

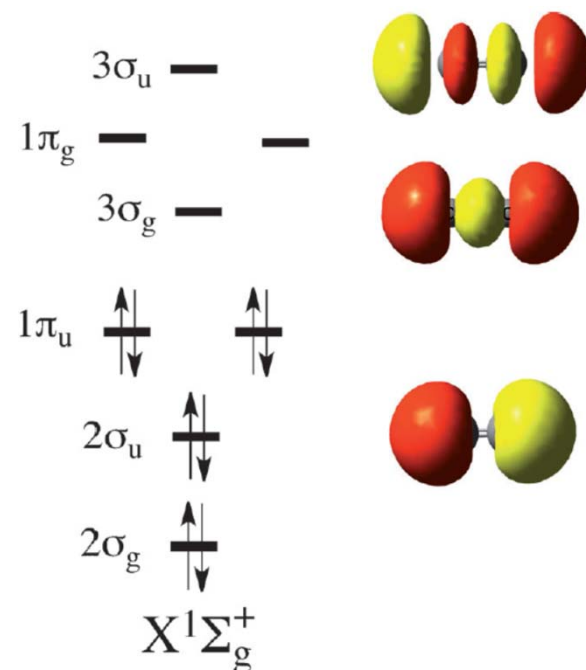
Multiple Bonding in C₂

C₂ – blue color of hot hydrocarbon flames

1802 Wollaston - the first reported emission spectrum of any molecule

One of the most abundant molecules in the universe, comets

Valence MO in
the ground state



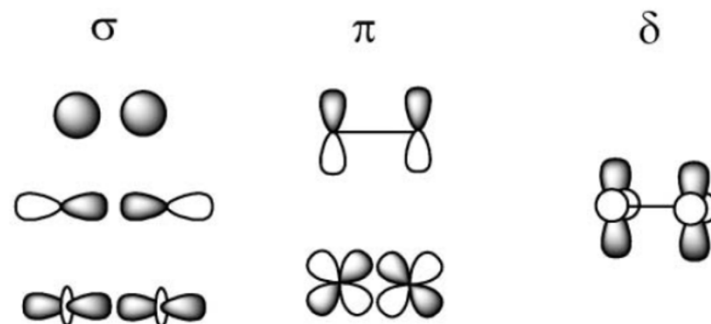
$$\text{Bond order} = (6 - 2)/2$$

2σ_g and 2σ_u^{*} orbitals are both filled = two π-bonds unsupported by an underlying σ-bond and two σ lone pairs



Multiple Bonding in C₂

The variation of **orbital overlap** as a function of **internuclear distance** shows that **maximum overlap** occurs at **shorter** distances for **π- and δ-bonds** than for **σ-bond**



π-bonds (unsupported by an underlying σ-bond) are shorter than σ+π-bonds

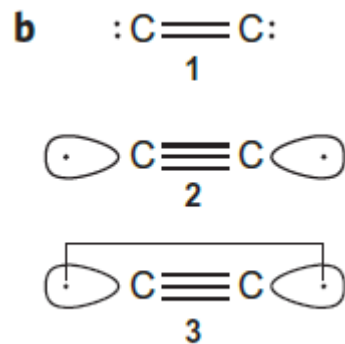
Bond	Å	C₂	$3\sigma_g$ $1\pi_u$ $2\sigma_u^*$ $2\sigma_g$	$1\Sigma_g^+$ 	$3\Pi_u$ 	$3\Sigma_g^+$ 	
H ₃ C-CH ₃	1.538			Bond length	1.240 Å	1.313 Å	1.370 Å
H ₂ C=CH ₂	1.338						
HC≡CH	1.203						



Inverted Bond

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

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



Triplet state $^3\Sigma_u^+$, electrons are unpaired
 26.4 kcal mol⁻¹ above the singlet GS
 Flip of the spins of the diradical to a
 singlet = the energy goes down

These electrons maintain a significant
 bonding interaction in the ground state

Bond order = 3

- $2\sigma_u^*$ is not antibonding but rather
 nonbonding

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

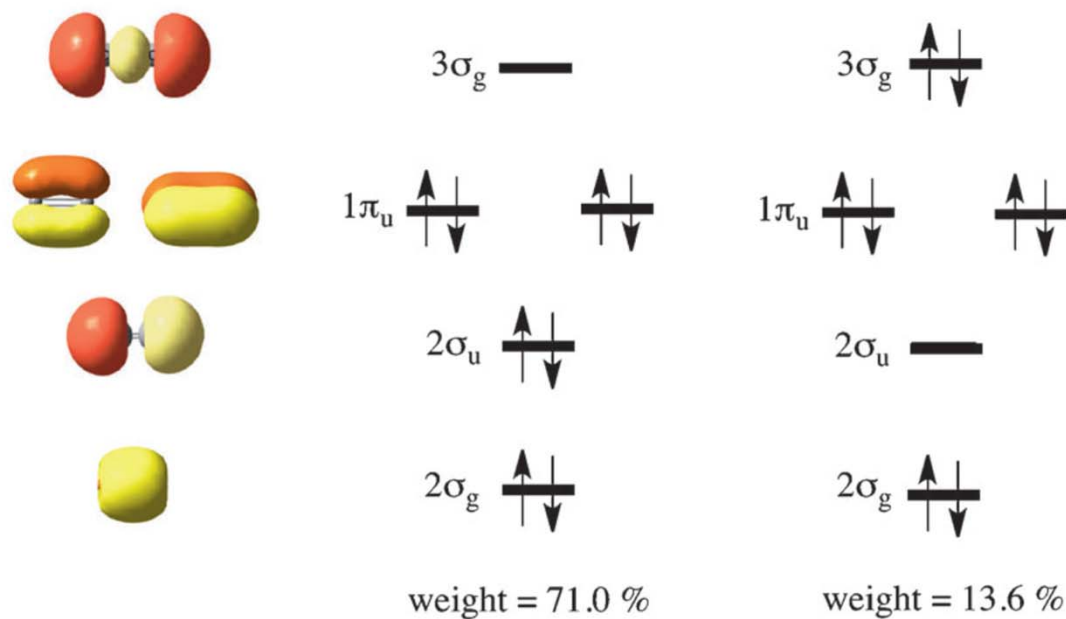
Bond order = 4

C_2 quadruply bonded, 3 internal bonds
 (1 strong σ + 2 π) and one weak
 '**inverted**' C-C bond



Quadruple Bonding in C₂

Full-valence CASSCF/6-31G* wave function



Significant contribution



Quadruple Bonding in C₂

Bonding between two atoms - a well-defined discrete **minimum** in the potential energy curve (PEC) plotted against the interatomic distance

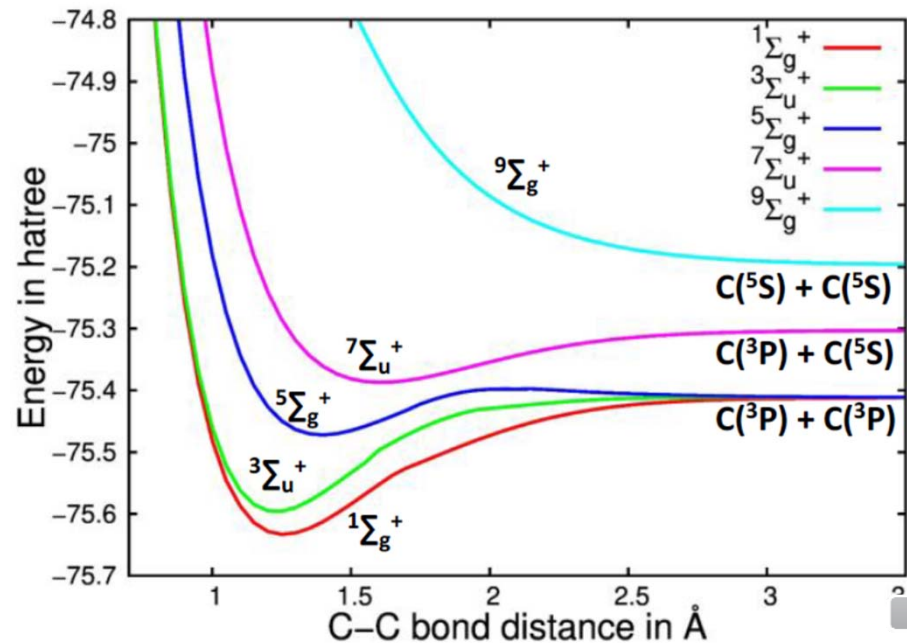
The multiply bonded diatomic species - generate high spin states by breaking bonding electron pairs, promote electrons from a bonding to the antibonding orbital with single occupation with parallel spins

The number of bonds in the ground state = at which high spin state **the purely dissociative PEC is reached**

All of the bonding interactions are annihilated at the ${}^9\Sigma_g^+$ state

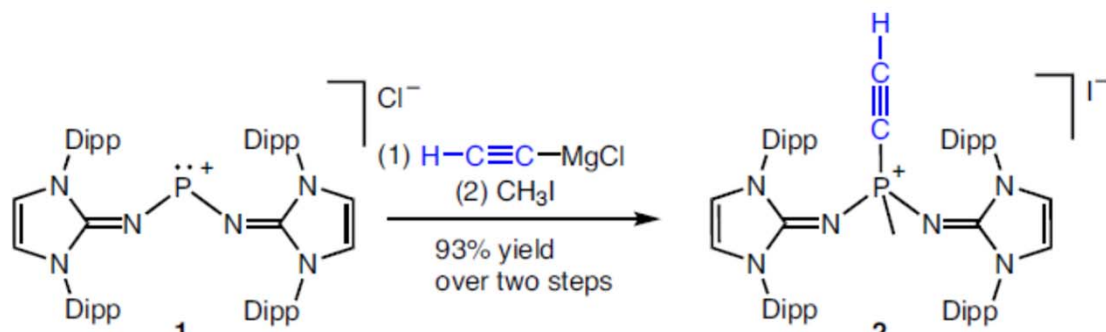
${}^7\Sigma_u^+$ state PEC has a minimum

The ground electronic state of C₂ has **four** bonds = 2 σ + 2 π

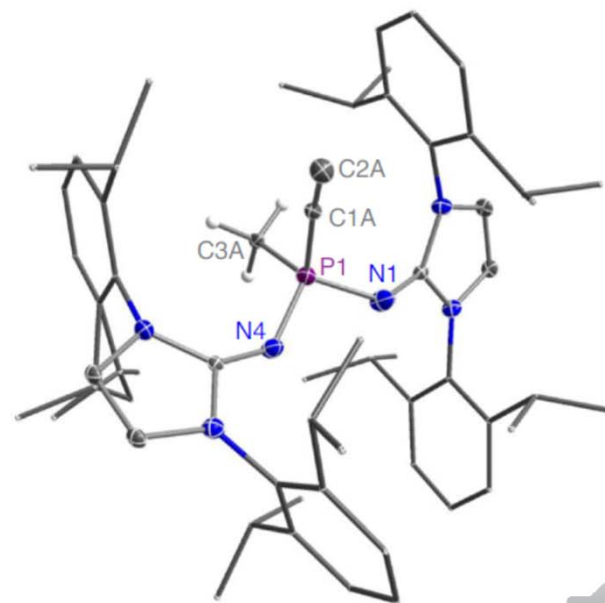
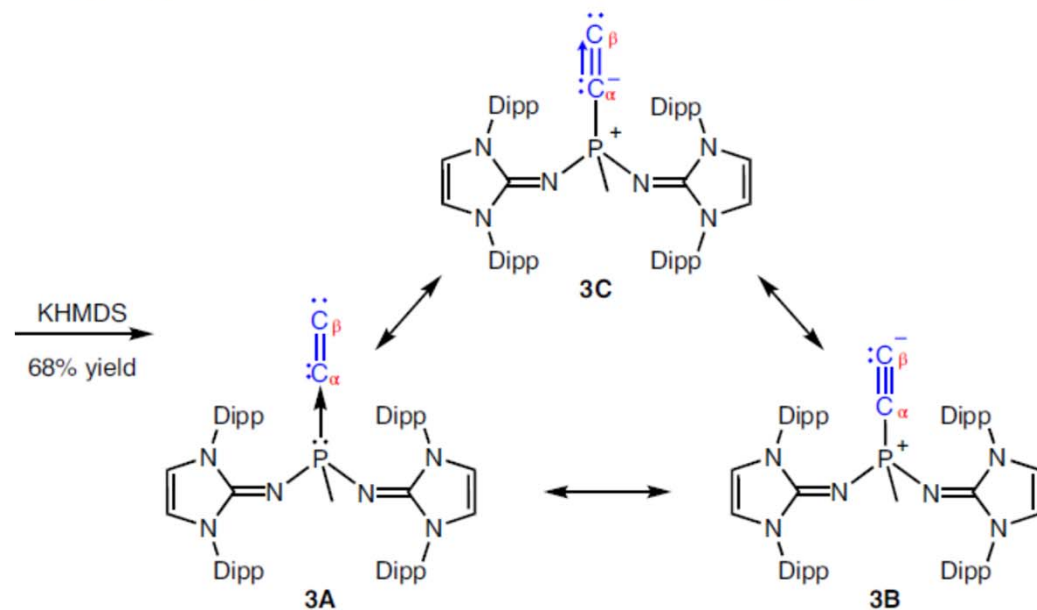


Synthesis of C₂

The two carbon atoms of the C₂ moiety both have carbene character



¹³C NMR
C_α (d, 98.9 ppm)
C_β (bs, 208.5 ppm)



Single-Electron Bonds

Single-electron Lanthanide-Lanthanide bonds inside fullerenes

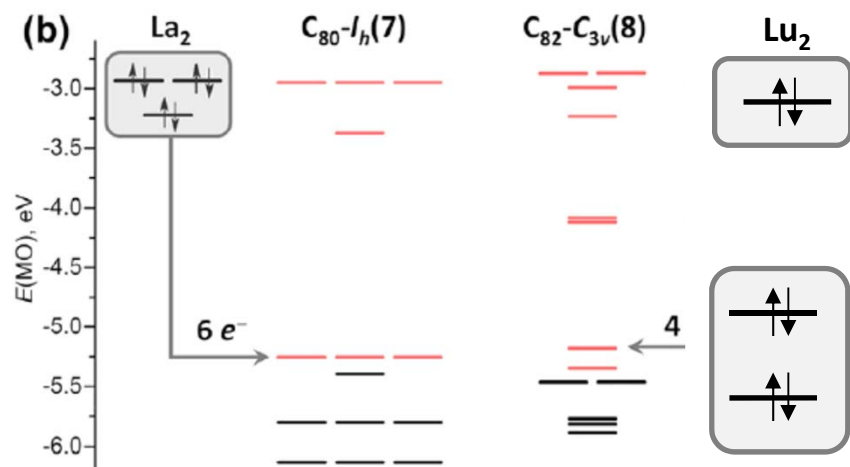
Ln–fullerene interaction = the transfer of metal valence electrons to the carbon cage

Early lanthanides (La, Ce, Pr, Nd) - complete transfer of 6 valence electrons = $(\text{Ln}^{3+})_2@C_{80}^{6-}$

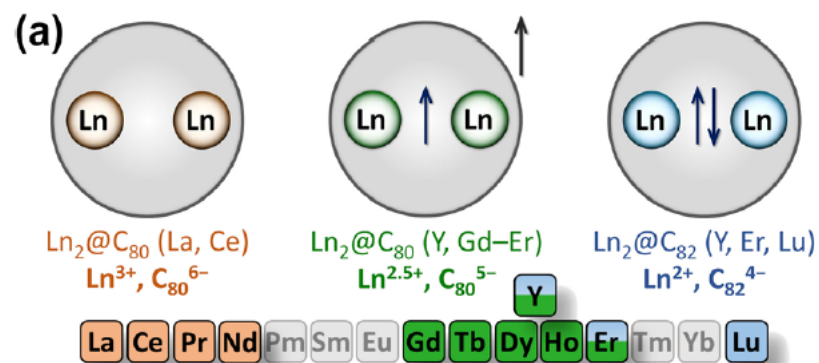
Middle lanthanides - transfer of only 5 electrons, 1 electron remains in the Ln–Ln σ -bonding orbital = $(\text{Ln}^{2.5+})_2@C_{80}^{5-}$ - **single-electron Ln–Ln bond**

Unstable in the neutral form, stabilized in $\text{Ln}_2@C_{79}\text{N}$

Late lanthanides (Lu) - transfer of only 4 electrons, 2 electrons remain in the Ln–Ln σ -bonding orbital = $(\text{Ln}^{2+})_2@C_{82}^{4-}$ - normal single 2-electron Ln–Ln bond



Black - occupied MOs; **red** - vacant MOs

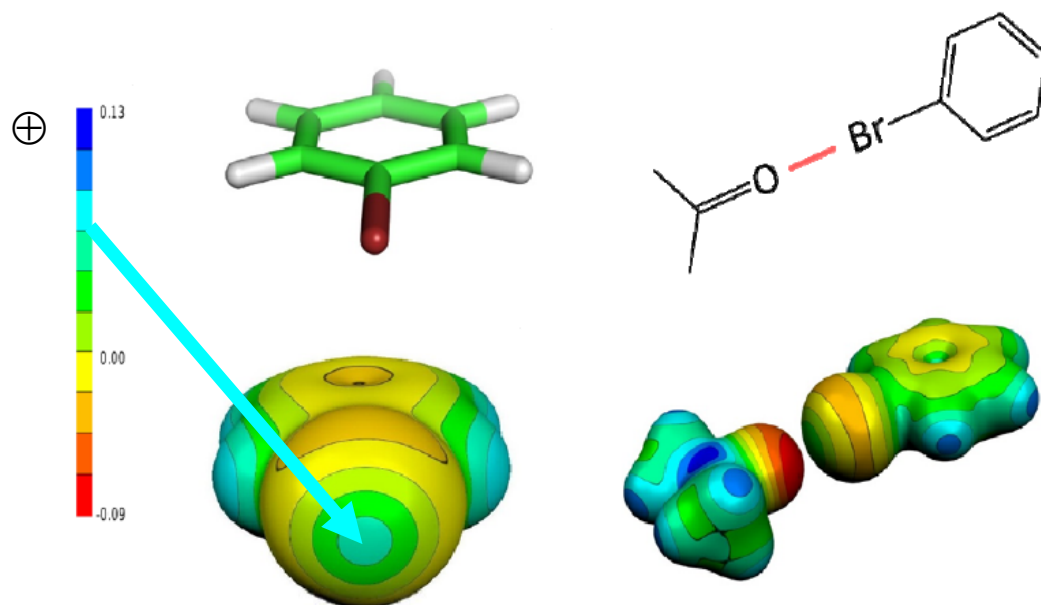


DOI: 10.1021/acs.accounts.9b00373
Acc. Chem. Res. 2019, 52, 2981–2993



Sigma Hole Interactions

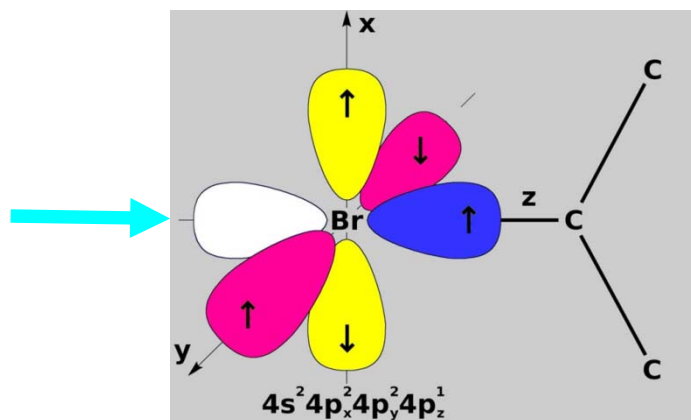
Electrostatic potential (ESP) – observable quantity



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 (Br) without hybridization
 $4p_z$ occupied by only one electron

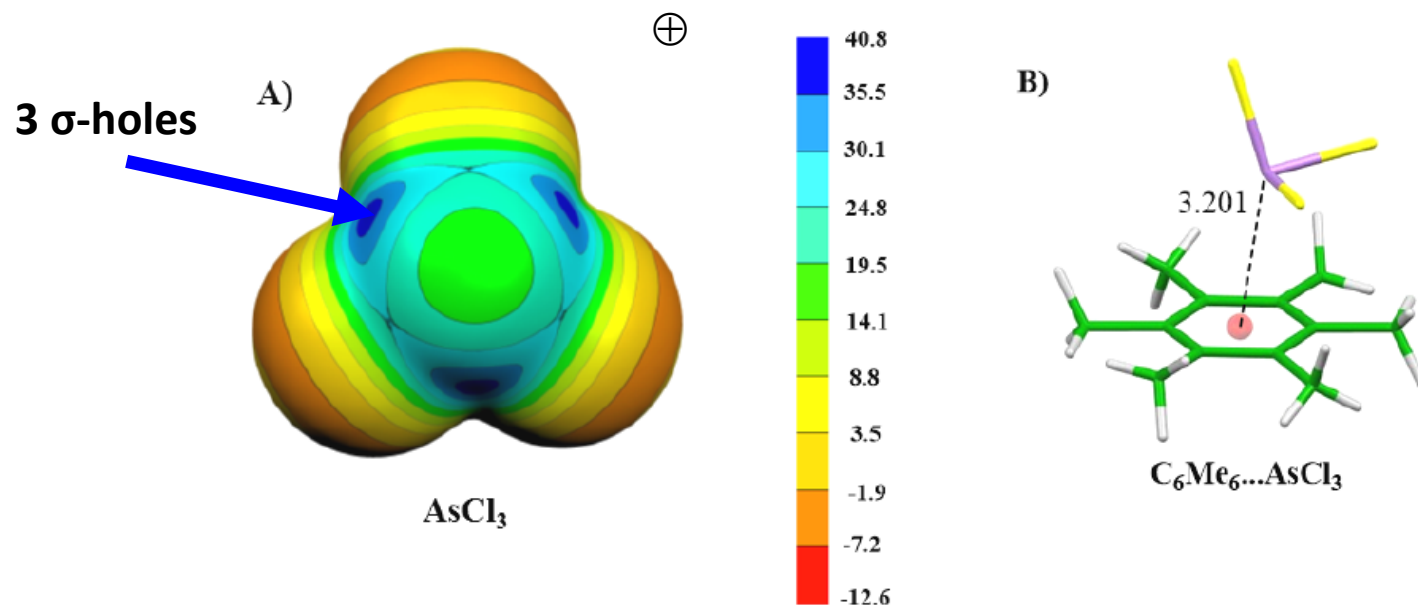


Sigma Hole Interactions

Electrostatic potential (ESP)

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|}$$

Pnictogen bonding



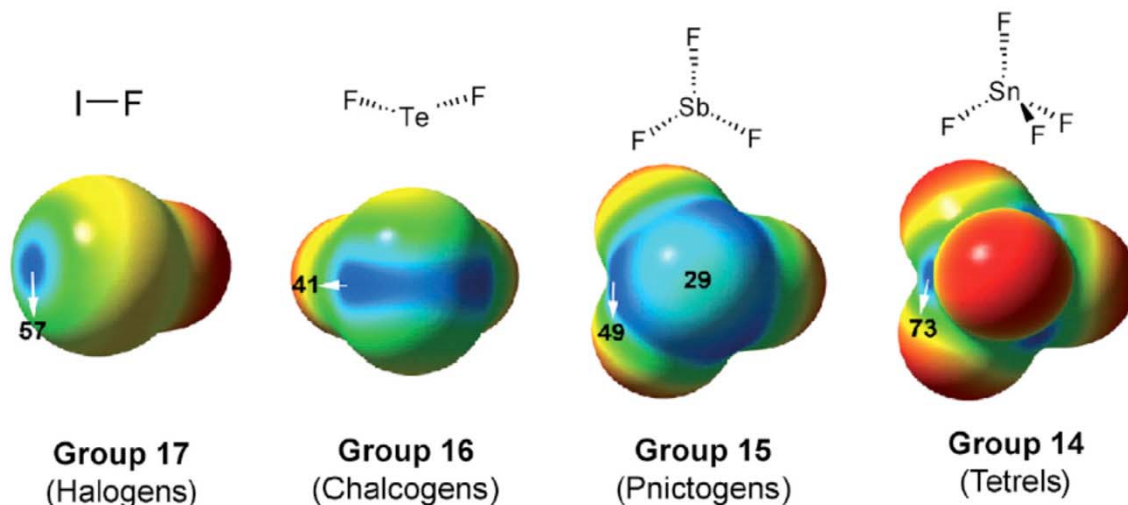
Bond strength 13–100 kJ mol⁻¹

H-bond in (H₂O)₂ 20 kJ mol⁻¹

Directionality increase Cl < Br < I

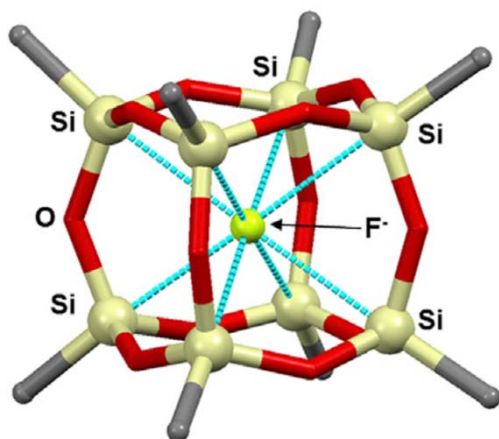


Sigma Hole Interactions

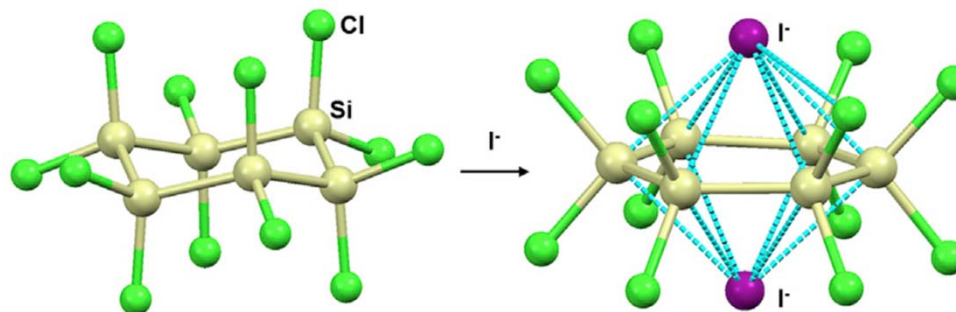


Halogen bonding
 Chalcogen bonding
 Pnictogen bonding
 Tetrel bonding

ESP values of the σ -holes in kJ mol^{-1}



Fluoride encapsulation
 Spherosilicate $\text{Si}_8\text{O}_{12}\text{R}_8$



Si_6X_{12} (X = Cl or Br) planarization
 inverse sandwich complexes

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

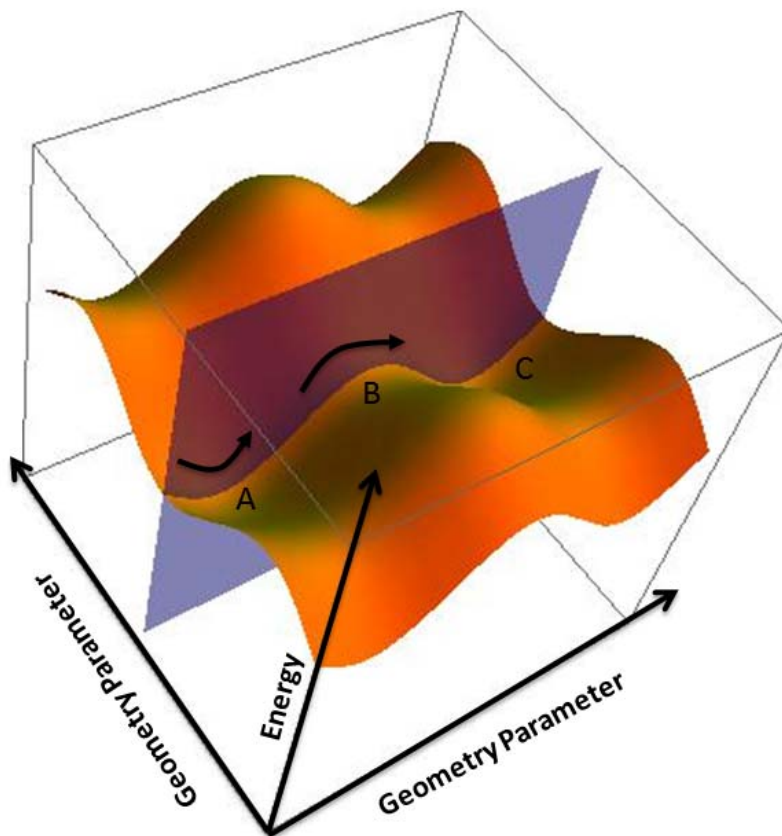
Isomers = molecular conformations corresponding to distinct minima on the PES, separated by an energy barrier high enough to impede immediate interconversion at room temperature, separable, 100–120 kJ mol⁻¹ or more

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

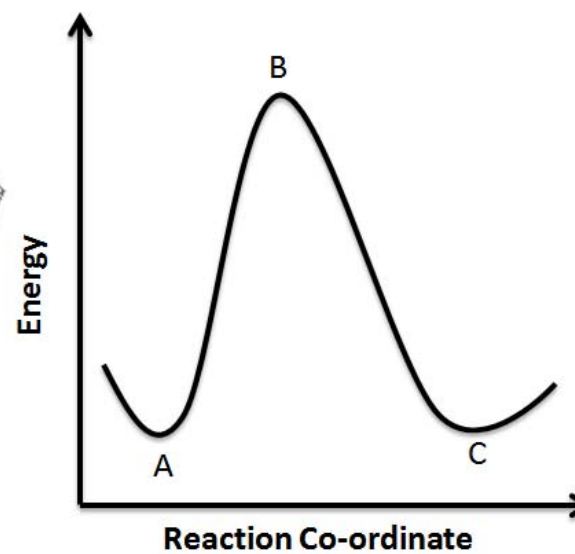


Bond-Stretch Isomers

The potential energy (hyper)surface (PES)



Interconversion
 $A \rightleftharpoons C$

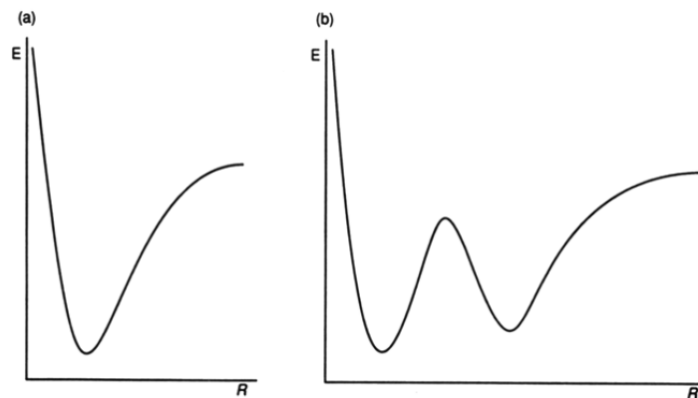


Bond-Stretch Isomers

1972 R. Hoffmann

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 $\text{Re}(\text{cis-Cl}_2)(\text{NCMe})(\text{NO})\text{-trans-}(\text{PMe}_3)_2$

Crystallizes in $P2_1/a$ with 44 molecules in the asymmetric unit

a dense and low-symmetry hydrogen bonding network

the $\text{Re-N}(\text{NO})$ and the $\text{Re-N}(\text{NCMe})$ distances vary by as much as 0.10 or 0.12 Å, respectively



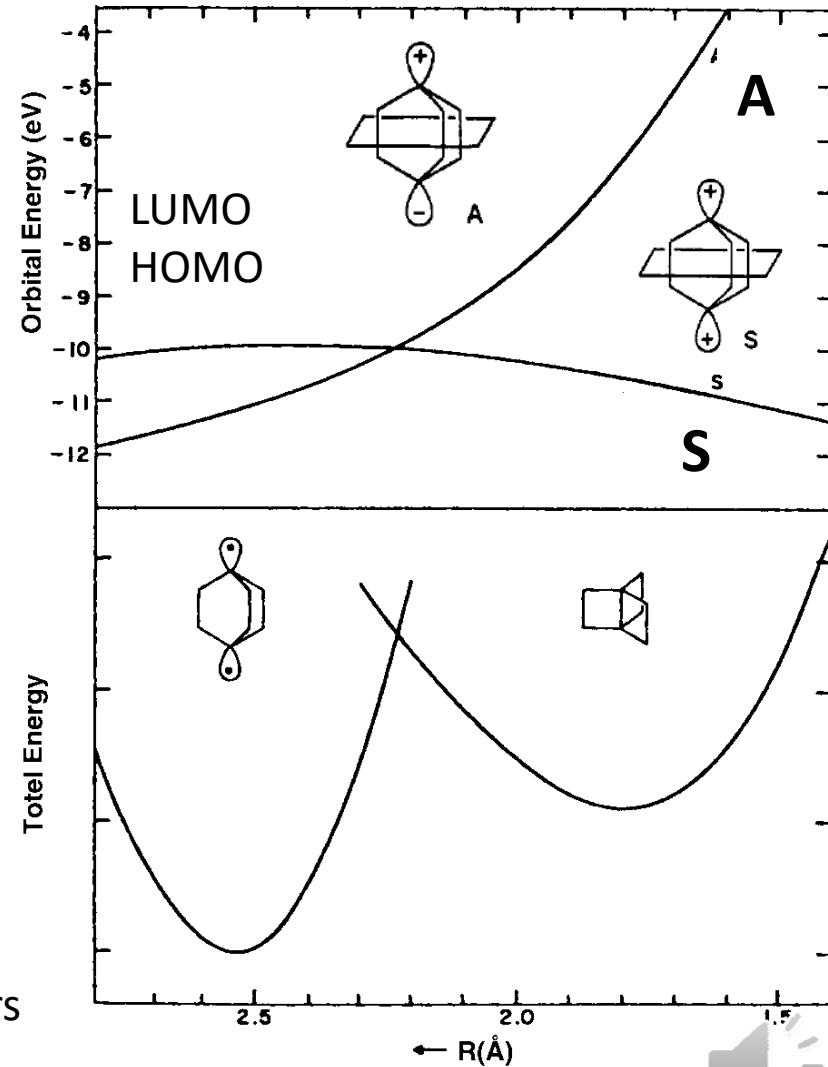
[2.2.2]propellane



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

A orbital = antibonding, antisymmetric

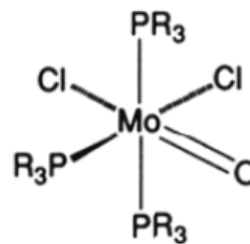
Interaction (through-bond coupling) between **A** and the high-lying σ^* orbitals of the C–C bonds (2–3, 5–6 and 7–8) results in a stabilization of **A**. A crossing between **A** and **S**, **A** becomes the HOMO when the transannular distance is larger than 2.25 Å and gives rise to a diradical form. 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)Cl₂(PMe₂Ph)₃ and Mo(O)Cl₂(PEt₂Ph)₃^a

	blue Mo(O)Cl ₂ (PMe ₂ Ph) ₃	green Mo(O)Cl ₂ (PEt ₂ Ph) 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.

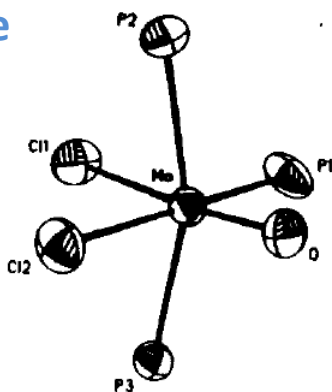
Chatt, J.; Manojlovic-Muir, L.; Muir, K. W. J. Chem. Soc. (D) 1971, 655-656
 Manojlovic-Muir, L.; Muir, K. W. J. Chem. Soc., Dalton Trans. 1972, 686-690



Not Bond-Stretch Isomers

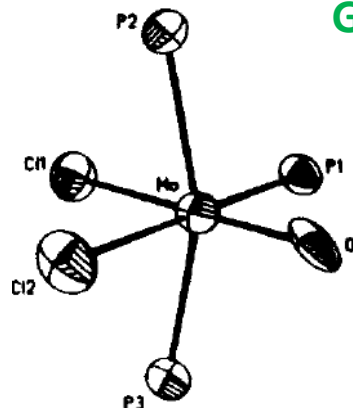
Distortional M=O isomers?

Blue

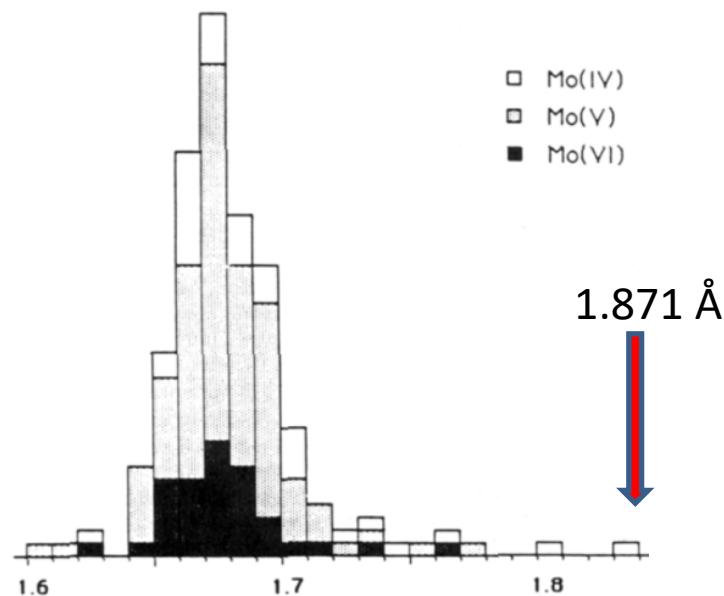


1.675(3) Å

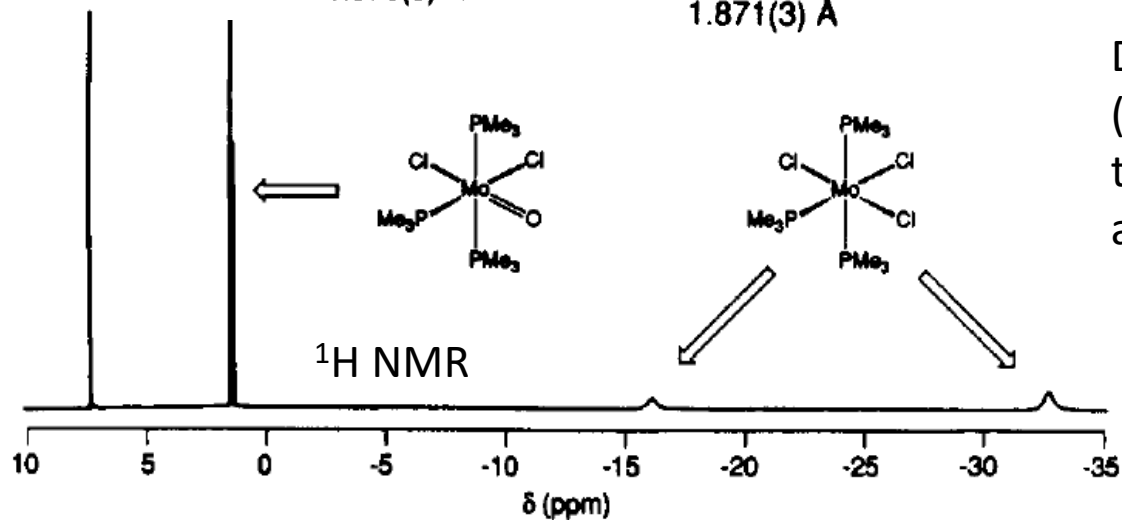
Green



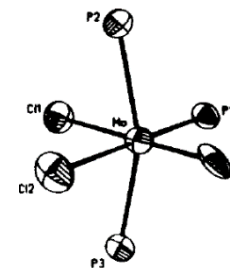
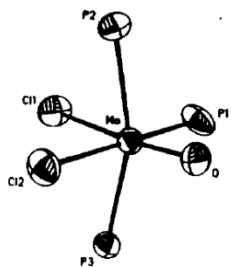
1.871(3) Å



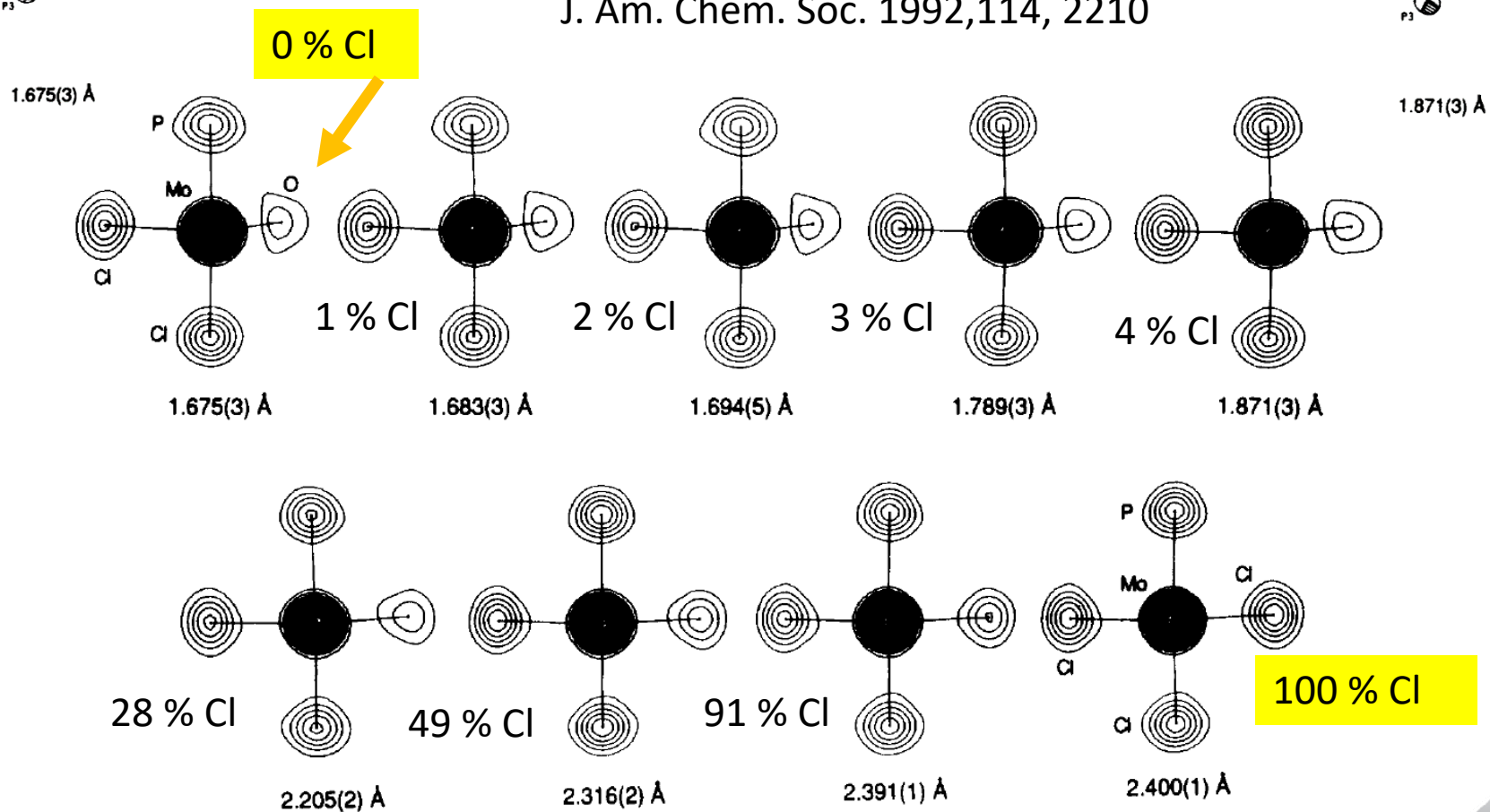
Distribution of Mo=O distances (Å) for monooxo complexes in the oxidation states +4, +5, and +6



Not Bond-Stretch Isomers



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

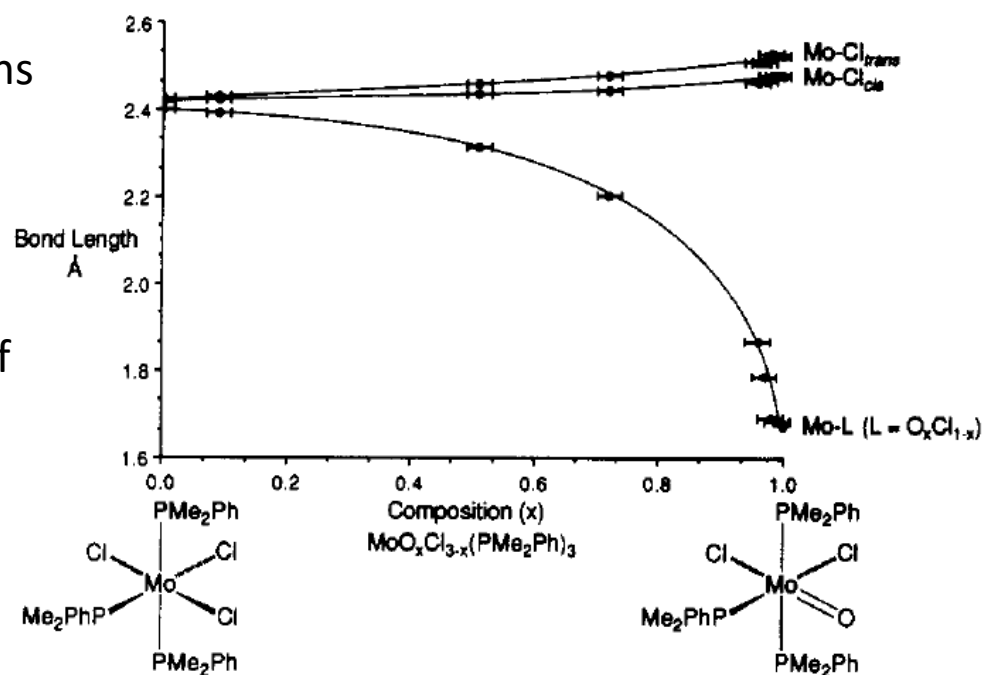


Not Bond-Stretch Isomers

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 Cr₂?

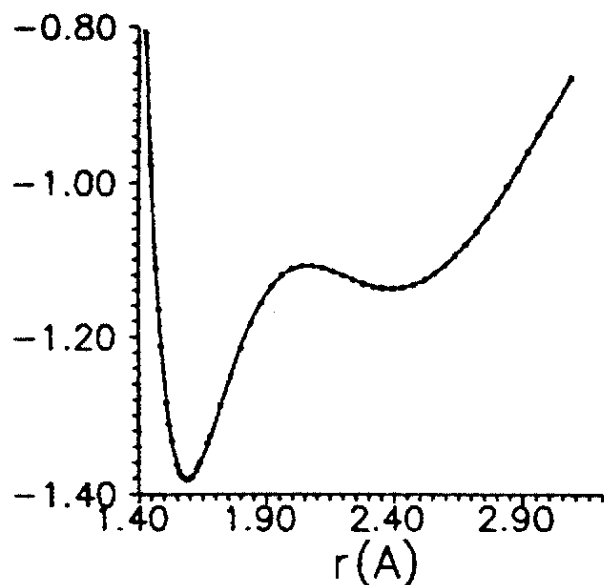
Valence electron configuration:

$(3d\sigma_g)^2(3d\pi_u)^4(3d\delta_g)^4(4s\sigma_g)^2$ **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



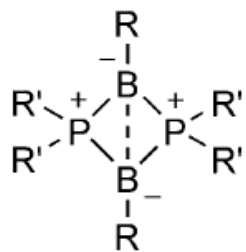
Balance between covalent **bonding (d-d)** at **short** distance and (s-s) bonding and antiferromagnetic coupling of the 3d electrons at long distance

Calculated 2nd minimum of the ground-state energy curve is extremely shallow

Corresponding isomer rather short-lived and difficult to trap and to characterize



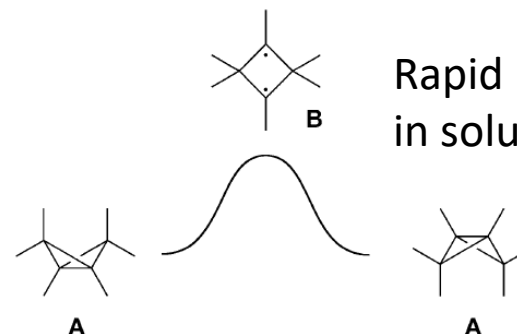
Not Bond-Stretch Isomers



1-5

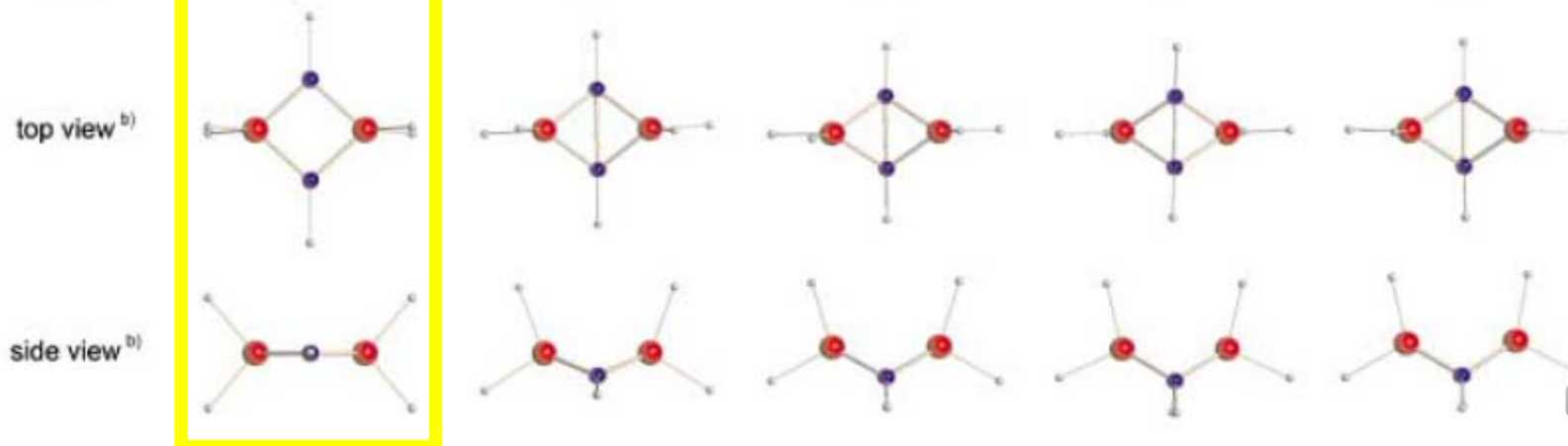
- 1: R=*t*Bu, R'=iPr,
- 2: R=Dur, R'=iPr
- 3: R=*t*Bu, R'=Ph,
- 4: R=Dur, R'=Et,
- 5: R=Ph, R'=Ph,

Not bond-stretch
isomers – different
compounds



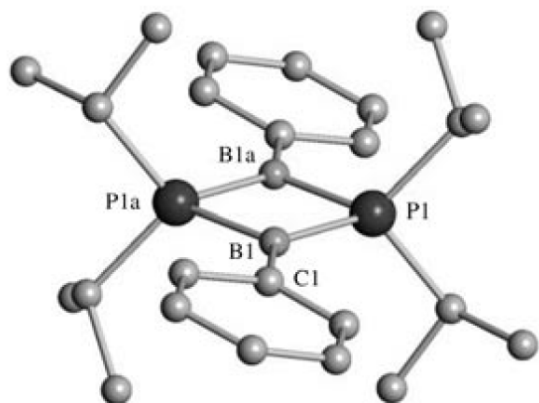
Rapid inversion
in solution at r.t.

compound	1 (iPr ₂ PB <i>t</i> Bu) ₂	2 (iPr ₂ PBDur) ₂	3 (Ph ₂ PB <i>t</i> Bu) ₂	4 (Et ₂ PBDur) ₂	5 (Ph ₂ 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



Bond-Stretch Isomers

Planar P_2B_2 core, B-B = 2.57 Å



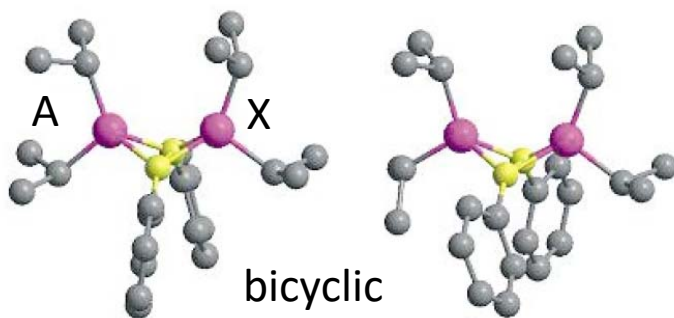
Changing populations
diradical → bicyclic
ratio of 1:7 at r.t.

Bicyclic – Diradical
coalescence

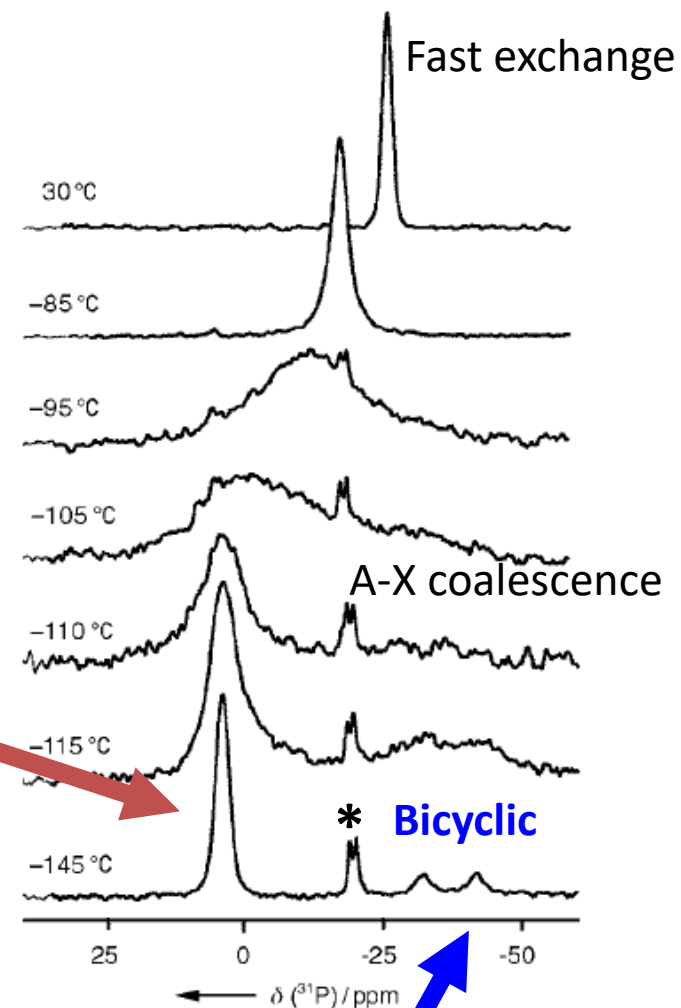
^{31}P solid-state NMR $\delta = 5.9$ ppm (diradical)

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

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



bicyclic



Diradical
 $\delta = 4.0$ ppm

* = impurity

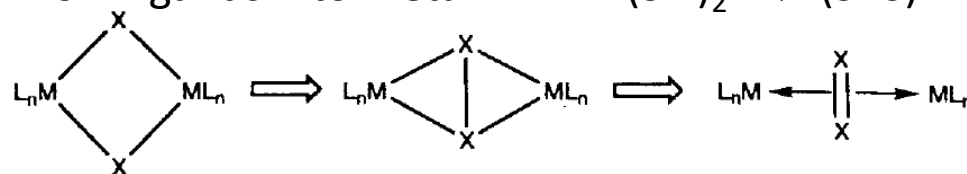
* **Bicyclic**

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

M₂X₂ Rings

Isomers with or without ligand–ligand bonds

Electron transfer from ligands X to metal M: $(S^{2-})_2 \rightarrow (S-S)^{2-} \rightarrow (S=S)^0$



FEC =	8	6	4
Metal configuration	$d^n M^{2+}$	$d^{n+1} M^{1+}$	$d^{n+2} M^0$
Bridge	$(X_2)^{x-}$	$(X_2)^{2-x}$	$(X_2)^{4-x}$

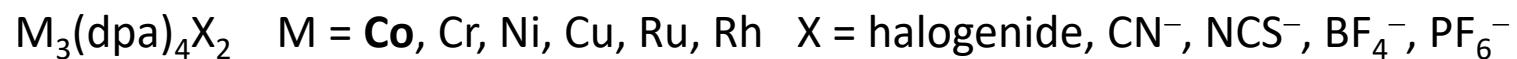
M	X	L ₂	β	Δ_{XX}
Experimental data				
Pd	Te	(PEt ₃) ₂	108	0.07
Pt	S	(PpyPh ₂) ₂	103	0.96
Pt	S	dppe	86	1.10
Pt	Se	(PPh ₃) ₂	100	0.70
Pt	Te	(PEt ₃) ₂	106	0.32
Pt	Te	(PPh ₃) ₂	100	0.32
Pt	Te	dppe	86	0.53

β is the LML bond angle

Δ_{XX} is the difference b/w the X–X distance and the atomic radii sum

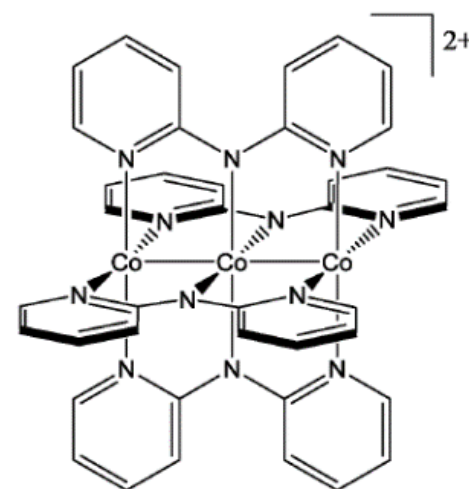
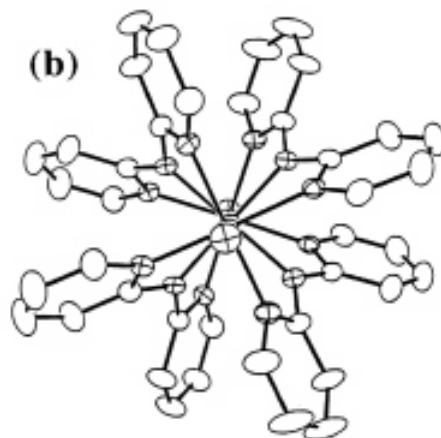
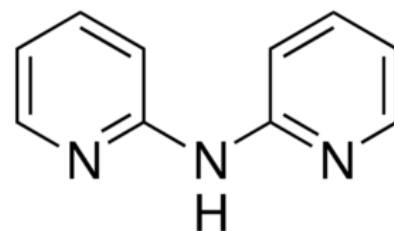
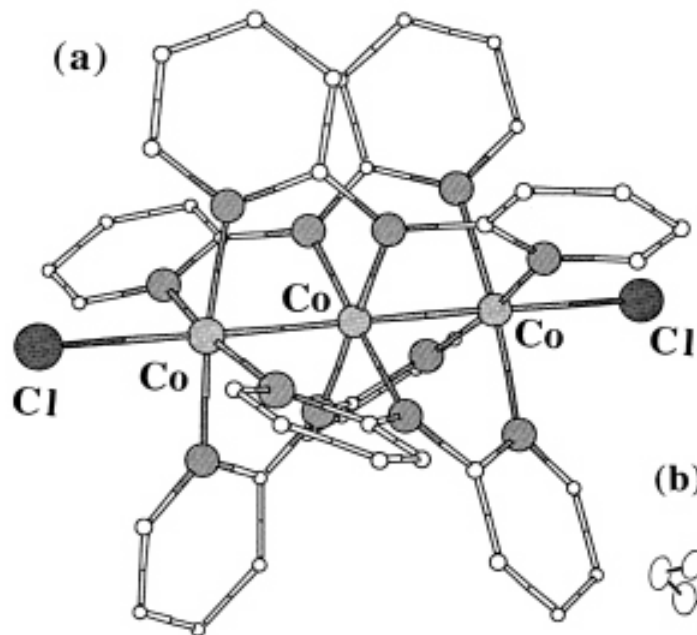


Linear Metal M-M-M Frameworks



Oxidation state of M?

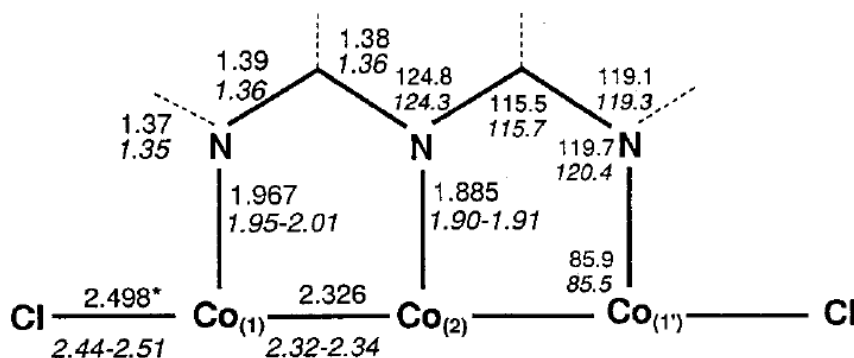
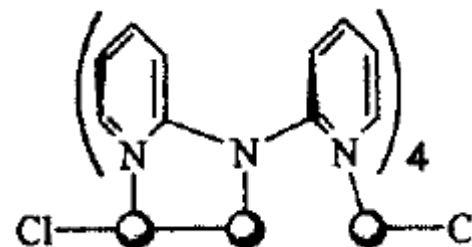
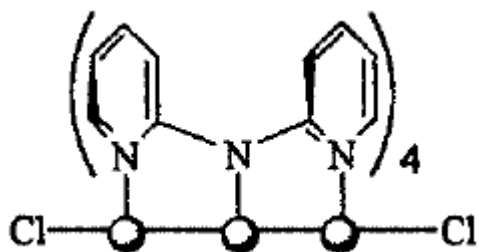
dpa = dipyridylamine



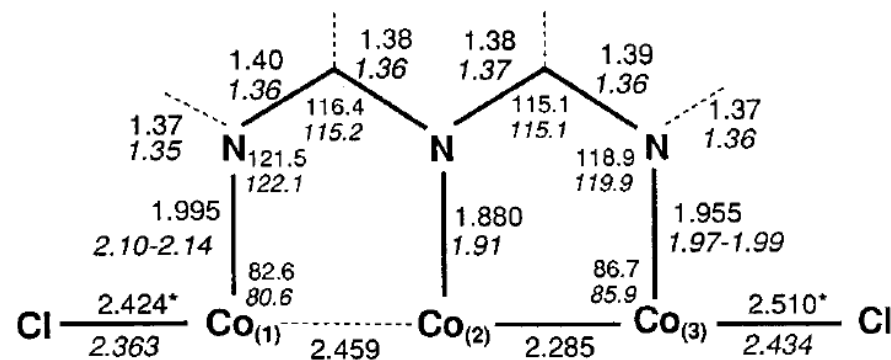
Linear Metal M-M-M Frameworks

$\text{Co}_3(\text{dpa})_4\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$
 symmetrical (*s*) Co₃ chain

$\text{Co}_3(\text{dpa})_4\text{Cl}_2 \cdot 2\text{CH}_2\text{Cl}_2$
 unsymmetrical (*u*) Co₃ chain



Unchanged on cooling



More symmetrical at low temperature

Both the *s* and the *u* isomers are in an $S = 1/2$ ground state at low temperature

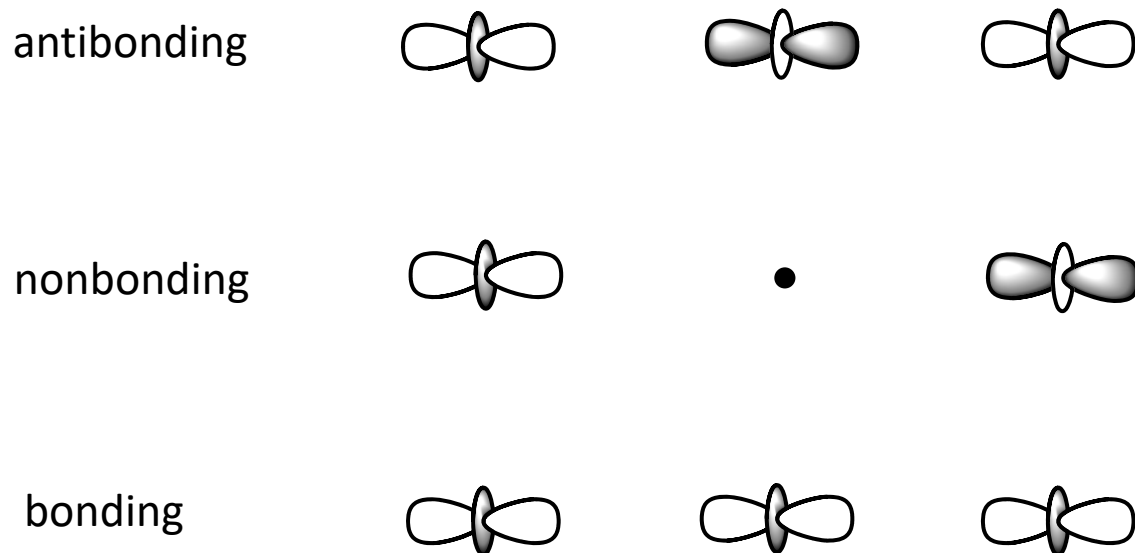


Linear Metal M-M-M Frameworks

Linear triatomic system: M-M-M (z is collinear with the framework axis)

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

Four orbital sets for M-M-M bonding:

One σ set - d_{z^2} orbital combinations
bonding - nonbonding - antibonding

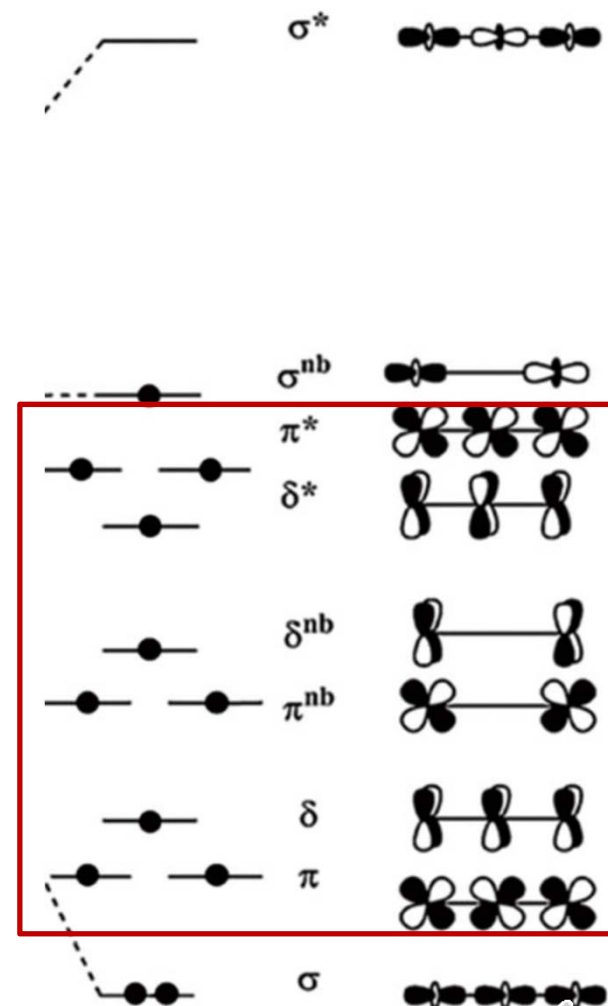
Two degenerate π sets - combinations of d_{xz} and d_{yz} orbitals

One δ set - combinations of d_{xy} orbitals

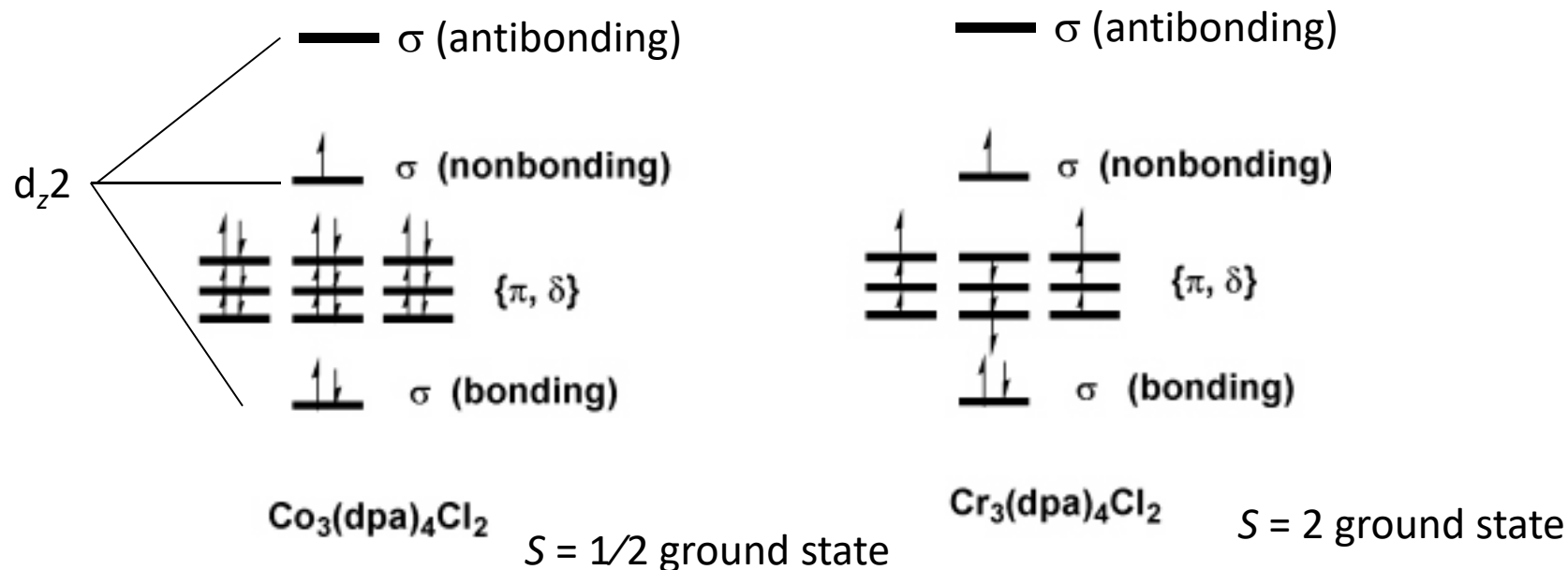
One δ set ($d_{x^2-y^2}$) accepts the lone pairs of the equatorial dpa ligands

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

The **nine metal MOs** belonging to the two π sets and to the remaining δ set are not split in energy
Degenerate set $\{2\pi, \delta\}$



Linear Metal M-M-M Frameworks



Three-electron, three-center system

18 electrons in the $\{2\pi, \delta\}$ 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** (2 bonding + 1 nonbonding), which are *delocalized* over the metal framework

Three-electron, three-center system

12 electrons, in the $\{2\pi, \delta\}$ singly occupied
10 unpaired electrons = 9 + 1

The **one electron** in the σ **nonbonding** orbital is shared between the **terminal** Cr
Unpaired electrons are *spin-coupled* =
→ antiferromagnetic interaction



Linear Metal M-M-M Frameworks

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

S = 5 state is destabilized by 30.8 kcal mol⁻¹



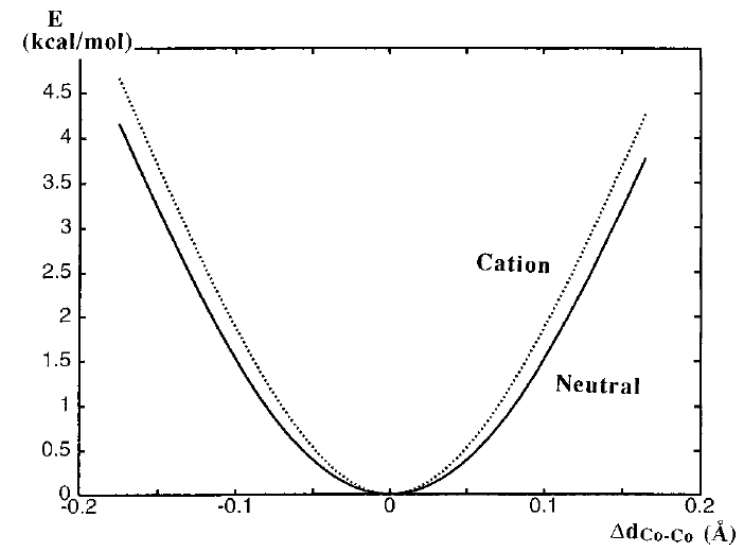
Bond-Stretch Isomers?

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



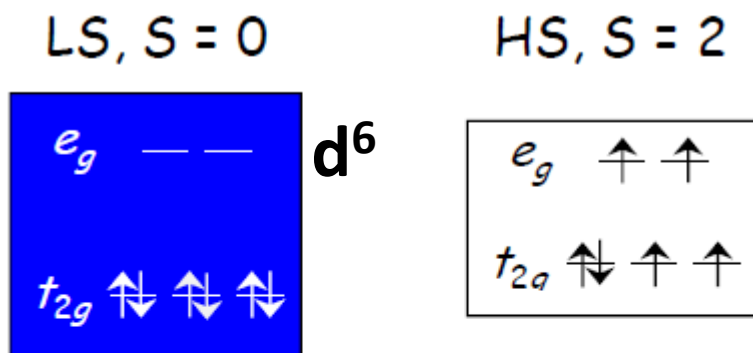
Cr-Cr-Cr

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

3d⁴ – 3d⁷ cations in O_h complexes
Only 3d metals



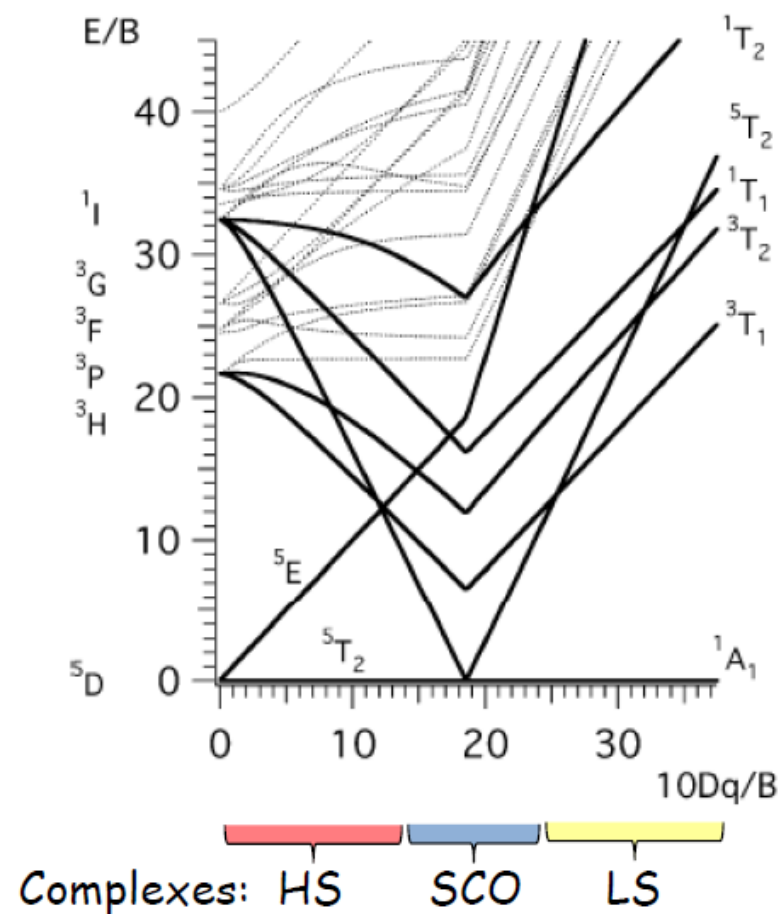
$$10Dq > \Pi$$

$$10Dq < \Pi$$

10Dq – ligand-field splitting

Π – electron pairing energy

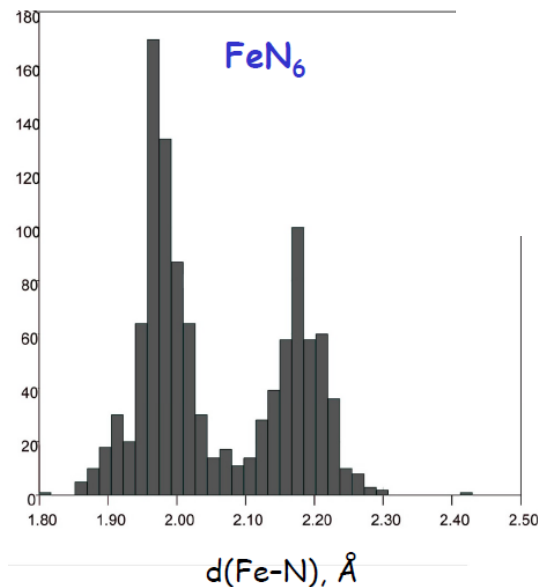
$$10Dq(\text{LS}) \neq 10Dq(\text{HS})$$



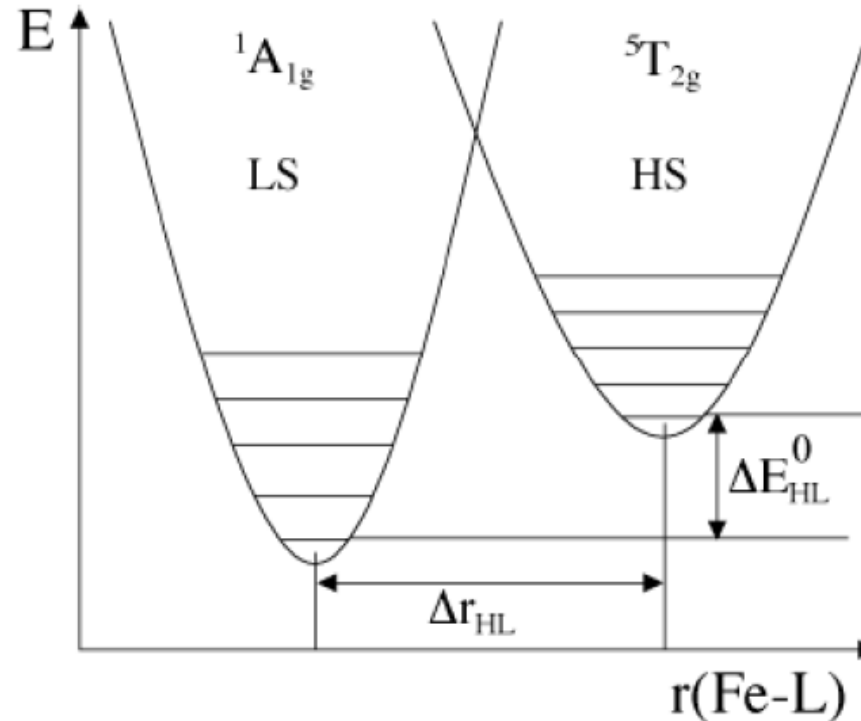
Spin Crossover (SCO)

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

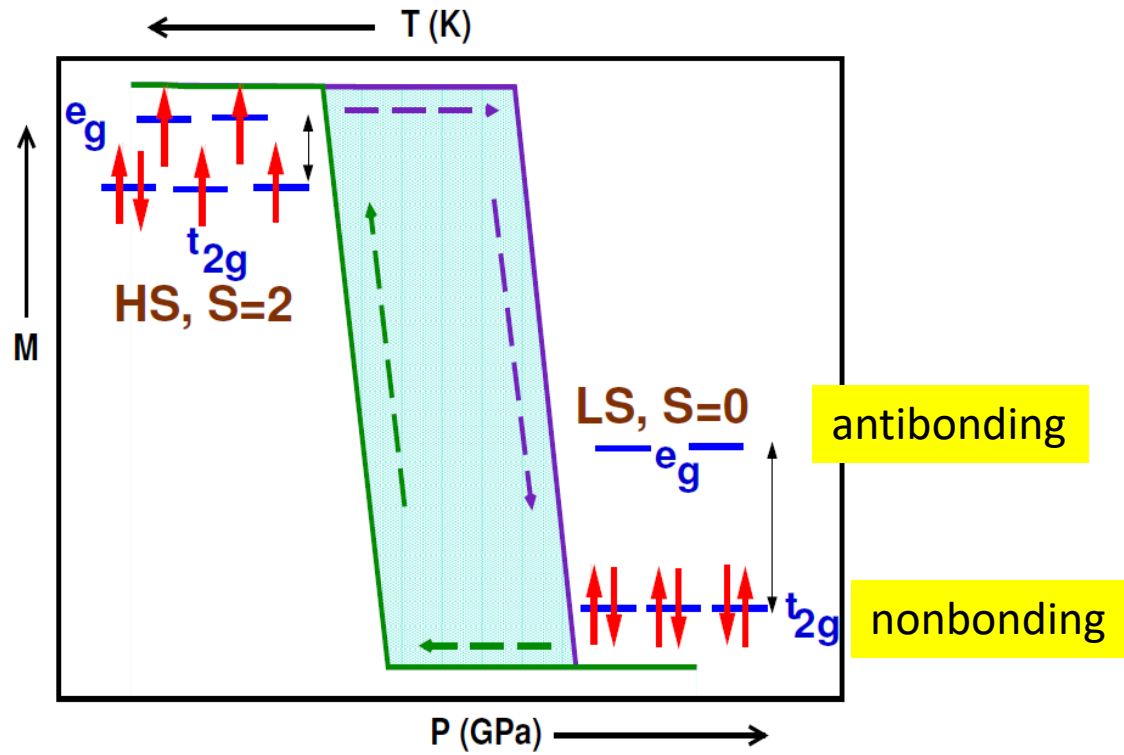


$r(\text{Fe-N})$: 1.95-2.00 \AA 2.15-2.20 \AA

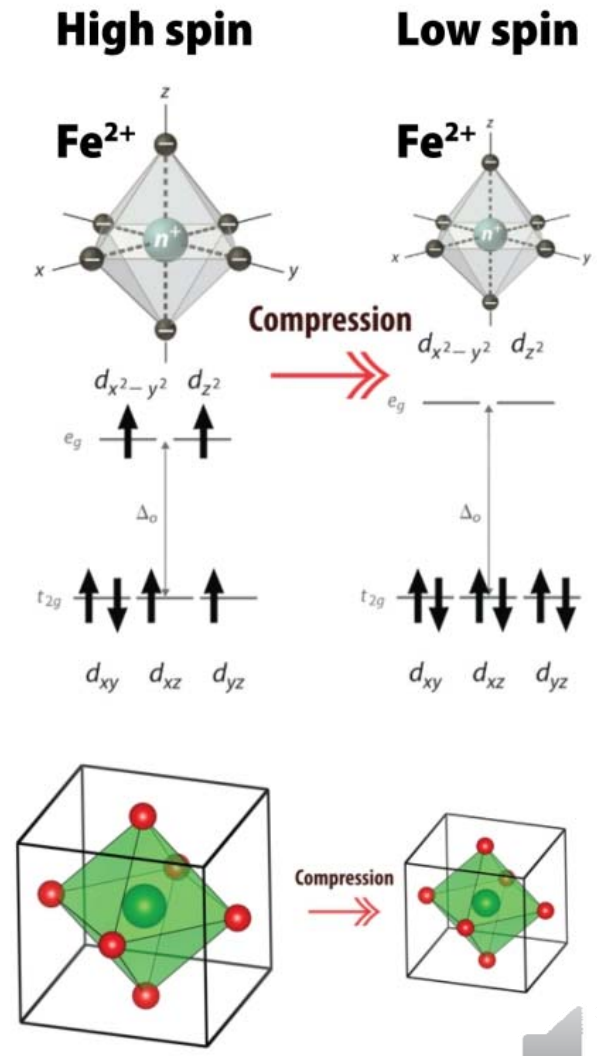
The Fe-N bond lengths and orbital overlap change upon SCO, and therefore $10Dq$ is different for the LS and HS states of the same complex



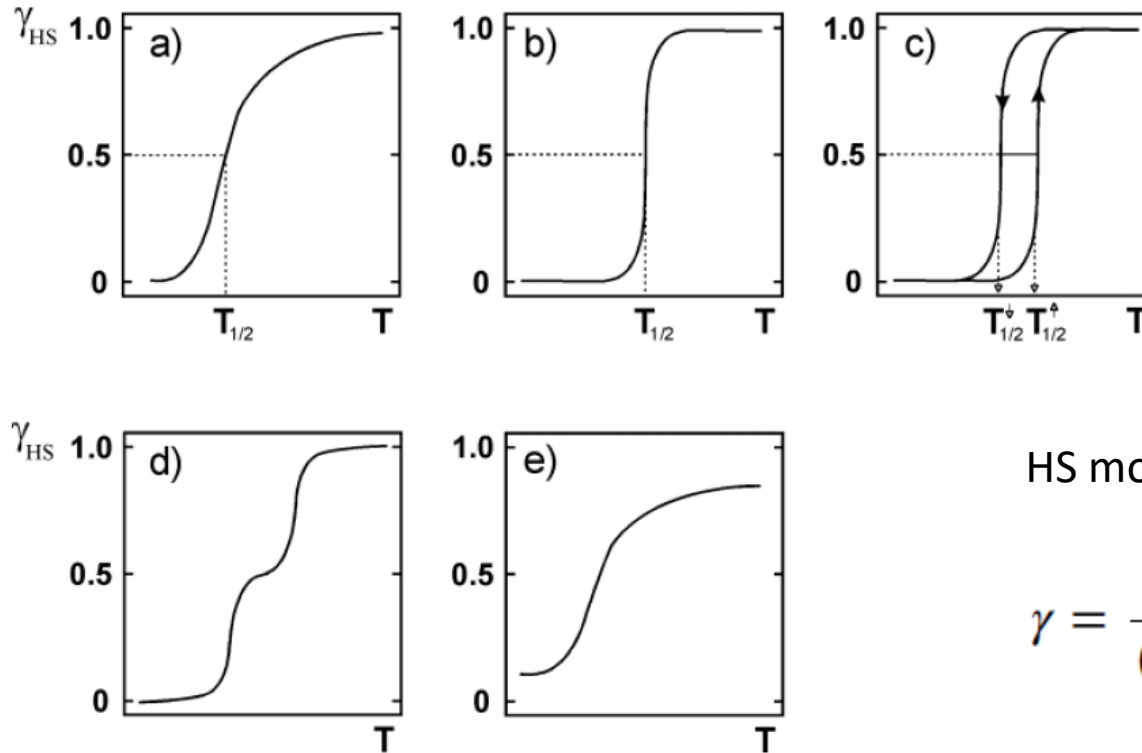
Spin Crossover (SCO)



Increasing pressure = bond shortening = better orbital overlap = increasing splitting bonding / antibonding levels



Spin Crossover (SCO)



HS molar fraction γ

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

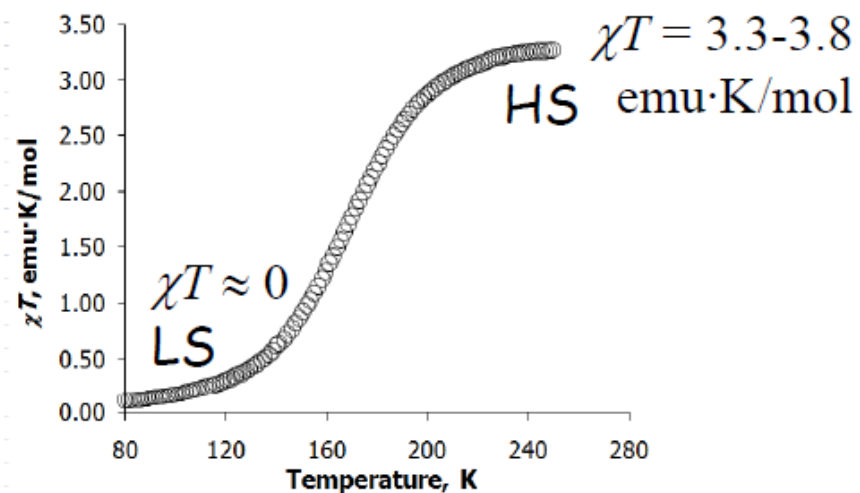
Types of SCO curves - γ_{HS} vs T

a = gradual; b = abrupt; c = abrupt with hysteresis; d = two-step; e = incomplete



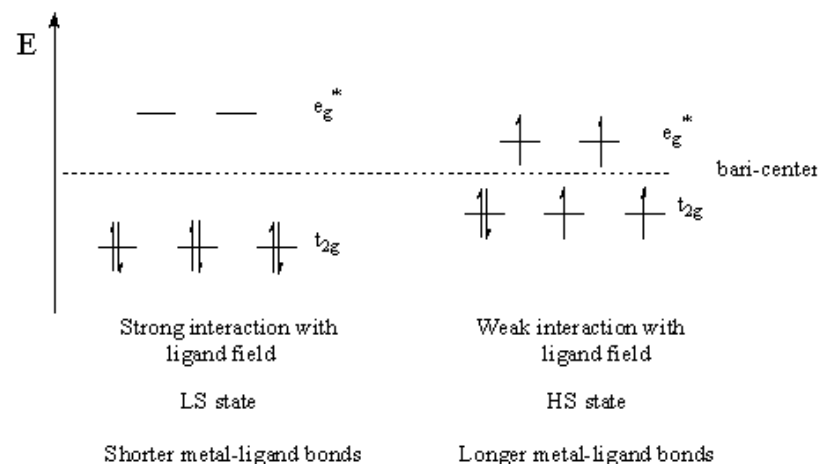
Spin State Isomers

Magnetometry



HS molar fraction γ

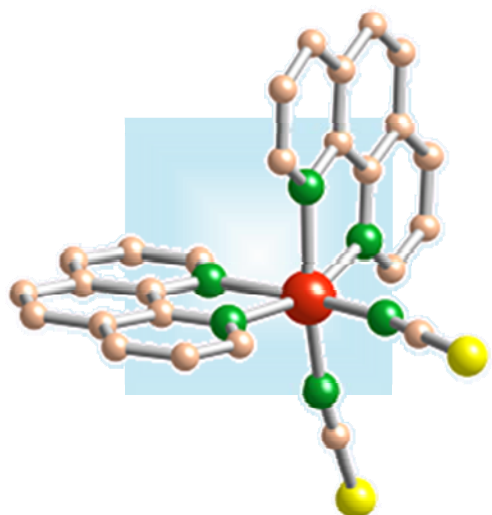
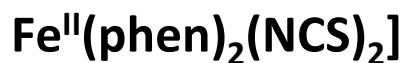
$$\gamma = \frac{\chi T - (\chi T)_{\text{LS}}}{(\chi T)_{\text{HS}} - (\chi T)_{\text{LS}}}$$



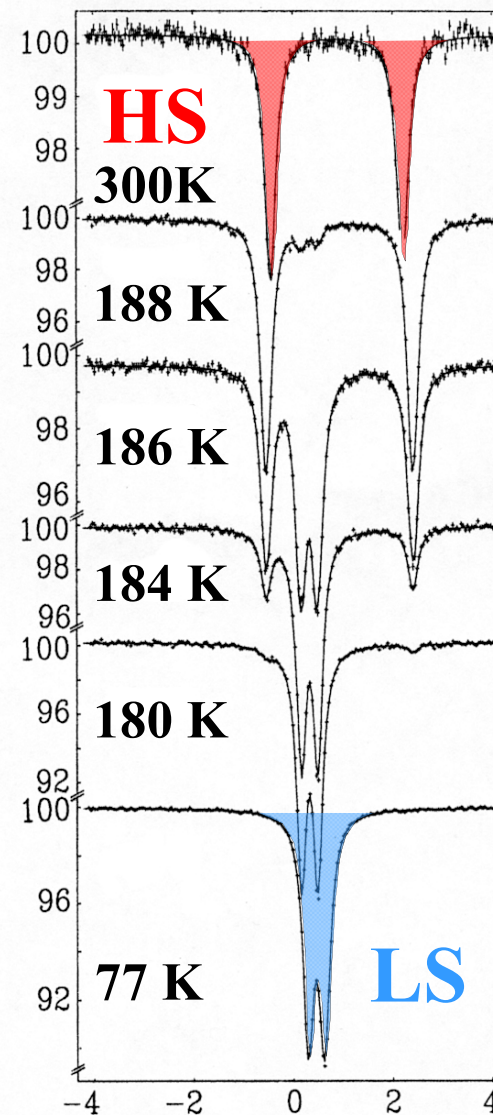
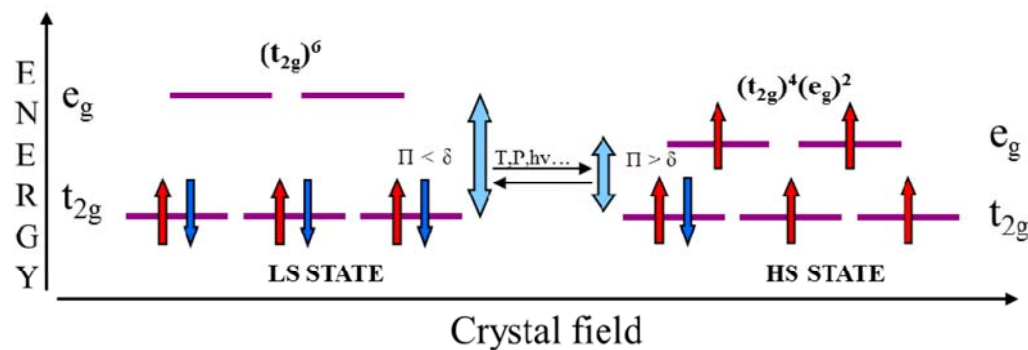
$$\chi_M T(50\% \text{HS}) = \frac{\chi_M T(\text{HS}) + \chi_M T(\text{LS})}{2}$$

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

Spin State Isomers



Moessbauer spectra



Relativistic Effects

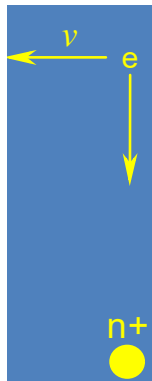
Einstein's special theory of relativity (1905)

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

space-time; a single continuum (one entity)

Bohr atomic model (1913)

$$v_{electron} = \left(\frac{2\pi e^2}{nh} \right) Z \quad a_0 = \frac{\epsilon_0 h^2}{mZe^2 \pi}$$



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

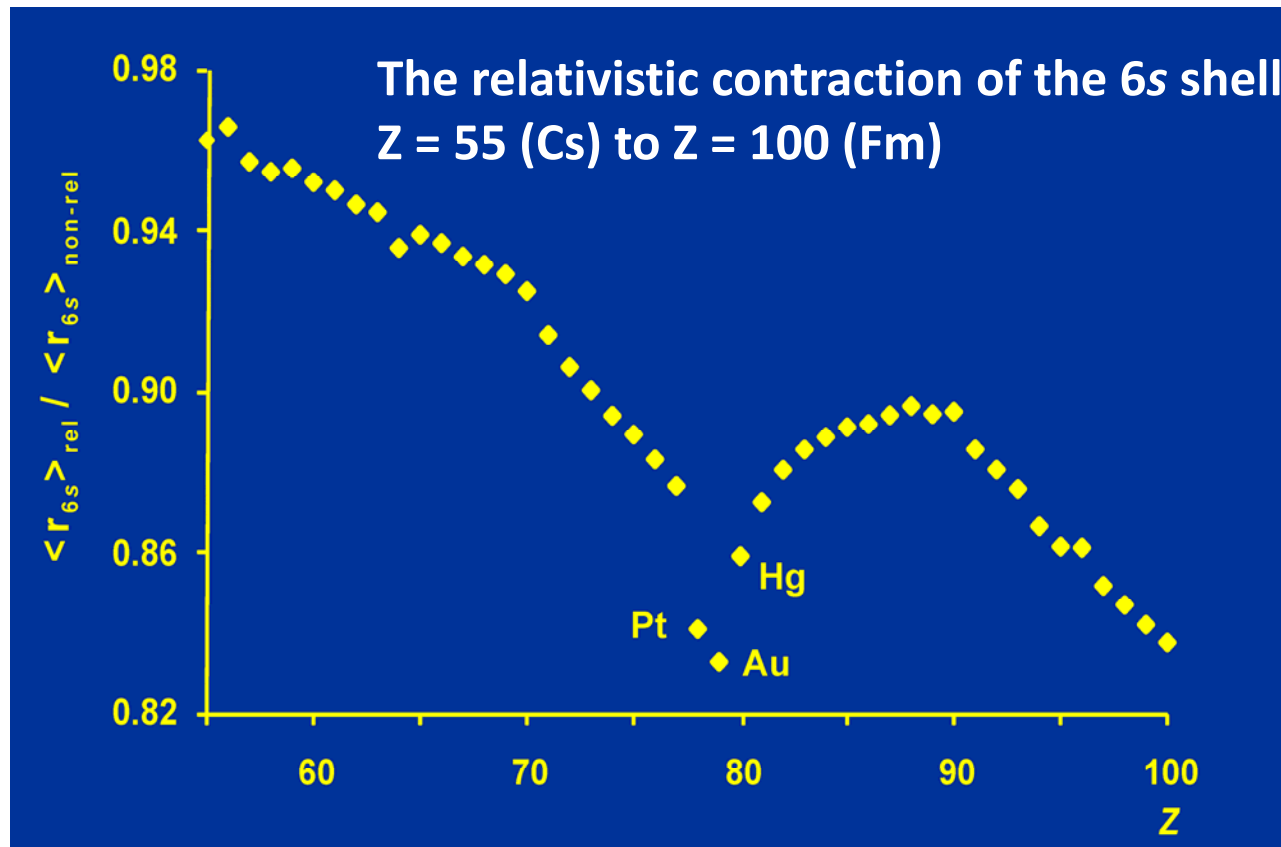
	1s electron velocity m/s	relativistic mass	relativistic radius contraction
H (Z = 1)	$v = 2.18 \cdot 10^6$ $v = 0.00727 \cdot c$	$m = 1.0000265 m_0$	~ 0 %
Au (Z = 79)	$v = 1.73 \cdot 10^8$ $v = 0.577 \cdot c$	$m = 1.23 m_0$	~ 20 %
Fm (Z = 100)	$v = 2.18 \cdot 10^8$ $v = 0.727 \cdot c$	$m = 1.46 m_0$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



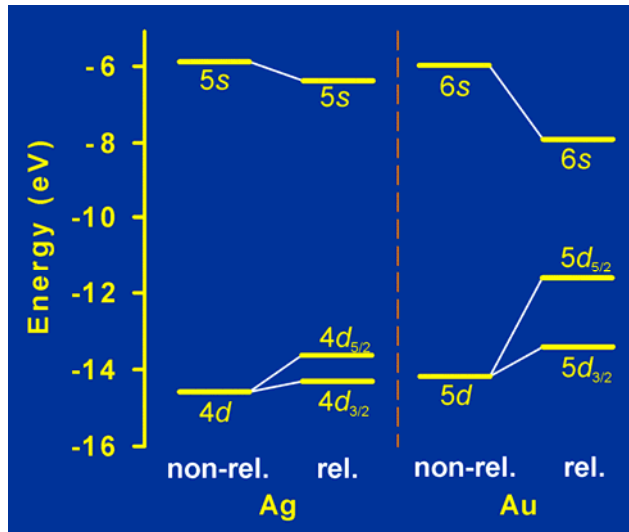
Relativistic Effects

Direct effects: stabilization (decrease) of s - and p -orbitals

Indirect effects: destabilization (expanding) of d - in f -orbitals due to the increased shielding by s - and p -orbitals



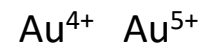
Relativistic Effects



[Kr] 4d¹⁰ 5s¹

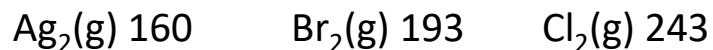
[Xe] 5d¹⁰ 6s¹

- 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)

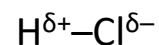
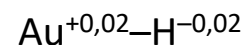
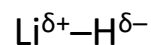


- **Au** - the highest electron affinity of all metals: simple reduction to auride anion Au⁻ (Cs⁺Au⁻ is known since 1931, it has CsCl structure) – **pseudohalogen**

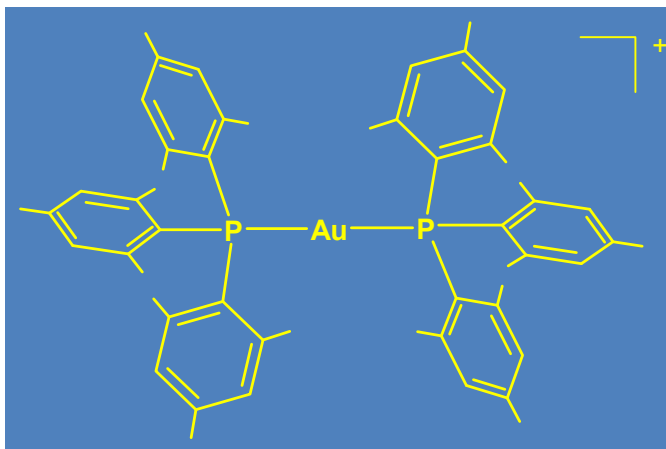
- Au₂(g) dissociation energy: 221 kJ/mol



- Gold is the most electronegative of all metals



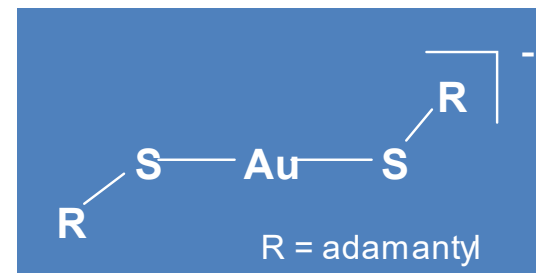
Relativistic Atomic Radius and Bond-Length Contractions



Expected order: $\text{Cu} < \text{Ag} < \text{Au}$

Actual order: $\text{Cu} < \text{Au} < \text{Ag}$

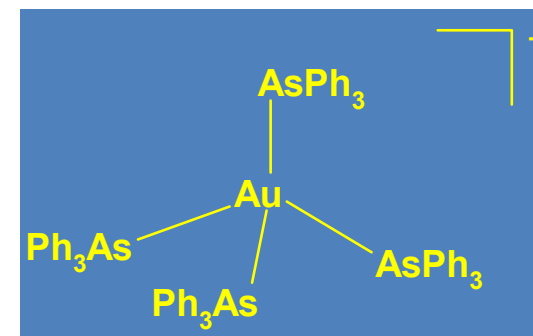
$d(\text{Ag-P})$ $d(\text{Au-P})$
2.44 Å 2.35 Å



$d(\text{Ag-S})$ $d(\text{Au-S})$
2.35 Å 2.30 Å

Distance, Å	Ag	Au
In solid state $d(\text{M-M})$	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

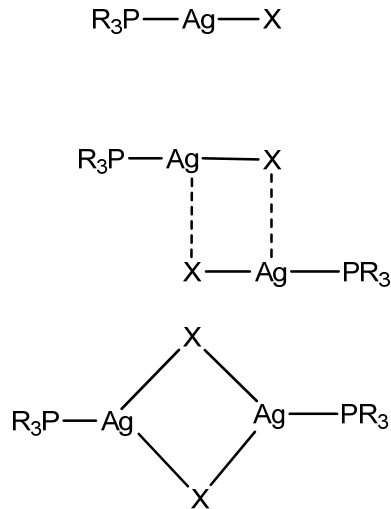
$d(\text{Ag-H})$ $d(\text{Au-H})$
1.62 Å 1.52 Å



$d(\text{Ag-As})$ $d(\text{Au-As})$
2.66 Å 2.59 Å



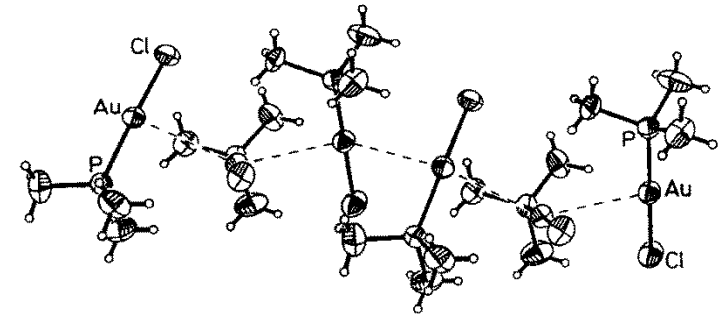
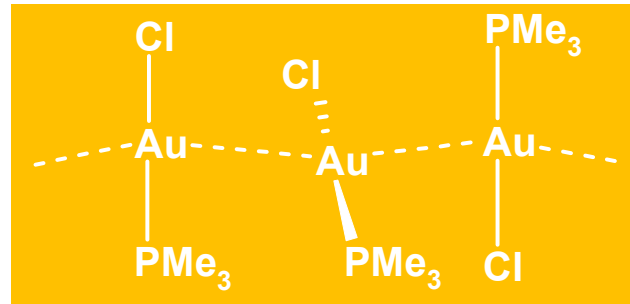
Aurophilicity



L-Au⁺ isolobal to H⁺, R⁺

metallophilicity or metallophilic interactions

d¹⁰-d¹⁰ Au⁺, Ag⁺, Cu⁺, Hg²⁺, Pt⁰, Pd⁰, Tl³⁺, also Ir



Attractive interactions Au^{1+...Au}1+:

d(Au-Au)
3.27 Å

Aurophilicity or aurophilic interaction

Two-coordinate Au 5d¹⁰ closed-shell interactions

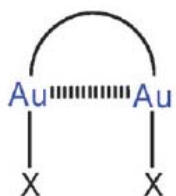
Energy comparable to hydrogen-bonding (5–10 kcal/mol)

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

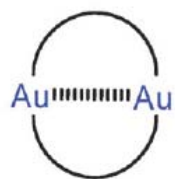
Correlation effects + relativistic effects ~20 %



Aurophilic Interactions



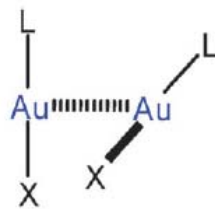
semi-supported



fully-supported

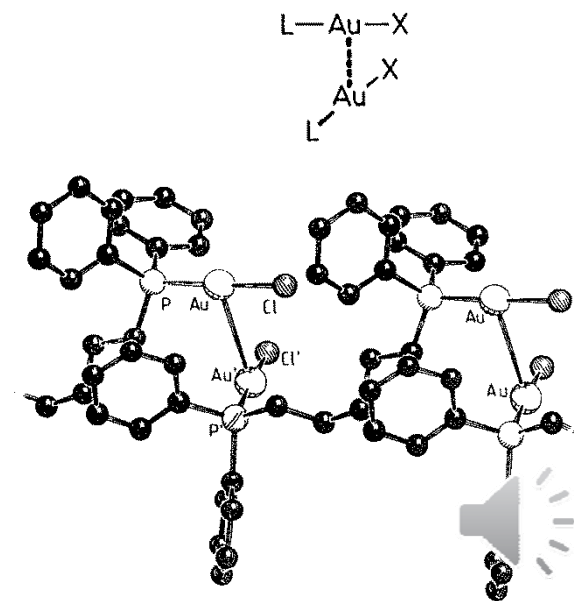
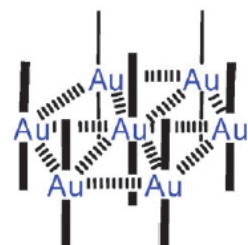
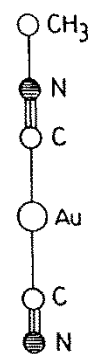
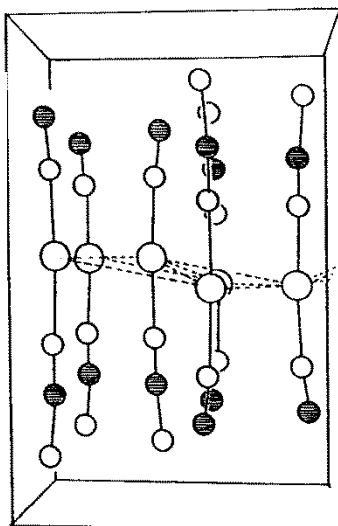
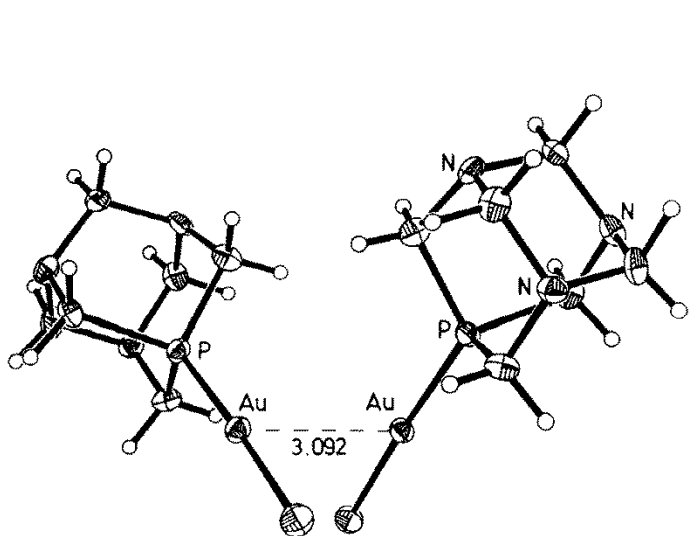
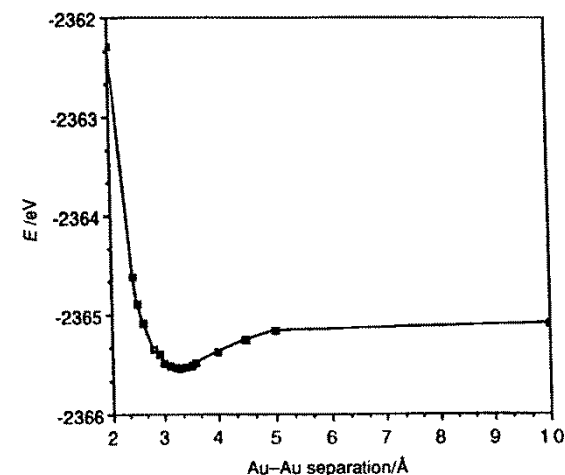


intramolecular



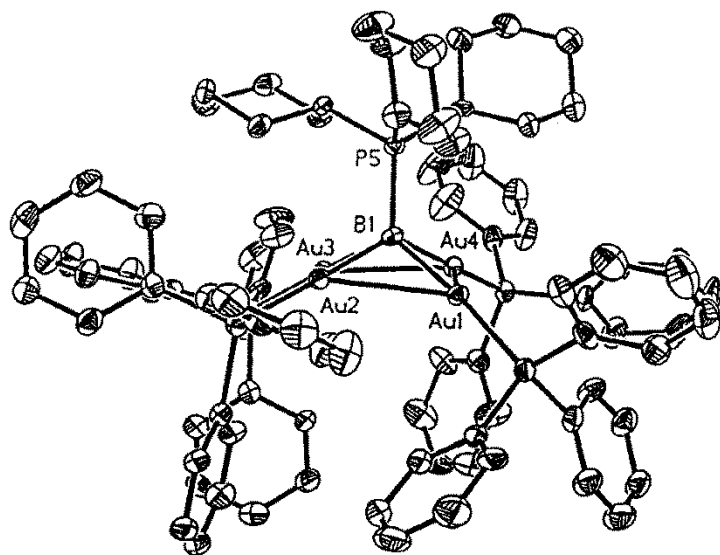
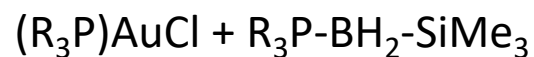
unsupported

intermolecular



Auration Reactions

L-Au⁺ isolobal to H⁺, R⁺



(a) *Homoleptic substitution*

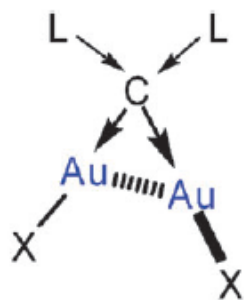
$C(AuL)_4$	—	—	—
$[C(AuL)_5]^+$	$[N(AuL)_4]^+$	$[O(AuL)_3]^+$	—
$[C(AuL)_6]^{2+}$	$[N(AuL)_5]^{2+}$	$[O(AuL)_4]^{2+}$	—
—	—	—	—
—	—	$S(AuL)_2$	—
—	$[P(AuL)_4]^+$	$[S(AuL)_3]^+$	$[Cl(AuL)_2]^+$
—	$[P(AuL)_5]^{2+}$	$[S(AuL)_4]^{2+}$	—
—	$[P(AuL)_6]^{3+}$	$[S(AuL)_5]^{3+}$	—
—	—	$[S(AuL)_6]^{4+}$	—
—	—	—	—
—	$[As(AuL)_4]^+$	$[Se(AuL)_3]^+$	$[Br(AuL)_2]^+$
—	—	$[Te(AuL)_3]^+$	—

(b) *Heteroleptic substitution*

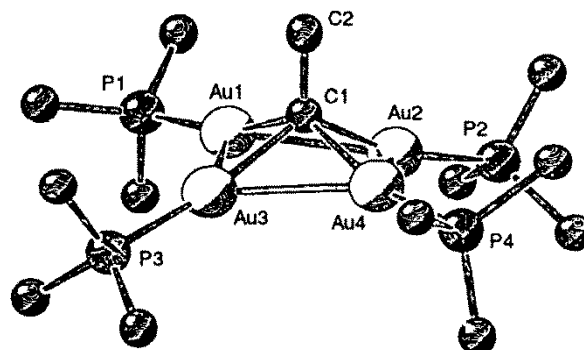
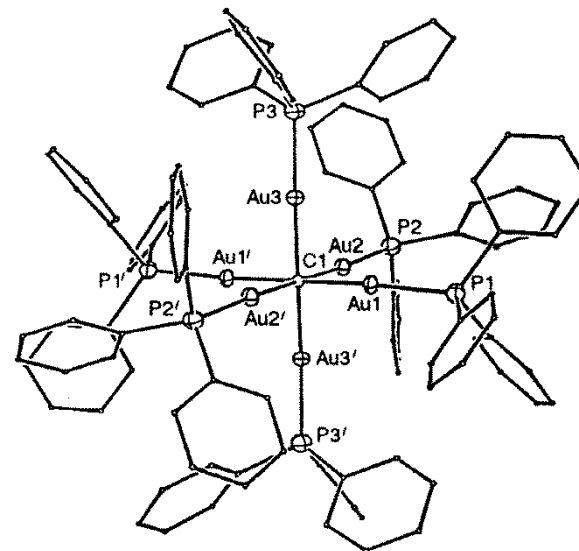
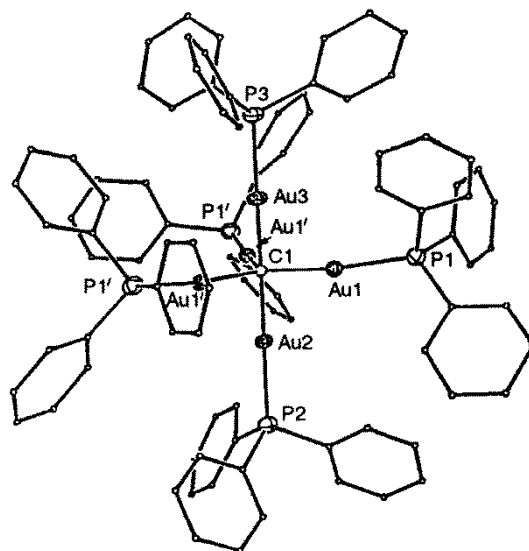
$RC(AuL)_3$	—	—	—
—	$[R_2N(AuL)_2]^+$	—	—
—	$[RN(AuL)_3]^+$	—	—
$[R_2C(AuL)_3]^+$	$[RN(AuL)_4]^{2+}$	—	—
—	$[RP(AuL)_3]^+$	$[RS(AuL)_2]^+$	—
—	$[RP(AuL)_4]^{2+}$	$[RS(AuL)_3]^+$	—
—	$[R_2P(AuL)_3]^{2+}$	—	—
$[(L)B(AuL)_4]^+$	—	$[RSe(AuL)_2]^+$	—



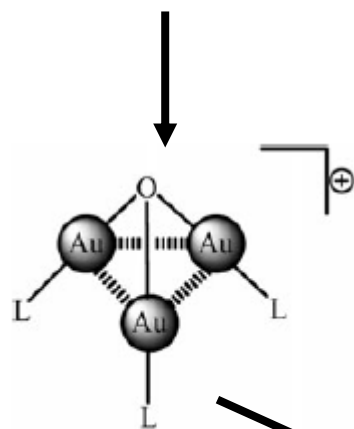
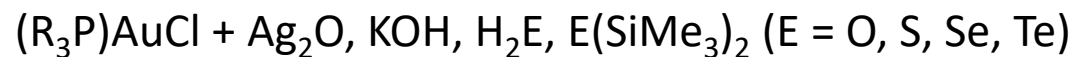
Auration Reactions



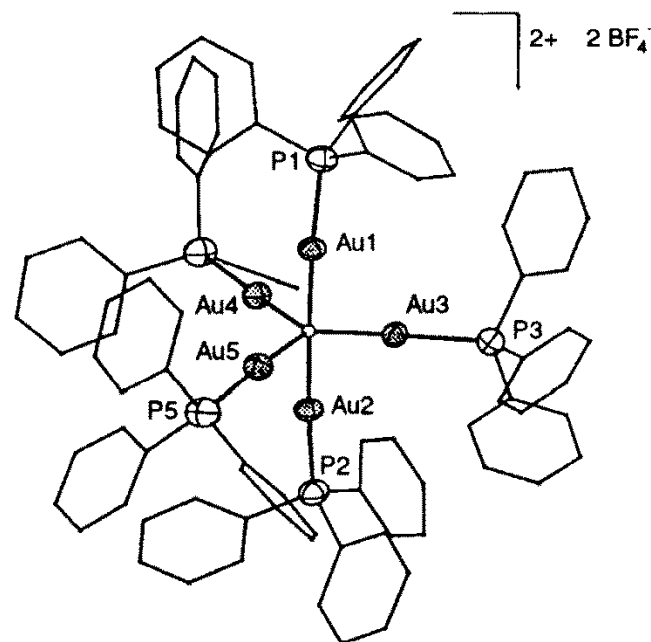
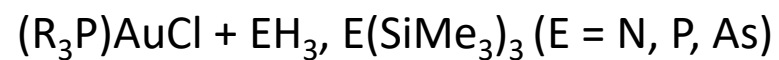
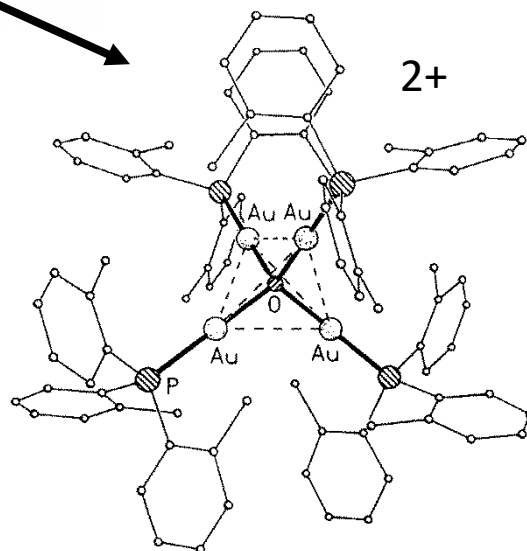
- 1 L = PR₃ , X = Cl
- 2 L = carbene, X = Cl
- 3 L = CN , X = Cl
- 4 L = PPh₂S , X = PPh₃



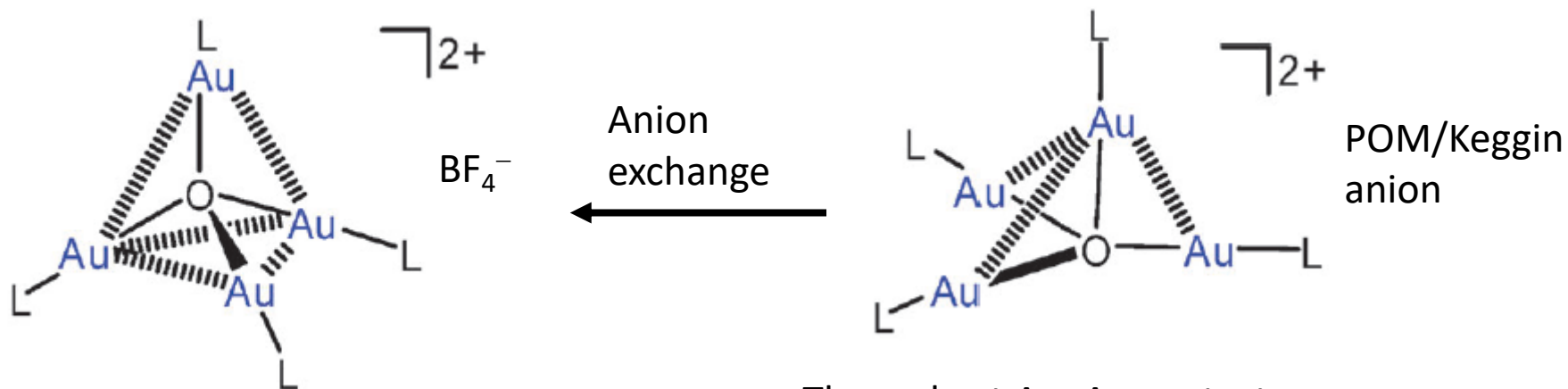
Auration Reactions



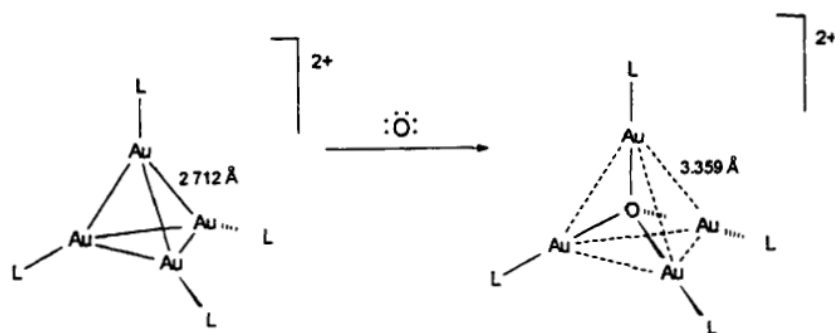
Strong aurating agent



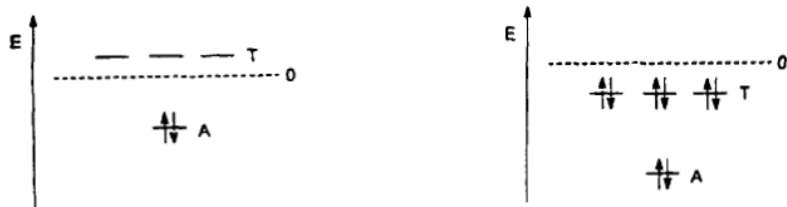
Auration Reactions



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



Solid-state ³¹P NMR
 two different types of phosphines
 (1 axial, 3 equatorial)
 Solution (in DMSO-d₆)
 equivalence of all four ligands
 $\delta^{31}\text{P} = 25 \text{ ppm}$



Bond Energies of Auophilic Interactions

Compound/model	Au–Au contact mode	Method	Bond energy/kcal mol ⁻¹
(CO)AuCl	Unsupported intermolecular	MP2	10.0
(Et ₃ P)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 ₃ PAu) ₂ C≡CB ₁₁ H ₁₁]	Unsupported inter-cationic	NMR	8.8
(dppe)Au ₂ [S ₂ C ₂ (CN) ₂]	Fully supported intramolecular	UV/vis	15.0
[(Xantphos) ₂ Au ₂] ²⁺	Fully supported intramolecular	NMR	11.6

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



Isolobal Analogs



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



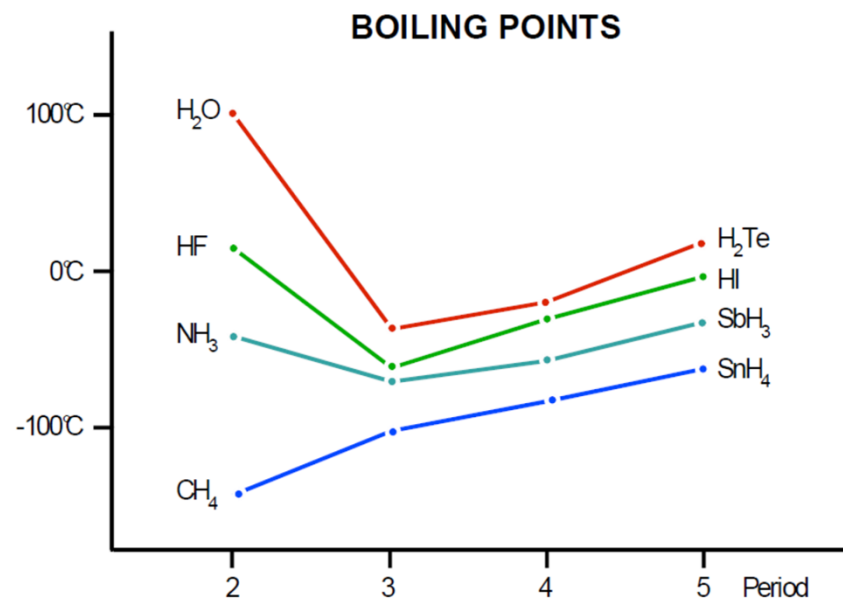
D–H bond elongates = weakened
D–H bond dipole increases
Dipole-dipole electrostatic energy increases
Attractive interaction increases

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

D–H bond weakened = elongated

D–H vibration decreases = RED SHIFT ($10 - 100 \text{ cm}^{-1}$)

D–H dipole increases = intensity in IR increases



Improper (Blue-Shifting) H-bond

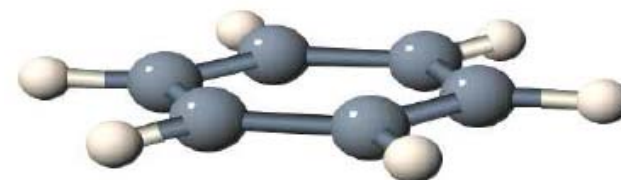
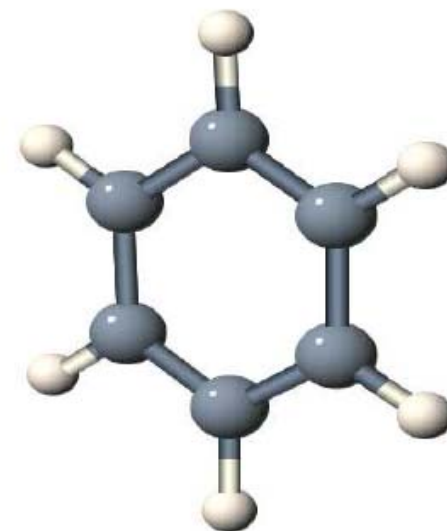
P. Hobza et al.: JPC A 102, 2501 (1998)
benzene...H-X (X = CH₃, CCl₃, C₆H₅)
P. Hobza, Z. Havlas: Chem. Rev. 100, 4253 (2000)

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

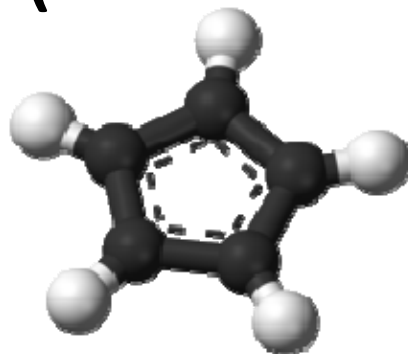
C–H strenghtening, shortening = **BLUE SHIFT**
Rehybridization of C

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



[Cp₂Co⁺]
salts in (solid state)

The blue spectra = an improper H-bond

a: [Co(CN)₆]³⁻

b: [PF₆]⁻

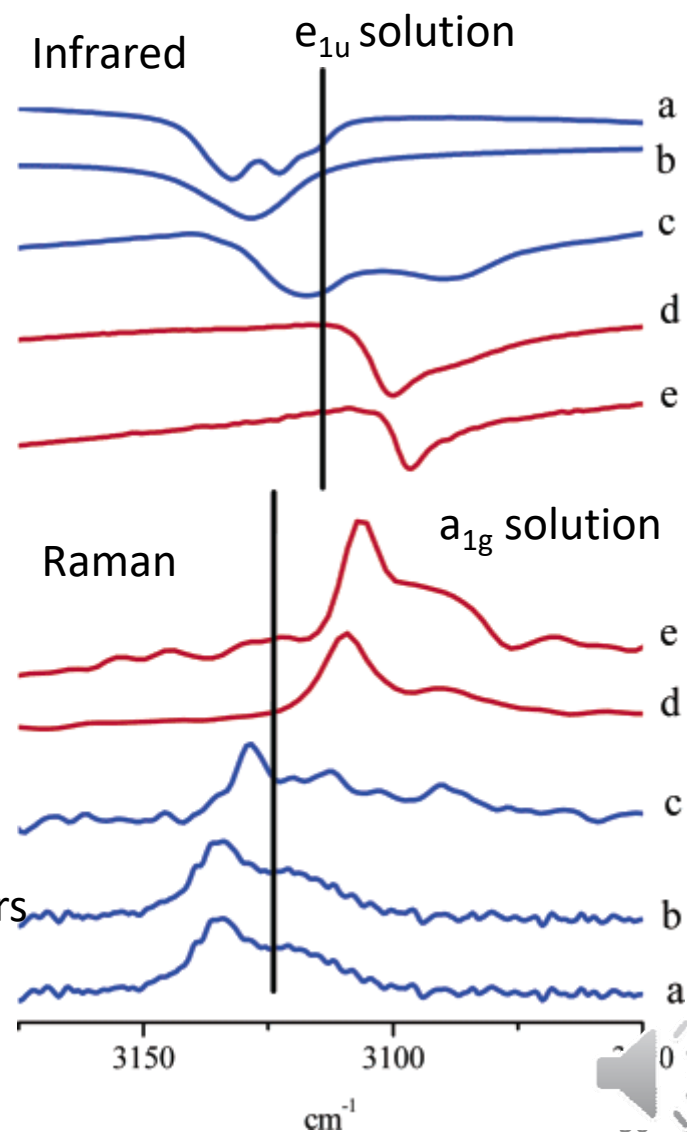
c: [Co(CO)₄]⁻

The red spectra = the proper H-bond

d: [Br₃]⁻

e: [I]⁻

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



Dihydrogen Bonds

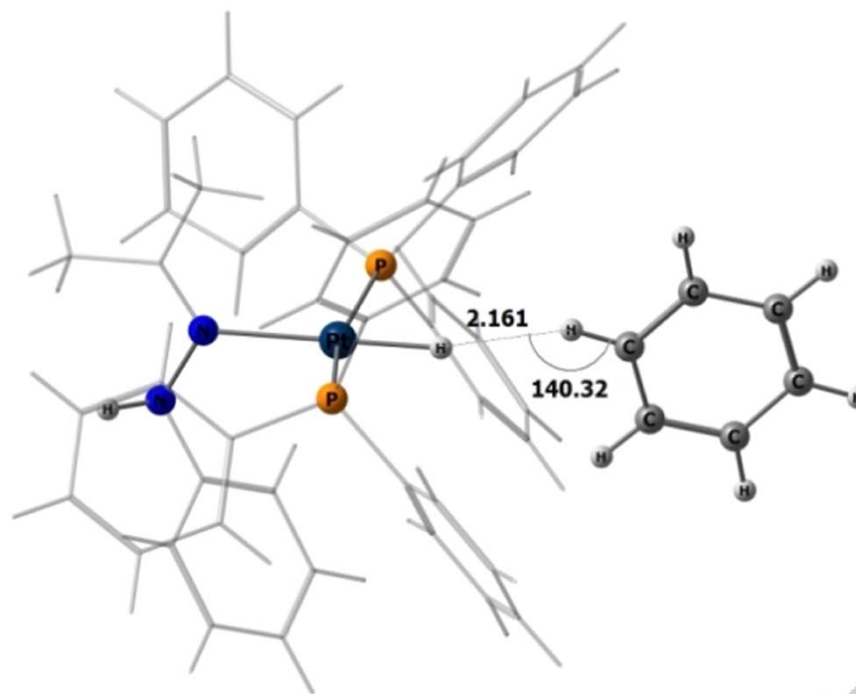
The dihydrogen bond = an interaction between a transition metal or main-group **hydride** (M–H) and a **protic** hydrogen moiety (H–X)

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(PhHNNC₃H₆)(PPh₃)₂]BF₄



NMR Spectral Criteria of Dihydrogen Bonding

- Shifts of the ^1H 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 ($T_{1\text{min}}$)

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, $J_{\text{H-H}}$ on metal polyhydrides
- 1D nuclear Overhauser effect (NOE) spectroscopy or 2D ^1H nuclear Overhauser enhancement spectroscopy (NOESY)

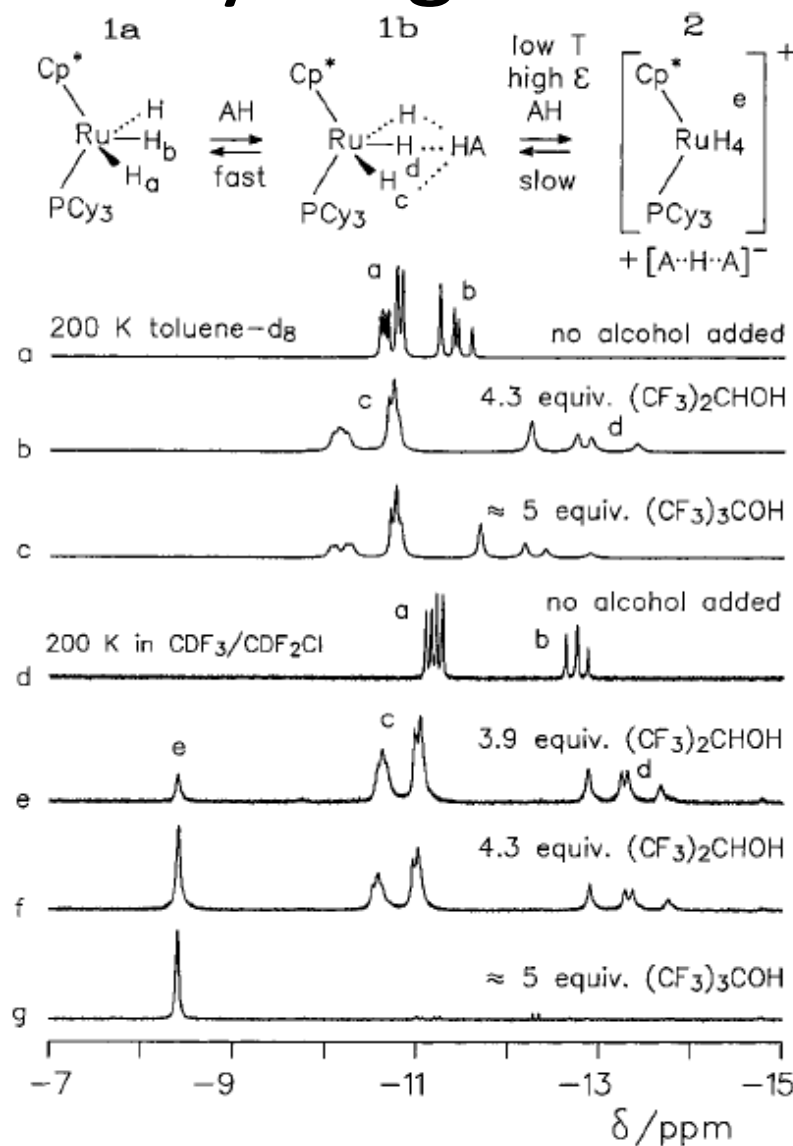
Estimation of H \cdots H distances from spin–lattice T_1 relaxation measurements
Short MH \cdots HX contacts cause strong homonuclear dipolar coupling that provides
an additional contribution to nuclear dipole–dipole relaxation

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



NMR Spectral Criteria of Dihydrogen Bonding

Hydride regions
500 MHz ^1H NMR



AB_2X spin system
 $\text{X} = \text{P}$

$J_{ab} = 80\text{ Hz}$

Increased coupling

$J_{ab} = 220\text{ Hz}$

One AB_2X 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 dihydrogen-bonded species

The formation of a dihydrogen bond $MH \cdots HX$ = appearance of a new wider and more intense band, ν_{XH}^{bonded} , of the proton donor

A band shift: $\Delta\nu_{XH} = \nu_{XH}^{\text{bonded}} - \nu_{XH}^{\text{free}}$ (**red shift** up to -450 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})

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

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

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



Enthalpies of Dihydrogen Bonds

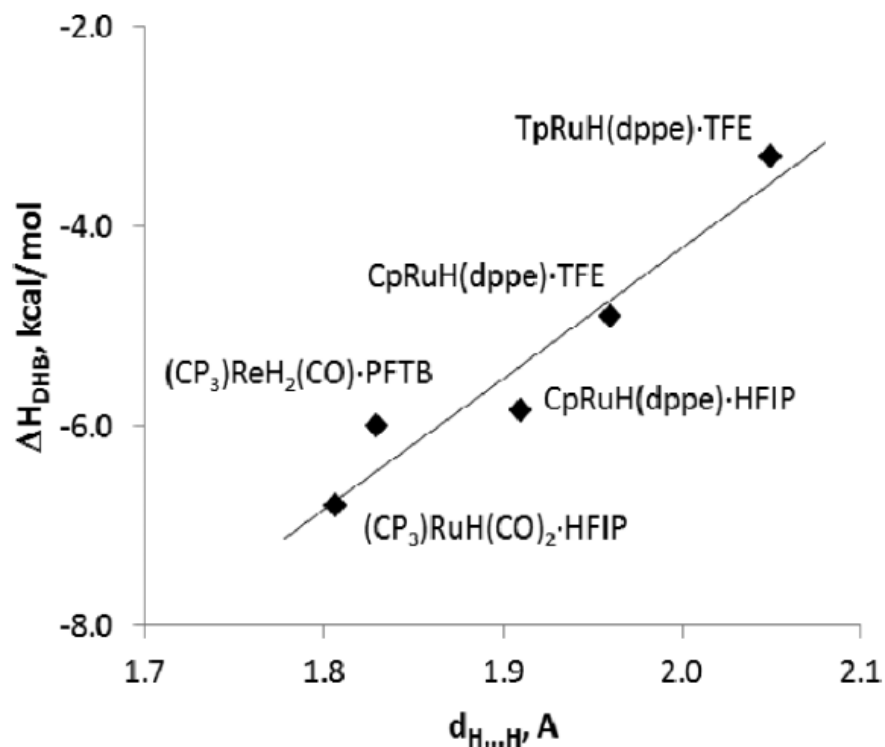
Complexes of Boron Tetrahydride with Different Proton Donors

ROH	ν_{σ} in CH_2Cl_2 (cm^{-1})	$\Delta\nu_{\text{OH}}$ (cm^{-1})	$-\Delta H_{\text{exp}}$ in CH_2Cl_2 (kcal/mol)	$r_{\text{H}\cdots\text{H}}$ (Å)
$\text{CFH}_2\text{CH}_2\text{OH}$	318	247	4.6	1.63
$\text{CF}_3\text{CH}_2\text{OH}$	324	290	5.2	1.55
$(\text{CF}_3)_2\text{CHOH}$	362	402	6.5	1.46

ν_{σ} = intermolecular $\text{H}\cdots\text{H}$ stretching mode



Enthalpies of Dihydrogen Bonds



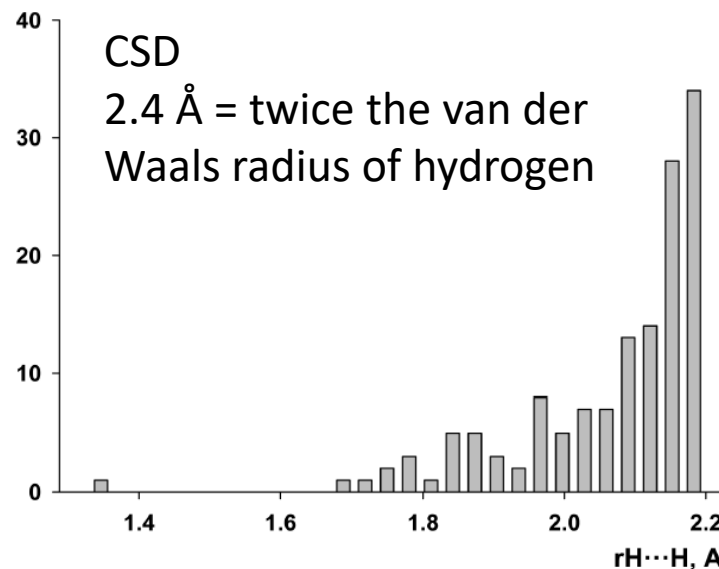
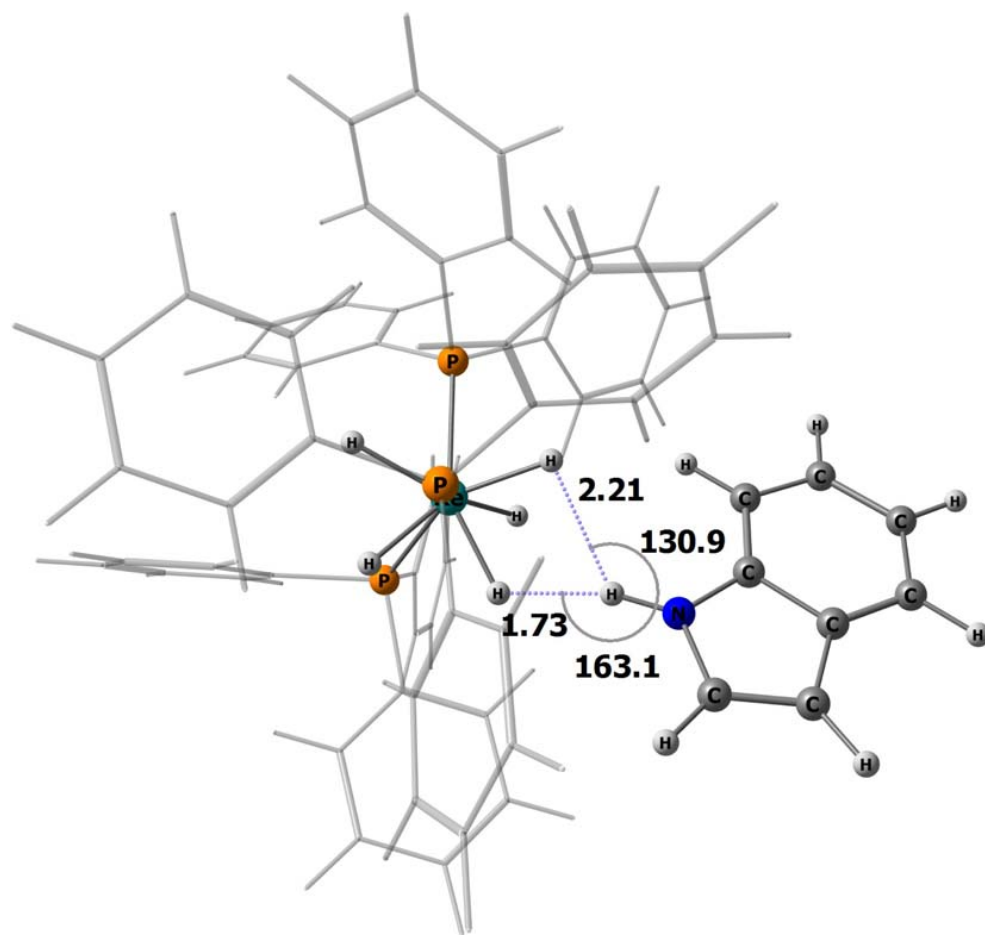
Correlation between the enthalpy of DHB formation ($\Delta H^\circ_{\text{DHB}}$; derived from IR data) and the H \cdots H distance (determined from NMR data on $T_{1\text{min}}$) for complexes of fluorinated alcohols

[TFE = $\text{CF}_3\text{CH}_2\text{OH}$, HFIP = $(\text{CF}_3)_2\text{CHOH}$, PFTB = $(\text{CF}_3)_3\text{COH}$]

in dichloromethane



Crystallographic Structural Data



Neutron diffraction crystal structure of $\text{ReH}_5(\text{PPh}_3)_3 \cdot \text{indole}$