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Gold(I) N-heterocyclic carbene based initiators for bulk ring-opening polymerization of L-lactide

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Abstract

Synthesis, structures, and catalysis studies of gold(I) complexes of N-heterocyclic carbenes namely, a di-O-functionalized [1-(2-hydroxy-cyclohexyl)-3-(acetophenone)imidazol-2-ylidene], a mono-O-functionalized [1-(2-hydroxy-cyclohexyl)-3-(benzyl)imidazol-2-ylidene] and a non-functionalized [1,3-di-*i*-propyl-benzimidazol-2-ylidene], are reported. Specifically, the gold complexes, [1-(2-hydroxy-cyclohexyl)-3-(acetophenone)imidazol-2-ylidene]AuCl (**1c**), [1-(2-hydroxy-cyclohexyl)-3-(benzyl)imidazol-2-ylidene]AuCl (**2c**), and [1,3-di-*i*-propyl-benzimidazol-2-ylidene]AuCl (**3b**), were prepared from the respective silver complexes **1b**, **2b**, and **3a** by treatment with (SMe_2)AuCl in good yields following the commonly used silver carbene transfer route. The silver complexes **1b**, **2b**, and **3a** were synthesized from the respective imidazolium halide salts by the reactions with Ag_2O. The N-heterocyclic carbene precursors, 1-(2-hydroxy-cyclohexyl)-3-(acetophenone)imidazolium chloride (**1a**) and 1-(2-hydroxy-cyclohexyl)-3-(benzyl)imidazolium chloride (**2a**), were synthesized by the direct reactions of cyclohexene oxide and imidazole with chloroacetophenone and benzyl chloride respectively. The gold (**1c**, **2c**, and **3b**) and the silver (**3a**) complexes along with a new O-functionalized imidazolium chloride salt (**1a**) have been structurally characterized by X-ray diffraction. The structural studies revealed that geometries around the metal centers were almost linear in these gold and silver complexes. The gold (**1c**, **2c**, and **3b**) complexes efficiently catalyze ring-opening polymerization (ROP) of L-lactide under solvent-free melt conditions producing polylactide polymer of moderate to low molecular weights with narrow molecular weight distributions.

Keywords: Gold; Silver; N-Heterocylic carbene; Ring-opening polymerization; Lactide

1. Introduction

Only recently, the catalytic potential of gold has started to unravel, with a display of quite an impressive range of transformations emerging by the day that varies from hydroarylation [1], to C–C [2] and C–O [3] bond formations, to hydrosilylation [4], to hydroamination [5], to carbonylation of amines [6], etc. As a consequence, gold, otherwise deemed as an unreactive coinage metal with limited utility in catalysis, has received unprecedented attention of late [7]. Not surprisingly, riding high on the successes of N-heterocyclic carbenes (NHCs) in homogeneous catalysis [8], the new gold–NHC based catalysts are spearheading the developments in this field with several first claims showing up against their names, and thereby underscoring the new-found role of gold in catalysis. For example, Herrmann and coworkers [9] reported the first-ever use of a Au–NHC complex in homogeneous catalysis in the form of the addition reaction of water to 3-hexyne, while Nolan and coworkers [10] reported the first example of a Au–NHC complex for ethyl diazoacetate assisted

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carbene transfer reaction and recently we [11] have reported the first example of a Au–NHC complex for the bulk ring-opening polymerization of L-lactide. The necessary motivation for research on the utility of gold in chemical catalysis arises from its low toxicity and from the thus far unexplored catalytic exploits of gold, which still remains a challenge till date. Moreover, the strong σ-donating nature of N-heterocyclic carbenes [12–14] facilitate tighter binding to metal, thereby imparting greater stability to the Au–NHC complexes, which generally are easy to synthesize and convenient to handle. Though new to catalysis, gold, however, is long known for its varied biomedical applications like, antimicrobial [15], antitumor [16,17], antiarthritic activities [18] and for therapeutic usages [19], etc.

For silver too, like gold, the utility in chemical catalysis is relatively a recent phenomenon, though much more is known about its catalytic applications than gold [20,21]. In this context it is worth mentioning that the Ag–NHC complexes, similar to their gold counterparts, have played an important role in realizing the catalytic potential of silver with the Ag–NHC complexes carrying out many important transformations like, ethyl diazoacetate (EDA) assisted carbene transfer reactions [22], catalytic preparation of 1,2-bis(boronate) esters [23], transesterification reactions, ring-opening polymerization of L-lactide [24,25], etc. Apart from catalysis, the Ag–NHC complexes are however long known for their role as effective transmetalating agents for synthesizing transition metal complexes of N-heterocyclic carbenes and have contributed significantly to the growth in this area [20,21].

As one of the primary objectives of our core program is centered on exploring the catalytic potentials of gold and silver, considered rather unreactive for catalysis, we became interested in designing gold and silver N-heterocyclic carbene complexes for their utility in chemical catalysis. In particular, the ring-opening polymerization of L-lactide is of interest to us because of its eco-friendliness as the polylactide polymers (PLA) are biodegradable while the lactide monomers can be generated from renewable resources by corn fermentation process or from agricultural starch wastes [26,27]. Furthermore, the polylactide polymers have found wide utility in medical and pharmaceutical applications because of their good mechanical strength and biodegradability [28,29]. Our specific interest in the bulk polymerization [30] of the L-lactide under solvent-free melt conditions, as opposed to the solution polymerization [31] is due to the preference for bulk polymerization for the large-scale production of PLAs. Though a much greater control is achieved in solution polymerization compared to the bulk polymerization, the solution polymerization suffers from certain limitations as owing to their higher reactivities they are often susceptible to the impurity levels and to the various unwanted reactions like, racemization and transesterification [32]. In this regard it is worth mentioning that we have recently reported the applications of gold [11] and silver [25] N-heterocyclic carbene complexes in the bulk ring-opening polymerization (ROP) of L-lactide.

Here in this contribution, we disclose the synthesis, structural characterizations, and catalysis studies of several gold based initiators, [1-(2-hydroxy-cyclohexyl)-3-(acetophenone)imidazol-2-ylidene]AuCl (**1c**), [1-(2-hydroxy-cyclohexyl)-3-(benzyl)imidazol-2-ylidene]AuCl (**2c**), and [1,3-di-*i*-propyl-benzimidazol-2-ylidene]AuCl (**3b**), respectively supported over a di-O-functionalized, a mono-O-functionalized and a non-functionalized N-heterocyclic carbene ligand for the ring-opening polymerization (ROP) of L-lactide under solvent-free melt conditions. Furthermore in this paper, we report the structural characterizations of a silver complex, [1,3-di-*i*-propyl-benzimidazol-2-ylidene]AgBr (**3a**), and a N-heterocyclic carbene precursor, 1-(2-hydroxy-cyclohexyl)-3-(acetophenone)imidazolium chloride (**1a**).

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. Ag_2O was purchased from SD-fine Chemicals (India) and used without any further purification. $(SMe_2)AuCl$ [33], chloroacetophenone [34] and 1,3-di-*i*-propylbenzimidazolium bromide [35] were synthesized according to reported 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), and multiplet (m). Infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrophotometer. Mass spectrometry measurements were done on a Micromass Q-Tof spectrometer. Polymer molecular weights were determined using a Waters GPC (Waters 2414 RI Detector) with PL-gel, 5μ Mixed-D (2×300 mm) Column, with polystyrene standards in chloroform, covered molecular weight range of 140–4×10^5. X-ray diffraction data for **1a**, **1c**, **2c**, **3a**, and **3b** were collected on Oxford diffraction XCALIBUR-S instrument. The 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). CCDC – 607580 (**1a**), CCDC – 614945 (**1c**), CCDC – 617398 (**2c**), CCDC – 616362 (**3a**), and CCDC – 614944 (**3b**) contain the Supplementary crystallographic data for this paper. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or [from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internet.) +44-1223/336-033; e–mail: deposit@ccdc.cam.ac.uk].

Table 1
X-ray crystallographic data for **1a**, **1c**, **2c**, **3a**, and **3b**

Compound	**1a**	**1c**	**2c**	**3a**	**3b**
Lattice	Orthorhombic	Triclinic	Orthorhombic	Orthorhombic	Monoclinic
Formula	$C_{17}H_{21}ClN_2O_2$	$C_{17}H_{20}AuClN_2O_2$	$C_{16}H_{20}AuClN_2O$	$C_{13}H_{18}AgBrN_2$	$C_{13}H_{18}AuClN_2$
Formula weight	320.81	516.77	488.76	390.07	434.71
Space group	*Pbca*	$P\bar{1}$	$P\bar{1}$	*Pcab*	$P2_1/n$
a (Å)	9.8239(11)	9.7287(15)	7.1702(7)	10.739(2)	9.624(3)
b (Å)	17.5170(11)	9.818(2)	9.440(2)	16.0940(8)	7.8258(8)
c (Å)	19.2733(12)	10.3135(10)	12.557(3)	16.953(4)	19.292(4)
α (°)	90.00	106.902(14)	103.64(2)	90.00	90.00
β (°)	90.00	98.713(10)	101.692(14)	90.00	100.641(19)
γ (°)	90.00	103.817(17)	93.724(13)	90.00	90.00
V (Å^3)	3316.7(5)	889.0(3)	803.1(3)	2930.2(9)	1428.0(5)
Z	8	2	2	8	4
Temperature (K)	293(2)	293(2)	150(2)	150(2)	150(2)
Radiation, λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
ρ_{calc} (g cm^{-3})	1.285	1.930	2.021	1.768	2.022
μ(Mo Kα) (mm^{-1})	0.239	8.434	9.325	4.084	10.470
θ (°)	27.48–2.11	24.99–3.25	25.00–3.04	25.00–3.16	25.00–3.38
Number of data	3294	3118	2793	2574	2476
Number of parameters	203	212	190	158	158
R_1	0.2212	0.0236	0.0565	0.0.346	0.0577
wR_2	0.2455	0.0479	0.1428	0.0642	0.1212
Goodness-of-fit	1.024	1.045	1.037	1.106	1.086

2.2. Synthesis of 1-(2-hydroxy-cyclohexyl)-3-(acetophenone)imidazolium chloride (*1a*)

Cyclohexene oxide (3.57 g, 36.4 mmol) and imidazole (2.47 g, 36.4 mmol) were heated at 60 °C for 12 h and the resulting sticky brown solid was dissolved in acetonitrile (*ca*. 20 mL). Chloroacetophenone (5.63 g, 36.4 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 (6.75 g, 58%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 9.70 (s, 1H, NC*H*N), 8.01 (d, 2H, $^3J_{HH} = 8$ Hz, *o*-C_6H_5), 7.59 (t, 1H, $^3J_{HH} = 8$ Hz, *p*-C_6H_5) 7.46 (t, 2H, $^3J_{HH} = 8$ Hz, *m*-C_6H_5) 7.35 (br, 1H, NC*H*CHN), 7.29 (br, 1H, NCHC*H*N), 6.18 (d, 1H, $^2J_{HH} = 15$ Hz, CH_2), 6.03 (d, 1H, $^2J_{HH} = 15$ Hz, CH_2), 4.18–4.12 (m, 1H, C_6H_{10}), 3.68–3.62 (m, 1H, C_6H_{10}), 2.16–2.01 (m, 2H, C_6H_{10}), 1.83–1.69 (m, 3H, C_6H_{10}), 1.45–1.29 (m, 3H, C_6H_{10}). ^{1}H NMR (CD_3OD, 400 MHz, 25 °C): δ 9.16 (s, 1H, NC*H*N), 7.55 (s, 1H, NC*H*CHN), 7.63 (s, 1H, NCHC*H*N),7.34–7.32 (m, 5H, C_6H_5), 5.44 (s, 2H, CH_2), 4.10–4.03 (m, 1H, C_6H_{10}), 3.69–3.64 (m, 1H, C_6H_{10}), 2.15–2.09 (m, 2H, C_6H_{10}), 1.90–1.82 (m, 3H, C_6H_{10}), 1.49–1.41 (m, 3H, C_6H_{10}). ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz, 25 °C) δ 191.3 (*C*O), 137.4 (N*C*N), 136.1 (*ipso*-C_6H_5), 134.8 (*o*-C_6H_5), 133.8 (*p*-C_6H_5), 129.2 (*m*-C_6H_5), 128.8 (N*C*HCHN), 123.9 (NCH*C*HN), 72.2 (C_6H_{10}), 66.8 (C_6H_{10}), 55.9 (*C*H_2), 34.5 (C_6H_{10}), 33.9 (C_6H_{10}), 31.6 (C_6H_{10}), 24.9 (C_6H_{10}). IR data cm^{-1} KBr pellet: 3282 (s) (ν_{OH}), 1694 (s) (ν_{CO}). LRMS (ES): *m/z* 285 [(NHC–Ligand)]$^+$. HRMS (ES): 285.1606 (NHC–Ligand)$^+$. Calc. 285.1603.

2.3. Synthesis of [1-(2-hydroxy-cyclohexyl)-3-(acetophenone)imidazol-2-ylidene]AgCl (*1b*)

A mixture of 1-(2-hydroxy-cyclohexyl)-3-(acetophenone)imidazolium chloride (**1a**) (1.50 g, 4.68 mmol) and Ag_2O (0.542 g, 2.34 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 brown solid (1.67 g, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 8.02 (d, 2H, $^3J_{HH} = 8$ Hz, *o*-C_6H_5), 7.62 (t, 1H, $^3J_{HH} = 8$ Hz, *p*-C_6H_5) 7.49 (t, 2H, $^3J_{HH} = 8$ Hz, *m*-C_6H_5) 7.07 (br, 1H, NC*H*CHN), 7.00 (br, 1H, NCHC*H*N), 5.87 (d, 1H, $^2J_{HH} = 15$ Hz, CH_2), 5.62 (d, 1H, $^2J_{HH} = 15$ Hz, CH_2), 4.21–4.16 (m, 1H, C_6H_{10}), 3.64–3.55 (m, 1H, C_6H_{10}), 2.12–2.03 (m, 2H, C_6H_{10}), 1.72–1.70 (m, 3H, C_6H_{10}), 1.37–1.21 (m, 3H, C_6H_{10}). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ 193.0 (*C*O), 181.4 (N*C*N–Ag), 133.9 (*ipso*-C_6H_5), 133.8 (*p*-C_6H_5), 128.7 (*m*-C_6H_5), 128.1 (*o*-C_6H_5), 122.5 (NCH*C*HN), 118.5 (N*C*HCHN), 72.2 (C_6H_{10}), 67.4 (C_6H_{10}), 53.3 (*C*H_2), 34.0 (C_6H_{10}), 32.2 (C_6H_{10}), 24.5 (C_6H_{10}), 24.1 (C_6H_{10}). IR data cm^{-1} KBr pellet: 3440 (s) (ν_{OH}), 1698 (m) (ν_{CO}). CHN Anal. Calc. for $C_{17}H_{20}AgClN_2O_2$: C, 47.74; H, 4.71; N, 6.55. Found: C, 47.25; H, 5.39; N, 6.11%.

2.4. Synthesis of [1-(2-hydroxy-cyclohexyl)-3-(acetophenone)imidazol-2-ylidene]AuCl (*1c*)

A mixture of [1-(2-hydroxy-cyclohexyl)-3-(acetophenone)imidazol-2-ylidene]AgCl (**1b**) (0.362 g, 0.846 mmol) and (SMe_2)AuCl (0.254 g, 0.848 mmol) in dichloromethane (*ca*. 15 mL) was stirred at room temperature for 6 h, when

the formation of a 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 (0.295 g, 68%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 8.01 (d, 2H, $^3J_{HH} = 8$ Hz, *o*-C_6H_5), 7.69 (t, 1H, $^3J_{HH} = 8$ Hz, *p*-C_6H_5) 7.55 (t, 2H, $^3J_{HH} = 8$ Hz, *m*-C_6H_5) 7.12 (br, 1H, NC*H*CHN), 7.07 (br, 1H, NCHC*H*N), 5.83 (d, 1H, $^2J_{HH} = 18$ Hz, CH_2), 5.69 (d, 1H, $^2J_{HH} = 18$ Hz, CH_2), 4.46–4.40 (m, 1H, C_6H_{10}), 3.98–3.91 (m, 1H, C_6H_{10}), 2.18–2.02 (m, 2H, C_6H_{10}), 1.86–1.84 (m, 3H, C_6H_{10}), 1.49–1.38 (m, 3H, C_6H_{10}). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ 190.5 (*C*O), 167.6 (N*C*N–Au), 132.3 (*ipso*-C_6H_5), 132.1 (*p*-C_6H_5), 127.1 (*m*-C_6H_5), 126.2 (*o*-C_6H_5), 121.0 (N*C*HCHN), 117.0 (NCH*C*HN), 78.6 (C_6H_{10}), 64.9 (C_6H_{10}), 55.2 (*C*H_2), 34.9 (C_6H_{10}), 32.8 (C_6H_{10}), 24.7 (C_6H_{10}), 23.8 (C_6H_{10}). IR data cm^{-1} KBr pellet: 3302 (s) (ν_{OH}), 1673 (m) (ν_{CO}). HRMS (ES): 481.1201 (NHC–Au)$^+$. Calc. 481.1190. CHN Anal. Calc. for $C_{17}H_{20}AuClN_2O_2$: C, 39.51; H, 3.90; N, 5.42. Found: C, 39.36; H, 3.76; N, 6.17%.

2.5. Synthesis of 1-(2-hydroxy-cyclohexyl)-3-(benzyl)-imidazolium chloride (*2a*)

Cyclohexene oxide (8.20 mL, 88.0 mmol) and imidazole (6.00 g, 88.1 mmol) were heated at 60 °C for 12 h and the resulting sticky brown solid was dissolved in acetonitrile (*ca.* 20 mL). Benzyl chloride (9.4 mL, 88.0 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 **2a** as a white solid (14.8 g, 57%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 10.1 (s, 1H, NC*H*N), 7.36–7.33 (m, 5H, C_6H_5), 7.06 (br, 2H, NC*H*CHN), 5.45 (d, 1H, $^2J_{HH} = 15$ Hz, CH_2), 5.38 (d, 1H, $^2J_{HH} = 15$ Hz, CH_2), 4.34–4.28 (m, 1H, C_6H_{10}), 3.67–3.61 (m, 1H, C_6H_{10}), 2.14–2.06 (m, 2H, C_6H_{10}), 1.81–1.71 (m, 2H, C_6H_{10}), 1.53–1.46 (m, 2H, C_6H_{10}), 1.36–1.32 (m, 2H, C_6H_{10}). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ 136.1 (N*C*HN), 133.1 (*ipso*-C_6H_5), 129.2 (*o*-C_6H_5), 129.1 (*p*-C_6H_5), 128.9 (*m*-C_6H_5), 121.2 (N*C*HCHN), 121.0 (NCH*C*HN), 72.0 (C_6H_{10}), 65.8 (C_6H_{10}), 53.0 (C_6H_{10}), 34.4 (C_6H_{10}), 31.2 (C_6H_{10}), 24.4 (C_6H_{10}), 23.9 (C_6H_{10}). IR data cm^{-1} KBr pellet: 3251 (s) ($\nu_{O–H}$). LRMS (ES): *m*/*z* 257, (NHC–Ligand)$^+$ 100%. HRMS (ES): 257.1658 (NHC–Ligand)$^+$. Calc. 257.1654.

2.6. Synthesis of {[1-(2-hydroxy-cyclohexyl)-3-(benzyl)-imidazol-2- ylidene]$_2$Ag}$^+$Cl$^-$ (*2b*)

A mixture of 1-(2-hydroxy-cyclohexyl)-3-(benzyl)imidazolium chloride (**2a**) (0.501 g, 1.71 mmol) and Ag_2O (0.199 g, 0.859 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 **2b** as a white solid (0.415 g, 74%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 7.25–7.15 (m, 5H, C_6H_5), 7.00 (br, 1H, NC*H*CHN), 6.87 (br, 1H, NC*H*CHN), 5.26 (d, 1H, $^2J_{HH} = 15$ Hz, CH_2), 5.14 (d, 1H, $^2J_{HH} = 15$ Hz, CH_2), 4.29–4.23 (m, 1H, C_6H_{10}), 3.68–3.62 (m, 1H, C_6H_{10}), 2.08–1.99 (m, 2H, C_6H_{10}), 1.71–1.66 (m, 2H, C_6H_{10}), 1.53–1.43 (m, 2H, C_6H_{10}), 1.38–1.31 (m, 2H, C_6H_{10}). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ 179.7 (N*C*N), 152.1 (*ipso*-C_6H_5), 135.9 (*o*-C_6H_5), 131.7 (*m*-C_6H_5), 123.4 (NCH*C*HN), 123.0 (*p*-C_6H_5), 121.0 (N*C*HCHN), 70.3 (C_6H_{10}), 66.0 (C_6H_{10}), 54.0 (*C*H_2), 34.8 (C_6H_{10}), 29.5 (C_6H_{10}), 24.5 (C_6H_{10}), 24.0 (C_6H_{10}). IR data cm^{-1} KBr pellet: 3419 (s) ($\nu_{O–H}$). LRMS (ES): *m*/*z* 619 [(NHC)$_2$Ag]$^+$. CHN Anal. Calc. for $C_{16}H_{20}AgClN_2O$: C, 48.08; H, 5.04; N, 7.01. Found: C, 47.58; H, 4.79; N, 6.58%.

2.7. Synthesis of [1-(2-hydroxy-cyclohexyl)-3-(benzyl)-imidazol-2-ylidene]AuCl (*2c*)

A mixture of {[1-(2-hydroxy-cyclohexyl)-3-(benzyl)imidazol-2- ylidene]$_2$Ag}$^+$Cl$^-$ (**2b**) (0.403 g, 0.509 mmol) and (SMe_2)AuCl (0.150 g, 0.509 mmol) in dichloromethane (*ca.* 15 mL) was stirred at room temperature for 6 h, when the formation of a off-white AgCl precipitate was observed. The reaction mixture was filtered and the solvent was removed under vacuum to obtain the product **2c** as a white solid (0.138 g, 45%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 7.38–7.32 (m, 5H, C_6H_5), 7.00 (br, 1H, NC*H*CHN), 6.90 (br, 1H, NCHC*H*N), 5.44 (d, 1H, $^2J_{HH} = 15$ Hz, CH_2), 5.35 (d, 1H, $^2J_{HH} = 15$ Hz, CH_2), 4.48–4.41 (m, 1H, C_6H_{10}), 3.93–3.86 (m, 1H, C_6H_{10}), 2.21–2.12 (m, 2H, C_6H_{10}), 1.87–1.80 (m, 2H, C_6H_{10}), 1.68–1.55 (m, 2H, C_6H_{10}), 1.49–1.41 (m, 2H, C_6H_{10}). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ 170.1 (N*C*N), 135.1 (*ipso*-C_6H_5), 129.0 (*m*-C_6H_5), 128.9 (*o*-C_6H_5), 128.6 (*p*-C_6H_5), 120.6 (N*C*HCHN), 118.8 (NCH*C*HN), 72.6 (C_6H_{10}) 67.4 (C_6H_{10}), 55.4 (C_6H_{10}), 34.7 (C_6H_{10}), 33.0 (C_6H_{10}), 24.8 (C_6H_{10}), 24.2 (C_6H_{10}). IR data cm^{-1} KBr pellet: 3426 (s) ($\nu_{O–H}$). CHN Anal. Calc. for $C_{16}H_{20}AuClN_2O$: C, 39.32; H, 4.12; N 5.73. Found: C, 39.14; H, 3.94; N, 5.44%.

2.8. Synthesis of [1,3-di-i-propyl-benzimidazol-2-ylidene]-AgBr (*3a*)

A mixture of 1,3-di-*i*-propyl-benzimidazolium bromide (1.89 g, 6.69 mmol) and Ag_2O (0.775 g, 3.35 mmol) in acetonitrile (*ca.* 30 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 **3a** as a white solid (1.57 g, 60%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.64 (dd, 2H, $^3J_{HH} = 7$ Hz, $^4J_{HH} = 3$ Hz, *o*-C_6H_4), 7.38 (dd, 2H, $^3J_{HH} = 7$ Hz, $^4J_{HH} = 3$ Hz, *m*-C_6H_4), 5.09 (sept, 2H, $^3J_{HH} = 8$ Hz, C*H*(CH_3)$_2$), 1.73 (d, 12H, $^3J_{HH} = 8$ Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ 185.4 (N*C*N–Ag), 132.5 (*ipso*-C_6H_4), 123.2 (*m*-C_6H_4), 112.2 (*o*-C_6H_4), 53.2 (*C*H(CH_3)$_2$), 22.1 (CH(*C*H_3)$_2$). IR Data cm^{-1} KBr pellet: 3058 (w), 2974 (s), 2931 (m), 2876 (w), 2730 (w), 2190 (w), 1959 (w), 1918 (w), 1796 (w),

1669 (m), 1603 (m), 1553 (w), 1475 (s), 1461 (s), 1424 (s), 1392 (s), 1363 (s), 1333 (s), 1289 (s), 1230 (s), 1207 (m), 1164 (s), 1132 (m), 1100 (s), 1021 (w), 940 (w), 882 (m), 799 (m), 781 (w), 754 (s), 656 (w), 559 (w), 521 (w). CHN Anal. Calc. for $C_{13}H_{18}AgBrN_2(CH_3CN)$ C, 41.79; H, 4.91; N, 9.75. Found: C, 42.74; H, 4.69; N, 9.01%.

2.9. Synthesis of [1,3-di-i-propyl-benzimidazol-2-ylidene]-AuCl (3b)

A mixture of [1,3-di-*i*-propyl-benzimidazol-2-ylidene]AgBr **3a** (0.329 g, 0.848 mmol) and $(SMe_2)AuCl$ (0.250 g, 0.848 mmol) in dichloromethane (*ca.* 30 mL) was stirred at room temperature for 6 hours when the formation of an off-white AgBr precipitate was observed. The reaction mixture was filtered and the solvent was removed under vacuum to obtain the product **3b** as a white solid (0.266 g, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.66 (dd, 2H, $^3J_{HH} = 7$ Hz, $^4J_{HH} = 3$ Hz, *o*-C_6H_4), 7.38 (dd, 2H, $^3J_{HH} = 7$ Hz, $^4J_{HH} = 3$ Hz, *m*-C_6H_4), 5.52 (sept, 2H, $^3J_{HH} = 8$ Hz, $CH(CH_3)_2$), 1.74 (d, 12H, $^3J_{HH} = 8$ Hz, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ 175.9 (N*C*N–Au), 132.3 (*ipso*-C_6H_4), 123.8 (*m*-C_6H_4), 113.1 (*o*-C_6H_4), 54.3 ($CH(CH_3)_2$), 21.6 ($CH(CH_3)_2$). IR Data cm^{-1} KBr pellet: 3058 (w), 2976 (m), 2932 (m), 2877 (w), 1604 (w), 1556 (w), 1478 (m), 1463 (m), 1435 (m), 1418 (s), 1399 (s), 1373 (m), 1311 (m), 1297 (w), 1231 (w), 1174 (m), 1142 (m), 1095 (m), 1025 (w), 936 (w), 894 (w), 816 (w), 749 (s), 650 (w), 548 (w). CHN Anal. Calc. for $C_{13}H_{18}AuClN_2$ C, 35.92; H, 4.17; N, 6.44. Found: C, 35.69; H, 3.36; N, 7.14%.

2.10. Polymerization experiments

Bulk polymerizations of L-lactide were carried out in vacuum-sealed glass ampoules. The glass ampoule was first charged with monomer (L-lactide) and dried for a period of 2 h under high vacuum at 50 °C. Subsequently, the catalyst (**1c** or **2c** or **3b**) was added keeping with the monomer to catalyst ratio ranging from 50 to 250. 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 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 not to influence the results.

3. Results and discussion

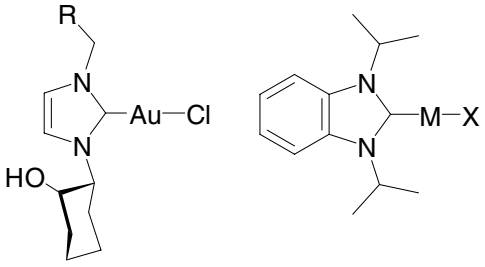
Three types of N-heterocyclic carbene systems namely, (i) di-O-functionalized, 1-(2-hydroxy-cyclohexyl)-3-(acetophenone)imidazol-2-ylidene, (ii) mono-O-functionalized, 1-(2-hydroxy-cyclohexyl)-3-(benzyl)imidazol-2-ylidene, and (iii) non-functionalized, 1,3-di-*i*-propyl-benzimidazol-2-ylidene, have been synthesized with the intent of designing new Au–NHC based initiators for utility in the ring-opening polymerization (ROP) of L-lactide (Fig. 1).

3.1. O-Functionalized N-heterocyclic carbenes

Both the di-O-functionalized, 1-(2-hydroxy-cyclohexyl)-3-(acetophenone)imidazolium chloride (**1a**), and the mono-O-functionalized, 1-(2-hydroxy-cyclohexyl)-3-(benzyl)imidazolium chloride (**2a**), were synthesized using an epoxide ring-opening reaction earlier reported by us [11] and by Arnold [36]. Specifically, the direct reactions of chloroacetophenone and benzyl chloride with cyclohexene oxide and imidazole gave the respective di-O-functionalized **1a** and the mono-O-functionalized **2a** imidazolium chloride salts in *ca.* 57–58% yield. The formations of the imidazolium chloride salts were evident from the appearances of the diagnostic (NC*H*N) peaks at 9.70 ppm (**1a**) and at 10.1 ppm (**2a**) in the ^{1}H NMR spectra while the corresponding (N*C*HN) resonances at 137.4 ppm (**1a**) and at 136.1 ppm (**2a**) in the ^{13}C NMR spectra. The carbonyl moiety (*C*=O) in **1a** appeared at 191.3 ppm in the ^{13}C NMR spectrum and at 1694 cm^{-1} in the infrared spectrum. The electrospray mass analysis showed peaks at *m*/*z* 285 (**1a**) and at *m*/*z* 257 (**2a**) corresponding to the individual cationic imidazolium fragments.

The imidazolium chloride salt **1a** has been structurally characterized by X-ray diffraction studies (Fig. 2). The C1–N1 [1.312(6) Å] and the C1–N2 [1.325(6) Å] distances in the di-O-functionalized imidazolium chloride salt **1a** is comparable to that observed for other reported analogs like, another di-O-functionalized 1-(2-hydroxy-cyclohexyl)-3-(*N*-*t*-butylacetamido)imidazolium chloride [1.326(6), 1.314(6) Å] [11] and a mono-O-functionalized 1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazolium chloride [1.320(2), 1.323(2) Å] [14]. The ∠N1–C1–N2 angle in **1a** was observed to be 108.8(5)° and is comparable to other reported complexes.

An interesting feature of the **1a** structure is that despite the presence of an OH group in the functionalized sidearm, a [Cl···H–C] type hydrogen bonding interaction between



R = COPh (**1c**) M = Ag, X = Br (**3a**)
R = Ph (**2c**) M = Au, X = Cl (**3b**)

Fig. 1. Silver and gold complexes of di-O-functionalized, mono-O-functionalized, and non-functionalized N-heterocyclic carbenes are shown.

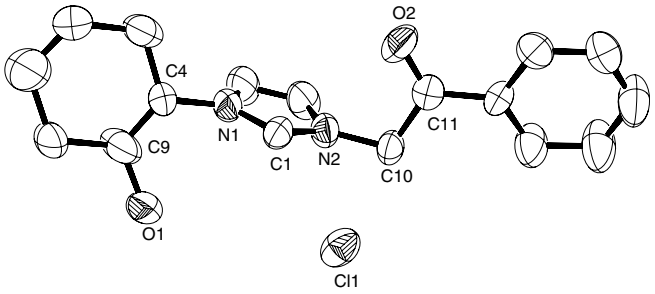


Fig. 2. ORTEP of **1a** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): N(1)–C(1) 1.312(6), N(2)–C(1) 1.325(6), N(2)–C(1)–N(1) 108.8(5).

the chloride anion (Cl1) and the 2-position imidazolyl (NC*H*N) proton was observed, a fact indicative of the highly acidic nature of 2-position imidazolyl (NC*H*N) proton and is further corroborated by the observed high downfield shift (9.70 ppm for **1a**) of the (NC*H*N) resonance in the ^{1}H NMR spectrum recorded in non-polar $CDCl_3$ solvent. Evidence in favor of the presence of [Cl···H–C] type hydrogen bonding interaction in solution further came from the methanol-d_4 ^{1}H NMR spectrum of **1a**, as methanol being more polar a solvent would disfavor the [Cl···H–C] type hydrogen bonding interaction and, indeed, the imidazolyl (NC*H*N) proton resonance was found to be significantly shifted by *ca*. 0.54 to 9.16 ppm (δ) in its methanol-d_4 ^{1}H NMR spectrum. However, definitive proof for the hydrogen bonding interaction came from the X-ray diffraction studies. Specifically, the Cl1···C1 distance of 3.386 Å in **1a** is significantly shorter than the sum of the individual van der Waals radii of Cl and C (3.45 Å) [37]. However, it is worth noting that in a related di-O-functionalized 1-(2-hydroxy-cyclohexyl)-3-(*N*-*t*-butylacetamido)imidazolium chloride [11], also containing a similar hydroxyl group in the functionalized sidearm, a [Cl···H–O] type hydrogen bonding interaction was observed with the Cl1···O distance being 3.091 Å instead of the [Cl···H–C] type hydrogen bonding interaction seen in **1a**. Quite expectedly, in another mono-functionalized 1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazolium chloride [14] which is bereft of any hydroxyl group, a [Cl···H–C] hydrogen bonding interaction was observed between the chloride anion and the 2-position imidazolyl (NC*H*N) proton with the Cl1···C1 distance being 3.373 Å.

The gold complexes of the di-O-functionalized NHC ligand **1c** and the mono-O-functionalized NHC ligand **2c** were synthesized by the commonly used silver carbene transfer route from the respective silver complexes **1b** and **2b** by treatment with (SMe_2)AuCl in 68% and 45% yields respectively. The gold complexes **1c** and **2c** are sufficiently air stable to allow manipulations in open-air. The silver complexes **1b** and **2b** were synthesized from the corresponding imidazolium halide salts **1a** and **2a** by the reaction with Ag_2O following a procedure earlier reported by Wang and Lin [38]. Apart from the Ag_2O route [38] which is by far the most popular method [21] a few other methods, although not very common, have been reported for synthesizing the Ag–NHC complexes *e.g.* from the reaction of free N-heterocyclic carbene with AgOTf [39,40] and also by the reaction of imidazolium halide salts with silver halide under phase transfer catalysis conditions [38]. Quite interestingly, there remains more versatility in methods available for sythesizing Au–NHC complexes than for the Ag–NHC complexes. For example, the Au–NHC complexes can be prepared by various methods like, (i) cleavage of electron-rich olefins [41], (ii) carbene transfer from group 6 carbonyl complexes [42], (iii) reactions of azolium salts or free NHCs with Au(I) precursors [43], (iv) protonation or alkylation of gold azolyl complexes [44], and (v) transmetalation *via* the reaction of Ag(I)-NHC complexes with Au(I) precursors [38].

The ^{1}H NMR spectra of the gold, **1c** and **2c**, and the silver complexes, **1b** and **2b**, are worth commenting on. The bridging methylene (–CH_2–) protons are diastereotropic in nature and thus appear as separate resonances in the gold **1c** (5.83, 5.69 ppm) and **2c** (5.44, 5.35 ppm) and the silver **1b** (5.87, 5.62 ppm) and **2b** (5.26, 5.14 ppm) complexes, displaying a two-bond vicinal coupling ($^2J_{H-H}$) of *ca*. 15 Hz. For example, similar diastereotopic hydrogens for the bridging methylene moiety (–CH_2–) has been observed by us [11] for an analogous NHC variant as well as by Peris and coworkers [45] for Ir complexes of 1-*n*-butyl-3-(2-pyridylmethyl)imidazol-2-ylidene ligand. Quite expectedly, the characteristic metal bound carbene (NC*C*N–M; M = Au, Ag) peaks appeared in the highly downfield shifted region of the ^{13}C NMR spectra for the gold, **1c** (167.6 ppm) and **2c** (170.1 ppm), and the silver, **1b** (181.4 ppm) and **2b** (179.7 ppm) complexes.

The molecular structures of the gold, **1c** and **2c**, complexes have been determined by X-ray diffraction studies (Figs. 3 and 4) that revealed the formations of neutral monomeric (NHC)AuCl type complexes exhibiting the commonly observed linear geometries at the metal centers characteristics of the d^{10} configurations of Au(I) [46]. The Au–C_{carb} distances of 1.991(4) Å (**1c**) and 1.987(14) Å (**2c**) are slightly shorter that the sum of the individual

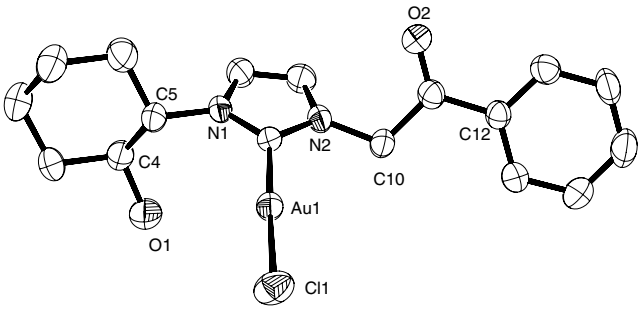


Fig. 3. ORTEP of **1c** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Au–C(1) 1.991(4), Au–Cl(1) 2.2921(11), N(1)–C(1) 1.344(5), N(2)–C(1) 1.356(5), C(1)–Au–Cl(1) 177.53(10), N(2)–C(1)–N(1) 105.9(3).

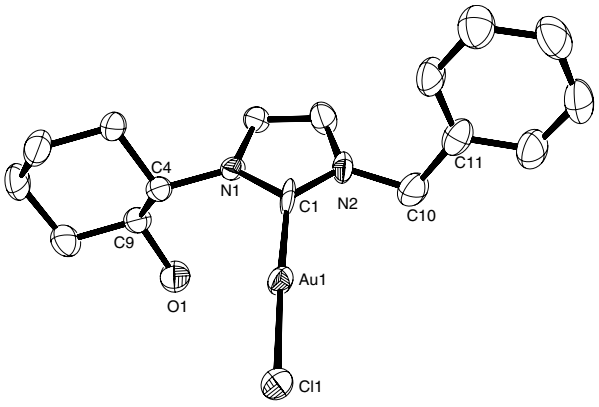


Fig. 4. ORTEP of **2c** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Au–C(1) 1.987(14), Au–Cl(1) 2.294(3), N(1)–C(1) 1.371(13), N(2)–C(1) 1.292(15), C(1)–Au–Cl(1) 177.3(3), N(2)–C(1)–N(1) 106.6(11).

covalent radii of Au and C (2.108 Å) [47] and is comparable to the other reported analogous gold complexes namely, [1-(2-hydroxy-cyclohexyl)-3-(*N*-*t*-butylacetamido)-imidazol-2- ylidene]AuCl [1.969(5) Å] [11] and [1,3-bis(R)-imidazol-2-ylidene]AuCl [48] {R = mesityl [1.998(5) Å], 2,6-di-*i*-propylphenyl [1.979(3) Å], cyclohexyl [1.990(13)-Å, 1.996(12) Å], and adamantyl [1.989(2) Å]} complexes.

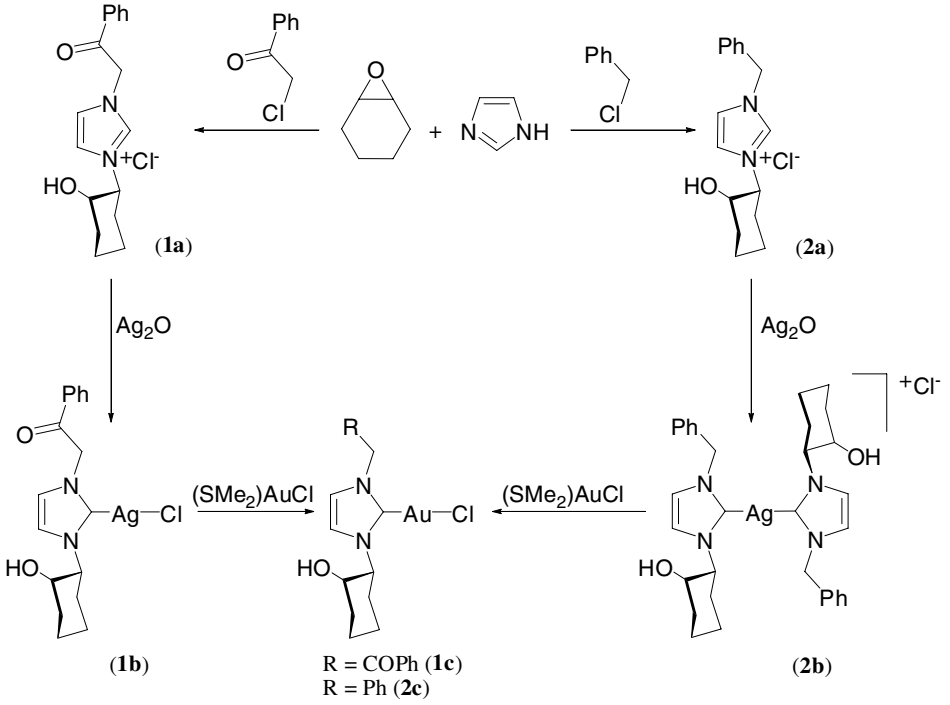
Interestingly, no chelation from the O-functionalized imidazolyl sidearm to the metal center was observed either in case of the di-O-functionalized **1c** complex having the (alkoxy O) O1···Au1 distance of 3.86 Å and the (carbonyl O) O2···Au1 distance of 4.94 Å or in the mono-O-functionalized **2c** complex that displayed the (alkoxy O) O1···Au1 distance of 4.07 Å. Similar lack of coordination from the O-functionalized imidazolyl sidearm to Au was earlier observed in a related analog [11] and is in accordance with the propensity of Au(I) towards adapting a linear geometry [46].

It is worth mentioning that compared to the Ag–NHC complexes [49–52], the gold analogs are relatively fewer [11,53–55] in number and they exhibit much less diverse structural motifs than their silver counterparts. Primarily, the neutral monomeric (NHC)AuX (X = halide) and cationic $[(NHC)_2Au]^+$ type structures are commonly observed for the Au–NHC complexes [56].

3.2. Non-functionalized N-heterocyclic carbene

The gold and silver complexes of the non-functionalized 1,3-di-*i*-propyl-benzimidazol-2-ylidene were synthesized following the same methodology as their O-functionalized counterparts, *i.e.* the gold, **1c** and **2c**, and the silver, **1b** and **2b**, complexes. Specifically, the silver complex [1,3-di-*i*-propyl-benzimidazol-2-ylidene]AgBr (**3a**) was synthesized from the reaction of 1,3-di-*i*-propyl-benzimidazolium bromide [35] with Ag_2O in 60% yield while the corresponding gold complex, [1,3-di-*i*-propyl-benzimidazol-2-ylidene]-AuCl (**3b**), was obtained from the silver complex **3a** by the treatment with $(SMe_2)AuCl$ in 72% yield (Scheme 1).

The molecular structures of the gold **3b** (Fig. 7) and the silver **3a** (Fig. 5) complexes have been determined by X-ray diffraction studies that revealed the formations of neutral (NHC)MX (M = Au, Ag; X = Cl, Br) type complexes. Quite expectedly, in accordance with the smaller covalent



Scheme 1.

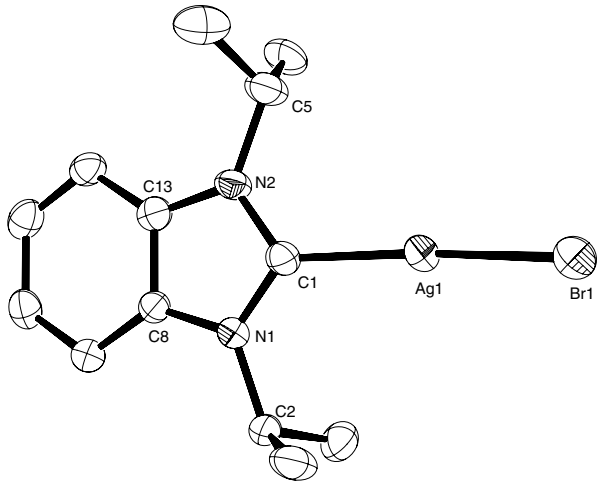


Fig. 5. ORTEP of **3a** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Ag1–C(1) 2.093(4), Ag1–Br(1) 2.4874(6), N(1)–C(1) 1.346(4), N(2)–C(1) 1.353(4), C(1)–Ag1–Br(1) 161.04(9), N(2)–C(1)–N(1) 106.1(3).

radii of Au compared to Ag [47,57], the observed Au–C_{carb} distance of 1.972(9) Å in the gold complex **3b** was indeed shorter than the Ag–C_{carb} distance of 2.093(4) Å in the silver complex **3a**. An important difference between the gold **3b** and the silver **3a** structures, however, is the existence of the intermolecular Ag···Br interactions in the latter, resulting in a head-to-tail dimeric $\{(NHC)AgBr\}_2$ type association containing a Ag_2Br_2 core (Fig. 6). The two equivalent intermolecular Ag(1)···Br(1a) and Ag(1a)···Br(1) distances of 2.8999(5) Å in **3a** is significantly shorter than the sum of the individual van der Waals radii of Br and Ag (3.59 Å) [37]. Similar intermolecular Ag···Br interactions have been observed by Lin and coworkers [58] for a analogous dimeric complex, $\{[1,3\text{-di-(R)-imidazol-2-ylidene}]AgBr\}_2$ (R = $C_{14}H_{29}$), with a Ag_2Br_2 core and displaying a intermolecular Ag···Br distance of 2.9248(8) Å (Scheme 2).

Worth comparing are the gold **3b** and the silver **3a** structures with the other reported [1,3-di-substituted-benzimidazol-2-ylidene] analogs. Unlike the neutral (NHC)-AgBr type complex obtained in the case of **3a**, having two bulky *i*-propyl substituents, from the reaction of the benzimidazolium halide salt with Ag_2O, the same reaction with diethyl analog of the benzimidazolium halide salt resulted in a cationic $\{[1,3\text{-di-ethyl-imidazol-2-ylidene}]_2Ag\}^+AgBr_2^-$ complex [38], displaying significant Ag···Ag interaction [d(Ag···Ag) = 2.954(4) Å]. Contrary to the different structural motifs observed in case of the silver complexes, the [1,3-di-substituted-benzimidazol-2-ylidene] complexes of gold, however, showed a neutral (NHC)AuCl type structures *e.g*, [1,3-di-methyl-benzimidazol-2-ylidene]AuCl [59] [1,3-di-ethyl-benzimidazol-2-ylidene]AuCl [59] and [1,3-di-*i*-propyl-benzimidazol-2-ylidene]AuCl (**3b**). It is interesting to note that intermolecular interactions, both Au···Au and π···π types, observed in the gold complexes decreased with increase in the steric bulk of the ancillary ligand, as the [1,3-di-methyl-benzimidazol-2-ylidene]AuCl showed Au···Au [d(Au···Au) = 3.1664(10) Å] and π···π [ring–ring distance = 3.45 Å] interactions, while the bulkier [1,3-di-ethyl-benzimidazol-2-ylidene]AuCl showed only π···π [ring–ring distance = 3.53 Å] interaction and the bulkiest in the series, [1,3-di-*i*-propyl-ben-

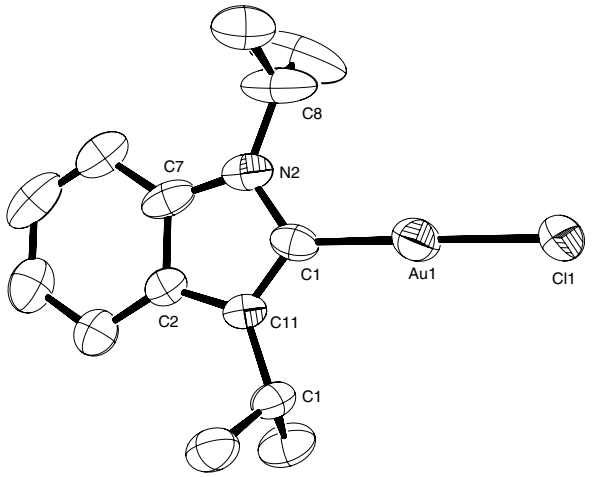


Fig. 7. ORTEP of **3b** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Au–C(1) 1.972(9), Au–Cl(1) 2.272(3), N(1)–C(1) 1.373(11), N(2)–C(1) 1.334(11), C(1)–Au–Cl(1) 178.1(2), N(2)–C(1)–N(1) 107.8(8).

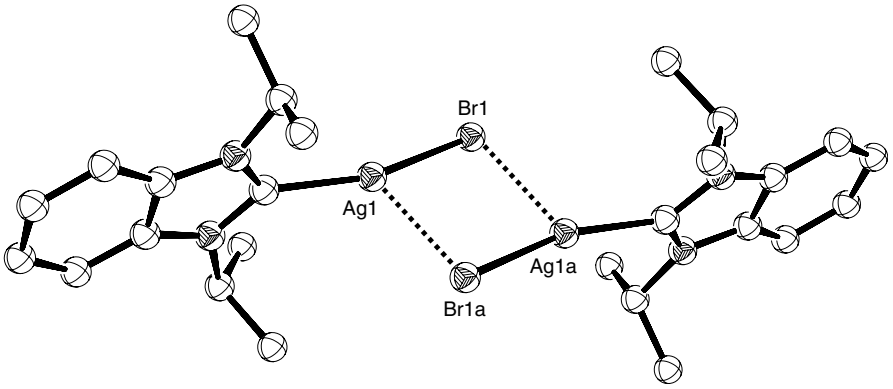
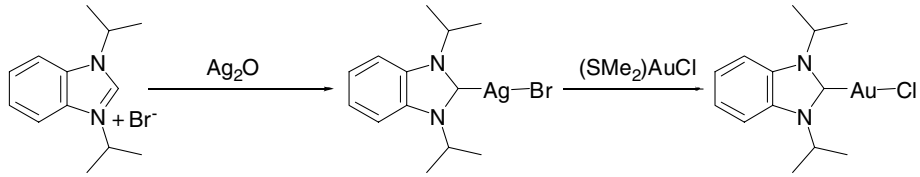


Fig. 6. Intermolecular Ag(1)···Br(1a) (2.900 Å) and Ag(1a)···Br(1) (2.900 Å) interactions observed in **3a**.



Scheme 2.

zimidazol-2-ylidene]AuCl (**3b**), was bereft of any such interaction.

Significantly enough, all of the di-O-functionalized **1c**, mono-O-functionalized **2c**, and the non-functionalized **3b** gold complexes efficiently catalyzed the ring-opening polymerization (ROP) of L-lactide under solvent-free melt conditions. It is worth noting that very little is known about the catalytic utility of gold in the ring-opening polymerization (ROP) of L-lactide and in this regard we have recently reported the first example of a Au–NHC based initiator, [1-(2-hydroxy-cyclohexyl)-3-(*N*-*t*-butylacetamido)imidazol-2-ylidene]AuCl [11], for the lactide polymerization. Building upon our initial discovery [11] the current set of gold compounds, **1c**, **2c**, and **3b**, thus offer scope for studying the effect of functionalization, in the forms of di-O-functionalized **1c** and the mono-O-functionalized **2c**, and also the effect of modification of the N-heterocyclic ring, in the form of benzimidazole backbone in **3b**, of the Au–NHC based initiators on the ring-opening polymerization (ROP) of L-lactide.

Specifically, a typical polymerization experiment would involve heating L-lactide and the catalyst, **1c**, **2c**, or **3b**, 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 maximum molecular weight in case of the di-O-functionalized **1c** (entry 2: $M_n = 9.2 \times 10^3$, Table 2) and the mono-O-functionalized **2c** (entry 2: $M_n = 8.4 \times 10^3$, Table 3) were obtained at [M]:[C] ratio 100:1 whereas for the non-functionalized **3b** (entry 3: $M_n = 1.0 \times 10^4$, Table 4) the same was obtained at 150:1 ratio for a 4 h run at 160 °C. The molecular weight distributions are almost similar for these Au–NHC based initiators, **1c** (PDI = 1.16–1.26), **2c** (PDI = 1.13–1.34), and **3b** (PDI = 1.13–1.48) [PDI = ploydispersity index].

The time dependence study showed steady increase in the polymer molecular weight with time with maximum molecular weight (M_n) observed for **1c** (9.3×10^3; entry 12, Table 2) and **2c** (1.0×10^4; entry 12, Table 3) after 8 h at 160 °C while the same for **3b** (1.0×10^4; entry 3, Table 4) was reached at 4 h at 160 °C after which it plateaued off. The temperature dependence study, carried out in the range 120–180 °C, too, showed similar increase in the

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

Entry	L-Lactide/(**1c**) ratio	Temp. (°C)	Time (h)	M_n	M_w/M_n	Conv. (%)
1	50	160	4	5.6×10^3	1.24	>99
2	100	160	4	9.2×10^3	1.18	>99
3	150	160	4	8.0×10^3	1.17	87
4	200	160	4	7.8×10^3	1.28	78
5	250	160	4	5.2×10^3	1.26	36
6	100	120	4	5.5×10^3	1.17	53
7	100	140	4	7.3×10^3	1.16	59
8	100	180	4	4.7×10^3	1.34	>99
9	100	160	1	3.7×10^3	1.19	42
10	100	160	2	4.1×10^3	1.22	66
11	100	160	3	7.3×10^3	1.24	81
12	100	160	8	9.3×10^3	1.26	92

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

Entry	L-Lactide/(**2c**) ratio	Temp. (°C)	Time (h)	M_n	M_w/M_n	Conv. (%)
1	50	160	4	4.7×10^3	1.25	>99
2	100	160	4	8.4×10^3	1.16	82
3	150	160	4	7.0×10^3	1.15	75
4	200	160	4	6.9×10^3	1.17	69
5	250	160	4	6.4×10^3	1.24	74
6	100	120	4	6.7×10^3	1.13	89
7	100	140	4	7.6×10^3	1.12	86
8	100	180	4	4.1×10^3	1.34	>99
9	100	160	1	2.5×10^3	1.18	49
10	100	160	2	2.7×10^3	1.14	32
11	100	160	3	4.1×10^3	1.26	94
12	100	160	8	1.0×10^4	1.20	>99

Table 4
Melt polymerization of L-lactide by **3b**

Entry	L-Lactide/(**3c**) ratio	Temp. (°C)	Time (h)	M_n	M_w/M_n	Conv. (%)
1	50	160	4	6.3×10^3	1.32	>99
2	100	160	4	7.4×10^3	1.37	98
3	150	160	4	1.0×10^4	1.26	90
4	200	160	4	6.8×10^3	1.27	93
5	250	160	4	5.8×10^3	1.26	87
6	100	120	4	5.1×10^3	1.13	37
7	100	140	4	5.7×10^3	1.19	73
8	100	180	4	5.8×10^3	1.34	>99
9	100	160	1	4.7×10^3	1.25	81
10	100	160	2	6.6×10^3	1.48	90
11	100	160	3	7.0×10^3	1.40	92
12	100	160	8	9.2×10^3	1.27	97

polymer molecular weight with temperature up to 160 °C for all the gold initiators, **1c** (9.2×10^3; entry 2, Table 2), **2c** (8.4×10^3; entry 2, Table 3), and **3b** (7.4×10^3; entry 2, Table 4), above which a decrease was observed for all the three initiators at 180 °C. It is worth noting that similar decrease in the polymer molecular weight at higher temperatures has been earlier observed by Liao [30] and by Albertson and Varma [28].

Worth is the comparison of the gold **1c**, **2c** and **3b** initiators with the only other reported Au–NHC initiator, [1-(2-hydroxy-cyclohexyl)-3-(*N*-*t*-butylacetamido)imidazol-2-ylidene]AgCl [11]. Quite interestingly, higher molecular weight polylactide polymers were consistently obtained in case of both the di-O-functionalized **1c** (4.7×10^3 to 8.4×10^3) and the mono-O-functionalized **2c** (5.2×10^3–9.2×10^3) initiators compared to that of the structurally related [1-(2-hydroxy-cyclohexyl)-3-(*N*-*t*-butylacetamido)-imidazol-2- ylidene]AgCl [11] complex (3.6×10^3–5.4×10^3) at all the [M]:[C] ratios (50:1, 100:1, 150:1, 200:1, and 250:1) after 4 h at 160 °C. The non-functionalized **3b** initiator, possessing benzimidzole framework, too, showed similar higher polymer molecular weights (5.8×10^3–10.0×10^3) at the same [M]:[C] ratios under analogous conditions (4 h at 160 °C).

4. Summary

In summary, gold and silver complexes of di-O-functionalized, mono-O-functionalized, and non-functionalized N-heterocyclic carbene ligands have been synthesized and characterized. The molecular structures of the gold complexes, [1-(2-hydroxy-cyclohexyl)-3-(acetophenone)-imidazol-2-ylidene]AuCl (**1c**), [1-(2-hydroxy-cyclohexyl)-3-(benzyl)imidazol-2-ylidene]AuCl (**2c**), [1,3-di-*i*-propyl-benzimidazol-2-ylidene]AuCl (**3b**), and the silver complex [1,3-di-*i*-propyl-benzimidazol-2-ylidene]AgBr (**3a**) along with an imidazoilum chloride salt, 1-(2-hydroxy-cyclohexyl)-3-(acetophenone)imidazolium chloride (**1a**), have been determined by X-ray diffraction studies. The structural comparisons of the gold and silver complexes revealed that geometries around the metal centers were almost linear. No chelations through the O-functionalized sidearm substituent of the N-heterocyclic ligands to the metal centers were observed in these gold and silver complexes. The gold (**1c**, **2c**, and **3b**) complexes efficiently catalyze ring-opening polymerization of L-lactide under solvent-free melt conditions producing polylactide polymer of moderate to low molecular weights with narrow molecular weight distributions.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.06.033.

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