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Short communication

Immobilization of cationic Al(III) salen in the interlayers of montmorillonite clay for the synthesis of cyclic carbonate

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ABSTRACT

Cationic Al(III) salen complex immobilized in the interlayer of montmorillonite clay **1-Mont** (0.25 mol%) was used as an effective immobilized catalyst for the synthesis of cyclic carbonates from various epoxides at atmospheric pressure with excellent conversion (99%), selectivity (99%) and high degree of catalyst recyclability.

1. Introduction

The cycloaddition of CO_2 to epoxides gives valuable cyclic carbonates, which have applications in various fields such as fine chemicals, speciality polymers, agrochemicals and as solvent in various organic synthesis processes [1,2]. Production of cyclic carbonates is largely done by using highly toxic and environmentally hazardous triphosgene [3]. Therefore, a search of an alternative route for the synthesis of cyclic carbonates is a hot area of research. In this context, cycloaddition of CO_2 to epoxides [4] is very attractive as epoxides are very reactive and can easily produce at large scale to meet the demand. The other feed stock–CO_2 needs no special emphasis as its use in the synthesis of valuable chemicals is always welcomed due to environmental reasons. A significant number of homogeneous/heterogeneous catalysts such as organic bases [5], ionic liquids [6], transition metal complexes [7], metal oxides [8], gold nanoparticle supported resins [9], ion exchange resins [10], supported amines [11], grafted ammonium/phosphonium salts [12], grafted ionic liquids [13], periodic mesoporous organosilicas [14] and covalent triazine framework [15] have been reported for the cycloaddition of CO_2 to epoxides. Among the homogeneous catalysts used, metal salen complexes [16] are the center of attraction over the last few decades due to easy tunable electronic and steric features that can accommodate a variety of transition metal ions to meet the desired outcome for this purpose. However, in most of the cases the reaction requires very high pressure of CO_2 and high temperature for the obtaining of cyclic carbonates in good yield. Al salen complexes initially explored by Lu et al. [17] was the most suitable catalyst for cycloaddition of epoxide and CO_2 owing to its higher activity at low catalyst loading as well as mild reaction condition, but there is still room for improvement specifically to address the issues related to protocol for catalyst synthesis, catalyst loading, reaction time and most importantly catalyst recyclability to offset the cost of the catalyst to make the overall process more economically attractive. To address the issue of recyclability, score of studies have been reported where active homogeneous catalysts have been immobilized on to different solid supports [18]. Among these, clays being inexpensive, easily available with large surface area and very high ion exchange capacity are potential catalyst support materials which have been exploited in various organic transformations [19,20]. In the past we have successfully used montmorillonite clay to support di-cationic Mn(III) salen complexes for epoxidation reaction [21]. Here we are reporting the use of di-cationic salen ligand synthesize by the condensation of *trans*-1, 2-diaminocyclohexane with salicylaldehyde having triphenylphosphinomethyl group at 5, 5′ positions [22] in preparation of its Al(III) salen complex **1** [23], its intercalation in the interlayer space of montmorillonite-type clay by cation exchange process to get the catalyst **1-Mont** for its use in cycloaddition of CO_2 to epoxides. The

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catalyst **1-Mont** was found to very active giving excellent conversion and selectivity (up to 99%) for cyclic carbonates at 1 atm pressure of CO_2 in 24 h with added advantage of 10 times recyclability.

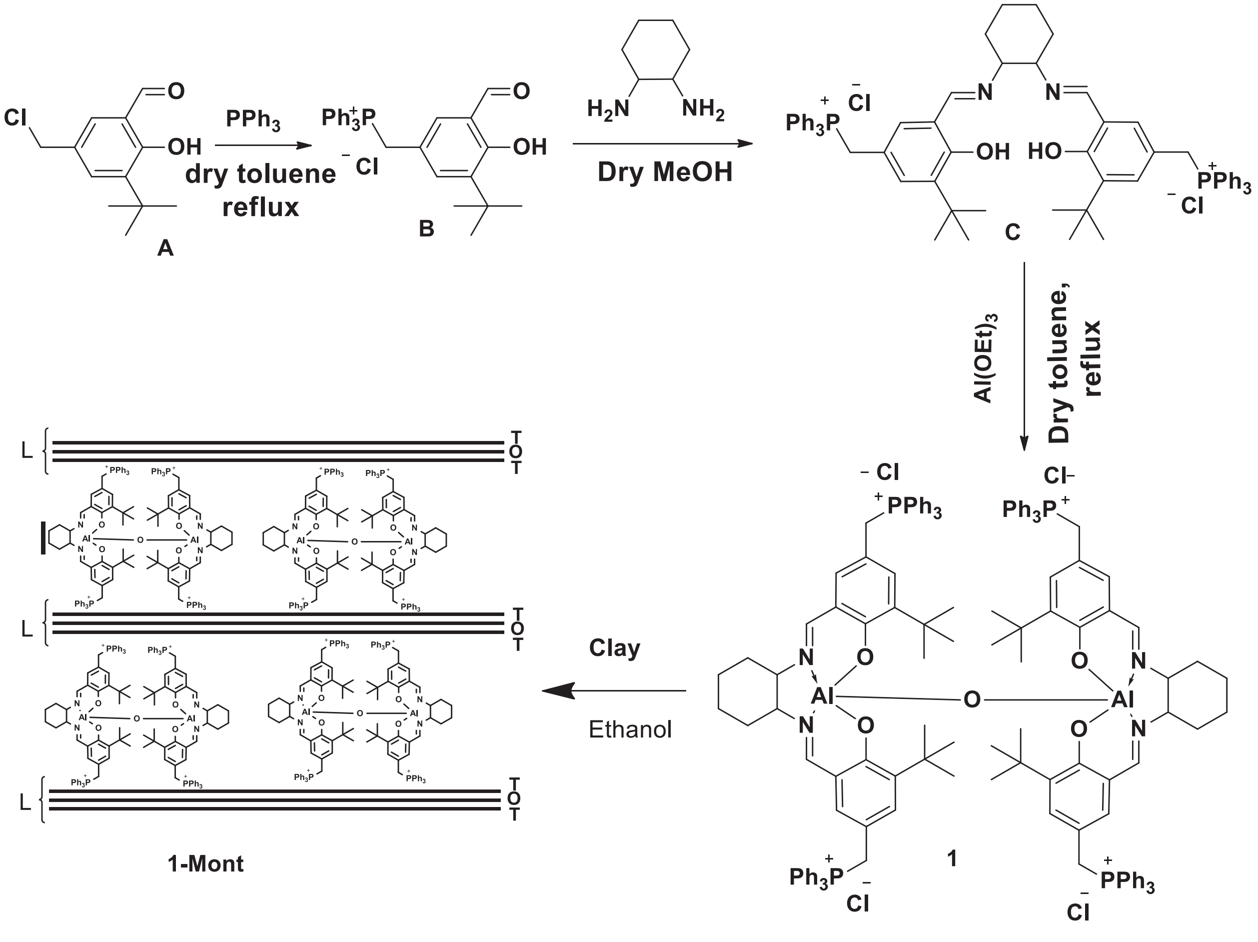
2. Experimental

2.1. General procedure for the synthesis of dicationic salen ligands C

Initially the cationic aldehyde **B** was synthesized from the interaction of 3-(*tert*-butyl)-5-chloromethyl salicylaldehyde **A** (1.13 g, 5 mmol) and triphenylphosphine (1.31 g, 5 mmol) together in dry toluene (100 ml) under refluxing condition. The solid thus obtained was filtered, washed several times with toluene, ether and dried to afford a white solid. In the next step to a cooled solution of cationic aldehyde **B** (489 mg, 1 mmol) in dry methanol (5 ml), a solution of *trans*-1, 2-diaminocyclohexane (125 mg, 1.1 mmol) was added drop wise and the reaction mixture was allowed to reflux for 6–8 h (checked on TLC). The yellow solution thus obtained was partially reduced on rotavapor and the salen ligand **C** [22] was precipitated out from the reaction mixture as yellow solid using hexane. Ligand **C** Yield: 95%. FT-IR (KBr): υ 1628 (C=N), 1440 (C=C) and 1276 cm^{-1} (Ar-O). ^1H NMR (500 MHz, $CDCl_3$): δ 1.12 (18H, s), 1.42-1.92 (8H, m), 3.28 (2H, m), 4.88 (2H, s), 5.47 (2H, s), 6.72 (2H, s), 6.85 (2H, s), 7.60–7.74 (30H, m), 8.03 (2H, s), 14.06 (2H, s). ^{13}C NMR (500 MHz $CDCl_3$): 23.97, 29.06, 30.05, 30.42, 32.71, 34.63, 71.38, 115.19, 115.12, 117.13, 118.45, 118.61, 130.12, 130.22, 132.32, 132.60, 134.21, 134.98, 137.87, 160.73, 164.91. Anal. Calcd. for $C_{66}H_{70}Cl_2N_2O_2P_2$ C 75.06, H 6.68, N 2.65. Found C 74.98, H 6.72, N 2.62. MALDI-TOF $(M\text{-}2Cl + K)^+$; 1023.53.

*2.2. General procedure for the synthesis of cationic aluminium(III) salen complex **1** and immobilized complex **1-Mont***

The salen ligand **C** (1 mmol) was dissolved in 20 mL of dry toluene in a three necked 50 mL round bottom flask to which $Al(OEt)_3$ (2 mmol) was added under an inert atmosphere and the reaction mixture was refluxed for 18 h by reported method [23]. After completion of the reaction (checked on TLC) the reaction mixture was cooled to room temperature and the solvent was evaporated on a rotavapor under reduced pressure. The solid residue thus obtained was dissolved in dichloromethane and the organic layer was washed successively with water, brine and dried over anhydrous Na_2SO_4. After complete removal of the solvent the desired complex **1** was obtained as yellow solid powder. An ethanolic 100-ml solution of the complex **1** (0.004 mmol) was stirred for 48 h with preactivated clay (4 g). The loaded sample **1-Mont** was centrifuged, washed thoroughly and extracted repeatedly with ethanol and CH_2Cl_2 on Soxhlet extractor till the washing become colorless. The characterization of the complex **1-Mont** was done by various physico-chemical techniques. Al(III) salen complex **1**: Yield 72%. FT-IR (KBr): υ 1631 (C=N), 1438 (C=C) and 1275 cm^{-1} (Ar-O). ^1H NMR (500 MHz, $CDCl_3$): δ 1.12 (36H, s), 1.40-1.87 (16H, m), 3.31 (4H, m), 5.47 (8H, s), 6.69 (4H, s), 6.90 (4H, s), 7.61-7.74 (60H, m), 8.06 (4H, s). ^{13}C NMR (125 MHz $CDCl_3$): 23.99, 29.09, 29.95, 30.32, 32.68, 34.59, 71.16, 114.08, 115.05, 117.42, 118.10, 118.80, 130.09, 130.18, 132.24, 132.61, 134.18, 134.94, 137.87, 160.80, 164.93. Anal. Calcd. for $C_{132}H_{136}Al_2Cl_4N_4O_5P_4$ C 72.79, H 6.29, N 2.57. Found C 72.80, H 6.40, N 2.60. MALDI-TOF $(M\text{-}Cl + K + H_2O)^+$; 2196.80 (Scheme 1).



Scheme 1. Synthesis of clay supported cationic aluminium salen complex **1-Mont**.