

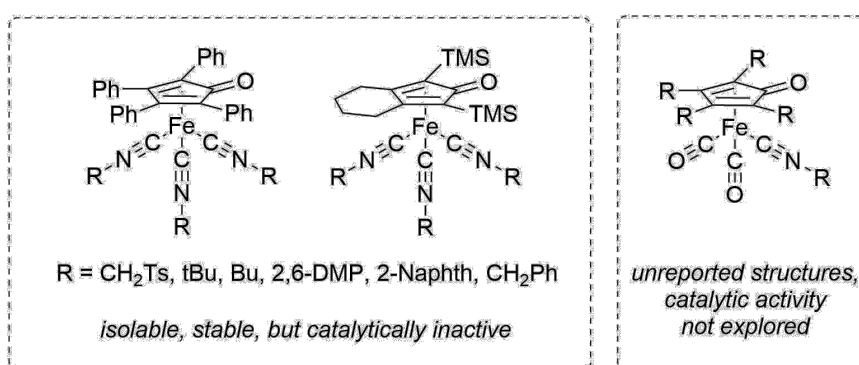
Introducing Isocyanide Ligands into the Cyclopentadienone Iron Complex Framework

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Cyclopentadienone iron complexes are well established as hydrogenation and transfer hydrogenation catalysts [1-2]. Most systems use a dicarbonyl complex with a free coordination site on iron as the active catalyst, although other configurations exist which replace one of the carbonyls by other ligands, such as, for example, phosphines [3] or NHC's [4].

Isocyanides (RNC, R = aryl, alkyl) are isoelectronic to CO and can be generally regarded as electron rich analogues to carbonyl ligands, i.e. they are better σ -donors and worse π -acceptors [5]. In contrast to CO, isocyanides offer a handle to vary the electronic and steric properties of the ligand by variation of the R substituent.



Recently, we have discovered that cyclopentadienone triisocyanide complexes can be easily prepared by irradiation (blue LED's) of the corresponding tricarbonyl complexes in the presence of the isocyanide of choice (R = CH₂Ts, ^tBu, Bu, 2,6-DMP, 2-Naphth, CH₂Ph) (Ts = toluenesulfonyl, DMP = dimethylphenyl, Naphth = naphthyl) (*manuscript submitted*). These complexes constitute the first instance of incorporation of isocyanides into the cyclopentadienone iron complex framework. Although these complexes are catalytically inactive in hydrogenation, presumably because of the lack of a straightforward way to create an empty coordination site, they show that isocyanides can be used in place of carbonyls.

In this work, we explore the synthesis of dicarbonyl monoisocyanide complexes. By removal of a carbonyl ligand with trimethylamine oxide, a free coordination site is created, opening up the possibility of catalysis. We investigate the catalytic activity of the complexes in hydrogenation and transfer hydrogenation reactions depending on the chosen isocyanide ligands.

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