Silver alkoxide and amino N-heterocyclic carbenes; syntheses and crystal structures

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Abstract

Silver(I) complexes of heterobidentate ligands that incorporate one or two N-heterocyclic carbene moieties coupled with an alcohol or amine group have been made by direct deprotonation of ligands of the form $[HOCR^1R^2CH_2(1\text{-}HC\{NCHCHNR\})][X]$, H_2L^1X (X = Br, I), $[H_2NR^1CHR^2CHR^2(1\text{-}HC\{NCHCHNR\})][Br]_2$ $H_3L^2X_2$ (X = Cl, Br), and $[H_2N\{CH_2CH_2(1\text{-}HC[NCHCHNMes])\}_2][X]_3$ $H_4L^3X_3$ (X = Cl, Br). Silver(I) oxide is sufficiently basic to deprotonate both the imidazolium and the alcohol functional groups of all but one of the L^1 ligand precursors, to afford rare examples of silver alkoxide complexes $[Ag(L^1)]$, stabilised by the soft donor carbene. Another complex of L^1 is characterised as the carbene alcohol adduct $[Ag(HL^1)_2I]$. The analogous reactions of silver(I) oxide with the amino imidazolium precursors afford silver amino-carbenes $[Ag(HL^2)Br]$ with the potentially bidentate L^2 ligand, and $[Ag(HL^3)X]$ (X = Cl, Br) with the potentially tridentate L^3 ligand. A single crystal X-ray diffraction study of the latter complex confirms that the neutral amine of the potentially tridentate L^3 ligand is unco-ordinated; instead the structure contains discrete chains of T-shaped silver bis(carbene) halide moieties that bridge to form a zig-zag 2-connected polymer. Protonolysis of two of the silver alkoxide and amino adducts, $[Ag(L^{1a})]$ and $[Ag(HL^{2a})Br]$, affords imidazolium complexes salts $[H_2L^{1a}][AgCl_2]$ and $[Ag(H_2L^{2a})Br][AgBr_2]$ that retain the Ag(I) centre as complex counterions. The single crystal X-ray structures of these salts have been determined and show the silver(I) cations are now incorporated into ladders or chains as silver(I) halo-anions, and a silver amine dative bond is present in the latter complex.

1. Introduction

N-heterocyclic carbenes (NHCs) are widely used as replacements for phosphines as supporting σ-bases in homogeneous late metal catalyst systems, and as rate accelerating additives in organic reactions catalysed by Lewis acidic metal cations [1–13]. Whilst almost all isolated NHCs are thermally stable indefinitely at room temperature, the strongly basic carbenes decompose in air, often rapidly. However, the silver(I) adducts, formed when an imidazolium precursor is deprotonated by basic silver(I) oxide or carbonate [14,15], are relatively air stable, yet sufficiently labile to be useful carbene transfer agents in solution [16–21]. We have been studying the chemistry of NHC ligands with an incorporated anionic functional group to allow us to isolate discrete carbene complexes of

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Lewis acidic transition metal cations and lanthanides. We have found that the Group 1 salts of both alkoxide, amide, and amino-functionalised NHC ligands can be readily synthesised to form kinetically inert complexes [4,22].

The synthesis of inert silver(I) carbene complexes that remain complexed in aqueous solvent systems, has recently been shown by Youngs et al. [23–25] to be an interesting new source of antimicrobial agents for medical applications. There are no simple silver alkoxides in the literature other than that of the tridentate alkoxy-dicarbene we have communicated, [Ag{OC(Ph)-(CH$_2${1-C[NCHCHNBu^t])$_2$}]$_2$ [26]. Noting the potential for using such complexes as precursors for silver or silver oxide nanoparticles [27], homogeneous catalysts [11,28,29], and perceiving that silver complexes often show interesting structural [30,31], and optical properties [32,33], we have studied the complexation of silver(I) by bidentate alkoxide carbene ligands [4]. For comparison, we also report herein the results of studies on the complexation of silver(I) by bidentate amino-carbene ligands, and a new tridentate amino carbene, [NH{CH$_2$-CH$_2$(C[NCHCHNMes])}$_2$], the first with two NHC groups. A simple, one-pot route to the tridentate amino-carbene ligand is also described.
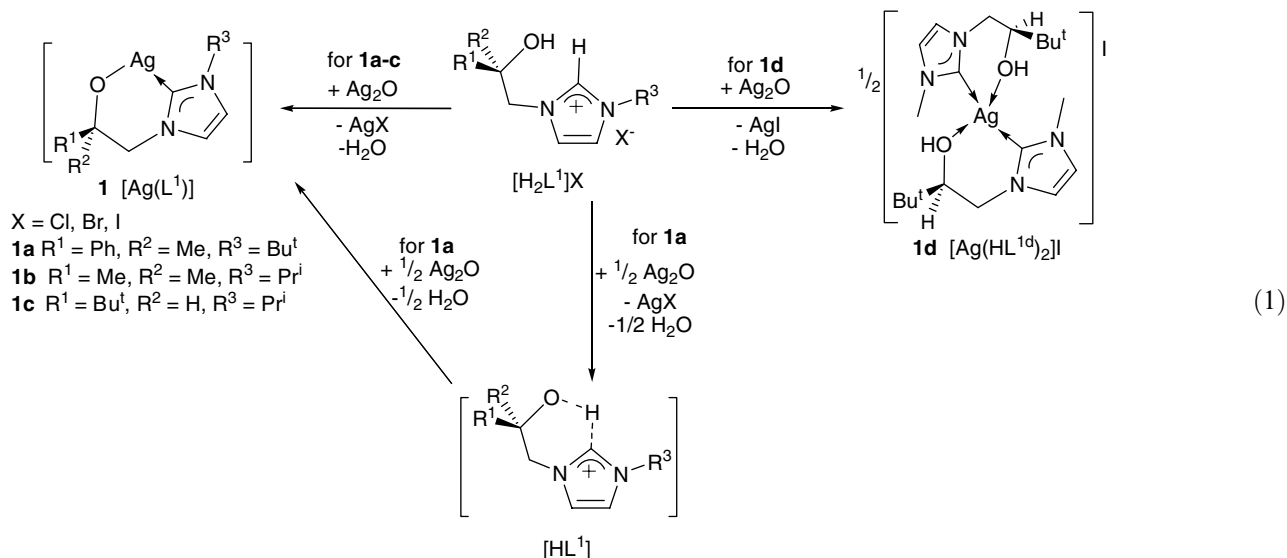
2. Results and discussion

2.1. Silver adducts of bidentate alkoxy carbene ligands

In turn, a sample of an alkoxide proligand – the non-halide containing zwitterionic [HL^{1a}], or the imidazolium alcohol [H$_2$L$^{1b–d}$]X (X = Cl, Br, or I) [4], was dissolved in dichloromethane, under a dinitrogen atmosphere, and a mixture of Ag$_2$O and activated 4 Å molecular sieves added. The black suspension was stirred for 12 h in the absence of light, during which time the suspended powder became a pale grey. The reaction mixture was filtered, and the volatiles removed under reduced pressure to afford the silver carbene [AgOCR^{1}R^{2}CH$_2$(1-C{NCHCHNR^3})], Ag(L^1), **1a**–**1c**, as colourless solids, in excellent yields, which could be recrystallised from dichloromethane/hexanes mixtures, Eq. (1). The reaction with [H$_2$L^{1d}]I does not afford the alkoxide-carbene adducts. Instead, a bis(carbene-alcohol) silver(I) salt is isolated, [AgOCHBu^{t}CH$_2$(1-C{NCHCHNMe})]I, [Ag(L^{1d})$_2$]I, **1d**, which was recrystallised to purity from 1,2-dichloroethane. The proligands [HL^{1a}], [H$_2$L^{1c}]X, and [H$_2$L^{1d}]X were made and used as racemates; one diastereomer of **1d** has been drawn in Eq. (1).

For the three alkoxide complexes **1a**–**c** ^{13}C{^{1}H} NMR spectroscopy of the bulk material shows a high frequency carbene resonance, with no observed coupling to the silver nucleus. Thus, deprotonation of both the NHC and alcohol groups to afford complexes of the [L^1] anion is achieved by the addition of silver oxide. The novelty of these products is in the fact that they are halide-free; NHC ligands studied to date have been almost exclusively those functionalised with neutral donor groups such as pyridyl or imine [16,19,21,34–37]. These tend to form cationic silver(I) bis(carbene) structures incorporating silver(I) polyhalo counteranions of the general form [Ag-(NHC)$_2$][AgX$_2$]. Youngs et al. [38] have already

1 [Ag(L^1)]

X = Cl, Br, I
1a R^1 = Ph, R^2 = Me, R^3 = Bu^t
1b R^1 = Me, R^2 = Me, R^3 = Pr^i
1c R^1 = Bu^t, R^2 = H, R^3 = Pr^i

1d [Ag(HL^{1d})$_2$]I

[HL^1]

(1)

Synthesis of silver(I) adducts of L^1

highlighted how the counterion X plays an important role in stabilising complexes of the form [Ag$_2${CH$_2$(1-C{NCHCHNMe})$_2$}][X]$_2$ against decomposition.

The deprotonation of [H$_2$L^{1d}]I does not afford a neutral, molecular silver(I) complex. Instead, ^{1}H NMR spectroscopy of the product **1d** confirms that the alcohol group remains protonated. The pK_a of the imidazolium group is about 24, [39] and that of a tertiary alkyl-substituted alcohol about 15, but we recently demonstrated that in the zwitterionic complex [HL^{1b}], formed by the treatment of [H$_2$L^{1b}]I with one equivalent of KH, the chemical behaviour of the remaining acidic H atom is as if it is bridged between the alkoxide and carbene groups; this may make it less easy to remove [40]. The zwitterionic species [HL^{1a}] is completely deprotonated to the silver alkoxide **1a**.

In contrast to the spectroscopic characteristics of the products **1a–c**, the ^{1}H NMR spectrum of **1d** shows that the OH proton is still present; a resonance is observed as a doublet at 2.40 ppm, with a $^3J_{HH}$ coupling of 5.4 Hz to the tertiary H of the chiral backbone carbon atom, suggesting a rigid backbone conformation, perhaps enforced by the alcohol functioning as a donor ligand to silver(I). The spectrum of **1d** also shows a magnetically distinct environment for each of the backbone CH$_2$ and CH protons of the ligand, unlike that seen for the cationic proligands [H$_2$L^{1a}]$^+$ or [H$_2$L^{1d}]$^+$. The formulation of **1d** drawn in Eq. (1) suggests a congested silver coordination sphere, which might also suggest why the *N*-methylated ligand L^{1d} can form this [Ag(L^1)$_2$]$^+$ cation in **1d**, while the larger *N-iso*-propyl substituted ligand L^{1c} is completely deprotonated to form the neutral [Ag(L^1)] conformation.

The silver alkoxide complexes **1a–d** are all soluble in halogenated solvents, and the elemental analytical data for **1c** include one equivalent of dichloromethane. The ligands with sterically less demanding *N*-alkyl groups tend to show peaks for fragments based on [Ag(L)$_2$]$^+$ in the mass spectrum, suggesting that a rearrangement to a bis(carbene) co-ordinated silver cation takes place. For the larger *N-iso*-propyl carbene ligand L^{1b}, the parent ion fragment [Ag(L^{1b})]$^+$ is observed by electrospray mass spectrometry.

All complexes **1a–d** decompose after prolonged exposure (96 h) to light or air, but are stable for about 24 h in undried chloroform solutions made up in air.

## 2.2. Silver adducts of bidentate amino-carbene ligands L^2

A dichloromethane solution of the alkyl ammonium imidazolium proligand [H$_3$L^{2a}]Br$_2$ [41] in a Schlenk flask was treated with a mixture of Ag$_2$O and activated 4 Å molecular sieves, and stirred in the absence of light, under a dinitrogen atmosphere for 12 h.

$$\text{(2)}$$
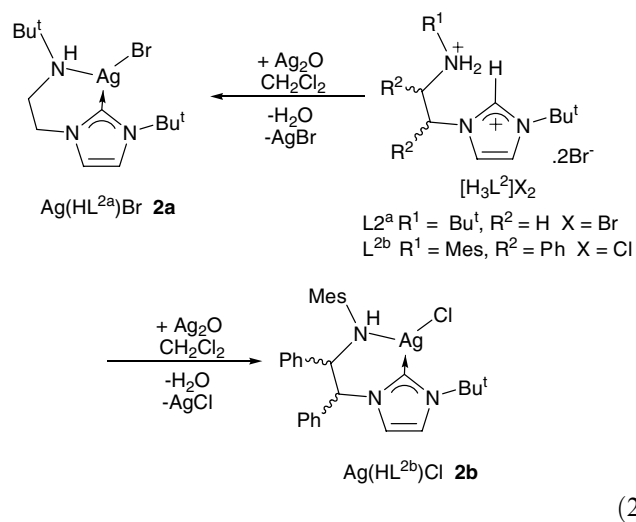
The grey-brown suspended mixture was filtered, and the volatiles removed under reduced pressure to afford [^{t}BuNHCH$_2$CH$_2$(C(AgBr)(NCHCHNBu^t))], [Ag(HL^{2a})-Br], **2a** as a pale brown powder, in poor isolated yield but good purity, Eq. (2). Complex **2b**, [Mes-NHCHPhCHPh(C(AgCl)(NCHCHNBu^t))], [Ag(HL^{2b})-Cl], which has a more sterically encumbered alkyl backbone linking the NHC and amino functional groups, is made by the same route, but isolated in significantly higher yield than **2a**, as a colourless solid. The ^{13}C{^{1}H} NMR spectrum obtained from the bulk material of **2a** shows a high frequency carbene resonance at 177.4 ppm, with no measurable silver coupling. This chemical shift compares with that of the free carbene HL^{2a}, at 211 ppm, suggesting complexation of the silver(I) cation. Silver oxide is not sufficiently basic to deprotonate a secondary amine, and the formulation of the two bulk products as the NH-containing [Ag(HL^2)Br] is confirmed by elemental analysis, and NMR spectroscopy. The (EI) mass spectrum of [Ag(HL^{2a})Br] shows no peaks attributable to a silver-containing fragment, which could either be due to the size of the carbene *N*-alkyl groups preventing a rearrangement to the [Ag(NHC)$_2$]$^+$ cation (which is usually observed by mass spectrometry), or the amine may be metal-bound, which would yield less stable, heteroleptic silver fragments in the spectrometer. Complex **2a** is surprisingly unstable in air and within seconds of exposure the compound becomes a thick oil, presumably due to the hygroscopic nature of the imidazolium salts that are being formed. However, the diphenyl substituted complex **2b** survives dissolution in an aqueous organic solvent mixture for up to 10 min before any decomposition to imidazolium-containing products is observed.

2.3. Silver adducts of tridentate amino bis(carbene) ligands L^3

$$(3)$$
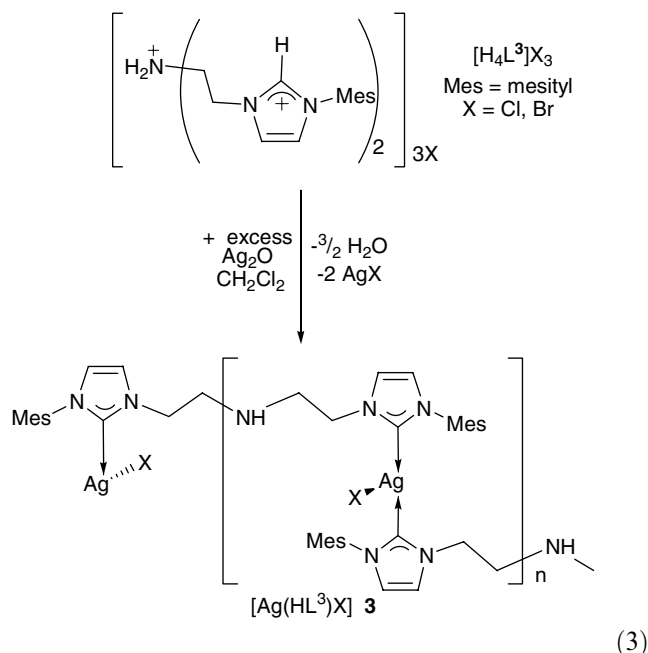
We have also prepared the diimidazolium precursor to a potentially tridentate, monoanionic amido ligand $[H_4L^3]X_3$ (X = Cl, Br) from the reaction of mesitylimidazole with di(chloroethyl)ammonium chloride or di(bromoethyl)ammonium bromide in acetonitrile at reflux temperatures. This one-pot route contrasts with that reported for the diamino-monoimidazolium salt reported recently [42]. The amine precursor di(bromoethyl)ammonium bromide is made by stirring $[H_4L^3]Cl_3$ with LiBr, and the product is difficult to separate from the LiCl byproduct so the proligand used is best formulated as $[H_4L^3]Br_3 \cdot 3LiCl$.

A dichloromethane solution of the diimidazolium alkylammonium salt $[H_4L^3]X_3$ (X = Cl or Br) stirred with a mixture of Ag_2O and activated 4 Å molecular sieves, in the dark under a dinitrogen atmosphere for 12 h, affords a grey suspension. After filtration, removal of volatiles from the pale yellow filtrate under reduced pressure, and recrystallisation from a dichloromethane/hexanes mixture, the new compound $[NH\{CH_2-CH_2(C(AgX)[NCHCHNMes])\}_2]$, $[Ag(HL^3)X]$, **3** is isolated as a pale yellow powder in good yield, Eq. (3). Complex **3** can readily be made bromide-free (i.e., all halide is chloride) from the proligand $[H_4L^3]Cl_3$. However, the reaction times for the synthesis of both $[H_4L^3]Br_3$ and $[Ag(HL^3)Br]$ are significantly reduced compared with the chloride analogues. Thus, for systems in which the counterion is unimportant, the halide mixture arising from the use of $[H_4L^3]Br_3$ is acceptable, and even preferential to the chloride-only system. The mass spectrum (EI) of the product shows fragments attributable

to a silver(I) ion co-ordinated by one complete L^3 ligand and portions of a second ligand. These fragments can be attributed to linear portions of the polymeric structure of **3**, drawn in Eq. (3), according to the single crystal structure determination results (vide infra).

Crystals suitable for single crystal X-ray analysis were grown by diffusion of hexanes into a solution of **3** in dichloromethane. The molecular structure of $[Ag(HL^3)X]_n$ is shown in Fig. 1. In this crystal, there is an occupational disorder between chloride and bromide ions (approximately 0.5:0.5 Cl:Br), due to the mixture of halide ions carried through from the ligand synthesis.

There is no evidence of silver-amine bonding in $[Ag(HL^3)Br]$ in the solid-state, but rather the CNC ligand bridges between adjacent metal centres to accommodate a conventional T-shaped silver geometry with a near-linear (164.5°) carbene–Ag–carbene moiety. This T-shaped geometry has been seen once before in organometallic silver(I) chemistry in a complex of a tripodal NHC ligand $[(TIME^{Me})_2Ag_3]_2[Ag_8Br_{14}]$ [43], while the $[Ag(NHC)_2]^+$ unit is ubiquitous [44,45]. The Ag–$C_{carbene}$ distances are 2.09 Å as expected for silver bis(carbene) complexes. The shortest intermolecular amine N–Br distance between different molecules is 4.416 Å, with no other obvious close contacts within the structure, H-bonding, or otherwise. Complex **3** is the first reported example of a Ag(I)–carbene chain polymer connected by the carbene ligands rather than through metal halochains [31,33,46].

Complex **3** is stable in chloroform solution in air, in the dark, for at least 24 h, but if water is added to the solution the complex shows partial decomposition to an insoluble powder. Addition of dilute aqueous HCl results in the immediate precipitation of AgCl and the ^1H NMR spectrum of the protonated ligand $[H_4L^3]Cl_3$ is regenerated quantitatively. A sample of **3** stored in air
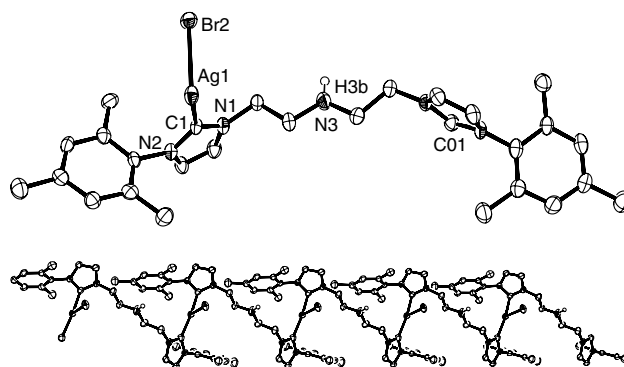

Fig. 1. Displacement ellipsoid drawing of a portion of the 1-D polymer **3**, $[Ag(HL^3)X]_n$, X labeled as bromide, but refined to 0.5Br:0.5Cl (50% probability). Lattice solvent and non-NH hydrogens omitted for clarity. Upper-asymmetric unit. Lower-portion of polymeric chain of (AgX)L. Selected distances (Å) and angles (°): Ag1–C1, 2.090(5); Ag1–C01 2.090(6), C1–Ag1–C01 164.5(2), Ag1–Br2 2.8522(10), C1–Ag1–Br2 97.5(2); C1–N1 1.348(7), C1–N2 1.348(7), N1–C1–N2 103.8(4).

as a solid in the dark is not hygroscopic like **2a**, but may be recovered unchanged after five days. Upon exposure of **3** to light, decomposition in solution takes place slowly over 4–5 days.

2.4. Silver halide adducts of the protonated alcohol and amino bis(carbene) ligands L^{1a} and L^{2a}

All examined crystals of $[Ag(L^1)]$ and $[Ag(HL^2)]X$ that appeared optically suitable for single crystal X-ray analysis showed weak or no diffraction. However, two samples produced small quantities of partially protonated imidazolium-based silver complexes which were both highly crystalline and suitable for single crystal X-ray diffraction studies.

2.5. Structure of a silver halo-alcohol-imidazolium salt based on L^{1a}

$$[H_2L^{1a}][AgCl_2]\ \mathbf{4}$$

$$(4)$$
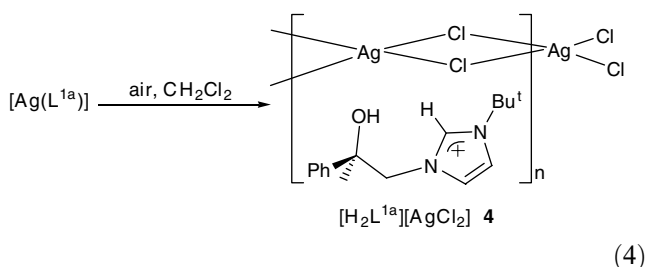
One crystal isolated from a solution of $[Ag(L^{1a})]$, which was identified as the imidazolium salt $[Ag(H_2L^{1a})_2Cl_2(NO_3)]$ **4**, formed either from a reprotonation of the silver alkoxide compound, Eq. (4), or from the co-crystallisation of the silver chloride byproduct with the free ligand. The nitrate ion in the lattice derives from an impurity in the silver oxide, which was not purified prior to use. The molecular structure of **4** is shown in Fig. 2.

There are two molecules of imidazolium alcohol $[H_2L^{1a}]^+$ in the asymmetric unit, which stack in double layers with π–π stacking interactions between the phenyl groups of the ligands. The layers form a repeating order of ABBCBB (A = $[AgCl_2]_n^-$, B = $[H_2L^{1a}]_n^+$, C = $[NO_3]_n^-$) with the silver(I) centres in **4** forming an infinite 1-D chain of AgCl diamonds comprising tetrahedral four co-ordinate silver(I) vertices joined by two μ₂-bridged chloride ions, with an average Ag–Cl distance of 2.610 Å. There are also geometries suggestive of H-bonding interactions; the distance between the alcohol O1 and Cl2 is 3.148 Å, but the imidazolium C–Cl2 distance is 3.587 Å, somewhat long for a H-bonding interaction, while the planar CH group is not obviously oriented towards the anion. There is no obvious interaction between either the Ag(I) or imidazolium cations and the nitrate ions in the layers.

2.6. Structure of a silver halo-amino-imidazolium salt based on L^{2a}

A small crop of crystals (<5%) isolated from a dichloromethane/hexane solution of $[Ag(HL^{2a})]Br$ at 5 °C were identified as an incompletely deprotonated adduct $[Ag(H_2L^{2a})Br][AgBr_2]$, **5**, Eq. (5)

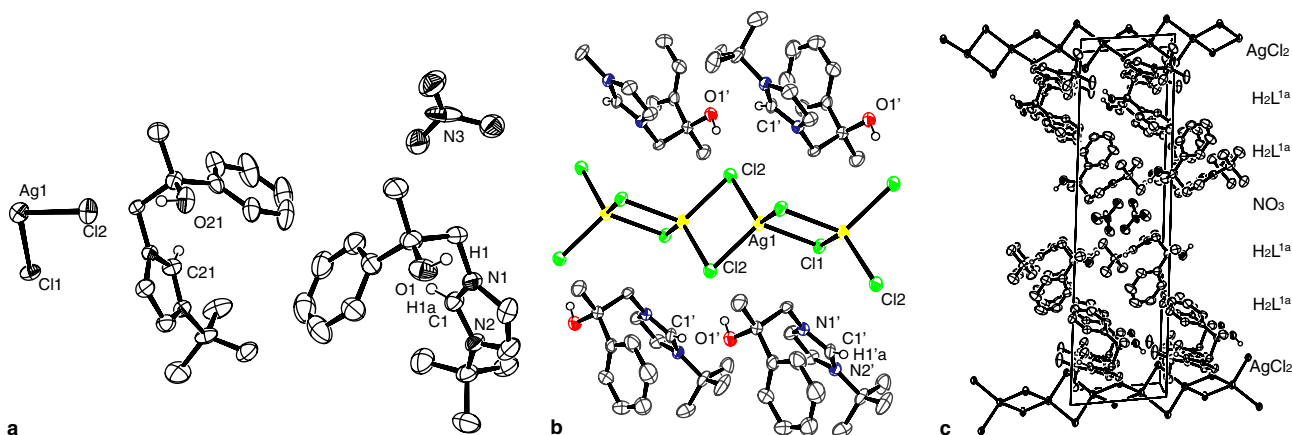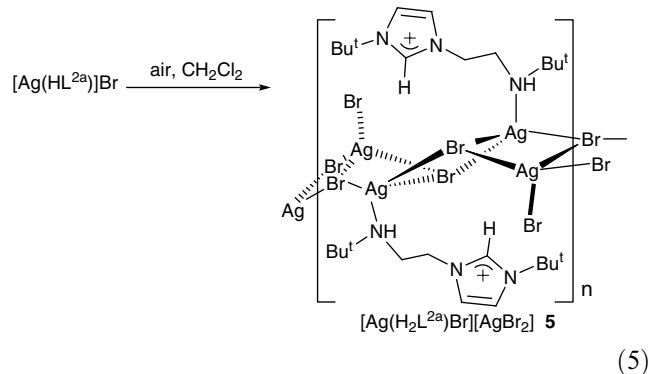$$[Ag(H_2L^{2a})Br][AgBr_2]\ \mathbf{5}$$

$$(5)$$

Fig. 2. Displacement ellipsoid drawing of $[Ag(H_2L^{1a})Cl_2]$, **4**; asymmetric unit (a), packing diagram (b), and cell contents (c) (50% probability). Hydrogen atoms not involved in hydrogen bonding omitted for clarity. Selected distances (Å) and angles (°): Ag1–Cl1 2.6044(11), Ag1–Cl2 2.6269(11), N1–C1 1.330(6), N21–C21 1.328(5); Cl1–Ag1–Cl2 118.72(4), Cl1–Ag1–Cl1 92.94(3), Cl1–Ag1–Cl2 119.65(4), Cl2–Ag1–Cl2 100.72(3), Ag1–Cl1–Ag1 87.06(3), Ag1–Cl2–Ag1 79.28(3), N1–C1–N2 108.4(4), N21–C21–N22 109.3(4).
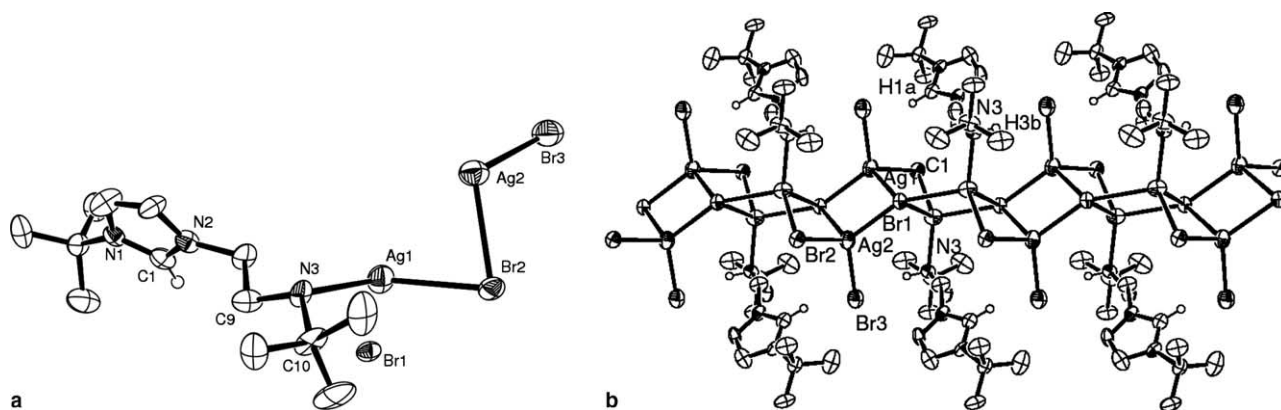
Fig. 3. Displacement ellipsoid drawing of [Ag(H$_2$L^{2a})Br][AgBr$_2$], **5**, and packing diagram of chains (50% probability). Non-H-bonded hydrogens omitted for clarity. Selected distances (Å) and angles (°): C1–N1 1.318(18), C1–N2 1.378(18), C2–C3 1.37(2), N3–Ag1 2.330(11), N1–C1–N2 107.1(13).

The structure of **5** is shown in Fig. 3. Both ^{1}H and ^{13}C NMR spectroscopy of the sample confirm that this imidazolium-based product is only present as a small fraction of the recrystallised sample.

Unlike **4**, the structure of **5** is based upon a polymeric ladder of [AgBr$_2$]$^-$, rather than a chain of diamonds. The crystal structure of **5** is centrosymmetric with the layer of cations lying on the opposite side of the [AgBr$_2$]$^-$ ladder generated by symmetry. As in **4**, the [AgBr$_2^-$]$_n$ co-ordination polymer runs between the protonated molecules of ligand, but this time two distinct co-ordination environments are observed for the silver(I) centres. The amine groups bind as neutral donors to alternate Ag(I) centres [Ag(1) in Fig. 3], and this binding gives these cations a distorted tetrahedral geometry, with N3 displaced by only 0.053 Å from the centre of the three bromide ions occupying the other three sites. The other half of the Ag(I) cations, Ag2, are also approximately tetrahedral, and are bonded to three bridging bromide anions with distances of 2.708, 2.736, and 2.838 Å [47,48], and a closer terminal bromide, distance 2.624 Å. Previously, neutral [AgBr]$_n$ and [49] ladders have been observed in N,N'-dimethyl substituted NHC adducts of Ag(I) [33,45], but here the two alternating types of silver(I) cations render the ladders more puckered. Two NH groups point at the terminal bromide, with geometries suggestive of H-bonding interactions; the imidazolium carbon C1–Br3 distance is 3.448 Å and the amine N3–Br3 distance is 3.406 Å, the structure of the imidazolium-metal halide core being essentially the same as that observed in the lithium bromide salt, [Li(H$_2$L^{2a})Br$_2$], which we have reported previously [41].

3. Conclusions

This work demonstrates that silver(I) alkoxide complexes are readily accessible using pendant N-heterocy-clic carbene functional groups to increase the stability of the complexes. This allows halide-free silver(I)–NHC complexes [Ag(L^1)] to be isolated for three alkoxy carbene ligands with different peripheral alkyl substituents. However, for one complex, [Ag(L^{1d})$_2$]I the alcohol group of the ligand remains protonated, so this complex forms the more traditionally observed silver(I) bis(NHC) cation with an iodide counter-ion. New bidentate amino-NHC and tridentate amino-bis(NHC) ligands HL^2 and HL^3 have been prepared, and their silver(I) complexes characterised. The tridentate ligand L^3 forms 1-D Ag(I) coordination polymers in which T-shaped silver cations bridge adjacent ligands; there is no evidence of amine co-ordination to the metal. The silver(I) complex **3** is the first reported example of an NHC-connected Ag(I)–carbene chain polymer. The molecular structures of two partially protonated silver alkoxide and silver amine complexes have been determined from single crystal diffraction studies; both contain anionic ribbons of silver halide packed between cationic layers of imidazolium moieties; the latter amine structure shows a silver(I)-amine dative bond, unlike in [Ag(L^3)Br].

4. Experimental

4.1. General details

All manipulations of air-sensitive materials were carried out under a dry, oxygen free argon or dinitrogen atmosphere, using standard Schlenk techniques (rotary pump for vacuum 10^{-4} mbar) or in a glove box (Mbraun Unilab or Saffron) under dry dinitrogen. All NMR spectra were recorded on a Bruker DPX 300 spectrometer, operating frequency 300 MHz (^{1}H), 75 MHz (^{13}C), variable temperature unit set to 300 K unless otherwise stated. Chemical shifts are reported in parts per million, and referenced to residual solvent proton

resonances calibrated against external TMS. IR spectra were recorded in the range 400–4000 cm^{-1} on a Nicolet Avatar 360 FT-IR spectrometer as nujol mulls between NaCl discs. Mass spectra (EI, ES and FAB) were run by A. Hollingworth on a VG autospec instrument. Elemental analyses were determined by Dr. S. Boyer at London Metropolitan University and by T. Spencer at the University of Nottingham.

All solvents used (diethyl ether, tetrahydrofuran, hexane, toluene, dichloromethane, 1,2-dichloromethane, acetonitrile and pyridine) were either degassed and purified by passage through activated alumina towers prior to use, or were freshly distilled from the appropriate drying reagent under dinitrogen, and thoroughly degassed prior to use. dichloromethane from CaH$_2$, 1,2-dichloroethane and pyridine from CaH$_2$. NMR spectroscopic grade benzene-d_6 and pyridine-d_5 were dried over potassium metal, thoroughly degassed by the freeze-thaw method and transferred under reduced pressure before use. Chloroform-d was dried over activated molecular sieves. The synthesis of [H$_2$L^1]Hal and [H$_3$L^2]Br$_2$ have been previously described [4,41].

4.2. Synthesis of [Ag(L^{1a})]

A Schlenk flask was charged with silver(I) oxide (0.050 g, 0.216 mmol), HL^{1a} (0.100 g, 0.388 mmol) and 4 Å molecular sieves (1.0 g). To this was added dichloromethane (10 ml) and the solution was stirred at room temperature in the absence of light for 12 h. The resultant mixture was filtered and the volatiles removed to yield a colourless solid, which was recrystallised from a mixture of dichloromethane and hexanes to yield colourless [Ag(L^{1a})] **1a** in 82% yield, 0.115 g. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.21–7.37 (m, 5H, ArH), 6.99 (s, 1H, NCHCHN), 6.93 (s, 1H, NCHCHN), 4.34 (s, 2H, NCH$_2$), 1.66 (s, 3H, CH$_3$), 1.54 (s, 9H, NC(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz): δ 143.5 (C$_i$), 128.9 (C$_m$), 127.7 (C$_p$), 124.9 (C$_o$), 121.1 (NCCN), 117.7 (NCCN), 74.6 (NCH$_2$C), 63.9 (NCH$_2$), 57.4 (C(CH$_3$)$_3$), 31.8 (C(CH$_3$)$_3$), 27.4 (CH$_3$). MS (ES): m/z 623 ([Ag(L^{1a})$_2$]$^+$, 100%).

4.3. Synthesis of [Ag(L^{1b})]

A Schlenk flask was charged with silver(I) oxide (0.75 g, 3.23 mol), H$_2$L^{1b}I (1.00 g, 3.23 mmol), dichloromethane (20 ml) and 4 Å molecular sieves (1.0 g). To this was added dichloromethane (10 ml) and the solution was stirred at room temperature in the absence of light for 12 h. The resultant mixture was filtered and the volatiles removed to yield a colourless solid, which was recrystallised from a mixture of dichloromethane and hexanes to yield a colourless solid characterised as [Ag(L^{1b})] **1b** in 53% yield, 0.49 g. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.26 (s, 1H,

NCHCHN), 6.98 (s, 1H, NCHCHN), 4.70 (sept, 1H, $^3J = 7.5$ Hz, NCH(CH$_3$)$_2$), 4.11 (s, 2H, NCH$_2$), 1.46 (d, 6H, $^3J = 7.5$ Hz, NCH(CH$_3$)$_2$), 1.22 (s, 6H, CH$_{32}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz): δ 179.9 (NCN), 123.4 (NCCN), 116.2 (NCCN), 77.2 (C(CH$_3$)$_2$), 69.7 (NCH$_2$), 62.1 (NCH(CH$_3$)$_2$), 27.3 (NCH(CH$_3$)$_2$), 23.8 (C(CH$_3$)$_2$). MS (ES): m/z 306 ([M]$^+$, 100%). Anal. Calcd. for C$_{10}$H$_{17}$N$_2$OAg: C, 41.52; H, 5.88; N, 9.69. Found: C, 41.70; H, 6.03; N, 9.51%.

4.4. Synthesis of [Ag(L^{1c})]

A Schlenk flask was charged with silver(I) oxide (0.208 g, 0.904 mmol), H$_2$L^{1c}I (0.300 g, 0.888 mmol), dichloromethane and 4 Å molecular sieves (1.0 g). To this was added dichloromethane (10 ml) and the solution was stirred at room temperature in the absence of light for 12 h. The resultant mixture was filtered and the volatiles removed to yield a colourless solid, which was recrystallised from a mixture of dichloromethane and hexanes to yield a colourless solid characterised as [Ag(L^{1c})] **1c** in 78% yield, 0.219 g. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.28 (d, 1H, $^3J = 1.8$ Hz, NCHCHN), 6.96 (d, 1H, $^3J = 1.8$ Hz, NCHCHN), 4.69 (sept, 1H, $^3J = 6.8$ Hz, NCH(CH$_3$)$_2$), 4.25 (dd, 1H, $^2J = 13.8$ Hz, $^3J = 1.9$ Hz, NCHH), 4.02 (dd, 1H, $^2J = 13.8$ Hz, $^3J = 9.7$ Hz, NCHH), 3.5 (dd, 1H, $^3J = 1.9$ Hz, $^3J = 9.7$ Hz, NCH$_2$CH), 1.44 (d, 6H, $^3J = 6.8$ Hz, NCH(CH$_3$)$_2$), 0.97 (s, 9H, C(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz): δ ppm 179.0 (NCN), 122.8 (NCCN), 116.6 (NCCN), 79.7 (NCH$_2$CH), 54.2 (NCH$_2$), 53.9 (NCH(CH$_3$)$_2$), 34.6 (C(CH$_3$)$_3$), 25.9 (C(CH$_3$)$_3$), 23.8 (NCH(CH$_3$)$_2$). MS (ES): m/z 527 ([Ag(L^{1c})$_2$]$^+$, 43%), 211 ([H$_2$L^{1c}]$^+$, 100%).

4.5. Synthesis of [Ag(HL^{1d})$_2$]I

A Schlenk flask was charged with silver(I) oxide (0.412 g, 1.78 mmol), H$_2$L^{1c}I (0.500 g 1.61 mmol), and 4 Å molecular sieves (1.0 g). To this was added dichloromethane (10 ml) and the solution was stirred at room temperature in the absence of light for 15 h. The resultant mixture was filtered and the volatiles removed to yield a colourless solid which was recrystallised from 1,2-dichloroethane, and characterised as [Ag(HL^{1d})$_2$]I **1d** in 89% yield, 0.542 g. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.13 (d, 1H, $^3J = 1.8$ Hz, NCHCHN), 6.96 (d, 1H, $^3J = 1.8$ Hz, NCHCHN), 4.31 (dd, 1H, $^3J = 1.7$ Hz, $^2J = 13.8$ Hz, NCHH), 3.87 (dd, 1H, $^3J = 10.0$ Hz, $^2J = 13.8$ Hz, NCHH), 3.80 (s, 3H, NCH$_3$), 3.53 (ddd, 1H, $^3J = 1.7$ Hz, $^3J = 5.4$ Hz, $^3J = 10.0$ Hz, NCH$_2$CH), 2.40 (d, 1H, $^3J = 5.4$ Hz, OH), 0.98 (s, 9H, C(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz): δ 179.2 (NCN), 121.8 (NCCN), 121.0 (NCCN), 79.2 (NCH$_2$CH), 43.2 (NCH$_2$), 38.0 (NCH$_3$), 33.7 (C(CH$_3$)$_3$), 24.8 (C(CH$_3$)$_3$).

MS (ES): m/z 183 ([H_2L^{1d}]$^+$, 100%), 471 ([M − I]$^+$, 52%). IR (Nujol mull): ν_{max}/cm^{-1} 3421br (OH). Anal. Calcd. for $C_{20}H_{36}N_4O_2AgI \cdot 2CH_2Cl_2$: C, 34.35; H, 5.24; N, 7.28. Found: C, 34.71; H, 5.20; N, 7.06%.

Due to the similarity of the complexes [Ag(L^1)] and their ready characterisation by NMR spectroscopy and mass spectrometry, only [Ag(L^{1b})] and [Ag(L^{1d})$_2$]I were characterised by microanalysis, as representative examples.

4.6. Synthesis of [Ag(HL^{2a})Br]

To a mixture of silver(I) oxide (1.21 g, 2.59 mmol), 4 Å molecular sieves (1.0 g) and [H_3L^{2a}]Br$_2$ (1.0 g, 5.19 mmol) in a Schlenk flask was added dichloromethane (5 ml). The suspension was stirred in the absence of light for 18 h and filtered. The volatiles were removed from the filtrate to yield [Ag(HL^{2a})Br] **2a** as a pale brown solid (0.14 g, 13%). ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ 1.02 (s, 9H, tBu), 1.70 (s, 9H, tBu), 2.94 (dd, 1H, $^3J_{HH} = 6.2$ Hz, $^2J_{HH} = 14.4$ Hz), 4.15 (t, $^3J_{HH} = 6.2$ Hz, 2H, CH$_2$), 7.08 (d, 1H, $^3J_{HH} = 1.9$ Hz), 7.11 (d, 1H, $^2J_{HH} = 1.9$ Hz). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 298 K): δ 28.03 (tBu), 30.82 (tBu), 42.74 (CH$_2$), 49.59 (CH$_2$), 53.62 (CMe$_3$), 56.73 (CMe$_3$), 117.31 (CH), 119.17 (CH), 177.36 (C$_{carbene}$). Anal. Calcd. for $C_{13}H_{25}N_3AgBr$: C, 37.98; H, 6.13; N, 10.22. Found: C, 38.19; H, 6.00; N, 10.39%.

4.7. Synthesis of [H$_3$L^{2b}]Cl$_2$

To a solution of 1-mesityl-1H-imidazole (1.52 g, 8.16 mmol) in acetonitrile (20 ml) was added a solution of N-(2-chloro-$trans$-1,2-diphenylethyl) methylaminium chloride (2.0 g, 8.16 mmol) in acetonitrile (20 ml). The mixture was stirred at reflux for 72 h, then cooled to room temperature. The volatiles were removed under reduced pressure and the resulting solid recrystallised from chloroform to yield [H$_3$L^{2b}Cl$_2$] as a colourless solid (2.8 g, 73.4%). M.p. 255–256 °C (dec), ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ 10.13 (s, 1H, N(CH)N), 8.31 (s, 1H, CH), 8.16 (bs, 2H, NH$_2^+$), 7.52 (s, 1H, CH), 7.00–7.54 (m, 14H, aromatic), 6.96 (d, $^3J_{HH} = 10.92$ Hz, 1H, CH), 5.70 (d, $^3J_{HH} = 10.32$ Hz, 1H, CH), 2.32 (s, 3H, CH$_3$), 2.23 (s, 3H, CH$_3$), 2.19 (s, 3H, CH$_3$), 1.98 (s, 3H, CH$_3$).

4.8. Synthesis of [Ag(HL^{2b})Cl]

To a mixture of silver(I)oxide (0.14 g, 0.61 mmol) and activated 4A molecular sieves (1 g) in a Schlenk flask was added a solution of [H$_3$L^{2b}]Cl$_2$ (0.1 g, 0.23 mmol) (0.1 g, 0.23 mmol) in dichloromethane (5 ml). The solution was stirred for 4 h at room temperature, the solution was filtered and the volatiles removed from the filtrate under reduced pressure. The pale brown solid

was recrystallised from thf to yield [Ag(HL^{2b})Cl] **2b** as a colourless solid (0.051 mg, 44%). ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ 1.57 (s, 3H, CH$_3$), 1.74 (s, 3H, CH$_3$), 1.92 (s, 3H, CH$_3$), 2.30 (s, 3H, CH$_3$), 4.62 (d, $^3J_{HH} = 5.72$ Hz, 1H, CH), 6.03 (d, $^3J_{HH} = 5.65$ Hz, 1H, CH), 6.91 (s, 1H, CH), 6.90–7.41 (m, 10H, aromatic), 7.71(s, 1H, CH). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 298 K): δ 16.29 (CH$_3$), 19.98 (CH$_3$), 29.89 (CH$_3$), 33.36 (CH$_3$), 67.5 (CH(Ph)), 70.05 (CH(Ph)), 119.02 (CH), 125.82 (CH), 126.65–140 (aromatic), 206.0 (C$_{carbene}$).

4.9. Synthesis of [H$_4$L^3]Br$_3$

To an acetonitrile solution of mesityl imidazole (2.87 g, 15.35 mmol, 20 ml) was added bis(2-dibromoethyl)amine hydrobromide (3.37 g, 7.67 mmol) and the mixture stirred at reflux for 48 h. The mixture was then filtered and volatiles removed from the filtrate under reduced pressure to afford the crude product as a brown oil. The oil was stirred in acetone to precipitate the pure product as a white powder which was washed with acetone (5 ml) and cold acetonitrile (2 × 5 ml) to give [H$_4$L^3]Br$_3$ as a colourless solid. Yield = 2.41 g, 46%. The pure product is hygroscopic. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 9.98 (s, 2H, CH{NCN}), 8.60 (s, 2H, CH), 7.15 (s, 2H, CH), 6.95 (s, 4H, Ar), 5.35 (s, br, 4H, CH$_2$), 4.15 (s, br, 4H, CH$_2$), 2.31 (s, 6H, p-Me), 2.14 (s, 12H, o-Me), NH not observed; ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz): δ 141.3 (NCN), 138.3 (Ar), 134.9 (Ar), 131.2 (Ar), 130.2 (Ar), 125.2 (CH), 123.7 (CH), 48.0 (CH$_2$), 46.6 (CH$_2$), 21.4 (p-Me), 18.7 (o-Me). HRMS (ES): [M − 2H − 2Br], calculated m/z = 522.2227, found 522.2231.

4.10. Synthesis of [H$_4$L^3]Cl$_3$

The trichloride salt is made analogously, yield 1.78 g, 42% ^{1}H NMR (CDCl$_3$, 300 MHz): δ 9.95 (s, 2H, CH{NCN}), 8.54 (s, 2H, CH), 7.17 (s, 2H, CH), 6.90 (s, 4H, Ar), 5.22 (s, br, 4H, CH$_2$), 3.36 (s, br, 4H, CH$_2$), 2.26 (s, 6H, p-Me), 2.06 (s, 12H, o-Me), NH not observed.

4.11. Synthesis of [Ag(HL^3)Cl]

To a dichloromethane solution of H$_4$L^{3}Cl$_3$ (165 mg, 0.3 mmol, 10 ml) in a Schlenk flask was added silver(I) oxide (116 mg, 0.5 mmol), 4 Å molecular sieves (1.0 g), and the mixture stirred in the dark for 12 h. The mixture was filtered and volatiles removed from the filtrate under reduced pressure to afford [Ag(HL^3)Cl] **3** as a colourless solid. Yield = 117 mg, 66.7%. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.47 (d, 2H, CH), 6.94 (s, 2H, CH), 6.93 (s, 4H, Ar), 4.31 (t, 4H, CH$_2$), 3.15 (m, 4H, CH$_2$), 2.32 (s, 6H, p-Me), 1.95 (s, 12H, o-Me);

Table 1
Crystal data for complexes **3**, **4**, and **5**

	3	4	5
Chemical formula	$C_{28}H_{35}AgBr_{0.51}Cl_{0.49}N_5$	$C_{32}H_{46}AgCl_2N_5O_5$	$C_{13.50}H_{27}Ag_2Br_3ClN_3$
M_r	607.83	759.50	722.30
Cell setting, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$
a (Å)	10.001 (2)	6.9149 (9)	15.945 (3)
b (Å)	10.906 (2)	10.0229 (13)	7.5712 (15)
c (Å)	13.068 (2)	26.353 (3)	19.643 (4)
α (°)	101.482 (3)	84.517 (2)	90
β (°)	100.737 (3)	83.738 (2)	93.876 (4)
γ (°)	92.156 (3)	83.389 (2)	90
V (Å^3)	1368.2 (7)	1797.1 (7)	2365.9 (8)
Z	2	2	4
D_x (Mg m^{-3})	1.475	1.404	2.028
Radiation type	Mo Kα	Mo Kα	Mo Kα
Number of reflections for cell parameters	1937	3482	2516
θ Range (°)	2.3–23.0	2.3–25.9	2.5–24.1
μ (mm^{-1})	1.56	0.75	6.84
Temperature (K)	150 (2)	150 (2)	150 (2)
Crystal form, colour	Block, colourless	Plate, colourless	Block, colourless
Crystal size (mm)	$0.13 \times 0.06 \times 0.06$	$0.36 \times 0.22 \times 0.04$	$0.18 \times 0.12 \times 0.08$
Data collection			
Diffractometer	Bruker SMART 1000 CCD area detector	Bruker SMART1000 CCD area detector	SMART1000 CCD area detector
Data collection method	ω	ω	ω
Absorption correction	Multi-scan	Numerical	Multi-scan
T_{min}, T_{min}	0.765, 1	0.771, 0.970	0.577, 1

$^{13}C\{^1H\}$ NMR (CDCl$_3$, 75 MHz): δ 139.7 (Ar), 135.5 (Ar), 134.8 (Ar), 129.6 (Ar), 122.9 (CH), 122.1 (CH), 52.1 (CH$_2$), 50.5 (CH$_2$), 21.2 (*p*-Me), 17.9 (*o*-Me). MS (ES): *m/z* = 442 [H2L] + (39%), 478 [H3LCl] + (59%), 548 [AgHL] + (100%), 584 [AgH$_2$LCl] + (48%), 617 [AgHL + C$_2$N$_3$H$_3$] + (71%), 661 [AgHL + (C$_2$N$_3$H$_3$-CH$_2$CH$_2$NH$_2$)] + (30%) found with correct isotope pattern. High resolution ESMS: calc. for [M − Cl]$^+$ (^{107}Ag isotope): 548.1938. Found: 548.1938. Anal. Calcd. for C$_{28}$H$_{35}$N$_5$AgBr: C, 57.49; H, 6.03; N, 11.97. Found: C, 57.34; H, 5.90; N, 11.87.

4.12. X-ray crystallography

Crystal data for compounds **3**, **4**, and **5** are given in Table 1. Crystals were examined on a Bruker AXS SMART 1000 area detector diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved variously by heavy-atom and direct methods and were refined by least-squares methods on F^2 values, with anisotropic displacement parameters for non-H atoms, and with constrained riding hydrogen geometries (except amine and ammonium hydrogens which were freely refined); U(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} for the parent atom. Programs were Bruker AXS SMART (control) and SAINT (integration) [50], and SHELXTL [51], and WINGX [52] for structure solution, refinement, and molecular graphics. CCDC 265422–265424 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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