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A Cationic (N-Heterocyclic carbene)silver Complex as Catalyst for Bulk Ring-Opening Polymerization of L-Lactides

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Synthetic, theoretical, and catalysis studies of a cationic functionalized N-heterocyclic carbene complex of silver, namely [{1-isopropyl-3-(*N*-phenylacetamido)imidazol-2-ylidene}$_2$-Ag]$^+$Cl$^-$ (**1b**), is reported. Specifically, **1b** was synthesized by the reaction of 1-isopropyl-3-(*N*-phenylacetamido)imidazolium chloride (**1a**) with Ag_2O in 64 % yield; **1a** was synthesized by the alkylation reaction of 1-isopropylimidazole with *N*-phenyl chloroacetamide in 90 % yield. The molecular structure of **1b** was determined by X-ray diffraction studies and was found to be active for polymerization of L-lactide at elevated temperatures under solvent-free melt conditions to give polylactide of moderate molecular weight with narrow molecular weight distribution. Density functional theory studies of the cationic species **2b**, derived from NHC silver complex **1b**, were employed to obtain an understanding of the structure, bonding, and electronic features of the molecule. Bonding in complex **2b** has been probed with the help of charge decomposition analysis (CDA), the atoms in molecules (AIM) approach as well as natural bond orbital (NBO) methods. The Ag–NHC bond has been found to be more covalent with NHC acting as an effective σ-donor. The π-backbonding from the metal atom to the ligand was found to be negligible. It has been noticed that the imidazole rings remain nearly orthogonal with respect to each other, in contrast to the experimental geometry. Intramolecular hydrogen bonds as well as Ag···O interaction involving the carbonyl oxygen atoms have been identified as additional stabilizing factors contributing towards the lower energy conformer of **2b** compared to the corresponding planar geometry.

Introduction

Ever since the first successful isolation of a stable singlet carbene by Arduengo,[1] there has been phenomenal growth in the field of N-heterocyclic carbene (NHC) chemistry.[2] As a consequence, the N-heterocyclic carbenes have found wide-spread application in chemical catalysis with new catalysts being discovered recently.[3] The growth in NHC chemistry has made a profound impact, particularly in the field of organometallic catalysis, with the NHC-based catalysts exhibiting superior performance over the traditional catalysts in many important transformations. For example, it is now a well-established fact that Grubbs' second-generation ROMP catalyst bearing NHC exhibits better efficiency over the original phosphane-based ruthenium catalyst, $(PCy_3)_2(Cl)_2Ru{=}CHPh$.[4–6] Not surprisingly, the trendy NHCs are fast replacing the phosphanes and are gradually emerging as the designer's choice of ligand in organometallic catalysis. Remarkably, the NHC transition metal complexes have exhibited catalytic activities for a truly impressive range of reactions covering the C–C coupling reaction,[7,8] olefin metathesis,[9] hydrogenation,[10,11] hydroformylation,[12] hydrosilylation,[13] CO/ethylene copolymerization,[14] and hydroboration[15] reactions to name a few. In addition to the newly found successes in organometallic catalysis, the NHCs have shown promise in organocatalysis as potent nucleophilic organic catalysts and are increasingly gaining popularity and acceptance in such roles. Recently, there have been several reports of organocatalysis by NHCs particularly in transesterification reactions[16] and in ring-opening lactide polymerization reactions.[17–19] Both the in-situ generated carbenes as well as the isolable stable singlet N-heterocyclic carbenes have been directly employed in these organocatalysis reactions.

The mainstay of N-heterocyclic carbene chemistry has been its silver complexes, which played an important role in the development of the field of NHCs.[20] The interest in NHC silver complexes is primarily due to it being an effec-

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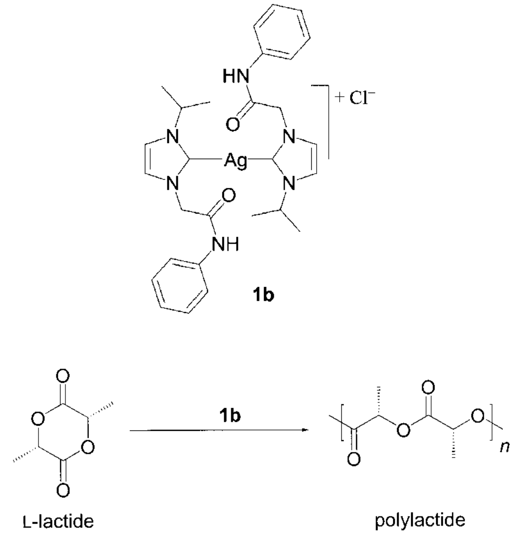
tive transmetallating agent, a property which is being extensively used for synthesizing other desired transition metal complexes. Lin[21] provided a commonly employed methodology for synthesizing the NHC silver complexes using Ag_2O, which represents by far the most popular route to these complexes. As an outcome of all the efforts toward designing new N-heterocyclic carbene systems, many silver complexes were synthesized and structurally characterized.[22–25] A notable feature of the silver complexes is their structural diversity in the solid state. For example, an NHC ligand with a sterically demanding mesityl substituent gave a neutral (NHC)AgCl-type complex with a 1:1 ligand/metal ratio, whereas the less bulky variant of the same ligand bearing a methyl substituent gave a cationic $(NHC)_2Ag^+$-type complex with a 2:1 ligand/metal ratio.[26]

Interestingly, apart from its exclusive use in transmetallation reactions, a few reports of the utility of NHC silver complexes in chemical catalysis have appeared lately. For instance, there have been reports of the NHC silver complexes exhibiting catalytic activity in ethyl diazoacetate (EDA) assisted carbene transfer reactions,[27] in transesterification reactions, and in ring-opening lactide polymerization reactions.[28] Thus, for the NHC silver complexes, the focus of research is gradually shifting from being solely used in transmetallation reactions to its applications in chemical catalysis, which has opened up a new frontier of research. As the catalytic applications of NHC silver complexes are relatively less explored, we became interested in investigating the catalytic properties of these complexes.

NHCs are often compared with the tertiary phosphane ligands because of their good σ-donating ability.[29] However, a closer scrutiny based on both theoretical[30–34] and experimental[35,36] results revealed that the NHCs are more strongly σ-donating than the phosphanes.[37] Another notable difference between the two is that the NHCs are generally easier to synthesize but harder to metallate while the reverse is true for phosphanes. In general, the success of NHCs can be attributed partly to their ease of synthetic accessibility and partly to the observed improved air, moisture,[38] and thermal stabilities[39] of the so-called NHC catalysts. The issue of improved stabilities of NHC metal complexes may be related to the nature of the metal–carbene (NHC) bond in these complexes and this requires a detailed theoretical study to gain a better understanding of these complexes. Alongside our main aim of designing new NHC silver complexes for applications in chemical catalysis, we became interested in carrying out a detailed theoretical analysis of our NHC silver complexes in order to gain insight into their reactivity pattern and catalytic potential. In this regard, we have recently communicated a detailed synthetic and theoretical study of a newly designed neutral monomeric NHC silver complex, [1-isopropyl-3-(2-*tert*-butyl-2-oxoethyl)imidazol-2-ylidene]AgCl.[40] In addition to the theoretical understanding, our interest is in the testing of these new NHC silver complexes for catalysis, particularly with regard to ring-opening polymerization (ROP) of L-lactides. Because of ecological reasons, the ROP of L-lactides is of current research interest. The polylactide polymers (PLAs), not only are biodegradable but they can also be generated from renewable resources (i.e. the L- and D-lactide monomers) by a corn fermentation process or from agricultural starch wastes.[41] Because of their good mechanical properties and biocompatibility, the PLAs have found wide utility in medical and pharmaceutical applications.[42,43] As the sequence of stereocenters in the polymer chain has a direct bearing on its mechanical properties, the ring-opening polymerization of cyclic lactides thus enjoys inherent advantage over α-olefin polymerizations that need intricate ligand design for control of polymer tacticity.

Herein, we report the synthesis and structural characterization of a silver complex, namely $[\{1\text{-isopropyl-3-}(N\text{-phenylacetamido})\text{imidazol-2-ylidene}\}_2Ag]^+Cl^-$ (**1b**), of a new functionalized N-heterocyclic carbene ligand along with a theoretical study. Furthermore, in this contribution we disclose that **1b** effectively catalyzes ring-opening polymerization of L-lactides (Scheme 1) at elevated temperatures under solvent-free melt conditions to give a polylactide polymer of moderate molecular weight with narrow molecular weight distribution.



Scheme 1.

Results and Discussion

Despite the phenomenal successes of NHCs and NHC metal complexes in chemical catalysis, the NHC silver complexes have so far shown only limited utility as catalysts. Recently, there was a report of NHC silver complexes catalyzing a carbene transfer reaction from ethyl diazoacetate to cyclohexane.[27] On another occasion, Waymouth and Hedrick reported NHC silver complexes as novel carbene delivery agents for ring-opening polymerization of L-lactides and for transesterification reactions.[28] These promising applications of NHC silver complexes in chemical catalysis have opened up a new frontier of research. As this area still remains largely unexplored, we became interested in designing novel N-heterocyclic carbene silver complexes and testing their catalytic utility in ring-opening polymerization of L-lactides.

Synthesis of [{1-Isopropyl-3-(*N*-phenylacetamido)imidazol-2-ylidene}$_2$Ag]$^+$Cl$^-$ (1b)

The N-heterocyclic carbene ligand precursor, 1-isopropyl-3-(*N*-phenylacetamido)imidazolium chloride (**1a**), was synthesized by the alkylation reaction of 1-isopropylimidazole with *N*-phenyl chloroacetamide in refluxing toluene in 90% yield (Scheme 2). Recently, Burgess[44] synthesized similar *N*-acetamidoimidazolium chloride derivatives, synthesized by analogous alkylation procedures, for preparing theNHC silver and palladium complexes. The NMR analysis of 1-isopropyl-3-(*N*-phenylacetamido)imidazolium chloride (**1a**) showed that the diagnostic imidazolium (N*CH*N) resonance appeared downfield-shifted at δ = 9.97 ppm in the ^{1}H NMR spectrum and at δ = 137.7 ppm in the ^{13}C NMR spectrum. As expected, the amide proton (CON*H*) resonance appeared downfield-shifted at δ = 11.37 ppm in the ^{1}H NMR spectrum, while the amide carbon (*C*ONH) resonance appeared at δ = 163.0 ppm in the ^{13}C NMR spectrum. The C–O stretching frequency of the amide group (CONH) appeared at 1697 cm^{-1} in the IR spectrum.

The silver complex, [{1-isopropyl-3-(*N*-phenylacetamido)-imidazol-2-ylidene}$_2$Ag]$^+$Cl$^-$ (**1b**), was prepared by the reaction of 1-isopropyl-3-(*N*-phenylacetamido)imidazolium chloride (**1a**) with Ag$_2$O in CH$_2$Cl$_2$ at room temperature in 64% yield (Scheme 2). Consistent with the formation of the silver complex, the (NC*H*N) resonance of the starting material was conspicuously absent at δ = 9.97 ppm in the ^{1}H NMR spectrum, while a new peak at δ = 179.5 ppm, corresponding to the silver-bound carbene (N*C*N) resonance, was observed in the ^{13}C NMR spectrum. The (*C*ONH) resonance appeared at δ = 165.0 ppm in the ^{13}C NMR spectrum. The carbonyl peak (ν_{CO}) of the amide moiety (CONH) appeared at 1694 cm^{-1} in the IR spectrum. The electrospray mass analysis gave a 100% abundance peak at *m*/*z* = 593 corresponding to the cationic [{1-isopropyl-3-(*N*-phenylacetamido)imidazol-2-ylidene}$_2$Ag]$^+$ fragment.

The molecular structure of [{1-isopropyl-3-(*N*-phenylacetamido)imidazol-2-ylidene}$_2$Ag]$^+$Cl$^-$ (**1b**) was determined by X-ray diffraction (Figure 1). In the complex, two [{1-isopropyl-3-(*N*-phenylacetamido)imidazol-2-ylidene}] ligands are found to be bound to the metal center. It is noteworthy that for a related NHC ligand, 1-isopropyl-3-(2-*tert*-butyl-2-oxoethyl)imidazolin-2-ylidene, a neutral monomeric complex [1-isopropyl-3-(2-*tert*-butyl-2-oxoethyl)-imidazolin-2-ylidene]AgCl[40] bearing a 1:1 ligand/metal ratio was obtained under analogous reaction conditions unlike the cationic 2:1 ligand/metal ratio observed in the present case. Köhler et al.[45] have recently demonstrated that for the same ligand both the cationic 2:1 NHC/metal complex and the neutral 1:1 NHC/metal complex could be isolated upon changing the polarity of the reaction medium. For example, the reaction in THF gave a neutral 1:1 NHC/metal complex of the type [(saturated NHC)AgCl] while the same in highly polar water gave a 2:1 NHC/metal complex of the type [(saturated NHC)$_2$Ag]$^+$BF$_4^-$.

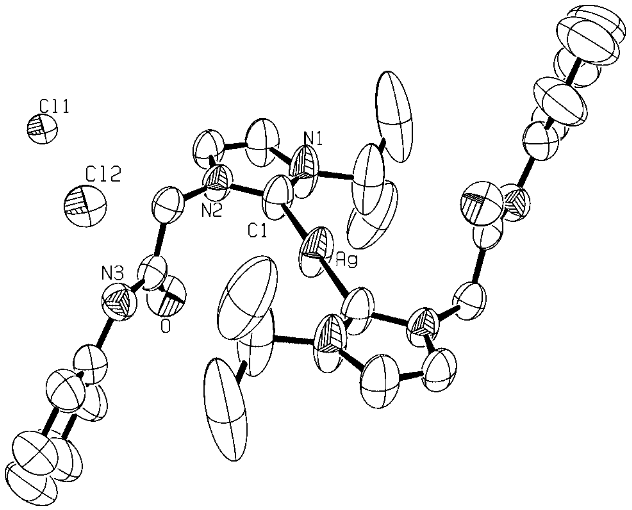
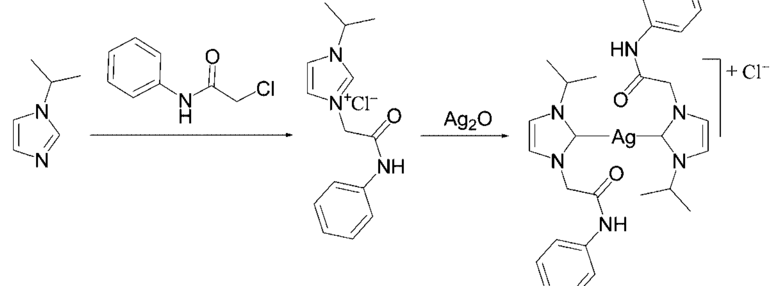


Figure 1. ORTEP of **1b**. The Cl$^-$ ion is disordered with Cl1 having 1/3 occupancy and Cl2 having 2/3 occupancy. Selected bond lengths [Å] and angles [°]: Ag–C(1) 2.085(3), N(1)–C(1) 1.350(4), N(1)–C(2) 1.379(4), C(1)–Ag–C(1) 180.000(1), N(2)–C(1)–N(1) 104.0(2), N(2)–C(1)–Ag 124.7(2), N(1)–C(1)–Ag 131.3(2).

Another notable feature of the **1b** structure is that the two imidazolyl rings surrounding the silver atom are coplanar. The isopropyl and the *N*-phenylacetamide substituents on the imidazole rings are at a *trans* disposition to each other presumably for steric reasons. The coordination geometry around the silver atom is linear [$\angle C_{carb}$–Ag–C_{carb} angle is 180.0(1)°] and is consistent with the preferred linear

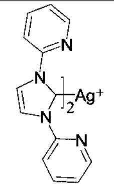
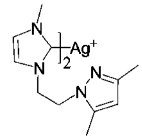
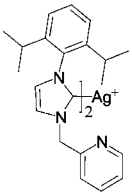
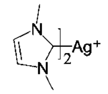
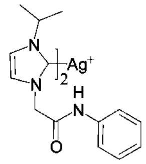


1a **1b**

Scheme 2.

geometry exhibited by two-coordinate Ag^I complexes having d^{10} configuration.[46] The chloride anion is disordered in the structure with Cl2 having 2/3 occupancy while Cl1 has 1/3 occupancy. The $Ag–C_{carb}$ bond length of 2.085(3) Å more closely resembles a single bond, being slightly shorter than the sum of the covalent radii of silver and carbon (2.111 Å)[47] and also falls well within the observed range of $Ag–C_{carb}$ bond lengths of other analogous complexes (Table 1). Furthermore, the $\angle(N–C_{carb}–N)$ angle of 104.0(2)° in **1b** is consistent with that observed for other analogous complexes (Table 1).

Table 1. Selected metrical data for some $[(N\text{-}R^1\text{-}N'\text{-}R^2\text{-imidazol-2-ylidene})_2Ag]^+$-type complexes.

Complexes	$d(C_{carb}–Ag)$/ [Å]	$\angle(N–C_{carb}–N)$/ [°]	$\angle(C_{carb}–Ag–C_{carb})$/ [°]	Ref.
	2.117(5) 2.106(6)	103.6(5) 103.5(5)	176.8(2)	[24]
	2.092(10) 2.088(11)	103.9(9) 105.0(9)	179.5(4)	[26]
	2.069(5) 2.074(5)	102.7(4)	175.90(19)	[77]
	2.096(6)[a] 2.084(5)[b]	105.3(6)[a] 104.6(5)[b]	180.0(4)[a] 180.0[b]	[78]
	2.085(3)	104.0(2)	180.0(1)	this work

[a] Counter anion is $AgCl_2^-$. [b] Counter anion is $AgBr_2^-$.

Important is the comparison of the structure of **1b** with a related $[(\text{saturated NHC})_2Ag]^+$ counterpart. For example, in an analogous saturated NHC silver complex, bis[(4*R*,5*S*)-4,5-diallyl-1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydro-3*H*-imidazolin-2-ylidene]silver(I) tetrafluoroborate,[45] the $\angle(N–C_{carb}–N)$ angle of 109.0(4)° is larger than the corresponding value of 104.0(2)° observed in the case of **1b** and this is presumably due to the differences in their respective N-heterocyclic ring geometries. The $Ag–C_{carb}$ bond lengths [2.082(4) and 2.087(4) Å] in bis[(4*R*,5*S*)-4,5-diallyl-1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydro-3*H*-imidazolin-2-ylidene]silver(I) tetrafluoroborate, however, compare well with the corresponding values of 2.085(3) Å observed in complex **1b**.

Density Funtional Theory Studies

Electronic structure calculations using the density functional theory were performed on the $[\{1\text{-isopropyl-3-}(N\text{-phenylacetamido})\text{imidazol-2-ylidene}\}_2Ag]^+$ cationic complex (**2b**) in order to gain further insights into structure and bonding. We used the B3LYP/SDD,6-31G* level of theory. Two major conformers differing in energy by about 2.66 kcal/mol were identified.[48] In the lower energy conformer the imidazole rings were found to remain nearly orthogonal to each other. In an earlier study by Frenking and co-workers on a series of unfunctionalized $(NHC)_2Ag^+$ complexes, the energy difference between such conformers was reported to be of the order of 5 kcal/mol with only a negligible barrier to interconversion.[33] A close inspection of the optimized structure with that obtained through X-ray crystallography revealed interesting facts. In the experimental structure, where the imidazole rings are coplanar, it appears that there is an obvious intermolecular hydrogen bonding interaction involving olefinic hydrogen atoms (C8–C10) from the imidazole unit with that of the carbonyl O atom from the functional side-arm of the neighboring NHC silver molecule.[49] Furthermore, additional intramolecular stabilization interactions were noticed in the nonplanar conformer rather than in the planar one (vide infra).

In general, agreement between computed and experimental geometrical parameters was found to be quite good (Table 2). Calculated structural parameters for the unbound carbene, in its singlet ground state, are indicated in Figure 2. It can be seen that the bond lengths in the imidazole ring do not undergo any major change, except for the $\angle(N–C_{carb}–N)$ angle, which shows a modest widening by about 1.8°. Since NHCs are known to act as efficient σ-donors through the carbenic carbon atom, one can expect only a minimal geometric distortion as predicted by the computed geometries in Figure 2.

The σ-donation increases the electron deficiency on the C_{carb} atom and thus facilitates a better $N\rightarrow C_{carb}$ π-donation. We have found an effective delocalization of the nitrogen lone pair electrons into the adjacent C–N bond with the help of natural bond orbital (NBO) analysis. Such delocalizations are responsible for shorter C–N distances in complex **2b** compared to that of the unbound carbene.[50] The computed natural population on C7 (and C42) revealed that the pπ atomic orbital is substantially more populated (1.14 e) in the complex **2b** than in the unbound singlet ground state (0.83 e).[51] The NPA charges on the imidazole nitrogen atoms were found to be increasingly positive upon complexation while the charges on the C_{carb} atoms remain unchanged. Similar observations on related systems have been made earlier and independently by Frenking[31] and Scherer.[32]

In order to gain better insight into the nature of the chemical bonding we carried out charge decomposition analysis (CDA) using the B3LYP wave function. CDA has been known to be a useful tool in analyzing the extent of back-bonding in organometallic systems.[52] The CDA results in **2b** show a significant $C_{carb}\rightarrow Ag$ σ-donation (*d* =

Table 2. Comparison between selected distances [Å] and angles [°] in **1b** (X-ray structure) and **2b** (computed structure).

Parameter[a]	Exp.	Calcd.	Parameter	Exp.	Calcd.
Ag–C1	2.085(3)	2.109	C2–C3	1.328(5)	1.357
Ag–C1	2.085(3)	2.109	C4–C5	1.507(4)	1.546
N1–C1	1.350(4)	1.356	C11–C12	1.473(10)	1.532
N1–C2	1.379(4)	1.388	C11–C13	1.526(12)	1.532
N1–C11	1.502(5)	1.484	C21–C22	1.378(6)	1.401
N2–C1	1.350(4)	1.363	C21–C26	1.388(6)	1.402
N2–C3	1.384(4)	1.388	C22–C23	1.390(7)	1.396
N2–C4	1.445(4)	1.453	C23–C24	1.369(12)	1.395
N3–C5	1.365(4)	1.361	C24–C25	1.326(11)	1.396
N3–C21	1.427(4)	1.422	C25–C26	1.383(7)	1.392
C5–O	1.206(3)	1.227	Ag–O	3.980	3.262
			Ag–O	3.980	3.220
C1–Ag–C1	180.0(1)	172.5	O–C5–N3	125.1(3)	125.6
C1–N1–C2	110.9(3)	111.1	O–C5–C4	122.7(3)	120.8
C1–N1–C11	124.5(3)	124.3	N3–C5–C4	112.2(3)	113.6
C2–N1–C11	124.4(3)	124.6	C12–C11–N1	111.5(5)	110.7
C1–N2–C3	111.5(2)	111.1	C12–C11–C13	113.6(6)	113.3
C1–N2–C4	123.3(2)	124.3	N1–C11–C13	106.8(6)	110.4
C3–N2–C4	125.1(2)	124.5	C22–C21–C26	120.9(4)	120.0
C5–N3–C21	127.5(3)	129.2	C22–C21–N3	122.9(4)	123.1
N2–C1–N1	104.0(2)	104.6	C26–C21–N3	116.1(4)	116.8
N2–C1–Ag	124.7(2)	125.5	C21–C22–C23	117.6(6)	119.1
N1–C1–Ag	131.3(2)	128.4	C24–C23–C22	120.7(7)	121.2
C3–C2–N1	107.5(3)	106.9	C25–C24–C23	121.3(6)	119.4
C2–C3–N2	106.2(3)	106.4	C24–C25–C26	120.4(7)	120.2
N2–C4–C5	112.3(2)	112.4	C25–C26–C21	119.0(5)	120.2
N3–C7–C42–N38	0.85	77.94			

[a] The calculated structure does not include chloride ions and thus refers to the cationic complex **2b**. The atom numbering is therefore different from that in the cif file. For optimized coordinates, please refer to the Supporting Information.

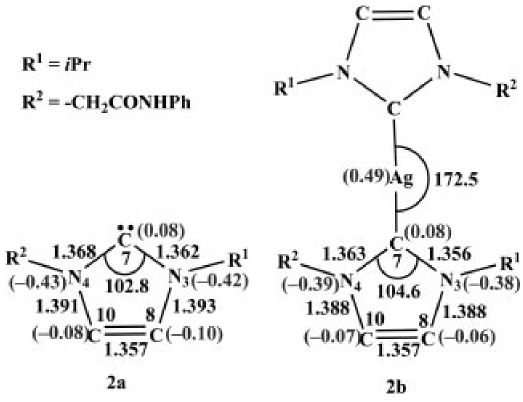


Figure 2. Calculated key structural parameters of free carbene **2a** and the complex **2b**. NPA charges are given in parentheses.

0.656) and a very negligible C_{carb}←Ag back-donation (*b* = 0.053). A *d*/*b* ratio of 11.4 and 12.4 between Ag and the two NHC ligands evidently underscores the ability of NHC to function as an effective σ-donor ligand (see Table S3, Supporting Information). The structural parameters as well as population analysis presented in the previous sections are in concurrence with the CDA result that the back-bonding in **2b** is not very significant.

Analysis of the topological features of electron density offers valuable information pertaining to the nature of chemical bonding in molecules. Bader's theory of "Atoms In Molecules" (AIM) has widely been applied to examine interesting bonding situations.[53] Topological properties such as the density at the bond critical point (ρ_{bc}), Laplacian of electron density ($\nabla^2\rho_{bc}$) as well as the total energy density (*H*) are analyzed. A covalent interaction is characterized by a negative value for $\nabla^2\rho_{bc}$ as well as $H < 0$. The value of *H* is widely accepted as a better descriptor in determining the nature of interaction than the $\nabla^2\rho_{bc}$ value.[54] Inspection of computed topological features in the present system, as given in Table 3, reveals that the C_{carb}–Ag bond is covalent. For **2b**, values of Laplacian $\nabla^2\rho_{bc}$ as well as total energy density H_{bc} for the C_{carb}–Ag bonds were found to be –0.07 and –4.5 au, respectively. These values suggest that the C_{carb}–Ag bond is more covalent than ionic. Further, the computed NPA charges on Ag (+0.49) and C_{carb} (+0.08) are consistent with this observation (Figure 2). All other bonds such as C–N and C=C of the imidazole ring were found to be more covalent, as expected. Another noticeable feature emerging from the AIM analysis pertains to the π-bonds in the imidazole rings. The characteristic ellipticity associated with π-bonds is clearly reflected in the computed ε values that are found to be as high as 0.4 for the C=C bonds. The C_{carb}–Ag bond exhibits the lowest value for ellipticity, again indicating lack of π-bonding interactions. Interestingly, the ε values for the N3–C8 and N4–C10 (also N38–C43 and N39–C45) bonds suggest a moderate π-character, presumably arising due to an N→C_{carb} π-donation into the carbene π-type orbital.

Table 3. Summary of the AIM analysis performed on **2b** at the AIM//B3LYP/SDD,6-31G* level of theory.[a]

Bond	ρ_{bc} [e·Å^{-3}]	$\nabla^2\rho_{bc}$ [e·Å^{-5}]	ε	H_{bc}
Ag1–C7	0.102	–0.071	0.04	–4.49
C7–N3	0.320	0.158	0.09	–14.68
C7–N4	0.314	0.150	0.06	–14.41
N3–C8	0.301	0.187	0.16	–12.52
N4–C10	0.299	0.173	0.17	–12.47
C8–C10	0.337	0.243	0.39	–13.19
Ag1–C42	0.102	–0.071	0.04	–4.50
C42–N38	0.320	0.158	0.08	–14.53
C42–N39	0.315	0.154	0.04	–14.56
N38–C43	0.301	0.186	0.17	–12.28
N39–C45	0.300	0.177	0.17	–12.61
C45–C43	0.337	0.243	0.39	–13.09
O2···H49	0.008	–0.007	0.13	–0.30
O37···H21	0.003	–0.003	0.13	–0.12
Ag1···O2	0.009	–0.006	0.50	–0.38
Ag1···O37	0.010	–0.007	0.61	–0.40

[a] See Figure 3 for atom numbers.

As mentioned earlier, the geometry of the lowest energy conformer has a nearly orthogonal disposition of the imidazole rings. In the optimized geometry, there are two interesting intramolecular hydrogen bonds, rendering additional stabilization as shown in Figure 3. The first one is between the hydrogen atom of the tethered isopropyl group of one imidazole ring with the carbonyl group of the other imidazole ring (2.91 Å, ρ = 0.003). The second hydrogen bonding interaction is between the methylene hydrogen atom and the carbonyl group attached to another imidazole ring (2.49 Å, ρ = 0.008). These intramolecular interactions were identified correctly by the AIM calculations, where the densities at the bond critical points (ρ_{bc}) were found to fall within the hydrogen bonding range.[55] There are also additional interactions between the carbonyl oxygen atoms from both imidazole rings and the silver atom (3.26 Å, ρ = 0.01). These interactions together could be responsible for the near orthogonal orientations of the imidazole rings in the gas-phase-optimized geometry.

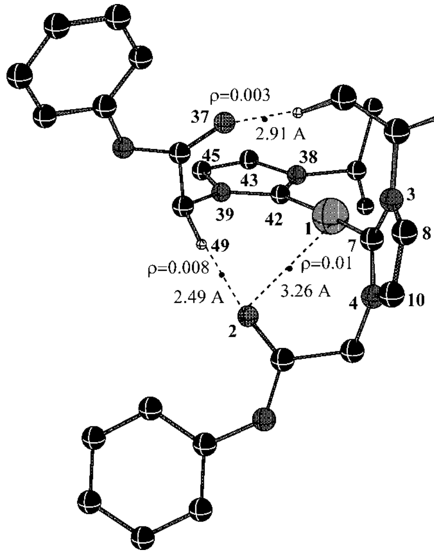


Figure 3. The B3LYP/SDD,6-31G* optimized geometry of **2b** showing weak intramolecular interactions and the corresponding densities at the bond critical points (ρ_{bc}) computed using the AIM theory (only selected hydrogen atoms are shown for clarity).

Polymerization Studies

The silver complex [{1-isopropyl-3-(*N*-phenylacetamido)-imidazol-2-ylidene}$_2$Ag]$^+$Cl$^-$ (**1b**) was found to be an active catalyst for ring-opening polymerization of L-lactides carried out at elevated temperatures under melt conditions in the absence of any solvent.[56] For example, a typical run involved heating of L-lactide and [{1-isopropyl-3-(*N*-phenylacetamido)imidazol-2-ylidene}$_2$Ag]$^+$Cl$^-$ (**1b**) in a sealed vessel under vacuum at designated temperatures for stipulated periods 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) at 160 °C showed that the maximum molecular weight (M_w = 12.2·10^3, Entry 2, Table 4) was obtained at a 100:1 monomer/catalyst ratio. The observed polydispersity index (PDI) was in the range 1.22–1.47. Consistent with the observed molecular weight distributions, the time dependence studies (Entries 2 and 7–9, Table 4) showed no correlation of the observed molecular weight with time thereby ruling out the possibility of a true living polymerization process. The temperature dependence study carried out in the range 100–180 °C[57] (Entries 2 and 10–13, Table 4) showed that the molecular weight of the polymer decreased with an increase in temperature, with the highest molecular weight observed at 100 °C (13.5·10^3, Entry 10, Table 4). The decrease in molecular weight with the increase in temperature may be caused by thermal depolymerization as well as an enhanced transesterification reaction occurring at elevated temperatures. In this regard, Liao et al.[56a] and Albertsson and Varma[42] have recently reported a similar decrease in polymer molecular weight with temperature, arising from thermal depolymerization and accelerated transesterification reactions.

Table 4. Melt polymerization of L-lactide by **1b**.

Entry	L-Lactide/**1b**	Temp. [°C]	Time [h]	M_w	M_w/M_n	Conv. [%]
1	50	160	4	8.1·10^3	1.37	90
2	100	160	4	12.2·10^3	1.40	98
3	250	160	4	9.2·10^3	1.41	78
4	500	160	4	6.6·10^3	1.28	46
5	750	160	4	5.3·10^3	1.23	35
6	1000	160	4	4.9·10^3	1.22	36
7	100	160	3	11.0·10^3	1.41	79
8	100	160	1.5	11.4·10^3	1.47	78
9	100	160	0.5	10.6·10^3	1.29	65
10	100	100	4	13.5·10^3	1.27	84
11	100	120	4	11.9·10^3	1.46	81
12	100	140	4	11.2·10^3	1.36	91
13	100	180	4	8.3·10^3	1.35	94

In order to gain insight into the nature of the active species in the catalytic cycle, the thermal stability of [{1-isopropyl-3-(*N*-phenylacetamido)imidazol-2-ylidene}$_2$Ag]$^+$Cl$^-$ (**1b**) was studied by a thermogravimetric analysis (TGA) experiment (Figure 4). Compound **1b** was found to be stable up to 180 °C above which drastic mass loss started to occur presumably caused by the generation of the carbene. Consistent with the TGA results, the attempts to trap the in-situ generated carbene from the thermal decomposition of **1b** with CS$_2$, carried out at a much lower temperature (60 °C), proved to be unsuccessful.[58]

In this regard, it is worth mentioning that Waymouth and Hedrick[28] have recently proposed a mechanism invoking in-situ generation of carbene from similar NHC silver complexes for the ring-opening polymerization of L-lactides. However, for sterically demanding NHC silver precatalysts that were thermally sufficiently stable and did not dissociate to generate carbenes at the polymerization temperature, the possibility of the silver complexes directly mediating the polymerization was also suggested to exist. A similar possibility of silver directly participating in the polymerization also exists in the case of **1b** and is in agreement with the TGA experiment that showed the complex did not undergo significant mass loss below 180 °C while the polymerizations were carried out at a lower temperature range (100–180 °C). Such direct metal-mediated polymerization would lead to the capping of polymer chain ends with NHC fragments (Scheme 3) and indeed, the characteristic resonances of the NHC moieties could be seen in both the ^{1}H NMR and ^{13}C NMR spectra of the polymer.[59] The MALDI spectrometric analysis of the polymer also confirms the presence of NHC chain end groups.[60] In this re-

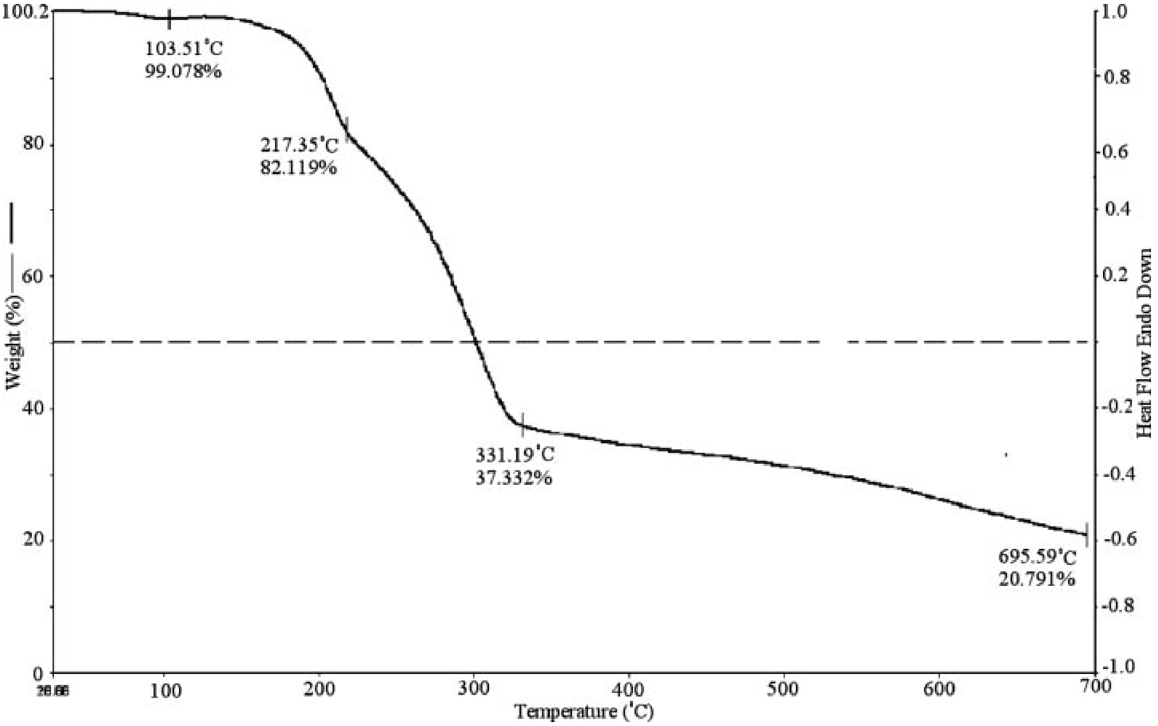
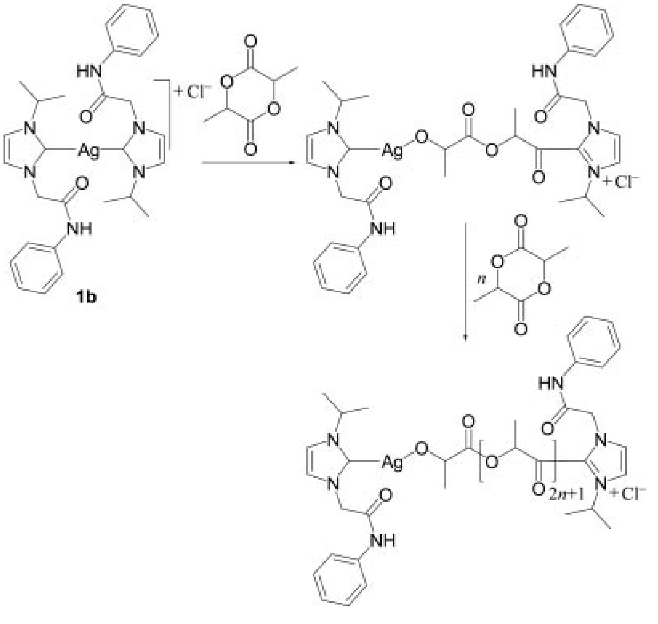


Figure 4. Thermogravimetric analysis of **1b** as a function of temperature.

gard it is worth mentioning that a (NHC)Y^{III} complex has been recently reported to exhibit metal-mediated coordination insertion polymerization of lactides.[61] However, the other possibility that minute amounts of carbene, generated during the thermal decomposition of **1b**, are responsible for the polymerization also cannot be ruled out completely. Currently, detailed mechanistic studies are underway to establish the identity of the active species responsible for the catalysis.



Scheme 3.

Conclusions

In summary, a new functionalized N-heterocyclic carbene ligand precursor, 1-isopropyl-3-(*N*-phenylacetamido)-imidazolium chloride (**1a**), was synthesized by the alkylation of 1-iso-proplyimidazole with *N*-phenyl chloroacetamide. The silver complex, [{1-isopropyl-3-(*N*-phenylacetamido)imidazol-2-ylidene}$_2$Ag]$^+$Cl$^-$ (**1b**), was synthesized by treatment of **1a** with Ag_2O. Complex **1b** has been structurally characterized by X-ray diffraction studies and was found to effectively initiate polymerization of L-lactide at higher temperatures under solvent-free melt conditions producing polylactide polymers with a narrow molecular weight distribution. Density functional theory studies and post-wave function analysis were able to establish that the functionalized NHC was acting as an effective σ-donor. Weak intramolecular stabilizing interactions were identified as responsible factors in contributing to the perpendicular dispositions of the imidazole rings, compared to the coplanar arrangement as revealed by the X-ray crystallographic study.

Experimental Section

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. Ag_2O was purchased from SD-Fine Chemicals (India) and used without any further purification. L-Lactide was purchased from Sigma Aldrich (Germany) and was subjected to polymerization without further purification. L-Lactide was stored at 4 °C as supplied, to avoid the formation of lactyl lactate. *N*-Phenyl chloroacetamide[62] and 1-

isopropylimidazole[63] were synthesized according to literature procedures. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded with a Varian 400 MHz NMR spectrometer. ^{1}H NMR peaks were labeled as singlet (s), doublet (d), triplet (t), and septet (sept). Infrared spectra were recorded with a Perkin–Elmer Spectrum One FT-IR spectrometer. Mass spectrometry measurements were carried out with a Micromass Q-Tof spectrometer. The thermal analysis was performed in N_2 (flow rate: 10 mL/min) with a heating rate of 10 °C/min using a Perkin–Elmer Pyris thermal analyzer. X-ray diffraction data were collected with a Bruker P4 diffractometer equipped with a SMART CCD detector, and crystal data collection and refinement parameters are summarized in Table 5. The structures were solved by direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 6.10). CCDC-297479 (for compound **1b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The polymer molecular weights were determined using a Waters GPC (Waters 2414 RI Detector) with PL-gel, a 5 µ-mixed-D (2×300 mm) column, with polystyrene standards in chloroform, and a covered molecular weight range of 140 to $4{\cdot}10^5$. The MALDI-TOF MS measurements were performed with a Voyager-DE STR Biospectrometry Workstation mass spectrometer. A 19 kV accelerating voltage was used with pulsed ion extraction (PIE). The positive ions were detected using the reflection mode (20 kV). A nitrogen laser (337 nm, 1 ns pulse width operating at 4 Hz) was used to produce laser desorption and 50 shots were scanned per spectra. The instrument was calibrated with four standards [Des-Arg 1, Bradykinn and Angiotensin-1, and ACTH (1-17)] by means of linear calibration. The sample was prepared with an α-cyanohydroxy cinnamic acid (CHC) matrix (10 mg /mL). A 1 µL analyte solution (10 mg/mL) was deposited onto the sample plate (stainless steel) and allowed to air-dry. Subsequently, a 1 µL matrix solution (50:50 v/v, CHC/acetonitrile) was added to the analyte.

Table 5. X-ray crystallographic data for **1b**.

Lattice	rhombohedral
Empirical formula	$C_{28}H_{34}AgClN_6O_2$
Formula mass	629.93
Space group	$R\bar{3}$
a [Å]	18.2066(8)
b [Å]	18.2066(8)
c [Å]	28.102(2)
α [°]	90
β [°]	90
γ [°]	120
V [Å^3]	8067.3(8)
Z	9
Temperature [K]	243(2)
Radiation, λ [Å]	0.71073
ρ(calcd.) [g·cm^{-3}]	1.167
μ(Mo-K_α) [mm^{-1}]	0.665
$\theta_{\max}$ [°]	28.30
No. of data	4167
No. of parameters	175
R_1	0.0461
wR_2	0.1326
GOF	1.030

Synthesis of 1-Isopropyl-3-(*N*-phenylacetamido)imidazolium Chloride (1a): *N*-Phenyl chloroacetamide (2.01 g, 11.8 mmol) and 1-isopropylimidazole (1.30 g, 11.8 mmol) were added to toluene (ca. 10 mL) and heated at 140 °C for 12 h during which a brown precipitate was formed. The precipitate was collected by filtration and washed with hot hexane (ca. 8 mL) and dried under vacuum to give the product as a brown crystalline solid (2.98 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 11.37 (s, 1 H, N*H*), 9.97 (s, 1 H, NC*H*N), 7.71 (d, $^3J_{H,H}$ = 7 Hz, 2 H, *o*-C_6H_5), 7.59 (s, 1 H, NC*H*CHN), 7.28 (s, 1 H, NCHC*H*N), 7.22 (t, $^3J_{H,H}$ = 7 Hz, 2 H, *m*-C_6H_5), 7.03 (t, $^3J_{H,H}$ = 7 Hz, 1 H, *p*-C_6H_5), 5.60 (s, 2 H, CH_2), 4.63 [sept, $^3J_{H,H}$ = 6 Hz, 1 H, C*H*(CH_3)$_2$], 1.52 [d, $^3J_{H,H}$ = 7 Hz, 6 H, CH(CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ = 163.0 (*C*O), 137.7 (N*C*N), 135.8 (*ipso*-C_6H_5), 128.4 (*o*-C_6H_5), 124.0 (N*C*HCHN), 123.7 (NCH*C*HN), 119.8 (*p*-C_6H_5), 118.9 (*m*-C_6H_5), 52.9 (CH_2), 51.9 [*C*(CH_3)$_2$], 22.6 [C(CH_3)$_2$] ppm. IR (KBr pellet): $\tilde{\nu}$ = 1697 (s) (ν_{CO}) cm^{-1}. LRMS (ES): m/z (%) = 244 (100) [NHC ligand]$^+$. HRMS (ES): calcd. for [NHC ligand]$^+$ 244.1450, found 244.1455.

Synthesis of [{1-Isopropyl-3-(*N*-phenylacetamido)imidazol-2-ylidene}$_2$Ag]$^+$Cl$^-$ (1b): The reaction was carried out under exclusion of light. A mixture of **1a** (1.81 g, 6.47 mmol) and Ag_2O (0.748 g, 3.23 mmol) in dichloromethane (ca. 25 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 (1.30 g, 64%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 11 (br., 1 H, N*H*), 7.78 (d, $^3J_{H,H}$ = 8 Hz, 2 H, *o*-C_6H_5), 7.29 (s, 1 H, NC*H*CHN), 7.20 (t, $^3J_{H,H}$ = 8 Hz, 2 H, *m*-C_6H_5), 7.02 (t, $^3J_{H,H}$ = 8 Hz, 1 H, *p*-C_6H_5), 6.99 (s, 1 H, NCHC*H*N), 5.27 (s, 2 H, CH_2), 4.60 [sept, $^3J_{H,H}$ = 7 Hz, 1 H, C*H*(CH_3)$_2$], 1.42 [d, $^3J_{H,H}$ = 7 Hz, 6 H, CH(CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ = 179.5 (N*C*N), 165.0 (*C*O), 138.0 (*ipso*-C_6H_5), 128.1 (*o*-C_6H_5), 123.5 (N*C*HCHN), 122.6 (NCH*C*HN), 119.5 (*p*-C_6H_5), 116.4 (*m*-C_6H_5), 54.4 [*C*(CH_3)$_2$], 53.5 (CH_2), 23.2 [C(CH_3)$_2$] ppm. IR (KBr pellet): $\tilde{\nu}$ = 1694 (s) (ν_{CO}) cm^{-1}. LRMS (ES): m/z (%) = 593 (100) [(NHC ligand)$_2$Ag]$^+$.

Computational Methods: The density functional theory calculations were performed on the [{1-isopropyl-3-(*N*-phenylacetamido)imidazol-2-ylidene}$_2$Ag]$^+$ cationic complex (**2b**) using the Gaussian98 suite of quantum chemical programs.[64] The Becke three-parameter exchange functional in conjunction with the Lee–Yang–Parr correlation functional (B3LYP) was employed in this study.[65,66] The Stuttgart-Dresden effective core potential (ECP), representing 19 core electrons, along with valence basis sets (SDD) was used for the silver atom.[67] All other atoms were treated with the 6-31G(d) basis set.[68] We will be designating the level of theory hereafter as B3LYP/SDD,6-31G*. Inspection of the metal–ligand donor–acceptor interactions was carried out using charge decomposition analysis (CDA).[69] CDA is a valuable tool for analyzing the interactions between molecular fragments in a quantitative fashion, with an emphasis on the electron donation.[70] The CDA calculations were performed with the program AOMIX using the B3LYP/SDD,6-31G* wave function.[71] Natural bond orbital analysis was performed using the NBO3.1 program as implemented in the Gaussian98 package.[72] Second-order perturbation energy analysis, natural charges,[73] and bond orders[74] for **2b** were calculated using the B3LYP wave function. The nature of the chemical bonding was further explored with Bader's "Atoms in Molecules" approach[75] using the AIM2000 program.[76]

Polymerization Experiments: Typical polymerization experiment: L-Lactide (1.01 g, 7.01 mmol) and **1b** (0.044 g, 0.070 mmol) were charged in an ampoule inside a glove box. The ampoule was taken out and put under vacuum at 50 °C for 15 min, after which the ampoule was sealed under vacuum and heated at 160 °C for 4 h. Under these conditions, the reaction mixture turned into a monomer melt in which polymerization occurred. Subsequently, the molten reactive polymer mixture was cooled by submerging the sealed ampoule into liquid nitrogen to stop the polymerization. The conversion of L-lactide monomer was determined using the size exclusion chromatography method. The analyses were performed on the crude reaction mixture, no precipitation was executed to avoid fractionation of the sample so as not to influence the results.

Supporting Information (see footnote on the first page of this article): Polymer characterization data, B3LYP-optimized coordinates for NPA data, and list of NBO delocalizations for **2b**.

Acknowledgments

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[49] See Figure S1 in the Supporting Information.
[50] Details of various delocalizations and the corresponding second-order perturbation energies obtained with NBO analysis are summarized in Table S1 in the Supporting Information.
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[59] It is noteworthy that the NHC end-groups were seen in the ^{1}H NMR and ^{13}C{^{1}H} NMR spectra of the polymer when analyzed directly from the melt as well as after dissolving in a minimum of dichloromethane and precipitating with hexane whereas no NHC resonances were observed when the precipitation of the polymer was done with methanol. See Figures S2 and S3 in the Supporting Information.
[60] A series of sodium (23 Da) cationized peaks of the polymers bearing NHC end groups can be recognized in the MALDI spectrum. See Figure S4 in Supporting Information. The mass (M_C) of the sodium cationized peak of the polymer bearing the (NHC)Ag (350 Da) and NHC (243 Da) end groups is given by $M_C = 72x + 350 + 243 + 23$ where x = number of repeat unit (72Da).
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