

# Silver(I) N-heterocyclic carbene halide complexes: A new bonding motif

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Received 6 June 2007; received in revised form 5 July 2007; accepted 10 July 2007

Available online 1 August 2007

## Abstract

Two new NHC silver halide salts have been synthesised and structurally characterised, and they show the two most common structural forms for such salts: the  $(\text{NHC})\text{AgX}$  and the  $(\text{NHC})_2\text{Ag}^+/\text{AgX}_2^-$  forms (both have a stoichiometry of 1 NHC:1 Ag:1 halide). A third new compound has been synthesised and structurally characterised: this compound has an unprecedented 2 NHC:1 Ag:1 halide stoichiometry and exhibits a planar arrangement of two coordinating NHCs, and a coordinating bromide about the central silver. The Ag–Br bond is long in the solid state and, together with solution NMR data, this suggests that a formulation of  $(\text{NHC})_2\text{Ag}^+\text{Br}^-$  might be more appropriate.

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*Keywords:* Silver; Carbene; NHC

## 1. Introduction

In the past five years the nitrogen stabilised heterocyclic carbene (NHC) ligand has progressed from being an academic curiosity to its present ubiquitousness: it is now considered as a versatile ligand that is often used in preference to the more usual phosphine [1]. Electronically, the NHC ligand is usually considered to be a better  $\sigma$  donor, and a weaker  $\pi$  acceptor, than the phosphine ligand [2], though evidence is not always clear cut [3]. Synthetic procedures leading to precursor imidazolium salts have been elucidated [4], and many routes that allow the introduction of an NHC ligand to a metal centre have been developed. The reaction of imidazolium salts with silver oxide giving an NHC complex of silver, which serves as a useful trans-metallating reagent, has proved particularly popular [5,6], and is the subject of this paper. Other interesting methods include the utilisation of an electron-reservoir complex, together with air, to generate NHCs [7], or the use of imidazolium-2-carboxylates which lose  $\text{CO}_2$  to gen-

erate NHCs [8], though, increasingly, direct reaction of the imidazolium salt with the metal has found favour [9–12]. More recently, NHC ligands have been shown not to be innocent spectators, but reactive intermediates themselves, with a number of new products being formed [13,14].

The reaction of imidazolium salts with silver oxide to form NHC complexes of silver is a commonly used method for the generation of NHC complexes of other metals and has recently been comprehensively reviewed [15]. In this paper we look at this reaction, and document the synthesis of a new type of silver NHC complex.

## 2. Results and discussion

The direct reaction of imidazolium salts with silver oxide has a clearly implied stoichiometry: 2 equiv. of imidazolium salt react with 1 equiv. of silver oxide generating 1 equiv. of water and 2 equiv. of an NHC complex of silver:  $2(\text{imidazolium halide}) + \text{Ag}_2\text{O} \rightarrow 2(\text{NHCAg halide}) + \text{H}_2\text{O}$

Excess silver oxide is often employed and, traditionally, light was excluded [5], though a recent report states that this precaution is unnecessary [16]. The silver product normally exhibits one of two formulations, either an

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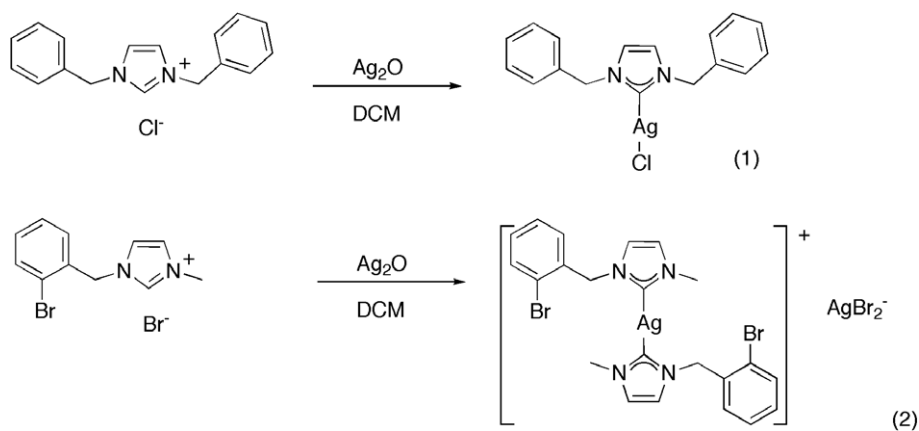
E-mail address: [j.rourke@warwick.ac.uk](mailto:j.rourke@warwick.ac.uk) (J.P. Rourke).

(NHC)AgX complex or an (NHC)<sub>2</sub>Ag<sup>+</sup> cation together with a AgX<sub>2</sub><sup>-</sup> anion. Thus when we react di(benzyl)imidazolium chloride with silver oxide we get complex (1) which has the (NHC)AgX formulation, and when we react methyl(2-bromobenzyl)imidazolium bromide with silver oxide we get complex (2) which has a (NHC)<sub>2</sub>Ag<sup>+</sup> cation with a AgBr<sub>2</sub><sup>-</sup> anion, Scheme 1.

The formulation of (1) and (2) in the solid state was determined by single crystal X-ray diffraction, Figs. 1 and 2, respectively. Both structures clearly show the coordination around the silver and both show additional packing features that commonly occur in silver salts of NHCs. In the structure of (1), two molecules of (NHC)AgCl are asso-

ciated about an inversion centre to give dimeric structures with lateral silver-chloride interactions. Whilst the length of the direct silver to chloride bond is 2.3695(8) Å, this additional interaction is substantially longer at 3.0347(9) Å; the Ag–Ag distance is 3.9947(8) Å and the Ag1–Cl–Ag1A angle is 94.5°. This type of side-on silver-halide interaction is present in eight of the 15 crystal structures recorded in the CCDC [17] that have the (NHC)AgX form.

In the structure of (2) an infinite chain of Ag–Ag interactions between alternating anion and cation extends along the *a*-axis of the cell, this Ag–Ag distance is 3.4866(11) Å, Fig. 3. Silver–silver interactions are present in four of the nine structures showing the form (NHC)<sub>2</sub>Ag<sup>+</sup>



Scheme 1.

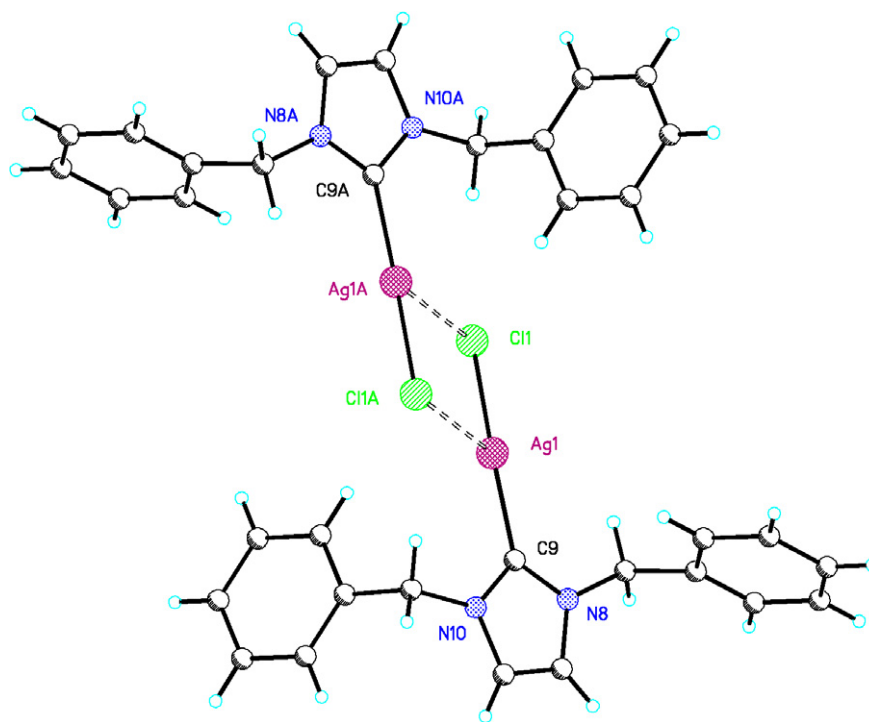


Fig. 1. The X-ray structure of (1). Selected bond lengths and angles: Ag1–C9 2.090(2) Å, Ag1–Cl1 2.3695(8) Å, Ag1–Cl1A 3.0347(9) Å, C9–Ag1–Cl1 163.08(6)°, Ag1–Cl1–Ag1A 94.52(4) Å.

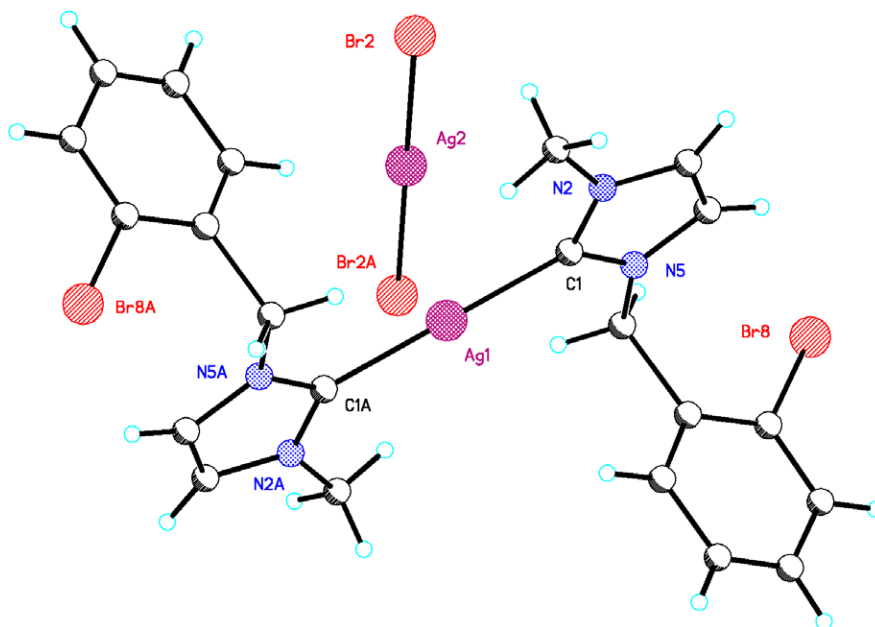


Fig. 2. The X-ray structure of (2). Selected bond lengths and angles: Ag1–C1 2.107(7), Ag2–Br2 2.4380(11) Å, C11–Ag1–C1A 180.0°, Br2–Ag2–Br2A 180.0°.

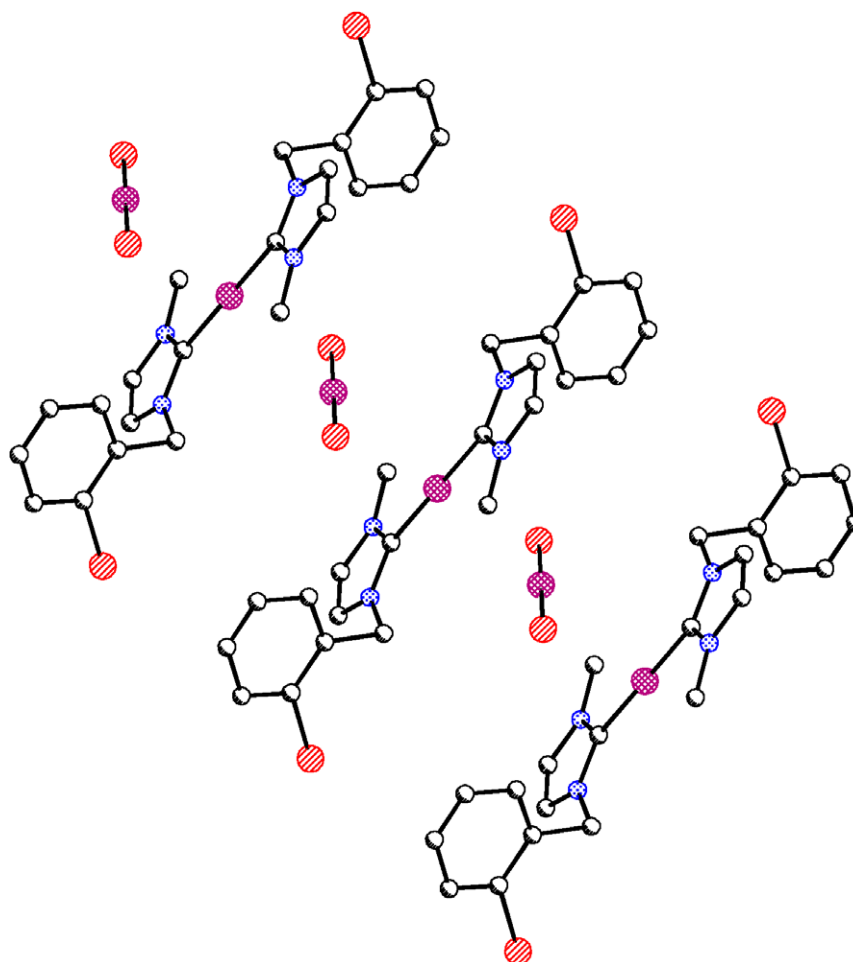


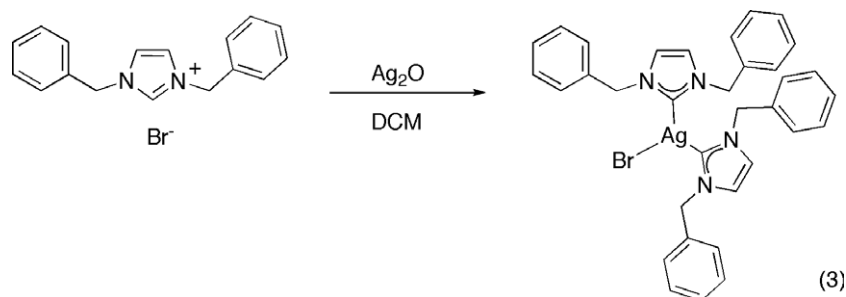
Fig. 3. The extended Ag–Ag chain that exists in the solid-state structure of (2). The Ag–Ag distance is 3.4866(11) Å, and the chain is perfectly straight.

cation/ $\text{AgX}_2^-$  anion present in the CCDC. Of these, two structures [5,18], have silver–silver contacts of 2.95 Å and 2.97 Å, between the  $(\text{NHC})_2\text{Ag}^+$  cation and the  $\text{AgX}_2^-$  anion, and no other close contacts. However two structures (in the same paper) of the dimethyl imidazolium derived silver NHC have infinite chains like that shown by (2) [19]; here the silver–silver distances are 3.189 Å for X = Cl and 3.208 Å for X = Br. Our longer Ag–Ag distance is almost certainly simply a steric effect: the larger 2-bromobenzyl groups present in (2) need more space than the simple methyl groups present in the previously reported structures.

A recent review [15] categorises all known silver(I) carbene complexes: as we indicate, the majority of mono(NHC) ligands with silver halides do adopt one of the  $(\text{NHC})\text{AgX}$  or the  $(\text{NHC})_2\text{Ag}^+/\text{AgX}_2^-$  forms. Another recent paper [16] attempts to rationalise the competition between the  $(\text{NHC})\text{AgX}$  and the  $(\text{NHC})_2\text{Ag}^+/\text{AgX}_2^-$

forms, and reports a dynamic equilibrium between the two forms in solution. Broadly speaking, the conclusion was drawn that increasing solvent polarity stabilised the  $(\text{NHC})_2\text{Ag}^+/\text{AgX}_2^-$  form over the  $(\text{NHC})\text{AgX}$  form. One of the implicit conclusions of the review, and the underlying assumption of the paper reporting the competition between the two forms is that the stoichiometry of the NHC silver salt is 1 NHC:1 Ag:1 halide. Consequently, we were more than a little surprised that the reaction of the bis(benzyl)imidazolium cation (albeit with a bromide counterion), under identical conditions to those that gave us (1) with silver oxide, gave us an unprecedented new compound (3), Scheme 2. The new compound has a 2 NHC:1 Ag:1 halide stoichiometry, and the crystal structure is shown in Fig. 4.

The structure shows an essentially planar arrangement of the two coordinating carbons, the bromide and the silver (which is only 0.019 Å away from the plane defined by



Scheme 2.

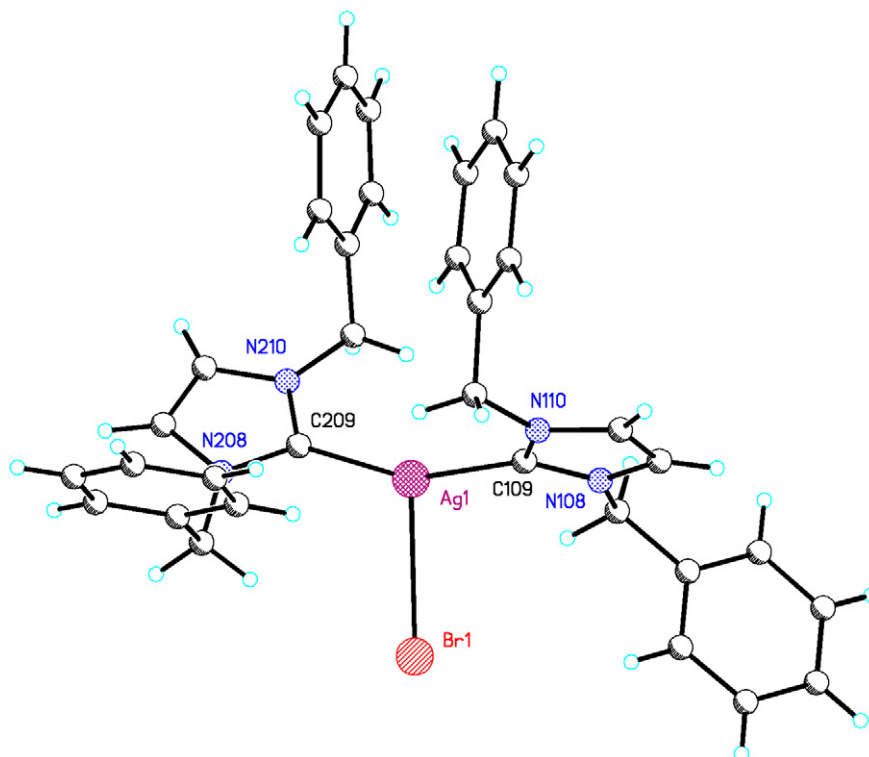
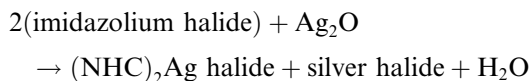


Fig. 4. The X-ray structure of (3). Selected bond lengths and angles: Ag(1)–C(209) 2.116(4) Å, Ag(1)–C(109) 2.117(4) Å, Ag(1)–Br(1) 2.8934(5) Å, C(209)–Ag(1)–C(109) 157.04(14)°, C(209)–Ag(1)–Br(1) 105.41(10)°, C(109)–Ag(1)–Br(1) 97.52(10)°.

C109, C209 and Br1), with the C–Ag–C angle being 157°. The Ag–Br distance is really quite long: at 2.8934(5) Å it is nearly half an Angstrom longer than the 2.4380(11) Å present in (2). A search of the CCDC reveals this distance to be in keeping with the longer, side on type of Ag–Br interactions (like that seen with Ag–Cl in the structure of (1)) where the average Ag–Br distance is 2.91 Å, and not the shorter direct bond (again like that seen with Ag–Cl in the structure of (1)) where the Ag–Br average distance is 2.46 Å. In addition, there are a number of contacts between hydrogens on adjacent molecules and the bromide at slightly less than the sum of the van der Waals radii of H and Br (3.05 Å) [20].

The stoichiometry of the reaction was still 1 imidazolium salt to 1 silver, but presumably an equivalent of silver bromide was generated, which was removed at the filtration step. Thus the overall reaction is



Quite why this particular imidazolium salt should react this way is still unknown to us, but it is repeatable. We attempted this reaction with varying proportions of silver oxide and dibenzylimidazolium bromide and, on each occasion, following filtration and precipitation, we isolated a white solid that analysed as (NHC)<sub>2</sub>AgBr. Chloroform solution NMR does not reveal any major differences in the <sup>1</sup>H spectra of (1) and (3), though the <sup>13</sup>C NMR does. The carbene carbon of (1) resonates at 151 ppm, whereas the equivalent resonance for (3) is at 182 ppm, very similar in fact to the carbene peak of (2), which resonates at 183 ppm. Together with the long Ag–Br distance observed in the solid-state structure, this would seem to imply that a better formulation for (3) would be (NHC)<sub>2</sub>Ag<sup>+</sup>Br<sup>−</sup>, with dissolution into separate ions in chloroform solution.

Compounds that have some degree of similarity to (3) are mentioned in the literature. There is a single reported example of a silver with two NHCs and a halide bound to it: in a similar fashion to our compound (3) the Ag–Br bond is quite long at 3.0676(13) Å, and the C–Ag–C angle is some way off linear (171.2(3)°) [21]. The NHC ligands used in this compound are actually tridentate and the anion is a complex [Ag<sub>8</sub>Br<sub>12</sub>]<sup>6−</sup> anion giving an overall stoichiometry that is essentially (NHC)AgX. One other previous report mentions a (NHC)<sub>2</sub>Ag<sup>+</sup> complex with a counter ion consistently analyses as I<sup>−</sup> · (0.4AgI) [22] giving a complex that can be considered as part of the way between the extremes of (NHC)AgX and (NHC)<sub>2</sub>AgX. This paper makes discusses likely reasons for this formulation (their NHC ligand had a pendant pyridine group), but they were unable to crystallise their sample and were not completely certain of the exact structure. Another paper reports [23] (without further discussion) the formation of a ((NHC)<sub>2</sub>Ag)<sub>3</sub>I<sup>2+</sup> cation where each of three silvers has two NHC ligands and a long interaction with an iodide; the charge balance is maintained with two iodide counterions. In this example the carbenes

again have pendant pyridine groups and now the overall ratio is the same as our complex (3): 2 NHC:1 Ag:1 halide.

### 3. Conclusions

Though there are many different coordination modes for silver in all the many reported crystal structures with NHC ligands, none have the 2 ligand:1 Ag:1 halide stoichiometry that we report here. Our bis(dibenzylimidazolium)silver bromide complex exhibits a previously unreported structure, and solution NMR would suggest that it might be better to consider it as (NHC)<sub>2</sub>Ag<sup>+</sup>Br<sup>−</sup>.

### 4. Experimental

All chemicals were used as supplied, unless noted otherwise. All NMR spectra were obtained on a Bruker Avance 400 or 500 in CDCl<sub>3</sub> and are referenced to external TMS, assignments being made with the use of decoupling, nOe and COSY pulse sequences. Elemental analyses were performed by Warwick Analytical Services. Symmetrical di(benzyl)imidazolium salts were synthesised via a literature route [24], and the unsymmetrical 1-methyl-3-(2-bromo)benzylimidazolium salt prepared via the reaction of methyl imidazole with 1-bromo-2-bromomethylbenzene.

#### 4.1. (1,3-Dibenzylimidazol-2-ylidene)silver chloride (1)

1,3-Dibenzylimidazolium chloride (224 mg, 7.87 × 10<sup>−4</sup> mol) and silver(I) oxide (91 mg, 3.94 × 10<sup>−4</sup> mol) were dissolved/suspended in dichloromethane (10 ml) and stirred, at room temperature, in air, in the dark for 15 h. The resulting solution was filtered and concentrated and the product precipitated by addition of excess diethyl ether. Yield: 181 mg (59%, 4.64 × 10<sup>−4</sup> mol).

δ<sub>H</sub>: 7.4 (6H, m); 7.25 (4H, m); 6.95 (2H, s, NHC ring); 5.3 (4H, s, benzyl).

δ<sub>C</sub>: 151.2 (carbene C); 135.3; 129.2; 128.8; 127.9; 121.6 (NHC ring); 55.9 (benzyl).

MS (LSIMS): *m/z* 605 (M<sup>+</sup>); 355 (M<sup>+</sup>−1,3-dibenzylimidazol-2-ylidene).

Microanalysis: Found (expected) C 51.7 (52.1); H 4.1 (4.1); N 7.0 (7.2); Cl 9.2 (9.1).

Crystal structure data: Triclinic, space group *P*1; *a* = 8.0808(17) Å, *b* = 9.954(2) Å, *c* = 10.398(2) Å, α = 88.613(5)°, β = 68.374(5)°, γ = 85.554(5)°. *D*(calc) = 1.678 Mg m<sup>−3</sup>. The structure was solved by direct methods using SHELXS with additional light atoms found by Fourier methods. Refinement was by full matrix least-squares on *F*<sup>2</sup> for 8192 reflection positions using SHELXTL [25].

Hydrogen atoms were added at calculated positions and refined using a riding model with freely rotating methyl groups. Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl hydrogen atoms) times the equivalent isotropic

displacement parameter of the atom to which the H-atom is attached.

The weighting scheme was calculated using  $w = 1/[\sigma^2(F_o^2) + (0.0303P)^2]$  where  $P = (F_o^2 + 2F_c^2)/3$ . Goodness of fit on  $F^2 = 0.965$ .  $R_1$  [for 3200 reflections with  $I > 2\sigma(I)$ ] = 0.0268,  $wR_2 = 0.0595$ .

#### 4.2. Bis(1-methyl-3-(2-bromo)benzylimidazol-2-ylidene) silver dibromoargentate (2)

1-Methyl-3-(2-bromo)benzylimidazolium bromide (249.3 mg,  $7.51 \times 10^{-4}$  mol) and silver(I) oxide (87 mg,  $3.76 \times 10^{-4}$  mol) were dissolved/suspended in dichloromethane (10 ml) and stirred, at room temperature, in air, in the dark for 15 h. The resulting solution was filtered and concentrated and the product precipitated by addition of excess diethyl ether. Yield: 214 mg (65%,  $2.44 \times 10^{-4}$  mol).

$\delta_H$ : 7.5 (2H, dd,  $^3J_{HH}$  8 Hz,  $^4J_{HH}$  2 Hz, o to Br); 7.25 (2H, dt,  $^3J_{HH}$  8 Hz,  $^4J_{HH}$  1 Hz, p to Br); 7.15 (2H, dd,  $^3J_{HH}$  8 Hz,  $^4J_{HH}$  2 Hz, o to benzyl); 7.1 (2H, dt,  $^3J_{HH}$  8 Hz,  $^4J_{HH}$  2 Hz, m to Br); 7.0 (4H, s, NHC ring); 5.4 (4H, s, benzyl); 3.9 (6H, s, Me).

$\delta_C$ : 183.0 (carbene C); 135.0; 133.3; 130.4; 130.3; 128.3; 123.6; 122.5 (NHC ring); 121.5 (NHC ring); 55.2 (benzyl); 39.1 (Me).

MS (LSIMS):  $m/z$  609 ( $M^+$ ).

Microanalysis: Found (expected) C 30.1 (30.1); H 2.5 (2.5); N 6.3 (6.4).

Crystal structure data: Triclinic, space group  $P1$ ;  $a = 6.973(2)$  Å,  $b = 8.566(3)$  Å,  $c = 11.532(4)$  Å,  $\alpha = 107.688(2)^\circ$ ,  $\beta = 91.7430(10)^\circ$ ,  $\gamma = 100.153(2)^\circ$ .  $D(\text{calc}) = 2.266$  Mg m $^{-3}$ . The structure was solved by direct methods using SHELXS with additional light atoms found by Fourier methods. Refinement was by full matrix least-squares on  $F^2$  for 4244 reflection positions using SHELXTL [25].

Hydrogen atoms were added at calculated positions and refined using a riding model with freely rotating methyl groups. Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl hydrogen atoms) times the equivalent isotropic displacement parameter of the atom to which the H-atom is attached.

The weighting scheme was calculated using  $w = 1/[\sigma^2(F_o^2) + (0.0734P)^2]$  where  $P = (F_o^2 + 2F_c^2)/3$ . Goodness of fit on  $F^2 = 0.908$ .  $R_1$  [for 1752 reflections with  $I > 2\sigma(I)$ ] = 0.0538,  $wR_2 = 0.1262$ .

#### 4.3. Bis(1,3-dibenzylimidazol-2-ylidene) silver bromide (3)

1,3-Dibenzylimidazolium bromide (455 mg,  $1.38 \times 10^{-4}$  mol) and silver(I) oxide (160 mg,  $6.90 \times 10^{-4}$  mol) were dissolved/suspended in dichloromethane (10 ml) and stirred, at room temperature, in air, in the dark for fifteen hours. The resulting solution was filtered and concentrated

and the product precipitated by addition of excess diethyl ether. 54% yield.

$\delta_H$ : 7.27 (6H, m); 7.19 (4H, m); 6.85 (2H, s, NHC ring); 5.24 (4H, s, benzyl).

$\delta_C$ : 182.1 (carbene C); 135.5; 129.2; 128.7; 127.9; 121.5 (NHC ring); 55.8 (benzyl).

MS (LSIMS):  $m/z$  684 ( $M^+$ ); 436 ( $M^+ - 1,3$ -dibenzylimidazol-2-ylidene).

Microanalysis: Found (expected) C 59.5 (59.7); H 4.5 (4.7); N 8.2 (8.2).

Crystal structure data: Monoclinic, space group  $P2(1)/n$ ;  $a = 13.3270(7)$  Å,  $b = 9.7802(5)$  Å,  $c = 24.0155(12)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 104.8420(10)^\circ$ ,  $\gamma = 90^\circ$ .  $D(\text{calc}) = 1.502$  Mg m $^{-3}$ . The structure was solved by direct methods using SHELXS with additional light atoms found by Fourier methods. Refinement was by full matrix least-squares on  $F^2$  for 4612 reflection positions using SHELXTL [25].

Hydrogen atoms were added at calculated positions and refined using a riding model with freely rotating methyl groups. Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl hydrogen atoms) times the equivalent isotropic displacement parameter of the atom to which the H-atom is attached.

Goodness of fit on  $F^2 = 1.033$ .  $R_1$  [for 5706 reflections with  $I > 2\sigma(I)$ ] = 0.0475,  $wR_2 = 0.1293$ . Data/restraints/parameters 7327/0/337. Largest difference Fourier peak and hole 1.664 and  $-1.504$  e Å $^{-3}$ .

## 5. Supplementary material

CCDC 649653, 649654 and 649655 contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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