

Metal organic chemistry

Electron counting
Oxidation states
Coordination numbers

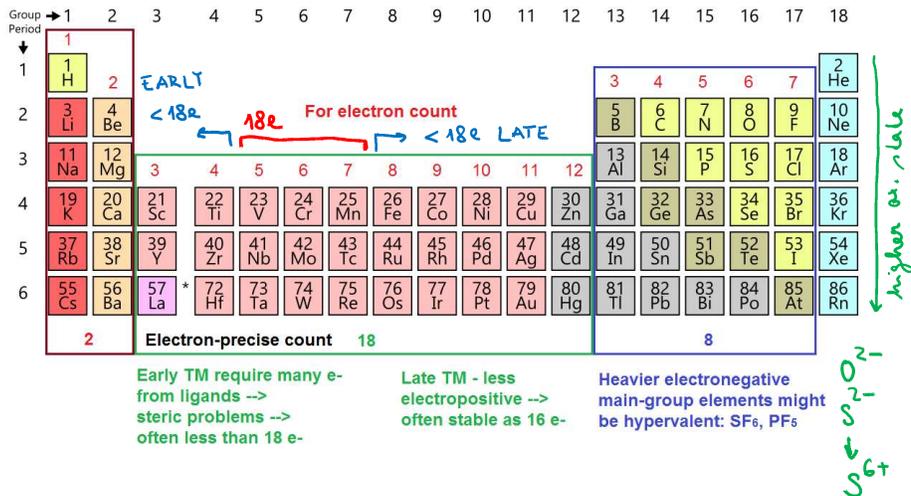
Trends in the periodic table

- Main group metals: Left and down: more electropositive

- Transition metals:

- middle: strongest preference for 18-e

- down: higher oxidation states more stable



Electron counting and oxidation state

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period 1	1 H	2 He																
Period 2	3 Li	4 Be	For electron count										5 B	6 C	7 N	8 O	9 F	10 Ne
Period 3	11 Na	12 Mg	3	4	5	6	7	8	9	10	11	12	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
Period 4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
Period 5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
Period 6	55 Cs	56 Ba	57 La*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
	2	Electron-precise count 18										8						

Early TM require many e- from ligands --> steric problems --> often less than 18 e-
Late TM - less electropositive --> often stable as 16 e-
Heavier electronegative main-group elements might be hypervalent: SF₆, PF₅

Electron count

Covalent bonds

1 – X (F, Cl, Br, OH, CN, RO, RCOO)
 2 – double bonds: O=, R₂C=
 3 – triple bonds: RC≡

Dative bonds

2 – M (CH₃CN, CO, THF, NH₃, ...)

Other dative bonds:

carbene

2 e

olefin

2 e

allyl

3 e

cyclopentadienyl

5 e

Electron counting

- Chemists are "sloppy" in writing structures. A "line" can mean a covalent bond, a dative bond, or even a part of a three-center two-electron bond.

→ Rewrite the structure properly before you start counting.

$d^0 \quad 10 + 1 + 2 + 3 = 16$

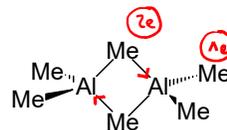
$d^4 \quad 4 + 2 \times 5 + 2 + 1 - 1 = 16$

$d^10 \quad 10 + 1 + 2 + 3 = 16$

$d^4 \quad 4 + 2 \times 5 + 2 + 1 - 1 = 16$

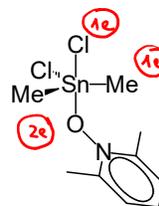
Main-group organometallics

- s and p orbitals
 - usually 8-e rule - with a lot of exceptions



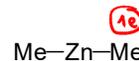
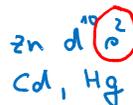
$$\text{Al} \quad 3 + 3 \times 1 + 2 = \underline{8}$$

- More electropositive and larger:
 - higher coordination numbers (regardless of the number of electrons)



$$\text{Sn} \quad 4 + 4 \times 1 + 2 = \underline{10}$$

- "Early" groups and electropositive:
 - lower coordination numbers



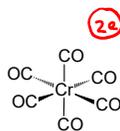
$$\text{zn} \quad 2 + 2 \times 1 = \underline{4}$$

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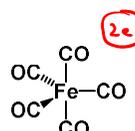
Transition-metal organometallics

- s, p and d orbitals
- 18-e rule:

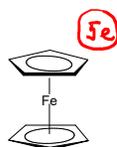
$$\text{Cr} = d^6 \quad 6 + 6 \times 2 = \underline{18}$$



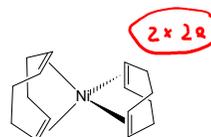
$$\text{Fe} = d^8 \quad 8 + 5 \times 2 = \underline{18}$$



$$\text{Fe} = d^8 \quad 8 + 2 \times 5 = \underline{18}$$



$$\text{Ni} = d^{10} \quad 10 + 2 \times 4 = \underline{18}$$



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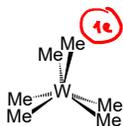
Transition-metal organometallics

- Lower electron counts

metals are sterically saturated:

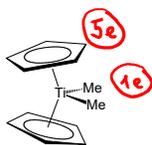
$$W = d^6$$

$$6 + 6 \times 1 = \underline{12}$$

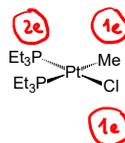


$$Ti = d^4$$

$$4 + 2 \times 5 + 2 = \underline{16}$$

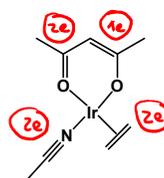


late transition metals – often 16e:



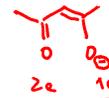
$$Pt = d^{10}$$

$$10 + 2 \times 2 + 2 \times 1 = \underline{16}$$



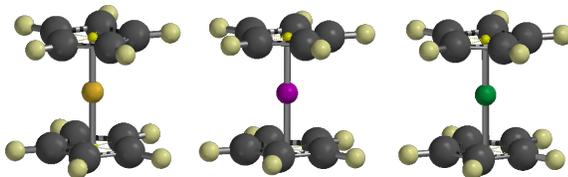
$$Ir = d^9$$

$$9 + 3 \times 2 + 1 = \underline{16}$$



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Prediction of stability of complexes

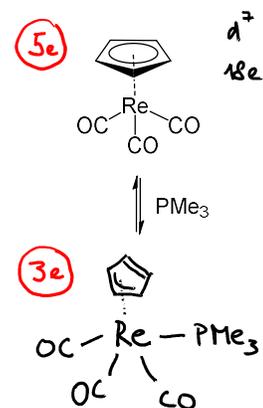


Ferrocene:
e-count:
Very stable.

Behaves as an aromatic organic compound in e.g. Friedel-Crafts acylation.

Cobaltocene:
e-count:
Strong reductant, reacts with air.
Cation (Cp₂Co⁺) is very stable.

Nickelocene:
e-count:
Chemically reactive, easily loses a Cp ring, reacts with air.



RING SLIPPAGE

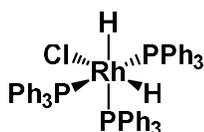
If there are too many electrons...

- Excess-electron compounds are relatively rare, especially for transition metals.
- "Too many electrons" means there might be fewer net covalent bonds than one thinks.
- An ionic model is required to explain part of the bonding.
- The "extra" bonds are relatively weak.
- Often generated by reduction (= addition of electrons).

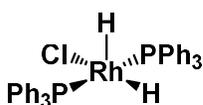
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If there are not enough electrons...

- Structures with a lower than ideal electron count are called **electron-deficient or coordinatively unsaturated**.
- They have unused (empty) valence orbitals.
- This makes them electrophilic, i.e. susceptible to attack by nucleophiles.
- Some unsaturated compounds are so reactive they will attack hydrocarbons, or bind noble gases.

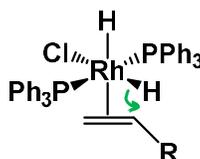


*unreactive
reaction promoted
by a loss of a ligand*

 $16e$


**REACTIVE
INTERMEDIATE**

*→ reacts with
a substrate*

 $18e$


→ hydrogenation

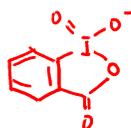
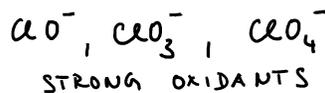
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Oxidation states

- Most elements have a clear preference for certain oxidation states. These are determined by (a.o.) electronegativity and the number of valence electrons.

Examples:

- Li: nearly always +1.
Has only 1 valence electron, so cannot go higher.
Is very electropositive, so doesn't want to go lower.
- Cl: nearly always -1.
Already has 7 valence electrons, so cannot go lower.
Is very electronegative, so doesn't want to go higher.

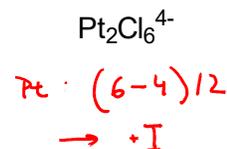
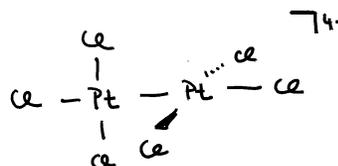
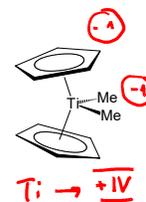
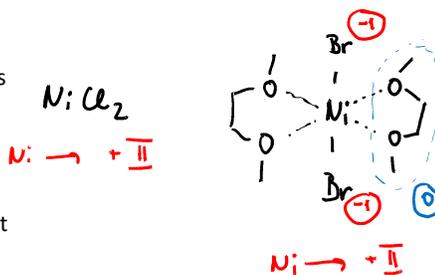


*2-iodoxybenzoic acid
oxidation of alcohols to aldehydes*

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How do you calculate oxidation states ?

1. Assign charges according to the electronegativities
Usually + at the metal
Multiple bonds: multiple + and - charges
2. Ignore dative bonds, consider just charges
3. Ignore bonds between atoms of the same element
4. Add together with the formal charge at the metal

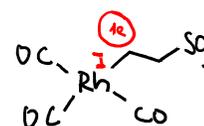
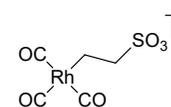
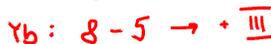
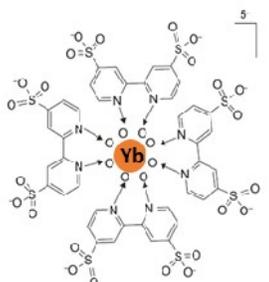


Homonuclear bonds \rightarrow

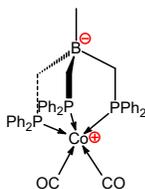
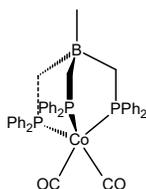
- Artificial, abnormal formal oxidation states.
- If you want to say something about stability, pretend the homonuclear bond is polar (for metals, typically with the + end at the metal you are interested in)
- For $[Pt_2Cl_6]^{4-}$ that would Pt^{II} and Pt^{II} - the normal oxidation states.

Handling charges

- Correct for the overall charge
- Eliminate all obvious places where a charge could belong \rightarrow pay attention to the hetero-atoms with unusual numbers of bonds.



- Even overall neutral molecules could have "hidden" charges!

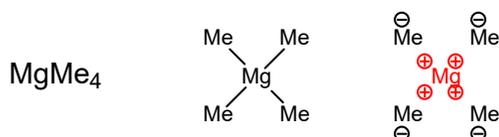


A boron atom with 4 bonds would be -1 (c.f. BH_4^-).

No other obvious centers of charge, so the Co must be +1.

Significance of oxidation states

- Oxidation states are formal.
- They do not indicate the "real charge" at the metal centre.
- However, they do give an indication whether a structure or composition is reasonable.
 - apart from the M-M complication
- They have more meaning when all bonds are relatively polar.
 - i.e. close to the fully ionic description used for counting
- Sometimes you can easily deduce that an oxidation state is "impossible", so the compound must be unstable



But Mg only has 2 valence electrons!
Any compound containing Mg⁴⁺ will not be stable.

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Normal oxidation states

s ¹		Maximum oxidation state										s ²		p ¹		p ²		p ³		p ⁴		p ⁵		2													
1		3		4		5		6		7		8		9		10		11		12		13		14		15		16		17		18		19		20	
H		Li		Be		B		C		N		O		F		Ne		Na		Mg		Al		Si		P		S		Cl		Ar		K		Ca	
21		22		23		24		25		26		27		28		29		30		31		32		33		34		35		36		37		38		39	
41		42		43		44		45		46		47		48		49		50		51		52		53		54		55		56		57		72		73	
81		82		83		84		85		86		87		88		89		90		91		92		93		94		95		96		97		98		99	

Noble metals
Coinage metals

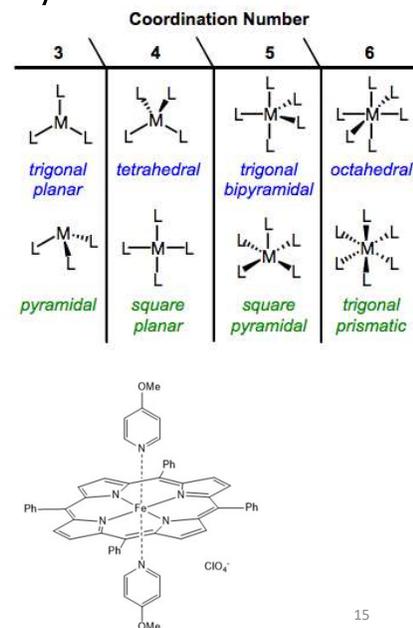
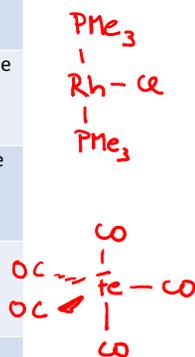
For group n or $n+10$:

- never $>n$ or $<-n$ (except group 11: frequently +2 or +3) → Cu^{II}, Au^{III} (d¹⁰ s¹)
- usually even for n even, odd for n odd → lots of exceptions
- usually ≥ 0 for metals
- usually $+n$ for very electropositive metals → Na⁺, Mg²⁺, Sc³⁺ BUT: Fe^{II/III}
- usually 0-3 for 1st-row transition metals of groups 6-11, often higher for 2nd and 3rd row → Cr^{III}, WCl₆
- electronegative ligands (F,O) stabilize higher oxidation states, NiCl₂
- π -acceptor ligands (CO) stabilize lower oxidation states Ni(CO)₄
- oxidation states usually change from m to $m-2$, m or $m+2$ in reactions

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Coordination number and geometry

Normal geometry	"Normal" geometry
2	linear or bent $\text{Me}_3\text{P}-\text{Au}-\text{Cl}$ $\text{H}-\text{O}-\text{H}$
3	planar trigonal, pyramidal; "T-shaped" often for d^8 14-e BF_3 NH_3
4	tetrahedral; square planar often for d^8 16-e CH_4 $\text{Ni}(\text{CO})_4$ $\text{H}_3\text{N}-\text{Pd}-\text{Cl}_2$ H_2O
5	square pyramidal, trigonal bipyramidal
6	octahedral



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What did you learn today?

- 1) Why organometallics
- 2) What are organometallic compounds
- 3) Trends in reactivity across the periodic table
- 4) Determine electron-counts, oxidation states, coordination numbers