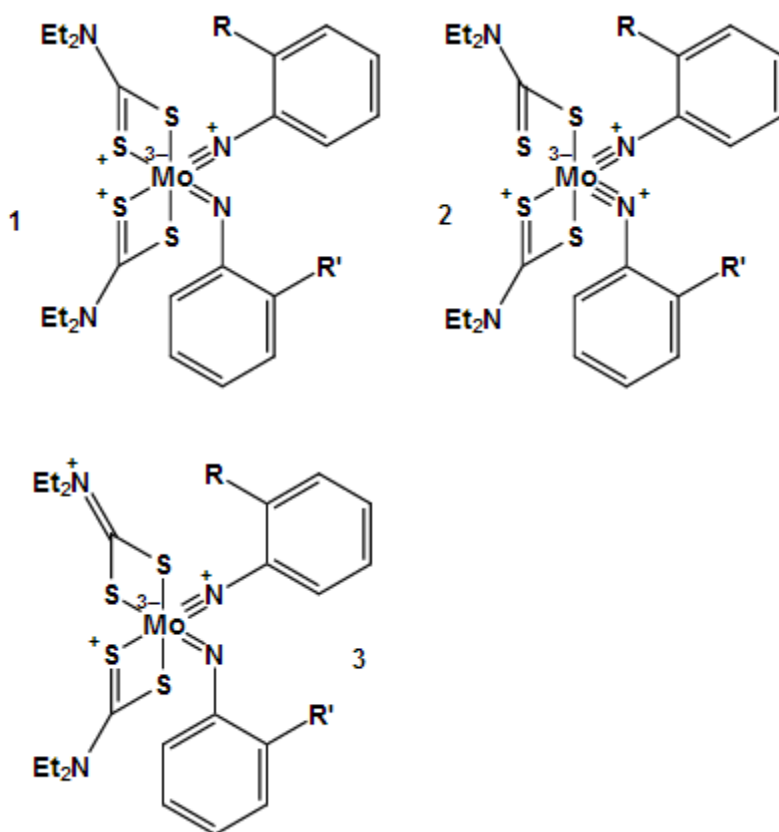


The butterfly effect in chemistry: bimodal bond angles

This potential example of a molecule on the edge of chaos was suggested to me by a student (thanks Stephen!), originating from an inorganic tutorial. It represents a class of Mo-complex ligated by two dithiocarbamate ligands and two aryl nitrene ligands (Ar-N:).



I focus on two specific examples[1], where $R=R' = \text{H}$ or Me , with crystal structures available for both. The reason for its appearance in a tutorial is that it provides a nice example of electron counting. Relocated to a tutorial on organic chemistry, it might also provide an interesting challenge for drawing a [Lewis](#) structure. So before we deal with the edge of chaos, let me start with the electron counting/Lewis structure. I have set out three possibilities for these above.

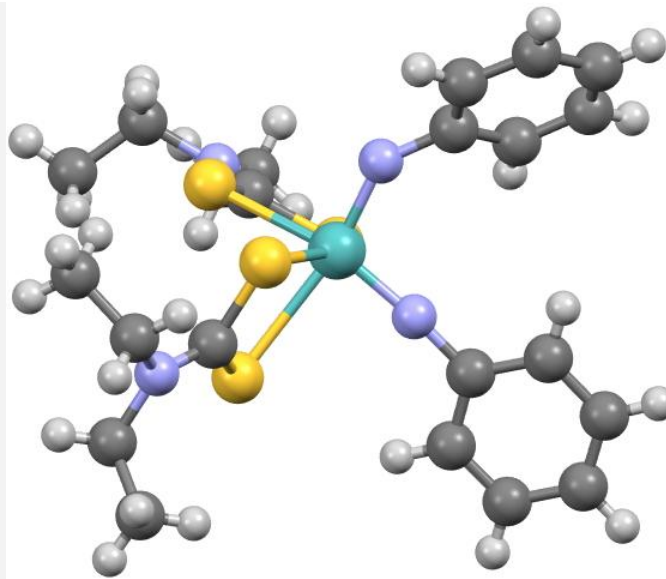
1. This one is drawn with nine bonds (= 9 electron pairs = 18 electrons) associated with the Mo. This is the 18-electron valence shell rule for transition elements, [originally set out by Langmuir](#). Of these nine bonds, six are normal, nominally covalent, shared electron bonds formed from the six valence electrons of the Mo (ground state electronic configuration $[\text{Kr}].4d^5.5s^1$) and six electron from the

ligands (two from a S- pair , and four from a N= pair). Three more bonds are formed by donation of electron pairs, two from S and one from N. This last results in the creation of (nominal) positive charges on each of the S atoms and on ONE of the nitrogen atoms (note not BOTH). In particular, one of the nitrene ligands now becomes sp-hybridised and hence linear, whilst the other remains sp² hybridized and hence bent. As a result, the Mo formally assumes a charge of **3-**.

2. This Lewis resonance form returns one S-Mo covalent electron pair to having lone pair status, and replaces the shared electron pair with a Mo-N bond formed from the remaining nitrogen lone pair. Both nitrogen atoms are now sp-hybridized, and hence linear.
3. This form removes an electron pair from one C=S double bond, and replaces it with a N=C double bond formed from the lone pair on the Et₂N group.
4. Structures **1** and **3** each show the nitrogen ligands to contribute a total of five bonds (ten shared electrons) to the Mo-N bonding. In the forms shown above, one N contributes 6, the other 4. But equally one might imagine a situation where partial bond orders of 2.5 allow each nitrogen to in effect contribute 5 electrons equally. This would result in the angle at each nitrogen being "half-bent" rather than having one fully bent and the other not bent at all. So now we have set up our molecule on the edge of chaos, where it might exist in a form best described by the resonance structures **1-3**, and an alternative form where the two nitrogen atoms are "half-bent".

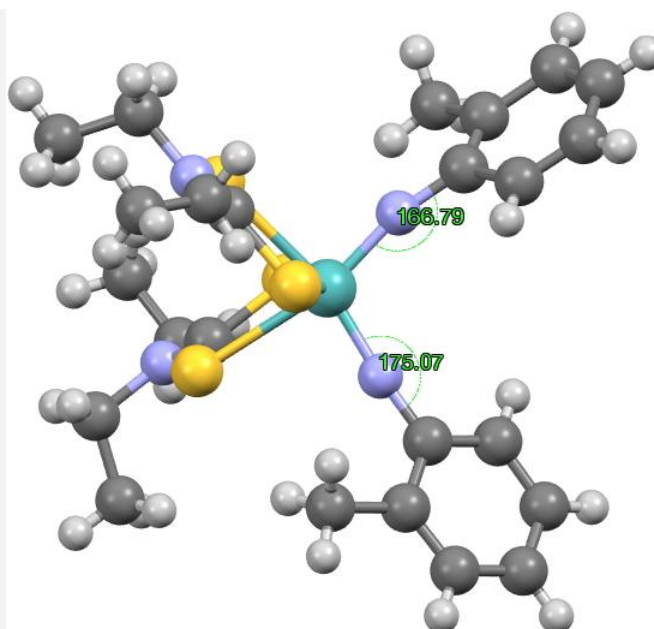
We can now apply the reality check of inspecting the crystal structure.

1. For R=H, one Mo-N-C angle is 171° and the other is 141°, a difference of 30°.
2. The consequence of the differentiated nitrogens is that the Mo-S bond immediately co-linear with the Co-N bond is 2.61Å for the linear nitrogen and 2.76 for the bent nitrogen. The lone pair on the bent nitrogen can stereoelectronically align with the Mo-S bond to lengthen it. But the p-orbital on the linear sp-nitrogen is precisely orthogonal to the Mo-S bond, and hence does not interact with it.



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What happens with R=Me? The two angles are now 167 and 175°, a mere 8° different. The system appears to have “flipped” from 6+4 bonding heading to 5+5 bonding, all because of an apparently innocuous change on the two aryl groups.



click for 3D

With this sort of behaviour, one has to ask if it might in fact be a crystallographic artefact. One way of checking this is to calculate the geometries of the two molecules, at the ω B97XD/Def2-TZVPD level in this instance. Any errors are at least systematic, and not subject to crystallographic effects. For R=H,[\[2\]](#) the two angles subtended at N are 175.1 and 146.6, a difference of 28.5°, in good agreement

with the crystallographic value of 30°. For R=Me, the values are 169 and 152°, a difference of 17°. It is certainly less than for R=H, but a bit more than is apparently measured (8°).

On balance, I think we probably can assign these two Mo complexes to the category of molecules on the edge of chaos, where the mere replacement of an *o*-H by an *o*-Me can have a big change on the angles at N.

References

1. P. Barrie, T.A. Coffey, G.D. Forster, and G. Hogarth, "Bent vs. linear imido ligation at the octahedral molybdenum(VI) dithiocarbamate stabilised centre", *J. Chem. Soc., Dalton Trans.*, pp. 4519-4528, 1999. <http://dx.doi.org/10.1039/A907382E>
2. Henry S. Rzepa., "Gaussian Job Archive for C22H30MoN4S4", 2013. <http://dx.doi.org/10.6084/m9.figshare.746899>

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