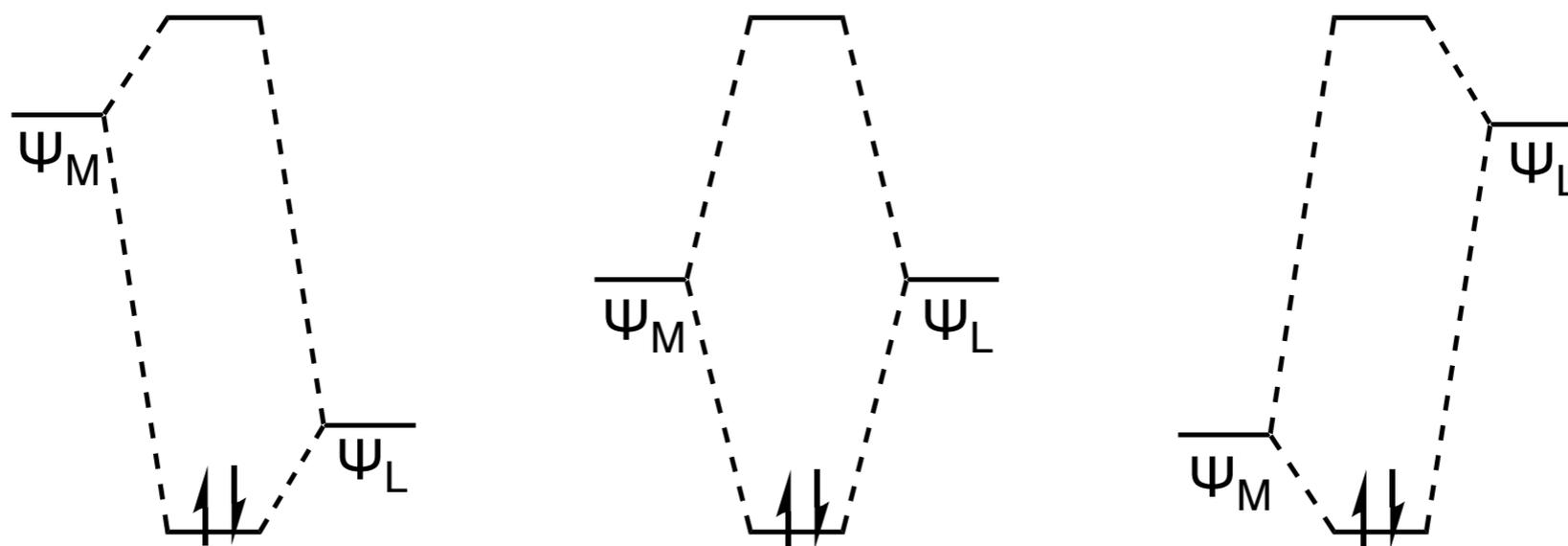


Inverted Ligand Fields
What is The Deal With Copper(III)?



MacMillan Group Meeting
June 15th, 2020
Cesar Nicolas Prieto Kullmer

Outline of Talk

Bonding Models of Coordination Complexes and Their Pitfalls – What are Inverted Ligand Fields?

Early Experimental and Computational Evidence for Inverted Ligand Fields

Copper (III) Complexes – Theoretical and Experimental Analysis of their Electronic Structure

The Implications of Inverted Ligand Fields for Organometallic Complex Reactivity

Outline of Talk

Bonding Models of Coordination Complexes and Their Pitfalls – What are Inverted Ligand Fields?

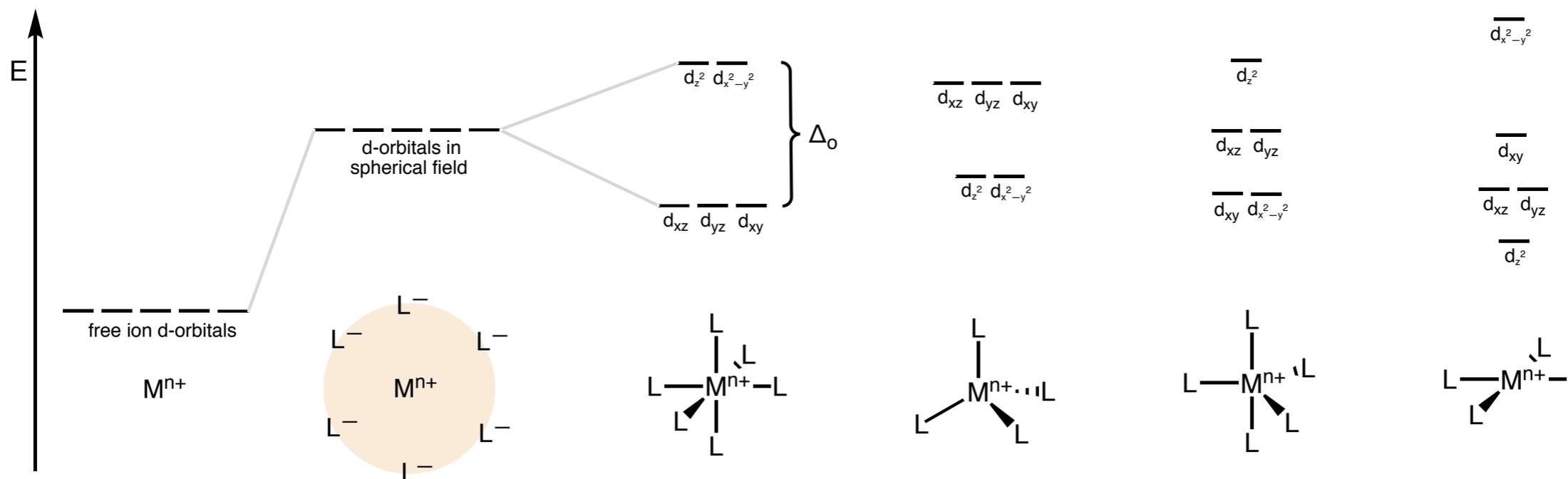
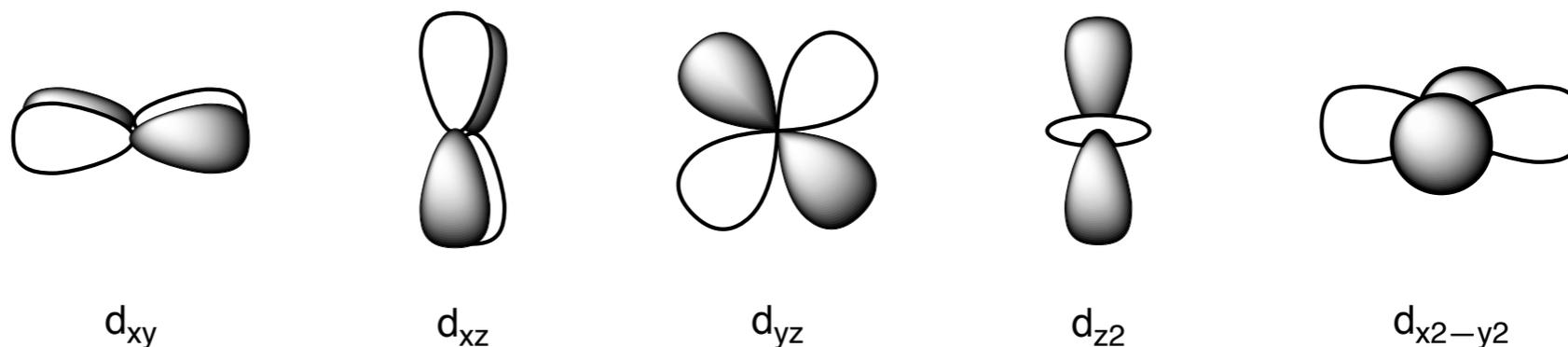
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Crystal Field Theory

d-orbitals:



■ relies only ligand—metal electronic repulsion

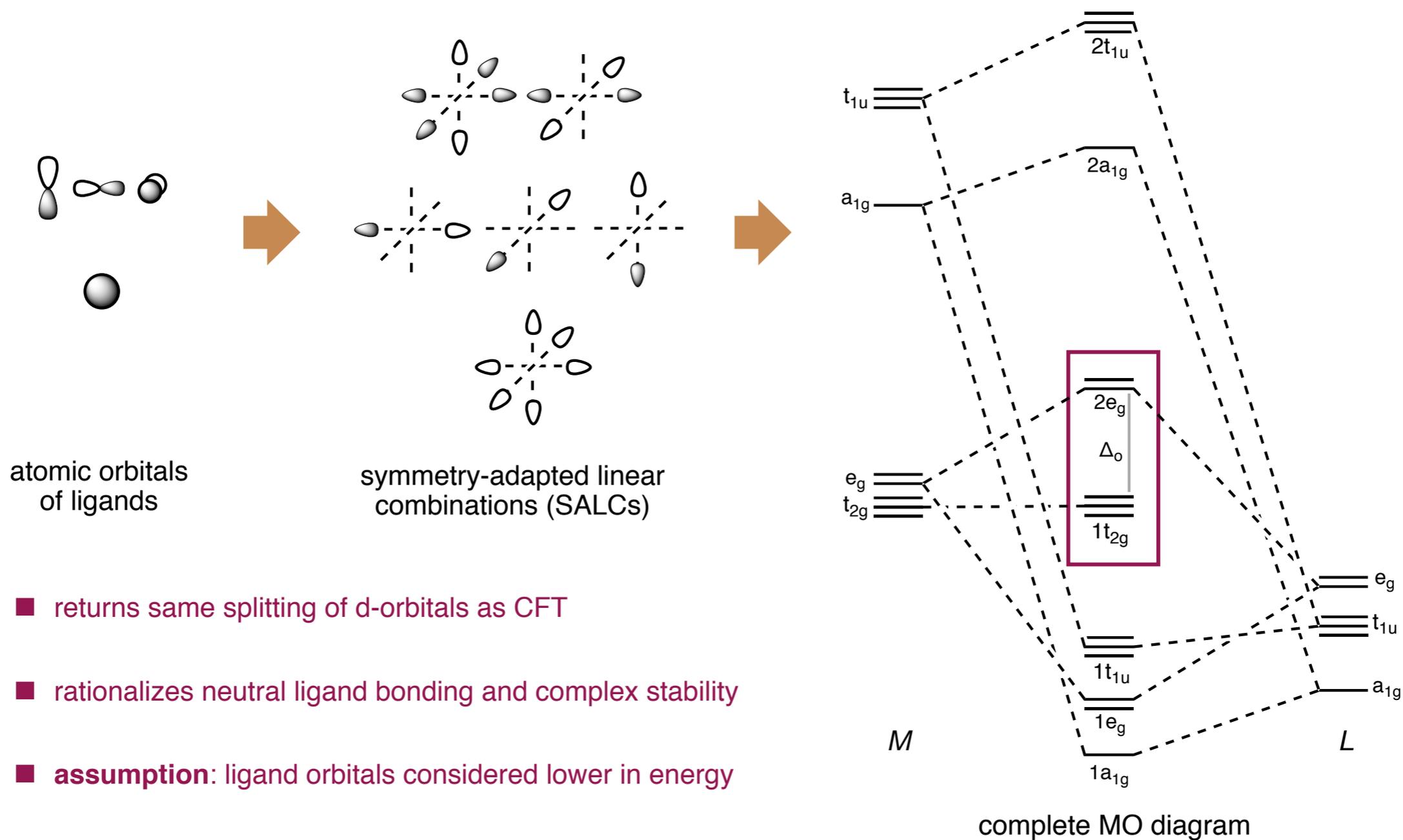
■ fails to predict certain ligand effects (i.e. OH⁻ vs. H₂O)

■ cannot account for neutral ligands

■ only considers d-orbitals

Ligand Field Theory

factors in ALL metal orbitals and ALL ligand orbitals



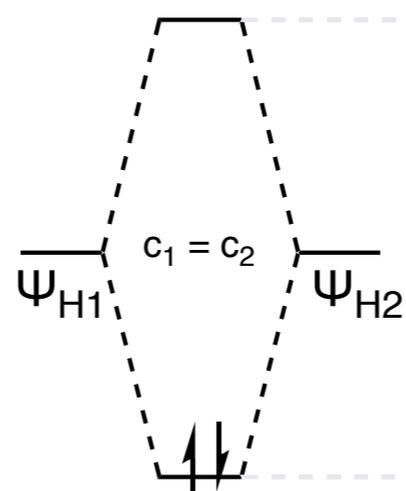
MO Shape and Composition

$$\Psi_{\text{anb}} = c_1\Psi_1 - c_2\Psi_2$$

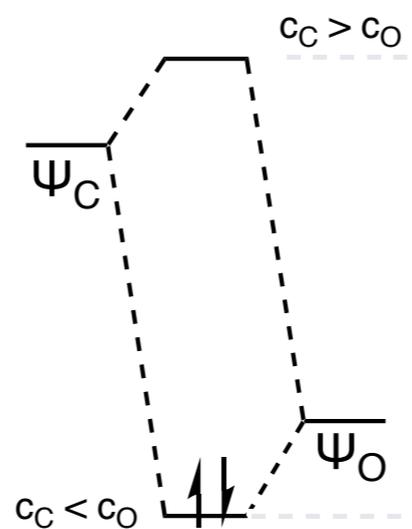
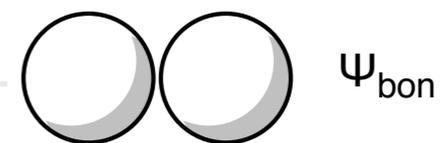
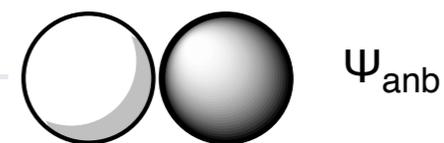
MO composition
reflects individual
AO contribution

$$\Psi_{\text{bon}} = c_1\Psi_1 + c_2\Psi_2$$

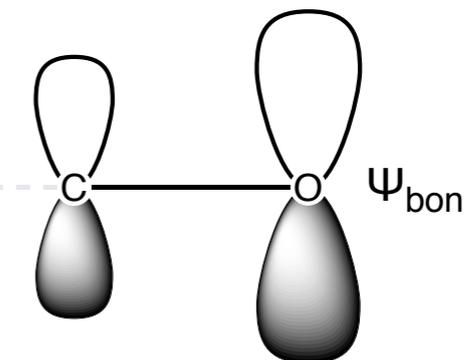
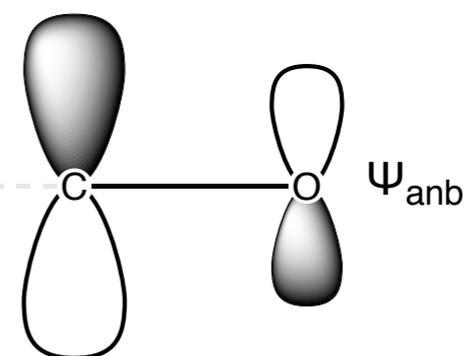
electrons of MO
reside mostly on
main contributor



non-polarized



polarized



Oxidation State Formalism

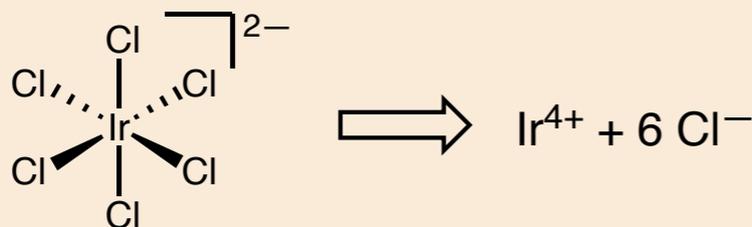
According to the IUPAC:

OS of an atom is the charge of this atom after ionic approximation of its heteronuclear bonds.

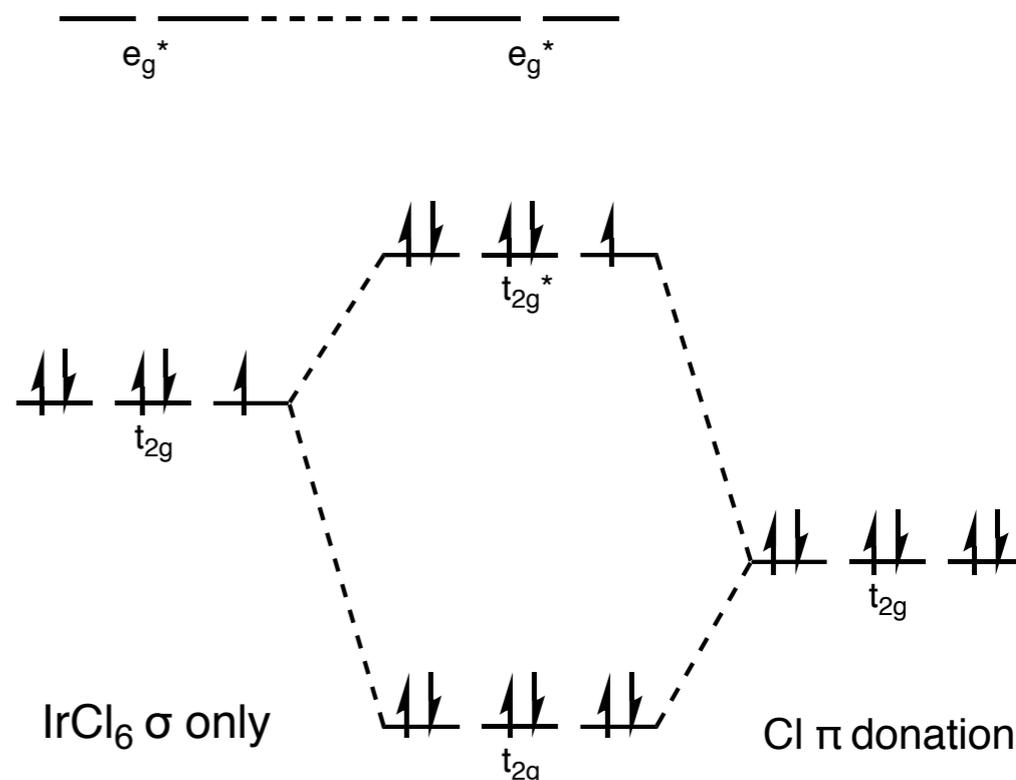
Why?

...underlying principle is that the ionic sign in an AB molecule is deduced from the electron allegiance in a LCAO-MO model:
The bond's **electrons are assigned to its main atomic contributor**.

tend to assign oxidation state based on electronegativity



- ESR hyperfine coupling w/ chlorine observed
- e^- hole 3% of time on any chlorine (18% total)



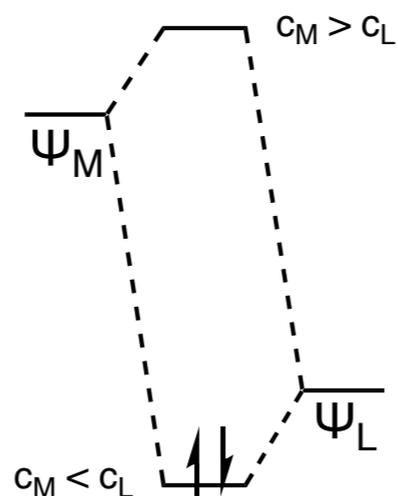
What if combined ligand contributions outweigh metal?

What is an inverted ligand field?

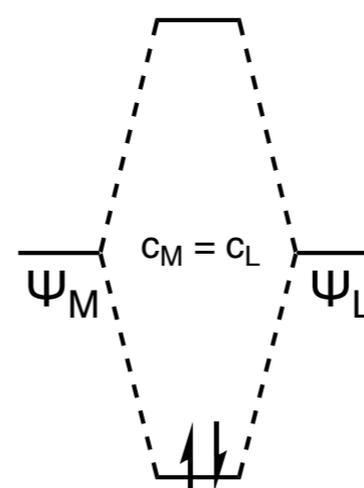
$$\Psi_{\text{anb}} = c_M \Psi_M - c_L \Psi_L$$

*MO composition
reflects individual
AO contribution*

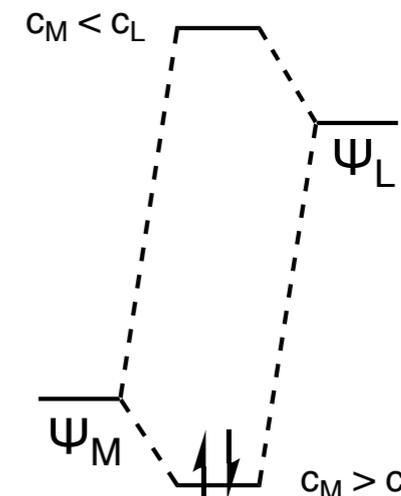
$$\Psi_{\text{bon}} = c_M \Psi_M + c_L \Psi_L$$



classical



covalent

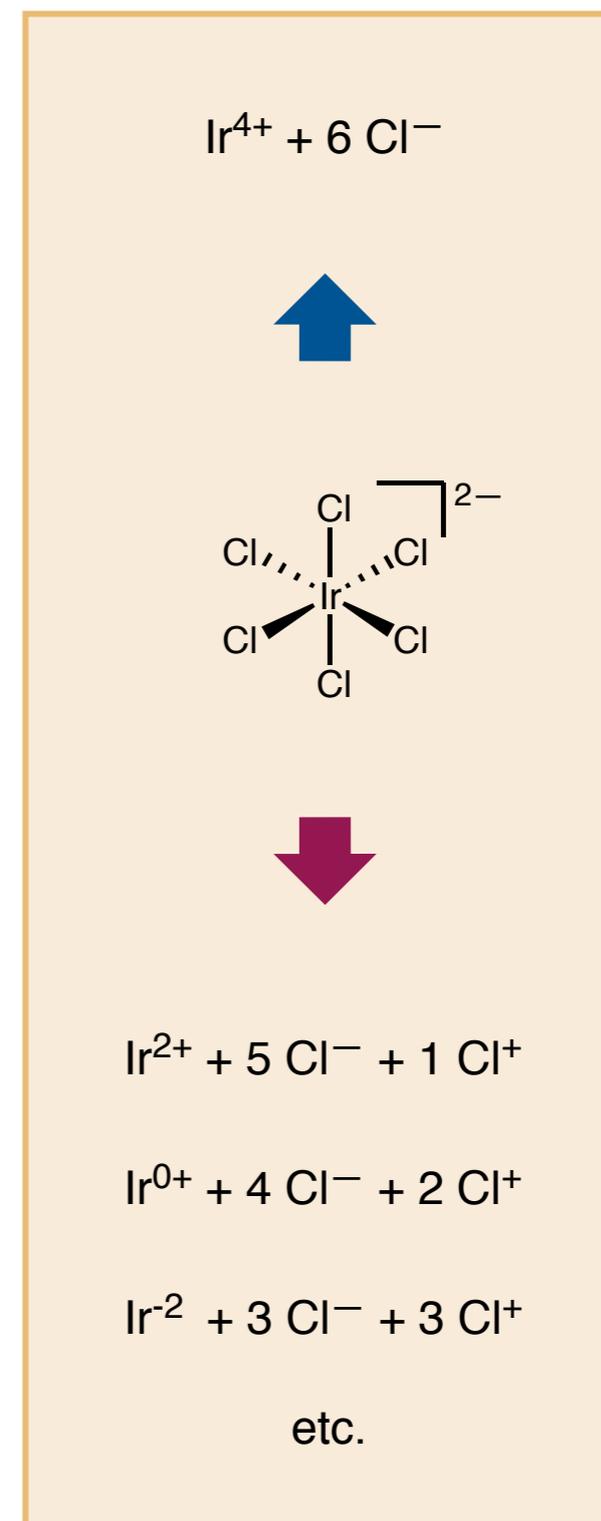
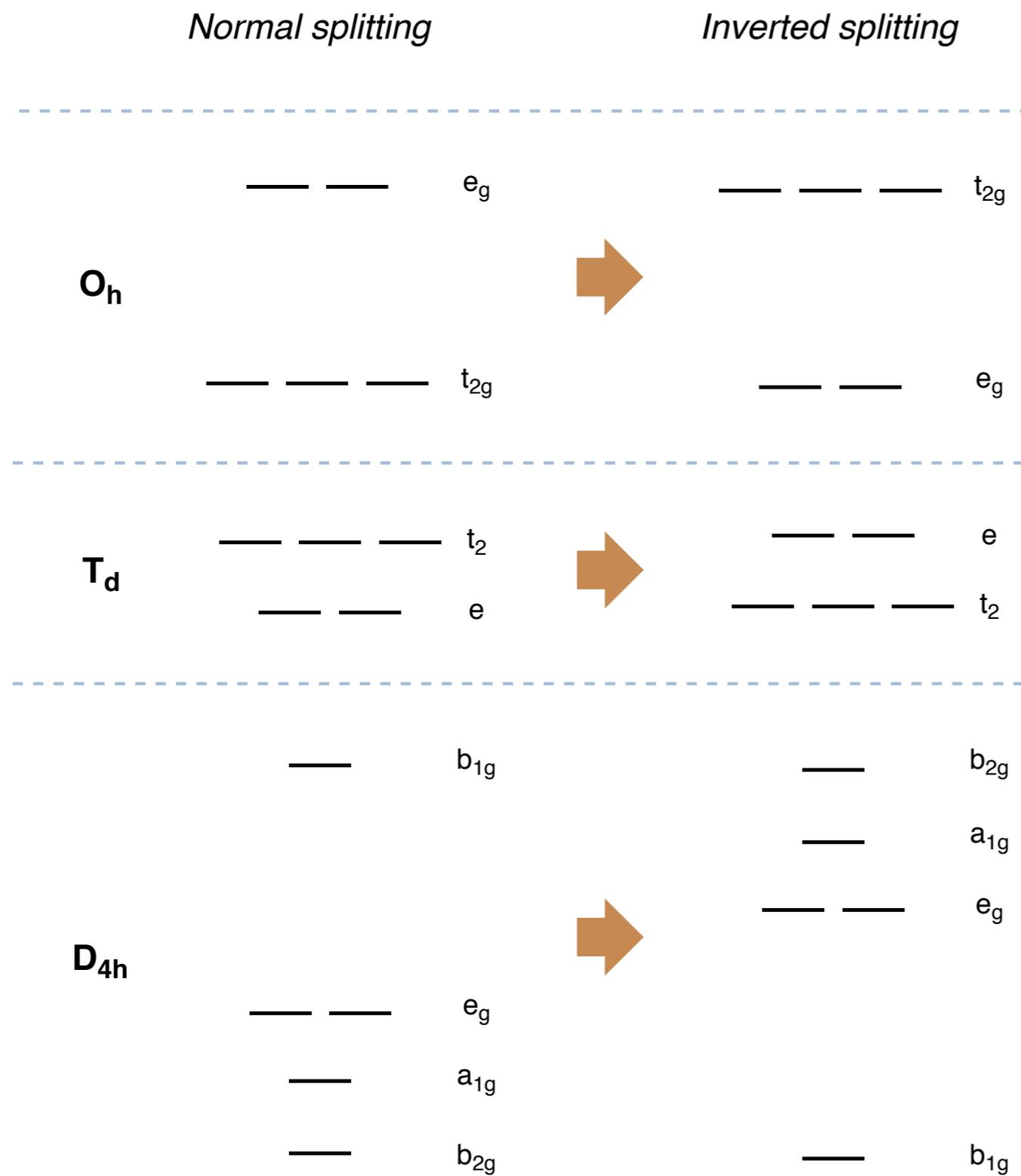


inverted

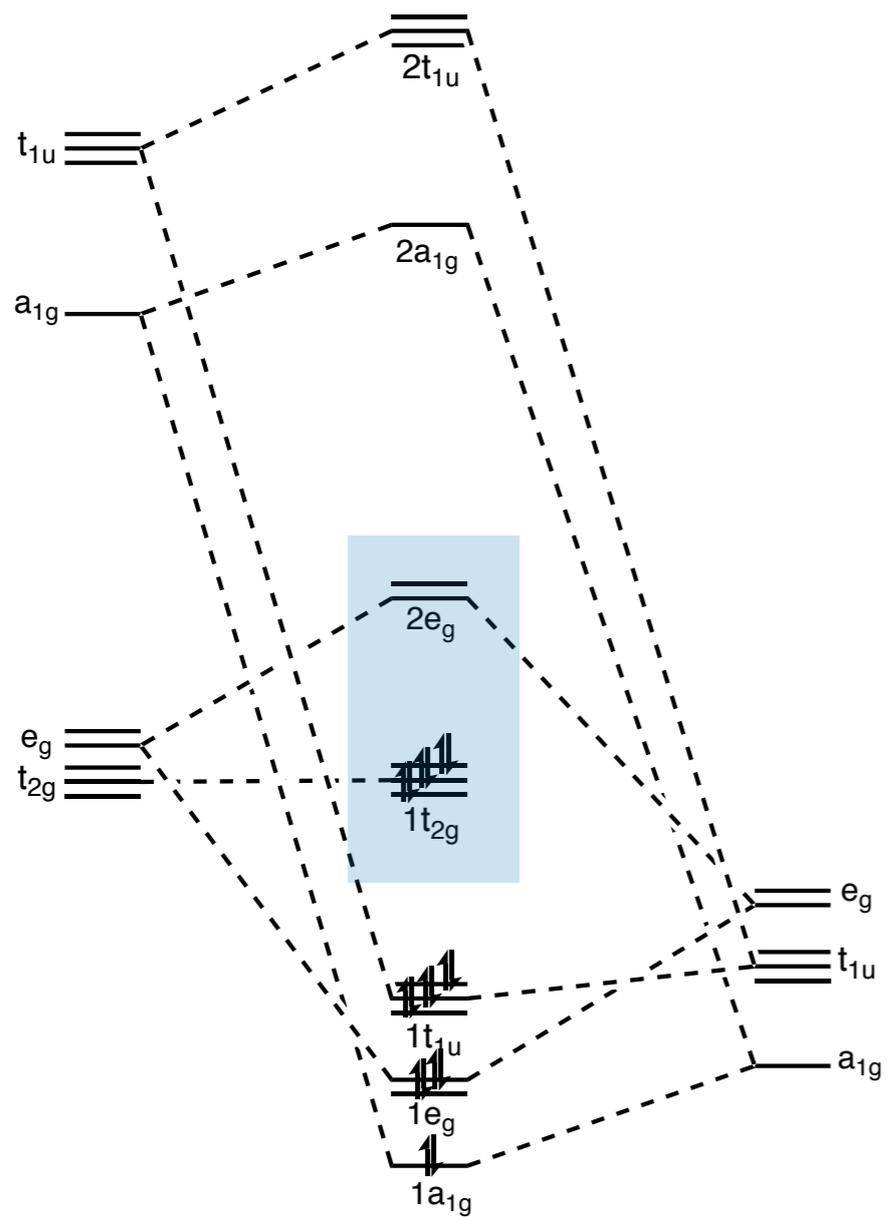
- inverted ligand fields show abnormal MO orderings and compositions
- HOMO and LUMO are ligand-based rather than metal-based

electrons do not reside on atoms as one would expect from oxidation state formalism

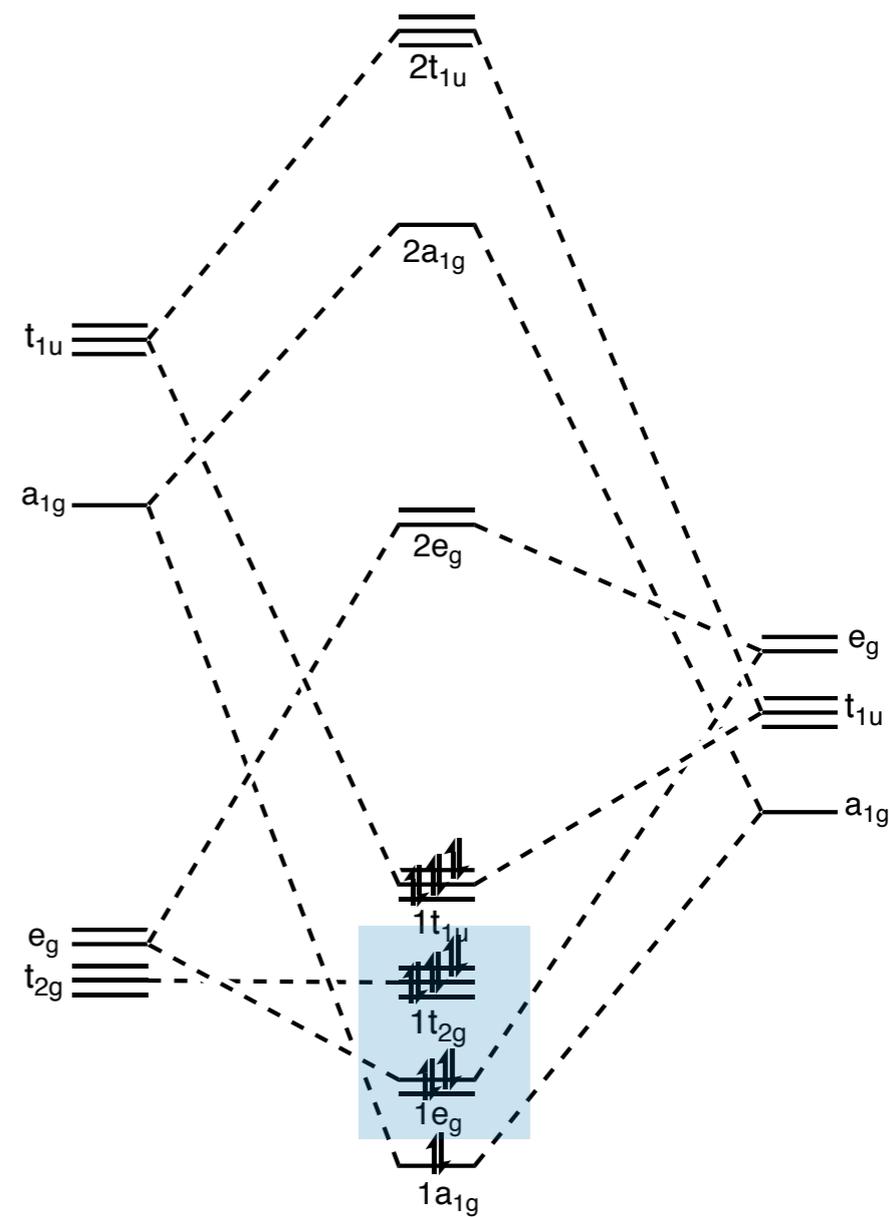
What is an inverted ligand field?



A Theoretical Inverted Octahedral Ligand Field



$M = 6 e^-$ normal MO diagram $L = 12 e^-$



$M = 10 e^-$ inverted MO diagram $L = 8 e^-$

only some MOs switch their order
the metal–centered MOs change their identity

Approaches to Ligand Field Inversion

lower metal-based orbitals

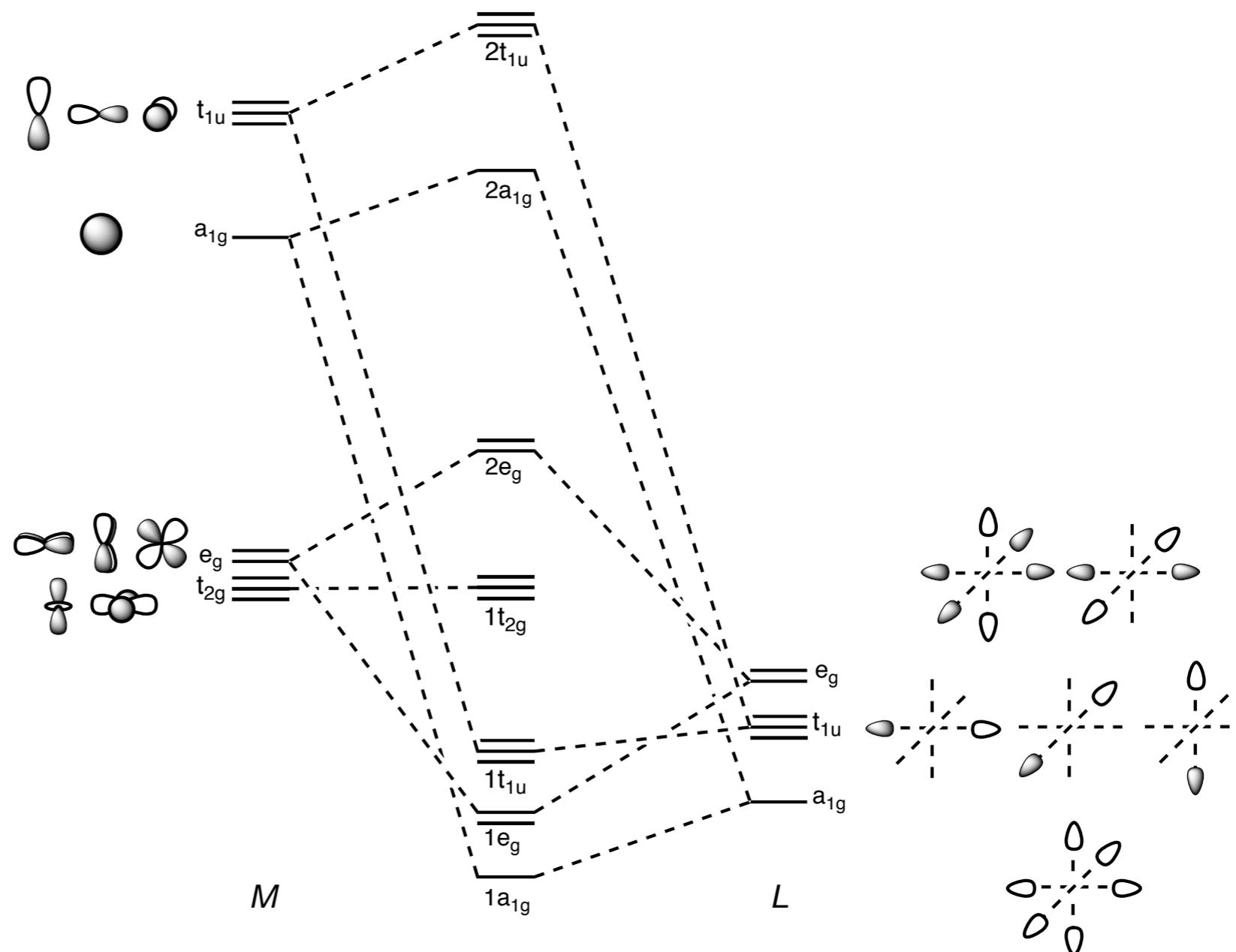
charged metal center

more electronegative metal

raise ligand-based orbitals

electron-releasing substituents

more electropositive elements



Outline of Talk

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Early Experimental and Computational Evidence for Inverted Ligand Fields

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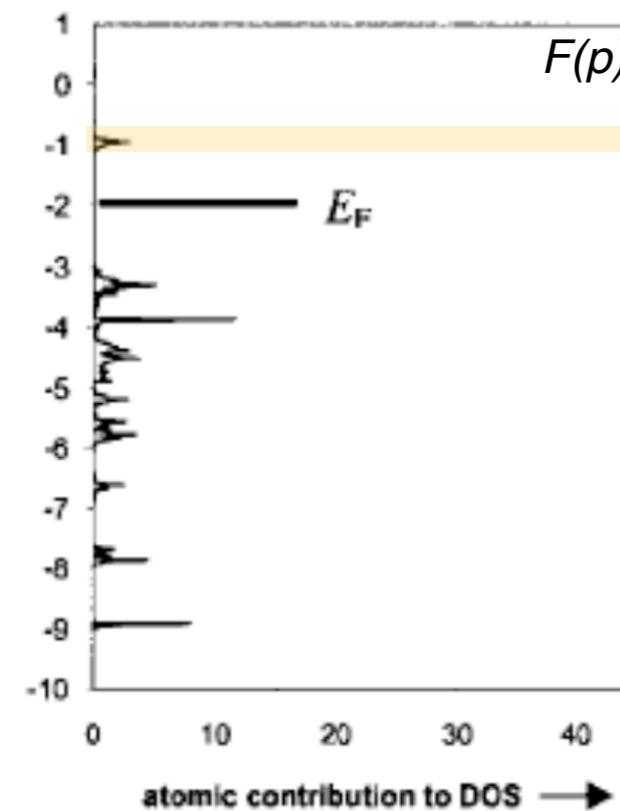
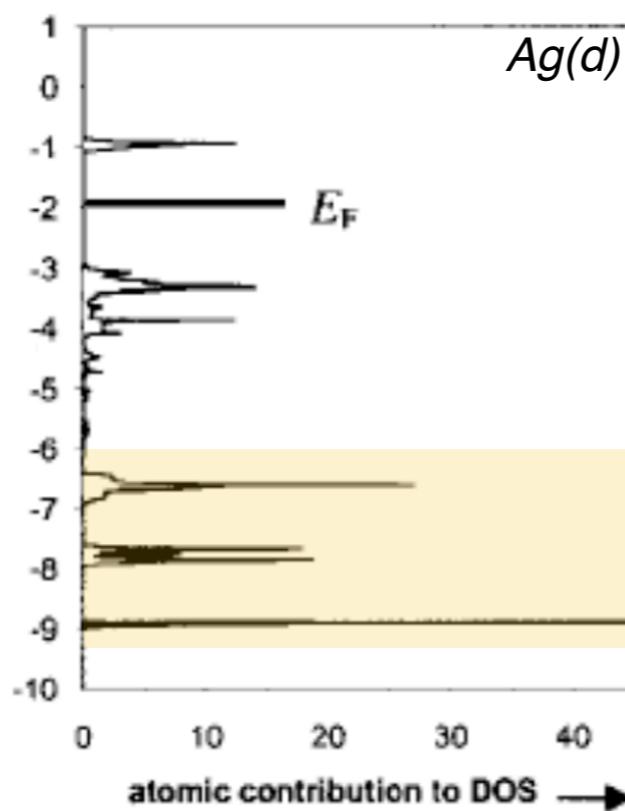
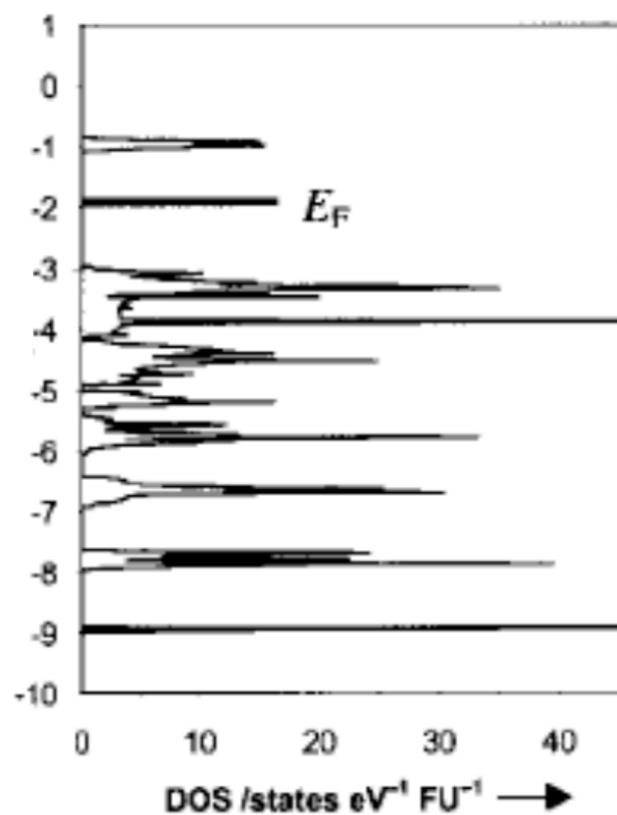
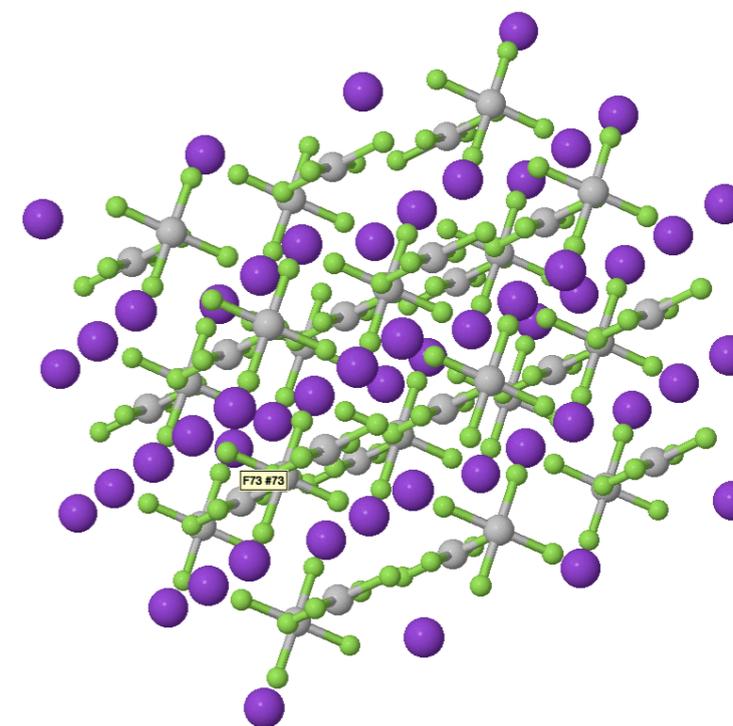
The Implications of Inverted Ligand Fields for Organometallic Complex Reactivity

Early Evidence — $KAgF_4$

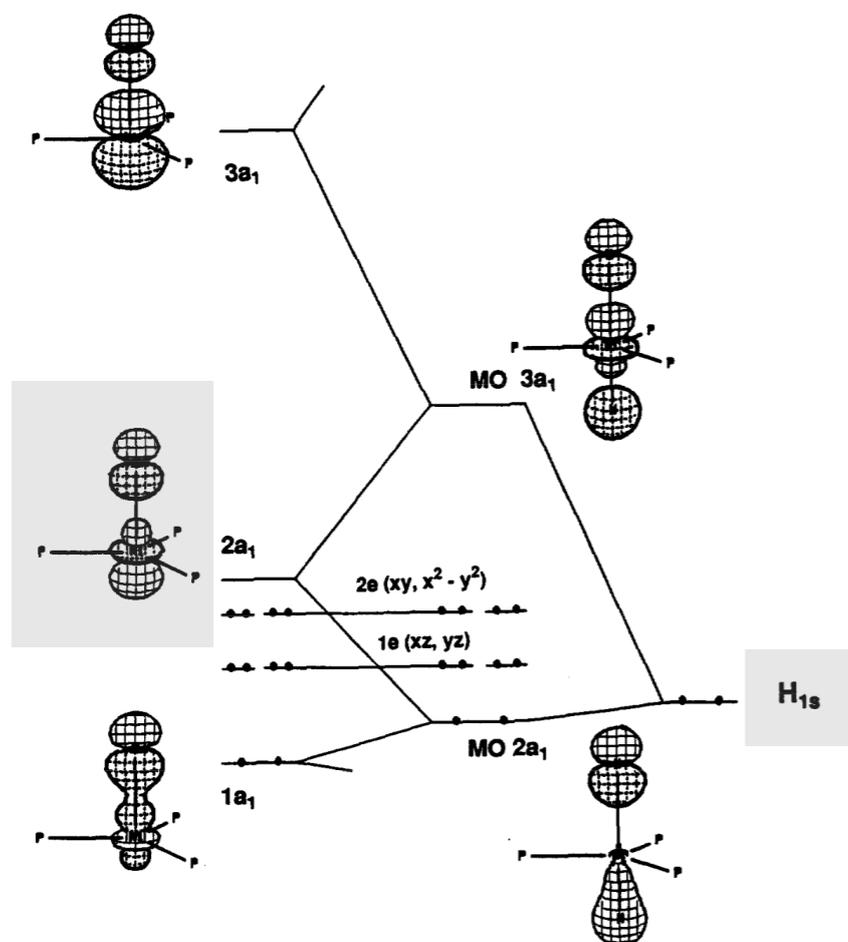
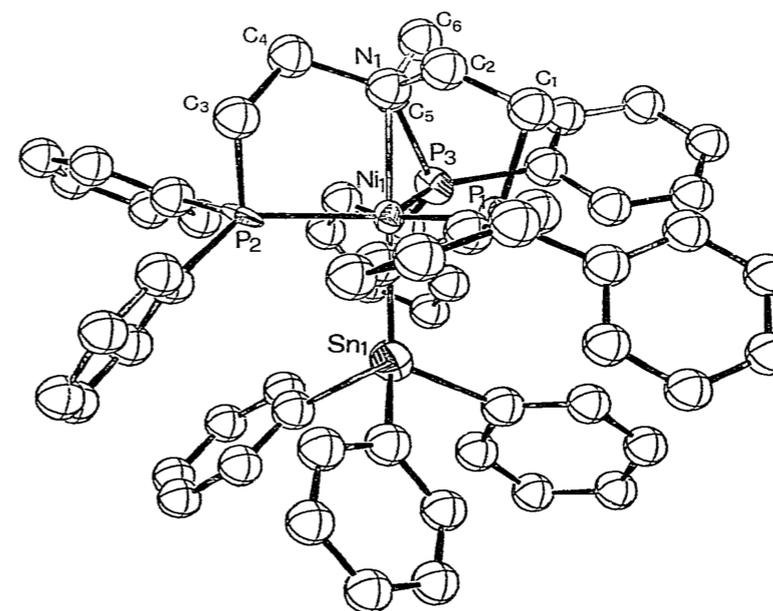
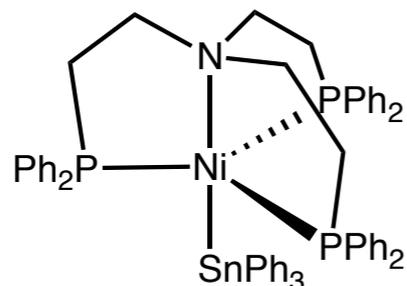
Solid containing formally Ag(III):

- Ag—F bonding (−6.5 to −9.0 eV): dominant Ag d—orbital contribution
- Ag—F anti bonding (−0.7 eV): excess F 2p—orbital contribution

... classical picture used for ionic inorganic compounds ... an ionic formulation of $KAgF_4$ as $K^I Ag^{III} (F^-)_4$, must be modified in this case...



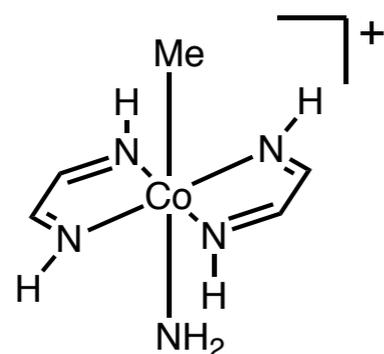
Early Evidence — $[Ni(SnPh_3)(np_3)]^+$



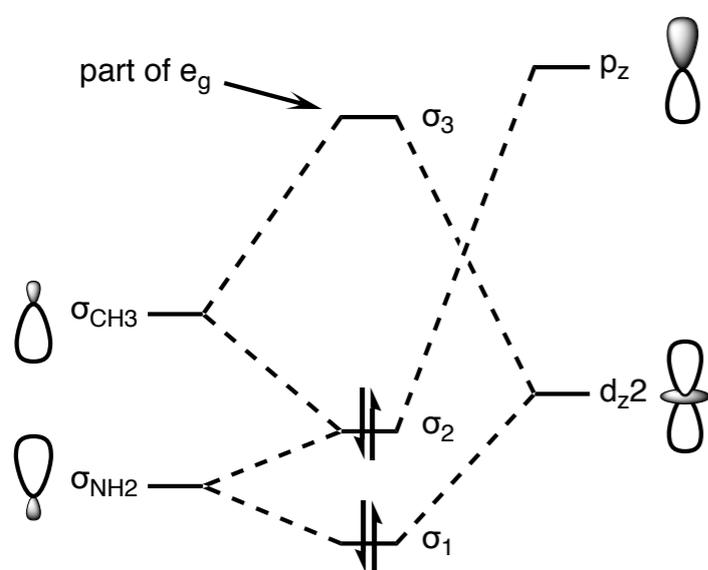
- $[Ni(np_3)]$ known to exist independently as stable complex
- donor—acceptor relationship between Ni and Sn inverted (σ -SnPh₃ ~ 2eV higher than 2a₁)
- metal is best described as d¹⁰ w/ SnPh₃⁺ ligand

σ -noninnocence: ambiguity on which atom is acting as the donor

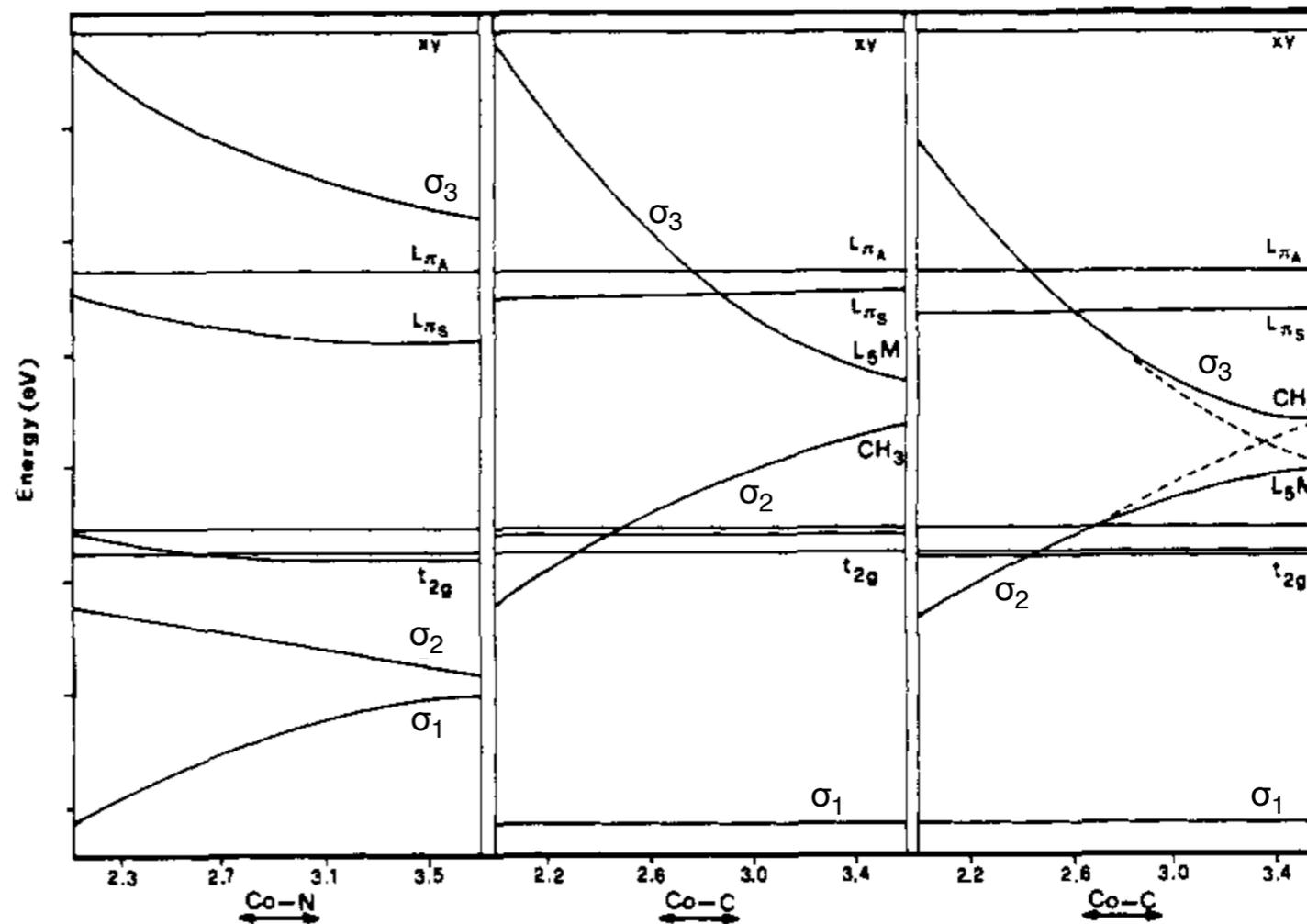
Early Evidence – Vitamin B₁₂ mimetics



Cobaloxime

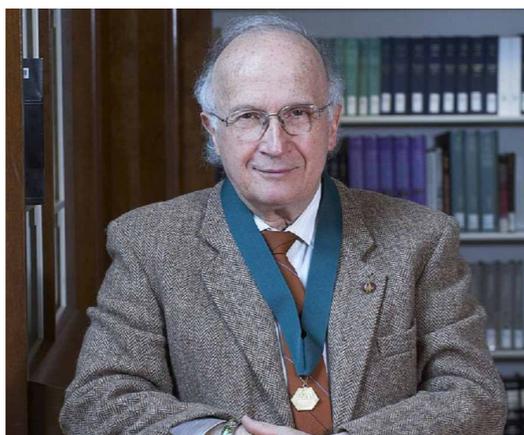


- σ₁ – NH₂, z² bonding
- σ₂ – p_z, CH₃ bonding +NH₂, z² antibonding
- σ₃ – p_z, CH₃ antibonding +NH₂, z² antibonding

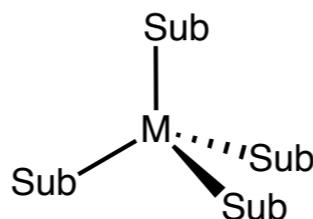


- Modulation of Co–N distance affects propensity metal to undergo inner-sphere e[−] transfer
- Intermediate Co–N distance shows avoided crossing at longer Co–C distances (allows for Co–C homolysis)

Computational Investigation of d^{10}



Roald Hoffmann



- Using EH_3 ($E = \text{N, P, As, Sb, Bi}$) $M = \text{Ni, Pd, Pt}$:

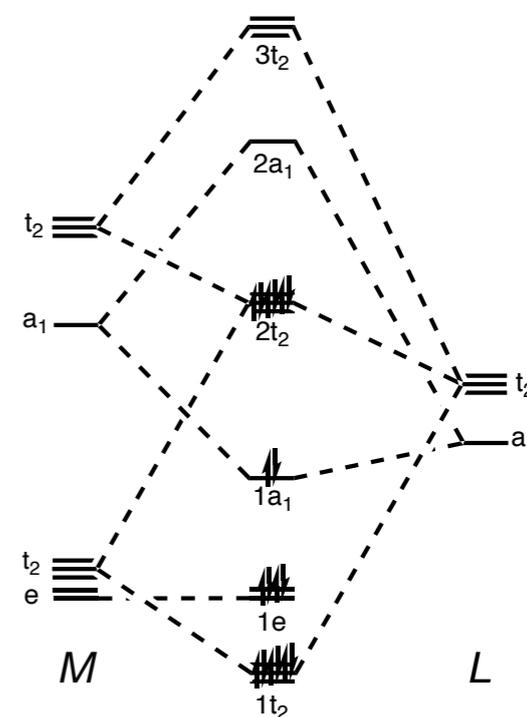
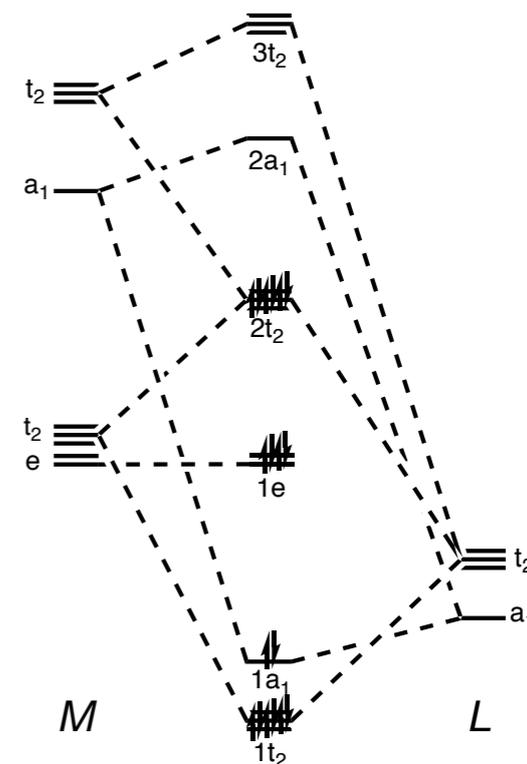
Inherent instability (decay into $\text{ML}_2 + 2\text{L}$) limits combinations to local minima

Donor ability of ligand does not correlate w/ electropositivity (inert electron pair effect)

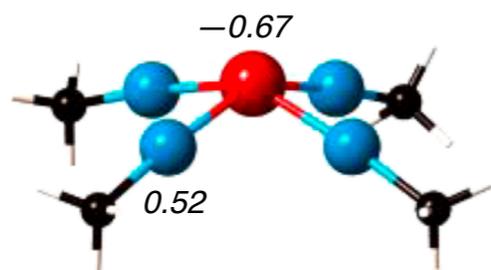
Varying metal did not return clear result due to realities of atomic orbital energies

- Using $\text{L} = \text{X}^-$, PH_3 $M = \text{Zn}^{2+}$:

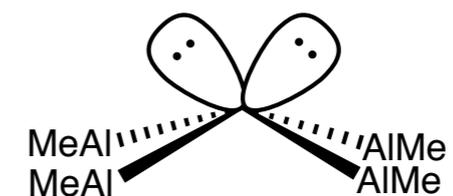
orbital	$[\text{ZnF}_4]^{2-}$			$[\text{Zn}(\text{PH}_3)_4](\text{BF}_4)_2$		
	energy(eV)	%Zn	%F	energy(eV)	%Zn	%L
$2t_2$	0.87	16	84	-11.03	8	92
$1a_1$	-1.70	19	81	-14.13	46	54
$1e$	-2.86	92	8	-17.73	99	1
$1t_2$	-3.14	82	18	-17.79	96	4



Inversion with a true transition metal



$[\text{Rh}(\text{AIme})_4]^+$
formally Rh(I)
effectively Rh(-I)

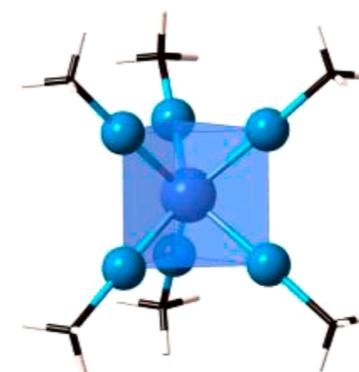


e_g (xz, yz) rehybridizes to form orbitals with significant lone-pair character

trigonal prismatic structure

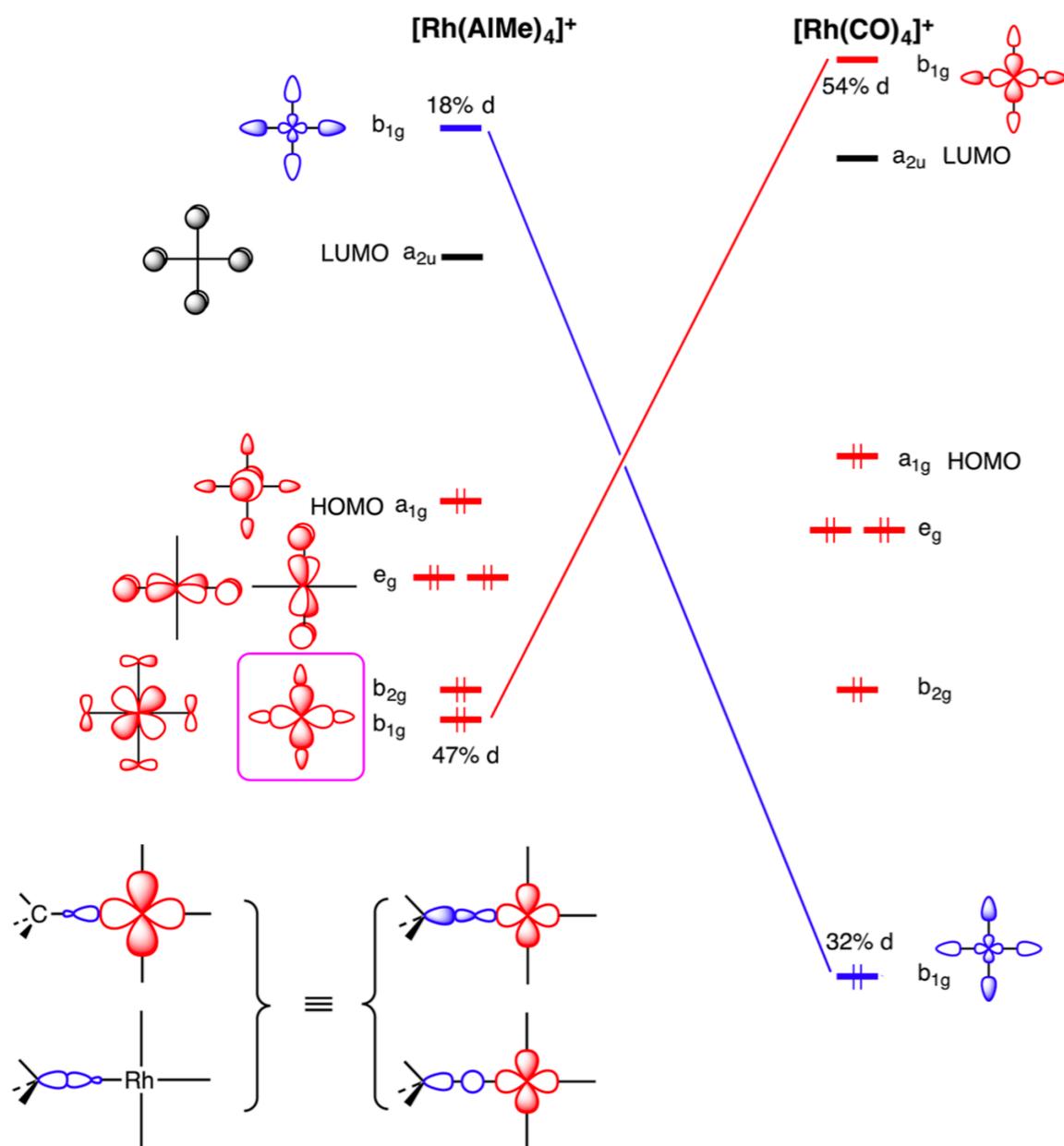
ECR₃ ligands highly electropositive
strong π acceptors
synthetically accessible

Can we see a similar effect in homoleptic hexacoordinate AIme complexes?



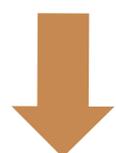
$\text{Mo}(\text{AIme})_6$

also optimizes into a trigonal prismatic structure

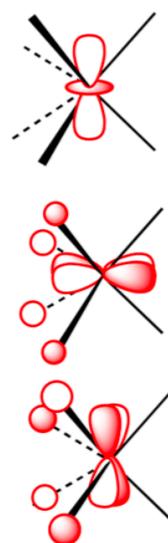


Inversion with a true transition metal

Mo(AlMe)₆
formally Mo(0)
effectively Mo(-IV)



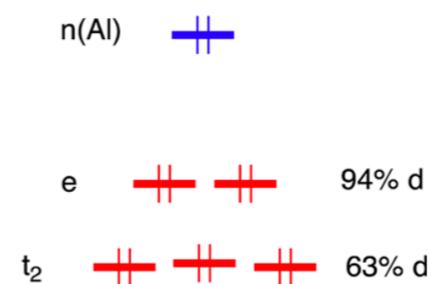
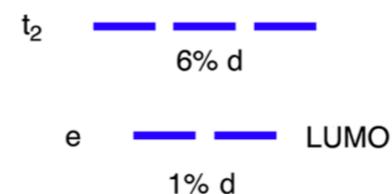
π-acidity of ligands
crucial to stability



inverted from that found in classical trigonal
prismatic complexes ($a'_1 < e' < e''$)



2 eV



Pd(AlMe)₄
formally Pd(0)
effectively Pd(0)



inverted orbital
splitting, ligand-
centered FMOs
tetrahedral structure
as expected for d^{10}
two e^- more than the
rhodium species



removal of e^- from Pd
to Rh occur from
ligand over metal

Outline of Talk

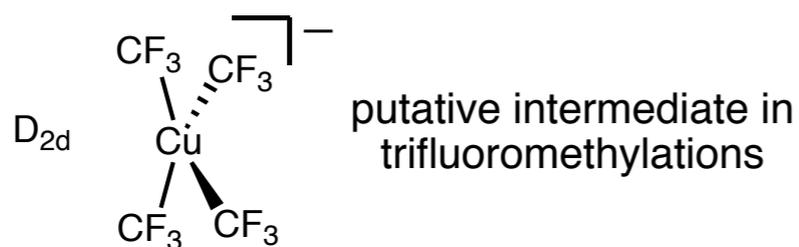
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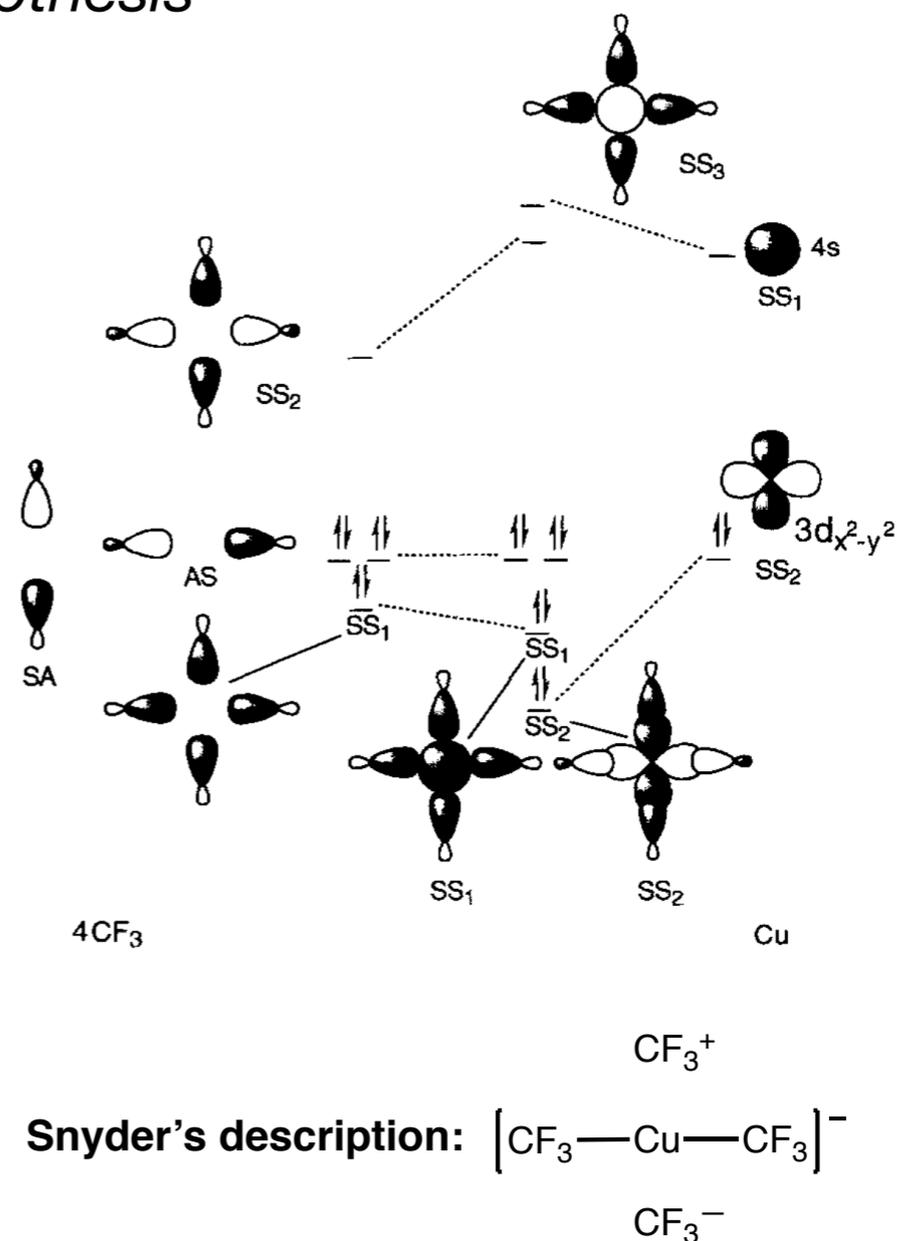
The Snyder Hypothesis



Snyder presumed that upon oxidation of $[\text{Cu}(\text{CF}_3)_4]^{3-}$ a ligand is oxidized

MO diagram implies that only **four** bonding electrons hold this complex together

both **HOMO** and **LUMO** ligand-based



DFT calculations reveal:

atomic charges: Cu (+0.71), C (+0.74), F (-0.39)

d population: d_{xy} , d_{xz} , d_{yz} , d_{z^2} 1.96–1.98, $d_{x^2-y^2}$ 1.77

CF_3 groups carry 25.4 electrons ($3\text{CF}_3^- + \text{CF}_3^+$)



- bonding is principally ionic and accompanied by two $5c/2e^-$ bonds
- depletion delocalized across all CF_3 ligands
- copper is best described as a Cu(I) species

The Snyder Hypothesis — Backlash

... Snyder has confused two important but fundamentally different concepts: the formal oxidation state, and partial charges as obtained, for example, from population analysis ...

- interprets filled d—orbitals as signs of Cu—C covalency
- invokes square—planar geometry as tell-tale sign of normal ligand field

Kraupp, M.; von Schnering, H. G. *Angew. Chem. int. Ed.* **1995**, 34, 986.

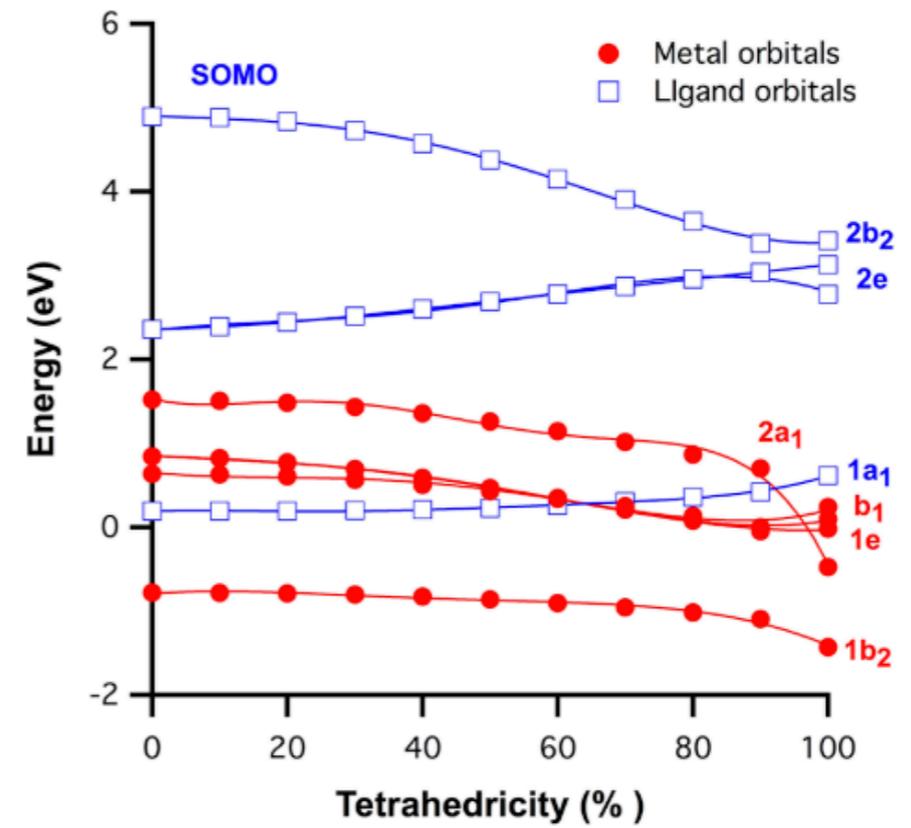
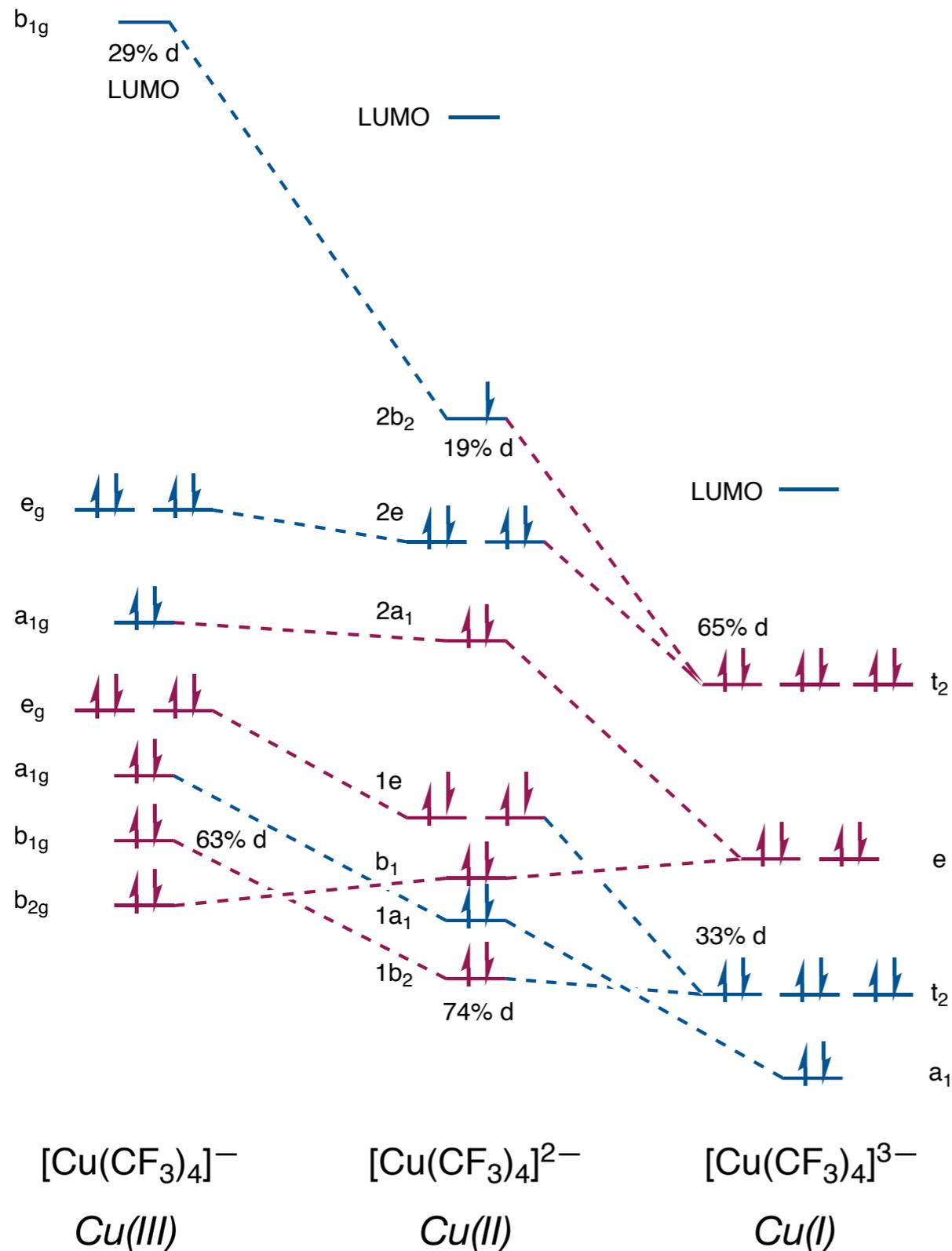
... designation of a formal oxidation state is entirely arbitrary ...uncritical application of the resulting oxidation values can lead to confusing and physically unrealistic descriptions for organic, organometallic, and inorganic species alike ...

- interprets high ionic bonding as sign that electrons do reside in d—orbitals
- ascribes copper a d^{10} configuration and a NONFORMAL Cu(I) oxidation state

Snyder, J. P. *Angew. Chem. int. Ed.* **1995**, 34, 986–987.

Comparing $[\text{Cu}(\text{CF}_3)_4]^n$

20 years later ...



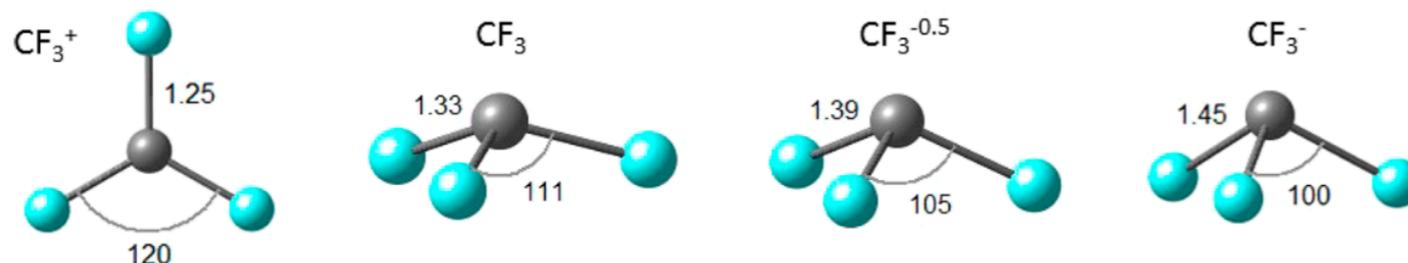
■ geometry defined by higher energy, ligand-based orbitals

■ Cu(I) shows IFL when forced into D_{2d} symmetry

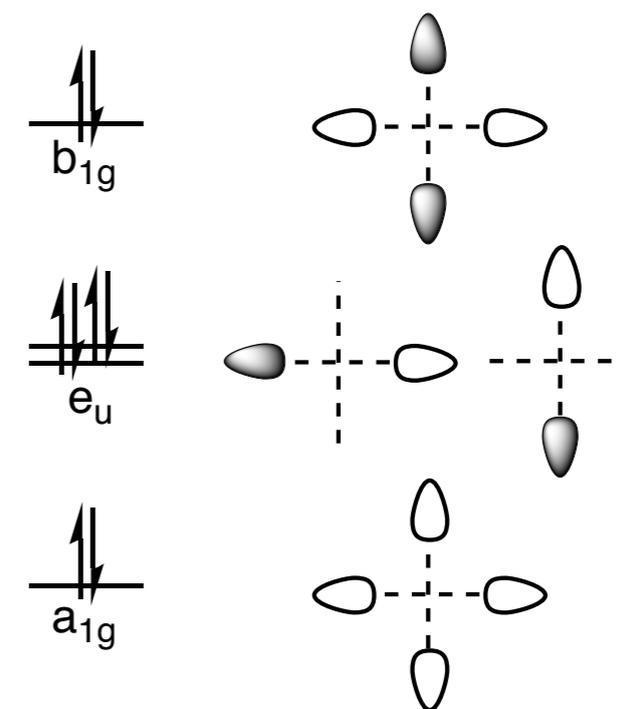
Ligand geometry influences ligand field inversion

Ligand Oxidation in $[\text{Cu}(\text{CF}_3)_4]^-$

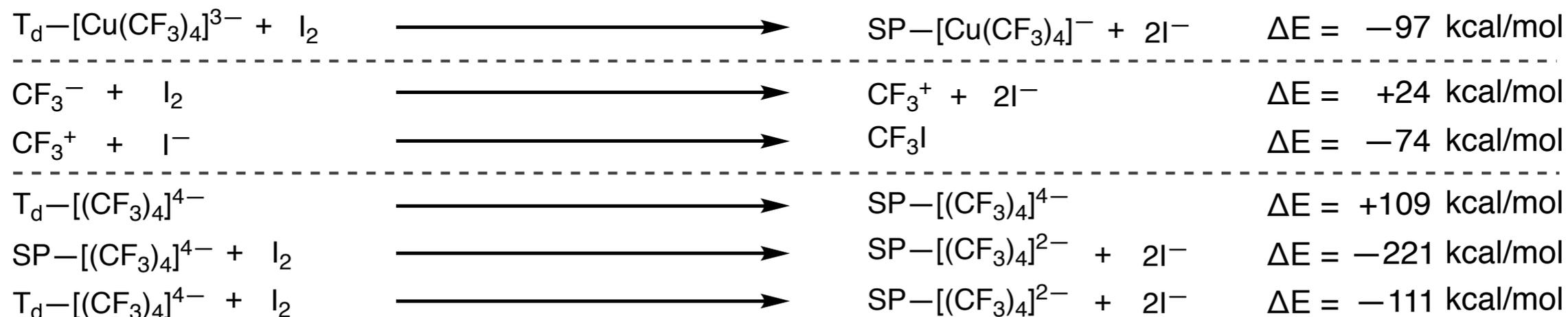
Ligand Geometry and Spatial Arrangement



optimized $[\text{Cu}(\text{CF}_3)_4]^-$: $d(\text{C-F}) = 1.37$, F-C-F angle of 105°
 optimized $[\text{Cu}(\text{CF}_3)_4]^{3-}$: $d(\text{C-F}) = 1.44$, F-C-F angle of 100°



Energetics of Ligand Oxidation



Combined Computational Evidence

[Cu(CF₃)₄]⁻ has an inverted ligand field and mainly ligand-centered FMOs

Energetics and Ligand Geometry support the existence of a CF₃⁺ ligand in the coordination sphere

Coordination geometry influences ligand field inversion due to inter-ligand interactions

How can we prove this experimentally?

Combined Computational Evidence

**[Cu(CF₃)₄]⁻ has an inverted ligand field
and mainly ligand-centered FMOs**

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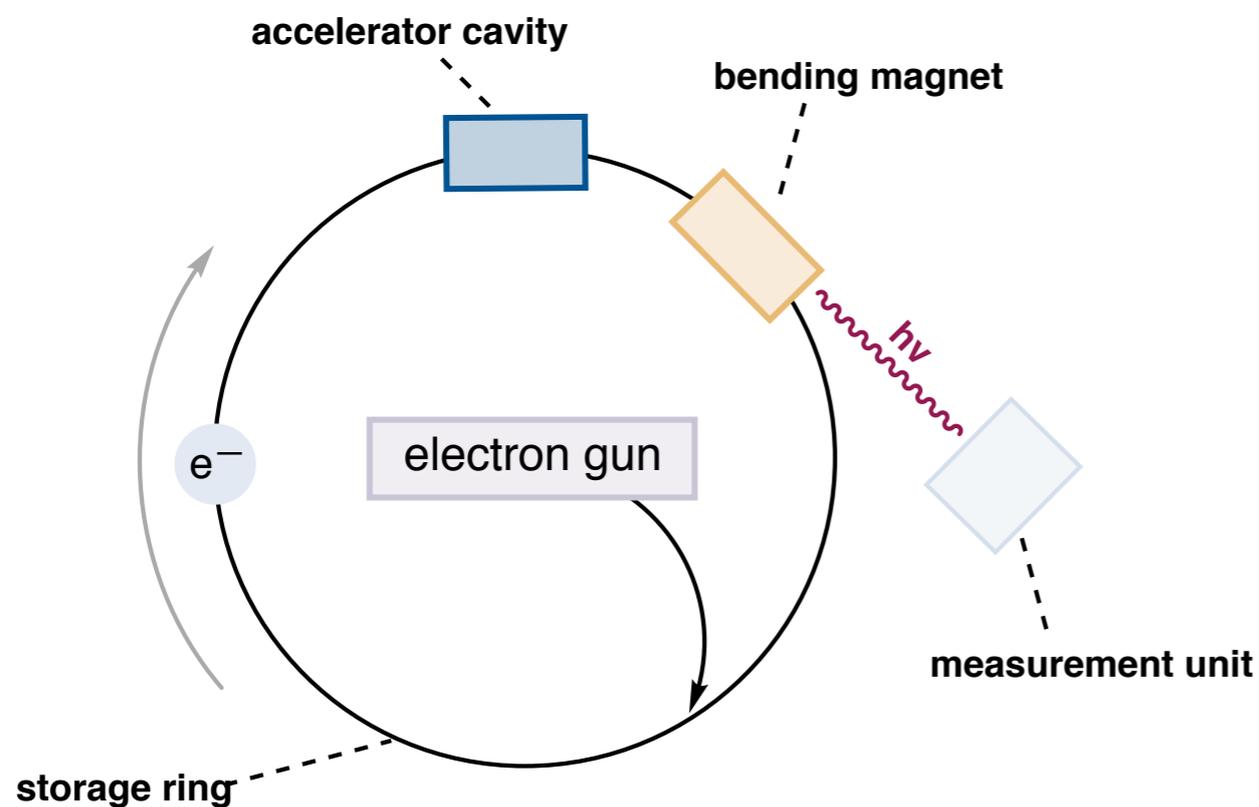
How can we prove this experimentally?

Synchrotron-based X-Ray Spectroscopy – A Primer

- relies on electronic excitation from core orbitals (e.g. 1s, 2s, 2p)
- element-specific orbital energy separations provide molecular/electronic information
- can focus on absorption (XAS) or emission (XES)
- requires access to synchrotron light source



ALBA synchrotron (Cerdanyola del Vallés)



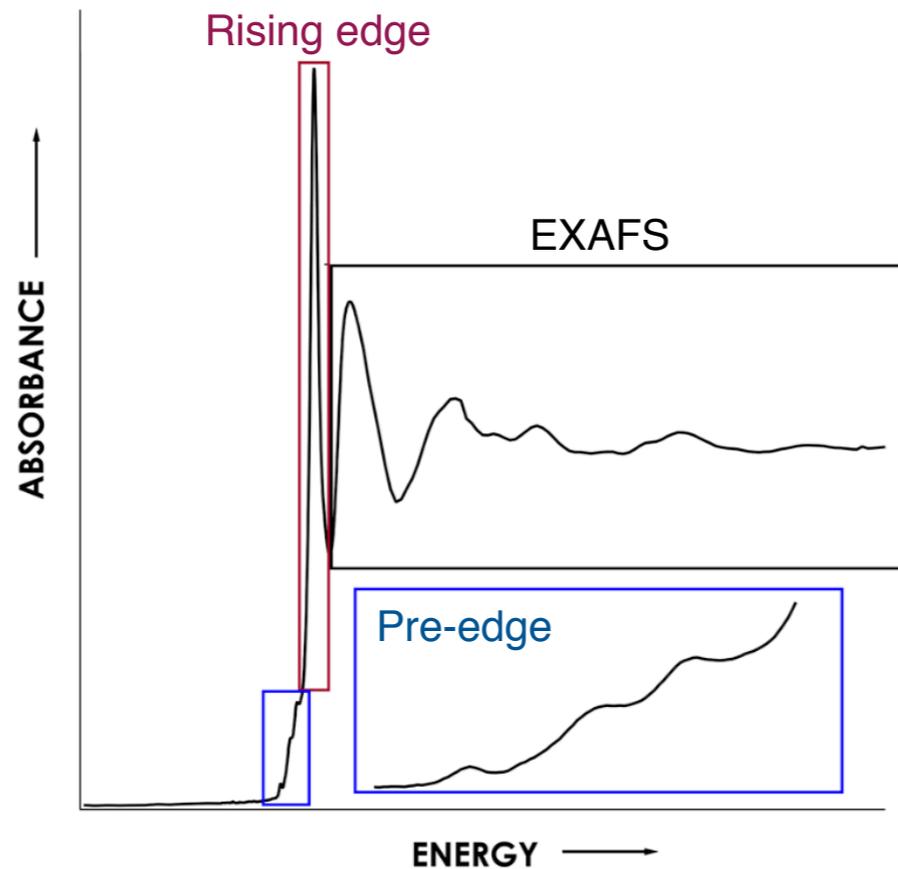
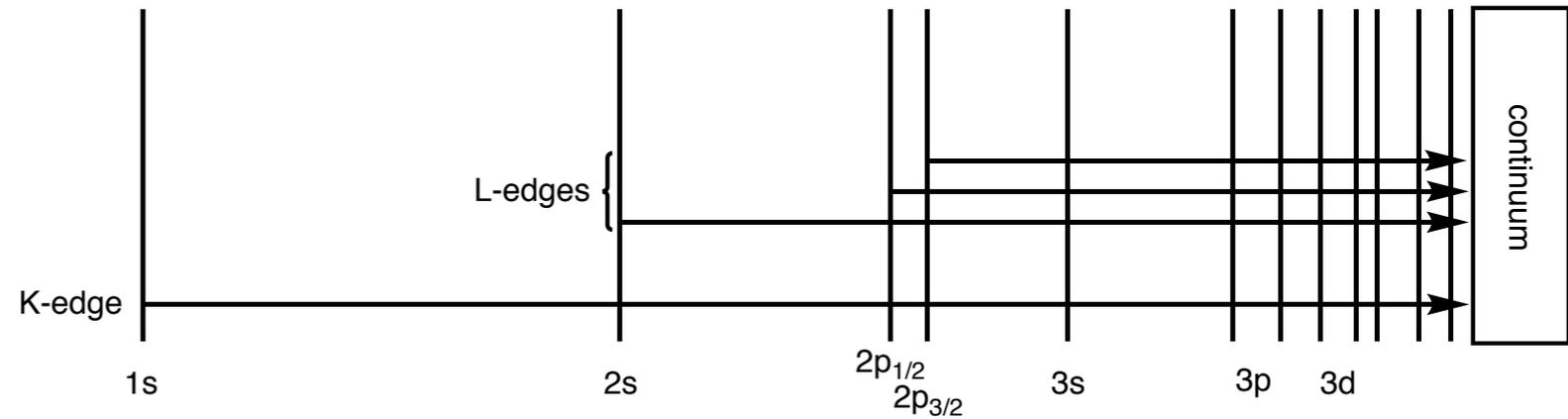
Synchrotron Radiation

Radiation that occurs when charged particles are accelerated in a curved path

$$P = \frac{2Ke^2}{3c^3} \left[\gamma^2 \frac{v^2}{r} \right]^2 = \frac{2Ke^2\gamma^4 v^4}{3c^3 r^2}$$

Edges in Core Spectroscopy

edge
core electron absorbs energy \geq binding energy



- **Pre-edge:** Excitation of core electron to bound state
- **EXAFS:** Photoelectron scattering interference patterns
- **Rising edge:** Mixture of transitions to bound states and near-edge scattering

transitions follow **selection rules**
 $\Delta L = 1, -1$
 $\Delta S = 0$

Synchrotron-based X-Ray Spectroscopy – A Primer

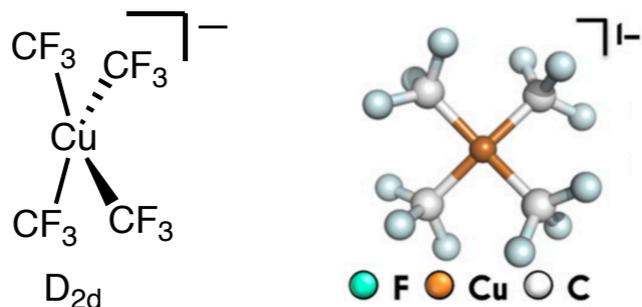
X-ray absorption spectroscopy

- **Metal K-Edge XAS:** Excitation from metal 1s.
 - Pre edge normally assigned as 1s - nd transitions (forbidden)
 - Ligand p orbital admixture raises intensity
- **Ligand K-Edge XAS:** Excitation from ligand 1s.
 - Excitations into ligand p orbital common (allowed)
 - Metal d-orbital admixture attenuates intensity
- **Metal L_{2,3}-Edge XAS:** Excitation from metal 2p.
 - Metal 2p → 3d transition allowed, attenuated by ligand p admixture
 - Yields two edges. Rel. inten. modulates by SO coupling/Auger effects.

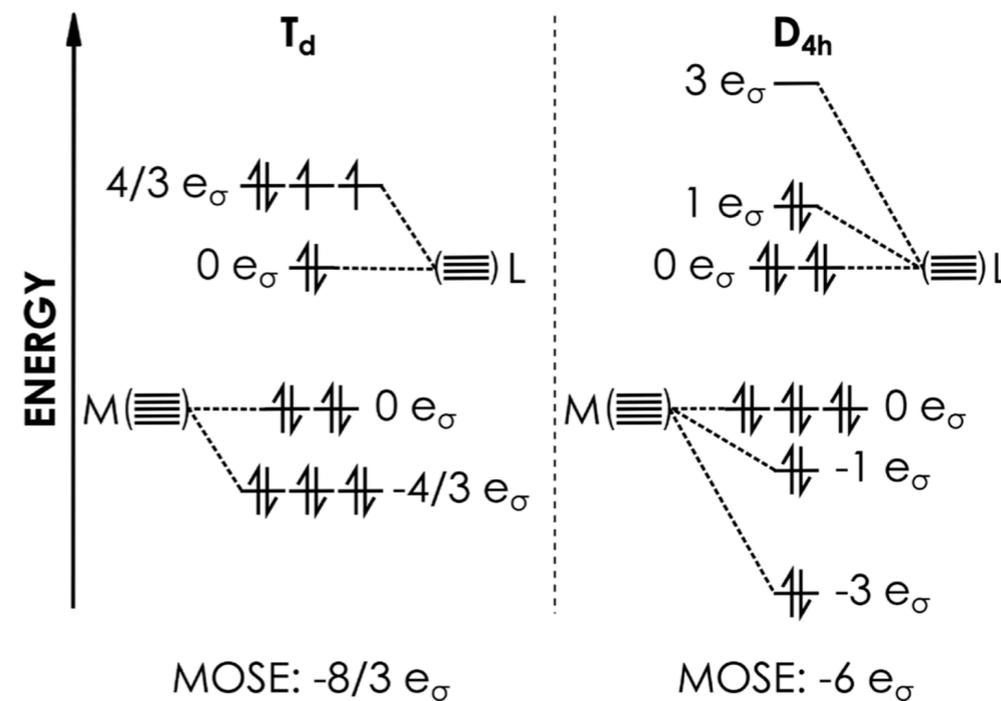
X-ray emission spectroscopy

- **K α XES:** Decay into 1s from 2p.
 - Two final 2p⁵ states yield two features (K α ₁ and K α ₂)
- **K β XES:** Decay into 1s from 3p.
 - Exchange interaction w/ unpaired 3d splits line (K β ' and K β _{1,3})
- **RIXS:** Excite w. energies that match transition to bound states and study temporal evolution of electronic state via emission.

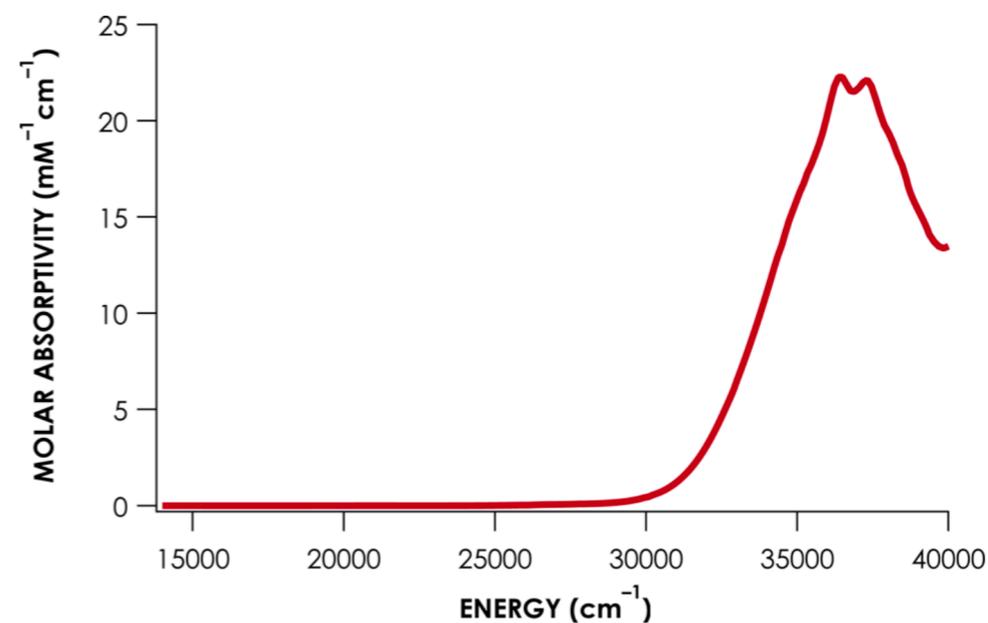
Experimental Verification of the IFL in $[\text{Cu}(\text{CF}_3)_4]^-$



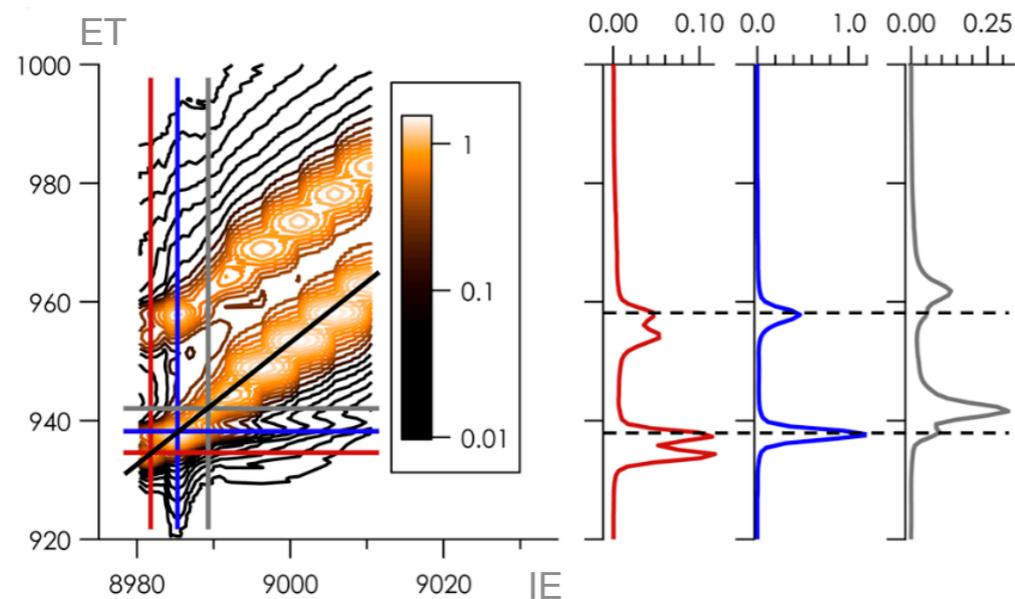
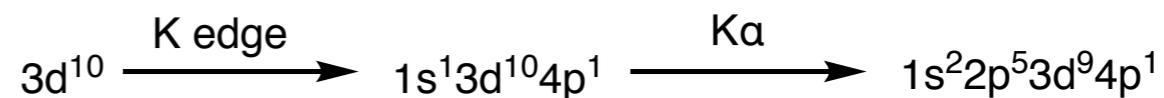
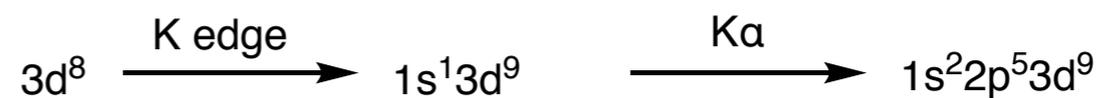
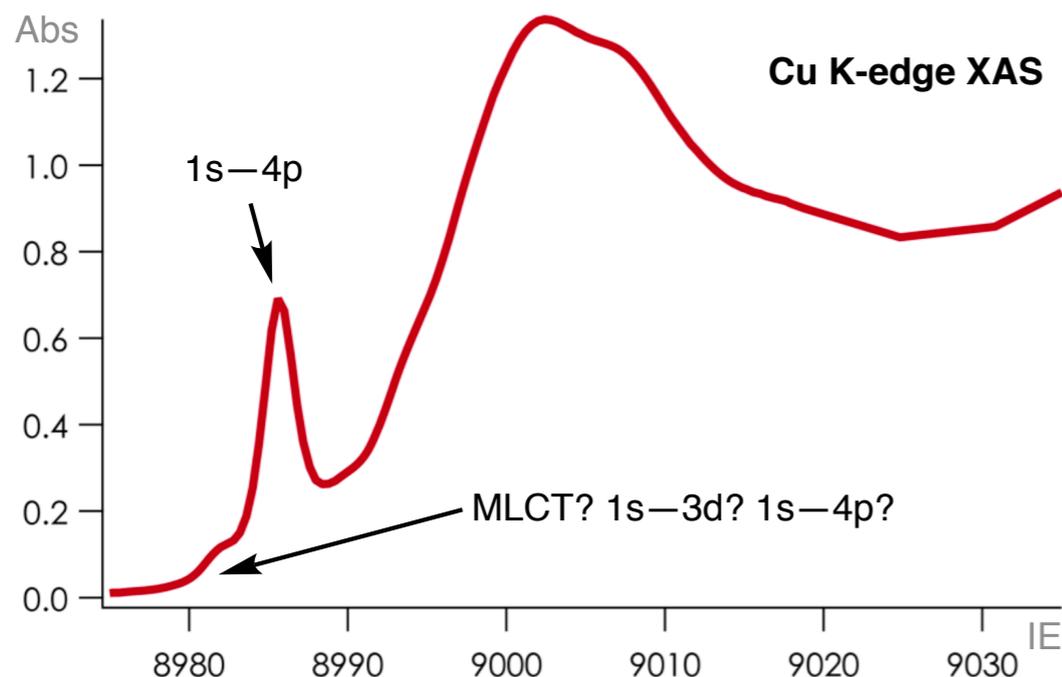
■ Inverted d^{10} favors D_{4h} over T_d in angular overlap approximations of MOs



- UV-vis should show d-d band in d^8 limit — not observed
- d—d band unlikely to be buried under CT band as this would imply a very large field splitting



Experimental Verification of the IFL in $[\text{Cu}(\text{CF}_3)_4]^-$

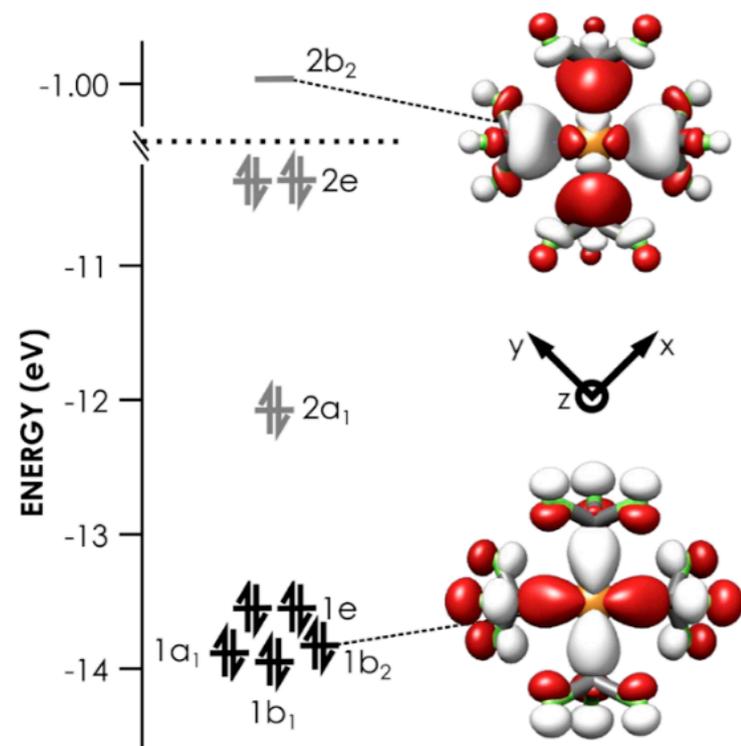


■ Cross peak observed for 8982 eV, results from concurrent 1s-4p excitation due to broad bandwidth

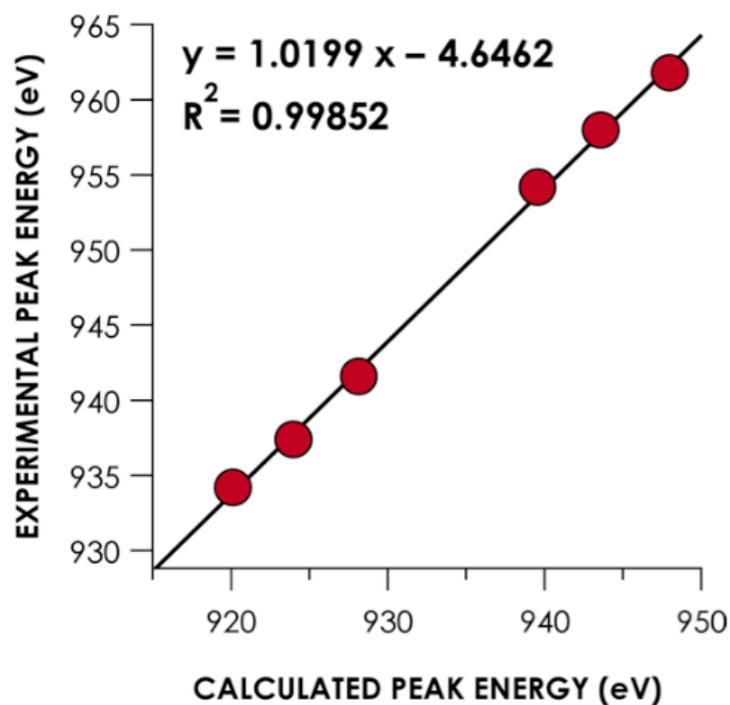
interorbital exchange interactions proportional to proximity of radial probability maxima (significant only for 2p-3d exchange)

Corrected peak at 8982 eV shows no cross peak, which excludes 1s-3d transition, and supports d^{10} assignment

Experimental Verification of the IFL in $[\text{Cu}(\text{CF}_3)_4]^-$

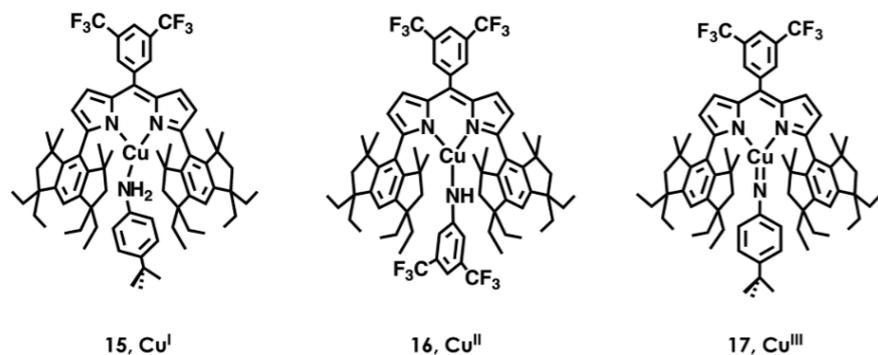
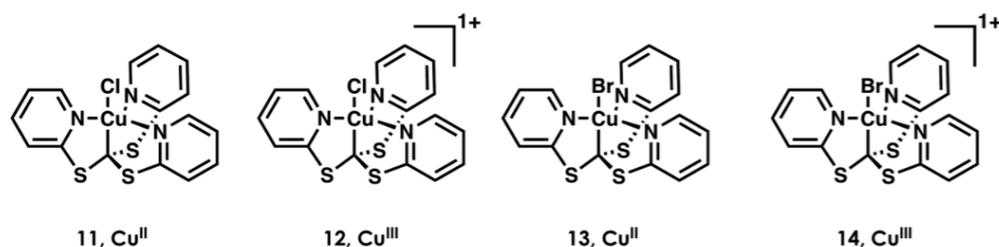
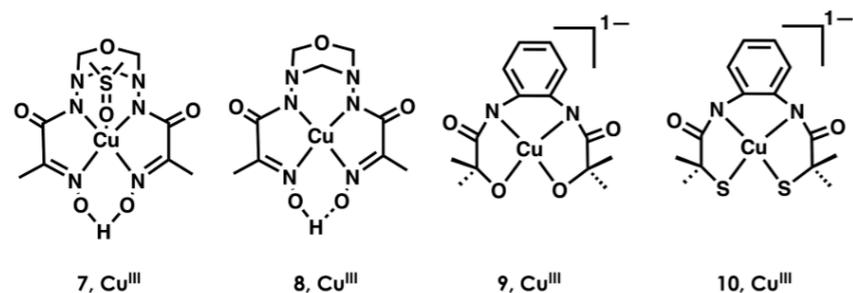
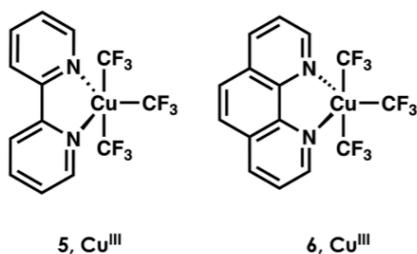
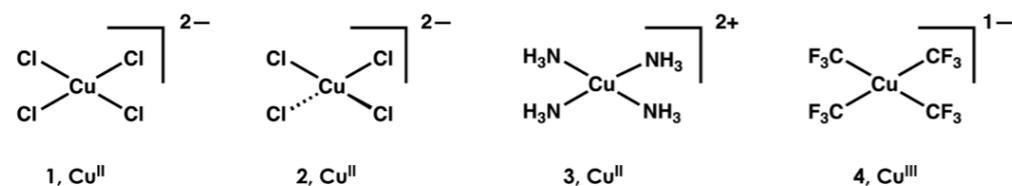


- Inverted d^{10} is predicted with all applied levels of theory
- Unoccupied $2b_2$ orbital is mostly of CF_3 character (% CF_3 = 58.9–63.8)
- No $d-d$ transition predicted (confirms UV–vis)
- K-edge XAS feature at 8982 eV identified as $1s-\text{CF}_3\sigma^*$, confirms other peak energies and assignments



TDDFT and ROCIS show high fidelity XAS transition estimation and allow for accurate designation of $L_{2,3}$ edge features in copper systems

The Myth of d^8 Copper(III)



■ Cu $L_{2,3}$ -edge XAS affords a direct means to estimate Cu 3d orbital contributions to vacant frontier MOs

■ $L_{2,3}$ main lines correspond to the $2p \rightarrow$ LUMO excitation

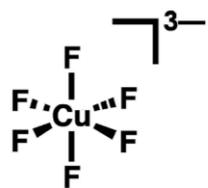
■ LUMO w/ ligand parentage disallows this transition ($\Delta L = 0$)

all Cu^{III} compounds show less than 50% d-character in LUMO

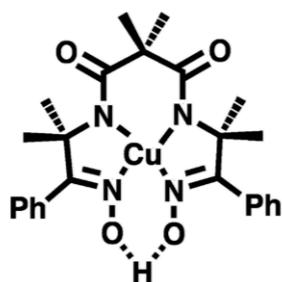


tell-tale sign of ligand field inversion and d^{10} configuration

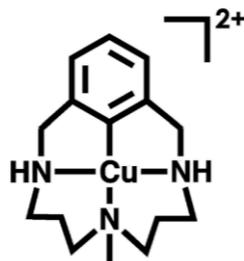
The Myth of d^8 Copper(III)



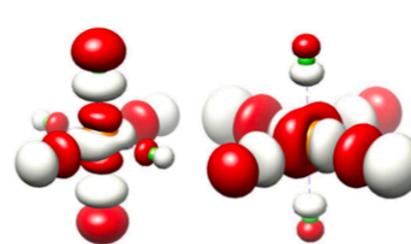
Klemm, 1955



Kruger, 1999



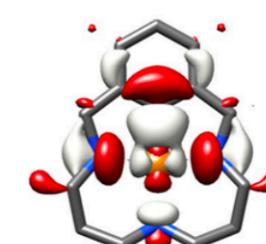
Stack, 2002



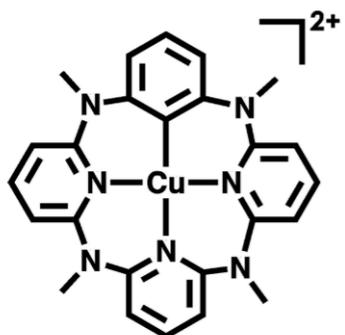
Klemm, 1955
61% Cu 3d



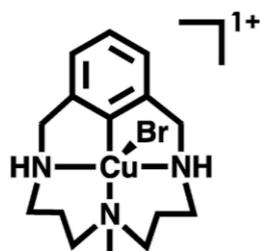
Kruger, 1998
41% Cu 3d



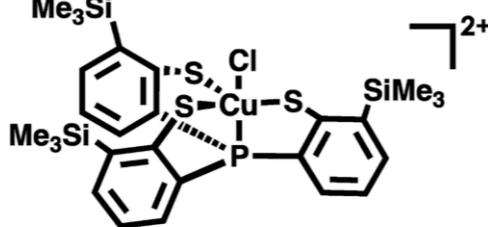
Stack, 2002
37% Cu 3d



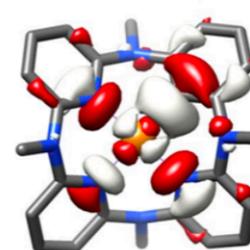
Wang, 2009



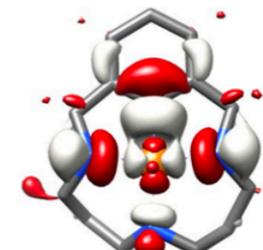
Ribas, 2010



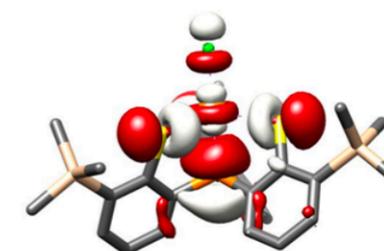
Lee, 2015



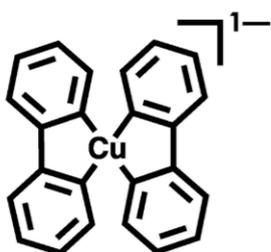
Wang, 2009
40% Cu 3d



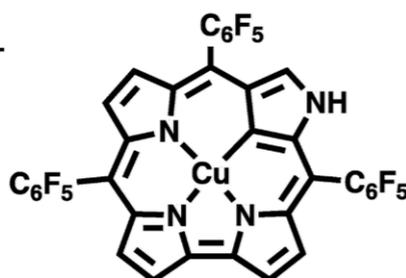
Ribas, 2010
35% Cu 3d



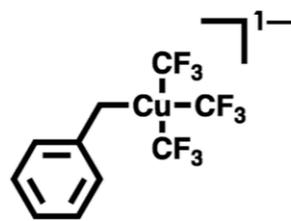
Lee, 2015
24% Cu 3d



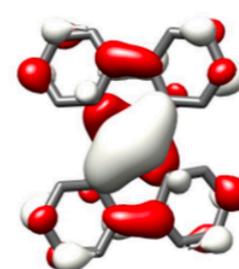
Xi, 2017



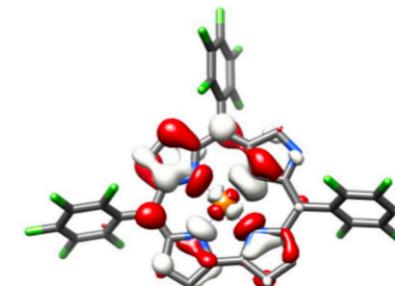
Furuta, 2018



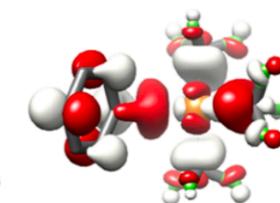
Liu, 2019



Xi, 2017
24% Cu 3d



Furuta, 2018
27% Cu 3d



Liu, 2019
26% Cu 3d

computational model can be applied to other formally copper(III) compounds

all except one show inverted ligand field

Outline of Talk

Bonding Models of Coordination Complexes and Their Pitfalls — What are Inverted Ligand Fields?

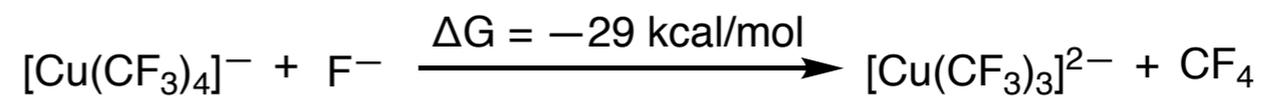
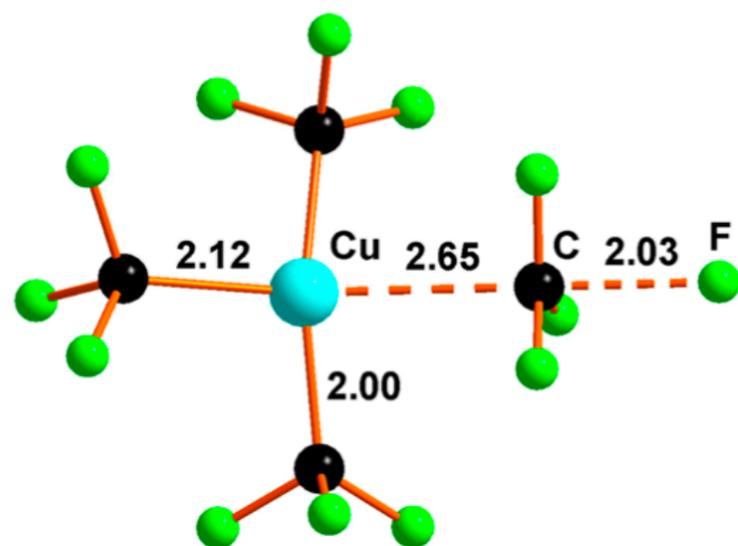
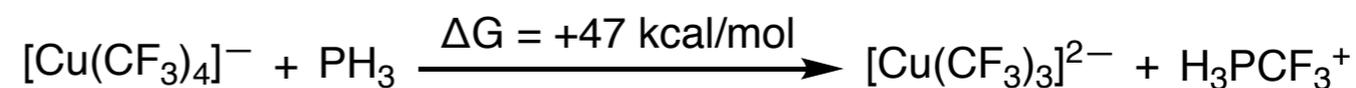
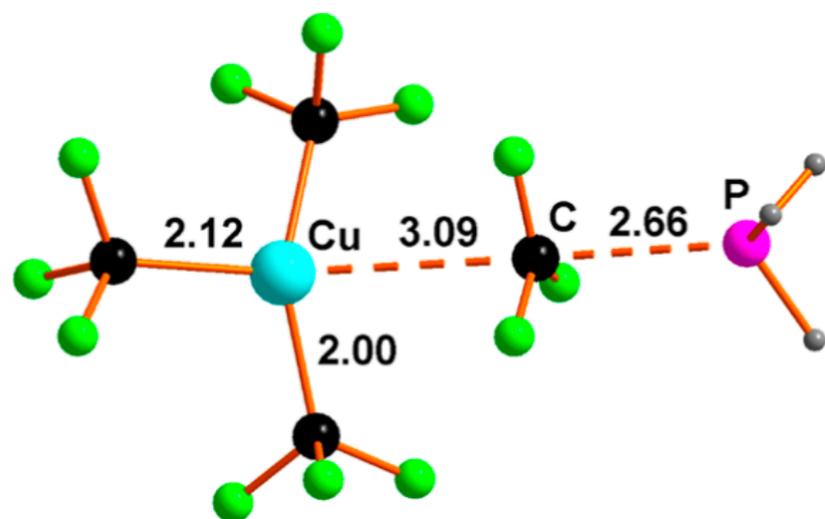
Early Experimental and Computational Evidence for Inverted Ligand Fields

Copper (III) Complexes — Theoretical and Experimental Analysis of their Electronic Structure

The Implications of Inverted Ligand Fields for Organometallic Complex Reactivity

Electrophilic Reactivity of $[\text{Cu}(\text{CF}_3)_4]^-$

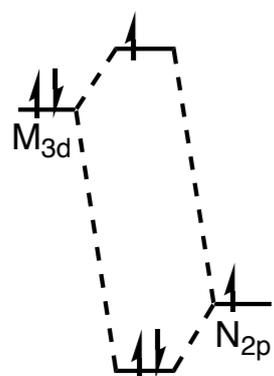
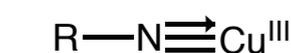
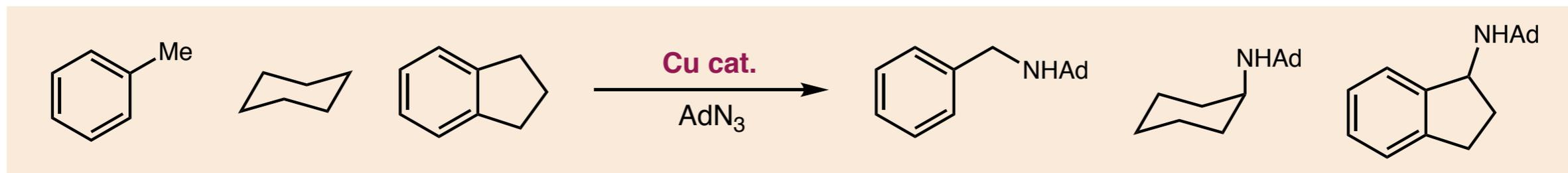
Some computation on $\text{S}_{\text{N}}2$ reactivity has been done:



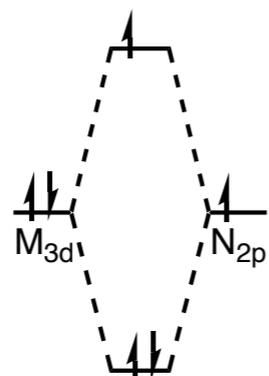
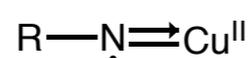
suffers from high activation energy ($\Delta G^\ddagger = +56 \text{ kcal/mol}$)

inverted field complexes as sources of electrophilic reactants is currently underexplored

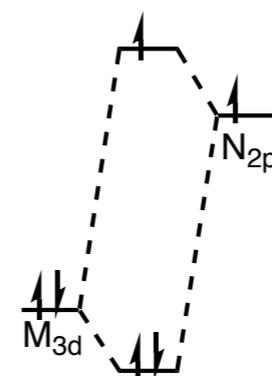
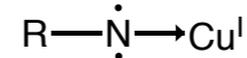
Impact on Copper-Catalyzed Nitrene Transfer



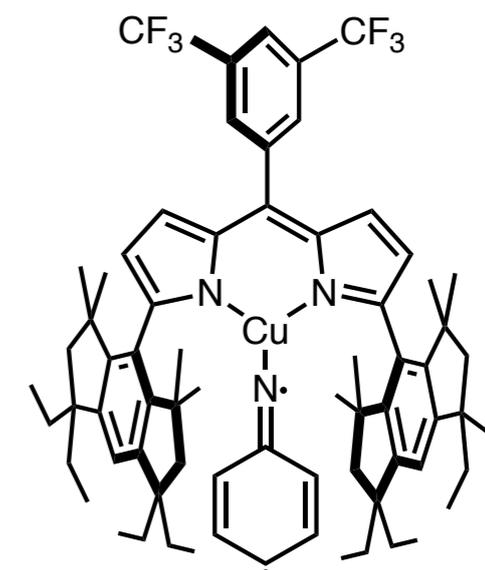
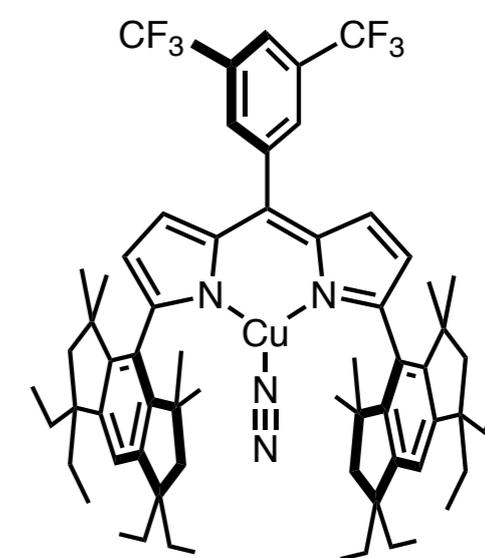
Imido (NR^{2-})



Iminyl (${}^2\text{NR}^-$)



Nitrene (${}^{1,3}\text{NR}$)



■ Crystal structure reveals dearomatized aryl moiety on nitrene

■ XAS points towards the hole being located on the nitrogen

■ Reactivity posited to stem from electron-deficient nitrogen

$\text{R}-\dot{\text{N}}:$
free nitrene

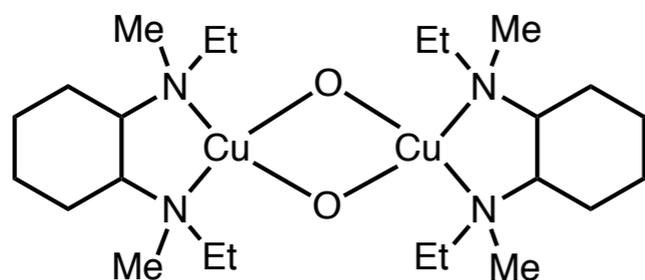
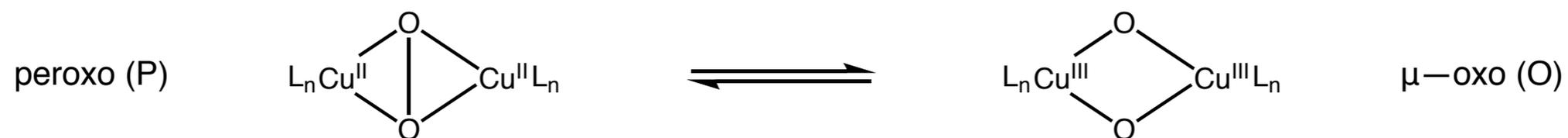
Peroxo-Bridged Dicopper(II) Complexes

Coupled binuclear copper (CBC) proteins: Bind dioxygen for a variety of biological functions

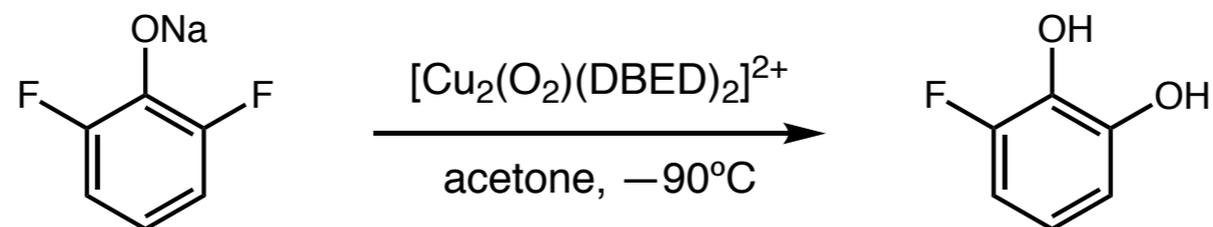
Hemocyanin

Catechol oxidase

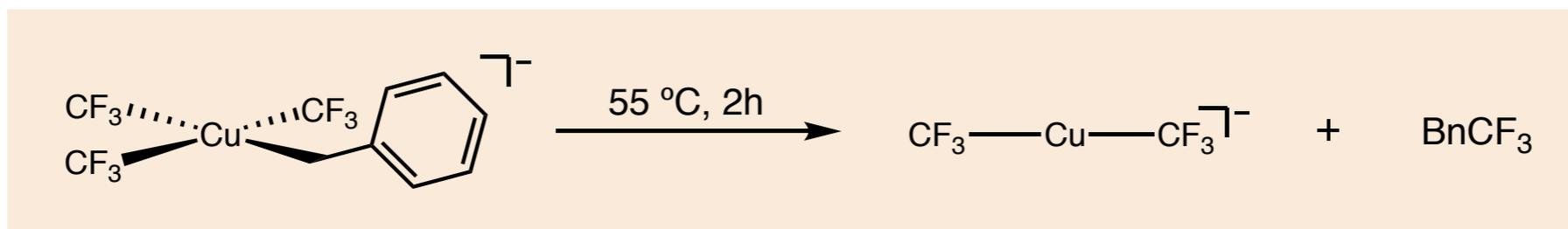
Tyrosinase



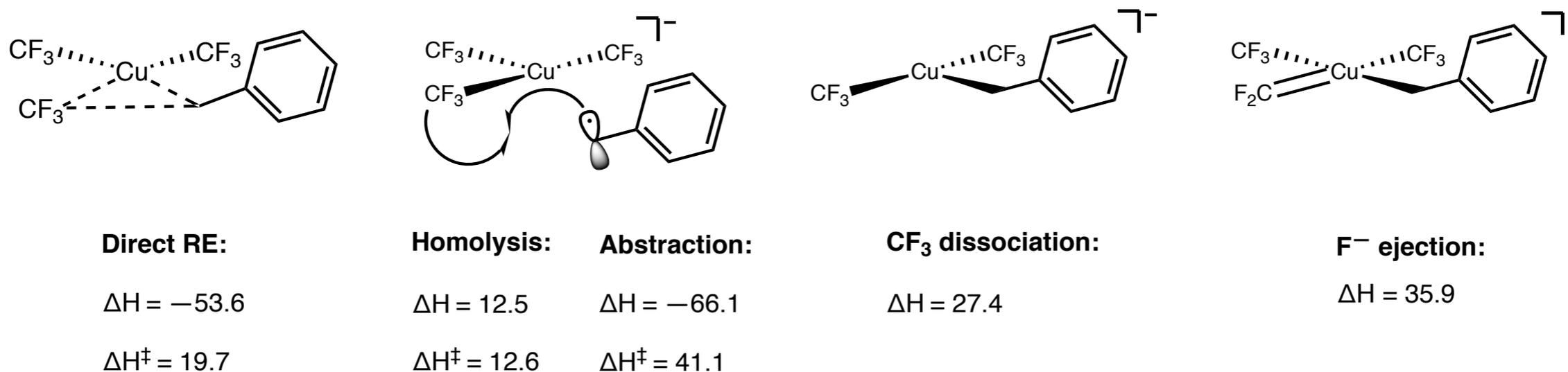
- $L_{2,3}$ -edge area reveals 40% Cu 3d-character in the SOMO
- Electron-deficient O^{2-} a highly oxidizing species that drives the reactivity of the complexes



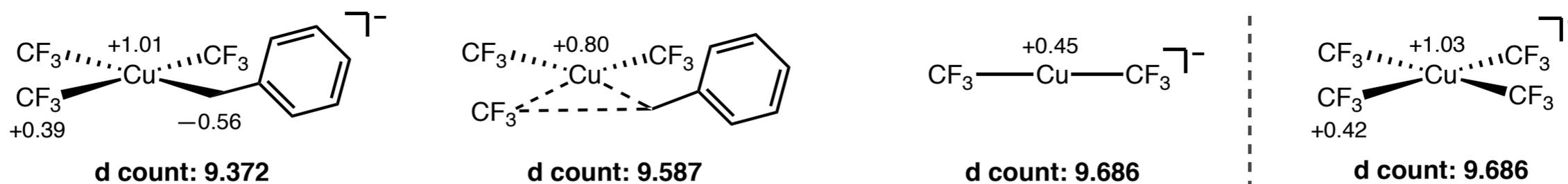
Impact on Reductive Elimination – Copper(III)



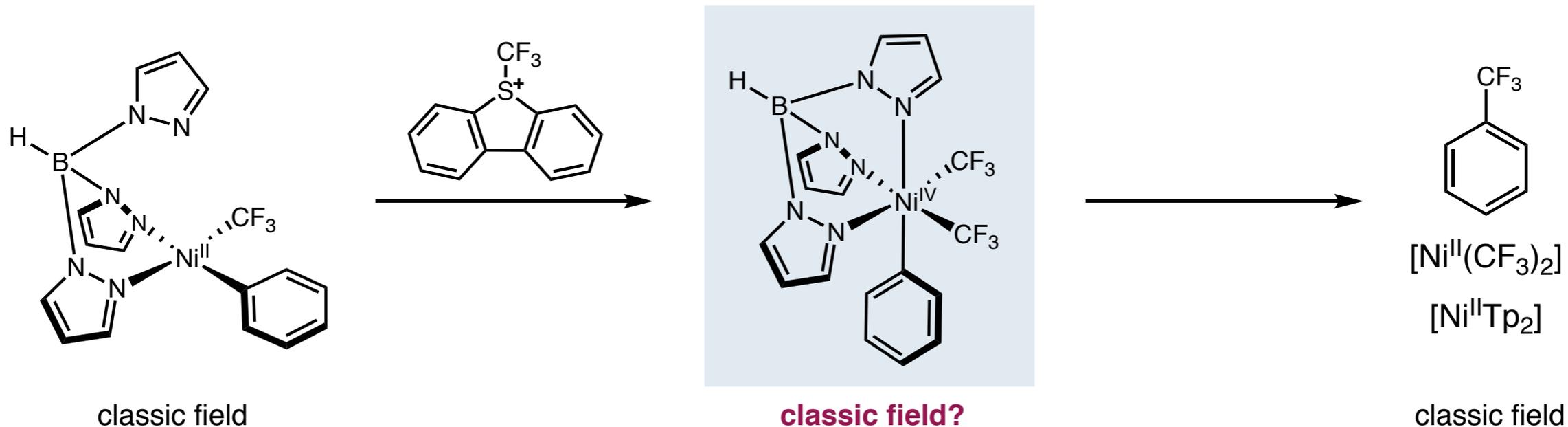
Possible Mechanisms



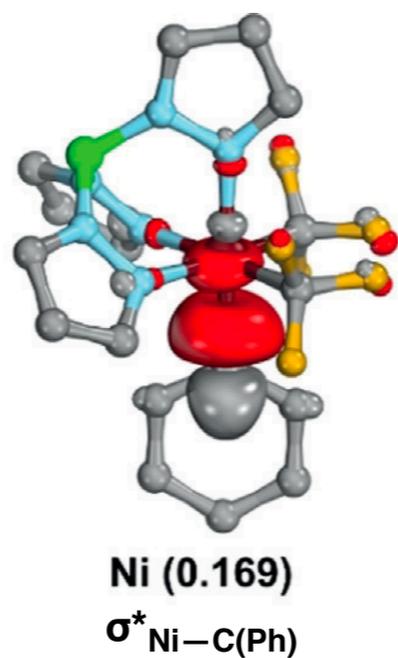
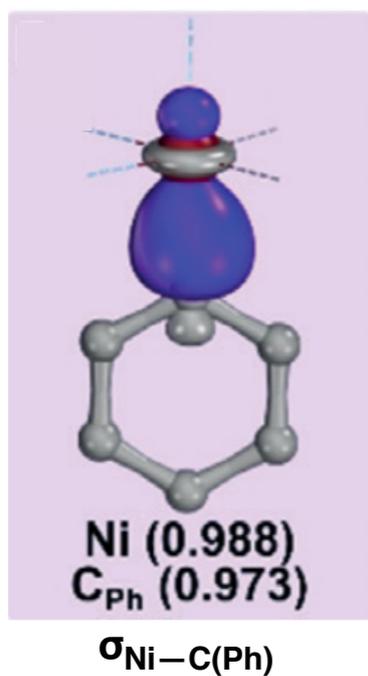
Population Analysis of Direct RE



Impact on Reductive Elimination – Nickel(IV)



Intrinsic Bond Orbitals (IBO)



- complex better described as Ni(II) w/ cationic aryl ligand
- cationic aryl conflicts with Hammett analysis ($\rho = -0.91$)
- e^- flow supports nucleophilic attack of CF_3^- on Ph^+
- TS shows Ni acting as LA activating π -system and interaction increases w/ electron-donating substituents

σ -noninnocence-induced masked aryl cation transfer

Outline of Talk

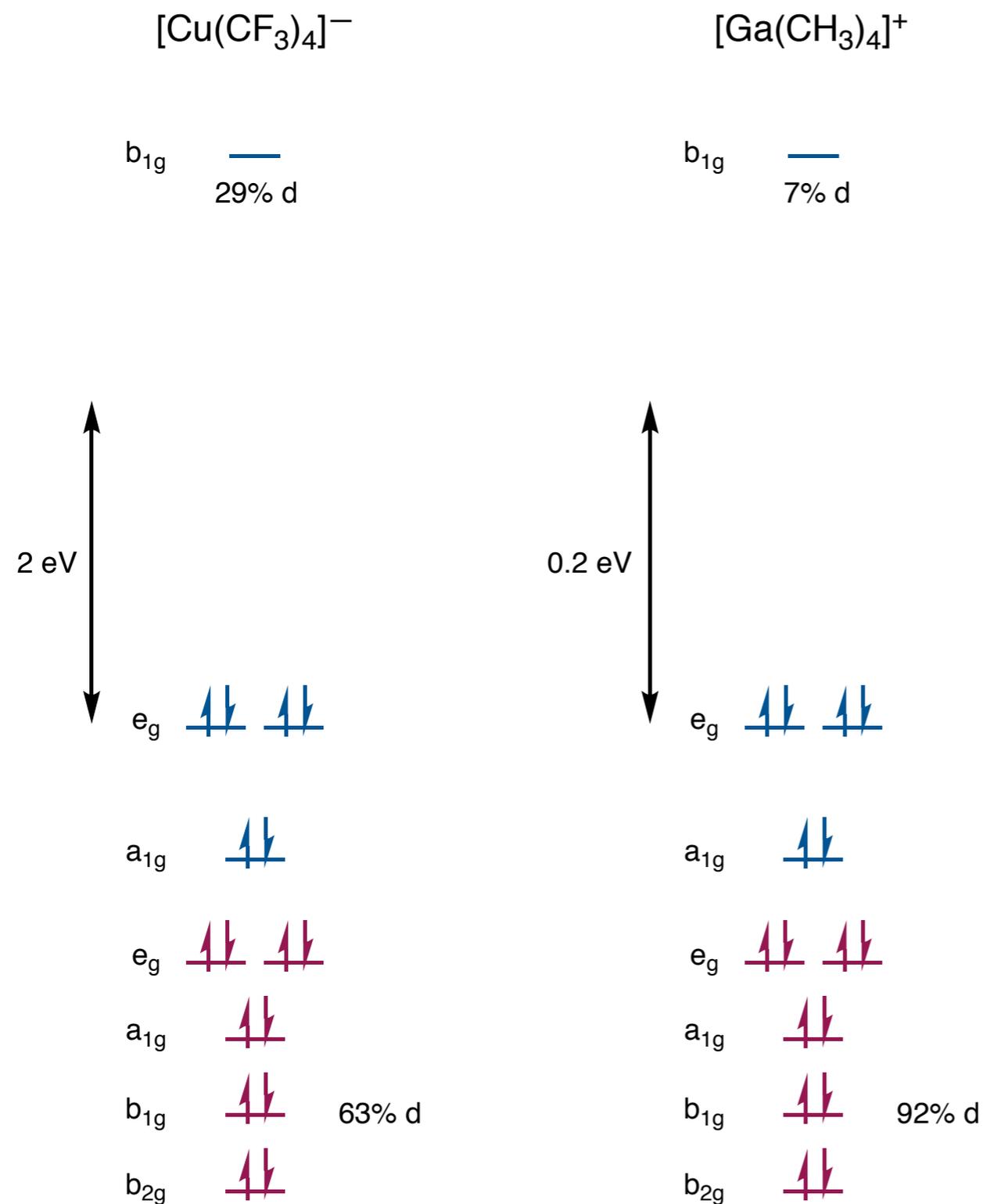
Bonding Models of Coordination Complexes and Their Pitfalls – What are Inverted Ligand Fields?

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Copper(III) — IFLs as Periodic Trend



- d-orbitals become contracted across a period
- main-group bonding treats d-orbitals as core orbitals
- transition-metal bonding treats d-orbitals as valence orbitals



IFLs reside at the transition of transition- and main-group bonding formalisms

Outline of Talk

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Questions?

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