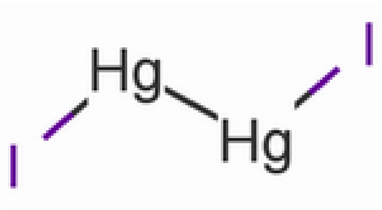
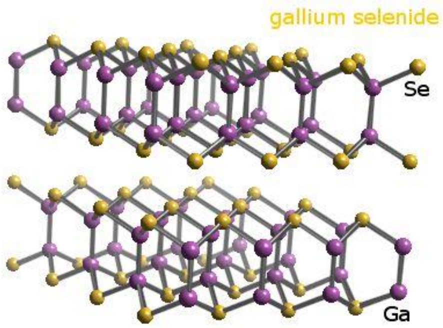
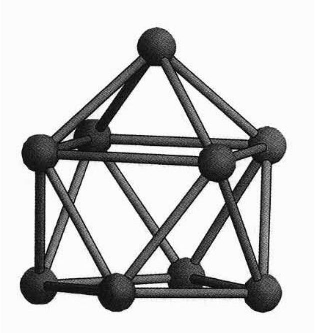
Metal-Metal Bonding

Types of Metal-Metal bonding

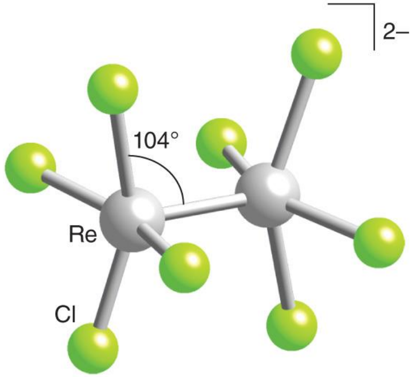


- Hg_2I_2

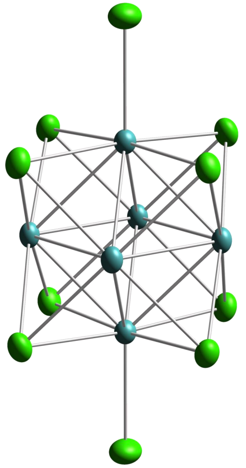




- $[Ge_9]^{4-}$ (Zintl Phases)

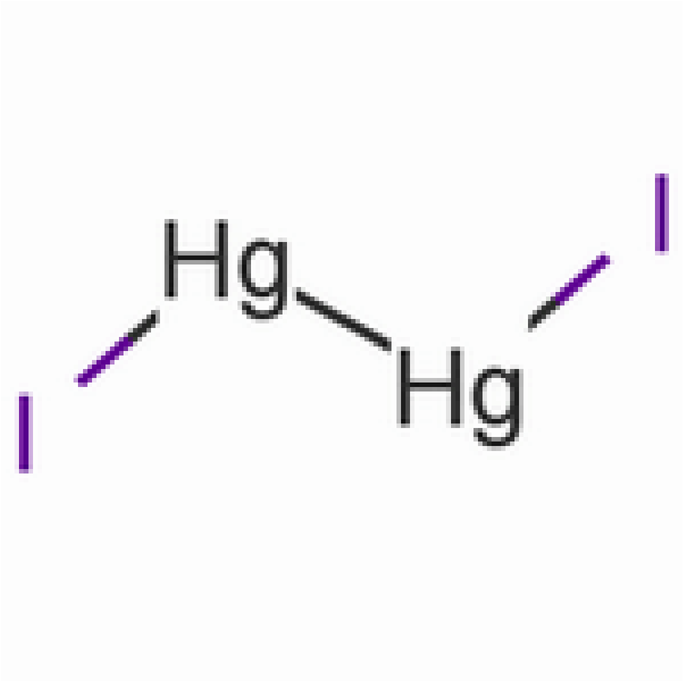


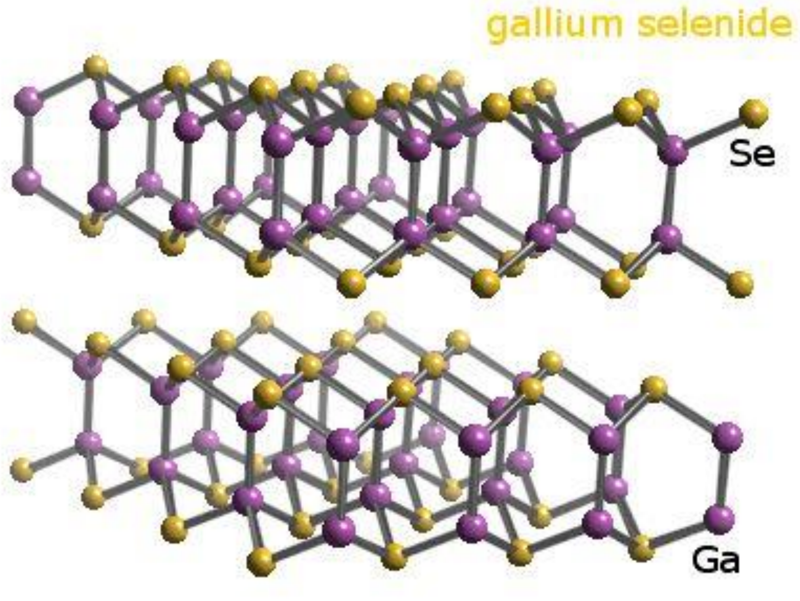
- $[Re_2Cl_8]^{2-}$ (Multiple Metal-Metal bonds)



- $[Mo_6Cl_{12}]^{2-}$ (Octahedral clusters)

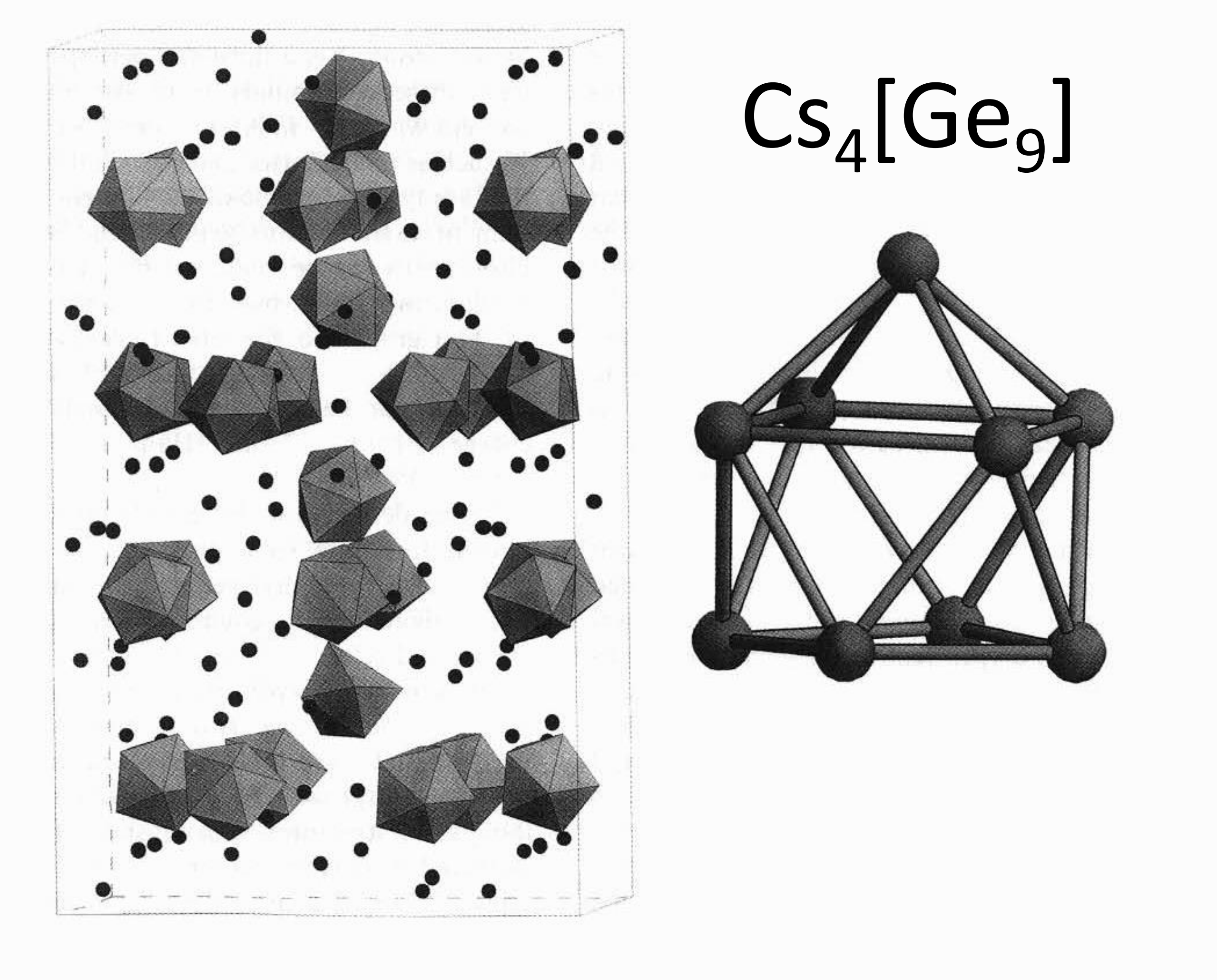
Metal-Metal bonds in p-block metals





Simple σ-bonding between the metals to completely fill the d-orbitals (d^{10})

Zintl Phases

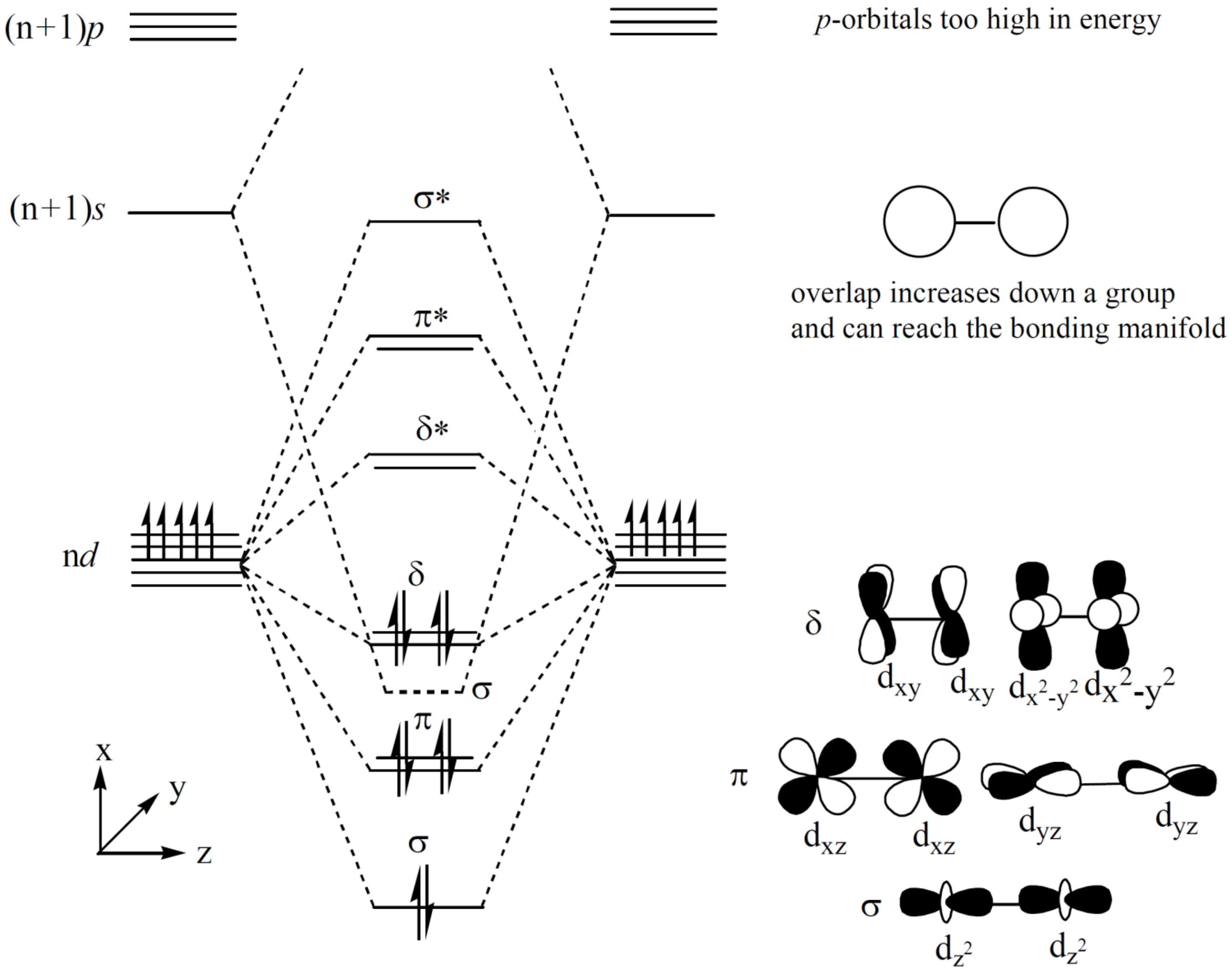


$Cs_4[Ge_9]$

Result from reduction of p-block elements with alkali metals.

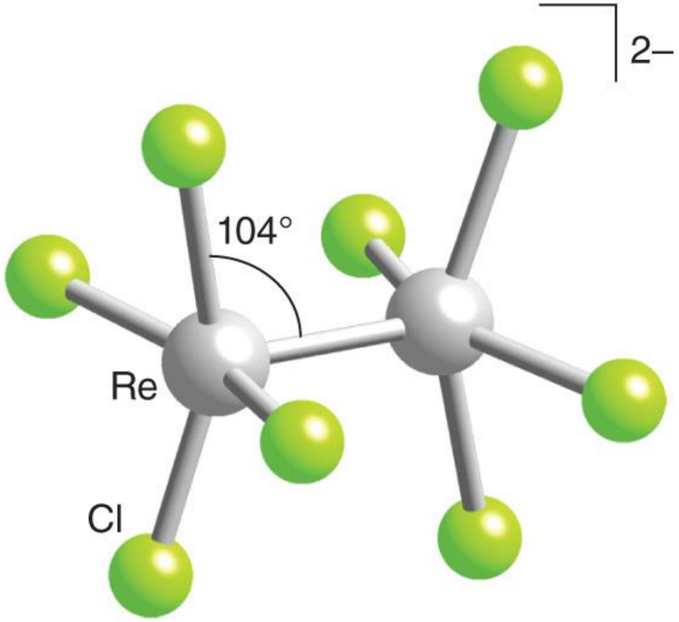
Direct donation of electrons to the conduction band of the metal

Molecular Orbitals in Metal-Metal Bonds



p-orbitals too high in energy

overlap increases down a group
and can reach the bonding manifold



18 e^-/EAN/Noble Gas (NG) Rule

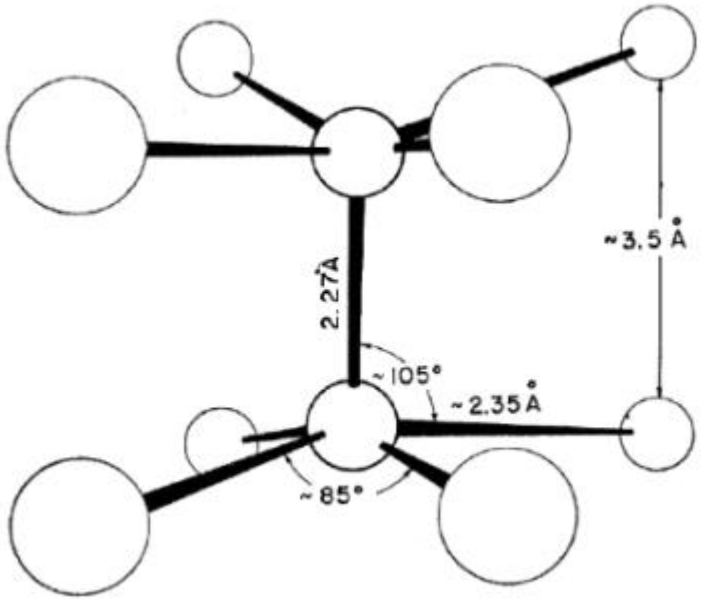
NLM—Covalent Model: Treat ligands as covalently bonded to the metal center

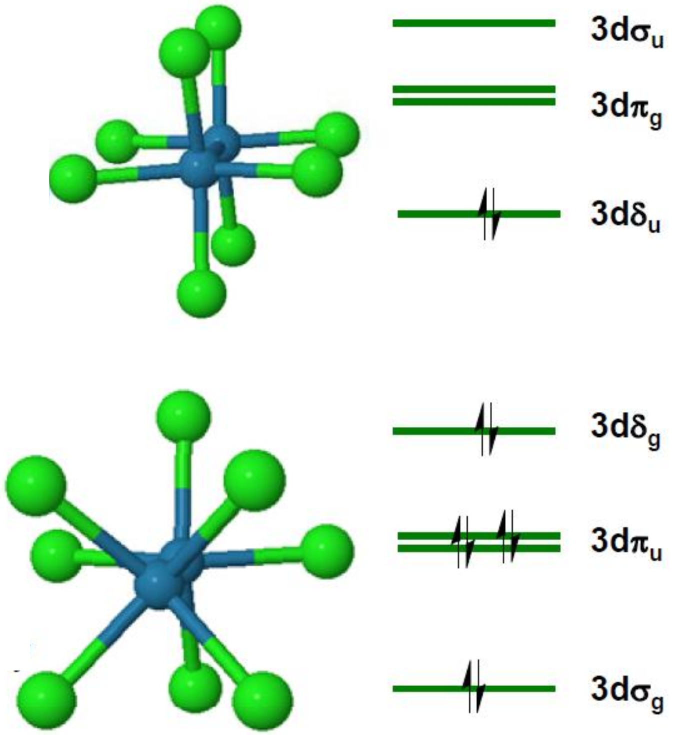
1. d e^- count of neutral metal
2. Contribution from ligands
3. For M-M bonds, add one electron
4. Possible adjustment for charge of complex

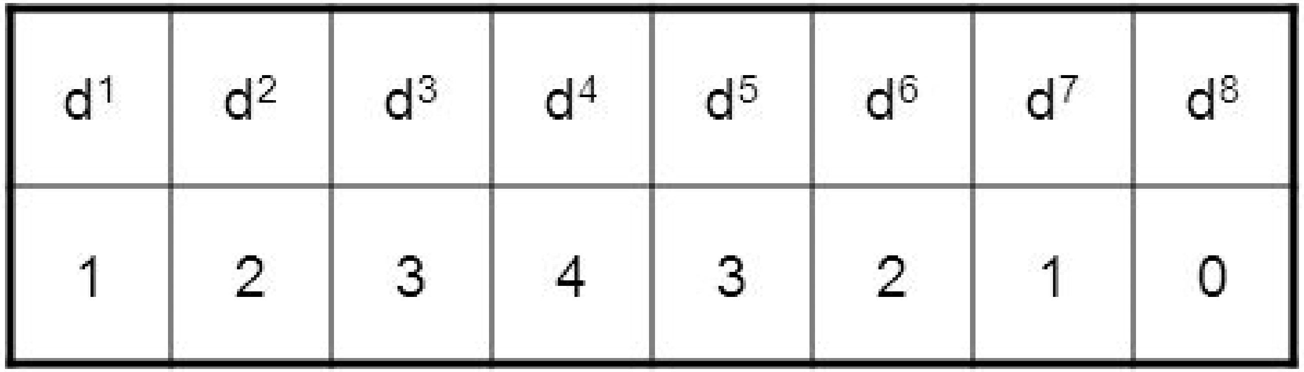
DPM—Ionic Model: Treat ligands as an ionic species and assign electrons to more electronegative atom; transition metal species may also be ionic and count its d-electrons. e.g. Mn^{2+}

Ligand	NLM	DPM
H	1	2 (H^-)
X	1	2 (X^-)
OH	1	2 (OH^-)
CO, PX_3	2	2
R	1	2 (R^-)
Cp	5	6 (Cp^-)

Bond Order in Metal-Metal Bonds







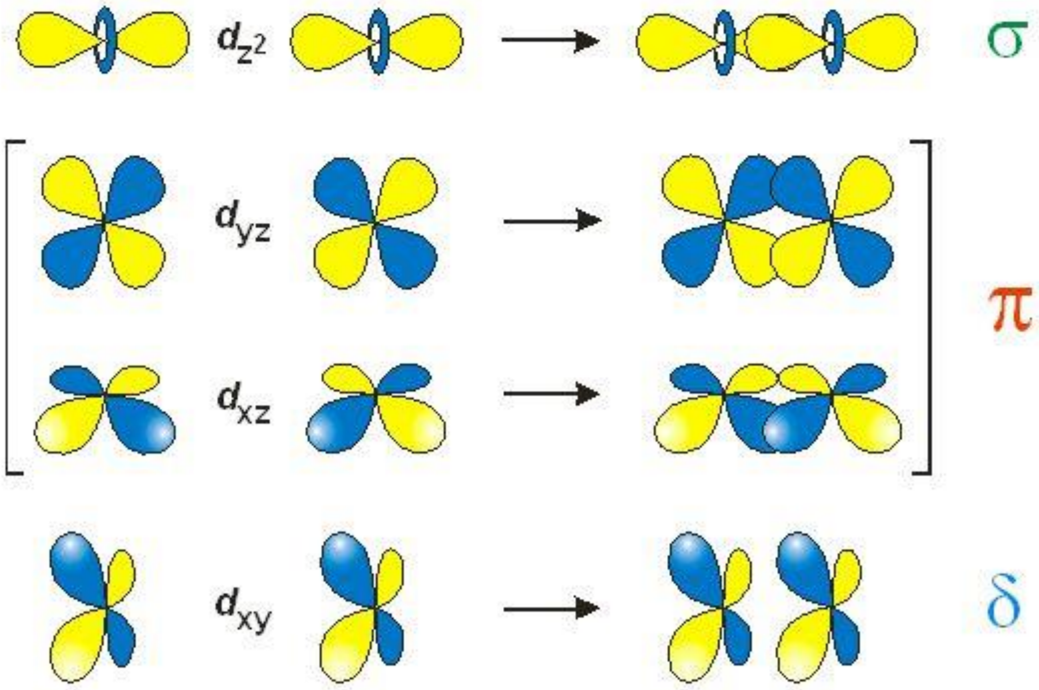
d¹	d²	d³	d⁴	d⁵	d⁶	d⁷	d⁸
1	2	3	4	3	2	1	0

Metal-Metal Bonding

Covalent: Electron precise bonds. M-M bond counts as one e- from each metal center. Most common type of M-M bonding.

Dative: Where one metal uses a filled *d* orbital "lone pair" to coordinate to an empty orbital on a second, more unsaturated metal. Most dative bonding situations can also be electron-counted as covalent bonds.

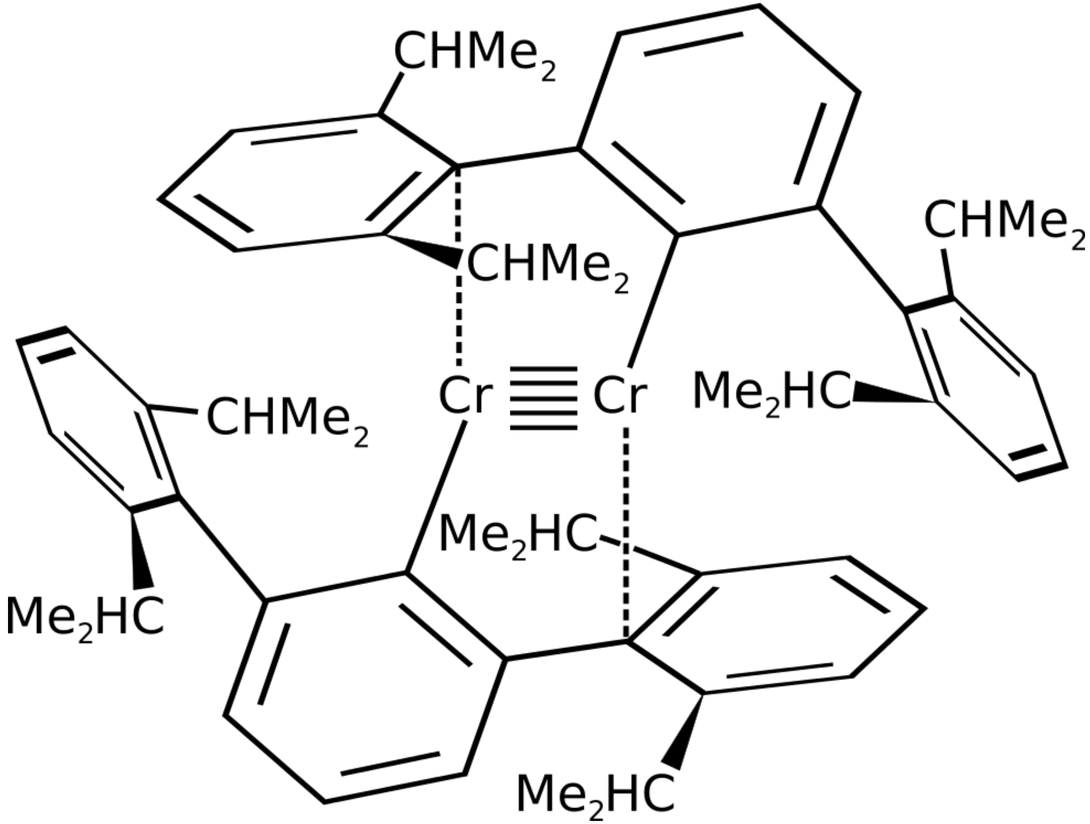
Symmetry: Weak metal-metal interactions caused by molecular orbital symmetry interactions of filled & empty M-M bonding and/or antibonding orbitals. Typically seen for d_8 metals. Not at all common.



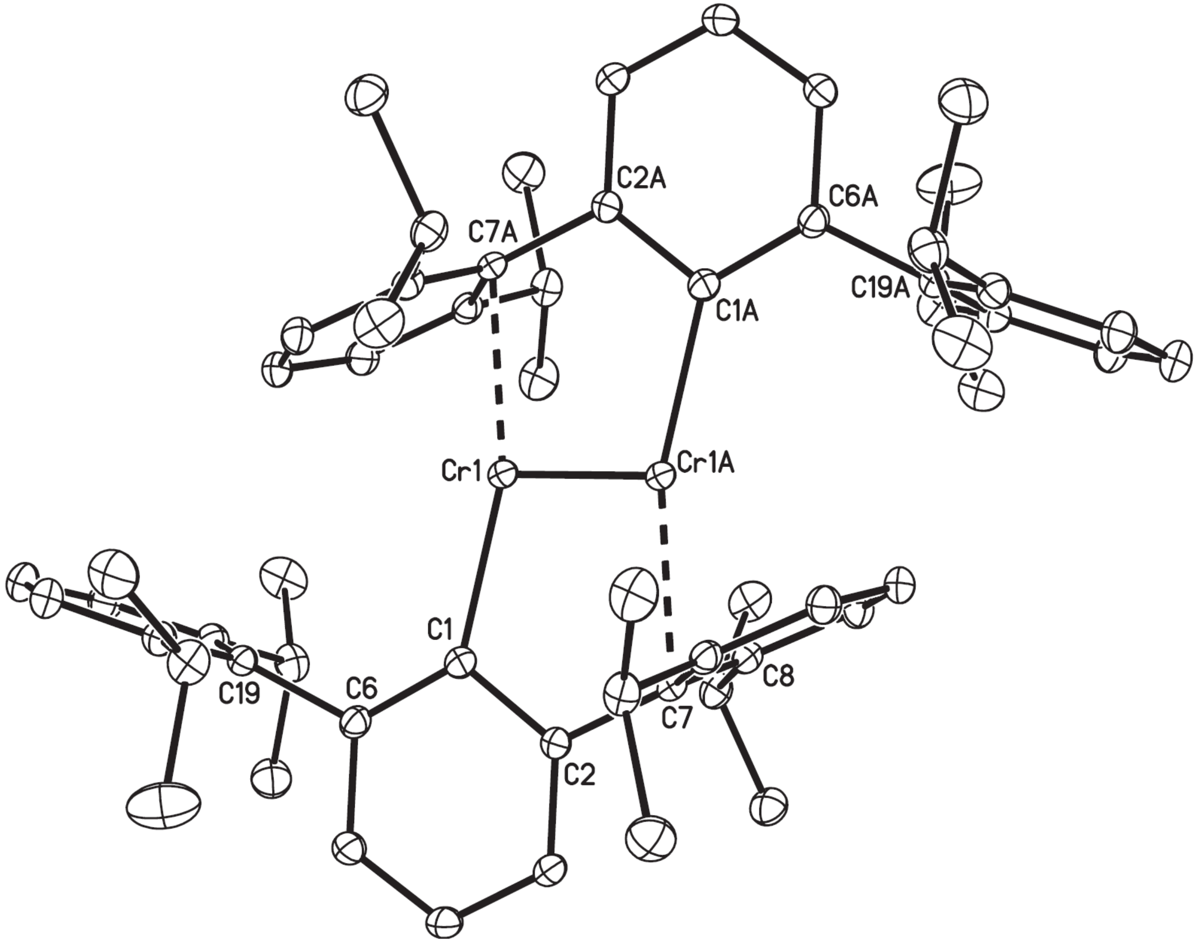
the $d_{x^2-y^2}$ orbitals (not shown) are used for M-L bonding

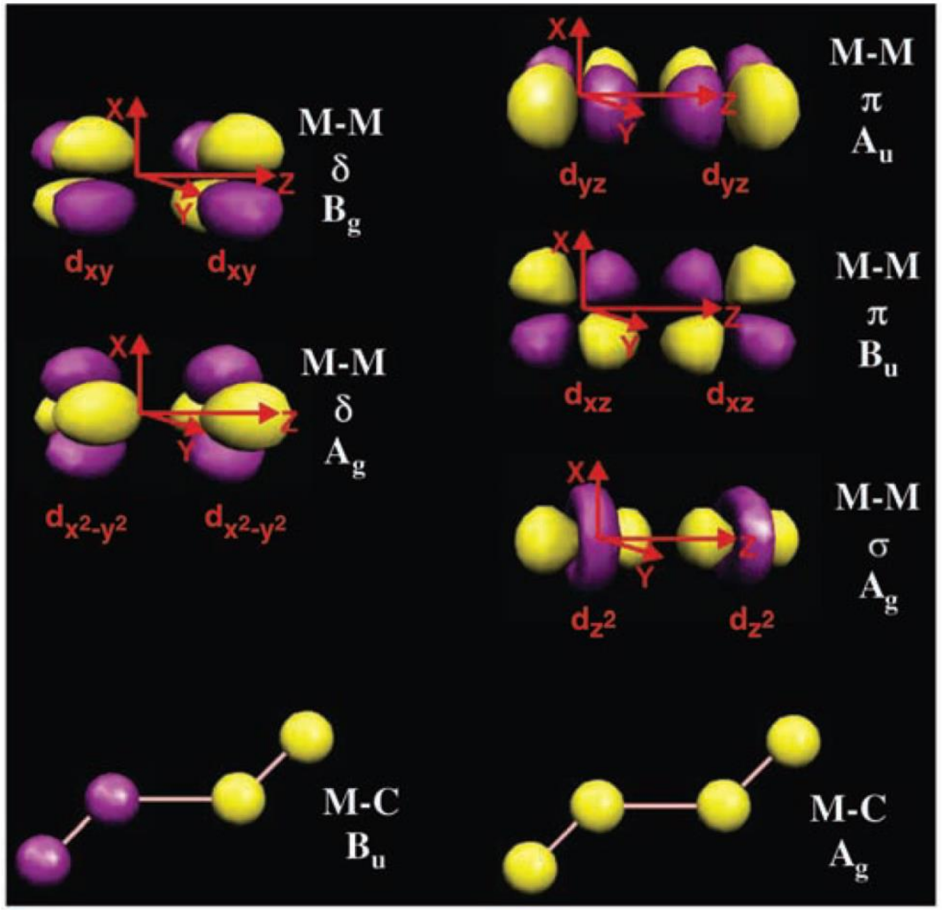
The Quintuple bond: Is this possible?

- Quintuple Metal-Metal Bonding

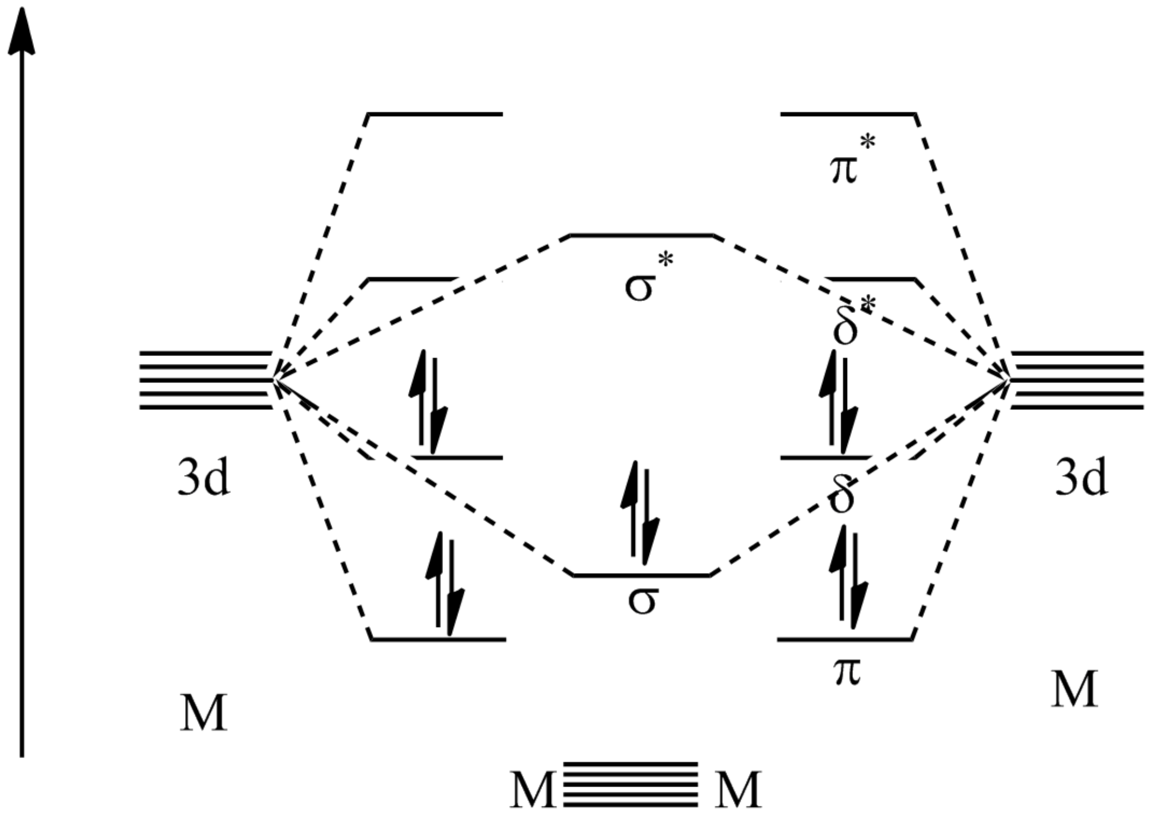


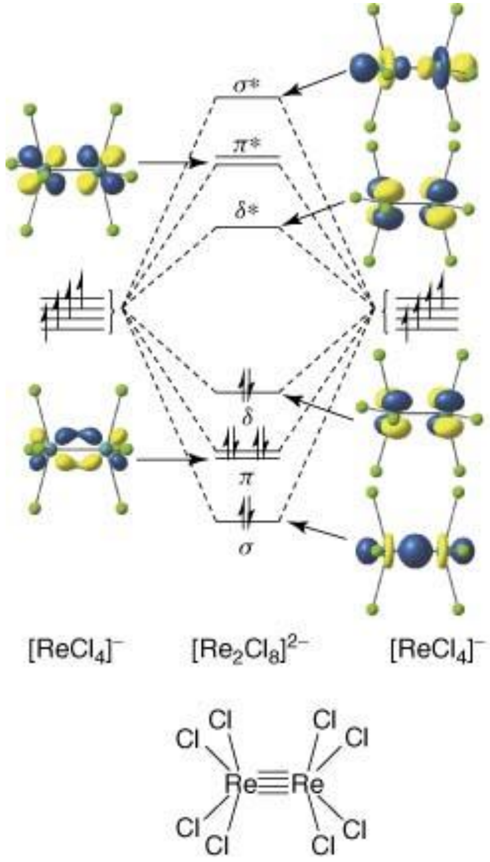
Low coordination number frees the 5th orbital

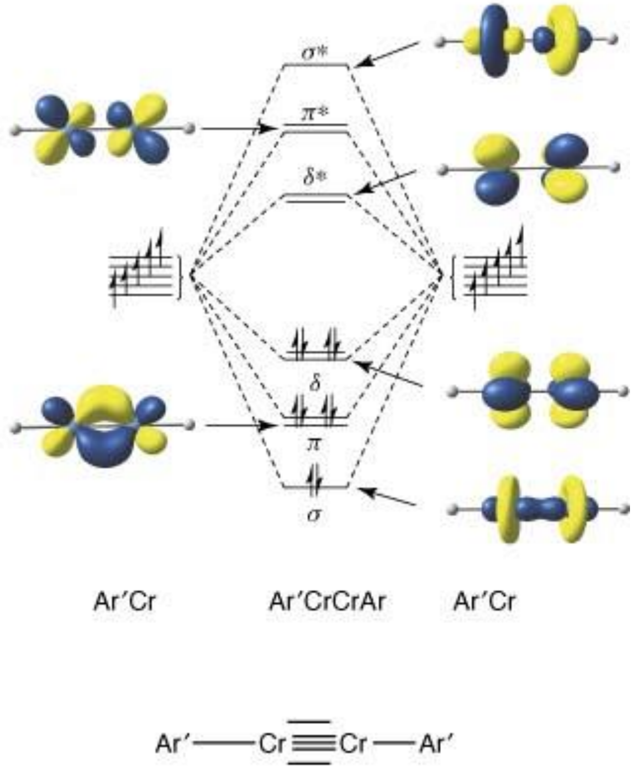




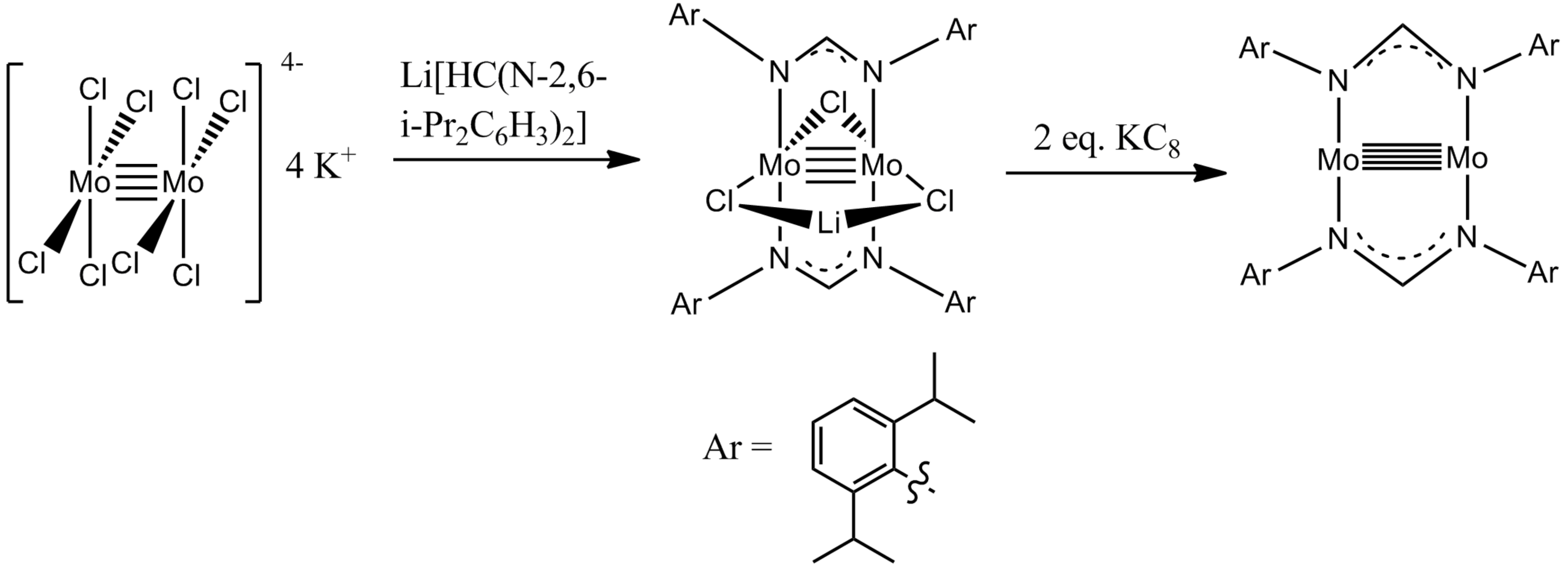
A M-ligand bond is required!



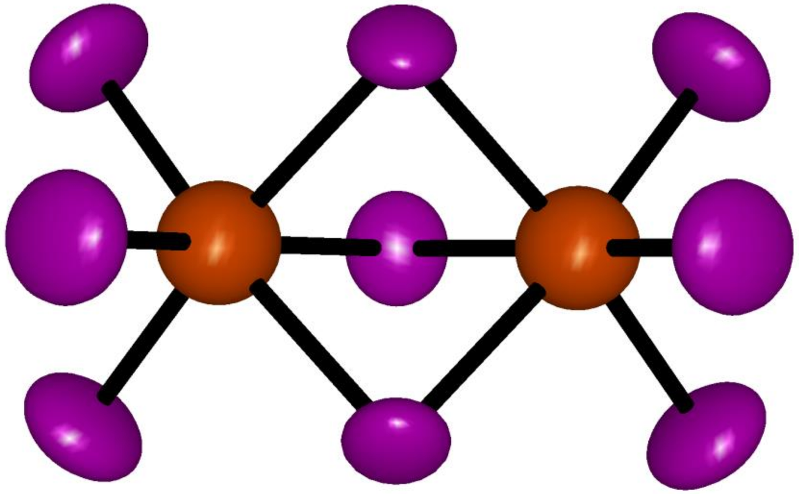




A recent example



$[M_2X_9]^{3-}$:When do we have a M-M bond?



d-orbitals increase in size Cr>Mo>W

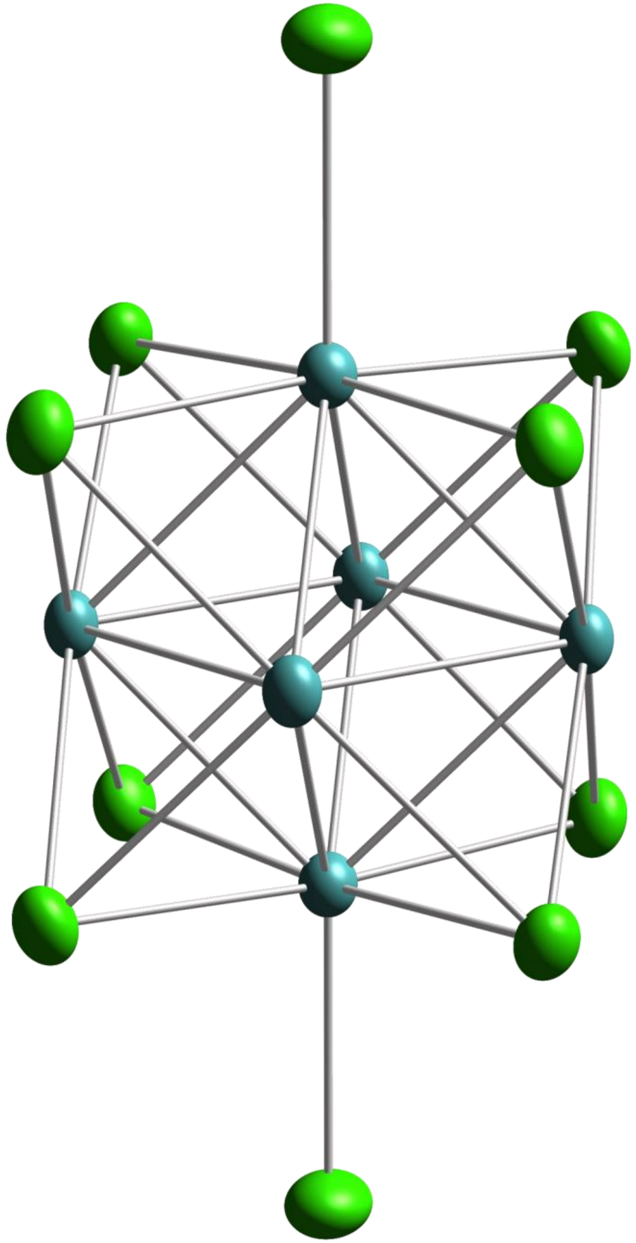
	Configuration	rM-M / pm	Magnetism	
$Cr_2Cl_9^{3-}$	$\sigma^2(\delta/\pi)^4$	310	Paramagnetic	No Cr-Cr bond because no d-orbital overlap
$Mo_2Cl_9^{3-}$	$\sigma^2(\delta/\pi)^4$	253-288	Variable	Cation dependent
$W_2Cl_9^{3-}$	$\sigma^2(\delta/\pi)^4$	242-250	Diamagnetic	Good d-orbital overlap

Metal-Metal Clusters

“$MoCl_2$” or…

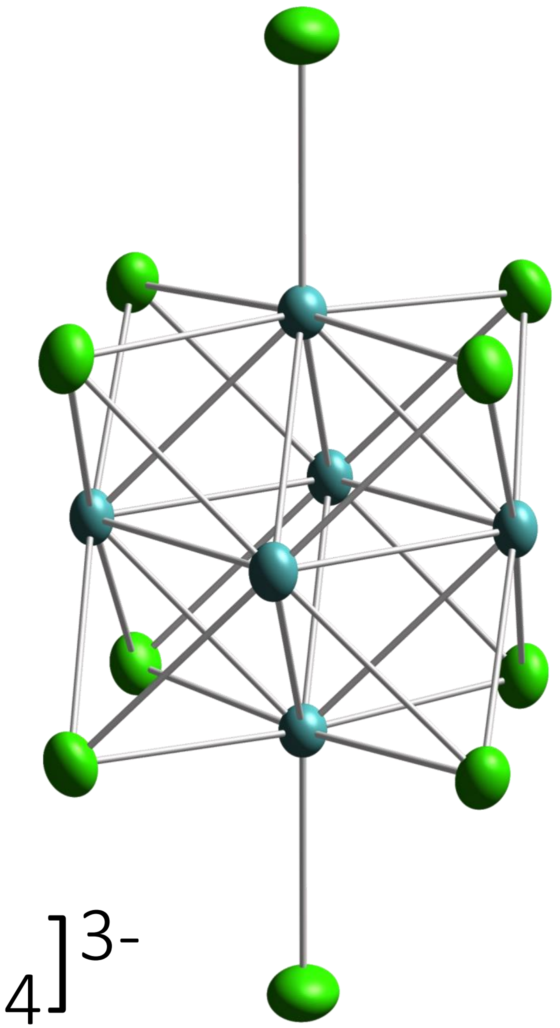
clusters based on the “$[Mo_6X_{14}]^{2-}$” building block

Termed Chevrel Phases in solid state chemistry



Exercise: Bond order in Metal-Metal Clusters

21 Sc $[Ar]3d^{1}4s^{2}$	22 Ti $[Ar]3d^{2}4s$	23 V $[Ar]3d^{3}4s^{2}$	24 Cr $[Ar]\ 3d^{5}4s^{1}$	25 Mn $[Ar]3d^{5}4s^{2}$	26 Fe $Ar]3d^{6}4s^{2}$	27 Co $[Ar]3d^{7}4s^{2}$	28 N $[Ar]3d^{8}4s^{2}$	29 Cu $[Ar]3d^{10}4s^{1}$	30 Zn $[Ar]3d^{10}4s^{2}$
39 Y $[Kr]4d^{1}5s^{2}$	40 Zr $[Kr]4d^{2}5s$	41 Nb $[Kr]4d^{3}5s^{2}$	42 Mo $[Kr]4d^{5}5s^{1}$	43 Tc $[Kr]4d^{5}5s^{2}$	44 Ru $Kr]4d^{7}5s^{1}$	45 Rh $[Kr]4d^{8}5s^{1}$	46 Pd $[Kr]4d^{10}$	47 Ag $[Kr]4d^{10}5s^{1}$	48 Cd $[Kr]4d^{10}5s^{2}$
57 La $[Xe]6s^{2}5d^{1}$	72 Hf $[Xe]5d^{2}6s$	73 Ta $[Xe]5d^{3}6s^{2}$	74 W $[Xe]5d^{4}6s^{2}$	75 Re $[Xe]5d^{5}6s^{2}$	76 Os $e]5d^{6}6s^{2}$	77 Ir $[Xe]5d^{7}6s^{2}$	78 Pt $[Xe]5d^{9}6s^{1}$	79 Au $[Xe]5d^{10}6s^{1}$	80 Hg $[Xe]5d^{10}6s^{2}$



$[Mo_6X_{14}]^{2-}$, $[Nb_6X_{12}]^{2+}$, $[Ta_6X_{14}]^{4-}$, $[Tc_6X_{14}]^{3-}$

Application of Inorganic Compounds: Catalysis!

Reaction	Core Metals	Catalyst	Reference
Alkene hydroformylation	Mo-Rh	$Mo_2RhCp_3(CO)_5$	[32]
Alkene hydroformylation	Rh	$Rh_4(CO)_{10+x}(PPh_3)_{2-x}$ (x=0,2)	[33]
CO hydrogenation	Ru-Os	$H_2RuOs_3(CO)_{13}$	[32]
CO hydrogenation	Ru-Co	$RuCo_2(CO)_{11}$	[32]
CO hydrogenation	Ir	$Ir_4(CO)_{12}$	[31][33][34]
CO hydrogenation	Fe	$Fe_3(CO)_{12}$	[35]
Alkene hydrogenation	Os-Ni	$H_3Os_3NiCp(CO)_9$	[32]
Alkene hydrogenation	Ni	$Ni_{2+x}Cp_{2+x}(CO)_2$ (x=0,1)	[33]
Alkyne hydrogenation	Os-Ni	$Os_3Ni_3Cp_3(CO)_9$	[32]
Hydrogenation of aromatics	Ni	$Ni_{2+x}Cp_{2+x}(CO)_2$ (x=0,1)	[33]
Acetaldehyde hydrogenation	Ni	$Ni_4(Me_3CNC)_7$	[33]
Alkene isomerization	V-Cr	$VCrCp_3(CO)_3$	[32]
Hydrocarbon isomerization	Fe-Pt	$Fe_2Pt(CO)_6(NO)_2(Me_3CNC)_2$	[32]
Butane hydrogenolysis	Rh-Ir	$Rh_{3+x}Ir_{3-x}(CO)_{16}$ (x=0,1,2)	[32]
Methanol hydrocarbonylation	Ru-Co	$Ru_2Co_2(CO)_{13}$	[32]
Hydrodesulfurization	Mo-Fe	$Mo_2Fe_2S_2Cp_2(CO)_8$	[32]
CO and CO_2 methanation	Ru-Co	$HRuCo_3(CO)_{12}$	[32]
Ammonia synthesis	Ru-Ni	$H_3Ru_3NiCp(CO)_9$	[32]

From Wikipedia