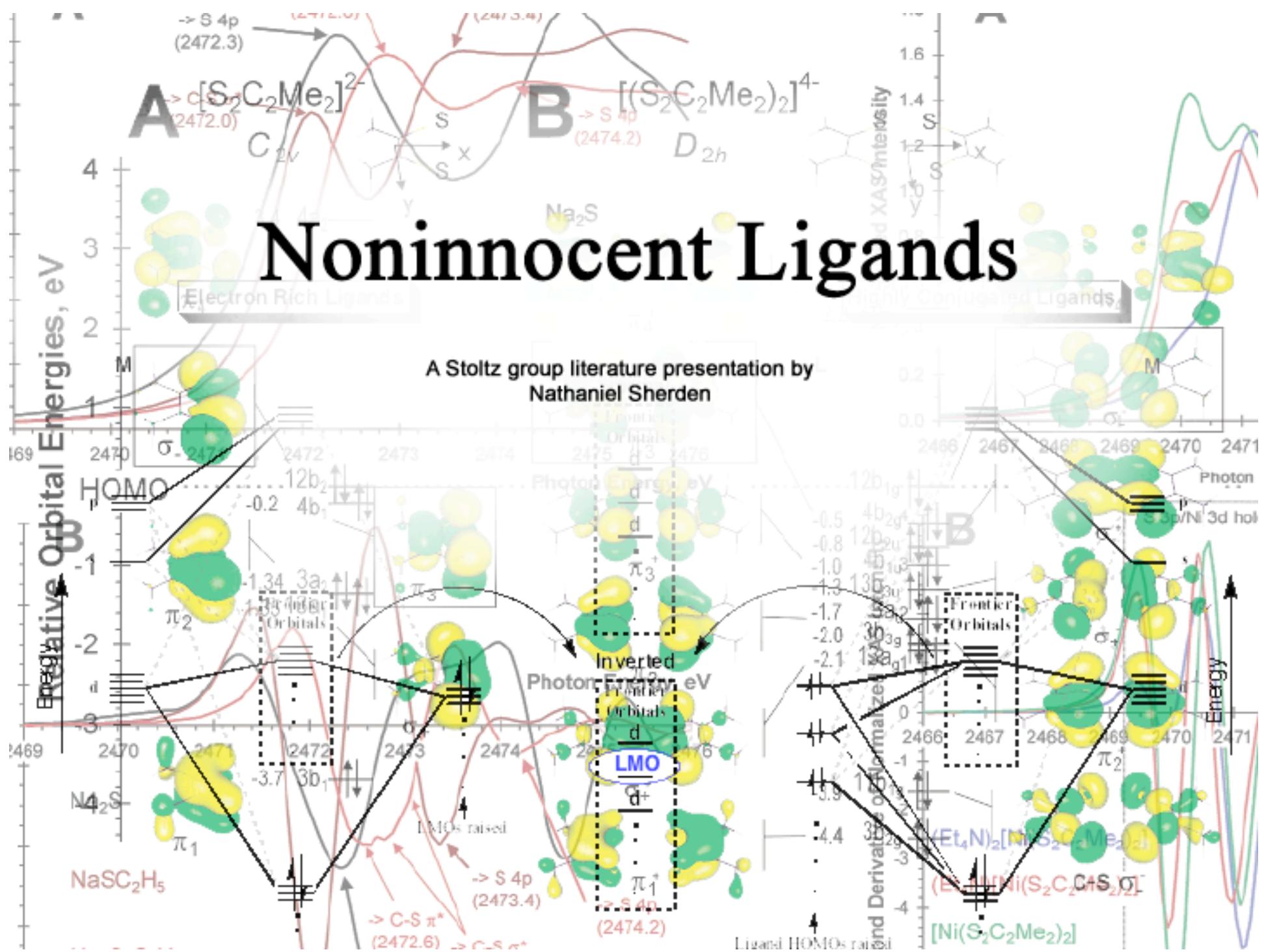


# Noninnocent Ligands

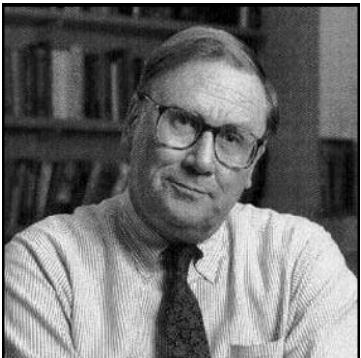


# ***Outline***

## **I. Introduction**

Noninnocence: an Illustrative Example  
Understanding Noninnocence  
Remedying a Misconception  
Trends and Examples

## **II. Determining noninnocence and electronic structure**



**Richard H. Holm**  
*Harvard*

Magnetism  
- *Magnetic susceptibility*  
- *SQUID*  
Structural Geometry  
Spectroscopy + DFT  
Advanced Methods  
- *ESR / EPR*  
- *MCD*



**Dr. Frank Neese**  
*Max-Plank-Institut*

## **IV. Application / Potential**

In Biology  
Nonsynthetic Applications  
Synthetic Applications

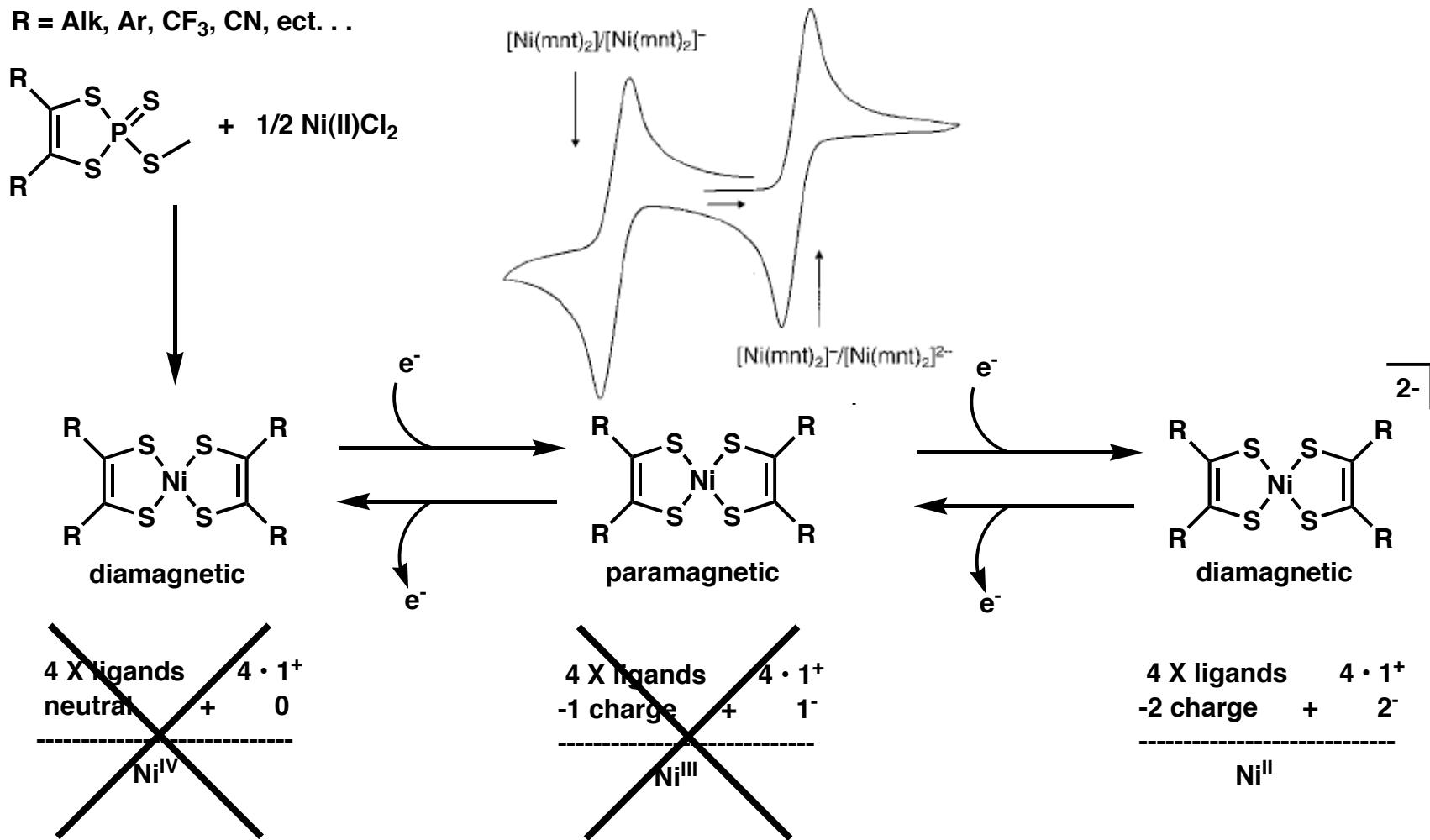
## **Review**

Butin KP, Beloglazkina YK, Zyk NV  
Metal complexes with non-innocent ligands  
USPEKHI KHMII 74 (6): 585-609 2005

## Noninnocence: an Illustrative Example

( No one can tell you what noninnocence is. You must see it for yourself. . . )

$R = \text{Alk, Ar, CF}_3, \text{CN, ect. . .}$



**All three complexes are actually nickel (II)**

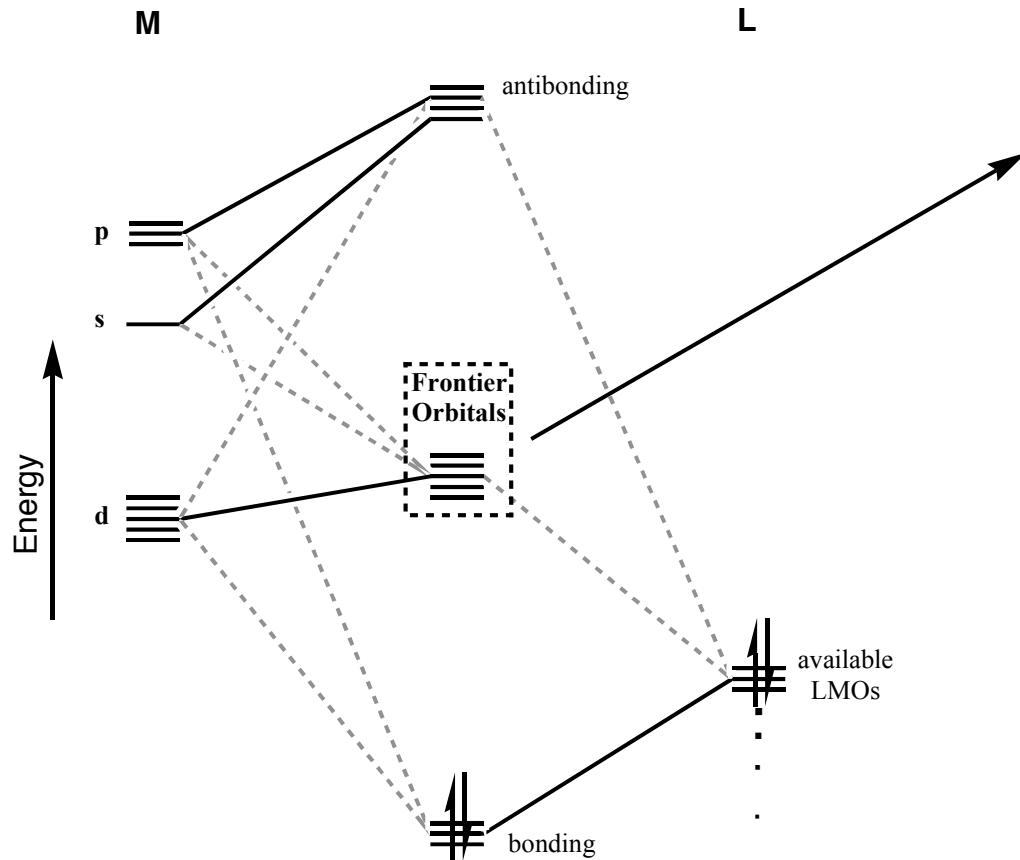
Schauzer, G. N.; Mayweg, V. P.; *J. Am. Chem. Soc.*, **1965**, 87, 1483-1489.

Lim, B. S.; Fomitchev, D. V.; Holm, R. H.; *Inorg. Chem.*, **2001**, 40, 4257-4262.

Wang, K.; Stiefel, E. I; *Science.*, **2001**, 291, 106-109.

# Understanding Noninnocence

## Generalized Classical Metal Bonding



## Some Classical Frontier Orbitals

### Tetrahedral

|       |                                |                                    |           |       |
|-------|--------------------------------|------------------------------------|-----------|-------|
| (nb)* | <u>xy</u>                      | <u>xz</u>                          | <u>yz</u> | $t_2$ |
| nb    | <u><u><math>z^2</math></u></u> | <u><u><math>x^2-y^2</math></u></u> |           | $e$   |

### Octahedral

|            |                                |                                    |           |
|------------|--------------------------------|------------------------------------|-----------|
| $\sigma^*$ | <u><u><math>z^2</math></u></u> | <u><u><math>x^2-y^2</math></u></u> | $e_g$     |
| nb         | <u>xy</u>                      | <u>xz</u>                          | <u>yz</u> |

$t_{2g}$

### Trigonal Bipyramidal

|            |                                |                             |
|------------|--------------------------------|-----------------------------|
| $\sigma^*$ | <u><u><math>z^2</math></u></u> | $a_1'$                      |
| (nb)*      | <u>xy</u>                      | <u><math>x^2-y^2</math></u> |
| nb         | <u>xz</u>                      | <u>yz</u>                   |

$e'$

### Square Planar

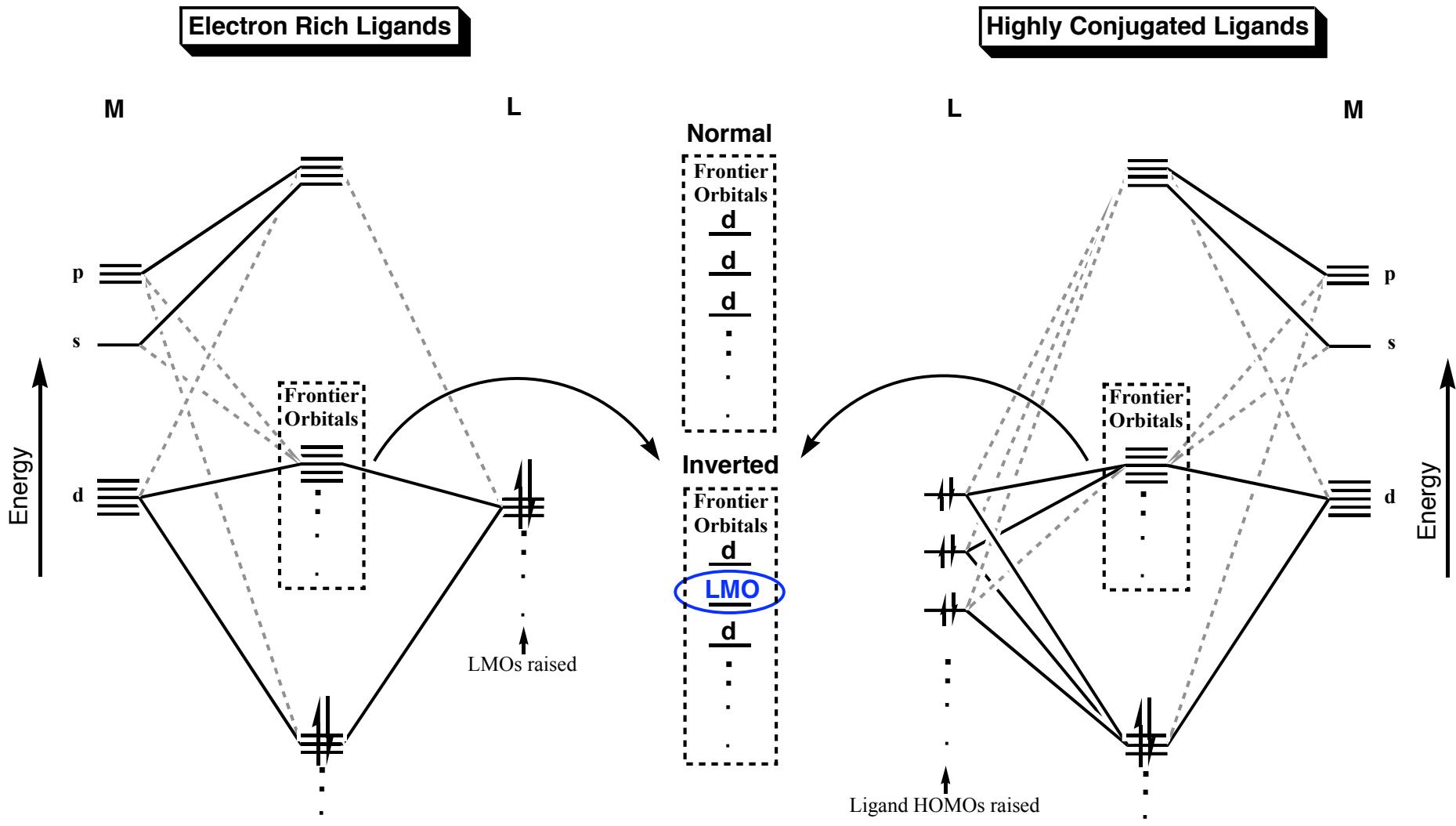
|            |                                    |                               |
|------------|------------------------------------|-------------------------------|
| $\sigma^*$ | <u><u><math>x^2-y^2</math></u></u> | $b_{1g}$                      |
| (nb)*      | <u><u><math>z^2</math></u></u>     | $a_{1g}$                      |
| nb         | <u><u><math>xz</math></u></u>      | <u><u><math>yz</math></u></u> |

$e_{1g}$

$b_{2g}$

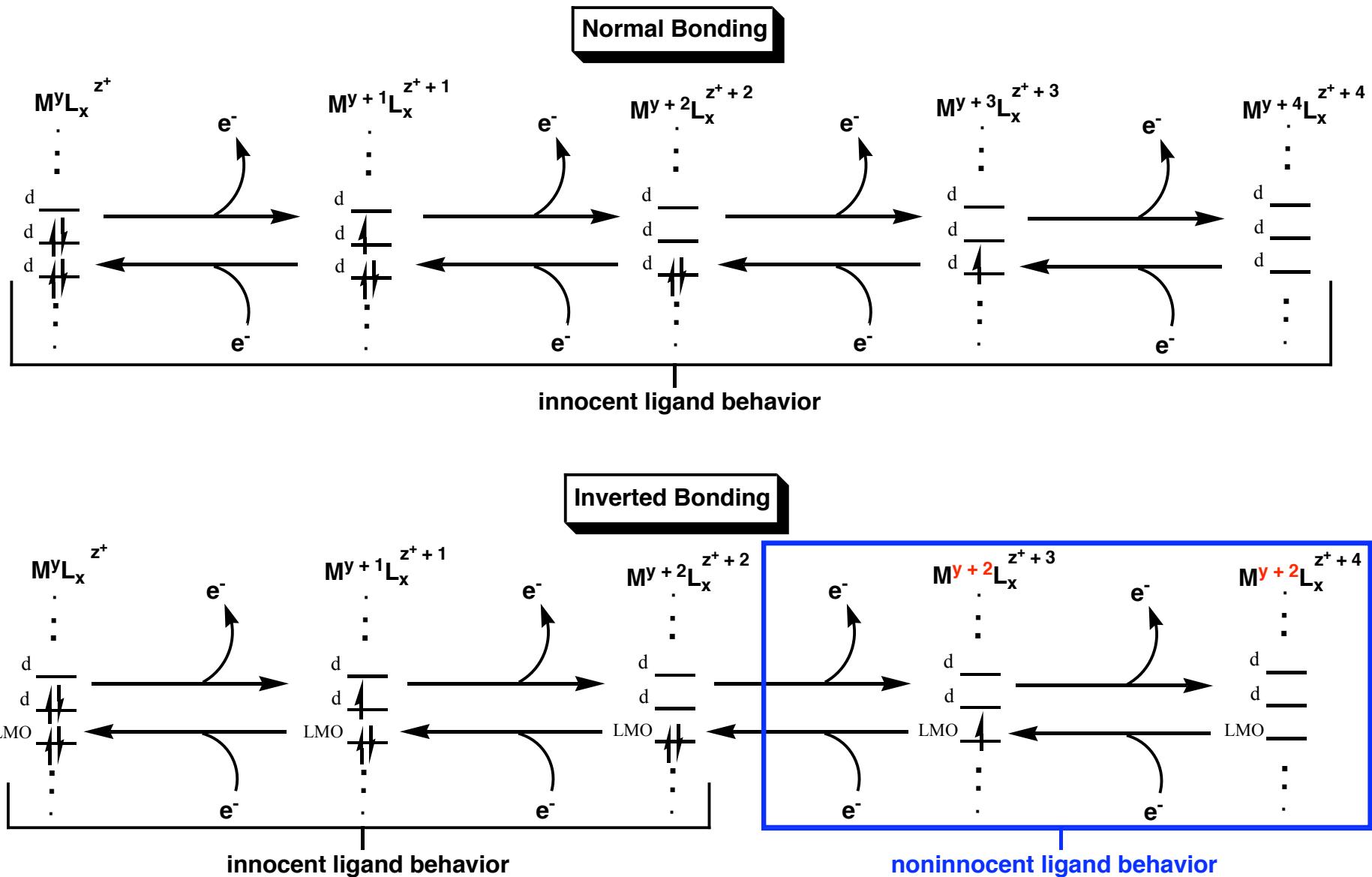
The metal frontier orbitals are a mixture of weakly bonding, nonbonding, and weakly antibonding orbitals. In classic metal complexes the character of these orbitals is almost entirely composed of the metal d set with very little ligand contribution. Practically all of a metal complex's chemistry takes place using these orbitals.

# *Understanding Noninnocence*



Szilagyi, S. K.; Lim, B. S.; Glaser, T.; Holm, R. H.; Hedman, B.; Hodgson, K. O.; Solomon, E. I.; *J. Am. Chem. Soc.*, **2003**, *135*, 9158.  
Spessard G. O.; Miessler G. L.; *Organometallic Chemistry*, Prentice-Hall Inc., **2000**.

# Understanding Noninnocence



## ***Remedying a Misconception***

There is **NO** group of ligands that are noninnocent. Rather noninnocence is a state that potentially any ligand can belong to under the right conditions. When a ligand is behaving in a noninnocent fashion it is said to be a noninnocent ligand, but this in no way implies that the ligand is always a non innocent ligand, is a non innocent ligand in any other systems, or even that it necessarily shares any similarity to or should be grouped electronically or chemically with any other ligands that also demonstrate noninnocence.

**Incorrect: Corrole is a noninnocent ligand.**

**Correct: In this system corrole is a noninnocent ligand.**

**Correct: Corrole is often a noninnocent ligand.**

**Correct: I like noninnocent ligands.**

**Incorrect: I like noninnocent ligands, like corrole.**

## ***Trends and Examples***

### **Metal Trends**

#### **Potential Metal Candidates**

|                  |           |           |           |                  |           |           |           |           |           |
|------------------|-----------|-----------|-----------|------------------|-----------|-----------|-----------|-----------|-----------|
| Sc<br>1.3        | Ti<br>1.5 | V<br>1.6  | Cr<br>1.6 | Mn<br>1.5        | Fe<br>1.8 | Co<br>1.9 | Ni<br>1.9 | Cu<br>1.9 | Zn<br>1.6 |
| Y<br>1.2         | Zr<br>1.4 | Nb<br>1.6 | Mo<br>1.8 | Tc<br>1.9        | Ru<br>2.2 | Rh<br>2.2 | Pd<br>2.2 | Ag<br>1.9 | Cd<br>1.7 |
| La-Lu<br>1.0-1.2 | Hf<br>1.3 | Ta<br>1.5 | W<br>1.7  | Re<br>1.9        | Os<br>2.2 | Ir<br>2.2 | Pt<br>2.2 | Au<br>2.4 | Hg<br>1.9 |
| Ac<br>1.1        | Th<br>1.3 | Pa<br>1.4 | U<br>1.4  | Np-No<br>1.4-1.3 |           |           |           |           |           |

**Electrostatic availability**

#### **System availability**

|                  |           |           |           |                  |           |           |           |           |           |
|------------------|-----------|-----------|-----------|------------------|-----------|-----------|-----------|-----------|-----------|
| Sc<br>1.3        | Ti<br>1.5 | V<br>1.6  | Cr<br>1.6 | Mn<br>1.5        | Fe<br>1.8 | Co<br>1.9 | Ni<br>1.9 | Cu<br>1.9 | Zn<br>1.6 |
| Y<br>1.2         | Zr<br>1.4 | Nb<br>1.6 | Mo<br>1.8 | Tc<br>1.9        | Ru<br>2.2 | Rh<br>2.2 | Pd<br>2.2 | Ag<br>1.9 | Cd<br>1.7 |
| La-Lu<br>1.0-1.2 | Hf<br>1.3 | Ta<br>1.5 | W<br>1.7  | Re<br>1.9        | Os<br>2.2 | Ir<br>2.2 | Pt<br>2.2 | Au<br>2.4 | Hg<br>1.9 |
| Ac<br>1.1        | Th<br>1.3 | Pa<br>1.4 | U<br>1.4  | Np-No<br>1.4-1.3 |           |           |           |           |           |

**Metal availability**

### **Ligand Trends**

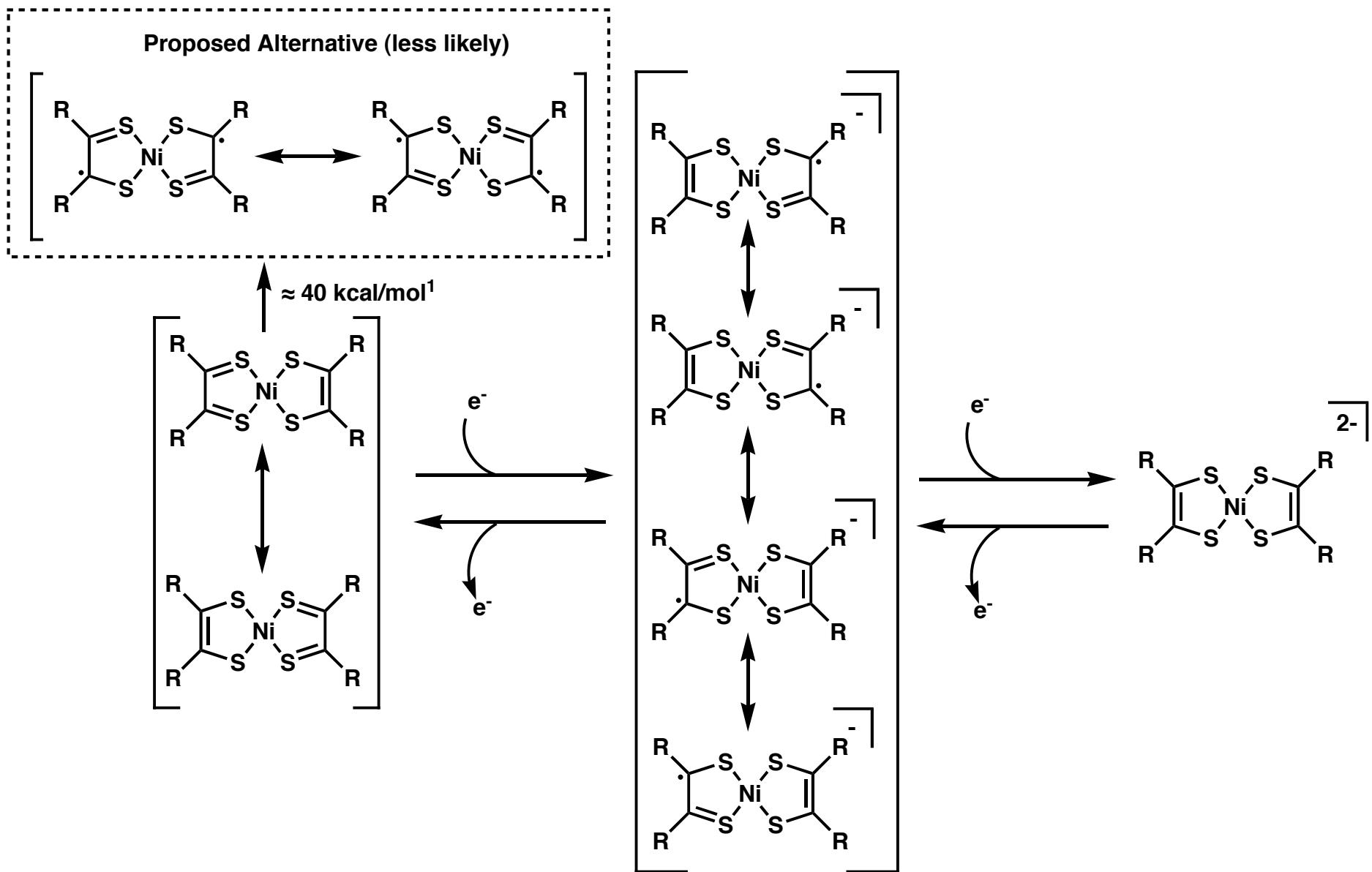
#### **Larger atoms in contact with the metal (P, S, ect...)**

- Larger Atoms have orbitals closer in size to metal orbitals
- Larger Atoms have orbitals closer in energy to the metal orbitals
- Larger Atoms are less electronegative (more electron rich)
- Larger Atoms can back bond through their sigma framework

#### **Conjugation / Aromaticity**

- $\pi^*$  orbitals allow for potent back bonding
- raises some of the ligand HOMOs to be closer to the metal orbitals in energy.

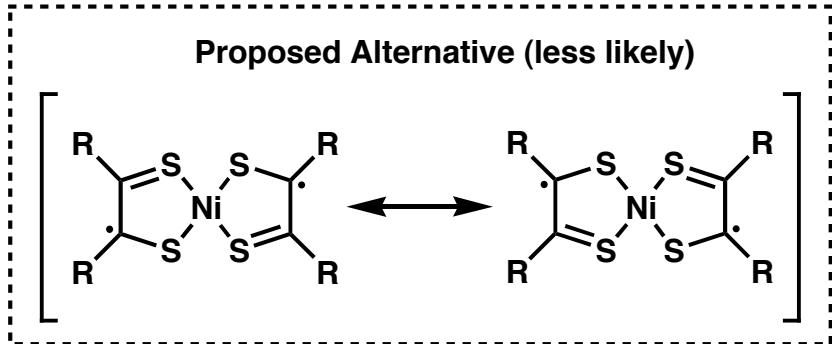
## Trends and Examples



1) Lim, B. S.; Fomitchev, D. V.; Holm, R. H.; *Inorg. Chem.*, **2001**, *40*, 4247-4262.

Szilagyi, S. K.; Lim, B. S.; Glaser, T.; Holm, R. H.; Hedman, B.; Hodgson, K. O.; Solomon, E. I.; *J. Am. Chem. Soc.*, **2003**, *135*, 9158.

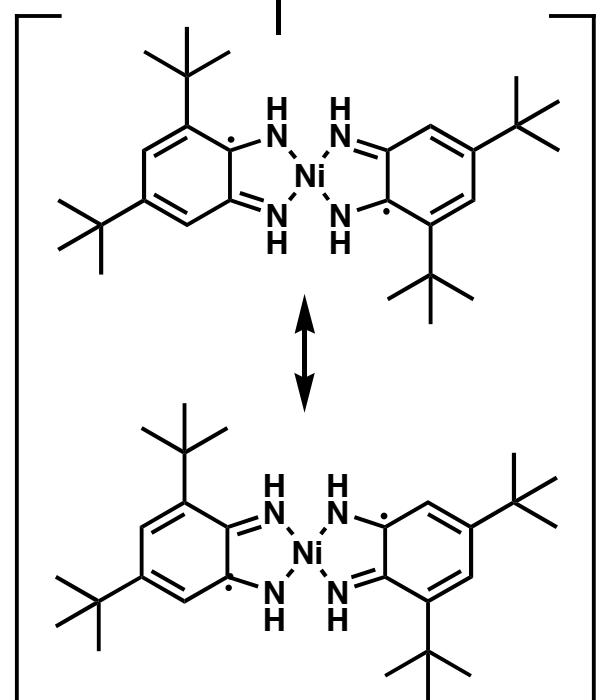
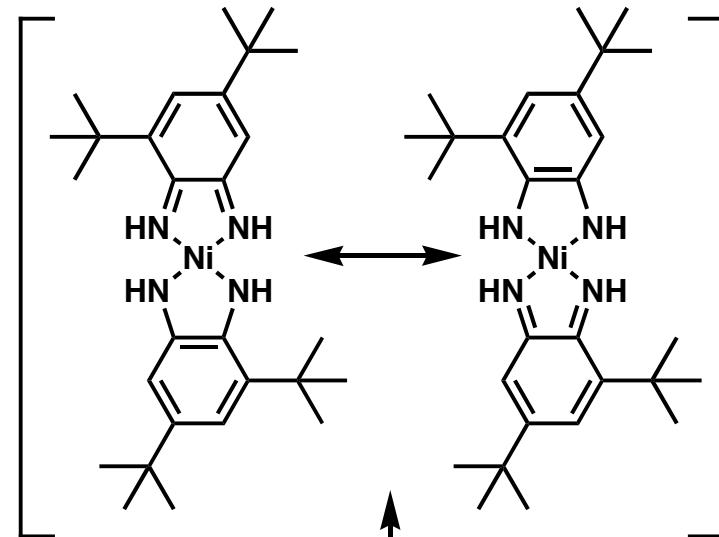
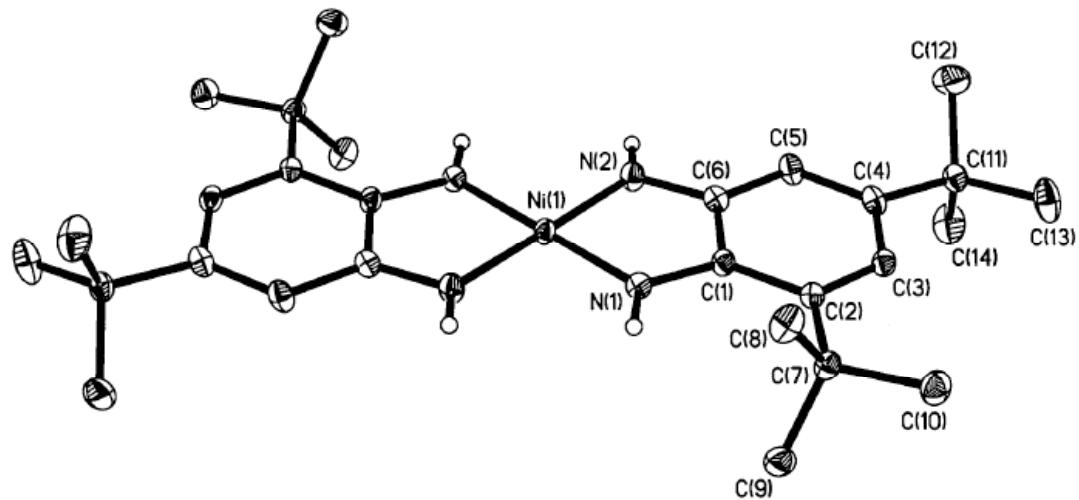
## Trends and Examples



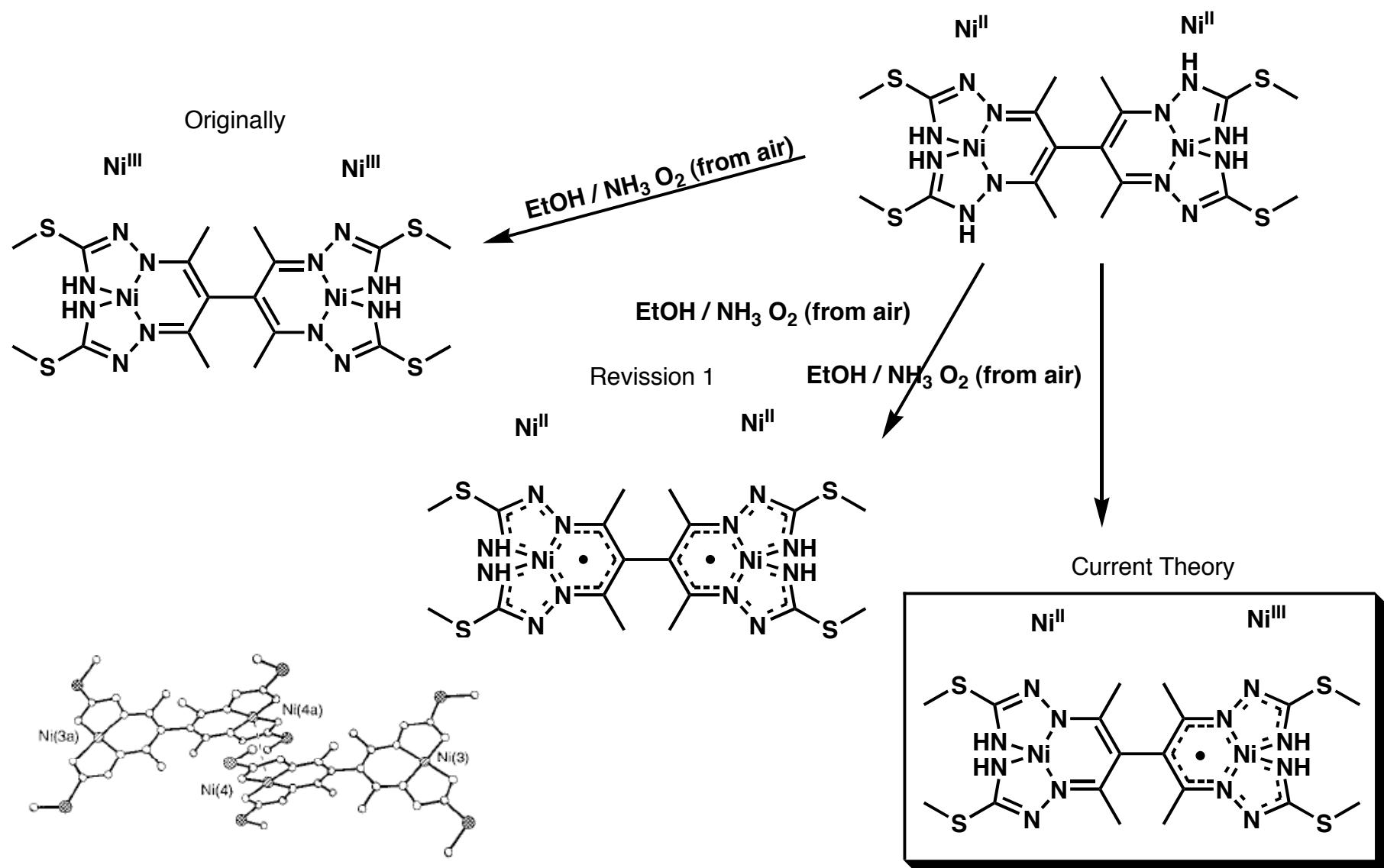
### Some Bond lengths

|       |          |       |          |
|-------|----------|-------|----------|
| Ni-N1 | 1.822(4) | C1-C6 | 1.429(6) |
| Ni-N2 | 1.826(4) | C1-C2 | 1.435(6) |
| N1-C1 | 1.356(5) | C2-C3 | 1.386(6) |
| N2-C6 | 1.347(5) | C3-C4 | 1.423(6) |
| C5-C6 | 1.415(6) | C4-C5 | 1.379(6) |

### Diamagnetic Nickel(II)



## Trends and Examples



Arion, V. B.; Gerbeleu, N. V.; Levitsky, V. G.; Simonov, Y. A.; Dvorkin, A. A.; Bourosh, P. N.; *J. Chme. Soc., Dalton Trans.*, 1994, 1913-1961.

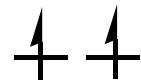
Arion, V.; Weighardt, K.; Weyhermueller, T.; Bill, E.; Leovac, V.; Rufinska, A.; *Inorg. Chem.*, 1997, 36, 661-669.

# Magnetism Explained in 5 Minuets or Bust

## Basic Localized Paramagnetism

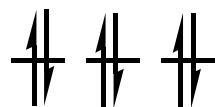
Paramagnetism is a term that refers to molecules with one or more unpaired electrons. Many metal containing complexes are paramagnetic. It is important to realize that high symmetry in metal complexes coupled with frontier orbitals that are often close in energy allows many metal complexes to have multiple unpaired electrons and also can cause metal complexes with an even over all electron count to be highly paramagnetic.

EX:



Ni<sup>II</sup>    d<sup>8</sup>

$$\sqrt{[3k\chi_m T] / (L\mu_0\mu_b^2)} = 0.7977\sqrt{(\chi_m T)} = \mu_{\text{eff}} = \sqrt{[n(n+2)]} = \mu_s$$



[Ni(en)<sub>3</sub>]<sup>2+</sup>

EX: VCl<sub>4</sub>(MeCN)<sub>2</sub> is d<sup>1</sup>  $\Rightarrow \sqrt{[1e^-(1e^-+2)]} = 1.73 \mu_b$   
observed = 1.77  $\mu_b$

## Complications

### Orbital Angular Momentum

$$\mu_{\text{eff}} = \sqrt{[S(S+2) + L(L+1)]} = \mu_s + \mu_L$$

where L is the orbital angular momentum

Magnetic effects from orbital angular momentum requires degeneracy such that the partially occupied orbital(s) in question can be transformed by symmetry elements into other vacant orbitals of identical energy.

### Spin-orbit coupling.

$$\mu_{\text{eff}} = (1 - \alpha\lambda / \Delta)\mu_s$$

$\alpha, \lambda, \Delta$  are composed of constants from various look up tables

Contributions are small in first row transition metals (only).

## A Quick Approximation

$$\lambda > 0 \text{ for } d^1 - d^4$$

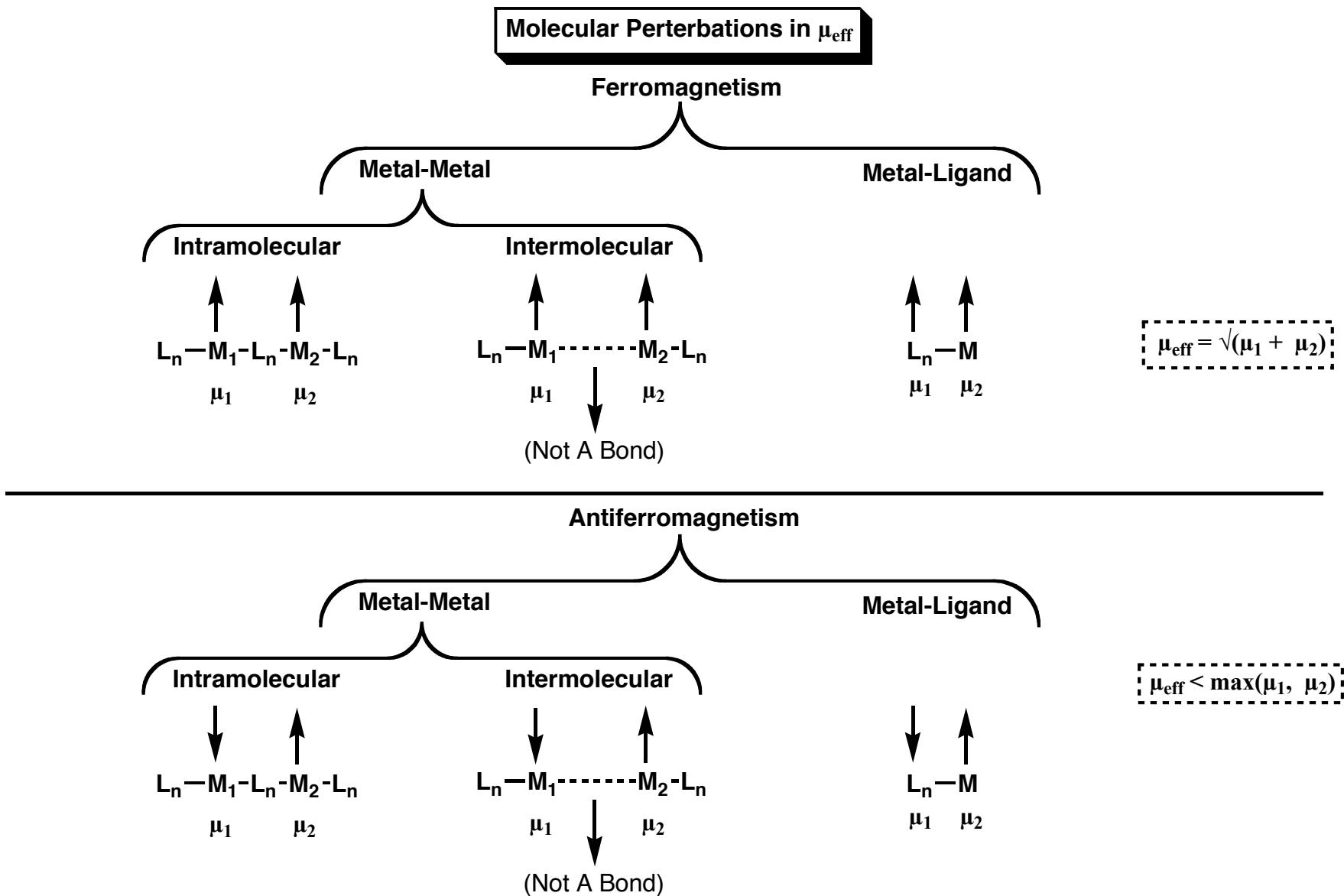
Then assume that:

$$\lambda < 0 \text{ for } d^6 - d^9$$

$$\mu_{\text{eff}} < \mu_s \text{ for } d^1 - d^4$$

$$\mu_{\text{eff}} > \mu_s \text{ for } d^6 - d^9$$

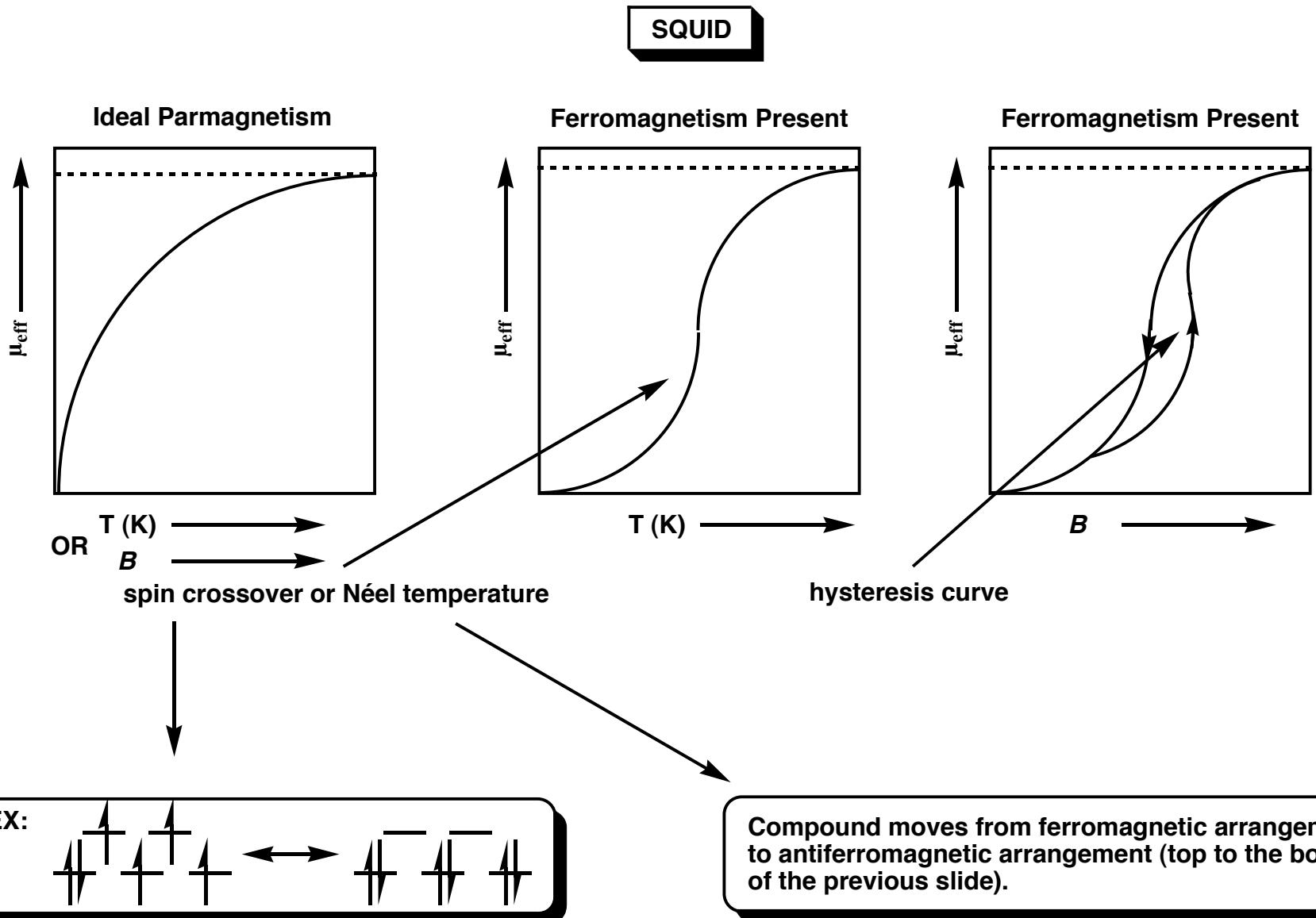
# Magnetism Explained in 5 Minuets or Bust



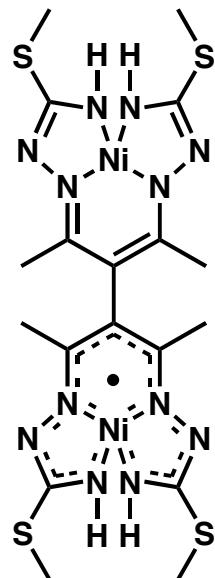
Results in diamagnetic complexes with complete canceling of magnetic moments, or ferrimagnetic complexes with incomplete canceling.

Housecroft, C. E.; Sharpe A. G.; *Inorganic Chemistry*, Pearson Education Limited, 2005.

# *Magnetism Explained in 5 Minuets or Bust*



# Magnetism Explained in 5 Minuets or Bust



## Experimental

(RT) Solution  $\mu_{\text{eff}} = 1.94 \pm 0.06 \mu_B$

(RT) Solid  $\mu_{\text{eff}} = 0.7 \mu_B$

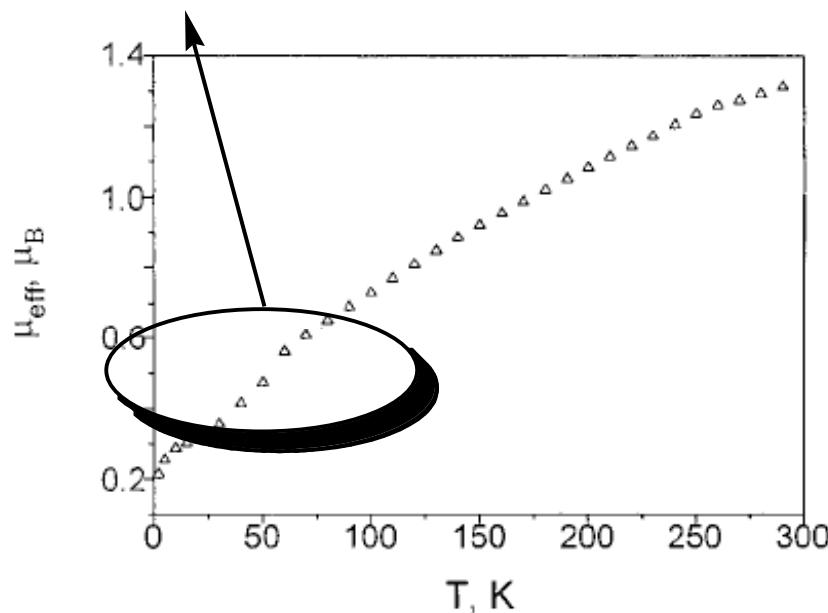
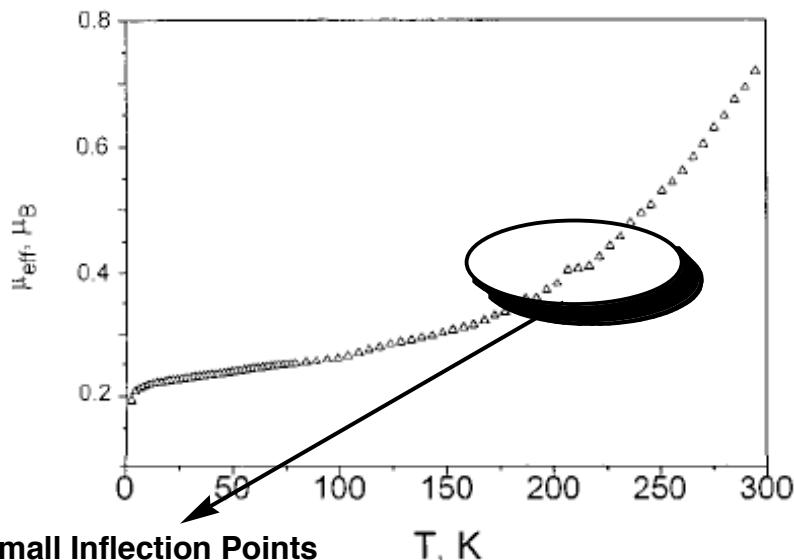
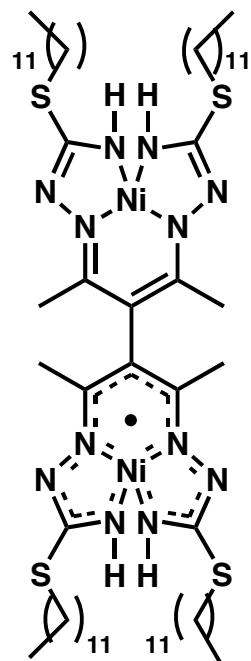
## Theoretical

$\text{Ni}^{\text{III}}$  (square planer)

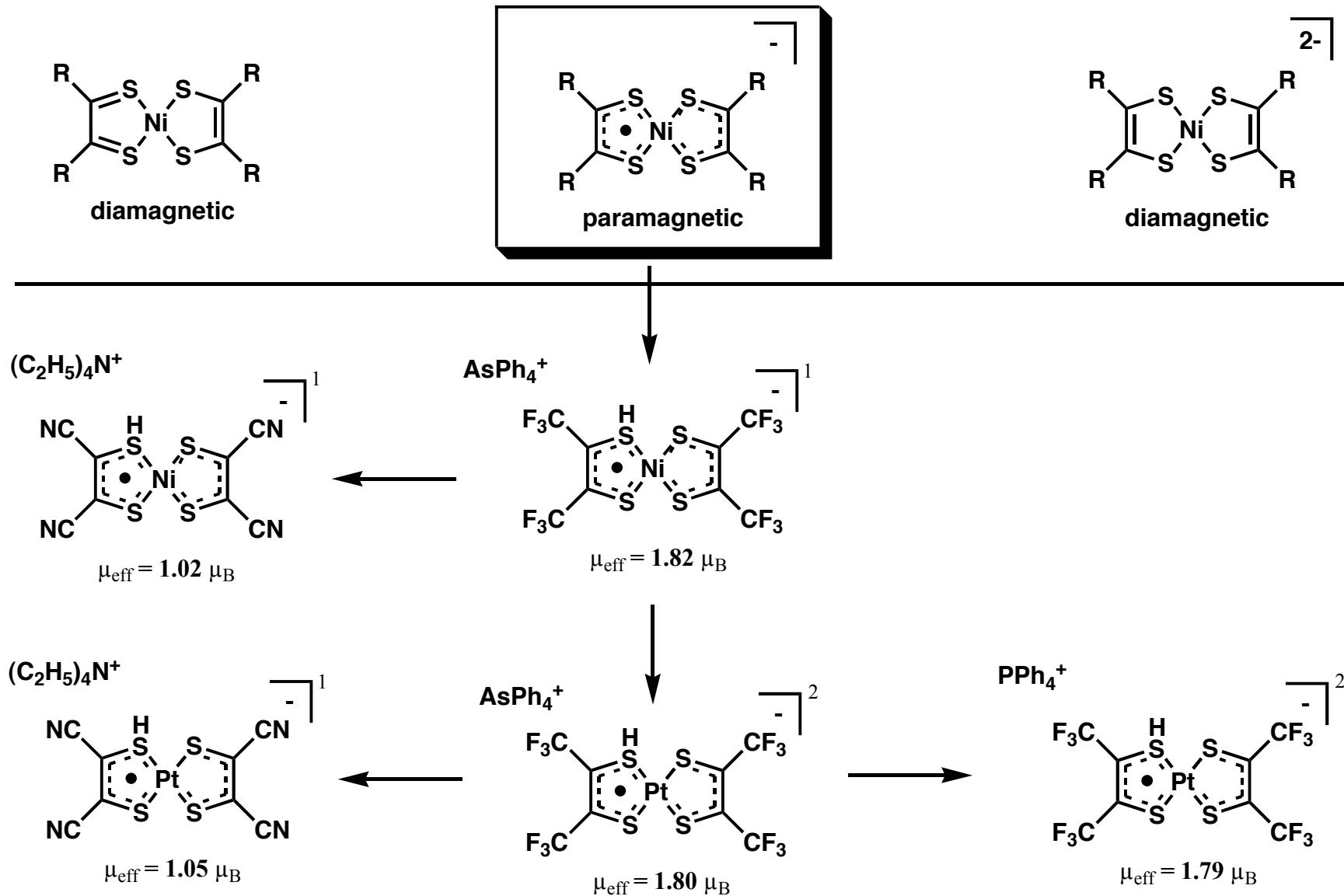
$$\sqrt{[1e^{-}(1e^{-} + 2)]} = 1.73 \mu_B$$

$2 \cdot \text{Ni}^{\text{III}}$  (square planer)

$$\sqrt{(1.73^2 + 1.73^2)} = 2.45 \mu_B$$



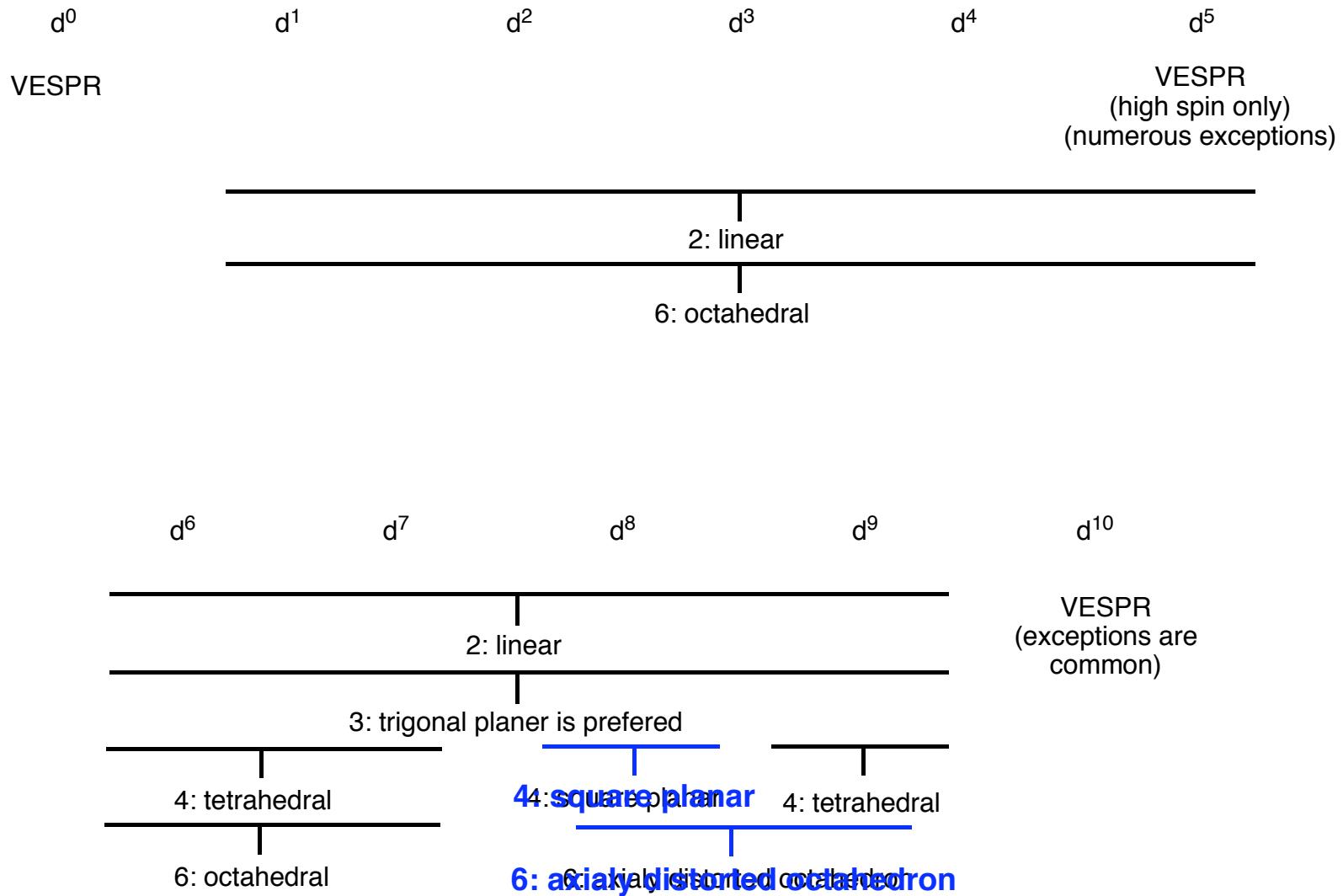
# Magnetism Explained in 5 Minuets or Bust



- 1) Davison, A.; Edelstein, N.; Holm, R. H.; Maki, H.; *Inorg. Chem.*, **1963**, 1227.  
 2) Davison, A.; Edelstein, N.; Holm, R. H.; Maki, H.; *Inorg. Chem.*, **1964**, 814.

# **Structural Geometry**

## **Transition Metal Geometry**



**Take these with a grain of salt, as transition metal geometries are all riddled with exceptions**

# **Structural Geometry**

## **Transition Metal Geometry**

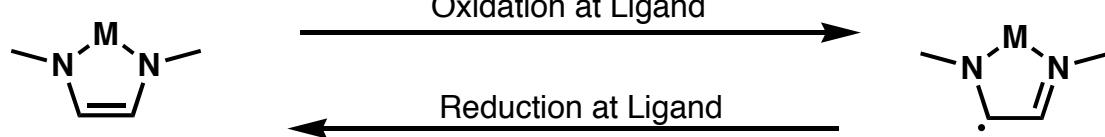
### **Ni, Pd, Pt preferred coordination counts by oxidation state**

| <b>0<sup>+</sup></b>            | <b>1<sup>+</sup></b> | <b>2<sup>+</sup></b>               | <b>3<sup>+</sup></b> | <b>4<sup>+</sup></b> |
|---------------------------------|----------------------|------------------------------------|----------------------|----------------------|
| 2 - 4<br>(4 is the most common) | 4                    | 4<br>(6 is also common for nickel) | 4-5                  | 6                    |

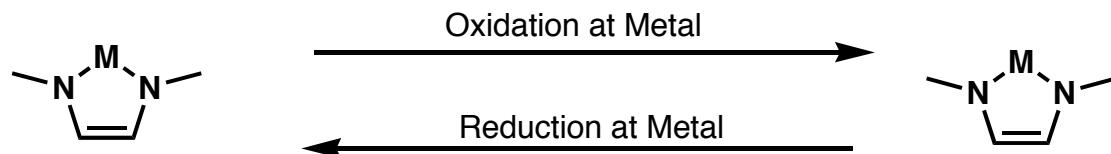
## **Ligand Geometry**

For p-block elements bound to metals, their usual VESPR geometry and standard bond lengths / angles are still just as valid. Paying attention to ligand atom hybridizations and bond lengths over large conjugated areas in a ligand is often an excellent way to figure out ligand oxidation states.

**EX:**



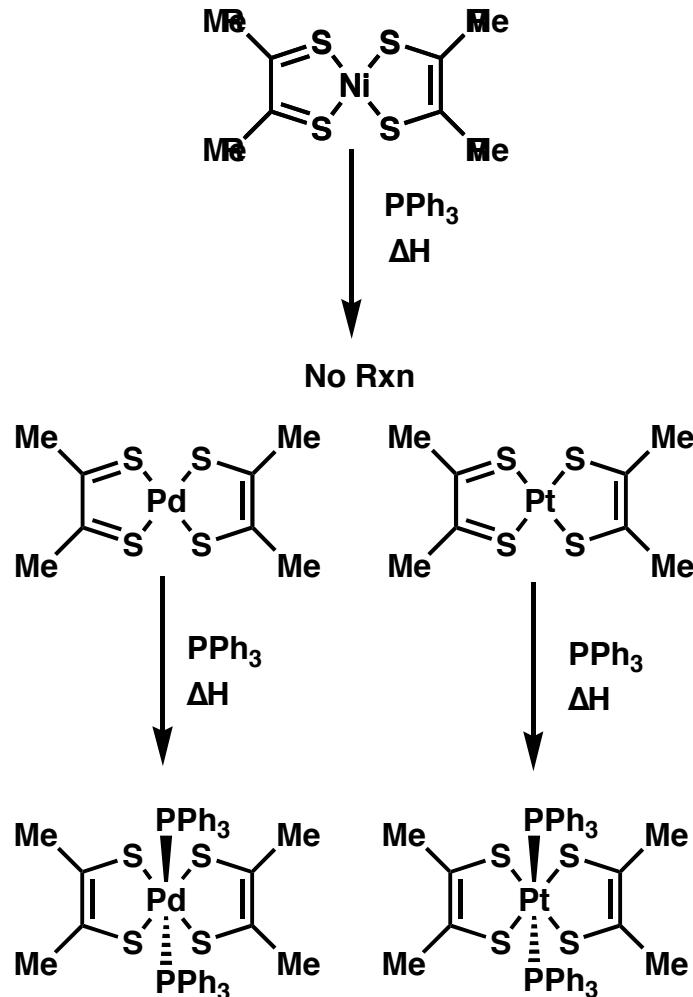
N-C-C-N total bond length should be within experimental error of  
N-C + C-C + N=C



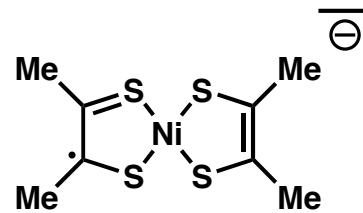
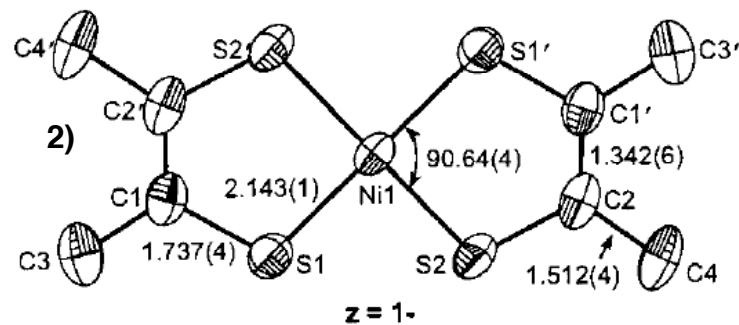
N-C-C-N total bond length should be within experimental error of  
2• N-C + C=C

## Structural Geometry

If this was actually nickel (IV) it should have six coordination sites filled, and be rigorously octahedral!



Square planar Nickel(III) species are exceedingly rare.<sup>1</sup> This square planar nickel geometry here suggests a Nickel (II) species.



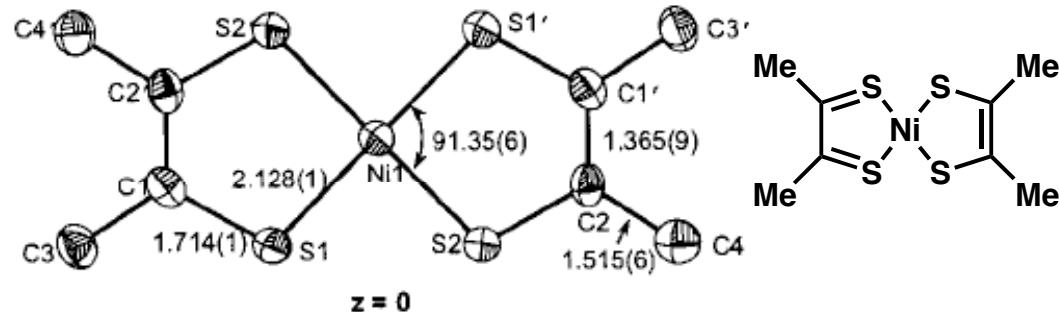
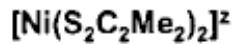
Note: this structural argument is not even close to being a sufficient condition for determining noninnocence or even ruling out the possibility of a nickel(III) species. It does suggest, however, that the electronic structure of this complex is unusual and warrants further examination.

1) Collins, T. J.; Nichols, T. R.; Uffelman, E. S. *J. Am. Chem. Soc.*, **1991**, *113*, 4708-4709.

2) Lim, B. S.; Fomitchev, D. V.; Holm, R. H.; *Inorg. Chem.*, **2001**, *40*, 4257-4262.

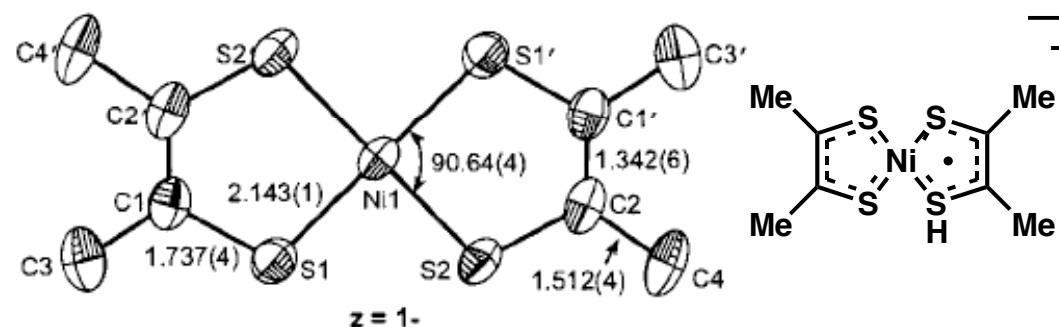
Schrauzer, G. N.; Mayweg, V. P.; *J. Am. Chem. Soc.*, **1965**, *87*, 1483-1489.

## Structural Geometry



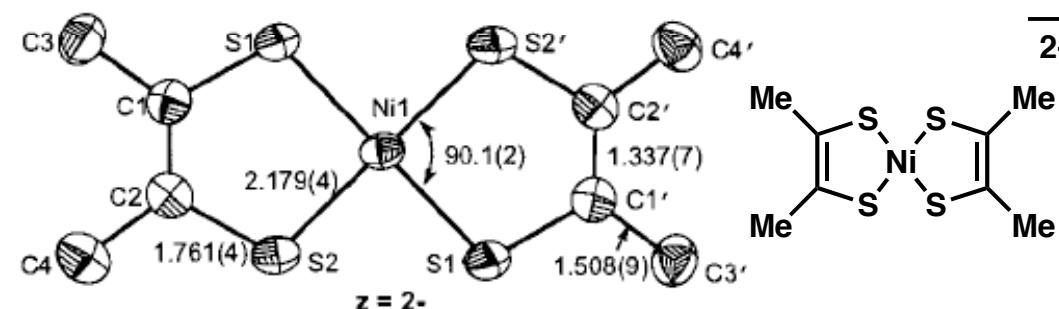
$$\text{S1}'\text{-C1}'\text{-C2-S2} + \text{S1-C1-C2}'\text{-S2}' \approx 9.586 \text{ (22) } \text{\AA}$$

$$2 \cdot \text{aromatic C-C} + 2 \cdot \text{S=C} + 2 \cdot \text{S-C} = 9.52 \text{ \AA}$$



$$\text{S1}'\text{-C1}'\text{-C2-S2} + \text{S1-C1-C2}'\text{-S2}' \approx 9.632 \text{ (28) } \text{\AA}$$

$$2 \cdot \text{aromatic C-C} + \text{S=C} + 3 \cdot \text{S-C} = 9.68 \text{ \AA}$$



$$\text{S1}'\text{-C1}'\text{-C2-S2} + \text{S1-C1-C2}'\text{-S2}' \approx 9.718 \text{ (30) } \text{\AA}$$

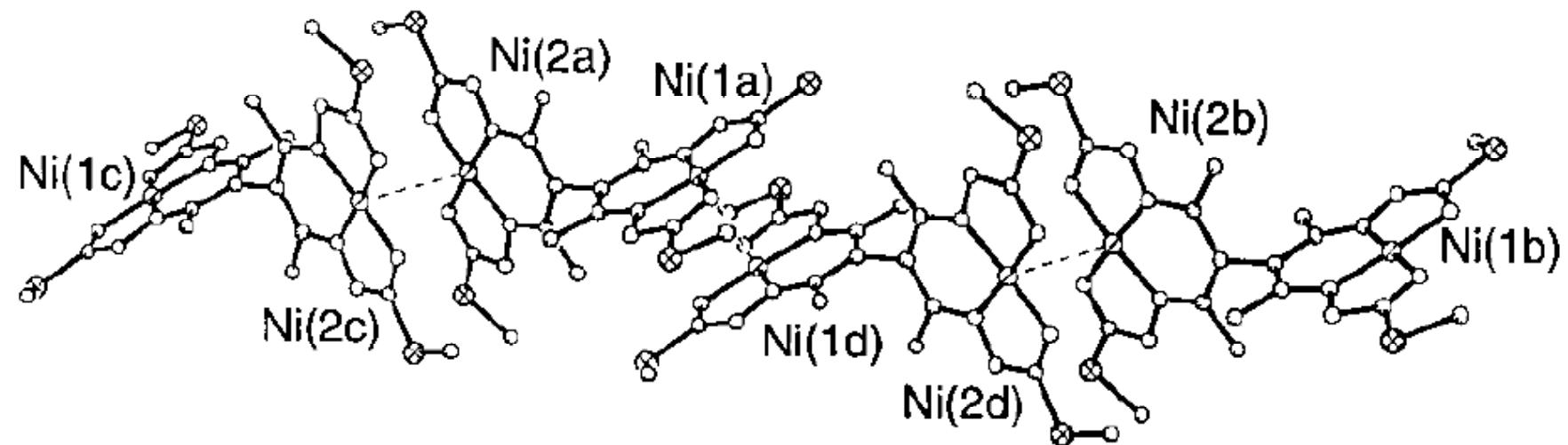
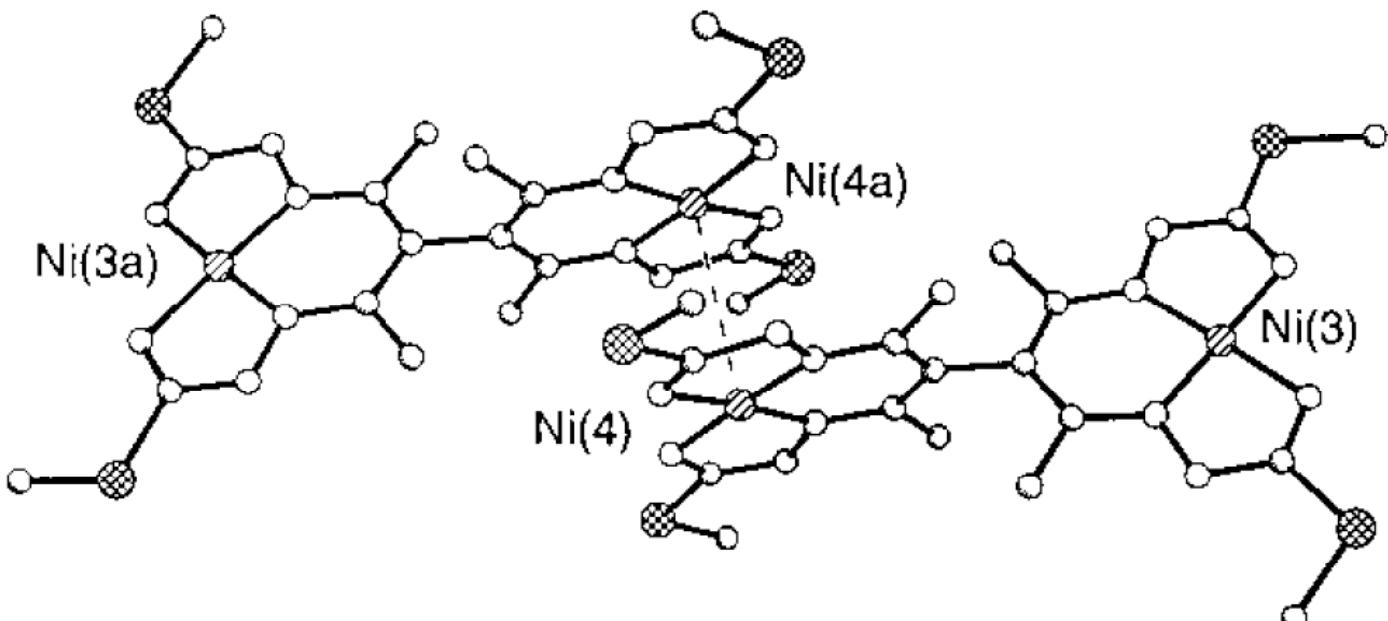
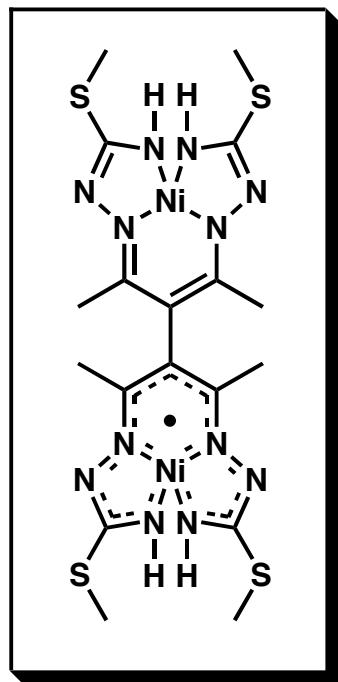
$$2 \cdot \text{C=C} + 4 \cdot \text{S-C} = 9.70 \text{ \AA}$$

$\text{C=C} = 1.33 \text{ \AA}$    aromatic  $\text{C-C} = 1.40 \text{ \AA}$     $\text{C=S} = 1.60 \text{ \AA}$     $\text{C-S} = 1.82$  (nonconjugated systems)   restandardized  $\text{C-S} = 1.76 \text{ \AA}$

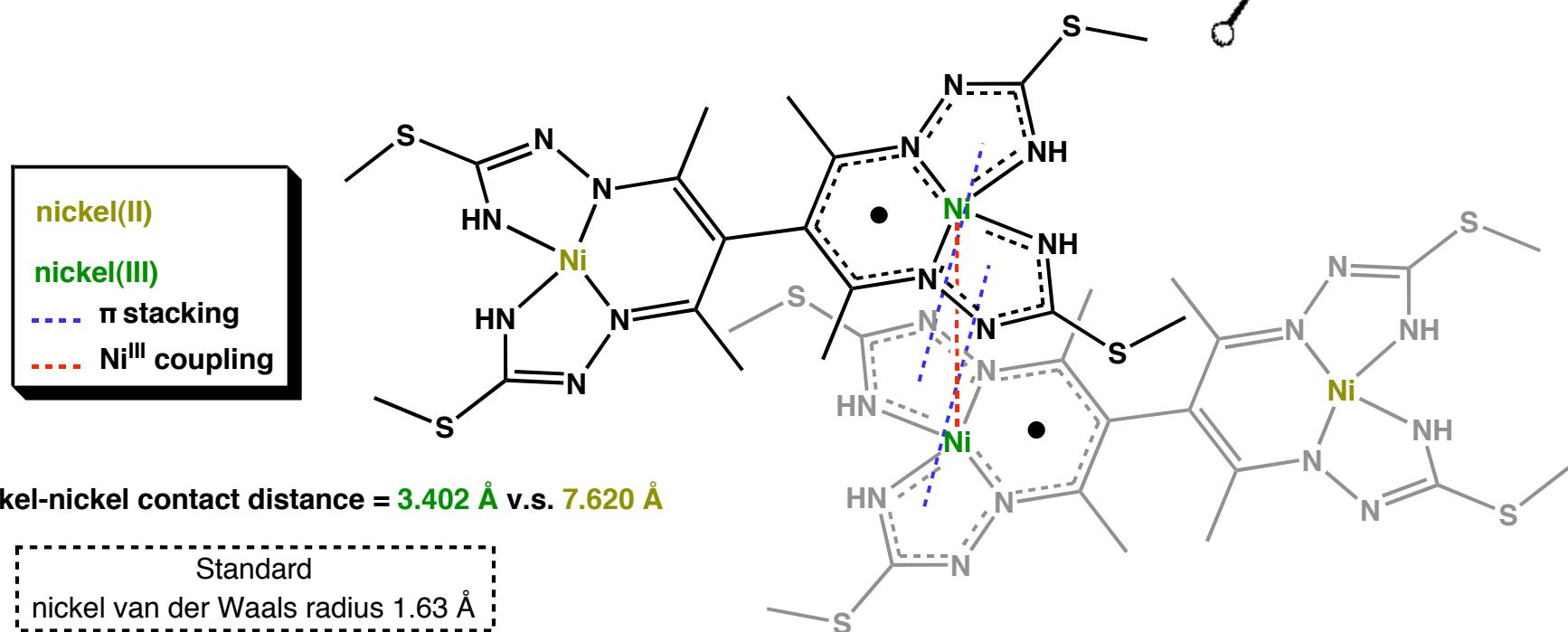
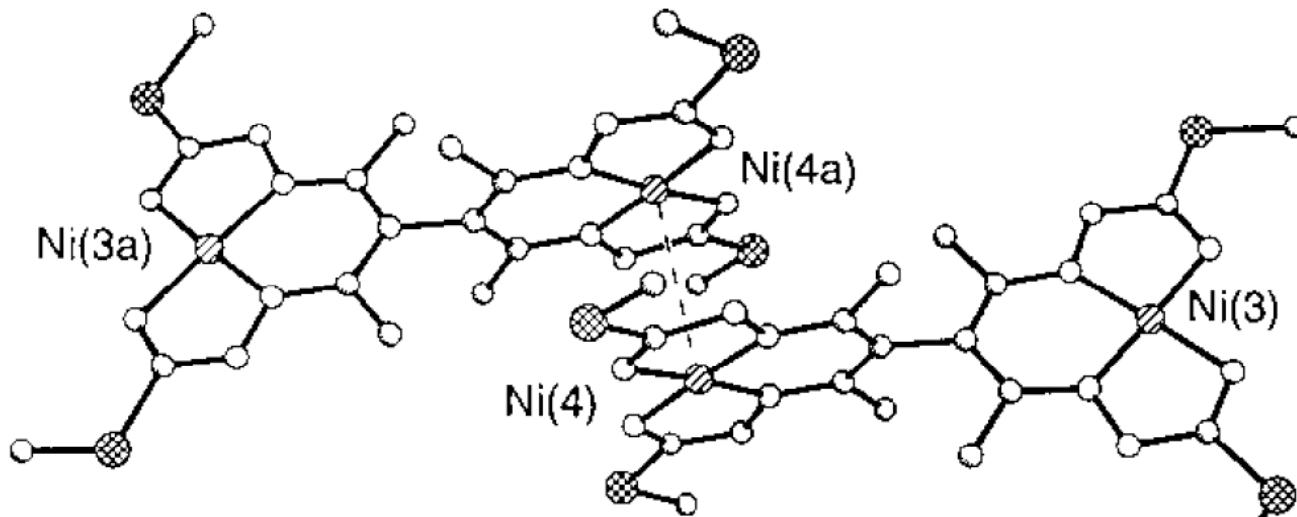
<http://chemviz.ncsa.uiuc.edu/content/doc-resources-bond.html>

2) Lim, B. S.; Fomitchev, D. V.; Holm, R. H.; *Inorg. Chem.*, 2001, 40, 4257-4262.

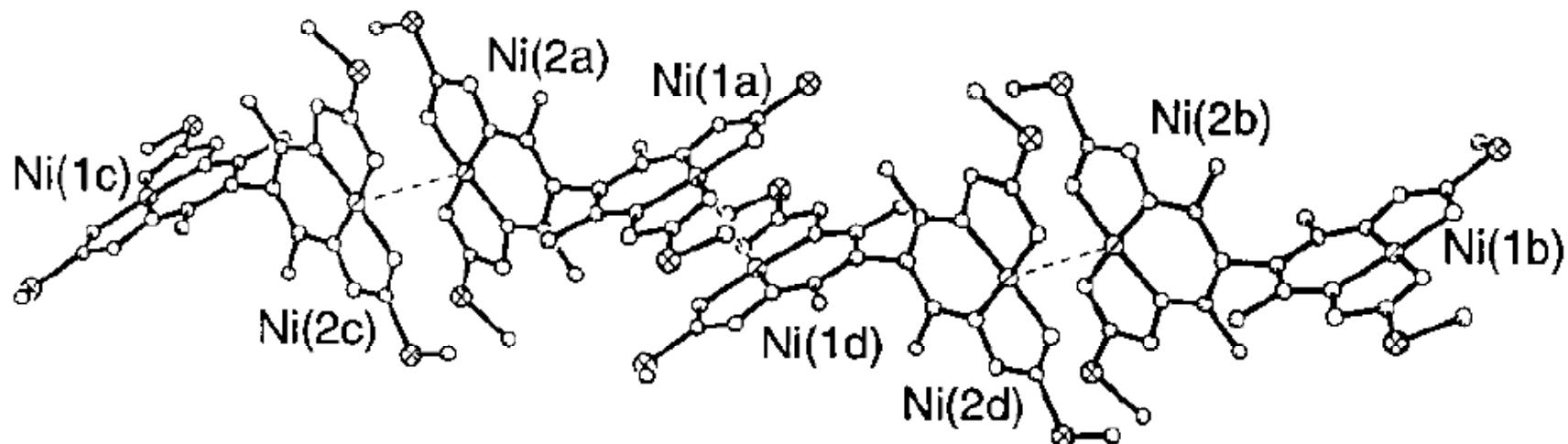
## *Structural Geometry*



## Structural Geometry

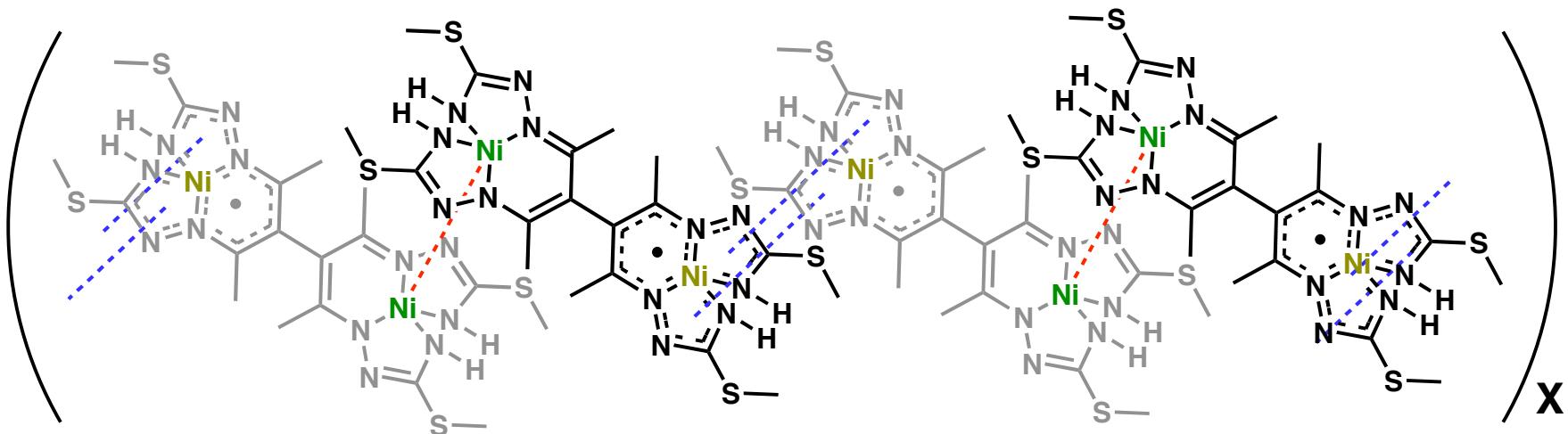


## Structural Geometry

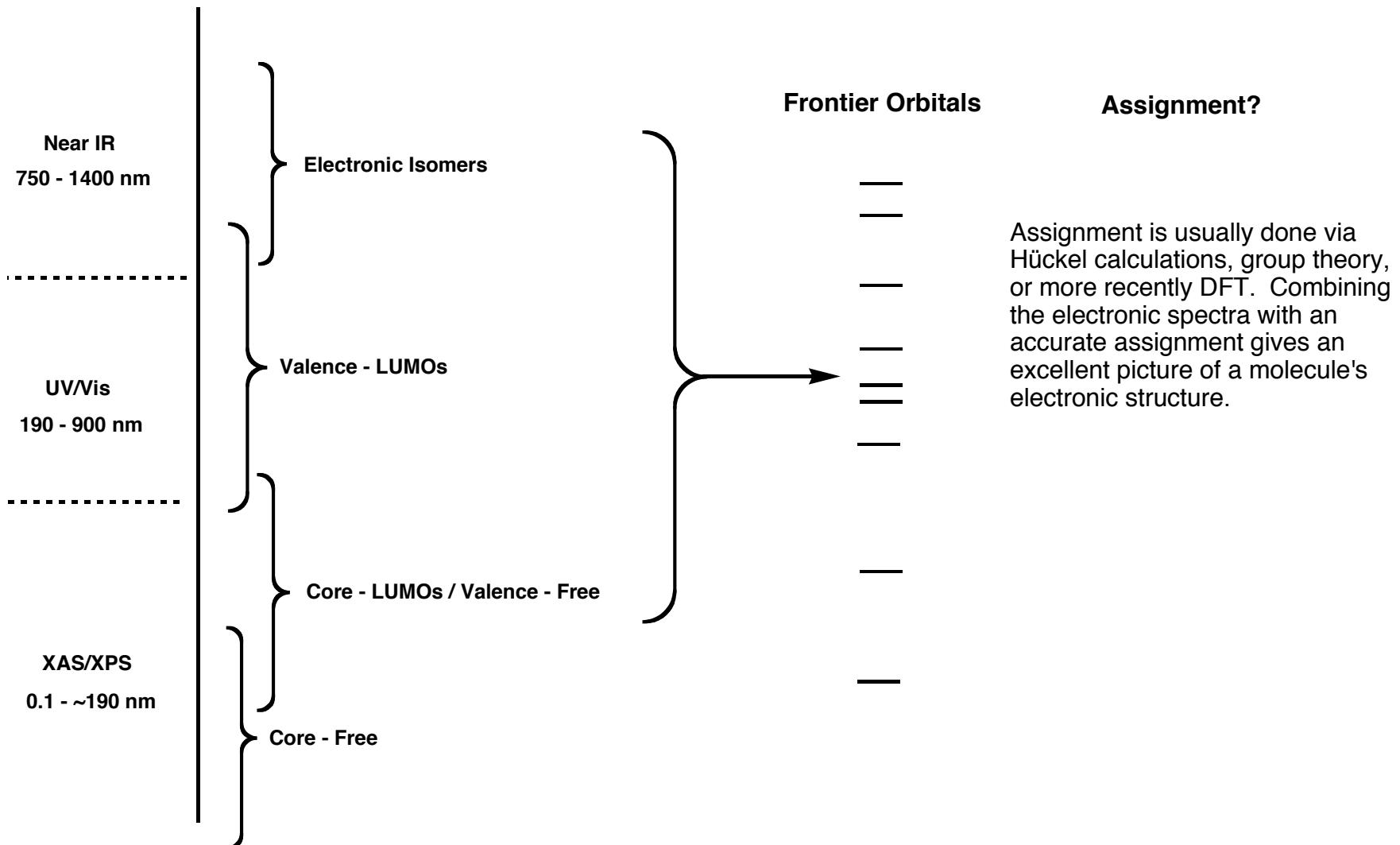


Standard  
nickel van der Waals radius 1.63 Å

Previous  
nickel-nickel contact distance = 3.402 Å v.s. 7.620 Å



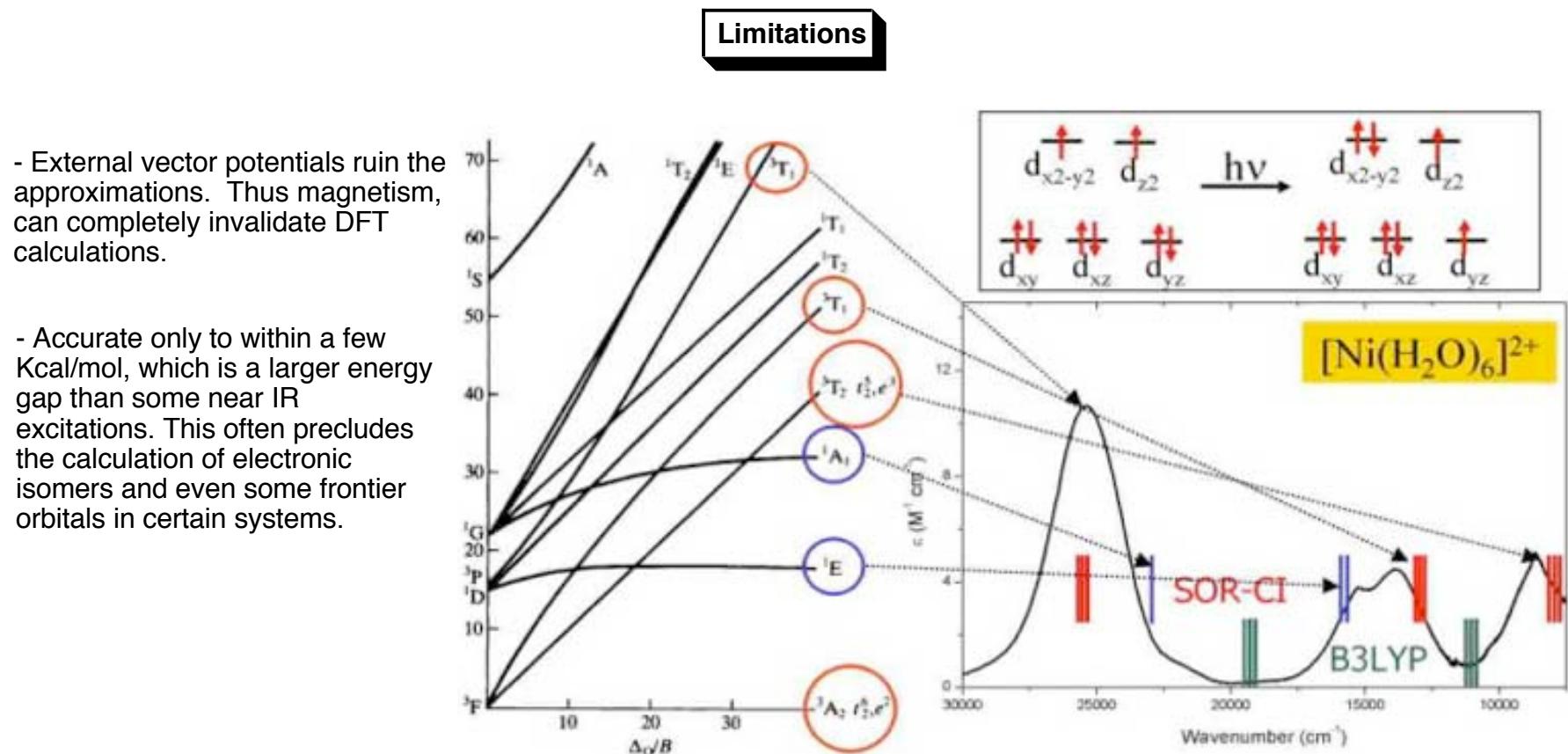
# *Electronic Spectra*



<http://www.theo-physik.uni-kiel.de/theo-physik/schattke/notes/berk97/>  
[http://www.casaxps.com/help\\_manual/XPSInformation/IntroductiontoXPS.htm](http://www.casaxps.com/help_manual/XPSInformation/IntroductiontoXPS.htm)

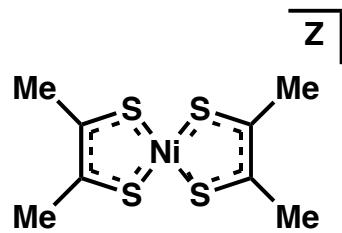
# Density Functional Theory

DFT is a quantum mechanics approximation method in which the computationally intensive interaction terms have been removed from the Hamiltonian and are replaced with a set of standard electron probability density fields. A set of specialized exchange-correlation functions are then applied to the preset fields to create more accurate electron distributions. Basis sets are collections of these exchange-correlation functions that have been adapted via standardization on certain systems. The current industry standard basis set is B3LYP. It is recommended that to get the most out of DFT, custom basis sets must be generated to match the experimentally measured properties of a given system.



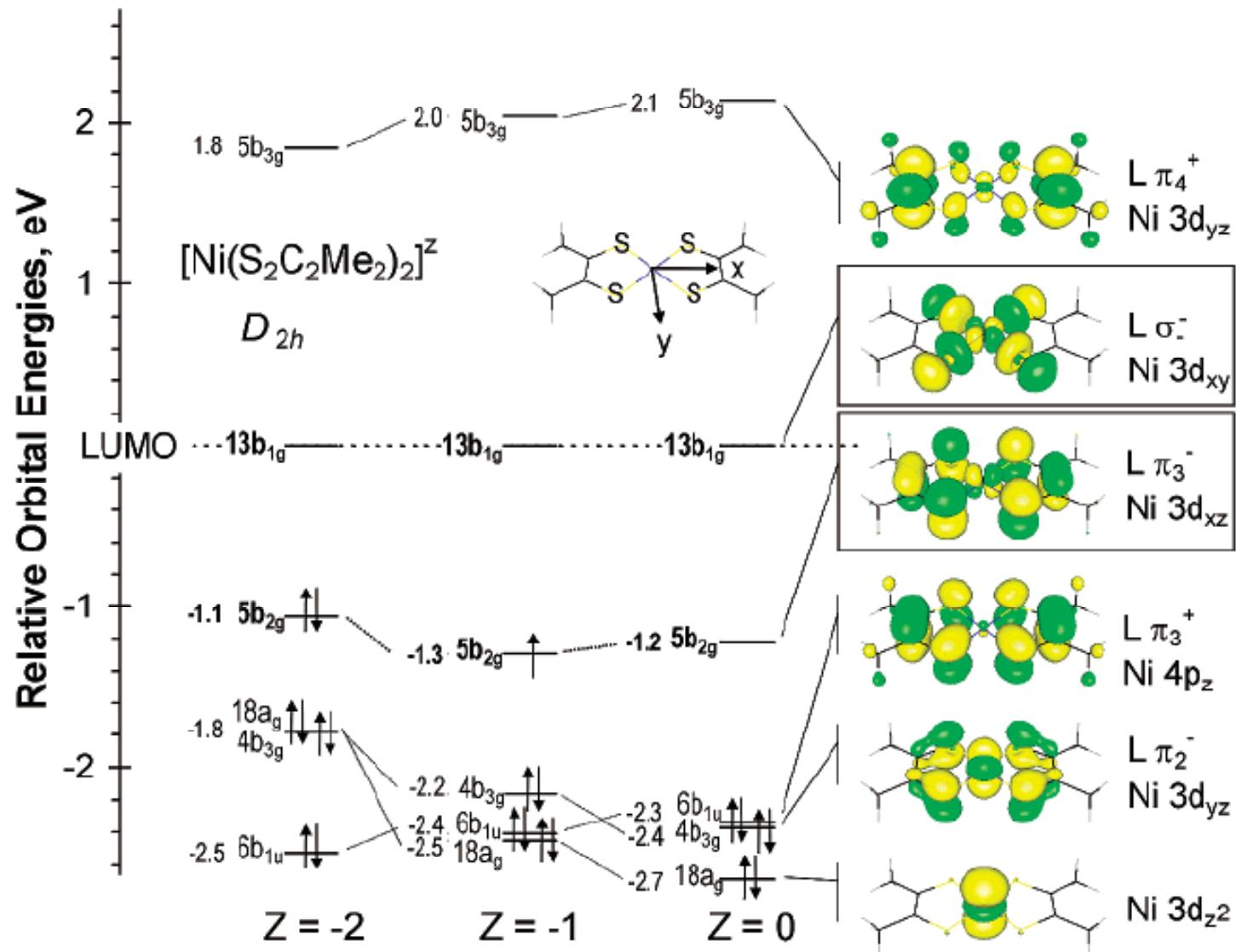
1) [http://ewww.mpi-muelheim.mpg.de/bac/mitarbeiter/neese/neese\\_en.php](http://ewww.mpi-muelheim.mpg.de/bac/mitarbeiter/neese/neese_en.php)  
[<http://www.physics.ohio-state.edu/~aulbur/dft.html>](http://www.physics.ohio-state.edu/~aulbur/dft.html)

## Density Functional Theory



$5b_{2g}$  is calculated to be composed of only ~25% Ni  $3d_{xz}$  thus depopulating this orbital has a ~75% effect on ligand oxidation state.

~25% Ni orbital character allows for a super exchange pathway between the two ligands, this is why the system does not exist as a diradical in its ground state, it can couple through the metal.

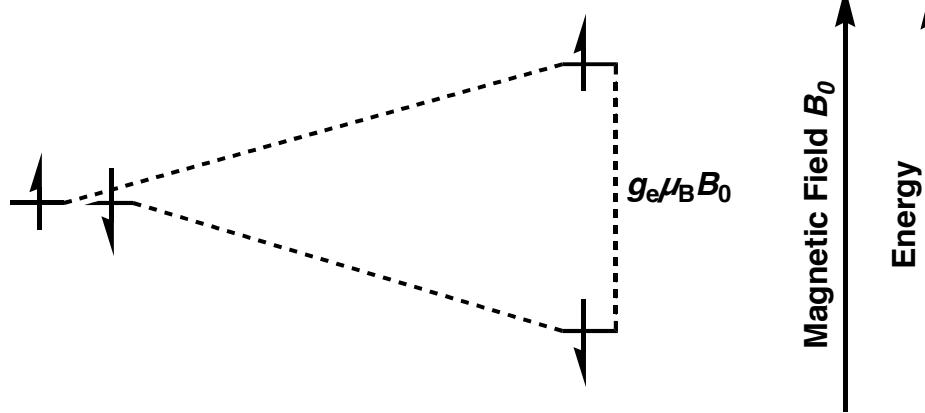


DFT calculations were preformed with a custom combination of basis sets that were statistically blended to match data from K-edge X-ray absorption spectra. Sets used in this process are: BS5, BSIV, B88, P86, LYP, PBE, PBE98, PBErev, PW86, PW91

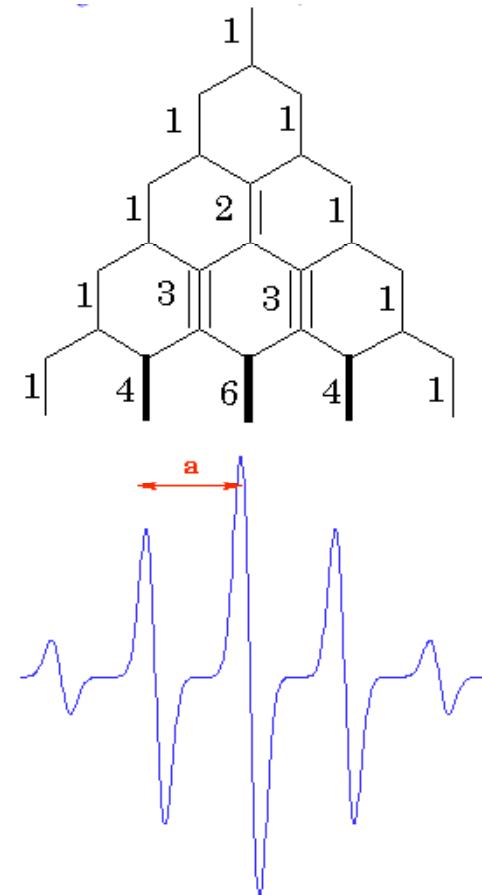
## ***Advanced Methods***

### **EPR / ESR**

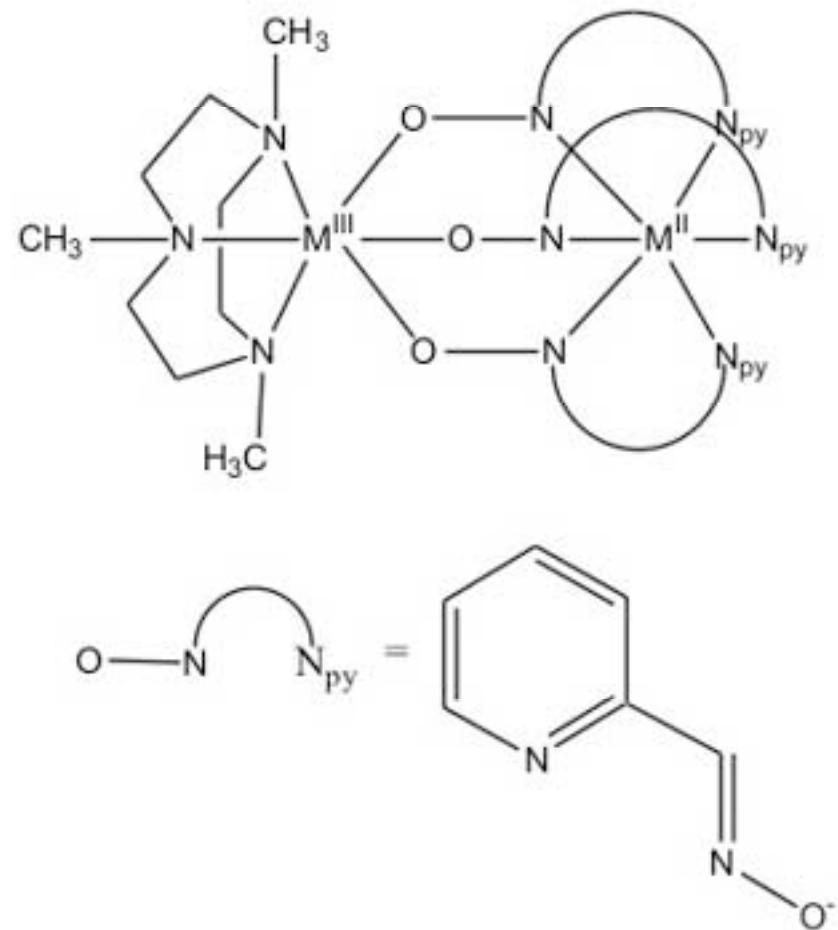
EPR is based on the same concept as NMR, but instead of magnetically aligning nuclei and perturbing their spins with radio waves, the instrument magnetically aligns unpaired electrons, and perturbs their spins with microwaves.



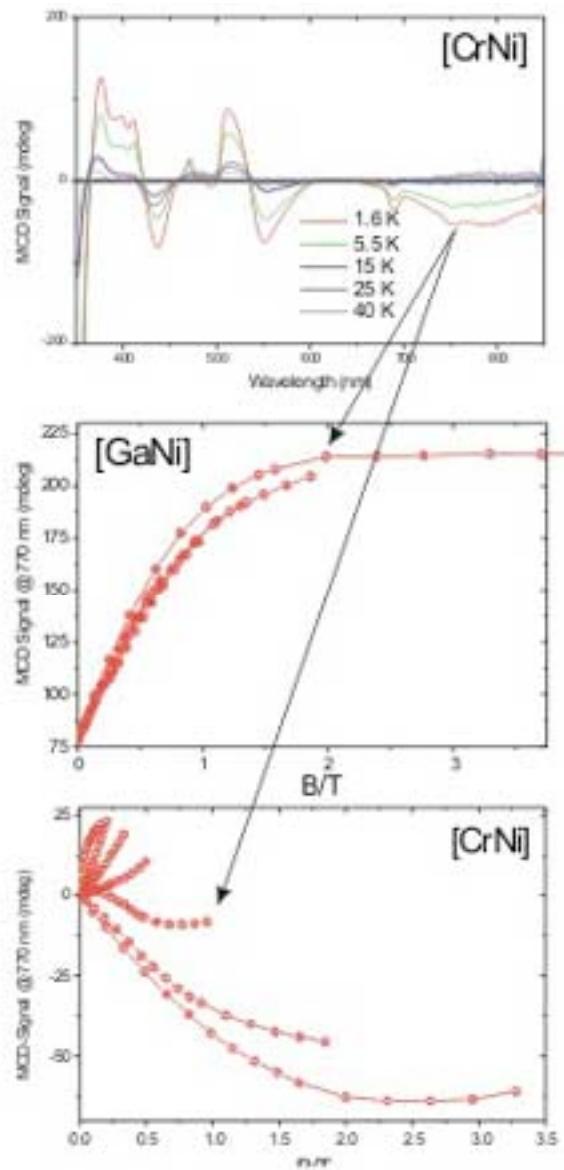
EPR not only gives a detailed picture of the number of unpaired electrons, but also via nuclear coupling, EPR can distinguish the atoms contributing to the molecular orbital(s) in which the unpaired electron(s) are situated. More detailed analysis of EPR spectra can give information about the spin orbital coupling, molecular and orbital degeneracy, and the shapes of the magnetic tensor.



## Advanced Methods



M.C.D



"In the presence of a longitudinal magnetic field, electronic transitions acquire circular polarization (the longitudinal Zeeman effect)."<sup>1</sup>

PRO:

- All material must have MCD spectra
- Good spectra provide rigorous assignment of oxidation states and electronic transitions (d-d, CT, p-p etc. . .)

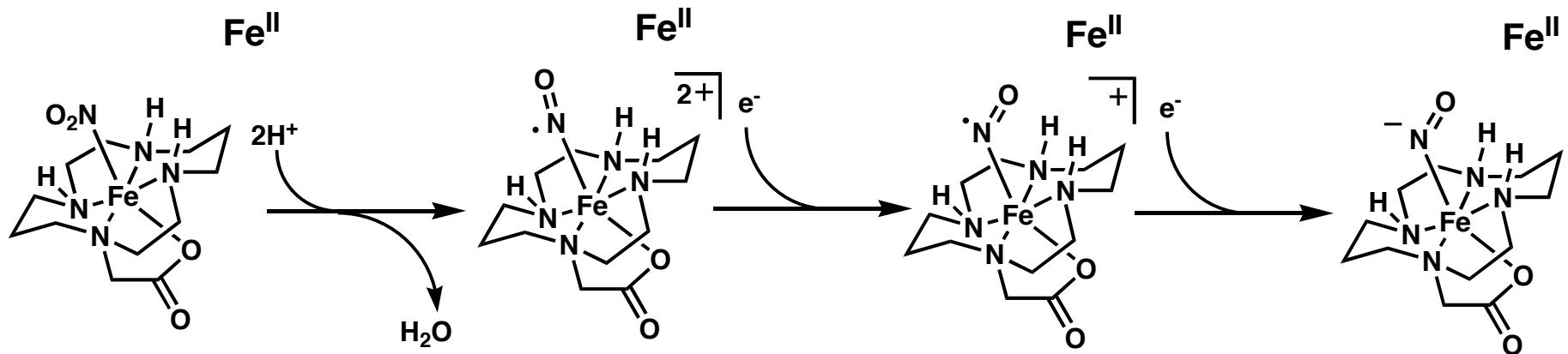
CON:

- Truly elucidating spectra only come from compounds that are:
  - 1) paramagnetic
  - 2) chiral
  - 3) have high symmetry

<sup>1</sup><http://www.bmb.ogi.edu/users/JWW/MCD00.html>

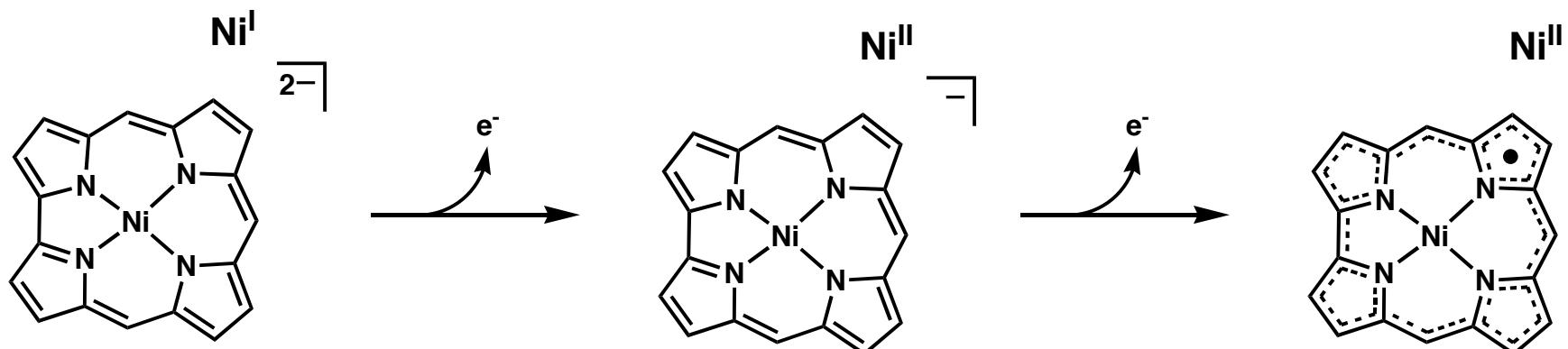
[http://ewww.mpi-muelheim.mpg.de/bac/mitarbeiter/neese/neese\\_en.php](http://ewww.mpi-muelheim.mpg.de/bac/mitarbeiter/neese/neese_en.php)

## *Biological Application*



Model system for the core of cytochrome c nitrite reductase

various corrole and porphyrin based systems<sup>2</sup>

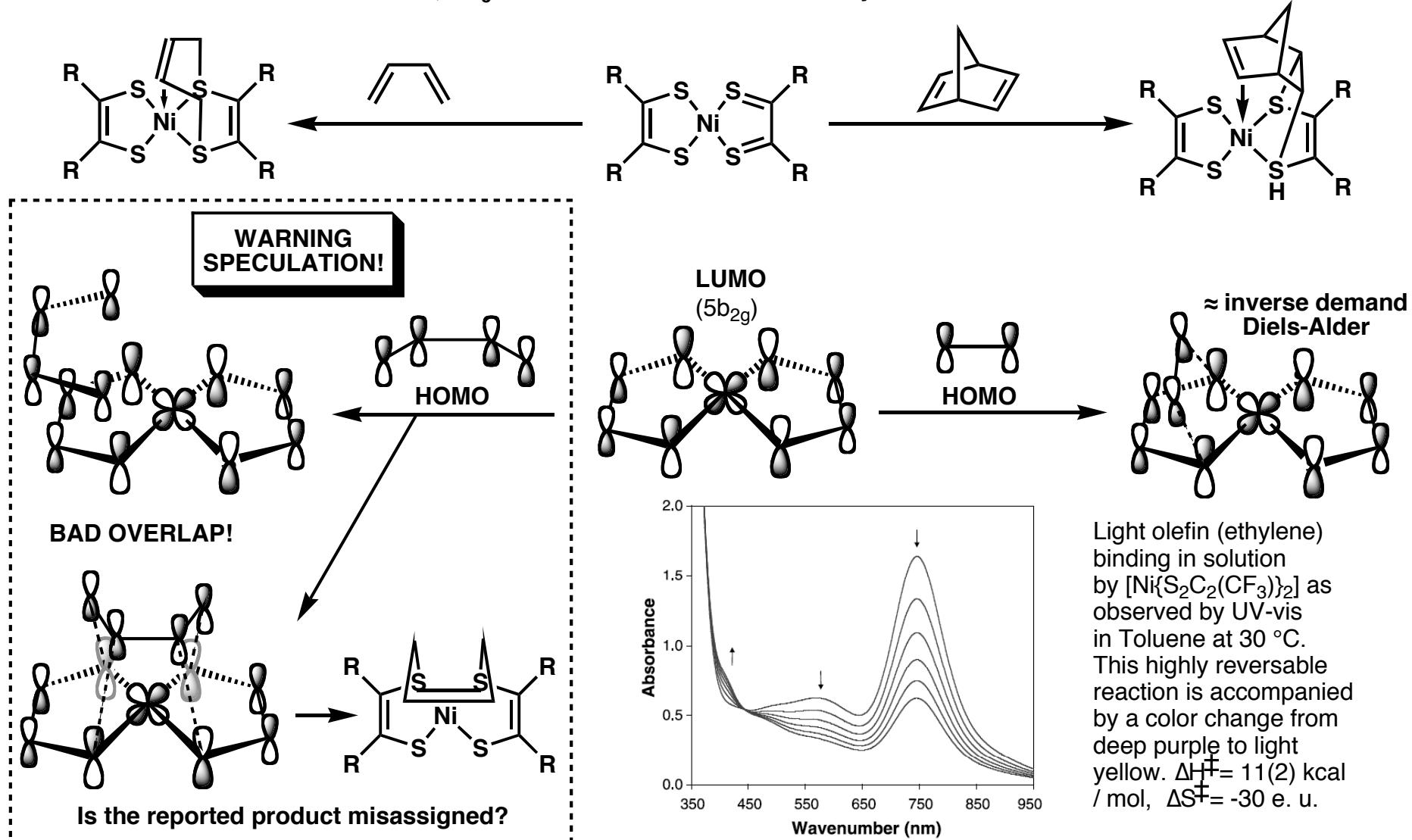


Study of Corroles on High Valent Metals

- 1) Serres, R. G.; Grapperhaus, C. A.; Bothe, E.; Bill E.; Weyhermüller, T.; Neese F.; Wieghardt, Karl.; *J. Am. Chem. Soc.*, **2004**, 126, 5138 - 5153.
- 2) Ghosh, A.; Wondimagegn, T; Parusel, A. B. J.; *J. Am. Chem. Soc.*, **2000**, 122, 5100-5104.

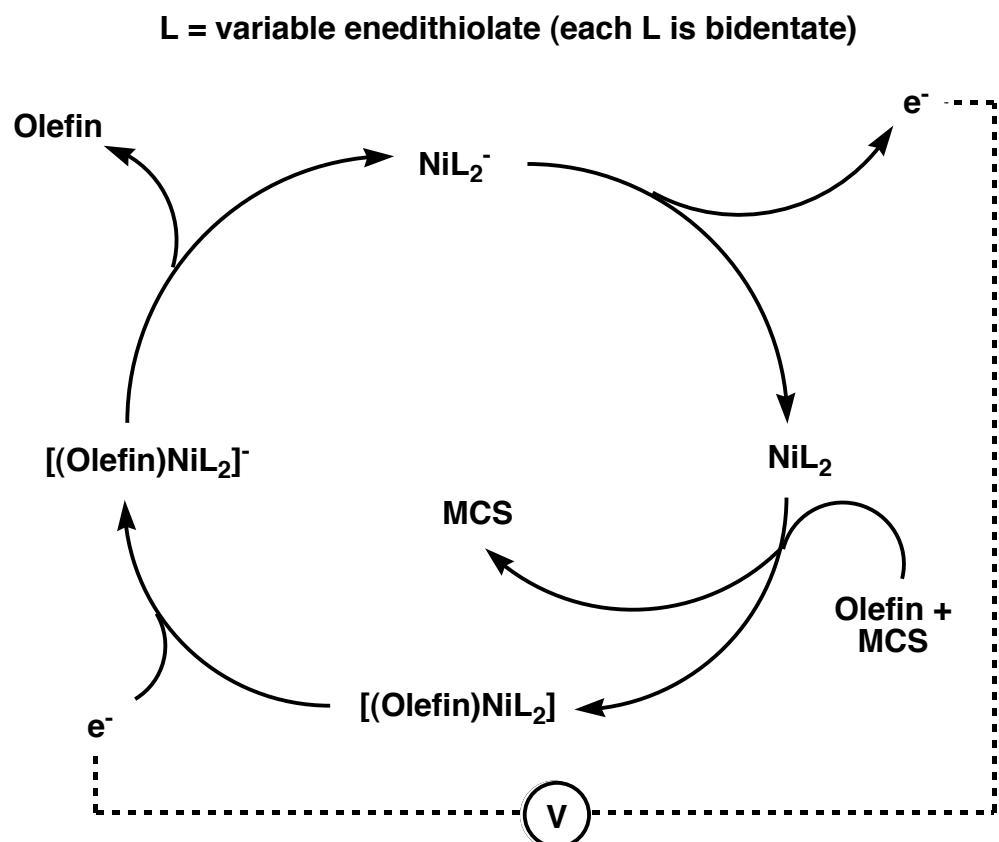
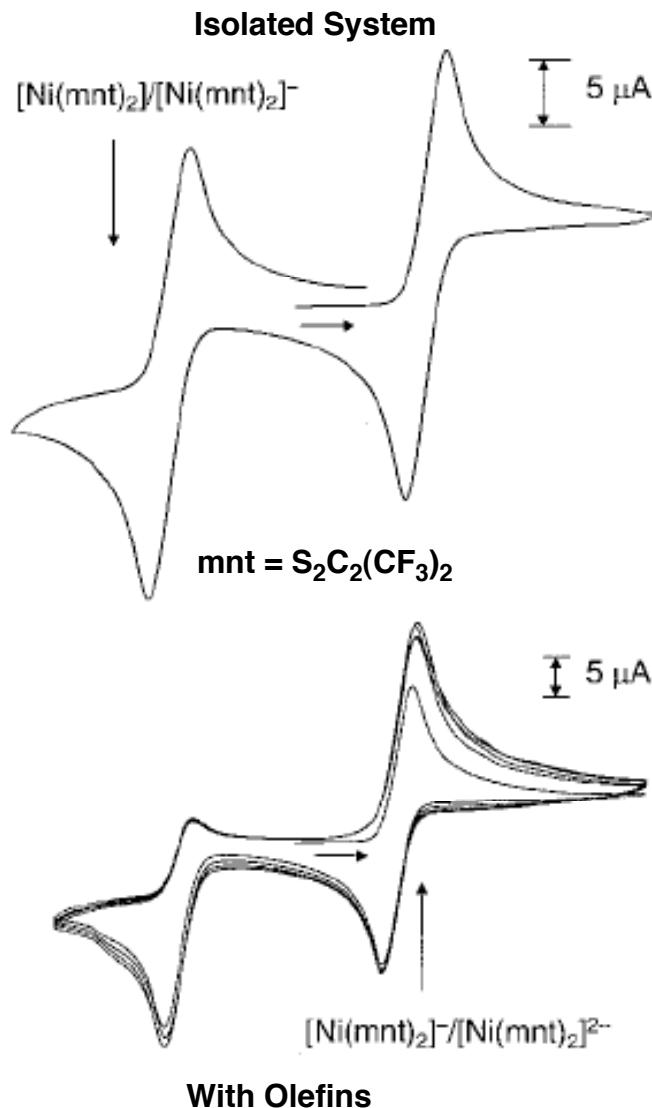
## Synthetic Applications

$R = \text{Ph, } \text{CF}_3$ . Theorized to be viable for many other substitutions



Schrauzer, G. N.; Mayweg, V. P.; *J. Am. Chem. Soc.*, **1965**, *87*, 1483-1489.  
 Szilagyi, S. K.; Lim, B. S.; Glaser, T.; Holm, R. H.; Hedman, B.; Hodgson, K. O.; Solomon, E. I.; *J. Am. Chem. Soc.*, **2003**, *125*, 9158.  
 Wang, K.; Stiefel, E. I; *Science*, **2001**, *291*, 106-109.

## Non-Synthetic Applications

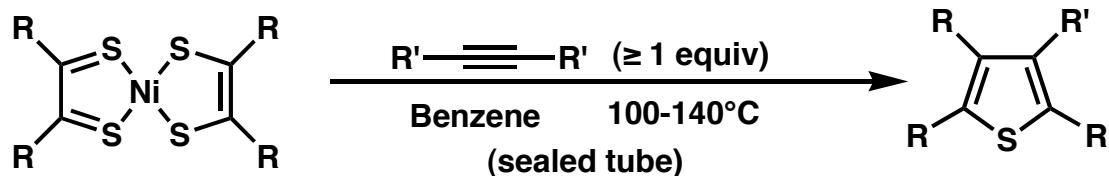


| Olefin                 | $K_{eq} (M^{-1})$ | $k (10^{-4} M^{-1}s^{-1})$ |     |
|------------------------|-------------------|----------------------------|-----|
|                        |                   | MePh                       | DCE |
| Ethylene               | 140               | 9                          | 51  |
| Propylene              | 70                | 25                         | 153 |
| 1-Hexene               | 60                | 11                         | 77  |
| <i>trans</i> -3-Hexene | 15                | 2                          | ND  |

## Synthetic Applications

$R = \text{alkyl, aryl}$

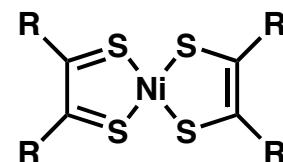
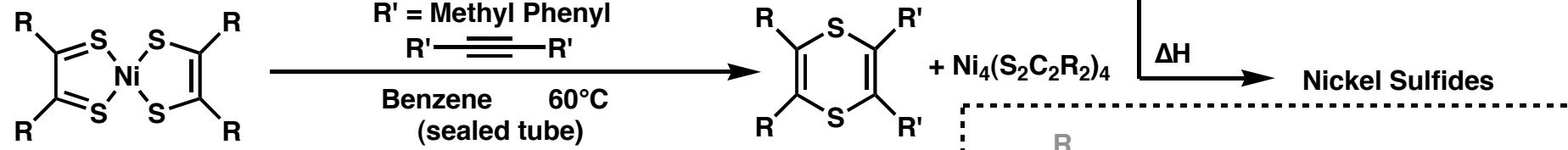
$R' = \text{alkyl, aryl, fluoralkyl, fluoraryl, esters}$



$R = \text{alkyl, aryl}$

(fast reacting substrates only)

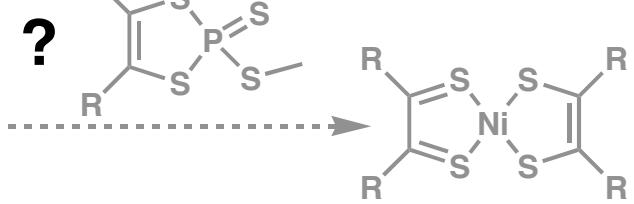
$R' = \text{Methyl Phenyl}$



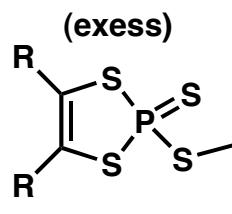
$\text{Ni}_{(s)}$  or  $\text{Ni}(\text{CO})_4$

$\text{Ni}_4(\text{S}_2\text{C}_2\text{R}_2)_4$

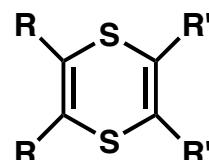
?



### Theoretical Section



$\text{NiCl}_2$  (cat.)



sulfide scavenger

