

Osmapentalyne: New member of metalla-aromatics

Metalla-aromatics are analogues of conventional organic aromatic molecules in which one of the CH groups is formally replaced by an isolobal transition-metal fragment. Their synthesis and reactivity have been investigated for the past three decades. Despite significant advances, challenges still remain in this field due to the limited number of convenient and versatile synthetic methods to construct stable and fully characterized metalla-aromatics, and the relative shortage of new topologies.

With the supports of the National Natural Science Foundation of China, the research team led by Prof. Xia Haiping from State Key Laboratory of Physical Chemistry of Solid Surfaces and College of Chemistry and Chemical Engineering, Xiamen University, has developed new methods to prepare metalla-aromatics, especially those possessing new topologies (*Angew Chem Int Ed* **2011**, 50: 1354–1358; **2012**, 51: 9838–9841; **2013**, 52: 9251–9255). Recently, great progress was made in the synthesis of first metallapentalyne (**II**), which shows characteristic Möbius aromaticity. The results have been published in *Nature Chemistry* (**2013**, 5: 698–703).

The combination of the anti-aromaticity and extreme ring strain hinders attempts to prepare pentalyne (**I**), an eight π electron antiaromatic bicycle. In sharp contrast, osmapentalyne (**II**) is found to be thermally viable, despite containing the smallest angles observed so far at a carbyne carbon.

The calculations led by Assoc. Prof. Zhu Jun reveal the aromatic character in osmapentalyne. For instance, both the computed isomerization stabilization energies (ISEs) and down-field magnetic properties ($^1\text{H-NMR}$) suggest the aromaticity in osmapentalyne. Further CMO-NICS analysis revealed that the net aromaticity in osmapentalyne can be attributed to the total diamagnetic contributions from the two Möbius-type MOs ($-18.0/-18.6$ ppm) and three Hückel-type MOs ($-1.9/-3.5$ ppm). Accordingly, the nature of the aromaticity in metallapentalyne can be regarded as mixed aromaticity with Craig-type Möbius aromaticity dominated. Hence, the incorporation of the osmium centre not only reduces the ring strain of the parent pentalyne, but also converts its Hückel antiaromaticity into Craig-type Möbius aromaticity in the metallapentalynes. The concept of aromaticity is thus extended to five-membered rings containing a metal-carbon triple bond.

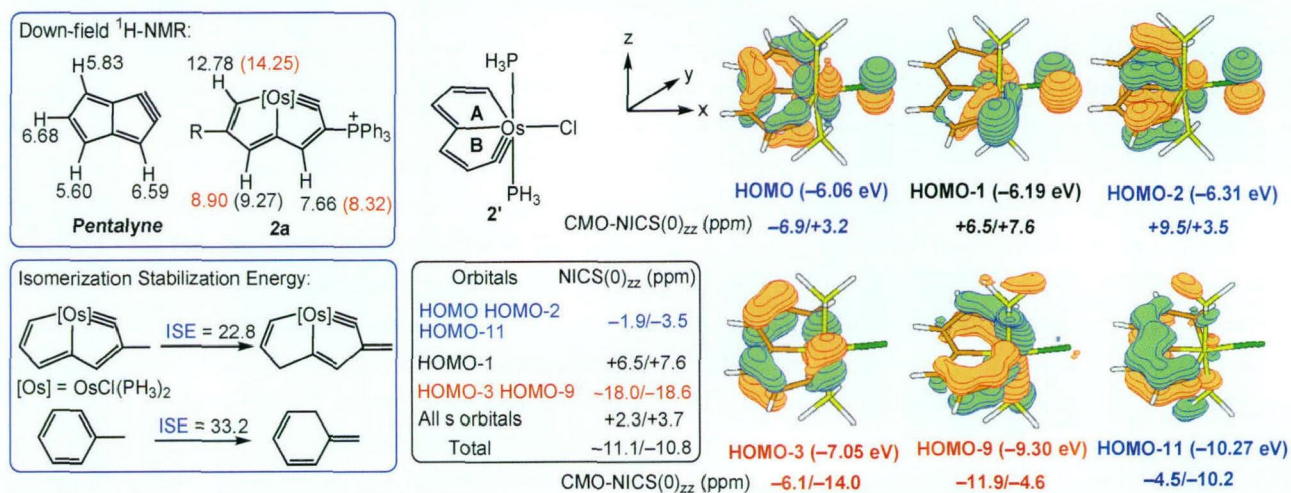
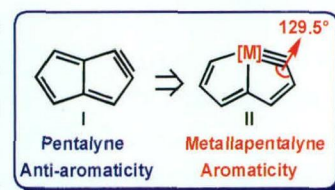


Figure Downfield ^1H chemical shifts, isomerization stabilization energy and NICS(0)_{zz} contributions of the occupied perimeter π -MOs of the model complex **2'**.