

Organometallic Chemistry

CHEM 534

Exam 1

October 9, 2008

Prof. Malachowski

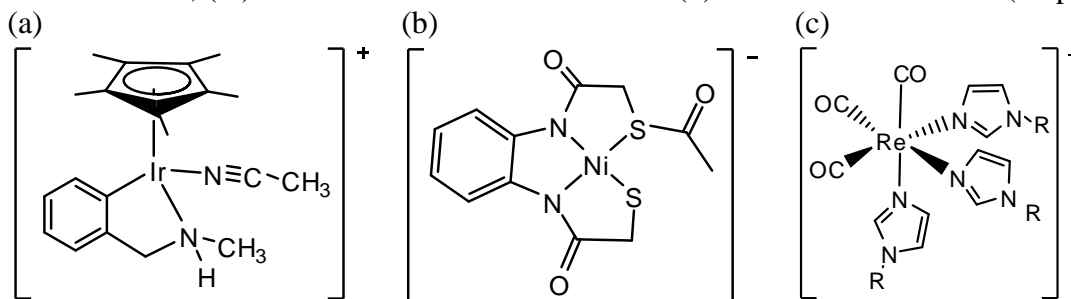
Name: Ron Paul

1. How could you distinguish between a square planar and a tetrahedral structure in a Ni(II) complex of which you have a pure sample, without using crystallography? (10 pts.)



Ni(II) in a tetrahedral geometry would be paramagnetic, while in the square planar it is not.

2. The three organometallic complexes shown below were reported in the most recent issue of the *Journal of the American Chemical Society* (2008, 130, issue 41). Choose TWO and provide the following: (i) identify each ligand as L-type or X-type; (ii) formal oxidation state of the metal; (iii) d^n electron count; (iv) total electron count of the metal (v) coordination number. (10 pts.)



(i) X-type: Cp (L_2X),
Phenyl L-type: N(H)CH₃,
NCCH₃

(ii) Ir⁺³

(iii) d^6

(iv) 18 e⁻s

(v) CN=6

(i) X-type: both N-C(O), S-
CH₂
L-type: S(CH₂)C(O)CH₃

(ii) Ni⁺²

(iii) d^8

(iv) 16 e⁻s

(v) CN=4

(i) X-type: none
L-type: all six

(ii) Re⁺

(iii) d^6

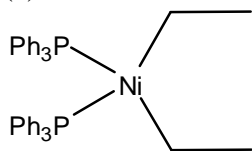
(iv) 18 e⁻s

(v) CN=6

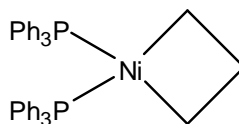
_____/20 pts.

3. Which of the two complexes below is more likely to undergo beta-elimination? Explain. (8 pts.)

(a)



(b)

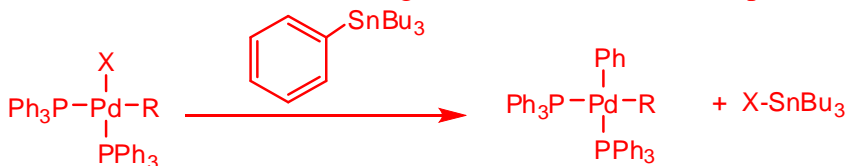


Complex (a) should undergo beta-elimination faster because its beta protons will be more available since the alkyl groups can freely rotate in (a), but are confined in a small ring in (b) and therefore not accessible to the Ni filled d orbitals.

4. Show two specific examples of reactions that make a metal-alkyl complex. Name the reaction type that you have shown (e.g. beta-elimination, oxidative addition, etc.). (12 pts.)

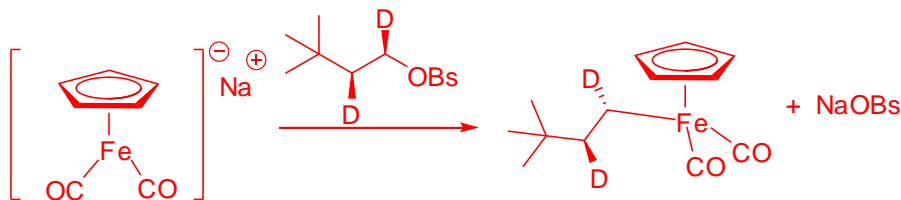
Possible answers include:

1) transmetalation or ligand substitution or nucleophilic attack on M

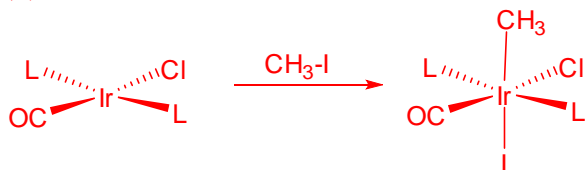


X=halide

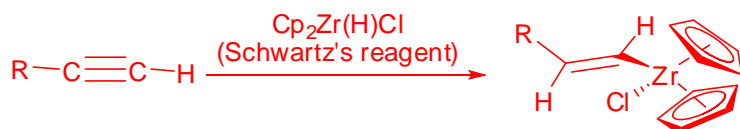
(2) electrophilic attack on metal



(3) oxidative addition

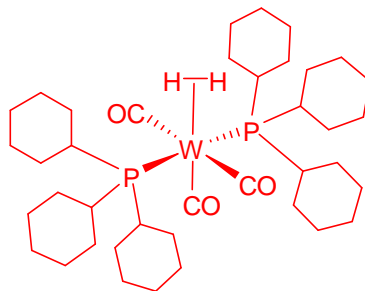


(4) 1,2-insertion



_____/20 pts.

5. The first dihydrogen σ complex was reported in 1984 by G. Kubas and co-workers (*JACS* **1984**, *106*, 451) and had the structure: $W(CO)_3(PCy_3)_2(\eta^2-H_2)$. (Cy=cyclohexyl)
 (a) Draw the structure of this complex if it has a meridional orientation. (6 pts.)



- (b) Suggest one reason why this complex may be stabilized in the sigma dihydrogen form as opposed to the classical di-hydride structure. (4 pts.)

The W may be relatively electron poor with three CO's (π acids engaged in backbonding) and this limits the e- density available to donate from W to the σ^* bond of the H-H. Donation to σ^* leads to formation of the classical dihydride complex.

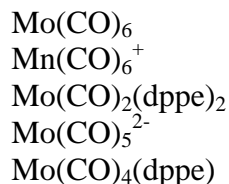
A second reason may be that the complex is coordinatively saturated (CN=6) and therefore can't fit two hydride ligands.

- (c) Suggest a way that you could test your reason from part (b). (4 pts.)

For reason one: replace one or more of the CO ligands with strong σ donors and/or π neutral or acidic ligands, e.g. $-CH_3$ or PMe_3 , to see if increasing electron density on W will cause the dihydride complex to form.

For reason two: replace one or both of the $P(Cy)_3$ ligands with PR_3 ligands that have a smaller cone angle, but similar electronic donation properties, e.g. PMe_3 or $P(CH_2CH_3)_3$.

6. List the following in order of decreasing reactivity with trimethylamine oxide on their CO groups. (10 pts.)



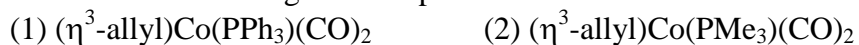
Least reactive

Most reactive



_____/24 pts.

7. Compare characteristics of the following two complexes.



a) Select the complex with the highest ν_{CO} and briefly explain your choice. (6 pts.)

As a stronger π acid PPh_3 in (1) will withdraw more e-density from the Co thereby reducing the back bonding to the CO ligands, increasing the strength of the CO bond and raising ν_{CO} .

b) Select the complex with the most sterically congested center and briefly explain your choice. (6 pts.)

Complex (1) PPh_3 has a much larger cone angle than PMe_3 and will therefore require greater space around the Co.

8. The rate law for CO exchange in $\text{Ni}(\text{CO})_4$ is: $\text{rate} = k[\text{Ni}(\text{CO})_4]$.



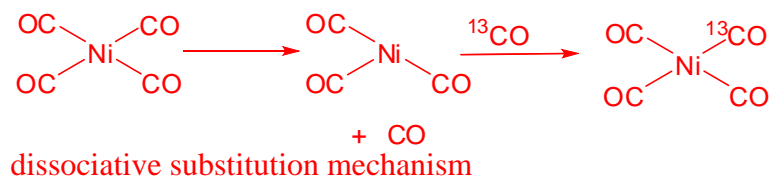
a) Provide the total electron count of $\text{Ni}(\text{CO})_4$: (3 pts.)

10 e-s (for Ni) + (4 x 2 e-'s for each CO) = 18e-'s

b) Provide the d^n electron count of Ni: (3 pts.)

No X type ligands, therefore Ni(0) and d^{10} .

c) Provide the best mechanism for the reaction that is consistent with the rate law. (7 pts.)

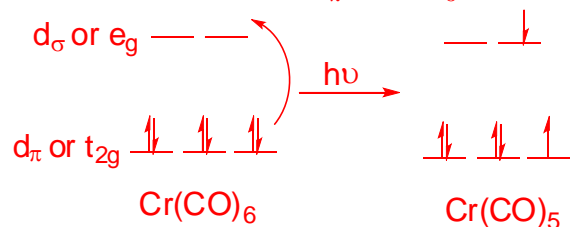


_____/25 pts

9. When $\text{Cr}(\text{CO})_6$ is irradiated with UV light, the following reaction occurs:

a) Draw the Cr d molecular orbitals before and after the irradiation to show the effect of the irradiation event. (6 pts.)

Octahedral geometry for $\text{Cr}(\text{CO})_6$ and therefore a two-over-three arrangement of Cr's d molecular orbitals. Light causes the promotion of one e- from d_π to the d_σ orbitals.



b) Explain why this results in the loss of one CO ligand. (5 pts.)

With the promotion of an electron to the anti-bonding d_σ orbital, there is a new e-/e- repulsion between the d_σ e- and one of the CO groups along the x, y or z axis. Furthermore, there is also one less e- for π backbonding and so the CO backbond will be compromised.

_____/11 pts