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 Pt²⁺ a little more direct. The electronic configurations are of course [Xe].4f¹⁴.5d¹⁰.6s⁰ and [Xe].4f¹⁴.5d⁸.6s⁰ 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 Cᵥ symmetry; in other words the metal is bound symmetrically to all four carbons. The four C-C lengths are all the same (1.46Å) and strongly suggest that four electrons from the cyclobutadiene are participating in bonding; the Pt²⁺ is clearly capable of accepting four electrons, two into 6s⁰ and two into 5d⁸. In the process, the cyclobutadiene looses its antiaromaticity. The molecular orbitals of this species are all lovely; I illustrate just one below.
If the Pt in this C₄ᵥ 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

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