

of the physical and biological sciences. It is equally true that the predictive power of these methods continues to grow. They are, of course, not a substitute for experiment. Indeed, the most successful applications of computational chemistry are those that are integrated with experimental programmes. Here, the integration is built into the whole approach, and perhaps most importantly, chemical knowledge and intuition enter into the computational procedures from the beginning. In this way materials design

— much discussed but not often achieved — becomes a reality.

The method is in its early stages: it may have much still to learn from the algorithms and protocols used in the atomic-based structure prediction methods. What is not in doubt is that we have a procedure that promises to have a substantial impact on the development of new functional materials with specific physical and chemical properties. As such it promises to be a major development in materials chemistry.

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## METALLACYCLES

# Breaking the rules

Chemists have long been interested in synthesizing compounds that push the boundaries of conventional molecular structure. — to ss ha1(o)GB

Owing to the fundamental rules of orbital symmetry, alkynes ( $\text{RC}\equiv\text{CR}$ ), allenes ( $\text{R}_2\text{C}=\text{C}=\text{CR}_2$ ) and cumulenes (such as  $\text{R}_2\text{C}=\text{C}=\text{C}=\text{CR}_2$ ) are linear, hence incorporation of these unsaturated structural motifs into small carbocyclic ring systems significantly deforms their geometry and causes enormous ring strain. However, synthetic chemists have always been driven by a “desire to make the molecule that violates the norm”<sup>1</sup>, and so ever more exotic, more unstable hydrocarbon structures have been created.

For hydrocarbons, the frontiers of “molecular sadism” have probably been reached by incorporating maximum degrees of unsaturation into the smallest possible ring systems, which results in highly distorted orbital symmetries. Numerous examples of organic compounds with ‘abnormal’ geometries have been stabilized, trapped or even synthesized in pure form in the past. Computational techniques have also been used to explore these frontiers and to predict the viability of such compounds<sup>2</sup>. An elegant approach for the synthesis of

such exotic cyclic structures includes the incorporation of metal atoms into the ring system (Fig. 1) — a strategy that has been exploited by Zhu, Xia and co-workers, who, writing in *Nature Chemistry*, describe the stabilization of an elusive antiaromatic bicyclic pentalyne<sup>3</sup>.

Addition of heteroatoms or metal centres to strained cyclic structures results in two different modes of stabilization. Heteroatoms in general have a longer bond distance to the attached carbon atoms than the equivalent C–C bond, and metal

centres can interact with the  $\pi$  electrons of the unsaturated moieties of the so-called metallacycle. These effects both give significant release of ring strain and therefore a reasonably stable, and in many cases isolable, organometallic complex. In addition to the interest in their structural features, some of these exotic molecules can also be regarded as model complexes for stoichiometric and catalytic conversions mediated by transition metal centres.

Examples of stabilization solely by a metal centre include metallacyclocumulenes (Rosenthal's group, **A**; Fig. 1)<sup>4</sup>, metallacycloallenes (Erker's<sup>5</sup> and Suzuki's<sup>6</sup> groups, **B**) and metallacycloalkynes, which have one isolated triple bond (Suzuki<sup>7</sup> and Rosenthal's<sup>8</sup> groups, **C**), as well as 4-membered metallacycloallenes (Schrock's group, **D**)<sup>9</sup>. In all cases the metal atom plays a significant role in the stabilization of the small cyclic structural elements. Two approaches were adopted to synthesize these species: (1) the direct complexation of unsaturated compounds such as butadiynes ( $\text{RC}\equiv\text{C}-\text{C}\equiv\text{CR}$ ) to **A**, of but-ene-yne ( $\text{RC}\equiv\text{C}-\text{CH}_2=\text{CR}_2$ ) to **B** and of alkenyl ( $-\text{CH}_2=\text{CR}_2$ ) to **C** with a metal centre; or (2) the reductive coupling of two alkynyl ( $\text{RC}\equiv\text{C}-$ ), or an alkynyl ( $\text{RC}\equiv\text{C}-$ ) and an alkenyl ( $-\text{CH}_2=\text{CR}_2$ ), generating unsaturated compounds that were subsequently complexed with a metal centre.

A combination of both metals and heteroatoms has allowed for the isolation of even more strained azacycloallenes (**F**), disilacyclopent-3-yne (**G**) and a series of different hetero-1-metallacyclobuta-2,3-dienes (**H**)<sup>10</sup>. From a theoretical point of view, there is some controversy over whether they should be classified as complexes or metallacycles with an aromatic character, or perhaps something between the two<sup>11</sup>.

Zhu, Xia and co-workers have now synthesized a series of very unusual metallacycles, in which a metal centre (osmium) is connected to an adjacent carbon atom through a triple bond. It features the smallest carbyne angles observed so far, and a rarely observed type of Möbius aromaticity

— rather than the destabilizing Hückel antiaromaticity that might be expected from an eight-electron system. Möbius aromaticity arises when compounds display a monocyclic array of molecular orbitals in which there is an odd number of out-of-phase overlaps, which shows the opposite pattern of aromaticity compared with Hückel systems. The spatial arrangement of the orbitals is also characteristic for Möbius strips, hence the name. In the described osmapentalynes, the special case of Craig-type Möbius aromaticity arises from the incorporation of  $d$  orbitals into the  $p$ -orbital (Möbius aromatic) ring system, resulting in the phase shift.

The synthesis produced a series of osmapentalynes complexes (**E**) in high yields, and was a relatively straightforward one-step coupling of alkyl propiolates with the pendant alkyne moiety of a substituted osmium alkenyl complex.

A key feature in the molecular structures of these osmapentalynes is their Os–C triple bonds and the full planarity throughout their pentalynes units. One mesomeric form of this structure can be described as a metallacycloallene. Density functional theory computations and magnetic studies of the complexes showed aromatic character, suggesting that incorporation of the osmium centre results in both release of the ring strain of the organic analogue pentalynes as well as conversion of Hückel antiaromaticity into rarely observed eight-centre-eight-electron Möbius aromaticity in the metallapentalynes. Xia and co-workers explain this unusual electronic feature on the basis of molecular orbital analysis; computation of the nucleus-independent chemical shift values — which are a good estimate of the degree of aromatization — corroborate these findings. The observed nucleus-independent chemical shift values for both fused rings are in the same range as for benzene, the most commonly known classical aromatic system.

Besides the spectacular organometallic aspects of these metallacycles, the osmapentalynes exhibit interesting optical

effects due to the combination of an electron-rich metal centre with a fused aromatic system. It is the pronounced near-infrared photoluminescence as well as the long emission lifetime of up to one microsecond that could make these molecules attractive for applications in materials science.

In the chemistry of less strained five-membered metallacycles such as metallacyclopentadienes, -pentenes and -pentanes, oxidative or hydrolytic work-up often gives rise to metal-free analogues. Also, these compounds are known to serve in catalytic applications such as cyclizations or oligomerizations, playing an important role either as key intermediates or as catalyst complexes. Such approaches might become of interest for this new class of compounds, to synthesize all-carbon or heteroatom-modified derivatives. Further studies on the reactivity of this new class of compounds that “violate the norm” may provide further insight into their structure and bonding.

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