CHARACTERIZATION AND REACTIVITY STUDIES ON A TERMINAL COPPER-NITRENE SPECIES

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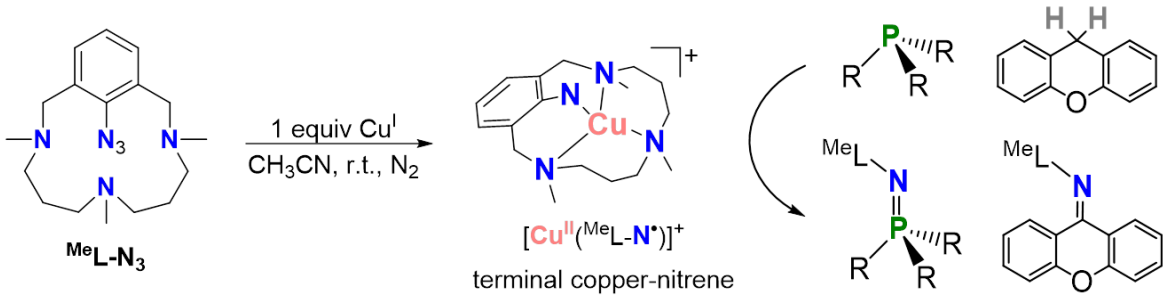
High-valent copper-nitrene species have been postulated as key intermediates in several copper-catalyzed reactions such as aziridination and amination reactions.[1] The high reactivity of these intermediates has eluded their characterization for decades, thereby making the mechanism ambiguous. However, seminal works have evidenced their formation. For instance, Warren et al. could crystallize a dicopper(II)-nitrene complex as a precursor of a terminal copper(III)-nitrene species.[2] Very recently, the Lewis acid adduct of a copper-nitrene intermediate has been trapped at -90 ºC and shown to be active in various oxidation reactions.[3,4]

Herein, we describe for the first time the synthesis and spectroscopic characterization of a room temperature stable terminal copper(II)-nitrene radical species in the absence of any Lewis acid (see Scheme).[5] The azide derivative of a triazamacrocyclic ligand has been employed as an ancillary ligand in the study, which has previously been utilized in the stabilization of aryl-Cu^{III} intermediates. This copper-nitrene species is able to perform nitrene-transfer to phosphines and H-atom abstraction from weak C-H bonds leading to the formation of oxidized products in modest yields.



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