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Experimental and theoretical studies of a silver complex of O-functionalized N-heterocyclic carbene

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Abstract

Experimental and theoretical studies of a silver complex namely, [1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazol-2-ylidene]AgCl (**1b**), supported over an O-functionalized N-heterocyclic carbene ligand are reported. Specifically, [1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazol-2-ylidene]AgCl (**1b**) was synthesized by reaction of 1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazolium chloride **1a** with Ag_2O in 42% yield. The 1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazolium chloride **1a** was synthesized by the alkylation reaction of 1-*i*-propylimidazole with α-chloropinacolone in 70% yield. The molecular structures of **1a** and **1b** have been determined by X-ray diffraction. Detailed theoretical investigation has been performed using the density functional theory method with the B3LYP functional. Bonding in **1b** has been probed with the help of charge decomposition analysis (CDA), atoms in molecule (AIM) approach as well as natural bond orbital (NBO) methods. The Ag–NHC bond has a dominantly covalent character with NHC acting as an effective σ-donor. The π-back-bonding from the metal to the ligand was found to be negligible.

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

1. Introduction

The field of N-heterocyclic carbene (NHC) chemistry has seen a phenomenal growth in recent years, with numerous new applications [1] in organometallic catalysis emerging day by day [2]. Recently, the transition metal–NHC complexes have been found to be efficient catalysts for many important transformations such as C–C coupling reaction [3,4], olefin metathesis [5], hydrogenation [6,7], hydroformylation [8], hydrosilylation [9], CO–ethlyene copolymerization [10] and hydroboration [11] reactions etc. In this context, the silver–NHC complexes deserve a special mention as they have played a pivotal role in the development of the N-heterocyclic carbene chemistry. This is particularly because the silver–NHC complexes, being effective transmetallating agents, provide a dependable and a convenient route to a whole gamut of transition metal complexes many of which have catalytic utilities. Furthermore, as an outcome of numerous efforts towards designing new N-heterocyclic carbene motifs, a large number of silver–NHC complexes were thus synthesized and their molecular structures determined [12–15]. Recent reports of the silver–NHC complexes exhibiting catalytic activity in ethyl diazoacetate (EDA) assisted carbene transfer reactions [16], *trans*-esterification reactions and in ring-opening lactide polymerization reactions [17], etc., not only underscores the importance of silver–NHC complexes in chemical catalysis but also represent an important emerging area of research.

The successes of NHCs in general and their silver complexes in particular can partly be attributed to its ease of synthetic accessibility and partly to the observed air, moisture and thermal stabilities of these complexes [7,13,18].

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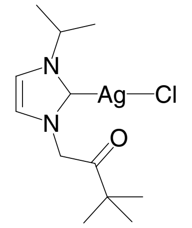
Because of their superior stability, the NHC catalysts are fast replacing their phosphine counterparts in organometallic catalysis and thus are becoming increasingly popular as “phosphine substitutes” in this area. A notable contrast between the NHCs and the phosphines is that in general the NHCs are easy to synthesize but are relatively difficult to metallate while the reverse is true in case of the phosphines. On the other hand, the parallel between NHCs and tertiary phosphines primarily arises from an accepted notion that both of them are generally good σ-donating ligands with minimal π-accepting properties [19]. In fact, recent IR studies on metal carbonyl complexes of NHCs and phosphines indicated that the σ-donating properties of NHCs are better than the phosphines [20,21]; a result that also conformed well with a comparative density functional theory study on NHC and phosphine complexes [22]. Despite relatively poor π-back-bonding [23] in NHCs, a few recent reports suggest the presence of such interactions in NHC–metal complexes [24–27].

Since, the exceptional stabilities of the metal–NHC complexes can directly be related to the nature of the metal–carbene bond, an insight into the bonding assumes additional relevance and a detailed study is desirable. A better understanding of the nature of metal–carbene bond would be useful in designing catalysts with superior performances. With this intent in mind we set out to synthesize silver complexes of new O-functionalized N-heterocyclic carbene ligands and study its properties theoretically. Our interest, in designing functionalized NHC ligands, is primarily based on our rationale that the chelation through the functionalized side arm may lead to complexes, and eventually the catalysts, with improved thermal stabilities. In particular, our reason for incorporating a $–CH_2COBu^t$ functionalized N-substituent is for achieving a stable six-membered chelating ring with the metal center in the NHC–metal complexes. For example, in case of the phosphine catalysts, the chelated ones have been reported to posses remarkably high thermal stabilities [28].

Here in this contribution we report the synthesis, structural characterization and theoretical studies of a silver complex namely, [1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazol-2-ylidene]AgCl (**1b**), supported over a new O-functionalized N-heterocyclic carbene ligand (Fig. 1).



1b

Fig. 1. The [1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazol-2-ylidene]AgCl complex is shown.

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. Chloropinacolone [29] and 1-*i*-propylimidazole [30] were synthesized according to the literature procedures. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian 400 MHz NMR spectrometer. ^1H and ^{13}C NMR peaks are labeled as singlet (s), doublet (d), triplet (t), and septet (sept). Infrared spectra were recorded on a Perkin–Elmer Spectrum One FT-IR spectrometer. Mass spectrometry measurements were done on a Micromass Q-Tof spectrometer.

2.2. Synthesis of 1-i-propyl-3-(2-oxo-2-t-butyl ethyl)imidazolium chloride (1a)

Chloropinacolone (1.03 g, 7.66 mmol) and 1-*i*-propylimidazole (0.845 g, 7.67 mmol) were taken in toluene (ca. 10 cm^3) and refluxed at 140 °C for 12 h during which a brown sticky mass was formed. The sticky substance was collected by filtration and was washed with hexane (ca. 15 cm^3) and dried under vacuum to give 1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazolium chloride (**1a**) as a brown viscous product (1.31 g, 70%). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): $\delta = 9.91$ (s, 1H, NC*H*N); 7.51 (s, 1H, NC*H*CHN); 7.46 (s, 1H, NCHC*H*N); 5.82 (s, 2H, CH_2); 4.70 (sept, $^3J_{H,H} = 6$ Hz, 1H, $CH(CH_3)_2$); 1.52 (d, $^3J_{H,H} = 6$ Hz, 6H, $CH(CH_3)_2$); 1.21 (s, 9H, $C(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): $\delta = 207.0$ (*C*O); 135.9 (N*C*HN); 123.9 (N*C*HCHN); 119.1 (NCH*C*HN); 53.9 (CH_2); 52.7 ($CH(CH_3)_2$); 42.9 ($C(CH_3)_3$); 25.7 ($C(CH_3)_3$); 22.5 ($CH(CH_3)_2$) ppm. IR Data cm^{-1} KBr pellet: 1721 (s) (ν_{co}). LRMS (ES): *m/z* 209 $(NHC\text{-}ligand)^+$ 100%. HRMS (ES): *m/z* 209.1657 $(NHC\text{-}ligand)^+$ Calculated 209.1654.

2.3. Synthesis of [1-i-propyl-3-(2-oxo-2-t-butyl ethyl)imidazol-2-ylidene]AgCl (1b)

A mixture of 1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazolium chloride (**1a**) (1.31 g, 5.35 mmol) and Ag_2O (0.615 g, 2.66 mmol) in dichloromethane (*ca.* 15 cm^3) was stirred for 4 h at room temperature. The reaction mixture was filtered and the filtrate was collected and dried under vacuum to give [1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazol-2-ylidene]AgCl (**1b**) as a dark brown solid (0.786 g, 42%). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): $\delta = 7.07$ (s, 1H, NC*H*CHN); 6.98 (s, 1H, NCHC*H*N); 5.12 (s, 2H, CH_2); 4.73 (sept, $^3J_{H,H} = 7$ Hz, 1H, $CH(CH_3)_2$); 1.48 (d, $^3J_{H,H} = 7$ Hz, 6H, $CH(CH_3)_2$); 1.29 (s, 9H, $C(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): $\delta = 207.8$ (*C*O); 179.3 (N*C*N); 122.5 (N*C*HCHN); 116.7

(NCH*C*HN); 55.4 (CH_2); 53.7 ($CH(CH_3)_2$); 43.0 ($C(CH_3)_3$); 25.8 ($C(CH_3)_3$); 23.3 ($CH(CH_3)_2$) ppm. IR Data cm^{-1} KBr pellet: 1719 (s) (ν_{co}). LRMS (ES): *m*/*z* 315 [(NHC-ligand)Ag]$^+$, *m*/*z* 523 [(NHC-ligand)$_2$Ag]$^+$.

2.4. X-ray crystallography

Single crystals of **1a** and **1b**, suitable for X-ray diffraction, were grown from toluene at 25 °C. A crystal of **1a** of approximate size 0.25 × 0.20 × 0.20 mm was mounted on a glass fiber with epoxy cement. Oxford diffraction X-calibur-S CCD diffractometer (graphite-monochromatized Mo Kα radiation) was used for the cell determination and intensity data collection. A crystal of **1b** of approximate size 0.40 × 0.35 × 0.30 mm was mounted on a glass fiber with epoxy cement. Unit cell dimensions were obtained using 25 centered reflections in the *θ range* 11.2100–14.1900 on a Nonius Mach3 diffractometer (graphite-monochromatized Mo Kα radiation) for the cell determination and intensity data collection. The structure were solved by direct methods SHELXS97 and refined by using SHELEX97 software. The non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were geometrically fixed and allowed to refine using a riding model.

2.5. Computational methods

The density functional theory calculations were performed using GAUSSIAN98 [31] suite of quantum chemical programs. The Becke three-parameter exchange functional in conjunction with Lee–Yang–Parr correlation functional (B3LYP) has been employed in this study [32,33]. Stuttgart–Dresden effective core potential (ECP), representing 19 core electrons, along with valence basis sets (SDD) is used for silver atom [34]. All other atoms are treated with 6-31G(d) basis set [35]. All stationary points are characterized as minima by evaluating Hessian indices on the respective potential energy surfaces.

Inspection of the metal–ligand donor–acceptor interactions was carried out using the charge decomposition analysis (CDA) [36]. CDA is a valuable tool in analyzing the interactions between molecular fragments on a quantitative fashion, with an emphasis on the electron donation [37]. The orbital contributions in the NHC–AgCl complex, **1b**, can be divided into three parts: (i) σ-donation from NHC → AgCl fragment; (ii) π-back donation NHC ← AgCl, and (iii) a repulsive interaction arising between the occupied MOs of these two fragments. The CDA calculations are performed using the program AOMIX using the B3LYP/SDD,6-31G(d) wave function [38].

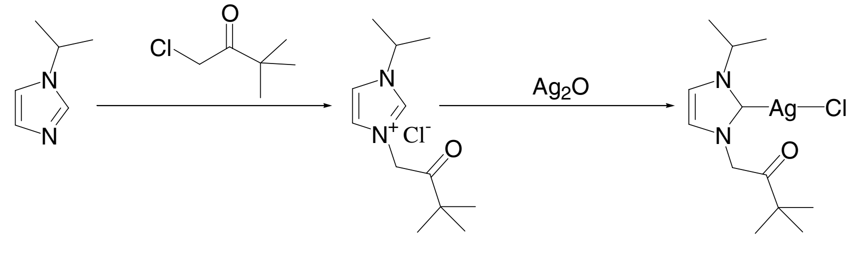
Natural bond orbital analysis is performed using the NBO3.1 program as implemented in the GAUSSIAN98 package [39]. Second order perturbation energy analysis, natural charges [40] and bond orders [41] for **1b** are calculated using the B3LYP/SDD,6-31G(d) wave function. The aromaticity in the free carbene as well as the corresponding silver complex was estimated with the *nucleus independent chemical shift* (NICS) method as suggested by Schleyer et al. [42]. The NICS values are calculated at 1 Å above the ring plane using the gauge independent atomic orbital (GIAO) formalism [43] at the B3LYP/SDD,6-311 ++ G(d,p) //B3LYP/SDD,6-31G(d) level of theory. The nature of the chemical bonding in **1b** was further explored with Bader's *Atoms in Molecules* approach [44] using the AIM2000 program [45].

3. Results and discussion

The Ag^I–NHC complexes display a wide variety of structural motifs in the solid-state that range from monomeric neutral covalent complexes (of the type [NHC]AgCl), to the cationic monomeric complexes (of the type $[(NHC)_2Ag]^+Y^-$; where Y^- = a halide or $Ag(halide)_2$ anion), to polymeric structures [46–49]. The structural diversity exhibited by silver–NHC complexes may be dependent upon several factors including the sterics. For example, a NHC ligand with a sterically demanding mesityl substituent gave a neutral (NHC)AgCl type complex with 1:1 ligand to metal ratio, whereas the less bulky variant of the same ligand bearing methyl substituent gave cationic $(NHC)_2Ag^+$ type complex having 2:1 ligand to metal ratio [50]. Recently, Köhler et al. [51] reported that for the same ligand, similar change in structure from a neutral 1:1 complex, (saturated NHC)AgCl, to a cationic 2:1 complex, [(saturated NHC)$_2$Ag]$^+$BF$_4^-$, could be achieved by increasing the polarity of the reaction medium. Specifically, when the Ag_2O metallation reaction was carried out in relatively less polar medium like THF then a neutral 1:1 complex, (saturated NHC)AgCl, was obtained, whereas when the same was done in much polar medium like water then a cationic 2:1 complex, [(saturated NHC)$_2$Ag]$^+$BF$_4^-$, was obtained. Another important quality of silver–NHC complexes that emerges out from the above study is the exceptional stability of these complexes in general and of the silver–carbene bond in particular, given the fact that one of the reactions was carried out in a highly polar solvent like water. In light of the above facts, understanding the structural diversity as well as the stability of silver–NHC complexes becomes important as these complexes may find use in designing of supramolecular architectures, in materials related applications as well as in chemical catalysis.

3.1. Synthesis of [1-i-propyl-3-(2-oxo-2-t-butyl ethyl)imidazol-2-ylidene]AgCl (**1b**)

The N-heterocyclic carbene ligand was prepared by slight modification of a procedure reported for a variant ligand [52] (Scheme 1). Specifically, the reaction of 1-*i*-propylimidazole with α-chloropinacolone gave 1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazolium chloride (**1a**) in 70% yield. As expected, the ^{1}H NMR spectrum of the compound showed the diagnostic (NC*H*N) resonance at 9.91 ppm while the corresponding carbon resonance (N*C*HN)



1a **1b**

Scheme 1.

appeared at 135.9 ppm in the ^{13}C NMR spectrum. The carbonyl moiety (–*C*O–) appeared at 207.0 ppm in the ^{13}C NMR spectrum while at 1721 cm^{-1} (ν_{co}) in the infrared spectrum. In the Electrospray Mass spectroscopy the 1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazolium cation appeared as a 209 (*m*/*z*) peak.

The molecular structure of the 1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazolium chloride (**1a**) has been determined by X-ray diffraction (Fig. 2). Of the central imidazolium ring, the two N1–C1 and N2–C1 bond distances are 1.320(2) Å and 1.323(2) Å, respectively, while the N2–C1–N1 angle is 108.54(16)°. It is interesting to note that a weak [C1–H···Cl1] hydrogen bonding interaction between the Cl^{-} anion with the acidic imidazolium proton (N1–C1*H*–N2) was observed as the [Cl1···C1] distance of 3.373 Å is slightly shorter than the van der Waals radii of Cl and C atoms (3.45 Å) [53].

The silver complex, [1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazol-2-ylidene]AgCl (**1b**), was obtained from the reaction of 1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazolium chloride (**1a**) with Ag_2O in 42% yield. Consistent with the formation of the silver complex **1b**, the silver–carbene resonance (N*C*N) appeared at 179.3 ppm in the ^{13}C NMR spectrum. In the infrared spectrum the carbonyl peak (ν_{co}) appeared 1719 cm^{-1}. The Electrospray Mass analysis showed a peak at 315 *m*/*z* corresponding to the [1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazol-2-ylidene]Ag^{+} cation, formed as a result of the Cl^{-} dissociation from the neutral complex **1b** along with a peak at 523 *m*/*z* corresponding to the [1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)-imidazol-2-ylidene]$_2$Ag^{+} cation. Such conversion of (NHC)Ag-halide complexes to (NHC)$_2$Ag^{+} and Ag(halide)$_2$ anion species under sampling conditions of Electrospray Mass spectrometry had been observed on previous occasions [47,51,54]. It was suggested that polar medium promotes the dissociation of (NHC)Ag-halide complexes to (NHC)$_2$Ag^{+} and Ag(halide)$_2$ anion species.

The definitive proof of the neutral monomeric nature of the silver complex **1b** came from the X-ray diffraction studies (Fig. 3). In the **1b** complex, the silver is in linear geometry being covalently bound to the NHC ligand on one side and to the chlorine on the other. The crystallographic data and the selected metrical data are listed in Tables 1 and 2, respectively. The Ag–C$_{carb}$ (Ag–C1) bond distance of 2.077(3) Å is slightly shorter than the sum of the covalent radii 2.111 Å [55] whereas the Ag–Cl (Ag–Cl1) bond distance [2.3294(9) Å] is comparable to the sum of the individual covalent radii of Ag and Cl (2.329 Å) [55]. Also, consistent with the two-coordinated d^{10} configuration of Ag^{I}, the angle at silver (C1–Ag–Cl1) is almost linear [172.38(10)°] [56]. Interestingly, The N1–C1–N2 [∠(N–

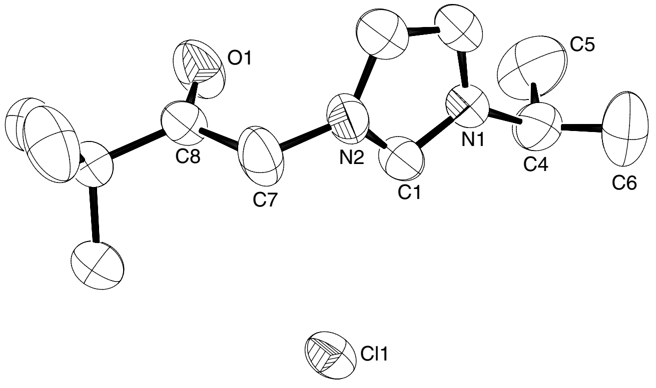


Fig. 2. ORTEP of **1a**. Selected bond lengths (Å) and angles (°): N(1)–C(1) 1.320(2), N(2)–C(1) 1.323(2), N(2)–C(1)–N(1) 108.54(16), C(1)–N(1)–C(4) 125.42(16), C(1)–N(2)–C(7) 124.80(17).

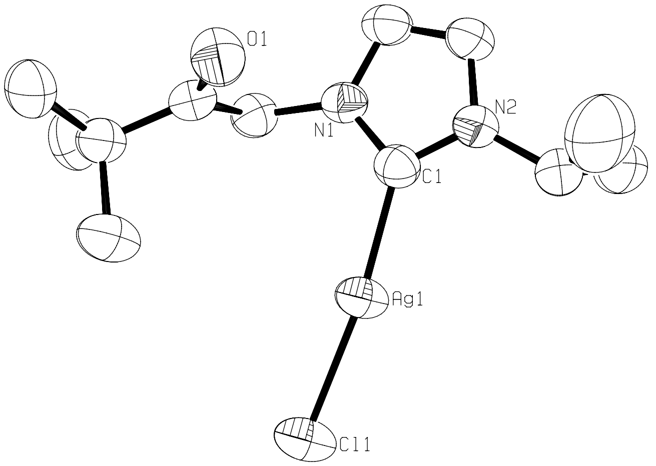


Fig. 3. ORTEP of **1b**. Selected bond lengths (Å) and angles (°): Ag(1)–C(1) 2.077(3), Ag(1)–Cl(1) 2.3294(9), N(1)–C(1) 1.352(4), N(2)–C(1) 1.348(4), C(1)–Ag(1)–Cl(1) 172.38(10), N(2)–C(1)–N(1) 104.2(3), N(2)–C(1)–Ag(1) 130.9(2), N(1)–C(1)–Ag(1) 124.7(2).

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

Compound	**1a**	**1b**
Chemical formula	$C_{12}H_{21}ClN_2O$	$C_{12}H_{20}AgClN_2O$
Molecular weight	244.76	351.62
Crystal system	Orthorhombic	Monoclinic
Space group	*pbca*	*P*21/*n*
Z	8	4
a (Å)	11.182(3)	11.3870(8)
b (Å)	11.2330(15)	10.6830(7)
c (Å)	22.799(8)	12.4460(12)
α (°)	90	90.00
β (°)	90	90.995(7)
γ (°)	90	90.00
V (Å)	2863.6(13)	1513.8(2)
D_{calc} (mg m^{-3})	1.135	1.543
Crystal dimensions (mm)	0.25 × 0.20 × 0.20	0.40 × 0.35 × 0.30
T (K)	293(2)	293(2)
Diffractometer	Oxford diffraction X-calibur-S CCD	Enraf nonius CAD-4 MACH(-3)
Radiation λ (Å)	0.71073	0.71073
θ Range (°)	3.13–30.19	2.51–24.99
No. of data collected	41467	2788
No. of unique data	4209	2660
Agreement between equivalent data (R_{int})	0.0606	0.0382
No. of parameters varied	145	159
μ (mm)	0.252	1.496
Absorption correction	Semi-empirical form equivalents	Psi-scan
$R1(F_o)$, $wR2(F_o^2)(I > 2\sigma)$	0.0472, 0.1201	0.0293, 0.0679

Table 2
Comparison of experimental and calculated[a]

Parameter	Experimental	Calculated	Parameter	Experimental	Calculated
Ag1–C1	2.077(3)	2.094	C2–C3	1.339(5)	1.357
Ag1–Cl1	2.3294(9)	2.327	C4–C5	1.496(6)	1.532
O1–C8	1.202(4)	1.215	C4–C6	1.498(6)	1.532
N1–C1	1.352(4)	1.364	C7–C8	1.524(5)	1.544
N1–C2	1.380(4)	1.386	C8–C9	1.511(5)	1.536
N1–C7	1.455(4)	1.453	C9–C12	1.523(5)	1.538
N2–C1	1.348(4)	1.357	C9–C10	1.527(5)	1.545
N2–C3	1.377(4)	1.389	C9–C11	1.539(5)	1.551
N2–C4	1.473(5)	1.479			
C1–Ag1–Cl1	172.38(10)	178.06	N2–C4–C6	109.9(4)	110.74
C1–N1–C2	111.4(3)	111.19	C5–C4–C6	113.4(4)	113.01
C1–N1–C7	123.2(3)	123.79	N1–C7–C8	112.0(3)	112.61
C2–N1–C7	125.3(3)	124.97	O1–C8–C9	123.0(3)	122.85
C1–N2–C3	111.1(3)	111.04	O1–C8–C7	119.5(3)	119.56
C1–N2–C4	124.0(3)	124.22	C9–C8–C7	117.4(3)	117.59
C3–N2–C4	124.9(3)	124.74	C8–C9–C12	109.9(3)	109.17
N2–C1–N1	104.2(3)	104.49	C8–C9–C10	106.0(3)	107.09
N2–C1–Ag1	130.9(2)	128.83	C12–C9–C10	110.1(3)	109.64
N1–C1–Ag1	124.7(2)	126.67	C8–C9–C11	111.3(3)	111.21
C3–C2–N1	106.2(3)	106.45	C12–C9–C11	110.0(3)	110.07
C2–C3–N2	107.1(3)	106.78	C10–C9–C11	109.4(3)	109.67
N2–C4–C5	110.0(4)	110.60			

Geometrical parameters (in Å and °, respectively, for bond length and angle) for **1b**.

[a] Geometries were obtained at the B3LYP level of theory with the SDD basis set for silver and 6-31G(d) basis set for rest of the elements.

C_{carb}–N)] angle of 104.2(3)° is shorter than that observed in **1a** 108.54(16)°.

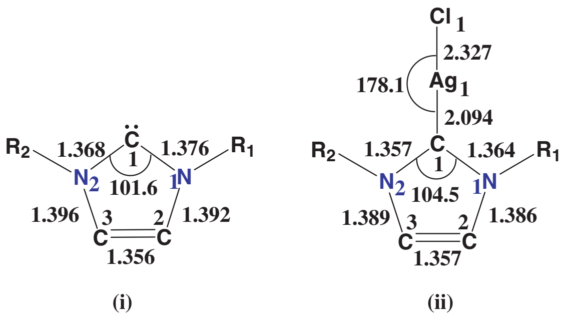
At this juncture, it would be interesting to compare the structure of [1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazol-2-ylidene]AgCl (**1b**) with related (saturated NHC)AgCl complexes. Köhler et al. [51] had observed that the ∠(N–C_{carb}–N) angle is larger in case of (saturated NHC)–silver complexes in comparison to the (NHC)–silver complexes. This was attributed to the different ring geometries of the 4,5-dihydroimidazole ring in the saturated NHC complex as oppose to that of the imidazole ring in the NHC complex. Similar observation is made in the present case, as the ∠(N–C_{carb}–N) angle of 109.8(3)° in the saturated NHC complex, [(4R,5S)-4,5-diallyl-1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydro-3H-imidazolin-2-ylidene]silver(I) chloride, [51] is significantly larger than that of 104.2(3)° observed in case of the NHC complex **1b**. However, the Ag–C_{carb} bond length [2.057(7) Å], the Ag–Cl bond length [2.305(2) Å] and the ∠(C_{carb}–Ag–Cl) angle 180.0° also differ from the corresponding values of 2.077(3) Å, 2.3294(9) Å and 172.38(10)°, respectively, in the **1b** complex.

It is noteworthy that instead of chelating to the silver atom, the carbonyl group of (2-oxo-2-*t*-butyl ethyl) substituent was found disposed away from silver (the O···Ag distance = 4.374 Å) and was found lying perpendicular to the plane containing the imidazole ring, the silver (Ag) and the chlorine (Cl)atoms.

Unlike the neutral monomeric 1:1 complex (NHC ligand to metal) observed in case of [1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazol-2-ylidene]AgCl (**1b**), a cationic monomeric complex, [(1-*i*-propyl-3-{N-phenylacetamido}imidazol-2-ylidene)$_2$Ag]$^+$Cl$^-$, [57] having 2:1 NHC ligand to metal ratio was obtained under analogous reaction conditions for a related NHC ligand bearing a *N*-phenylacetamide substituent. Similar 2:1 cationic monomeric silver complexes have been observed in case of both symmetrically as well as unsymmetrically substituted N-hetercocylic carbene ligands. The Ag–C_{carb} (Ag–C1) bond distance [2.077(3) Å] in [1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazol-2-ylidene]AgCl (**1b**) compare well with that observed in these cationic complexes namely, [(*N*,*N*′-dimethyl-imidazol-2-ylidene)$_2$Ag]$^+$[AgCl$_2$]$^-$ [2.084(5) Å] [48], [(*N*,*N*′-dipyridyl-imidazol-2-ylidene)$_2$Ag]$^+$[BF$_4$]$^-$ [2.117(5) Å, 2.106(6) Å] [14], [(1-{2-[3,5-dimethylpyrazol-1-yl]ethyl}-3-methyl-imidazol-2-ylidene)$_2$Ag]$^+$[AgCl$_2$]$^-$ [2.092(10) Å, 2.088(11) Å] [50] and [(1-2,6-diisopropylphenyl-3-{2-pyridylmethyl}imidazol-2-ylidene)$_2$Ag]$^+$[AgCl$_2$]$^-$ [2.069(5) Å, 2.074(5) Å] [47].

3.2. Density functional theory studies

In order to gain further insights on the NHC–AgCl bonding in **1b**, we have carried out a detailed theoretical investigation with the density functional theory. The key findings are described in the following sections. The calculated geometrical parameters of **1b** are found to be in good agreement with the experimental values obtained from the X-ray crystallographic study (Table 2). The geometrical changes in free NHC associated with AgCl binding is determined by comparing the optimized geometries of free (in its singlet ground state) and AgCl bound systems. The changes are found to be very minimal, in concert with an earlier report by Frenking et al. on similar series of ligands [23]. Key geometrical features of **1b** and the free ligand are summarized in Fig. 4 [58]. It is evident that the imidazole ring has undergone very little geometrical changes upon binding to AgCl. While the computed ∠(N–C_{carb}–N) angle showed widening by about 3.0°, the C=C bond length (1.357 Å) remained nearly unchanged. The AgCl bond length in **1b** showed no variation compared to free AgCl (2.328 Å). Interestingly, the C_{carb}–N bonds are shortened upon binding with AgCl, compared to that in the free ligand (*vide infra*).



(i) (ii)

R_1 = -CH$_2$C(O)CMe$_3$
R_2 = -CHMe$_2$

Fig. 4. Comparison of key geometrical parameters of (i) free carbene ligand and (ii) **1b** obtained at the B3LYP/SDD,6-31G(d) level of theory.

The AgCl–carbene bond dissociation energy is calculated to be 50.8 kcal/mol at the B3LYP/SDD,6-31G(d) level of theory. This value is in good agreement with the earlier estimates at similar levels of theory [23,25]. The nature of binding interaction in NHC–AgCl has been probed by post-wave function analysis using the natural bond orbital (NBO) method [39]. Important electron delocalizations and atomic populations have been analyzed [59]. It is noticed that the Ag → ligand donation is very small. The σ*(Ag–C_{carb}) acts as an acceptor and helps to delocalize the chlorine lone pair electrons. Such an interaction is expected to weaken the Ag–C_{carb} bond in **1b**. An interesting observation pertains to the calculated natural charges (NPA) on the nitrogen atoms in **1b**, which are found to be less negative compared to the free NHC-ligand [60]. The σ-donation by NHC increases the electron deficiency on the carbene C_{carb} and ensues a better N → C_{carb} π-donation. Evidently, the optimized C–N bond length is found to be shorter in **1b** compared to that in the free NHC-ligand (Fig. 4). Further, the p–π population on the donor center in **1b** is found to be higher while the populations on the nitrogen atoms are slightly lower than in the free NHC-ligand [61]. This observation can be ascribed to effective delocalization of nitrogen lone pair electrons into the adjacent C–N bond.

The charge decomposition analysis (CDA) has been known to be a useful tool in analyzing the extent of back-bonding in organometallic systems [23,62]. The CDA results in **1b** showed a significant C_{carb} → AgCl σ-donation ($d = 0.624$) and a very negligible C_{carb} ← AgCl back-donation ($b = 0.080$). A d/b ratio of 7.8 evidently underscores the ability of NHC to function as an effective σ-donor ligand. The structural parameters as well as population analysis presented in the previous sections is in concurrence with the CDA result that the back-bonding in **1b** is not very significant.

The nature of bonding in **1b** is further examined with topological analysis of the electron density using the Bader's theory of atoms in molecule (AIM) [63]. In the AIM formalism, topological properties of electron density 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 indicator in determining the nature of interaction than $\nabla^2\rho_{bc}$ [64]. Inspection of computed topological features in the present system, as given in Table 3, reveals that the C_{carb}–Ag bond is evidently covalent. This observation is further supported by the near-zero charge on the carbenic carbon computed using the natural population analysis [60]. Thus, the involvement of any major electrostatic contribution can be ruled out in NHC–AgCl interaction. The π-character of bonds is inspected by calculating bond ellipticity (ε) values. It is found that ellipticity is close to zero for the C_{carb}–Ag bond and highest for the imidazole C2–C3 bond. Thus, the C_{carb}–Ag bond lacks π-character while the imidazole C2–C3 bond do exhibit π-bond characteristics. Interestingly, the ε values for the N1–C2 and N2–C3 bonds suggest a moderate π-character. This arises due to $N \rightarrow C_{carb}$ π-donation into the carbene π-type orbital as described in previous sections. The computed electron density at the ring critical point of the free imidazole carbene ring (0.053) is found to be little depleted when complexed with AgCl [65].

Electron delocalizations in cyclic systems can be probed by calculating the magnetic shielding tensor with methods such as nucleus independent chemical shift (NICS). The NICS values at the ring centre of a cyclic conjugated system can be used as a descriptor for aromaticity [42,66]. According to Schleyer et al. classical aromatic compounds have a high negative chemical shifts at the ring centroid, whereas anti-aromatic compounds possess a positive chemical shift. The NICS values computed using the gauge independent atomic orbital (GIAO) method [43] indicates that the imidazole ring in the free (singlet ground state) as well as the AgCl bound complex is fairly aromatic. The computed values were found to be −11.71 and −11.55 ppm, respectively, for free and bound NHC. It is also interesting to note that the change in the NICS value upon complex formation with AgCl is nearly negligible. This observation supports the fact that the σ-type lone pair on the NHC is predominantly used for bonding with AgCl without any significant participation from the π-type orbitals on the carbenic carbon. Further, comparison of natural populations on d-orbitals of the silver center in the free as well as NHC bound AgCl reveals interesting aspects. While the population on the silver s-orbital increases upon complex formation the $d_{x^2-y^2}$ population was found to be slightly depleted. Thus, by combining all the computed details, it is quite sensible to believe that the back-bonding interactions is quite negligible in **1b**.

Table 3
Topological features of **1b** computed at the AIM/B3LYP//B3LYP/SDD,6-31G(d) level of theory

Bond	ρ_{bc} (e Å^{-3})	$\nabla^2\rho_{bc}$ (e Å^{-5})	ε	H_{bc}
Ag1–C1	0.104	−0.076	0.040	−3.36
Ag1–Cl1	0.080	−0.062	0.002	−2.38
C1–N1	0.314	0.154	0.060	−11.24
C1–N2	0.318	0.153	0.080	−11.33
N1–C2	0.301	0.177	0.160	−10.03
N2–C3	0.300	0.184	0.180	−9.77
C2–C3	0.337	0.242	0.394	−10.36

4. Summary

In summary, a new O-functionalized N-heterocyclic carbene ligand precursor, 1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazolium chloride (**1a**), was synthesized by the alkylation of 1-*i*-proplyimidazole with α-chloropinacolone. A neutral monomeric silver complex, [1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazol-2-ylidene]AgCl (**1b**), was synthesized by the treatment of 1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazolium chloride (**1a**) with Ag_2O and has been structurally characterized by X-ray diffraction studies. The CDA analysis using the B3LYP wave function exhibited a σ-donation/back-donation (d/b) ratio of 7.8, indicating the ability of NHC to function as an effective σ-donor ligand. Topological analysis of electron density as well as the NPA charges revealed that the metal–ligand bond in **1b** is covalent. The aromaticity in the imidazole ring of the unbound NHC, as given by the NICS values, was found to be only minimally affected upon binding with the AgCl. The results obtained from CDA, NBO as well as other indicators all agree with the fact that the back bonding in **1b** is negligible.

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Appendix A. Supplementary material

Crystallographic data for the structural analysis of 1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazolium chloride (**1a**) and 1-*i*-propyl-3-(2-oxo-2-*t*-butyl ethyl)imidazol-2-ylidene]AgCl (**1b**) have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 603748 is for **1a** and 296645 for **1b**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; email: deposit@ccdc.cam.ac.uk or www: http://

www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.05.037.

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