

## Publication

### Expanded ring and functionalised expanded ring *N*-heterocyclic carbenes as ligands in catalysis

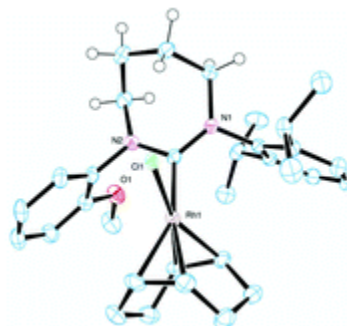
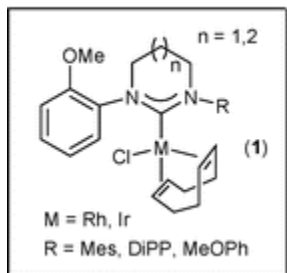
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#### Abstract

The synthesis of new functionalised 6- and 7-membered NHC (*N*-heterocyclic carbene) precursors bearing anisidyl or pyridine *N*-substituents, both symmetrically and non-symmetrically substituted is reported. Their corresponding rhodium(I) and iridium(I) complexes,  $M(\text{COD})(\text{NHC})\text{Cl}$ , were also prepared and characterised. The unusual Rh(III)/Rh(I) salt,  $[\text{Rh}(\eta^2\text{-NHC-py})_2\text{Cl}_2][\text{Rh}(\text{COD})\text{Cl}_2]$ , was obtained with one of the pyridyl-functionalised NHC ligands. Single-crystal X-ray analyses have been obtained for the majority of the complexes and NHC salts. The activity of these complexes was tested in the hydrogenation of a range of substrates with molecular hydrogen, including 1-cyclooctadiene and 2-methyl styrene, where they show enhanced activity and stability in comparison to non-functionalised NHC analogues, operating under exceptionally mild conditions (ambient temperature and atmospheric pressure).



## Donor-Functionalised Expanded Ring N-Heterocyclic Carbenes:

### Highly Effective Ligands in Ir-Catalysed Transfer Hydrogenation

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#### Abstract

The performances of a number of Rh<sup>I</sup> and Ir<sup>I</sup> complexes of type [M(NHC)(COD)Cl] in the transfer hydrogenation of ketones were tested under a variety of reaction conditions, and with a variety of substrates, allowing comparison of Rh- and Ir-NHC complexes, and also comparison of the influence of the NHC ligand on catalytic performance. Notably, of the Rh<sup>I</sup> and Ir<sup>I</sup> complexes with symmetrically substituted NHCs only those bearing cyclohexyl substituents were active, with Rh<sup>I</sup> complexes of saturated 5-, 6- and 7-NHCs with N-Mes substituents, [Rh(5,6,7-Mes)(COD)Cl], showing no activity in transfer hydrogenation under the test conditions. Rh<sup>I</sup> and Ir<sup>I</sup> complexes of unsymmetrical *o*-methoxyphenyl donor-functionalised NHCs (df-NHC) with differing carbene ring sizes were also tested in transfer hydrogenations, with the Rh<sup>I</sup> complexes displaying no catalytic activity. However, the corresponding df-NHC Ir<sup>I</sup> complexes were found to be extremely effective catalysts. Catalyst tests also demonstrated the excellent stability of these complexes.

