**Literature Discussion: Coordination Bonding with Main Group Metals(?)**

The coordinate covalent bonding model is very useful for describing the bonding in ligand complexes of transition metals – but what about the main group metals such as Sn, Pb, and Bi? A recent communication by Gilliard and coworkers described the synthesis of a novel compound of bismuth metal combined with a cyclic(alkyl)(amino)carbene (CAAC) ligand, a type of ligand that has been extensively studied in complexes of transition metals and lighter main group elements.

**READ** the following paper on the synthesis of a carbene-bismuthinidene complex:

Wang, G., Freeman, L. A., Dickie, D. A., Mokrai, R., Benkö, Z., Gilliard, R. J. *Chem. Eur. J*. **2019**, *25*, 4335-4339.

Glossary of some terms and acronyms:

* Pnictogen – a Group 15 element (i.e., P, As, Sb, Bi)
* Carbene – an organic molecule featuring a neutral carbon atom with two substituents and a lone pair
* CAAC – “cyclic(alkyl)(amino)carbene”, a type of stable carbene where the carbene C is adjacent to one bulky amino group and one bulky alkyl group within a 5-membered ring
* DFT – a type of computational chemistry that models the geometry, energy levels, and molecular orbitals of small compounds

**CONSIDER** the following questions, which we will discuss during class:

1. What was the goal of the experiments described in this paper? According to the authors, why have subvalent bismuthinidenes been difficult to create as opposed to pnictinidenes of lighter Group 15 elements?
2. How is the carbene carbon stabilized in the CAAC molecule? How does the CAAC act as a ligand?
3. What happened in the first attempt to reduce (CAAC)BiPhCl2 with KC8? Why did the authors think this attempt failed, and what did they do to fix it?
4. What were the two successful versions of the synthesis utilizing the Be(0) reagent? What was the difference between these approaches? Did one work better than the other?
5. What evidence do the researchers present that they indeed synthesized Compound 3?
6. What evidence do the researchers present for the proposed “partial double bond character” of the carbene C – Bi bond in Compound 3? How can this double bond be described in terms of orbital overlaps?
7. What is the best model to describe the C – Bi bonding in Compound 3: a covalent, ionic, or coordinate (dative) bonding model? Why?

**Name: \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_**

**Literature Discussion 1 Worksheet**

**COMPLETE** the following preparatory exercises (to be turned in at the beginning of class):

1. Define the term “carbene-pnictinidene” and sketch the three possible resonance forms of such a molecule as proposed by the paper.
   1. What is the oxidation state of the Pn element in a pnictinidene?
   2. What is the “normal” oxidation state expected for an element such as bismuth in compounds? How does this compare to its oxidation state in “subvalent” bismuthinidenes?
2. Sketch the Lewis structures of the CAAC ligand and the BiPhCl2 reagent, respectively.
   1. How would a hybridization model describe the orbitals at C in the carbene?
   2. How would a hybridization model describe the orbitals at Bi in BiPhCl2?
   3. What geometry would be expected at Bi in BiPhCl2 by VSEPR theory?
3. Sketch the Lewis structure of BeCl2.
   1. How would a hybridization model describe the orbitals at Be in BeCl2?
   2. What geometry would be expected at Be in BeCl2 by VSEPR theory?
4. Sketch the Lewis structure of the (CAAC)BiPh Compound 3, including the main resonance form(s) that the paper argues describe this compound.
   1. What geometry would be expected at Bi in Compound 3 by VSEPR theory (considering all relevant resonance forms)? How does this compare to what the authors actually observed?