MAX-PLANCK-INSTITUT
FÜR KOLLOID- UND
GRENZFLÄCHENFORSCHUNG

ORGANOTRANSITION METAL COMPLEXES:
HISTORY, STRUCTURE AND BONDING

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Biomolecular Systems
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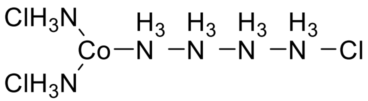
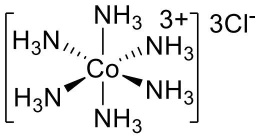
1.1.1 HISTORY – COMPLEX STRUCTURES

$CoCl_3$•$6NH_3$?



Blomstrand-Jorgensen chain theory



"Werner complex"

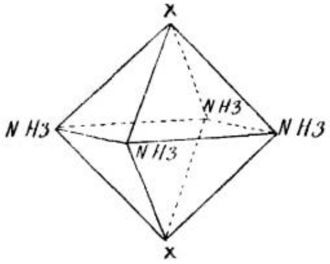
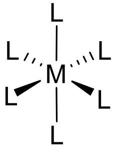
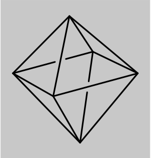


Fig. 2.



octahedral complex



octahedron

prevailing belief 1890s
oxidation state = coordination number

Werner complexes
(Alfred Werner - Nobel prize 1913)

POD #1

Using chemistry knowledge at 1890, which experiment could support Werner’s proposed structure?

Conductivity studies → 3 Cl^-

$AgNO_3$ ↓AgCl

Werner, *Z. Anorg. Chem.* **1893**, 3, 267. DOI: 10.1002/zaac.18930030136. (EN translation in Kauffman, “Classics in coordination chemistry”)

1.1.1 HISTORY – WERNER COMPLEXES

Werner complexes (Alfred Werner - Nobel prize 1913)

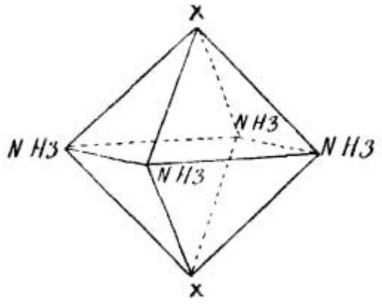


Fig. 2.

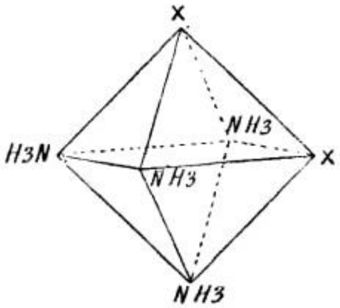
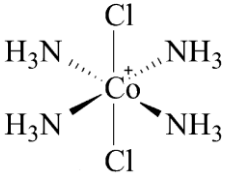
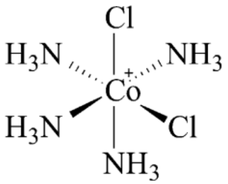


Fig. 3.



trans (known)

green



cis (predicted)

purple

ML_n generic representation

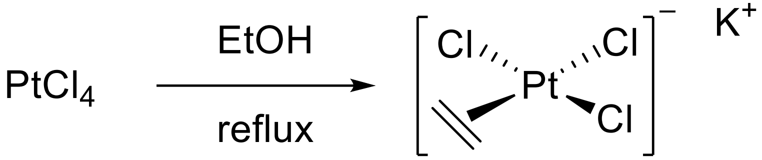
e.g. ML_6:

$[Ni(H_2O)_6]^{2+}$ hexaaquanickel

$Mo(CO)_6$ molybdenum hexacarbonyl

1.1.2 HISTORY – ZEISE'S SALT

Zeise, a pharmacist, in 1831:



Structural debate in the 19th century

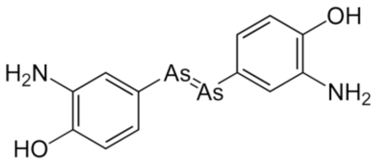
Single-crystal XRD only in 1969

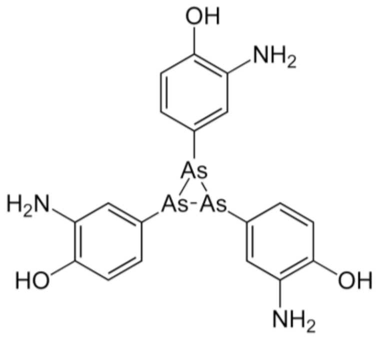
Zeise, W. C. Annalen der Physik und Chemie 1831, 97, 497. DOI: 10.1002/andp.18310970402.
Owston, P. G. *et al.*, *Acta Crystall. B* **1969**, *25* (9), 1753. DOI: 10.1107/S0567740869004699.

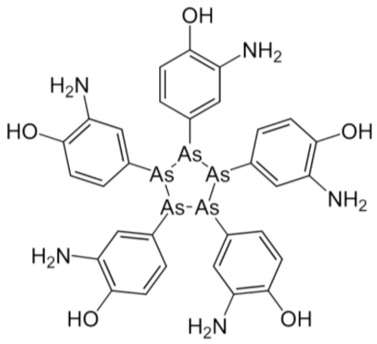
1.1.3 HISTORY – SALVARSAN

Paul Ehrlich’s Salvarsan – “magic bullet”

1910s 1st antimicrobial drug (syphilis)

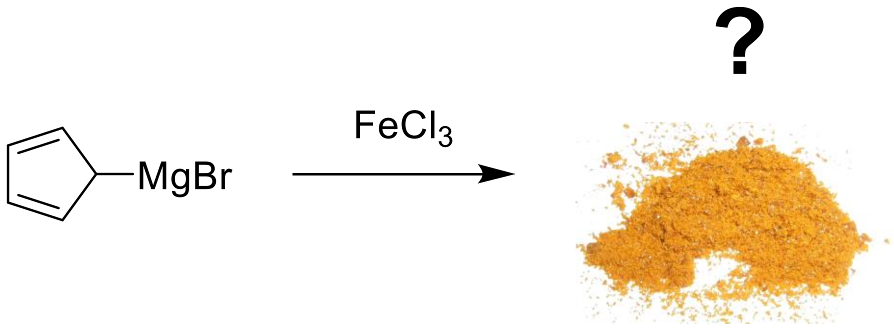




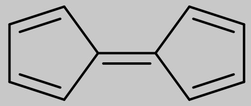


1.1.4 HISTORY

1951, Paulson and Kealy:



fulvalene



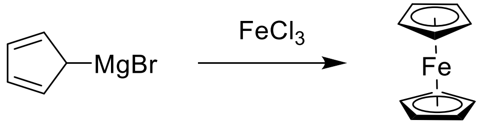
(not observed)

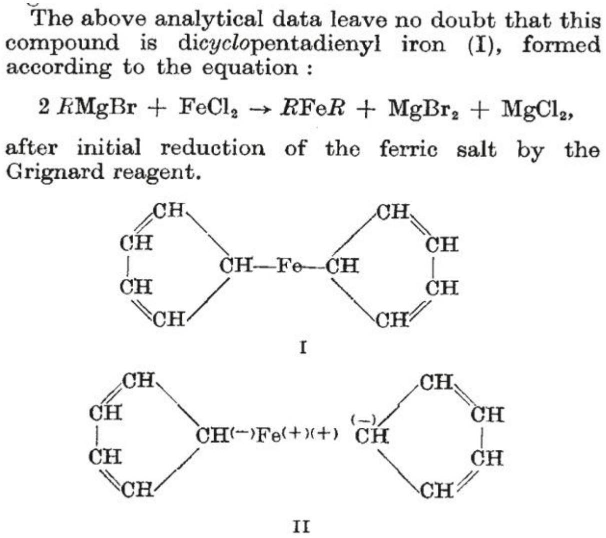
POD #2

Which analytical techniques from 1950 would you use to **identify and characterize it**?

Kealy and Pauson, Nature 1951, 168 (4285), 1039–1040. DOI: 10.1038/1681039b0.

1.1.4 HISTORY – FERROCENE





The above analytical data leave no doubt that this compound is dicyclopentadienyl iron (I), formed according to the equation :

$$2\,R\text{MgBr} + \text{FeCl}_2 \rightarrow R\text{Fe}R + \text{MgBr}_2 + \text{MgCl}_2,$$

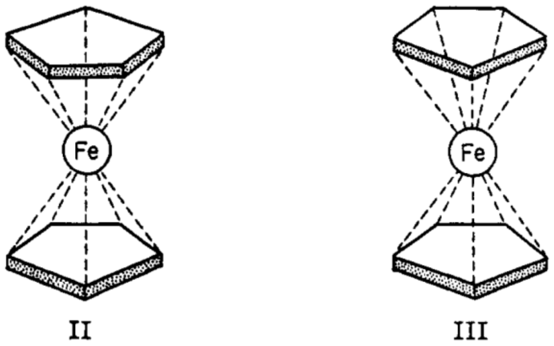
after initial reduction of the ferric salt by the Grignard reagent.

I

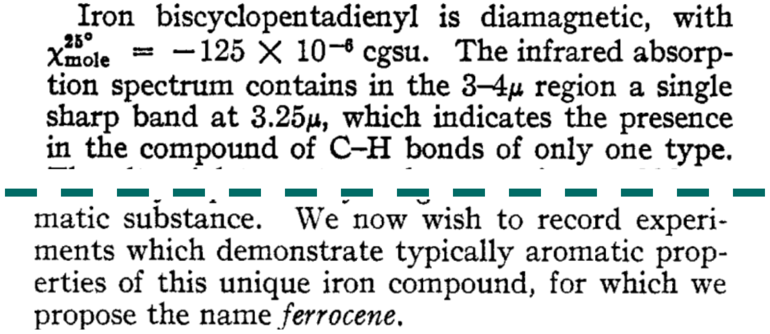
II

Kealy and Pauson, *Nature* **1951**, *168*, 1039.

DOI: 10.1038/1681039b0.



II III

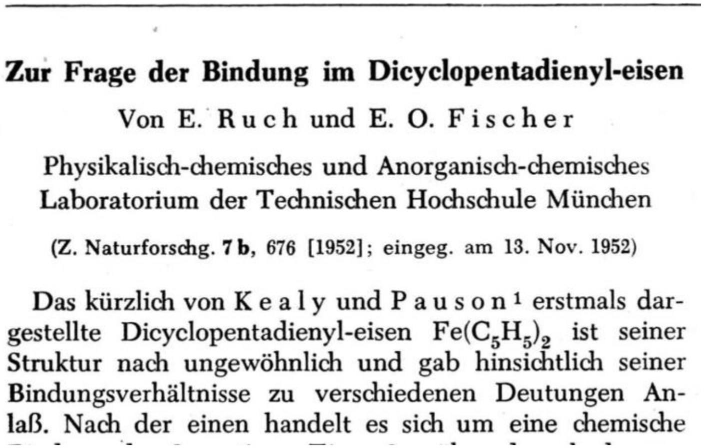


Iron biscyclopentadienyl is diamagnetic, with $\chi^{25°}_{\text{mole}} = -125 \times 10^{-6}$ cgsu. The infrared absorption spectrum contains in the 3–4μ region a single sharp band at 3.25μ, which indicates the presence in the compound of C–H bonds of only one type.

matic substance. We now wish to record experiments which demonstrate typically aromatic properties of this unique iron compound, for which we propose the name *ferrocene*.

Winkilson, Woodward *et al.*, *JACS* **1952**, 74 (8), 2125.
Woodward *et al.*, *JACS* **1952**, 74 (13), 3458.

DOI: 10.1021/ja01128a527.



Zur Frage der Bindung im Dicyclopentadienyl-eisen

Von E. Ruch und E. O. Fischer

Physikalisch-chemisches und Anorganisch-chemisches Laboratorium der Technischen Hochschule München

(Z. Naturforschg. **7 b**, 676 [1952]; eingeg. am 13. Nov. 1952)

Das kürzlich von Kealy und Pauson[1] erstmals dargestellte Dicyclopentadienyl-eisen $Fe(C_5H_5)_2$ ist seiner Struktur nach ungewöhnlich und gab hinsichtlich seiner Bindungsverhältnisse zu verschiedenen Deutungen Anlaß. Nach der einen handelt es sich um eine chemische

(Ernst Otto Fischer
and Geoffrey Winkilson
Nobel prize 1913)

Ruch and Fischer, *Z. Naturforsch., B* **1952**, *7*, 676.

DOI: 10.1515/znb-1952-1209.

1.2.1 STRUCTURE – 18 ELECTRON “RULE”

18 electron “rule” (aka effective atomic number or noble-gas rule)

Stable, diamagnetic, mononuclear organotransition metal complexes almost always contain 18 (or fewer) valence electrons.

- works best for small, high-field, monodentate ligands, such as H and CO.
- group 11 the highest tendency to become 16e. When these metals are 16e, they normally become square planar, as in $RhClL_3$, $IrCl(CO)L_2$, $PdCl_2L_2$, $[PtCl_4]^{2-}$, and $[AuMe_4]^-$ (L= PR_3).

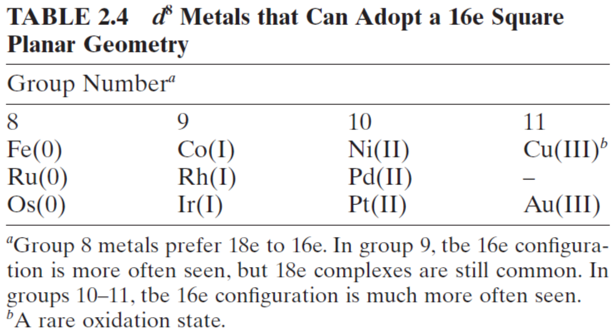


TABLE 2.4 ***d*^{8} Metals that Can Adopt a 16e Square Planar Geometry**

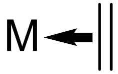
Group Number[a]			
8	9	10	11
Fe(0)	Co(I)	Ni(II)	Cu(III)[b]
Ru(0)	Rh(I)	Pd(II)	–
Os(0)	Ir(I)	Pt(II)	Au(III)

[a] Group 8 metals prefer 18e to 16e. In group 9, tbe 16e configuration is more often seen, but 18e complexes are still common. In groups 10–11, tbe 16e configuration is much more often seen.
[b] A rare oxidation state.

1.2.1 STRUCTURE – LIGAND TYPES

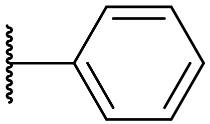
“L-type” (neutral / dative)

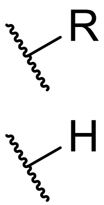
NH_3
PR_3
OH_2
CO



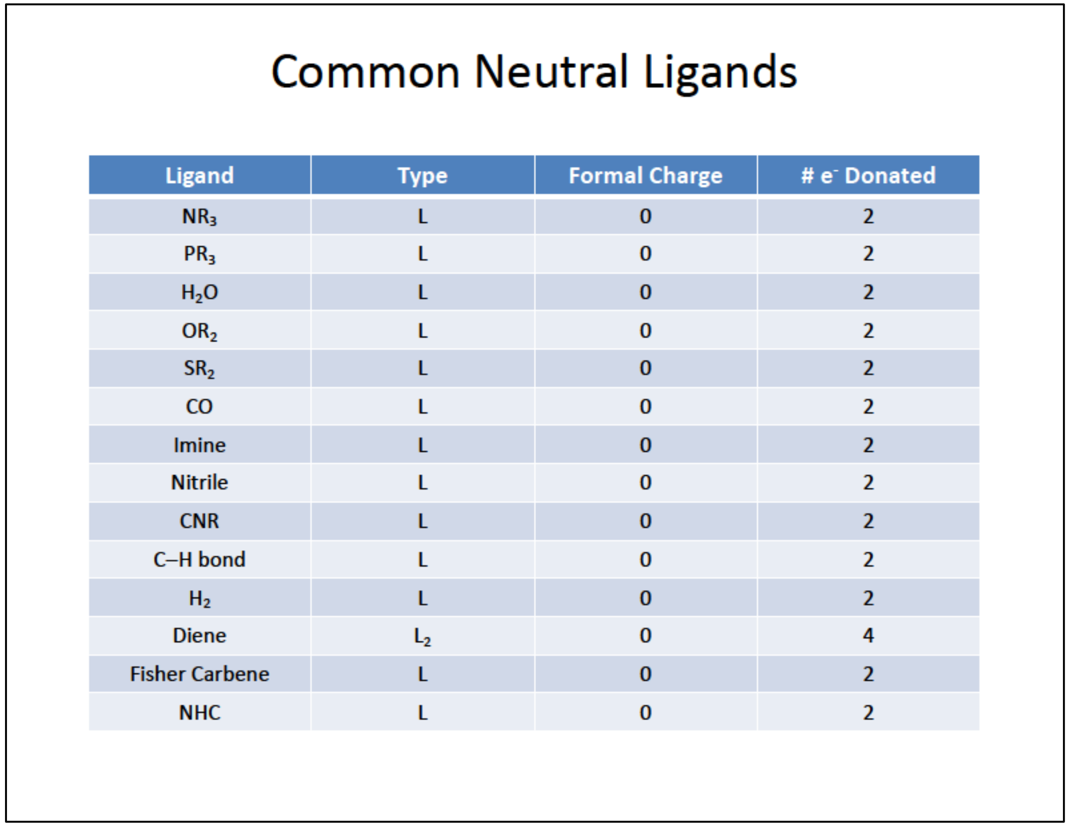
“X-type” (anionic)

Cl-
OR-





Handout on blackboard:



Common Neutral Ligands

Ligand	Type	Formal Charge	# e^- Donated
NR_3	L	0	2
PR_3	L	0	2
H_2O	L	0	2
OR_2	L	0	2
SR_2	L	0	2
CO	L	0	2
Imine	L	0	2
Nitrile	L	0	2
CNR	L	0	2
C–H bond	L	0	2
H_2	L	0	2
Diene	L_2	0	4
Fisher Carbene	L	0	2
NHC	L	0	2

1.2.1 STRUCTURE – OXIDATION STATE

Oxidation state

Charge left on the metal after all ligands are removed to give closed shell species

For complex ions also consider overall charge, e.g. Cp_2Fe is Fe(II) but Cp_2Fe^+ is Fe(III)

d^n electron count

d-electrons = metal group – oxidation state

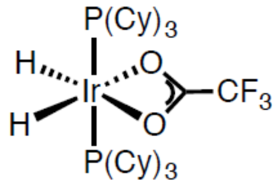
Overall electron count

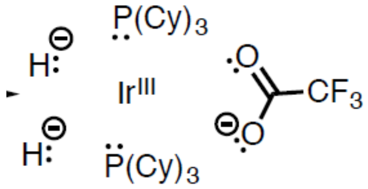
d-electrons + ligand electrons (all $2e^-$ if ionic model)

Note: d-electron count in complexes != d electrons in atomic configuration (aufbau)

Cobalt: [Ar] $4s^2\,3d^7$ **Co-complex**: [Ar] $4s^0\,3d^9$

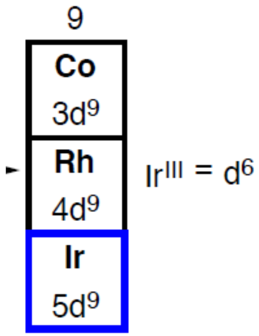
1.2.2 STRUCTURE – ELECTRON COUNTING





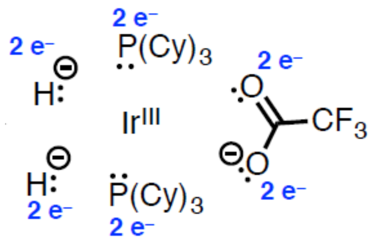
Step 1: oxidation state

- Assign ligand type (anionic, neutral, cationic…)
- Determine the total charge of the ligands
- Add/subtract the overall charge of the metal complex to/from ligand charge
- The oxidation state will be equal, with opposite charge



Step 2: d-electron count

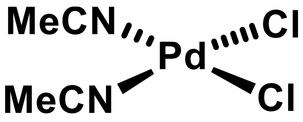
- From the metal group number subtract the oxidation state



Step 3: complex electron count

Add the number of electron donated by each ligand to the metal's d-electron count

1.2.2 STRUCTURE – ELECTRON COUNTING – EXERCISE

		$[CpMo(CO)_3(H_2O)]^+$	$Ru(NO)(PPh_3)_2Cl_3$
	Pd – Group 10	Mo – Group 6	Ru – Group 8
Which type of ligands?	2 L-type 2 X-type	1 L_2X + 3 L + 1 L	1 X* + 2 L + 3 X
Oxidation state?	+2	+2	+2
d-electron count?	10 - 2 = d^8	6 - 2 = d^4	8 - 2 = d^6
Total electron count?	8 + 4 + 4 = 16	4 + 6 + 6 + 2 = 18	6 + 12 = 18
			* linear form

1.2.1 STRUCTURE – ANALOGIES

Isoelectronic analogy

Complexes with the same number of d-electrons, similar ligands and geometry.

e.g. $[Co(CO)_4]^-$ and $Ni(CO)_4$ but, with a bit of a stretch, also $CpMn(CO)_3$ and $[CpRu(CO)_3]^+$

Isolobal analogy

Complexes with the same number, symmetry, approximate energy and shape of frontier orbitals are said to be isolobal.

1.2.1 STRUCTURE – VOCABULARY

Coordination number

Number of electron pairs donated to the metal.

e.g. CN=4 for $Pd(PPh_3)_4$

Hapticity (η)

Number of contiguous atoms in a ligand that are directly coordinated with the metal.

e.g. η^5 *for ferrocene*

Denticity (κ)

Number of atoms of a ligand that is bound through non-contiguous atoms.

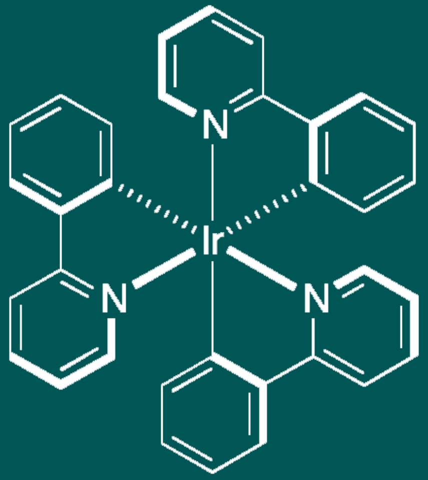
e.g. κ^3 *for a pincer ligands*

Mu (μ)

The greek letter mu indicates the number of metals to which a ligand is bound.

e.g. μ^2 *for a bridging halide*

"paddle-wheel"

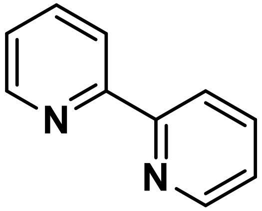


Ir(ppy)3

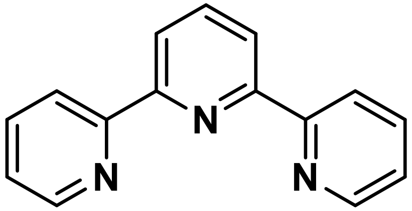
1.2.1 STRUCTURE – VOCABULARY – DENTICITY

K_{eq} monodentate vs. bidentate?

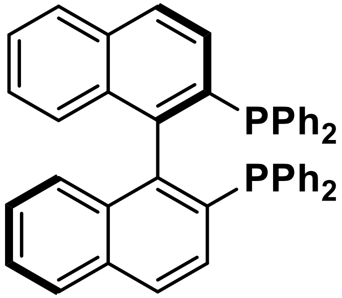
10^5 more stable!



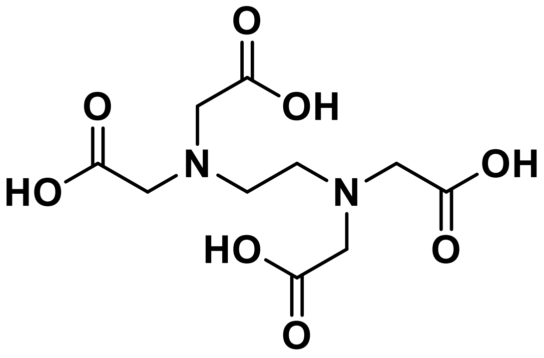
bipyririne
bpy



terpyridine
terpy



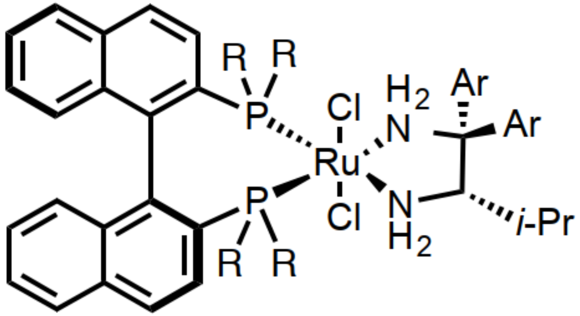
(R)-binap



ethylenediaminetetraacetic acid
EDTA

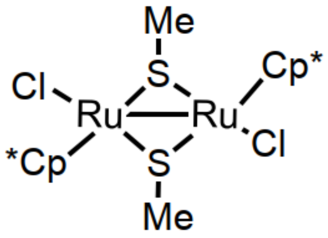
1.2.1 STRUCTURE – POD #3

For the structures below, **provide the coordination number, metal oxidation state, d-electron count, and overall electron count.**

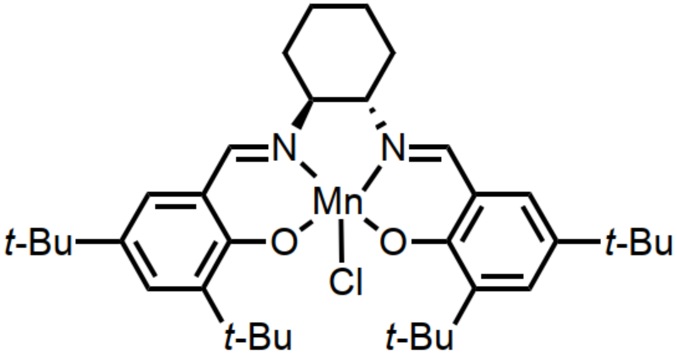


Ru Group 8
2X 4 L: OS 2 CN 6
d-6
e-count 18

Noyori’s catalysts



Ru Group 8
2X 2X4L 2X2L: OS 3 CN 6
d-5
e-count 18

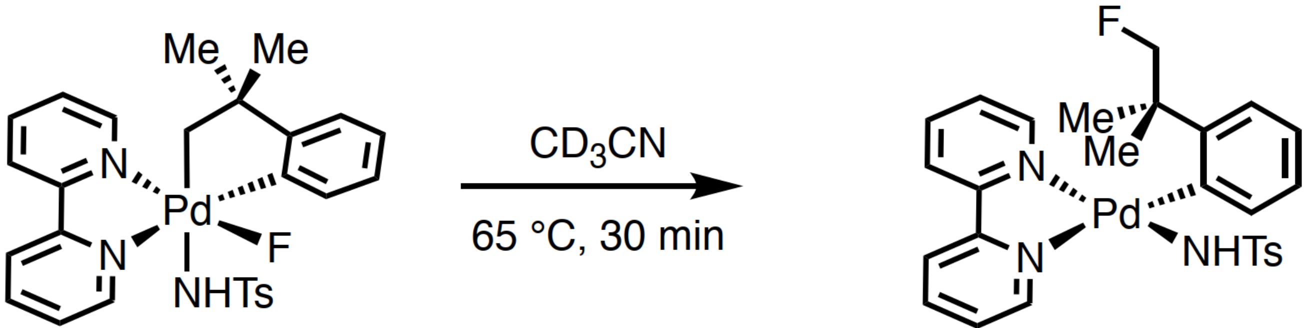


Mn Group 7
3X 2L: OS 3 CN 5
d-4
e-count 14

Jacobsen's catalyst

1.2.1 STRUCTURE – SUMMARY OF DAY1 – POD #1

Cyclometallated palladium species A rapidly undergoes reductive elimination to give B.



A

CN 6, Pd(IV)

d-6

e-count 18

B (major)

CN 4, Pd(II)

d-8

e-count 16

For both complexes, provide the (a) coordination number, (b) d-electron count, (c) geometry, (d) metal oxidation state, and (e) total electron count

Sanford and co-workers, *JACS,* **2014**, 136 (11), 4097. DOI: 10.1021/ja411433f

1.2.2 PERIODIC TRENDS IN TRANSITION METALS

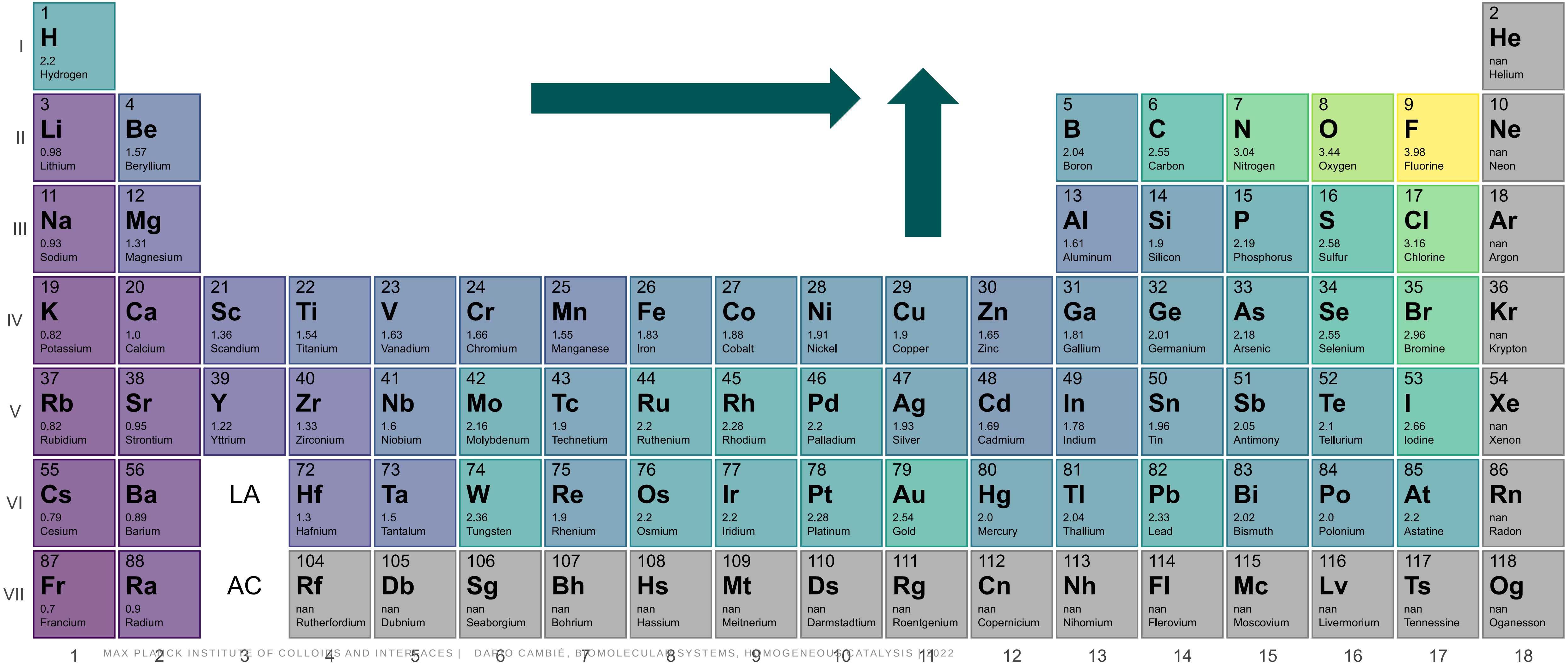
- A change in the metal greatly affects the properties of the resulting complexes

Caveats:

- Most trends are not contiguous throughout transition series
- Trends in properties when comparing elements are different than for complexes

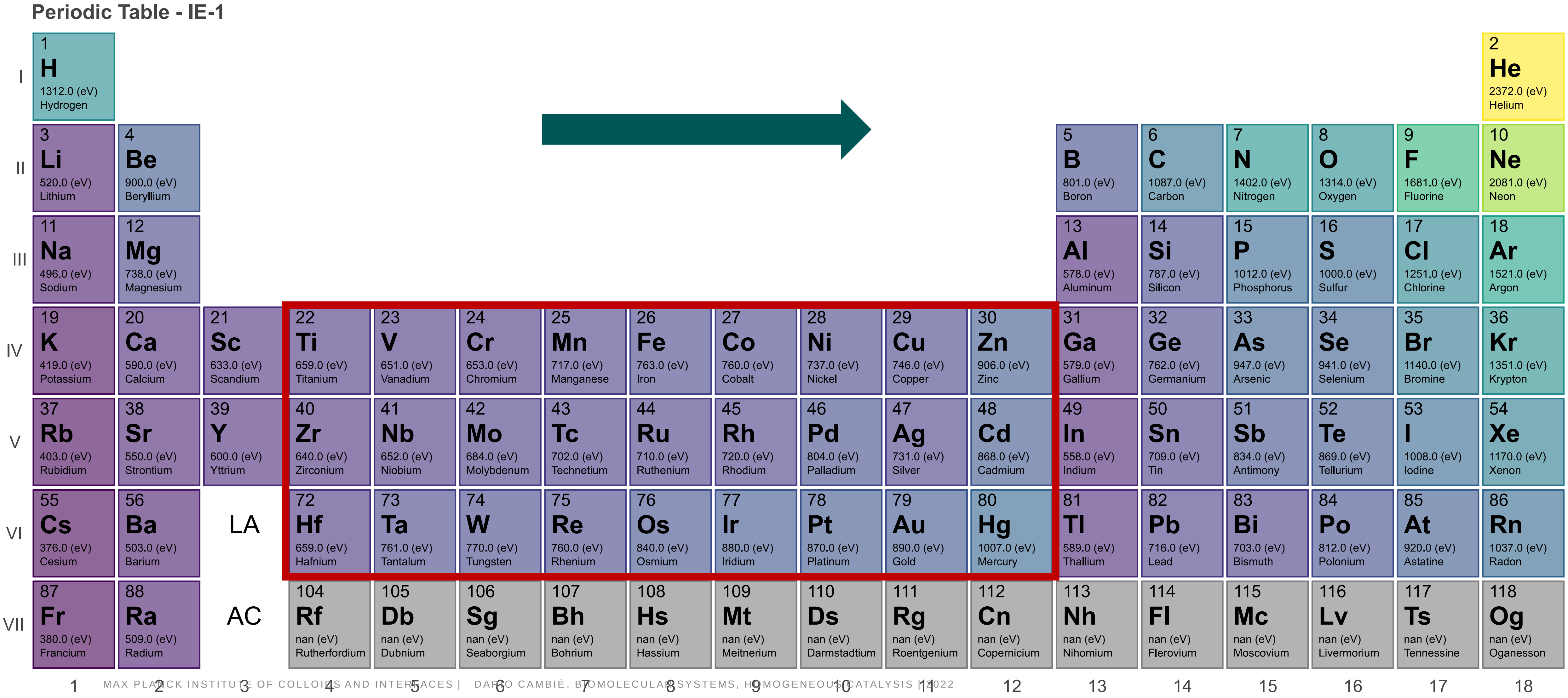
1.2.2 PERIODIC TRENDS – ELECTRONEGATIVITY

Periodic Table - electronegativity



I	1 **H** 2.2 Hydrogen																	2 **He** nan Helium
II	3 **Li** 0.98 Lithium	4 **Be** 1.57 Beryllium											5 **B** 2.04 Boron	6 **C** 2.55 Carbon	7 **N** 3.04 Nitrogen	8 **O** 3.44 Oxygen	9 **F** 3.98 Fluorine	10 **Ne** nan Neon
III	11 **Na** 0.93 Sodium	12 **Mg** 1.31 Magnesium											13 **Al** 1.61 Aluminum	14 **Si** 1.9 Silicon	15 **P** 2.19 Phosphorus	16 **S** 2.58 Sulfur	17 **Cl** 3.16 Chlorine	18 **Ar** nan Argon
IV	19 **K** 0.82 Potassium	20 **Ca** 1.0 Calcium	21 **Sc** 1.36 Scandium	22 **Ti** 1.54 Titanium	23 **V** 1.63 Vanadium	24 **Cr** 1.66 Chromium	25 **Mn** 1.55 Manganese	26 **Fe** 1.83 Iron	27 **Co** 1.88 Cobalt	28 **Ni** 1.91 Nickel	29 **Cu** 1.9 Copper	30 **Zn** 1.65 Zinc	31 **Ga** 1.81 Gallium	32 **Ge** 2.01 Germanium	33 **As** 2.18 Arsenic	34 **Se** 2.55 Selenium	35 **Br** 2.96 Bromine	36 **Kr** nan Krypton
V	37 **Rb** 0.82 Rubidium	38 **Sr** 0.95 Strontium	39 **Y** 1.22 Yttrium	40 **Zr** 1.33 Zirconium	41 **Nb** 1.6 Niobium	42 **Mo** 2.16 Molybdenum	43 **Tc** 1.9 Technetium	44 **Ru** 2.2 Ruthenium	45 **Rh** 2.28 Rhodium	46 **Pd** 2.2 Palladium	47 **Ag** 1.93 Silver	48 **Cd** 1.69 Cadmium	49 **In** 1.78 Indium	50 **Sn** 1.96 Tin	51 **Sb** 2.05 Antimony	52 **Te** 2.1 Tellurium	53 **I** 2.66 Iodine	54 **Xe** nan Xenon
VI	55 **Cs** 0.79 Cesium	56 **Ba** 0.89 Barium	LA	72 **Hf** 1.3 Hafnium	73 **Ta** 1.5 Tantalum	74 **W** 2.36 Tungsten	75 **Re** 1.9 Rhenium	76 **Os** 2.2 Osmium	77 **Ir** 2.2 Iridium	78 **Pt** 2.28 Platinum	79 **Au** 2.54 Gold	80 **Hg** 2.0 Mercury	81 **Tl** 2.04 Thallium	82 **Pb** 2.33 Lead	83 **Bi** 2.02 Bismuth	84 **Po** 2.0 Polonium	85 **At** 2.2 Astatine	86 **Rn** nan Radon
VII	87 **Fr** 0.7 Francium	88 **Ra** 0.9 Radium	AC	104 **Rf** nan Rutherfordium	105 **Db** nan Dubnium	106 **Sg** nan Seaborgium	107 **Bh** nan Bohrium	108 **Hs** nan Hassium	109 **Mt** nan Meitnerium	110 **Ds** nan Darmstadtium	111 **Rg** nan Roentgenium	112 **Cn** nan Copernicium	113 **Nh** nan Nihomium	114 **Fl** nan Flerovium	115 **Mc** nan Moscovium	116 **Lv** nan Livermorium	117 **Ts** nan Tennessine	118 **Og** nan Oganesson
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18

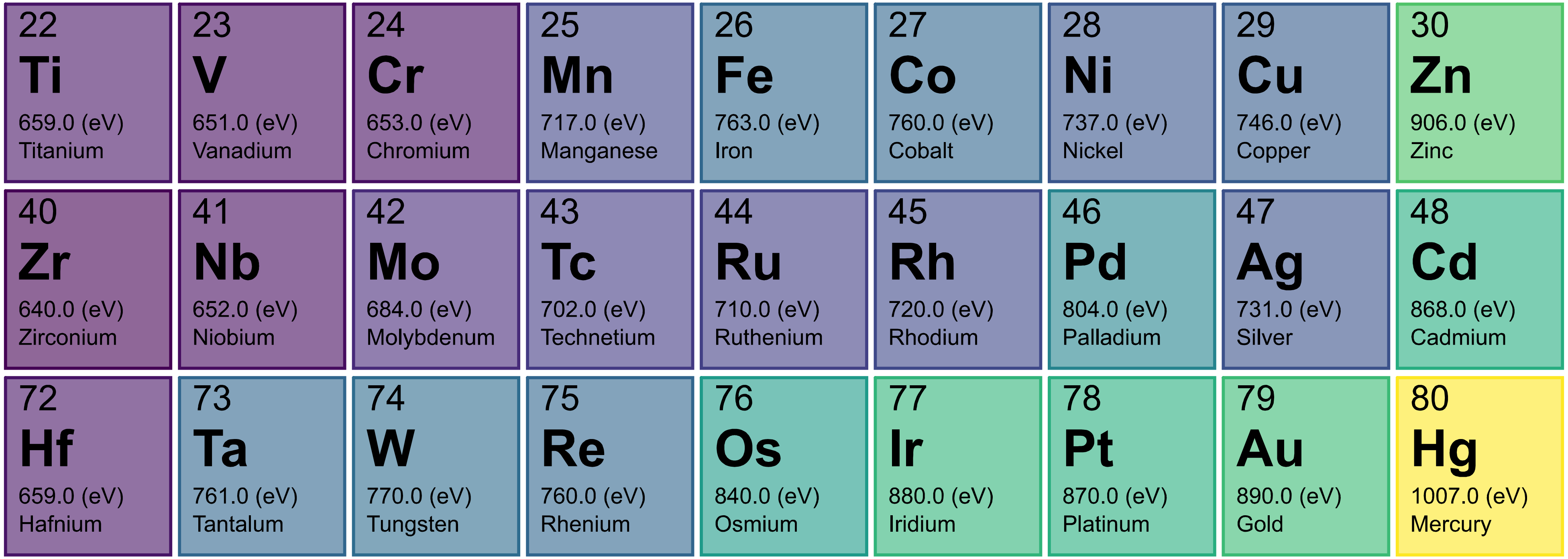
1.2.2 PERIODIC TRENDS – IONIZATION POTENTIAL



Periodic Table - IE-1

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
I	1 **H** 1312.0 (eV) Hydrogen																	2 **He** 2372.0 (eV) Helium
II	3 **Li** 520.0 (eV) Lithium	4 **Be** 900.0 (eV) Beryllium											5 **B** 801.0 (eV) Boron	6 **C** 1087.0 (eV) Carbon	7 **N** 1402.0 (eV) Nitrogen	8 **O** 1314.0 (eV) Oxygen	9 **F** 1681.0 (eV) Fluorine	10 **Ne** 2081.0 (eV) Neon
III	11 **Na** 496.0 (eV) Sodium	12 **Mg** 738.0 (eV) Magnesium											13 **Al** 578.0 (eV) Aluminum	14 **Si** 787.0 (eV) Silicon	15 **P** 1012.0 (eV) Phosphorus	16 **S** 1000.0 (eV) Sulfur	17 **Cl** 1251.0 (eV) Chlorine	18 **Ar** 1521.0 (eV) Argon
IV	19 **K** 419.0 (eV) Potassium	20 **Ca** 590.0 (eV) Calcium	21 **Sc** 633.0 (eV) Scandium	22 **Ti** 659.0 (eV) Titanium	23 **V** 651.0 (eV) Vanadium	24 **Cr** 653.0 (eV) Chromium	25 **Mn** 717.0 (eV) Manganese	26 **Fe** 763.0 (eV) Iron	27 **Co** 760.0 (eV) Cobalt	28 **Ni** 737.0 (eV) Nickel	29 **Cu** 746.0 (eV) Copper	30 **Zn** 906.0 (eV) Zinc	31 **Ga** 579.0 (eV) Gallium	32 **Ge** 762.0 (eV) Germanium	33 **As** 947.0 (eV) Arsenic	34 **Se** 941.0 (eV) Selenium	35 **Br** 1140.0 (eV) Bromine	36 **Kr** 1351.0 (eV) Krypton
V	37 **Rb** 403.0 (eV) Rubidium	38 **Sr** 550.0 (eV) Strontium	39 **Y** 600.0 (eV) Yttrium	40 **Zr** 640.0 (eV) Zirconium	41 **Nb** 652.0 (eV) Niobium	42 **Mo** 684.0 (eV) Molybdenum	43 **Tc** 702.0 (eV) Technetium	44 **Ru** 710.0 (eV) Ruthenium	45 **Rh** 720.0 (eV) Rhodium	46 **Pd** 804.0 (eV) Palladium	47 **Ag** 731.0 (eV) Silver	48 **Cd** 868.0 (eV) Cadmium	49 **In** 558.0 (eV) Indium	50 **Sn** 709.0 (eV) Tin	51 **Sb** 834.0 (eV) Antimony	52 **Te** 869.0 (eV) Tellurium	53 **I** 1008.0 (eV) Iodine	54 **Xe** 1170.0 (eV) Xenon
VI	55 **Cs** 376.0 (eV) Cesium	56 **Ba** 503.0 (eV) Barium	LA	72 **Hf** 659.0 (eV) Hafnium	73 **Ta** 761.0 (eV) Tantalum	74 **W** 770.0 (eV) Tungsten	75 **Re** 760.0 (eV) Rhenium	76 **Os** 840.0 (eV) Osmium	77 **Ir** 880.0 (eV) Iridium	78 **Pt** 870.0 (eV) Platinum	79 **Au** 890.0 (eV) Gold	80 **Hg** 1007.0 (eV) Mercury	81 **Tl** 589.0 (eV) Thallium	82 **Pb** 716.0 (eV) Lead	83 **Bi** 703.0 (eV) Bismuth	84 **Po** 812.0 (eV) Polonium	85 **At** 920.0 (eV) Astatine	86 **Rn** 1037.0 (eV) Radon
VII	87 **Fr** 380.0 (eV) Francium	88 **Ra** 509.0 (eV) Radium	AC	104 **Rf** nan (eV) Rutherfordium	105 **Db** nan (eV) Dubnium	106 **Sg** nan (eV) Seaborgium	107 **Bh** nan (eV) Bohrium	108 **Hs** nan (eV) Hassium	109 **Mt** nan (eV) Meitnerium	110 **Ds** nan (eV) Darmstadtium	111 **Rg** nan (eV) Roentgenium	112 **Cn** nan (eV) Copernicium	113 **Nh** nan (eV) Nihomium	114 **Fl** nan (eV) Flerovium	115 **Mc** nan (eV) Moscovium	116 **Lv** nan (eV) Livermorium	117 **Ts** nan (eV) Tennessine	118 **Og** nan (eV) Oganesson

1.2.2 PERIODIC TRENDS – IONIZATION POTENTIAL



22 **Ti** 659.0 (eV) Titanium	23 **V** 651.0 (eV) Vanadium	24 **Cr** 653.0 (eV) Chromium	25 **Mn** 717.0 (eV) Manganese	26 **Fe** 763.0 (eV) Iron	27 **Co** 760.0 (eV) Cobalt	28 **Ni** 737.0 (eV) Nickel	29 **Cu** 746.0 (eV) Copper	30 **Zn** 906.0 (eV) Zinc
40 **Zr** 640.0 (eV) Zirconium	41 **Nb** 652.0 (eV) Niobium	42 **Mo** 684.0 (eV) Molybdenum	43 **Tc** 702.0 (eV) Technetium	44 **Ru** 710.0 (eV) Ruthenium	45 **Rh** 720.0 (eV) Rhodium	46 **Pd** 804.0 (eV) Palladium	47 **Ag** 731.0 (eV) Silver	48 **Cd** 868.0 (eV) Cadmium
72 **Hf** 659.0 (eV) Hafnium	73 **Ta** 761.0 (eV) Tantalum	74 **W** 770.0 (eV) Tungsten	75 **Re** 760.0 (eV) Rhenium	76 **Os** 840.0 (eV) Osmium	77 **Ir** 880.0 (eV) Iridium	78 **Pt** 870.0 (eV) Platinum	79 **Au** 890.0 (eV) Gold	80 **Hg** 1007.0 (eV) Mercury

1.2.2 PERIODIC TRENDS – IONIZATION POTENTIAL

Electronegativity

- Early TM very electropositive -> often in highest oxidation state (e.g. Zr(IV) and Ta(V)), if lower they are easily oxidized
- Late TM more electronegative -> Pd(IV) is harder than Pd(0) and Pd(II)

Ionization potential

- energies of d-orbitals can be estimated from ionization potential
- Higher oxidation states are more accessible for earlier TM, (e.g. Zr^{2+} vs. Pd^{2+})
- Trends within group are more complex
  - Generally, higher oxidation states are more accessible for $3^{rd} > 2^{nd} > 1^{st}$ row. (e.g. Pt^{4+} vs. Ni^{4+})

1.2.2 PERIODIC TRENDS – SIZE AND METAL-LIGAND BOND STRENGTH

- Which trend for size (atomic radii)? **1st < 2nd ≈ 3rd** *(lanthanide contraction!)*

- Which trend for C–X bond strength for X = F, Cl, Br, I? C-F **>** C-Cl **>** C-Br **>** C-I
- Which trend for M–C bond strength for M = 1st 2nd and 3rd row? 3rd **>** 2nd **>** 1st
  - *better spatial overlap between metal w/ ligand orbitals*
  - *closer match of energies of ligand orbitals with the metal (esp. 3rd row)*

HARD/SOFT ACID/BASE THEORY (HSAB)

- Hard acids form more stable complexes with hard bases
- Soft acids form more stable complexes with soft bases

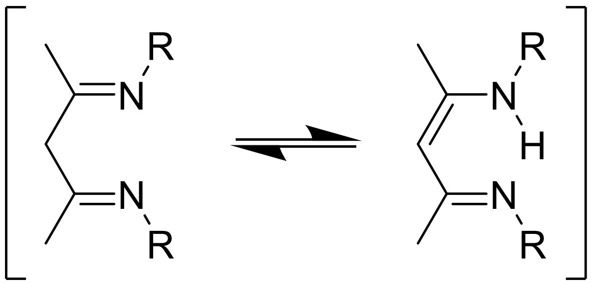
- **Hard**: small, densely charge, non polarizable **1st row**
- **Soft**: large, diffusely charged, polarizable **2nd / 3rd row**

1.2.3.1 GEOMETRY – VSEPR THEORY

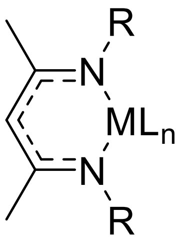
Coord. #	Possible geometry	Example
2	linear	$[Au(CN)_2]^-$, $[CuCl_2]^-$
"	bent	$SnCl_2$
3	trigonal planar	$[AgCl_3]^{2-}$
"	pyramidal	Rare!
"	T-shaped	

1.2.3.1 EXAMPLE OF T-SHAPE

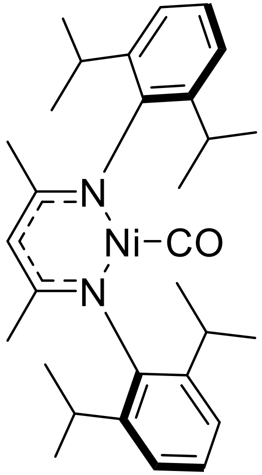
3D STRUCTURE LINK



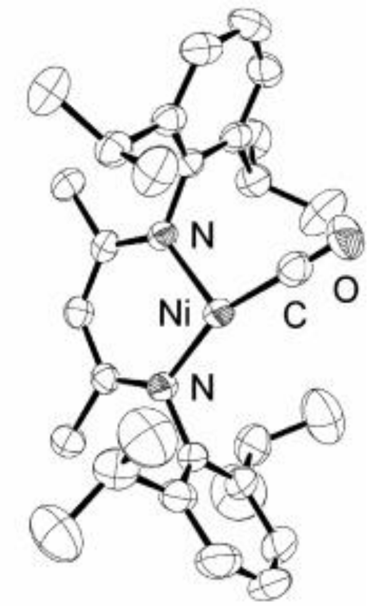
HNacnac



Nacnac



$L^{Me}Ni(CO)$
(L = (dipp)Nacnac)



$L^{Me}Ni(CO)$

T geometry

Holland and co-workers, *Inorg. Chem.* **2005**, 44, 22, 7702. DOI: 10.1021/ic0510213

1.2.3.1 STRUCTURE – GEOMETRY – VSEPR THEORY

VSEPR is rudimentary!

Limits

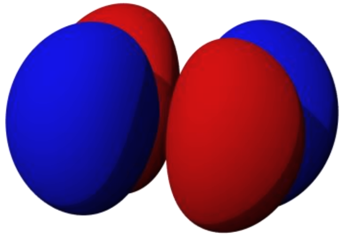
- Magnetism
- Color
- Distortions
- Sq. planar vs. tet.?

Coord. #	Possible geometry	Example
2	linear	$[Au(CN)_2]^-$, $[CuCl_2]^-$
“	bent	$SnCl_2$
3	trigonal planar	$[AgCl_3]^{2-}$
“	pyramidal	Rare!
“	T-shaped	
4	**square planar**	$RhCl(PPh_3)_3$
“	**tetrahedral**	$Pd(PPh_3)_4$, $TiCl_4$
5	trigonal pyramidal	$Fe(CO)_5$
“	square pyramidal	$VO(acac)_2$
6	**octahedral**	Werner complex, $Fe(H_2O)_6^{2+}$

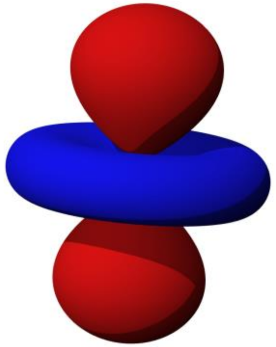
1.2.3.2 STRUCTURE – GEOMETRY – CRYSTAL FIELD THEORY

- Developed in 1930s (Bethe and van Fleck)
- Describes breaking of degeneracies of electron orbital states due to a static electric field
- Ligands are treated as point charges (NOT a bonding description)
- Negative charge on ligand and positive charge on metal create electrostatic interaction
- As ligands approach the metal, the electrons from the ligand will be closer (repulsion) to some d-orbitals than others
  - closer d-electrons have higher energy
  - Splitting affected by metal oxidation state (higher ox. state -> higher splitting), ligand (higher field higher splitting) and geometry (CN)

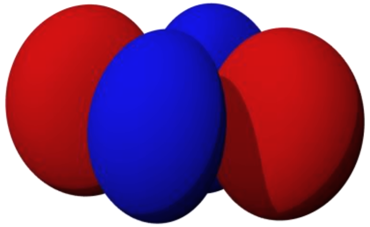
1.2.3.2 STRUCTURE – GEOMETRY – CRYSTAL FIELD THEORY



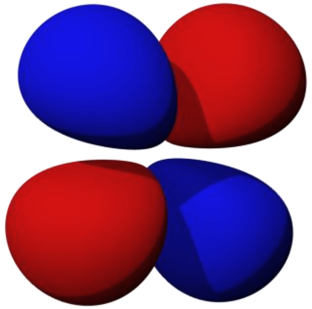
$d_{x^2-y^2}$



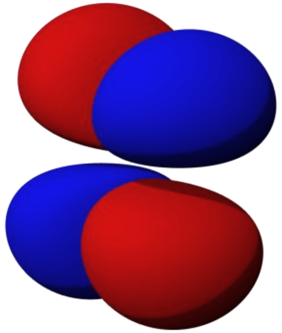
d_{z^2}



d_{xy}

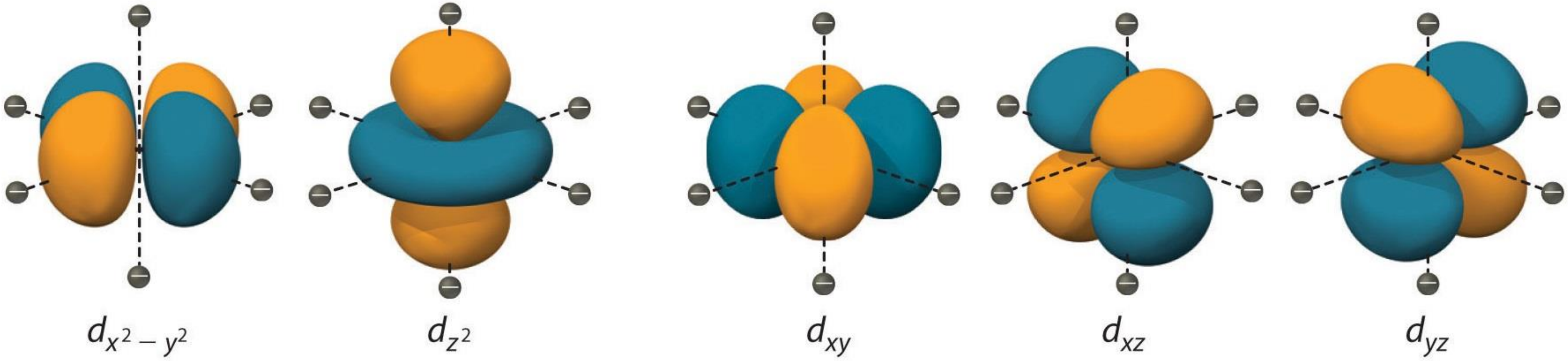


d_{xz}

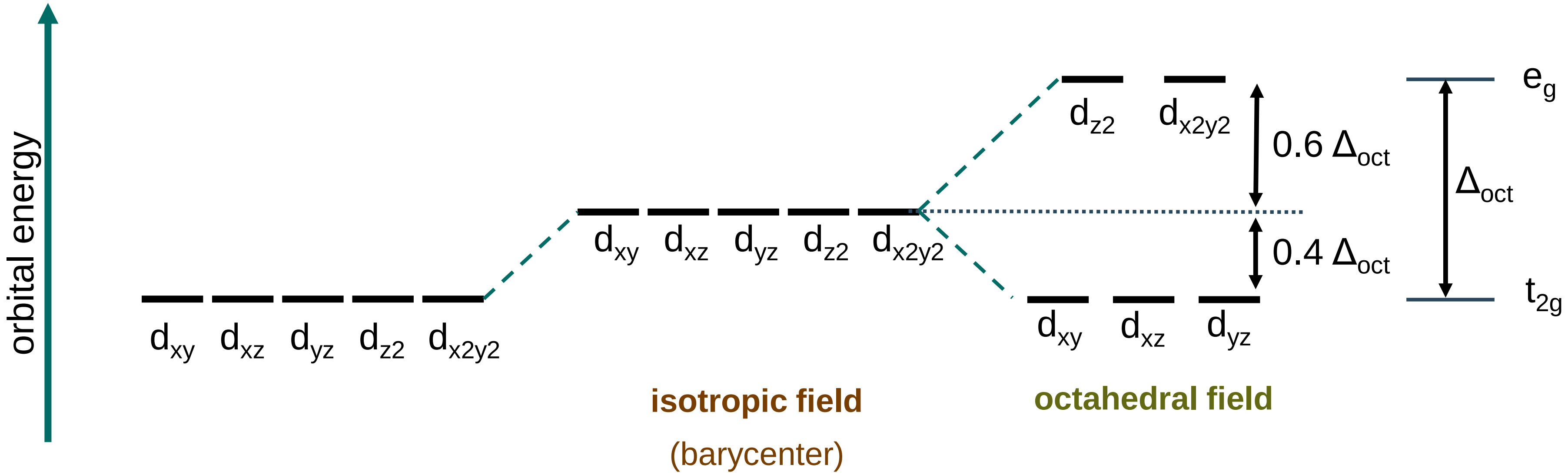


d_{yz}

1.2.3.2 STRUCTURE – GEOMETRY – OCTAHEDRAL LIGAND FIELD



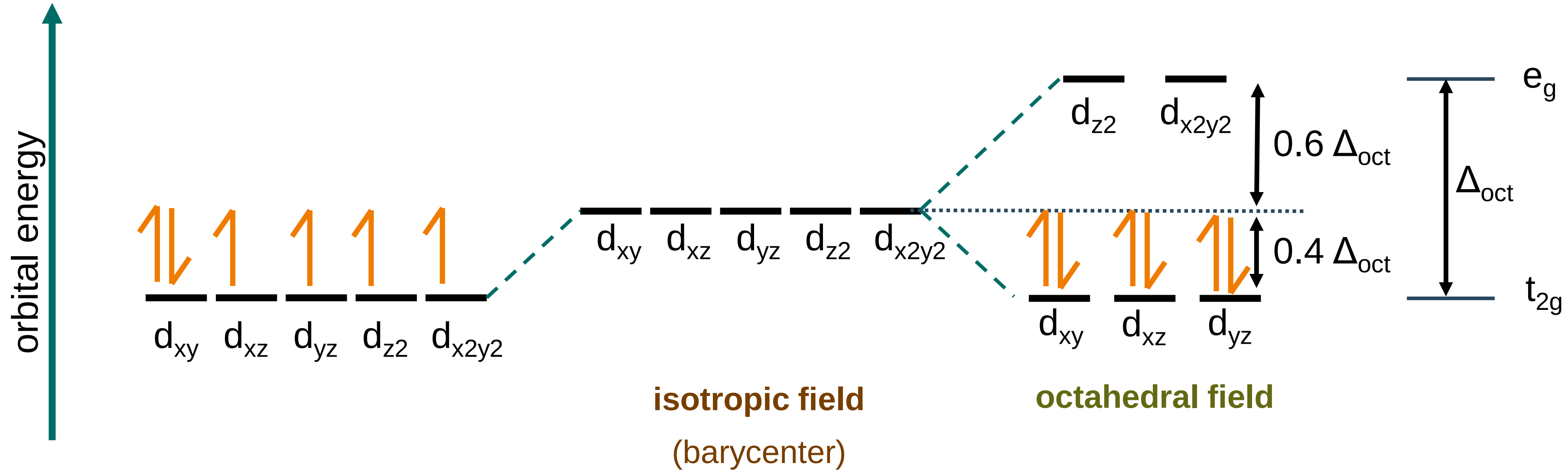
1.2.3.2 GEOMETRY – OCTAHEDRAL LIGAND FIELD



$\Delta_{oct} \approx 400 – 2500$ nm
0.5 – 3.1 eV
12 – 71 Kcal/mol

1.2.3.2 GEOMETRY – OCTAHEDRAL LIGAND FIELD

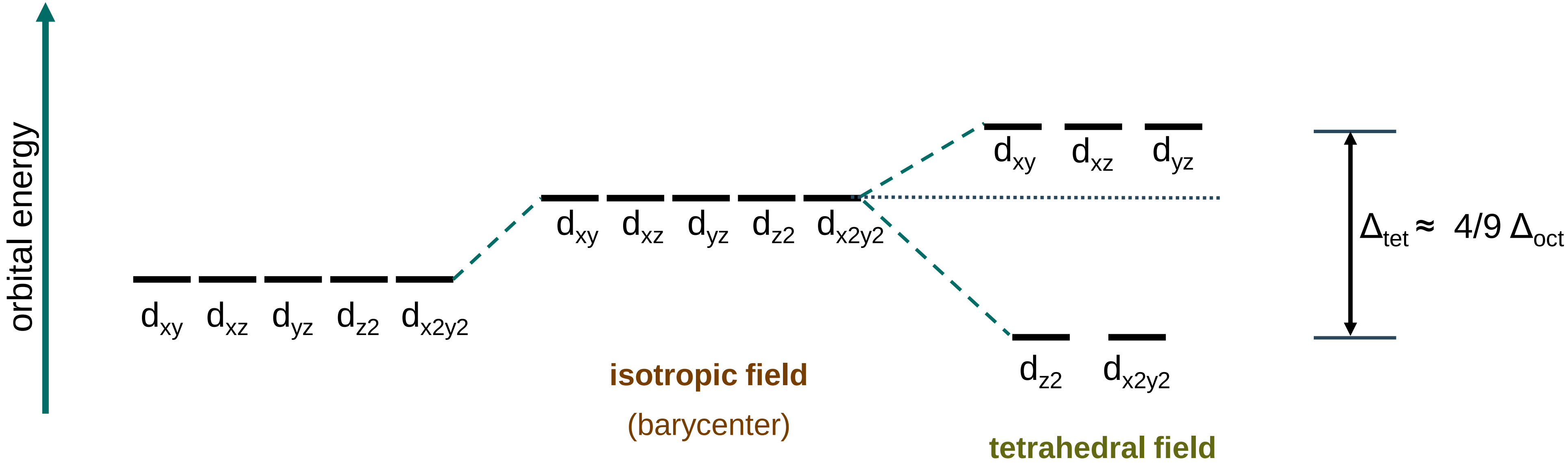
Common for d^0, d^3, d^5, d^6



1.2.3.2 GEOMETRY – TETRAHEDRAL LIGAND FIELD

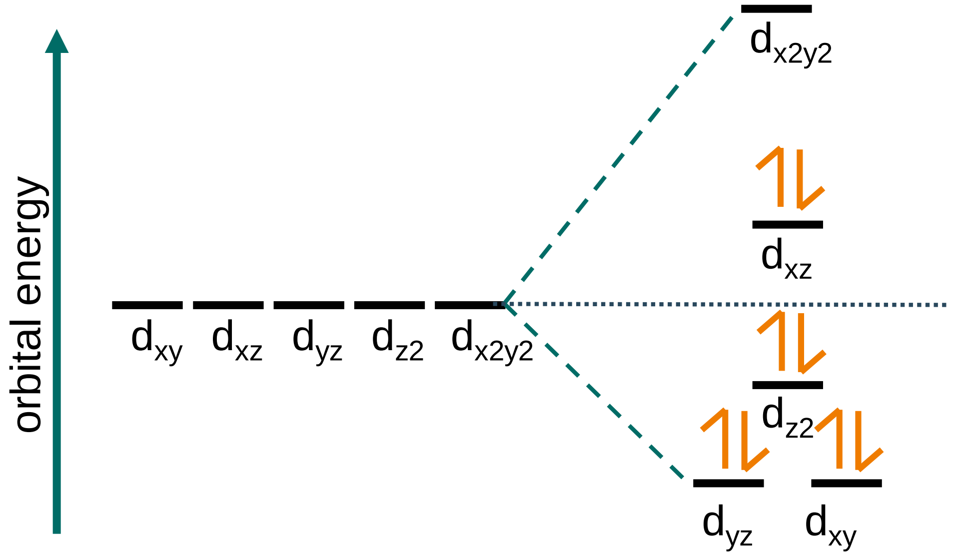
Common for d^0, d^5, d^{10}

often high spin (energy for higher orbital < energy to pair two spins)

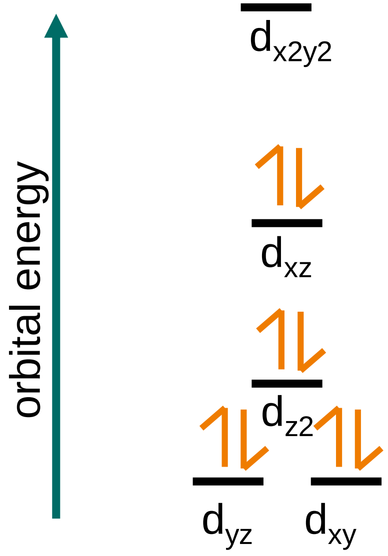


1.2.3.2 GEOMETRY – SQUARE PLANAR LIGAND FIELD

Common for d^8

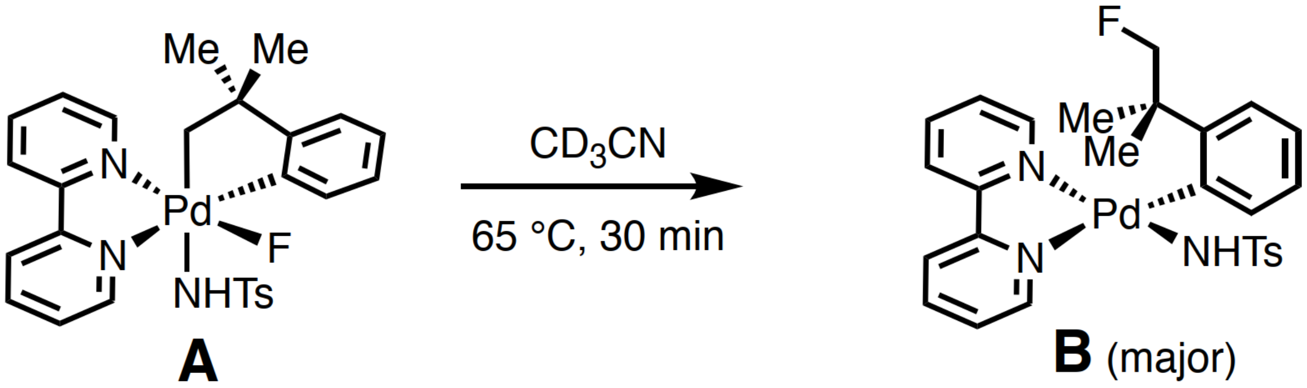


square planar field



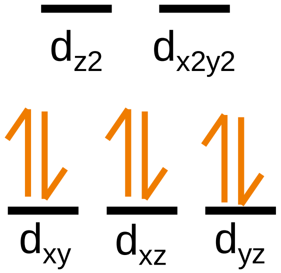
1.2.3.2 POD #1 PART B

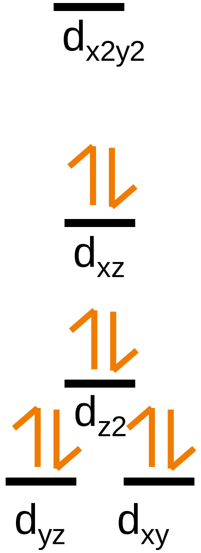
Cyclometallated palladium species A rapidly undergoes reductive elimination to give B.



A

B (major)





b. For both complexes, provide the **d-orbital diagrams predicted from CFT**.

Sanford and co-workers, *JACS,* **2014**, 136 (11), 4097. DOI: 10.1021/ja411433f

1.2.3.2 CFT – SPECTROCHEMICAL SERIES

Empirically derived trend of ligands

low-field
low Δ

$I^{-} < Br^{-} < Cl^{-} < F^{-} < H_2O < NH_3 < PPh_3 < CO < H$

high-field
high Δ

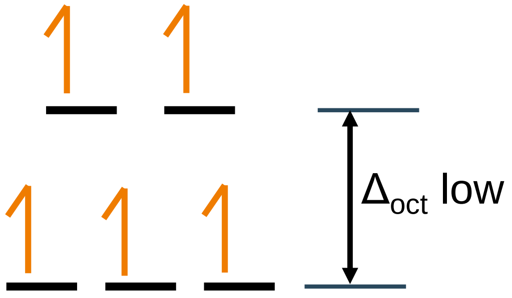
1.2.3.2 CFT – HIGH-SPIN VS. LOW-SPIN

Diamagnetic no unpaired electrons

Paramagnetic unpaired electrons

e.g. Fe^{3+}, d^5, octahedral

low spin e.g. $[Fe(NO_2)_6]^{3+}$



high spin e.g. $[FeBr_6]^{3-}$

Aufbau principle: lower energy orbitals should be completely filled before filling higher energy orbitals

Hund's rule: if two or more orbital of equal energy are available, electrons will occupy them singly before filling them in pairs

1.2.3.3 POD #3

low-field
low Δ

$I^- < Br^- < Cl^- < F^- < H_2O < NH_3 < PPh_3 < CO < H$

high-field
high Δ

Predict whether the following complexes are high or low spin:

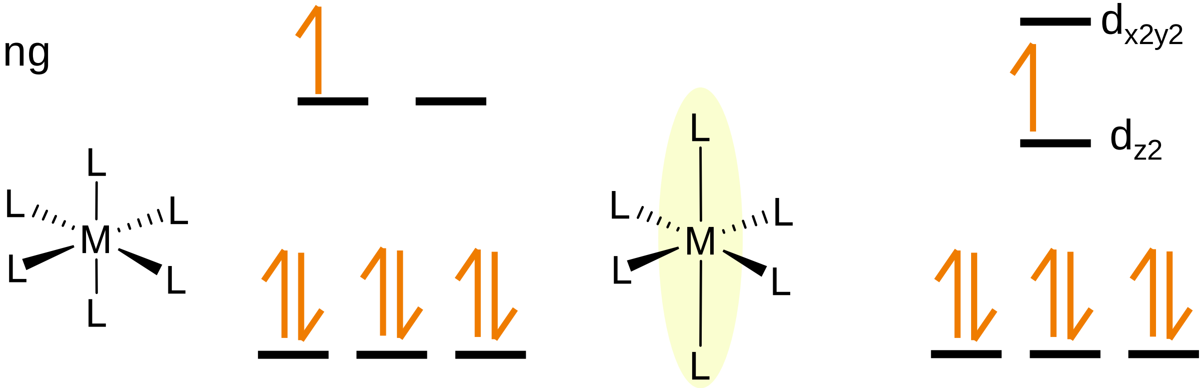
$[Co(H_2O)_6]^{3+}$	**$[CoF_6]^{3-}$**	**$[Ni(CN)_4]^{2-}$**
Co(III) d6 18e	Co(III) d6 18e	Ni(II) d8 16e
low spin	**high spin**	**low spin**

Spectrochemical series for ligands + metal nature (e.g. 1st row vs. 2nd row)

1.2.3.2 CFT – JAHN-TELLER EFFECT

Spontaneous symmetry breaking

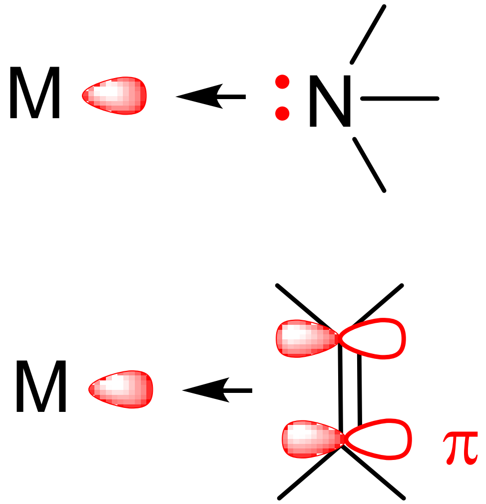
e.g. d^7 low spin

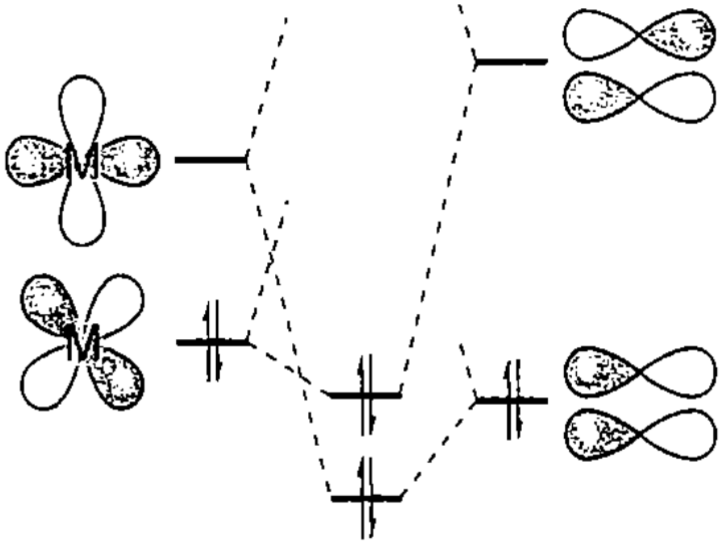


Octahedral complex with unpaired electrons given elongation of one axis -> symmetry breaking

Happens whenever a set of degenerate orbitals are unequally occupied

1.3 BONDING – SIGMA σ



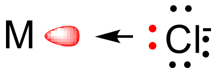


A **B**

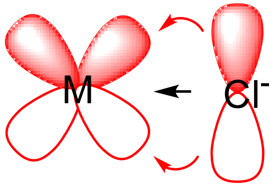
1.3 BONDING – PI π

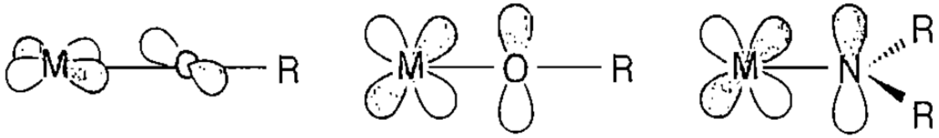
Ligand-to-metal π-bonding (“π-donating”)

σ-bonding



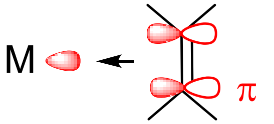
π-bonding



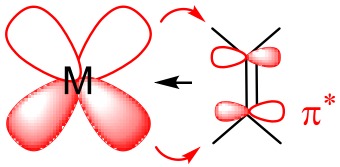


Metal-to-ligand π-bonding (“π-accepting”)

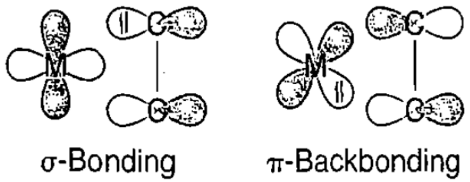
σ-bonding



π-bonding



[Dewer-Chatt-Duncanson Model]

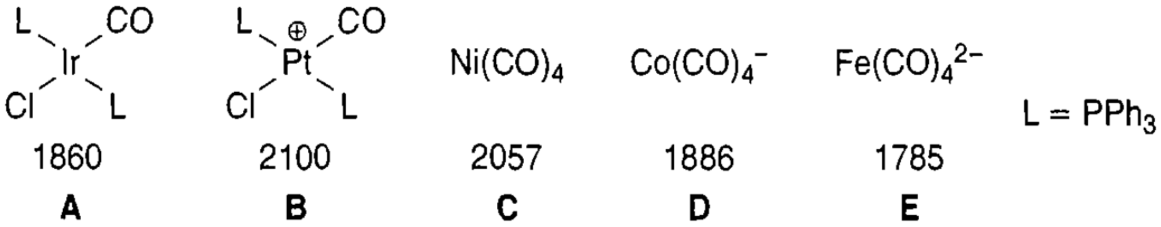


1.3 BONDING – PI π – PHOSPHINES, H_2, CO

- **Phosphines**
  sigma: LP phosphine to M **pi:** *d* M to sigma*

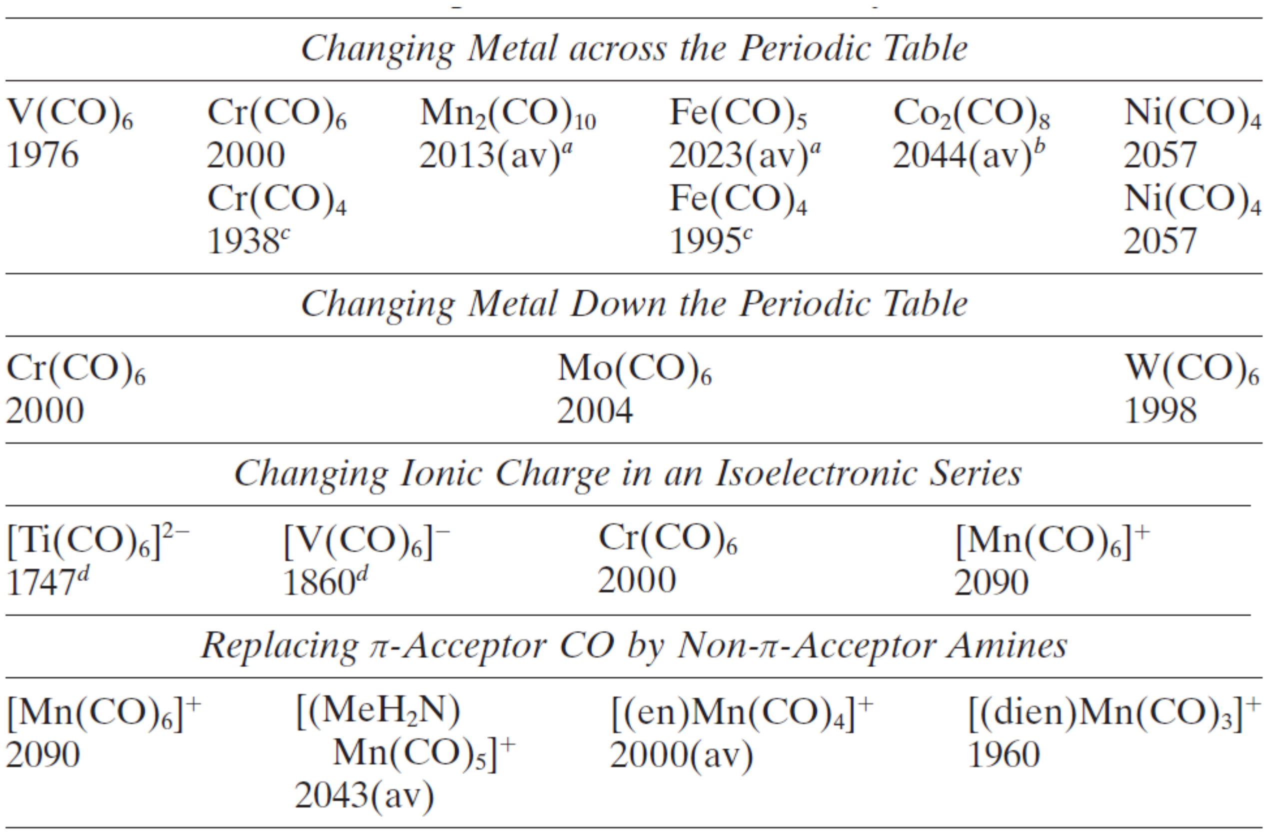
- **H_2**
  sigma: sigma H_2 bond to M **pi:** *d* M to sigma* -> H-H from 0.74Å (H_2) to 0.82-1.5Å (M-H_2)

- **CO**
  sigma: LP CO to M **pi:** *d* M to pi* -> CO from 2143 cm^{-1} to… (strong bond, 10-40 kcal/mol)



1.2.2 PERIODIC TRENDS – METAL-LIGAND BOND

Backdonation lowers ν(CO)



Changing Metal across the Periodic Table					
$V(CO)_6$ 1976	$Cr(CO)_6$ 2000 $Cr(CO)_4$ 1938[c]	$Mn_2(CO)_{10}$ 2013(av)[a]	$Fe(CO)_5$ 2023(av)[a] $Fe(CO)_4$ 1995[c]	$Co_2(CO)_8$ 2044(av)[b]	$Ni(CO)_4$ 2057 $Ni(CO)_4$ 2057
Changing Metal Down the Periodic Table					
$Cr(CO)_6$ 2000			$Mo(CO)_6$ 2004		$W(CO)_6$ 1998
Changing Ionic Charge in an Isoelectronic Series					
$[Ti(CO)_6]^{2-}$ 1747[d]	$[V(CO)_6]^{-}$ 1860[d]		$Cr(CO)_6$ 2000	$[Mn(CO)_6]^{+}$ 2090	
Replacing π-Acceptor CO by Non-π-Acceptor Amines					
$[Mn(CO)_6]^{+}$ 2090	$[(MeH_2N)Mn(CO)_5]^{+}$ 2043(av)		$[(en)Mn(CO)_4]^{+}$ 2000(av)	$[(dien)Mn(CO)_3]^{+}$ 1960	

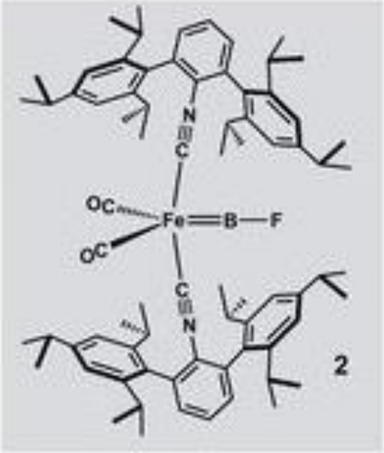
Crabtree, Table 2.10, Effect of Changing Metal, Net Ionic Charge, and Ligand Set on ν(CO) in the Infrared Spectrum of Metal Carbonyls

POD #2

CO is one of the most important ligands in organometallic chemistry. **Draw possible isoelectronic ligands.**

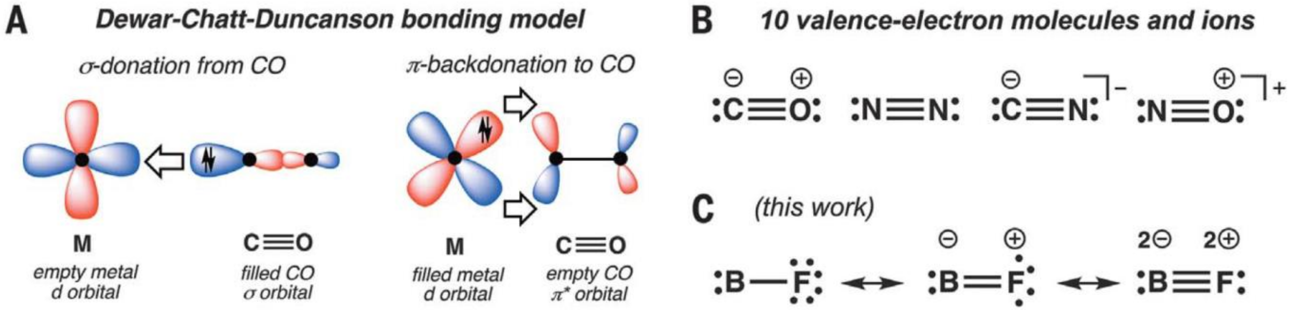
	CO,	N_2,	CN^-,	NO^+	BF
cm^{-1}	2092	2075			2056

For the ligands above, predict if their respective σ-donating and π-accepting ability, and **design an experiment** to test your prediction.



2

IR (CO), P-NMR (phosphine), direct NMR…



Figueroa and co-workers, *Science*, **2019,** 363, 1203. DOI: 10.1126/science.aaw6102

1.3 BONDING – DELTA Δ

Not encountered in the course, e.g. explains M-M quadruple bond.

Via overlap of d-orbitals.