

Organic Azide and Auxiliary-Ligand-Free Complexes of Coinage Metals Supported by N-Heterocyclic Carbenes

Dash C.

Wang G.

Muñoz-Castro A.

Ponduru T.T.

Zacharias A.O.

Yousufuddin M.

Dias H.V.R.

Organic azide complexes of copper(I) and silver(I), [(SIPr)CuN(1-Ad)NN][SbF₆], [(SIPr)CuN(2-Ad)NN][SbF₆], [(SIPr)CuN(Cy)NN][SbF₆], and [(SIPr)AgN(1-Ad)NN][SbF₆] have been synthesized by using Ag[SbF₆] and the corresponding organic azides with (SIPr)CuBr and (SIPr)AgCl (SIPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene). The copper and silver organic azide complexes were characterized by various spectroscopic techniques and X-ray crystallography. Group trends of isoelectronic Cu(I), Ag(I), and Au(I) organic azide complexes are presented on the basis of experimental data and a detailed computational study. The $\tau_{\text{asym}}(\text{N}_3)$ values of the metal-bound 1-AdNNN in [(SIPr)MN(1-Ad)NN]⁺ follow the order Ag < Cu < Au. DFT calculations show that gold(I) forms the strongest bond with 1-AdNNN in this series, while silver has the weakest interaction. Furthermore, auxiliary ligand free coinage metal N-heterocyclic carbene complexes, [(SIPr)M][SbF₆], have been synthesized via metathesis reactions of (SIPr)MCl (M = Cu, Ag, Au) with Ag[SbF₆]. X-ray crystal structures of dinuclear [(SIPr)Ag]₂[SbF₆]₂ and [(SIPr)Au]₂[SbF₆]₂ are also reported. They show close metallophilic contacts. [(SIPr)Au]₂[SbF₆]₂ reacts with OEt₂, SMe₂, and CNtBu to afford [(SIPr)Au(OEt₂)][SbF₆], [(SIPr)Au(SMe₂)][SbF₆], and [(SIPr)Au(CNtBu)][SbF₆] adducts, respectively. © 2019 American Chemical Society.