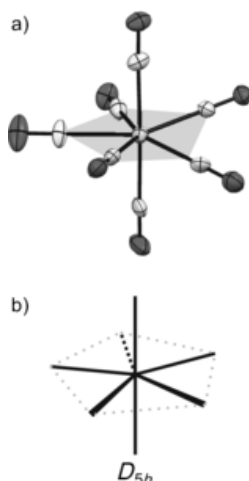


Inorganic Chemistry Cumulative Exam
Thursday, January 12, 2017
Neal Mankad

1. The bifluoride anion $[\text{HF}_2]^-$ exemplifies the so-called **three-center two-electron** (3c-2e) bond.
 (a) Give a general definition of "3c-2e bond".
 (b) Provide a qualitative MO analysis of $[\text{HF}_2]^-$ and explain how it fits within your definition.

2. Dunbar and coworkers recently reported¹ the synthesis and characterization of the heptacyanotungstate(IV) anion, i.e. $[\text{W}(\text{CN})_7]^-$, which adopts a D_{5h} geometry as shown below. How many $\text{C}\equiv\text{N}$ stretching bands do you expect to be observable by IR spectroscopy? A D_{5h} character table is provided for your reference.

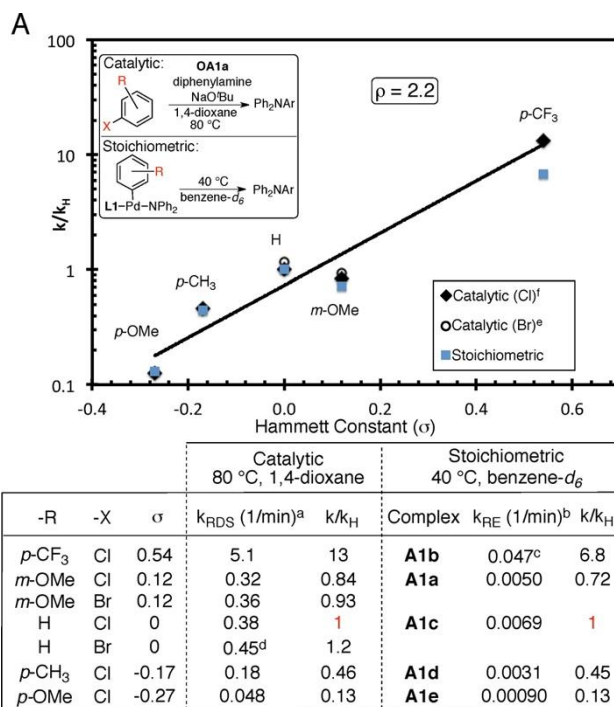


Character table for D_{5h} point group

	E	$2C_5$	$2(C_5)^2$	$5C_2$	σ_h	$2S_5$	$2(S_5)^3$	$5\sigma_v$	linear, rotations	quadratic
A'_1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A'_2	1	1	1	-1	1	1	1	-1	R_z	
E'_1	2	$2\cos(2\pi/5)$	$2\cos(4\pi/5)$	0	2	$2\cos(2\pi/5)$	$2\cos(4\pi/5)$	0	(x, y)	
E'_2	2	$2\cos(4\pi/5)$	$2\cos(2\pi/5)$	0	2	$2\cos(4\pi/5)$	$2\cos(2\pi/5)$	0		(x^2-y^2, xy)
A''_1	1	1	1	1	-1	-1	-1	-1		
A''_2	1	1	1	-1	-1	-1	-1	1	z	
E''_1	2	$2\cos(2\pi/5)$	$2\cos(4\pi/5)$	0	-2	$-2\cos(2\pi/5)$	$-2\cos(4\pi/5)$	0	(R_x, R_y)	(xz, yz)
E''_2	2	$2\cos(4\pi/5)$	$2\cos(2\pi/5)$	0	-2	$-2\cos(4\pi/5)$	$-2\cos(2\pi/5)$	0		

¹ Birk, F. J., Pinkowicz, D. & Dunbar, K. R. The Heptacyanotungstate (IV) Anion: A New 5d Transition- Metal Member of the Rare Heptacyanometallate Family of Anions. *Angew. Chem.* (2016). doi:10.1002/ange.201602949

3. Recently, Buchwald and coworkers conducted stoichiometric C-N reductive elimination studies using isolated arylpalladium(II) amido complexes that were identified as resting states during Pd-catalyzed C-N coupling.² As shown below, Hammett studies indicated that Pd(II) intermediates derived from electron-deficient aryl halides undergo reductive elimination more slowly than those derived from electron-rich aryl halides.



- (a) Provide an explanation for this observation that takes into account the factors generally impacting rates of reductive elimination.
- (b) Give your hypothesis for how *ortho*-substitution on the aryl halide would impact the rate of reductive elimination.

4. The neutral and cationic states of ferrocene, i.e. FeCp₂ and [FeCp₂]⁺, are used as standards for nonaqueous electrochemistry because they are so stable and well understood. The dicationic state of ferrocene is comparatively elusive. Meyer and coworkers recently reported³ the synthesis and characterization of the decamethylferrocene dication, i.e. [FeCp*₂]²⁺ (where Cp* = η⁵-C₅Me₅). Give the following information about [FeCp*₂]²⁺: (a) oxidation state of Fe, (b) d-electron count of Fe, (c) total valence electron count of Fe, and (d) number of unpaired electrons in [FeCp*₂]²⁺. For part (d), give a qualitative d-orbital splitting diagram to show how you arrived at your answer.

² Arrechea, P. L. & Buchwald, S. L. Biaryl Phosphine Based Pd(II) Amido Complexes: The Effect of Ligand Structure on Reductive Elimination. *J. Am. Chem. Soc.* **138**, 12486–12493 (2016).

³ Malischewski, M., Adelhardt, M., Sutter, J., Meyer, K. & Seppelt, K. Isolation and structural and electronic characterization of salts of the decamethylferrocene dication. *Science* **353**, 678–682 (2016).