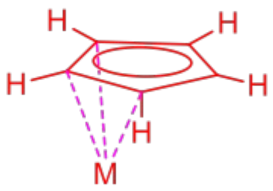
1



2

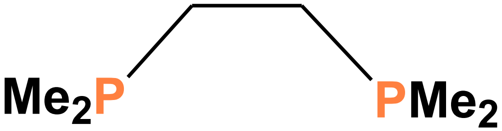


3

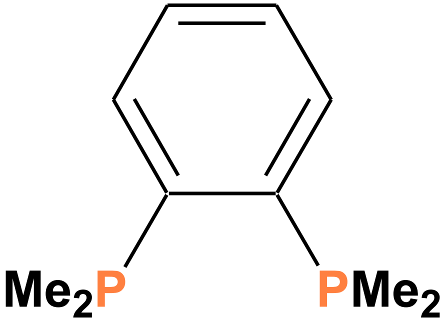


Problem: Which of the following ligands will chelate the ***strongest*** to a generic metal center? Why?

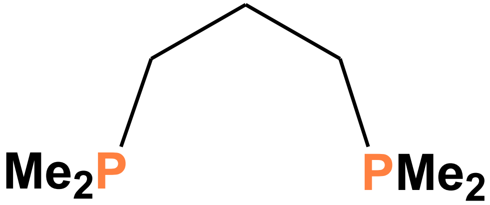
A)



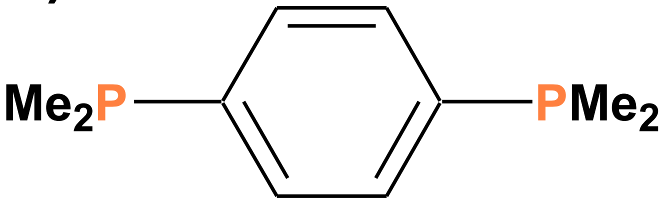
B)



C)

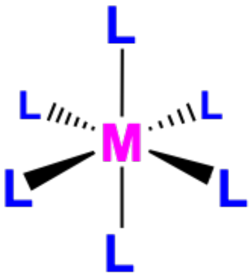


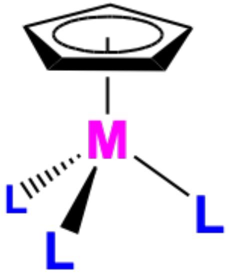
D)



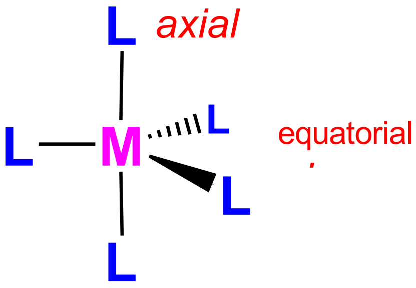
Common Coordination Geometries

6-Coordinate: ***Octahedral*** **(90° & 180° angles)**

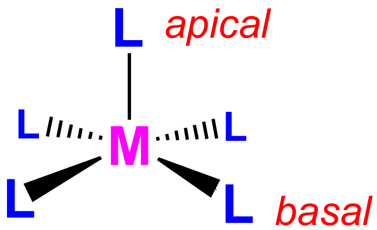




5-Coordinate: ***Trigonal Bypyramidal or Square Pyramidial***

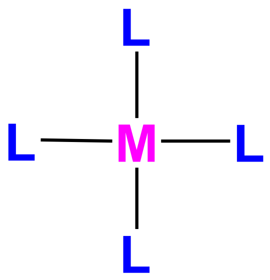


(90° & 120°)

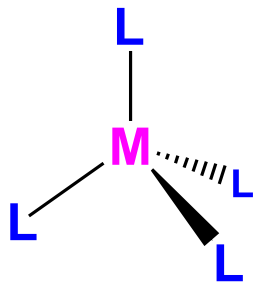


(~100° & 90°)

4-Coordinate: *Square Planar or Tetrahedral*



(90° & 180°)



(109°)

Square planar geometry is generally limited to **Rh, Ir, Ni, Pd, Pt,** and **Au** in the d^8 electronic state when coordinated to 2e- donor ligands.

Problem: **Sketch structures for the following:**

a) $[(\eta^5\text{-Cp})\text{RuCl}(=\text{CHCO}_2\text{Et})(\text{PPh}_3)]$

b) $[\text{Co}_2(\mu\text{-CO})_2(\text{CO})_6]$ (Co-Co bond; several possible)

c) *[trans*-$\text{HRh}(\text{CO})(\text{PPh}_3)_2]$ $[\text{Rh}(+1) = d^8]$

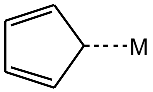
d) $[\text{Ir}_2(\mu\text{-Cl})_2(\text{CO})_4]$ $[\text{Ir}(+1) = d^8]$

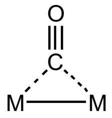
e) $[(\eta^5\text{-Cp})_2\text{TiCl}_2]$

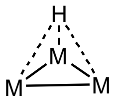
Exercises

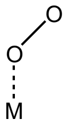
Describe the following

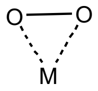
using η and/or μ

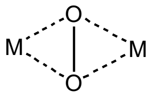


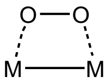


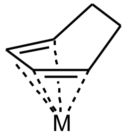


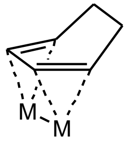


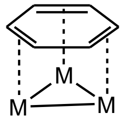












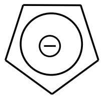
Overview of Types of Organometallic Complexes*:*

4 Main Types:

1) Ionic (charge separated)

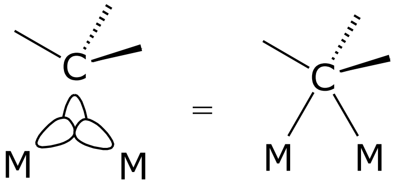
Only with the most electropositive, early elements. Highly reactive and unstable. More stable if R can be stabilised by delocalisation or steric bulk.

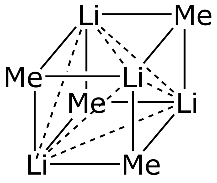
e.g. $Na^+C_5H_5^-$ charge is delocalised in aromatic ring

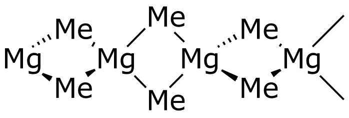


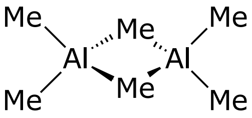
2) Electron deficient

Insufficient electrons to fill valence orbitals and form 2-centre-2electron bonds between all atoms. This results in multi-centre bonding between R and two or more metal centres.









e.g. 3-centre-2-electron bond.

Overview of Types of Organometallic Complexes:

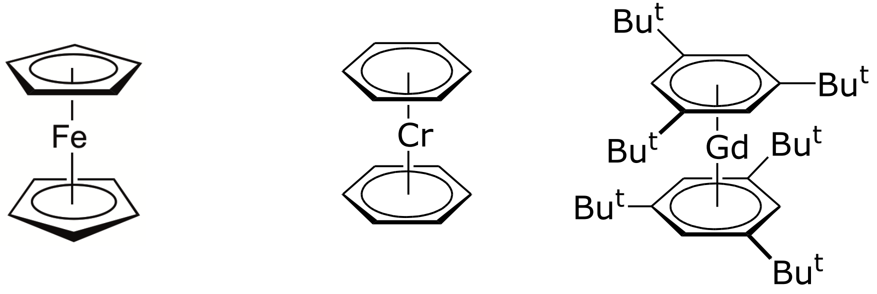
3) σ-Bonding only

Occurs with closed-shell transition metal and main group centres, often leading to volatile compounds.

e.g. ZnR_2, $PbEt_4$, $InMe_3$, SnR_4.

4) π-Bonding

This is the interaction of π and π^* orbitals of organic ligands with metal-based orbitals. This is especially prevalent with transition metals and zero-valent lanthanides.



Gd-C = 2.63 Å

e.g. Ferrocene, *bis*-benzene chromium, *bis*-(1,3,5-$Bu^t_3C_6H_3$)-gadolinium

Formal Oxidation State (O.S.) of a Metal:

O.S. = charge on complex – [sum of formal ligand charges]

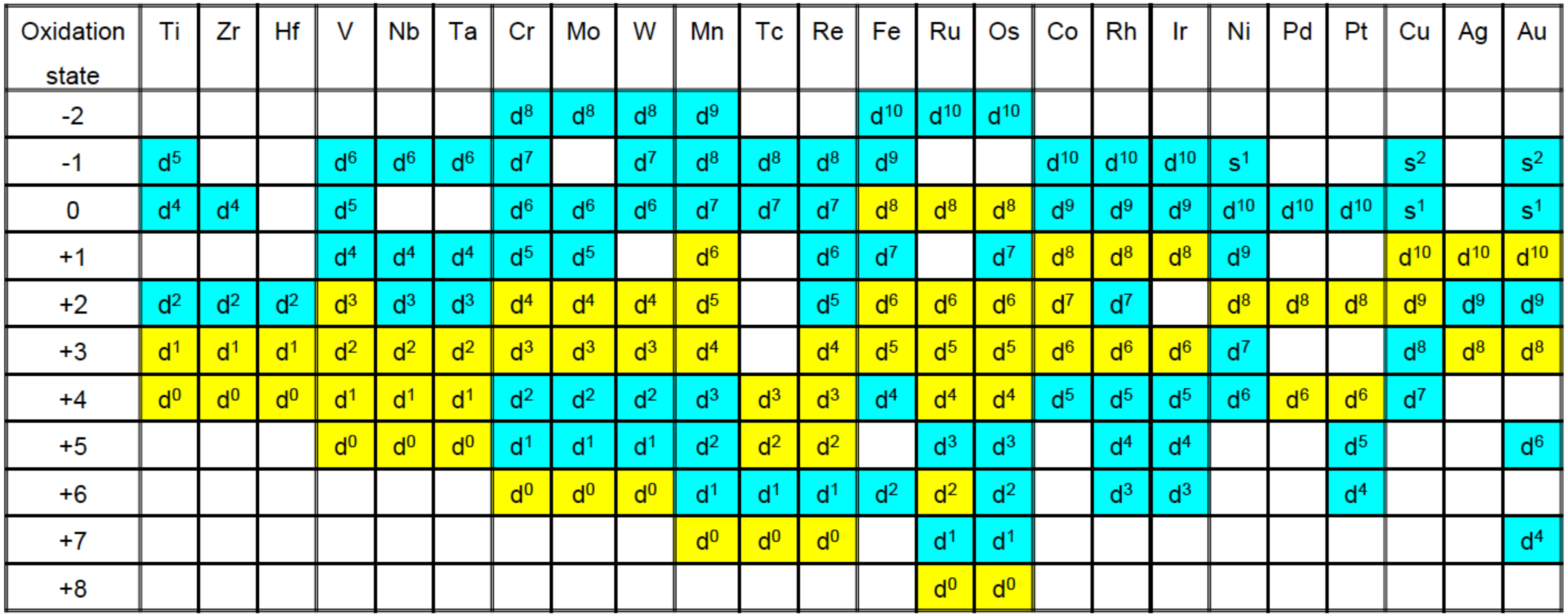
N.B. these are the charges formally assigned to the ligands on removal from the metal centre.

Examples:

$[TiCl_4]$	O.S. = 0 – [4 × –1] = +4
$[Mo(CO)_6]$	O.S. = 0 – [6 × 0] = 0
$[Mn(NH_3)_2(CH_3)_2]$	O.S. = 0 – [(2 × 0) + (2 × –1)] = +2
$[NH_4]_2[CrCl_4]$	O.S. = –2 – [4 × –1] = +2
$[TiCl_2(PPh_3)_4]$	O.S. = 0 – [(2 × –1) + (4 × 0)] = +2

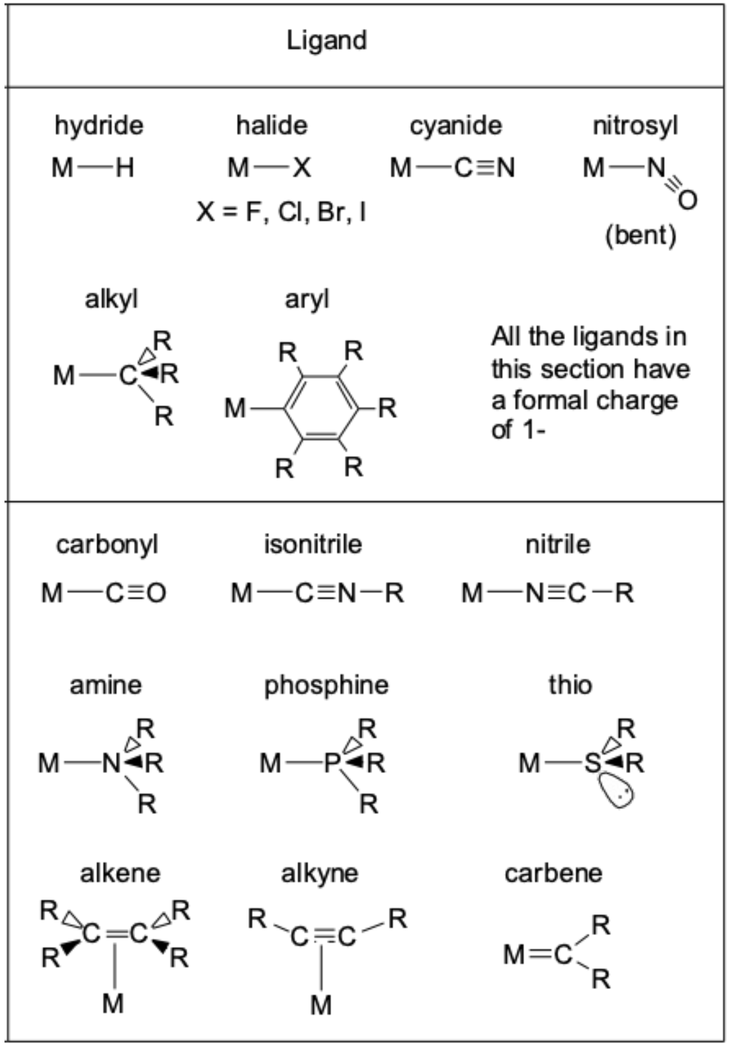
To assign charges and electron counts it is important to know how organics bind to the metal. For organic ligands, the electrons in a shared bonding electron pair are assigned to the more electronegative atom.

Oxidation States of transition metals

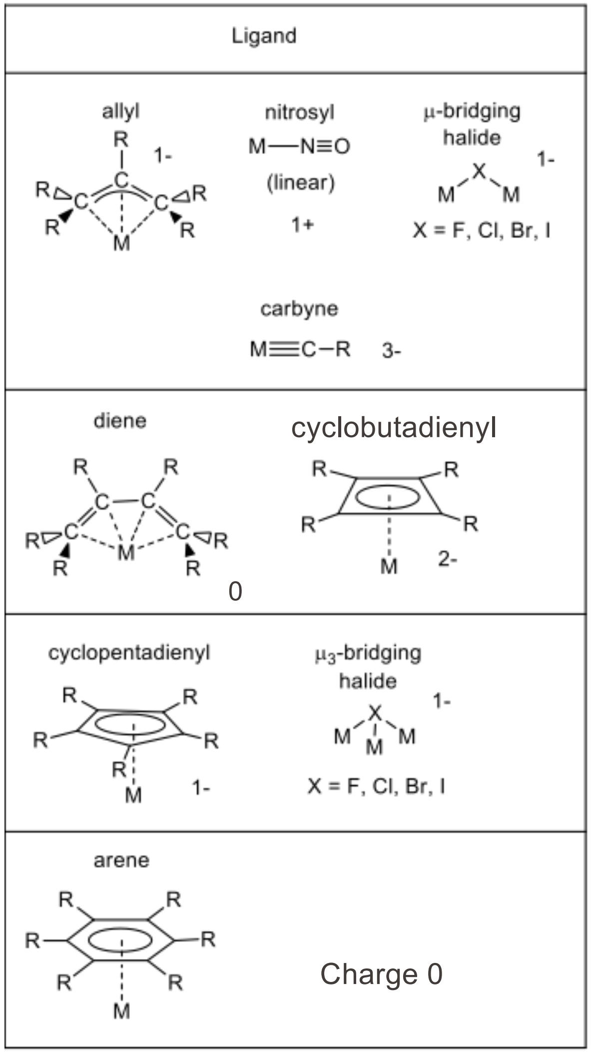
The accessible oxidation states of the transition elements. Blue are less commonly observed oxidation states and yellow are those which dominate.

Oxidation state	Ti	Zr	Hf	V	Nb	Ta	Cr	Mo	W	Mn	Tc	Re	Fe	Ru	Os	Co	Rh	Ir	Ni	Pd	Pt	Cu	Ag	Au
-2							d^8	d^8	d^8	d^9			d^{10}	d^{10}	d^{10}									
-1	d^5			d^6	d^6	d^6	d^7		d^7	d^8	d^8	d^8	d^9			d^{10}	d^{10}	d^{10}	s^1			s^2		s^2
0	d^4	d^4		d^5			d^6	d^6	d^6	d^7	d^7	d^7	d^8	d^8	d^8	d^9	d^9	d^9	d^{10}	d^{10}	d^{10}	s^1		s^1
+1				d^4	d^4	d^4	d^5	d^5		d^6		d^6	d^7		d^7	d^8	d^8	d^8	d^9			d^{10}	d^{10}	d^{10}
+2	d^2	d^2	d^2	d^3	d^3	d^3	d^4	d^4	d^4	d^5		d^5	d^6	d^6	d^6	d^7	d^7		d^8	d^8	d^8	d^9	d^9	d^9
+3	d^1	d^1	d^1	d^2	d^2	d^2	d^3	d^3	d^3	d^4		d^4	d^5	d^5	d^5	d^6	d^6	d^6	d^7			d^8	d^8	d^8
+4	d^0	d^0	d^0	d^1	d^1	d^1	d^2	d^2	d^2	d^3	d^3	d^3	d^4	d^4	d^4	d^5	d^5	d^5	d^6	d^6	d^6	d^7		
+5				d^0	d^0	d^0	d^1	d^1	d^1	d^2	d^2	d^2		d^3	d^3		d^4	d^4			d^5			d^6
+6							d^0	d^0	d^0	d^1	d^1	d^1	d^2	d^2	d^2		d^3	d^3			d^4			
+7										d^0	d^0	d^0		d^1	d^1									d^4
+8														d^0	d^0									

Common Ligands

Ligands with Charge 0



All the ligands in this section have a formal charge of 1-



Charge 0

d^n Electron Count in Transition Metal Compounds:

d^n gives you the number of electrons formally associated with metal-centred (i.e. d) orbitals in a transition metal compound:

d^n = metal group number – O.S.

Examples:

$[TiCl_4]$	$d^n = 4 - 4 = 0$
$[Mo(CO)_6]$	$d^n = 6 - 0 = 6$
$[Mn(NH_3)_2(CH_3)_2]$	$d^n = 7 - 2 = 5$
$[NH_4]_2[CrCl_4]$	$d^n = 6 - 2 = 4$
$[TiCl_2(PPh_3)_4]$	$d^n = 4 - 2 = 2$

Do not confuse ion configurations in *complexes* with *atomic* configurations.

d^n Electron Count in Transition Metal Compounds:

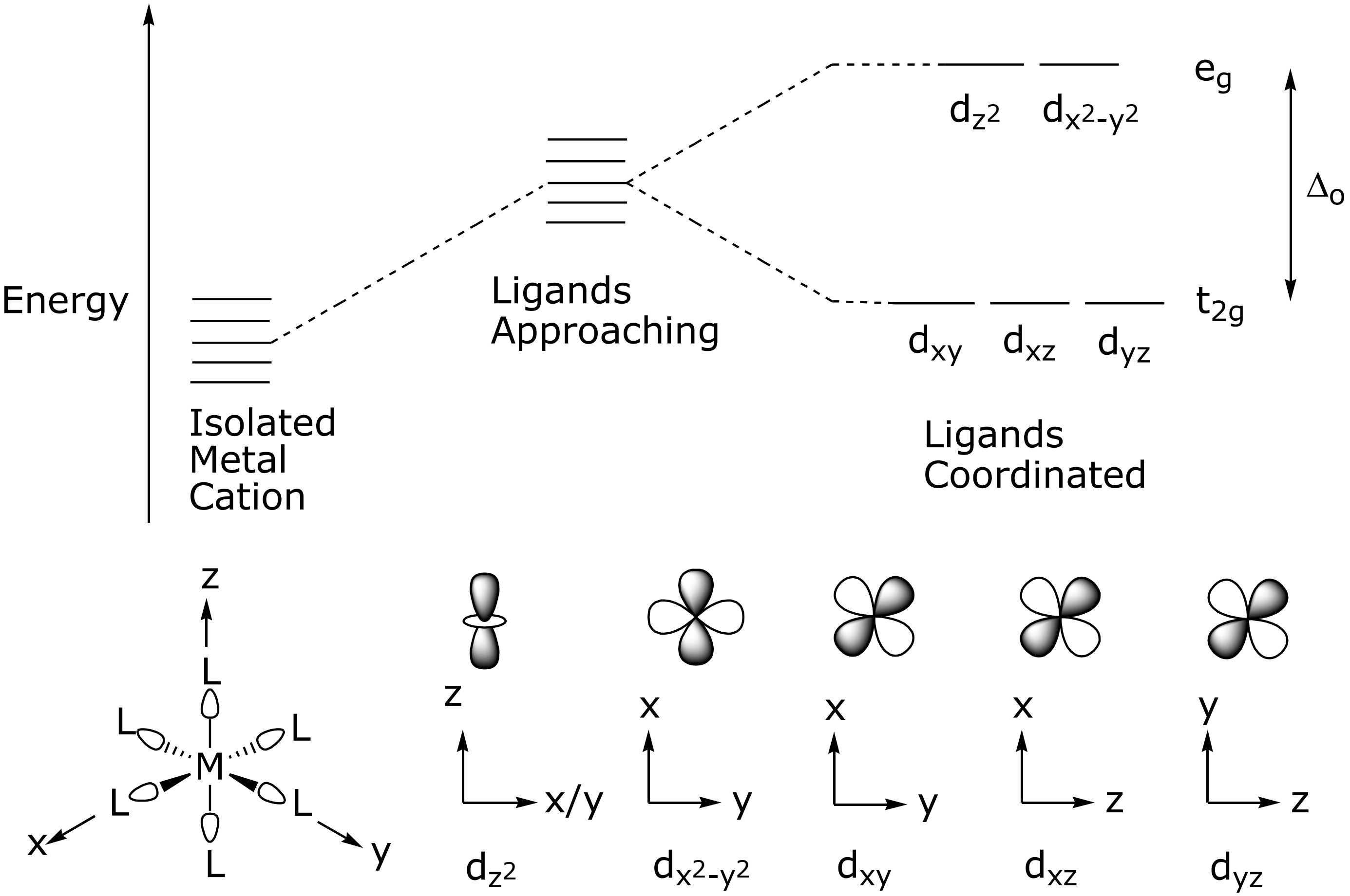
d^n gives you the number of electrons formally associated with metal-centred (i.e. d) orbitals in a transition metal compound:

$$\mathbf{d^n = metal\ group\ number - O.S.}$$

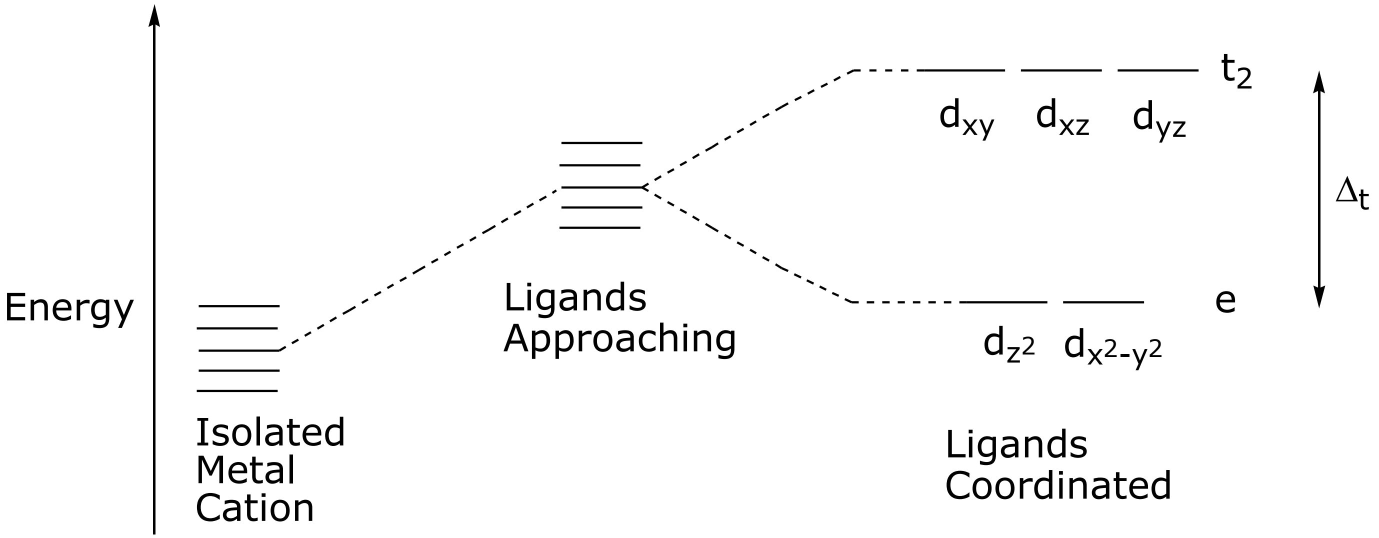
Do not confuse ion configurations in *complexes* with *atomic* configurations.

d^3							d^{10}		
21 Sc $3d^1 4s^2$	22 Ti $3d^2 4s^2$	23 V $3d^3 4s^2$	24 Cr $3d^5 4s^1$	25 Mn $3d^5 4s^2$	26 Fe $3d^6 4s^2$	27 Co $3d^7 4s^2$	28 Ni $3d^8 4s^2$	29 Cu $3d^{10} 4s^1$	30 Zn $3d^{10} 4s^2$
39 Y $4d^1 5s^2$	40 Zr $4d^2 5s^2$	41 Nb $4d^3 5s^2$	42 Mo $4d^5 5s^1$	43 Tc $4d^5 5s^2$	44 Ru $4d^7 5s^1$	45 Rh $4d^8 5s^1$	46 Pd $4d^{10} 5s^0$	47 Ag $4d^{10} 5s^1$	48 Cd $4d^{10} 5s^2$
57 La $5d^1 6s^2$	72 Hf $5d^2 6s^2$	73 Ta $5d^3 6s^2$	74 W $5d^4 6s^2$	75 Re $5d^5 6s^2$	76 Os $5d^6 6s^2$	77 Ir $5d^7 6s^2$	78 Pt $5d^9 6s^1$	79 Au $5d^{10} 6s^1$	80 Hg $5d^{10} 6s^2$
89 Ac $6d^1 7s^2$	104 Rf $6d^2 7s^2$	105 Db $6d^3 7s^2$	106 Sg $6d^4 7s^2$	107 Bh $6d^5 7s^2$	108 Hs $6d^6 7s^2$	109 Mt $6d^7 7s^2$	110 Ds $6d^9 7s^1$	111 Rg $6d^{10} 7s^1$	112 Cn $6d^{10} 7s^2$

Crystal Field Theory of Coordination Complexes – Octahedral (see Prof Queen course)



Crystal Field Theory of Coordination Complexes – Tetrahedral

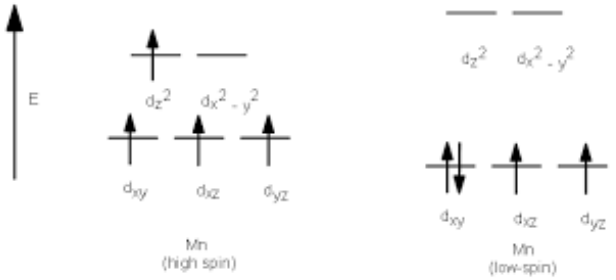


- $\Delta_t \approx {}^4/_9 \, \Delta_o$

Crystal Field Theory of Coordination Complexes (see Prof. Queen Course)

Factors that affect Δ:

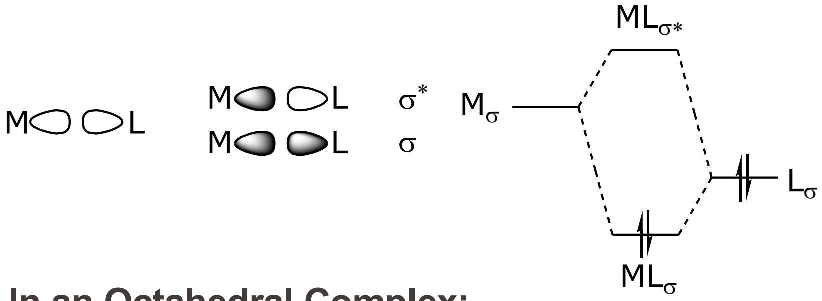
- Metal oxidation state - higher O.S. bigger Δ.
- Nature of M^+ - 5d > 4d > 3d.
- Number and geometry of ligands.
- Nature of ligands – strong vs weak field ligands.
- $I^- < Br^- <$ SCN- $< Cl^- < NO_3^- < N_3^- < F^- < OH^- < H_2O < SCN^- <$ py $< NH_3 <$ en $<$ bipy $<$ phen $< NO_2^- < PPh_3 < CN^- < CO$
- Larger Δo leads to low spin complex



But: Crystal field theory is an *ionic* model, but for *covalent* compounds we need molecular orbital theory.

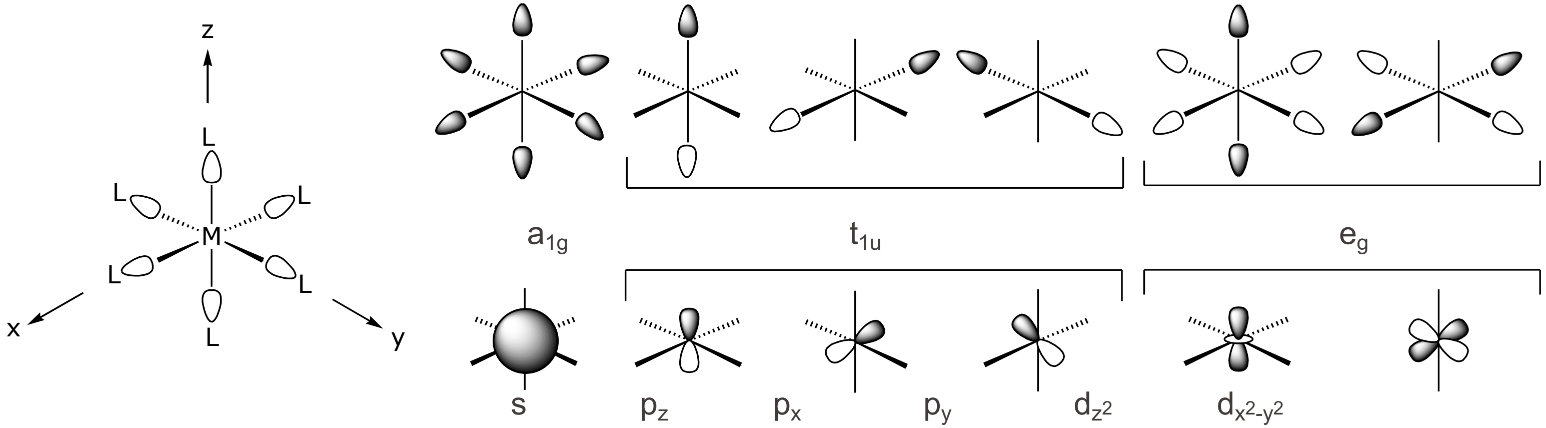
Molecular Orbital Theory for Coordination Complexes – Octahedral (course Queen)

For Single M–L σ-Bond:

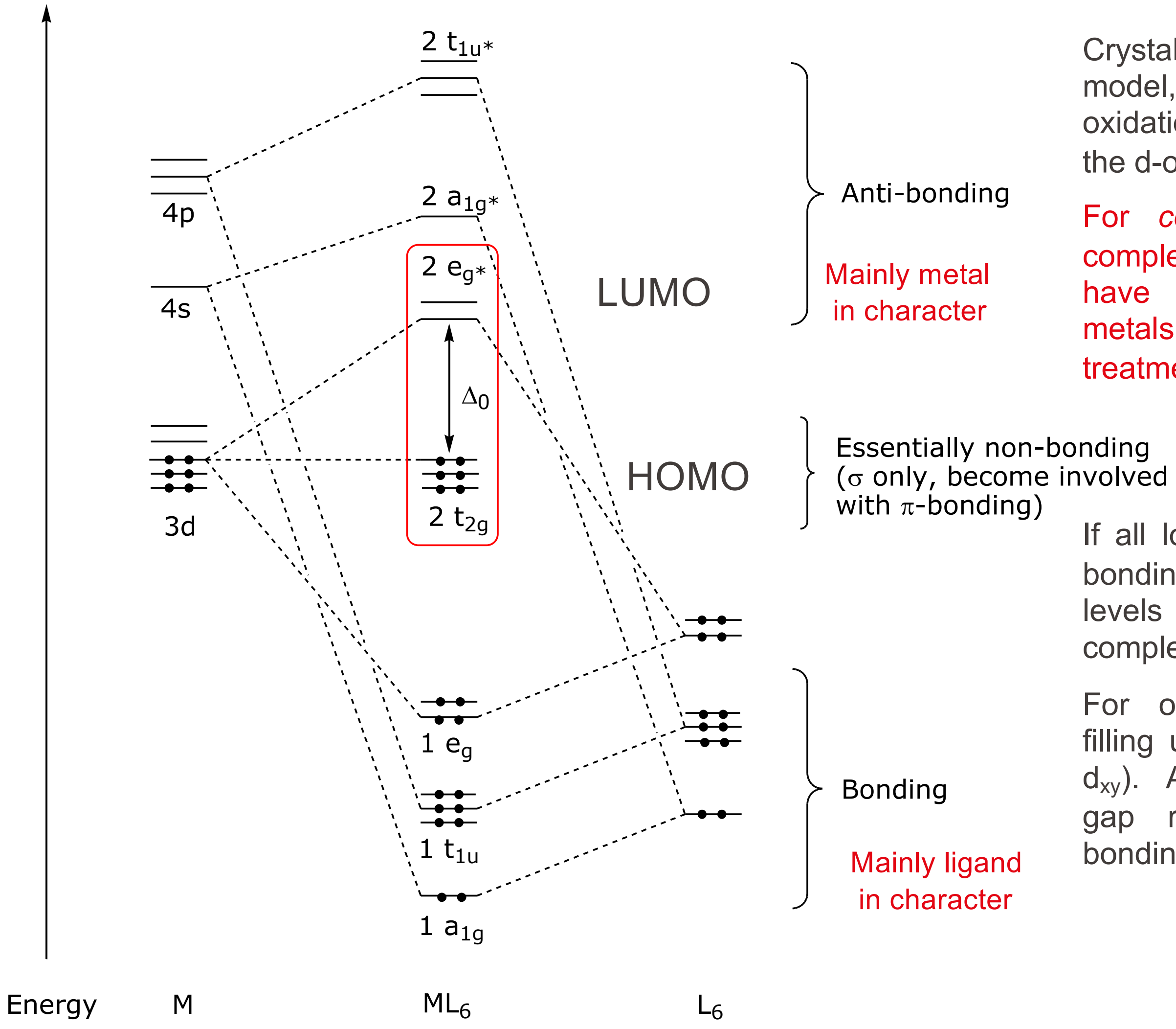


In an Octahedral Complex:

Six L_σ orbitals treated as a group and need to match various combinations to symmetry of metal orbitals to get overlap leading to σ-bonds (LCAO approach).



Molecular Orbital Theory for Coordination Complexes – Octahedral (see course Queen)



Crystal Field theory is an *ionic* model, suitable for high oxidation state metals where the d-orbitals are contracted.

For *covalent* organometallic complexes, which usually have low oxidation state metals, a Molecular Orbital treatment is better.

If all low energy metal-ligand bonding and non-bonding levels are filled then a stable complex will result.

For octahedral this means filling up to t_{2g} level (d_{xz}, d_{yz}, d_{xy}). A large HOMO-LUMO gap results and no anti-bonding orbitals are filled.

The Eighteen- (and Sixteen-) Electron Rule:

Stable organometallic complexes are formed when the sum of the (neutral) metal valence electrons plus the sum of the electrons considered to be donated by the ligands (taking into account any net charge) equals 18.

For square planar complexes an analogous sixteen-electron rule is used.

Note that it is complexes with $d^n > 2$ and strong π-acceptor ligands that most faithfully obey this rule.

Why Eighteen? (or sixteen electrons for d8 metals with fours ligands)

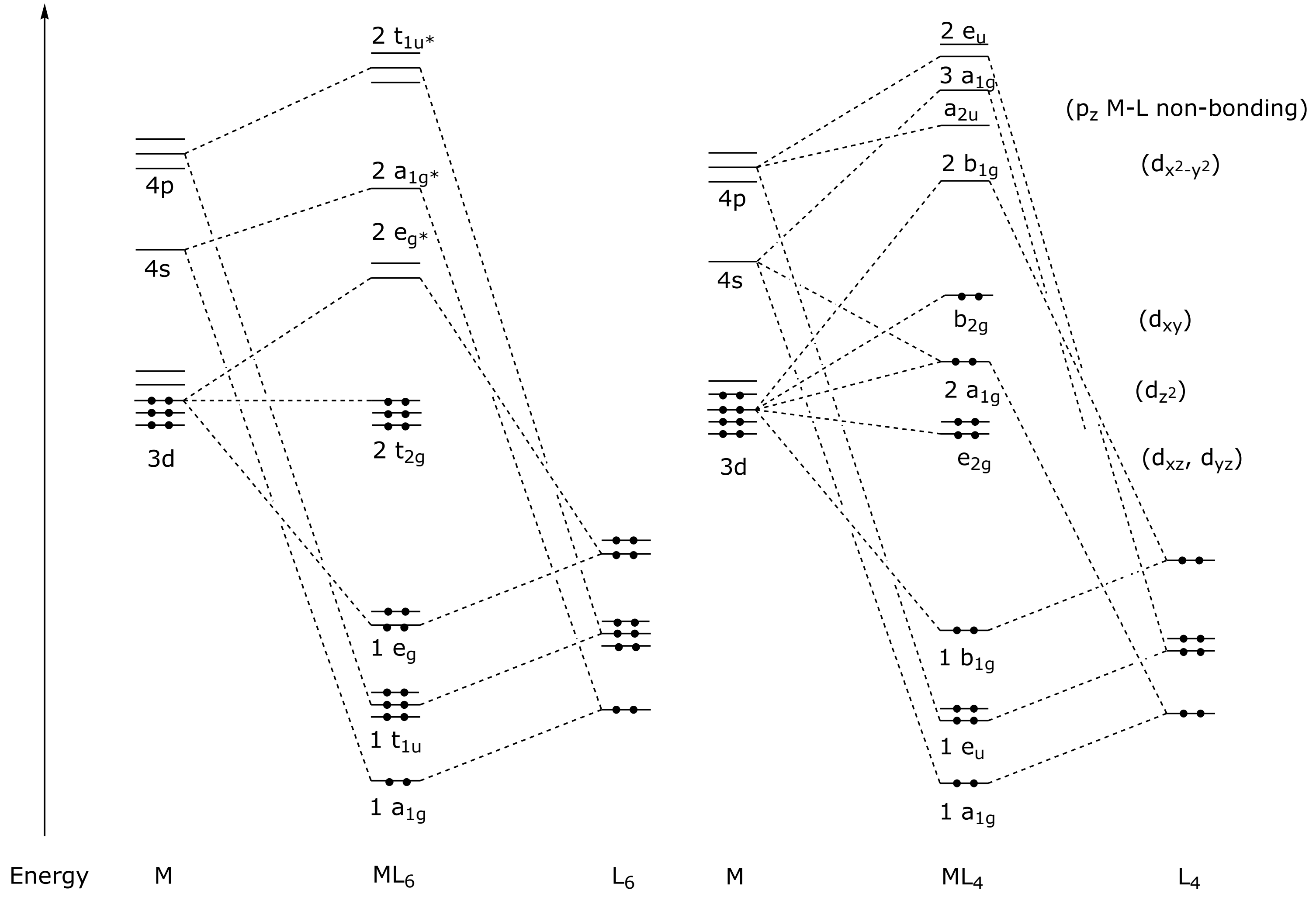
- *Octet rule:* 1s + 3p = 8 electrons (closed shell)

- *18-electron rule:* 1s +3p +5d = 18 electrons (closed shell)

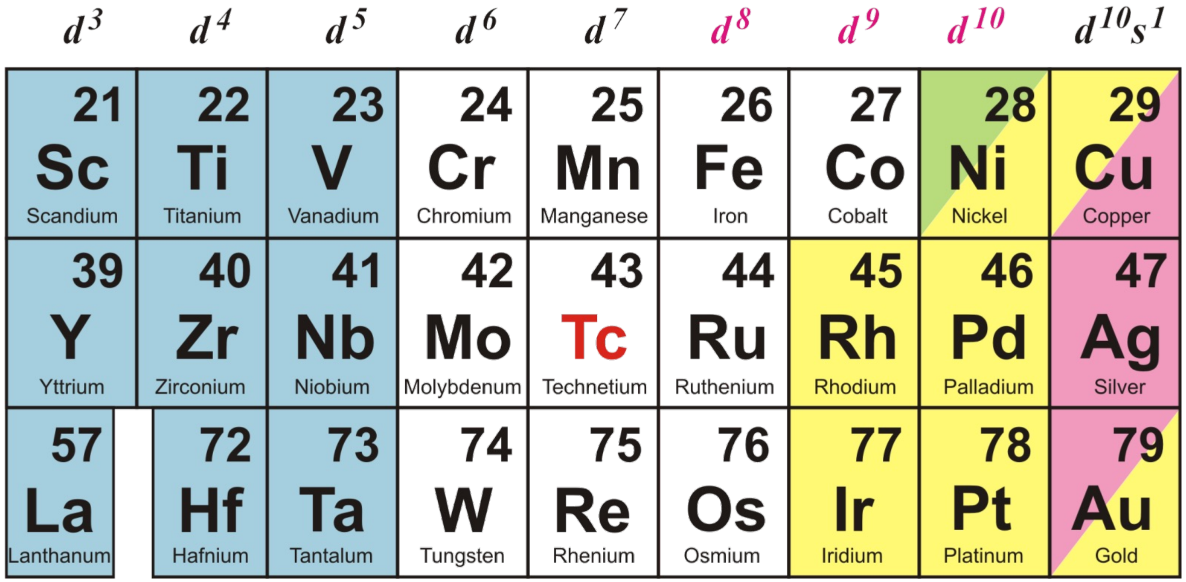
- **For 16 and 18 electron complexes the bonding and non-bonding orbitals are *full* and the anti-bonding orbitals are *empty*.**

There are examples where the 18 electron rule is violated. However, it serves as a useful rule-of-thumb in predicting stability and reactivity.

The Eighteen- (and Sixteen-) Electron Rule:



Lots of General Exceptions to the 18-Electron “Rule”



d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}	$d^{10}s^1$
21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper
39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver
57 La Lanthanum	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold

Early Transition Metals

16e- and sub-16e- configurations are common

Coordination geometries higher than 6 relatively common

Middle Transition Metals

18e- configurations are common

Coordination geometries of 6 are common

Late Transition Metals

16e- and sub-16e- configurations are common

Coordination geometries of 5 and lower are common: d^8 = square planar

Coordinative Unsaturation:

This is a very important concept in organometallic chemistry.

Compounds which have less than an 18-electron count are said to be "coordinatively unsaturated" and there may be a tendency to add further ligands.

- This is because there must be one or more vacant orbital(s) available.

e.g. $[Ni(CN)_4]^{2-} + CN^- \rightarrow [Ni(CN)_5]^{3-}$

16-electron 18-electron

Conversely, complexes with an 18-electron count are said to be "*coordinatively saturated*" and will most likely lose a ligand in order for any reactivity to occur.

Pauling Electroneutrality Principle:

Neutral molecules, or those with a ±1 or ±2 charge are more likely to form than highly charged species.

- The greater the charge or polarisation the greater the tendency to react.

Stability and Preventing Decomposition:

Stability:

- In this context, stability refers to a lack of decomposition of the pure compound in the absence of a reaction partner, e.g. H_2O, O_2.
- We must distinguish between thermodynamic stability (stable or unstable) and kinetic stability (inert or labile).
- Compared with M–N, M–O, and M-halide bonds, M–C must be considered *weak*.

Main Group Alkyl	B.E./kJmol^{-1}	T.M. Alkyl	B.E./kJmol^{-1}
CMe_4	358	$Ti(CH_2Bu^t)_4$	198
$SiMe_4$	311	$Zr(CH_2Bu^t)_4$	249
$GeMe_4$	249	$Hf(CH_2Bu^t)_4$	266
$SnMe_4$	217		
$PbMe_4$	152		

General Trends:

M–C bond enthalpy (B.E., strength) *decreases* with increasing atomic number for main group elements but *increases* as a transition metal triad is descended.

Therefore, transition metal alkyls should be more stable than lead alkyls, whose formation is endothermic and they possess only weak Pb–C bonds. But:

Compound	T_{dec}	Compound	T_{dec}
$TiMe_4$	> −50 ° C	$PbMe_4$	> 200 ° C (b.p. 110 ° C)
$TiEt_4$	Existence doubtful	$PbEt_4$	> 100 ° C

- **The reason for the difference in stability is therefore not thermodynamic but *kinetic*.**

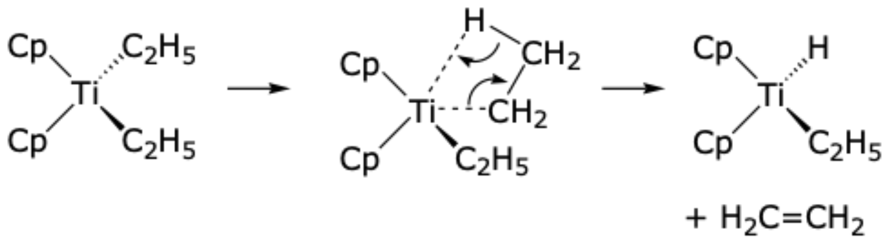
$PbEt_4$ decomposes by M–C bond homolysis (a high energy process) as Pb has a full octet, its 5d shell is filled, and the 6d and σ-* levels are energetically inaccessible.

e.g.

$$PbEt_4 \xrightarrow{\Delta} PbEt_3^{\bullet} + Et^{\bullet}$$

This contrasts to transition metal organometallics with vacant d-orbitals that may decompose by (concerted, lower energy) β- or reductive-elimination.

e.g.



Preventing Decomposition:

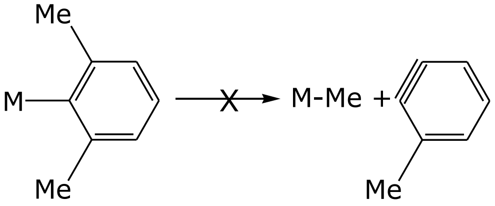
1) Use Ligands Stable to β-Hydride Elimination:

e.g.

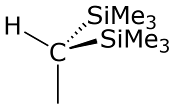
CH_3 CH_2Ph CH_2CMe_3

CH_2SiMe_3 $CH(SiMe_3)_2$ $C(SiMe_3)_3$

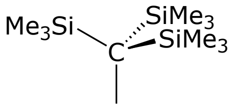
2) Formation of arynes from arenes can be prevented by using *ortho*-substituents which are ≠H.



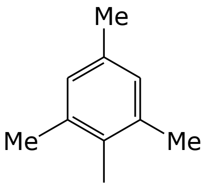
3) Use Bulky Ligands:



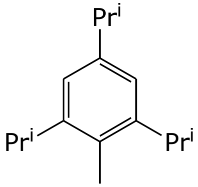
Disyl



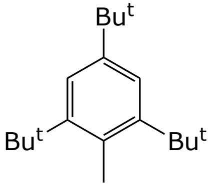
Trisyl



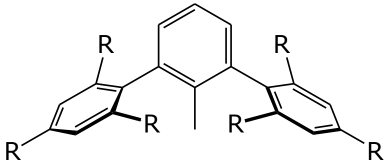
Mes



Tripp



Mes*

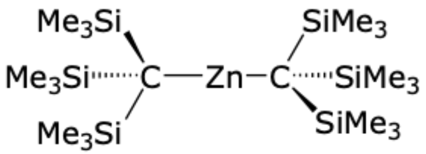


Terphenyl

4) Saturate the Coordination Sphere:

By either:

- Using extra ligands, e.g. $TiMe_4$ unstable, but $TiMe_4(Me_2PCH_2CH_2PMe_2)$ is stable at RT.
- Ligands which occupy more than one coordination site, e.g. Cp.
- Use ligands with pendant coordinating groups, e.g. C_6H_4-2-CH_2NMe_2.
- Use sterically demanding ligands. e.g.



c.f. $ZnMe_2$ is pyrophoric

Stable to air and
boiling (!) HCl

5) Obey the Pauling Electroneutrality Principle:

The less charged a species, the less reactive it will be.

6) Make 18-electron Compounds:

Compounds obeying the 18(16) electron rule are inherently more stable.