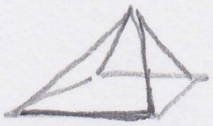
Answers – Chapter 22

1. (a) $B_5H_9 \equiv (BH_2)_4BH$

$BH = 2e^-$
$4\,BH_2 = 12$
$\overline{\quad 14}$

$n = 5$
$14 = 2(5) + x$
$x = 4$ ∴ nido oct.



(b) $C_2B_4H_8 \equiv (CH_2)_2(BH)_4$

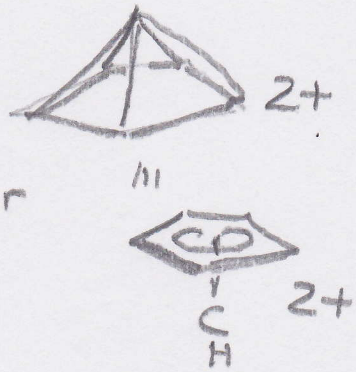
$2CH_2 = 8e^-$
$4\,BH = 8$
$\overline{\quad 16}$

$n = 6$
$16 = 2(6) + x$
$x = 4$ ∴ nido pentagonal bipyr.

(c) $C_6H_6^{2+}$

$6CH = 18e^-$
$2+ = -2$
$\overline{\quad 16}$

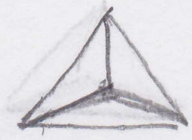
$n = 6$
$16 = 2(6) + x$
$x = 4$ ∴ nido pentagonal bipyr



(d) B_4H_8

$4BH_2 = 12e^-$

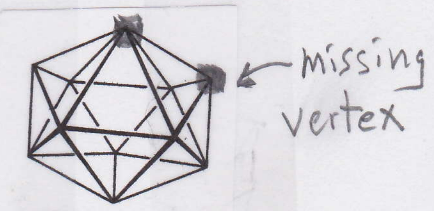
$n = 4$
$12 = 2(4) + x$
$x = 4$ ∴ nido trigonal bipyr.



(e) $B_9H_{15} \equiv (BH)_3(BH_2)_6$

$3\,BH = 6e^-$
$6\,BH_2 = 18$
$\overline{\quad 24}$

$n = 9$
$24 = 2(9) + x$
$x = 6$ ∴



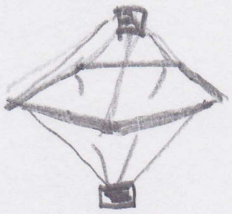
octadecahedron
N = 11

arachno octadecahedron

(f) $C_5H_5^-$

$5CH = 15e^-$
$-1 = \underline{1}$
16

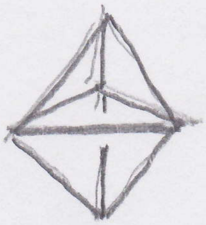
$n=5$
$16 = 2(5) + x$
$x = 6 \therefore$ aracho
pentagonal bipyr.



(g) $Ni_5(CO)_{12}^{2+} \equiv [Ni(CO)_2]_3[Ni(CO)_3]_2^{2+}$

$3\,Ni(CO)_2 = 6e^-$
$2\,Ni(CO)_3 = 8$
$2+ = \underline{-2}$
12

$n=5$
$12 = 2(5) + x$
$x = 2 \therefore$ closo
trigonal byr.



(h) $Co_4Ni_2(CO)_{14}^{2-} \equiv [Co(CO)_2]_4[Ni(CO)_3]_2^{2-}$

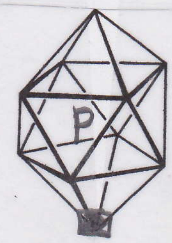
$4\,Co(CO)_2 = 4e^-$
$2\,Ni(CO)_3 = 8$
$2-$ $\underline{12}$
14

$n = 6$
$14 = 2(6) + x$
$x = 2 \therefore$ closo oct.

(i) $Rh_9P(CO)_{21}^{2-} \equiv [Rh(CO)_2]_6[Rh(CO)_3]_3P^{2-}$

$6\,Rh(CO)_2 = 6e^-$
$3\,Rh(CO)_3 = 9$
$P = 5$
$2^- = \underline{2}$
22

$n = 9$
$22 = 2(9) + x$
$x = 4 \therefore$ nido
bicapped square prism



bicapped square antiprism
N = 10

(j) $Cp_2Co_2C_2B_6H_8 \equiv (CpCo)_2(CH)_2(BH)_6$

$2CpCo = 4e^-$
$2\,CH = 6$
$6\,BH = \underline{12}$
22

$n = 10$
$22 = 2(10) + x$
$x = 2 \therefore$ closo bicap. sq. prism

above without the missing vertex

k) $CCo_8(CO)_{18}^{2-} \equiv [Co(CO)_2]_6[Co(CO)_3]_2C^{2-}$

$6\,Co(CO)_2 = 6e^-$ $\quad n = 8$

$2\,Co(CO)_3 = 6$ $\quad 18 = 2(8) + x$

$C = 4$ $\quad x = 2 \therefore$ closo

$2- = \underline{2}$ $\quad$ dodecahedron

$18e^-$

dodecahedron
N = 8

l) $C_2H_4Pt(PPh_3)_2$

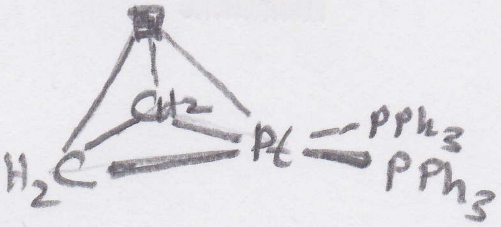
$2CH_2 = 8e^-$ $\quad n = 3$

$Pt(PPh_3)_2 = \underline{2}$ $\quad 10 = 2(3) + x$

10 $\quad x = 4 \therefore$

nido tetrahedron

or - arachno trig. byr. ?

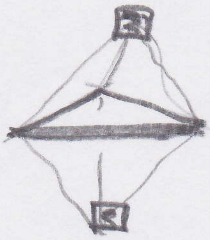


m) $Os_3(CO)_{12}$ $\quad n = 3$

$3\,Os(CO)_4 = 12e^-$ $\quad 12 = 2(3) + x$

$x = 6 \therefore$

arachno trig. byr.

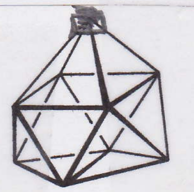


n) $Cp_4Co_4P_4$ $\quad n = 8$

$4\,CpCo = 8e^-$ $\quad 20 = 2(8) + x$

$4P = \underline{12}$ $\quad x = 4 \therefore$ nido

20 $\quad$ tricapped trig. prism



tricapped trigonal prism
N = 9

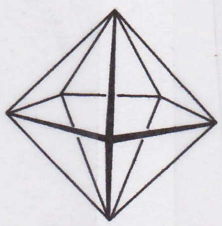
o) $C_2B_4H_6Pt(PEt_3)_2$

$2CH = 6e^-$ $\quad n = 7$

$4\,BH = 8$ $\quad 16 = 2(7) + x$

$Pt(PEt_3)_2 = \underline{2}$ $\quad x = 2 \therefore$ closo

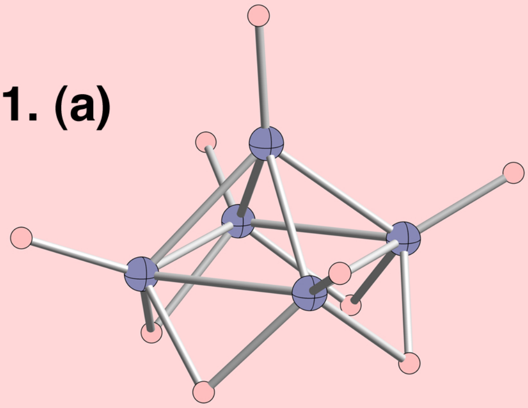
16 $\quad$ pentagonal bipyramid



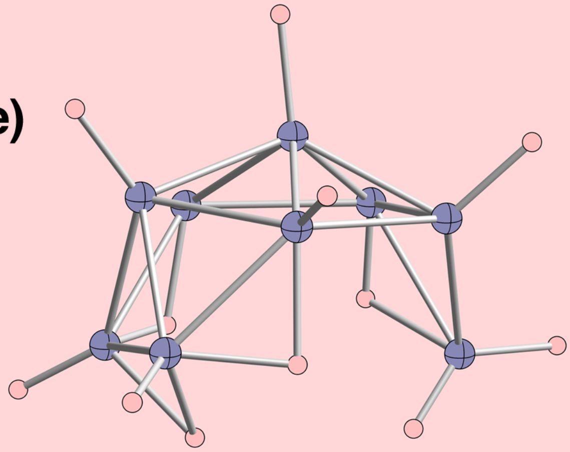
pentagonal bipyramid
N = 7

* The real structures of most are on the next pages

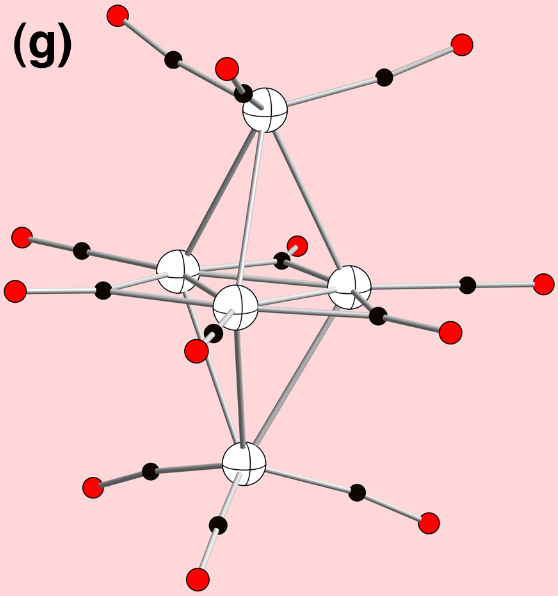
1. (a)



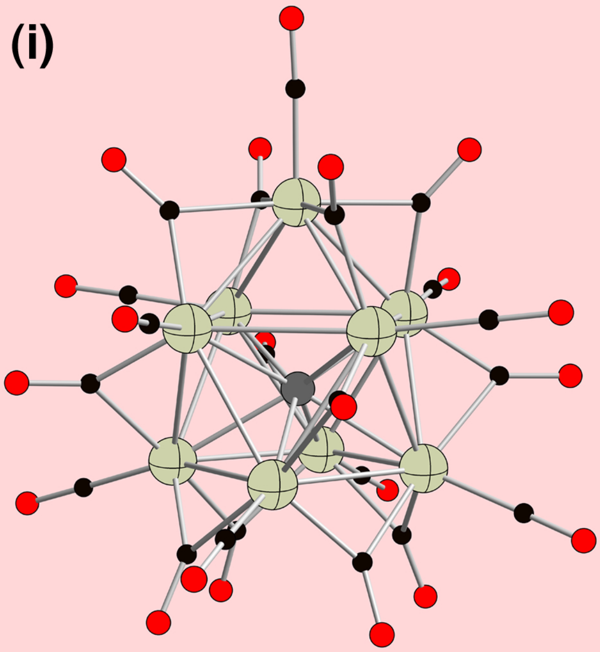
(e)



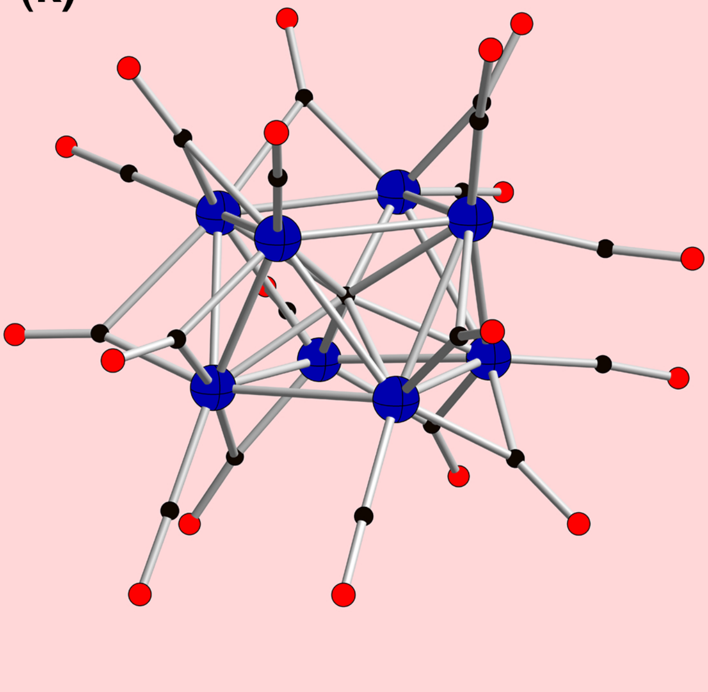
(g)



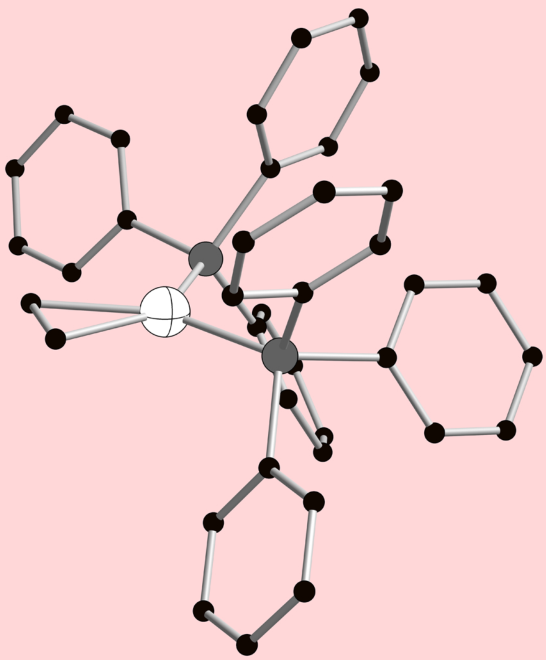
(i)

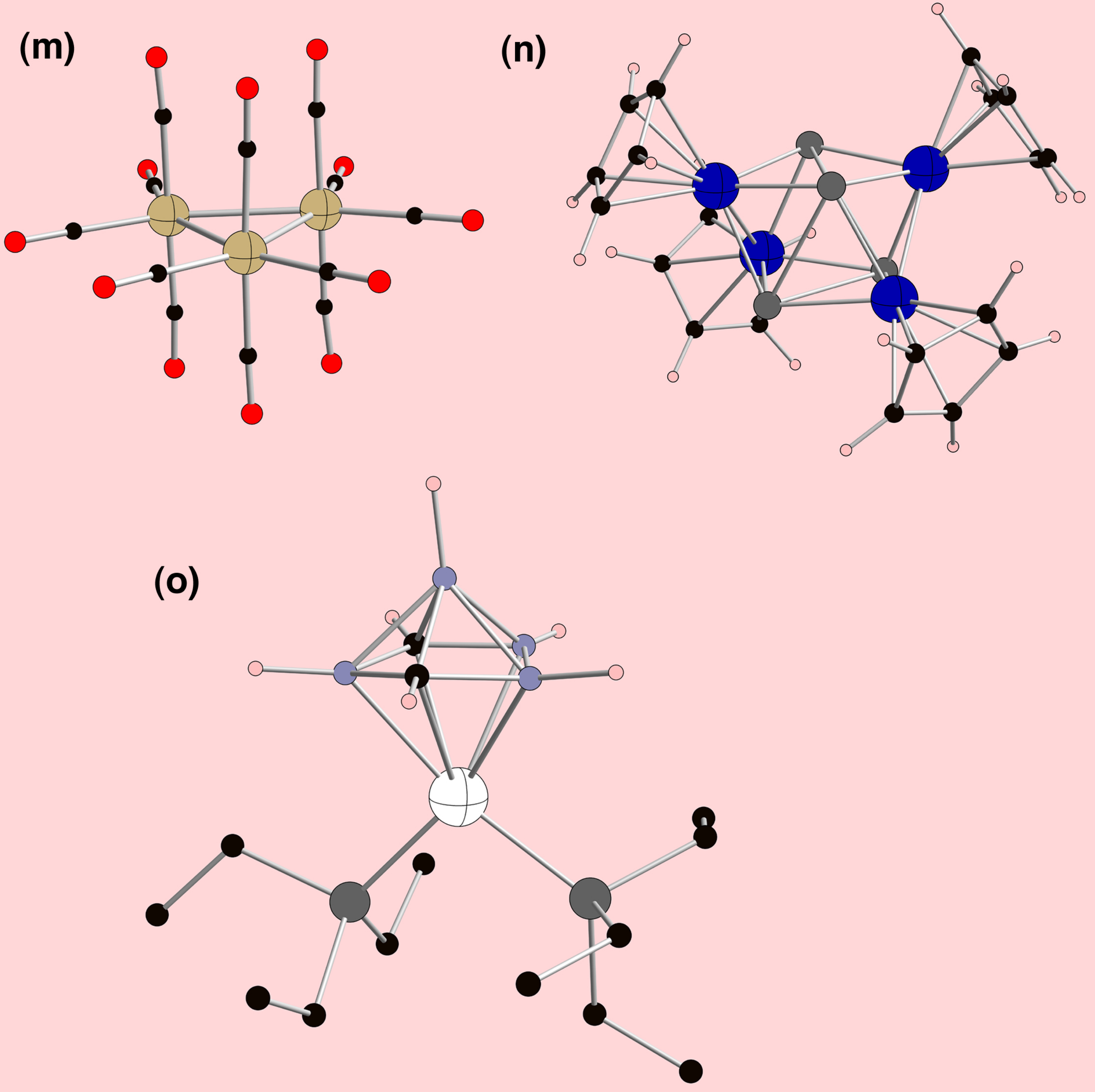


(k)



(l)




(m)
(n)
(o)

2. (a) For a trigonal bipyramid the number of skeletal electrons = $2(5)+2=12e^-$. $3CpCo = 6e$ so $x+y = 12-6 = 6e^-$

	X	Y	$\#e^-$	
i)	CpNi	CpNi	6	these will work
ii)	$Fe(CO)_4$	CpCo	6	
iii)	$Ru(CO)_4$	NH	8	
iv)	$Fe(CO)_3$	$Fe(CO)_3$	4	
v)	CpCo	BH	4	

(b) For an icosahedron $2(12)+2=26$ skeletal e^-. There are $10BH = 20e^-$, so $x+y = 26-20 = 6e^-$

	X	Y	$\#e^-$	
i)	Bi	S	7	
ii)	S	S	8	
iii)	P	CH	6	these will work
iv)	P	Bi	6	
v)	BH	Bi	5	

(c) For arachno bicapped square antiprism – $2(8)+6=22e^-$
$4CpRh = 8$ & $2Re(CO)_4 = 6$ ∴ $x+y = 22-14 = 8e^-$

	X	Y	$\#e^-$s	
i)	$Rh(CO)_3$	S	7	
ii)	PMe	PMe	8	these will work
iii)	$Rh(CO)_4$	CpPt	8	
iv)	GeMe	GeMe	6	
v)	In-OMe	Br	8	

3. (a) $Ba_3Pb_5 = Pb_5^{6-}$

$5Pb = 10e^-$
$6- = \underline{6}$
16

$16 = 2(5) + x$
$x = 6 -$

should be arachno pentagnol bipyr. – a nido octahedron should have 2 less e^-

$Cs_4Pb_9 \equiv Pb_9^{4-}$

$9Pb = 18e^-$
$4- = \underline{4}$
22

$22 = 2(9) + x$
$x = 4$ ∴ nido bicapped square prism
Consistent with structure

(b) $Re_6(CO)_{18}(P\text{-}Me)_4$

$6\,Re(CO)_3 = 6e^-$
$3\,PMe = \underline{12}$
18

$18 = 2(9) + x$
$x = 0$! needs 2 more e^- (or one more CO) to be a closo tricapped trigonal prism

$Rh_{10}(CO)_{22}P^{3-} \equiv [Rh(CO)_2]_8[Rh(CO)_3]_2P^{3-}$ ← encapsulated

$8Rh(CO)_2 = 8e^-$
$2\,Rh(CO)_3 = 6$
$P = 5$
$3- = \underline{3}$
$22e^-$

$22 = 2(10) + x$
$x = 2$ ∴ Closo bicapped square antiprism which is consistent with the structure

(c) $Cp_6 Ni_6$

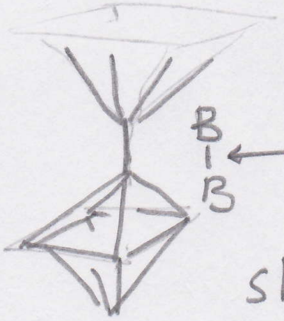
$6\ NiCp = 18e^-$ $\quad 18 = 2(6) + X$

$X = 6$ - not an arachno dodecahedron

a closo octahedron has 4 less e^-'s.

Li_2B_6 - an octahedron should have 14 skeletal e^-'s.

Each vertex of the octahedron is connected to another vertex, i.e.



B
|
B ← 2 center / 2 e^- bond

∴ each B brings 2 skeletal e^- to the octahedron

Therefore, $6(2) + \underset{\uparrow \text{ from Li}}{2} = 14$ skeletal e^-'s - just the right number for a closo octahedron

4. (a) The polyhedron on the left is a nido $N = 11$ while that on the right is a nido $N = 12$; 2 B atoms are shared so

$F(e) = 19 + 2 + 0 + 2 = 23$ pairs $\equiv 46 e^-$

$14\ BH = 28 e^-$
$1\ BH_2 = 3$
shared atoms → $2B = 6$
$2S = 8$
$-1 = 1$
$\overline{46 e^-}$

(b) The two polyhedra are nido $N=7$; the Me_5C_5 are nido, $N=7$, and 2 B atoms have shared verticies, so

$F(e) = 4+22+2+4 = 32$ pairs $\equiv 64e^-$

$2BH_2 = 6e^-$
$2BH = 4$
$14\ CR = 42$
$2\ Co = 6$
shared verticies $\rightarrow 2B = \underline{6}$
64

(c) The 4 polyhedra are all nido; 3 shared B atoms, and 2 Rh shared verticies, so

$F(e) = 4+29+2+4 = 39$ pairs $\equiv 78e^-$

$5BH_2 = 15e^-$
$9BH = 18$
shared $\rightarrow 3B = 9$
$10\ CMe = 30$
shared $\rightarrow 2Rh = \underline{6}$
$78e^-$

(d) Two polyhedra with Si sharing two verticies, so

$F(e) = 2+22+1 = 25$ pairs $\equiv 50e^-$

$18\ BH = 36$
$4\ CH = 12$
shared $\rightarrow Si = \underline{4}$
$52e^-$

2 extra electrons so Si slips by ~0,3 Å towards the 2 carbon atoms in each ring to accomidate the extra 2 electrons

5. (a) There are two polyhedra, two shared B atoms along one edge and both polyhedra are nido, ∴

$F(e) = 2+18+2 = 22$ pairs $\equiv 44e^-$

$6\ BH_2 - 18e^-$
$10\ BH - 20$
shared → $2B - \underline{6}$
$44e^-$

(b) This is identical to (a) except a CpCo has replaced a BH and since CpCo ⟷ BH (both donate 2 skeletal electrons) $CpCoB_{17}H_{21}$ should and does have 44 skeletal electrons

(c) This is a similar structure to the other two with one important difference, there are a B_3 face is now shared between the two polyhedra which are both nido, ∴

$F(e) = 2+19+2 = 23$ pairs $= 46e^-$

$5BH_2 = 15e^-$
$10\ BH = 20$
shared → $3B = 9$
$Pt(PR_3)_2 = \underline{2}$
$46e^-$

6. (a) $CpFeB_7C_3H_9Me$ - 2 polyhedra with one closo and the other nido, Fe shares verticies between the two.

$F(e) = 2 + 16 + 1 + 1 = 20$ pairs $\equiv 40e^-$

$8\ CR = 24e^-$
$7\ BH = 14$
shared $\rightarrow$ $Fe = 2$
$40e^-$

(b) Two polyhedra - both closo with shared V atom

$F(e) = 2 + 21 + 1 = 24$ pairs $\equiv 48e^-$

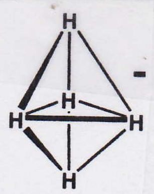
$6\ CR = 18e^-$
$14\ BH = 28$
shared $\rightarrow$ $V = -1\ (?)$
$45e^-$ $\rightarrow$ a more likely scenerio is to have high spin V where 3 unpaired electrons are in t_{2g} leaving $2e^-$ for the skeletal e⁻ count which then is 48 and agrees with the mno rule.

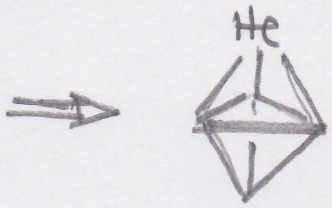
(c) $(B_7C_3H_9Me)_2Pd$ is just like the above except that Pd donates $4e^-$; so there are 2 electrons too many. As a consequence Pd moves to an η^4 position on both rings and the polyhedra bend $1\ BCH_2$ unit away from the Pd.

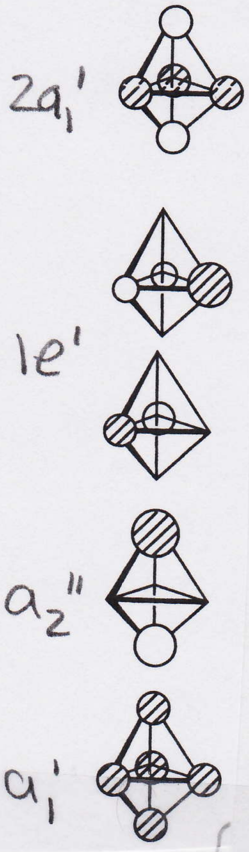
7. Recall that $e_i \approx e_i^{(0)} + e_i^{(1)} + e_i^{(2)}$

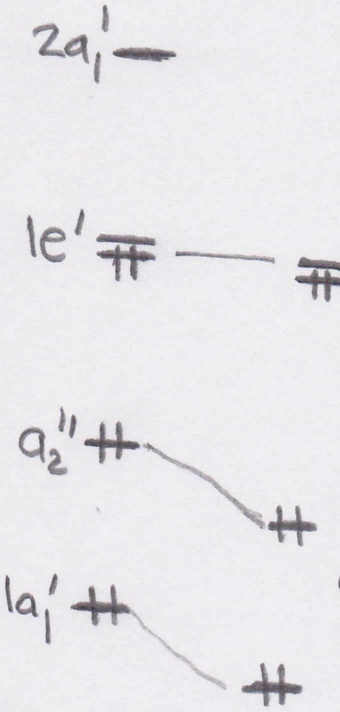
$$e_i^{(1)} = \left(c_{\alpha i}^{(0)}\right)^2 \delta\alpha \qquad e_i^{(2)} = \sum_{j \neq i} \frac{\left(c_{\alpha i}^{(0)} c_{\alpha j}^{(0)} \delta\alpha\right)^2}{e_i^{(0)} - e_j^{(0)}}$$

H → He $\delta\alpha = (-)$

D_{3h} 

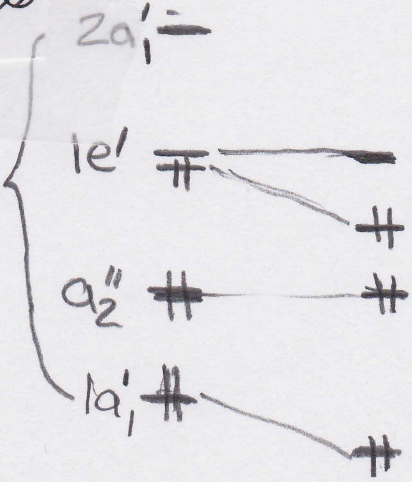






} no coefficient on axial H ∴ the molecule is still Jahn-Teller unstable

$e^{(1)} = (-)$ and since the coefficient is large this will be sizable - <u>but</u> $e^{(2)}$ will be small since the contribution from $1a_1' = (+)$ and $2a_1' = (-)$.



$e^{(1)}$ again is large - about the same as the axial isomer, <u>but</u> now $e^{(2)}$ is large and $(-)$ - $1e'$ is close to $2a_1'$ and farther away from $1a_1'$

About the same $e^{(1)}$ and $e^{(2)}$ as in the axial case

So the equatorial isomer opens an energy gap and provides more stabilization (via the $e^{(2)}$ term in $1e'$ versus a_2'')