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Review

Recent advances in annellated NHCs and their metal complexes

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Dedicated to Professor G. K. Lahiri on his 60th birthday

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ABSTRACT

N-Heterocyclic carbenes (NHCs) have emerged as one of the most useful class of ligands for metal complexes primarily due to their relatively easy synthesis, broad structural and stereoelectronic diversity, and their ability to form stable compounds with different metal ions. Among a vast number of variants known, annellated systems which feature fused ring(s) on the basic framework of NHC have drawn wide attention for their unique structural and stereoelectronic properties. The annellation has been attributed to have a significant effect on the ligating behavior of NHCs. The actual effect depends on the nature of the annellated system and the position in the parent scaffold where annellation takes place. The transition metal complexes bearing annellated NHCs have the potential to exhibit superior activity and/or selectivity in catalytic transformations. Besides, the fusion of ring(s) provides further scope for the functionalization of NHC. The NHCs annellated to suitably functionalized scaffolds have been used to design the stimuli-modulable systems. The use of NHCs fused to extended aromatic systems has paved the way for improving the efficacies of the catalytic systems using non-covalent interactions. Metal complexes containing annellated NHCs have afforded compounds with interesting photophysical and electronic properties. Herein we classify annellated NHCs based on their structural attributes. The effects of annellation on the ligand behavior of NHCs and the catalytic utility of metal complexes featuring these annellated carbenes, along with a host of other promising applications, are described.

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Abbreviations: ATH, asymmetric transfer hydrogenation; BIm, benzimidazolin-2-ylidene; BIMes, 1,3-dimesitylbenzimidazolin-2-ylidene; BI*t*Bu, 1,3-di-*tert*-butylbenzimidazolin-2-ylidene; CAAC, cyclic (alkyl)(amino)carbenes; DAC, diamidocarbene; DFT, density functional theory; Dipp, 2,6-diisopropylphenyl; DMSO, dimethyl sulfoxide; dppb, 1,4-bis(diphenylphosphino)butane; dppf, 1,1′-bis(diphenylphosphino)ferrocene; dppp, 1,3-(diphenylphosphino)propane; dppm, bis(diphenylphosphino)methane; dppv, 1,2-bis(diphenylphosphino)ethylene; ee, enantiomeric excess; Et, ethyl; equiv, equivalent; Fc^+/Fc, ferrocenium/ferrocene; hmb, hexamethylbenzene; HOMO, highest occupied molecular orbital; IAd, 1,3-diadamantylimidazol-2-ylidene; I*i*Pr, 1,3-diisopropylimidazol-2-ylidene; Im, imidazolin-2-ylidene; IMes, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene; *i*Prs, isopropyl; IPr, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; IR, infrared; I*t*Bu, 1,3-di-*tert*-butylimidazol-2-ylidene; LUMO, lowest unoccupied molecular orbital; Me, methyl; Mes, mesityl; MLCT, metal-to-ligand charge transfer; NBO, natural bond orbital; *n*Bu, *n*-butyl; n.d, not determined; NHC, N-heterocyclic carbene; NMR, nuclear magnetic resonance; Np, neopentyl; *o*-Tol, 2-methylphenyl; Ph, phenyl; phen, phenanthroline; ppy, 2-phenylpyridine; py, pyridine; RCM, ring closing metathesis; rt, room temperature; SIm, imidazolidin-2-ylidene; SIMes, 1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene; SIPr, 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene; *t*Bu, *tert*-butyl; TEMPO, 2,2,6,6-tetramethylpiperidinyloxyl; TEP, Tolman electronic parameter; Tf, trifluoromethylsulfonyl; TH, transfer hydrogenation; UV, ultra-violet.

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