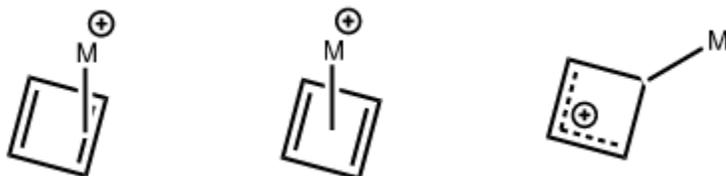
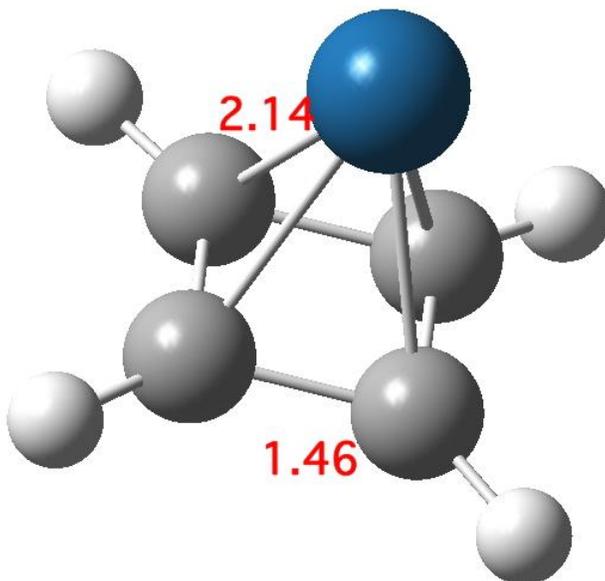


Au and Pt π -complexes of cyclobutadiene

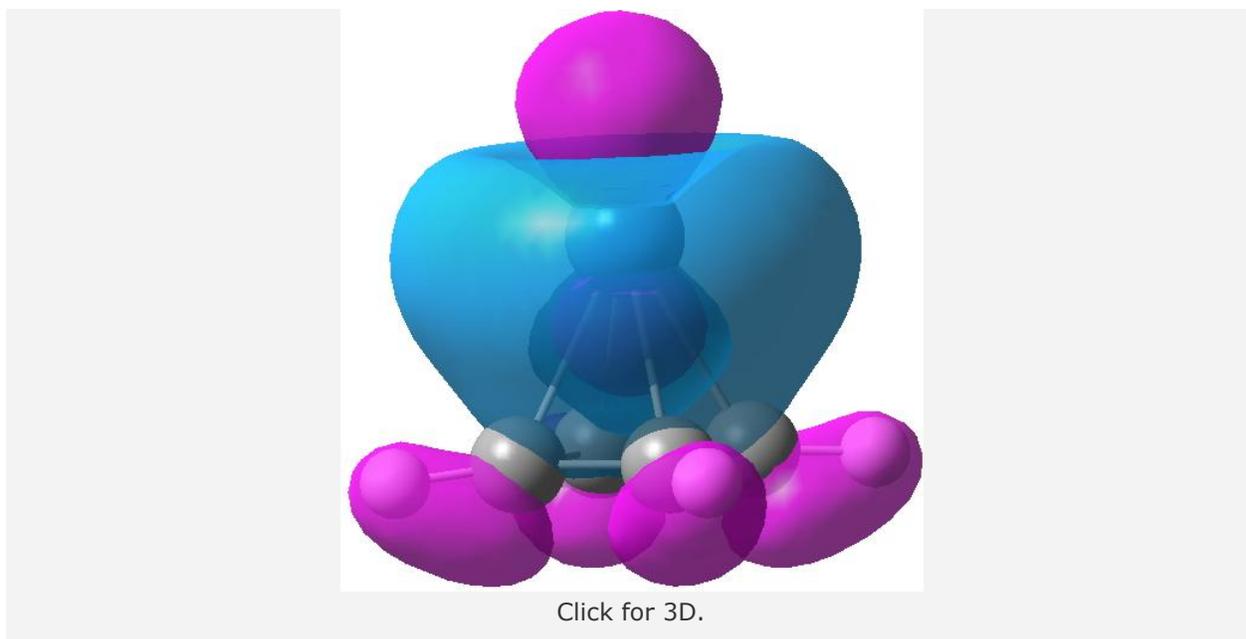
In the [preceding post](#), I introduced Dewar's n -complex theory for alkene-metal compounds, outlining the molecular orbital analysis he presented, in which the filled n -MO of the alkene donates into a Ag^+ empty metal orbital and back-donation occurs from a filled metal orbital into the alkene n^* MO. Here I play a little "what if" game with this scenario to see what one can learn from doing so.



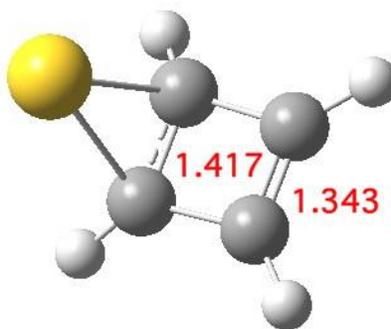
Firstly, I will use Au^+ instead of Ag^+ , so as to make a comparison with Pt^{2+} a little more direct. The electronic configurations are of course $[Xe].4f^{14}.5d^{10}.6s^0$ and $[Xe].4f^{14}.5d^8.6s^0$ respectively. I will also replace a simple ethene with cyclobutadiene, the intent here being that this cyclo-diene is a very much better n -donor due to its anti-aromatic character. It also now has the possibility of acting as a four or a two-electron donor. I started with $M=Pt^+[1]$ by adding another double bond to the structure of the ethene complex.



Optimising this starting structure in fact moves the metal and the final geometry has C_{4v} symmetry; in other words the metal is bound symmetrically to all four carbons. The four C-C lengths are all the same (1.46\AA) and strongly suggest that four electrons from the cyclobutadiene are participating in bonding; the Pt^{2+} is clearly capable of accepting four electrons, two into $6s^0$ and two into $5d^8$. In the process, the cyclobutadiene loses its antiaromaticity. The molecular orbitals of this species are all lovely; I illustrate just one below.

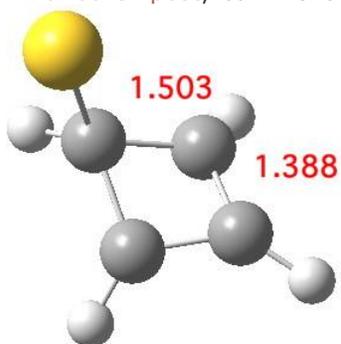


If the Pt in this C_{4v} structure is mutated into Au^+ , the resulting optimised stationary point exhibits a negative force constant characteristic of a transition state[2]. As the d-shell is already fully, the Au can only accept two electrons, and this is therefore a nice illustration of the "18-electron" rule in operation. So, the Au^+ complex must exist in at least one lower energy form. For example, one where the Au^+ is coordinated to only one alkene is 94 kcal/mol lower in free energy.[3] This form results in electrons from the coordinated alkene being donated into the 6s Au orbital, and this action reduces the anti-aromaticity of the cyclobutadiene ring.



Another isomer also achieves this result, resulting in a further lowering in free energy of 11.0 kcal/mol[4] The anti-aromaticity this time is eliminated by forming an allyl cation on the ring. I have

described this mode in [another post](#), commenting on the effect when a guanidinium cation interacts



with cyclobutadiene.

We have learnt that cyclobutadiene has many modes for eliminating 4n-electron antiaromaticity and other destabilising influences upon the ring. It can accept four electrons from a suitable acceptor (Pt^{2+}), or two electrons from Au^+ in two different ways.

References

1. Henry S. Rzepa., "Gaussian Job Archive for C4H4Pt(2+)", 2013.<http://dx.doi.org/10.6084/m9.figshare.703546>
2. Henry S. Rzepa., "Gaussian Job Archive for C4H4Au(1+)", 2013.<http://dx.doi.org/10.6084/m9.figshare.703547>
3. Henry S. Rzepa., "Gaussian Job Archive for C4H4Au(1+)", 2013.<http://dx.doi.org/10.6084/m9.figshare.703576>
4. Henry S. Rzepa., "Gaussian Job Archive for C4H4Au(1+)", 2013.<http://dx.doi.org/10.6084/m9.figshare.703577>

Source: <http://www.ch.imperial.ac.uk/rzepa/blog/?p=10498>