HIGHLY STABLE DIIMINE SILVER(I) CATALYSTS THAT INCORPORATE CO₂ INTO ALKYNES FRAMEWORKS

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Carbon dioxide is a potentially valuable and highly accessible C1 feedstock. However, the application of this ubiquitous gas in industrial processes is comparably limited due to thermodynamic restraints and general inertness towards C-activation. This work addresses the development of novel room temperature stable cationic silver(I) complexes supported by N,N'-chelating α,α -dimines, that demonstrate high alkynophilicity. These complexes are highly efficient in incorporating CO₂ into organic alkynes frameworks,^[2,3] affording cyclic carbonates and carbamates under mild conditions. The unusual high stability of these silver(I) pre-catalysts was accomplished by employing a η^2 : η^2 -chelating *cis*-cyclo-octadiene which was predicted through DFT calculations. The ability of these novel α, α -dimines silver(I) complexes to catalyse the incorporation of CO₂ into a propargylic alcohols/amines and the subsequent cyclisation was evaluated using a variety of terminal and internal alkynes substrates was evaluated in the presence of different non-nucleophilic nitrogen bases. All reactions were performed at 25 °C under 1 to 6 bars of CO₂ pressure affording the corresponding αalkylidene cyclic products, which are employed as precursors for drugs and polymers. This family of catalysts shows high conversion at atmospheric CO₂ pressure, using 1-5 mol% catalyst loading. The reaction pathway proved was fully modelled with DFT/solvent corrections, showing the deprotonation of the propargyl alcohols or amines as the rate limiting step.



 $E= O \text{ or } NH R_1 = H \text{ or aryl} R_2 \text{ and } R_3 = alkyl \text{ or aryl}$

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