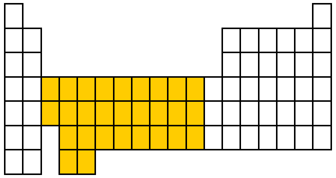
Oriol Planas

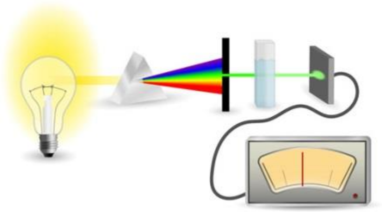
IC: Fundamentals, Techniques and Examples

Cornella group meeting
19/10/2018

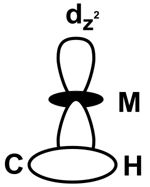
Disclaimer: This topic presentation pretends to be a quick inorganic/transition-metal chemistry guide for organic chemistry users. This is not a comprehensive review of chemical bonding, molecular symmetry, etc.



Bonding in Transition Metals



Spectroscopic techniques



Influence of bonding to reactivity

This topic presentation covers

- **Basics of Transition-Metal bonding**, including
    1. Werner coordination theory
    2. Valence bond theory
    3. Crystal Field theory
- **Paramagnetic species characterization techniques**, including
    1. Evans method
    2. EPR spectroscopy
    3. Mössbauer spectroscopy
    4. X-Ray Absorption spectroscopy
- ***Examples* connected with theoretical reasoning, including**
    1. C-H activation
    2. The oxo-wall

NOT covered:

- Symmetry operations and complex orbital mixing
- Physical/mathematical basis of spectroscopic techniques

This presentation will omit mathematical treatment of physical phenomena and some hard-core physical inorganic chemistry reasoning. When the concepts turn qualitative you will see the following sign:

Bonding in Transition Metals

Alfred Werner - **Nobel Prize in Chemistry (1913)** for his **„coordination theory (1893)“** of transition metal complexes.

- Described the meaning of ***the „mysterious dot“ in $CoCl_3$•$6NH_3$***
- Explained the ***formation of isomers*** of formula $[Co(NH_3)_nCl_{6-n}]$
- Discovered ***the first non carbon-based chiral compound***

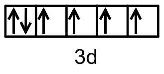
His main contributions to TM-bonding are summarized in his concept of valence, which is divided depending on the ligand:

1- Primary valence (Co-Cl bond) : ionizable, non-directional (oxidation state)
2- Secondary valence: non-ionizable, directional (coordination number)

Linus Pauling - **Nobel Prize in Chemistry (1954)** for his **„Valence Bond theory“ (1930)** *(The Nature of the Chemical Bond)* introducing concepts such as **hybridization** and **covalency**. To examples: Co^{3+} and Ni^{2+}:

[Co] = [Ar] **$3d^7$ $4s^2$**
[Co^{3+}] = [Ar] **$3d^6$**

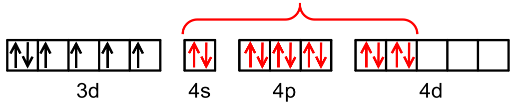
Six **empty orbitals** required to accommodate the ligands'



6L

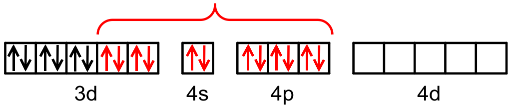
sp^3d^2 (high-spin complex, O_h)

Outer orbital complex: *reactive, labile and paramagnetic*



or

d^2sp^3 (low-spin complex, O_h)



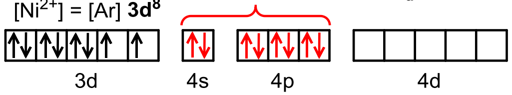
Inner orbital complex: *stable, inhert and diamagnetic*

sp – lineal complex
sp^2 – trigonal planar complex
sp^3 - Tetrahedral complex
d^2sp^3 – Octahedral complex
dsp^2 – Tetrahedral complex
dsp^3 - Trigonal bypiramidal complex

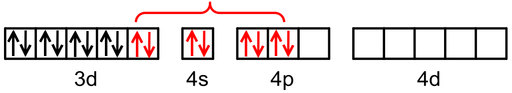
[Ni] = [Ar] **$3d^8$ $4s^2$**
[Ni^{2+}] = [Ar] **$3d^8$**

4L

sp^3 (paramagnetic, T_d)



dsp^2 (diamagnetic, D_{4h})



Simplistic model, misleading distinction between high- and low-spin, no spectroscopic properties…

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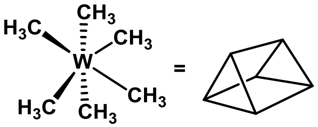
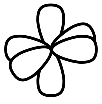
Gillespie-Nyholm theory or the **Valence Shell Electron Pair Repulsion theory (1957) –** Useful to rationalize organic compounds geometries through lone-pair/bond repulsions, although it has major limitations when applied to coordination chemistry.



JACS, ***1990***, 4547

Simple VSEPR predicts $\mathbf{d^2sp^3}$ **hybrids** and Oh geometry

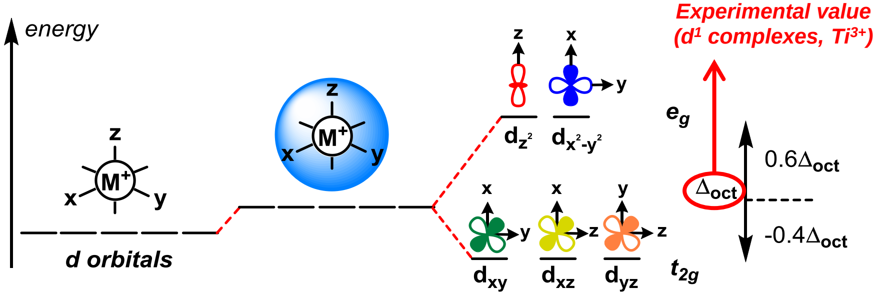
Note: VSEPR considers the effect of lone pairs, thus ions with different d-occupancy should have different geometries.



$\mathbf{d^2sp^3}$

Kepert Model – Does not consider non-bonding orbitals. Fails at D_{4h} complexes.

Crystal Field Theory (Van Bleck, 1932) – Electrostatic model which predicts that the d orbitals in a metal complex are not degenerate. The pattern of splitting of the d orbitals depends on the crystal field, this being determined by the arrangement and type of ligands.



Factors governing the magnitude of Δ_{oct}

(a) Oxidation state of the metal ion
(b) Row of the metal ion
(χ) σ-donor and π-acceptor properties of ligands

Δ_{oct} (*weak field*) < Δ_{oct} (*strong field*)

Spectrochemical series of ligands – Experimentally determined series. Incorporates both the effect of σ and π bonding.

Weak field ligands

$O_2^{2-} < I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3^- < F^- < NCO^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < CH_3CN < py < NH_3 <$ bipy $<$ phen $< NO_2^- < PPh_3 < CN^- < CO$

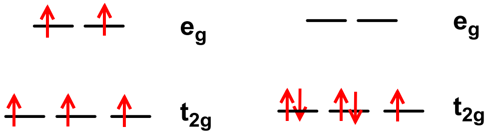
Strong field ligands

Spectrochemical series of metal ions

Mn(II) < Ni(II) < Co(II) < Fe(III) < Co(III) < Ru(III) < Mo(III) < Rh (III) < Ir(III)

Increasing field strenght

GOING DEEPER – **What determines the ground state configuration of a d^5 ion?**



High-spin

CFSE

$2*0.6\Delta_{oct}-3*0.4\Delta_{oct} = 0$

Low-spin

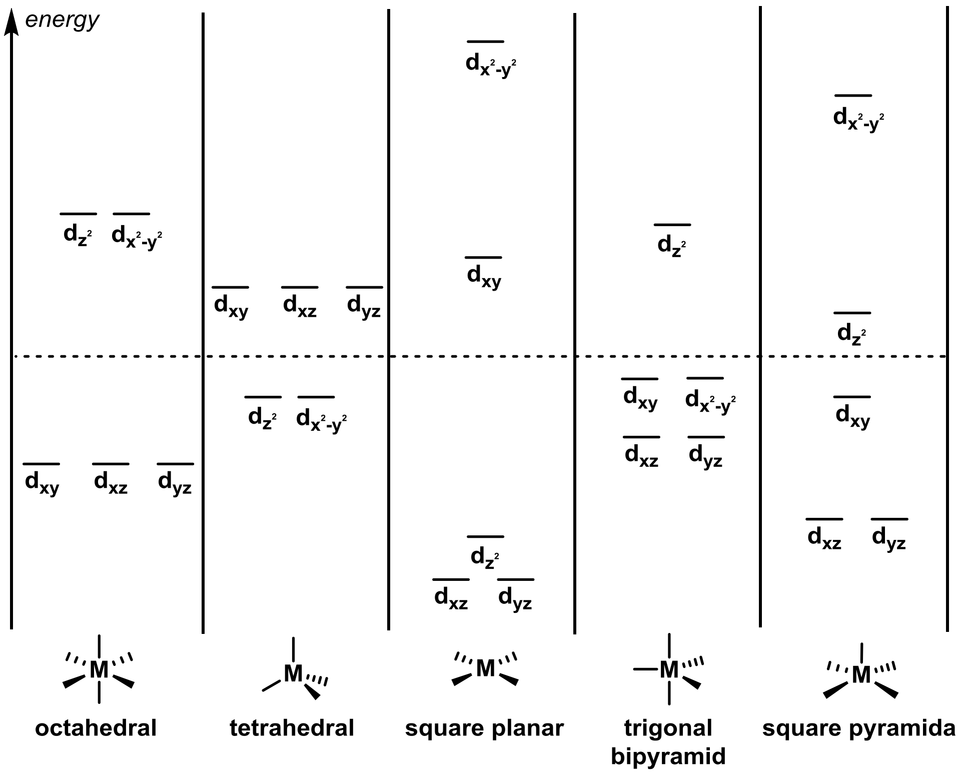
CFSE

$-2\Delta_{oct} + 2P$

The preferred configuration is that with the lower energy and depends on whether it is energetically preferable to pair the fourth electron or promote it to the e_g level.

P = electron-pairing energy

Crystal field splitting diagrams for some common fields



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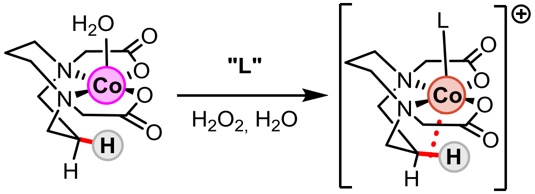
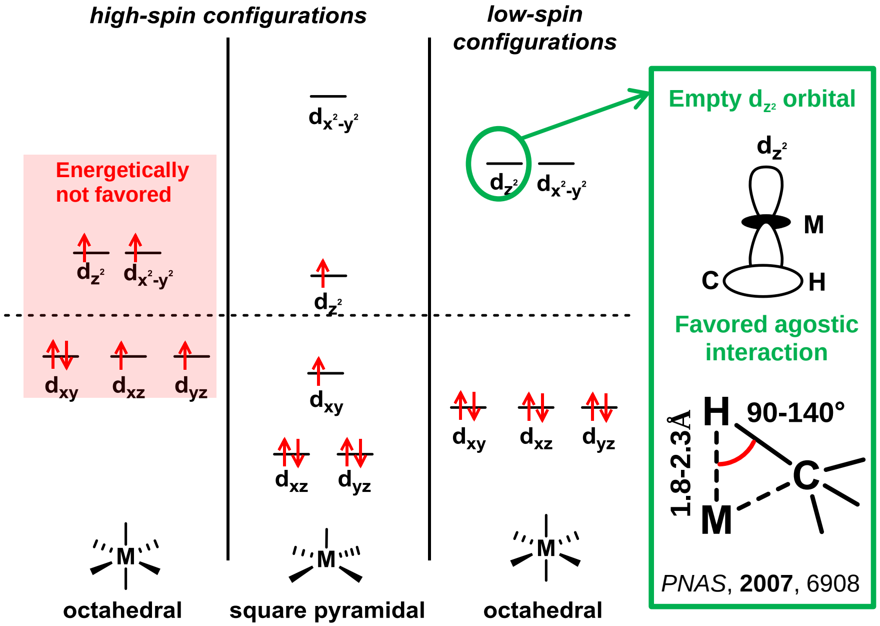
AN EXAMPLE – How the ligands effect C-H activation through **crystal field splitting** and **geometry modification**

JACS, ***1986***, 7122; IC, ***1991***, 3875.



The C-H activation step **works with strong field ligands** (CN^-, NO_2^-, SO_3^{2-} and NH_3) while **with weak field ligands** (Cl, SCN^- or H_2O) **no production** of the organometallic alkyl-Co(III) complex **was observed.**



PNAS, **2007**, 6908

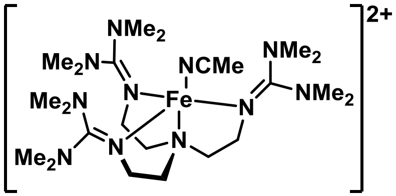
Stronger field ligands also

- Ease the oxidation of Co(II) to Co(III), as the unpaired electron is higher in energy.
- Only intermediate isolated with L = SO_3^{2-}. Trans effect -> As the trans influences, the agostic interaction is weaker, thus the acidity of the C-H bond decreases.

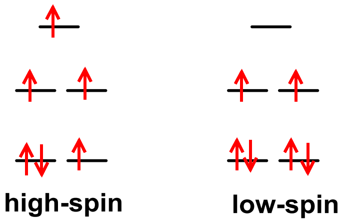
REVIEW IT YOURSELF: Dewar-Chatt-Duncanson model (must know)

Characterizing paramagnetic species (basics): magnetism and broad NMRs

For an organic chemist, a broad NMR is a consequence of a paramagnetic species that makes the analysis impossible. Typical thoughts: "Impossible to follow" or "I will never know which is that species that make my ^{1}H-NMR messy" What if your intermediate has unpaired electrons? Is it possible to characterize it?



ACIE, ***2009***, 3622



When I do a H-NMR I see broad signals, shifted peaks… why?

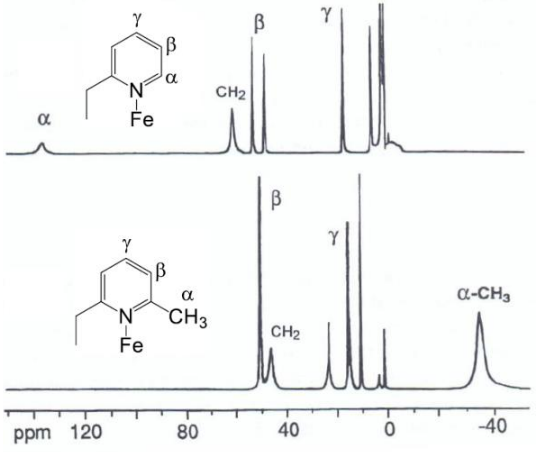
unpaired electron

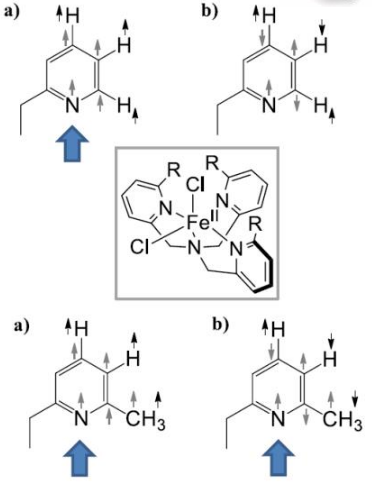
- *Modification of the chemical shift = magnetic moment of the unpaired electron,* ***dominant contribution, wide spectral window (-100 to 300 ppm)***
- *Short relaxation times* ***= broad signals, loss of couplings***

Modification of the chemical shift – Fermi contact interaction

Spin delocalization vs. Spin polarization

Fe(II) O_h complex, d^6





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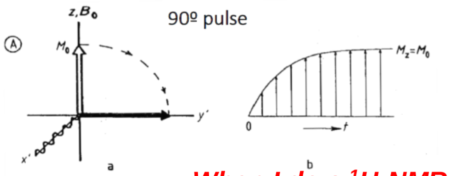
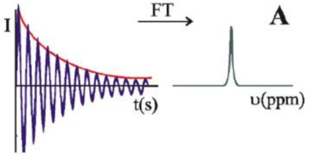
Broad signals and loss of couplings – Short relaxation times



Longitudinal relaxation, T_1
Energy dissipated into the environment. Related to time to recover equilibrium (M_0)
Interaction between the nuclei and electronic magnetic moment (through-space)

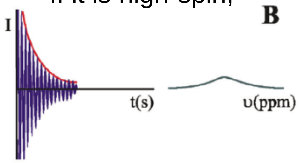
When I do a ^{1}H-NMR of an O_h Fe(II) complex…

If it is low-spin,



Diamagnetic signal: long relaxation time, well-resolved signal, few scans

If it is high-spin,



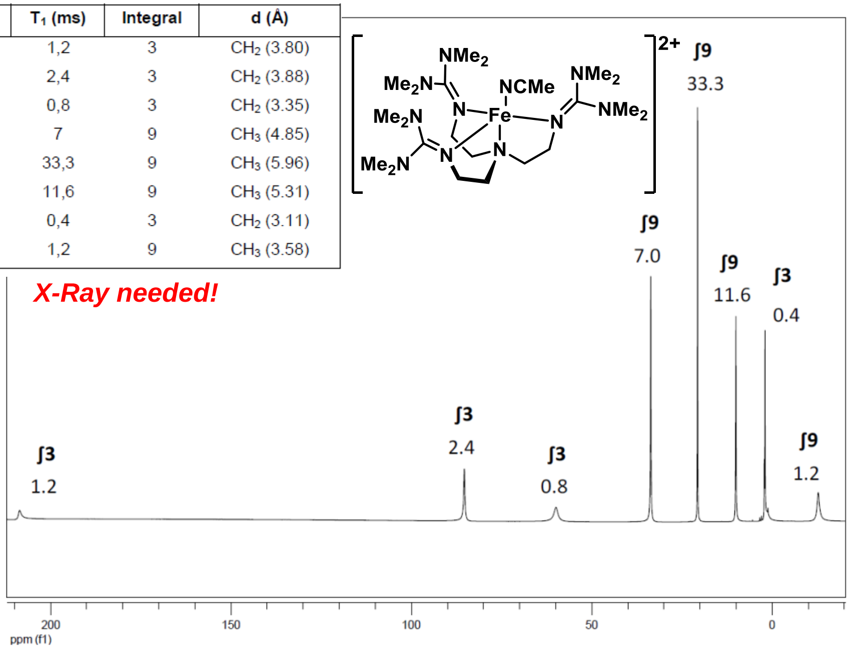
Paramagnetic signal: short relaxation time, low resolution, many scans

Determining T_1 (not trivial) we can optimize the integral of each signal as well as assign every proton signal in a paramagnetic NMR, due to

$$T_1 \propto r^6$$

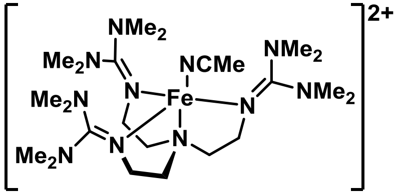
δ (ppm)	T_1 (ms)	Integral	d (Å)
213,5	1,2	3	CH_2 (3.80)
85,6	2,4	3	CH_2 (3.88)
60,2	0,8	3	CH_2 (3.35)
33,8	7	9	CH_3 (4.85)
20,7	33,3	9	CH_3 (5.96)
10,1	11,6	9	CH_3 (5.31)
1,9	0,4	3	CH_2 (3.11)
-13,1	1,2	9	CH_3 (3.58)

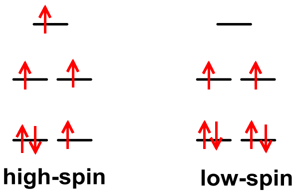
X-Ray needed!



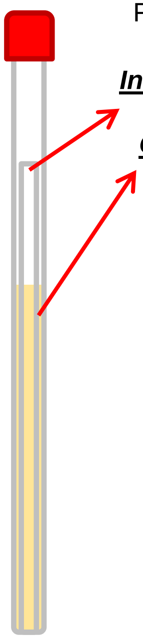
Characterizing paramagnetic species: other techniques

(a) The Evans method – D. F. Evans, J. Chem. Soc. 1959, 2003. The Evans method is a useful NMR technique to measure the magnetic susceptibility of a paramagnetic sample and subsequently calculate the number of unpaired electrons in paramagnetic complexes.



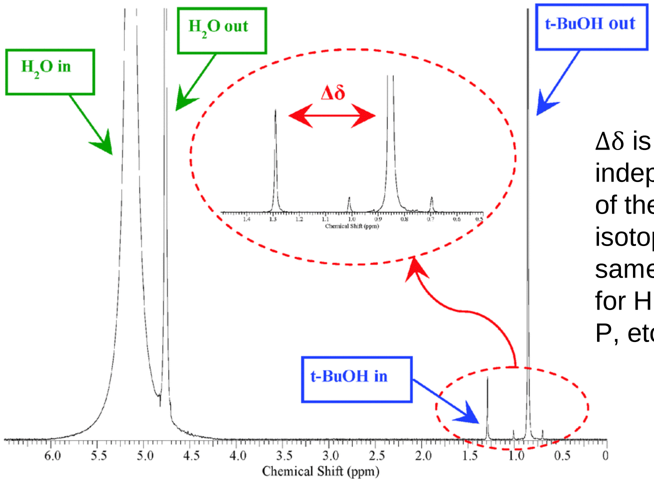


Fe(II), C_{3v}, d^6 – **two possible spin configurations**



Inner tube – Reference compound (TMS, CH_2Cl_2..) and solvent

Outer tube – Reference, solvent and sample in known [C]



Δδ is independent of the isotope: same shift for H, C, F, P, etc.

Magnetic susceptibility (X_m, ml mol^{-1})

T = temperature

$$X_m = \frac{-3\Delta\delta \cdot 10^{-6}}{4\pi c} \implies \mu_{eff} = 2.828\sqrt{Xm \cdot T}$$

c = concentration (M)
$\Delta\delta$ = chemical shift between inner and outer reference

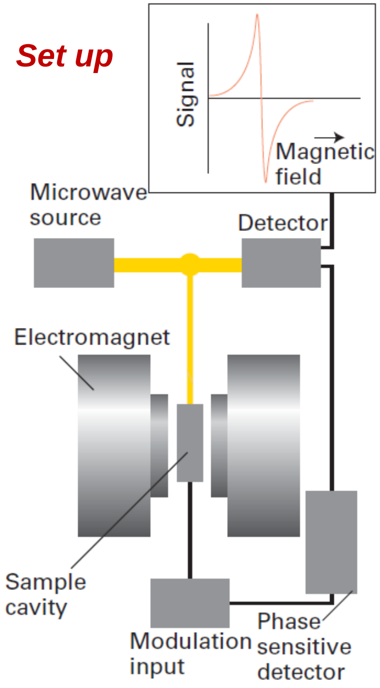
$$\Downarrow$$

$$\mu_{eff} = \sqrt{n(n+2)}$$

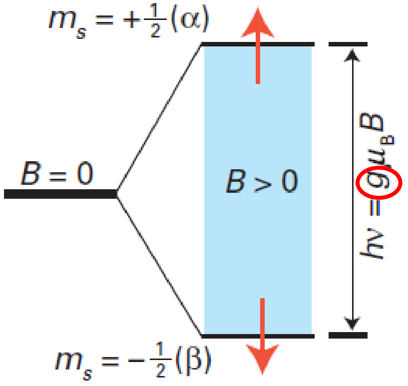
n = unpaired electrons

(c) EPR spectroscopy – Magnetic resonance on unpaired electrons. Study of paramagnetic species (radicals, main-group radicals and d-metal ions).

Set up



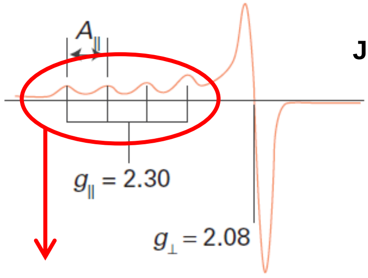
1 unpaired electron (s = ½), the application of an external magnetic field (B) produces a difference in energy between ms = ½ and ms = -½ .



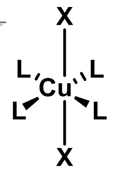
Sample irradiated with a constant MW frequency (usually 9GHz; X-band)

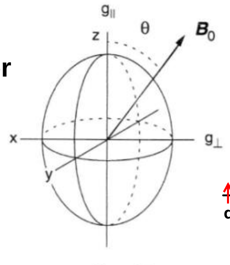
g-value – characteristic for every oxidation and spin state

For a free electron ***g = 2.0023***. In compounds = value altered by spin-orbit coupling which changes the local magnetic field experienced by the electron. One species could have more than one g-value depending on the angle that the magnetic field experiences!

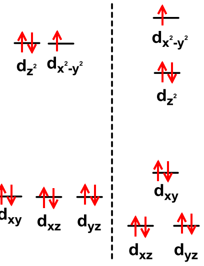


Jahn-Teller



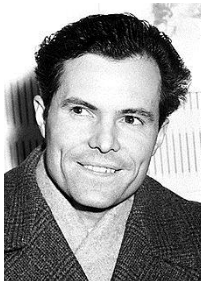


g ellipsoid



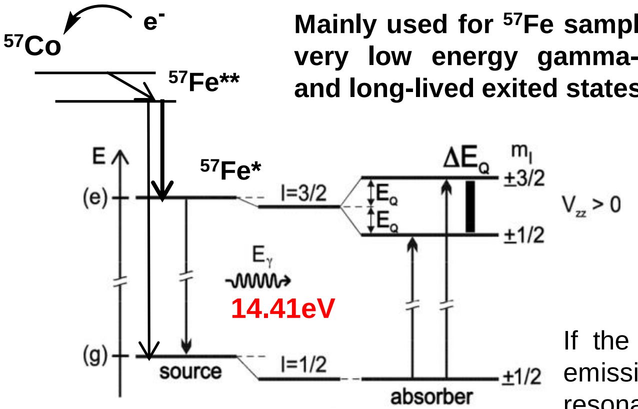
Hyperfine coupling with nucleus!
Cu; I = 3/2, 2I+1 lines of the same intensity

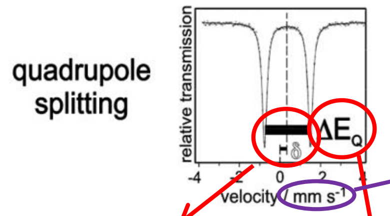
(c) Mössbauer spectroscopy – Rudolf Mössbauer discovered the recoiless emission of gamma-rays by a nucleus, which is then absorbed resonantly.



Rudolf Mössbauer
28yo, discovery
32yo, Nobel Prize

Mainly used for ^{57}Fe samples: very low energy gamma-ray and long-lived exited states

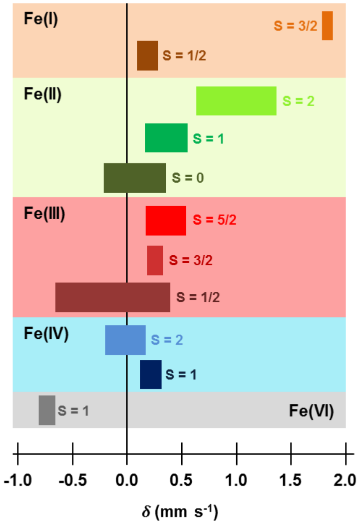




Isomer shift

Quadrupole splitting

If the sample is pure ^{57}Fe, the emission will be absorbed resonantly. Other types of ^{57}Fe samples will resonate differently due to magnetic and electric field variations. How do we tune the gamma-emision then? **Doppler-Effect!**



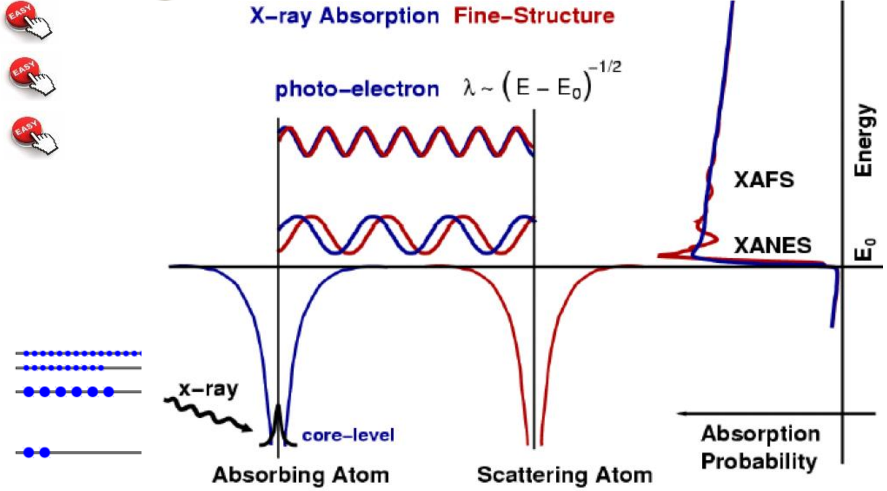
(a) Isomer shift (δ) – ΔE between the sample and that of metallic ^{57}Fe. Depends on the magnitude of the electron density at the nucleus (s electrons).

(b) Quadrupole splitting – Due to anisotropic distribution of electric field, spectrum splits in two lines of separation **ΔE_Q**. Oxidation state and distribution of d-electron density (spin).

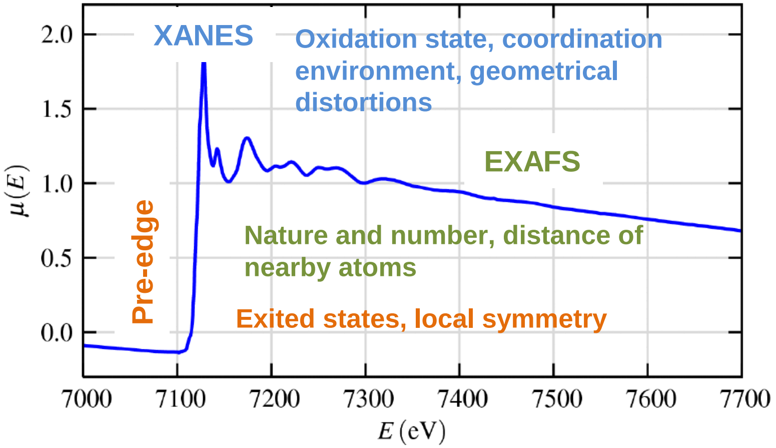
Other useful nucleus:
^{119}Sn, ^{129}I and ^{197}Au

(c) X-Ray Absorption Spectroscopy – Extremely useful to determine the oxidation state of an element in a compound and to investigate ist local environment.

X-Ray emission excites an inner shell electron, which is removed leaving a hole. This hole is filled by higher layer electrons, thus emmiting X-Ray radiation. (+Auger effect). The absorbtion energy depends both on the ***metal*** and on the ***surrounding atoms***.



What should I, an OC, know from this technique?



XANES: Oxidation state, coordination environment, geometrical distortions

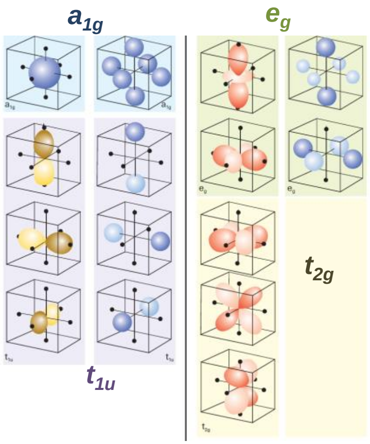
EXAFS: Nature and number, distance of nearby atoms

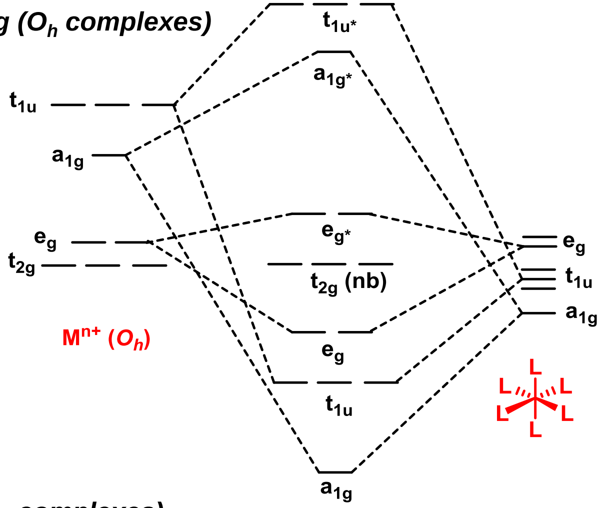
Pre-edge: Exited states, local symmetry

Molecular orbital theory (MOT) and Ligand Field Theory

The crystal field theory is extremely useful but has several limitations: ***ionic compounds***, ***covalent bonding*** and place of ligands in spectrochemical series. That is solved by the Molecular Orbital Theory – Ligand Field Theory.

(1) No metal-ligand p bonding (O_h complexes)

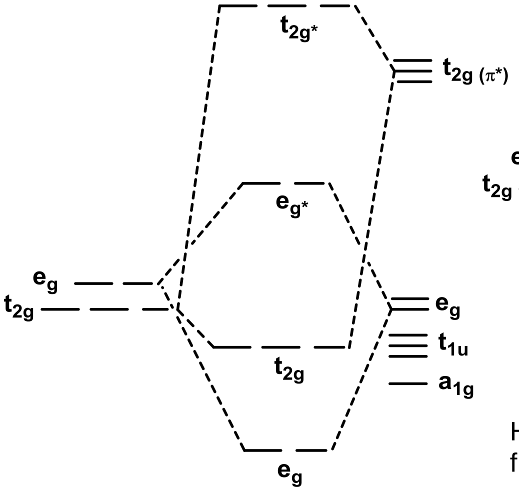




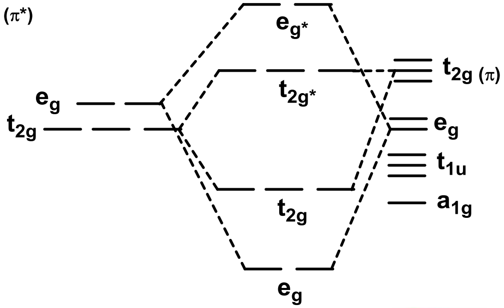
(2) Metal-ligand p bonding (O_h complexes)

The t_{2g} set is non-bonding at σ-complexes, but overlaps with symmetry allowed ligand orbitals to give π-interactions

π-acceptor, strong field



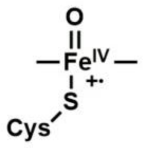
π-donor, weak field



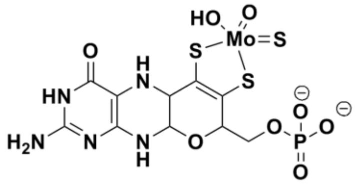
How do you rationalize ligand field with CO and CN^-? I^- and F^-?

AN EXAMPLE – THE OXO WALL

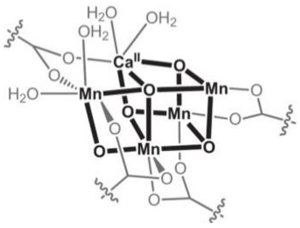
Metal-oxo compounds are involved in OAT and HAT reactions in **natural systems** such as



Cyt P450

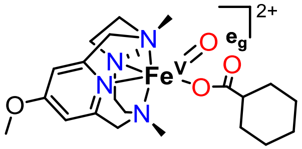


Xanthine oxidase

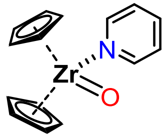


OEC - PSII

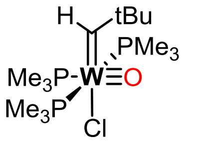
However, metal-oxo compounds can proceed from synthetic routes



JACS, ***2018***, 3916

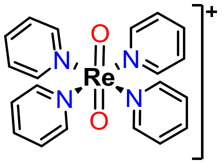


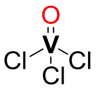
JACS, ***1993***, 4917.

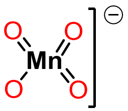


OM, ***2012***, 7278

Indeed, **early transition metal-oxo compounds are ubiquitous**…



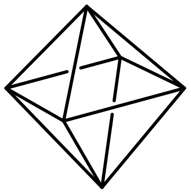




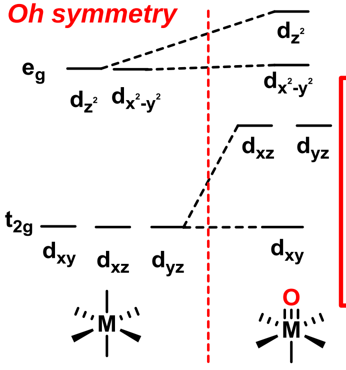
What about **late transition metal-oxo complexes**?

Crystal Field splitting in Oh symmetry

Ballhausen and Gray
IC, ***1962***, 111



$V(O)(OH_2)_5^{2+}$

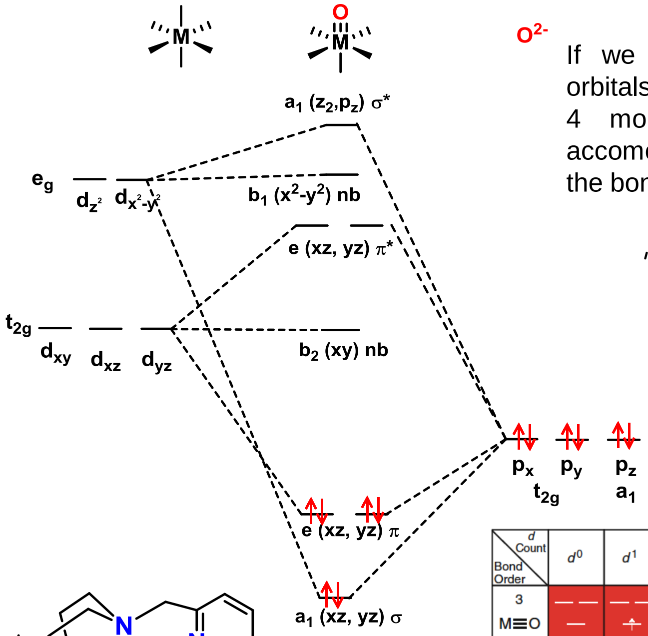


See also: Struct. Bond. ***2012***, 17

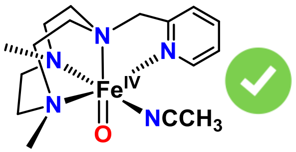
O^{2-}

THE OXO LIGAND
- Dianionic
- Monodentate
- Sometimes bridging
- Weak field ligand

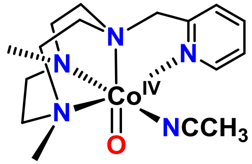
MOT treatment of the M=O bond and consequences



If we first fill the p and s orbitals with the O^{2-} ligand, only 4 more electrons can be accomodated without lowerig the bond order…

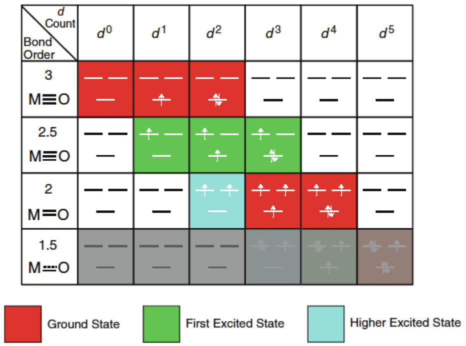


Iron(IV) ion
4 d-electrons = $4s^2\ 3d^2$
BO = 2

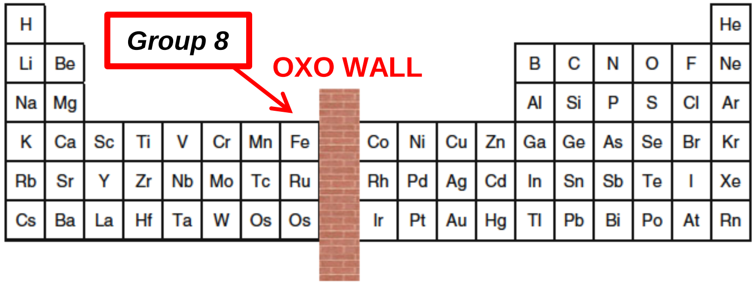


Cobalt(IV) ion
5 d-electrons = $4s^2\ 3d^3$
BO = 1.5

NOPE



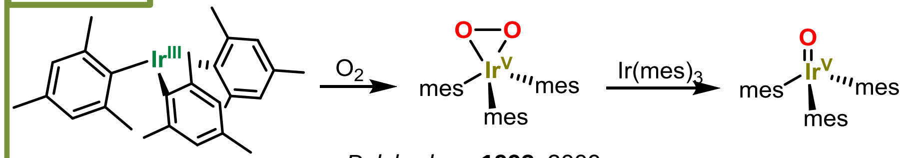
Fe, Ru and Os can form tetragonal –yl complexes
The same cannot be said for Co, Rh and Ir



AN EXAMPLE – BEYOND THE OXO WALL

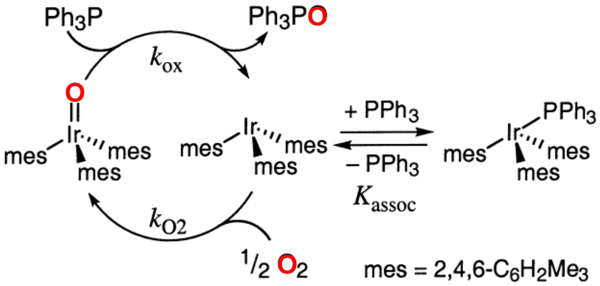
Is there something beyond the oxo-wall? Late metal-oxo complexes?

Group 9

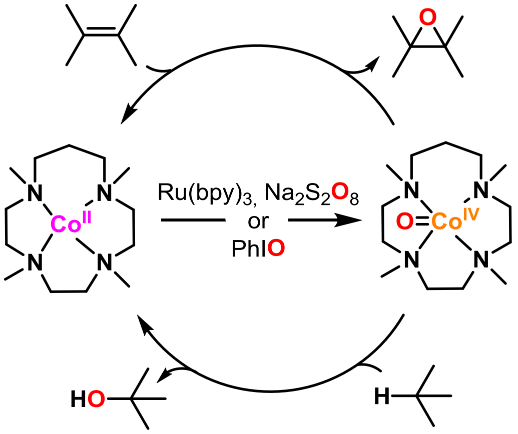


Polyhedron, **1993**, 2009

Highly electron-rich Ir^{III}, rare example of stable Ir^{V} (d^4)

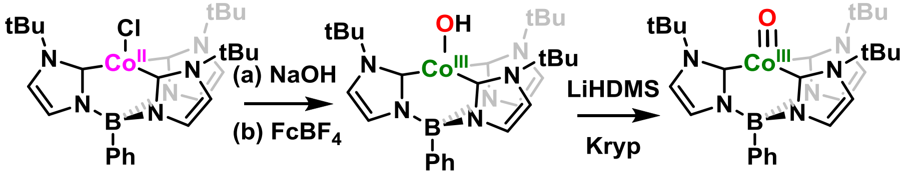


Ir^{V}=O Not only stable but catalytically active in the oxidation of PPh_3!



Co(IV), d^5 metal ion
Capable of oxidizing double bonds (OAT) and weak C-H bonds (HAT)

Co(III), d^6 metal ion

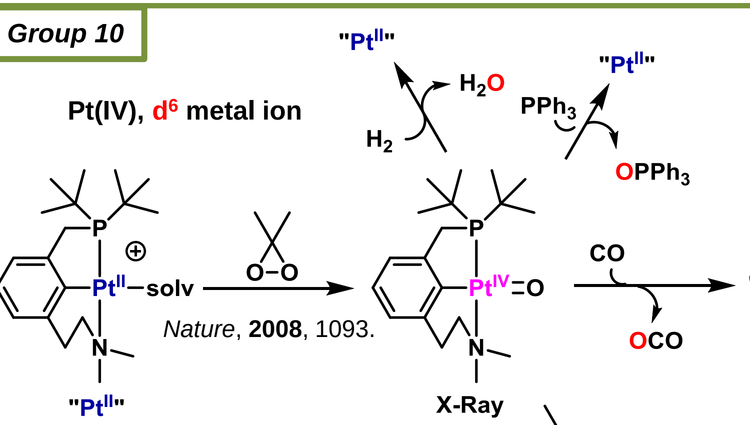


JACS, **2018**, 13176

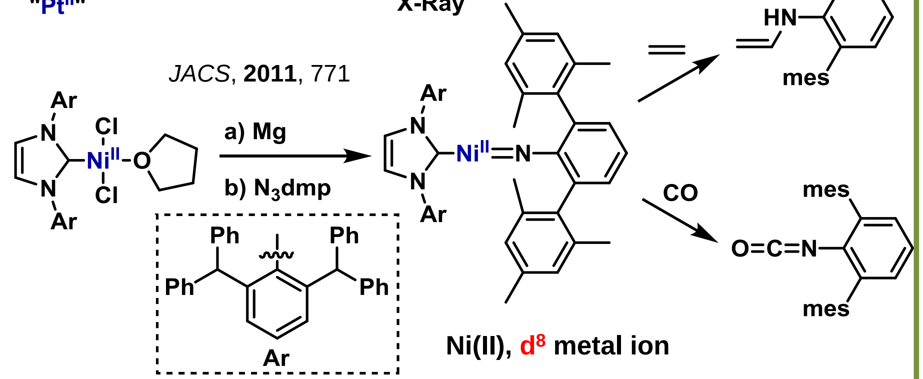
Group 10

Pt(IV), d^6 metal ion

Highly electrophilic oxidants! (stoichometric reactivity)



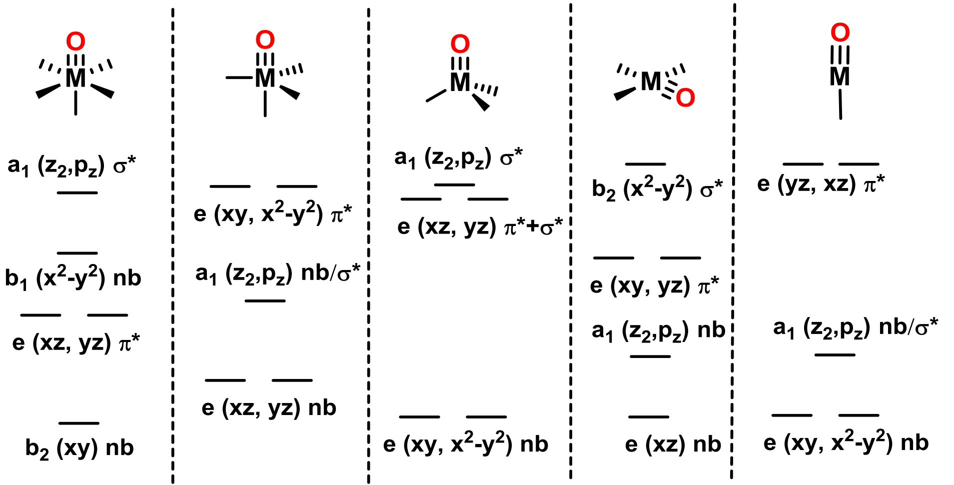
Nature, **2008**, 1093.



JACS, **2011**, 771

Ni(II), d^8 metal ion

The **oxo-wall** is not true? **d^5**, **d^6** and **d^7** ions **with oxo** and **nitrido** bonds?



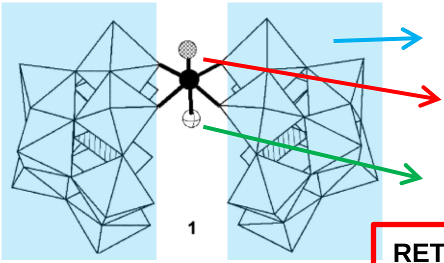
AN EXAMPLE – BEYOND THE OXO WALL

In 2004, Prof. Craig L. Hill broke the oxo-wall with seminal publications on polyoxometalated compounds, but his papers were strongly criticized by the inorganic community…

Prof. Craig L. Hill
Emory University
Atlanta, Georgia

Group 10

First O_h late-TM-oxo, Pt(IV) (d^6)



Polyoxometalate $[PW_9O_{24}]^{9-}$

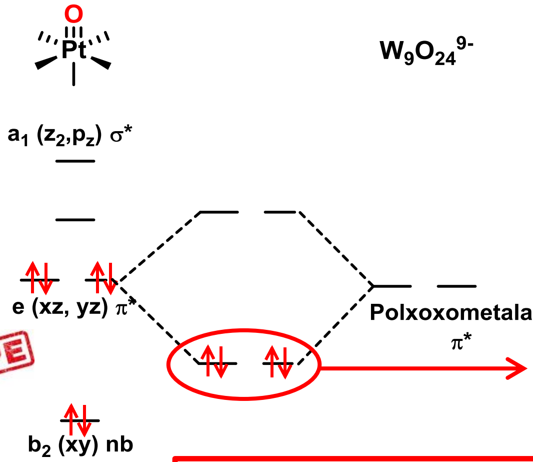
OXO-ligand (Pt=O, 1.72A)

H_2O-ligand in axial position

Science, **2004**, 2074

Characterization

- X-Ray (100 and 30K)
- Neutron Diffraction
- Magnetic susceptibility
- Elemental analysis
- Raman
- ^{31}P NMR
- UVvis



Stabilized π* electrons!

NOPE

RETRACTED IN 2012
(a) Wrong crystal refinement analysis (instead of a Pd was a W, site occupancy 0.5)
(b) Pd(II) incorporated in the polyoxometalate

IC, **2012**, 7025

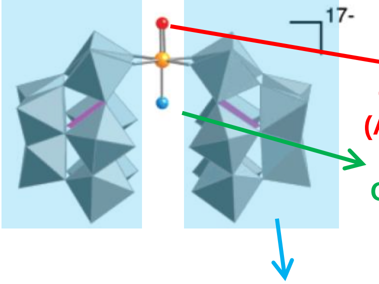
NOPE

RETRACTED IN 2012
(a) X-Ray refines 100% well if no Au is considered in the crystal structure
(b) Reaction of PPh_3 with $HAuCl_4$ and H_2O
(c) Inconsistencies in ^{17}O NMR still not resolved

IC, **2012**, 7025

Group 11

Extremely rare O_h Au(III)-oxo, Au(III) (d^8)



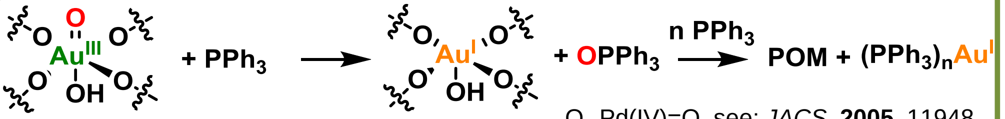
OXO-ligand (Au=O, 1.76A)

OH-ligand in axial position

Polyoxometalate $[PW_9O_{24}]^{9-}$

Characterization

- X-Ray (173, 90 and 30K)
- Neutron Diffraction
- Magnetic susceptibility
- Elemental analysis
- Electrochemistry
- FT-IR
- Redox titration
- DSC
- EXAFS
- ^{31}P NMR
- ^{17}O NMR



O_h Pd(IV)=O, see: *JACS*, **2005**, 11948
Also retracted

O_h Fe(III)=O, Costas, Que and Roithová. *JACS*, **2018**, 140, 14391

> "If one were to look at any one of the techniques, it might have been possible to pick holes in the analysis, but when taken together all the data could seem compelling and the referees decided that the results should be published. You need an extraordinary amount of data to be convincing, and they did provide a lot of data." *Prof. Clark Landis, UWisconsin-Madison*

> "One, we just published the new paper which not only gives considerable new data on these materials (originally formulated as noble metal terminal oxo compounds) but also refers to the data in the original papers and two, if we didn't retract them, all the authors, but particularly me, would doubtless be getting emails on the initial papers for years to come. This would be a nightmare." *Craig. L. Hill after retractions*

More reading: Organotransition Metal Chemistry: From Bonding to Catalysis, Ed. John Hartwig; Inorganic Chemistry, Ed. Shriver and Atkins; Concise Inorganic Chemistry, Lee; Modern Physical Organic Chemistry, Anslyn and Dougherty; Principles of Inorganic chemistry, Pfenning.