Inorganic Chemistry Cumulative Exam
Thursday, October 1, 2015
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1. If you have been following the news this week, you know that scientists from Georgia Tech, NASA, and other institutions found evidence for the existence of liquid water on Mars!!!! While you and I likely read about this in the mainstream press, the data was reported in the scientific journal, *Nature Geoscience*, on 28 September 2015. Interestingly for inorganic chemists, the main evidence supporting the newsworthy claims comes from analysis of the infrared (IR) spectra of key Martian samples containing the perchlorate anion, ClO_4^-. The data clearly show that perchlorate is found complexed to metal cations such as Mg^{2+} and Na^+, and comparison to terrestrial samples confirms that these perchlorate salts are present in *hydrated* form.

   a. Draw the Lewis structure of ClO_4^-, and make sure to depict it in its correct geometry according to the principles of VSEPR. If more than one resonance structure is reasonable, draw all of them. Assign the point group of this anion.
   b. There are four Cl-O bonds in this anion. If the anion is "free", i.e. not complexes to any cation, how many Cl-O stretching vibrations are expected in its IR spectrum? Use group theory to obtain your answer. Character tables are provided.
   c. If perchlorate is complexed to a metal cation, its symmetry will be lowered, and this will be reflected in the IR spectroscopy. Two possible binding modes are shown below, but without the geometry at Cl indicated. Assign point groups for each case. Use group theory to determine how many of the four Cl-O stretching vibrations are expected to be IR-active in each case.

$$M-O-ClO_3 \qquad M\underset{O}{\overset{O}{<}}\hspace{-0.3em}>ClO_2$$

2. Although less newsworthy than water on Mars, homogeneous catalysts for hydrogenation of unsaturated organic substrates have always been a main focus of the organometallic community. Some of the classic systems for hydrogenation are among the most well studied homogeneous catalysts in history, and much of our knowledge of organometallic systems generally comes from studies on this specific application. This question reviews knowledge of these historically important systems.

   a. Geoffrey Wilkinson (Nobel Prize 1973) and coworkers, including his student John Osborn, reported one of the earliest (and still most famous) examples of a catalyst for homogeneous hydrogenation of alkenes. Provide the structure of "Wilkinson's catalyst" and assign the metal's formal oxidation state and *d*-electron count.
   b. Two mechanisms for alkene hydrogenation by Wilkinson's catalyst are accepted, and the operative mechanism in any individual case likely depends on reaction conditions and the nature of the substrate. For a generic terminal alkene, provide one of the two accepted mechanisms. Assign the metal's formal oxidation state and *d*-electron for each catalytic intermediate.
   c. A more active catalyst was later reported by John Osborn and his student, Richard Schrock (Nobel Prize 2005). This catalyst, now known as the Schrock-Osborn catalyst

(shown below), is essentially a cationic derivative of Wilkinson's catalyst. Assign the metal's formal oxidation state and *d*-electron count.
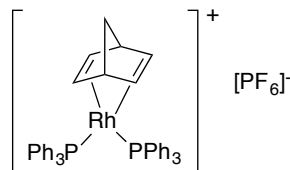
d. Provide a qualitative explanation for why the Schrock-Osborn catalyst tends to be more active than Wilkinson's catalyst. Use insights from your answer to part (b) in your explanation.

e. Wilkinson's catalyst and the Schrock-Osborn catalyst both utilize Rh. Other key advances with precious metal catalysts based on Rh, Ir, and Ru were made by Knowles (Nobel Prize 2001), Crabtree, and Noyori (Nobel Prize 2001), respectively. Choose any one of these discoveries and describe it.

f. Recently, there has been a push to develop sustainable catalysts based on non-precious metals. Because such metals typically cannot perform oxidative addition like the precious metals above, new ways to break the H_2 bond are needed. One recent approach, from Jonas Peters (Schrock's student's student and my Ph.D. advisor) and coworkers, is shown below. It involves a [Co-B] unit that is capable of adding 2 equivalents of H_2 to give a species active for alkene hydrogenation. Assign the Co formal oxidation state and *d*-electron count for each species shown. Based on your answer, explain how this H_2 activation is similar or different from a classical H_2 oxidative addition by, for example, Wilkinson's catalyst.
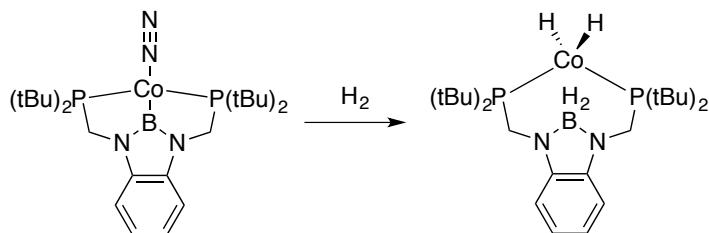
g. Another key advance that has emerged recently is the concept of frustrated Lewis pairs (FLPs), which allow for metal-free H_2 activation. Here, a *p*-block Lewis acid and a *p*-block Lewis base cooperate to break the H_2 bond, in many cases giving active catalyst mixtures for hydrogenation of ketones, aldehydes, imines, etc. A typical FLP and its activation of H_2 are shown below. Assign the formal oxidation states of B and P in all species shown. Based on your answer, explain how this H_2 activation is similar or different from a classical H_2 oxidative addition by, for example, Wilkinson's catalyst. In the pair that results from H_2 activation by the FLP, which species should be considered "protic" and which one "hydridic"?
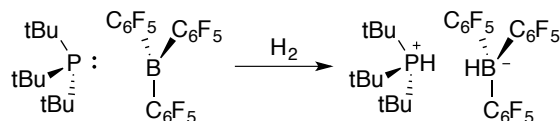
Character table for T_d point group

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	linear, rotations	quadratic
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

Character table for D_{3h} point group

	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$	linear, rotations	quadratic
A'_1	1	1	1	1	1	1		x^2+y^2, z^2
A'_2	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x, y)	(x^2-y^2, xy)
A''_1	1	1	1	-1	-1	-1		
A''_2	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

Character table for D$_{2d}$ point group

	E	2S$_4$	C$_2$ (z)	2C'$_2$	2σ$_d$	linear, rotations	quadratic
A$_1$	1	1	1	1	1		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	z	xy
E	2	0	-2	0	0	(x, y) (R$_x$, R$_y$)	(xz, yz)

Character table for C$_{3v}$ point group

	E	2C$_3$ (z)	3σ$_v$	linear, rotations	quadratic
A$_1$	1	1	1	z	x^2+y^2, z^2
A$_2$	1	1	-1	R$_z$	
E	2	-1	0	(x, y) (R$_x$, R$_y$)	(x^2-y^2, xy) (xz, yz)

Character table for C$_{2v}$ point group

	E	C$_2$ (z)	σ$_v$(xz)	σ$_v$(yz)	linear, rotations	quadratic
A$_1$	1	1	1	1	z	x^2, y^2, z^2
A$_2$	1	1	-1	-1	R$_z$	xy
B$_1$	1	-1	1	-1	x, R$_y$	xz
B$_2$	1	-1	-1	1	y, R$_x$	yz