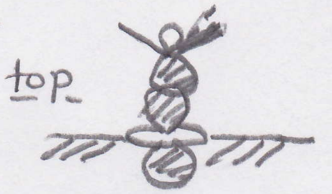
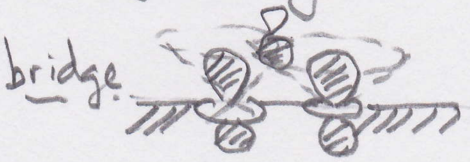
Answers - Chapter 23

1.(a) The sp^3 hybridized orbital on the methyl group, n, will interact most strongly with metal z^2 at the on-top geometry:

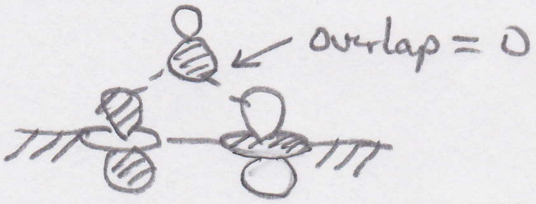


} note: this interaction will be the same through the z^2 band(s).

For the bridge site, the total overlap with z^2 is much less, first because the nodal cones lie close to n and second only the lower portions of the z^2 band have the correct symmetry:

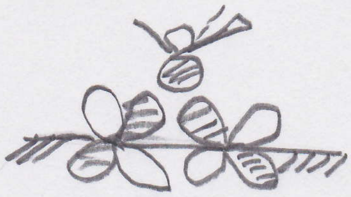


lower portion of z^2



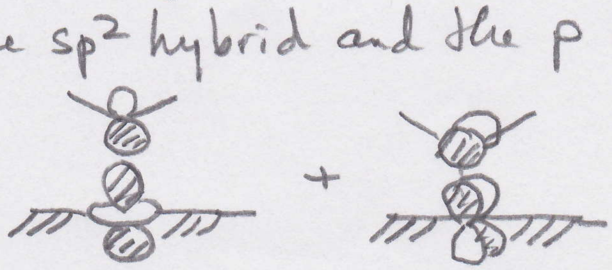
upper portion of z^2

There is additionally a contribution with yz, but this has the same problem in that only the lower portion now has the correct symmetry:



The cap has the same problem, only worse. So the order of stability should be top > bridge > cap.

For methylene there are two orbitals that can interact: the sp^2 hybrid and the p AO. So on-top:

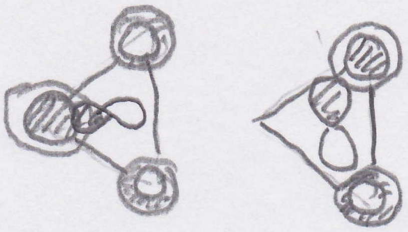


For the bridge, there are several interactions

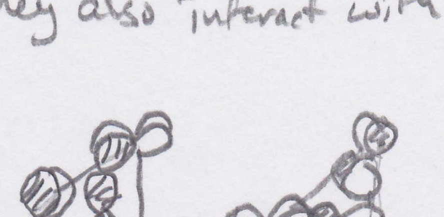
For the cap, the interactions with the sp^2 hybrid are very similiar, but the overlap to the p AO is not as large, i.e. from the top:

So now the bridge is favored over the top and cap.

Finally, for CH the cap geometry is ideal since the two p AOs on CH can overlap strongly with an e set of z^2:



And the sp hybrid interacts with the a_1 combination of z^2. They also interact with xz/yz combinations, i.e.



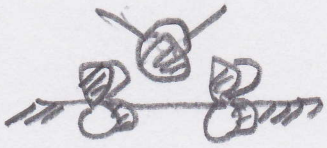
etc. So cap > bridge > top

(b) The relative energies in kcal/mol are given below for two very different levels of computation:

Pt(111) B3LYP	top	bridge	cap
CH_3	0	27	31
CH_2	26	0	23
CH	86	18	0

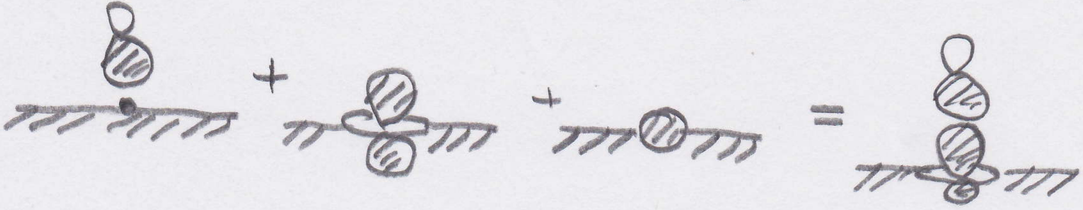
Co(0001) EHT	top	bridge	cap
CH_3	0	25	32
CH_2	0	0	14
CH	12	7	0

(b) The interactions for the perpendicular geometry are shown on the previous page. In the parallel geometry the interaction with the sp^2 hybrid is the same. There now is only one interaction with the p AO:

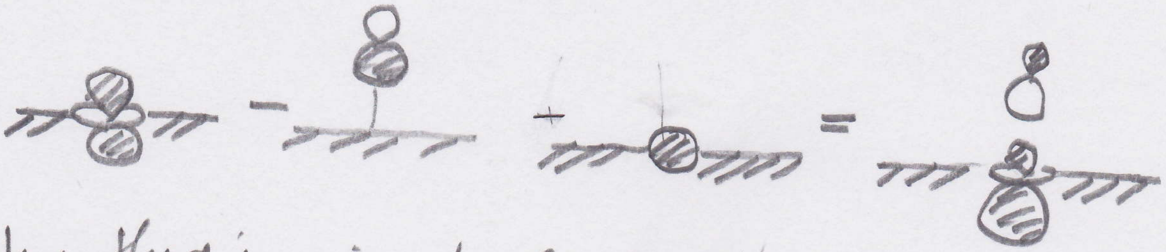


so the perpendicular geometry is much more stable.

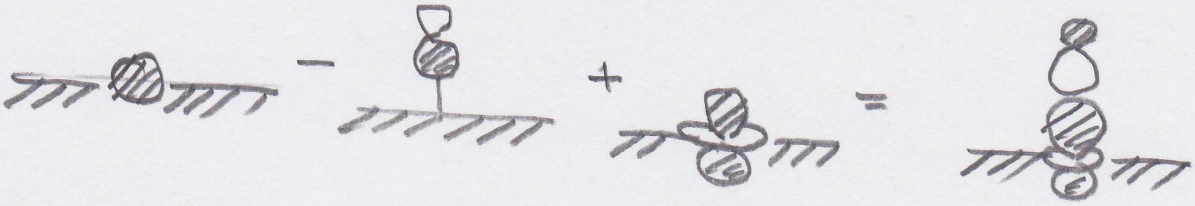
2. (a) This region is primarily the sp^3 hybrid on carbon with some z^2 and s. It is strongly Co–C bonding – so the orbitals here are predominately



(b) the region from -12 to -3 eV is predominately z^2 with some Co s and CH_3 n. The COOP curve shows a small negative Co-C overlap population in this region. This is consistent with interactions like:



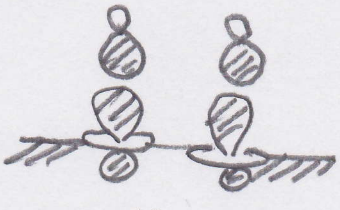
(c) Here there is primarily Co s and strong Co-C antibonding, so the interactions are



3. (a) For the late transition metals the reaction pathway should go from top to bridge to top. But for an early transition metal it would appear that the best path is from top to cap to top.

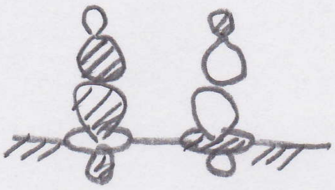
(b) On going to the early transition metals, the Fermi level rises and the metal d band becomes depopulated so that antibonding interactions to CH_3 n at the capping and bridge geometries become smaller. Furthermore, the d and s AOs become more diffuse so that overlaps at bridging and capping geometries becomes more competitive with the m-top ones.

4. (a) From about -11 to -14 eV there are two main peaks for the n orbitals. These are the symmetric and antisymmetric combinations at $\theta = 0°$, i.e.



n_s

&



n_a

The corresponding m-c antibonding combinations are at ~ -3 to 11 eV. As θ increases the n_s combination is stabilized and n_a is pushed upwards. At $\theta = 30°$ the n_a combinations lie around the Fermi level. On going to $\theta = 60°$, n_a is pushed up more and n_s is stabilized.

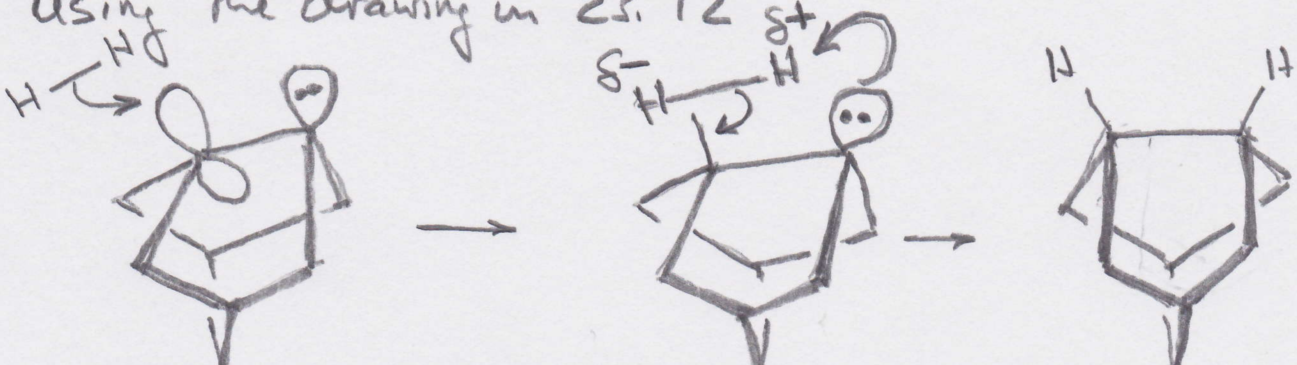
(b) The n_a combinations need to be destabilized enough so that they lie above the Fermi level. This is the electronic origin of much of the activation barrier. The Fermi level lies higher in energy for early transition metals so the energy associated with the destabilization of n_a when it is filled is larger.

(c) Early metals have low barriers for migration so getting the alkyl groups close to one another is facile. However, the coupling barrier is high. The exact reverse holds true for late transition metals. Transition metals in the middle should be the best place to look, i.e. Fe, Co, Ru, etc.

5. (a) The black circles become pyramidal – they must have a lone pair pointing away from the surface. Therefore, Se, the more electronegative element must be the black circles.

(b) NH_3 is a nucleophile so it should attack the Cd. Using (a) NH_3 will attack the white circles and BH_3, an electrophile, will attack Se, the black ones.

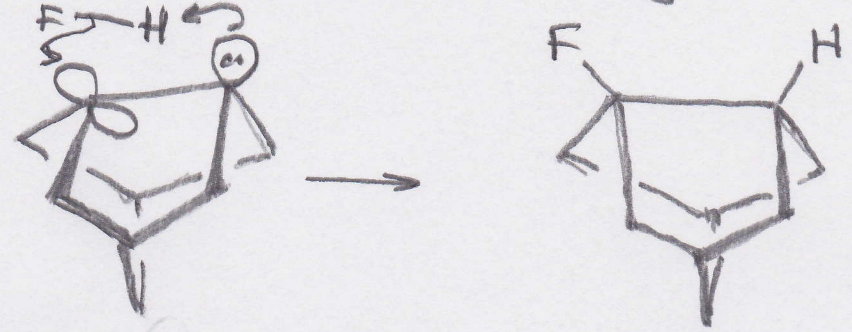
6. Using the drawing in 23.72



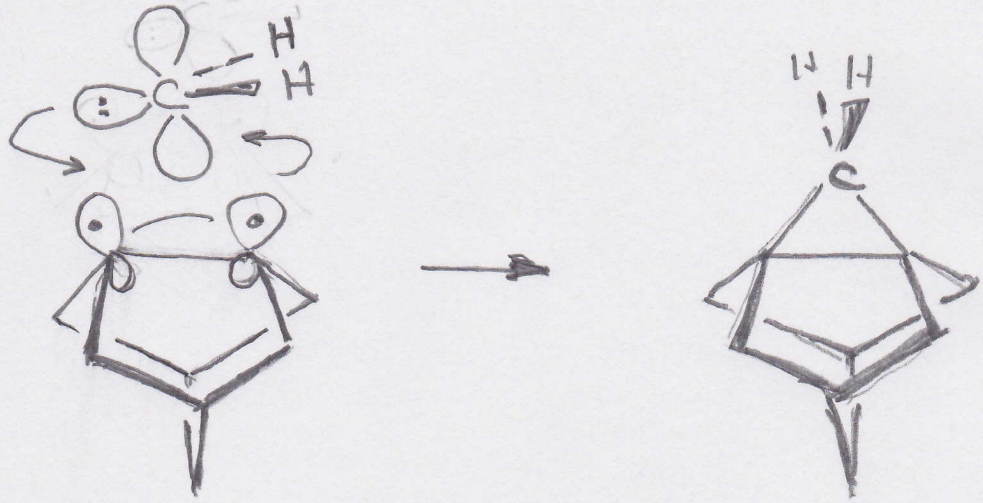
(H$_2$ σ interacts with the empty p AO on Si)

(The H$_2$ unit slips over to the right and the H atoms are polarized in the way shown – why? ;-)
consider the polarization with H$_2$ σ & σ* interacting with Si p AO

The mechanism for H–F is likely to be:



7.



This is exactly like the addition of CH_2 to ethylene – see 11.13 – 11.15 and the discussion around them.