IPr*^{Thia} – wingtip-flexible, sterically hindered, modular, N,C/S,C-chelating thiazole-donor N-heterocyclic carbene ligands

Autorzy

Pamela Podchorodecka

Błażej Dziuk

Robert Junga

Roman Szostak

Michal Szostak

Elwira Bisz

Rok wydania

2024

Czasopismo

Dalton Transactions

Numer woluminu

53

Strony

14975-14985

DOI

10.1039/d4dt01468e

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

N-Heterocyclic carbenes (NHCs) represent a pivotal class of ligands in coordination chemistry owing to their unique electronic properties. In particular, hemilabile N-heterocyclic carbenes have garnered significant attention over the past decade due to their capacity to transiently coordinate to metals and open coordination sites. However, hemilabile NHC ligands have been predominantly limited to N, O and P donors, while NHC ligands bearing versatile S-donors have been severely underdeveloped. Herein, we report wingtip-flexible, sterically hindered NHC ligands that feature N,C/S,C-chelating thiazole donors in combination with the powerful IPr* (IPr* = (2,6-bis(diphenylmethyl)-4-methylphenyl)imidazol-2-ylidene) scaffold. These ligands are prepared using a highly modular S_NAr arylation of thiazole derivatives. Full structural and electronic characterization is reported. The ligands feature a high barrier to rotation around the *N*-thiazole axis (10 kcal mol^{-1}). The ligands are evaluated for their steric, electron-donating and π-accepting properties as well as coordination chemistry to Ag(I), Pd(II), Rh(I) and Se. Preliminary studies on Ag, Pd and Rh catalysis are presented. The efficiency of the approach is highlighted by preparing a library of unsymmetrical imidazolium precursors. The mono-IPr* wingtip provides a highly hindered yet sterically flexible environment adjusting to metal centers, while the *N*-thiazolyl wingtip displays a fluxional behavior that interchanges from the hard/soft N,C to soft/soft S,C coordination. Considering the importance of hemilabile N-heterocyclic carbene ligands in metal stabilization in inorganic and organometallic chemistry, we expect that this class of ligands will be of broad interest.

Adres publiczny

http://dx.doi.org/10.1039/d4dt01468e

Strona internetowa wydawcy

https://www.rsc.org/