

New Pyridine Dicarbene Pincer Ligands with Ring Expanded N-Heterocyclic Carbene Donors and their Transition Metal Complexes

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Imidazol-based N-Heterocyclic Carbenes (abbr. NHCs) are without doubt one of the most prominent and well-explored class of the NHC family and exploited as ancillary ligands^[1]. Conversely, Ring-Expanded NHCs (abbr. RE-NHCs), despite displaying as ligands superior σ -donor characteristics and distinct steric effects, have been less explored and rarely employed as donors in ligand architectures^[2]. Attracted by the versatility of the rigid Pincer architecture and the increased thermal stability of their transition metal complexes^[3], two novel pyridine dicarbene Pincer ligand precursors with RE-NHCs were synthesised (Figure 1).

In situ generation of the free dicarbene **L**₁ by deprotonation of the **L**₁·2HBr and concomitant reaction with suitable metal precursors, or metalation of the **L**₁·2HBr by aminolysis with metal bis(trimethylsilyl)amide metal precursors, afforded the complexes depicted in Figure 2. However, the coordination chemistry of **L**₂ has not yet been studied due to its inherent instability. The complexes **Ni**₁ and **Cr**₁, when activated with MAO, were catalysts of moderate activity for the oligomerisation and polymerisation of ethylene, respectively. Experimental data supported by DFT calculations showcased that compared to imidazolylidene analogues, **L**₁ acts as a stronger electron donor and can indirectly modulate geometries and electronic structures of metals by sterics effected through the arrangement of wingtips^[4].

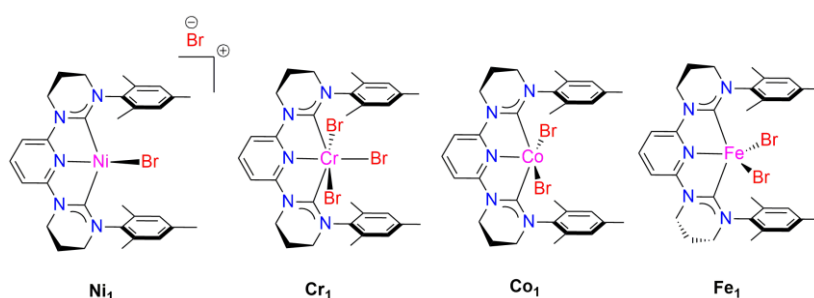


Figure 1: Ligand Precursors **L**₁·2HBr & **L**₂·HBr.

Figure 2: Metal Complexes of **L**₁.

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