## Efficient modulation of the donor sites of triazolylidene metal complexes for enhancing catalytic activity

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N-heterocyclic carbene (NHC) metal complexes have shown versatile applicability in a wide variety of catalytic transformations. [1] Mesoionic NHCs, such as 1,2,3-triazolylidenes, are an interesting sub-class of NHCs, exhibiting even stronger  $\sigma$ -donation and additional beneficial properties in, for instance, redox catalysis. [2] Introducing specific functional groups into NHC ligands is often highly beneficial for enhancing catalytic performance of the complexes, though generally such functionalization requires a challenging multi-step synthetic procedure. Such multi-step ligand by ligand synthesis can be simplified by a post-modification procedure. [3,4] We have developed a system that is based on a chloro-functionalized triazolylidene ligand (see Figure). Chloride substitution on the complex allows for postmodification of the ligand and the formation of novel chelating systems, some of which are hard to make by any other route. Here we demonstrate the potential of this approach by the synthesis and catalytic screening of a variety of donor-functionalized Ir and Ru complexes. The rapid access to a wide range of functionalized triazolylidene metal complexexs gives immediate information on the best systems for a specific catalytic reaction. The versatility of the method will be discussed as well as the effect of the functional donor sites on different types of catalysis.

$$R^{-N} \xrightarrow{N-N} CI \xrightarrow{E^{-}} R^{-N} \xrightarrow{N-N} [M] = E$$

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