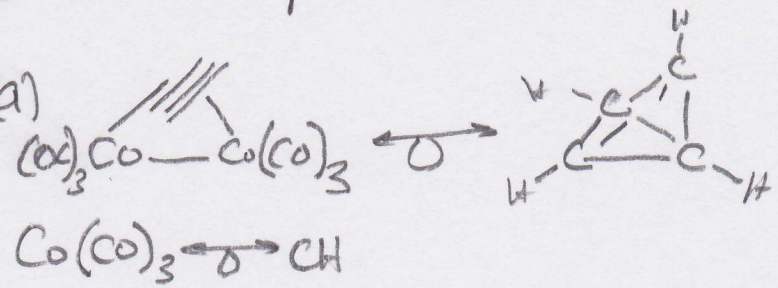
Answers – Chapter 21

1. (a)

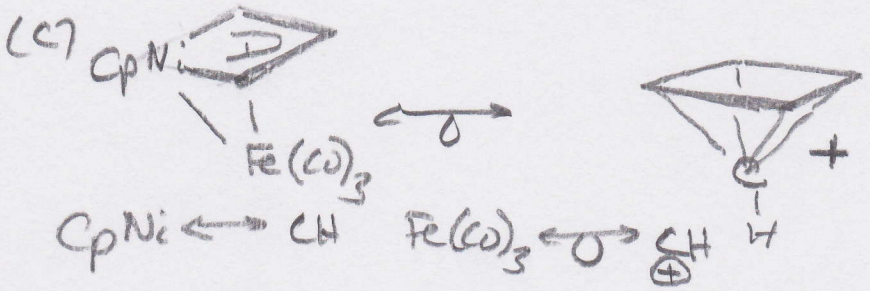


$Co(CO)_3 \leftrightarrow O \rightarrow CH$

(b) $(OC)_5Re-Pt(CO)_2-Re(CO)_5 \leftrightarrow O \rightarrow CH_3-CH_2-CH_3$

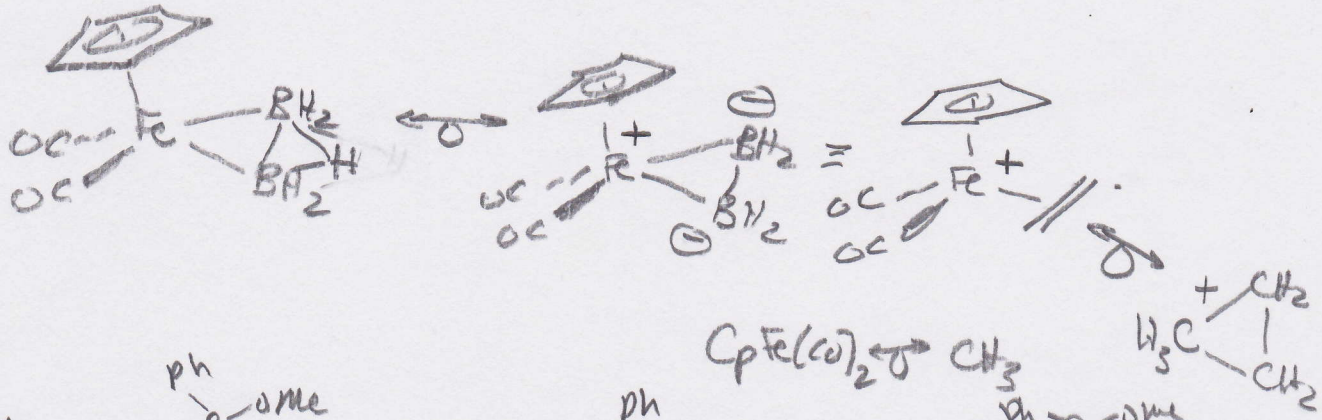
$Re(CO)_5 \leftrightarrow O \rightarrow CH_3 \quad Pt(CO)_2 \leftarrow CH_2$

(c)



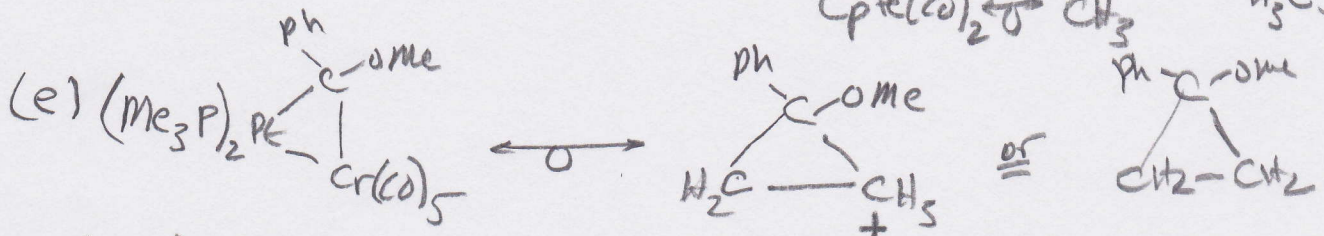
$CpNi \leftrightarrow CH \quad Fe(CO)_3 \leftrightarrow O \rightarrow CH$

(d)



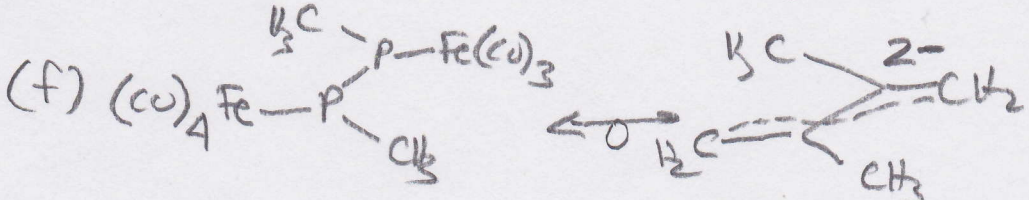
$CpFe(CO)_2 \leftrightarrow O \rightarrow CH_3$

(e)



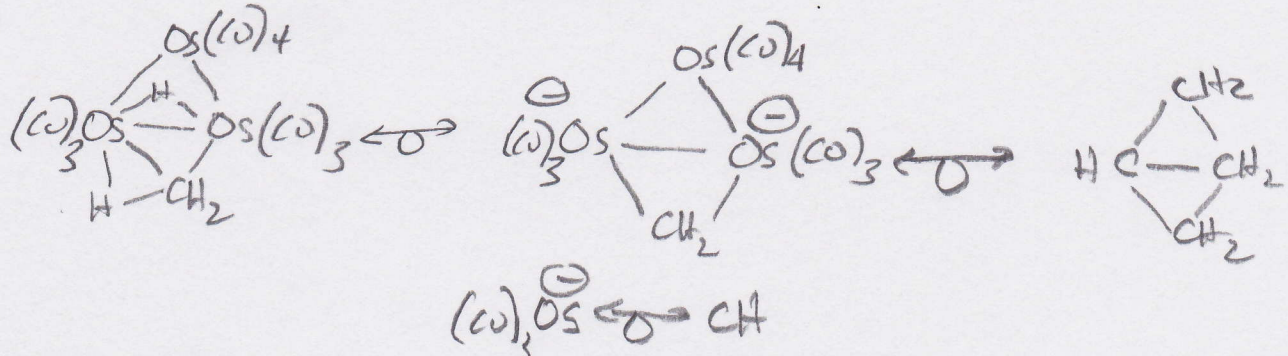
$(Me_3P)_2Pt \leftrightarrow O \rightarrow CH_2 \quad (CO)_5Cr \leftrightarrow O \rightarrow CH_3^+$ or $(CO)_5Cr \leftrightarrow O \rightarrow CH_2$

(f)



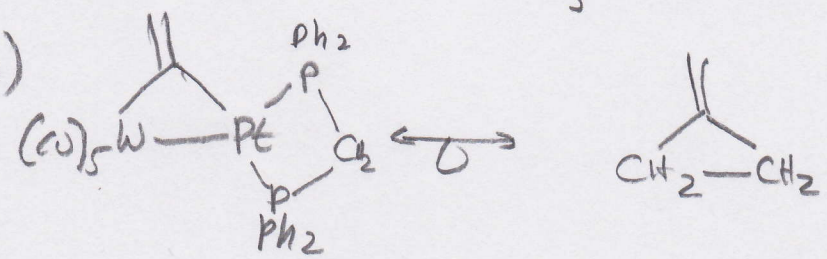
$Fe(CO)_4 \leftrightarrow O \rightarrow CH_2 \quad P \rightarrow O \rightarrow C^{\ominus}$

(g)



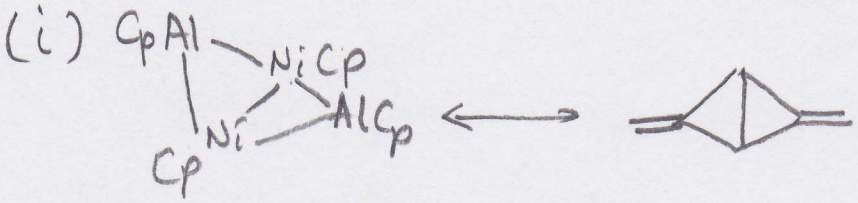
$(CO)_3Os \leftrightarrow CH$

(h)



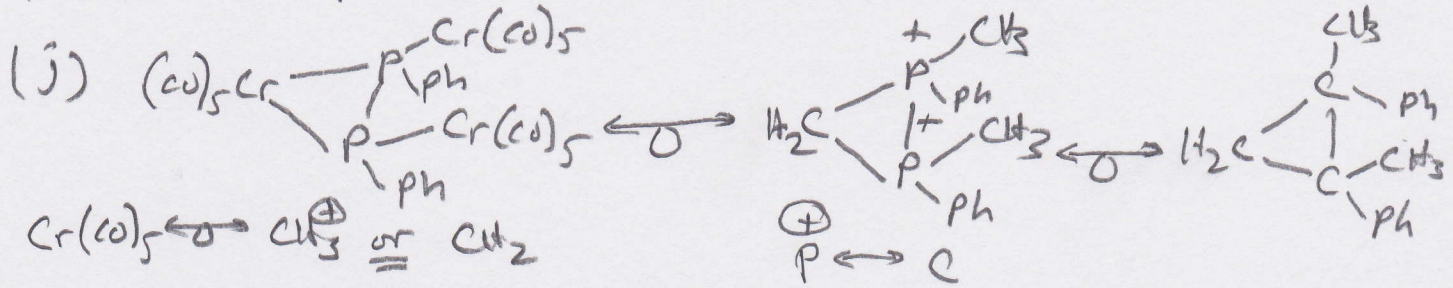
$(R_3P)_2Pt \leftrightarrow CH_2 \quad W(CO)_5 \leftrightarrow CH_2$

(i)



$CpNi \leftrightarrow CH \quad CpAl \leftrightarrow CO \text{ or } C{=}CH_2$

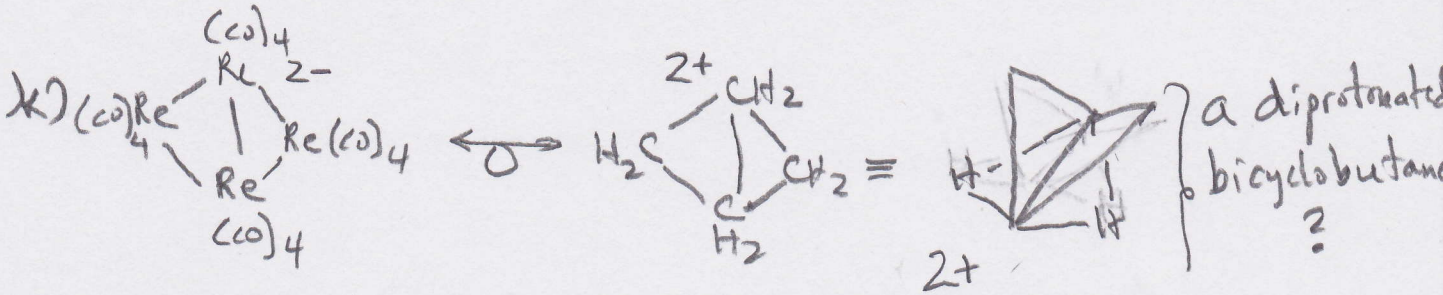
(j)



$Cr(CO)_5 \leftrightarrow CH_3^{\oplus} \text{ or } CH_2$

$P \leftrightarrow C$

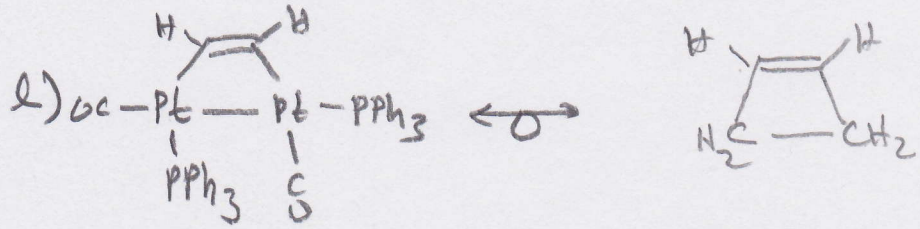
(k)



a diprotonated bicyclobutane ?

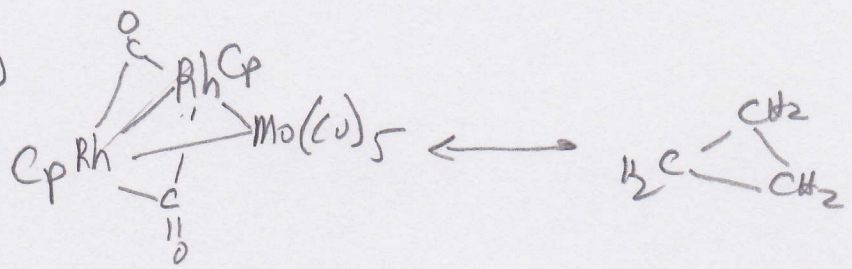
$Re(CO)_4 \leftrightarrow CH_2^+ \quad Re(CO)_4^- \leftrightarrow CH_2$

(l)



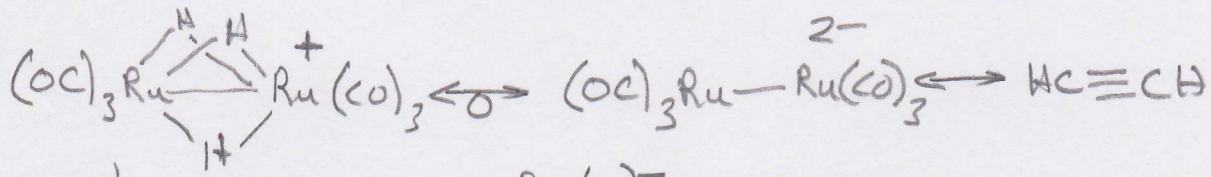
$Pt(CO)PPh_3 \leftrightarrow CH_2$

(m)



$CpRh(CO) \leftrightarrow CH_2 \quad M(CO)_5 \leftrightarrow CH_2$

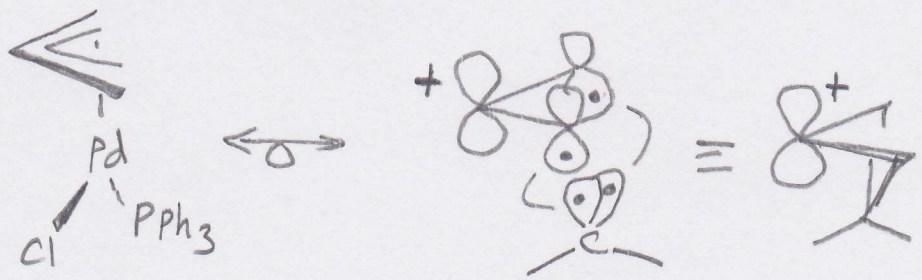
(n)



The bonding here was covered in problem 20, & (a) & (b)

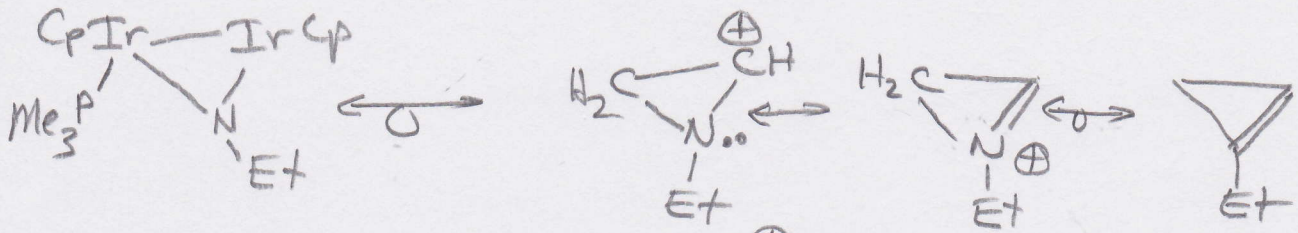
$Ru(CO)_3^{-} \leftrightarrow CH$

(o)



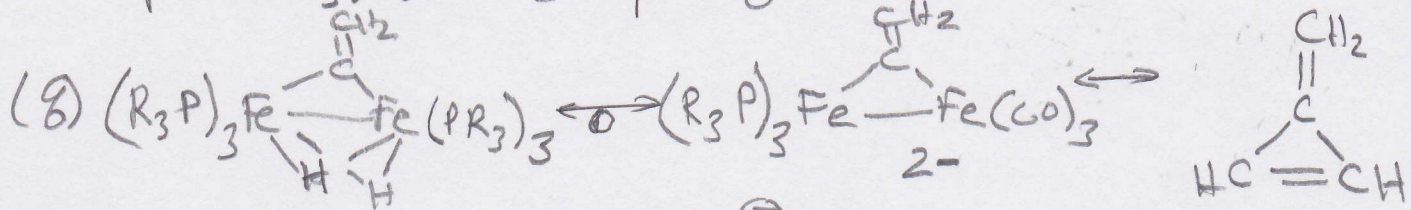
$Pd(Cl)(PPh_3) \leftrightarrow CH_2$

(p)



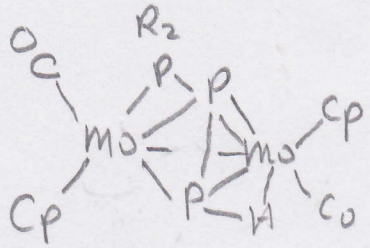
$CpIr(PMe_3) \leftrightarrow CH_2 \quad CpIr \leftrightarrow CH$

(q)

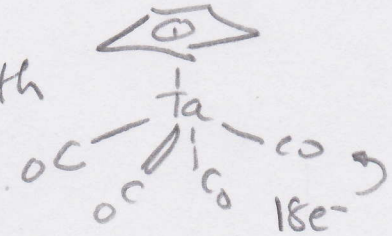


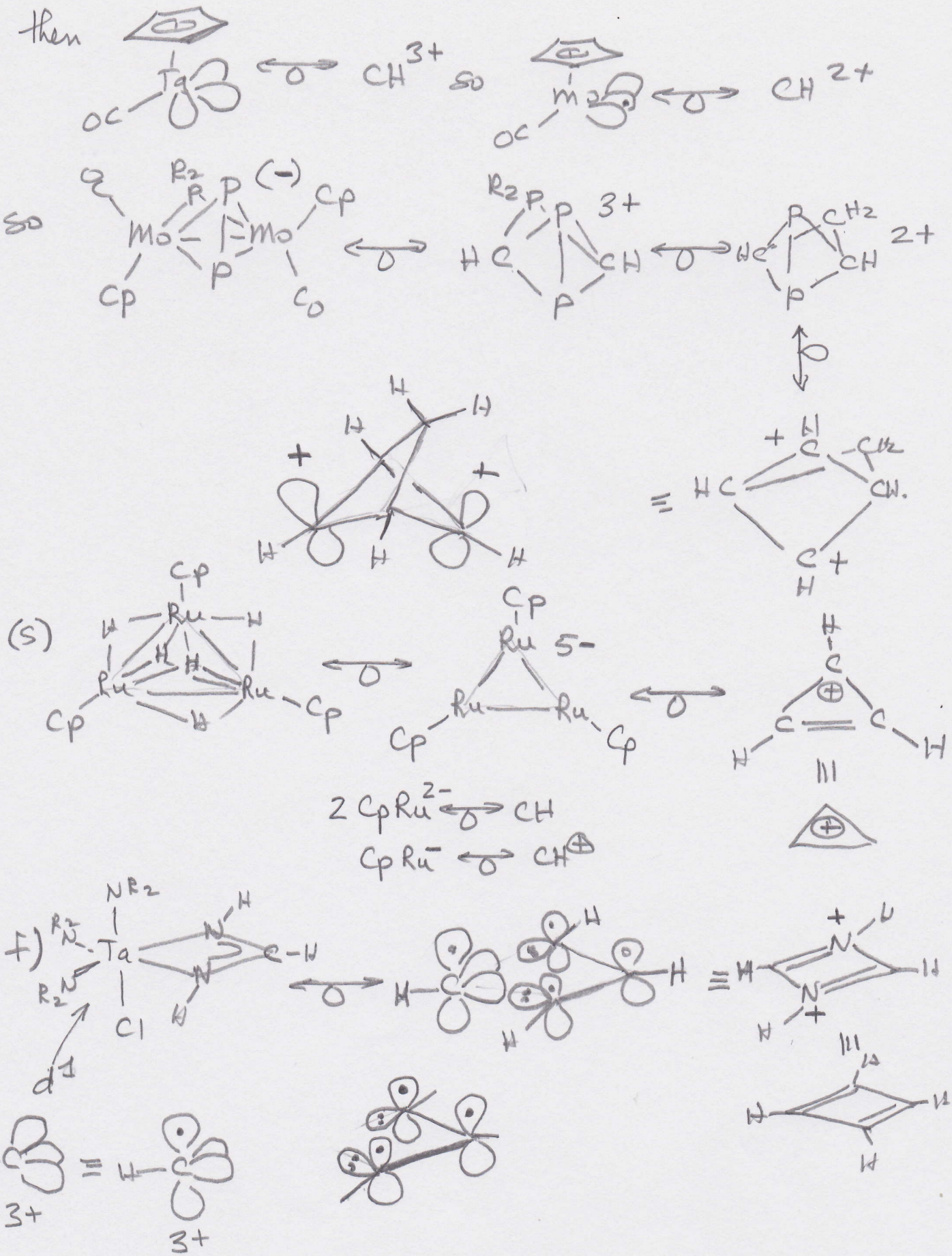
$(R_3P)_3Fe^{\ominus} \leftrightarrow CH$

(r)

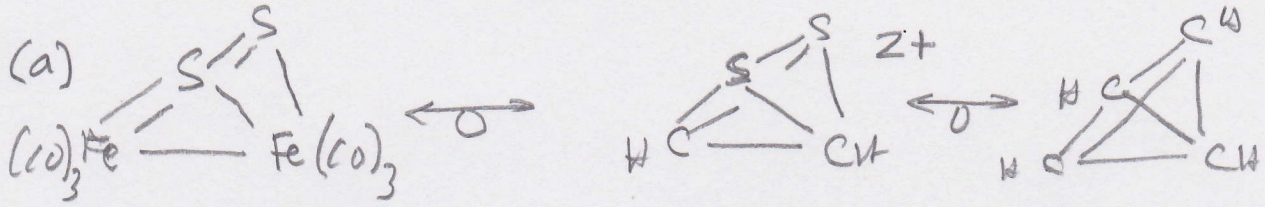


For $CpMo(CO)_3$ start with

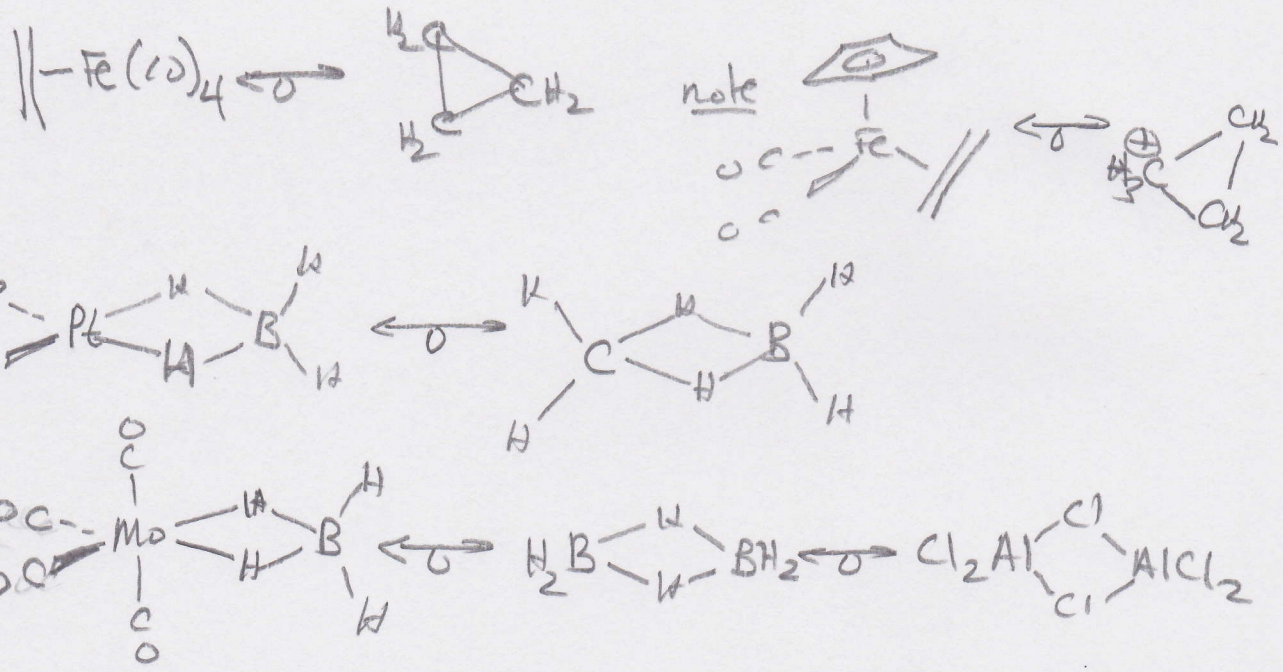



then
CH 3+
so
CH 2+
so
(-)
3+
2+
(5)
5-
2 CpRu 2-
CH
CpRu-
CH
f)
d1
3+
3+

2. (a)



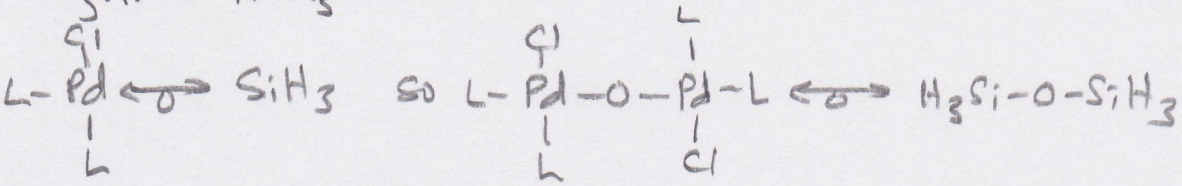
(b)



note:

$Mo(CO)_4 \leftrightarrow BH_2$

d) $Cl_3Al-O-AlCl_3$ 2 less electrons than $H_3Si-O-SiH_3$

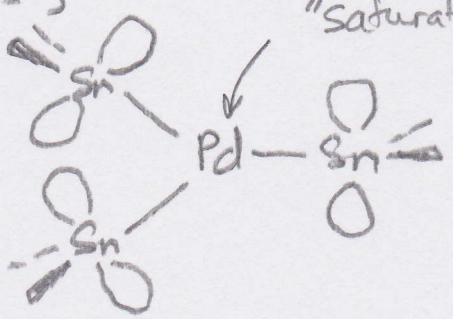


e) $CpW(CO)_2-W(CO)_2Cp \leftrightarrow HC\equiv CH$

$CpW(CO)_2 \leftrightarrow HC$

3. The answer here is that all three are isolobal, sort of, maybe...

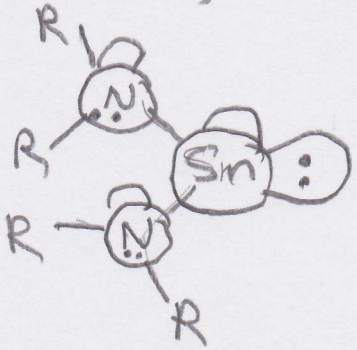
The $Pd[Sn(NR_2)_2]_3$ structure is a d^{10}, 16 electron ML_3 complex. The $Sn(NR_2)_2$ groups are analogous to a carbene so there are two center-two electron (2c-2e) Pd-Sn bonds;



"saturated" 16 e⁻ / d^{10} metal

} there will be back-bonding from the Pd d set to the empty p AO's on Sn

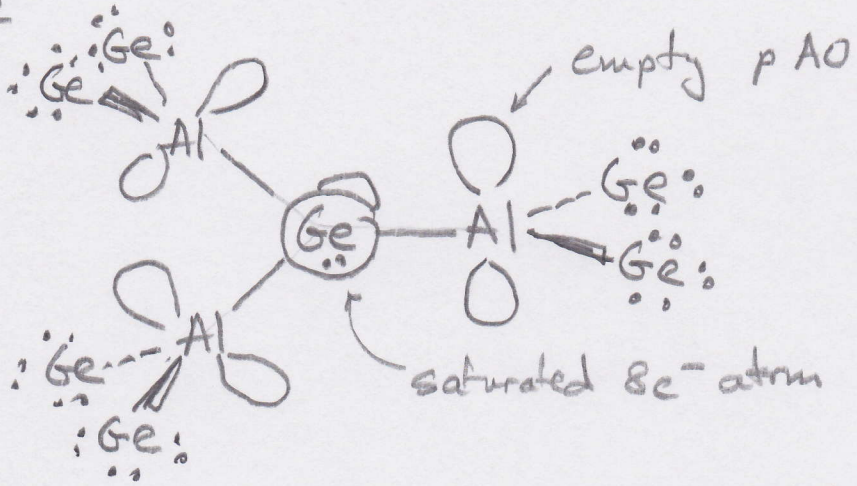
And, of course, there is a full octet at the nitrogens:



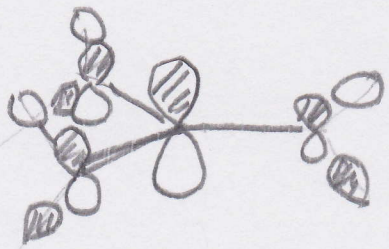
For $Al_3Ge_7^{2-}$ there are a total of $(3\times3)+(7\times4)+2 = 57e^-$

Let there be 2c-2e Al-Ge bonds. There are 9, so $9\times2 = 18e^-$. Let the outside 6 Ge atoms to be totally saturated, $8e^-$ (like the N atoms in the Pd complex) so each Ge has 3 lone pairs and $6\times3\times2 = 36e^-$. This gives a grand total of $18+36 = 54\ e^-$, $3e^-$ short of the 57 available. Putting $2e^-$ on the

central Ge atom and the last electron in the "Ba sea" uses all of the electrons. So the electronic structure looks like



The filled p AO on the central Ge atom is stabilized by the σ^*_π orbitals on the Ge-Al-Ge bonds



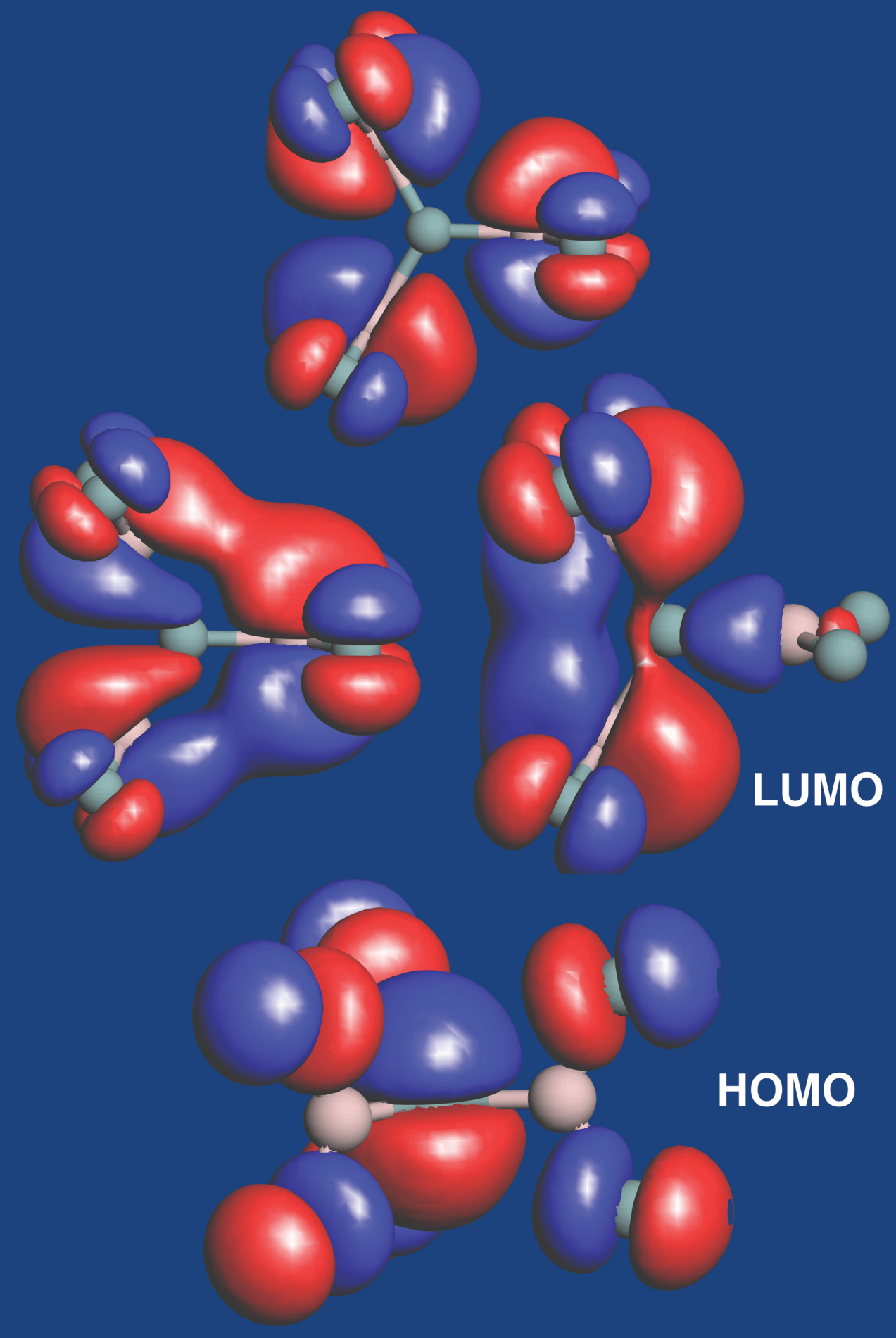
actually σ_π also mixes in so this is really the middle level of a 3 orbital mixing with small coefficients on Al

NOTE: The Homo-Lumo gap was 3,6 eV at the EHT level!

A plot of this MO and the 3 tangential pAOs (LUMOs) at the extended Hückel level is given on the next page.

So forgiving the extra electron in $Ba_{10}Al_3Ge_7$, it would appear to be isolobal to the Pd complex.

The $Ca_{10}Si_3Pt_7$ compound is more difficult to decipher. Let us start by assuming that Ca donates its 2 electrons which gives $Si_3Pt_7^{20-}$. We'll also assume that


LUMO
HOMO

we start with Pt(0) - d^{10}. So there are $3\times4+20=32$ extra electrons to assign. There are three possible/plausible models to choose from:

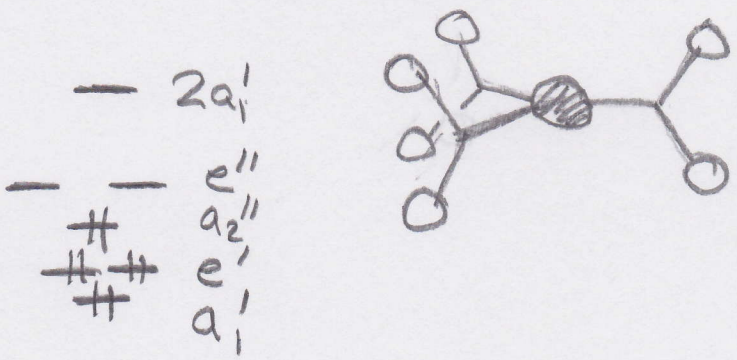
model 1: the Si atoms are saturated, 8 e^-. The Pt atoms are divided into Pt(1-) and Pt(2-) oxidation states and the electrons are placed in 3 (4c-6e) bonds in the Pt-Si region. Full details can be found in the Ponec and coworkers paper. Obviously, this is not isolobal to the other two.

model 2:

Let each Pt-Si bond be of the 2c-2e type giving $9\times2=18e^-$. Let the Si tangential set be fully occupied which makes for 6 more electrons. Letting the central Pt atom to be Pt(2-) - $d^{10}s^2$, then the remaining, outside Pt atoms are $d^{10}s^1$. So the total number of electrons: $18+6+2+6=32e^-$ just enough! This is actually the situation for an extended Hückel calculation on $Si_3Pt_7^{20-}$.

But, there is a problem. The Pt s AO's are the highest occupied ones. There are 7 Pt s AOs

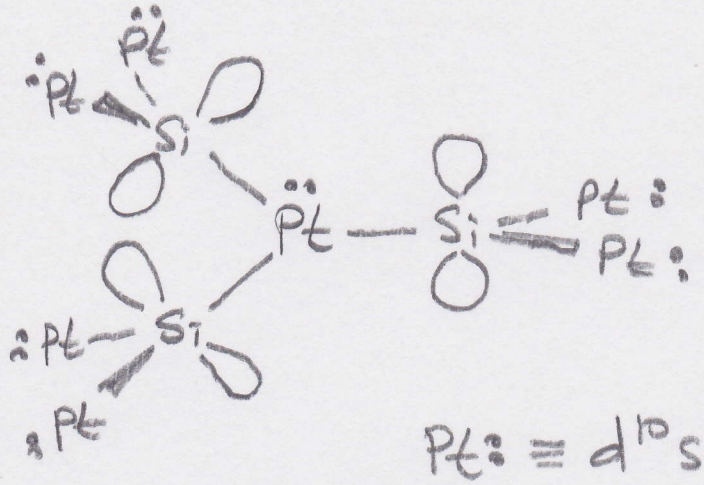
with 8 electrons in them. It is easy to take symmetry adapted combinations they will be:



These combinations are over a small range and so we might expect a significant Pt DOS at the Fermi level. The DFT calculations by Ponou and coworkers do not show this feature. Obviously this model does not make the compound isolobal to the other two.

Model 3: There are 5 Ca--Pt contacts to each of the outside Pt atoms within 3.2Å and 6 Ca--Pt contacts within 3.2 Å. Thus, it is reasonable to expect Ca--Pt interactions that stabilize the Pt based orbitals including the Pt s combinations. Indeed, there is significant Ca character in the filled portion of the calculated DOS. So in this model there are again all Pt-Si 2c-2e bonds. Every Pt is $d^{10}s^2$; i.e. Pt(2-) and the Si p in-plane tangential orbitals are empty. So the total electron count is

$(9\times2)+(7\times2)=32$! In other words:



Pt: $\equiv d^{10}s^2$ which is a saturated electron count

This is precisely the same picture as in the previous two compounds. I like it!

Extended Hückel plots of the Pt's AOs and the tangential Si p set are shown on the next page.

Pt s AOs

tangential
Si p AOs