Inorganic Chemistry Cumulative Exam
January 2019
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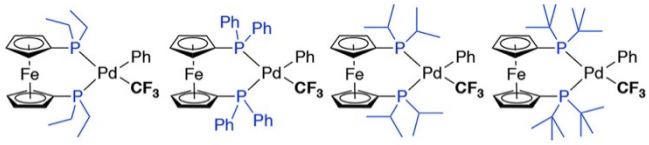
1. Trifluoromethylated organic compounds are valuable in many areas including pharmaceuticals and agrochemicals. Thus, fundamental aspects of metal-catalyzed trifluoromethylation is an area of great interest. Recently, Sanford and coworkers studied the rates of Ph-CF_3 reductive elimination from the series of complexes shown below.

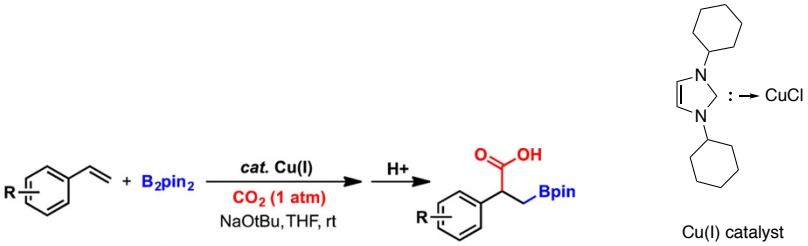
(a) **Assign oxidation states** to ***both*** metal centers in these complexes. Explain how your assignment accounts for the observed square planar geometry at Pd.

(b) **Rank** the complexes in order of Ph-CF_3 reductive elimination rate, from ***fastest to slowest***.



Reference: *Organometallics*, Article ASAP, **DOI:** 10.1021/acs.organomet.8b00828

2. A frontier area in catalysis is to discover systems that incorporate CO_2 into value-added chemicals. In this context, recently Popp and coworkers reported a Cu(I)-catalyzed borylcarboxylation reaction of styrenes, as shown below. **Propose** a reasonable catalytic ***mechanism*** for this transformation.



Reference: *Org. Lett.*, **2016**, *18* (24), pp 6428–6431

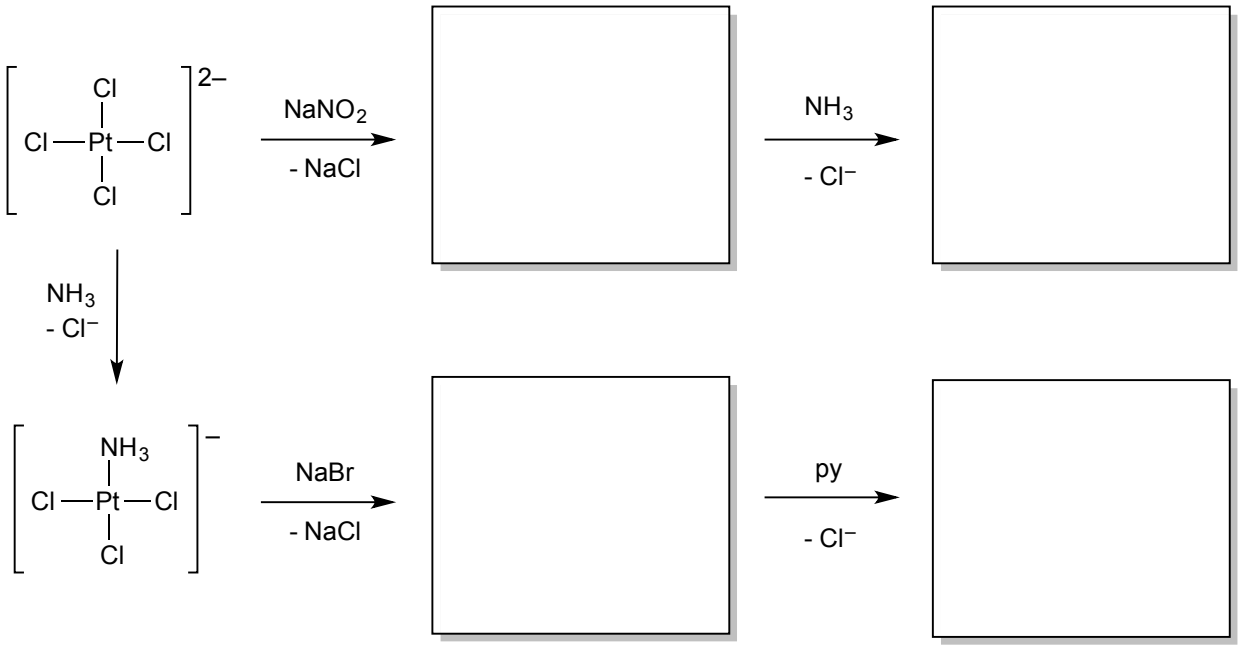
3. (a) For a complex of the type $W(CO)_5(PR_3)$, **how many** CO stretching vibrations are ***IR-active***? Show your work. (A character table is provided at the back of the exam, should you need it.)
(b) A table of IR data is provided below for various $W(CO)_5(PR_3)$ derivatives. Fill in the empty column from this list of phosphines: **PCl_3, PMe_3, PF_3, $P(OEt)_3$**.

IR data for $W(CO)_5(PR_3)$ complexes

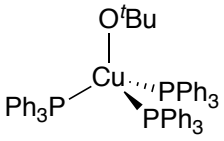
PR_3	**A_1 stretch (cm^{-1})**
	2103
	2094
	2078
	2071

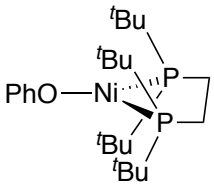
4. Assuming each reaction below goes by an associative substitution mechanism, fill in the boxes with your predicted products. For each complex, be sure to indicate both the *cis*/*trans* ***stereochemistry*** and the ***charge*** of the coordination complex.

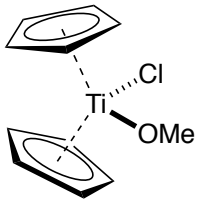
***trans*-effect:**
(weak) F^-, HO^-, H_2O < NH_3 < py < Cl^- < Br^- < I^-, SCN^-, NO_2^-, $SC(NH_2)_2$, Ph^- < SO_3^{2-} < PR_3 < AsR_3, SR_2, H_3C^- < H^-, NO, CO, NC^-, C_2H_4 (strong)

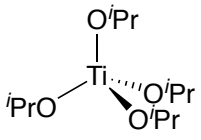


5. **Predict** whether each of the metal-alkoxide (M-O-R) units below will be ***bent or linear*** at oxygen. Use the metal center's valence electron count to justify your answer, and show your work.









Character table for C_{4v} point group

	E	$2C_4$ (z)	C_2	$2\sigma_v$	$2\sigma_d$	linear, rotations	quadratic
A_1	1	1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		x^2-y^2
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	(x, y) (R_x, R_y)	(xz, yz)