Comments on Structure-Bonding Representations.

Introduction.

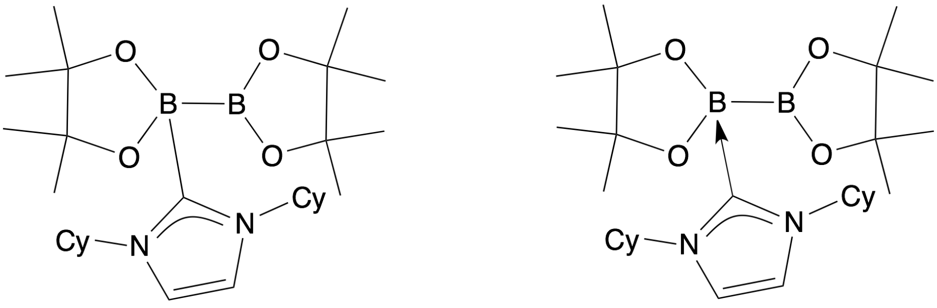
In organic chemistry, compounds and their structures (where structure means "relative atom positions"), and the bonding between two atoms are represented by Lewis diagrams with great success. For the most part, bonds between atoms are shown with one, two or three black lines for single, double or triple bonds. Occasionally, an arrow is used to represent a donor bond, for example, N→O in trimethylamine-N-oxide. Further, it is understood that, for example, the alternating single-double bonds in the benzene ring is one of two structures, which are in resonance and that the C – C bond lengths are all the same.

The bonding in inorganic compounds is often more complex than that in organic compounds and so in order to determine covalent bond classification of the molecule it is necessary to draw correct and complete structure-bonding (S-B) representations. However, it is often the case that the representations as drawn in the literature are either incorrect or, more often, incomplete. Although in many cases it may not be difficult to deduce the nature of the compound, in other cases the representation could be undecipherable.

Authors choose to draw Lewis–type representations with different degrees of attention to the representation of the bonding, whilst for the most part successfully conveying the atom structure. Commonly, the distinction between M-X and M←L bonds is ignored and the latter is drawn without an arrow. Much of the time this does not cause difficulties as experienced chemists can readily identify the different classes of ligands and can, for example, count the electron number of the compound correctly. Nonetheless it would be a helpful practice if authors would provide, e.g. in the supplementay data, a correct drawing of a structure-bonding representation, together with the corresponding ML_lX_x or MX_xZ_z class.

A few examples of incomplete representations taken from recent literature are discussed below.

(i). A recent paper describes the crystal structure of the CyNHC adduct of B_2pin_2, and the Lewis diagram drawn for this structure is shown below in Figure 1 (A).



A B

Figure 1.

As seen in Figure 1 (A), the boron atom is not attached to the carbon atom CyNHC ligand by an arrow and, therefore, to many chemists, the boron on the left hand side would appear to be tetravalent BX_4. In fact, the carbene donates two electrons to the boron as indicated by the arrow in Figure 1 (B), and so the boron is trivalent.

The absence of the arrow in Figure 1 (A) obscures consideration of the possibility that the carbene could act as a bridging μ-L group and, as such, bridge the two boron atoms. The fact that it does not is shown by the crystal structure. This is most likely due to steric interactions by the bulky CyNHC molecule.

(ii) Another paper describes the synthesis and crystal structure of a titanocene catecholborane compound. The crystal structure is shown in Figure 2 (a) and a Lewis bond representation of the structure as presented in the paper is shown in Figure 2 (b), in which there are two short black lines to indicate the attachment of the borane ligands to the titanium center. This Lewis representation is not useful for the determination of the class of the titanium. A DFT discussion of the bonding is provided in the article but this is not translated into a S-B representation.

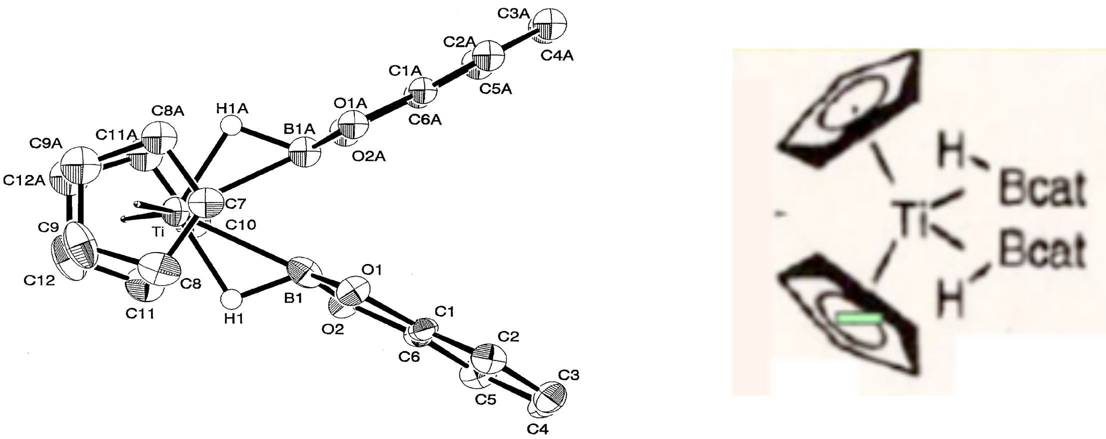


Figure 2. (a) (b)

A subsequent paper "Bonding Analysis of Titanocene Borane σ-Complexes" by Wai Han Lam and Zhenyang Lin, *Organometallics* **2000**, *19*, 2625-2628, describes detailed DFT studies of the bonding in this complex. The authors identified "an unusual three-center-two-electron bond involving the B-Ti-B triangle". However, the Lewis diagram in this paper, as shown in Figure 3 (b), suggests that the titanium atom is 6-valent (!) and that the boron atoms are tetravalent. Further, in the Lewis diagrams shown in (b) and (c), the bridging hydrogen is shown to be apparently divalent rather than as a μ-X bond, such as in diborane where the half-arrow representation is now commonly used. These Lewis diagrams were clearly not intended to show the details of the primary bonding or the unusual 3c-2e bond that was identified. This compound is interesting and an example of a μ-L bond and two correct CBC representations are shown in Figure 3 (e) and (f). Once the S-B representation is drawn as in (e) the class of the titanium in this compound is shown to be ML_4X_4 derived from a combination of $(L_2X)_2$ for the 2 Cp ligands, L_2 for the two bridging hydrides and a single Z for the two boron atoms. These ligand functions combine to give ML_6X_2Z which transforms to ML_5X_4 (using LZ = X_2), which has an electron number of 18 with a d^0 configuration.

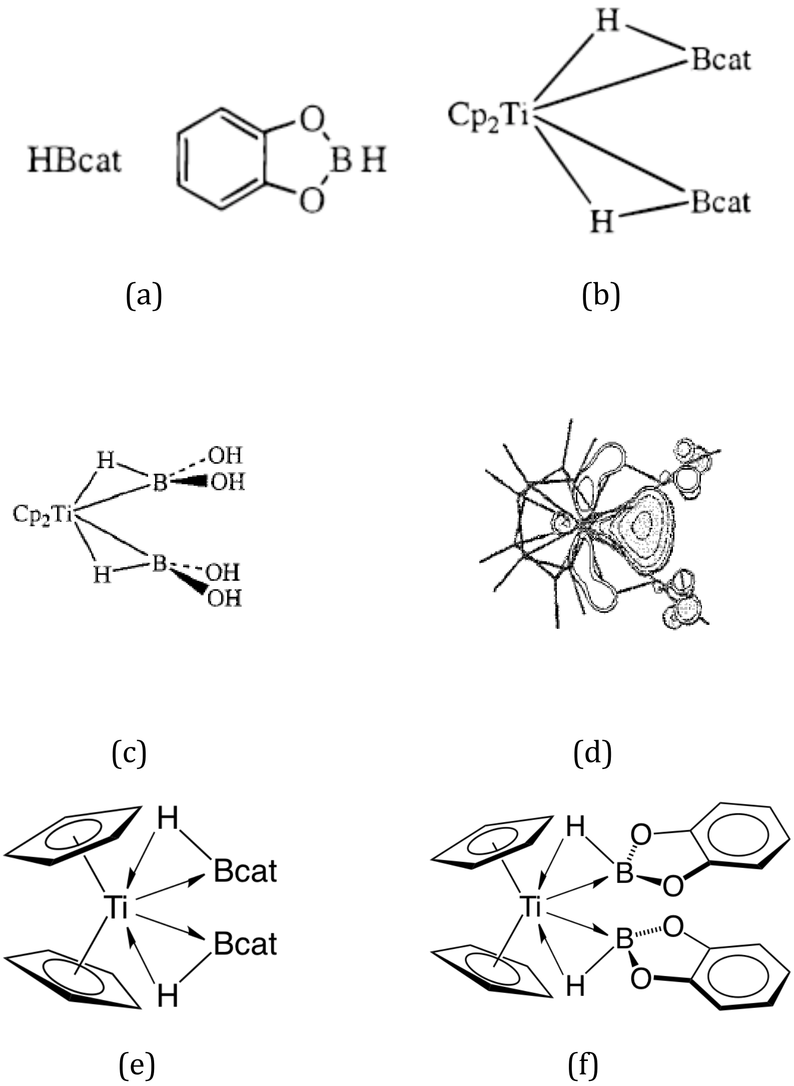


Figure 3. (a) The catecholborane ligand. (b) The Lewis diagram presented in the paper. (c) The Lewis diagram of the (hypothetical) molecule used for the DFT calculation. (d) The d-orbital of the titanium “lone pair” in the xy plane bonding with the two empty orbitals on the boron atoms. This is the 3c-2e bond. In CBC it is classified as a μ-L bond. (e) The CBC S-N representation of the titanocene-diborane compound. (f) The CBC S-N representation of the titanocene-diborane compound showing the catecholate ligand.

(iii) Other examples of incomplete Lewis representations are given in a paper that describes about ten interesting new titanium compounds. Three of these compounds are shown as drawn the paper in Figure 4 (line A). None of these representations distinguish between X and L donor ligands, and the *linear* $NOBu^t$ ligand is drawn as X_2 rather than X_2L. The

CBC representations are shown in line B below each Figure 4 in line A. The class of the titanium is given under each structure in line B.

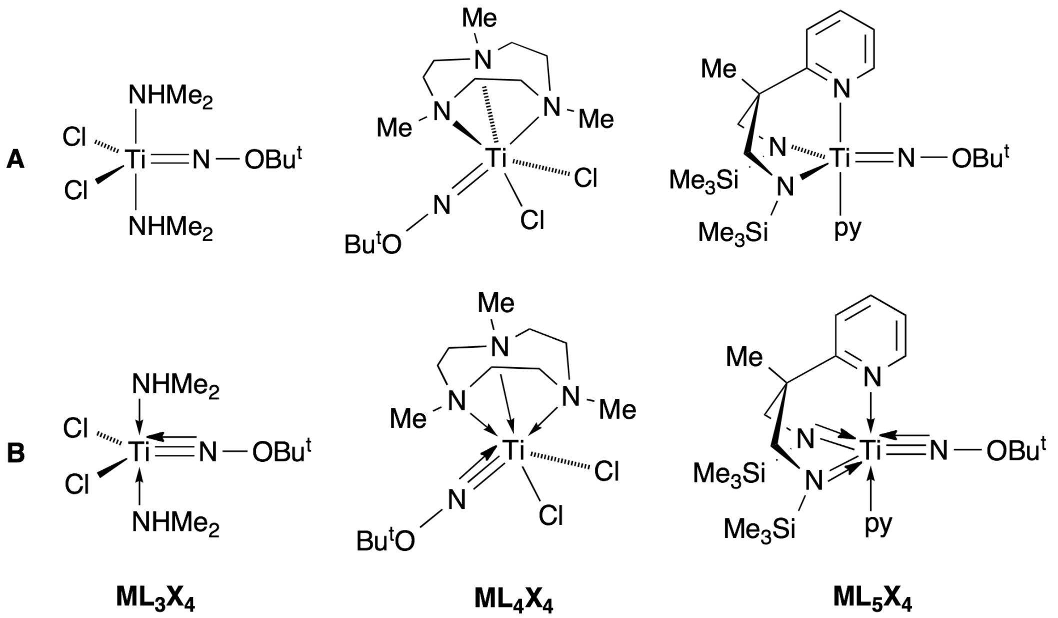


Figure 4.

Note that for the third compound (on the rhs), the CBC representation (line B) has two of the nitrogen ligand atoms classed as LX. This is because their environment is planar (as shown in the crystal structure diagram) so that they are almost certainly donating their electron pairs to the titanium. Therefore, the class of the titanium in this compound is TiL_5X_4. This is an unusual 18-electron titanium VN = 4 compound. Such compounds are quite rare because the LBN is 9 and a compact ligand system is required to avoid steric overcrowding.

Conclusion.

The drawing of a correct S-B representation provides the direct understanding of the class of a compound and hence the nature of the primary bonding and its chemistry. In most cases, the bonding is clearly apparent from the S-B representation. If one cannot draw a correct S-B representation, then this may mean that there is not a clear understanding of the bonding in the compound.