

IPr^{*}BndiNHC – sterically adaptable benzyl-linked dinuclear N-heterocyclic carbenes

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Streszczenie

N-Heterocyclic carbenes (NHCs) represent one of the most important ligand classes in inorganic and organometallic chemistry due to their strong σ -donor properties and the sterically hindered environment around the metal centers. Recently, dinuclear ligand frameworks have received special attention owing to their potential for adaptable steric properties and metal–metal cooperative interactions. Herein, we report the synthesis of a series of sterically hindered di-nuclear N-heterocyclic carbenes featuring the modular IPr^{*} (IPr^{*} = (2,6-bis(diphenylmethyl)-4-methylphenyl)imidazol-2-ylidene) framework and benzyl linkers. A series of di- and mono-gold(I) complexes bearing IPr^{*}-based bis-NHC ligands have been synthesized to investigate the effect of aromatic linkers on the structure and catalytic activity. Two common linkers, 1,2-bis(methyl)benzene and 2,4-bis(methyl)mesitylene, were employed to modulate the geometry and steric environment of dinuclear IPr^{*}-type N-heterocyclic carbenes. Structural analysis revealed that the linker substitution strongly affects the conformation of the di-NHC scaffold as indicated by changes in the interplanar NHC–NHC angles (22–78°) and buried volume (% V_{bur} = 39–52%). The catalytic activity of the complexes was evaluated in carboxylative cyclization of propargylamines and hydration of diphenylacetylene. Complexes with the bis(methyl)benzene linker displayed higher activity in carboxylative cyclization, while complexes incorporating the bulkier 2,4-bis(methyl)mesitylene linker showed higher activity in alkyne hydration. In view of the importance of sterically adaptable di-nuclear ligands in various facets of inorganic and organometallic chemistry, we anticipate that this class of N-heterocyclic carbenes will find broad application in modulating the steric environment around metal centers.

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