

Unexpected intramolecular: N -arylciano-?-diketiminato cyclization in new aminoquinoline derivative complexes of aluminium for CO₂ fixation into cyclic carbonates

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New 4-amino-3-iminoquinoline derivative ligands (L1-4) were synthesized through an intramolecular exo-dig cyclization of anionic β -diketiminates, containing an N-benzonitrile moiety. The effect of the alkali-metal in this reaction was investigated and an inverse effect between the size of the cation and the cyclization rate was revealed. The effect of the reaction temperature was also studied, in which a direct dependence was observed. Kinetic and theoretical studies were performed in an attempt to clarify the reaction mechanism, obtaining a first-order reaction rate dependence with an activation energy of 20.6 kcal mol⁻¹, with DFT-based calculations supporting the proposed mechanism. In addition, four new aluminium complexes were isolated in high yields (C1-4), which were evaluated as catalysts for the preparation of cyclic carbonates from epoxides and CO₂, thus becoming the first examples of the use of β -diketiminato ligands in this catalytic process. The reactions were performed at 80 °C and 1 bar CO₂ pressure under solvent-free conditions. We were able to prepare a large variety of cyclic carbonates in excellent selectivities and yields, employing the aluminium complex C3. The L1-4 ligands and C1-4 complexes were characterized using NMR,

FT-IR, HRMS, and X-ray diffraction methods.