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First Example of a Gold(I) *N*-Heterocyclic-Carbene-Based Initiator for the Bulk Ring-Opening Polymerization of L-Lactide

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Synthesis, structure, and catalysis studies of two Au- and Ag-based initiators, namely, [3-(*N-tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene]AuCl (**1c**) and [3-(*N-tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene]AgCl (**1b**), for the bulk ring-opening polymerization of L-lactide are reported. Specifically, gold complex **1c** was obtained from silver complex **1b** by the transmetalation reaction with $(SMe_2)AuCl$. Silver complex **1b** was synthesized by the treatment of 3-(*N-tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazolium chloride (**1a**) with Ag_2O. Compound **1a** was synthesized directly from the reaction of *N-tert*-butyl-2-chloroacetamide, cyclohexene oxide, and imidazole. The molecular structures of **1a**, **1b**, and **1c** have been determined by X-ray diffraction studies. The formation of neutral monomeric complexes with linear geometries at the metal centers was observed for both **1b** and **1c**. The Au and Ag complexes **1c** and **1b** successfully catalyzed the bulk ring-opening polymerization of L-lactide at elevated temperatures under solvent-free melt conditions to produce moderate to low molecular weight polylactide polymers with narrow molecular weight distributions.

Introduction

The long-standing notion of gold being an expensive and unreactive coinage metal with limited utility is gradually changing. Various new applications of Au^I complexes in pharmaceuticals,[1] chemical vapor depositions,[2] and in homogeneous catalysis[3] have been recently reported. Compared to the other coinage metals (i.e. Cu and Ag), Au has seen relatively few applications and poses a formidable challenge in utility-oriented research. Quite significantly, a recent report detailed the use of a Au^I complex supported over a sterically demanding *N*-heterocyclic carbene (NHC) ligand as a catalyst for the ethyl diazoacetate-assisted carbene-transfer reaction;[3] this represents an important breakthrough in this field of chemistry and adds further promise to the use of gold in chemical catalysis. The growing utility of NHCs in homogeneous catalysis is now well-recognized, and a plethora of NHC-based catalysts have been developed in recent years for a wide variety of transformations, such as C–C coupling reactions,[4,5] olefin metatheses,[6] hydrogenations,[7,8] hydroformylations,[9] hydrosilylations,[10] CO-ethylene copolymerizations,[11] hydroboration[12] reactions, and so forth. Interestingly enough, despite the numerous NHC-transition metal complexes that exist, the Au–NHC complexes are surprisingly few in number and have seldomly been employed in catalysis.[13]

A growing number of new applications have appeared lately for the Ag^I–NHC counterparts however, and their catalytic utility has just begun to unfold.[14,15] Specifically, the Ag^I–NHC complexes have been found to be active catalysts for several chemical transformations, such as, ethyl diazoacetate (EDA)-assisted carbene-transfer reactions,[16] catalytic preparation of 1,2-bis(boronate) esters,[17] transesterification reactions, and ring-opening lactide polymerization reactions.[18] It is noteworthy that even though the applications of Ag^I–NHC complexes in chemical catalysis is a recent phenomenon, they are long-known for their use as transmetalation agents for the synthesis of other transition metal–NHC complexes.[14,15] Like its heavier congener, the Au analogue, biomedical applications, particularly with regard to antimicrobial activities, have recently been reported for Ag^I–NHC complexes.[19,20] Thus far, the popularity of Ag–NHC complexes can be ascribed to their broadly based applications, to their synthetic accessibility, and to their air and moisture stabilities, which make them user-friendly and hence convenient to handle.[14,15]

As the catalytic utility of Au–NHC complexes remains largely unexplored and that of the Ag–NHC complexes is just beginning to emerge, we became interested in the design of Au and Ag complexes for their potential application in homogeneous catalysis. In particular, we were interested in

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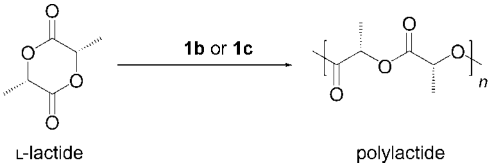
the design of Au–NHC and Ag–NHC based initiators for the ring-opening polymerization (ROP) of L-lactide. In this regard, we have recently reported a Ag–NHC complex as an initiator for the bulk ROP of L-lactide.[21] Although there exists a few reports on the use of Ag^I–NHC complexes for the ROP of L-lactides,[18,21] we are unaware of any such report in the case of the Au^I–NHC complexes.

Of late, the ROP of L-lactide has attracted considerable attention by virtue of its eco-friendliness. Not only is the polylactide polymer (PLA) biodegradable, but the lactide monomer can also be generated from renewable resources by a corn fermentation process or from agricultural starch wastes.[22,23] Because of their good mechanical properties and biocompatibility, PLAs have found wide utility in medical and pharmaceutical applications.[24,25] Various metals, such as Zn, Al, and Sn, have been extensively utilized for the synthesis of PLAs.[22a] The specific objective of our program is centered around the design of novel initiators for the bulk polymerization of L-lactides, which are often used for the large-scale production of PLAs. It is interesting to note that even though PLAs can be synthesized by both solution polymerization[26] and bulk polymerization,[27] solution polymerization suffers from certain disadvantages such as being susceptible to impurity levels and to various unwanted reactions, namely, racemization and transesterification, and hence is not conducive for the large-scale production of PLAs.[28] Our approach towards the design of initiators for bulk polymerization involved the utilization of functionalized NHCs as we rationalized that the presence of functional groups would enhance the solubility of the initiators in the monomer melt.

Here in this contribution, we disclose the first example of Au^I–NHC-based initiator **1c** along with Ag^I–NHC-based initiator **1b** for the bulk ROP of L-lactide (Figure 1). Specifically, both the gold and the silver complexes, namely, [3-(*N-tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene]AuCl (**1c**) and [3-(*N-tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene]AgCl (**1b**), effectively catalyze the ROP of L-lactide at elevated temperatures under solvent-free melt conditions to afford polylactide polymers of moderate to low molecular weights with narrow molecular weight distributions [Equation (1)]. We also disclose the synthesis and structural characterizations of both the Au (**1c**) and Ag (**1b**) complexes supported over a novel difunctionalized *N*-heterocyclic carbene ligand, 3-(*N-tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene.



(1)

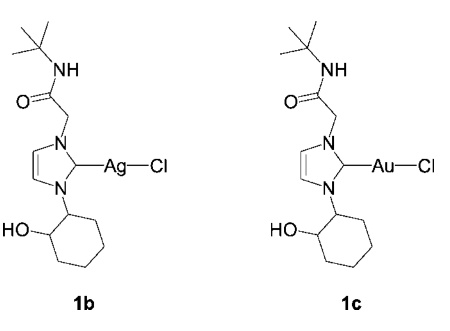
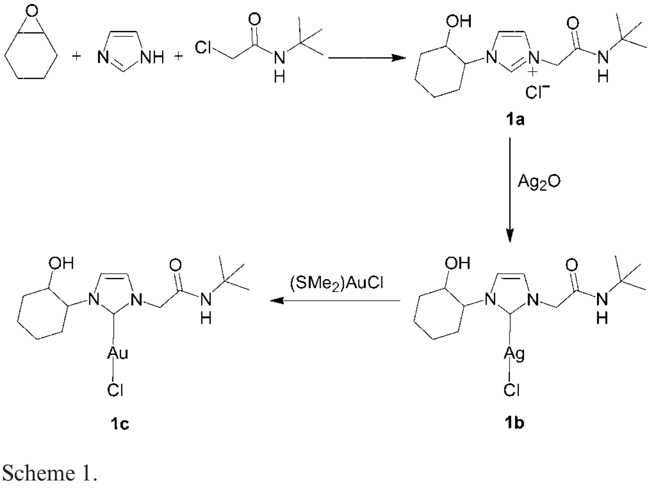


Figure 1. The complexes [3-(*N-tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene]AgCl (**1b**) and [3-(*N-tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene]AuCl (**1c**).

Results and Discussion

A difunctionalized *N*-heterocyclic carbene ligand, 3-(*N-tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene, with two functionalized imidazolyl *N*-substituents, a 2-hydroxycyclohexyl moiety and an *N-tert*-butylacetamido moiety, was synthesized by a modified procedure reported by Arnold and coworkers.[29] Specifically, the NHC precursor, 3-(*N-tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazolium chloride (**1a**), was obtained from the direct reaction of *N-tert*-butyl-2-chloroacetamide, cyclohexene oxide, and imidazole in 96% yield (Scheme 1). The formation of imidazolium salt **1a** was confirmed by the appearance of the diagnostic (NC*H*N) resonance at δ = 9.31 ppm in the ^{1}H NMR spectrum and the corresponding carbon resonance (N*C*HN) at δ = 136.3 ppm in the ^{13}C NMR spectrum. The most interesting aspect of the ^{1}H NMR spectrum is the diastereotopic nature of the two bridging methylene proton (-CH_2-) resonances which appear as two doublets at δ = 5.16 ppm and 4.96 ppm and display a geminal coupling between the two protons ($^2J_{H,H}$ = 15 Hz). For example, similar diastereotopic hydrogens for the bridging methylene moiety (-CH_2-) have been reported for Ir complexes with a 1-*n*-butyl-3-(2-pyridylmethyl)imidazol-2-ylidene ligand.[30] The carbonyl moiety (-*C*ONH-) appeared at δ = 163.8 ppm in the ^{13}C NMR spectrum and at 1671 cm^{-1} (ν_{co}) in the infrared spectrum. In the electrospray mass spectrum the 3-(*N-tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazolium cation appeared as a peak at *m*/*z* = 280 and was further substantiated by HRMS results.



Scheme 1.

The imidazolium halide salt **1a** has been structurally characterized by X-ray diffraction studies (Figure 2). The N1–C9 and N2–C9 bond lengths are 1.326(6) Å and 1.314(6) Å, respectively, and the N2–C9–N1 angle is 107.9(5)° for **1a** and is comparable with other imidazolium halide salts. For example, in a CN-functionalized imidazolium salt, 1-CH_2CN-3-methylimidazolium chloride, the C–N bond lengths are 1.348(3) Å and 1.336(3) Å and the N–C–N angle is 107.6°.[31]

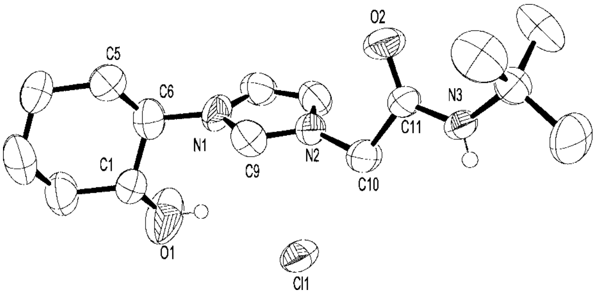


Figure 2. ORTEP drawing of **1a** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths [Å] and angles [°]: N1–C9 1.326(6), N2–C9 1.314(6), N2–C9–N1 107.9(5).

The silver complex, [3-(*N*-*tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene]AgCl (**1b**), was synthesized by the reaction of 3-(*N*-*tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazolium chloride (**1a**) with Ag_2O in dichloromethane at room temperature in 86% yield with the convenient methodology developed by Lin and coworkers.[32] The ^{1}H NMR spectrum of **1b** confirmed the absence of the reactant imidazolium (NC*H*N) peak in the ca. 9 ppm region. The ^{13}C NMR spectrum showed a new peak at δ = 181.6 ppm, which corresponds to the silver-bound carbene (N*C*N) resonance; the peak at δ = 136.3 ppm attributable to reactant **1a** (N*C*HN) was absent as a result of its deprotonation by Ag_2O and is indicative of the formation of **1b**. The two diastereotopic protons of the bridging methylene (-CH_2-) group appeared shifted as two doublets at δ = 4.94 ppm ($^{2}J_{H,H}$ = 15 Hz) and 4.82 ppm ($^{2}J_{H,H}$ = 15 Hz), respectively, compared to that of **1a**. The carbon resonance of the bridging methylene (-CH_2-) group appeared at δ = 54.4 ppm in the ^{13}C NMR spectrum. In the infrared spectrum, the amide carbonyl (-CONH-) appeared at 1673 cm^{-1} while the hydroxy group appeared as a broad peak at 3302 cm^{-1}.

The definitive proof for the structure of **1b** came from X-ray diffraction studies (Figure 3), which revealed a neutral monomeric complex bearing a 1:1 (NHC ligand/metal) stoichiometry. The silver center of **1b** was found to be two-coordinate, displays a linear geometry [∠ C1–Ag1–Cl1 = 172.66(11)°], and is consistent with the most common geometry displayed by d^{10} silver(I) ions.[33] The Ag–C_{carb} (Ag1–C1 = 2.066(4) Å) bond length of **1b** is shorter than the sum of the individual covalent radii of Ag and C (2.111 Å),[34a] but is comparable to that observed in other related (NHC)AgCl-type complexes. For example, a Ag–C_{carb} bond length of 2.056(7) Å was observed in the case of [1,3-*bis*(mesityl)imidazol-2-ylidene]AgCl,[35] while that of 2.098(2) Å was observed in another functionalized NHC complex, [1-(2-benzylideneamino-3,5-di-*tert*-butylbenzyl)-3-(*tert*-butyl)imidazol-2-ylidene]AgCl.[36] However, it is to be noted that the extent of π-backbonding in Group 11 metal–NHC (Cu, Au, Ag) complexes still remains a matter of debate with independent theoretical calculations carried out by Frenking[37] and Meyer,[38] who propose opposing views. In addition, a recent study by Cundari[39] concluded that a shortening of the metal–carbene bond up to 4% can be attributed to the change in hybridization state of the carbene carbon as a consequence of the enhanced *s*-character of the in-plane carbene lone pair σ-bonded to the metal in the metal–NHC complexes. The Ag1–Cl1 bond length of 2.3264(11) Å in **1b**, however, matches more closely with the sum of individual covalent radii of Ag and Cl (2.329 Å)[34a] and is in agreement with a single-bond character.

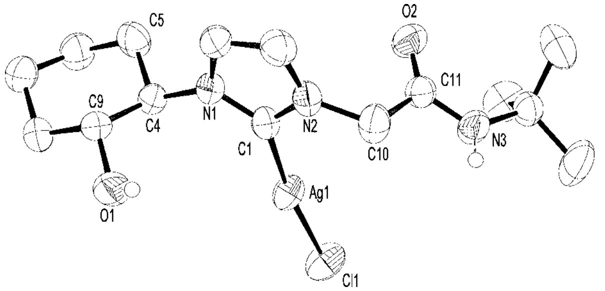


Figure 3. ORTEP drawing of **1b** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths [Å] and angles [°]: Ag–C1 2.066(4), Ag–Cl1 2.3264(11), N1–C1 1.350(4), N2–C1 1.345(5), C1–Ag–Cl1 172.66(11), N2–C1–N1 110.9(3).

Another notable structural feature of **1b** is that both of the *N*-substituents, that is, the 2-hydroxycyclohexyl and the *N*-*tert*-butylacetamido moieties, are disposed *trans* to each other with respect to the plane that contains the central imidazole ring and the silver center. The 2-hydroxy cyclohexyl O atom (O1···Ag1 = 4.176 Å) and the *N*-*tert*-butylacetamido O atom (O2···Ag1 = 4.199 Å) are located equidistant from the central Ag atom but in approximately diagonally opposite directions (*trans* orientation). Furthermore, the 2-hydroxycyclohexyl and the *N*-*tert*-butylacetamido moieties are perpendicular to the imidazole ring where the dihedral angle is 111.2° (C9–C4–N1–C1) and 85.6° (C1–N2–C10–C11), respectively.

The treatment of silver complex **1b** with (SMe_2)AuCl yielded the gold complex, [3-(*N*-*tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene]AuCl (**1c**), along with the precipitation of off-white AgCl in 77% yield. It is interesting to note that there are several methods available for the synthesis of Au–NHC complexes: (1) cleavage of electron-rich olefins,[40] (2) carbene transfer from Group 6 carbonyl complexes,[41] (3) reactions of azolium salts or free NHCs with Au^{I} precursors,[42] (4) protonation or alkylation of gold azolyl complexes,[43] and (5) transmetalation by the reaction of Ag^{I}–NHC complexes with Au^{I} precursors.[32] The popularity of the transmetalation method is primarily a result of the fact that the generation of free carbenes from the imidazolium salts with the use of strong bases often promotes decomposition reactions, and also the generated free carbenes are often difficult to handle because of their air and moisture sensitivities.[13] The ^{1}H NMR spectrum of **1c** shows two diastereotopic bridging methylene protons (-CH_2-) that appear as two sets of doublets at δ = 5.01 ppm ($^2J_{H,H}$ = 15 Hz) and 4.40 ppm ($^2J_{H,H}$ = 15 Hz). The Au-bound carbene (N*C*N) peak appears slightly shifted at δ = 170.2 ppm compared to the Ag-bound carbene (N*C*N) resonance at δ = 181.6 ppm in the ^{13}C NMR spectrum. In the infrared spectrum, the carbonyl peak of the amido (-CONH-) moiety appears at 1676 cm^{-1} while the cyclohexyl hydroxy peak appears at 3439 cm^{-1}.

The X-ray diffraction study revealed that the molecular structure of gold complex **1c** (Figure 4) is isomorphous with silver complex **1b**. The *N*-substituents, 2-hydroxycyclohexyl and *N*-*tert*-butylacetamido, were found to be perpendicular to the imidazole ring, and the dihedral angles between each of these two moieties and the imidazolium ring is 112.1(5)° (C9–C4–N2–C1) and 83.7(6)° (C11–C10–N1–C1), respectively. Notably, the 2-hydroxycyclohexyl O atom and the *N*-*tert*-butylacetamido O atom are disposed *trans* to each other with respect to the central imidazole ring and they also point away from the Au atom in diagonally opposite directions. The O1···Au1 (2-hydroxycyclohexyl O atom) and the O2···Au1 (*N*-*tert*-butylacetamido O atom) distances are 4.082 Å and 4.109 Å, respectively. Consistent with a shorter covalent radii of Au compared to Ag,[34] the Au1–C1 bond [1.969(5) Å] in **1c** was indeed shorter than the corresponding Ag1–C1 bond [2.066(4) Å] in **1b**. Another noticeable difference is that the N1–C1–N2 angle [105.2(4)°] in **1c** is slightly greater than the value seen in **1b** [104.3(3)°].

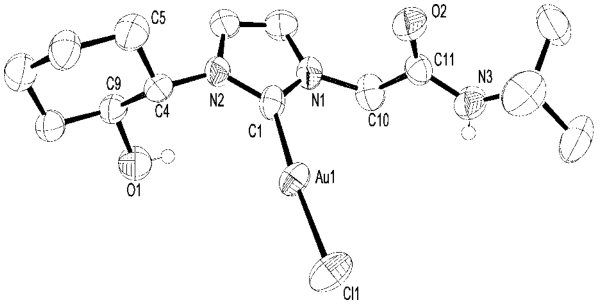


Figure 4. ORTEP drawing of **1c** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths [Å] and angles [°]: Au–C1 1.969(5), Au–Cl1 2.2845(13), N1–C1 1.332(6), N2–C1 1.355(5), C1–Au–Cl1 175.30(15), N2–C1–N1 111.3(4).

It is worth noting that compared to the numerous Ag^I–NHC complexes that are known, the Au^I–NHC complexes are surprisingly few in number. Correspondingly, the structural diversity exhibited by Ag^I–NHC complexes are more varied and diverse[35,36,44,45] when compared to their gold counterparts,[46–48] which commonly exhibit neutral monomeric (NHC)AuX (X = halide) and cationic $[(NHC)_2Au]^+$ type structures.[13] In this regard, Nolan and coworkers[49] have recently reported a series of neutral monomeric gold complexes, [1,3-bis(R)imidazol-2-ylidene]AuCl (R = mesityl, 2,6-di-*i*-propylphenyl, cyclohexyl and adamentyl); the bond lengths and bond angles of which are comparable to that observed in **1c**.

Because of their synthetic ease and air and moisture stabilities, there is a growing emphasis on the catalytic utility of Au and Ag complexes of the (NHC)MX (M = Au, Ag, X = halide) type. Research in this area may facilitate their use as precursors in the preparation of other important compounds.

Quite significantly, both Au and Ag complexes **1c** and **1b** efficiently catalyze the bulk ROP of L-lactide under solvent-free melt conditions at elevated temperatures. To the best of our knowledge, **1c** represents the first example of a Au^I–NHC based initiator for the ROP of L-lactide. Even though there exists a report of solution polymerization[18] and a report of the bulk polymerization[21] of L-lactide by Ag^I–NHC complexes, we are not aware of any such polymerization by Au^I–NHC complexes. Bulk polymerization exhibits certain advantages over solution polymerization: (1) no solvent is required, (2) it is less vulnerable to impurity levels and unwanted side reactions, (3) it is often useful for the large-scale production of PLAs.[28]

Specifically, a typical polymerization experiment would involve the heating of L-lactide and the catalyst, **1b** or **1c**, 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) showed that the maximum molecular weight in the case of **1b** (Entry 2: $M_n = 5.1\cdot10^3$, Table 1) as well as in **1c** (Entry 2: $M_n = 5.4\cdot10^3$, Table 2) were obtained at [M]:[C] ratio 100:1 for a 4 h run at 160 °C. The molecular weight distributions are almost similar for both catalysts **1b** (PDI = 1.10–1.53) and **1c** (PDI = 1.07–1.35). Interesting would be the comparison of the polymerization results of **1b** and **1c** with that of the other reported Au and Ag–NHC complexes. As we are unaware of any Au–NHC complex known for the ROP of L-lactide, such a comparison can only be drawn for the Ag–NHC complexes.[18,21] For example, for a cationic 2:1 (NHC ligand/metal) silver-NHC complex supported over a mono-functionalized NHC ligand re-

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

Entry	L-Lactide/**1b** ratio	Temp. [°C]	Time [h]	M_n	M_w/M_n	Conversion [%]
1	50	160	4	$3.6\cdot10^3$	1.39	98
2	100	160	4	$5.1\cdot10^3$	1.23	93
3	150	160	4	$4.9\cdot10^3$	1.24	86
4	200	160	4	$4.8\cdot10^3$	1.16	67
5	250	160	4	$4.5\cdot10^3$	1.14	53
6	300	160	4	$4.1\cdot10^3$	1.13	42
7	100	120	4	$4.2\cdot10^3$	1.10	78
8	100	140	4	$4.9\cdot10^3$	1.17	96
9	100	180	4	$4.9\cdot10^3$	1.31	96
10	100	160	1	$3.0\cdot10^3$	1.19	67
11	100	160	2	$4.0\cdot10^3$	1.25	92
12	100	160	3	$4.4\cdot10^3$	1.20	95
13	100	160	6	$5.1\cdot10^3$	1.29	98
14	100	160	8	$4.6\cdot10^3$	1.53	99

cently reported by us[21] for the bulk polymerization of L-lactide under analogous melt conditions, higher molecular weight polymers were obtained as compared to that of **1b** and **1c**. However, it should be noted that in the present study neutral monomeric (NHC)MCl (M = Ag and Au) type complexes, supported over a different difunctionalized NHC ligand, were examined as initiators for lactide polymerizations.

Table 2. Melt polymerization of L-lactide by **1c**.

Entry	L-Lactide/**1c** ratio	Temp. [°C]	Time [h]	M_n	M_w/M_n	Conversion [%]
1	50	160	4	$3.9\cdot10^3$	1.23	96
2	100	160	4	$5.4\cdot10^3$	1.17	80
3	150	160	4	$5.0\cdot10^3$	1.13	56
4	200	160	4	$3.8\cdot10^3$	1.22	42
5	250	160	4	$3.6\cdot10^3$	1.21	31
6	300	160	4	$3.6\cdot10^3$	1.13	29
7	100	120	4	$2.7\cdot10^3$	1.13	56
8	100	140	4	$4.3\cdot10^3$	1.17	74
9	100	180	4	$4.1\cdot10^3$	1.12	97
10	100	160	1	$2.0\cdot10^3$	1.07	27
11	100	160	2	$2.8\cdot10^3$	1.11	41
12	100	160	3	$3.4\cdot10^3$	1.11	61
13	100	160	6	$4.1\cdot10^3$	1.22	74
14	100	160	8	$5.1\cdot10^3$	1.35	90

The time-dependence study showed that the average molecular weight (M_n) of the polymer increased with time for the first 6 h in the case of **1b** and for the first 4 h in the case of **1c**, after which it reached saturation. The temperature-dependence study was carried out in the range 120–180 °C and showed that for both **1b** and **1c** the molecular weight increased steadily with the temperature till 160 °C after which point it started to decrease. The decrease in molecular weight may be attributed to the depolymerization that takes place at higher temperatures. A similar decrease in the molecular weight at higher temperatures has been reported by Liao[27a] and by Albertson and Varma.[24] Detailed mechanistic studies are underway to establish the nature of the active species responsible for the catalysis. In this regard, it is worth mentioning that there have been reports of both metal-mediated polymerization[21] as well as carbene-mediated lactide polymerization.[52]

It is interesting to note that despite the fact that the Au–C_{carb} bond energy (76.3 kcal/mol) is significantly stronger than the Ag–C_{carb} bond energy (53.1 kcal/mol) in (NHC)-MCl (M = Ag and Au) complexes,[37] comparable polymer molecular weights were observed in the case of **1b** (M_n = $3.0–5.1\cdot10^3$) and **1c** (M_n = $2.0–5.4\cdot10^3$). At this juncture, it will be worthwhile to compare the activity of **1c**, with representative examples of other metal-based catalysts for the bulk ROP of L-lactide. For example, the zinc complexes of the picolyl carbene ligand, namely, ethyl zinc iodide·1-mesityl-3-picolylimidazol-2-ylidene adduct and its bis-ligand adduct gave PLAs with M_n = $(6.1–20)\cdot10^3$, when the polymerization was carried out at 140 °C.[26b] The molecular weight distributions (PDI = 1.78–2.45) for PLAs obtained from these picolylcarbene-based zinc complexes are, however, higher as compared to that of **1b** or **1c**. Similarly, the Co, Ni, Cu, and Zn complexes of a Schiff base ligand derived from salicylidene and L-aspartic acid, also yielded PLAs with a viscosity average molecular weight in the order of $(4.86–11.1)\cdot10^3$ at 130 °C over a period of 24 h.[53] Furthermore, PLAs with a relatively narrow molecular weight distribution (PDI = 1.12–1.32) have been obtained with M_n = $(1.93–2.3)\cdot10^4$ with the use of Red-Al as a catalyst in the temperature range of 110–135 °C.[27b] In addition, a series of titanatranes with varying ring sizes have been successfully employed to achieve molecular weights [M_n = $(1.6–3.36)\cdot10^4$] with PDI in the range of 1.42–1.97 at 130 °C.[27c] Recently, various ferric alkoxides [$Fe(OR)_3$; R = Et, Pr, *i*Pr, Bu] have been reported for moderate molecular weight PLAs [M_n = $(1.78–13.97)\cdot10^4$] with PDI = 1.60–1.98; however, the polymerization have been carried out up to 72 h at 130–150 °C.[27a] We believe that, as a first example of a Au-based initiator for the bulk polymerization of L-lactide, the Au–NHC complex **1c** would encourage further research in the utility of gold in this area.

Conclusion

In summary, two new silver and gold complexes, namely, [3-(*N*-*tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene]AgCl (**1b**) and [3-(*N*-*tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene]AuCl (**1c**), supported over a difunctionalized *N*-heterocyclic carbene ligand have been synthesized. The **1a**, **1b**, and **1c** complexes have been structurally characterized by X-ray diffraction studies. The comparison of structures **1b** and **1c** show the formation of neutral monomeric complexes that have a 1:1 (NHC ligand/metal) stoichiometry. Notably, in neither structure **1b** nor structure **1c** was the chelation of the functionalized sidearms to the metals observed. This is in agreement with the two-coordinated d^{10} configurations of the Au^I and Ag^I ions that prefer linear geometries. The gold and silver complexes **1c** and **1b** effectively catalyze the ROP of L-lactide under solvent-free melt conditions to produce the polylactide polymer of moderate to low molecular weight with a narrow molecular weight distribution. Gold complex **1c** represents the first example of a Au^I–NHC based initiator for the ROP of L-lactide.

Experimental Section

General Procedures: All manipulations were carried out with a glove box and/or 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. $(SMe_2)AuCl$[50] and *N*-*tert*-butyl-2-chloroacetamide[51] were synthesized according to literature procedures. ^1H- and $^{13}C\{^1H\}$ NMR spectra were recorded in $CDCl_3$ with a Varian 400 MHz NMR spectrometer. ^1H NMR peaks are labeled as singlet (s), doublet (d) and multiplet (m). Infrared spectra were recorded with a Perkin–Elmer Spectrum One FTIR spectrometer. Mass spectrometry measurements were performed with a Micromass Q-Tof spectrometer. Polymer molecular weights were determined with a Waters GPC (Waters 2414 RI Detector) and with PLgel, 5µ Mixed-D (2×300 mm) column, with polystyrene standards in chloroform, with a covered molecular weight range of l40 to $4\cdot10^5$. X-ray diffraction data for **1b** was collected with a NONIUS-MACH3 diffractometer and that of **1a** and **1c** was collected on Oxford diffraction XCALIBUR-S instrument. The crystal data collection and refinement parameters are summarized in Table 3. 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-606428 (**1a**), CCDC-606429 (**1b**), and CCDC-606427 (**1c**) contain 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.

Table 3. X-ray crystallographic data for **1a**, **1b** and **1c**.

Compound	**1a**	**1b**	**1c**
Lattice	monoclinic	orthorhombic	orthorhombic
Formula	$C_{15}H_{26}ClN_3O_2$	$C_{15}H_{25}AgClN_3O_2$	$C_{15}H_{24}AuClN_3O_2$
Formula weight	315.84	422.70	510.79
Space group	*P21/n*	*Pabc*	*Pcab*
a [Å]	14.799(4)	9.8760(11)	9.879(2)
b [Å]	5.648(5)	19.0390(11)	18.800(2)
c [Å]	21.571(3)	19.2450(12)	19.391(3)
α [°]	90.00	90.00	90.00
β [°]	105.802(15)	90.00	90.00
γ [°]	90.00	90.00	90.00
V [Å^3]	1734.8(16)	3618.6(5)	3601.4(11)
Z	4	8	8
Temperature [K]	293(2)	293(2)	293(2)
Radiation (λ [Å])	0.71073	0.71073	0.71073
ρ(calcd.) [g cm^{-3}]	1.209	1.884	1.884
μ(Mo-K_α) [mm^{-1}]	0.228	1.271	8.328
θ max [°]	32.2342	12.2000	2.99–30.16
No. of data	3051	3182	5309
No. of parameters	194	211	203
R_1	0.0821	0.0320	0.0316
wR_2	0.2143	0.0708	0.0560
GOF	1.102	0.964	0.827

Synthesis of 3-(*N-tert*-Butylacetamido)-1-(2-hydroxycyclohexyl)imidazolium Chloride (1a): Cyclohexene oxide (0.656 g, 6.69 mmol) and imidazole (0.455 g, 6.69 mmol) were heated at 60 °C for 12 h and the resulting sticky brown solid was dissolved in acetonitrile (ca. 20 mL). *N-tert*-Butyl-2-chloroacetamide (1.00 g, 6.69 mmol) was added to the solution and the reaction mixture was heated at 90 °C for 2 h. A white precipitate was collected by filtration and was recrystallized from acetonitrile (ca. 10 mL) and dried under vacuum to give the product **1a** as a white solid (2.02 g, 96%). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 9.31 (s, 1 H, NC*H*N), 8.19 (br., 1 H, N*H*), 7.44 (br., 2 H, NC*H*CHN), 5.16 (d, ^2J = 15 Hz, 1 H, CH_2), 4.96 (d, ^2J = 15 Hz, 1 H, CH_2), 4.12–4.00 (m, 1 H, $\mathrm{C_6}H_{10}$), 3.62–3.56 (m, 1 H, $\mathrm{C_6}H_{10}$), 2.12–1.98 (m, 4 H, $\mathrm{C_6}H_{10}$), 1.78–1.68 (m, 4 H, $\mathrm{C_6}H_{10}$), 1.30 [s, 9 H, C(CH_3)$_3$] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ = 163.8 (*C*O), 136.3 (N*C*HN), 123.1 (N*C*HCHN), 120.1 (NCH*C*HN), 51.8 (*C*$\mathrm{H_2}$), 34.3 (*C*$\mathrm{_6H_{10}}$), 31.2 (*C*$\mathrm{_6H_{10}}$), 30.9 [*C*($\mathrm{CH_3}$)$_3$], 28.5 [C(*C*$\mathrm{H_3}$)$_2$], 24.5 (2C, *C*$\mathrm{_6H_{10}}$), 23.9 (2C, *C*$\mathrm{_6H_{10}}$) ppm. IR (KBr): ṽ = 3213 (br, OH), 1671 (s, CO) cm^{-1}. LRMS (ES): *m*/*z* (%) = 280 [100, (NHC–Ligand)$^+$]. HRMS (ES): calcd. for (NHC–Ligand)$^+$ 280.2025; found 280.2022.

Synthesis of [3-(*N-tert*-Butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene]AgCl (1b): A mixture of 3-(*N-tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazolium chloride **1a** (2.98 g, 9.53 mmol) and Ag_2O (1.11 g, 4.77 mmol) in dichloromethane (ca. 25 mL) was stirred at room temperature for 6 h. The reaction mixture was filtered and the solvent was removed under vacuum to give the product **1b** as a white solid (3.46 g, 86%). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 8.19 (br., 1 H, N*H*), 7.03 (br., 2 H, NC*H*CHN), 4.94 (d, ^2J = 15 Hz, 1 H, CH_2), 4.82 (d, ^2J = 15 Hz, 1 H, CH_2), 4.25–4.20 (m, 1 H, $\mathrm{C_6}H_{10}$), 3.68–3.55 (m, 1 H, $\mathrm{C_6}H_{10}$), 2.13–2.04 (m, 4 H, $\mathrm{C_6}H_{10}$), 1.80–1.70 (m, 4 H, $\mathrm{C_6}H_{10}$), 1.34 [s, 9 H, C(CH_3)$_3$] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ = 181.6 (N*C*N–Ag), 166.6 (*C*O), 123.0 (N*C*HCHN), 117.8 (NCH*C*HN), 54.4 (*C*$\mathrm{H_2}$), 34.4 (*C*$\mathrm{_6H_{10}}$), 32.9 (*C*$\mathrm{_6H_{10}}$), 32.3 [*C*-($\mathrm{CH_3}$)$_3$], 28.6 [C(*C*$\mathrm{H_3}$)$_2$], 24.9 (2 C, *C*$\mathrm{_6H_{10}}$), 24.4 (2 C, *C*$\mathrm{_6H_{10}}$) ppm. IR (KBr): ṽ = 3302 (br, OH), 1673 (s, CO) cm^{-1}. LRMS (ES): *m*/*z* = 386 (NHC–Ag)$^+$, 667 (NHC)$_2$Ag]$^+$.

Synthesis of [3-(*N-tert*-Butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene]AuCl (1c): A mixture of [3-(*N-tert*-butylacetamido)-1-(2-hydroxycyclohexyl)imidazol-2-ylidene]AgCl **1b** (0.277 g, 0.651 mmol) and (SMe_2)AuCl (0.193 g, 0.651 mmol) in dichloromethane (ca. 15 mL) was stirred at room temperature for 6 h, when the formation of an off-white AgCl precipitate was observed. The reaction mixture was filtered and the solvent was removed under vacuum to obtain the product **1c** as a white solid (0.259 g, 77%). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 9.12 (br., 1 H, N*H*), 7.12 (br., 1 H, NC*H*CHN), 6.93 (br., 1 H, NC*H*CHN), 5.01 (d, ^2J = 15 Hz, 1 H, CH_2), 4.40 (d, ^2J = 15 Hz, 1 H, CH_2), 4.35–4.29 (m, 1 H, $\mathrm{C_6}H_{10}$), 3.76–3.70 (m, 1 H, $\mathrm{C_6}H_{10}$), 2.07–2.01 (m, 4 H, $\mathrm{C_6}H_{10}$), 1.80–1.67 (m, 4 H, $\mathrm{C_6}H_{10}$), 1.30 [s, 9 H, C-(CH_3)$_3$] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ = 170.2 (N*C*N–Au), 165.7 (*C*O), 123.6 (N*C*HCHN), 117.7 (NCH*C*HN), 54.4 (*C*$\mathrm{H_2}$), 41.0 (*C*$\mathrm{_6H_{10}}$), 34.0 (*C*$\mathrm{_6H_{10}}$), 32.4 [*C*($\mathrm{CH_3}$)$_3$], 29.7 [C(*C*$\mathrm{H_3}$)$_2$], 24.9 (2 C, *C*$\mathrm{_6H_{10}}$), 24.3 (2 C, *C*$\mathrm{_6H_{10}}$) ppm. IR (KBr): ṽ = 3439 (br, OH), 1676 (s, CO) cm^{-1}.

Polymerization Experiments: Bulk polymerizations of L-lactide were carried out in vacuo-sealed glass ampoules. Firstly, the glass ampoule was charged with monomer (L-lactide) and dried for a period of two hours under high vacuum at 50 °C. Subsequently, the catalyst (**1b** or **1c**) was then added with the monomer to catalyst ratio in the range of 50–300. The ampoule was sealed under high vacuum and immersed in an oil bath. Polymerizations were carried out in the temperature range 120–180 °C. After a predetermined time (1–8 h) the glass ampoule was removed and subsequently the molten reactive polymer mixture was cooled while the sealed ampoule was immersed in liquid nitrogen to stop the polymerization, and thereafter the samples were removed for analysis. The analyses were performed on the crude reaction mixture; no precipitation was executed in order to avoid fractionation of the sample.

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