Silver N-heterocyclic carbene complexes as initiators for bulk ring-opening polymerization (ROP) of L-lactides

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Abstract

Synthetic, structural and catalysis studies of two silver complexes namely, [(1-(2,4,6-trimethylphenyl)-3-(N-phenylacetamido)imidazol-2-ylidene]2Ag}+Cl2b, supported over an amido-functionalized N-heterocyclic carbene ligand, and [1-((i-propyl)-3-(benzyl)imidazol-2-ylidene]AgCl 2b, supported over a non-functionalized N-heterocyclic carbene ligand, are reported. Specifically, 1b, a cationic complex bearing 2:1 NHC ligand to metal ratio, was obtained from the reaction of 1-(2,4,6-trimethylphenylimidazole) with Ag 2O in 52% yield. The corresponding 1a was synthesized by the alkylation reaction of 1-(2,4,6-trimethylphenylimidazole) with N-phenyl chloroacetamide in 73% yield. The other silver complex 2b, a neutral complex bearing 1:1 NHC ligand to metal ratio, was obtained from the reaction of 1-(i-propyl)imidazolium chloride with AgClO in 42% yield. The 2a was synthesized by the alkylation reaction of 1-(i-propylimidazole) with benzyl chloride in 45% yield. The molecular structures of the imidazolium chloride, 1a, and the silver complexes, 1b and 2b, have been determined by X-ray diffraction studies. The silver complexes, 1b and 2b, successfully catalyze bulk ring-opening polymerization (ROP) of L-lactides at elevated temperatures under solvent-free melt conditions producing moderate to low molecular weight polylactide polymers having narrow molecular weight distributions.

Keywords: Carbenes; Functionalized NHC; Organometallic complex; Silver–NHC complex

1. Introduction

There has been a recent surge of interest in silver N-heterocyclic carbene chemistry with the emergence of diverse range of applications of these complexes that span from biomedical applications to homogeneous catalysis [1,2]. For example, Youngs and coworkers have recently reported antimicrobial activities of water soluble silver–NHC complexes [3] that showed improved activity upon encapsulation in polymer mats due to greater bio-availability of active silver species in the polymer matrix [4]. Apart from the biomedical applications, the silver–NHC complexes have also been reported to exhibit catalytic activities for several chemical transformations like, ethyl diazoacetate (EDA) assisted carbene transfer reactions [5], catalytic preparation of 1,2-bis(boronate) esters, [6] in trans-esterification reactions and in ring-opening lactide polymerization reactions [7]. Though originally known for their transmetallation property, the new found applications in homogeneous catalysis as well as in medicine are redrawing the role of these silver–NHC complexes and, thus, are opening up new frontiers of research.

Another notable feature of the silver–NHC complexes is its structural diversity in the solid state [1,2]. Depending upon the type of the ligands used and the reaction conditions employed, the silver–NHC complexes display a variety of motifs that range from monomeric to oligomeric to
polymeric structures [8–11]. The aggregated structures are particularly important with regard to designing supramolecular architectures and in materials related applications. Though, the reasons determining the structural intricacies of these complexes are yet to be fully understood, the obvious factors like steric, electronics and reactions conditions play a significant role. For example, a NHC ligand with a sterically demanding mesityl substituent gave a neutral (NHC)AgCl type complex having 1:1 ligand to metal ratio, whereas the less bulky variant of the same ligand bearing methyl substituent gave a cationic (NHC) Ag+ type complex having 2:1 ligand to metal ratio [12]. Furthermore, Köhler and coworkers [13] have recently shown that the formation of either type of the complexes, i.e. the cationic 2:1 (NHC to metal) complex or the neutral 1:1 (NHC to metal) complex could be favored by simply changing the reaction conditions.

We became interested in designing new silver–NHC complexes, through functionalization of the N-heterocyclic carbene ligand, particularly, because of their potential applications in homogeneous catalysis. Specifically, we were interested in designing new N-heterocyclic carbene based initiators for ring-opening polymerization (ROP) of L-lactides. Ring-opening polymerization (ROP) of L-lactides is important on account of being eco-friendly as not only the polylactide polymer (PLA) is biodegradable but also the lactide monomer can be generated from renewable resources by corn fermentation process or from agricultural starch wastes [14,15]. Moreover, the PLAs have been widely used in medical and pharmaceutical applications [16,17] because of their good mechanical properties and biocompatibility. The PLA synthesis is generally carried out by solution polymerization [18] and by bulk polymerization [19]. Owing to its high reactivity, the solution polymerization is susceptible to unwanted reactions like, racemization, trans-esterifications, especially to the impurity levels. Thus, for the large-scale production of PLA for commercial purposes, the bulk melt polymerization is preferred as it does not suffer from the limitations faced by the solution polymerization [20]. Because of the aforementioned reasons we became interested in designing initiators for bulk polymerizations of L-lactides. In this regard, we have recently reported gold and silver–NHC complexes as initiators for ring-opening polymerization (ROP) of L-lactide [21]. We rationalized that the functionalization of N-heterocyclic carbene ligand would provide extra stability to these metal catalysts through chelation of the functionalized side arm to the metal center. For example, in case of the phosphine catalysts, the chelated ones have been reported to possess remarkably high thermal stabilities [22]. For comparison, the syntheses of non-functionalized N-heterocyclic carbene based initiators were also undertaken (Fig. 1).

Here in this contribution, we report the synthesis and structural characterizations of two such new silver complexes namely, [1-(2,4,6-trimethylphenyl)-3-(N-phenylacetamido)imidazol-2-ylidene)2Ag] Cl− 1b and [1-(i-propyl)-3-(benzylimidazol-2-ylidene)AgCl 2b supported respectively over an amido-functionalized NHC ligand, and an non-functionalized NHC ligand. Furthermore, in this contribution we disclose that both the silver complexes, 1b and 2b, effectively catalyze ring-opening polymerization (ROP) of L-lactid at elevated temperatures under solvent-free melt conditions to give polylactide polymers of moderate to low molecular weights with narrow molecular weight distributions (Eq. 1).

**Fig. 1.** The amido-functionalized, [[1-(2,4,6-trimethylphenyl)-3-(N-phenylacetamido)imidazol-2-ylidene)2Ag] Cl− 1b, and the non-functionalized, [1-(i-propyl)-3-(benzylimidazol-2-ylidene)AgCl 2b, silver complexes are shown.

**Eq. 1.** Ring-opening polymerization (ROP) of L-lactide by 1b and 2b.

### 2. Experimental

#### 2.1. General procedures

All manipulations were carried out using a combination of a glovebox and standard Schlenk techniques. Solvents were purified and degassed by standard procedures. L-Lactide was purchased from Sigma Aldrich, Germany and was subjected to polymerization without further purification. Ag2O was purchased from SD-fine chemicals (India) and used without any further purification. N-Phenylchloroacetamide [23], 1-i-propylimidazole [24] and 2,4,6-trimethylphenylimidazole [25] were synthesized according to literature procedures. 1H and 13C {1H} NMR spectra were recorded in CDCl3 on a Varian 400 MHz NMR spectrometer. 1H NMR peaks are labeled as singlet (s), doublet (d), triplet (t), and septet (sept). Infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer. Mass spectrometry measurements were done on a Micromass Q-Tof spectrometer. Thermal-gravimetric analysis of catalyst (1b and 2b) were carried out using NETZSCH STA 409PC Luxx Differential Scanning Calorimeter in the
temperature range of 25–700 °C at the rate of 10 °C/min under nitrogen flow (60 mL/min). Molecular weights of the polymers were determined using a Waters GPC (Waters 2414 RI Detector) with PL-gel, 5 μm Mixed-D (2 x 500 mm) Column, with polystyrene standards in chloroform that covered a molecular weight range of 160 to 4 x 10^5. MALDI-TOF MS measurements have been performed with a AXIMA CFR KRATOS Analytical mass spectrometer, employing a 19 kV accelerating voltage with pulsed ion extraction (PIE). The positive ions are detected via ionization mode (20 kV). Laser desorption is achieved by a nitrogen laser (337 nm, 1 ns pulse width, operating at 4 Hz), and each spectrum scans 500–1000 shots. The instrument has been linearly calibrated with three standards Insulin, Insulin B chain, Bradykinin, Angiotensin-1 and ACTH. The sample is prepared with a χ-cyano-4-hydroxy cinnamic acid (CHC) matrix (10 mg/mL). One microliter of analyte solution (10 mg/mL) is deposited onto the stainless steel sample plate, and allowed to air-dry. Subsequently, a 1 μL matrix solution (30:70 v/v CHC with 0.1% TFA: acetonitrile) is added into the analyte. The differences between the measured and the calculated masses of peaks are within 0.47–3.91 Da, corresponding to polymer chains bearing NHC–Ag and NHC fragments of 1b as end groups.

2.2. Synthesis of 1-(2,4,6-trimethylphenyl)-3-(N-phenylacetamido)imidazolium chloride 1a

N-Phenylethoxycarbamide (0.659 g, 3.87 mmol) and 2,4,6-trimethylphenylimidazole (0.721 g, 3.87 mmol) were taken in toluene (ca. 10 mL) and heated at 140 °C for 15 h during which a white precipitate was formed. The precipitate was collected by filtration and was washed with hot hexane (ca. 15 mL) and dried under vacuum to give the product as white crystalline solid (1.00 g, 73%). 1H NMR (CDCl3, 400 MHz, 25 °C), δ 11.3 (s, 1H, NH); 9.54 (s, 1H, NCN); 7.78 (s, 1H, NCHCN); 7.64 (d, 2H, 3JH-H = 8 Hz, o-C6H3); 7.13 (t, 2H, 3JH-H = 8 Hz, m-C6H3); 7.00 (s, 1H, NCHC/N); 6.95 (t, 1H, 3JH-H = 7 Hz, p-C6H3); 6.91 (s, 2H, m-C6H2{2,4,6-Me3}); 5.80 (s, 2H, CH2); 2.26 (s, 3H, p-C6H2{2,4,6-Me3}); 1.97 (s, 6H, o-C6H2{2,4,6-Me3}). 13C{1H} NMR (CDCl3, 100 MHz, 25 °C), δ 162.9 (CO); 141.2 (ipso-C6H3); 138.5 (ipso-C6H2{2,4,6-Me3}); 137.9 (NHCN); 134.2 (o-C6H2{2,4,6-Me3}); 130.5 (p-C6H2{2,4,6-Me3}); 129.7 (m-C6H2{2,4,6-Me3}); 128.5 (o-C6H3); 124.3 (NCHCN); 124.1 (NCHCN); 122.2 (p-C6H3); 120.0 (m-C6H3); 52.7 (CH2); 20.9 (p-C6H2{2,4,6-Me3}); 17.4 (o-C6H2{2,4,6-Me3}). IR data cm⁻¹ 1697 (s) (νC=O). HRMS (ES): m/z 320.1767 (NHC-ligand)+ calculated 320.1763.

2.3. Synthesis of [1-(2,4,6-trimethylphenyl)-3-(N-phenylacetamido)imidazol-2-ylidene]AgCl 1b

A mixture of 1-(2,4,6-trimethylphenyl)-3-(N-phenylacetamido)imidazolium chloride 1a (1.46 g, 4.10 mmol) and Ag2O (0.479 g, 2.07 mmol) in dichloromethane (ca. 20 mL) was stirred at room temperature for 4 h. The reaction mixture was filtered and the solvent was removed under vacuum to give the product as a light yellow solid (0.813 g, 52%). 1H NMR (CDCl3, 400 MHz, 25 °C), δ 11.0 (br, 1H, NH); 7.75 (d, 2H, 3JH-H = 8 Hz, o-C6H3); 7.34 (s, 1H, NCHCN); 7.16 (t, 2H, 3JH-H = 8 Hz, m-C6H3); 6.97 (t, 1H, 3JH-H = 7 Hz, p-C6H3); 6.73 (s, 1H, NCHCN); 6.72 (s, 2H, m-C6H2{2,4,6-Me3}); 5.35 (s, 2H, CH2); 2.32 (s, 3H, p-C6H2{2,4,6-Me3}); 1.60 (s, 6H, o-C6H2{2,4,6-Me3}). 13C{1H} NMR (CDCl3, 100 MHz, 25 °C), δ 182.8 (broad, NCO); 165.0 (CO); 138.5 (ipso-C6H3); 138.2 (ipso-C6H2{2,4,6-Me3}); 135.0 (o-C6H2{2,4,6-Me3}); 134.5 (p-C6H2{2,4,6-Me3}); 128.8 (m-C6H2{2,4,6-Me3}); 128.5 (o-C6H3); 123.8 (NCHCN); 123.2 (NCHCN); 121.7 (p-C6H3); 119.7 (m-C6H3); 54.3 (CH2); 21.0 (p-C6H2{2,4,6-Me3}); 17.2 (o-C6H2{2,4,6-Me3}). IR data cm⁻¹ 1698 (s) (νC=O). HRMS (ES): m/z 745.2410 [NHC]2Ag]+ calculated 745.2420.

2.4. Synthesis of 1-(i-propyl)-3-(benzyl)imidazolium chloride 2a

Benzylic chloride (3.10 g, 24.6 mmol) and 1-(i-propyl)imidazol-2-ylidene AgCl 2b

A mixture of 1-(i-propyl)-3-(benzyl)imidazolium chloride 2a (1.80 g, 7.61 mmol) and Ag2O (0.879 g, 3.80 mmol) in dichloromethane (ca. 20 mL) was stirred for 4 h at room temperature. The solution was filtered and the solvent was removed under vacuum to give the product as a light brown sticky solid (1.10 g, 42%). 1H NMR (CDCl3, 400 MHz, 25 °C), δ 7.36 (t, 3H, 3JH-H = 8 Hz, m/p-C6H3); 7.24 (d, 2H, 3JH-H = 6 Hz, o-C6H3); 7.05 (s, 1H, NCHCN); 6.96 (s, 1H, NCHCN); 5.26 (s, 2H, CH2); 4.75 (sept, 1H, 3JH-H = 7 Hz, CH(CH2){3}); 1.48 (d, 6H, 3JH-H = 7 Hz, CH(CH2){3}). 13C{1H} NMR (CDCl3, 100 MHz, 25 °C), δ 177.0 (NCO); 135.1 (ipso-C6H3);
127.9 (ο-C$_6$H$_3$); 127.1 (p-C$_6$H$_3$); 126.8 (m-C$_6$H$_3$); 120.8 (NCHCHN); 117.3 (NCHCHN); 54.4 (C(CH$_3$)$_2$); 53.1 (CH$_2$); 22.8 (C(CH$_3$)$_2$). HRMS (ES): m/z 307.0367 ([NHCCl$\text{Ag}^+$] calculated 307.0364. Anal. Calc. for C$_{13}$H$_{16}$AgClN$_2$: C 45.44%; H 4.69%, N 8.15%. Found: C 46.67%; H 4.40%, N 7.88%.

2.6. X-ray crystallography

Single crystals of 1a, 1b, and 2b suitable for X-ray diffraction, were grown from acetonitrile at 25 °C. X-ray diffraction data were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector, and crystal data collection and refinement parameters are summarized in Table 1. The structures were solved using direct methods and subsequently refined using a riding model. The hydrogen atoms nitrogen or oxygen (N–H, O–H) were located from the difference map and refined, while the hydrogen atoms attached to carbon (C–H) were geometrically fixed and subsequently refined using a riding model.

2.7. Polymerization experiments

Bulk polymerizations of L-lactide were carried out in vacuum-sealed glass ampoules. Firstly, the glass ampoule was charged with monomer (L-lactide) and dried for a period of 2 h under high vacuum at 50 °C. Subsequently, the catalyst (1b or 2b) was added keeping with the monomer to catalyst ratio ranging from 50 to 300. The ampoule was sealed under high vacuum and immersed in an oil bath.

Polymerizations were carried out in the temperature range 100–180 °C. After a predetermined time (0.5–8 h) the glass ampoule was removed and subsequently, the molten reactive polymer mixture was cooled while immersing sealed ampoule in liquid nitrogen to stop the polymerization and thereafter samples were removed for analysis. The analyses were performed on the crude reaction mixture, no precipitation was executed to avoid fractionation of the sample in order to not to influence the results.

3. Results and discussion

3.1. Amido-functionalized N-heterocyclic carbene complex of silver(I)

The 1-(2,4,6-trimethylphenyl)-3-(N-phenylacetamido)imidazolium chloride 1a was synthesized by the alkylation reaction of 2,4,6-trimethylphenylimidazole with N-phenylchloroacetamide in 73% yield (Scheme 1). The $^1$H NMR spectrum of 1a in CDCl$_3$ showed the characteristic imidazolium proton peak (NCHN) at 9.54 ppm while the corresponding carbon resonance (NCHN) appeared at 137.9 ppm in CDCl$_3$ in the $^{13}$C NMR spectrum. The amido (–CONH–) and the bridging methylene (–CH$_2$–) resonances appeared at 11.30 ppm and at 5.80 ppm respectively in the $^1$H NMR spectrum and at 162.9 ppm (–CONH–) and 52.7 ppm (–CH$_2$–) respectively in the $^{13}$C NMR spectrum. The infrared spectrum showed the carbonyl resonance of the amido group (–CONHz) at 1697 cm$^{-1}$.

The 1-(2,4,6-trimethylphenyl)-3-(N-phenylacetamido)imidazolium chloride 1a was determined by X-ray diffraction (Fig. 2). Two crystallo-

![Scheme 1](image-url)

Table 1

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graphically unique molecules were present in the unit cell. It is interesting to note that both the mesityl [26] and the N-phenylacetamido (–CH₂CONHPh) [27] substituents lie upright to the plane of the imidazole ring presumably due to the steric reasons. The two equivalent C–N bond distances [N12–C203 = 1.324(3) Å, N22–C203 = 1.322(3) Å, N13–C103 = 1.331(3) Å, N12–C103 = 1.312(3) Å], which are shorter than the sum (1.472 Å) of the individual single bond covalent radii of C (0.772 Å) and N (0.70 Å) [28], suggest partial double bond character of the C–N bonds due to the π-electron delocalization in the imidazole ring. The imidazolium C–N bond distances [N22–C203 = 1.324(3) Å, N23–C203 = 1.322(3) Å, N13–C103 = 1.331(3) Å, N12–C103 = 1.312(3) Å] in 1a are consistent with that observed for related compounds such as, 1-(ethyl)-3-(methyl)imidazolium chloride [1.348(3) Å and 1.336(3) Å] [30]. It is interesting to note that weak hydrogen bonding interaction between the Cl⁻ anion with the amide proton (–CONH–) has been found in the 1a structure. For example, the Cl⁻···N21 (3.244 Å) and the Cl⁻···N11 (3.236 Å) distances between the Cl⁻ anion and the amide nitrogen (–CONH–) are slightly shorter than the sum of the van der Waals radii of Cl and N atoms (3.31 Å) [31]. Another interesting observation that emerges out is that the Cl⁻ anion prefers to interact with the amide proton (–CONH–) instead of hydrogen bonding to the acidic proton at the 2-imidazolium position (NCHN). For example, in case of a non-functionalized imidazolium halide like, 1-(ethyl)-3-(methyl)imidazolium bromide, [29] which is bereft of any NH or OH protons, show extensive hydrogen bonding of the Br⁻ anion not only with the acidic proton of the 2-position (NCHN) but also with that of the olefinic protons of the 4- and 5-positions of the imidazole ring. Hydrogen bondings in imidazolium halide salts are quite common and have been extensively studied by NMR [32,33], and X-ray diffraction [34,29,30] techniques. The [1-(2,4,6-trimethylphenyl)-3-(N-phenylacetamido)imidazol-2-ylidene][Ag]Cl⁻ 1b was synthesized by the reaction of 1-(2,4,6-trimethylphenyl)-3-(N-phenylacetamido)imidazolium chloride 1a with Ag₂O in 52% yield following a methodology reported by Lin and coworkers [35]. Lin’s versatile Ag₂O methodology for synthesizing the Ag(I)–NHC complexes is particularly useful in cases when the generation of free carbenes from the imidazolium salts becomes difficult. Especially for imidazolium salts having base sensitive functional groups, the generations of free carbenes are often found to be challenging. It is noteworthy that with Ag₂O, the deprotonation of the acidic proton at the imidazolium 2-position (NCHN) was observed instead of the amide proton (–CONH–) of the functionalized side arm. This observation is in contrary to that observed for the hydrogen bonding interaction in the crystal structure of 1a, where the Cl⁻ anion preferred to interact with the amide proton (–CONH–) instead of the imidazolium 2-position (NCHN) proton. The characteristic imidazolium proton peak (NCHN) at 9.54 ppm was conspicuously absent in the product ¹H NMR spectrum in CDCl₃ owing to deprotonation by the weakly basic Ag₂O. Consistent with the formation of the singlet car bene, an additional broad peak corresponding to the metal coordinated carbene (NCN) was seen at 182.8 ppm in the ¹³C NMR spectrum in CDCl₃. The amide carbonyl (–CONH–) peak appeared at 165.0 ppm in the ¹³C NMR spectrum and at 1698 cm⁻¹ in the infrared spectrum. The electrospray mass spectrometry showed a molecular ion peak at 745 m/z corresponding to the cationic [[1-(2,4,6-trimethylphenyl)-3-(N-phenylacetamido)imidazol-2-ylidene][Ag]⁺Cl⁺] species.

The definitive proof of the [[1-(2,4,6-trimethylphenyl)-3-(N-phenylacetamido)imidazol-2-ylidene][Ag]⁺Cl⁻] species

Fig. 2. ORTEP of 1a with thermal ellipsoids drawn at 50% probability level. Two crystallographically unique molecules are present in the unit cell and only one of them is shown. Hydrogen atoms on carbon are omitted for clarity. Selected bond lengths (Å) and angles (°): N22–C203 1.324(3), N23–C203 1.322(3), N22–C203–N23 108.7(2), H-bond angles N11–H11A···Cl2 173°, N21–H21A···Cl1 174°, O3–H301···Cl2 173°, O3–H302···Cl1 169°, O4–H401···Cl2 173°, O4–H402···Cl1 160°.

Fig. 3. ORTEP of 1b with thermal ellipsoids drawn at 50% probability level. Solvent molecules present in the unit cell are not shown. Hydrogen atoms on carbon are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag–Cl1 2.076(3), Ag–C41 2.071(3), N1–C11 1.553(3), N2–C11 1.344(3), N4–C41 1.354(3), N5–C41 1.351(3), Cl1–Ag–C41 174.49(10), N2–C11–N1 104.5(2), N4–C41–N5 104.2(2). H-bond angles N3–H3A···Cl1 175°, N6–H6A···Cl1 171°, C57–H57C···O1 161°.
structure came from X-ray diffraction studies (Fig. 3). The molecular structure showed that two amido-functionalized ligands were bound to the center silver atom resulting in a cationic 2:1 complex. The geometry around silver is almost linear [C11–Ag–C41 174.49(10)°] and is consistent with the d10 configuration of silver(I) ion. The Ag–C carb bond distances [Ag–C11 = 2.076(3) Å and Ag–C41 = 2.071(3) Å] are comparable to the sum of the individual covalent radii of Ag and C (2.111 Å) [28]. Quite interestingly, the amido side arm of the complex 1b was found to be disposed away form the silver instead of chelating to the metal center as was expected. Similar non-chelation of the functionalized side arm to the metal center has been reported for groups like 2-pyridyl and 2-pyridinylmethyl moieties in case of silver–NHC complexes [9,36]. It is worth noting that in a functionalized Pd–NHC complex reported by Waymouth [37] and coworkers the chelation to the metal center through the enolate-O of a 2-oxo-2-phenylethyl functionalized side arm was however observed.

Another notable feature of the 1b structure is that the two imidazole rings were found to be non-coplanar having a N1–C11–C41–N4 dihedral angle of 57.7°. At this juncture it is worth mentioning that the analogous cationic 2:1 (NHC:silver) complexes have been found to exhibit both coplanar as well as non-coplanar orientations of the imidazole rings. For example, the non-coplanar structures have been reported for \{[1,3-di(2-pyridyl)imidazol-2-ylidene]Ag\} _2^+ BF_4^- [38] (dihedral angle N4–C14–Cl–N2 = 41.9°) and for \{[1,2,6-diisopropylphenyl]-3- (2-pyridylmethyl)imidazol-2-ylidene]Ag\} _2^+ AgBr_2^- [9] (dihedral angle N6–C47–C1–N2 = 32.3°) whereas the coplanar structures with dihedral angles almost close to 0° have been reported for \{[1,3-di(2-pyridyl)imidazol-2-ylidene]Ag\} _2^+ AgCl_2^- [10] and \{[1,2-(3,5-dimethylpyrazol-1-yl)ethyl]-3-(methyl)imidazol-2-ylidene]Ag\} _2^+ AgCl_2^- [12]. Theoretical study recently reported by Frenking and coworkers [39] suggests that both the coplanar and the non-coplanar perpendicular orientations of the imidazole rings are very close in energy. Quite interestingly, the Cl⁻ anion was found to be in the hydrogen bonding (Cl⁻···H–N) distance with one of the amido proton (–CONH–) of the side-arm substituent. The Cl⁻···N3 distance of 3.189 Å is shorter than the sum of the individual van der Waals radii (3.31 Å) and, thus, is consistent with a hydrogen bonding interaction [31]. Notably, the Cl⁻···N3 distance (3.189 Å) in 1b is even shorter than that observed in case of the similar interaction in 1a (Cl⁻···N2 = 3.244 Å and Cl2···N11 = 3.236 Å), suggesting a stronger hydrogen bond in the former. Similar Cl⁻···N distances have been observed in other compounds displaying Cl⁻···H–N (amido) hydrogen bonding interactions. For example, 3.2648(16) Å in [N(2,6-diisopropylphenyl)-3-bis(2-pyridylmethyl)amino]-propanamide)copper(I) chloride [40]. 3.341(3) Å and 3.325(3) Å in (Et₂N)_2[CuH₂ImMe(Cl)] Cl] (H₂ImMe = 2,6-bis[N,N₂⁺(2-acetamidophenyl)carbamoyl]pyridine [41], 3.2127(19) Å in [[(L')Zn(Cl)]Cl] [L' = (6-NHCObu₂-2-pyridylmethyl)-bis(2-pyridylmethyl)amine] [42] and 3.325(9) Å in (1)\(_2^+\)Cl⁻·H₂O] (1 = 3-methylamido-3',4'-ethylenedithiotetrahydrofulvalene) [43].

Important is the comparison of the structures of 1-(2,4,6-trimethylphenyl)-3-(N-phenylacetamido)imidazolium chloride 1a with \{(1-(2,4,6-trimethylphenyl)-3-(N-phenylacetamido)imidazol-2-ylidene)Ag\} _2^+ Cl⁻ 1b. Quite noticeably, marked decrease in the N–C–N bond angle was observed on going from that in 1a [108.7(2)°, 109.4(2)°] to 1b [104.5(2)°, 104.2(2)°]. This was further accompanied by the increase in the average C–N bond distance on going from 1a [1.321(3) Å] to 1b [1.351(7) Å]. Shorter C–N bond distance along with the N–C–N angle, being closer to 120°, in 1a suggests that the imidazolium ring in 1a is relatively more aromatic compared to that in 1b. As was observed in 1a, both the mesityl and the N-phenylacetamido (−CH₃CONHPh) groups in 1b were found to be perpendicular to that of the imidazole ring [44].

3.2. Non-Functionalized N-heterocyclic carbene complex of silver(I)

A non-functionalized imidazolium chloride salt, 1-(i-propyl)-3-(benzyl)imidazolium chloride 2a, was synthesized analogously by the reaction of i-propylimidazole with benzyl chloride in 45% yield (Scheme 1). The characteristic imidazolium peak (NCHN) and the bridging methylene (−CH₂−) peak appeared each as singlets at 10.6 ppm and at 5.59 ppm respectively in the \(^1\)H NMR spectrum in CDCl₃ and the corresponding resonances appeared at 135.0 ppm (NCHN) and at 52.4 ppm (−CH₂−) in the \(^13\)C NMR spectrum in CDCl₃. Consistent with the formation of 2a, Electrospray Mass analysis showed a cationic [1-(i-propyl)-3-(benzyl)imidazolium]⁺ species at 201 m/z and was further confirmed by HRMS results.

The silver complex, [1-(i-propyl)-3-(benzyl)imidazol-2-ylidene]AgCl 2b, was obtained from the reaction of 1-(i-propyl)-3-(benzyl)imidazolium chloride 2a with Ag₂O in 42% yield. Characteristic to the product formation, the silver coordinated imidazolium carbene resonance (NCN) appeared as a sharp peak at 177.0 ppm in the \(^13\)C NMR spectrum in CDCl₃. The bridging methylene peak (−CH₂−) appeared as singlet at 5.26 ppm in the \(^1\)H NMR spectrum in CDCl₃ and at 53.1 ppm in the \(^13\)C NMR spectrum in CDCl₃.

The molecular structure of [1-(i-propyl)-3-(benzyl)imidazol-2-ylidene]AgCl 2b has been determined by X-ray diffraction (Fig. 4). A neutral monomeric 1:1 complex containing one NHC ligand and a silver ion obtained in 2b is in sharp contrast to the cationic 2:1 complex observed in case of the amido-functionalized NHC ligand. The Ag–Cl bond distance of 2.3435(7) Å (Ag–Cl) compares well with the sum of the individual covalent radii of Ag and Cl (2.329 Å) [28]. The angle at silver is slightly bent from the linearity with the Cl–Ag–Cl angle being 166.08(7)°.

Important is the structural comparison of 1b and 2b, which reveals that amido-functionalization of the side-arm substituents has very little effect on the bonding of
the N-heterocyclic carbene moiety to the silver. For example, the Ag–C\textsubscript{carb} bond distance of 2.077(2) Å (Ag–Cl) in 2b compare well with the Ag–C\textsubscript{carb} bond distances [Ag–C\textsubscript{11} = 2.076(3) Å and Ag–Cl = 2.077(2) Å] in 1b. Similarly, the NCN bond angles in 1b [N1–C1–N2 = 1.353(3) Å, N2–C11 = 1.344(3) Å and N4–C41 = 1.354(3) Å, N5–C41 = 1.351(3) Å] and in 2b [N1–C1–N2 = 1.350(3) Å, N2–C11 = 1.353(3) Å, N4–C41 = 1.350(3) Å, N5–C41 = 1.351(3) Å] are also comparable. The coordination geometry of silver is linear in 1b (C11–Ag–C41 = 174.49(10)°) whereas it is slightly distorted from linearity in 2b (C1–Ag–C1 = 166.08(7)°).

The two silver complexes 1b and 2b, efficiently catalyze the ring-opening polymerization (ROP) of L-lactides under solvent-free melt conditions at elevated temperatures. Specifically, a typical polymerization experiment would involve heating L-lactide and the catalyst, 1b or 2b, for a given monomer to catalyst ratio in a sealed vessel under vacuum at a designated temperature for a specific period of time. Under these conditions the reaction mixture would form a monomer melt in which the polymerization would occur. The variation of the [M]/[C] ratio (M = monomer, C = catalyst) polymerization run showed that maximum molecular weight (entry 5: \( M_n = 6.3 \times 10^3 \)), Table 2) was obtained at [M]/[C] ratio 250:1 in case of 1b whereas the same (entry 3: \( M_n = 9.0 \times 10^3 \), Table 3) was obtained at [M]/[C] ratio 150:1 in case of 2b for a 4 h run at 160 °C. The polydispersity indexes are almost similar for both these catalysts 1b (PDI = 1.05 – 1.35) and 2b (PDI = 1.06 – 1.42). It is interesting to note that the polymer molecular weights obtained in case of a 1b and 2b is slightly shorter than that of a related cationic 2:1 (NHC ligand:metal) silver complex (maximum \( M_n = 12.2 \times 10^3 \)) we recently reported for bulk polymerization of l-lactide under analogous melt conditions [21b].

The time dependence study showed that for both 1b and 2b, the number average molecular weight (\( M_n \)) of the polymer increased with time for the 4 h after which it gradually reached toward saturation whereas the molecular weight distribution (PDI) remained constant all throughout the course of the polymerization (Fig. 5). Such an observation is consistent with a pseudo-living polymerization process [45]. The temperature dependence study carried out in the range (100–180 °C) showed that in case of 1b molecular weight (\( M_n \)) increased steadily with temperature whereas for 2b the \( M_n \) reached a maximum at 160 °C after which it started to decrease. The decrease in molecular weight may be attributed due to depolymerization taking place at higher temperatures. Similar decrease in molecular weight at higher temperatures has been reported by Liao [19a] and Albertson and Varma [16]. Interestingly, comparison between the silver complexes revealed that slightly higher molecular weight polymer is obtained in case of 2b than in 1b.

The stability of the catalysts, 1b and 2b, were assessed by the thermogravimetric analysis (TGA) which showed
that compound 1b is stable up to 300 °C whereas slow mass loss was observed after 95 °C for compound 2b (Fig. 6). It is noteworthy that remarkable stability of 1b is similar to that observed for analogous cationic 2:1 (NHC ligand:metal) silver complex namely, [(1-i-propyl-3-{N-phenylacetamido}imidazol-2-ylidene)2Ag]+Cl− [21b], which too was stable up to 180 °C. The extreme stability of cationic 2:1 (NHC ligand:metal) silver complexes, like that of 1b, point toward a metal mediated polymerization (Scheme 2). It is worth noting that metal mediated polymerization of lactide has recently been reported by us [21b], for a silver–NHC complex, and by Arnold [46], for an Y(III)–NHC complex. A consequence of metal mediated mechanism is the capping of the polymer chain-ends by NHC fragments. Indeed, the MALDI spectrometric analysis of polymer confirms the presence of NHC end groups (Fig. 7) [47]. It is worthy of mention that for the relatively less thermally stable neutral silver–NHC complex 2b, the other possibility of carbene mediated mechanism cannot be ruled out entirely. Detailed mechanistic studies to establish the nature of the active species responsible for catalysis by 2b are underway.

4. Conclusion

In summary, two new silver complexes, 1b and 2b, supported respectively over an amido-functionalized and a non-functionalized N-heterocyclic carbene ligands have been synthesized. The silver complexes, 1b and 2b, along with the amido-functionalized N-heterocyclic carbene ligand precursor, 1a, have been structurally characterized by X-ray diffraction studies. A cationic 2:1 (NHC ligand:metal) complex obtained in case of the amido-functionalized ligand is in sharp contrast to the neutral 1:1 (NHC ligand:metal) complex obtained in case of the non-functionalized ligand. Structural comparison of 1b with 2b reveal that amido-functionalization of the side arm had little bearing on its structures. The silver complexes, 1b and 2b, effectively catalyze the ring-opening polymerization (ROP) of l-lactide under solvent-free melt conditions producing polylactide polymer of moderate to low molecular weight with narrow molecular weight distribution.
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Appendix A. Supplementary data

CCDC 604566, 604565, and 604564 contain the supplementary crystallographic data for 1-(2,4,6-trimethylphenyl)-3-(N-phenylacetamido)imidazolium chloride \(1a\), \([1-(2,4,6-trimethylphenyl)-3-(N-phenylacetamido)imidazol-\)

Fig. 7. A zoomed MALDI-TOF MS spectrum of the polylactide polymer.

Scheme 2. Proposed scheme for ring-opening polymerization of lactide by 1b.
2-ylidene]2Ag}+Cl− 1b, and [1-(i-propyl)-3-(benzyl)imidazol-2-ylidene]AgCl 2b. These data can be obtained free of charge
or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK;

References


[26] The dihedral angle between the mesityl group and the imidazole ring in 1a that has two crystallographically unique molecules in the unit cell is 79.9° (C122–C121–N13–C130) and 100.6° (C226–C221–N23–C230). See the CIF file in Supporting information.

[27] The dihedral angle between the N-phenylacetamido (-CH2CONHPH) group and the imidazole ring in 1a that has two crystallographically unique molecules in the unit cell is 68.7° (C101–C102–N12–C103) and 64.2° (C201–C202–N22–C203). See the CIF file in Supporting information.


(C45–C44–N5–C41) and 77.2° (C15–C14–N2–C11). See the CIF file in Supporting information.


[47] Specifically, a series of sodium (23 Da) cationized peaks of the polymers bearing NHC end groups can be recognized in the MALDI spectrum. The mass ($M_C$) of the sodium cationized peak of the polymer bearing the NHC–Ag (426 Da) and NHC (319 Da) end groups is given by, $M_C = 72x + 426 + 319 + 23$ where $x =$ number of repeat unit (72 Da).