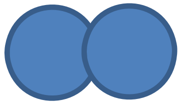
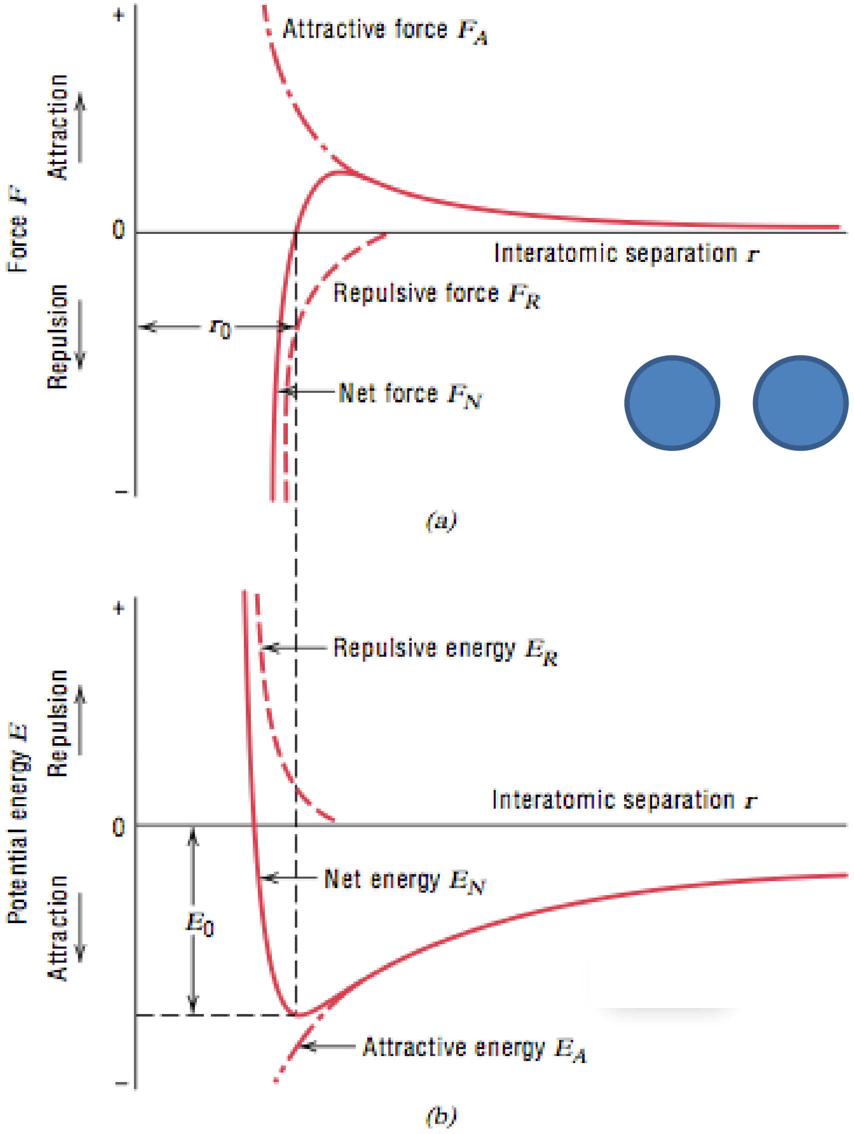
Bonding

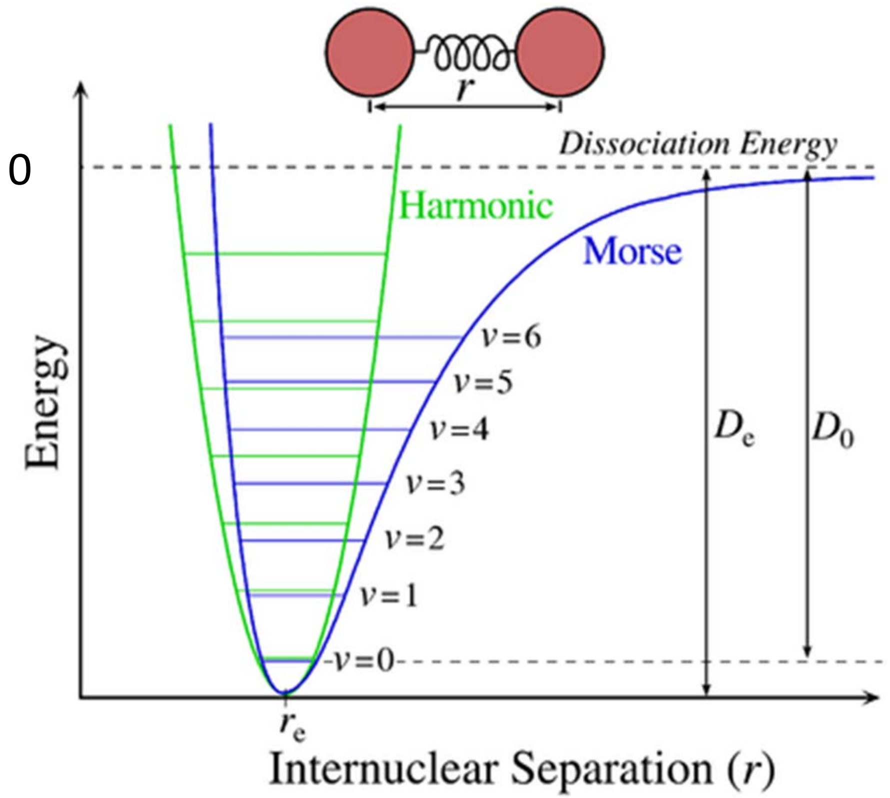
Potential Energy of a Bond





Stretching vibration

Bond Length and Temperature



Experimental Mo≡Mo bond distance:
at room temp. 2.23 Å, at LN2 t. 2.18 Å

Harmonic oscillator in quantum mechanics
Quantized vibrational energies
$E^n = (v + \frac{1}{2})h\nu$

Morse - Potential energy curve for a diatomic molecule

D_0 = bond dissociation energy

The ground-state energy is not 0

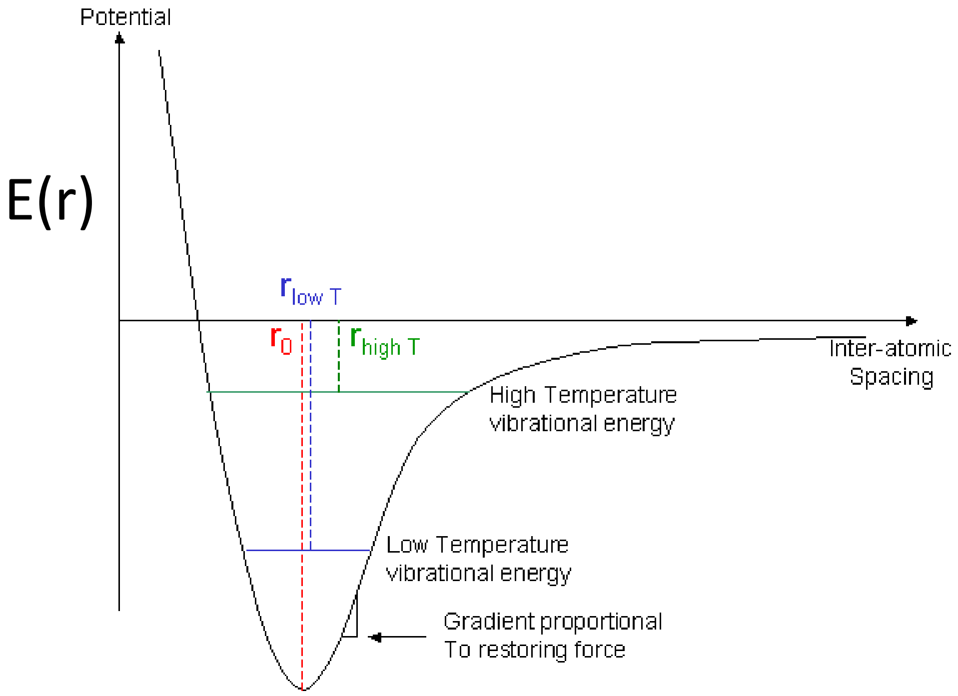
$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Bond	wavenumber cm^{-1}
C–H	3000
C–D	2200

The C–H bond is a stronger spring
The C–D bond has lower zero-point energy
Force constant *k* does not change with isotopic H/D substitution

Bond Length and Temperature

$$E(r) = D_e(1 - e^{a(r-r_e)})^2$$



$E^n = (v + ½)h\nu$

Potential energy curve is not parabolic (harmonic) but unsymmetrical

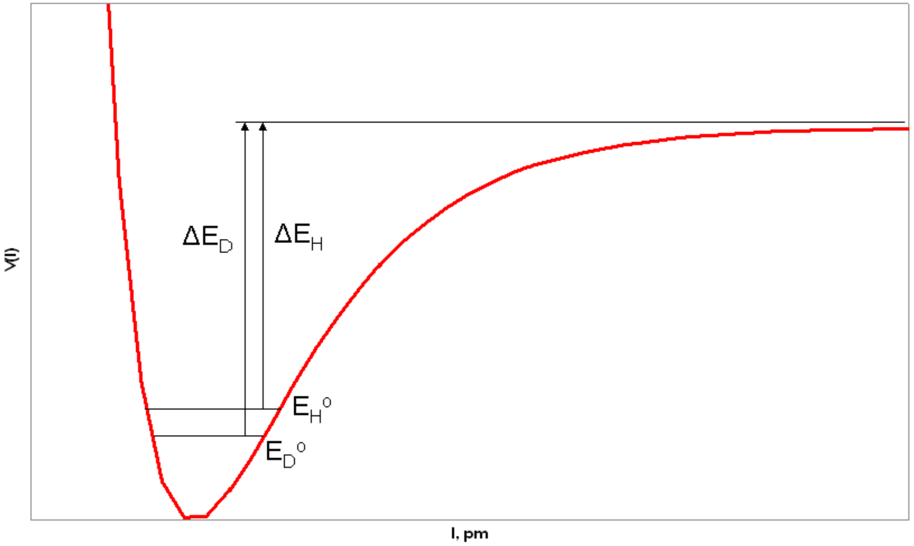
99.9 % of C–H bonds are in the ground vibrational state (v = 0) at room temperature

At high temperature, more high vibronic states are populated

Middle points move towards longer r

Bond Length and Isotopes

Is the C–H bond longer or shorter than the C–D bond?



A Morse potential curve

The zero point vibrational energy (ZPE) is the lowest possible energy of a system, the ground state energy.

E_D^o and E_H^o (for v = 0)

the ZPE of R–H and R–D (R is much heavier than H or D) depend upon the reduced mass of the molecule.

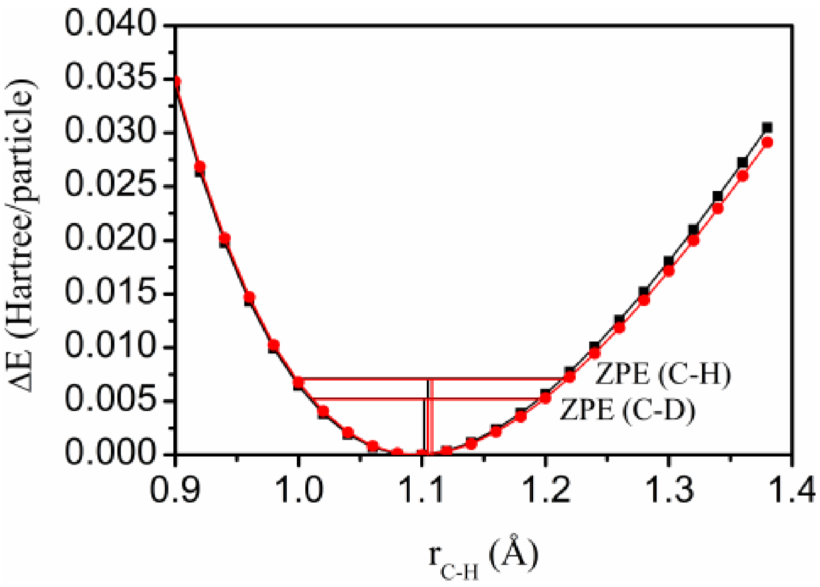
The **heavier** the molecule or atom, the **lower** the frequency of vibration and the **smaller** ZPE.

Lighter molecules or atoms have a **greater** frequency of vibration and a **higher** ZPE.

Deuterium is **heavier** than hydrogen and therefore has the **lower** zero point energy.

Bond Length and Isotopes

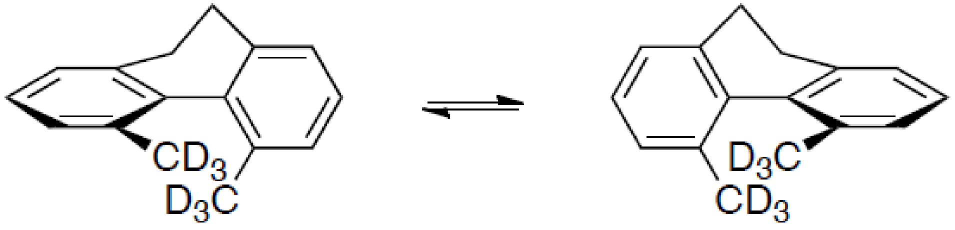
Is the C–H bond longer or shorter than the C–D bond?



Due to the anharmonicity of the C–H/C–D vibrational potential energy function and the lower ZPE of a C–D bond

the average C–D bond length is typically ~0.005 Å **shorter** than an equivalent C–H bond.

Secondary Isotope Effect - Steric effect of a CD_3 group **smaller** than CH_3.

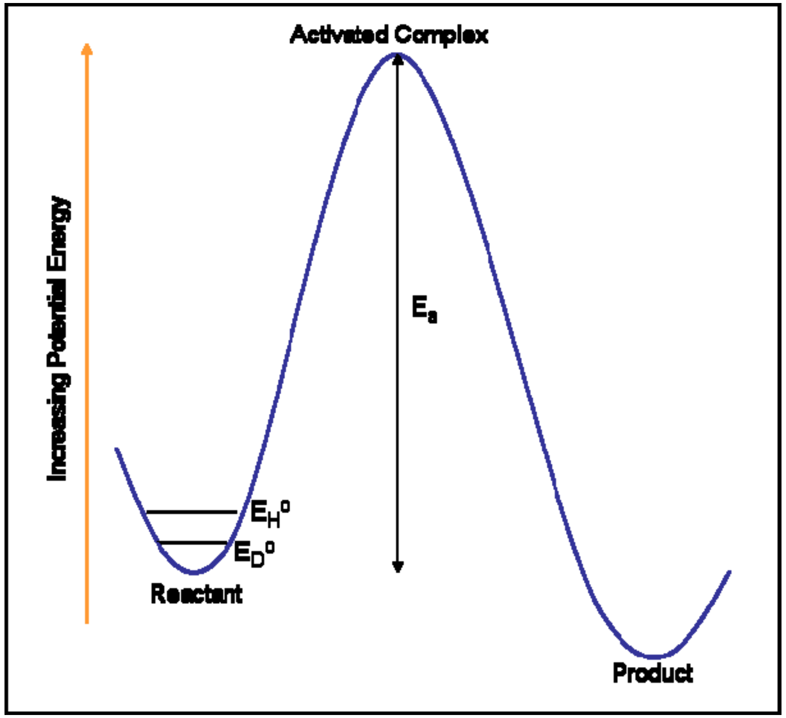


$k_H/k_D = 0.86$

Kinetic Isotope Effects

The **kinetic** isotope effect (KIE) = isotopically substituted molecules exhibit different reaction rates, the change in rate of a reaction due to isotopic substitution.
An isotopic substitution **does not influence the electronic** potential energy surface.

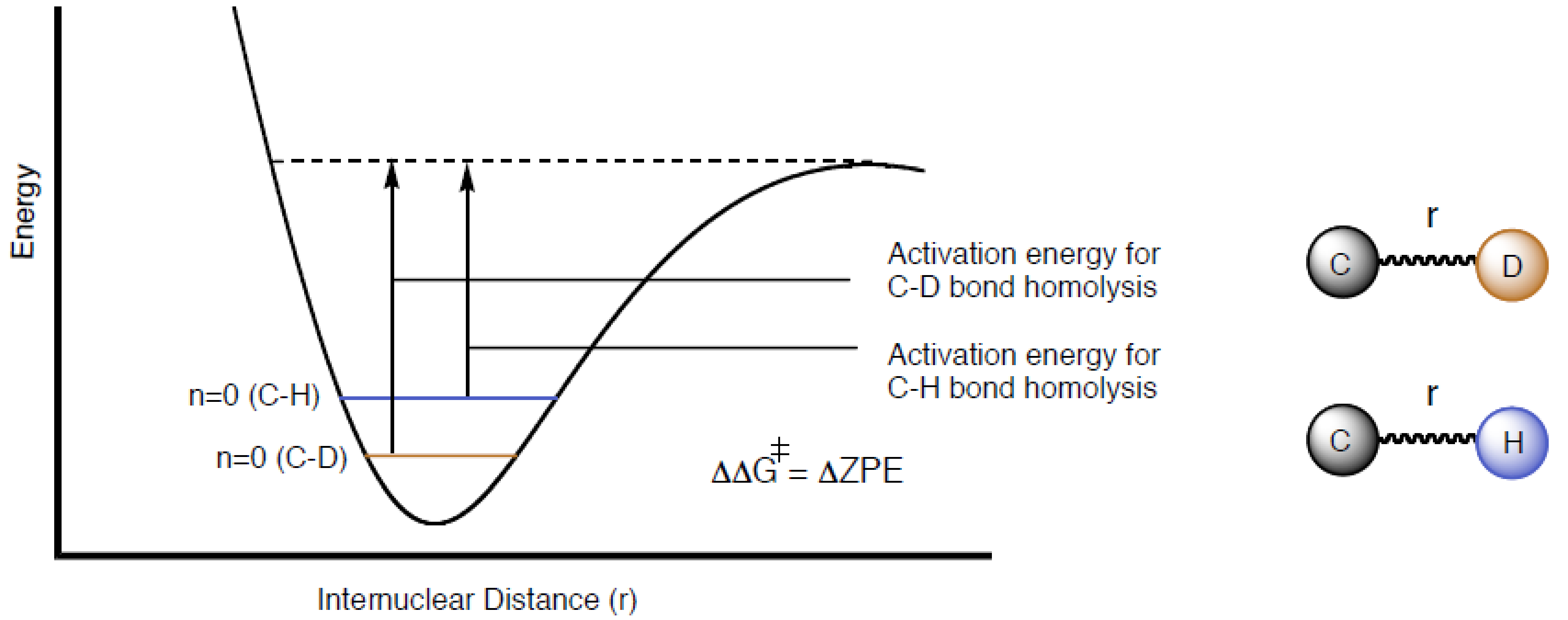
hydrogen (^1H) - deuterium (^2H) - tritium (^3H)
carbon (^{12}C , ^{13}C), nitrogen (^{14}N, ^{15}N), oxygen (^{16}O, ^{18}O), chlorine (^{35}Cl, ^{37}Cl)



Different bond dissociation energies for R–D and R–H: E_D is greater than E_H
This difference in energy due to isotopic replacement results in differing rates of reaction *k* – the rate determining step

The effect is measured in kinetic isotope effects:
The reaction rate for the conversion of R–D is slower than the reaction rate for the conversion of R–H.

Kinetic Isotope Effects



Different bond dissociation energies for C–D and C–H:
E_D is greater than E_H - differing rates of reaction *k* – the rate determining step

The kinetic isotope effects:
The reaction rate for the conversion of **C–D** is **slower** than the reaction rate for the conversion of C–H

Kinetic Isotope Effects

Isotope replacement does not change the electronic structure of the molecule or the potential energy surfaces of the reactions

The greater the mass the more energy is needed to break bonds. A **heavier** isotope forms a **stronger bond** - less of a tendency to dissociate. The increase in energy needed to break the bond results in a **slower reaction** rate and the observed isotope effect:

the ratio k_H/k_D = 1 to 7

Heavy atom isotope effects = the substitution of carbon, oxygen, nitrogen, sulfur, and bromine, with effects that are much smaller and are usually between 1.02 and 1.10. The maximum isotopic rate ratio is proportional to the square root of the inverse ratio of isotopic masses.

Secondary kinetic isotope effects = rate changes due to isotopic substitutions at a site other than the bond breaking site in the rate determining step of the reaction, α , β , and γ effects

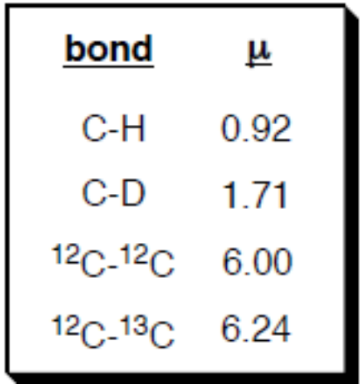
Kinetic Isotope Effects

Harmonic oscilator frequency
Bond stretching frquency

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$



bond	µ
C-H	0.92
C-D	1.71
^{12}C-^{12}C	6.00
^{12}C-^{13}C	6.24

Zero point energy

$$E^0 = \frac{1}{2}h\nu$$

Reaction rate

$$k = Ae^{-\frac{E^0}{kT}}$$

Isotope effect

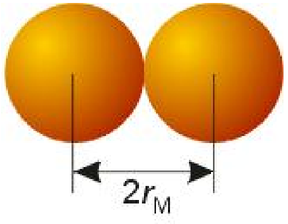
$$\frac{k_H}{k_D} = e^{\frac{h(\nu_D - \nu_H)}{2kT}}$$

Pauling’s Rules

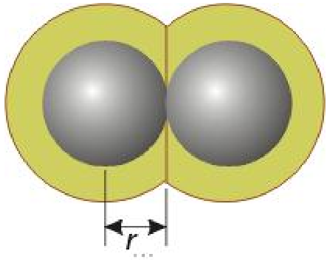
Five principles which could be used to determine the structures of complex ionic/covalent crystals

Pauling’s Rule no. 1 Coordination Polyhedra

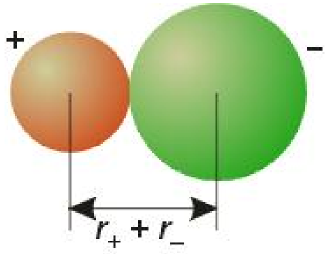
A coordinated polyhedron of anions is formed about each cation.
Cation-Anion distance is determined by sums of ionic radii.
Cation coordination environment is determined by radius ratio.



1 Metallic radius



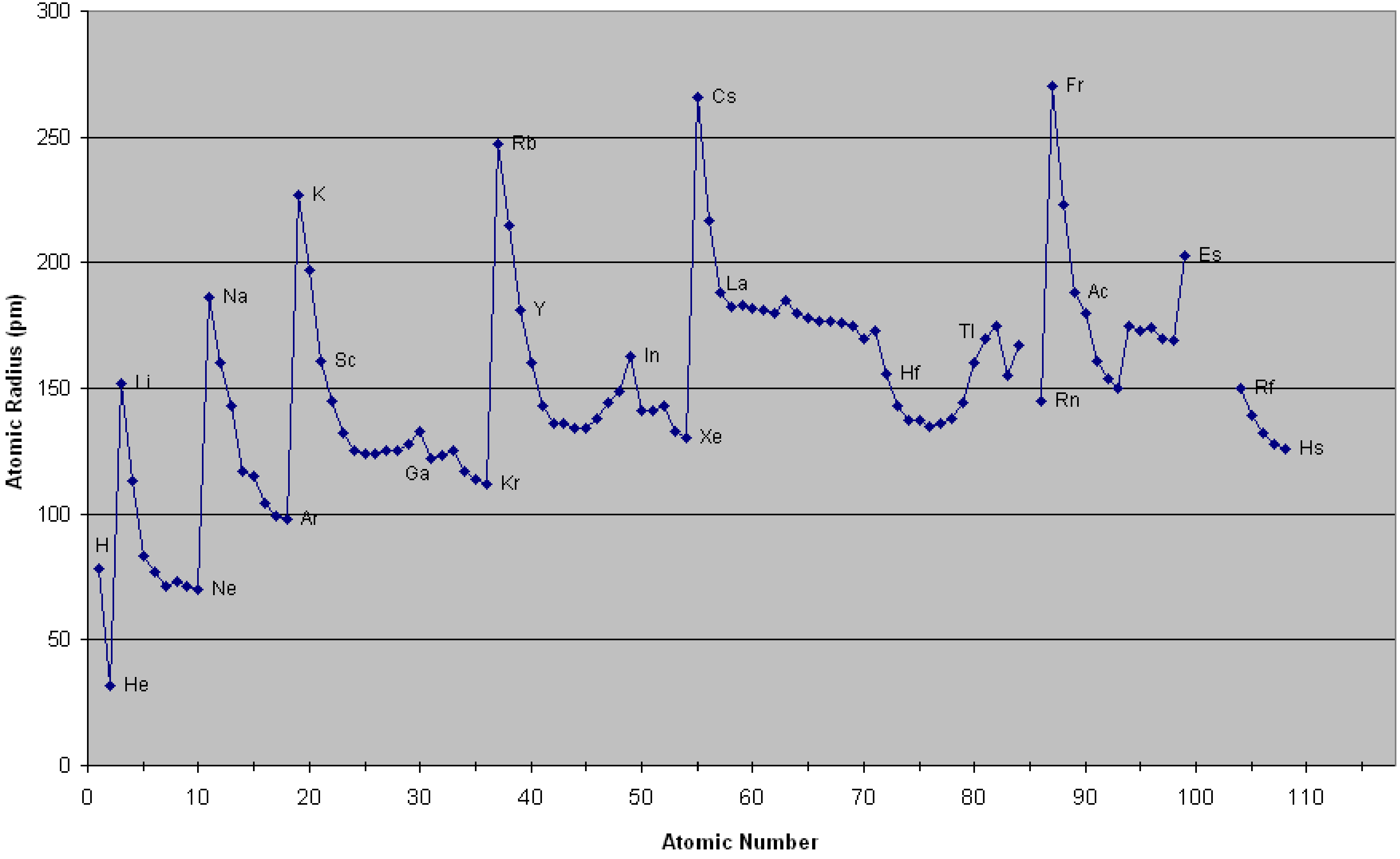
2 Covalent radius



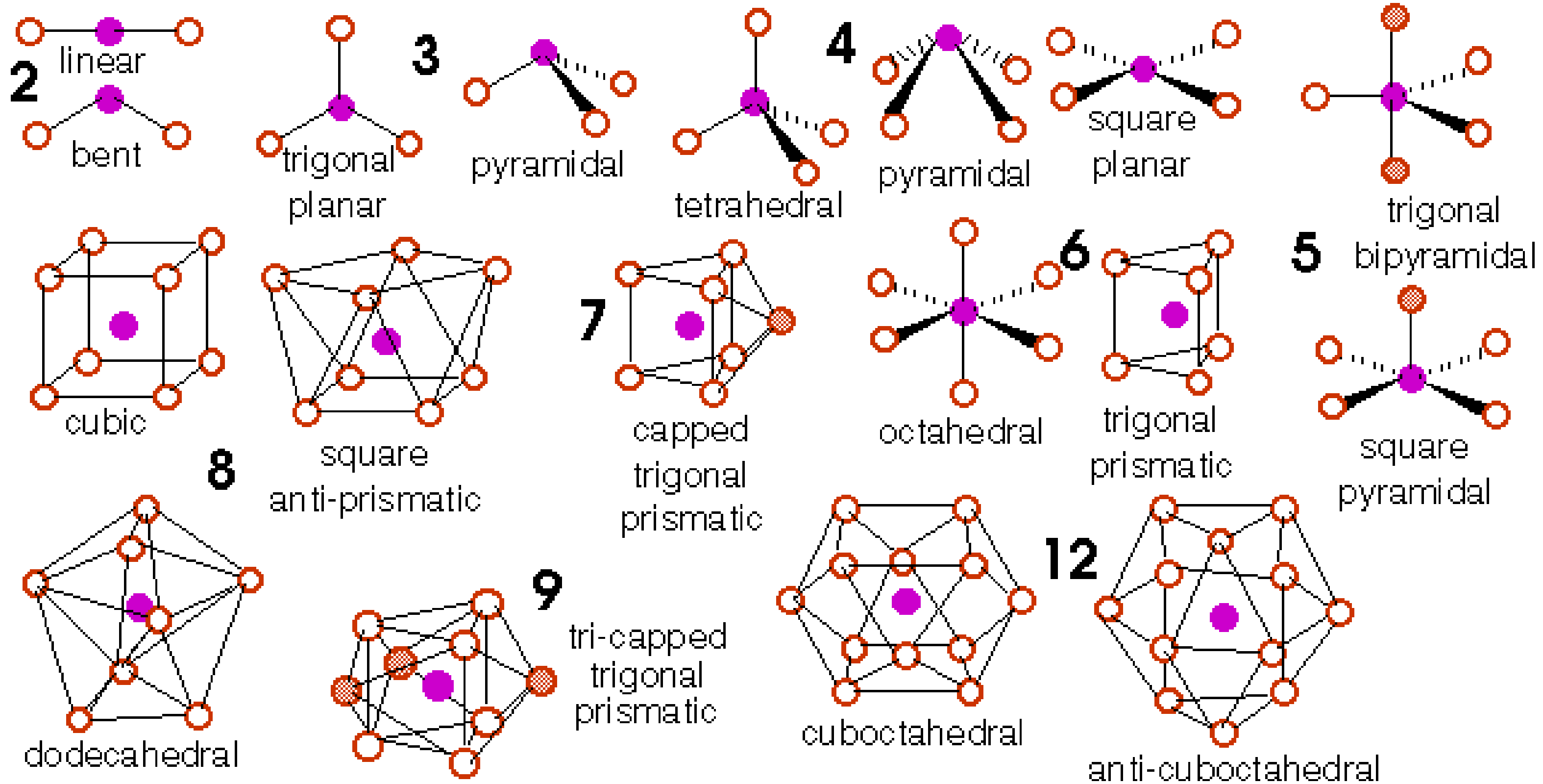
3 Ionic radius

$r(O^{2-})$ = 140 pm (Linus Pauling)

Periodic Trends in Atomic Radii



Coordination Polyhedra



Bond Length

Pauling $R(A-B) = r_A + r_B$

Schomaker-Stevenson Rule

polar bonds are shorter than the sum of covalent radii

Original c = 9 pm, n = 1
Modified c = 8.5 pm, n = 1.4

$$R(A-B) = r_A + r_B - c\left|\chi_A - \chi_B\right|^n$$

Allred-Rochow electronegativities give the best fit

Ionic Radii

R.D. Shannon and C.T. Prewitt, Acta Cryst. B25, 925-945 (1969)
R.D. Shannon, Acta Cryst. A32, 751-767 (1976)

As the coordination number (CN) increases, the Ionic Radius increases

Sr^{2+}

CN	Radius, Å
6	1.32
8	1.40
9	1.45
10	1.50
12	1.58

As the oxidation state increases, cations get smaller (6-fold coordination, in Å)

Mn^{2+}	0.810
Mn^{3+}	0.785
Mn^{4+}	0.670
Ti^{2+}	1.000
Ti^{3+}	0.810
Ti^{4+}	0.745

Ionic Radii

The radius increases down a group in the periodic table.
The exception - 4d/5d series in the transition metals - the lanthanide contraction

(6-fold coordination, in Å)

Al^{3+}	0.675
Ga^{3+}	0.760
In^{3+}	0.940
Tl^{3+}	1.025

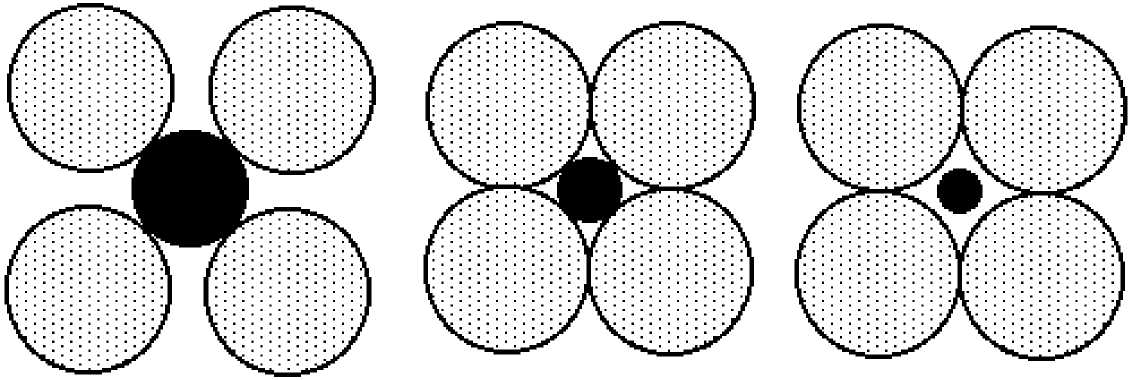
Ti^{4+}	0.745
Zr^{4+}	0.86
Hf^{4+}	0.85

Right to left across the periodic table the radius decreases.

(6 coordinate radii, in Å)

La^{3+}	1.172
Nd^{3+}	1.123
Gd^{3+}	1.078
Lu^{3+}	1.001

Cation/Anion Radius Ratio



$r_{cation}/r_{anion} >$ ideal
Stable

$r_{cation}/r_{anion} =$ ideal
Stable

$r_{cation}/r_{anion} <$ ideal
Unstable

CN	r/R
12 – hcp/ccp	**1.00 (substitution)**
8 – cubic	**0.732 – 1.00**
6 – octahedral	**0.414 – 0.732**
4 – tetrahedral	**0.225 – 0.414**

optimal radius ratio
for
given CN
ions are in touch

Pauling's Rules

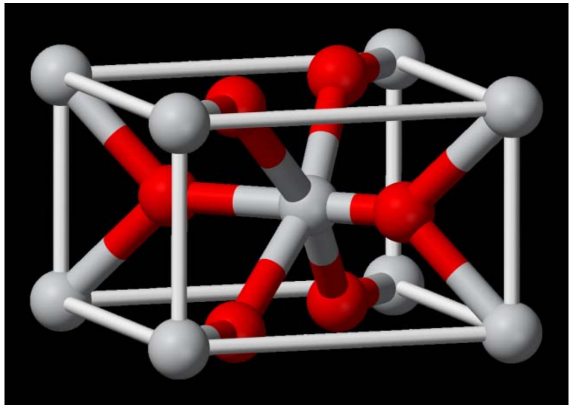
Pauling's Rule no. 2 Bond strength and the bond order conservation principle (a rule of local electroneutrality)

$$v_i = \Sigma s_{ij} = \Sigma \frac{z_i}{CN}$$

The strength of an electrostatic bond: s_{ij} = valence / CN
The bond valence sum of each ion equals its oxidation state.
The valence of an ion (V_i, equal to the oxidation state of the ion) is equal to a sum of the valences of its bonds (s_{ij}).

In a stable ionic structure the charge on an ion is balanced by the sum of electrostatic bond strengths (s_{ij}) to the ions in its coordination polyhedron.

TiO_2 (Rutile) Ti - oxidation state of +4, coordinated to 6 oxygens.
$V_{Ti} = +4 = 6\ (s_{ij})$ $s_{ij} = +2/3$



The bond valence of oxygen, coordinated by 3 Ti atoms
$V_o = 3\ (s_{ij}) = 3\ (-2/3) = -2$

Each bond has a valence of s_{ij} with respect to the cation
and $-s_{ij}$ with respect to the anion.

Bond Strength

Brown, Shannon, Donnay, Allmann:
Correlation of the valence of a bond s_{ij} with the (experimental) bond distance d_{ij}.

$$s_{ij} = \exp\frac{R_{ij} - d_{ij}}{b}$$

R_{ij} = standard single bond lenght - determined empirically from (many) structures where bond distances and ideal valences are accurately known.

Tables of R_{ij} values for given bonding pairs (i.e. Nb-O, Cr-N, Mg-F, etc.) have been calculated, just as tables of ionic radii are available.

A constant *b* = 0.30 - 0.37

$R = d$ $s = e^0 = 1$
$R < d$ $s = e^{-1} < 1$ a bond longer than R is weaker than 1
$R > d$ $s = e^1 > 1$ a bond shorter than R is stronger than 1

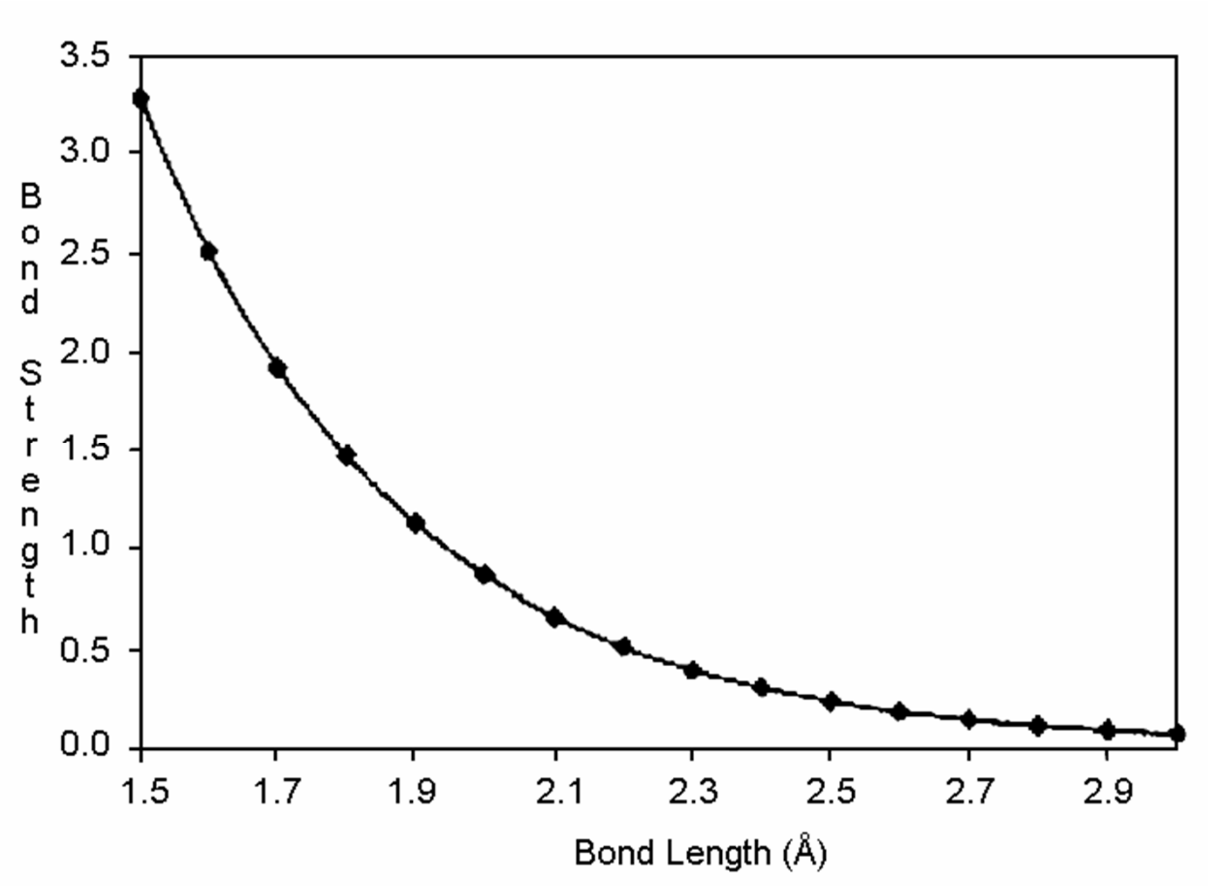
Bond Strength

Correlation of the valence of a bond s_{ij} with the (experimental) bond distance d_{ij}.

$$s_{ij} = \exp \frac{R_{ij} - d_{ij}}{b}$$

$$v_i = \Sigma s_{ij} = \Sigma \frac{z_i}{CN}$$

Use of the bond valence concept
A) To check experimentally determined structures for correctness, or bonding instabilities
B) To predict new structures
C) To locate light atoms such as hydrogen or Li ion, which are hard to find experimentally
D) To determine ordering of ions which are hard to differentiate experimentally, such as Al^{3+} and Si^{4+}, or O^{2-} and F^-
E) To check/confirm oxidation states of atoms (Co^{2+} /Co^{3+} , Fe^{2+} / Fe^{3+})


3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Bond Strength
1.5
1.7
1.9
2.1
2.3
2.5
2.7
2.9
Bond Length (Å)

Bond Strength

Correlation of the valence of a bond s_{ij} with the (experimental) bond distance d_{ij}.

$$s_{ij} = \exp\frac{R_{ij} - d_{ij}}{b}$$

$$v_i = \Sigma s_{ij} = \Sigma \frac{z_i}{CN}$$

$FeTiO_3$ (mineral Ilmenite) possesses the **corundum** structure – an hcp array of oxides with cations filling 2/3 of octahedral holes.

Decide which oxidation states are present: Fe(II) Ti(IV) or Fe(III) Ti(III)

Bond Distances (d_{exp}, Å)	Tabulated R_{ij} values	Constants
Fe–O = 3×2.07 and 3×2.20	R_0(Fe–O) = 1.795 Å	b = 0.30
Ti–O = 3×1.88 and 3×2.09	R_0(Ti–O) = 1.815 Å	b = 0.37

Oxygen valence and coordination number O?
Each oxygen is bound to Fe and Ti with both bond distances.

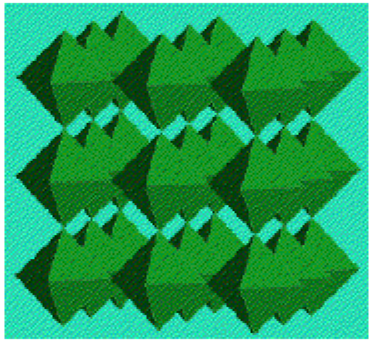
Pauling’s Rules

Pauling’s Rule no. 3   Polyhedral Linking

The presence of shared edges, and particularly shared faces decreases the stability of a structure. This is particularly true for cations with large valences and small coordination numbers.

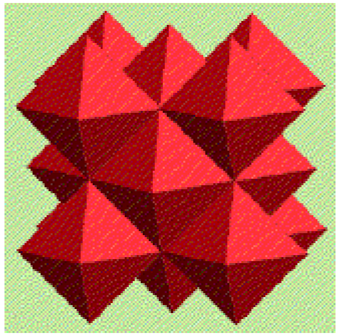
Avoid shared polyhedral edges and/or faces.

ReO_3



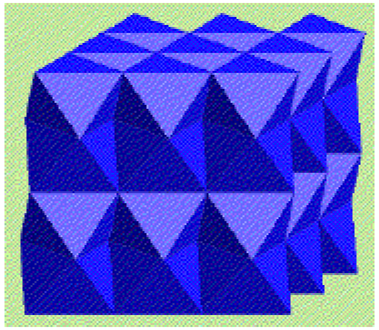
Vertex-Sharing Only

NaCl



Edge-Sharing

NiAs

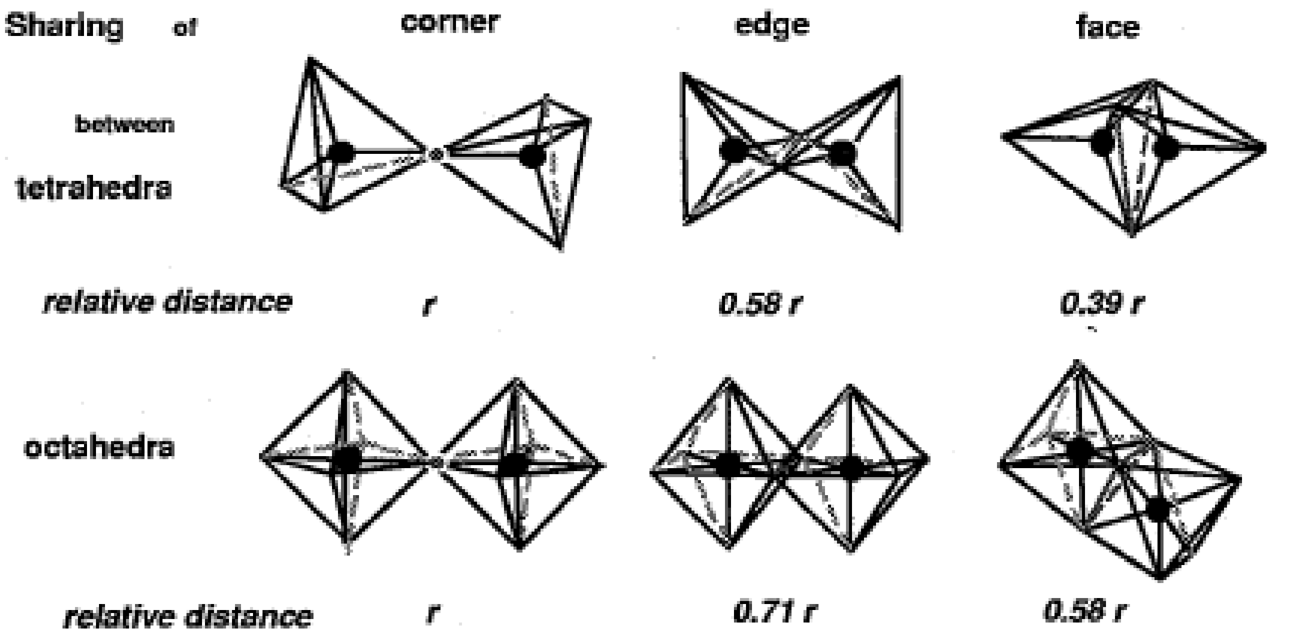


Face-Sharing in Columns

Polyhedral Linking

The Coulombic interactions - maximize the cation-anion interactions (attractive), and minimize the anion-anion and cation-cation interactions (repulsive).

- increasing the coordination number
- decreasing the cation-anion distance



The cation-cation distance decreases, (the Coulomb repulsion increases) as the

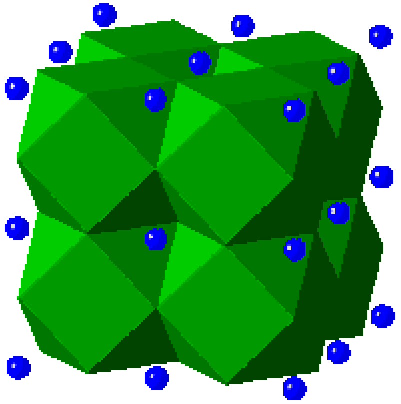
- degree of sharing increases (corner < edge < face)
- CN decreases (cubic < octahedral < tetrahedral)
- cation oxidation state increases (this leads to a stronger Coulomb repulsion)

Pauling's Rules

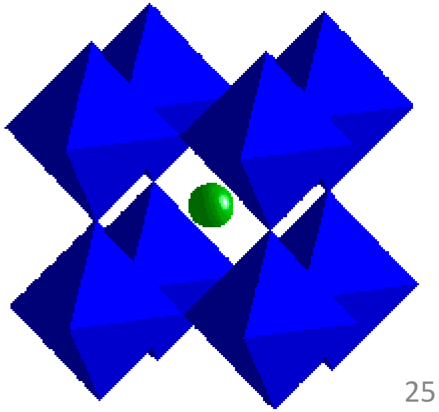
Pauling's Rule no. 4 Cation Evasion

In a crystal containing different cations those with large valence and small coord. number tend not to share polyhedral elements (anions).

Perovskite, $CaTiO_3$



Ca^{II} 12-coordinate **CaO_{12}** cuboctahedra share **FACES**



Ti^{IV} 6-coordinate **TiO_6** octahedra share only **VERTICES**

Pauling’s Rules

Pauling’s Rule no. 5 Environmental Homogeneity

the rule of parsimony

The number of chemically different coordination environments for a given ion tends to be small.

Once the optimal chemical environment for an ion is found, if possible all ions of that type should have the same environment.

Covalent Radius of Fluorine

1938 Brockway - electron diffraction on F_2(g)
R(F–F) = 145 pm   d(F) = 73 pm

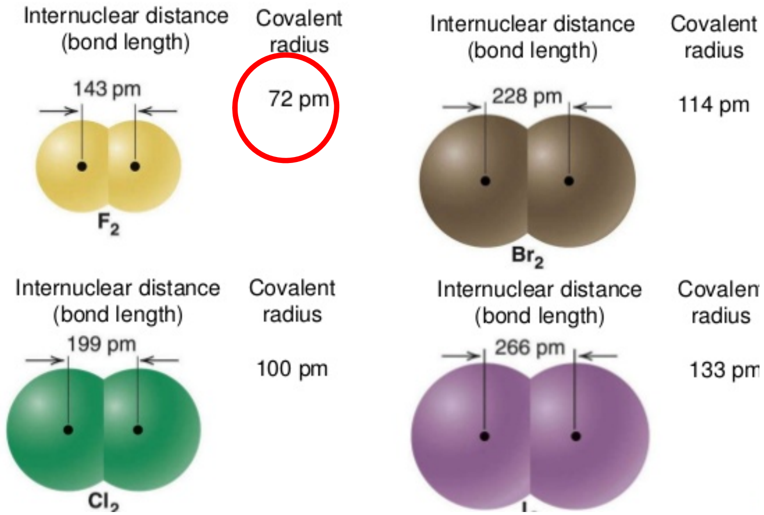
1960 Pauling – backbonding in A–F

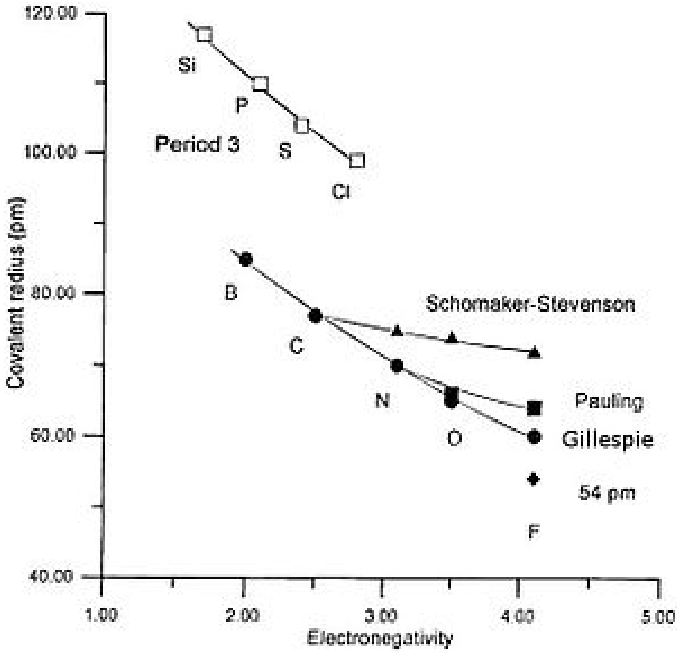
1990 Reed and Schleyer – pi bonding in A–F

1992 Gillespie and Robinson - 54 pm
Longer if a lone pair on EAF_n
Shorter in an incomplete octet BF_3

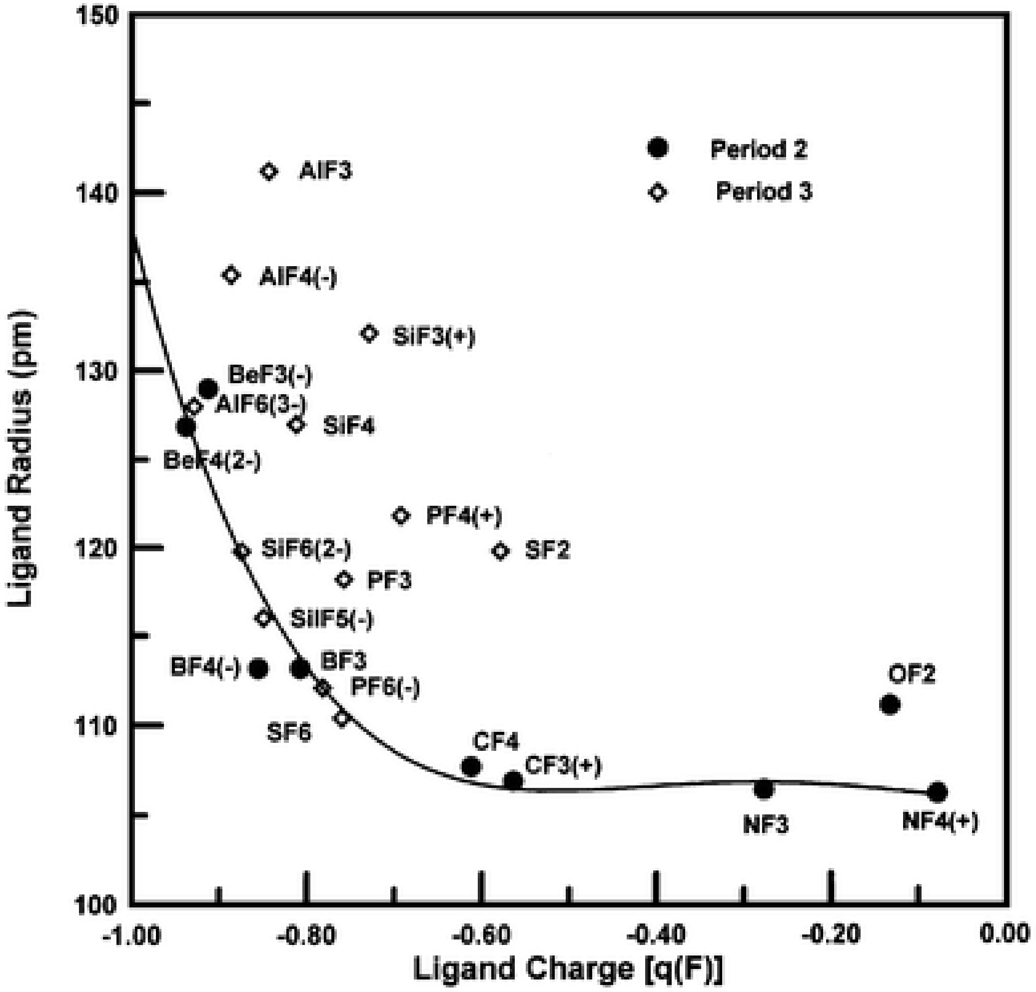
1997 Gillespie - 60 pm, the X–F bond length decreases with a decreasing CN, the smaller the bond angle (<F-A-F) the longer the bond length

2009 Pyykkö - 64 pm in a single bond, 59 pm in a double bond and 53 pm in triple bond character





Covalent Radius of Fluorine



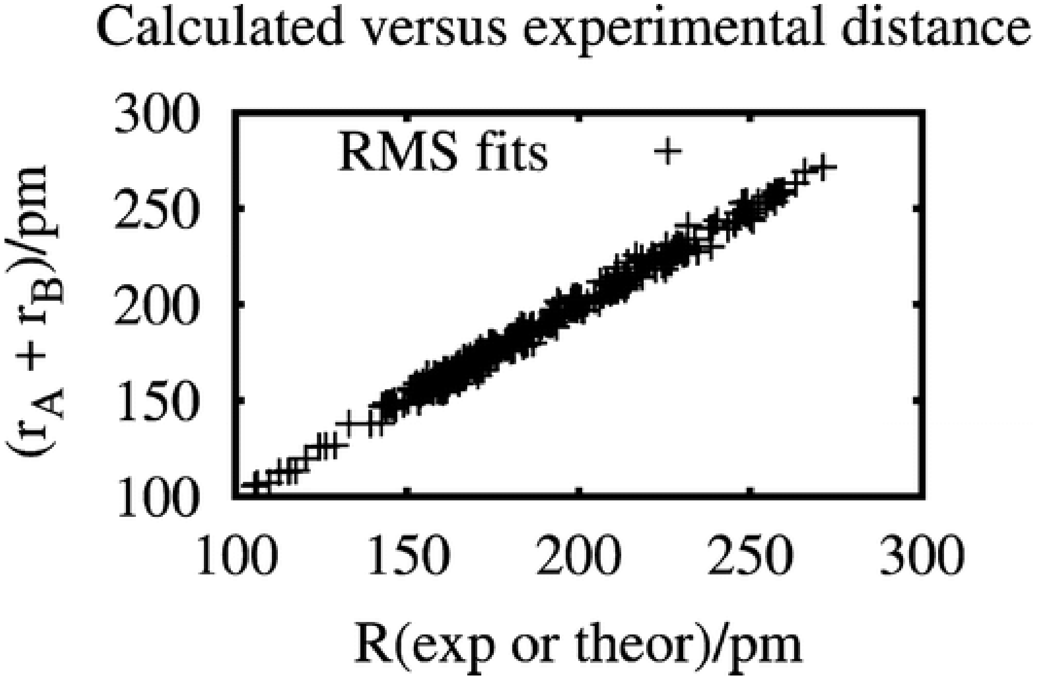
Period 2
Fluorine radii decrease across the 2nd period with increasing electronegativity of the central atom and therefore with decreasing ligand charge.

Period 3
The six-coordinated fluorides fall on the same smooth curve as for
the Period 2 fluorides = close-packed.

The 3- and 4-coordinated fluorides of the Period 3 elements do not fall on this curve = not close packed.

Additive Covalent Radii

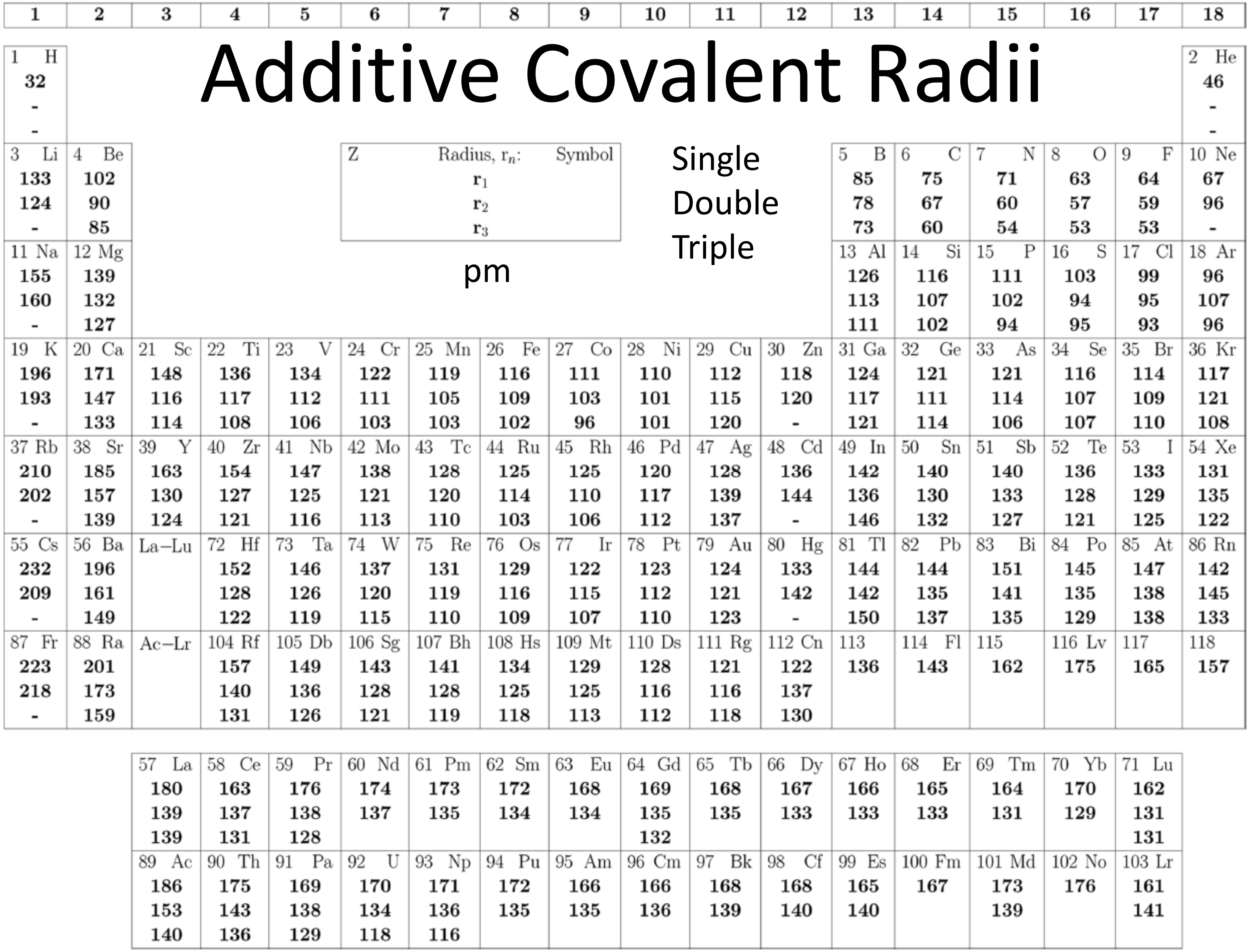
Additive covalent radii = approximate a bond length as the sum of two atomic radii
Predominantly covalent



the A−B bond is not
too ionic

Pekka Pyykkö J. Phys. Chem. A, 2015, 119 (11), 2326–2337

Additive Covalent Radii



Z Radius, r_n: Symbol
r_1 Single
r_2 Double
r_3 Triple

pm

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 32 - -																	2 He 46 - -
3 Li 133 124 -	4 Be 102 90 85											5 B 85 78 73	6 C 75 67 60	7 N 71 60 54	8 O 63 57 53	9 F 64 59 53	10 Ne 67 96 -
11 Na 155 160 -	12 Mg 139 132 127											13 Al 126 113 111	14 Si 116 107 102	15 P 111 102 94	16 S 103 94 95	17 Cl 99 95 93	18 Ar 96 107 96
19 K 196 193 -	20 Ca 171 147 133	21 Sc 148 116 114	22 Ti 136 117 108	23 V 134 112 106	24 Cr 122 111 103	25 Mn 119 105 103	26 Fe 116 109 102	27 Co 111 103 96	28 Ni 110 101 101	29 Cu 112 115 120	30 Zn 118 120 -	31 Ga 124 117 121	32 Ge 121 111 114	33 As 121 114 106	34 Se 116 107 107	35 Br 114 109 110	36 Kr 117 121 108
37 Rb 210 202 -	38 Sr 185 157 139	39 Y 163 130 124	40 Zr 154 127 121	41 Nb 147 125 116	42 Mo 138 121 113	43 Tc 128 120 110	44 Ru 125 114 103	45 Rh 125 110 106	46 Pd 120 117 112	47 Ag 128 139 137	48 Cd 136 144 -	49 In 142 136 146	50 Sn 140 130 132	51 Sb 140 133 127	52 Te 136 128 121	53 I 133 129 125	54 Xe 131 135 122
55 Cs 232 209 -	56 Ba 196 161 149	La–Lu	72 Hf 152 128 122	73 Ta 146 126 119	74 W 137 120 115	75 Re 131 119 110	76 Os 129 116 109	77 Ir 122 115 107	78 Pt 123 112 110	79 Au 124 121 123	80 Hg 133 142 -	81 Tl 144 142 150	82 Pb 144 135 137	83 Bi 151 141 135	84 Po 145 135 129	85 At 147 138 138	86 Rn 142 145 133
87 Fr 223 218 -	88 Ra 201 173 159	Ac–Lr	104 Rf 157 140 131	105 Db 149 136 126	106 Sg 143 128 121	107 Bh 141 128 119	108 Hs 134 125 118	109 Mt 129 125 113	110 Ds 128 116 112	111 Rg 121 116 118	112 Cn 122 137 130	113 136	114 Fl 143	115 162	116 Lv 175	117 165	118 157

57 La 180 139 139	58 Ce 163 137 131	59 Pr 176 138 128	60 Nd 174 137	61 Pm 173 135	62 Sm 172 134	63 Eu 168 134	64 Gd 169 135 132	65 Tb 168 135	66 Dy 167 133	67 Ho 166 133	68 Er 165 133	69 Tm 164 131	70 Yb 170 129	71 Lu 162 131 131
89 Ac 186 153 140	90 Th 175 143 136	91 Pa 169 138 129	92 U 170 134 118	93 Np 171 136 116	94 Pu 172 135	95 Am 166 135	96 Cm 166 136	97 Bk 168 139	98 Cf 168 140	99 Es 165 140	100 Fm 167	101 Md 173 139	102 No 176	103 Lr 161 141

Pekka Pyykkö J. Phys. Chem. A, 2015, 119 (11), 2326–2337

The Same or Not the Same

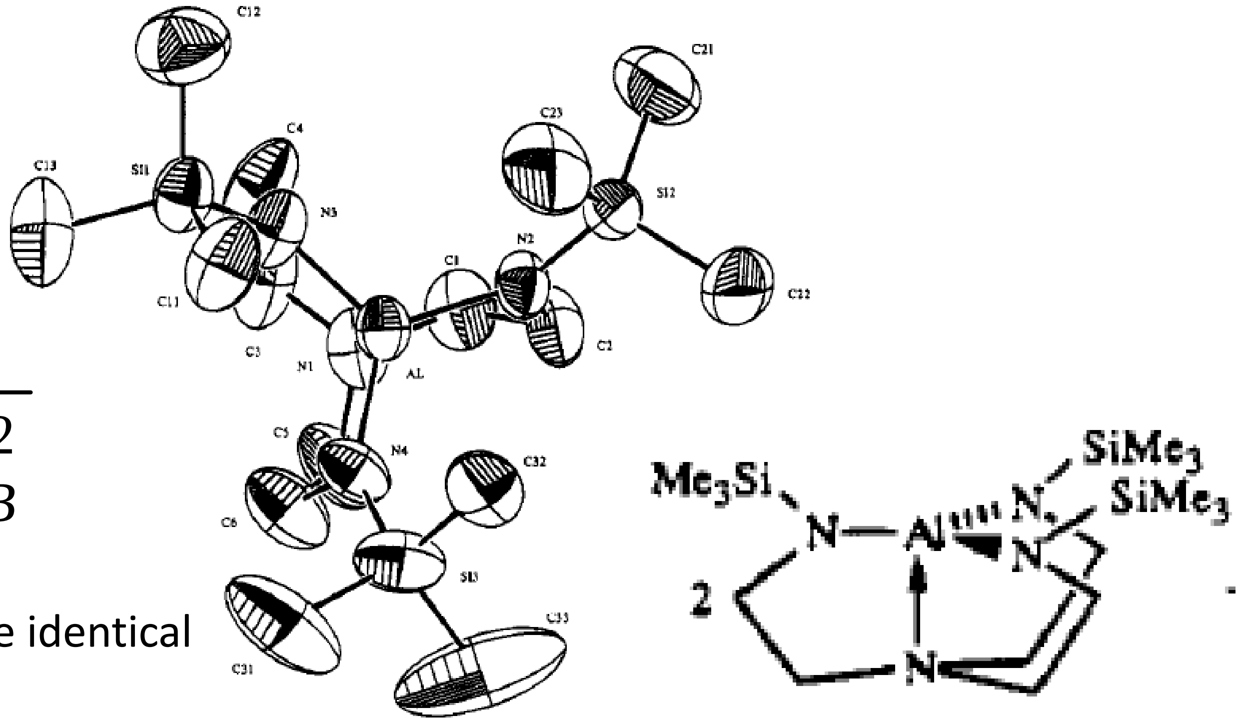
Three sigma criterion

$$\Delta = A \pm B$$

$$\sigma_{\Delta} = \sqrt{\sigma_A^2 + \sigma_B^2}$$

$$\Delta < 3\sigma_{\Delta}$$ A, B – are identical

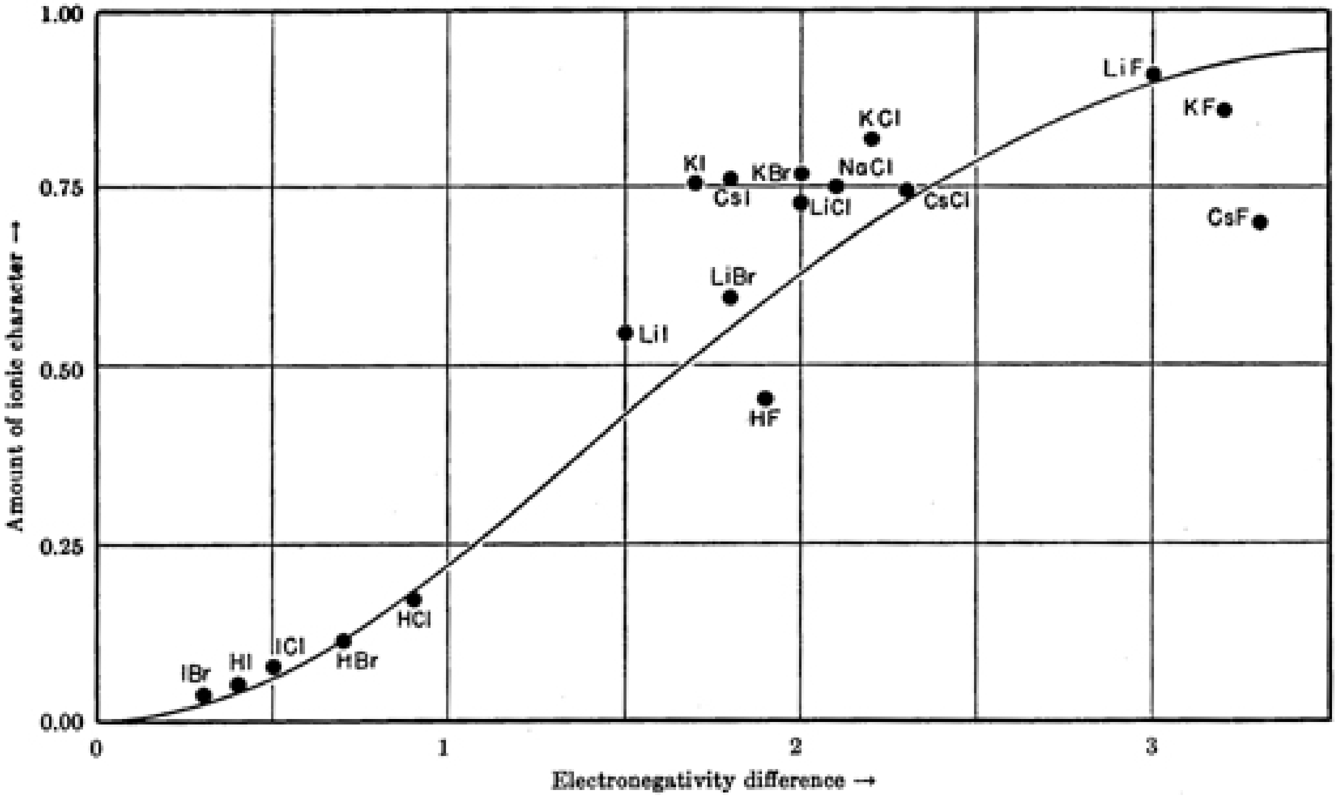
$$\Delta > 3\sigma_{\Delta}$$ A, B – are different



Crystallographically imposed C_3 axis??

Al-N(1) 1.983(6)	
Al-N(2) 1.805(5)	Si(2)-N(2) 1.684(5)
Al-N(3) 1.812(6)	Si(1)-N(3) 1.697(6)
Al-N(4) 1.810(6)	Si(3)-N(4) 1.690(6)

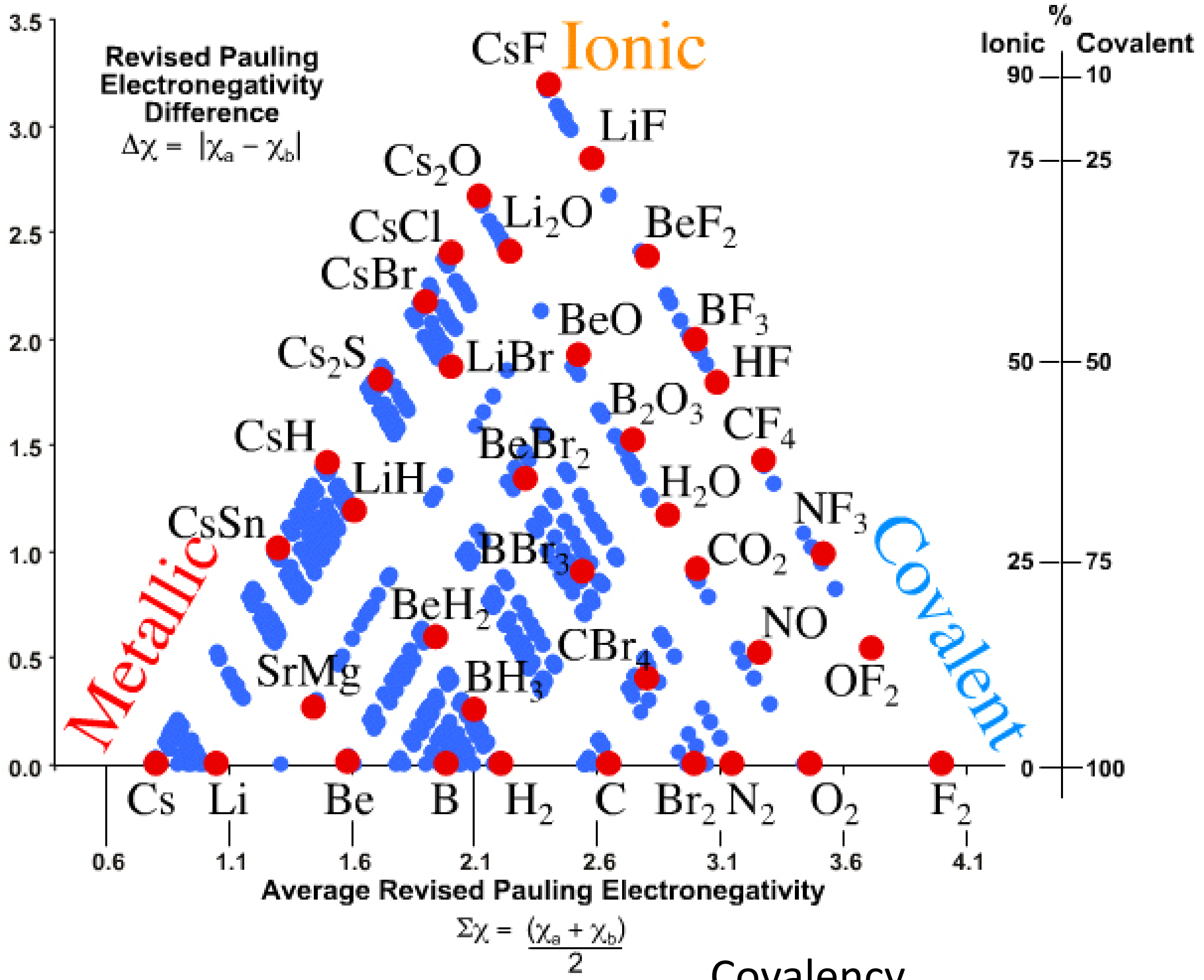
Ionic Character vs. Electronegativity



$$i = 1 - \exp[-0.21(\chi_A - \chi_B)^2]$$

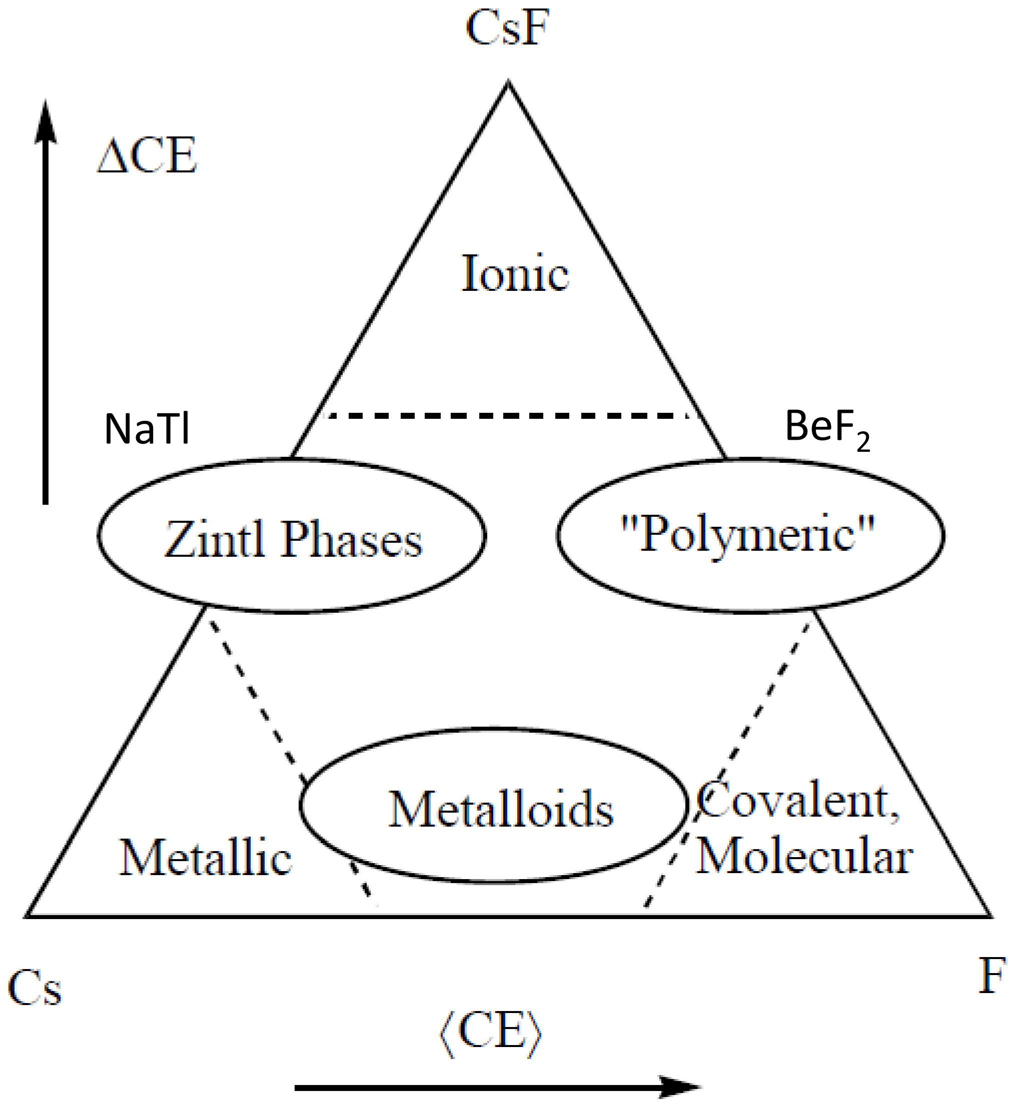
van Arkel-Ketelaar Triangle

Ionicity



Covalency

van Arkel-Ketelaar Triangle



CsF

ΔCE

Ionic

NaTl

BeF_2

Zintl Phases

"Polymeric"

Metalloids

Metallic

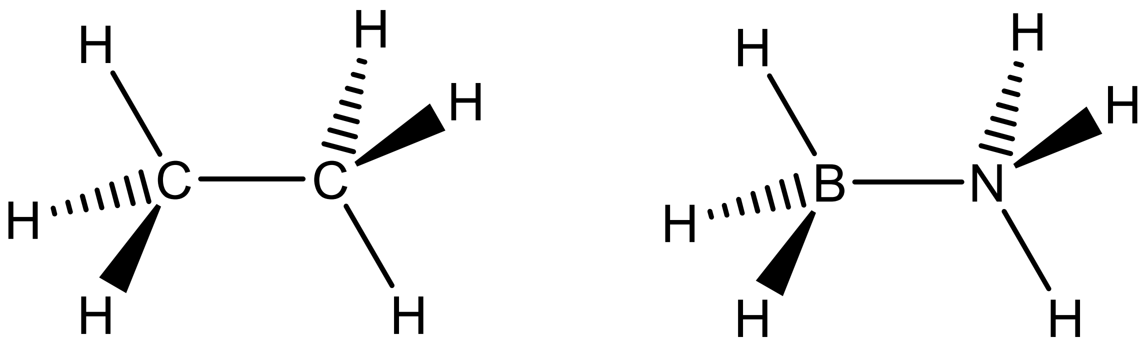
Covalent, Molecular

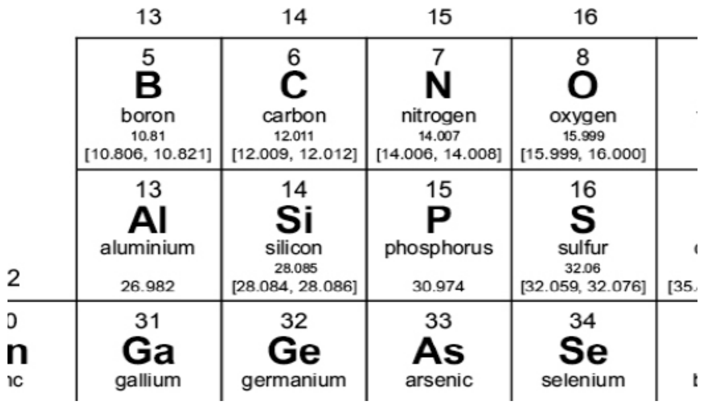
Cs

F

$\langle CE \rangle$

Normal vs. Dative Bond





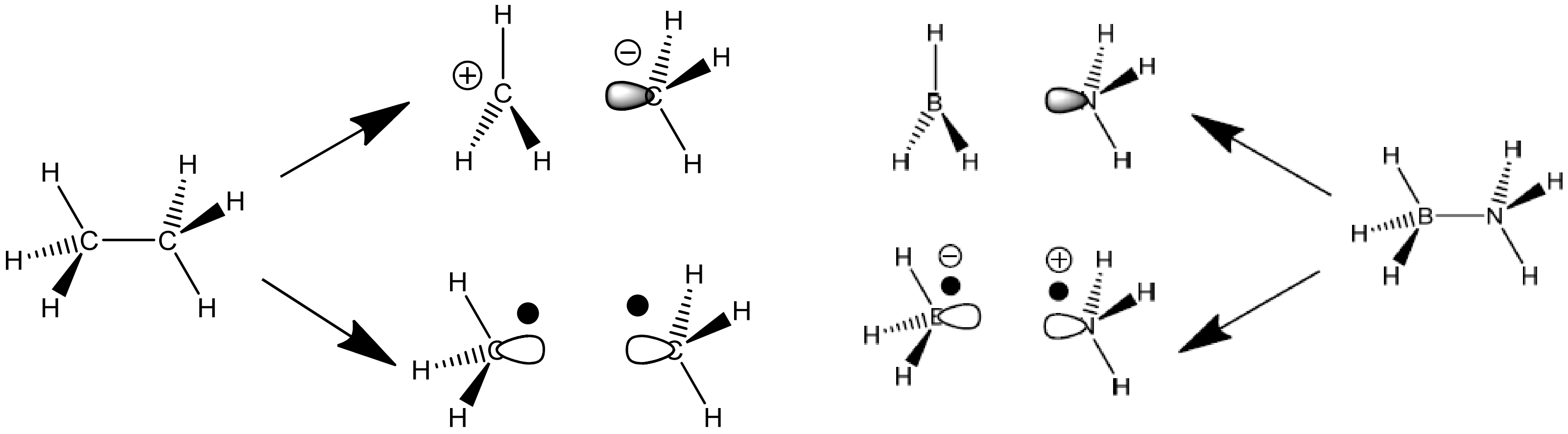
13	14	15	16
5 **B** boron 10.81 [10.806, 10.821]	6 **C** carbon 12.011 [12.009, 12.012]	7 **N** nitrogen 14.007 [14.006, 14.008]	8 **O** oxygen 15.999 [15.999, 16.000]
13 **Al** aluminium 26.982	14 **Si** silicon 28.085 [28.084, 28.086]	15 **P** phosphorus 30.974	16 **S** sulfur 32.06 [32.059, 32.076]
31 **Ga** gallium	32 **Ge** germanium	33 **As** arsenic	34 **Se** selenium

Normal vs. Dative Bond

Heterolytic Bond Cleavage

Charged + Diamagnetic

Neutral + Diamagnetic



Neutral + Radicals

Charged + Radical

Homolytic Bond Cleavage

Badger’s Rule

Badger’s rule relates vibrational frequencies to bond distances for various atomic pairs.

$$r_e = \left(\frac{C_{ij}}{k}\right)^{\frac{1}{3}} + d_{ij}$$

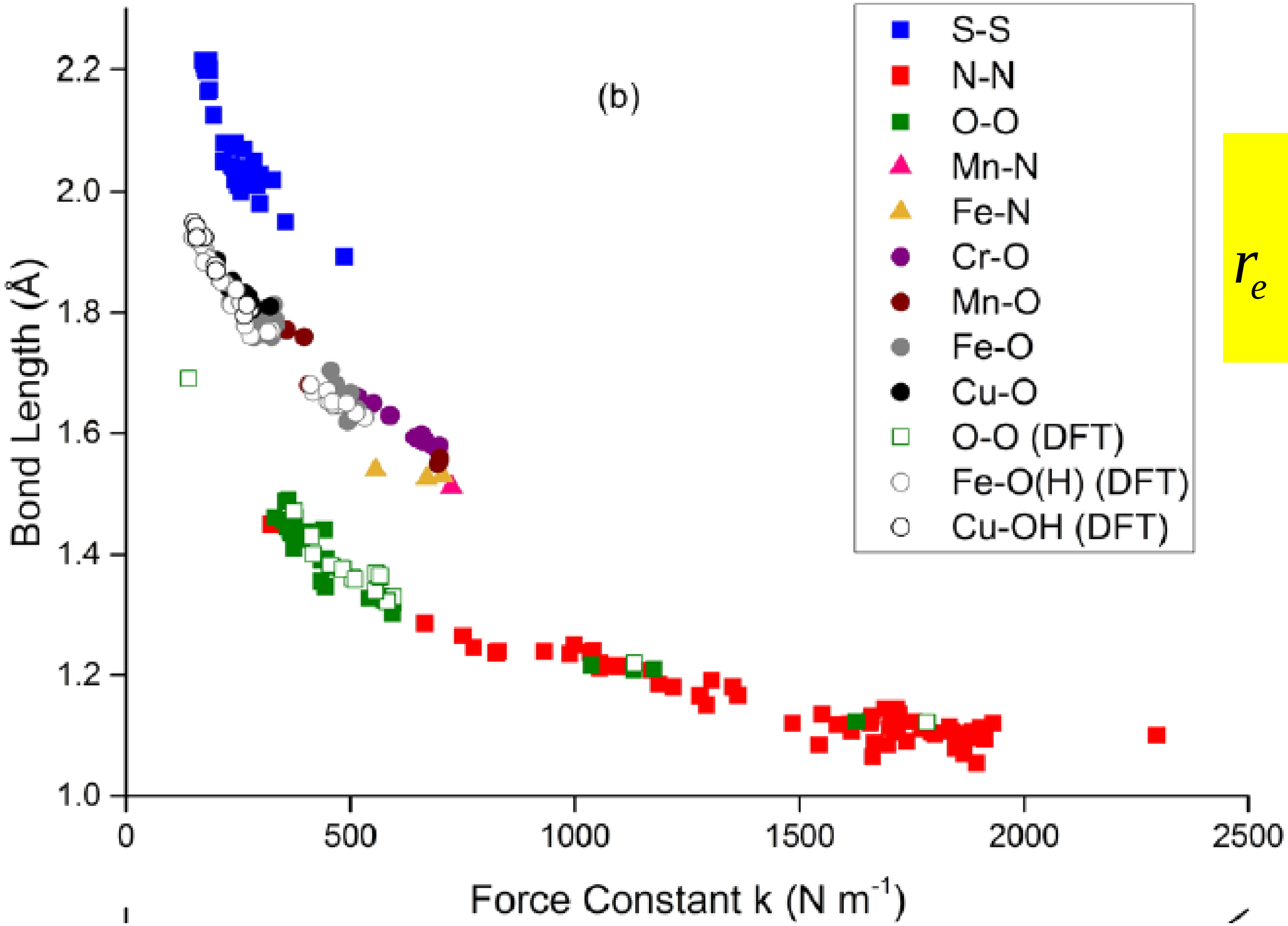
r_e = equilibrium bond distance
k = force constant (can be substituted with ν, the stretching frequency)
C_{ij} and d_{ij} = empirically fitted values for a particular atomic pair i-j

Plots of bond distances vs $\nu^{-2/3}$ or $k^{-1/3}$ for a set of compounds comprising a particular atomic pair are fit to equation to determine C_{ij} and d_{ij}, which then allows a newly measured force constant or vibrational frequency to be used to calculate an unknown bond distance (or vice versa).

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \Rightarrow k = \mu(2\pi\nu)^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

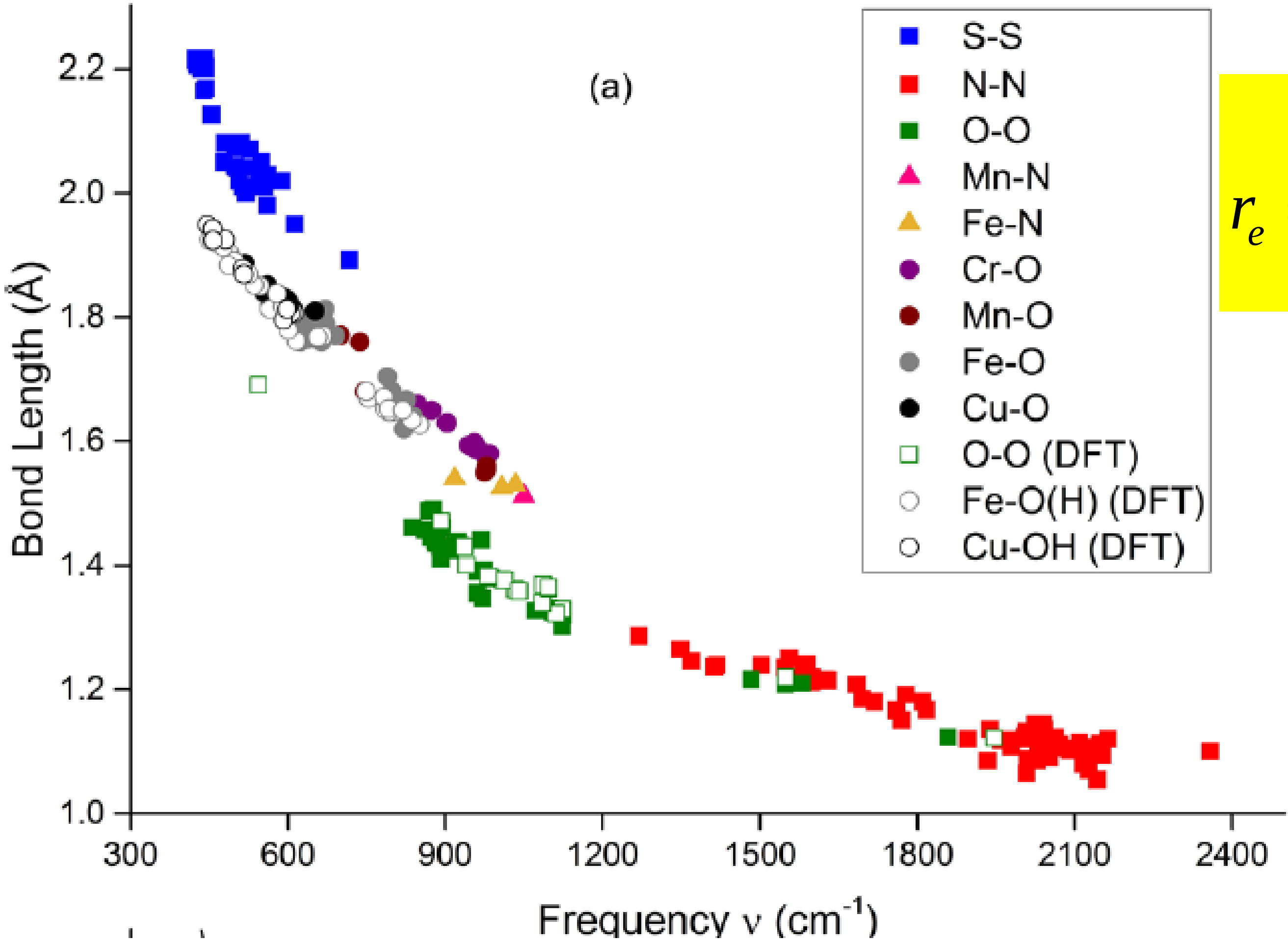
Badger's Rule



$$r_e = \left(\frac{C_{ij}}{k}\right)^{\frac{1}{3}} + d_{ij}$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Badger’s Rule

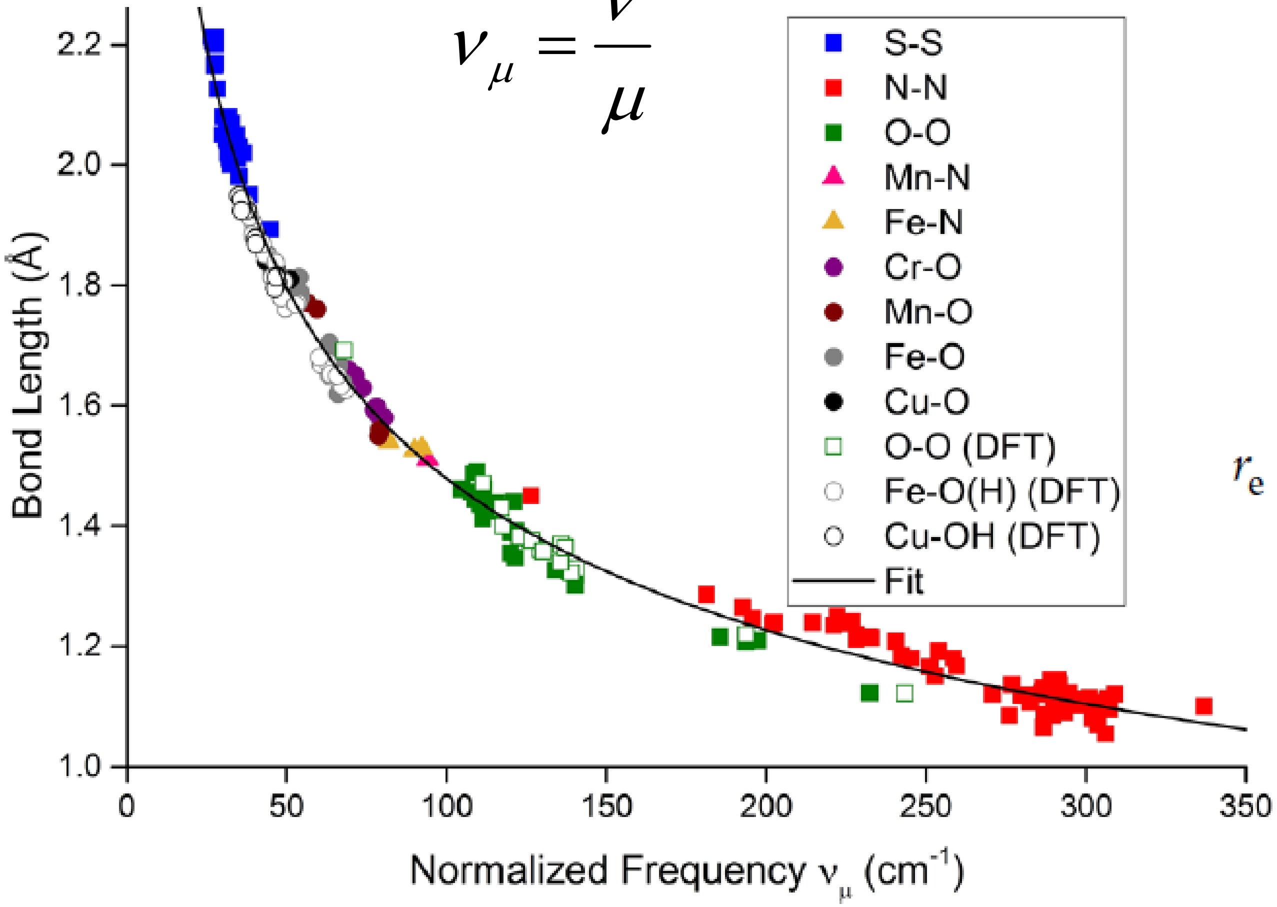


$$r_e = \left(\frac{C_{ij}}{\mu (2\pi\nu)^2} \right)^{\frac{1}{3}} + d_{ij}$$

Normalized Badger’s Rule

Normalized frequency

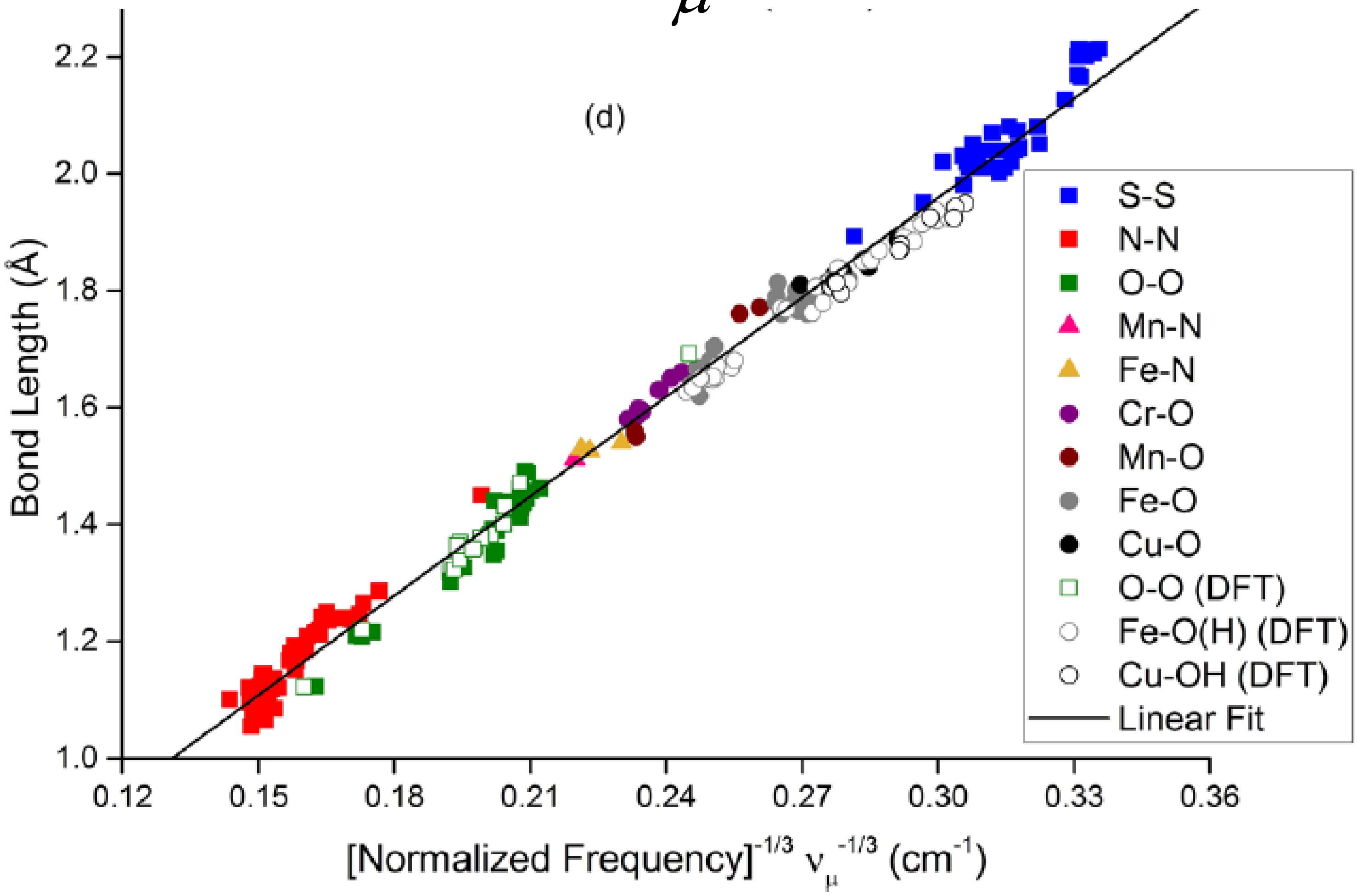
$$\nu_\mu = \frac{\nu}{\mu}$$



$$r_e = \left(\frac{181}{\nu_\mu}\right)^{1/3} + 0.259$$

Normalized Badger's Rule

Normalized frequency $\nu_{\mu} = \frac{\nu}{\mu}$



Bond Order

Not an observable quantity

G. N. Lewis 1916
Electron sharing between two atoms
Bond order = a measure of the number of electrons shared between two atoms
Resonance structures

G. Herzberg
Bond order is equal to half the difference between the number of bonding electrons and the number of antibonding electrons in the (diatomic) molecule
Not a quantum chemical quantity, not calculated from the wave function, semi-integer *formal* bond order

Bond Order

R. S. Mulliken

A non-integral bonding power of either sign is attributable to every outer electron - the Mulliken population analysis

The effective bond order (EBO)

Each bonding orbital *i* has a natural orbital (NO) occupation number b_i. The corresponding antibonding orbital has the occupation number ab_i

a = 0 – full bond, a = 1 – no bond

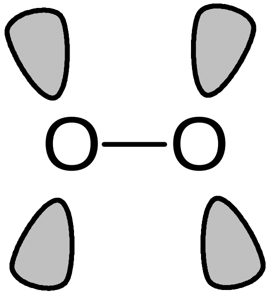
$$\mathrm{EBO} = \sum_i \frac{(b_i - ab_i)}{2}$$

The delocalization index between two any atoms in a system corresponds to the (fractional) number of electron pairs shared or exchanged between these atoms

Multiple Bonds

Dominant form of oxygen is O=O, a colourless paramagnetic gas.
Ozone (O_3) is the only other allotrope.
Why does not it form O_8 ?

Lone-pair repulsion across the short O-O distance.
O is small, and its orbitals highly contracted, and so electrons feel a lot of e-e repulsion.



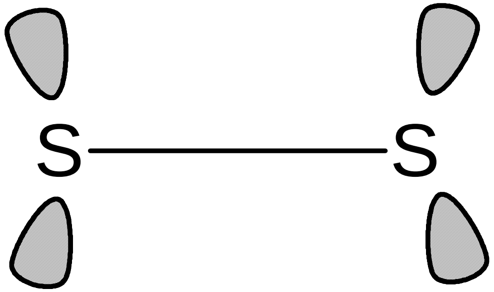
Bond energies

$O_2 \longrightarrow$ -O-O-

Bond
Energies: 350 2 × 145
$\Delta H = 350 + (2 \times -145) = +60 \text{ kJ mol}^{-1}$

$S_2 \longrightarrow$ -S-S-

Bond
Energies: 270 2 × 155
$\Delta H = 270 + (2 \times -155) = -40 \text{ kJ mol}^{-1}$



S=S is thermodynamically unstable wrt -S-S- (*catenation*) but stable above 700 °C (Why?)

π-Bonds

Diffuseness of orbitals

2s and 2p orbitals are only shielded from the nucleus by the 1s electrons. Therefore they are highly contracted, and π-overlap is efficient for the second period elements.

3s and 3p orbitals in the 3rd row and higher elements are more diffuse, and so this side-on p-p overlap is less effective.

Repulsion between core electrons

Second-row elements have only two core electrons (He). Third-row (Ne) and heavier elements (Ar-Kr-Xe) have a significantly larger number of core electrons that cause repulsion between two heavy elements bonded to each other. This prevents the atoms to approach each other closer and form stronger π bonds.

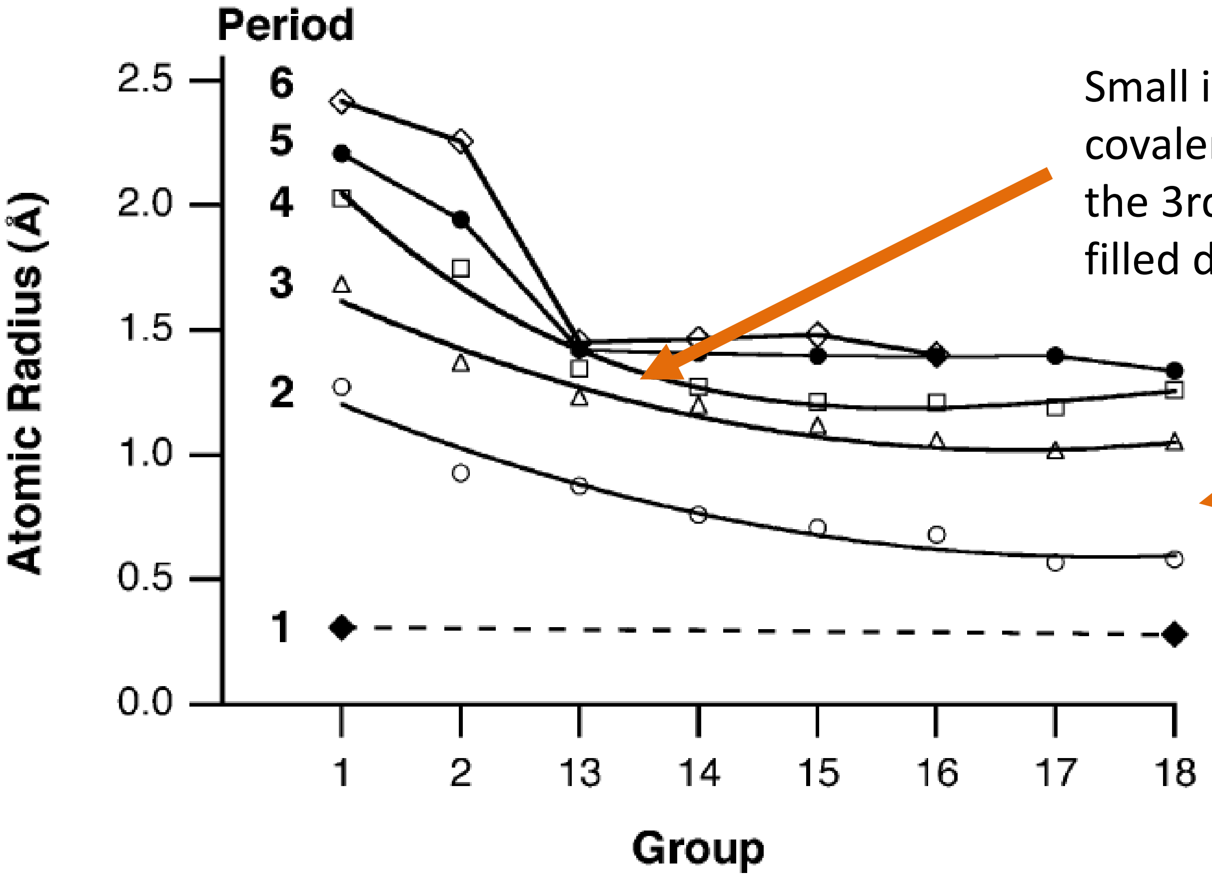
Atomic size

the large jump (50 %) in the covalent radii between the 2nd and 3rd rows of the periodic table (for example, C (0.77 Å), Si (1.17 Å). Higher coordination numbers observed for the 3rd row.

Thermochemistry

π -bond energies in heavy double bonds too small to prevent polymerization.

Atomic Radii

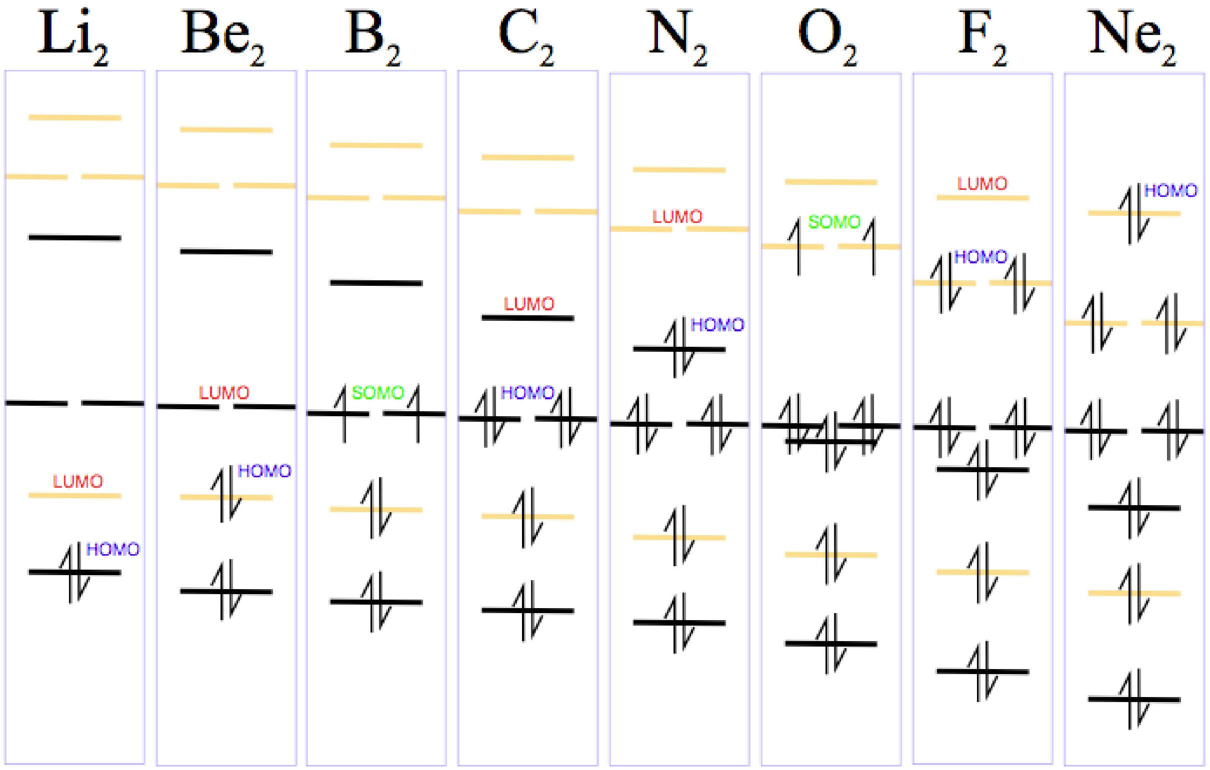


Small increase in the covalent radii between the 3rd and 4th rows - filled d^{10} - poor shielding

~50% increase in the covalent radii between the 2nd and 3rd rows

B. Cordero et al. *Dalton Trans.*, 2008, 2832–2838

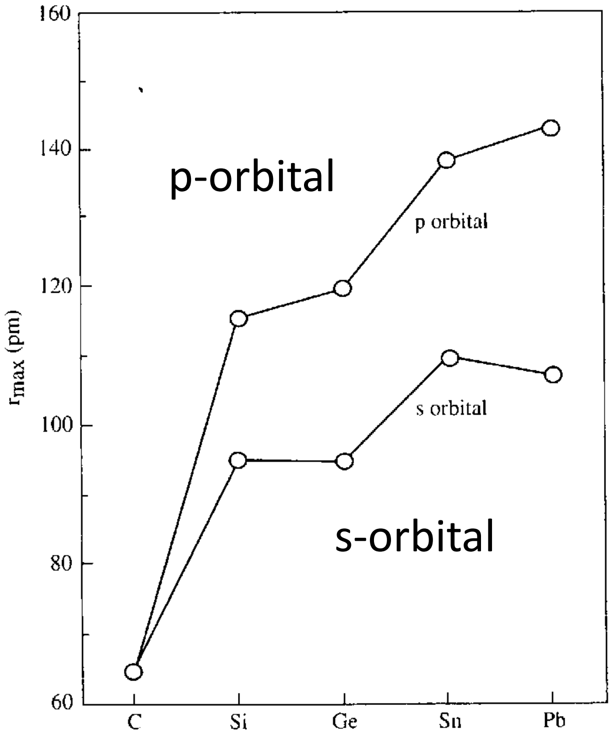
Bonding in Diatomic Moelcules

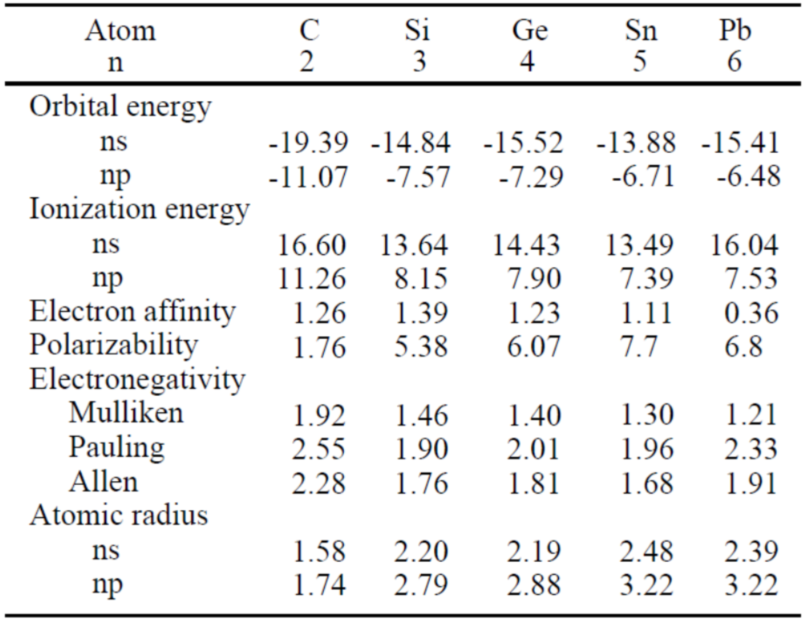


bond order = (electrons in bonding MOs – electrons in antibonding MOs) / 2

1	0	1	2	3	2	1	0
Li–Li	Be Be	B–B	C=C	N≡N	O=O	F–F	Ne Ne
known in the gas phase	dimer unknown	known in the gas phase paramagnetic diradical	known in the gas phase at high temp.	stable gas	stable gas paramagnetic diradical. Singlet & triplet states	stable gas	dimer unknown

π-Bonds





Atom n	C 2	Si 3	Ge 4	Sn 5	Pb 6
Orbital energy					
ns	-19.39	-14.84	-15.52	-13.88	-15.41
np	-11.07	-7.57	-7.29	-6.71	-6.48
Ionization energy					
ns	16.60	13.64	14.43	13.49	16.04
np	11.26	8.15	7.90	7.39	7.53
Electron affinity	1.26	1.39	1.23	1.11	0.36
Polarizability	1.76	5.38	6.07	7.7	6.8
Electronegativity					
Mulliken	1.92	1.46	1.40	1.30	1.21
Pauling	2.55	1.90	2.01	1.96	2.33
Allen	2.28	1.76	1.81	1.68	1.91
Atomic radius					
ns	1.58	2.20	2.19	2.48	2.39
np	1.74	2.79	2.88	3.22	3.22

Carbon - 2s and 2p electrons approximately **the same spatial extension** (the core electrons occupy only the 1s orbital).
Heavier Group 14 elements, the *n*p valence electrons (*n* > 2) are **spatially separated** from *n*s due to Pauli repulsion with the (*n*–1)p electrons in the inner shell.

Difficult to hybridize *n*s and *n*p orbitals for heavier atoms, tend to preserve the valence *n*s electrons as core-like electrons while carbon shows a preference for an effective hybridization of the s and p - the strong overlap binding ability.

π-Bonds

In Group 14 all double-bonded E=E species are unstable!

Exothermic !

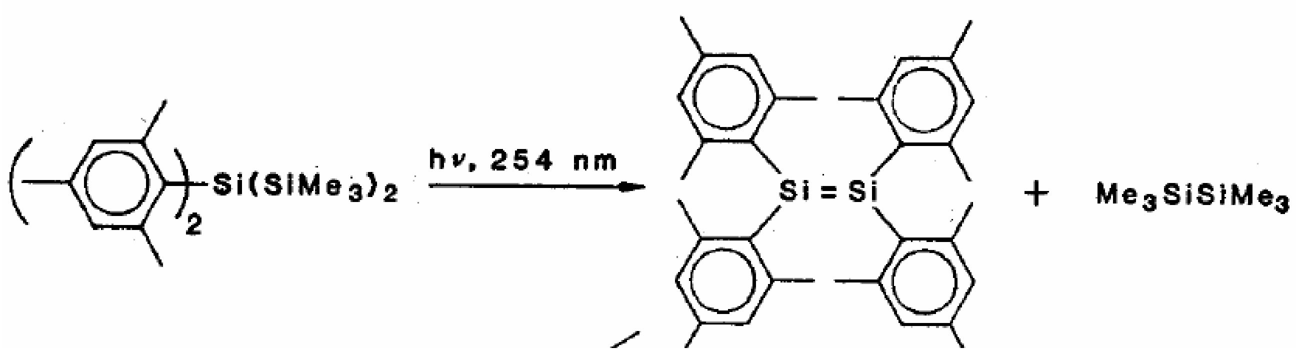
kJ mol^{-1}	E=E	E-E	ΔH
C	602	$-2(356)$	-110
Si	310	$-2(226)$	-142
Ge	270	$-2(188)$	-106
Sn	190	$-2(151)$	-112

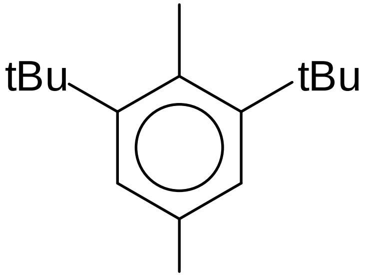
1933 at ICI
R. Gibson, E. Fawcett
High pressure
polyethylene

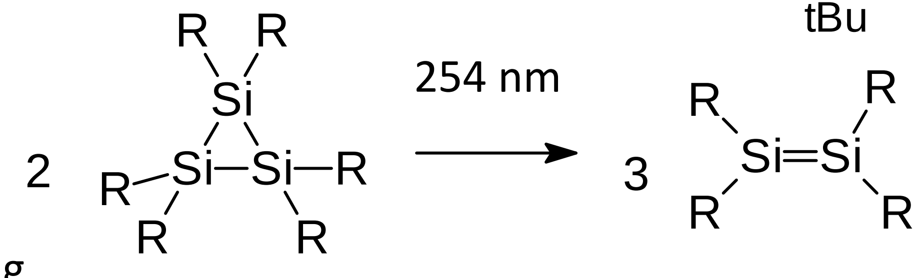
C=C double bonds are thermodynamically less stable than two corresponding single bonds and are kinetically stabilized. The preparation of polymers involves a catalyst to overcome the kinetic barrier and induce an exothermic reaction.

The Si=Si bond are much weaker, the driving force for polymerization is large, hard to prevent polymerization.

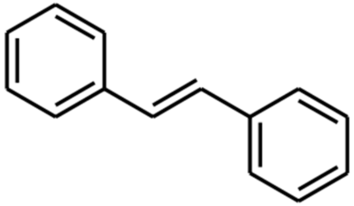
Stabilisation of Si=Si







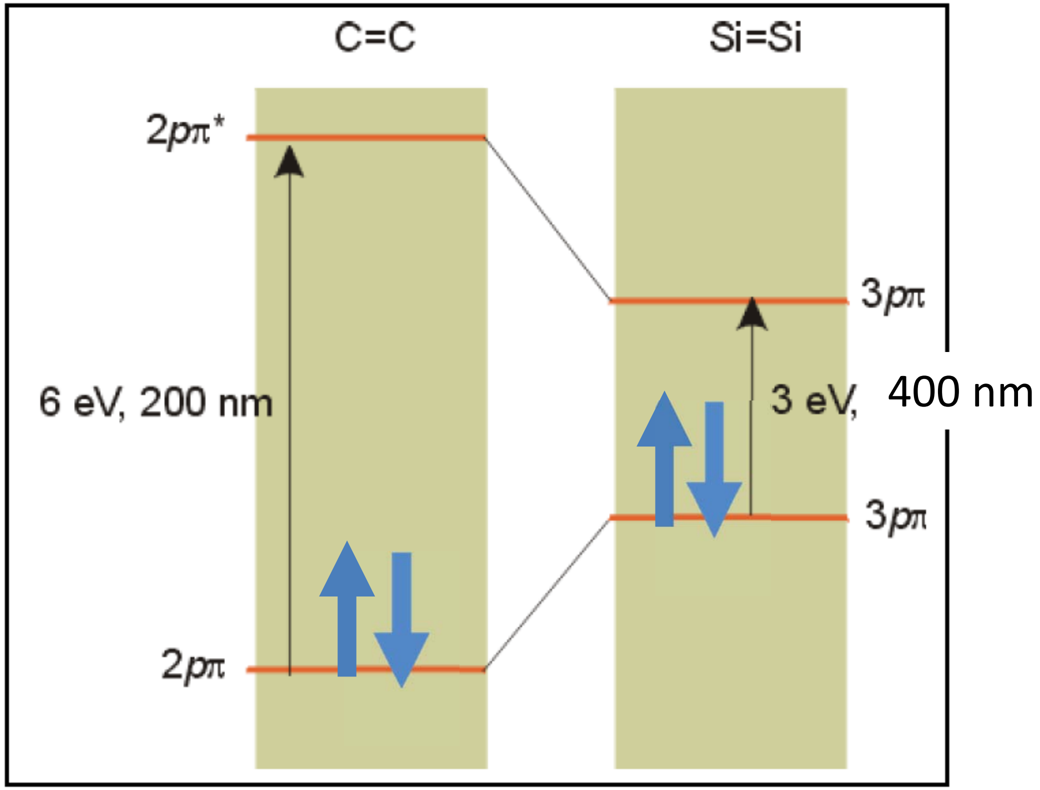
Bulky groups can inhibit catenation
Si=Si 216.0 pm
a typical Si–Si 232 pm - 8% shortening
Tetraphenylethene - C=C 12% shortening
the Z → E isomerization energy of unsymmetrical disilene, (Mes)(tBu)Si=Si(tBu)(Mes)
the barrier to inversion $E_{act} = 131$ kJ mol^{-1}
trans-stilbene only 179 kJ mol^{-1}
The barrier in the disilene is high



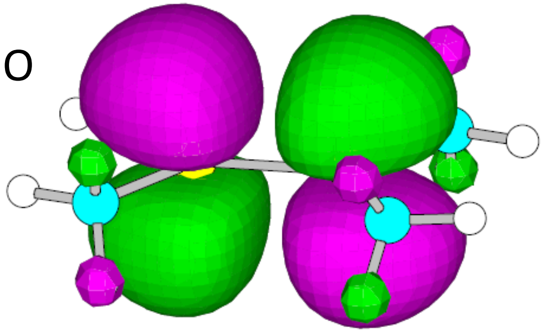
West, R.; Fink, M.J.; Michl, J. *Science* **1981**, *214*, 1343
Masamune, S. et al. *J. Am. Chem. Soc.* **1982**, *104*, 1150

π-Bonds

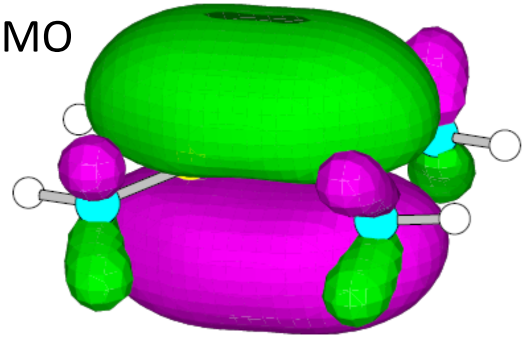
Differences in reactivity?



LUMO

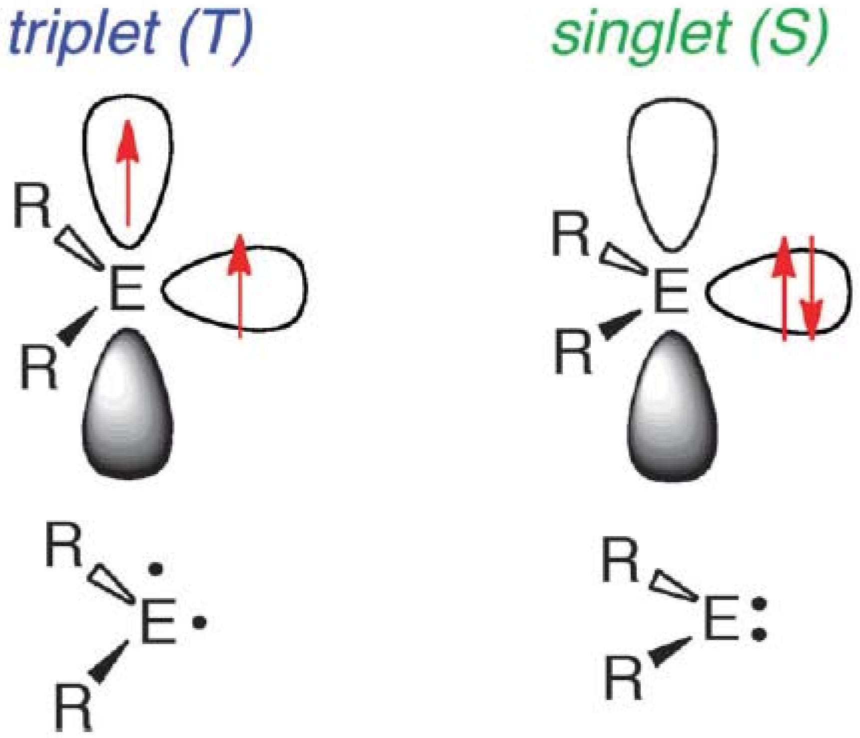


HOMO



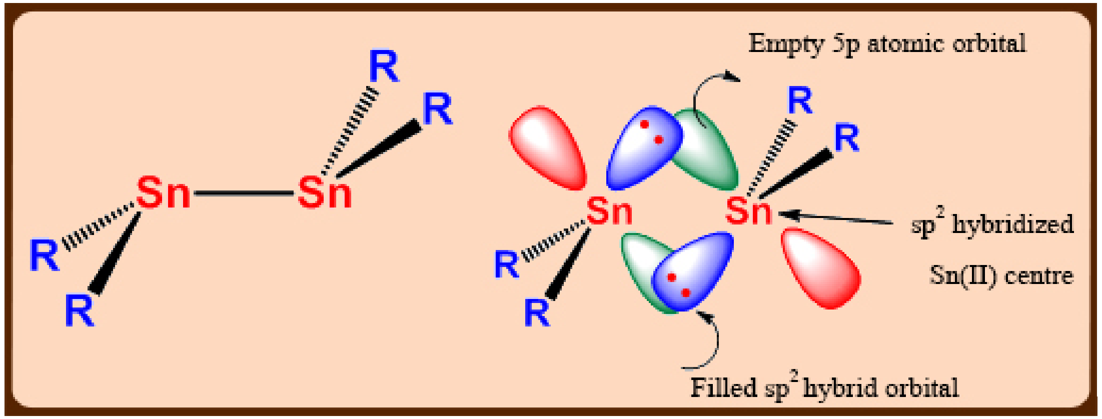
Triplet - Singlet

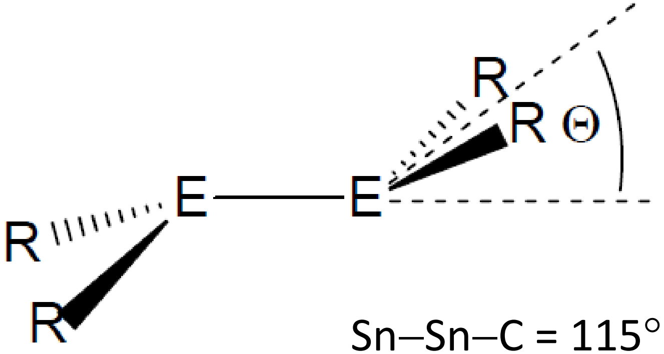
R_2C carbene triplet
R_2Sn singlet



Stabilisation of Sn=Sn

$Sn[N(SiMe_3)_2]_2 + 2\ Li[CH(SiMe_3)_2] \rightarrow Sn[CH(SiMe_3)_2]_2 + 2Li[N(SiMe_3)_2]$





Sn–Sn–C = 115°

Distannene = the first isolable species with multiple bonding between two heavier main group elements.

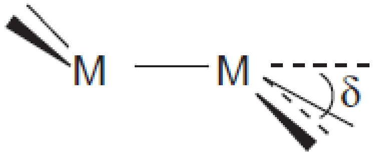
Sn-Sn distance = 2.768(1) Å
Sn elemental = 2.80 Å
$Ph_3Sn–SnPh_3$ = 2.770(4) Å

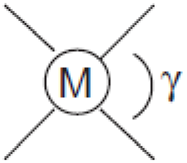
Lappert. M.F. et al. *J. Chem. Soc., Chem. Commun*. **1976**, 261

Distannene Sn=Sn

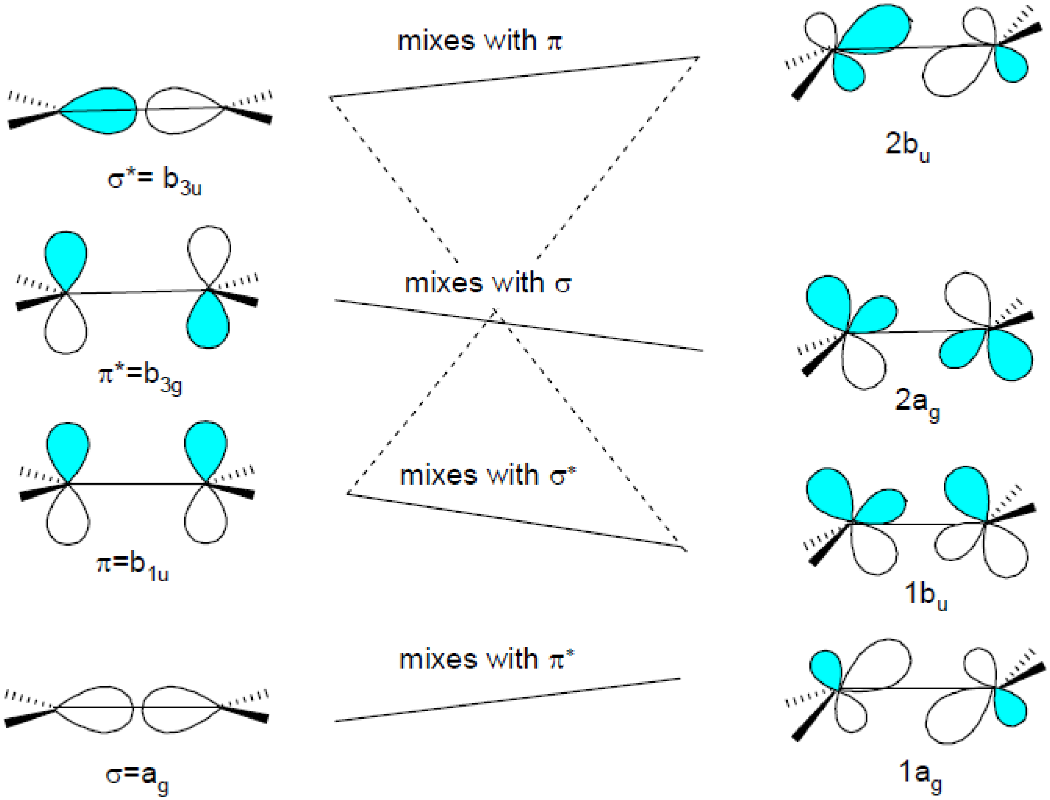
Double Bond in Heavy Elements

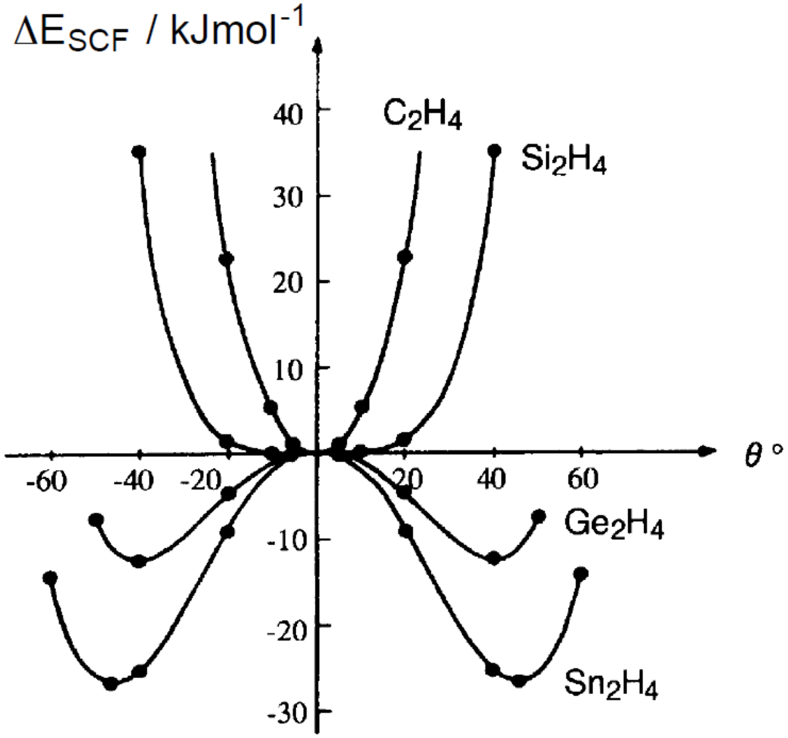
Compound	M–M/Å	δ*/°	γ*/°
$[Ge(C_6H_3Et_2\text{-}2,6)_2]_2$	2.213(2)	12	10
$[Ge(C_6HMe_3\text{-}2,3,4\text{-}Bu^t\text{-}6)_2]_2$	2.2521(8)	0	20.4
$[Ge(SiMePr^i_2)_2]_2$	2.267(1)	0	6.5
$[Ge(SiPr^i_3)_2]_2$	2.298(1)	0	16.4
$[Ge(Mes)(C_6H_3Pr^i_2\text{-}2,6)]_2$	2.301(1)	36	7
$[Ge\{CH(SiMe_3)_2\}_2]_2$	2.347(2)	32	0
$[GeCl(C_6H_3Mes_2\text{-}2,6)]_2$	2.443(2)	39	0
$\{GeN(Bu^t)(CH_2)_3N(Bu^t)SiN(Bu^t)(CH_2)_2N(Bu^t)\}_2$	2.451(2)	41.3	42.3
$[\{Ge(SiBu^t_3)_2\}_2Ge(SiBu^t_3)_2]$	2.239(4)	—	—
$[\{Ge(SiBu^t_3)\}_3][BPh_4]$	2.226(4)	—	—
$[Ge(C_6H_3Mes_2\text{-}2,6)]_3^{\bullet}$	2.35(7)	—	—
$K[\{Ge(C_6H_3Mes_2\text{-}2,6)\}_3]$	2.422(2)	—	—
$[Sn\{CH(SiMe_3)_2\}_2]_2$	2.768(1)	41	0
$[Sn\{Si(SiMe_3)_3\}_2]_2$	2.8247(6)	28.6	63.2
$[Sn\{C_6H_2(CF_3)_3\text{-}2,4,6\}\{Si(SiMe_3)_3\}]_2$	2.833(1)	41.5	0
$[Sn(C_6HMe_3\text{-}2,3,4\text{-}Bu^t\text{-}6)_2]_2$	2.910(1)	21.4, 64.4	—
$[Sn\{C_6H_2(CF_3)_3\text{-}2,4,6\}_2]_2$	3.639(1)	46	0
$[K(THF)_6][\{SnC_6H_3Trip_2\text{-}2,6\}_2]$	2.8123(9)	95.20	0
$[Pb\{C_6H_2(CF_3)_3\text{-}2,4,6\}\{Si(SiMe_3)_3\}]_2$	3.537(1)	40.8	0

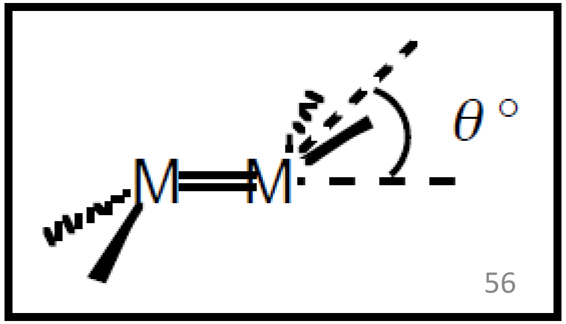




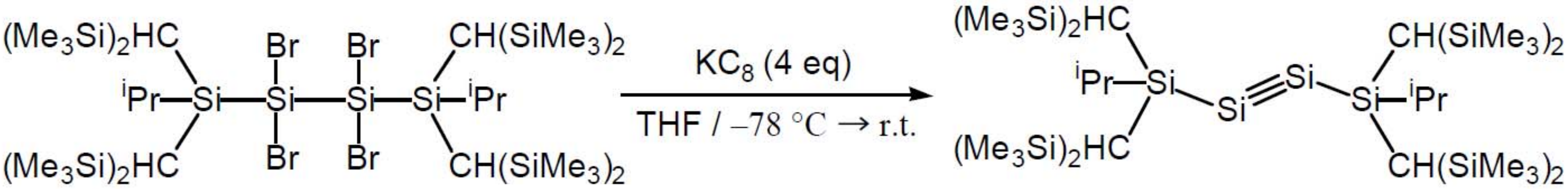
Double Bond in Heavy Elements

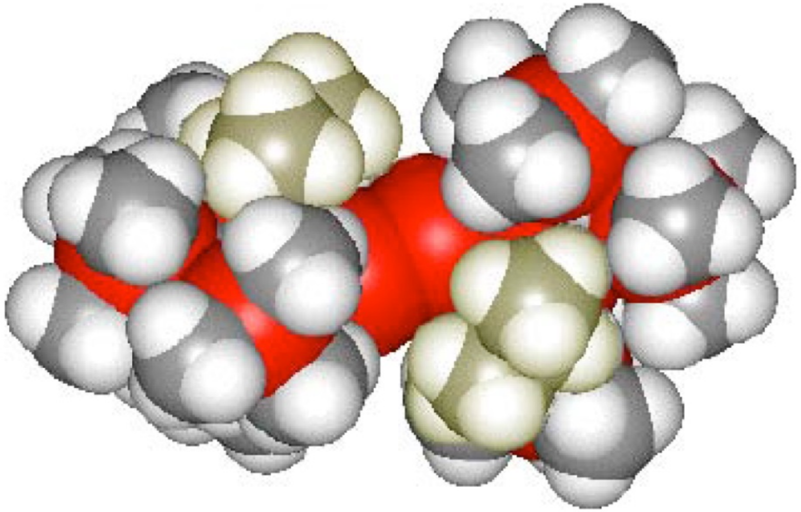






Triple Bond - Disilyne



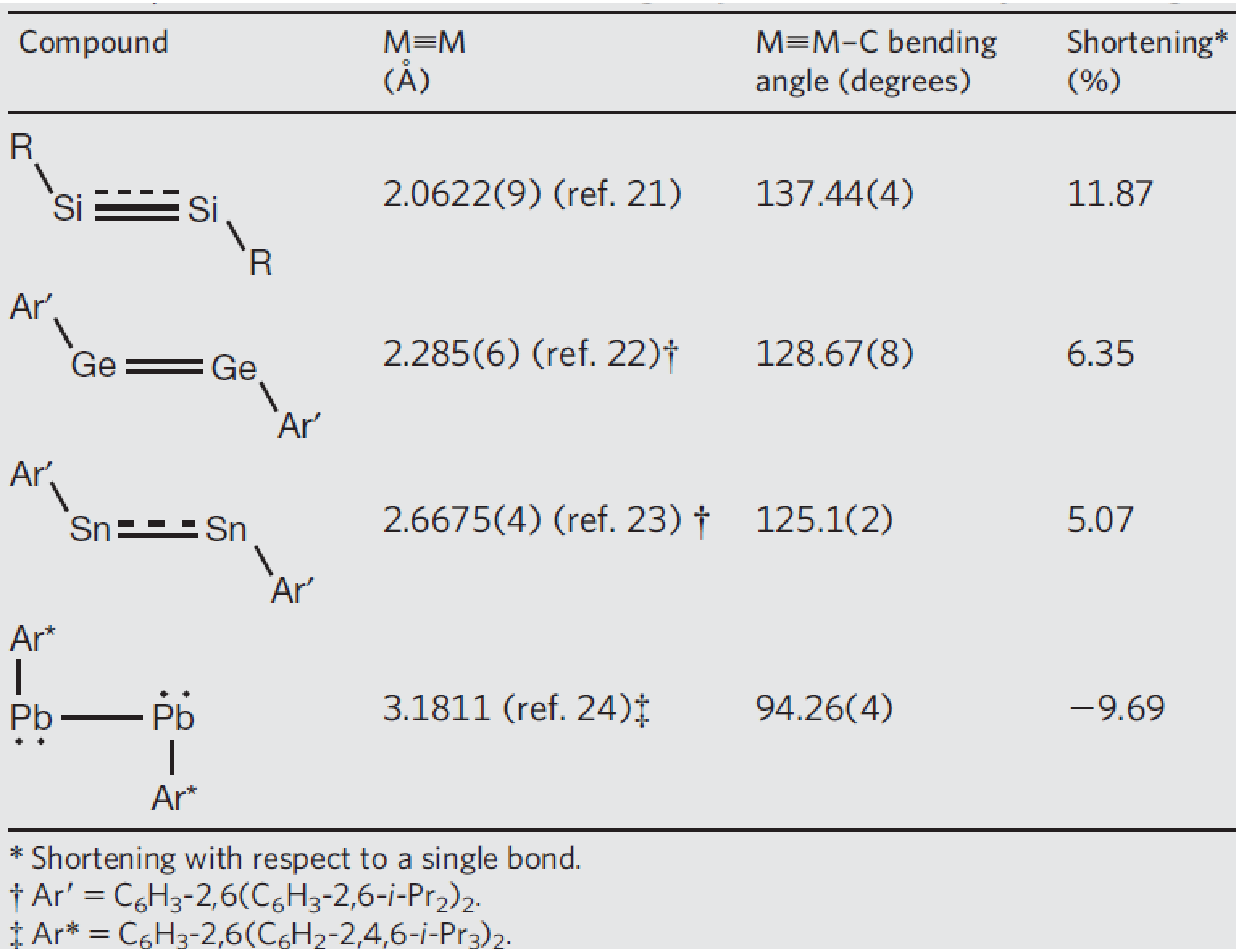


Si≡Si 2.0622(9) Å
half the magnitude of the bond shortening of alkynes/alkenes

the substituents at the Si≡Si group are trans-bent, a bond angle of 137.44(4)°

Sekiguchi, A.; Kinjo, R.; Ichinohe, M. *Science* **2004**, *305,* 1775

Heavier Gr14 Alkyne Analogues



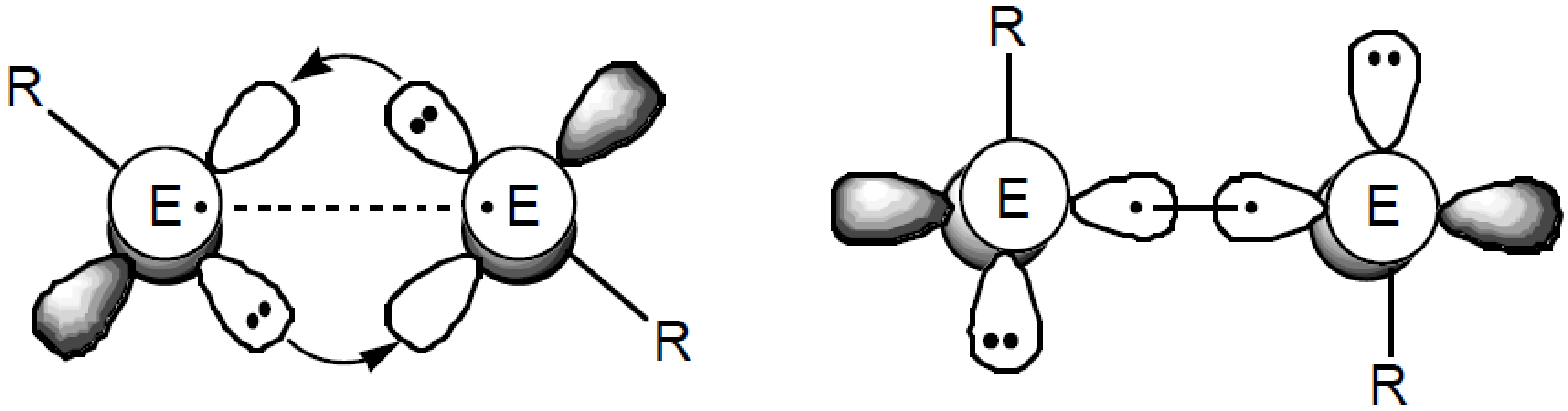
Compound	M≡M (Å)	M≡M–C bending angle (degrees)	Shortening* (%)
R Si Si R	2.0622(9) (ref. 21)	137.44(4)	11.87
Ar′ Ge Ge Ar′	2.285(6) (ref. 22)†	128.67(8)	6.35
Ar′ Sn Sn Ar′	2.6675(4) (ref. 23) †	125.1(2)	5.07
Ar* Pb Pb Ar*	3.1811 (ref. 24)‡	94.26(4)	−9.69

* Shortening with respect to a single bond.

† Ar′ = C_6H_3-2,6(C_6H_3-2,6-*i*-Pr_2)$_2$.

‡ Ar* = C_6H_3-2,6(C_6H_2-2,4,6-*i*-Pr_3)$_2$.

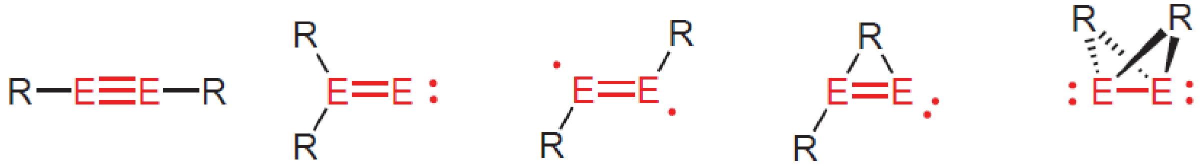
Heavier Gr14 Alkyne Analogues

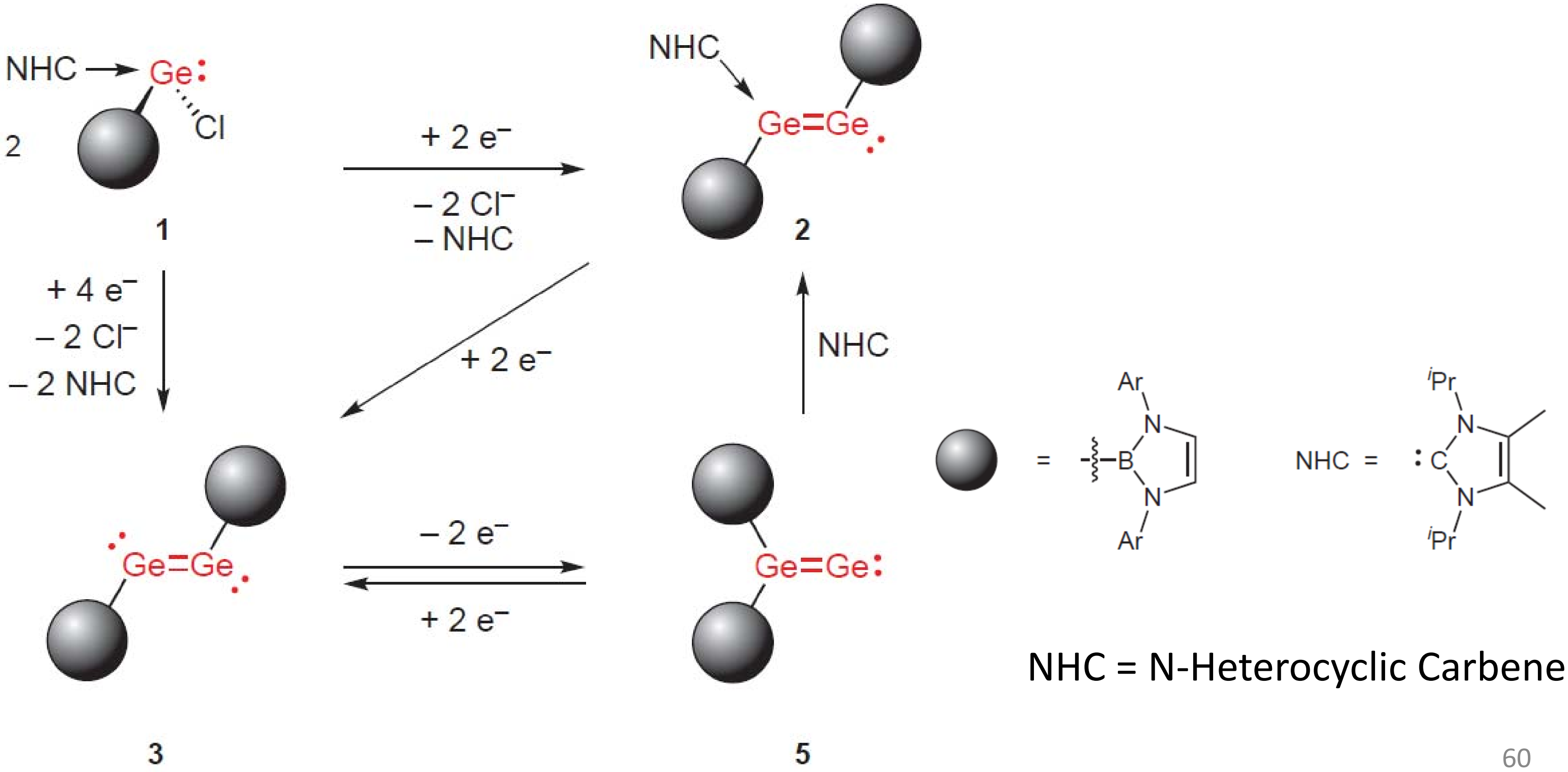


The 6s^2 valence electrons are stabilized by relativistic effects - they participate less in bonding.

The Pb-Pb single bond formed by head-to-head overlap of 6p orbitals, which have
a larger radius than 6s and hence form longer bonds

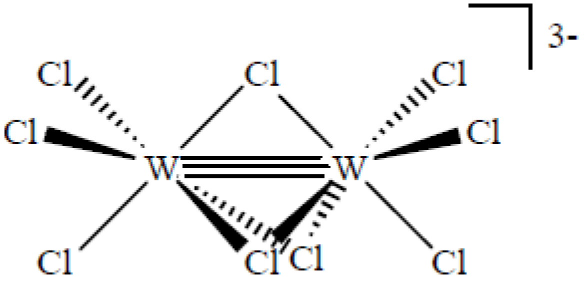
Vinylidene / Acetylene Isomers



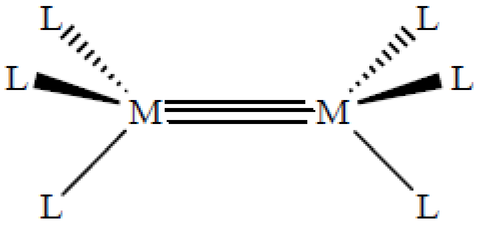


NHC = N-Heterocyclic Carbenes

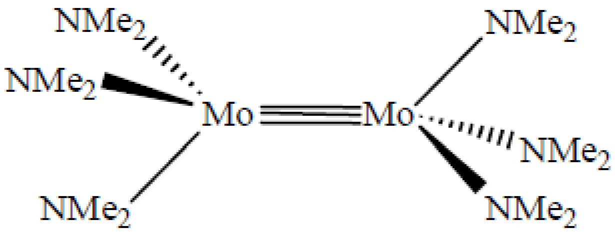
Triple M≡M Bond



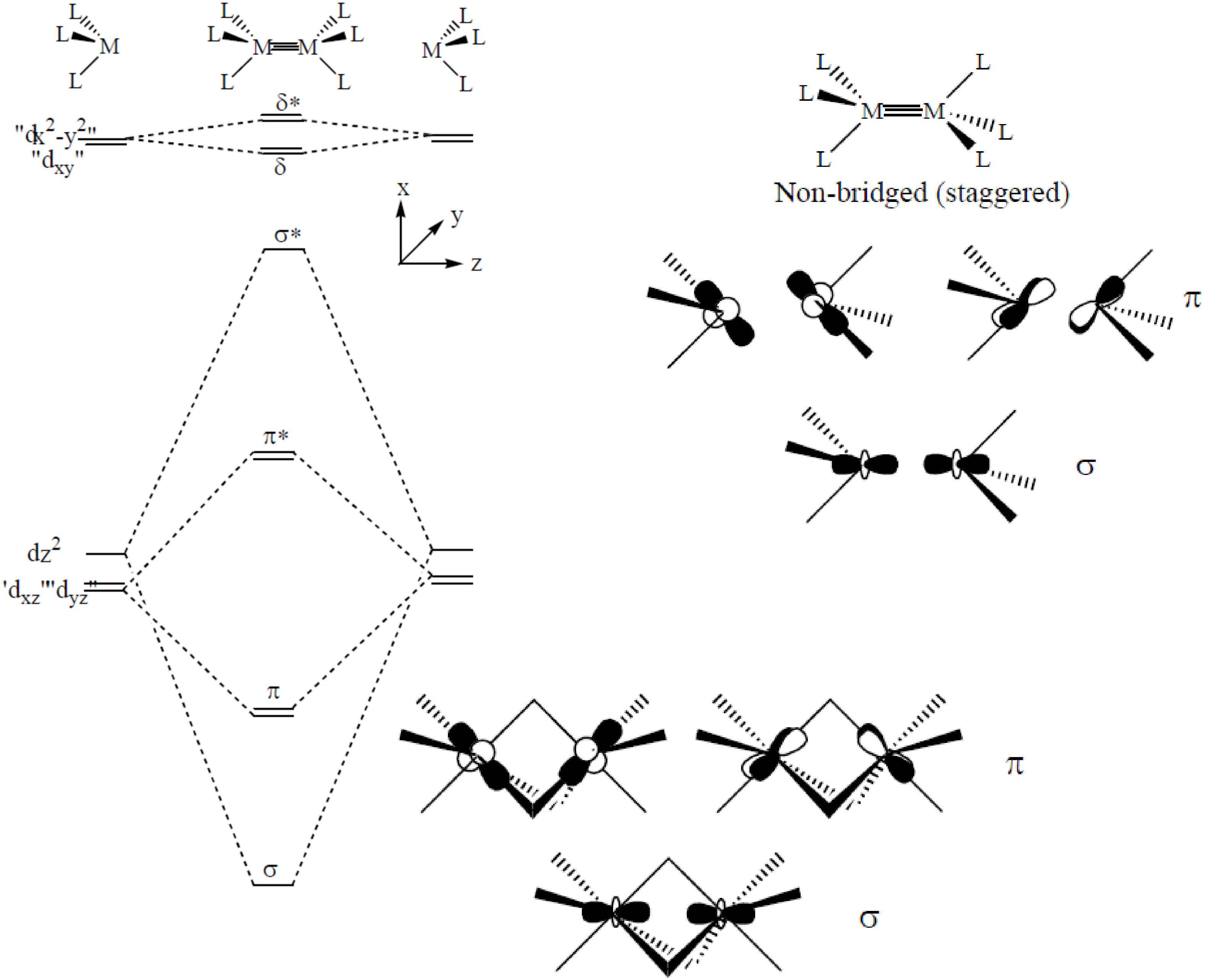
Bridged



Non-bridged (eclipsed)

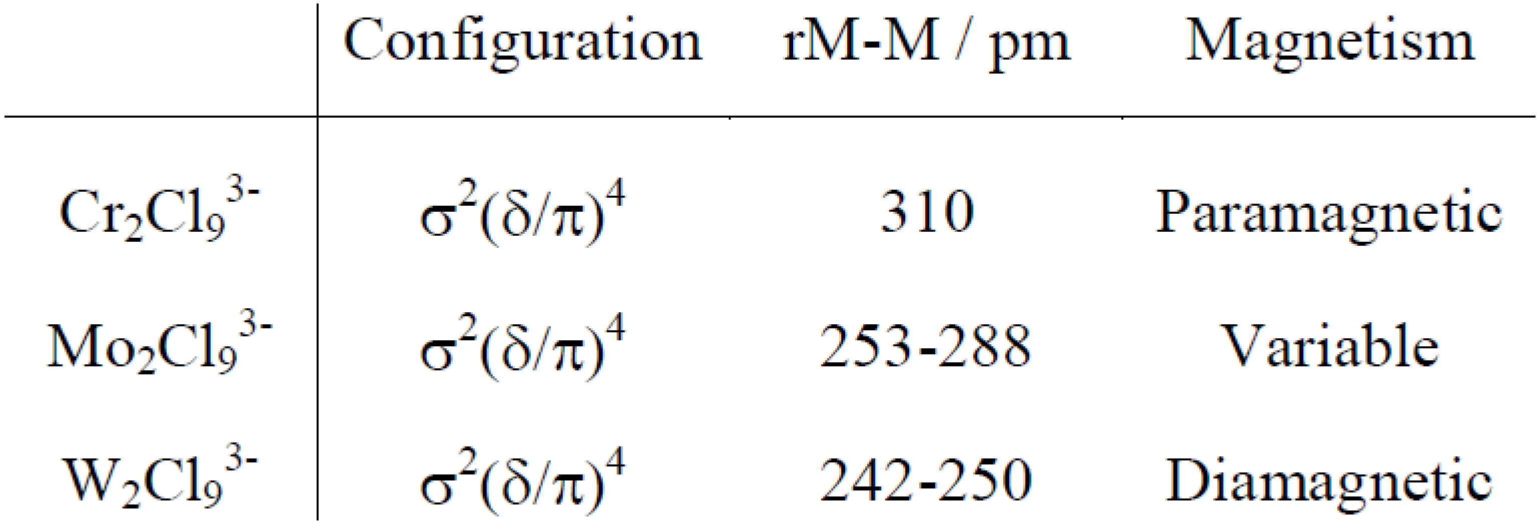


Non-bridged (staggered)



Non-bridged (staggered)

Triple $M{\equiv}M$ Bond



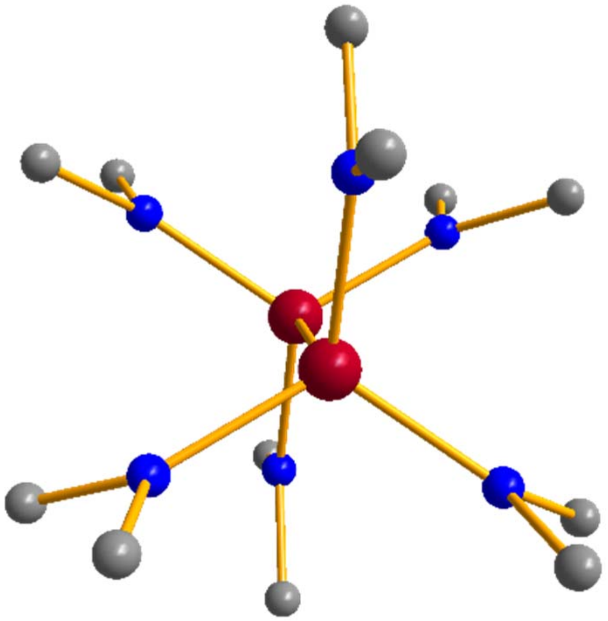
	Configuration	rM-M / pm	Magnetism
$Cr_2Cl_9^{3-}$	$\sigma^2(\delta/\pi)^4$	310	Paramagnetic
$Mo_2Cl_9^{3-}$	$\sigma^2(\delta/\pi)^4$	253-288	Variable
$W_2Cl_9^{3-}$	$\sigma^2(\delta/\pi)^4$	242-250	Diamagnetic

$Cr_2Cl_9^{3-}$ two $CrCl_3$ fragments held together by 3 bridging Cl, no d-orbital overlap, no direct Cr-Cr bond, paramagnetic with 6 unpaired electrons.

$Mo_2Cl_9^{3-}$ the Mo-Mo distance depends on the cation present in the crystal structure, variable bonding and magnetism.

$W_2Cl_9^{3-}$ good overlap and a triple W-W bond with no unpaired electrons.

Triple M≡M Bond

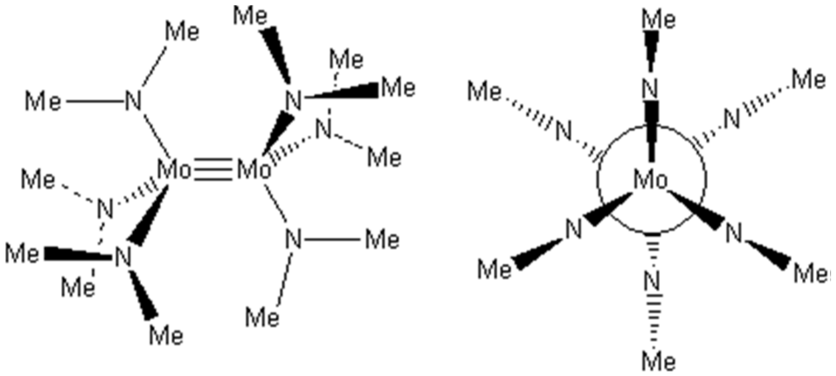


$Mo_2(NMe_2)_6$
a $\sigma^2\pi^4$ triple bond
a short Mo–Mo bond length of 2.214(2) Å

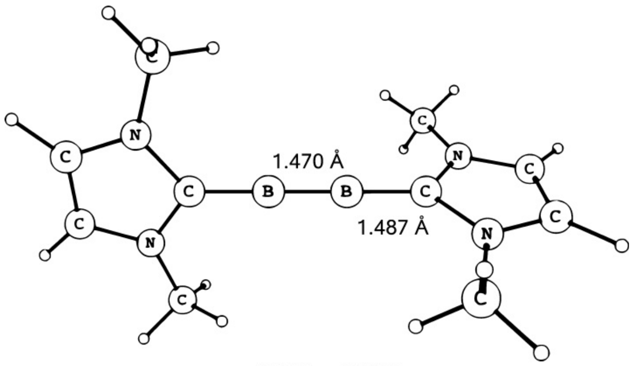
M.H. Chisholm, F.A. Cotton, B.A. Frenz, W.W. Reichert, L.W. Shive, B.R. Stults, J. Am. Chem. Soc. 98 (1976) 4469

$W_2(NMe_2)_6$
a W–W bond length of 2.294(1) Å

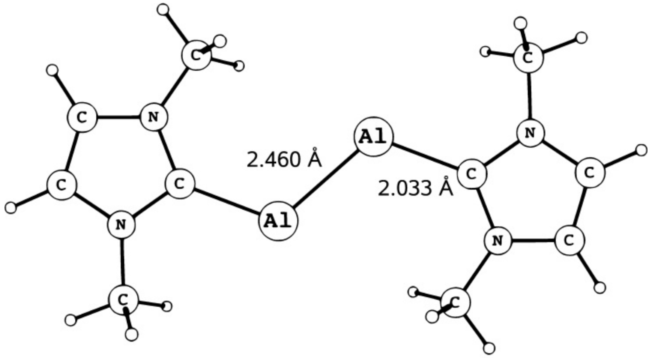
M.H. Chisholm, F.A. Cotton, M. Extine, B.R. Stults, J. Am. Chem. Soc. 98 (1976) 4477



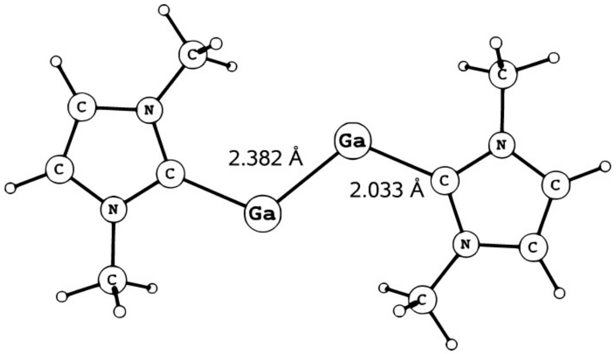
Triple M≡M Bond in Gr13



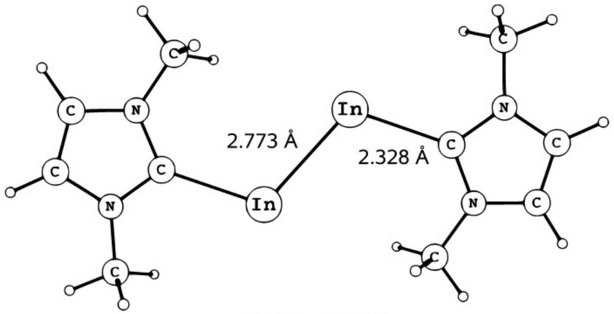
a(CBB) = 180.0°



a(CAlAl) = 117.8°
d(CAlAlC) = 180°



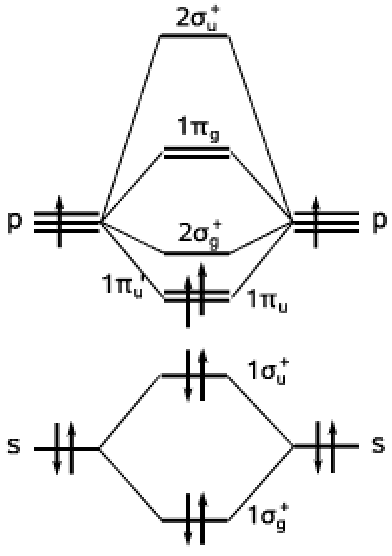
a(CGaGa) = 117.5°
d(CGaGaC) = 180°



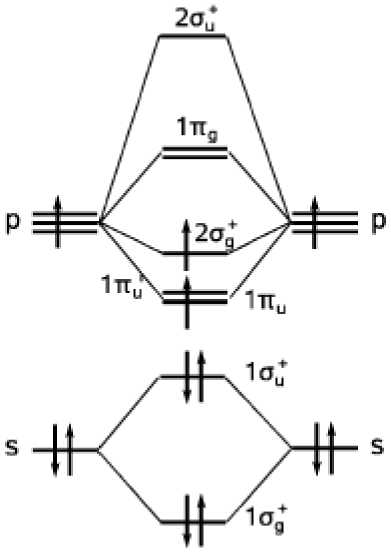
a(CInIn) = 113.0°
d(CInInC) = 180°

N. Holzmann, A. Stasch, C. Jones, G. Frenking, *Chem. Eur. J.* **2011**, *17*, 13517.

Triple E≡E Bond in Gr13



a) $X(B_2)\ ^3\Sigma_g^-$

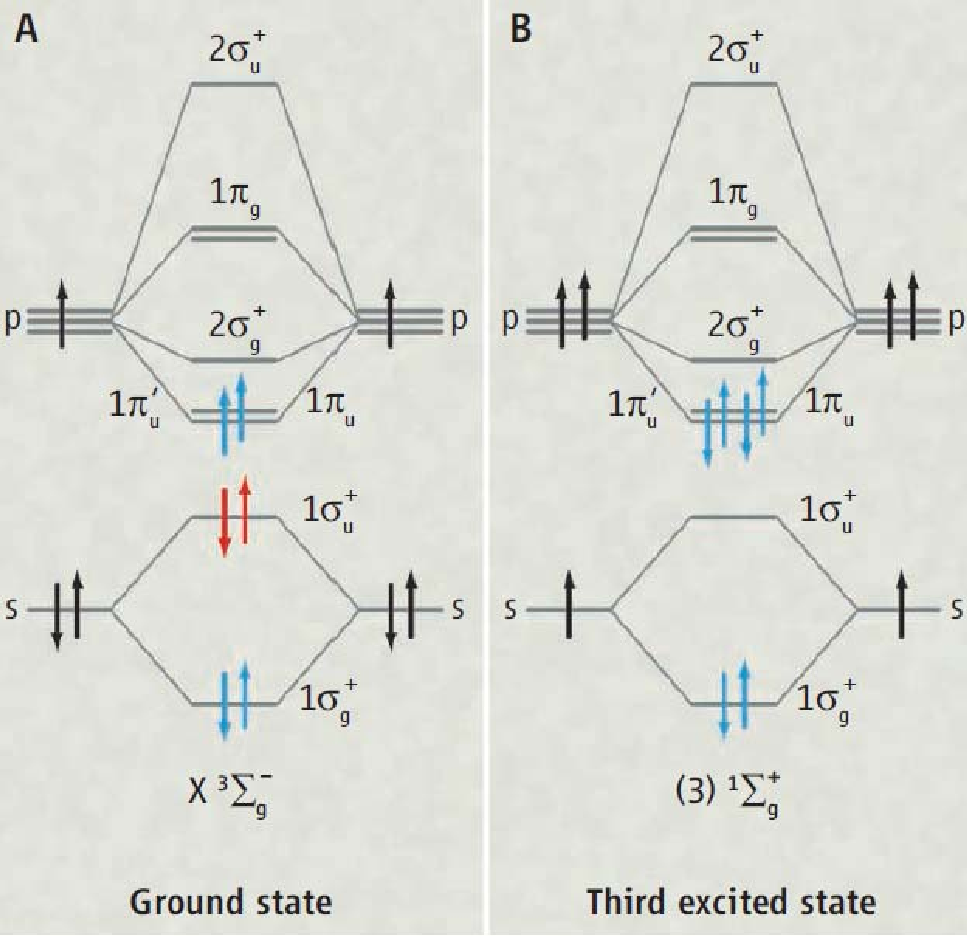


c) $X(E_2)\ ^3\Pi_u$

ground state of B_2

ground state of E_2 (E = Al–In)

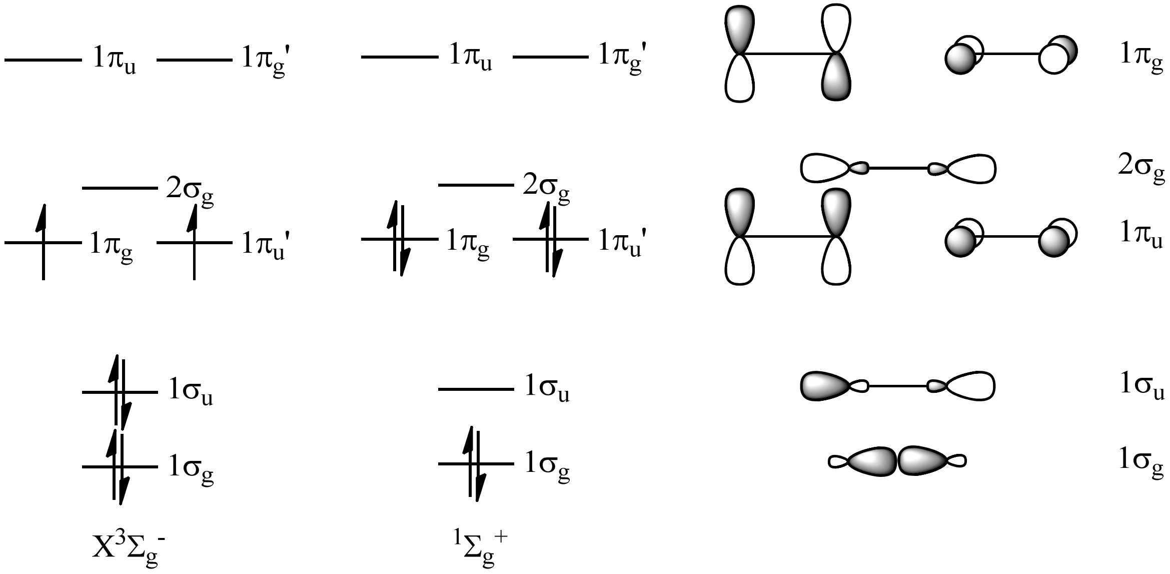
Triple E≡E Bond in Gr13

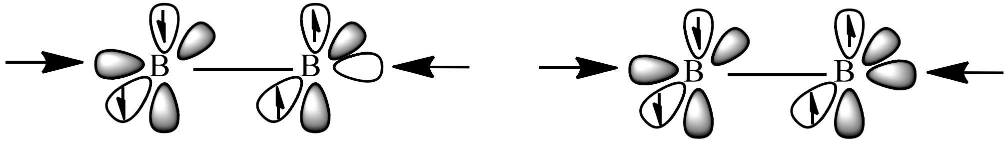


The ground state, seen in ligand free B_2, has two doubly occupied bonding orbitals (blue) but one doubly occupied antibonding orbital (red), giving a bond order of 1 and hence a single bond.

In contrast, the third excited state observed in (NHC)→B≡B←(NHC) has three doubly occupied bonding orbitals and hence a triple bond.

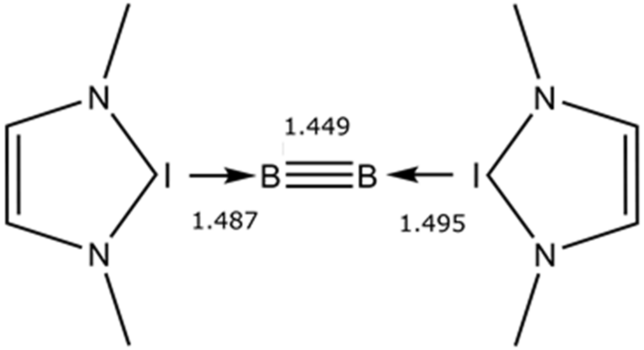
Triple E≡E Bond in Gr13



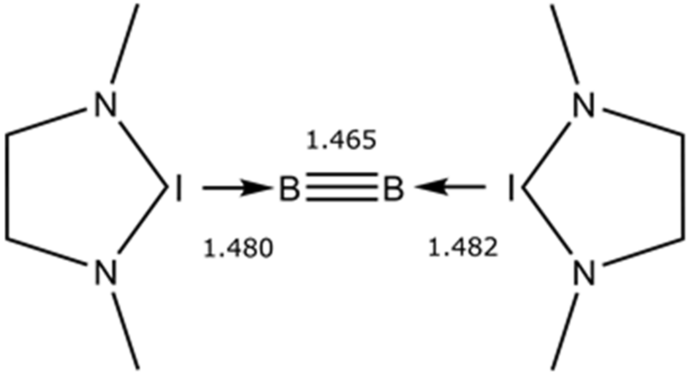


$B_2[X^3\Sigma_g^-] \longrightarrow B_2[(3)^1\Sigma_g^+]$ = 106.6 kcal/mol

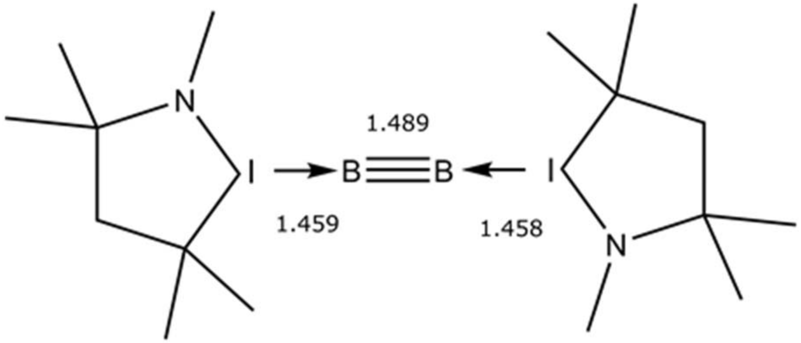
$B_2(NHC)_2 \longrightarrow B_2[X^3\Sigma_g^-] + 2\ NHC$ = 187.7 kcal/mol



Braunschweig et al., *Science* **2012,** *336*, 1420.



Braunschweig et al., *Angew. Chem. Int. Ed*. **2014**, *53*, 9082.

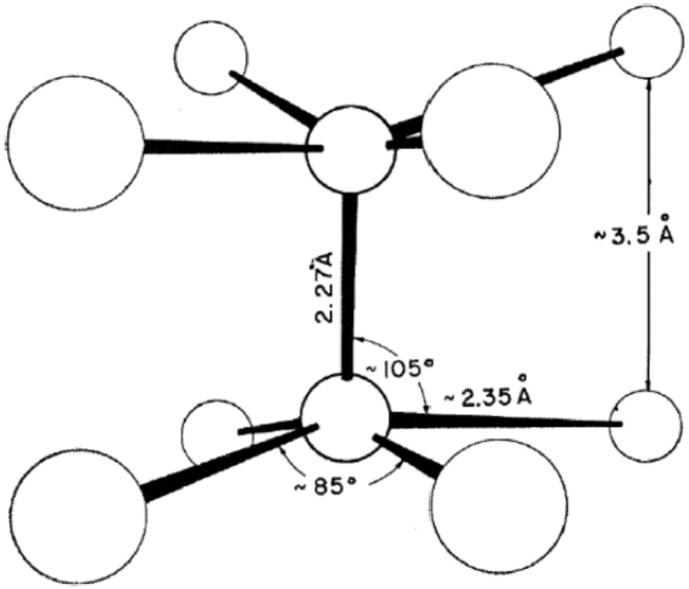


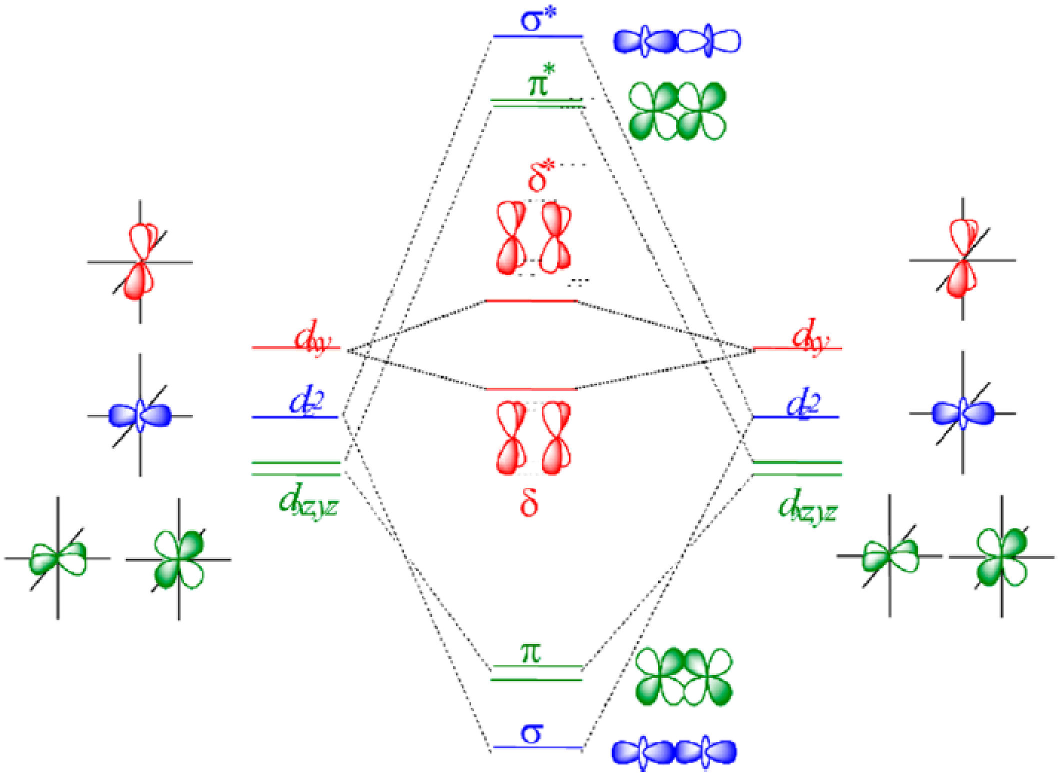
Braunschweig et al., *Angew. Chem. Int. Ed*. **2015**, *online*.

Quadruple Bond

1964 – F. A. Cotton – the first bond order higher than 3

$[Re_2Cl_8]^{2-}$





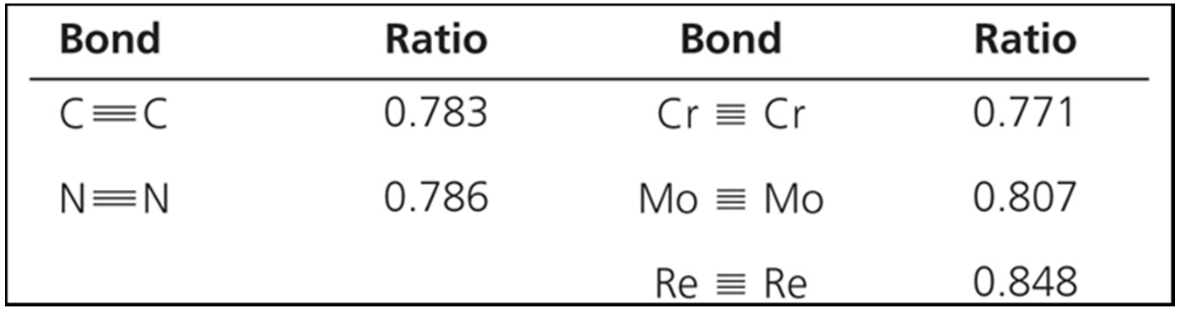
Eclipsed

δ–δ* transition   14700 cm^{-1} (1.82 eV)

EBO = 3.2

the sum of the partial bond orders 0.92 (σ), 1.74 (π) and 0.54 (δ)

Formal Shortness Ratio (FSR)



Bond	Ratio	Bond	Ratio
C≡C	0.783	Cr ≣ Cr	0.771
N≡N	0.786	Mo ≣ Mo	0.807
		Re ≣ Re	0.848

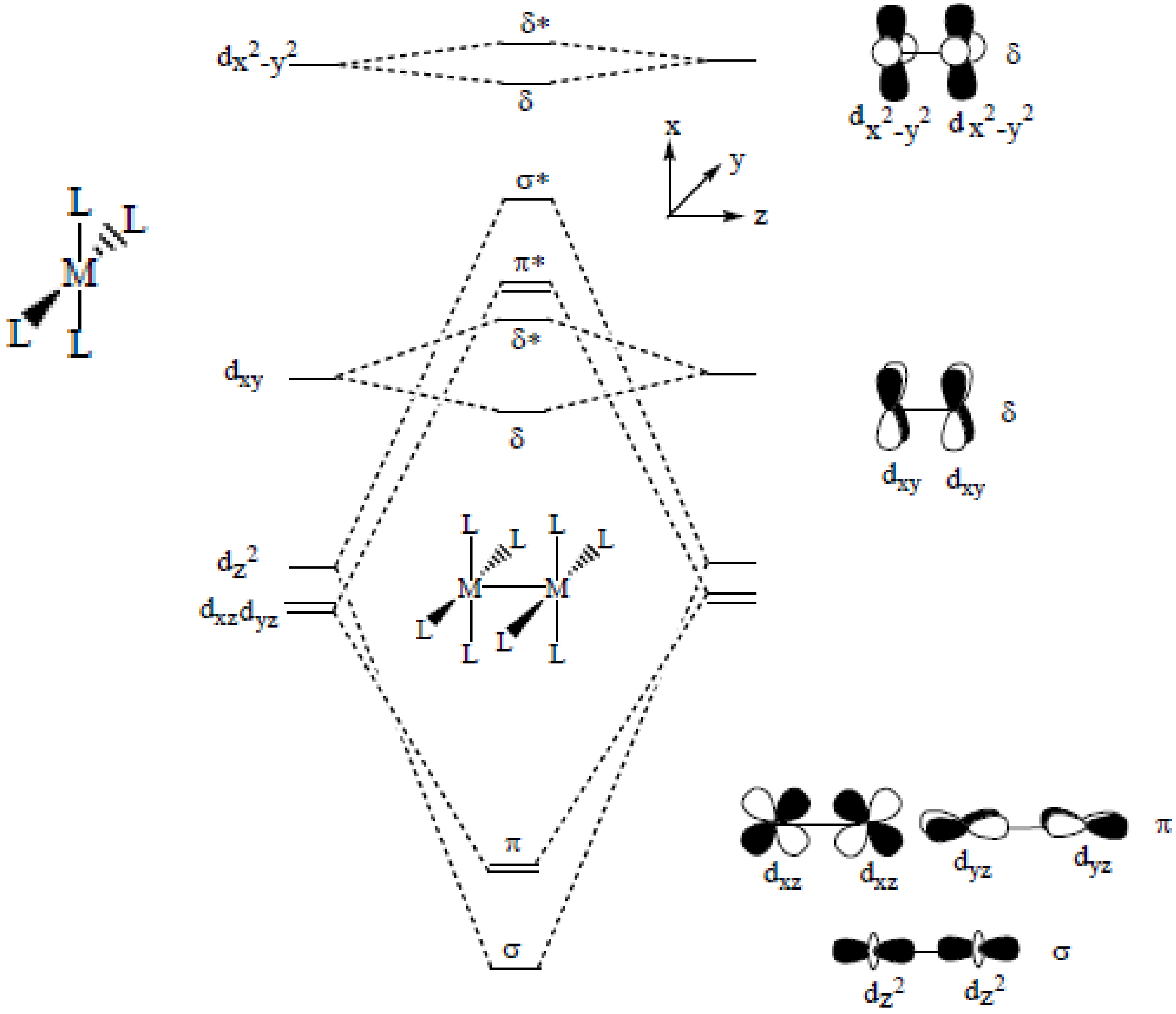
F. A. Cotton - A short bond?

The FSR is a dimensionless number given by the ratio of the atom–atom distance, *d*, of a bond and the sum of the radii of the two atoms involved, $r_A + r_B$:

FSR = $d/(r_A + r_B)$

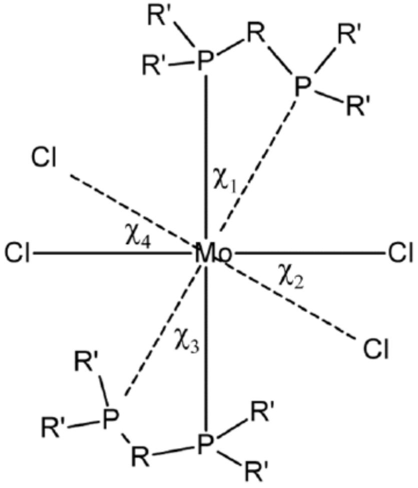
The advantage of this formalism is its interelement applicability. The FSR is a useful tool for comparing formal multiple bonding and short metal–metal distances

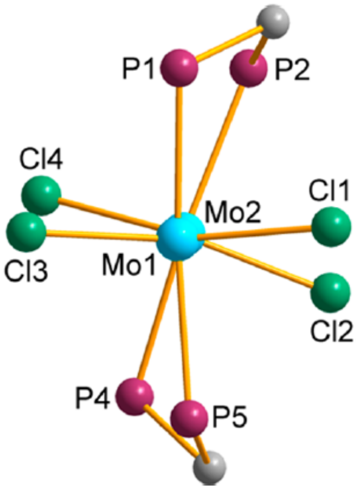
Quadruple Bond



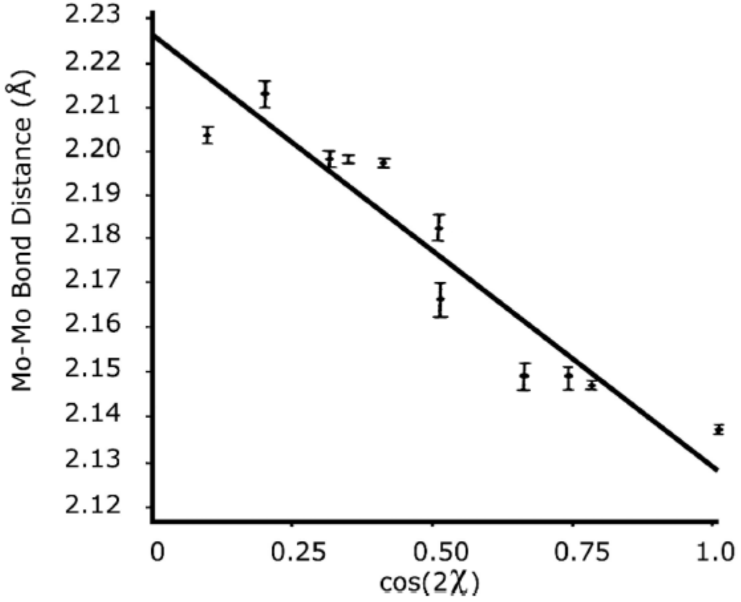
Quadruple Bond

the Mo−Mo distances changes as torsional strain is introduced by bridging diphosphines with concomitant diminution of the d_{xy}−d_{xy} overlap, i.e., the δ bond.





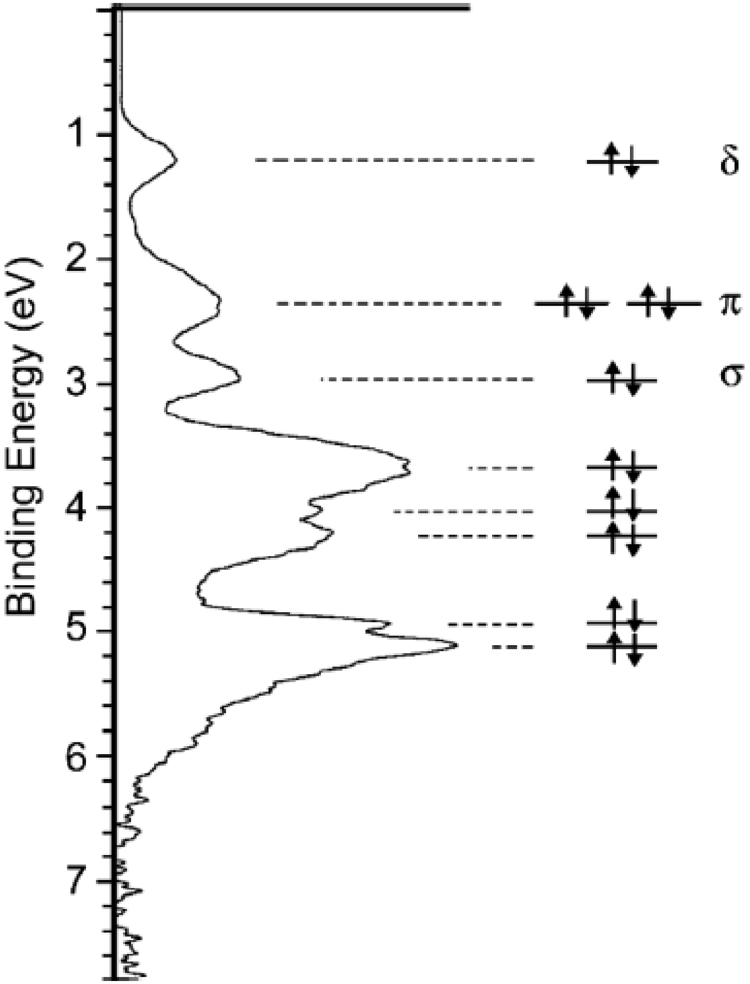
$Mo_2X_4(PR_3)_4$ and $Mo_2X_4(diphosphine)_2$
X = Cl and Br



internal twist
rotation about the metal−metal bond
average of 4 torsion angles

χ = 0° - an eclipsed configuration (b.o. = 4)
χ = 45° - a staggered configuration (b.o. = 3)

Quadruple Bond in PES



PES spectrum of the $[Re_2Cl_8]^{2-}$ anion

1 eV = 1.6×10^{-19} J

Oxidation $Mo_2(TiPB)_4$ to $[Mo_2(TiPB)_4]^+$

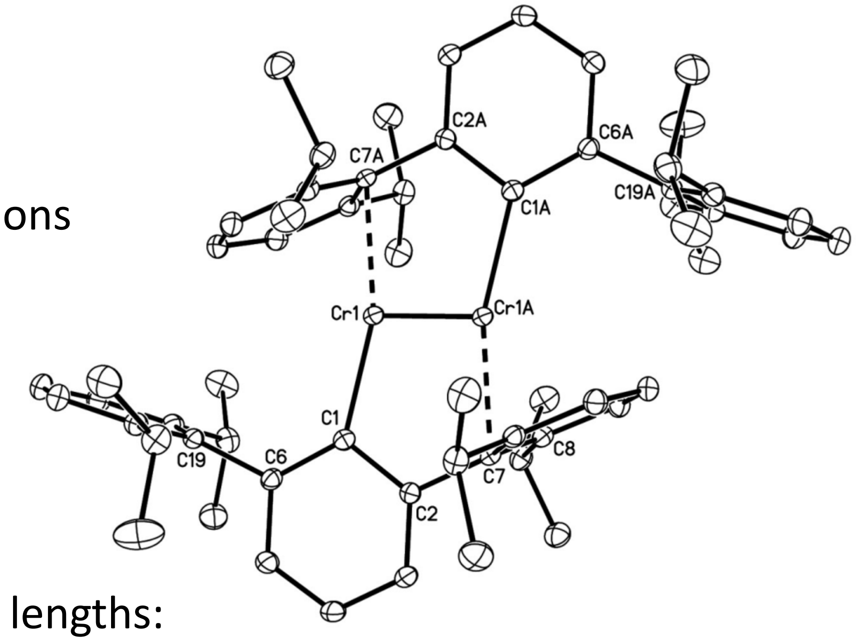
$Mo_2^{4+} \rightarrow Mo_2^{5+}$
one unpaired electron (EPR)

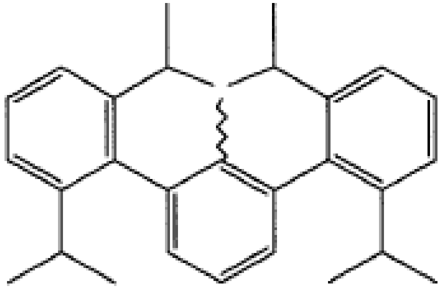
Mo−Mo distance 0.06 Å longer
electron removed from a bonding δ orbital

b.o. = 3.5

Quintuple Cr-Cr Bonding

Strategies for stabilization of multiple bonds
Maximum of valence electrons at metal
Minimum number of attached ligands
Bulky ligands to prevent intermolecular reactions
Monovalent m-terfenyl ligands





Bond lengths:
Cr-Cr = 1.8351 Å
Cr(1)-C(1A) = 2.131 Å
Cr(1)-C(7A) = 2.2943 Å
Bond angle: Cr(1A)-Cr(1)-C(1) = 102.78°

T. Nguyen, A. D. Sutton, M. Brynda, J.C. Fettinger, G. J. Long, P. P. Power, *Synthesis of stable compound with fivefold bonding between two chromium(I) centers*, Science **2005**, 310, 844. Doi 10.1126/science.1116789

Quintuple Cr-Cr Bonding

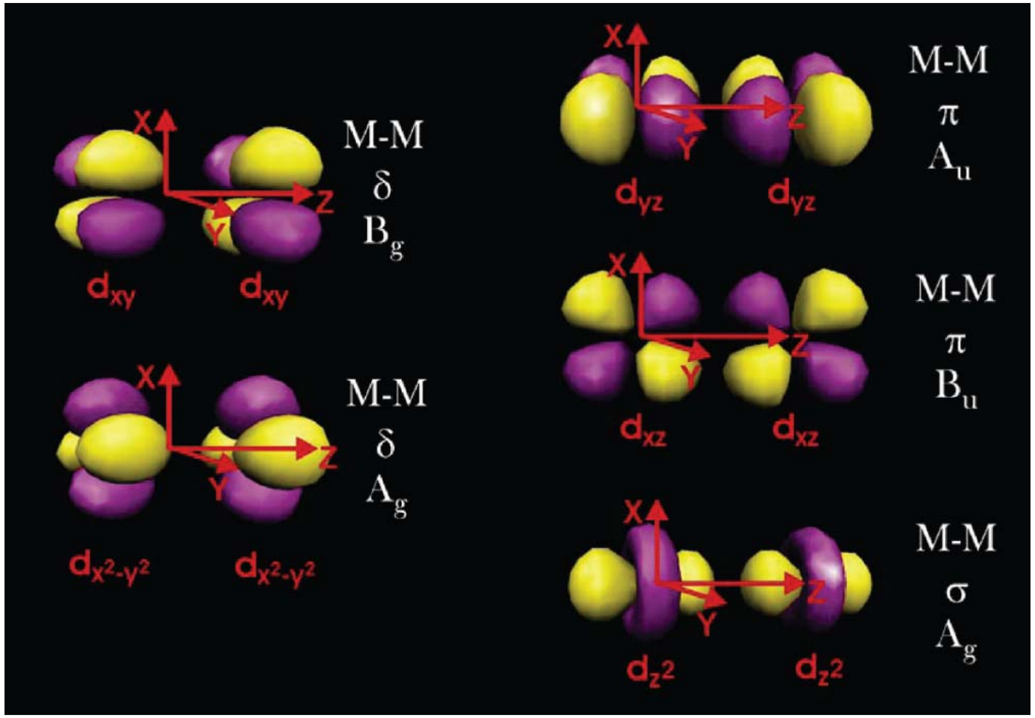
$CrCl_2(THF)_2$ + LiAr' → ½ $[Cr(\mu\text{-}Cl)Ar']_2$ + LiCl

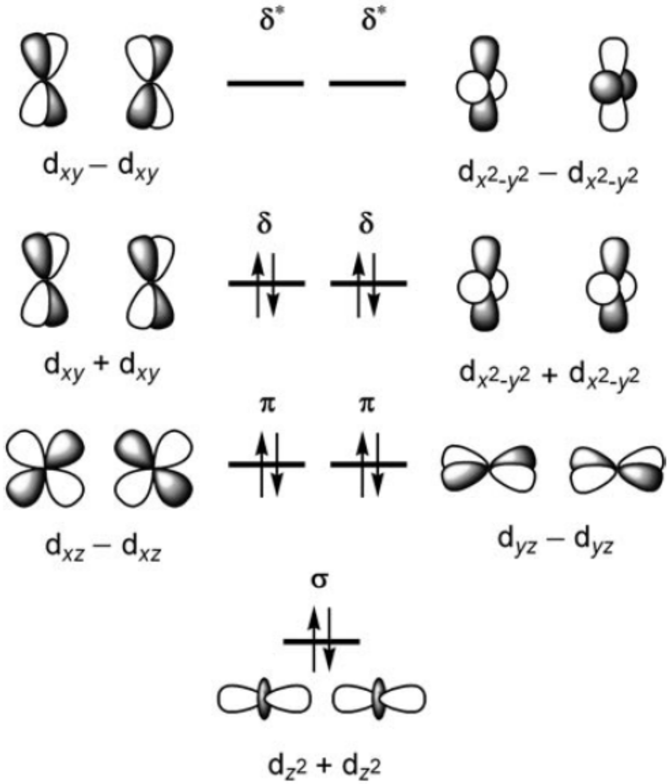
in THF, Ar' = $C_6H_3\text{-}2,6(C_6H_3\text{-}2,6\text{-}iPr_2)_2$

$[Cr(\mu\text{-}Cl)Ar']_2$ + 2 KC_8 → $[Cr_2(C_6H_3\text{-}2,6\text{-}(C_6H_3\text{-}2,6\text{-}iPr_2)_2)_2]$
+ KCl

Quintuple Cr-Cr Bonding

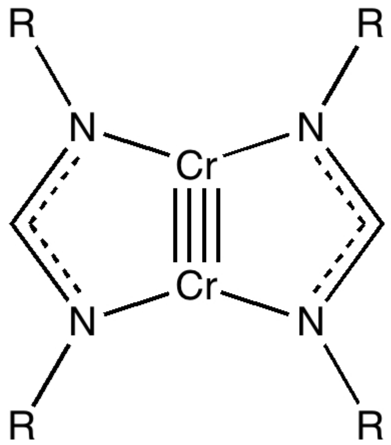
Cr-Cr bonding = $\sigma + 2\pi + 2\delta$

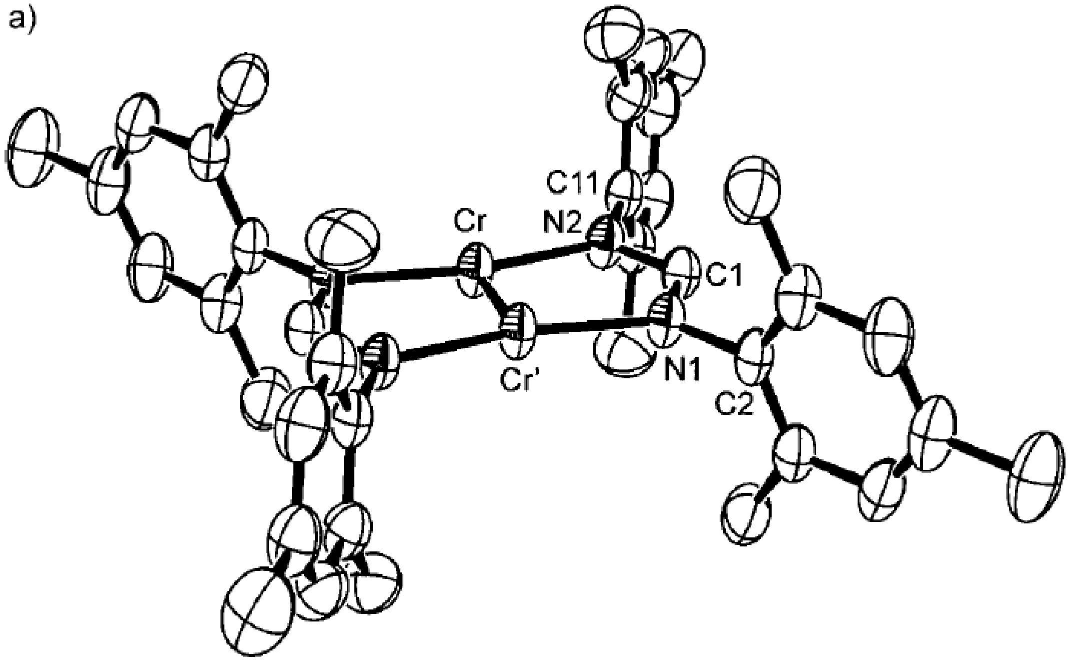




Quintuple bond = five electron pairs play a role in holding the metal atoms together. It does not imply that the bond order is five or that the bonding is very strong since the ground state of the molecule mixes with higher energy configurations with less bonding character. This gives lower, usually non-integer, bond orders.

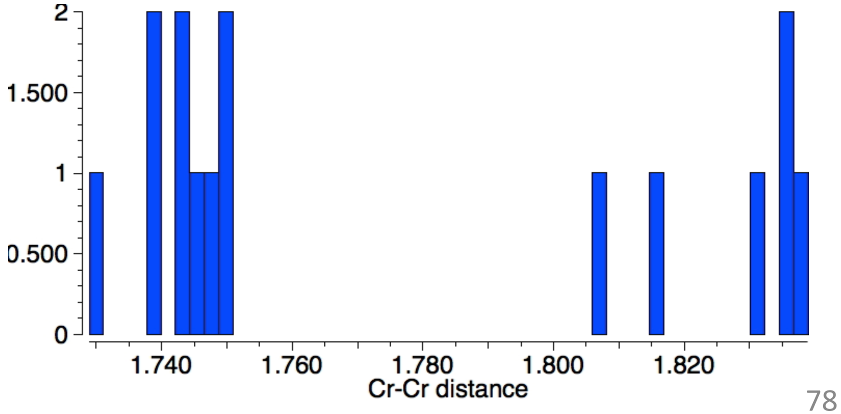
Quintuple Cr-Cr Bonding





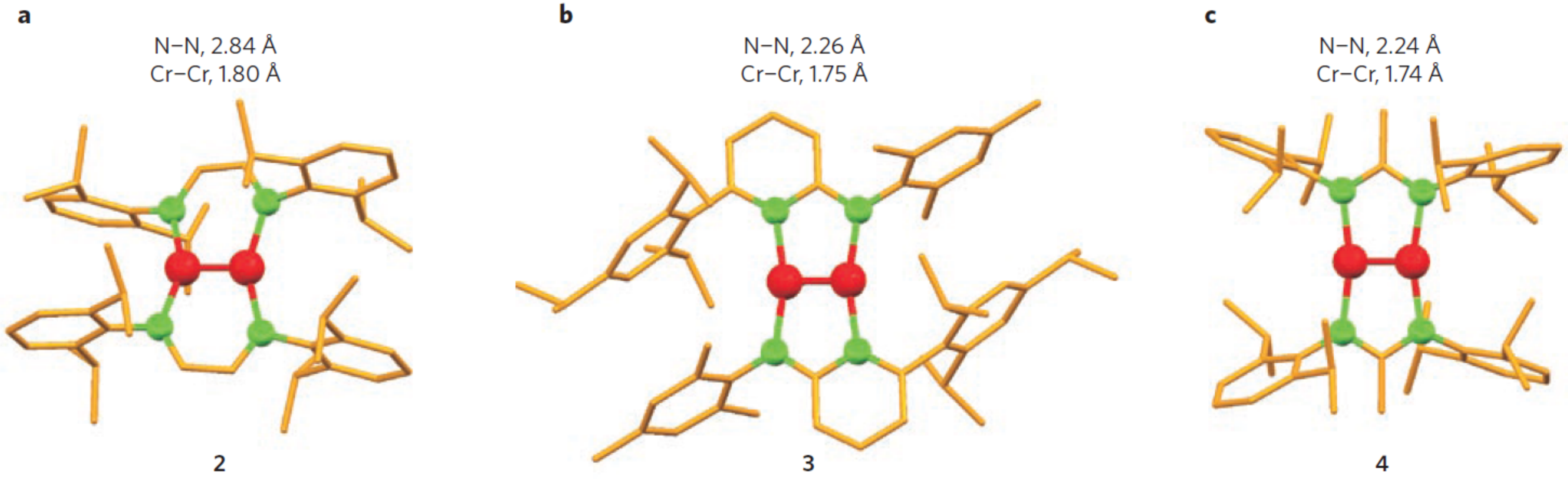
Cr-Cr
R = Mes 1.7404(8) Å
R = Xylyl 1.7397(9) Å

Cottons “formal shortness ratio” (FSR)
FSR = 0.733
the FSR of dinitrogen is 0.786



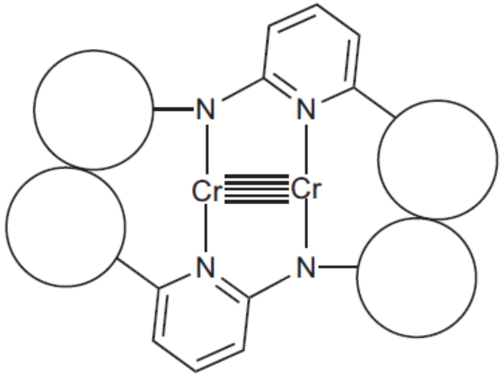
Quintuple Cr-Cr Bonding

The Hein– Cotton concept
three-atom bridging ligands to establish short metal–metal distances

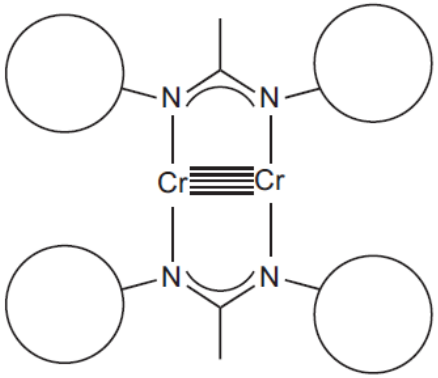


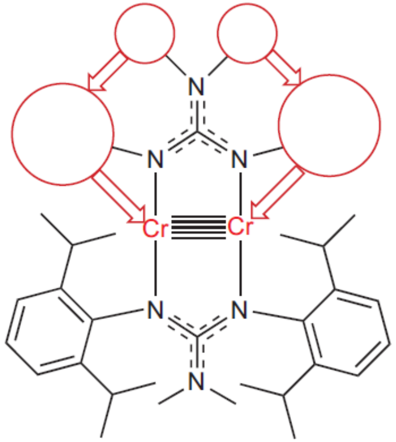
Importance of the ligand in establishing short metal–metal bonds:
The N–N distances correlate with the Cr–Cr bond lenghts.

The Shortest M–M Bond

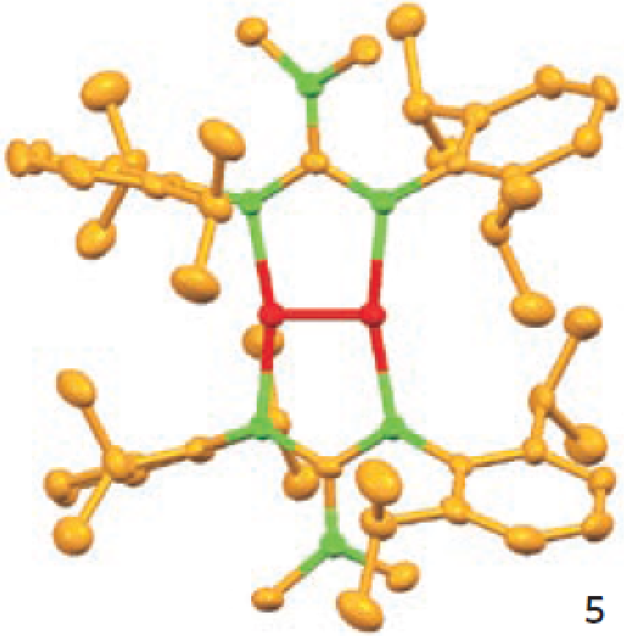


a





Cr–Cr, 1.7293(12) Å



5

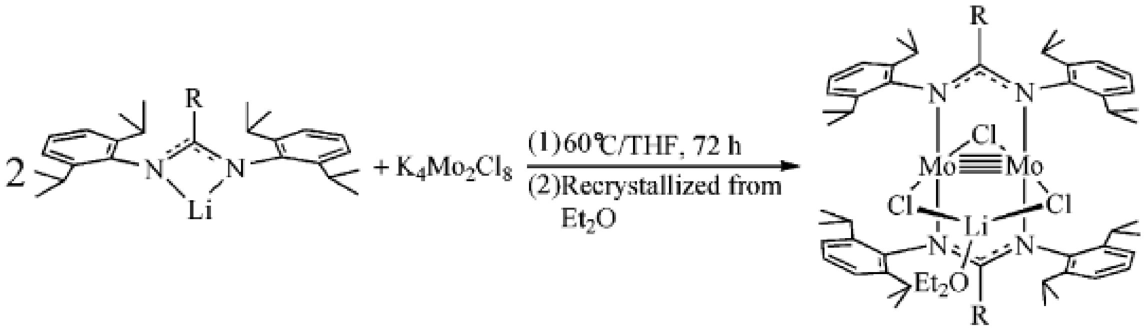
Steric pressure

a bulky substituent at the bridging carbon

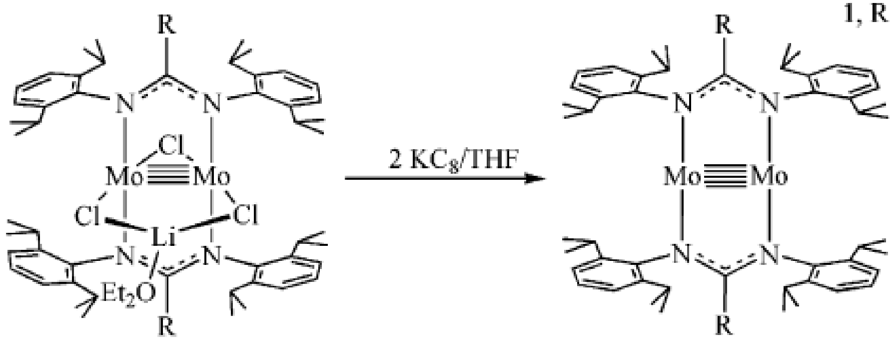
a further reduced M-M distance

Guanidinates π system is delocalized and planar

Quintuple Mo-Mo Bond

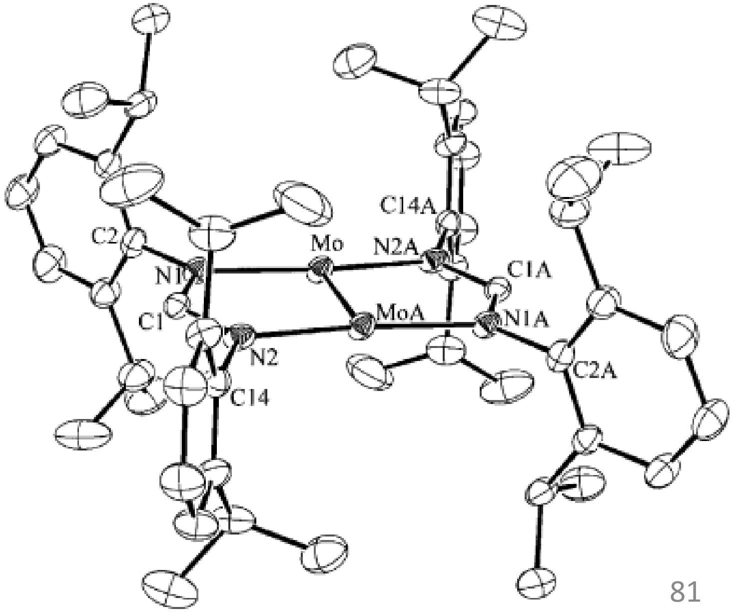


1, R = H; **2**, R = Ph



3, R = H; **4**, R = Ph

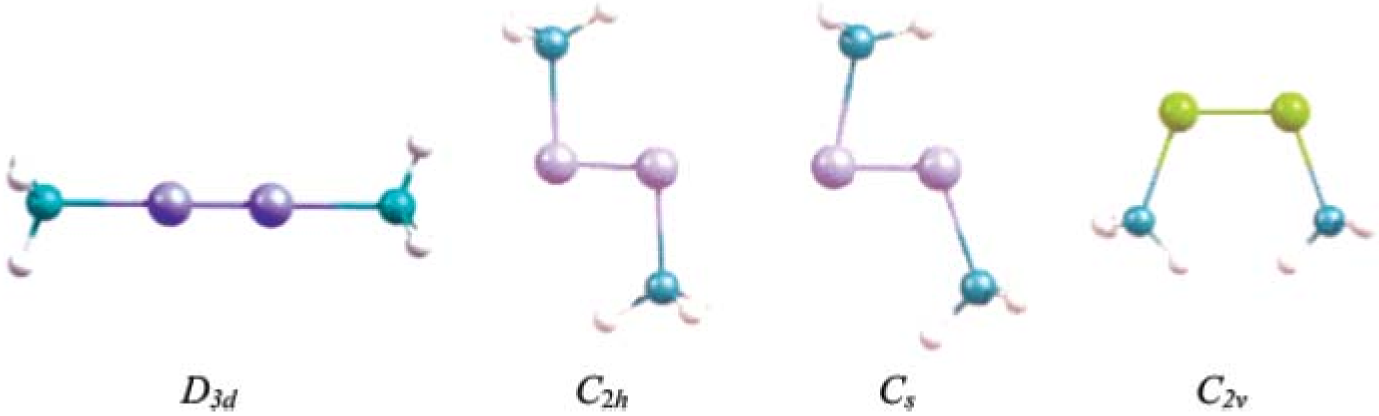
diamagnetic



Mo-Mo quintuple bond lengths
3 - 2.0187(9) Å
4 - 2.0157(4) Å,

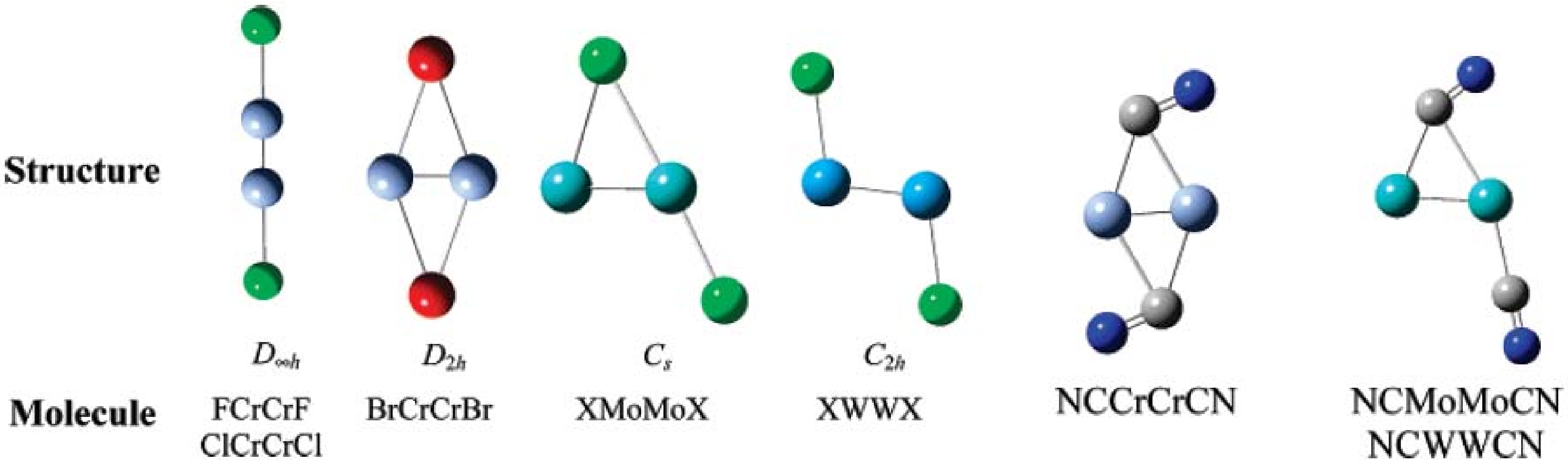
the shortest Mo-Mo quadruple bond
2.037(3) Å

Bonding in R-MM-R



R. Hoffmann - the potential energy surfaces of RMMR
R = H, F, Cl, Br, CN, and CH_3; M = Cr, Mo, and W
The potential energy surface is complex with several local minima.
The linear geometry is always a minimum, but almost never the global minimum;
A preference for either a trans-bent conformation or one of the R groups bridging
The potential energy surface is relatively flat, the lowest energy conformation - the best compromise between maximization of the MM bonding and minimization of orbital interactions that are MR antibonding
the MM quintuple bond persists

Bonding in R-MM-R



R. Hoffmann - the potential energy surfaces of RMMR, R = H, F, Cl, Br, CN, and CH_3; M = Cr, Mo, and W.

The potential energy surface is complex with several local minima.

The linear geometry is always a minimum, but almost never the global minimum;

A preference for either a trans-bent conformation or one of the R groups bridging

The potential energy surface is relatively flat, the lowest energy conformation - the best compromise between maximization of the MM bonding and minimization of orbital interactions that are MR antibonding

the MM quintuple bond persists

Sextuple Bonding in Gr6 M_2 Dimers

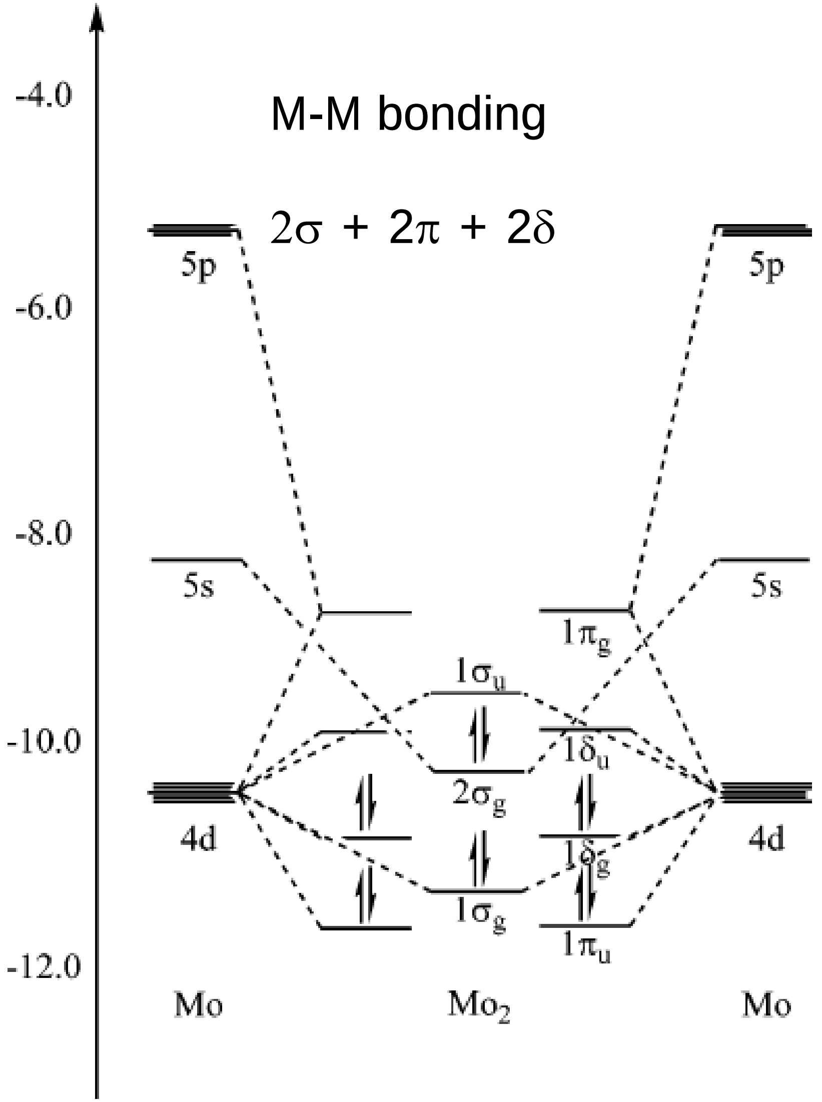
M_2 (M = Cr, Mo, W)

Matrix isolation
IR and UV spectroscopy
Short M-M distances
Singlet ground state

Laser-evaporated Cr_2 in the gas phase
d(Cr-Cr) = 1.68 Å

Spectroscopic studies of Cr_2 generated from pulsed photolysis of $Cr(CO)_6$
d(Cr-Cr) = 1.71 Å

Mo-Mo molecule
in the gas phase at low temperatures
d(Mo-Mo) = 1.93 Å



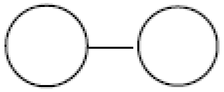
M-M bonding

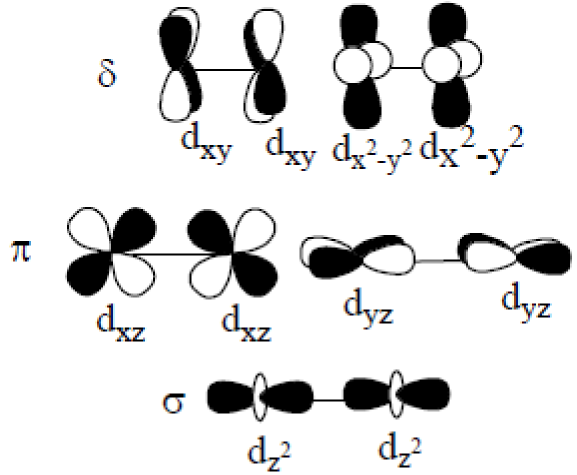
$2\sigma + 2\pi + 2\delta$

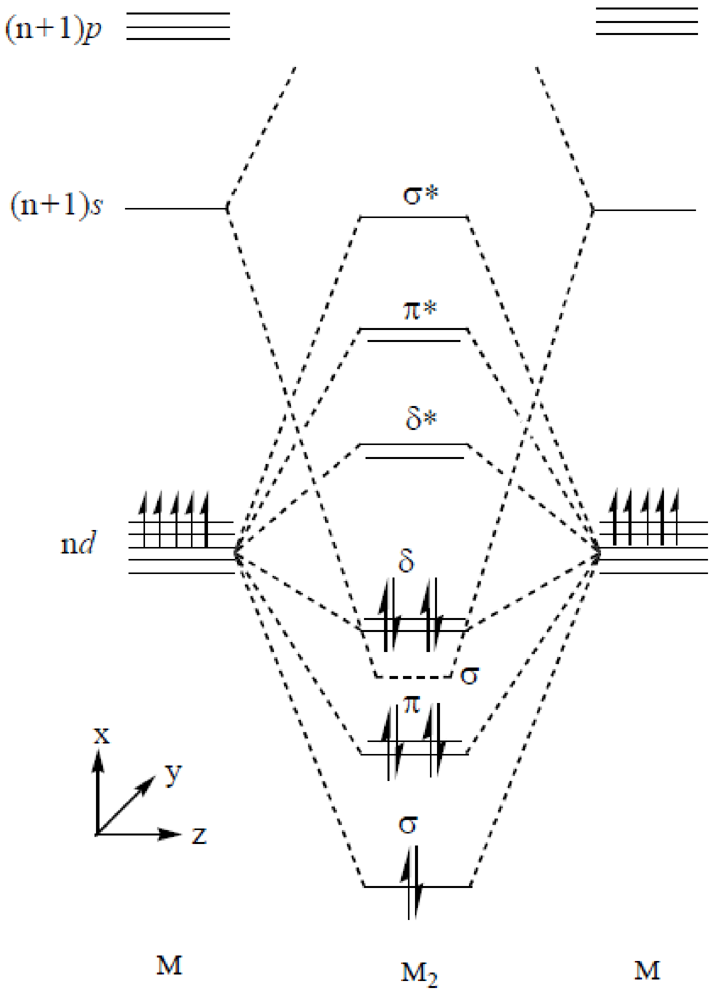
Sextuple Bonding in Gr6 M_2 Dimers

p-orbitals too high in energy

M_2 (M = Cr, Mo, W)





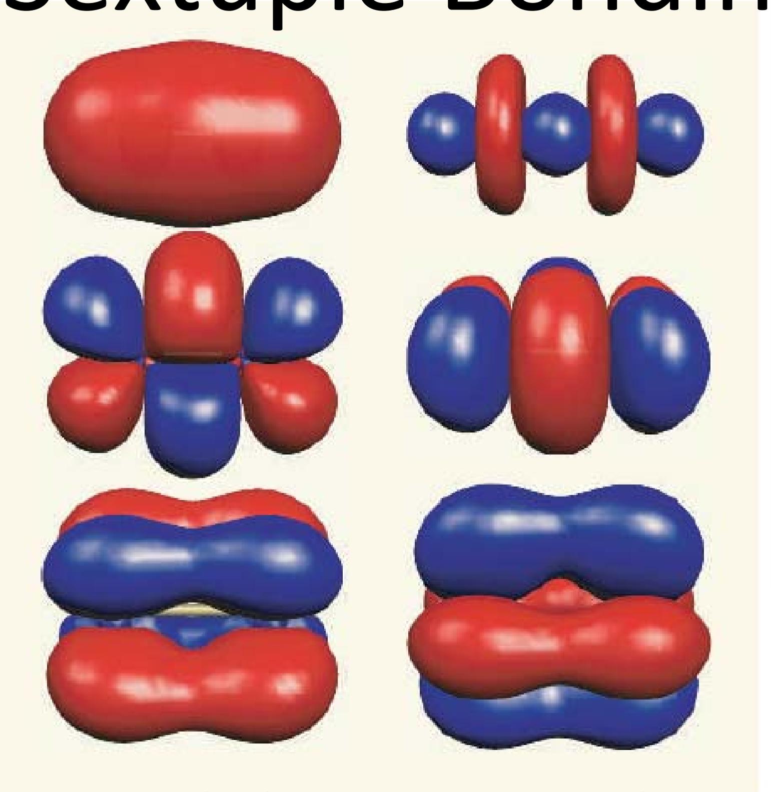


overlap **increases down** a group and can reach the bonding manifold

δ-bonds are weaker than π-bonds due to poor overlap between orbitals.

M-M bonding energy increases down a group which is in contrast to the *p*-block.

Sextuple Bonding in Gr6 M_2 Dimers

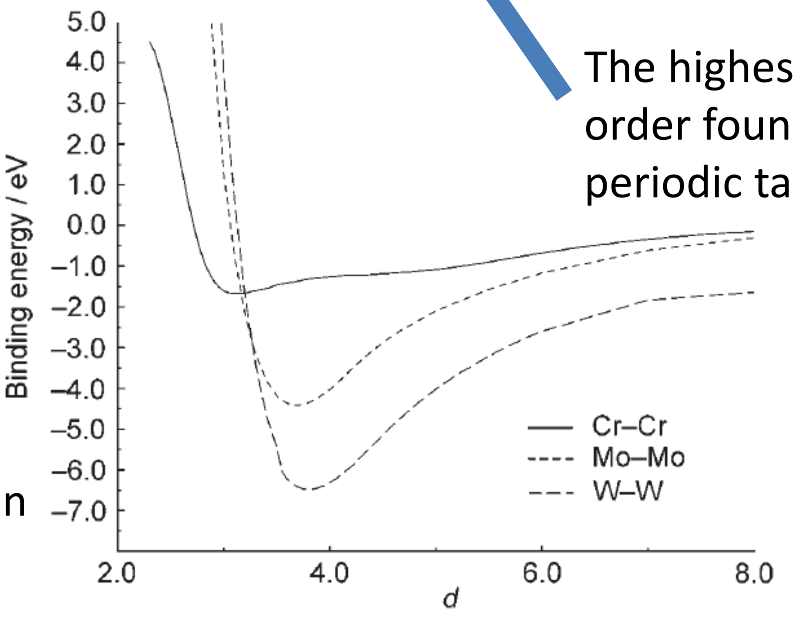


Cr_2 – poor delta bonding, 4 AF coupled electrons, larger 4s orbitals generate a considerably longer bond than the 3d-3d. This unbalance weakens the 3d bonds and makes the 4s bond repulsive at equilibrium geometry, the repulsive interaction between the closed 3p, which have about the same radial extension as 3d.

Effective bond order (EBO)
Dissociation energy (DE)

M	EBO	d(M-M), Å	DE, eV
Cr	3.5	1.66	1.65
Mo	5.2	1.95	4.4
W	5.2	2.01	5.4

The highest bond order found in the periodic table



Multiple Bonding

The bond energy only 1.66 eV for Cr_2 sextuple bond
but 3.17 eV for quintuple bond in [PhCrCrPh]
= no direct relation between bond order and bond energy, a complex quantity depends on many factors, such as atomic promotion energy, the interplay between attractive nuclear forces and electron repulsion, spin–orbit coupling-decreases the bond energy

Bond orders higher than 6?
Lanthanides – 4f orbitals?
Actinides – 5f orbitals participate in bonding

The EBO is always smaller than the maximum formal bond order (MBO = the number of electrons forming the bond divided by two)

Molecule	**MBO**	**EBO**	**D_0 [eV]**
Cr_2	6	3.5	1.6
[PhCrCrPh]	5	3.5	3.2
Ac_2	3	1.7	1.2
Th_2	4	3.7	3.3
Pa_2	**5**	**4.5**	**4.0**
U_2	6	4.2	1.2

Multiple Bonding Trends In Groups

Main-Group Elements

Tendency to multiple bonding **decreases down the group**
s + 3×p orbitals available
s/p size difference increases and propensity to hybridization decreases down the group

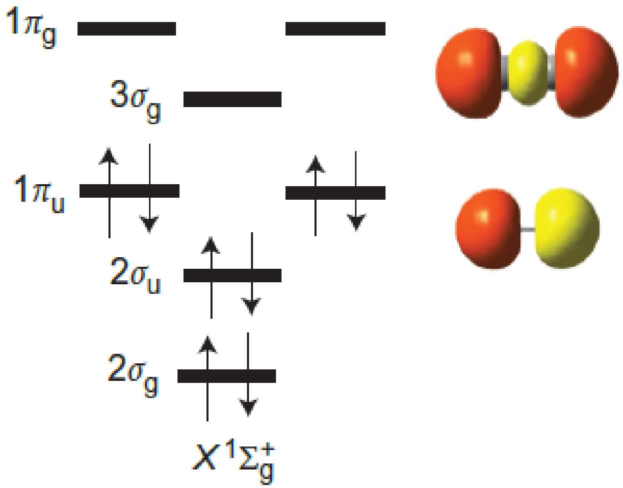
Transition Metals

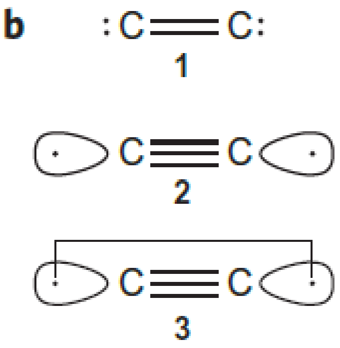
Multiple bonding **increases down the group**
s + 5×d orbitals available
difference in size between the smaller nd and larger (n+1)s orbitals decreases down the group
relativistic effects contract s and p orbitals while d and f are expanded
the s and d orbitals in second- and especially third-row transition metals are more equal in size. This greater equivalency in size considerably enhances the bond strength

Inverted Bond

isoelectronic molecules C_2, CN^+, BN, and CB^- singlet ground state $X^1\Sigma_g^+$

valence bond (VB) theory and full configuration interaction (FCI)





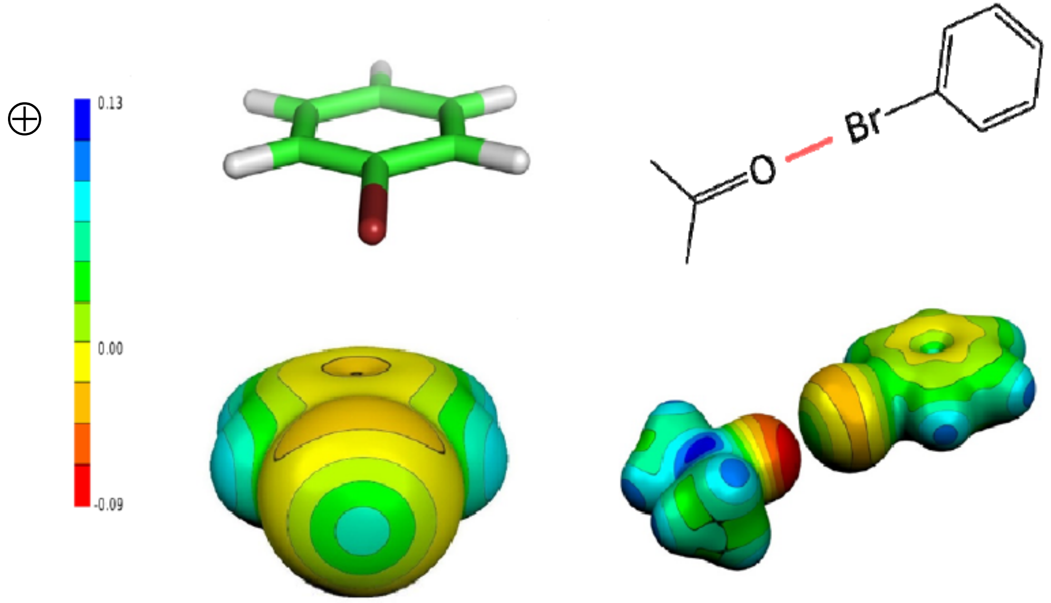
bond order = 2
$2\sigma_g$ and $2\sigma_u$ orbitals are both filled, two π-bonds unsupported by an underlying σ-bond and two σ lone pairs.

bond order = 3
sp-hybridized carbons, one σ- and two π-bonds, two electrons in the outwardly pointing hybrids

triplet state $c^3\Sigma_u^+$, electrons are unpaired, 26.4 kcal mol^{-1} above the ground state
these electrons maintain a significant bonding interaction in the ground state

Sigma Hole Interactions

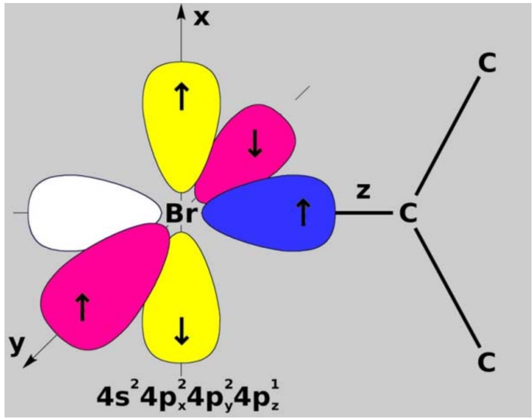
Electrostatic potential (ESP) – observable quantity



Halogen/chalcogen/pnictogen/tetrel bonding

= a noncovalent interaction between a covalently-bonded atom of Groups 14–17 and a negative site, *e.g.* a lone pair of a Lewis base or an anion.

σ-hole = a region of positive electrostatic potential on the extension of one of the covalent bonds to the atom caused by the anisotropy of the atom's charge distribution

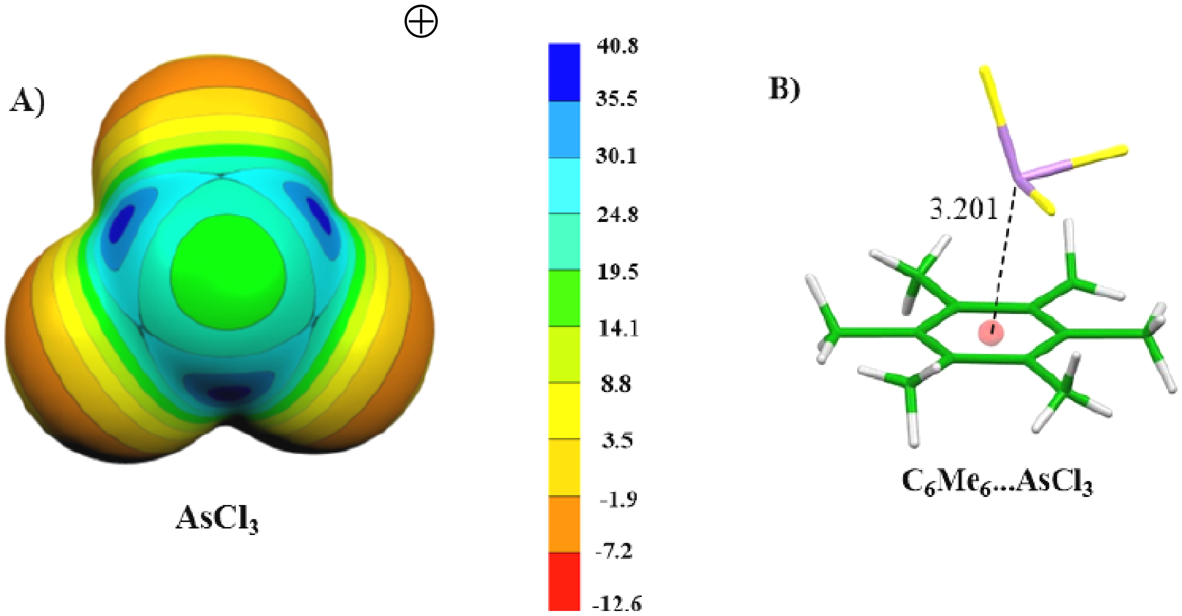


Heavy atoms without hybridization
$4p_z$ occupied by only one electron

Sigma Hole Interactions

Electrostatic potential (ESP)

$$V(\boldsymbol{r}) = \sum_{\mathrm{A}} \frac{Z_{\mathrm{A}}}{|\boldsymbol{R}_{\mathrm{A}} - \boldsymbol{r}|} - \int \frac{\rho(\mathbf{r}')\mathrm{d}\boldsymbol{r}'}{|\boldsymbol{r}' - \boldsymbol{r}|}$$



$AsCl_3$

$C_6Me_6...AsCl_3$

Bond strength 13 – 100 kJ mol^{-1}
H-bond in $(H_2O)_2$ 20 kJ mol^{-1}

Directionality increase Cl < Br < I

Bond-Stretch Isomers

Isomerism

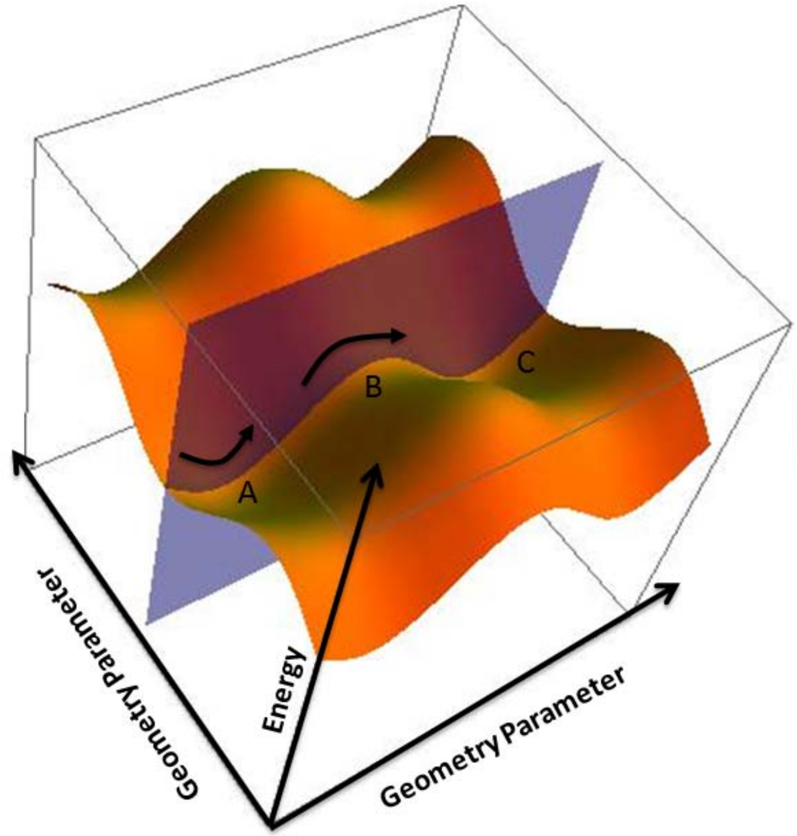
- the *molecular conformation* specifies a combination of relative atomic positions conferring on the molecule a certain stability.
- the *potential energy (hyper)surface* (PES) characterizes through its minima the various molecular conformations that could be expected for a given assembly of atoms, and defines by means of saddle points the thermodynamic pathways interconnecting them.

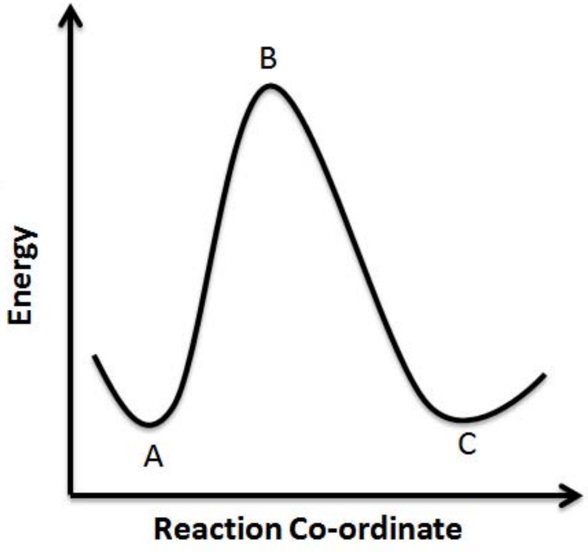
Isomers = molecular conformations corresponding to distinct minima on the PES, separated by an energy barrier high enough to impede immediate interconversion at room temperature, separable, 100 - 120 kJ mol^{-1} or more.

Conformers = barrier is lower, not separable under ambient conditions, but could be observed and characterized at lower temperature.

Bond-Stretch Isomers

the potential energy (hyper)surface (PES)

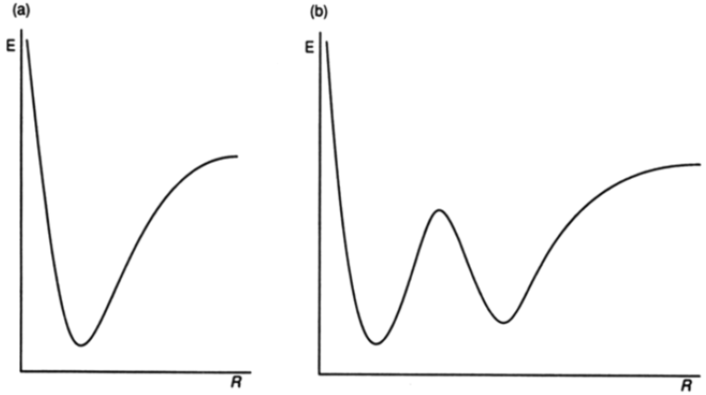




Bond-Stretch Isomers

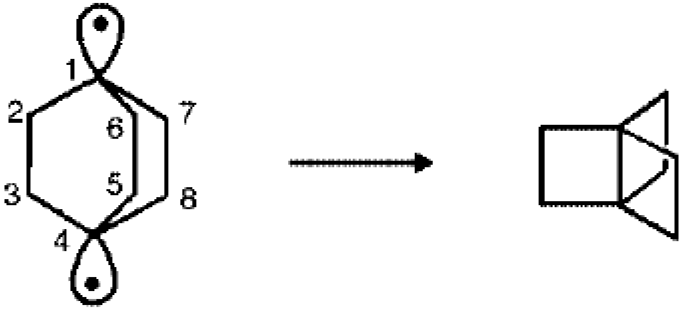
R. Hoffmann 1972
Bond-stretch *isomers* = distinct, separable and stable at room temperature

Bond-stretch isomerism (BSI) = the unusual phenomenon whereby molecules differ only in the length of one or more bonds



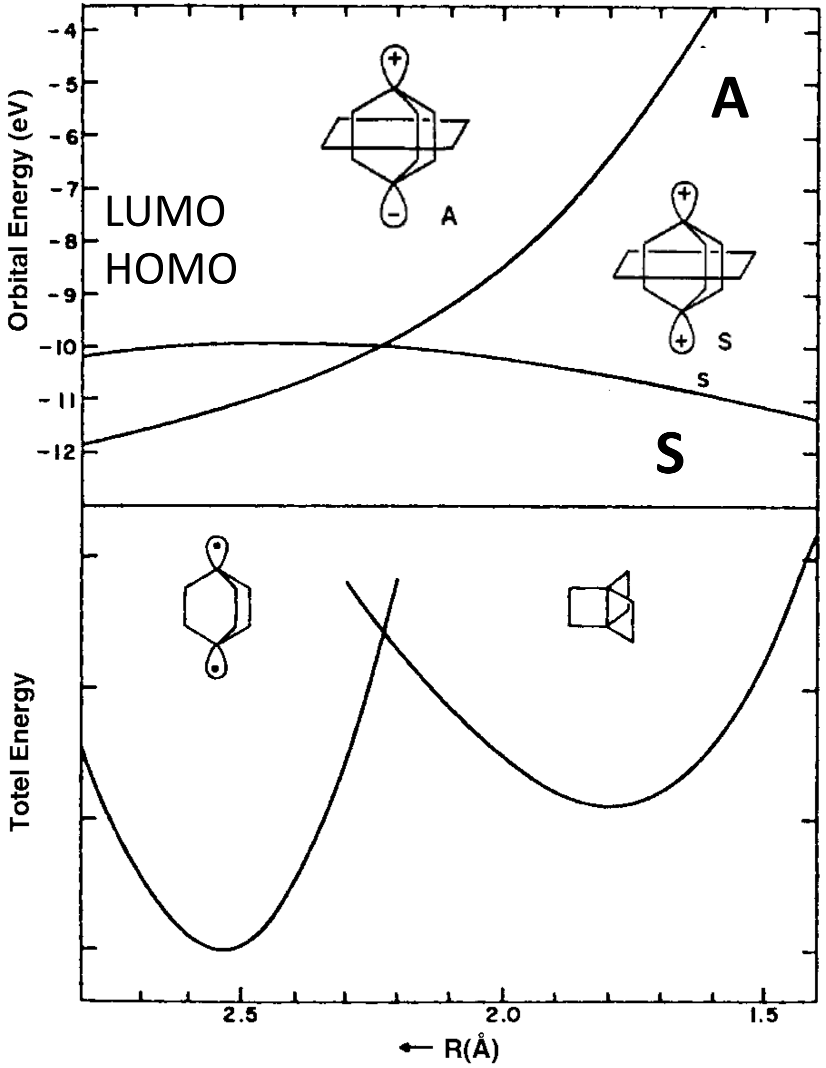
NOT Bond-stretch *isomers*:
Complex Re(*cis*-Cl_2)(NCMe)(NO)-*trans*-$(PMe_3)_2$
Crystallizes in $P2_1/a$ with 44 molecules in the asymmetric unit
a dense and low-symmetry hydrogen bonding network
the Re–N(NO) and the Re–N(NCMe) distances vary by as much as 0.10 or 0.12 Å, respectively.

[2.2.2]propellane



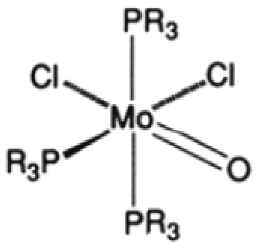
S orbital = symmetric combination wrt σ_h, transannular C–C bond
A orbital = antibonding, antisymmetric

Interaction (through-bond coupling) between **A** and the high-lying σ^* orbitals of the C–C bonds (2–3, 5–6 and 7–8) results in a stabilization of **A**.
A crossing between **A** and **S**, **A** becomes the HOMO when the transannular distance is larger than 2.25 Å and gives rise to a diradical form.
The orbital crossing makes the interconversion between the diradical and the tricyclic form symmetry forbidden and should generate isomers = equilibrium conformations separated by an energy barrier



Not Bond-Stretch Isomers

Blue



Green

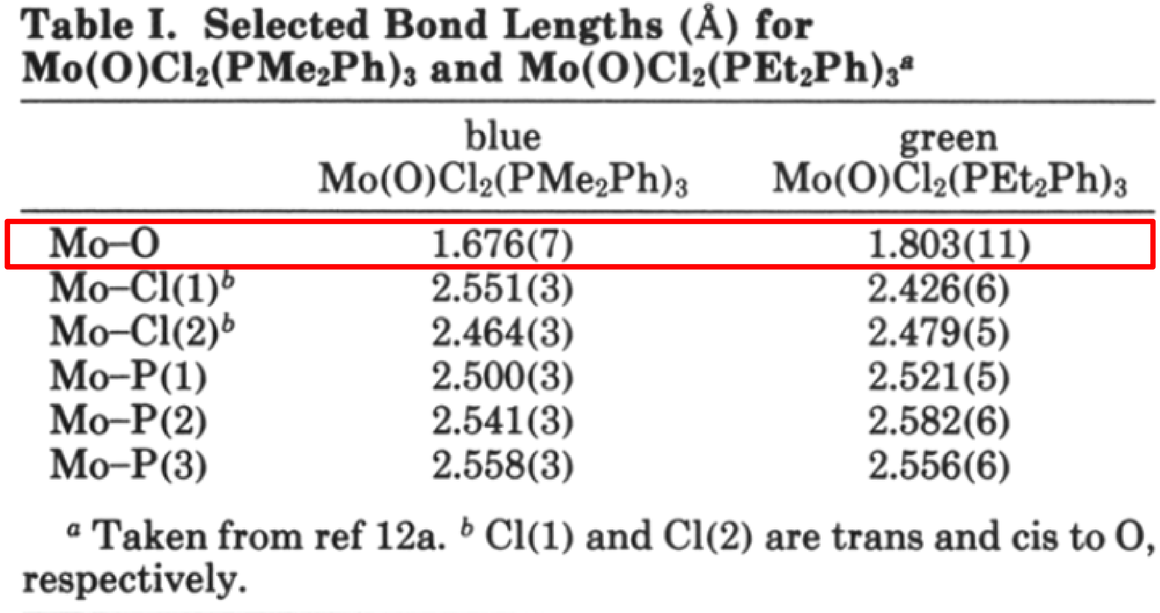


Table I. Selected Bond Lengths (Å) for $Mo(O)Cl_2(PMe_2Ph)_3$ and $Mo(O)Cl_2(PEt_2Ph)_3$[a]

	blue $Mo(O)Cl_2(PMe_2Ph)_3$	green $Mo(O)Cl_2(PEt_2Ph)_3$
Mo–O	1.676(7)	1.803(11)
Mo–Cl(1)[b]	2.551(3)	2.426(6)
Mo–Cl(2)[b]	2.464(3)	2.479(5)
Mo–P(1)	2.500(3)	2.521(5)
Mo–P(2)	2.541(3)	2.582(6)
Mo–P(3)	2.558(3)	2.556(6)

[a] Taken from ref 12a. [b] Cl(1) and Cl(2) are trans and cis to O, respectively.

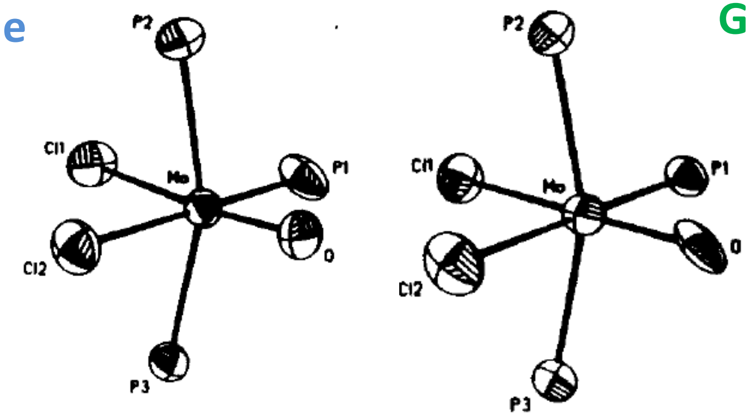
Chatt, J.; Manojlovic-Muir, L.; Muir, K. W. J. Chem. Soc. (D) 1971, 655-656
Manojlovic-Muir, L.; Muir, K. W. J. Chem. Soc., Dalton Trans. 1972, 686-690

Not Bond-Stretch Isomers

Distortional M=O isomers?

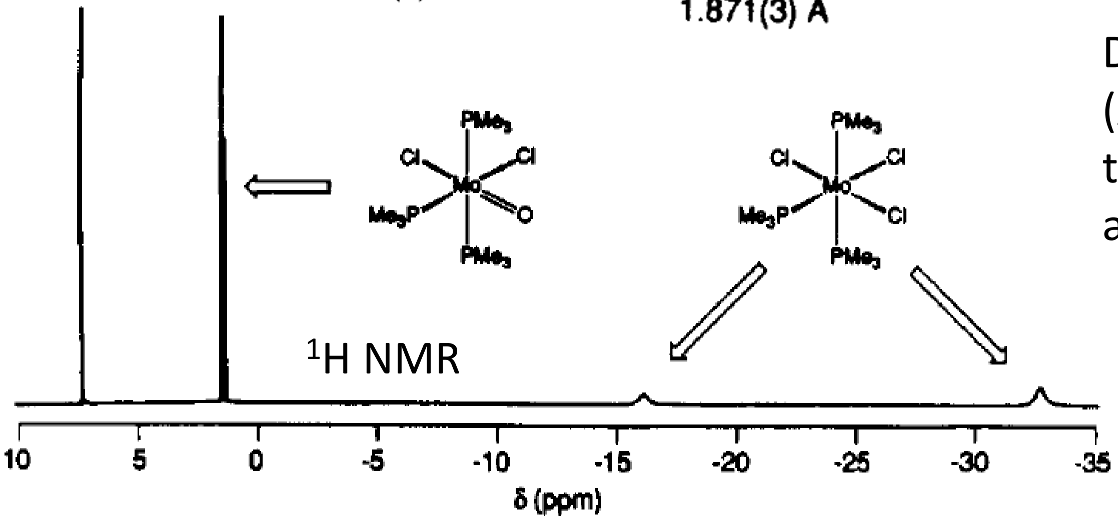
Blue

Green

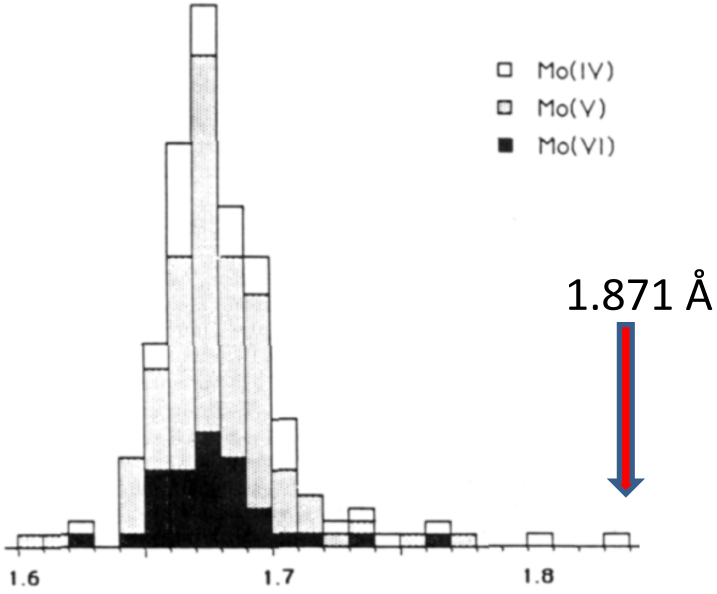


1.675(3) Å

1.871(3) Å

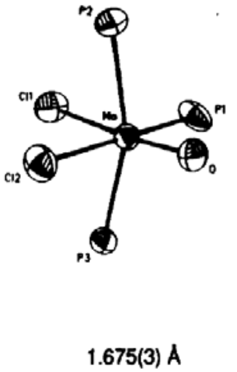


^{1}H NMR

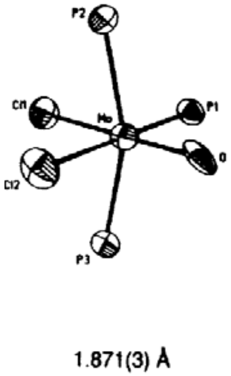


Distribution of Mo=O distances (Å) for monooxo complexes in the oxidation states +4, +5, and +6.

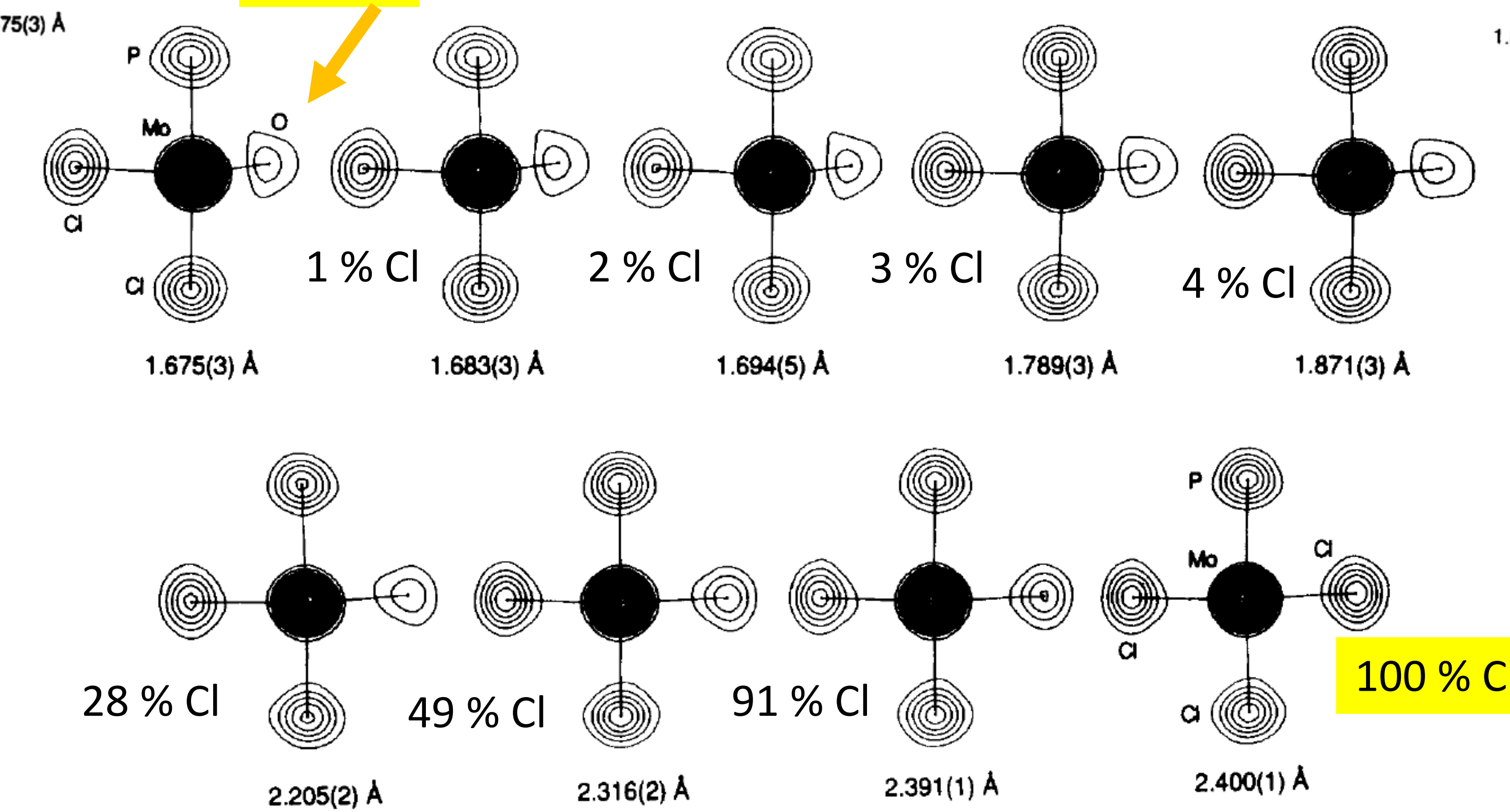
Not Bond-Stretch Isomers



Yoon, K.; Parkin, G.; Rheingold, A. L.
J. Am. Chem. Soc. 1992,114, 2210



0 % Cl



1 % Cl

2 % Cl

3 % Cl

4 % Cl

28 % Cl

49 % Cl

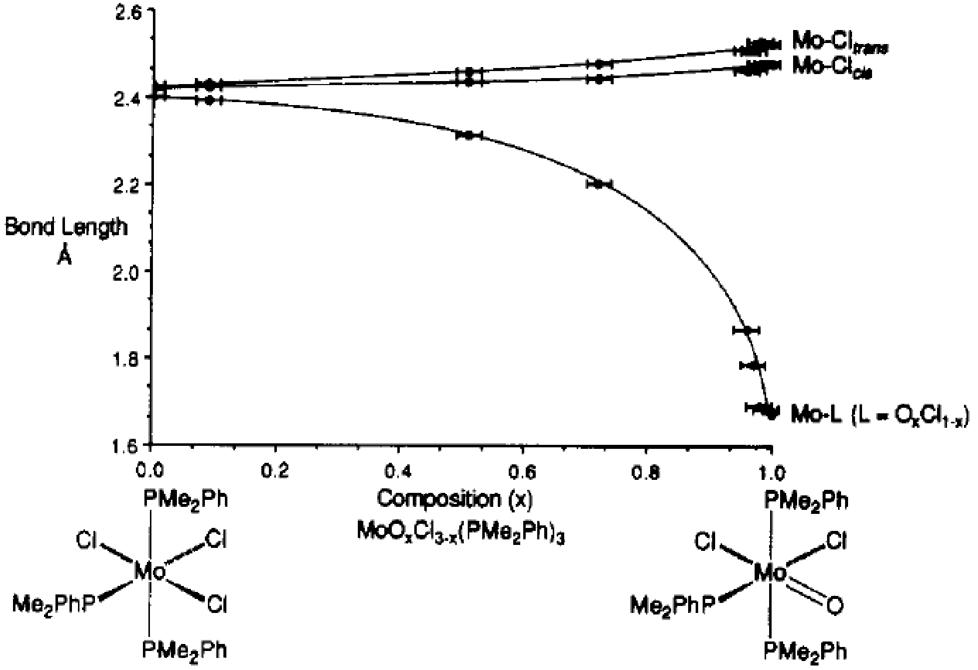
91 % Cl

100 % Cl

Not Bond-Stretch Isomers

Crystallographic disorder
difficult to detect, results in the incorrect determination of bond lengths and the incorrect formulation of compounds

Cocrystallization of structurally related molecules resulting in the formation of single-crystal solid solutions



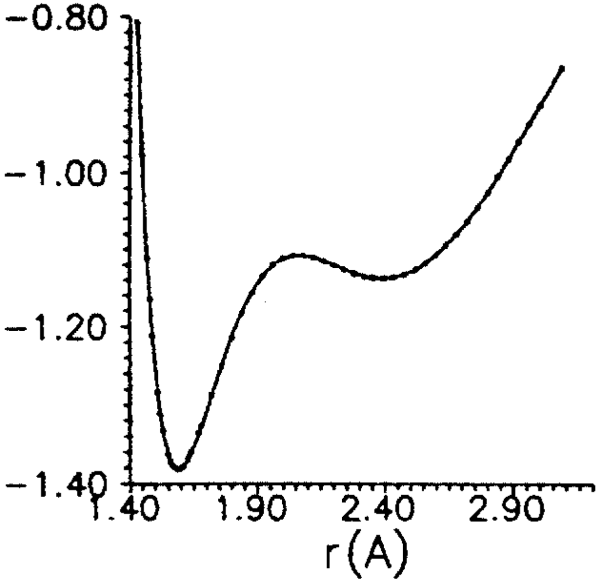
Yoon, K.; Parkin, G.; Rheingold, A. L. J. Am. Chem. Soc. 1992,114, 2210

Chromium Dimer?

Valence electron configuration:
$(3d\sigma_g)^2(3d\pi_u)^4(3d\delta_g)^4(4s\sigma_g)^2$ sextuple bond, Cr–Cr distance: 1.6788 Å (2.5 Å in Cr metal)
Singlet, observed dissociation energy = 1.44 ± 0.05 eV

The optimal bonding regions are quite different for the 3d and 4s orbitals

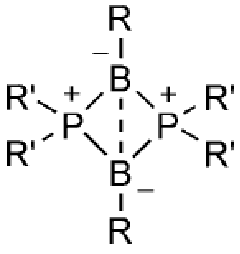
1st minimum: *R*e = 1.59 Å; *D*e = 1.38 eV
2nd minimum: *R*e = 2.40 Å; *D*e = 1.14 eV



Balance between covalent bonding (d-d) at short distance and (s-s) bonding and antiferromagnetic coupling of the 3d electrons at long distance

Calculated 2nd minimum
of the ground-state energy curve is extremely shallow
corresponding isomer rather short-lived and difficult to trap and to characterize

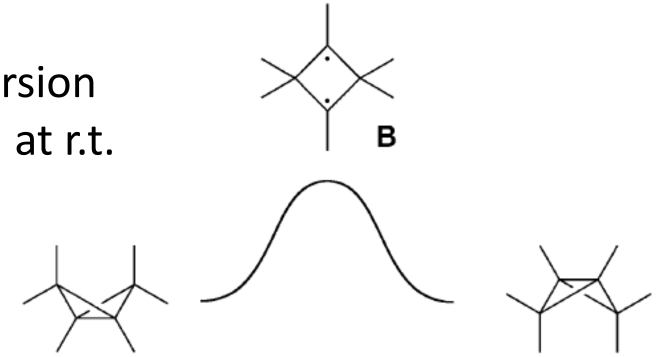
Not Bond-Stretch Isomers

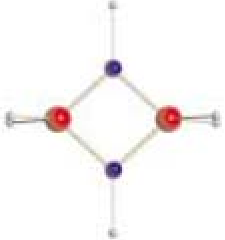
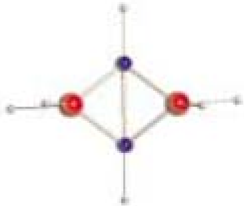
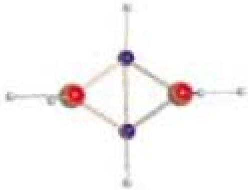
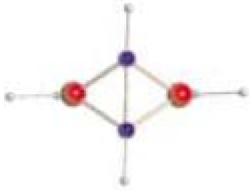
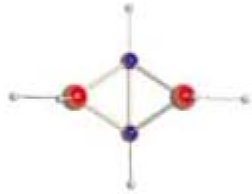
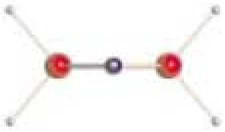
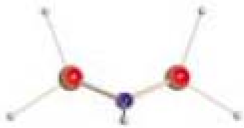
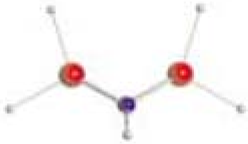
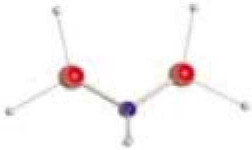


1–5

1: R=*t*Bu, R'=*i*Pr,
2: R=Dur, R'=*i*Pr
3: R=*t*Bu, R'=Ph,
4: R=Dur, R'=Et,
5: R=Ph, R'=Ph,

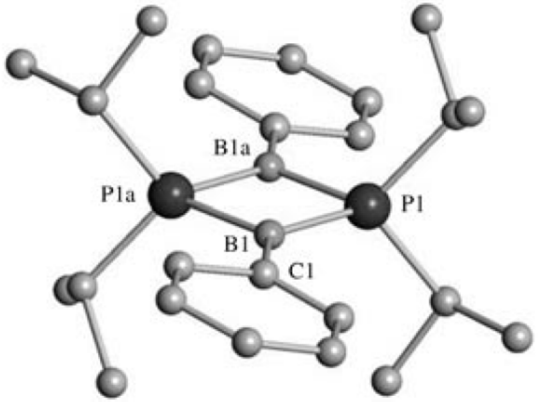
Rapid inversion
in solution at r.t.



compound	**1** $(i\text{Pr}_2\text{PB}t\text{Bu})_2$	**2** $(i\text{Pr}_2\text{PBDur})_2$	**3** $(\text{Ph}_2\text{PB}t\text{Bu})_2$	**4** $(\text{Et}_2\text{PBDur})_2$	**5** $(\text{Ph}_2\text{PBPh})_2$
δ ^{31}P (ppm)[a]	+3	–26	–56	–55	–54
δ ^{11}B (ppm)[a]	+25	–13	–12	–19	–13
B–B (Å)	2.57	2.24	1.99	1.89	1.83
τ (°)	180	130	118	115	114
top view[b]					
side view[b]					

Bond-Stretch Isomers

Planar P_2B_2 core, B-B = 2.57 Å



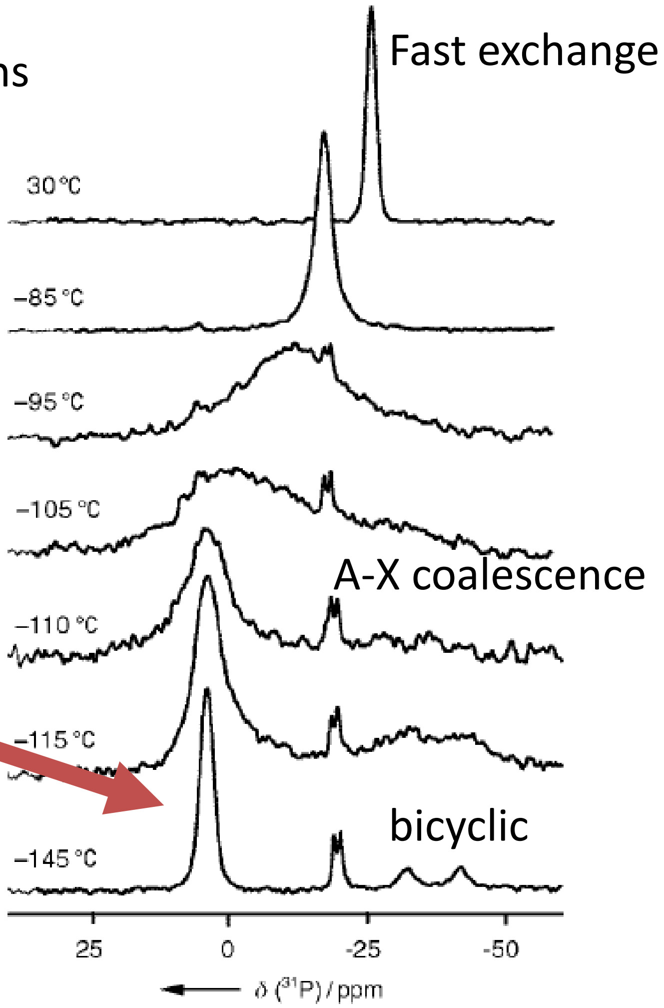
^{31}P solid-state NMR $\delta = 5.9$ ppm (diradical)

^{31}P solution $\delta = -28$ ppm (bicyclic)
^{11}B solution $\delta = -9$ ppm (bicyclic)

Changing populations
diradical → bicyclic
ratio of 1:7 at r.t.

bicyclic – diradical
coalescence

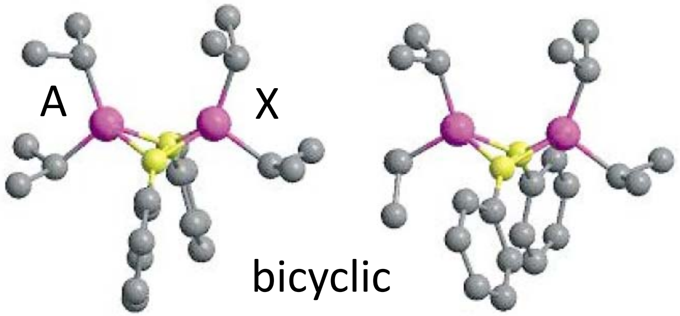
Diradical
$\delta = 4.0$ ppm



Fast exchange

A-X coalescence

bicyclic

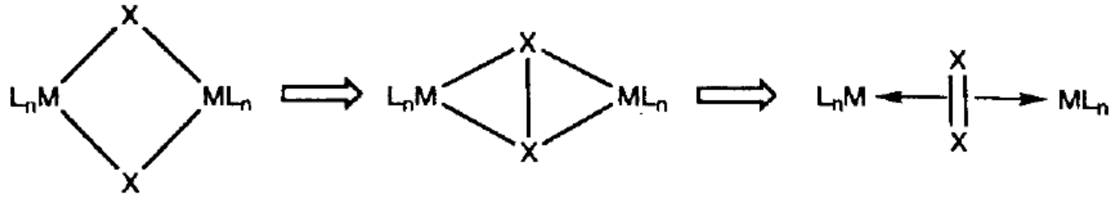


bicyclic

$\delta = 32.2$ and 41.8 ppm
(A:X = 1:1)

M_2X_2 Rings

Isomers with or without ligand–ligand bonds
Electron transfer from ligands X to metal M



FEC =	8	6	4
Metal configuration	d^n	d^{n+1}	d^{n+2}
Bridge	$(X_2)^{x-}$	$(X_2)^{2-x}$	$(X_2)^{4-x}$

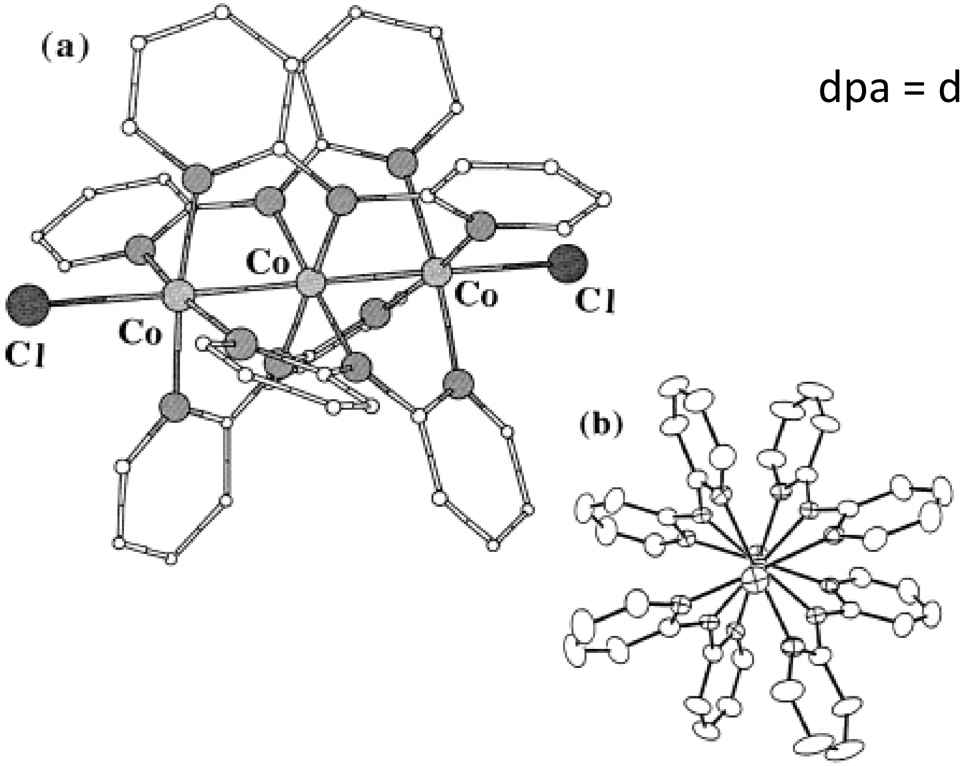
M	X	L_2	β	Δ_{XX}
Experimental data				
Pd	Te	$(PEt_3)_2$	108	0.07
Pt	S	$(PpyPh_2)_2$	103	0.96
Pt	S	dppe	86	1.10
Pt	Se	$(PPh_3)_2$	100	0.70
Pt	Te	$(PEt_3)_2$	106	0.32
Pt	Te	$(PPh_3)_2$	100	0.32
Pt	Te	dppe	86	0.53

β is the LML bond angle, Δ_{XX} is the difference b/w the X–X distance and the atomic radii sum.

Linear Metal M-M-M Frameworks

$M_3(dpa)_4X_2$ M = Cr, Co, Ni, Cu, Ru, Rh X = halogenide, BF_4^-, PF_6^-

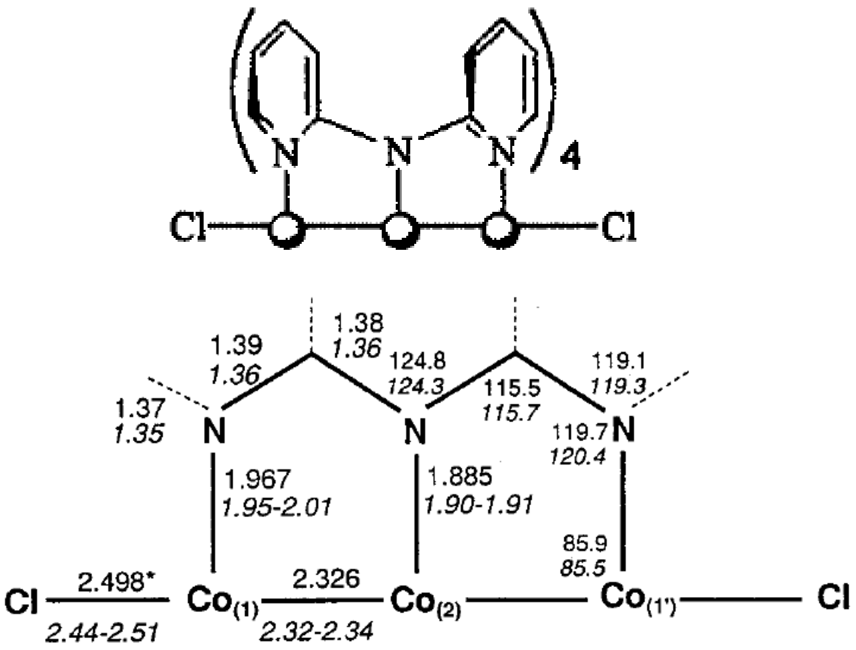
Ox. state of M?



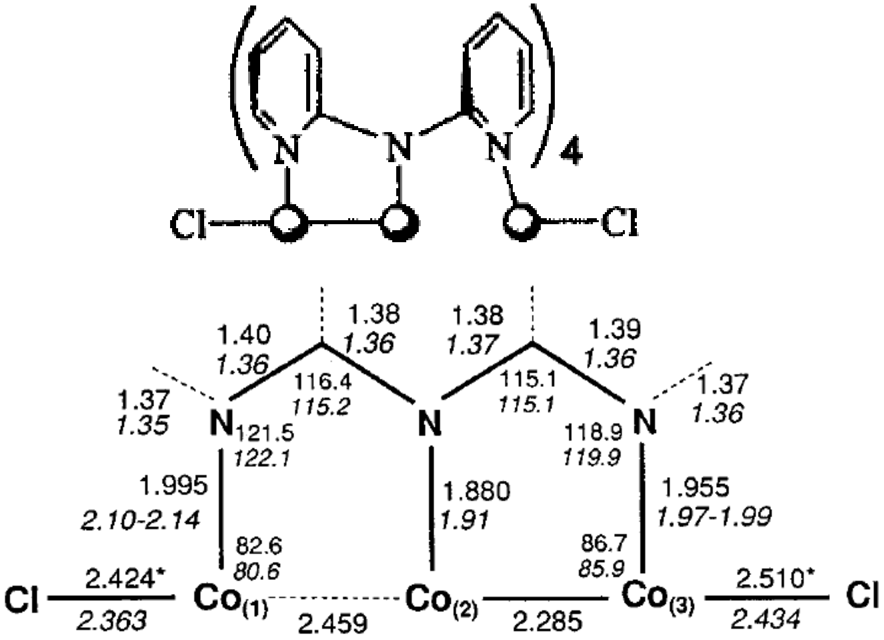
dpa = dipyridylamine

Linear Metal M-M-M Frameworks

symmetrical (*s*) Co3 chain



unsymmetrical (*u*) Co3 chain



less unsymmetrical at low temperature

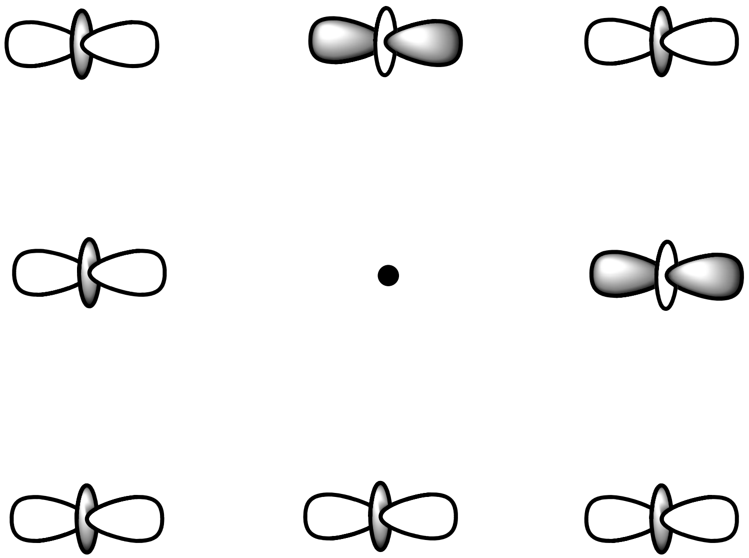
both the *s* and the *u* isomers are in an S = 1⁄2 ground state at low temperature

Linear Metal M-M-M Frameworks

Linear triatomic system: M-M-M

the equivalent atomic orbitals of every type give rise to a set of three molecular orbital (MO) combinations:

(i) a bonding MO, lowest in energy
(ii) a nonbonding, antisymmetric, localized on the terminal atoms
(iii) an antibonding MO



Linear Metal M-M-M Frameworks

Five orbital sets:

One σ set - d_{z^2} orbital combinations (z is collinear with the framework axis)

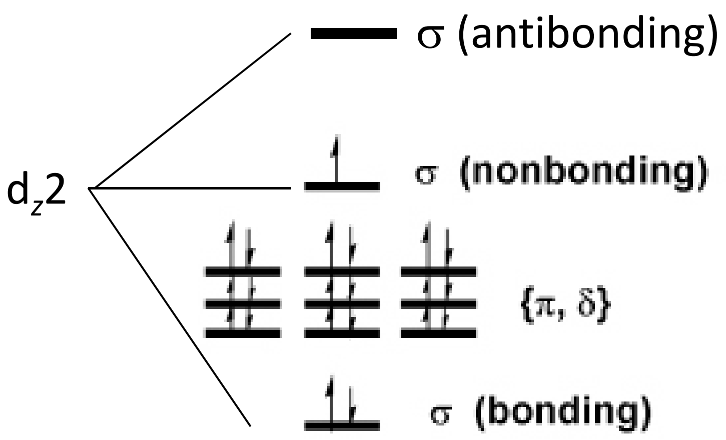
Two degenerate π sets - combinations of d_{xz} and d_{yz} orbitals

Two δ sets - combinations of d_{xy} and $d_{x^2-y^2}$ orbitals.
One δ set accepts the lone pairs of the equatorial dpa ligands

The 3d atomic orbitals are compact in space and the 3d–3d overlap between π and δ orbitals is weak except at supershort distances

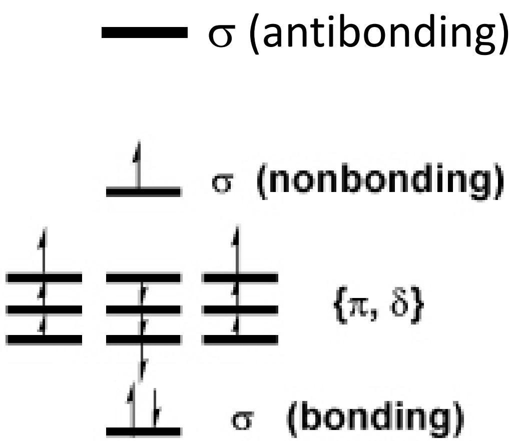
The nine metal MOs belonging to the two π sets and to the remaining δ set are not split in energy

Linear Metal M-M-M Frameworks



$Co_3(dpa)_4Cl_2$

S = 1⁄2 ground state



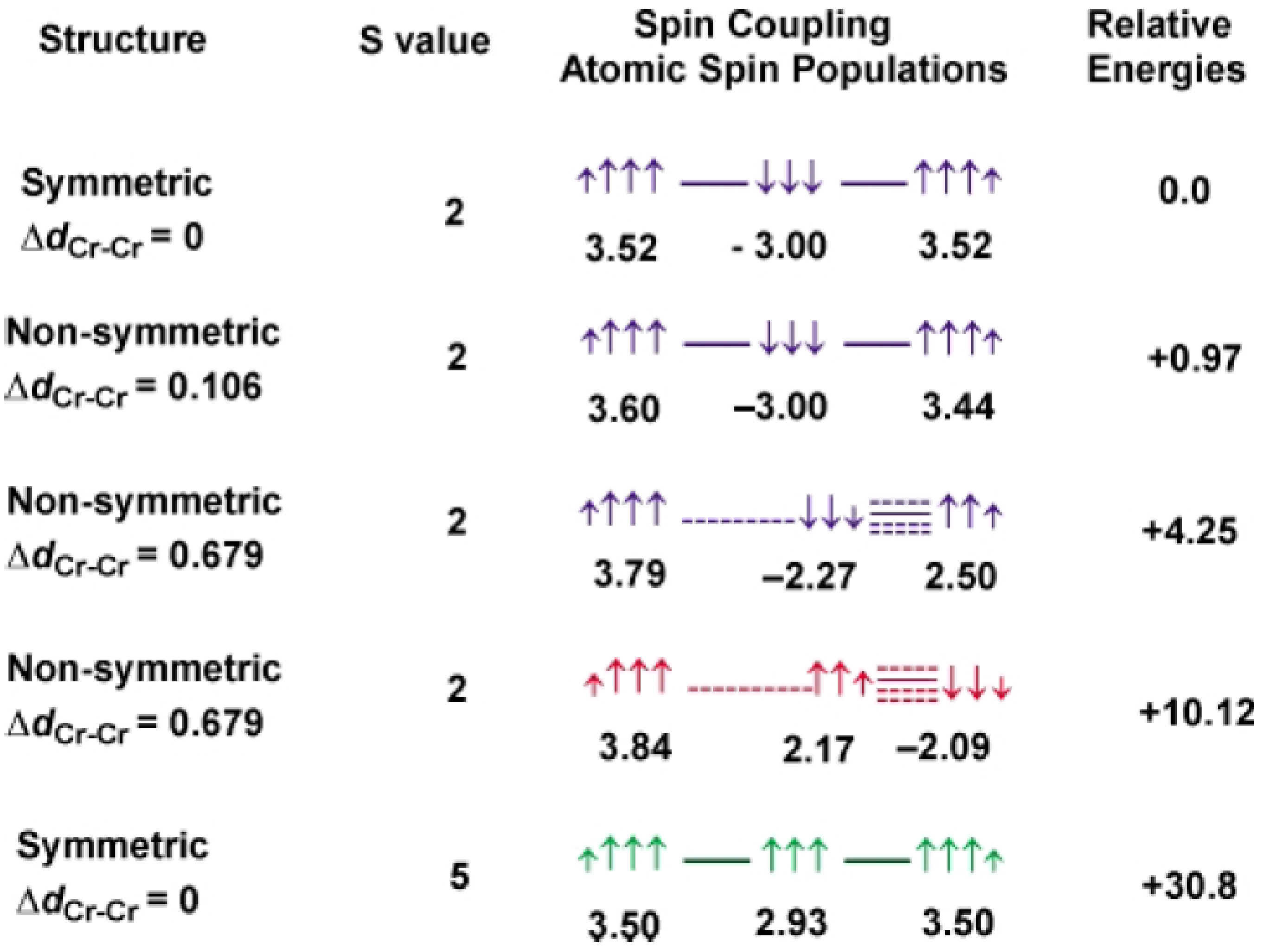
$Cr_3(dpa)_4Cl_2$

S = 2 ground state

Three-electron, three-center system
18 electrons in the π and δ orbital sets do not take part in any metal–metal interaction, *localized* on individual metal atoms
The bonding in the M-M-M fragment is exclusively due to the 3 σ electrons, which are *delocalized* over the metal framework

Three-electron, three-center system
12 electrons in the π/δ block singly occupied, the 10 unpaired electrons—including the one in the σ nonbonding orbital and shared between the terminal Cr atoms—are *spin-coupled*-antiferromagnetic interaction

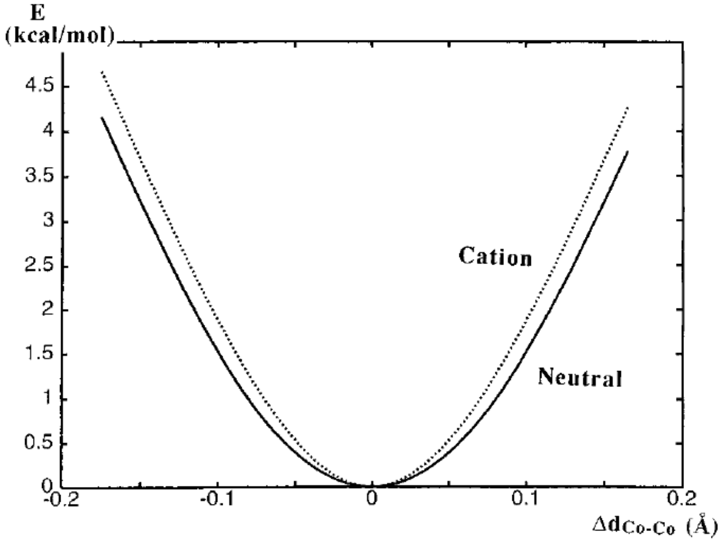
Linear Metal M-M-M Frameworks



Structure	S value	Spin Coupling Atomic Spin Populations	Relative Energies	
Symmetric $\Delta d_{Cr\text{-}Cr} = 0$	2	↑↑↑↑ — ↓↓↓ — ↑↑↑↑ 3.52 - 3.00 3.52	0.0	
Non-symmetric $\Delta d_{Cr\text{-}Cr} = 0.106$	2	↑↑↑↑ — ↓↓↓ — ↑↑↑↑ 3.60 –3.00 3.44	+0.97	
Non-symmetric $\Delta d_{Cr\text{-}Cr} = 0.679$	2	↑↑↑↑ ---------- ↓↓↓ ≡ ↑↑↑ 3.79 –2.27 2.50	+4.25	AF to bonding
Non-symmetric $\Delta d_{Cr\text{-}Cr} = 0.679$	2	↑↑↑↑ ---------- ↑↑↑ ≡ ↓↓↓ 3.84 2.17 –2.09	+10.12	Short = bonding Long = ferromg
Symmetric $\Delta d_{Cr\text{-}Cr} = 0$	5	↑↑↑↑ — ↑↑↑ — ↑↑↑↑ 3.50 2.93 3.50	+30.8	

state ($S = 5$) is destabilized by 30.8 kcal mol^{-1}

Bond-Stretch Isomers?



Co-Co-Co
A ground-state potential energy curve (PES) has only one shallow minimum
corresponding to the *s* conformation

Both the shape of this PES and the symmetric position of its minimum are consequences of the three-electron, three-center bond

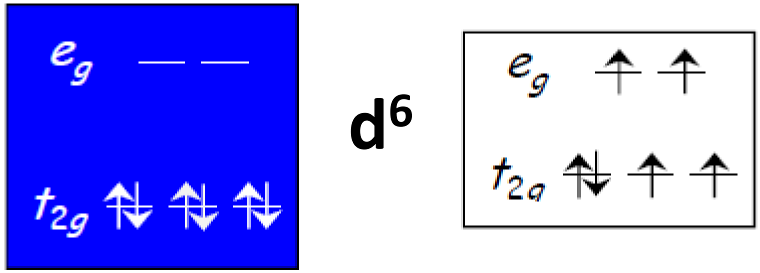
The crystal forces could influence the molecular geometry or population of a low-energy, high-spin excited state induce a temperature-dependent distortion of the framework

Cr-Cr-Cr
A shallow, symmetric PES governed by σ metal electrons
π and δ electrons, though localized on the metal atoms take part in the bonding through their magnetic coupling

Spin State Isomers

$3d^4$ –$3d^7$ cations in O_h complexes

LS, S = 0 HS, S = 2

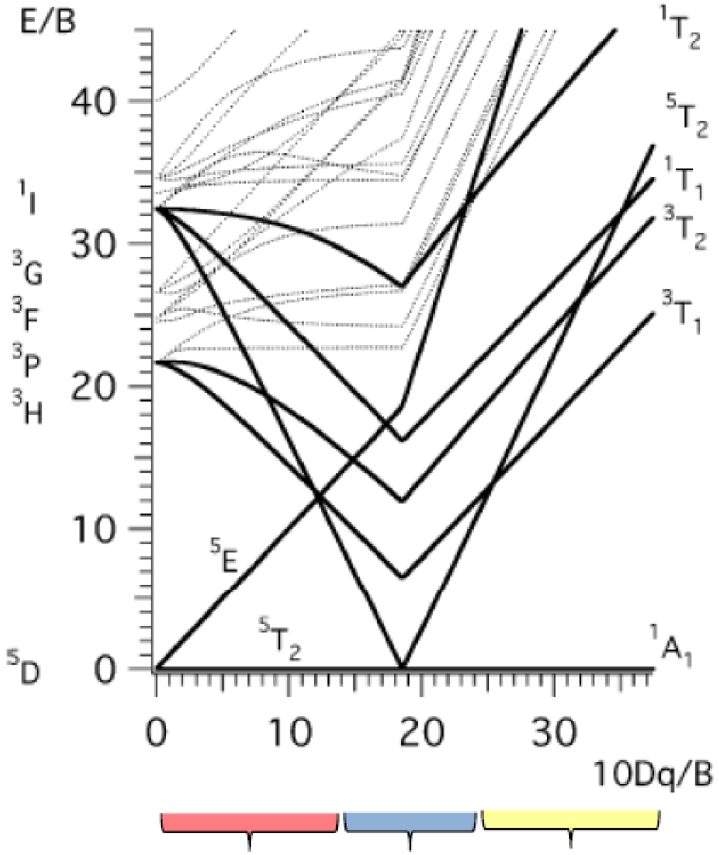


10Dq > Π 10Dq < Π

10Dq – ligand-field splitting

Π – electron pairing energy

10Dq(LS) ≠ 10Dq(HS)



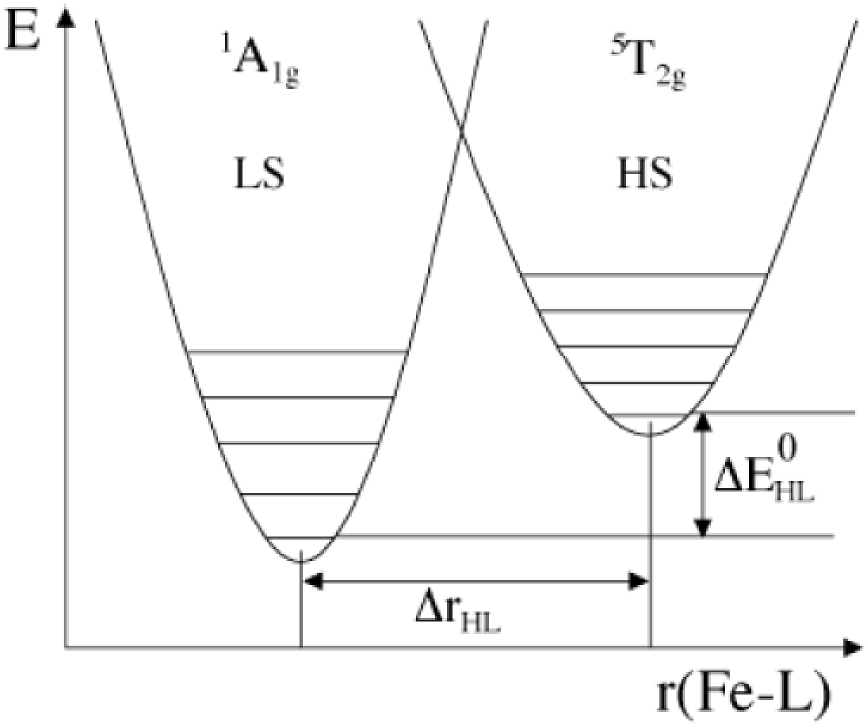
Complexes: HS SCO LS

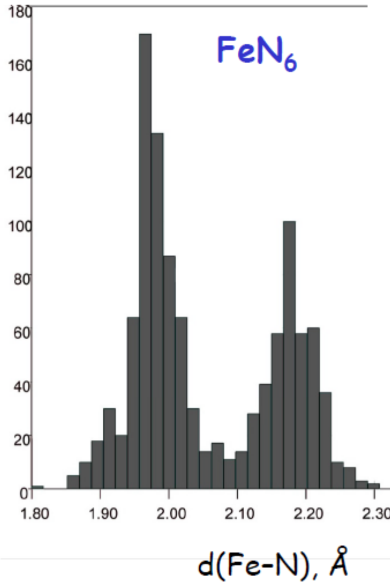
Spin Crossover (SCO)

a reversible change in the spin state of from low spin (LS) to high spin (HS) affected by the application of external stimuli:

- Temperature
- Pressure
- Photoexcitation
- Magnetic field
- Electric fields

Fe(II) complexes (O_h) - most abundant cases

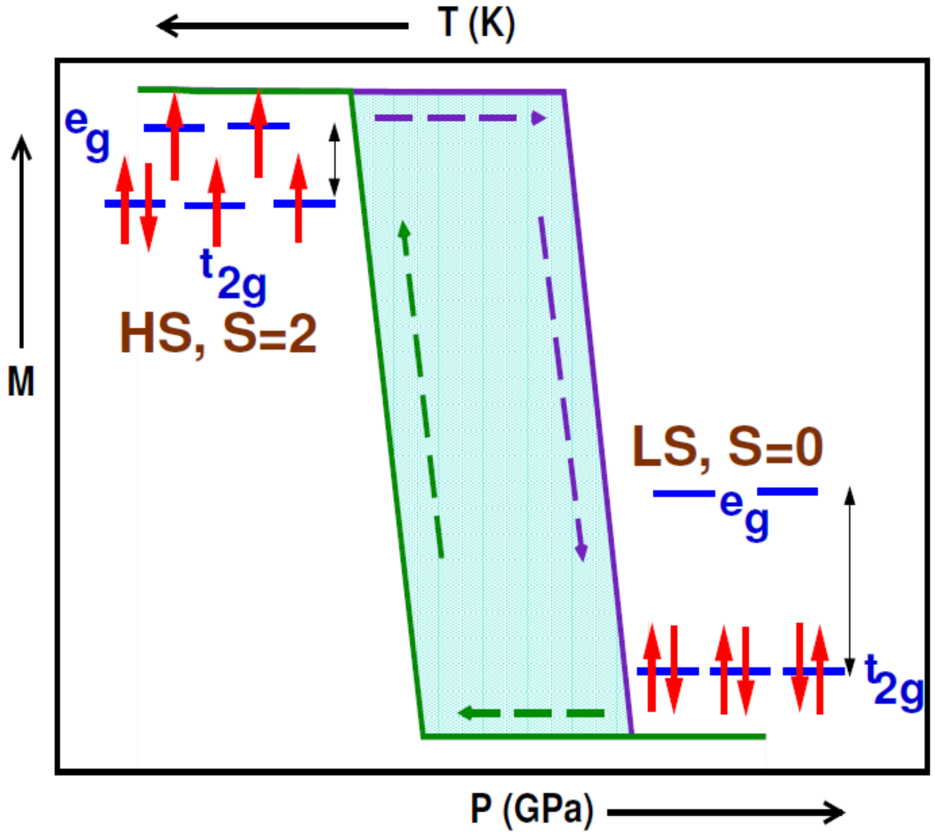




r(Fe–N): 1.95-2.00 Å 2.15-2.20 Å

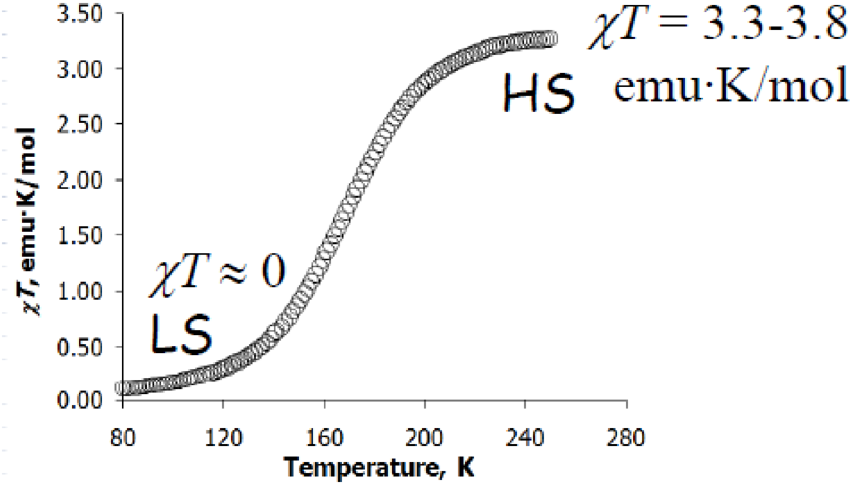
the Fe-N bond lengths and orbital overlap change upon SCO, and therefore 10Dq is different for the LS and HS states of the same complex

Spin Crossover (SCO)



Spin State Isomers

Mangetometry



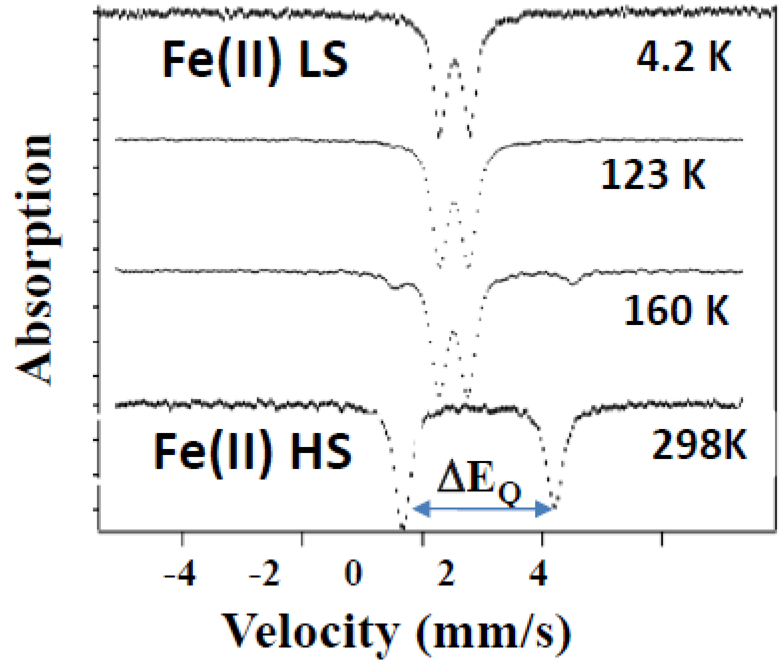
$$\chi_{\mathrm{M}} T(50\%\mathrm{HS}) = \frac{\chi_{\mathrm{M}} T(\mathrm{HS}) + \chi_{\mathrm{M}} T(\mathrm{LS})}{2}$$

$$\mu_{\mathrm{eff}}(50\%\mathrm{HS}) = \frac{\mu_{\mathrm{eff}}(\mathrm{HS}) + \mu_{\mathrm{eff}}(\mathrm{LS})}{\sqrt{2}}$$

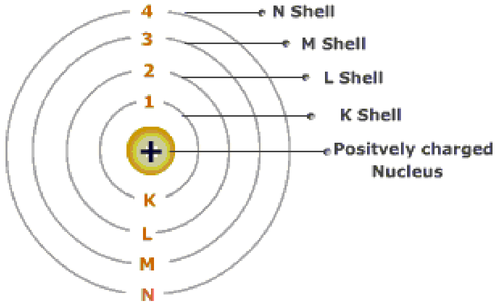
HS molar fraction γ

$$\gamma = \frac{\chi T - (\chi T)_{\mathrm{LS}}}{(\chi T)_{\mathrm{HS}} - (\chi T)_{\mathrm{LS}}}$$

^{57}Fe Mössbauer Spectroscopy



Relativistic Effects



Einstein’s special theory of relativity (1905)

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

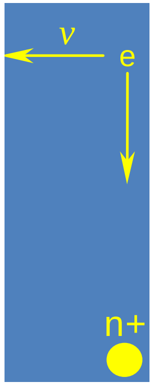
space–time; a single continuum (one entity)

Bohr atomic model (1913)

$$a_0 = \frac{\varepsilon_0 h^2}{mZe^2\pi}$$

$$v_{electron} = \left(\frac{2\pi e^2}{nh}\right) Z$$

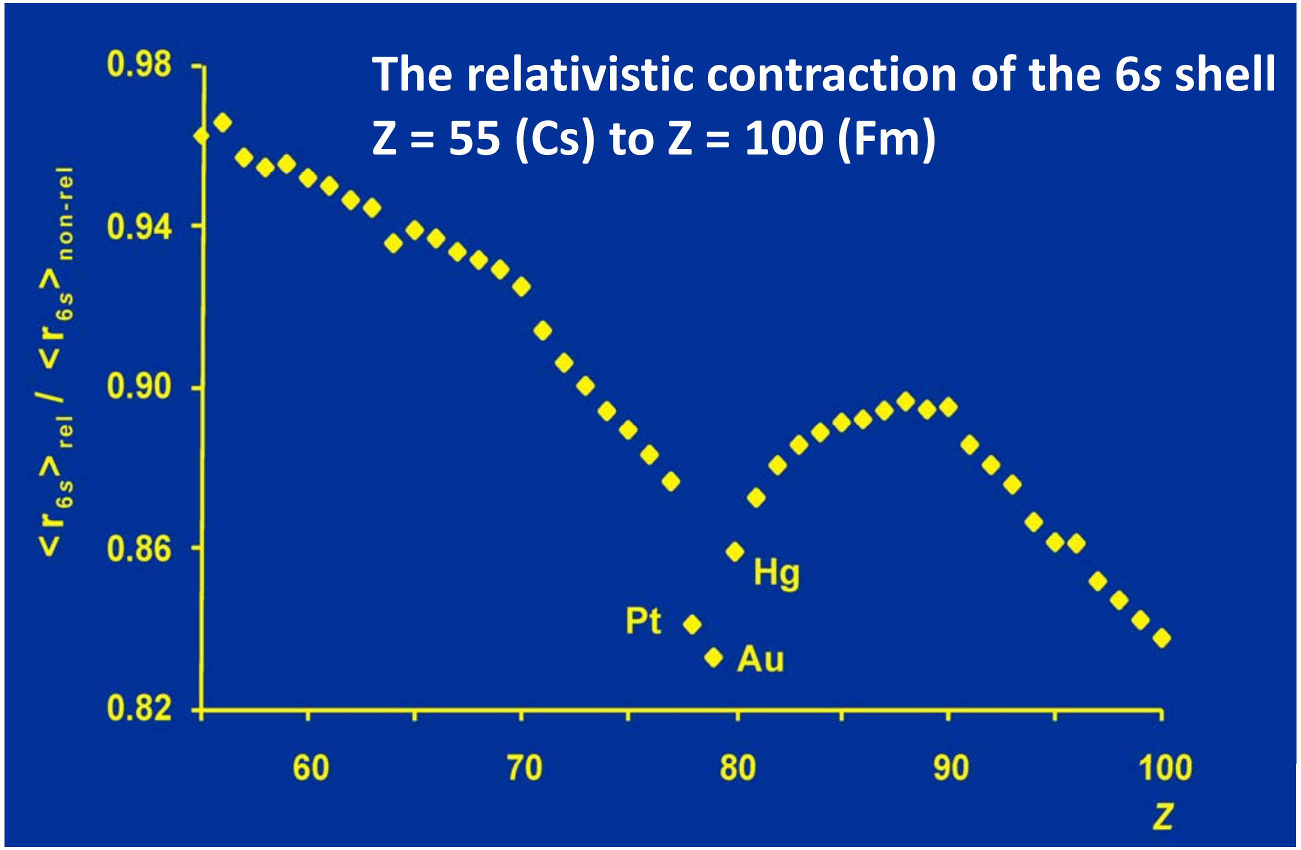
a_0 – Bohr radius
ε_0 – permittivity of free space
h – Planck constant
m – mass of an electron
Z – atomic number
e – elementary charge
$c = 3 \cdot 10^8$ m/s



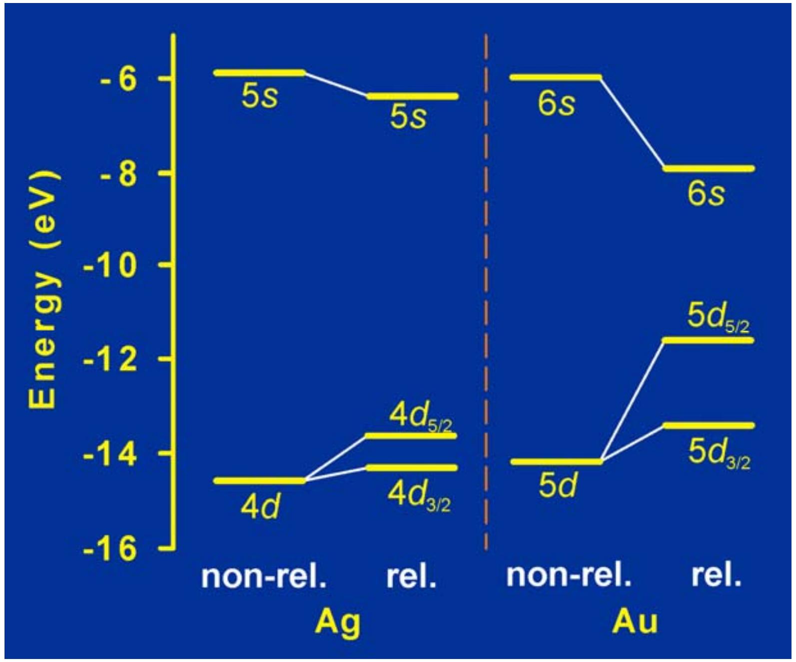
	1*s* electron velocity m/s	relativistic mass	relativistic radius contraction
H (Z = 1)	$v = 2.18 \cdot 10^6$ $v = 0.00727 \cdot c$	$m = 1.0000265\ m_0$	**~ 0 %**
Au (Z = 79)	$v = 1.73 \cdot 10^8$ $v = 0.577 \cdot c$	$m = 1.23\ m_0$	**~ 20 %**
Fm (Z = 100)	$v = 2.18 \cdot 10^8$ $v = 0.727 \cdot c$	$m = 1.46\ m_0$	**~ 30 %**

Relativistic Effects

- **direct effect:** stabilization (decrease) of *s*- and *p*-orbitals
- **indirect effect:** destabilization (expanding) of *d*- in *f*-orbitals due to the increased shielding by *s*- and *p*-orbitals



The relativistic contraction of the 6*s* shell
Z = 55 (Cs) to Z = 100 (Fm)



[Kr] $4d^{10}\,5s^1$ [Xe] $5d^{10}\,6s^1$

- color **Cu**, **Au**, **Ag** instead **Cu**, **Ag**, **Au**
- very high first ionization energy (Au 9.23 eV, Ag 7.58 eV, Cu 7.73 eV)

Au^{1+}/**Ag^{1+}** **Au^{3+}**/Ag^{3+} Au^{4+} Au^{5+}

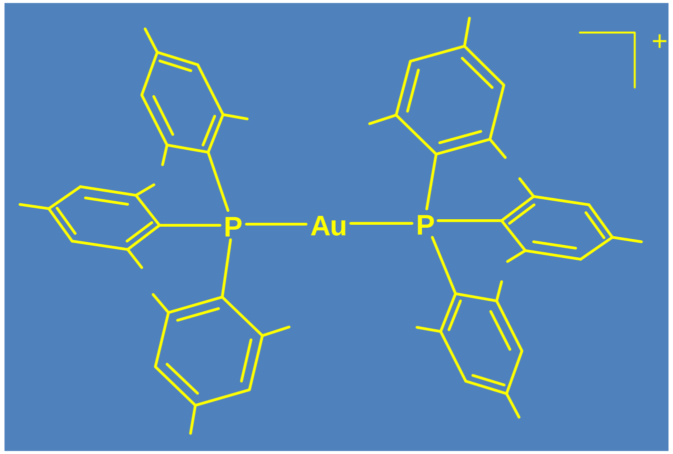
- the highest electron affinity of all metals: simple reduction to auride anion Au^- (Cs^+Au^- is known since 1931, it has CsCl structure) – **pseudohalogen**
- Au_2(g) dissociation energy: 221 kJ/mol

Ag_2(g) 160 Br_2(g) 193 Cl_2(g) 243

- gold is the most electronegative of all metals

$Li^{\delta+}–H^{\delta-}$ $Au^{+0,02}–H^{-0,02}$ $H^{\delta+}–Cl^{\delta-}$

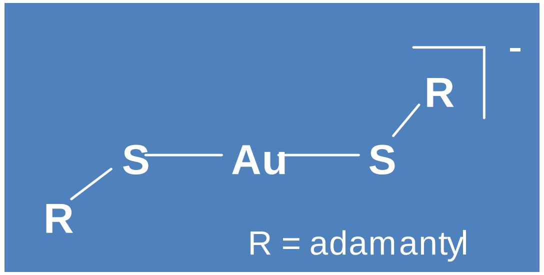
Relativistic Atomic Radius and Bond-Length Contractions



Expected order: **Cu < Ag < Au**

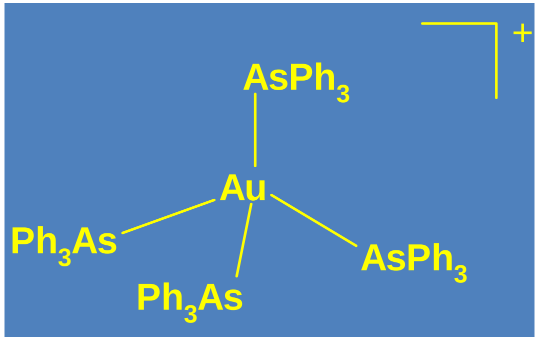
Actual order: **Cu < Au < Ag**

d(Ag–P)	**d(Au–P)**
2.44 Å	**2.35 Å**



d(Ag–S)	**d(Au–S)**
2.35 Å	**2.30Å**

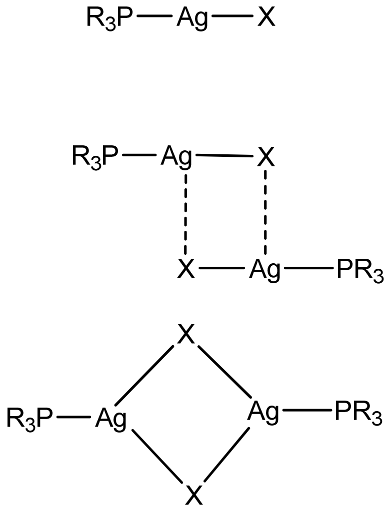
Distance, Å	**Ag**	**Au**
In solid state d(M–M)	**2.889**	**2.885**
Ionic radius for two-coordinate M^{1+}	**1.33**	**1.25**
Ionic radius for four-coordinate M^{1+}	**1.46**	**1.37**

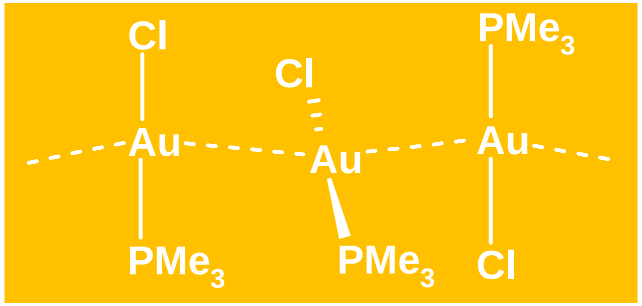


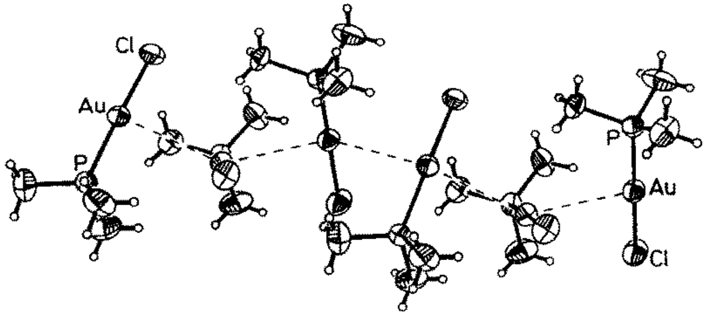
d(Ag–As)	**d(Au–As)**
2.66 Å	**2.59 Å**

d(Ag–H)	**d(Au–H)**
1.62 Å	**1.52 Å**

Aurophilicity







d(Au–Au)
3.27 Å

Attractive interactions $Au^{1+}\cdots Au^{1+}$:

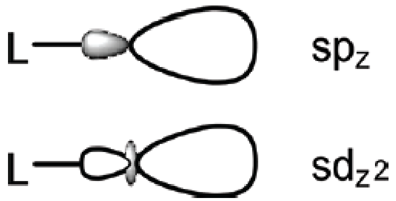
aurophilicity or aurophilic interaction

two-coordinate Au $5d^{10}$ closed-shell interactions

energy comparable to hydrogen-bonding (5–10 kcal/mol)

distances shorter 2.50–3.50 Å then the sum of van der Waals radii (3.80 Å) or d(Au-Au) in ccp (2.89 Å)

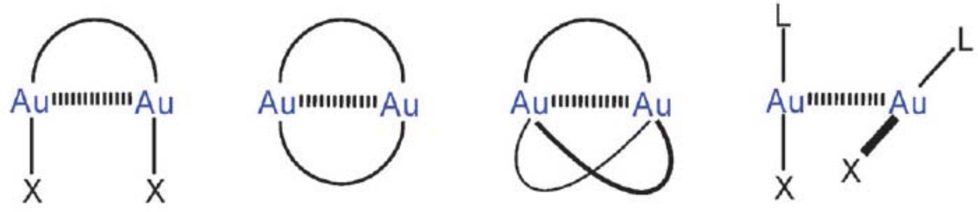
correlation effects + relativistic effects ~20 %



L-Au^+ isolobal to H^+, R^+

metallophilicity or metallophilic interactions
d^{10}-d^{10} Au^+, Ag^+, Cu^+, Hg^{2+}, Pt^0, Pd^0, Tl^{3+}, also Ir

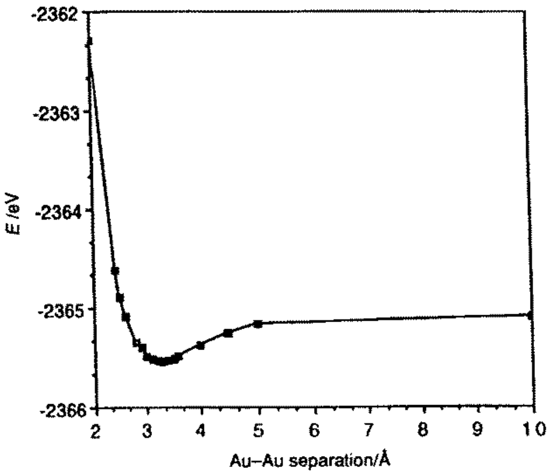
Aurophilic Interactions

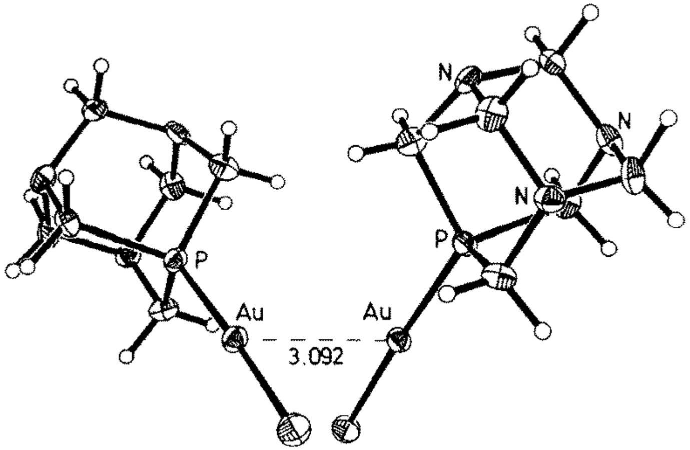


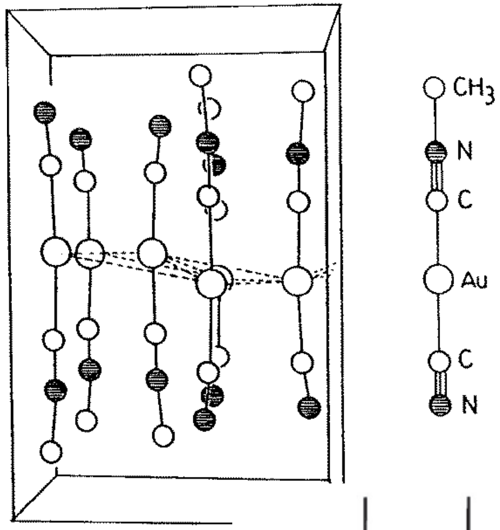
semi-supported fully-supported unsupported

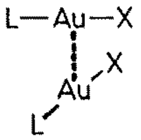
intramolecular

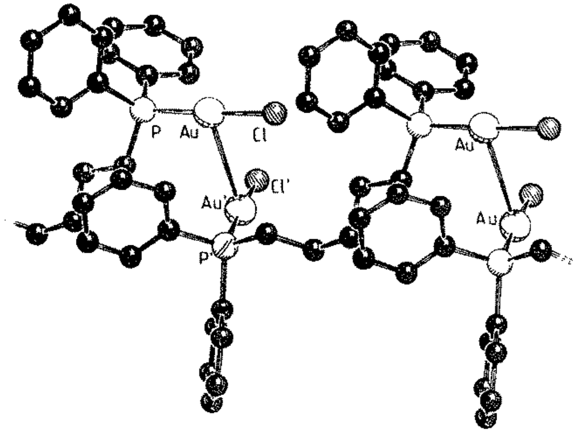
intermolecular

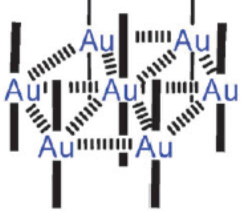








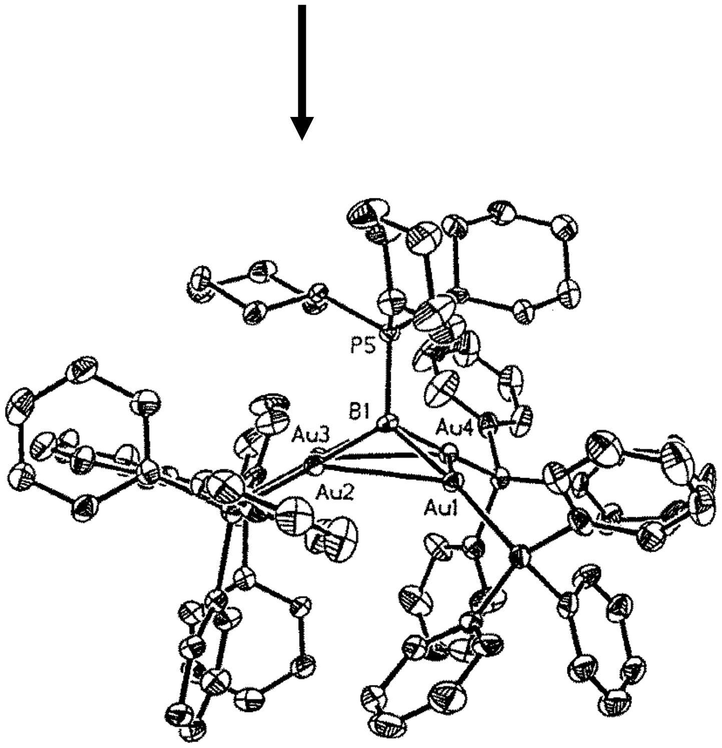


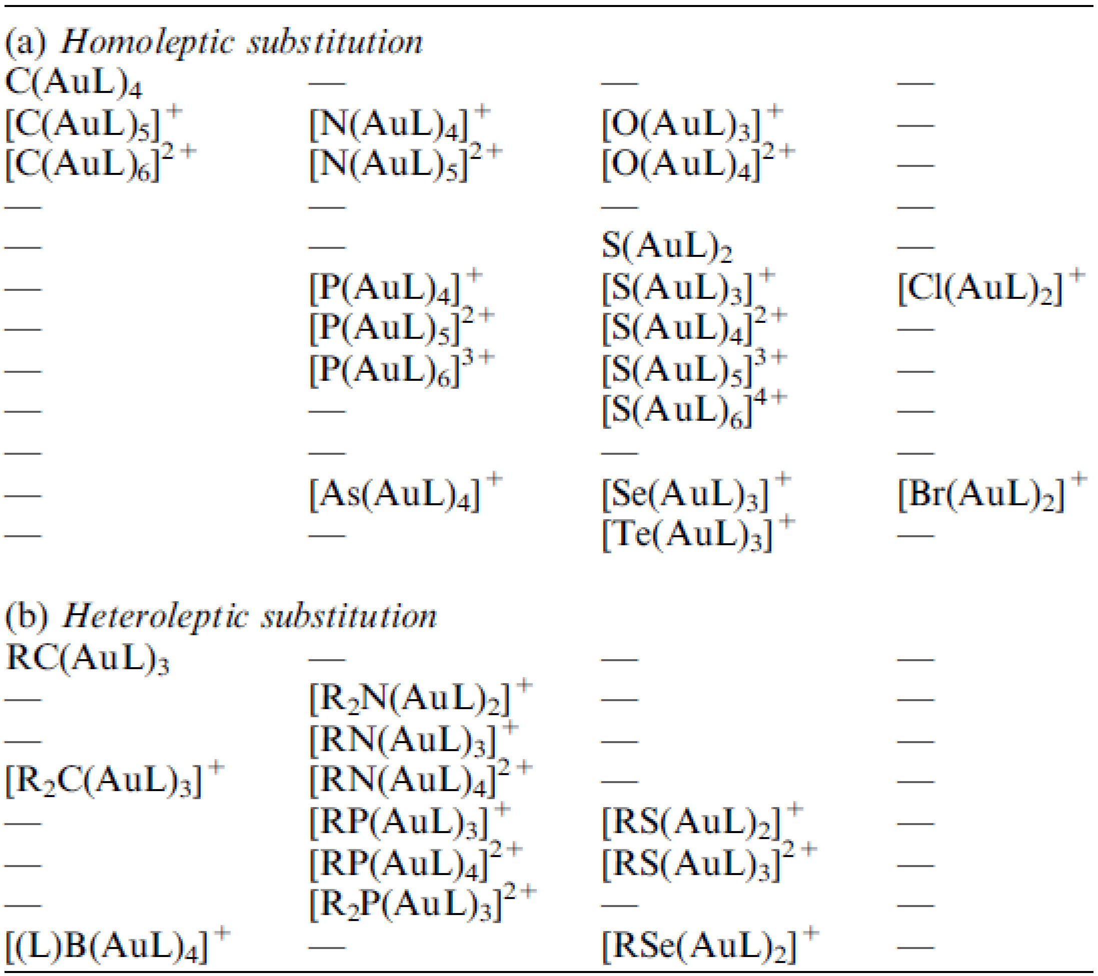


Auration Reactions

L-Au$^+$ isolobal to H$^+$, R$^+$

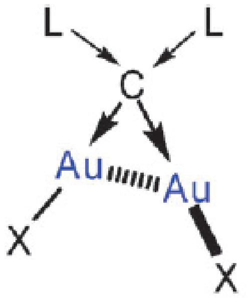
$(R_3P)AuCl + R_3P\text{-}BH_2\text{-}SiMe_3$



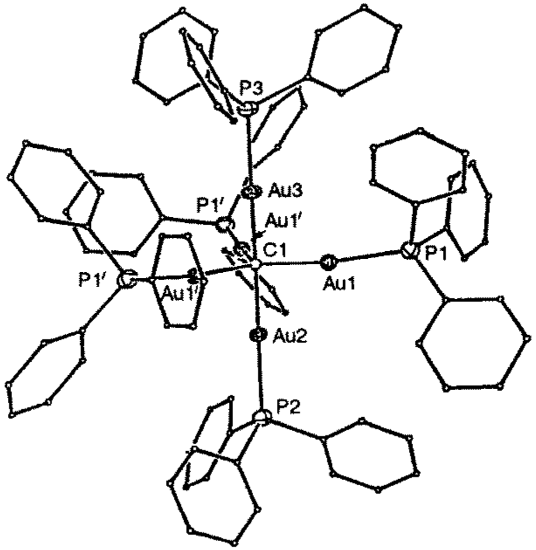


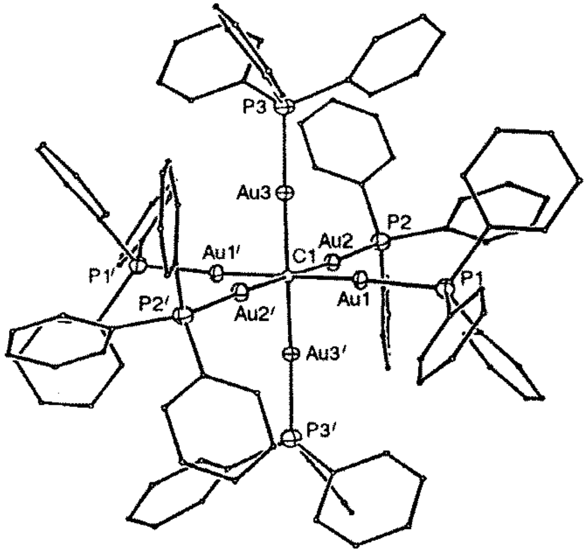
(a) *Homoleptic substitution*			
$C(AuL)_4$	—	—	—
$[C(AuL)_5]^+$	$[N(AuL)_4]^+$	$[O(AuL)_3]^+$	—
$[C(AuL)_6]^{2+}$	$[N(AuL)_5]^{2+}$	$[O(AuL)_4]^{2+}$	—
—	—	—	—
—	—	$S(AuL)_2$	—
—	$[P(AuL)_4]^+$	$[S(AuL)_3]^+$	$[Cl(AuL)_2]^+$
—	$[P(AuL)_5]^{2+}$	$[S(AuL)_4]^{2+}$	—
—	$[P(AuL)_6]^{3+}$	$[S(AuL)_5]^{3+}$	—
—	—	$[S(AuL)_6]^{4+}$	—
—	—	—	—
—	$[As(AuL)_4]^+$	$[Se(AuL)_3]^+$	$[Br(AuL)_2]^+$
—	—	$[Te(AuL)_3]^+$	—
(b) *Heteroleptic substitution*			
$RC(AuL)_3$	—	—	—
—	$[R_2N(AuL)_2]^+$	—	—
—	$[RN(AuL)_3]^+$	—	—
$[R_2C(AuL)_3]^+$	$[RN(AuL)_4]^{2+}$	—	—
—	$[RP(AuL)_3]^+$	$[RS(AuL)_2]^+$	—
—	$[RP(AuL)_4]^{2+}$	$[RS(AuL)_3]^{2+}$	—
—	$[R_2P(AuL)_3]^{2+}$	—	—
$[(L)B(AuL)_4]^+$	—	$[RSe(AuL)_2]^+$	—

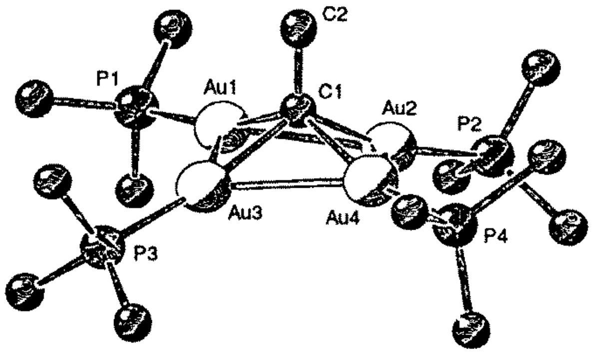
Auration Reactions



1 L = PR$_3$, X = Cl
2 L = carbene, X = Cl
3 L = CN , X = Cl
4 L = PPh$_2$S , X = PPh$_3$

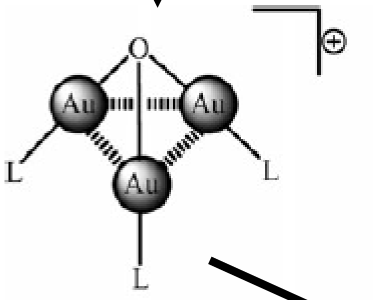






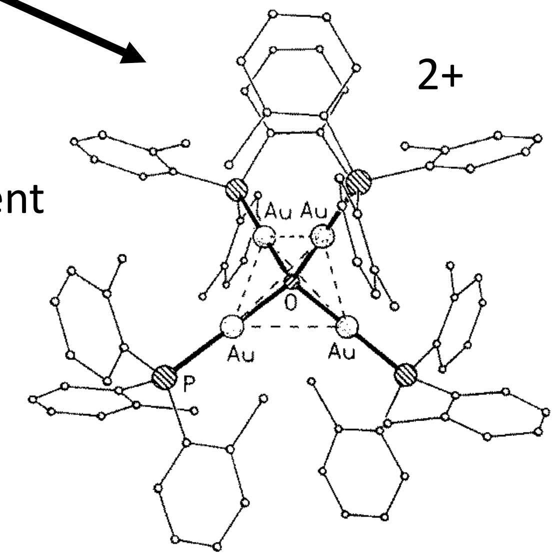
Auration Reactions

$(R_3P)AuCl + Ag_2O, KOH, H_2E, E(SiMe_3)_2$ (E = O, S, Se, Te)

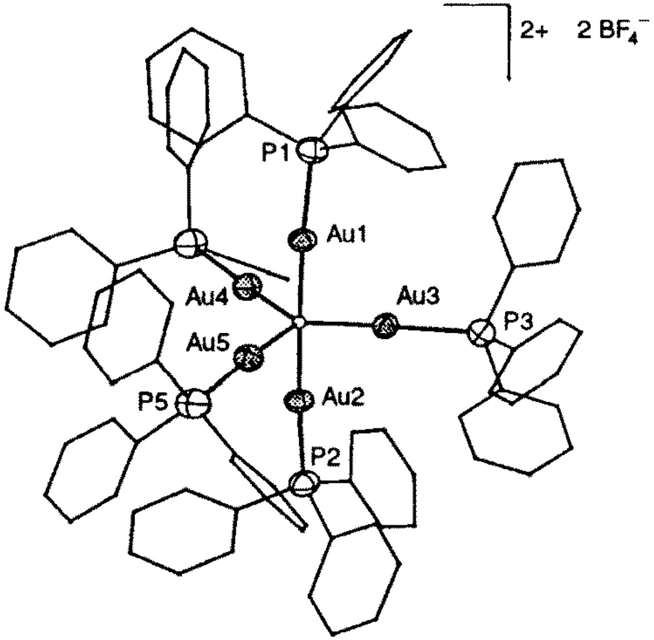


$(R_3P)Au^+ BF_4^-$

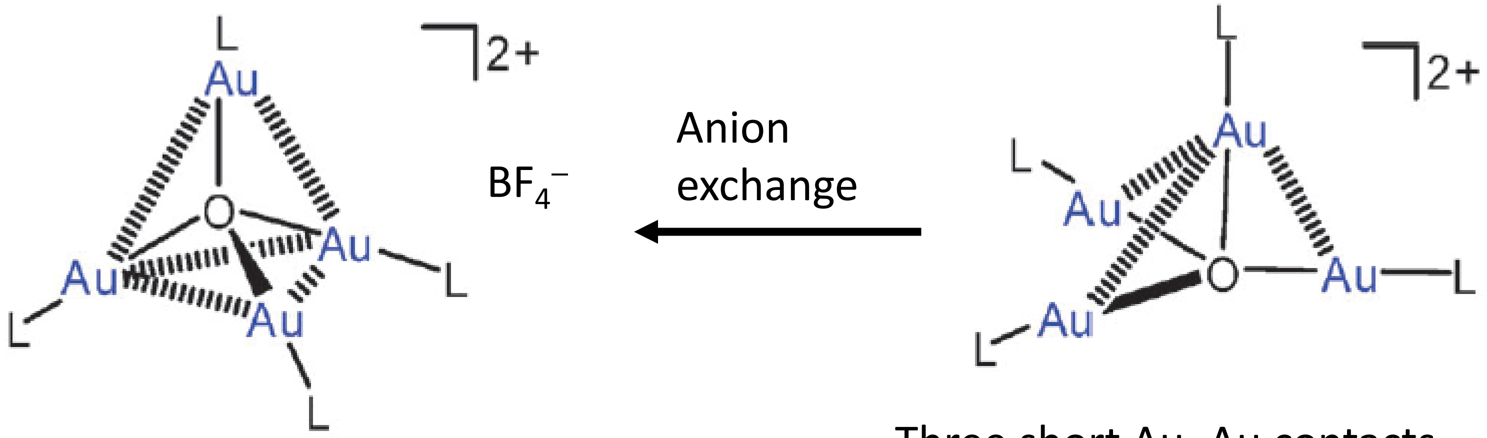
Strong aurating agent



$(R_3P)AuCl + EH_3, E(SiMe_3)_3$ (E = N, P, As)



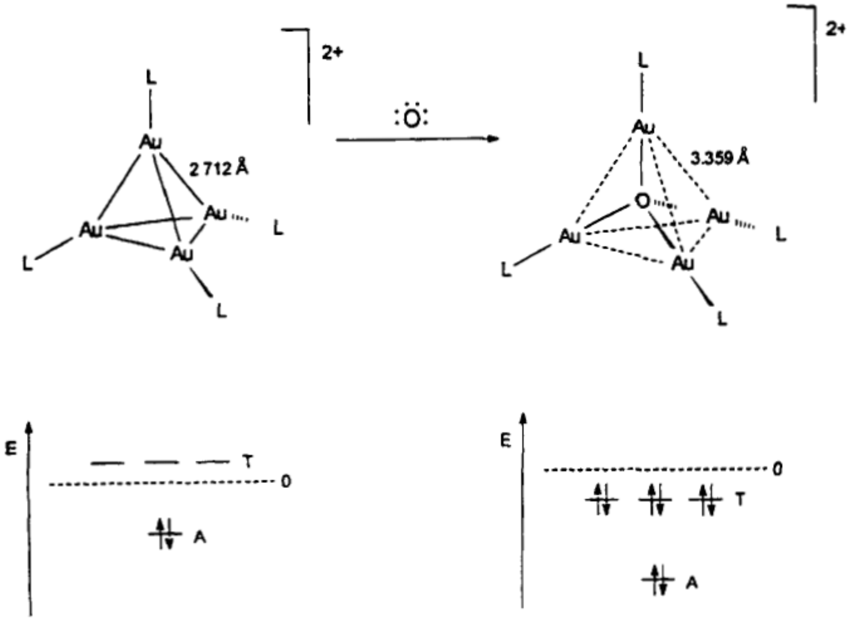
Auration Reactions



BF_4^-

Anion exchange

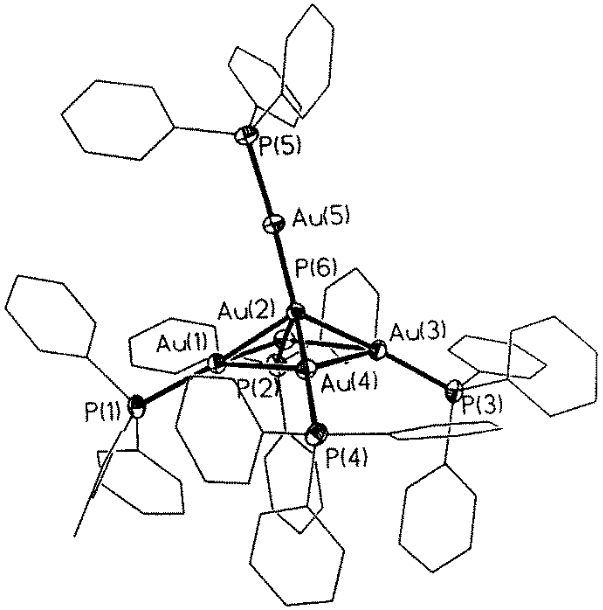
POM/Keggin anion

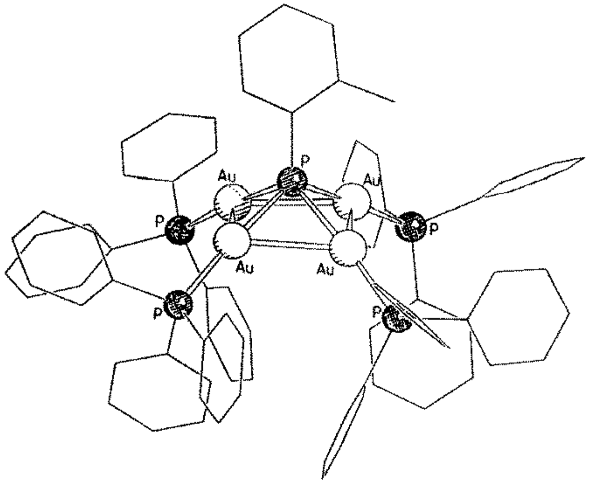


Three short Au–Au contacts
(apical–equatorial, average 2.94 Å)
three long Au–Au distances
(equatorial–equatorial, average 3.60 Å)

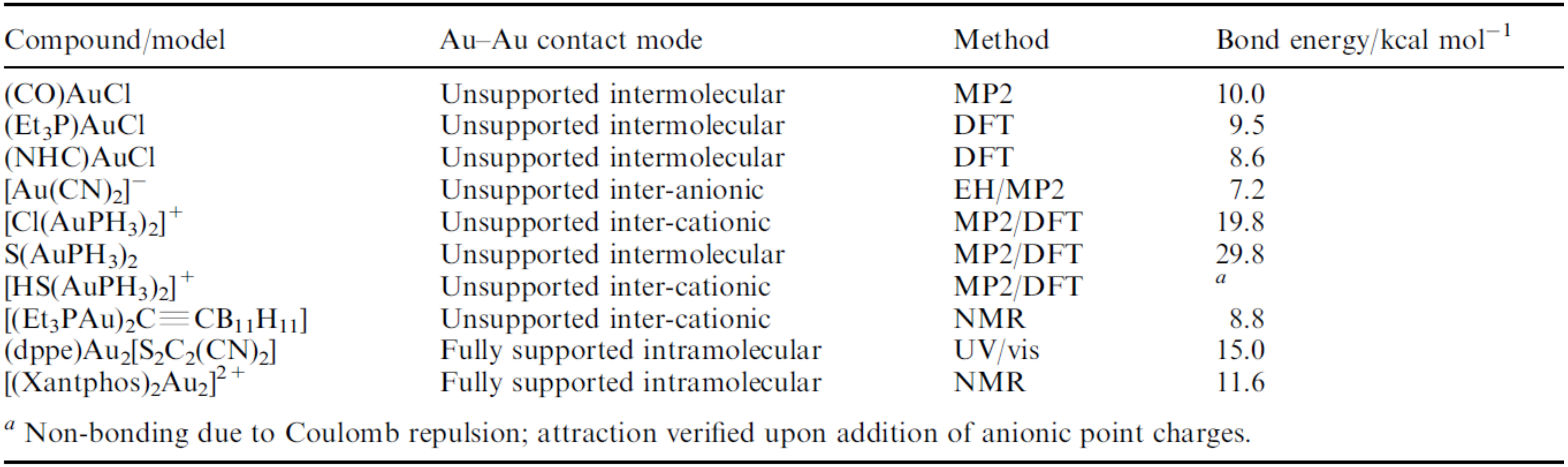
Solid-state ^{31}P NMR
two different types of phosphines
(1 axial, 3 equatorial)
Solution (in DMSO-d_6)
equivalence of all four ligands
$\delta\ ^{31}P = 25$ ppm

Auration Reactions





Bond Energies of Aurophilic Interactions



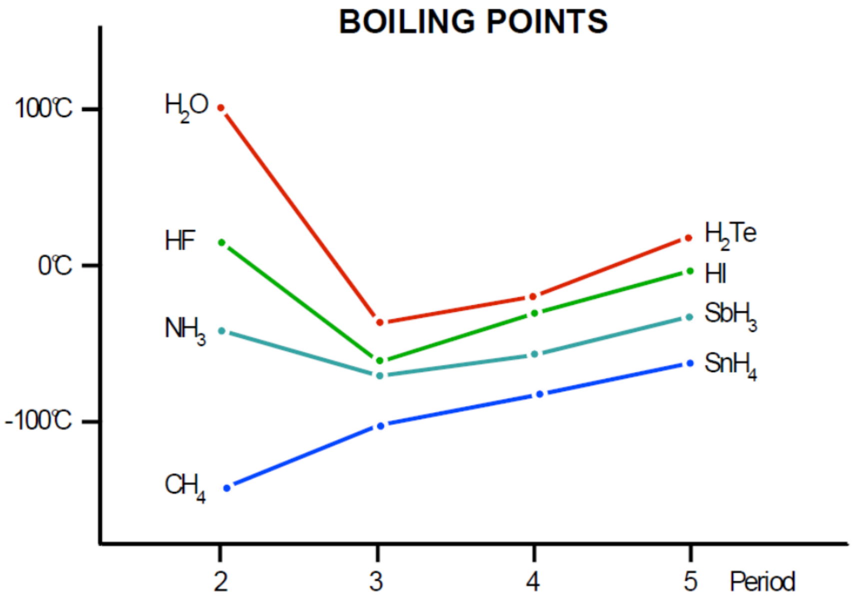
Compound/model	Au–Au contact mode	Method	Bond energy/kcal mol^{-1}
(CO)AuCl	Unsupported intermolecular	MP2	10.0
$(Et_3P)AuCl$	Unsupported intermolecular	DFT	9.5
(NHC)AuCl	Unsupported intermolecular	DFT	8.6
$[Au(CN)_2]^-$	Unsupported inter-anionic	EH/MP2	7.2
$[Cl(AuPH_3)_2]^+$	Unsupported inter-cationic	MP2/DFT	19.8
$S(AuPH_3)_2$	Unsupported intermolecular	MP2/DFT	29.8
$[HS(AuPH_3)_2]^+$	Unsupported inter-cationic	MP2/DFT	[a]
$[(Et_3PAu)_2C{\equiv}CB_{11}H_{11}]$	Unsupported inter-cationic	NMR	8.8
$(dppe)Au_2[S_2C_2(CN)_2]$	Fully supported intramolecular	UV/vis	15.0
$[(Xantphos)_2Au_2]^{2+}$	Fully supported intramolecular	NMR	11.6

[a] Non-bonding due to Coulomb repulsion; attraction verified upon addition of anionic point charges.

H^+	R^+	LAu^+
H_2O	R_2O	$(LAu)_2O$
H_3O^+	R_3O^+	$(LAu)_3O^+$
H_4O^{2+}	R_4O^{2+}	$(LAu)_4O^{2+}$
H_3N	R_3N	$(LAu)_3N$
H_4N^+	R_4N^+	$(LAu)_4N^+$
H_5N^{2+}	R_5N^{2+}	$(LAu)_5N^{2+}$
H_4C	R_4C	$(LAu)_4C$
H_5C^+	R_5C^+	$(LAu)_5C^+$
H_6C^{2+}	R_6C^{2+}	$(LAu)_6C^{2+}$

Hydrogen Bond

D–H•••••A



D–H bond elongates = weakened
D–H bond dipole increases
Dipole-dipole electrostatic energy increases
Attractive interaction increases

Charge transfer from A (lone pair, pi density) to sigma* (antibonding) MO of D–H

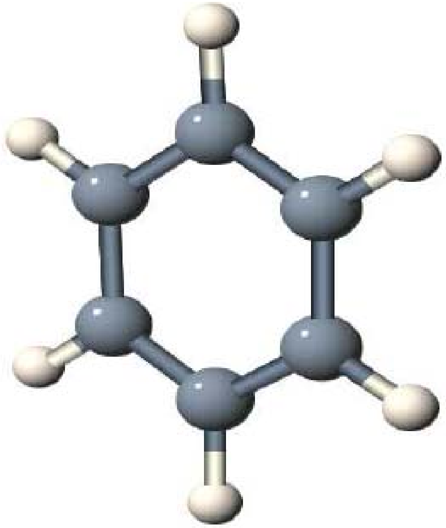
D–H bond weakened = elongated

D–H vibration decreases = RED shift (10 – 100 cm^{-1})

D–H dipole increases = intensity in IR increases

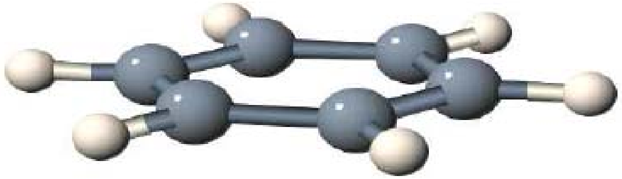
Improper (Blue-Shifting) H-bond

P. Hobza et al.: JPC A 102, 2501 (1998)
benzene…H-X (X = CH_3, CCl_3, C_6H_5)
P. Hobza, Z. Havlas: Chem. Rev. 100, 4253 (2000)



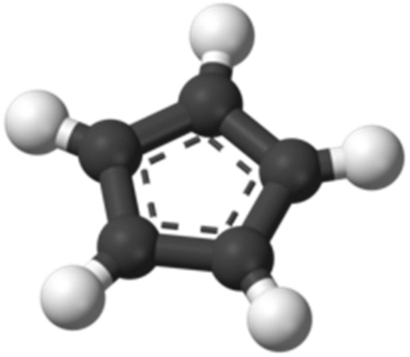
Charge transfer from electron donor to distant parts of electron acceptor (restructuralization of acceptor electrons)

C–H strenghtening, shortening = **BLUE SHIFT**
Rehybridization of C



Indirect mechanism
a two-step mechanism - a charge transfer from the proton acceptor to a remote part of the proton donor, followed by a structural reorganization of the proton donor itself

Improper (Blue-Shifting) H-bond

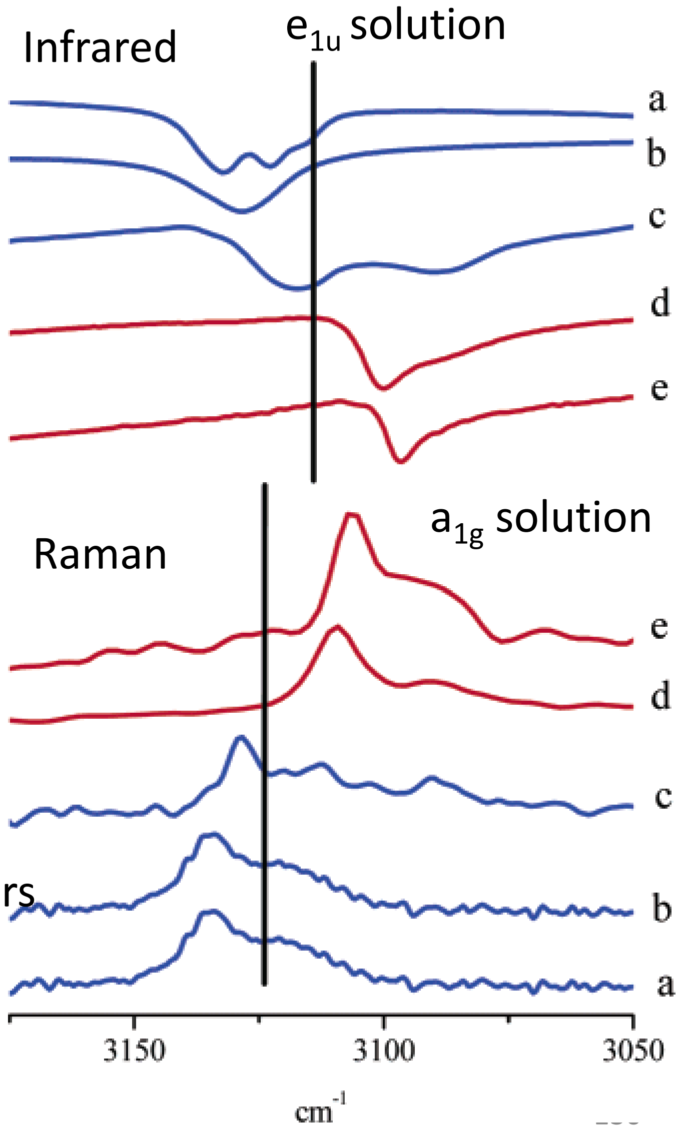


$[Cp_2Co^+]$
salts in (solid state)

The blue spectra = an improper H-bond
a: $[Co(CN)_6]^{3-}$
b: $[PF_6]^-$
c: $[Co(CO)_4]^-$

The red spectra = the proper H-bond
d: $[Br_3]^-$
e: $[I]^-$

a_{1g} = the in-phase displacement of all the C-H vibrators



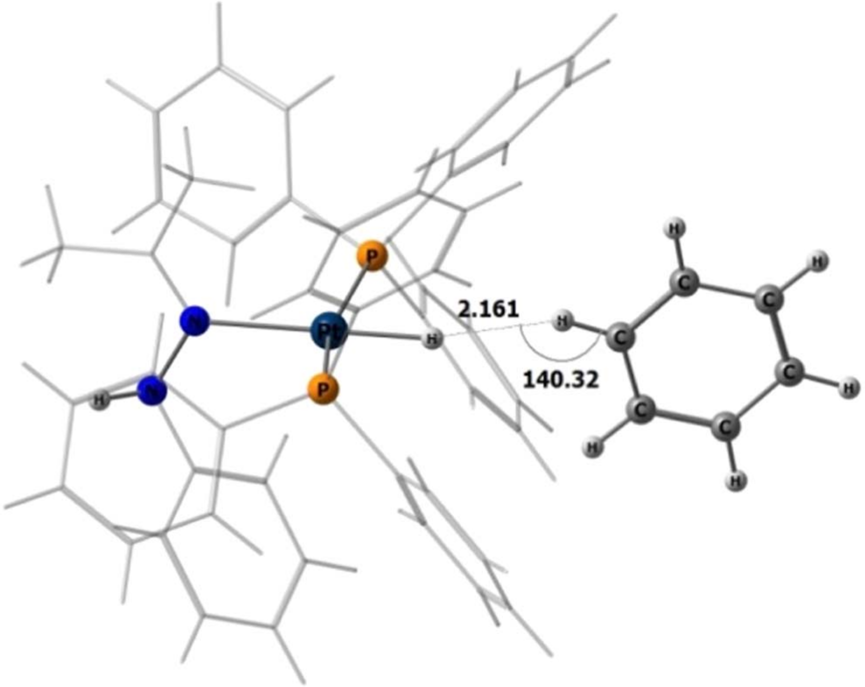
J. Am. Chem. Soc. 2004, 126, 7418-7419

Dihydrogen Bonds

The dihydrogen bond = an interaction between a transition metal or main-group **hydride** (M–H) and a **protic** hydrogen moiety (H–X)

intra- and intermolecular proton−hydride hydrogen bonds

Play a role in:
- crystal packing
- potential hydrogen-storage materials
- organometallic reaction mechanisms



X-ray crystal structure
of trans-[$PtH(PhHNNC_3H_6)(PPh_3)_2]BF_4$

NMR Spectral Criteria of Dihydrogen Bonding

- shifts of the ^{1}H resonance of HX to lower field by 2–4 ppm
- high-field shift of the hydride (M–H) signal by 0.1−0.8 ppm and a 1.5−3-fold decrease of its longitudinal relaxation time (T_{1min})

rapid exchange on the NMR time scale of free and hydrogen-bonded molecules
weighted average between free and dihydrogen bonded hydrides

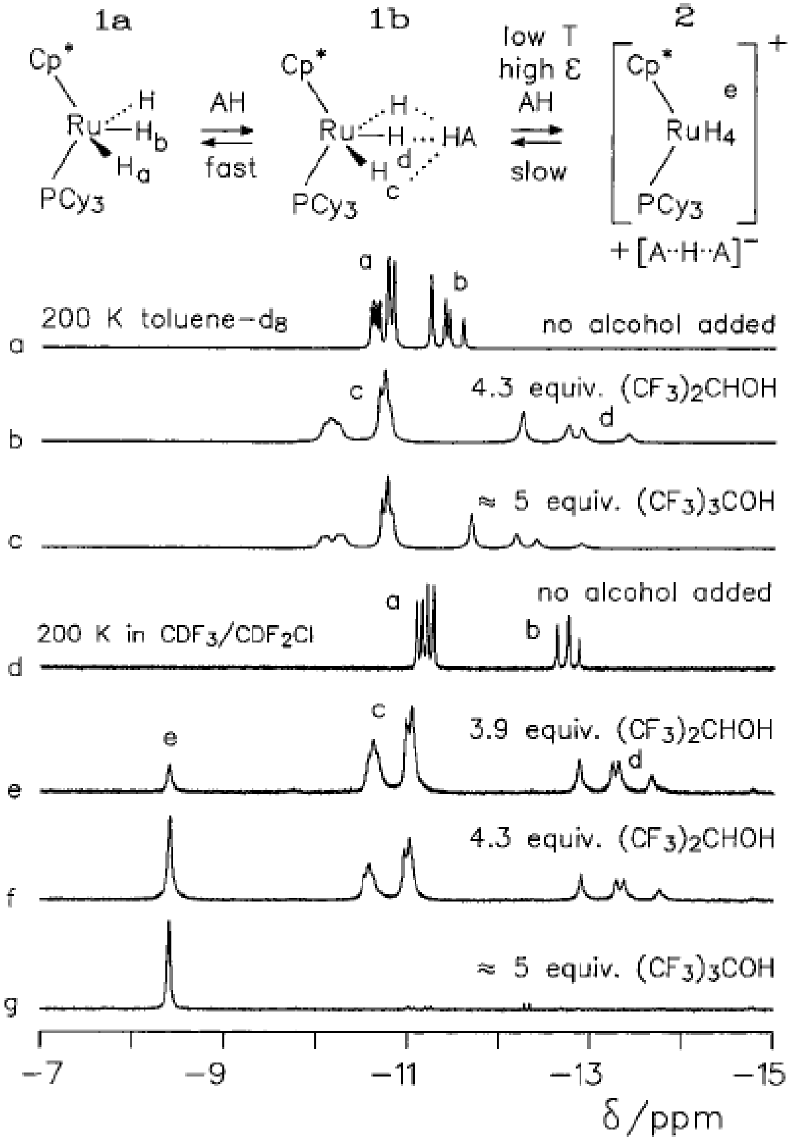
- an enhancement of H−H exchange coupling, J_{H-H} on metal polyhydrides
- 1D nuclear Overhauser effect (NOE) spectroscopy or 2D ^{1}H nuclear Overhauser enhancement spectroscopy (NOESY)

estimation of H···H distances from spin−lattice T_1 relaxation measurements
short MH···HX contacts cause strong homonuclear dipolar coupling that provides an additional contribution to nuclear dipole−dipole relaxation

$$r_{H-H} = 5.815\left(\frac{T_{1\min}}{\nu}\right)^{\frac{1}{6}}$$

NMR Spectral Criteria of Dihydrogen Bonding

Hydride regions
500 MHz ^{1}H NMR



AB$_2$X spin system

J_{ab} = 80 Hz

J_{ab} = 220 Hz

one AB$_2$X multiplet is observed = an average over the fast exchanging 1a/1b

IR Spectroscopy Criteria of Dihydrogen Bonding

IR short time scale - detection of separate absorptions for free and hydrogen-bonded species.
The formation of a dihydrogen bond MH···HX = appearance of a new wider and more intense band, ν_{XH}^{bonded}, of the proton donor

a band shift: $\Delta\nu_{XH} = \nu_{XH}^{bonded} - \nu_{XH}^{free}$ (red shift up to $-450\ \mathrm{cm}^{-1}$)

elongation of the proton-donating HX bond

Enthalpies of intermolecular hydrogen bonds ΔH_{HB}
changes in the IR band positions ($\Delta\nu_{XH}$) and intensities (ΔA_{XH})
(in kcal mol^{-1})

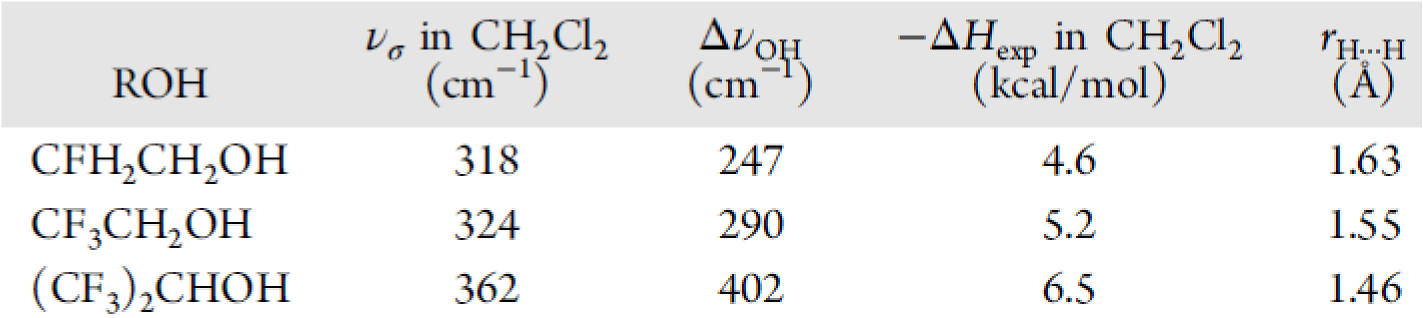
$$\Delta H_{\mathrm{HB}} = -18\Delta\nu_{\mathrm{HX}}/(\Delta\nu_{\mathrm{HX}} + 720)$$

$$\Delta H_{\mathrm{HB}} = -0.30\Delta\nu_{\mathrm{HX}}{}^{1/2}$$

$$\Delta H_{\mathrm{HB}} = -2.9\Delta \mathrm{A}_{\mathrm{HX}}{}^{1/2} = -2.9(A_{\mathrm{bonded}}{}^{1/2} - A_{\mathrm{free}}{}^{1/2})$$

Enthalpies of Dihydrogen Bonds

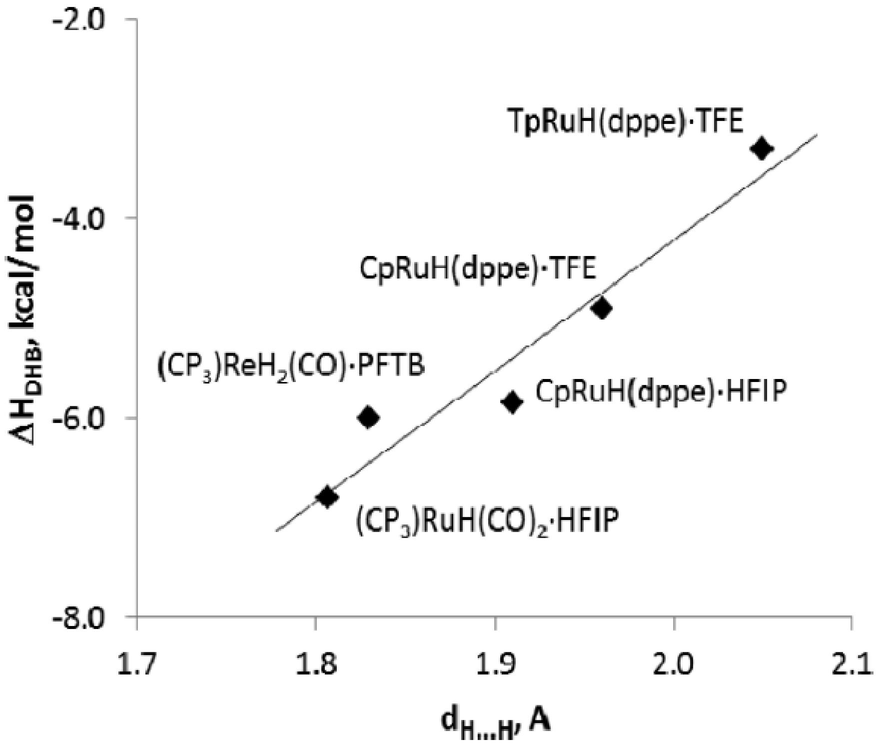
Complexes of Boron Tetrahydride with Different Proton Donors



ROH	ν_σ in CH_2Cl_2 (cm^{-1})	$\Delta\nu_{OH}$ (cm^{-1})	$-\Delta H_{exp}$ in CH_2Cl_2 (kcal/mol)	$r_{H\cdots H}$ (Å)
CFH_2CH_2OH	318	247	4.6	1.63
CF_3CH_2OH	324	290	5.2	1.55
$(CF_3)_2CHOH$	362	402	6.5	1.46

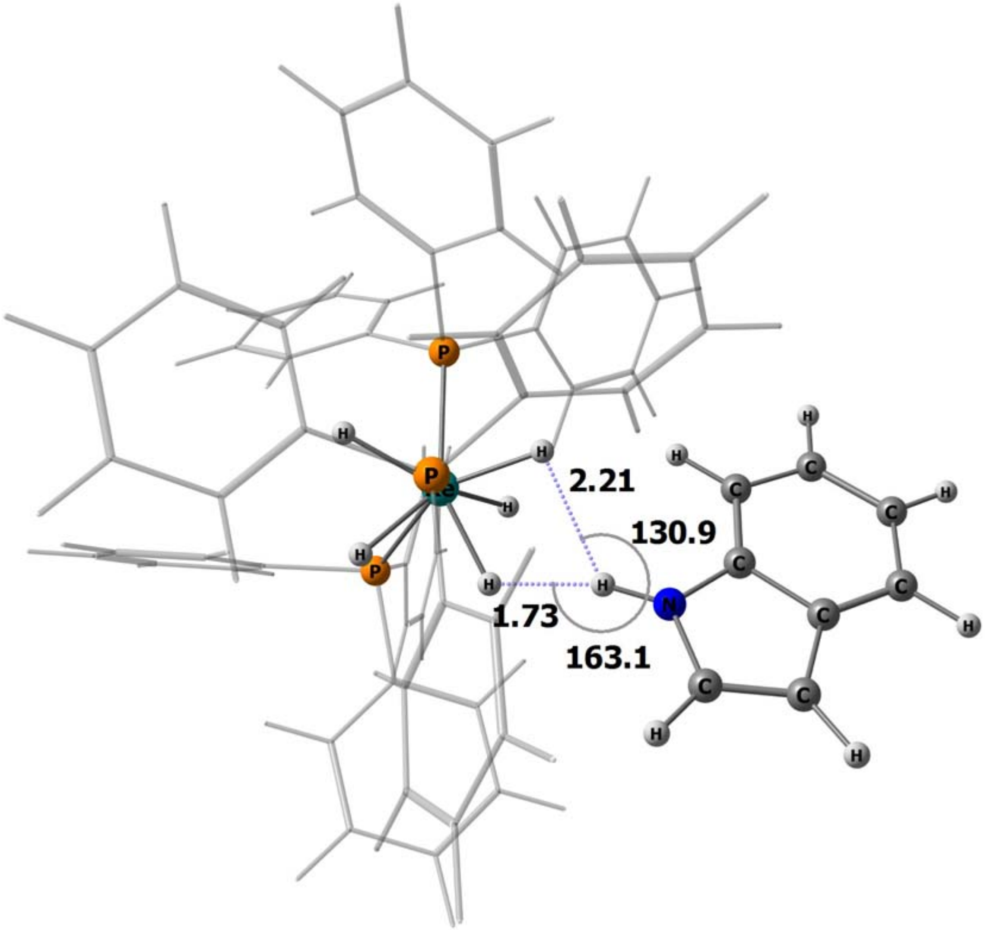
ν_σ = intermolecular H···H stretching mode

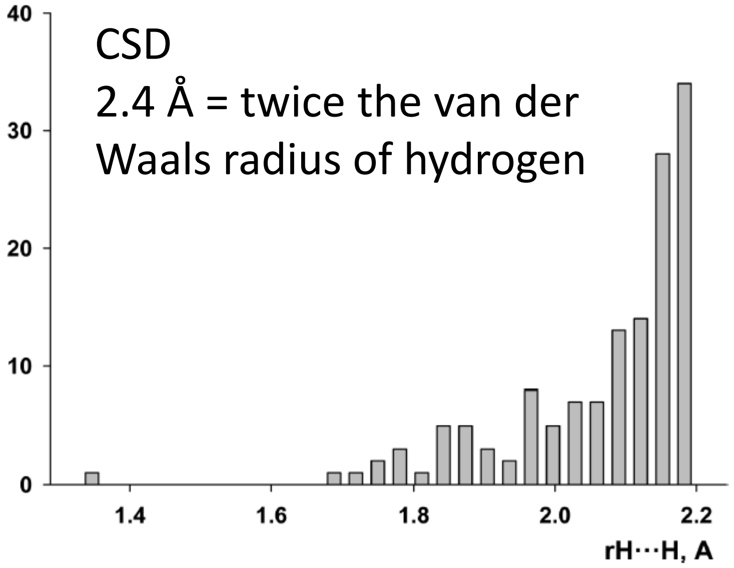
Enthalpies of Dihydrogen Bonds



Correlation between the enthalpy of DHB formation (ΔH°DHB; derived from IR data) and the H···H distance (determined from NMR data on T_{1min}) for complexes of fluorinated alcohols
[TFE = CF_3CH_2OH, HFIP = $(CF_3)_2CHOH$, PFTB = $(CF_3)_3COH$]
in dichloromethane

Crystallographic Structural Data




CSD
2.4 Å = twice the van der Waals radius of hydrogen

Neutron diffraction crystal structure of $ReH_5(PPh_3)_3$·indole