Towards the formation of a [Cobalt(TAML-Cl)] Nitrene from a Primary Amine.
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Abstract

The formation of a [Co(TAML-Cl2)] nitrene from a primary amine was investigated. A goal of this research was to employ this nitrene for C-H amination reactions. [Co(TAML-Cl2)] has an oxidation state of [CoIII(TAML-Cl2)]- as an anion, but can be oxidized towards [CoIV(TAML-Cl2)]. This oxidation has been performed previously by CAN, but not in a stoichiometric fashion. In this research, oxidation towards [CoIV(TAML-Cl2)] was achieved by 1.25 equivalents of [Thi]BF4. [CoIV(TAML-Cl2)] was investigated for its ability to form a metal nitrene complex with a primary amine, namely pTsNH2. To achieve this, the reaction between xanthene and pTsNH2 in the presence of 1,4-tetrachlorobenzoquinone was examined to screen for C-H amination products. For the formation of a nitrene it is necessary that 2 protons and 2 electrons are transferred, which can be accepted by 1,4-tetrachlorobenzoquinone. Analysis by 1H-NMR and RP-HPLC however showed that no nitrene formation most likely occurs. Finally the stepwise deprotonation and oxidation of pTsNH2 was investigated. Na[pTsNH] was synthesized, which was able to form a nitrogen radical in the presence of [CoIV(TAML-Cl2)], but most likely no nitrene between oxidized Na[pTsNH] and [CoIV(TAML-Cl2)] is formed.