Relativistic effects on dative carbon-coinage metal bond. Evaluation of NHC-MCl (M = Cu, Ag, Au) from relativistic DFT

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Abstract
The use of different N-heterocyclic carbene (NHC) as dative ligands benefits from their capabilities ranging from strong to weak σ-donor according to the Tolman electronic parameter (TEP), well spread in the formation of monometallic complexes, and recently extended to metallic nanocluster and surfaces. Here, we set to explore the role of relativistic effects in determining the stabilization of the dative carbon–metal bond on coinage metal complexes given by NHC-MCl species (M = Cu, Ag, Au), by quantifying their contribution to the different terms related to the bond formation by comparing scalar relativistic and non-relativistic DFT calculations. Our results show a strong contribution to the stabilization of the NHC-M bond, increasing along with the group, from the lighter Cu atom (7.9%) to Ag (15.3%), and most notoriously for the heavier member, Au (39.9%). This observation is similar along the different stabilizing terms related to the C-M bond, where the acceptor character of the metal center is affected, resulting in a stronger σ-donor interaction from the involved ligand. Thus, the theoretical evaluation of carbon–metal bonds requires the equal footing treatment of relativistic effects along with the group, which is beneficial for the theoretical evaluation of ligand capabilities prior to the engaging exploration of the efficient formation of related complexes involving lighter to heavy metallic centers.

Author keywords
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