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FULL PAPER

N-Functionalised heterocyclic carbene complexes of silver

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N-Functionalised imidazol-2-ylidene carbene complexes of Ag^{I} have been prepared by interaction of the corresponding imidazolium salt with Ag_2O in dichloromethane or 1,2-dichloroethane in the presence of molecular sieves or with Ag_2CO_3 in 1,2-dichloroethane. In an analogous way disilver(I) complexes of *o*-phenylenedimethylenebis(imidazol-2-ylidene) have been obtained. Their structures, as determined by X-ray crystallography, indicate that the carbene ligand acts as monodentate from the carbene end or as a bridge between two different metal atoms. In one case the silver is coordinated by two carbene ligands. In the majority of the structurally characterised complexes the metal centres adopt linear geometries with M–C(carbene) bond lengths in the range of 207–210 pm characteristic of a single bond.

There is growing interest in the use of nucleophilic Arduengo type carbenes as ligands on transition metals.[1] This stems from recent reports describing unprecedented catalytic activity of nucleophilic carbene complexes in important reactions such as Pd-catalysed Heck and Suzuki couplings, CO-ethylene copolymerisations, Ru-catalysed olefin metathesis and Rh-catalysed hydrosilylations.[2] The electronic characteristics of nucleophilic carbenes as ligands have been compared to those of the well studied phosphines.[3] The thermodynamic stability of the resulting complexes, in combination with the vast opportunities of ligand design, show immense potential for new catalysts. The synthesis of mixed donor carbene complexes has been the topic of recent reports by us[4] and others.[5] Potentially hemilabile carbene ligands could prove useful in stabilising catalytic centres while creating a degree of coordinative and electronic unsaturation, in the presence of substrates. In the first of a series of papers in this topic we describe the synthesis and the full characterisation of mixed donor *N*-functionalised imidazolium salts and their conversion into silver(I) carbene complexes. Silver carbene complexes are well known and some of them are structurally characterised.[6,7] However, the compounds described here are the first structurally characterised examples with mixed donor carbene ligands.

Results and discussion

N-Functionalised imidazolium salts

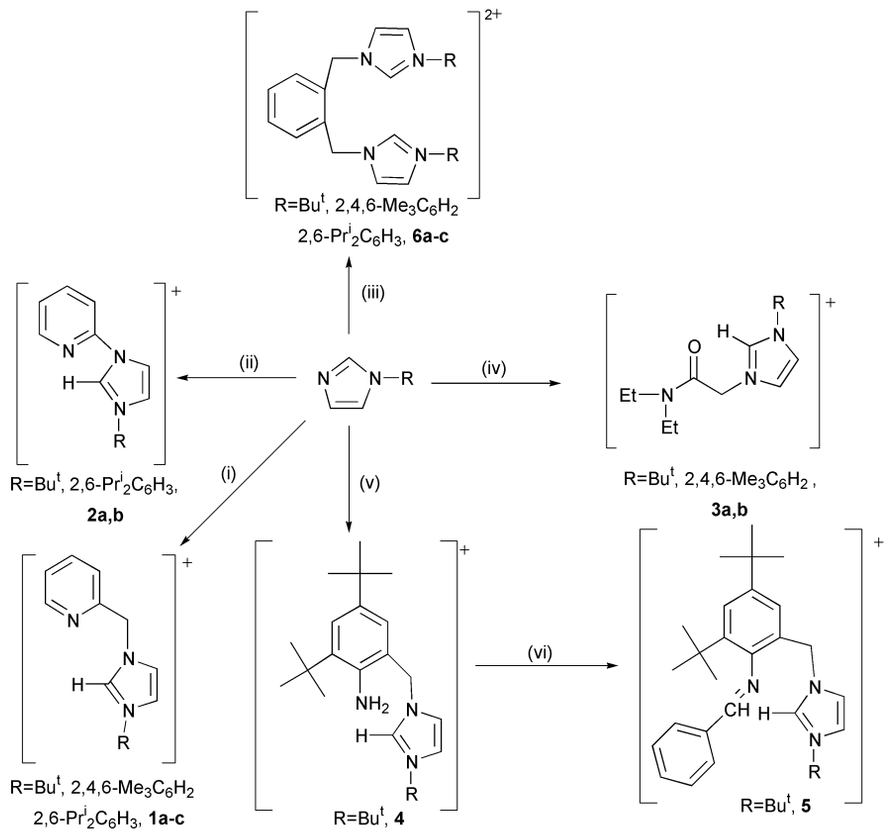
The new functionalised imidazolium salts were prepared by quaternisation of substituted alkyl and aryl imidazoles (see Scheme 1). The use of bulky substituents is expected to differentiate the reactivity of the resulting carbene complexes from the known, easily available 1-methylimidazolium analogues. In addition the crystallinity of the isolated compounds is generally expected to be better. The quaternisation reactions proceed selectively and at good rate in polar solvents like methanol, ethanol and 1,4-dioxane. The white solids obtained were characterised by analytical and spectroscopic methods. The majority of them crystallised as hydrates and the crystal structure of **1a** shows an interaction of the water molecule with the bromine.[8]

N-Functionalised carbene complexes of silver

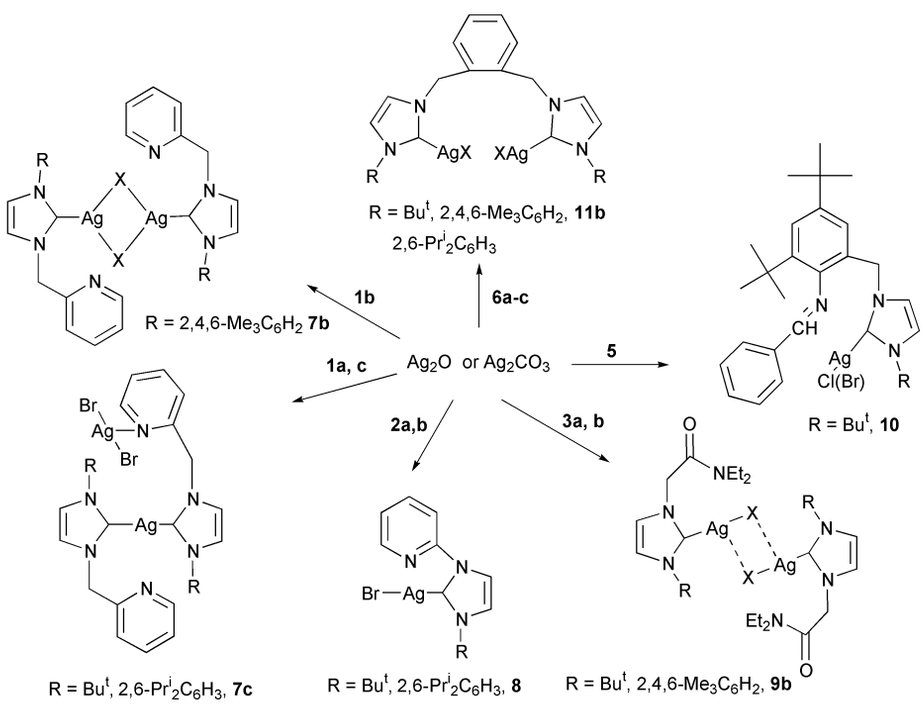
Silver carbene complexes were prepared by modification and extension of the method reported by Wang and Lin,[6] *i.e.* by interaction of the imidazolium salts with Ag_2O or Ag_2CO_3 as shown in Scheme 2. We found that: (i) with the relatively unreactive bulky imidazolium salts (**6a–6c**) the reaction took place only in refluxing 1,2-dichloroethane, whereas for all other imidazolium salts it was faster; (ii) under these conditions substantial exchange of bromide for chloride was observed; (iii) when complexes **7c** and **8** were synthesized at higher temperatures in 1,2-dichloroethane the formation of by-products was increased (see below); (iv) the purity of the products is improved by addition of activated 4 Å molecular sieves to the reaction medium; (v) Ag_2CO_3 in refluxing chlorinated solvents could be used instead of Ag_2O although the reaction times were usually longer. We have been unable to prepare the carbene complexes from silver halides and base under phase transfer catalysis as reported by Wang and Lin.[6] The identity of the silver carbene complexes was established by a combination of analytical and spectroscopic techniques. Electrospray mass spectroscopy in acetonitrile solution was of low diagnostic value, because conversion of Ag(ligand)Br into $[Ag(ligand)_2]^+$ was observed under the sampling conditions employed. This was further confirmed by using an acetonitrile solution of a crystal of **9b,** which by X-ray diffraction was shown to be Ag(ligand)Br; the molecular ion observed in this case corresponded to $[Ag(ligand)_2]^+$.

The formation of the carbene complexes was established by a weak peak below δ 165 in the $^{13}C\text{-}\{^1H\}$ NMR spectra which was assigned to the 2*C*-imidazol-2-ylidene (carbene) carbon, and by the absence of the downfield peak for the 2*H*-imidazolium proton in the ^1H NMR spectra (usually observed in non-protic solvents below δ 9).

The structures of the isolated silver carbene complexes in the solid state as determined by X-ray diffraction show considerable variety. Figs. 1 and 2 show the structures of **7c** and **8** respectively, important bond lengths and angles are given in Table 1. As shown, **7c** contains one silver atom coordinated by two carbene moieties and the second silver atom coordinated by two bromides and one pyridine group. The geometry around Ag(1) is linear and around Ag(2) is trigonal planar. The twist



Scheme 1 Reagents and conditions: (i) 2-$BrCH_2$py, EtOH; (ii) 2-Brpy, 150 °C; (iii) α,α′-dibromoxylene, 1,4-dioxane; (iv) $BrCH_2NEt_2$, 1,4-dioxane; (v) 2-($BrCH_2$)-4,6-$Bu^t_2C_6H_2NO_2$ followed by $N_2H_4{\cdot}H_2O$/Pd/C; (vi) PhCHO, HCO_2H.



Scheme 2 The synthesis of silver complexes. See Experimental section for details. Compounds in bold have been structurally characterised.

angle between the two planes, defined by the carbene rings, is 33.5°. The dihedral angle formed between the plane of the picolyl and carbene rings is 89°. The molecule adopts a conformation which keeps the picolyl rings away from each other. There is no evidence of Ag · · · Ag interaction. The Ag–C bond length is 206.9 pm, similar to those observed by Wang and Lin[6] and Arduengo *et al.*[7] In contrast, the solid state structure of **8** comprises a silver atom coordinated by a carbene carbon and a bromide in a linear geometry. There are no close contacts to the pyridyl nitrogen. The Ag–C bond lengths in both structures are similar. Why **7c** and **8** adopt different structures is not clear. The ligand with the carbene moiety directly linked to the pyridine (as in **8**) is more rigid than the one with a methylene linker between the two rings (**7c**). Although the introduction of a second ligand to **8** would have increased unfavourable steric interligand interactions, these do not seem to inhibit the formation of $[Ag(ligand)_2][AgBr_2]$. In depth NMR studies involving **7c** and **8** show many interesting features. The

Table 1 Selected bond lengths (pm) and angles (°) for structurally characterised compounds

	7b	7c	8	9b	10	11b
Ag–C(1)/Ag–C(2)	207(2)	206.9(5)/207.4(5)	207.5(7)	209.9(3)	209.8(2)	206.1(7)/209.2(8)
Ag–X(1)/Ag–X(2)	237.3(4)/295.2(4)	249.1(1)/250.9(1)	242.1(1)	241.0(1)/290.7(1)	237.1(1)	234.2(2)/238.9(2)
C(1)–Ag(1)–X(1)/C(2)–Ag–Ag(2)	162.5(5)/94.6(5)	—	176.1(2)	157.3(1)/110.3(1)	162.92(7)	177.4(2)/163.3(2)
C(1)–Ag–C(2)	—	175.9(2)	—	—	—	—
Ag–N(1)	—	246.7(4)	—	—	—	—
Ag···Ag	336.7(5)	—	—	—	—	—
X–Ag–X	102.4(2)	154.5(1)	—	90.14(3)	—	—
N–Ag–X	—	108.8(1)/95.8(1)	—	—	—	—
Twist of R against imidazole ring	—	88.8(2)/89.5(2)	84.8(3)	80.8(1)	—	—
Twist of imidazole against imidazole	—	33.5(1)	—	—	—	—
Angle imidazole–pyridine	—	77.8(2)/86.5(2)	31.5(3)	—	—	—

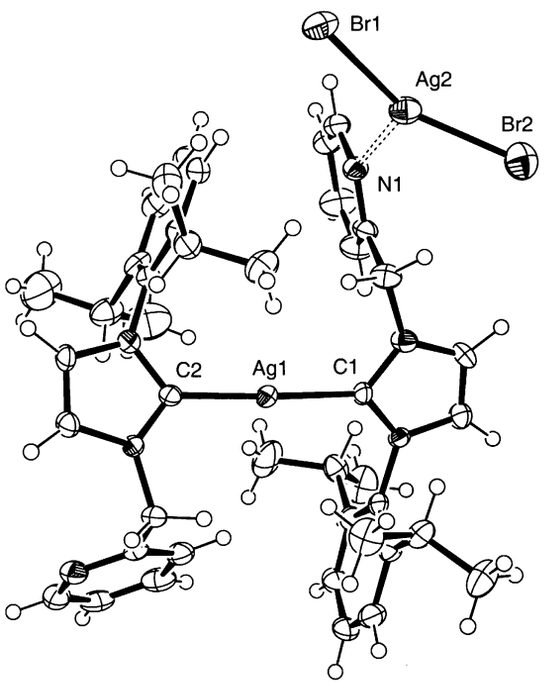


Fig. 1 An ORTEP[9] diagram of the crystal structure of silver carbene complex **7c** (50% probability thermal ellipsoids, as in all cases shown).

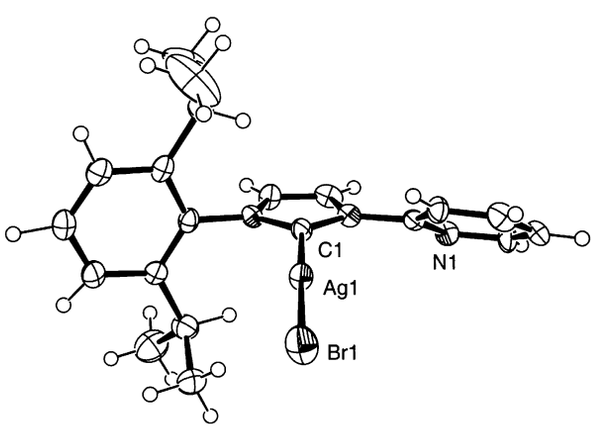


Fig. 2 An ORTEP diagram of the crystal structure of silver carbene complex **8**.

appearance of the spectra is dependent on the concentration of the sample, probably due to intermolecular interactions in solution. Dilute samples display sharp spectra, as given in the Experimental section, whereas concentrated samples display broad spectra. Furthermore, the spectra are temperature dependent. Pure (by NMR) **7c** and **8** are obtained when the preparations are carried out at lower temperatures (40 °C). However, in refluxing 1,2-dichloroethane by-products were

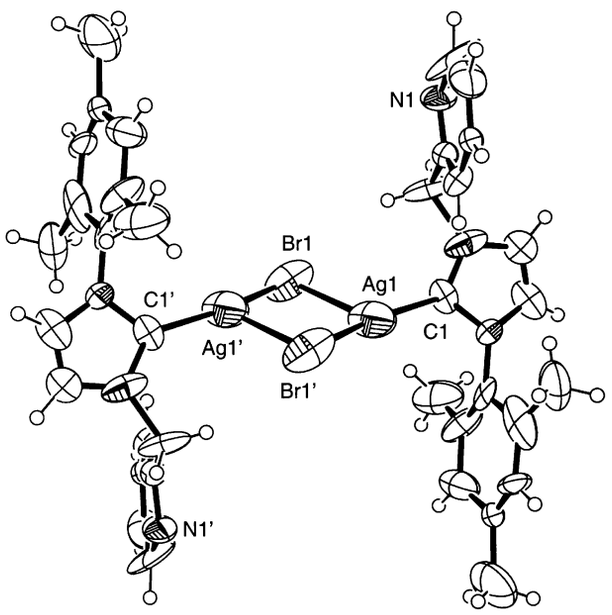


Fig. 3 An ORTEP diagram of the crystal structure of the dimeric silver carbene complex **7b**; see text for details.

formed (as shown by NMR spectroscopy) which we were unable to isolate. The ^{1}H NMR spectra of these mixtures show two sets of peaks, which are assignable to two different silver carbene complexes; their ^{1}H NMR spectra have the same symmetry but are slightly shifted. The major component is identical to that obtained from the low temperature preparations (see Experimental section). The presence of these two species persists within the range −80 to +50 (for **7c**) and −80 to −10 °C (for **8**), showing no indication of interconversion. Furthermore, analytical data for both impure (by NMR) and pure **7c** and **8** support the presence of compounds with the same stoichiometry. Crystals of **7c** and **8** suitable for X-ray diffraction were grown from solutions containing only one species. The crystal structures show that the isolated **7c** is [Ag(ligand)$_2$][AgBr$_2$] and **8** is Ag(ligand)Br. Therefore, we think that plausible formulations for the observed by-products are the isostoichiometric Ag(ligand)Br (in the case of **7c**) and [Ag(ligand)$_2$][AgBr$_2$] (in the case of **8**).

It is interesting that the structure of compound **7b** has also been determined.† Although twinned crystals were reproducibly obtained, and therefore did not allow refinement of the data to a level acceptable for publication, the connectivity can be deduced unequivocally; (Fig. 3). Here the molecule comprises two silver atoms bridged by bromides while the ligand acts as

† Crystal data: $C_{18}H_{19}Ag_1Br_1N_3$, $M = 465.14$, monoclinic, space group $P2/n$, $a = 977.52$, $b = 1686.7$, $c = 1090.9$ pm, $\beta = 95.11°$, $V = 1.7915(5)$ nm^3, $Z = 4$, $T = 150$ K, $\mu = 3.358$ mm^{-1}, no. of data collected = 3686, No. unique data = 1916, $R1$ with $F_o^2 > 2\sigma(F_o)^2 = 0.206$.

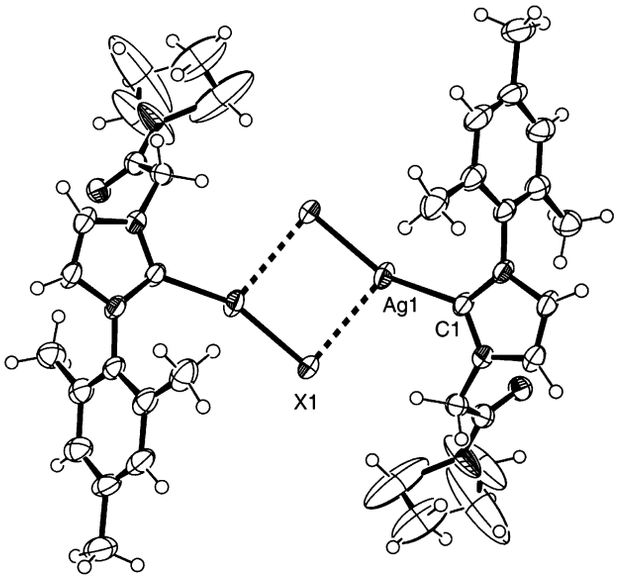


Fig. 4 An ORTEP diagram of the crystal structure of silver carbene complex **9b**.

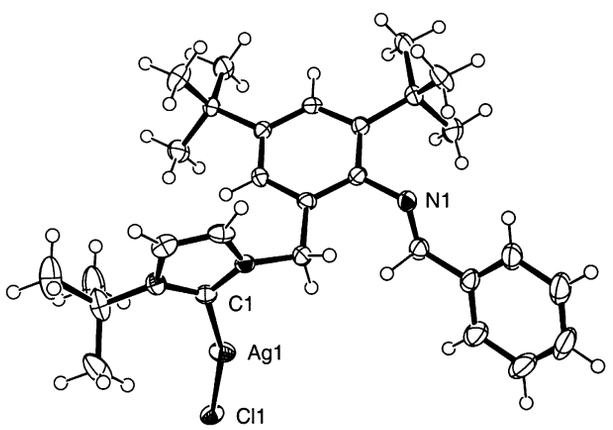


Fig. 5 An ORTEP diagram of the crystal structure of silver carbene complex **10**.

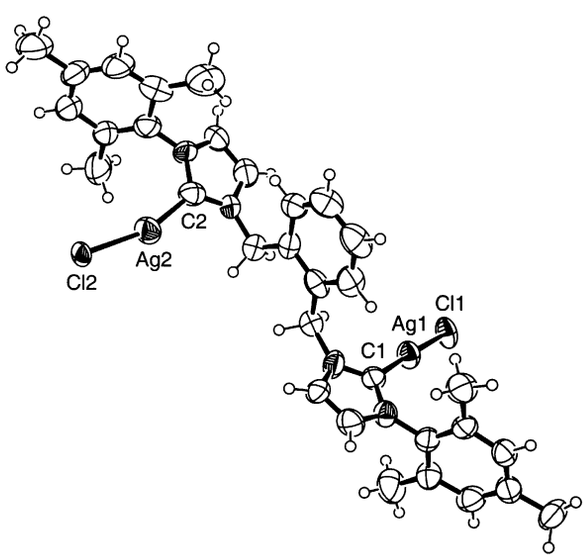


Fig. 6 An ORTEP diagram of the crystal structure of silver carbene complex **11b**.

monodentate from the carbene end (see also the structure of **9b**). The geometry of the chelate ring is rhombic and the Ag···Ag distance 334 pm, indicating a weak metal–metal interaction. The C–Ag–Br vector is almost linear.

Interaction of compounds **3a**, **3b** or **5** with Ag_2O gave the corresponding silver carbene complexes. The ^{1}H NMR spectra of **9a**, **9b** and **10** in chlorinated solvents show the presence of only one species. The structures of **9b** and **10** are shown in Figs. 4 and 5; important bond lengths and angles are given in Table 1. In both, the coordination sphere of silver comprises one carbene moiety and one halide. There is no intra- or intermolecular interaction of the amide or imine functionalities with silver atoms. The bond lengths and angles are in the normal range for this type of compound. The partial occupation of the halide positions by chloride has no effect on the geometrical parameters of the metal centre while it improves the R_1 of the structures. Support for the incorporation of chloride is given from analytical data (see Experimental section). The chlorine atoms possibly originate from the chlorinated solvents used. Hydrochloric acid washed glassware, used during the work up, is a less likely alternative.

Finally, interaction of the bis-imidazolium salts **6a**–**6c** with an excess of Ag_2O leads to isolation of the disilver dicarbene complexes **11a–11c**. The structure of **11b** was determined by X-ray diffraction study and is shown in Fig. 6; important bond lengths and angles are given in Table 1. In **11c** both silver atoms adopt a linear geometry, with one carbene moiety and one halide per silver. In the conformation observed the silver atoms are '*anti*'. All other geometrical parameters are comparable to those of the compounds described above.

Experimental

Elemental analyses were carried out by the University College London Microanalytical Laboratory. NMR data were recorded on Bruker AMX-300 and AM 360 spectrometers, operating at 300 and 360 MHz (^{1}H), respectively. The spectra were referenced internally using the signal from the residual protio-solvent (^{1}H) or the signals of the solvent (^{13}C). Mass spectra (electrospray ionisation) were obtained from acetonitrile solutions on a VG Biotec platform. The calculated isotopic envelopes agree well with the experimentally observed pattern. Commercial chemicals were from Acros, Aldrich and Avocado; the light petroleum had bp 40–60 °C. The following starting materials were prepared following literature methods: 1-*tert*-butylimidazole,[10] 1-mesitylimidazole and 1-(2,6-diisopropylphenyl)imidazole,[11] 2-bromomethylpyridine hydrobromide,[12] 2,6-bis(bromomethyl)pyridine hydrobromide,[13] 2-bromo-*N*,*N*-diethylacetamide,[14] 2-bromomethyl-4,6-di(*tert*-butyl)nitrobenzene.[15]

Preparations

3-*tert*-butyl-1-(2-pyridylmethyl)imidazolium bromide hydrate 1a. 2-(Bromomethyl)pyridine hydrobromide (4 g, 1.6 mmol) was neutralised using a saturated aqueous solution of sodium carbonate. The liberated 2-bromomethylpyridine was extracted into diethyl ether (3 × 50 cm^3) at 0 °C, dried with magnesium sulfate and filtered. The filtrate was concentrated to *ca.* 100 cm^3. 1-*tert*-Butylimidazole (1.95 g, 1.6 mmol) in methanol (100 cm^3) at 0 °C was added, the ether removed under reduced pressure and the solution stirred at room temperature overnight. Evaporation of the volatiles under reduced pressure left compound **1a** as a white solid. Yield: 3.80 g, 80%. mp 65 °C. MS (ES): *m*/*z* 216 (M^+). δ_H(DMSO-d_6) 1.6 (9H, s, $(CH_3)_3C$), 5.6 (2H, s, CH_2), 7.5 (1H, m, 5-CH of py), 7.6 (1H, d, 3-CH of py), 7.9 and 8.1 (2 × 1H, s, 4,5-imidazolium CH), 8.0 (1H, t, 4-CH of py), 8.6 (1H, d, 6-CH of py) and 9.6 (1H, s, 2-imidazolium CH) (Found: C, 49.68; H, 6.43; N, 13.88. $C_{13}H_{20}BrN_3O$ requires C, 49.69; H, 6.42; N, 13.37%).

3-Mesityl-1-(2-pyridylmethyl)imidazolium bromide hydrate 1b. This was obtained following a procedure similar to that described for compound **1a**, using 2-bromomethylpyridine

hydrobromide (3 g, 1.2 mmol) and 1-mesitylimidazole (2.2 g, 1.2 mmol). Yield: 2.9 g, 70%. mp 210 °C (decomp). MS (ES): *m*/*z* 278 (M^+). $\delta_H(CDCl_3)$ 2.0 (6H, s, *o*-mesityl CH_3), 2.3 (3H, s, *p*-mesityl CH_3), 6.1 (2H, s, CH_2), 6.9 (2H, s, mesityl CH), 7.0 and 8.0 (2 × 1H, s, 4,5-imidazolium CH), 7.2 (1H, m, 5-CH of py), 7.7 (1H, t, 4-CH of py), 7.9 (1H, d, 3-CH of py), 8.5 (1H, m, 6-CH of py) and 10.4 (1H, s, 2-imidazolium CH) (Found: C, 56.42; H, 5.42; N, 11.03. $C_{18}H_{22}BrN_3O$ requires C, 57.45; H, 5.89; N, 11.17%).

3-(2,6-Diisopropylphenyl)-1-(2-pyridylmethyl)imidazolium bromide hydrate 1c. This was obtained following a similar procedure using 2-bromomethylpyridine hydrobromide (3 g, 1.2 mmol) and 1-(2,6-diisopropylphenyl)imidazole (2.75 g, 1.2 mmol). Yield: 3.4 g, 70%. mp 220 °C (decomp). MS (ES): *m*/*z* 320 (M^+). $\delta_H(CDCl_3)$ 1.1 and 1.2 (2 × 6H, d, $CH(CH_3)_2$), 2.3 [2H, septet, $CH(CH_3)_2$], 6.2 (2H, s, CH_2), 7.1 and 8.3 (2 × 1H, s, 4,5-imidazolium CH), 7.3 (2H, d, 3,5-$Pr^i_2C_6H_2$H), 7.3 (1H, m, 5-CH of py), 7.5 (1H, t, 4-$Pr^i_2C_6H_2H$), 7.8 (1H, t, 4-CH of py), 8.0 (1H, d, 3-CH of py), 8.5 (1H, d, 6-CH of py) and 10.1 (1H, s, 2-imidazolium CH).

3-(2,6-Diisopropylphenyl)-1-(2-pyridyl)imidazolium bromide 2. A 100 cm^3 Schlenk flask equipped with a small stirrer bar, charged with 2-bromopyridine (2.2 g, 7.8 mmol) and 1-(2,6-diisopropylphenyl)imidazole (2.23 g, 9.75 mmol), was evacuated and then heated in an oil bath at 150 °C for 3–4 days. During the heating period the imidazole which sublimed onto the colder parts of the apparatus was melted back into the reaction mixture. After cooling to room temperature the brown residue was washed three times with ether and the insoluble solid product isolated by filtration and dried *in vacuo* at room temperature. Yield: 2.26 g, 95%. mp >220 °C. MS (ES): *m*/*z* 306 (M^+). $\delta_H(CDCl_3)$ 1.2 and 1.3 [2 × 6H, d, $CH(CH_3)_2$], 2.4 [2H, septet, $CH(CH_3)_2$], 7.3 (2H, d, $Pr^i_2C_6H_2$H), 7.5 (1H, t, $Pr^i_2C_6H_2H$), 7.5, 8.1, 8.5 and 9.1 (4 × 1H, pyridyl H), 7.4 and 9.3 (2 × 1H, d, 4,5-imidazolium H) and 10.9 (1H, s, 2-imidazolium H).

1-*tert*-Butyl-3-(*N*,*N*-diethylcarbamoylmethyl)imidazolium bromide 3a. 2-Bromo-*N*,*N*-diethylacetamide (2 g, 10 mmol) and 1-*tert*-butylimidazole (1.9 g, 15 mmol) were dissolved in 1,4-dioxane (50 cm^3) and the solution was heated at 100 °C overnight. After cooling to room temperature a colourless oil separated. The supernatant was decanted and the oil triturated with ether until it solidified. The white solid product was separated by filtration and dried *in vacuo*. Yield: 2.4 g, 75%. mp 118 °C. MS (ES): *m*/*z* 238 (M^+). $\delta_H(CDCl_3)$ 1.1 and 1.3 (2 × 3H, t, diastereotopic CH_2CH_3), 1.7 [9H, s, $C(CH_3)_3$], 3.2 and 3.5 (2 × 2H, q, diastereotopic CH_2CH_3), 5.7 (2H, s, CH_2), 7.3 and 7.6 (2 × 1H, s, 4,5-imidazolium H) and 10.3 (1H, s, 2-imidazolium H).

3-(*N*,*N*-Diethylcarbamoylmethyl)-1-mesitylimidazolium bromide 3b. This was obtained following a procedure similar to the one described for compound **3a** using 2-bromo-*N*,*N*-diethylacetamide (2 g, 10 mmol) and 1-mesitylimidazole (2.3 g, 12.5 mmol). After cooling to room temperature the white solid product was isolated by filtration, washed with ether and dried *in vacuo*. Yield: 3.0 g, 80%. mp 175 °C. MS (ES): *m*/*z* 300 (M^+). $\delta_H(CDCl_3)$ 1.1 and 1.3 (2 × 3H, t, diastereotopic CH_2CH_3), 2.1 (6H, s, *o*-mesityl CH_3), 2.3 (3H, s, *p*-mesityl CH_3), 3.4 and 3.6 (2 × 2H, q, diastereotopic CH_2CH_3), 6.0 (2H, s, CH_2), 6.9 [2H, s, *m*-mesityl H], 7.2 and 7.9 (2 × 1H, s, 4,5-imidazolium H) and 10.3 (1H, s, 2-imidazolium H).

1-(2-Amino-3,5-di-*tert*-butylbenzyl)-3-*tert*-butylimidazolium bromide 4. A solution of 2-bromomethyl-4,6-di-*tert*-butylnitrobenzene (2 g, 6.1 mmol) and 1-*tert*-butylimidazole (1.15 g, 9.1 mmol) in 1,4-dioxane (50 cm^3) was heated at 70 °C for 3 hours. After cooling to room temperature the volatiles were evaporated under reduced pressure and the residue was triturated with ether until it solidified. The yield of the white solid nitro compound was quantitative. MS (ES): *m*/*z* 372 (M^+). mp 184 °C. $\delta_H(CDCl_3)$ 1.3 and 1.4 {2 × 9H, s, $C_6H_2[C(CH_3)_3]_2$}, 1.7 [9H, s, $NC(CH_3)_3$], 5.6 (1H, s, CH_2), 7.3 and 7.6 (2 × 1H, s, 4,5-imidazolium H), 7.5 and 8.2 {2 × 1H, s, $C_6H_2[C(CH_3)_3]_2$} and 10.9 (1H, s, 2-imidazolium H). This compound (1 g, 2.2 mmol) was dissolved in degassed absolute ethanol (100 cm^3), and Pd/C (0.3 g, 10% PdC) and hydrazine hydrate (10 cm^3) were then added. The mixture was refluxed under nitrogen for 12 hours and, after cooling to room temperature, filtered. The volatile components were evaporated under reduced pressure, and the oily residue was washed with ether (3 × 30 cm^3) and dissolved in chloroform. The chloroform solution was dried with $MgSO_4$ and the product crystallised by addition of ether and then cooling to −20 °C. Yield: 0.60 g, 65%. mp 184 °C. MS (ES): *m*/*z* 342 (M^+). $\delta_H(CDCl_3)$ 1.3 and 1.4 {2 × 9H, s, $C_6H_2[C(CH_3)_3]_2$}, 1.7 [9H, s, $NC(CH_3)_3$], 4.2 (2H, br s, NH_2), 5.8 (2H, s, CH_2), 7.3 and 7.6 (2 × 1H, s, 4,5-imidazolium H), 7.5 and 8.2 {2 × 1H, s, $C_6H_2[C(CH_3)_3]_2$} and 10.7 (1H, s, 2-imidazolium H).

1-(2-Benzylideneamino-3,5-di-*tert*-butylbenzyl)-3-*tert*-butylimidazolium bromide 5. A solution of compound **4** (1.5 g, 4.4 mmol), benzaldehyde (2.2 g, 20 mmol) and HCO_2H (0.5 cm^3) in absolute ethanol was refluxed until the consumption of **4** was complete according to ^{1}H NMR. Removal of the volatiles under reduced pressure and trituration of the residue with ether gave crude **5** as an off-white powder. This was dissolved in chloroform, dried with $MgSO_4$ and then concentrated. Addition of ether followed by cooling to −20 °C gave analytically pure **5** as white crystals. Yield: 1.1 g, 60%. mp > 220 °C. MS (ES): *m*/*z* 430 (M^+). $\delta_H(CDCl_3)$ 1.3 {18H, s, $C_6H_2[C(CH_3)_3]_2$}, 1.6 [9H, s, $NC(CH_3)_3$], 5.7 (2H, s, CH_2), 7.3 and 7.6 (2 × 1H, s, 4, 5-imidazolium H), 7.3–7.4 and 7.8–7.9 (5H, m, C_6H_5CH=N), 7.5 and 8.2 {2 × 1H, s, $[(CH_3)_3C]_2C_6H_2$}, 8.4 (1H, s, C_6H_5CH=N) and 10.4 (1H, s, 2-imidazolium H).

3,3′-Di-*tert*-butyl-1,1′-*o*-phenylenedimethylenebis(imidazolium) dibromide 6a. A solution of 2,2′-dibromo-*o*-xylene (1.0 g, 3.8 mmol) and 1-*tert*-butylimidazole (2.00 g, 8.3 mmol) in 1,4-dioxane (100 cm^3) was heated at 100 °C overnight. After cooling to room temperature compound **6a** precipitated as a white powder which was collected by filtration. Additional product was isolated from the supernatant by removal of the volatiles under reduced pressure and trituration of the resultant oil with ether. Yield: 1.92 g, 92%. mp 247 °C (decomp). MS (ES): *m*/*z* 176.3 ($\frac{1}{2}$ M^{2+}). $\delta_H(D_2O)$ 1.5 [18H, s, $C(CH_3)_3$], 5.5 (4H, s, CH_2), 7.2 and 7.6 (2 × 2H, s, 4,5-imidazolium H), 7.3 and 7.5 (2 × 2H, m, xylyl) and 8.8 (2H, s, 2-imidazolium H). $\delta_C(D_2O)$ 31.5 [$C(CH_3)_3$], 52.8 (CH_2), 63.0 [$C(CH_3)_3$], 123.2, 124.9, 133.3, 133.6, 134.3 and 136.4 (xylene and imidazolium C) (Found: C, 50.85; H, 5.99; N, 10.48. $C_{22}H_{34}Br_2N_4O$ requires C, 49.82; H, 6.46; N, 10.56%).

3,3′-Dimesityl-1,1′-*o*-phenylenedimethylenebis(imidazolium) dibromide 6b. This was obtained by following the same procedure as for compound **6a** using 2,2′-dibromo-*o*-xylene (1.0 g, 3.8 mmol) and 1-mesitylimidazole (1.55 g, 8.3 mmol). Yield: 2.2 g, 92%. mp 254 °C (decomp.). MS (ES): *m*/*z* 238.4 ($\frac{1}{2}$ M^{2+}). $\delta_H(D_2O)$ 2.0 (12H, s, *o*-mesityl CH_3), 2.2 (6H, s, *p*-mesityl CH_3), 6.3 (4H, s, CH_2), 6.9 (4H, s, *m*-mesityl H), 7.2 and 8.3 (2 × 2H, s, 4,5-imidazolium H), 7.2 and 7.3 (2 × 2H, m, xylyl) and 10.1 (2H, s, 2-imidazolium H). $\delta_C(CDCl_3)$ 18.2 and 21.5 (mesityl CH_3), 50.5 (CH_2), 123.8, 124.9, 129.7, 130.2, 130.4, 131.1, 133.1, 134.7, 138.0 and 141.6 (xylene, mesityl and imidazolium C) (Found: C, 58.16; H, 5.86; N, 7.36. $C_{32}H_{38}Br_2N_4O$ requires C, 58.73; H, 5.85; N, 8.56%).

3,3′-Bis[(2,6-diisopropylphenyl)-1,1′-*o*-phenylenedimethylene-bis(imidazolium) dibromide 6c. This was obtained by following the same procedure as for compound **6a** using 2,2′-dibromo-*o*-xylene (1.0 g, 3.8 mmol) and 1-(2,6-diisopropylphenyl)imidazole (1.90 g, 8.3 mmol). Yield: 2.13 g 78%. MS (ES): *m*/*z* 280.5 ($\frac{1}{2}$ M^{2+}). $\delta_H(CDCl_3)$ 1.1 and 1.2 [2 × 12H, d, diastereotopic $CH(CH_3)_2$], 2.2 [4H, septet, $CH(CH_3)_2$], 6.1 (4H, s, CH_2), 7.1 and 8.7 (2 × 2H, s, 4,5-imidazolium H), 7.2 (2H, m, xylyl), 7.2 (4H, d, *m*-$Pr^i_2C_6H_2H$), 7.5 (2H, t, *p*-$Pr^i_2C_6H_2H$), 7.8 (2H, d, xylyl) and 10.7 (2H, s, 2-imidazolium H). $\delta_C(CDCl_3)$ 24.2 and 24.6 [$CH(CH_3)_2$)], 28.8 [$CH(CH_3)_2$], 53. 7 (CH_2), 124.25, 124.39, 124.82, 130.38, 132.04, 138.61, 139.19, 145.36 and 153.54 (xylene, phenyl and 4,5-imidazolium C); 2-imidazolium-*C*H not observed (Found: C, 59.52; H, 6.46; N, 7.60. $C_{19}H_{26}BrN_2O$ requires C, 60.32; H, 6.93; N, 7.40%).

Silver complexes. In method A a substituted imidazolium salt was refluxed with an excess of Ag_2O in dichloromethane or 1,2-dichloroethane for 3–48 hours. In some cases, addition of activated 4 Å molecular sieves to the reaction mixture improved the yield and purity of the product. After completion, the reaction mixture was filtered, dried over $MgSO_4$ (if sieves had not been used), the volatiles were removed under reduced pressure and the solid product was washed with ether and dried *in vacuo*. In most cases the products obtained at this stage were spectroscopically and analytically pure. If not, purification is possible by recrystallisation. In Method B a substituted imidazolium salt was refluxed with an excess of Ag_2CO_3 in dichlomethane or 1,2-dichloroethane for 3–48 hours. Isolation and purification of the product was accomplished as described in method A.

[1-tert-butyl-3-(2-pyridylmethyl)imidazol-2-ylidene]silver bromide ***7a***. Prepared by method A using compound **1a** (0.24 g, 0.77 mmol) and Ag_2O (0.16 g, 0.58 mmol) in dichloromethane (30 cm^3) and heating to 40 °C for two days. The solid obtained was dissolved in toluene, the solution filtered and the solvent removed under reduced pressure. The resulting yellow powder was washed with ether and dried *in vacuo*. Yield: 0.28 g, 90%. $\delta_H(CDCl_3)$ 1.6 (9H, s, $C(CH_3)_3$), 5.4 (2H, s, CH_2), 7.1 and 7.2 (2 × 1H, d, 4,5-imidazol-2-ylidene H), 7.2 (2H, d, 3,5-H of py), 7.6 (1H, dt, 4-pyridyl H of py), 8.5 (1H, dd, 6-H of py). $\delta_C(CDCl_3)$ 31.6 [$C(CH_3)_3$], 53.6 [$C(CH_3)_3$)], 57.9 (CH_2), 119.1, 120.2, 122.2 and 123.2 (pyridyl and 4,5-imidazol-2-ylidene C), 137.1, 149.6 and 154.9 (pyridyl C) and 178.6 (2-imidazol-2-ylidene C).

[1-Mesityl-3-(2-pyridylmethyl)imidazol-2-ylidene]silver bromide ***7b***. Prepared by method B, using compound **1b** (0.4 g, 1.07 mmol) and Ag_2CO_3 (0.17 g, 0.64 mmol) in dichloromethane (30 cm^3) and heating to 40 °C for two days. Work up as described for **7a** gave a pale yellow solid. Yield: quantitative. X-Ray diffraction quality crystals were obtained by cooling a saturated solution of dichloromethane-light petroleum (bp 40–60 °C) (1 : 1) to 4 °C. MS (ES): *m*/*z* 427, [Ag(ligand)-MeCN]$^+$; 663, [Ag(ligand)$_2$]$^+$. $\delta_H(CDCl_3)$ 1.9 (6H, s, *o*-mesityl CH_3), 2.3 (3H, s, *p*-mesityl CH_3), 5.4 (2H, m, CH_2), 6.9 (2H, s, *m*-mesityl H), 7.2 and 7.3 (2 × 1H, d, 4,5-imidazol-2-ylidene H), 7.2 (2H, m, 3,5-H of py), 7.7 (1H, dt, 4-H of py), and 8.6 (1H, d, 6-H of py). $\delta_C(CDCl_3)$ 17.8 (*o*-mesityl CH_3), 21.2 (*p*-mesityl CH_3), 57.4 (CH_2), 121.9, 122.5, 123.1, 123.7, 129.6, 134.8, 137.7, 140.1 and 150.1 (mesityl, pyridyl and 4,5-imidazol-2-ylidene C) and 173.9 (2-imidazol-2-ylidene C) (Found: C, 47.70; H, 4.22; N, 8.94. $C_{18}H_{19}AgBrN_3$ requires C, 46.48; H, 4.12; N, 9.03%).

1-(2,6-Diisopropylphenyl)-3-(2-pyridylmethyl)imidazol-2-ylidene]silver bromide ***7c***. Prepared by method B using compound **1c** (2.0 g, 5.17 mmol) and Ag_2CO_3 (1.06 g, 3.88 mmol) in dichloromethane (50 cm^3) and heating to 40 °C for two days, quantitative yield of a white solid. X-Ray diffraction quality crystals were obtained by cooling a saturated solution of THF–ether (1 : 1) to 4 °C. MS (ES): *m*/*z* 469, [Ag(ligand)-MeCN]$^+$; 748, [Ag(ligand)$_2$]$^+$. $\delta_H(CDCl_3)$ 1.1 and 1.2 [2 × 6H, d, $CH(CH_3)_2$], 2.4 [2H, septet, $CH(CH_3)_2$], 5.5 (2H, s, CH_2), 7.0 and 7.3 (2 × 1H, d, 4,5-imidazol-2-ylidene H), 7.2–7.4 (4H, m, 3,5-H of py, H of *m*-$Pr^i_2C_6H_3$), 7.5 (1H, t, H of *p*-$Pr^i_2C_6H_3$), 7.8 (1H, dt, 4-H of py) and 8.6 (1H, d, 6-H of py). $\delta_C(CDCl_3)$ 24.2 and 24.6 ($CH(CH_3)_2$), 28.3 ($CH(CH_3)_2$), 56.9 (CH_2), 122.1, 122.2, 123.3, 124.1, 124.2, 130.3, 134.6, 137.3, 145.6, 149.7 and 154.9 ($Pr^i_2C_6H_3$, pyridyl, 4,5-imidazol-2-ylidene C). The carbene carbon was not observed.

1-(2,6-Diisopropylphenyl)-3-(2-pyridyl)imidazol-2-ylidene]-silver bromide ***8***. Prepared by method B using compound **2** (2.0 g, 4.78 mmol) and Ag_2CO_3 (0.99 g, 3.58 mmol) in dichloromethane (50 cm^3), heating at 40 °C for two days. Yield quantitative. X-Ray diffraction quality crystals were grown by layering a dichloromethane solution with ether. MS (ES): *m*/*z* 455, [Ag(ligand)MeCN]$^+$; 719, [Ag(ligand)$_2$]$^+$. $\delta_H(CDCl_3)$ 1.0 and 1.3 [2 × 6H, d, $CH(CH_3)$], 2.5 (2H, septet, $CH(CH_3)_2$), 6.3 and 7.8 (2 × 1H, d, 4,5-imidazol-2-ylidene H), 7.0–7.2 (5H, m, *m*, *p*-H of $Pr^i_2C_6H_3$, 3,5-H of py), 8.1 (1H, d, 6-H of py), 8.5 (1H, dt, 4-H of py). $\delta_C(CDCl_3)$ 24.4 [$CH(CH_3)$], 28.2 [$CH(CH_3)$], 115.6, 119.9, 123.9, 124.3, 130.6, 134.9, 139.6, 145.5, 148.9 and 150.4 ($Pr^i_2C_6H_3$, pyridyl, 4,5-imidazol-2-ylidene C). The carbene carbon was not observed (Found: C, 49.35; H, 4.78; N, 8.52. $C_{20}H_{23}AgBrN_3$ requires C, 48.71; H, 4.70; N, 8.52%).

[1-tert-Butyl-3-(N,N-diethylcarbamoylmethyl)imidazol-2-ylidene]silver bromide ***9a***. Prepared by method A using compound **3a** (1 g, 3.2 mmol) and Ag_2O (1.139 g, 4.9 mmol) in 1,2-dichloroethane at 105 °C for 12 hours in the presence of molecular sieves. After filtration the solvent was removed *in vacuo*. The resulting solid was washed with ether, yielding a hygroscopic solid. Yield 0.542 g, 49.6%. MS (ES): *m*/*z* 584, [Ag(ligand)$_2$]$^+$. $\delta_H(CDCl_3)$ 1.1 and 1.3 (2 × 3H, t, diastereotopic CH_2CH_3), 1.7 [9H, s, $C(CH_3)_3$], 3.35 and 3.45 (2 × 2H, q, diastereotopic CH_2CH_3), 5.6 (2H, s, CH_2), 7.08 and 7.12 (2 × 1H, s, 4,5-imidazol-2-ylidene H). $\delta_C(CDCl_3)$ 12.9, 13.0, 14.4 and 14.6 (CH_2CH_3) 30.0 and 31.9 [$C(CH_3)_3$], 41.0, 41.1, 41.9 and 42.0 (CH_2CH_3), 57.9 and 60.2 [$C(CH_3)_3$], 65.8 (CH_2) 118.3, 118.9, 121.6 and 124.5 (4,5-imidazol-2-ylidene C), 163.9 and 165.2 (C=O) and 179.0 (2-imidazol-2-ylidene C).

1-(N,N-Diethylcarbamoylmethyl)-3-mesitylimidazol-2-ylidene]silver chloride ***9b***. Prepared by method A using compound **3b** (2 g, 5.3 mmol) and Ag_2O (1.8 g, 7.9 mmol) in 1,2-dichloroethane at 90 °C for 4 hours in the presence of molecular sieves. Work up as for **9a**. Yield quantitative. X-Ray diffraction quality crystals were obtained by layering of a dichloromethane solution with ether. MS (ES): *m*/*z* 707, [Ag(ligand)$_2$]$^+$. $\delta_H(CDCl_3)$ 1.2 and 1.4 (2 × 3H, t, $N(CH_2CH_3)_2$], 2.1 (6H, s, *o*-mesityl CH_3), 2.4 (3H, s, *p*-mesityl CH_3), 3.5 [4H, q, $N(CH_2CH_3)_2$], 5.2 (2H, s, CH_2) and 6.9 (2H, s, *m*-mesityl H). $\delta_C(CDCl_3)$ 13.9 and 14.7 [$N(CH_2CH_3)_2$], 17.8 and 21.2 [*o,p*-mesityl CH_3], 41.0 and 41.8 [$N(CH_2CH_3)_2$], 52.8 (CH_2), 123.2, 129.5, 135.0 and 139.6 (mesityl, 4,5-imidazol-2-ylidene CH) and 167 (2-imidazol-2-ylidene C) (Found: C, 48.37; H, 5.59; N, 9.28, $C_{18}H_{25}AgBr_{0.08}Cl_{0.92}N_3O$ requires C, 48.44; H, 5.65; N, 9.42%).

1-(2-Benzylideneamino-3,5-di-tert-butylbenzyl)-3-tert-butylimidazol-2-ylidene] silver bromide ***10***. Prepared by method A using compound **5** (0.15 g, 0.3 mmol) and Ag_2O (0.04 g, 0.13 mmol) in dichloromethane (30 cm^3) by heating at 40 °C overnight. X-Ray diffraction quality crystals were grown by cooling a saturated solution of THF–ether (1 : 1) to 4 °C. Yield 90%. MS (ES): *m*/*z* 579, [Ag(ligand)MeCN]$^+$; 967, [Ag(ligand)$_2$]$^+$. $\delta_H(CDCl_3)$ 1.3 [9H, s, $CC(CH_3)_3$], 1.3 [9H, s, $CC(CH_3)_3$], 1.6 [9H, s, $NC(CH_3)_3$], 5.1 (2H, s, CH_2), 6.8 and 7.1 (2 × 1H, d, 4,5-imidazol-2-ylidene H), 7.0 and 7.4 (2 × 1H, d, 3,5-H of C_6H_2), 7.2 (1H, d, *p*-H of phenyl), 7.5 (2H, m, *o*-H of phenyl), 7.8 (2H, dd, *m*-H of phenyl) and 8.1 (1H, s, PhC*H*=N). $\delta_C(CDCl_3)$ 30.4, 31.3 and 31.5 [$C(CH_3)_3$], 34.4, 35.7 and 54.2

Table 2 Crystallographic data for complexes **7c**, **8**, **9b** **10** and **11b**

	7c	8	9b	10	11b
Chemical formula	$C_{42}H_{50}Ag_2Br_2N_6$	$C_{20}H_{23}AgBrN_3$	$C_{18}H_{25}AgBr_{0.08}Cl_{0.92}N_3O$	$C_{29}H_{39}AgClN_3$	$C_{32.5}H_{35}Ag_2Cl_3N_4$
Formula weight	1014.44	493.19	446.34	572.95	803.73
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1nb$	$P2_1/n$	$C2/c$	$P\bar{1}$	$P2_1/a$
a/pm	1277.37(1)	1088.37(4)	2653.98(2)	968.84(2)	1728.53(3)
b/pm	1655.30(1)	1641.54(6)	1044.89(1)	1147.09(2)	1270.79(3)
c/pm	2013.44(2)	1141.27(4)	1688.53(2)	1377.50(2)	1858.79(4)
α/°				71.937(1)	
β/°		103.155(2)	125.90(1)	85.779(1)	117.407(1)
γ/°				76.949(1)	
V/nm^3	4.25728(6)	1.9855(2)	3.79301(6)	1.41783(4)	3.6247(1)
Z	4	4	8	2	4
T/K	150	150	150	150	150
μ/mm^{-1}	2.833	3.035	1.373	0.826	1.327
No. data collected	37682	2801	21107	14216	35356
No. unique data	8211	2167	5526	7942	9486
R_{int}	0.0660	0.0331	0.0362	0.0375	0.0821
Final $R(\|F\|)$ for $F_o > 2\sigma(F_o)$	0.0386	0.0454	0.0542	0.0403	0.0734
Final $R(F^2)$ for all data	0.0504	0.0519	0.0678	0.0626	0.1598

[$C(CH_3)_3$], 57.4 (CH_2), 118.5, 119.5, 123.2, 124.1, 124.2, 128.1, 128.8, 129.0, 131.9, 135.5, 139.8, 146.3 and 149.1 (phenyl, benzyl, 4,5-imidazol-2-ylidene C) and 163.2 (2-imidazol-2-ylidene C) (Found: C, 58.31; H, 6.66; N, 6.78. $C_{29}H_{39}AgBr_{0.5}Cl_{0.5}N_3$ requires C, 58.52; H, 6.60; N, 7.06%).

[3,3′-Di-tert-butyl-1,1′-o-phenylenedimethylenebis(imidazol-2-ylidene)]dichlorodisilver ***11a***. Prepared by method A using compound **6a** (1.0 g, 1.6 mmol) and Ag_2O (0.555 g, 2.4 mmol) in 1,2-dichloroethane (30 cm^3) in the presence of molecular sieves. After refluxing overnight the reaction mixture was filtered, the filtrate pumped to dryness and the resulting solid washed with light petroleum giving the product as a pale brown solid. The solid was precipitated by layering a saturated solution of dichloromethane with ether, filtered and dried *in vacuo*. Yield: 0.892 g, 71%. mp 152 °C (decomp). MS (ES): *m*/*z* 458, [Ag(ligand)]$^+$. $\delta_H(CDCl_3)$ 1.6 [18H, s, $C(CH_3)_3$], 5.4 (4H, s, CH_2), 6.8 and 7.3 (2 × 2H, dd, xylene H), 7.0 and 7.2 (2 × 2H, d, 4,5-imidazol-2-ylidene H). $\delta_C(CDCl_3)$ 31.6 [$C(CH_3)_3$], 53.6 (CH_2), 57.7 [$C(CH_3)_3$], 119.5 and 120.1 (4,5-imidazol-2-ylidene C) 128.3, 128.8 and 133.9 (xylene C) and 179.6 (2-imidazol-2-ylidene C).

[3,3′-Dimesityl-1,1′-o-phenylenedimethylenebis(imidazol-2-ylidene)]disilver ***11b***. Prepared by method A using compound **6b** (1.0 g, 1.6 mmol) and Ag_2O (0.56 g, 2.4 mmol) in 1,2-dichloroethane (30 cm^3) in the presence of molecular sieves. Work up as for **11a**. X-Ray diffraction quality crystals were grown by layering a saturated solution of dichloromethane with ether. Yield 0.80 g, 66%. mp 158 °C. MS (ES): *m*/*z* 582, [Ag(ligand)]$^+$. $\delta_H(CDCl_3)$ 1.9 (12H, s, *o*-mesityl CH_3), 2.3 (6H, s, *p*-mesityl CH_3), 5.6 (4H, s, CH_2), 6.9 (4H, s, *m*-H of mesityl), 6.9 and 7.4 (2 × 2H, s, 4,5-imidazol-2-ylidene H) and 7.3 (4H, m, xylyl H). $\delta_C(CDCl_3)$ 17.6, 20.9 (*o*,*p*-mesityl CH_3), 52.4 (CH_2), 122.4 and 122.9 (4,5-imidazol-2-ylidene C), 127.4, 128.7 and 129.1 (xylyl C), 134.2, 134.4, 135.3 and 139.1 (mesityl C). Carbene carbon not observed. The isolated product contains half a molecule of dichloromethane per formula unit (Found: C, 48.23; H, 4.33; N, 6.55. $C_{32.5}H_{35}Ag_2Cl_3N_4$ requires C, 48.57; H, 4.39; N, 6.97%).

Dichloro[3,3′-bis(2,6-diisopropylphenyl)-1,1′-o-phenylenedimethylenebis(imidazol-2-ylidene)]disilver ***11c***. Prepared by method A using compound **6c** (1.0 g, 1.4 mmol) and Ag_2O (0.48 g, 2.1 mmol) in 1,2-dichloroethane (30 cm^3) in the presence of molecular sieves. Work up as for **11a**. Yield 0.92 g, 62%. mp 170 °C. MS (ES): *m*/*z* 667.6, [Ag(ligand)]$^+$. $\delta_H(CDCl_3)$ 1.1 and 1.2 [2 × 12H, s, $CH(CH_3)_2$], 2.3 [4H, septet, $CH(CH_3)_2$], 5.5 (4H, s, CH_2), 7.0 and 7.2 (2 × 2H, s, 4,5-imidazol-2-ylidene H), 7.2 and 7.7 (2 × 2H, m, xylyl), 7.4 (4H, m, *m*-H of $Pr^i_2C_6H_3$) and 7.5 (2H, m, *p*-H of $Pr^i_2C_6H_3$). $\delta_C(CDCl_3)$ 24.39 and 24.80 [$CH(CH_3)_2$], 28.43 [$CH(CH_3)_2$], 56.88 (CH_2), 121.72, 122.80, 123.91, 124.38, 130.69, 135.89, 138.88, 145.72 and 155.80 (phenyl, xylyl, 4,5-imidazol-2-ylidene C). Carbene carbon not observed. The isolated product contains half a molecule of dichloromethane per formula unit (Found: C, 52.00; H, 5.56; N, 7.58. $C_{38.5}H_{47}Ag_2Cl_3N_4$ requires C, 52.08 ; H, 5.34; N, 6.31%).

Crystal structure determinations of compounds 7b, 7c, 8, 9b, 10 and 11b

A summary of the crystal data, data collection and refinement for compounds **7c**, **8**, **9b**, **10** and **11b** is given in Table 2. All data sets were collected on a Enraf Nonius KappaCCD area detector diffractometer with rotating anode FR591 and an Oxford Cryosystems low-temperature device operating in omega scanning mode with phi scans to fill the Ewald sphere. The programs used for control and integration were COLLECT, SCALEPACK and DENZO.[16] The crystals were mounted on a glass fibre with silicon grease. Accurate lattice parameters were determined from least-squares refinement of all reflections $F^2 > 4\sigma(F^2)$. An empirical absorption correction was made by the SORTAV[17] method from symmetry-related measurements. The structures were solved by heavy-atom Patterson methods (SHELXS 97).[18] Refinement was carried out by full-matrix least squares techniques (SHELXL 97).[19] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included using a riding model.

The chemical identity of the halogen atoms in the three complexes **9b**, **10** and **11b** was investigated carefully considering all possible combinations between chlorine and bromine. Therefore, the molecular formulation presented in each case corresponds to the combination with low R values and low anisotropic thermal parameters for chlorine and/or bromine atoms. The molecular formulations found by X-ray diffraction for all complexes are consistent with the other experimental data.

Compound **7b** was also investigated by X-ray single crystal diffraction. Unfortunately, it repeatedly showed a very poor diffraction pattern. The pictures taken indicated at all times a partly amorphous or twinned system. However, it was possible to solve the structure without problems and all non-hydrogen atoms have been located unambiguously and their positions refined with anisotropic thermal parameters. In spite of this final quality it is not enough for publication; the dimensions associated with the metal co-ordination spheres are accurate enough to be included in Table 1.

The crystals of compound **11b** were of particularly poor quality. The structure contains 0.5 molecule of highly disordered solvent CH_2Cl_2 and was treated in the manner described by Sluis and Spec (228 e cell^{-1}).[20] The total potential solvent accessible volume was found to be 496.6×10^6 pm^3 cell^{-1}. Recrystallisation from other solvents was unsuccessful.

CCDC reference number 186/2257.

See http://www.rsc.org/suppdata/dt/b0/b007504n/ for crystallographic files in .cif format.

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