# Unexpected intramolecular N-arylcyano-beta-diketiminate cyclization in new aminoquinoline derivative complexes of aluminium for CO2 fixation into cyclic carbonates

da Costa, D. M., Borja, L., Verdugo, C., Martinez, J., Quintero, C., Jaque, P., ... & Rojas, R. S. (2019). Unexpected intramolecular N-arylcyano-β-diketiminate cyclization in new aminoquinoline derivative complexes of aluminium for CO 2 fixation into cyclic carbonates. New Journal of Chemistry, 43(30), 12059-12068. <10.1039/c9nj02499a> Accessed 20 Feb 2021.

## Abstract

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-diketiminate 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..