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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]$_2$Ag}$^+$Cl$^-$ **1b**, 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-trimethylphenyl)-3-(*N*-phenylacetamido)imidazolium chloride **1a** 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)-3-(benzyl)imidazolium chloride **2a** with Ag_2O 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

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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 sterics, 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 $(NHC)_2Ag^+$ 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)$_2$Ag]$^+$Cl$^-$ **1b** and [1-(*i*-propyl)-3-(benzyl)imidazol-2-ylidene]AgCl **2b** supported

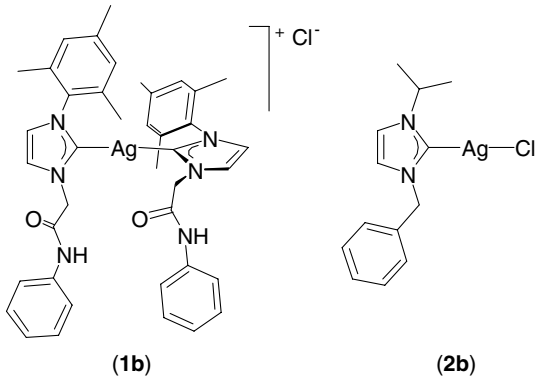
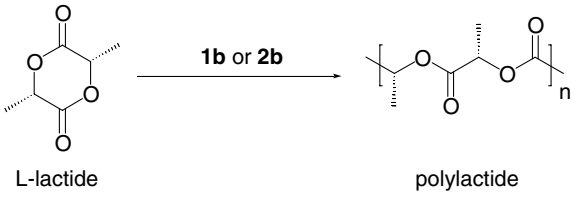


Fig. 1. The amido-functionalized, {[1-(2,4,6-trimethylphenyl)-3-(*N*-phenylacetamido)imidazol-2-ylidene]$_2$Ag}$^+$Cl$^-$ **1b**, and the non-functionalized, [1-(*i*-propyl)-3-(benzyl)imidazol-2-ylidene]AgCl **2b**, silver complexes are shown.

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-lactides 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).



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. Ag_2O 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 ^{13}C {^1H} NMR spectra were recorded in $CDCl_3$ 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-gravimeteric 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 (2×300 mm) Column, with polystyrene standards in chloroform that covered a molecular weight range of l60 to 4×10^5. 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, Bradykinn, Angiotensin-1 and ACTH. The sample is prepared with a α-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-Phenylchloroacetamide (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%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C), δ 11.3 (s, 1H, N*H*); 9.54 (s, 1H, NC*H*N); 7.78 (s, 1H, NC*H*CHN); 7.64 (d, 2H, $^3J_{HH} = 8$ Hz, *o*-C_6H_5); 7.13 (t, 2H, $^3J_{HH} = 8$ Hz, *m*-C_6H_5); 7.00 (s, 1H, NCHC*H*N); 6.95 (t, 1H, $^3J_{HH} = 7$ Hz, *p*-C_6H_5); 6.91 (s, 2H, *m*-C_6H_2{2,4,6-Me_3}); 5.80 (s, 2H, CH_2); 2.26 (s, 3H, *p*-C_6H_2{2,4,6-*Me*$_3$}); 1.97 (s, 6H, *o*-C_6H_2{2,4,6-*Me*$_3$}). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C), δ 162.9 (*C*O); 141.2 (*ipso*-C_6H_5); 138.5 (*ipso*-C_6H_2{2,4,6-Me_3}); 137.9 (N*C*HN); 134.2 (*o*-C_6H_2-{2,4,6-Me_3}); 130.5 (*p*-C_6H_2{2,4,6-Me_3}); 129.7 (*m*-C_6H_2{2,4,6-Me_3}); 128.5 (*o*-C_6H_5); 124.3 (N*C*HCHN); 124.1 (NCH*C*HN); 122.2 (*p*-C_6H_5); 120.0 (*m*-C_6H_5); 52.7 (CH_2); 20.9 (*p*-C_6H_2{2,4,6-*Me*$_3$}); 17.4 (*o*-C_6H_2{2,4,6-*Me*$_3$}). IR data cm^{-1} 1697 (s) (ν_{co}). 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]$_2$Ag}$^+$Cl$^-$ **1b**

A mixture of 1-(2,4,6-trimethylphenyl)-3-(*N*-phenylacetamido)imidazolium chloride **1a** (1.46 g, 4.10 mmol) and Ag_2O (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%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C), δ 11.0 (br, 1H, N*H*); 7.75 (d, 2H, $^3J_{HH} = 8$ Hz, *o*-C_6H_5); 7.34 (s, 1H, NC*H*CHN); 7.16 (t, 2H, $^3J_{HH} = 8$ Hz, *m*-C_6H_5); 6.97 (t, 1H, $^3J_{HH} = 7$ Hz, *p*-C_6H_5); 6.73 (s, 1H, NCHC*H*N); 6.72 (s, 2H, *m*-C_6H_2{2,4,6-Me_3}); 5.35 (s, 2H, CH_2); 2.32 (s, 3H, *p*-C_6H_2{2,4,6-*Me*$_3$}); 1.60 (s, 6H, *o*-C_6H_2{2,4,6-*Me*$_3$}). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C), δ 182.8 (broad, N*C*N); 165.0 (*C*O); 138.5 (*ipso*-C_6H_5); 138.2 (*ipso*-C_6H_2{2,4,6-Me_3}); 135.0 (*o*-C_6H_2{2,4,6-Me_3}); 134.5 (*p*-C_6H_2{2,4,6-Me_3}); 128.8 (*m*-C_6H_2{2,4,6-Me_3}); 128.5 (*o*-C_6H_5); 123.8 (N*C*HCHN); 123.2 (NCH*C*HN); 121.7 (*p*-C_6H_5); 119.7 (*m*-C_6H_5); 54.3 (CH_2); 21.0 (*p*-C_6H_2{2,4,6-*Me*$_3$}); 17.2 (*o*-C_6H_2{2,4,6-*Me*$_3$}). IR data cm^{-1} 1698 (s) (ν_{co}). HRMS (ES): *m*/*z* 745.2410 [(NHC)$_2$Ag]$^+$ calculated 745.2420.

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

Benzyl chloride (3.10 g, 24.6 mmol) and 1-*i*-propyl imidazole (2.71 g, 24.6 mmol) were taken in toluene (*ca.* 10 mL) and heated at 140 °C for 14 h during which a brown 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 brown sticky solid (2.61 g, 45%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C), δ 10.6 (s, 1H, NC*H*N); 7.62 (s, 1H, NCHC*H*N); 7.52 (d, 2H, $^3J_{HH} = 7$ Hz, *o*-C_6H_5); 7.49 (s, 1H, NC*H*CHN); 7.25 (t, 2H, $^3J_{HH} = 7$ Hz, *m*-C_6H_5); 7.17 (t, 1H, $^3J_{HH} = 8$ Hz, *p*-C_6H_5); 5.59 (s, 2H, CH_2); 4.78 (sept, 1H, $^3J_{HH} = 7$ Hz, $CH(CH_3)_2$); 1.56 (d, 6H, $^3J_{HH} = 7$ Hz, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C), δ 135.0 (N*C*HN); 133.2 (*ipso*-C_6H_5); 128.7 (*o*-C_6H_5); 128.6 (*p*-C_6H_5); 128.5 (*m*-C_6H_5); 121.7 (N*C*HCHN); 120.0 (NCH*C*HN); 52.6 ($CH(CH_3)_2$); 52.4 (CH_2); 22.5 ($CH(CH_3)_2$). HRMS (ES): *m*/*z* 201.1385 (NHC-ligand)$^+$ calculated 201.1392.

2.5. Synthesis of [1-(i-propyl)-3-(benzyl)imidazol-2-ylidene]AgCl **2b**

A mixture of 1-(*i*-propyl)-3-(benzyl)imidazolium chloride **2a** (1.80 g, 7.61 mmol) and Ag_2O (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 an light brown sticky solid (1.10 g, 42%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C), δ 7.36 (t, 3H, $^3J_{HH} = 8$ Hz, *m*/*p*-C_6H_5); 7.24 (d, 2H, $^3J_{HH} = 6$ Hz, *o*-C_6H_5); 7.05 (s, 1H, NC*H*CHN); 6.96 (s, 1H, NCHC*H*N); 5.26 (s, 2H, CH_2); 4.75 (sept, 1H, $^3J_{HH} = 7$ Hz, $CH(CH_3)_2$); 1.48 (d, 6H, $^3J_{HH} = 7$ Hz, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C), δ 177.0 (N*C*N); 135.1 (*ipso*-C_6H_5);

127.9 (o-C_6H_5); 127.1 (p-C_6H_5); 126.8 (m-C_6H_5); 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 $[(NHC)Ag]^+$ 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 standard difference map techniques, and were refined by full-matrix least-squares procedures on F_2 with SHELXTL (Version 6.10). For all structures the hydrogen atoms on 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.

Table 1
X-ray crystallographic data for **1a**, **1b** and **2b**

Compound	**1a**	**1b**	**2b**
Lattice	Orthorhombic	Triclinic	Monoclinic
Formula	$C_{20}H_{24}ClN_3O_2$	$C_{43.5}H_{46}AgClN_6O_2$	$C_{13}H_{16}AgClN_2$
Formula weight	373.87	828.18	343.60
Space group	$Pca2(1)$	$P\bar{1}$	$P2(1)/c$
a (Å)	16.9660(10)	10.3763(7)	10.4891(9)
b (Å)	7.7816(4)	15.0117(10)	9.7563(9)
c (Å)	30.4169(18)	15.4734(9)	13.5900(13)
α (°)	90.00	80.5310(10)	90.00
β (°)	90.00	83.6870(10)	97.884(2)
γ (°)	90.00	82.2810(10)	90.00
V (Å^3)	4015.7(4)	2346.3(3)	2377.6(2)
Z	8	2	4
Temperature (K)	243(2)	243(2)	243(2)
Radiation (λ, Å)	0.71073	0.71073	0.71073
ρ(calcd.), g cm^{-3}	1.237	1.303	1.657
μ(Mo Kα), mm^{-1}	0.209	0.531	1.637
θ_{max} (°)	28.28	28.34	28.30
No. of data	26,227	16,222	9309
No. of parameters	487	591	155
R_1	0.0410	0.0426	0.0283
wR_2	0.0900	0.0950	0.0651
GOF	1.002	1.007	1.011

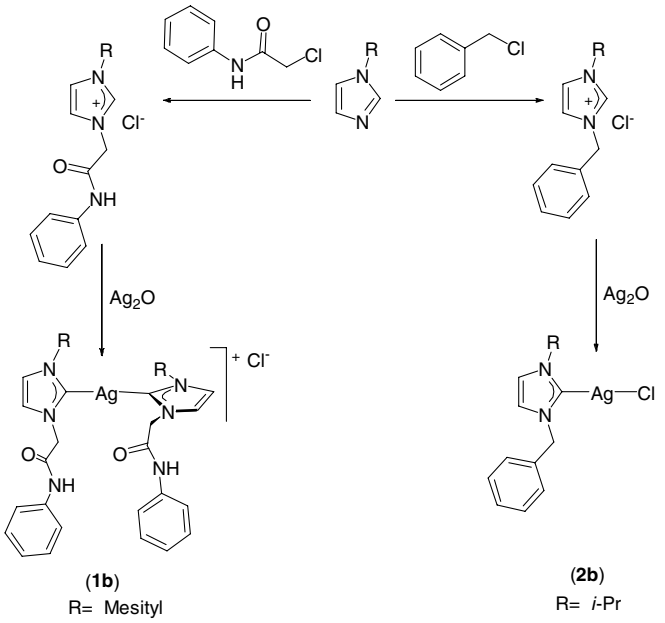
Polymerizations were carried out in the temperature range 100–180 °C. After a predetermined time (0.5–8 h) the glass ampoule was removed and subsequently, the molten reactive polymer mixture was cooled while immersing sealed ampoule in liquid nitrogen to stop the polymerization and thereafter samples 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 (NC*H*N) at 9.54 ppm while the corresponding carbon resonance (N*C*HN) appeared at 137.9 ppm in $CDCl_3$ in the ^{13}C NMR spectrum. The amido (–CON*H*–) 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 (–*C*ONH–) and 52.7 ppm (–*C*H$_2$–) respectively in the ^{13}C NMR spectrum. The infrared spectrum showed the carbonyl resonance of the amido group (–CONH–) at 1697 cm^{-1}. The electrospray mass analysis gave a 100% abundance peak at 320 m/z corresponding to the cationic [1-(2,4,6-trimethylphenyl)-3-(*N*-phenylacetamido)imidazolium]$^+$ species.

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



Scheme 1.

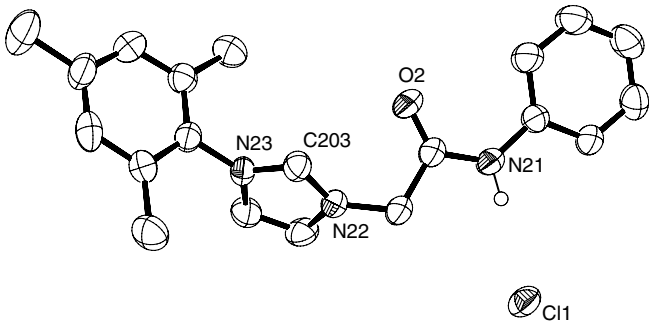


Fig. 2. ORTEP of **1a** with thermal ellipsoids drawn at 50% probability level. Two crystallographically unique molecules are present in the unit cell and only one of them is shown. Hydrogen atoms on carbon are omitted for clarity. Selected bond lengths (Å) and angles (°): N22–C203 1.324(3), N23–C203 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°.

graphically unique molecules were present in the unit cell. It is interesting to note that both the mesityl [26] and the *N*-phenylacetamido (–CH_2CONHPh) [27] substituents lie upright to the plane of the imidazole ring presumably due to the steric reasons. The two equivalent 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], 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 bromide [1.327(5) Å and 1.323(6) Å] [29] and 1-(cyano methylene)-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 (–CON*H*–) has been found in the **1a** structure. For example, the Cll···N21 (3.244 Å) and the Cl2···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 (–CON*H*–) instead of hydrogen bonding to the acidic proton at the 2-imidazolium position (NC*H*N). 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 (NC*H*N) 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 $\{[1\text{-}(2,4,6\text{-trimethylphenyl})\text{-}3\text{-}(N\text{-phenylacetamido})\text{-imidazol-2-ylidene}]_2Ag\}^+Cl^-$ **1b** was synthesized by the reaction of 1-(2,4,6-trimethylphenyl)-3-(*N*-phenylacetamido)imidazolium chloride **1a** with Ag_2O in 52% yield following a methodology reported by Lin and coworkers [35]. Lin's versatile Ag_2O 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 Ag_2O, the deprotonation of the acidic proton at the imidazolium 2-position (NC*H*N) was observed instead of the amide proton (–CON*H*–) 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 (–CON*H*–) instead of the imidazolium 2-position (NC*H*N) proton. The characteristic imidazolium proton peak (NC*H*N) at 9.54 ppm was conspicuously absent in the product ^{1}H NMR spectrum in $CDCl_3$ owing to deprotonation by the weakly basic Ag_2O. Consistent with the formation of the singlet carbene, an additional broad peak corresponding to the metal coordinated carbene (N*C*N) was seen at 182.8 ppm in the ^{13}C NMR spectrum in $CDCl_3$. The amide carbonyl (–*C*ONH–) peak appeared at 165.0 ppm in the ^{13}C 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 $\{[1\text{-}(2,4,6\text{-trimethylphenyl})\text{-}3\text{-}(N\text{-phenylacetamido})\text{imidazol-2-ylidene}]_2Ag\}^+$ species.

The definitive proof of the $\{[1\text{-}(2,4,6\text{-trimethylphenyl})\text{-}3\text{-}(N\text{-phenylacetamido})\text{imidazol-2-ylidene}]_2Ag\}^+Cl^-$ **1b**

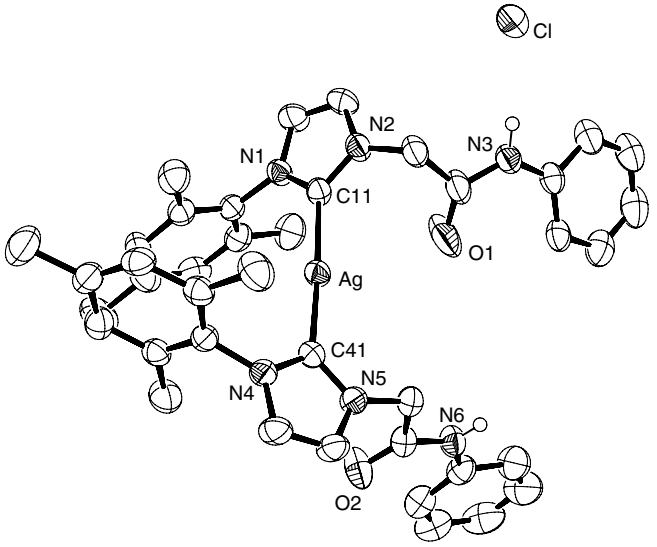


Fig. 3. ORTEP of **1b** with thermal ellipsoids drawn at 50% probability level. Solvent molecules present in the unit cell are not shown. Hydrogen atoms on carbon are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag–C11 2.076(3), Ag–C41 2.071(3), N1–C11 1.353(3), N2–C11 1.344(3), N4–C41 1.354(3), N5–C41 1.351(3), C11–Ag–C41 174.49(10), N2–C11–N1 104.5(2), N4–C41–N5 104.2(2). H-bond angles N3–H3A···Cl 175°, N6–H6A···Cl 171°, C57–H57C···O2 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 d^{10} 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 $\{[1,3\text{-di(2-pyridyl)imidazol-2-ylidene}]_2Ag\}^+BF_4^-$ [38] (dihedral angle N4–C14–C1–N2 = 41.9°) and for [1-(2, 6-diisopropylphenyl)-3- (2-pyridylmethyl)imidazol-2-ylidene]$Ag^+AgBr_2^-$ [9] (dihedral angle N6–C47–C20–N8 = 32.3°) whereas the coplanar structures with dihedral angles almost close to 0° have been reported for $\{[1,3\text{-di(methyl)imidazol-2-ylidene}]_2Ag\}^+$- $AgCl_2^-$ [10] and {1-[2-(3, 5-dimethylpyrazol-1-yl)ethyl]- 3-(methyl)-imidazol-2-ylidene]$Ag^+AgCl_2^-$ [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** (Cl1···N21 = 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-pyridyl-methyl)amino]-propanamide]copper(I) chloride [40], 3.341(3) Å and 3.325(3) Å in $(Et_4N)_2[CuH_2\mathbf{1}^{Me}(Cl)\ Cl]$ ($H_2\mathbf{1}^{Me}$ = 2,6-bis[*N*,*N*′-(2-acetamidophenyl)carbamoyl]pyridine [41], 3.2127(19) Å in [(**L**′)Zn(Cl)](Cl) [**L**′ = (6-NHCOBu^t-2-pyridylmethyl)-bis-(2-pyridylmethyl)amine] [42] and 3.325(9) Å in $(\mathbf{1})_2[Cl\cdot H_2O]$ (**1** = 3-methylamido-3′,4′-ethylenedithiotetrathiafulvalene) [43].

Important is the comparison of the structures of 1-(2,4,6-trimethylphenyl)-3-(*N*-phenylacetamido)imidazolium chloride **1a** with $\{[1\text{-}(2,4,6\text{-trimethylphenyl})\text{-}3\text{-}(N\text{-phenylacetamido})\text{imidazol-2-ylidene}]_2Ag\}^+Cl^-$ **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 (–CH_2CONHPh) 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 (NC*H*N) and the bridging methylene (–CH_2–) peak appeared each as singlets at 10.6 ppm and at 5.59 ppm respectively in the ^{1}H NMR spectrum in $CDCl_3$ and the corresponding resonances appeared at 135.0 ppm (N*C*HN) and at 52.4 ppm (–*C*H_2–) in the ^{13}C NMR spectrum in $CDCl_3$. 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 Ag_2O in 42% yield. Characteristic to the product formation, the silver coordinated imidazolium carbene resonance (N*C*N) appeared as a sharp peak at 177.0 ppm in the ^{13}C NMR spectrum in $CDCl_3$. The bridging methylene peak (–CH_2–) appeared as singlet at 5.26 ppm in the ^{1}H NMR spectrum in $CDCl_3$ and at 53.1 ppm in the ^{13}C NMR spectrum in $CDCl_3$.

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 C1–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

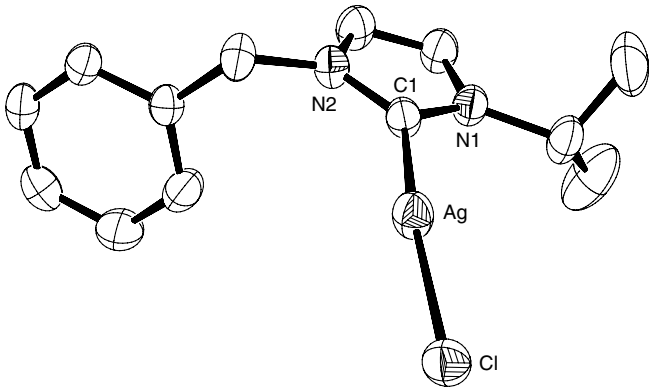


Fig. 4. ORTEP of **2b** with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms on carbon are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag–C1 2.077(2), Ag–Cl 2.3435(7), N1–C1 1.358(3), N2–C1 1.350(3), N1–C1–N2 104.8(2), C1–Ag–Cl 166.08(7).

the *N*-heterocyclic carbene moiety to the silver. For example, the Ag–C_{carb} bond distance of 2.077(2) Å (Ag–C1) in **2b** compare well with the Ag–C_{carb} bond distances [Ag–C11 = 2.076(3) Å and Ag–C41 = 2.071(3) Å] in **1b**. Similarly, the NCN bond angles in **1b** [N1–C11–N2 = 104.5 (2)° and N4–C41–N5 = 104.2(2)°] and in **2b** [N1–C1–N2 = 104.8(2)°] along with the C–N bond distances in **1b** [N1–C11 = 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 = 1.358(3) Å, N2–C1 = 1.350(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–Cl = 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: $M_w = 6.3 \times 10^3$, Table 2) was obtained at [M]:[C] ratio 250:1 in case of **1b** whereas the same (entry 3: $M_w = 9.0 \times 10^3$, 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 $M_w = 12.2 \times 10^3$) 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

Table 2
Melt polymerization of L-lactide by **1b**

Entry	L-Lactide/(**1b**) ratio	Temperature (°C)	Time (h)	M_n	M_w/M_n	Conversion (%)
1	50	160	4	5.3×10^3	1.28	90
2	100	160	4	5.3×10^3	1.29	92
3	150	160	4	5.3×10^3	1.29	92
4	200	160	4	6.2×10^3	1.19	81
5	250	160	4	6.3×10^3	1.23	77
6	300	160	4	6.1×10^3	1.20	75
7	250	100	4	3.2×10^3	1.13	55
8	250	120	4	5.2×10^3	1.09	76
9	250	140	4	5.0×10^3	1.15	67
10	250	180	4	7.2×10^3	1.34	99
11	250	160	0.5	3.0×10^3	1.05	21
12	250	160	1	3.5×10^3	1.15	36
13	250	160	2	4.6×10^3	1.11	51
14	250	160	3	5.3×10^3	1.30	52
15	250	160	6	7.0×10^3	1.35	91
16	250	160	8	7.6×10^3	1.30	98

Table 3
Melt polymerization of L-lactide by **2b**

Entry	L-lactide/(**2b**) ratio	Temperature (°C)	Time (h)	M_n	M_w/M_n	Conversion (%)
1	50	160	4	5.2×10^3	1.42	98
2	100	160	4	5.6×10^3	1.36	99
3	150	160	4	9.0×10^3	1.23	96
4	200	160	4	7.5×10^3	1.23	86
5	250	160	4	6.8×10^3	1.25	88
6	300	160	4	6.9×10^3	1.21	69
7	150	100	4	3.9×10^3	1.20	47
8	150	120	4	4.4×10^3	1.16	44
9	150	140	4	6.9×10^3	1.09	74
10	150	180	4	6.9×10^3	1.35	99
11	150	160	0.5	2.8×10^3	1.06	21
11	150	160	1	4.1×10^3	1.19	58
12	150	160	2	5.4×10^3	1.29	86
13	150	160	3	7.1×10^3	1.28	92
14	150	160	6	9.4×10^3	1.26	99
15	150	160	8	9.6×10^3	1.36	99

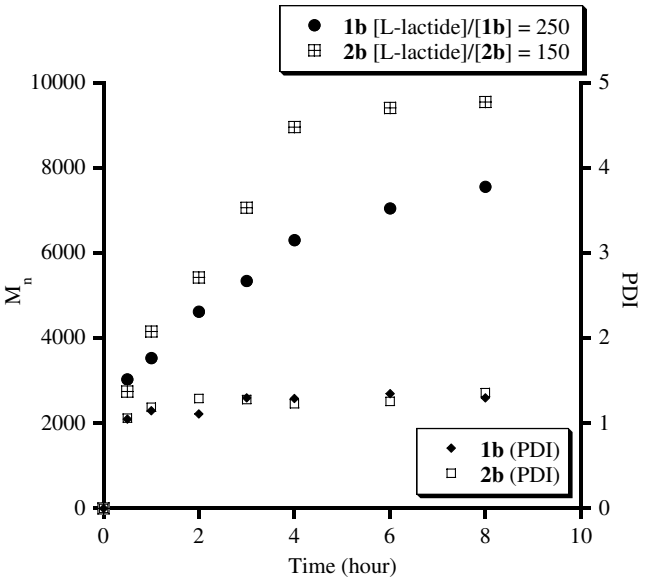


Fig. 5. Plot of M_n and PDI vs. time for the ring-opening polymerization (ROP) of **1b** (monomer to catalyst ratio = 250) and **2b** (monomer to catalyst ratio = 150) at 160 °C.

that compound **1b** is stable upto 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 a analogous cationic 2:1 (NHC ligand:metal) silver complex namely, [(1-*i*-propyl-3-{*N*-phenylacetamido}imidazol-2-ylidene)$_2$Ag]$^+$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-functionlized *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.

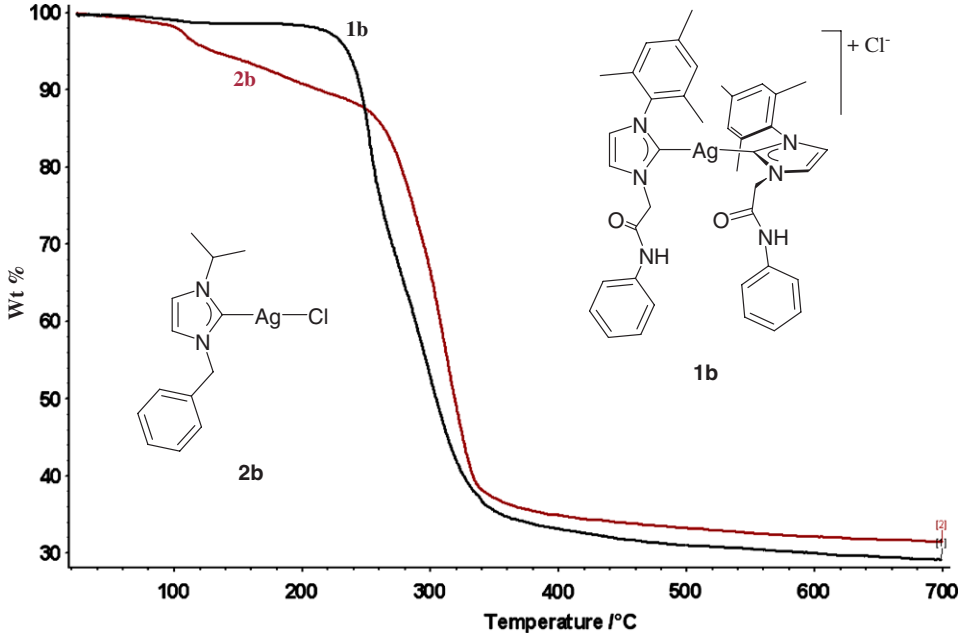
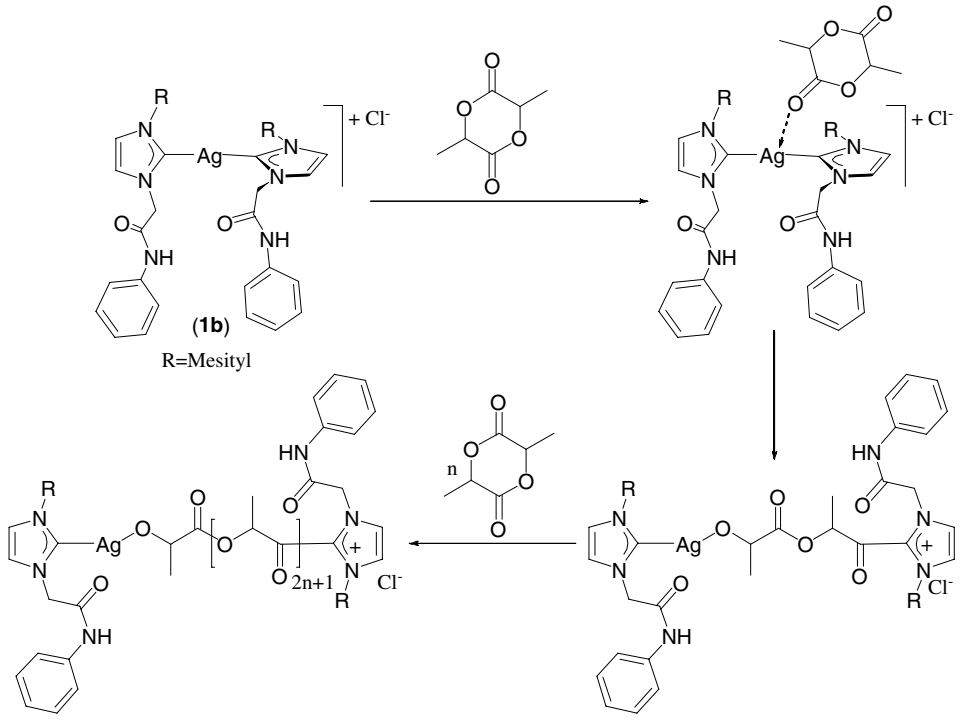


Fig. 6. Thermogravimetric analysis of **1b** and **2b** as a function of temperature.



Scheme 2. Proposed scheme for ring-opening polymerization of lactide by **1b**.

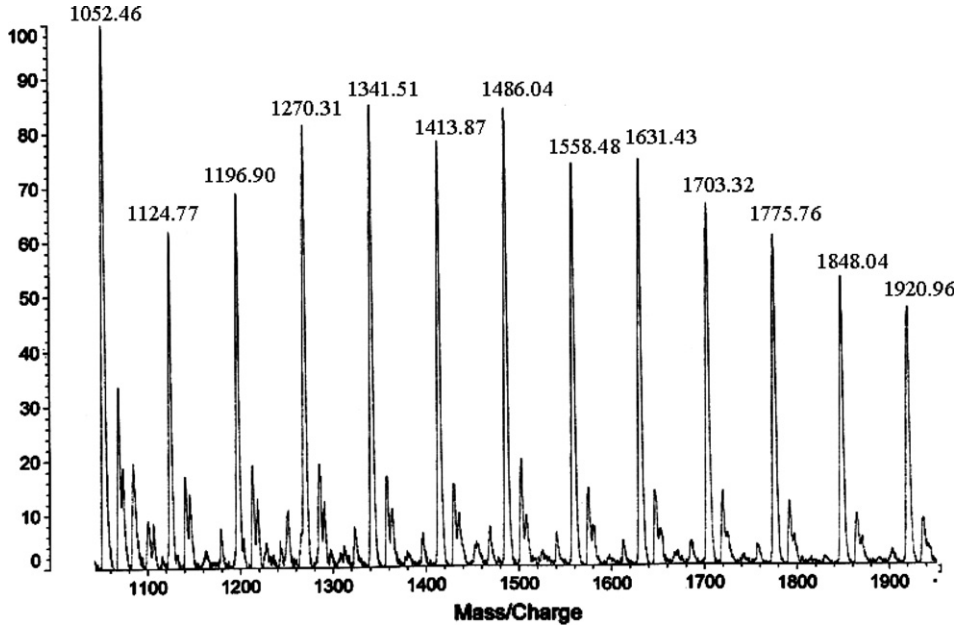


Fig. 7. A zoomed MALDI-TOF MS spectrum of the polylactide polymer.

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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-

2-ylidene]$_2$Ag}$^+$Cl$^-$ **1b**, and [1-(*i*-propyl)-3-(benzyl)imidazol-2-ylidene]AgCl **2b**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.12.022.

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