APPLICATION OF DEFINABLE, ISOLABLE AND HIGHLY STABLE MONO-COORDINATED DIIMINE SILVER(I) COMPLEXES IN CARBOXYLTIVE CYCLISATION REACTIONS

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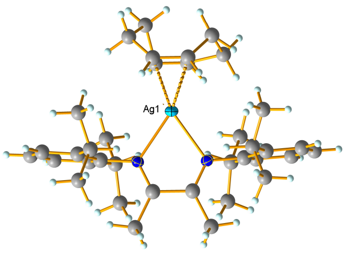
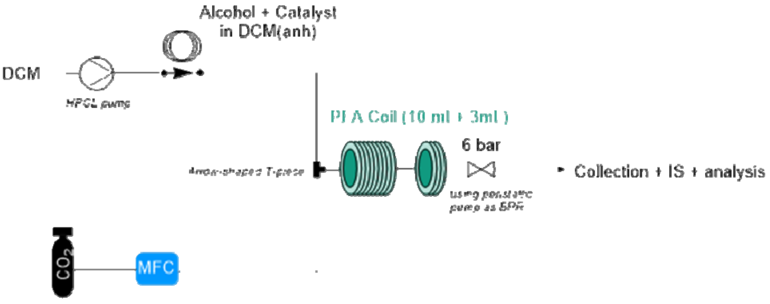
Carbon dioxide is a potentially valuable and highly accessible C_1 feedstock. However, the application of this ubiquitous gas in industrial processes is comparably limited due to thermodynamic restraints and general inertness towards C-activation. This work addresses the development of novel room-temperature and air-stable cationic silver(I) centers supported by *N,N'*-chelating α,α-diimines, that demonstrate high alkynophilicity. These complexes are highly efficient in incorporating CO_2 into organic alkynes frameworks,[1,2] affording cyclic carbonates and carbamates under mild conditions. The unusually high stability of these silver(I) pre-catalysts was accomplished by employing a co-ligand; η^2:η^2-chelating cis-cyclo-octadiene which stabilizing effects were predicted through DFT calculations. The ability of these novel α,α-diimines silver(I) complexes to catalyze the incorporation of CO_2 into a propargylic alcohols/amines and the subsequent cyclisation was evaluated using a variety of terminal and internal alkynes substrates in the presence of the base DBU. All reactions were performed at 25 °C under 1 to 6 bars of CO_2 pressure, affording the corresponding α-alkylidene cyclic products, which are employed as precursors for drugs and polymers. This series of organoargentate-based catalysts demonstrated high conversion after only 80 minutes under atmospheric CO_2 pressure and at 5 mol% catalyst loading. The scalability of the reaction has been proven using flow chemistry affording quantitative yields with half the catalyst loading, and only 3 equivalents of CO_2; the residence time being approximately 30 minutes. The reaction pathway was fully modelled with DFT/solvent corrections, showing the deprotonation of the propargyl alcohols or amines as the rate-limiting step. Hence the project demonstrated the optimized and succesful merging of coordination and flow chemistry.





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[1] Yamada, W.; Sugawara, Y.; Cheng, H.M.; Taketo Ikeno, T.; Yamada, T. *Eur. J. Org. Chem.* ***2007**, 2604–2607*

[2] Yoshida, S.; Fukui, K.; Kikuchi, S.; Yamada, T. *Chem. Lett.* ***2009**, 38, 786-787*