

Pyykkö, Schmidbaur, Seppelt

Note Title

4/7/2005

↓
Relativistic
Effects

↓
Au chemistry.

↓
F chemistry

$$\langle v_r \rangle \approx \frac{Z}{137} \cdot c \text{ for a } 1s \text{ electron}$$

Hg, $Z = 80$, 58% speed of light!

1s radius smaller by 23%!

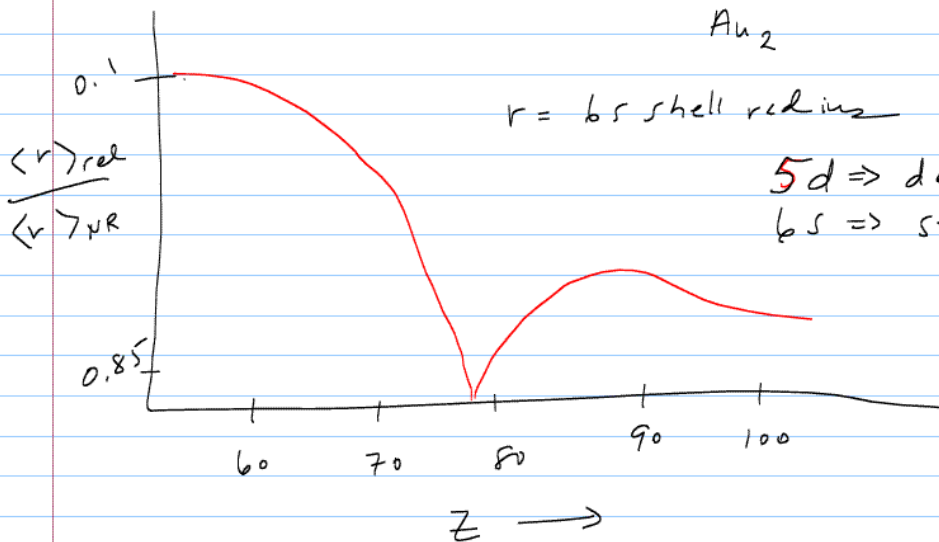
Orthogonality: 2s, 3s, 4s, 5s, 6s follow suit

l, s no longer "good" \underline{J} $s_{1/2}$, $p_{1/2}$, $p_{3/2}$

benchmark molecules

AuH

Au₂



5d \Rightarrow depts. / expands
6s \Rightarrow stays / contracts

Observables affected by Relativity:

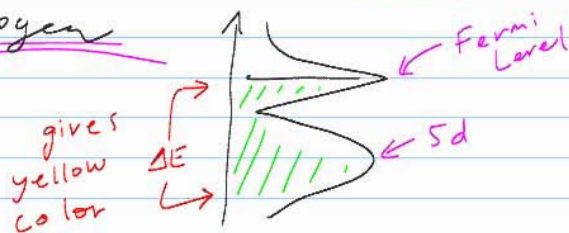
IP: 7.057 NR
 9.197 R
 9.226 exp

Au atom

EA: 1.283 NR } half the EA
 2.295 R } due to relativity!
 2.309 exp

similar to iodine!

Au as a pseudo-halogen



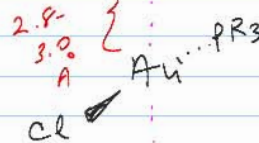
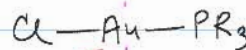
Closed-Shell Interactions

Au^{I} d^{10} ions

d^8 ion Ir^{I}

Te^{I} s^2 ion

Hg^0



dispersion, VDW interaction, "Aurophilicity"

comparable to strong H bond.

Pyykkö predicts $W Au_{12}$ triply stabilized!

Au_{12} icosahedron

12 Au 6s orbitals: $a_g + t_{1u} + h_g + t_{2u}$

structure

W-Au 2.68 Å

Au-Au 2.81 Å

20 Au-Au pairs!
100 kJ mol⁻¹ × 20

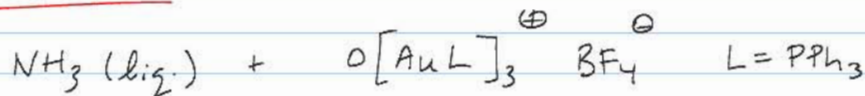
W: s, p, d
obeys 18 e rule!

surface stab.

⊙ SR⁻

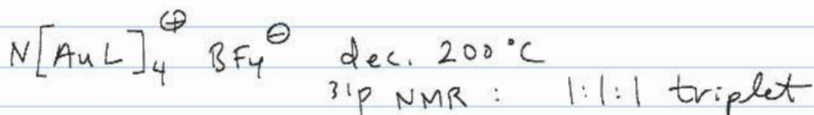
⊙ Xe atoms

Schmidbauer: auration



↓ -60°
yellow slurry

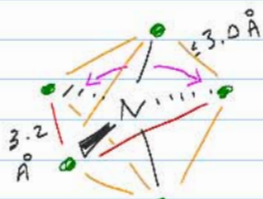
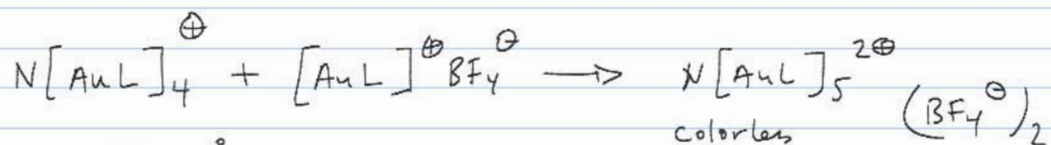
(analog of Me_3O^+)



high-symm: ¹⁴N-coupling

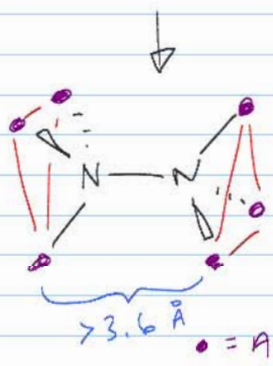
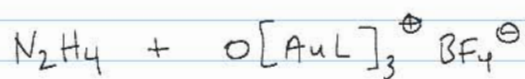
"Au^I as a proton analog"

Nature, 1990 : Hypercoordination of N

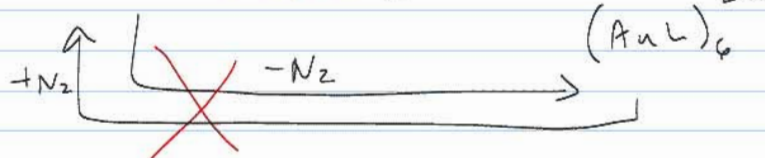
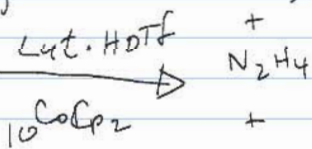


colorless ppt
no ^{14}N coupling observed
 \Rightarrow fluxional

Sharp: Science, 1997, 275, 1460-62

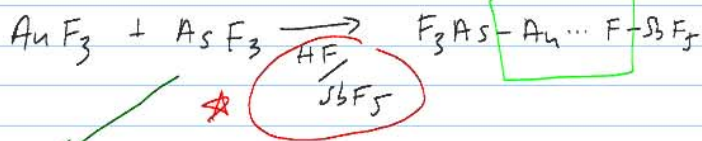


yellow-
yellow orange



Seppelt Science 2000, 290 117

• AuXe^{\oplus} proposed
Pykkö



• Possible Pt-Xe
in Bartlett's
work.

\Rightarrow Xe "mild and weakly coord.
reducing agent!"

• AuF elusive

red xtals

