

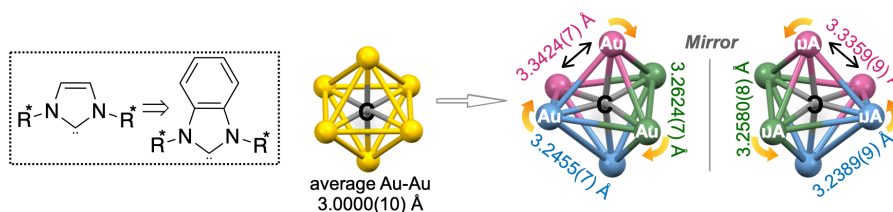
## Chiral twist in gold(I) octahedron generating asymmetric carbon centre

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Chiral twists are ubiquitous and bring unique asymmetric geometries to nature.<sup>1</sup> Chirality in metal clusters, especially group 11 metals, is of great interest for future applications as asymmetric catalysts, chiral sensors, and chiroptical materials.<sup>1</sup> Direct utilization of enantiomerically pure precursors through metal coordination was an effective protocol for introducing chirality into coinage metal clusters, but it is still challenging to enantioselectively generate an intrinsic metal core. Chiral bidentate or polydentate ligands were commonly used in ligand libraries.<sup>2</sup> However, in a few studies on optically pure monodentate ligands, a single-point coordination was more difficult than expected, leading to unique metal geometries.

Studies on an intriguing family of gold clusters with hypervalent C-centres, which are isolobal analogs of hydrocarbon cations, are important for understanding the mechanistic intermediates of acid-catalysis and for exploring luminescent materials.<sup>3-5</sup> The generation of chiral-at-cluster in the C@Au<sub>6</sub> system is of particular interest, as asymmetric induction with gold motifs can also provide new chirality to interstitial carbon. In this study, single-crystal X-ray diffraction analyses revealed that ligand modification from optically pure imidazolyliene-based N-heterocycle carbene (NHC) to benzimidazolyliene-based NHC twisted the common hexagold core into an essentially enantiomer, causing regioselective extension and cleavage of Au-Au bonds. The unique arrangement of NHC stabilizers and intraligand interactions probably contribute to the stabilization of asymmetrical hexagold motif. Interestingly, this chiral twist pattern was maintained even in solution as shown by the circular dichroism spectrum. This study shows that monodentate-ligation of NHC generated essential chirality in the hexagold core, forming a new type of asymmetric hypervalent carbon centre.



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