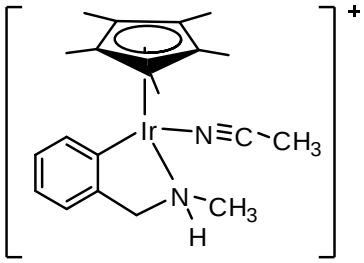
Organometallic Chemistry Name:_____
CHEM 534
Exam 1
October 9, 2008
Prof. Malachowski

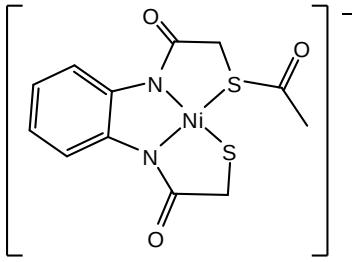
1. How could you distinguish between a square planar and a tetrahedral structure in a Ni(II) complex of which you have a pure sample, without using crystallography? (10 pts.)

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.)

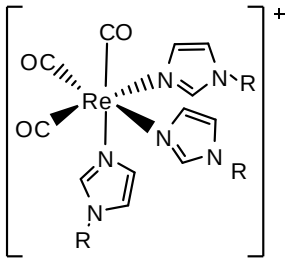
(a)



(b)



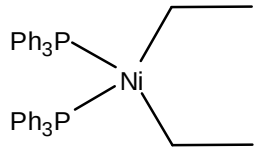
(c)



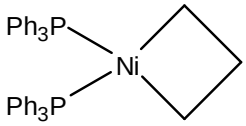
_____/20 pts.

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

(a)



(b)



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.)

_____/20 pts.

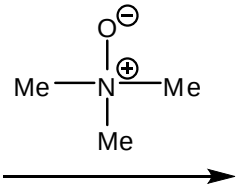
5. The first dihydrogen σ complex was reported in 1984 by G. Kubas and co-workers (*JACS* **1984**, *106*, 451) and had the structure: $W(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)$. (Cy=cyclohexyl)
(a) Draw the structure of this complex if it has a meridonal orientation. (6 pts.)

(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.)

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

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

$Mo(CO)_6$
$Mn(CO)_6^+$
$Mo(CO)_2(dppe)_2$
$Mo(CO)_5^{2-}$
$Mo(CO)_4(dppe)$



Least reactive Most reactive

_____<_____<_____<_____<_____

_____/24 pts.

7. Compare characteristics of the following two complexes.

(a) (η^3-allyl)Co(PPh_3)($CO)_2$ (b) (η^3-allyl)Co(PMe_3)($CO)_2$

a) Select the complex with the highest υ_{CO}. (6 pts.)

b) Select the complex with the most sterically congested center. (6 pts.)

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

$$Ni(CO)_4 + {}^{13}CO \rightarrow Ni(CO)_3({}^{13}CO) + CO$$

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

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

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

_____/25 pts

9. When $Cr(CO)_6$ 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.)

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

_____/11 pts