Hybridization and hypervalency in transition-metal and main-group bonding

- (The Absence of) Radial Nodes of Atomic Orbitals,
- an Important Aspect in Bonding Throughout the Periodic Table
- Consequences for p-Block Elements: Hybridization Defects,
- Hypervalency, Bond Polarity, etc....
- Consequences für the Transition Metal Elements
- Non-VSEPR Structures of d0 Complexes

Martin Kaupp, Winter School on Quantum Chemistry, Helsinki, Dec. 13-17, 2009
Analogy between Wave Functions and Classical Standing Waves

Vibrations of a string fixed at both ends. Base tone and the first two harmonics are shown.

Note the nodes (zero crossings)!! They result from the necessary orthogonality of the modes.
The Nodes of the Radial Solutions

Table 13.1. Hydrogenic radial wavefunctions†

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<th>n</th>
<th>l</th>
<th>( R_{n,l} )</th>
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<td>1s</td>
<td>1</td>
<td>0</td>
<td>( 2 \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-\frac{1}{2}\rho} )</td>
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<td>2s</td>
<td>2</td>
<td>0</td>
<td>( \frac{1}{2\sqrt{2}} \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} (2 - \rho) e^{-\frac{1}{2}\rho} )</td>
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<tr>
<td>2p</td>
<td>2</td>
<td>1</td>
<td>( \frac{1}{2\sqrt{6}} \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} \rho e^{-\frac{1}{2}\rho} )</td>
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<tr>
<td>3s</td>
<td>3</td>
<td>0</td>
<td>( \frac{1}{9\sqrt{3}} \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} (6 - 6\rho + \rho^2) e^{-\frac{1}{2}\rho} )</td>
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<tr>
<td>3p</td>
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<td>( \frac{1}{9\sqrt{6}} \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} (4 - \rho) \rho e^{-\frac{1}{2}\rho} )</td>
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<tr>
<td>3d</td>
<td>3</td>
<td>2</td>
<td>( \frac{1}{9\sqrt{30}} \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} \rho^2 e^{-\frac{1}{2}\rho} )</td>
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</table>

\( R \) is the product of an exponential \( e^{-(1/2)\rho} \) and of an associated Laguerre polynomial; \( \rho = 2Zr/na_0 \)

1s, 2p, 3d, 4f: no „primogenic repulsion“ (Pekka Pyykkö)
PERIODENSYSTEM DER ELEMENTE

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<th>NAME DES ELEMENTES</th>
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Hybridization Defects and their Consequences in p-Block Chemistry
X-H Binding Energies of Monohydrides XH, and "Saturated" Hydrides MHn

Radial Extent and Energies of Valence Orbitals


AO-Energies from Moore Tables

r-expectation values from Desclaux tables (DHF)
Reasons for Hybridization (1)

(a) better bonding overlap

(b) (radial) reduced antibonding overlap

(c) (angular)
10.6. Beschreibung von Bindungen durch MO’s, gebildet aus Hybrid-AO’s

Tab. 11. Zusammenhang zwischen Bindungsfestigkeit und Hybridisierungsgrad.

<table>
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<th>n</th>
<th>Partner</th>
<th>(E_{\text{bind}})</th>
<th>% p</th>
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<td>0</td>
<td>s, h</td>
<td>2(\beta = 2.000\beta)</td>
<td>0</td>
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<td>1</td>
<td>di, h</td>
<td>2(\sqrt{2}\beta = 2.828\beta)</td>
<td>50</td>
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<td>2</td>
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<td>(\frac{2}{3}(\sqrt{3} + \sqrt{5}) = 2.788\beta)</td>
<td>67</td>
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<td>3</td>
<td>te, h</td>
<td>((1 + \sqrt{3})\beta = 2.732\beta)</td>
<td>75</td>
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<tr>
<td>\infty</td>
<td>p, h</td>
<td>2(\beta = 2.000\beta)</td>
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<tr>
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<td>s, s'</td>
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<td>((2 + \frac{4}{3}\sqrt{2})\beta = 3.886\beta)</td>
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<td>((2 + \sqrt{3})\beta = 3.732\beta)</td>
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<td>\infty</td>
<td>p, p'</td>
<td>2(\beta = 2.000\beta)</td>
<td>100</td>
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</table>

Abb. 56. Abhängigkeit der Bindungsfestigkeit vom Hybridisierungsgrad.


W. Kutzelnigg, Einführung in die Theoretische Chemie, Vol. 2
Mulliken gross populations for valence AOs in XHₙ hydrides without free electron pairs

Hybridization Defects (2)

\[ \cos(180-\theta) = \frac{a_2}{1-a_2} \]

(a2 = s-character, 1-a2 = p-character)

Holds only for orthogonal hybrids!

*A posteriori* hybridization analyses from DFT calculations (BP86/TZVP)
Explanations of the Inert-Pair Effect

1) Promotion energies increase down the group

2) Drago: Binding energies decrease down the group
   □ promotion energies are not overcompensated anymore

3) Extension following Kutzelnigg:
   Promotion does not take place anymore
   □ no good hybrids and weakened covalent bonds in higher oxidation state
Why is Inorganic Lead Chemistry Dominated by PbII, but Organolead Chemistry by PbIV?


decreasing stability:

\[
R4Pb > R3PbX > R2PbX2 > RPbX3 > PbX4
\]

\(R = \text{alkyl, aryl; } X = \text{halogen, OR, NR2, OOCR, etc…….}\)
Substituent Effects on 1,2-Elimination Reactions of Pb(IV) Compounds

\[
PbMe_n F_{4-n} \quad PbMe_n F_{2-n} + F_2
\]

\[
PbMe_n F_{4-n} \quad PbMe_{n-1} F_{3-n} + MeF
\]

\[
PbMe_n F_{4-n} \quad PbMe_{n-2} F_{4-n} + C_2 H_6
\]

\[
PbF_4 \quad PbMeF_3 \quad PbMe_2 F_2 \quad PbMe_3 F \quad PbMe_4
\]

\[\Delta E_{\text{react.}} \text{ (kJ mol}^{-1}\text{)}\]


QCISD/DZ+P data
Substituent Effects on 1,1-Elimination Reactions of Pb(IV) Compounds

\[ \text{PbMenF}_4-n \rightarrow \text{PbMenF}_2-n + \text{F}_2 \]

\[ \text{PbMenF}_4-n \rightarrow \text{PbMen}^{-1}\text{F}_3-n + \text{MeF} \]

\[ \text{PbMenF}_4-n \rightarrow \text{PbMen}^{-2}\text{F}_4-n + \text{C}_2\text{H}_6 \]

\[ \Delta E_{\text{React. (kJ mol}^{-1})} \]


QCISD/DZ+P data
Hybridization Defects (3)

h(E): NPA/NLMO Hybridization results from DFT calculations (BP86)
Influence of Electronegative Substituents on Hybridization in Pb$^{IV}$ Compounds

$\text{J. Am. Chem. Soc. 1993, 115, 1061.}$
Bent's Rule: Basic Principles


exceptions: a) large steric effects, b) very different sizes of substituent orbitals (e.g. H vs. Hg), c) counteracting effects for very light central atoms d) transition metal systems (cf. also Huheey text book)

larger angles between more electropositive substituents

more s-character of central atom is directed towards less electronegative substituent, more p-character to more electronegative substituent
Bent's rule effects in organolead fluorides

Bent's Rule: Counteracting Effects

negative hyperconjugation counteracts EN effects

negative hyperconjugation “switched off“
	negative hyperconjugation small for heavier elements

/6-31G*, E(Lewis)

Reed/Schleyer
JACS 1987, 109, 7362.
Bent’s Rule and Lone Pairs

h: NPA/NLMO Hybridization

results from DFT calculations (BP86)
Inversion Barriers and Hybridization

- Everything that enhances hybridization defects increases inversion barrier and decreases angles!

- e.g. $\text{NH}_3 << \text{PH}_3 < \text{AsH}_3 < \text{SbH}_3 < \text{BiH}_3$
- $\text{NLi}_3 << \text{NH}_3 << \text{NF}_3$
- $\text{NH}_3 << \text{NH}_2\text{F} << \text{NHF}_2 << \text{NF}_3$
Further Peculiarities of 1st-Row (2. Period) Elements (p-Block)

important: size, electronegativity, hybridization defects

particularly weak bonds for F2, H2O2, N2H4, ..........
e.g. BDE (kJ mol-1):  F2 155, Cl2 240, Br2 190, I2 149.
(cf. also low EA of fluorine atom!)
explanation: „lone-pair bond weakening effect“ (Sanderson),
(less pronounced for heavier homologues)

preference for ⋅⋅⋅ multiple bonding compared to chain-linked single
bonds
e.g.: O2 vs S8, CO2 vs. SiO2, ketones vs. silicones

e.g. BDE (kJ mol-1):
Binding Energies
Preference for multiple bonding compared to chain-linked single bonds

Increments (\(\theta\) /\(\bar{\theta}\), in kJ mol\(^{-1}\)):

Also: bond ionicity
cf. silicates, etc…!

BDEs (kJ mol\(^{-1}\)):

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<th>C-X</th>
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Abbildung 2.51 Elektronegativität der Hauptgruppen. Die Elektronenzahl $Z$ nimmt innerhalb der Perioden die Elektronenzahlenaufsteigend. Rechts oben im PSE stehen daher die Elemente wie $B$ und $C$ als Halbmetalleg, während unten die typischen Metalle wie $Li$ und $Be$ stehen. Die Formel $\Delta \chi = 0.102 \cdot \sqrt{\Delta}$ beschreibt die Abhängigkeit der Elektronegativität von der Elektronenzahl.

\[
\chi_{\text{AR}} = 0.359 \cdot \frac{Z_{\text{eff}}}{r^2} + 0.744
\]
Silicon-Oxygen Bonds

Electronegativity
Si: 1.74  O: 3.50

H₃C⁻O⁻CH₃

Electron-Localisation-Function

H₃Si⁻O⁻SiH₃

Electron-Localisation-Function

The Si-O Bond has a Strong Ionic Character
Summary: Hybridization Defects and Related Phenomena in p-Block Main-Group Chemistry

- 2p shell has no primogenic repulsion and is thus compact
- this favors isovalent hybridization in the 2nd period
- electronegative substituents enhance hybridization defects
- for the heavier p-block elements, hybridization defects are important for inert-pair effect, inversion barriers, Bent’s rule effects, double-bond rule
Hypervalency?
On Myth and Reality of d-Orbital-Participation in Main-Group Chemistry
On the Definition of Hyper-(co)-Valency

MgF$_6^{4-}$  SiF$_6^{2-}$  SF$_6$

covalency increases

ionicity increases

certainly no hypervalency

hypervalency?
A Working Definition of Hypervalency

We regard a molecule as hypervalent if at least for one atom the bonding situation requires more valence orbitals than available for the free atom.
The Early History of Hypervalency, Part 1

electron pair theory, octet rule
Lewis 1916; Kossel 1916; Langmuir 1919

directed valency, spmdn hybrids, electroneutrality principle
Pauling 1931, 1940, 1948

3-center-4-electron-bond
Pimentel 1951; Hach, Rundle 1951
Limiting Bonding Situations:
Example of Different Lewis Structures for XeF2

\[ |F-Xe^+| \quad \text{covalent, hypervalent} \]

\[ |F| \quad |Xe| \quad |F| \quad \text{partially ionic, delocalized} \]

\[ |F^-| \quad |Xe^2+| \quad |F^-| \quad \text{ionic} \]
3-Center-4-Electron MO Model

\[ \text{F} \downarrow \quad \text{Xe}^+ \downarrow \text{F}^\downarrow \quad \text{F}^- \quad \text{Xe}^+ \downarrow \text{F}^\downarrow \]

\[ \sigma_a \]
\[ \sigma_n \]
\[ \sigma_b \]

\[ \pi_a \]
\[ \pi_n \]
\[ \pi_b \]
Modified 3-Center-4-Electron MO Model

\[ \left[ \overline{F} \right] + \left[ \overline{Xe + F} \right] + \left[ \overline{F} - Xe \right] \]

\( \sigma_a \)

\( \sigma_n \)

\( \sigma_b \)

\( \pi_a \)

\( \pi_n \)

\( \pi_b \)
The Early History of Hypervalency, Part 2

discovery of noble-gas compounds  
Chernik et al.; Claasen et al.; Bartlett, Hoppe; since 1962:

first ab initio calculations  
since ca. 1970

first improved wave functions, Mulliken population analyses  
since ca. 1975:
The Role of $d$-Polarization-Functions

\[ p\pi + \lambda \ d\pi = \text{polarized } p\pi \]

electric field
weak points of Mulliken population analysis:
strong basis-set dependence
unphysical (partly negative) populations
failure for transition to ionic bonding
Improved Analyses of Accurate Wave Functions

modified Roby/Davidson population analysis
Ahlrichs et al. 1976, 1985;
Wallmeier, Kutzelnigg 1979

„Natural Population Analysis“ (NPA),
„Natural Bond Orbital Analysis“ (NBO)
Reed, Weinhold 1986; Reed, Schleyer 1990

„Natural Resonance Theory“ (NRT)
Weinhold et al., 1995

energy contributions from d-orbitals
Magnusson 1986, 1990, 1993

topological analysis of electron density (QTAIM)
Cioslowski, Mixon 1993

„Generalized Valence Bond“ (GVB) theory
• Hay 1977, Cooper et al. 1994 (full-GVB)

one-center expansion of one-particle density matrix
• Häser 1996

Since late 1990’s
QTAIM based on experimental densities
(e.g. D. Stalke et al.)
“Natural Population Analysis”
“Natural Bond Orbital Analysis”
Weinhold et al. 1984, 1988

- **AO basis**: original basis set
  - occupancy-weighted Löwdin orthogonalization

- **NAO basis**: “natural atomic orbitals”
  - “natural minimal basis set” (strongly occupied)
  - “natural Rydberg basis set” (sparsely occupied)

- **NHO basis**: “natural hybrid orbitals”

- **NBO basis**: “natural bond orbitals”
  - NBO-Lewis-structure

- **NLMO basis**: “natural resonance theory” (NRT)
  - superposition of NBO-Lewis structures
  - Weinhold et al. 1995
NRT-Analysis of Sulfate Ion

NRT weight:

0%

66.2%

12x1.9% = 22.8%

11%

NRT at HF/6-31G* level

Weinhold et al., 1995
Which NRT-Lewis Structure Describes the Perchlorate Ion Best?

NRT weight:

0%

60.9%

12x2.0% = 24.0%

15%

NRT at HF/6-31G* level
Weinhold et al., 1995
NRT Weights (w) for Various Lewis Structures in Oxo Anions and Sulfur Oxides

species

NRT at HF/6-31G* (MP2/6-31G*) level
Weinhold et al., 1995
Hyperconjugation Exemplified by Cyclopentadiene
Negative Hyperconjugation Exemplified by Difluoromethane

\[ \text{F} \quad \text{C} \quad \text{F} \]
\[ \text{H} \quad \text{H} \quad \text{H} \]

\[ \text{F}^- \quad \text{C} \quad \text{F}^+ \]
\[ \text{H} \quad \text{H} \quad \text{H} \]

\[ \text{F}^+ \quad \text{C} \quad \text{F}^- \]
\[ \text{H} \quad \text{H} \quad \text{H} \]

\[ \text{F} \quad \text{C} \quad \text{F} \quad \pi(F) \]
\[ \text{H} \quad \text{H} \quad \text{H} \]

\[ \sigma^*(C-F) \]
Negative Hyperconjugation in F3PO

σ*(P-F) (to e*-MO)

π(O) (to e-MO)
....and for \( \pi \)-backbonding in phosphane complexes....

\[
\sigma^* (P-F) \quad \pi (M)
\]
Musher's Classification of „Hypervalent“ Compounds

(Musher 1969)
MO-Diagram of SF\(_6\)
Summary: Hypervalency, d-Orbital-Participation in p-Block Main-Group Chemistry

- in normal valent and „hypervalent“ p-block main-group systems, d-functions serve as „polarization functions“ but not as true valence orbitals

- hypervalent Lewis structures usually obtain small or no weight!

- ionic bonding contributions dominate, assisted by delocalization (3-c-4-el.-bonding, negative hyperconjugation)

in PF₅, SF₆ etc., delocalization is more complex due to...
### Transition Metal Systems

<table>
<thead>
<tr>
<th>Period</th>
<th>Group</th>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>Li, Be</td>
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<tr>
<td>2</td>
<td>2</td>
<td>Be, Mg,</td>
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<tr>
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<td>3</td>
<td>Sc, Y,</td>
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<td>4</td>
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<td>5</td>
<td>5</td>
<td>Zr, Nb,</td>
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<td>6</td>
<td>6</td>
<td>Hf, Ta,</td>
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<td>7</td>
<td>7</td>
<td>Pt, Au,</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>Au, Ag,</td>
</tr>
</tbody>
</table>

The periodic table highlights the transition metals, which are found in the 4th, 5th, and 6th periods of the periodic table.
Radial Orbital Densities of the Manganese Atom

$J. \text{Comput. Chem.} \ 2007, \ 28, \ 320$
The problem of the outermost core shells in transition-metal atoms

\[ M \quad L \]

\[(n-1)d\]

\[(n-1)s, p\]

outermost core shell

Pauli repulsion

\[ \text{stretched bond} \]

The problem is most pronounced for the 3d elements (nodelessness of the 3d shell)

- weak bonds, low-lying excited states, strong (nondynamical) correlation effects

The 4d shell is already better suited for bonding overlap.
The 5d shell even more so due to its relativistic expansion.

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The problem of the outermost core shells in transition-metal atoms

The problem is most pronounced for the 3d elements (nodelessness of the 3d shell)
- weak bonds, low-lying excited states, strong (nondynamical) correlation effects

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The 5d shell even more so due to its relativistic expansion.

Non-VSEPR Structures and Bonding for d0-Systems
Non-VSEPR Structures of d0-Systems

VSEPR = valence-shell electron-pair-repulsion model
Practical Relevance of d0-Systems

- e.g. catalysis
- Mo-Cofactor (after Rajagopalan, Johnson)
- ZrO₂, ferroelectric perovskites

- e.g. bioinorganic chemistry

- e.g. materials
The Question of Bending of the Alkaline Earth Dihalides

linearization energies in kJ/mol from SDCI calculations

(J. Am. Chem. Soc. 1991, 113, 6012)
Factors Controlling the Structures of d0 Systems

maximization of d-orbital participation in \( \sigma \)-bonding

mutual repulsion and polarization of the ligands

regular, "VSEPR" structures

maximization of \( \sigma \)-bonding

distorted, "non-VSEPR" structures

polarization of central-atom semi-core orbitals by the ligands, "inverse polarization" of cation

Review:
d-Orbital-Contributions to HOMO in d0 MX2-Complexes

b) bent structure

(e.g. SrX₂, BaX₂)
BaH2: Electron Localization Function (ELF, color scale) projected on electron density (cloud of points)
force constants from polarized ion model too low for Be and Mg complexes but too high for Ca, Sr, and Ba complexes
outer-core polarization and d-orbital participation cannot be separated completely!
Factors Controlling the Structures of d0 Systems

maximization of d-orbital participation in \( \sigma \)-bonding

distorted, „non-VSEPR“ structures

polarization of central-atom semi-core orbitals by the ligands, „inverse polarization“ of cation

mutual repulsion and polarization of the ligands

maximization of \( \pi \)-bonding

Review:
Low Ligand-Ligand Repulsion for Neutral Ligands
J. Phys. Chem. 1992, 96, 7316

\[ \Delta E(\text{MP2})_{\text{Lin}} = 0.6 \text{ kJ/Mol} \]

\[ \Delta E(\text{HF})_{\text{Plan}} = 0.4 \text{ kJ/Mol} \]
$\Delta E({\text{MP2}})_{\text{Lin}} = 0.2 \text{ kJ/Mol}$
Factors Controlling the Structures of d0 Systems

maximization of d-orbital participation in \( \sigma \)-bonding

distorted, „non-VSEPR“ structures

polarization of central-atom semi-core orbitals by the ligands, „inverse polarization“ of cation

mutual repulsion and polarization of the ligands

maximization of \( \sigma \)-bonding

Review:
Effects of $\pi$-Bonding

**C2v(in-plane)**

<table>
<thead>
<tr>
<th>X: Li</th>
<th>BeH</th>
<th>BH2</th>
<th>CH3</th>
<th>NH2</th>
<th>OH</th>
<th>F</th>
</tr>
</thead>
</table>

$\Delta E_{\text{lin}}$/kJ mol$^{-1}$

- C2v(in-plane)
  - $\Delta E_{\text{HF}} = 0.0$ kJ mol$^{-1}$

- C2v(out-of-plane)
  - $\Delta E_{\text{HF}} = +15.7$ kJ mol$^{-1}$

**Diagram:**

- $118.4^\circ$
  - C2v(in-plane)
  - $\Delta E(\text{HF}) = 0.0$ kJ mol$^{-1}$

- $128.8^\circ$
  - C2v(out-of-plane)
  - $\Delta E(\text{HF}) = +15.7$ kJ mol$^{-1}$
MR2 (M = Ca, Yb, Eu; R = C[Si(CH3)3]3)
Structural Preferences of d0 MX3 Complexes

π-Acceptor-Type d-Orbitals for Linear and Bent MX2 d0 Complexes

\( \pi_{ip}', 'b2' \)

\( \pi_{op}', 'a2' \)

\( \pi_{op}', 'a2' \)

\( \pi_{ip}', 'a1' \)

\( \pi_{op}', 'b1' \)
\( \pi\)-Bonding Favors Bent Structure in some Cases!

\[ \text{ScF}_2^+ \]

- \( \sigma \) (bold line)
- \( \pi_{ip} \) (red dashed line)
- \( \pi_{av} \) (blue dotted line)
- \( \pi_{op} \) (green dotted line)
π-Bonding Favors Bent Structure in some Cases!

<table>
<thead>
<tr>
<th>ZrO₂</th>
<th>( \pi_{\text{op}} )</th>
<th>( \pi_{\text{ay}} )</th>
<th>( \pi_{\text{ip}} )</th>
<th>( \sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>10</td>
<td>18</td>
<td>17</td>
<td>10</td>
</tr>
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<td>170</td>
<td>11</td>
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<td>18</td>
<td>11</td>
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<td>160</td>
<td>12</td>
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<td>12</td>
</tr>
<tr>
<td>150</td>
<td>13</td>
<td>21</td>
<td>20</td>
<td>13</td>
</tr>
<tr>
<td>140</td>
<td>14</td>
<td>22</td>
<td>21</td>
<td>14</td>
</tr>
</tbody>
</table>

\( \pi_{\text{av}} \): Average π-Bonding.
Inversion of Bent’s rule for d0-Systems

(CH3)2SiCl2

Si

Cl

Cl

107.50

114.20

(CH3)2TiCl2

Ti

Cl

Cl

117.30

102.80

GED data, Haaland et al., 1996.
Examples for Nonoctahedral Complexes with Sulfur Ligands

See, e.g.:
Inorg. Chem. 1993, 32, 2085
Inorg. Chem. 1989, 28, 773, etc....

Fig. 1 An ORTEP drawing of the complex anion \([\text{Mo}\{\text{O}_2\text{CC(S)-Ph}_2\}\_3]^2^-\) showing 50% probability ellipsoids and the atom labelling scheme. Hydrogen atoms omitted for clarity.

typical ligand types:
Are d<sup>0</sup> ML<sub>6</sub> Complexes Always Octahedral? The X-ray Structure of Trigonal-Prismatic [Li(tmed)]<sub>2</sub>[ZrMe<sub>6</sub>]

Paige M. Morse and Gregory S. Girolami

School of Chemical Sciences
University of Illinois at Urbana—Champaign
505 S. Mathews, Urbana, Illinois 61801

Figure 1. Molecular structure of [Li(tmed)]<sub>2</sub>[ZrMe<sub>6</sub>]. The methyl groups of the tmed ligands have been omitted for clarity. Important bond distances (Å) and angles (deg) are as follows: Zr–C7 = 2.43 (1), Zr–C8 = 2.37 (1), Zr–C9 = 2.35 (1), Li–C7 = 2.17 (2), Li–C8′ = 2.16 (2), C7–Zr–C8′ = 89.0 (4), C7–Zr–C9 = 82.4 (4), C8′–Zr–C9 = 84.7 (4), C7–Zr–C7′ = 78.2 (4), C8–Zr–C9 = 77.5 (4), C7–Zr–C8 = 141.5 (3), C7–Zr–C9′ = 128.2 (3), C8–Zr–C8′ = 121.0 (3), C9–Zr–C9′ = 143.5 (4).

The Structure of $\text{W(CH}_3\text{)}_6$

- Minimum: $2.15 \, \text{Å}$
- Transition state: $2.21 \, \text{Å}$
- Energy: $+17 \, \text{kJ/mol}$

<table>
<thead>
<tr>
<th>species:</th>
<th>config.</th>
<th>structure, $\Delta E^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$WMe_6$</td>
<td>$d^0$</td>
<td>$C_3$, 25 (NR: 53)</td>
</tr>
<tr>
<td>$MoMe_6$</td>
<td>$d^0$</td>
<td>$C_3$, 39</td>
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<tr>
<td>$CrMe_6$</td>
<td>$d^0$</td>
<td>$C_3$, 12</td>
</tr>
<tr>
<td>$MMe_6^-$ (M=V,Ta)</td>
<td>$d^0$</td>
<td>$D_3$</td>
</tr>
<tr>
<td>$NbMe_6^-$</td>
<td>$d^0$</td>
<td>$(C_3, 1)$</td>
</tr>
<tr>
<td>$MMe_6^{2-}$ (M=Ti,Zr,Hf)</td>
<td>$d^0$</td>
<td>$D_3$</td>
</tr>
<tr>
<td>$ReMe_6^+$</td>
<td>$d^0$</td>
<td>$C_3$, 93</td>
</tr>
<tr>
<td>$TcMe_6^+$</td>
<td>$d^0$</td>
<td>$C_3$, 112</td>
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<tr>
<td>$ReMe_6$, TcMe_6</td>
<td>$d^1$</td>
<td>$D_3$</td>
</tr>
<tr>
<td>$OsMe_6$, RuMe_6</td>
<td>$d^2$</td>
<td>$D_3$</td>
</tr>
</tbody>
</table>

$^a$energy difference between $D_3$ and $C_3$ structure in kJ/Mol (GGA-DFT level)
MO Rationalization of Nonoctahedral d0 Structures

Landis' sd-Hybridization Model (1)
(J. Am. Chem. Soc. 1998, 120, 1842)

Figure 1. Shapes and idealized bond angles for various sd hybrid orbitals.
Preferred coordination arrangements for sd5 hybrids.
Energetics of Baylar Twist for MX6 d0 Complexes

Relative energies (kJ mol\(^{-1}\)) between \(D3h\) and \(Oh\) structures of group 6 hexahalide complexes

No convergence for CrBr6, CrI6, MoI6.
Mo(SH)₆: intermediate between octahedral and trigonal prismatic
Importance of trigonal prismatic intermediates and transition structures of certain molybdenum enzymes

The Structure of WCl5CH3

Cs oct.

81.90

2.39 Å

78.10

2.19 Å

Cl

W

2.32 Å

Cl1

Cl2

Cl3

Cl4

Cl5

79.90

2.35 Å

83.30

79.90

85.30

2.35 Å

102.10

Cl

<Cl1-W-Cl5 = 97.90

<Cl1-W-Cl2 = 179.80

<Cl3-W-Cl4 = 166.30

<Cl1-W-Cl3 = 87.00

Cs trig. prism

transition state

minimum

+19 kJ/mol

BP86/A

BP86 data, relative energies in kJ/mol

Angew. Chemie 1999, 111, 3219
The Structure of WCl₄(CH₃)₂

- trans oct. C₂ (min. 0.0)
- “intermediate” C₂ (min. +6.5)
- cis oct. C₂ᵥ (TS +25.7)
- cis tp “other face”, C₂ᵥ (TS +8.5)
- tp “same face”, Cₛ (TS +14.5)

BP86 data, relative energies in kJ/mol
Angew. Chemie 1999, 111, 3219
The Structure of WCl$_3$(CH$_3$)$_3$

- Oct. fac. C$_{3v}$ (TS +61.2)
- Oct. merid. Cs (TS +26.0)
- tp “across” C1 (min. 0.0)
- tp “same face” C3 (min. +2.3)

BP86 data, relative energies in kJ/mol
Angew. Chemie 1999, 111, 3219
Limits of the Isolobal Principle

Examples of Unsymmetrical Metal Coordination in Oxide Materials

*5d vs. 4d comparisons:
KTaO₃ is regular octahedral (cubic) and paraelectric, KNbO₃ is distorted (rhombohedral) and ferroelectric at lower temperatures. LiTaO₃ has a ferroelectric transition at lower temperature (950 K) than LiNbO₃ (1480 K). More ionic bonding and larger band gap with 5d vs. 4d, due to relativistic effects!
Structures of the Dihydride Dimers $M_2H_4$ ($M = \text{Mg, Ca, Sr, Ba}$)
(relative MP2 Energies in kJ/Mol)

<table>
<thead>
<tr>
<th>Structure</th>
<th>$M_2H_4$ Energies (kJ/Mol)</th>
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</thead>
<tbody>
<tr>
<td>D2h</td>
<td>0.0</td>
</tr>
<tr>
<td>0.0</td>
<td>+20.1</td>
</tr>
<tr>
<td>+56.0</td>
<td></td>
</tr>
<tr>
<td>C2v</td>
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<tr>
<td>3</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
</tr>
<tr>
<td>C3v</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>+115.0</td>
</tr>
<tr>
<td>+5.9</td>
<td>0.0</td>
</tr>
<tr>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>D4h</td>
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<tr>
<td>5</td>
<td>+507.0</td>
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<td>+130.4</td>
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<tr>
<td>C2v</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

J. Am. Chem. Soc. 1993, 115, 11202
Summary: Understanding Non-VSEPR Structures in d0-Complexes

-d0 complexes with purely σ-bonded ligands tend to violate VSEPR and related models, in spite of increased ligand repulsion.

-while extended VSEPR models are not useful in rationalizing the distorted structures, both MO and VB models are successful for simple homoleptic complexes.

-σ-bonding is much more important in d0 complexes than in related p-block complexes, due to the availability of inner d-orbitals.

-the interrelation between σ-bonding and bond angles is complicated, due to the involvement of different d-orbitals.

-the “anti-Bent’s-rule” structure of TiCl2(CH3)2 is due to Ti-Cl σ-bonding!

-additional σ-donor ligands influence the angles between σ-donor ligands in heteroleptic complexes.
Thank you for your attention!
Structure of Mo(butadiene)₃
Extreme Resonance Structures for tris(Butadiene)-Molybdenum and Related Complexes

1, Mo$^0$, d$^6$

2, Mo$^{VI}$, d$^0$
Intermediate Resonance Structures for tris(Butadiene)-Molybdenum and Related Complexes

3 \times 3, \text{Mo}^{\text{II}}, d^4

3 \times 4, \text{Mo}^{\text{IV}}, d^2

(NRT analysis: 3\times 10\%)
\[
\begin{align*}
\Psi_4 & \quad a'' \quad e'' \\
\Psi_3 & \quad a' \quad e' \\
\Psi_2 & \quad e'' \\
\Psi_1 & \quad a' \\
\end{align*}
\]
"Non-Berry" Rearrangement of TaH5
Trends of the s- and d-valence orbitals in the transition metal series

a) radial size

from Dirac-Fock calculations (Desclaux)

Trends of the s- and d-valence orbitals in the transition metal series

b) orbital energies

from Dirac-Fock calculations (Desclaux)

<table>
<thead>
<tr>
<th>Element</th>
<th>Valenz-Elektronenkonfiguration</th>
<th>Element</th>
<th>Valenz-Elektronenkonfiguration</th>
<th>Element</th>
<th>Valenz-Elektronenkonfiguration</th>
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<tr>
<td>Sc</td>
<td>3d(^1)4s(^2)</td>
<td>Y</td>
<td>4d(^1)5s(^2)</td>
<td>La</td>
<td>5d(^1)6s(^2)</td>
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<tr>
<td>Ti</td>
<td>3d(^2)4s(^2)</td>
<td>Zr</td>
<td>4d(^2)5s(^2)</td>
<td>Hf</td>
<td>5d(^2)6s(^2)</td>
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<tr>
<td>V</td>
<td>3d(^3)4s(^2)</td>
<td>Nb</td>
<td>4d(^4)5s(^1)</td>
<td>Ta</td>
<td>5d(^3)6s(^2)</td>
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<tr>
<td>Cr</td>
<td>3d(^5)4s(^1)</td>
<td>Mo</td>
<td>4d(^5)5s(^1)</td>
<td>W</td>
<td>5d(^4)6s(^2)</td>
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<tr>
<td>Mn</td>
<td>3d(^5)4s(^2)</td>
<td>Tc</td>
<td>4d(^6)5s(^1)</td>
<td>Re</td>
<td>5d(^5)6s(^2)</td>
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<tr>
<td>Fe</td>
<td>3d(^6)4s(^2)</td>
<td>Ru</td>
<td>4d(^7)5s(^1)</td>
<td>Os</td>
<td>5d(^6)6s(^2)</td>
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<tr>
<td>Co</td>
<td>3d(^7)4s(^2)</td>
<td>Rh</td>
<td>4d(^8)5s(^1)</td>
<td>Ir</td>
<td>5d(^7)6s(^2)</td>
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<tr>
<td>Ni</td>
<td>3d(^8)4s(^2)</td>
<td>Pd</td>
<td>4d(^10)5s(^0)</td>
<td>Pt</td>
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<td>Cu</td>
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<td>Ag</td>
<td>4d(^10)5s(^1)</td>
<td>Au</td>
<td>5d(^10)6s(^1)</td>
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<tr>
<td>Zn</td>
<td>3d(^10)4s(^2)</td>
<td>Cd</td>
<td>4d(^10)5s(^2)</td>
<td>Hg</td>
<td>5d(^10)6s(^2)</td>
</tr>
</tbody>
</table>

Why??
Radialverteilung der (Pseudo)-Valenzorbitale des Bariums

On the relative energies of 3d- and 4s orbitals

The 3d orbitals are always lower in energy (and smaller!) than 4s. Stronger electron repulsion in 3d may nevertheless favor 4s occupation.
Ca atom: radial orbital densities

3p orbital (outermost core shell)

3d orbital (valence shell)

Fig. 1. Radial electron density distribution $r\phi(r)$ of the calcium atom (in atomic units): $3p^6$ of $^1S$ (---), $3d^1$ of $^1D$ (---), $4s^2$ of $^1S$ (---), and $4p^1$ of $^3P$ (---). The $\phi(r)$ are developed on the basis of table 1 except that of $3p^6$.