INORGANIC CHEMISTRY CUMULATIVE EXAM
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Frustrated Lewis Pairs

The Department recently hosted Douglas Stephan, from Toronto, for a seminar on his work with "Frustrated Lewis Pairs." This is an excellent opportunity to explore some fundamental and also some very applied examples from inorganic chemistry.

1. (25 points).
(a) Describe what is meant by a Lewis pair, including at least three examples.
Then, (b) describe why the idea of a "frustrated" Lewis pair may be important in developing new chemistry.

In addition, show how:
(c) Lewis pairs are a form of acid-base theory;
(d) How Lewis pairs may be of fundamental importance in catalysis of reactions involving organic transformations; and
(e) how Lewis pairs can alter the electronics of a molecule through resonance interactions.

2. (35 points—getting started).

(a) The basic discovery of FLPs came about because of the reactivity of a bifunctional compound, $(C_6H_2Me_3)_2PH(C_6F_4)BH(C_6F_5)_2$, **1.** This material, Stephan and coworkers found, reversibly reacts with H_2. Explain how this transformation occurs and also predict the detailed three-dimensional structure of the original FLP example.

(b) With the transformations of **1** in hand, it was a logical step to advance to *bimolecular* FLPs, which also carry out H_2 examples. Give an example of such a bimolecular FLP (hint: consider the structure of **1**).

(c) An early 'hit' for the importance of FLPs was the development of metal free catalysis of hydrogenation. Provide a mechanism by which an FLP could catalytically activate H_2 for the reduction of a target substrate, for example an aldimine.

(d) Doug talked about several examples of aldimine reduction, which is much easier than carbonyl reduction. Why?

3. (15 points—CO_2) Stephan did not talk about CO_2 in detail, but it has been on his list of substrates for activation. An article in *JACS* (2010, 132 (6), pp 1796–1797) discussed how he could stoichiometrically activate CO_2 by (a) Treatment with $PMes_3$ (Mes = mesityl) with two equivalents of $AlCl_3$ to get an intermediate 2, that is then reduced by NH_3BH_3 to make methanol. Propose the structure of **2** and also describe the mechanism of its formation and of its reduction to methanol.

4. (25 points). Recent work by Stephan and coworkers has moved in an exciting new direction through the development of chemistry for *electrophilic phosphonium cations*, such as $[P(C_6F_5)_3F]^+$.

(a) Describe the bonding of **3** around the phosphorus.

(b) How can **3** and similar phosphonium cations react as an electrophile? Why would the corresponding ammonium salt **not** work?

(c) Describe one application of an EPC in chemistry (hint: consider what Stephan discussed with respect to the chemistry of fluorine-containing substrates).