Nature of the dative Nitrogen-Coinage metal bond in molecular Motors. Evaluation of NHC-M pyrazine bond (M = Cu, Ag, Au) from relativistic DFT

Olea-Ulloa, Carolinaa;
Guajardo-Maturana, Raulb;
Rodríguez-Kessler, Peter L.c
Muñoz-Castro, Alvaro

Abstract
The use of different N-heterocyclic carbene (NHC) coordinated to coinage metals are useful caps for generating mechanical bonds towards donor-nitrogen fragments, leading to the characterization of efficient molecular motors. Here, we account for the nature of the formation of mechanical bonds on [(NHC-M)2pyz]2+ (M = Cu, Ag, Au; pyz = pyrazine) complexes. The NHC-M pyrazine interaction is of main electrostatic character given by the Lewis acidic σ-hole characteristics of the NHC-M caps, and the Lewis basic features of the aromatic pyrazine ring, accounting for the 69.9 %, 71.8 %, and 68.8 %, for Cu, Ag, and Au species, respectively. The rotational barrier is calculated at 10.2, 8.6, and 6.0 kcal mol−1, respectively, which is given by the variation of the NHC-M pyrazine interaction, and structural arrangements, accounting for 54.0/46.0 %, 59.3/40.7 %, and, 79.8/20.2 %, for Cu, Ag, and Au, respectively. Hence, the rotational barrier for the gold counterpart is less affected by structural factors. Relativistic effects on the N-coinage metal bond interaction are crucial for the account of the experimentally observed rotational barrier. Thus, the theoretical evaluation of mechanical bonds allows to gain further insights into the fundamental nature of the interaction and how structural factors affect the formation of molecular motors relevant to guide design and synthetic efforts.