



Synthesis, molecular structures and solution NMR studies of *N*-heterocyclic carbene–amine silver complexes

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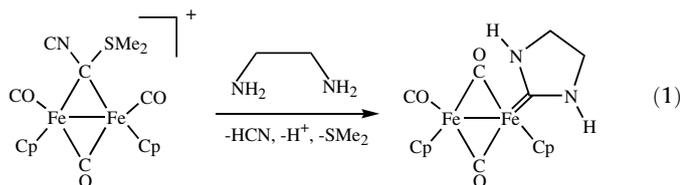
ABSTRACT

The synthesis of the Boc-protected 1-(2-aminoethyl)-3-methylimidazolium salts [BocNHCH₂CH₂ImMe]⁺X⁻ [**2**]⁺X⁻ (X = I, PF₆) and their straightforward transformation into [NH₂CH₂CH₂ImMe]⁺X⁻ [**3**]⁺X⁻ is reported. The reaction between [**2**]⁺X⁻ and Ag₂O leads to the formation in the solid state of three different bonding motifs: a biscarbene salt [(NHC–NHBoc)₂Ag]PF₆ (**4**)PF₆, NHC–NHBoc = 1-(2-BocNH-ethyl)-3-methyl-imidazolium-2-ylidene), a tetranuclear complex [Ag(NHC–NHBoc)₂]₂[Ag₂I₄] (**5**), and a polymeric silver “staircase” [(NHC–NHBoc)₂–Ag₄–I₄]_n (**6**) composed of Ag₄I₄ clusters. The same reaction carried out with [**3**]⁺X⁻ showed that a primary silver mono-NHC–NH₂ carbene complex of the type [(NHC–NH₂)Ag]⁺ (**7**) is likely to form but it is unstable in solution. The solid state molecular structures of [**4**]⁺PF₆⁻, **5** and **6** were determined by X-ray diffraction analysis, whereas PGSE NMR experiments were employed to investigate the hydrodynamic dimension of the imidazolium salts and silver complexes and, consequently, to gain information on the level of aggregation in solution. PGSE NMR studies were complemented by NOE NMR investigations in order to obtain information on anion–cation relative orientation within aggregates.

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1. Introduction

For several years within our group one research line has dealt with the study of carbene ligands in diiron complexes, including heteroatom substituted (Fischer type) alkylidenes, in both bridging and terminal coordination modes [1]. In the course of these studies, in 1995, we found that the reaction of diiron μ -alkylidene complexes such as [Fe₂{ μ -C(CN)SMe₂}(μ -CO)(CO)₂(Cp)₂][SO₃CF₃] with ethylenediamine results in the cleavage of the C–S and C–C bonds at the μ -alkylidene carbon yielding to [Fe₂{CN(H)(CH₂)₂N(H)}(μ -CO)(CO)₂(Cp)₂] (Eq. (1)) in which an *N*-heterocyclic carbene ligand is bound to an iron metal centre [2].



Recently our interest in this area has been renewed since complexes containing the *N*-heterocyclic carbene (NHCs) ligands have emerged

as one of the most important classes of compound used for a great number of transition metal mediated catalytic reactions [3].

The heterocyclic carbene moiety offers great possibilities for fine-tuning the ligand structure, and, thereby, the catalytic properties, through the introduction of appropriate substituents at the nitrogen atoms or at the 5-membered ring carbon atoms. The combination of ligand donor units with very different coordination properties in a di- or polydentate spectator ligand may permit a stereoelectronic control of the reactivity at the remaining coordination sites in a transition metal complex. Consequently, a strong motivation is leading to design polydentate NHC carbene ligands functionalized with a neutral or anionic donor group linked by an organic spacer [4]. Moreover, taking advantage of the ability of *N*-heterocyclic carbenes to form strong σ -bonds with the metal, it can serve as an anchoring point for the immobilization of the metal complexes onto solid supports [5].

Therefore several hybrid ligands based on NHC have been reported including those having an N-atom at the other terminus (NHC–N) in the form of a pyrazolyl [6], pyridine [7], oxazoline [8] sterically demanding imine [9] and amido/amine groups [10]. With regard to the NHC–amine case we were interested in expanding the library of this type of ligands focusing our attention on the NHC–NH₂ system that, as far as we know, has been firstly obtained by Douthwaite et al. by slow hydrolysis of NHC–imino complexes of palladium [9e].

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We herein report on the synthesis of the Boc-protected 1-(2-aminoethyl)-3-methylimidazolium salts [BocNHCH₂CH₂ImMe]X [2]X (X = I, PF₆), their straightforward transformation into [NH₂CH₂CH₂ImMe]X [3]X together with the syntheses and characterization of new silver NHC–amine complexes. The X-ray molecular structural studies of three silver carbene complexes show considerable differences depending on the coordinating or only weakly coordinating nature of the counterions [11]: when X = I, the tetranuclear complex of the type [Ag(NHC–NH₂Boc)₂][Ag₂I₄] (5, NHC–NH₂Boc = 1-(2-BocNH-ethyl)-3-methyl-imidazol-2-ylidene) is obtained but on standing in solution it gradually affords a polymeric silver “staircase” of the type [(NHC–NH₂Boc)₂–Ag₄–I₄]_n, (6) composed of Ag₄I₄ clusters. On the contrary when X = PF₆ the crystal structure consists of two independent and stable bis carbene [(NHC–NH₂Boc)₂Ag]PF₆ molecules [4]PF₆ in a 1:1 enantiomeric mixture. In order to gain a better understanding of the dynamic behaviour, level of aggregation and cation–anion relative orientation present in solution, the imidazolium salts [2]X and silver complexes were studied by PGSE (Pulsed Gradient Spin Echo) [12] and NOE [13] NMR techniques. Diffusion measurements for NHC-complexes are still scarce [14,15] and, as far as we know, the information herein reported represent the first data for NHC–Ag complexes. Finally the reactivity of [3]I toward Ag₂O is also presented and discussed.

2. Results and discussion

2.1. Ligand synthesis

Inspired by the recent work of Song et al. [16] in which a new functionalized ionic liquid, 1-(2-aminoethyl)-3-methylimidazolium hexafluorophosphate [NH₂CH₂CH₂ImMe][PF₆] was synthesized from 1-methylimidazole and 2-bromoethylamine hydrobromide, we decided to exploit this synthetic procedure to prepare the NHC–amine precursor. However, we found that the synthesis is thwarted by competitive oligomerization of the amine that invariably give a mixture of several products as depicted in Scheme 1. The major, ethanol soluble product, 3-methylimidazolium bromide (A), can be easily separated from the ethanol-insoluble B, C and D salts (see also Section 4).

In addition, considering what previously reported by Douthwaite et al. [10d], namely that the synthesis of the imidazolium salt NHC-precursors by reaction of *N*-alkyl imidazoles with halogenalkylamines requires protection of the amine functionality in or-

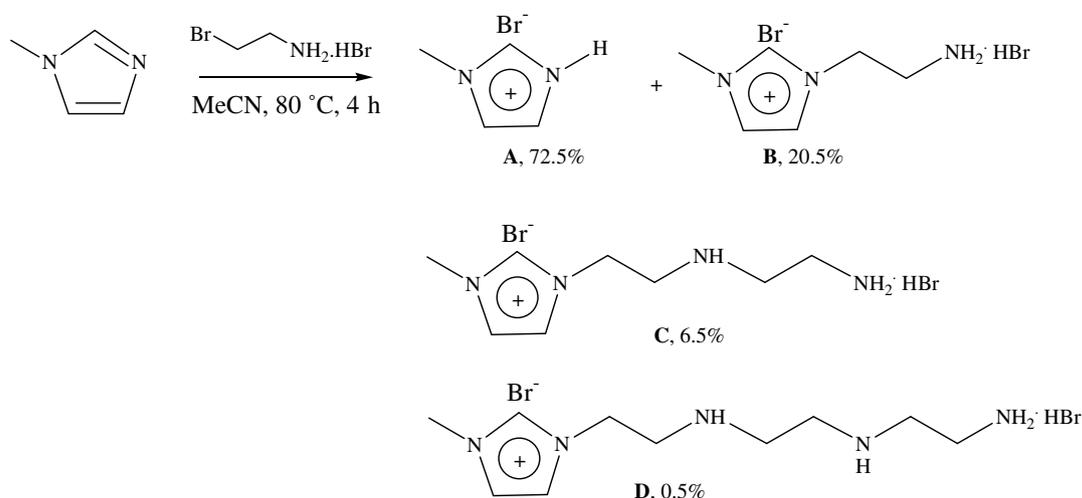
der to avoid competitive oligomerization side reactions, we tried to modify the synthetic protocol reacting 1-methylimidazole with the *N*-protected, *N*-Boc-bromoethylamine. However, in this case, we found that no reaction occurs at room temperature whilst by heating the reaction mixture the only result is the decomposition of the latter reagent. Consequently our first step was that of preparing, by modifying a synthetic procedure recently described in a Canadian patent [17] the starting molecule (2-imidazol-1-yl-ethyl)-carbamic acid *tert*-butyl ester hereafter abbreviated as BocNHCH₂CH₂Im, 1.

The *N*-quaternization of 1 with an excess of MeI led, in quantitative yields, to the methylimidazolium salt [BocNHCH₂CH₂ImMe]I, [2]I that readily underwent to an anion exchange with AgPF₆ to afford [2]PF₆. The subsequent thermolytic deprotection of the –NH₂ functionality of neat [2]I and [2]PF₆ derivatives cleanly gave the 1-(2-aminoethyl)-3-methylimidazolium salts [NH₂CH₂CH₂ImMe]X [3]I and [3]PF₆ although for the latter harsher conditions were required (Scheme 2).

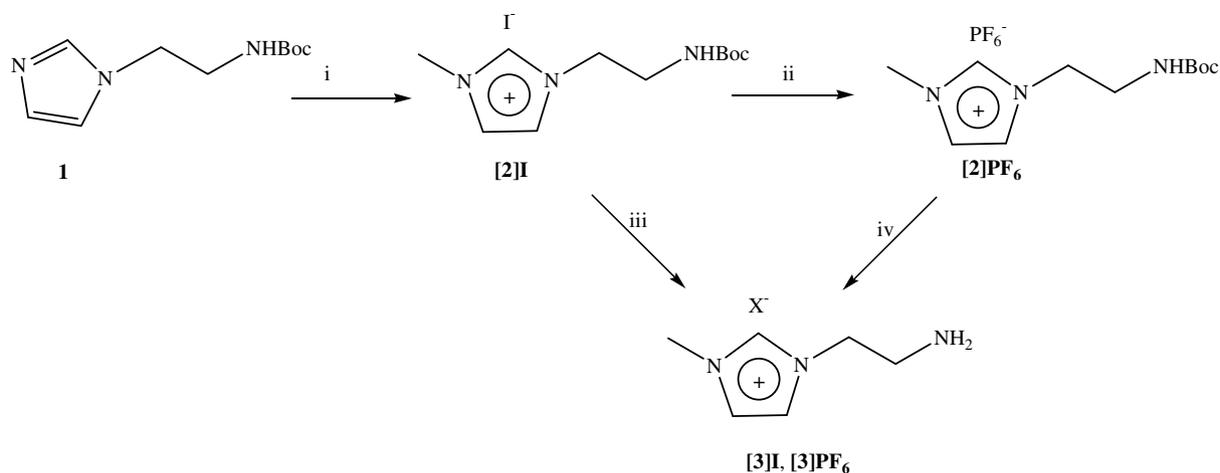
Compounds 2 and 3 are very viscous air-stable liquids. Unlike 2, the deprotected [3]I is insoluble in THF and chlorinated solvents, partially soluble in acetonitrile and completely soluble in DMSO and water, whereas [3]PF₆ is completely soluble only in water. Assignments for ¹H and ¹³C chemical shifts have been unambiguously confirmed by gCOSY, gHSQC and HMBC experiments. With the exception of the spectra in D₂O that, as often observed, did not show the downfield peak for the imidazolium proton [18], the NCHN resonance was found in the interval δ 9.70–8.70 (ca. δ 137 for the corresponding NCHN carbon). The imidazole backbone protons (CH_{imid}) invariably appear as broad singlets for 2, while in the deprotected case [3]I, probably due to strong intermolecular interactions favoured by the polar solvents used (CD₃CN, DMSO-*d*₆), the appearance of the signals is dependent on the concentration and in dilute samples a doublets of doublets multiplicity with resonances at 7.74 and 7.71 with ³J_{H,H} = 2.0 and ⁴J_{H,H} = 1.6 Hz can be observed.

2.2. Synthesis and characterization of silver aminocarbene complexes

The use of the silver base Ag₂O has been found a very advantageous method in order to trap the carbene molecule and has recently been comprehensively reviewed [19,20]. The imidazolium [2]I was hence treated with a slurry of Ag₂O in dichloromethane in a 2:1 molar ratio and stirred at room temperature for 2 h in the dark and under argon. The resulting grey suspension was filtered and the volatiles removed under reduced pressure to afford

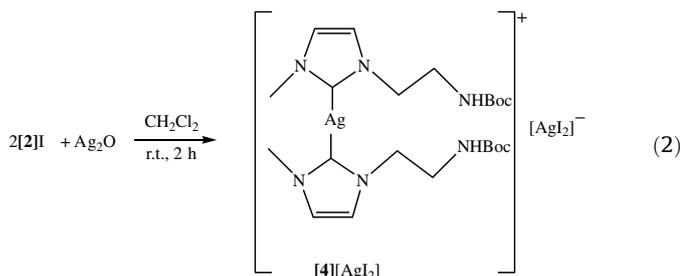


Scheme 1. Reaction between 1-methylimidazole and 2-bromoethylamine hydrobromide.



Scheme 2. Reagents and conditions: (i) MeI(excess), THF, rt, overnight; (ii) AgPF₆, CH₂Cl₂, 4 h; (iii) 185 °C, 30 min under argon; (iv) 210 °C, 3 h under argon.

in quantitative yields the silver complex **[4][AgI₂]** as a white solid that was analyzed by different spectroscopic techniques (Eq. (2)).



In the ¹H NMR spectrum in CDCl₃ the complete disappearance of the high frequency peak for the imidazolium proton was coupled with the appearance in the ¹³C NMR spectrum of a sharp singlet at δ 184.9 assigned to a Ag–C_{carbene} carbon (no ¹³C–¹⁰⁷Ag/¹⁰⁹Ag coupling was observed); the CH_{imid} carbons at δ 121.7 and 121.4 ppm, are, like the Ag–C_{carbene} chemical shift, perfectly in keeping with the values reported in the literature for other imidazol-2-ylidene–silver complexes [19,21]. The electrospray ionization mass spectrometry analysis in methanol indicated the presence in solution of the silver salt [Ag(NHC–NHBoc)₂]⁺[AgI₂][–] with peaks at 557 (100) *m/z* for [M]⁺ (C₂₂H₃₈AgN₆O₄) and at 361 (100) *m/z* for [AgI₂][–] with the observed isotopic distribution in perfect agreement with the calculated one. The carbonyl stretching frequency (ν_{CO}) of the carbamate group appeared at 1716 cm^{–1} in the IR spectrum in THF whilst the IR-Microscopy showed a strong N–H stretching absorption at 3339 cm^{–1} and a ν_{CO} at 1701 cm^{–1}. The silver complex is completely soluble in halogenated solvents, THF, acetone but insoluble in diethyl ether and petroleum ether.

Colourless crystals suitable for an X-ray crystal structure determination were obtained from a double layer acetone/hexane at –20 °C. As illustrated in Fig. 1 (selected bonds and angles are indicated in Table 1) the crystal structure consists of a [Ag₂I₄]^{2–} fragment sandwiched between two identical [Ag(NHC–NHBoc)₂]⁺ complexes (**5**) and it is analogous to the one reported by Chen and Liu [22].

The similarities are found in the quasi-planar geometry showed by the imidazolium rings, connected through Ag(1), as well as in their almost linear arrangement as indicated by the C–Ag(1)–C angle of 170.9(3)°. Furthermore, the Ag(1)–C bonds are 2.081(7) and 2.077(9) Å, slightly shorter but in line with the ones previously observed [21]. The Ag–I distances within the [Ag₂I₄]^{2–} anion, namely 2.6902(9) Å for I(2)–Ag(2), 2.7871(9) Å for I(1#1)–Ag(2) and

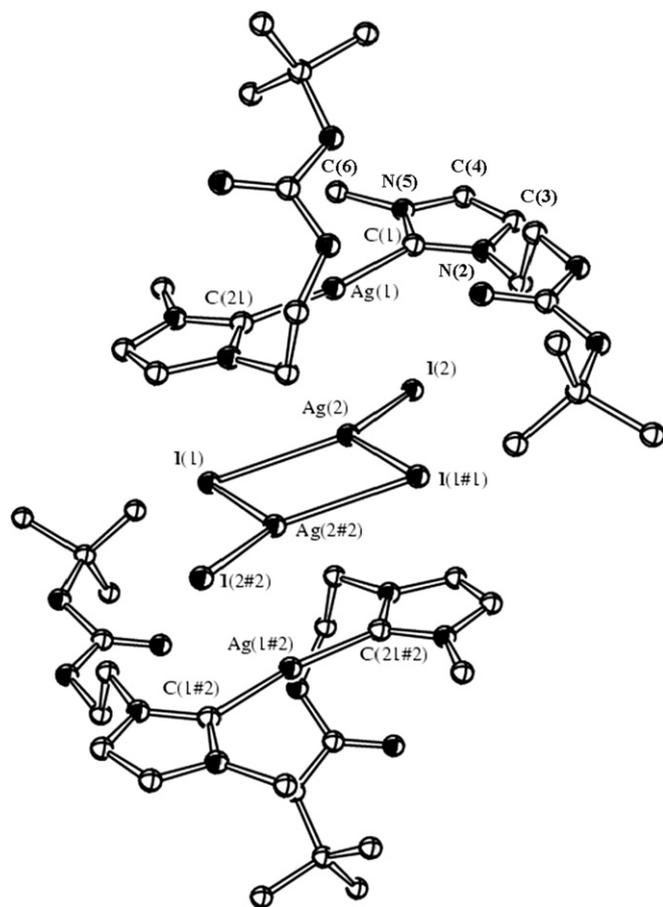


Fig. 1. ORTEP diagram (30% probability thermal ellipsoids) of **5** (for sake of clarity hydrogen atoms have been omitted).

2.8390(9) Å for I(1)–Ag(2), are also comparable. There are, however, major differences with regard to the Ag–Ag bond distances, the intermolecular interactions and the crystal packing. As a matter of fact the Ag(1)–Ag(2) contact connecting the complex to the anionic fragment is 3.2873(10) Å long, and a second long distance of 3.2421(14) Å is found between the two Ag(2) atoms of the latter, while the values Chan and Liu report are 3.042 and 2.9643(16) Å, respectively. This might be due to the fact that, unlike theirs, the structure we present displays important intermolecular hydrogen

Table 1
Selected bond lengths (Å) and angles (°) for **5**, **6** and **[4]PF₆**

5		6		[4]PF₆	
Ag(1)–C(21)	2.077(7)	I(1)–Ag(4#2)	2.882(2)	Ag(1)–C(1)	2.062(7)
Ag(1)–C(1)	2.081(7)	I(1)–Ag(4)	2.919(2)	Ag(1)–C(17)	2.088(6)
Ag(1)–Ag(2)	3.2873(10)	I(2)–Ag(4)	2.816(3)	C(1)–N(5)	1.348(8)
Ag(2)–I(2)	2.6902(9)	I(2#1)–Ag(3)	2.855(2)	C(1)–N(2)	1.374(8)
Ag(2)–I(1#1)	2.7871(9)	I(2)–Ag(3)	2.868(2)	N(2)–C(3)	1.378(9)
Ag(2)–I(1)	2.8390(9)	Ag(3)–C(1)	2.167(16)	C(3)–C(4)	1.300(11)
Ag(2)–Ag(2#2)	3.2421(14)	Ag(4)–I(1#2)	2.882(2)	C(4)–N(5)	1.393(9)
Ag(2#2)–I(1)	2.7871(9)	Ag(4)–Ag(3)	3.132(3)	N(5)–C(6)	1.454(9)
C(1)–N(2)	1.354(8)	Ag(4)–Ag(4#2)	3.117(3)	C(1)–Ag(1)–C(17)	177.8(2)
C(1)–N(5)	1.348(9)	C(1)–N(1)	1.31(2)	N(5)–C(1)–N(2)	103.4(5)
C(4)–N(5)	1.373(9)	C(1)–N(2)	1.32(2)	N(5)–C(1)–Ag(1)	130.7(5)
C(3)–C(4)	1.327(11)	C(2)–N(2)	1.32(2)	N(2)–C(1)–Ag(1)	125.7(5)
C(3)–N(2)	1.360(9)	C(2)–C(3)	1.37(3)	C(1)–N(2)–C(3)	110.6(6)
C(21)–Ag(1)–C(1)	170.9(3)	C(3)–N(1)	1.37(2)	C(1)–N(2)–C(7)	125.5(5)
C(21)–Ag(1)–Ag(2)	91.48(18)	Ag(4#2)–I(1)–Ag(4)	64.99(6)	C(3)–N(2)–C(7)	123.6(6)
C(1)–Ag(1)–Ag(2)	90.99(19)	Ag(4)–I(2)–Ag(3)	88.47(6)	C(4)–C(3)–N(2)	107.7(7)
I(2)–Ag(2)–I(1#1)	123.97(3)	C(1)–Ag(3)–I(2)	124.6(5)	C(3)–C(4)–N(5)	107.4(6)
I(2)–Ag(2)–I(1)	124.56(3)	I(2)–Ag(4)–I(1)	100.96(6)	C(1)–N(5)–C(4)	110.9(6)
I(1#1)–Ag(2)–I(1)	109.63(3)	I(2)–Ag(4)–Ag(4#2)	121.05(9)	C(1)–N(5)–C(6)	123.9(6)
I(2)–Ag(2)–Ag(2#2)	167.71(4)	I(1#3)–Ag(4)–Ag(4#2)	114.52(10)	C(4)–N(5)–C(6)	125.2(6)
I(1#1)–Ag(2)–Ag(2#2)	55.57(2)	I(1#2)–Ag(4)–Ag(4#2)	58.08(6)		
I(1)–Ag(2)–Ag(2#2)	54.07(2)	I(1)–Ag(4)–Ag(4#2)	56.93(6)		
I(2)–Ag(2)–Ag(1)	100.49(3)				

bonds that build an arrangement of infinite $[\text{Ag}(\text{NHC}-\text{NHBoc})_2]^+$ chains and, consequently, weaken the Ag(1)–Ag(2) interactions. The elongation of the Ag–Ag distance within the $[\text{Ag}_2\text{I}_4]^{2-}$ anion seems to be another consequence of the network assembled by the intermolecular interactions. More specifically, hydrogen bonds involve the intermolecular $\text{NH}\cdots\text{O}=\text{C}$ donor–acceptor carbamic couples, with values between 2.890(8) and 2.821(8) Å.

In order to obtain suitable crystals for X-ray diffractions different crystallization attempts were necessary. During these procedures, and already after the first crystallization from acetone–hexane, we noticed the presence of a white solid material only soluble in CDCl_3 warmed at 65 °C. The NMR spectra run on the heterogeneous sample at room temperature showed one single set of resonances identical to those observed for the crude material **[4]** $[\text{AgI}_2]$ whereas the NMR of the same sample made homogeneous after heating at 65 °C, revealed the presence of a second, identical but higher frequency shifted, set of signals attributed to a second NHC–Ag species **6**. The relative intensity of these new resonances increased with the number of re-crystallization steps: after two steps the presence of **6**, estimated by NMR of ca. 8% raised up to ca. 50% after four times.

During one of these re-crystallization steps we obtained crystals whose morphology appeared different from **5** and whose structure, shown in Figs. 2a and 2b (selected bonds and angles are indicated in Table 1), represents a rare example of multinuclear, polymeric silver complex with a staircase-type structure composed of Ag_4I_4 cluster fragments that aggregate to give an infinite ribbon stair structure, to which the carbene units are coordinate on both sides via C–Ag bonds [22,23].

The perspective view shown in Fig. 2b highlights the complex step structure of the AgI polymer, which propagates along the *b* axis.

The unit cell contains an independent carbene molecule, two independent silver atoms [Ag(3) and Ag(4)] and two independent iodine atoms [I(1) and I(2)]. The silver atom Ag(3) shows a quasi-planar trigonal coordination, if we exclude the long Ag(3)–Ag(4) interaction [3.132(3)], being directly bonded to the carbenic C1 atom [2.167(16) Å] and to two I(2) atoms with bond lengths equal to 2.855(2) and 2.868(2) Å (Fig. 2b). There is also a forth long contact of 3.306 Å between Ag(3) and I(1) that would give a pseudo

tetrahedral coordination to Ag(3) if kept into account. The other Ag atom, Ag(4), indeed possesses this last type of coordination, being completely internal to the cluster structure and bonded to four I atoms through contacts whose lengths vary from 2.816(3) to 2.919(2) Å. There is also an additional, fairly long Ag(4)–Ag(4) contact [3.117(3) Å]. The wide range observed for the Ag–I bond distances [2.816(3)–2.919(2) Å] is comparable to what found in the literature for analogous compounds [22]. The relatively long Ag–Ag distances observed [3.117(3) and 3.132(3) Å] suggest that they are quite weak and the ribbon stair frame is mainly stabilized by the multiple bridging iodides. These distances are less than the sum of the van der Waals radii of 3.44 Å for silver [24], but are in the range observed for ligand-unsupported $\text{Ag}^{\text{I}}-\text{Ag}^{\text{I}}$ distances (2.80–3.30 Å) [25]. As far as the iodine atoms are concerned, they all are tri-coordinated to Ag atoms and the main difference stands in their position: I(1) is internal to the Ag_4I_4 cluster unit and has also got an additional forth long contact with Ag(3), I(2) is peripheral. The carbene molecules are positioned onto both sides of the ribbon stair structure, bonded to every peripheral Ag atoms. The rings protrude outward along the polymeric AgI chain and the X-ray crystal packing pattern (Fig. 2b) showed that although they are not stacked, they lay on parallel planes distant 3.362 Å from each other. The 5-membered rings are planar and all the bond lengths in the ring are, within the experimental errors, very close to those observed for other similar complexes [9f]. The Ag–C bond distance of 2.167(16) Å is somewhat longer than those of known silver carbene complexes (2.052–2.090 Å) [26], but identical to that observed for a similar staircase-type structure [2.161(9) Å] [22]. With regard to the carbamic moiety, the X-ray analysis showed a positional disorder hence in the solid state it can be found in two different regions of the unit cell, one occupied for about 69%, the other for the remaining 31%. This is reasonable if we consider that the carbamic moiety is actually the most external fraction of the structure, nevertheless the disorder is partially controlled by intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds [2.480 Å in the prevailing isomer, 2.794 Å in the minor one].

The reaction of **[2]PF₆** with Ag_2O in a 2:1 molar ratio, under basic PTC (phase transfer catalyst)/ OH^- conditions in the presence of $[\text{NBu}_4]\text{PF}_6$ and NaOH [19b,27] formed the simple biscarbene salt **[4]PF₆** (Eq. (3)) in 71% yield (NMR).

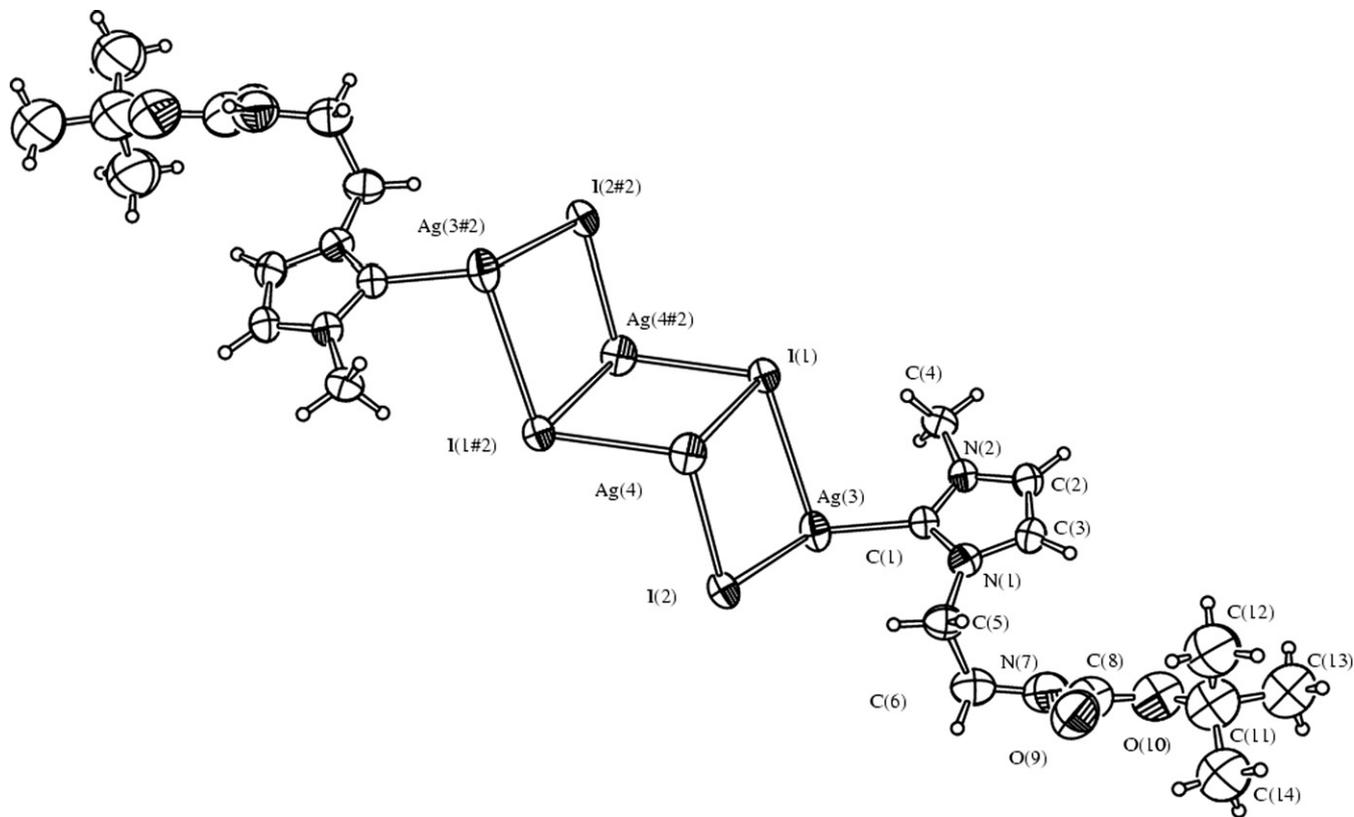
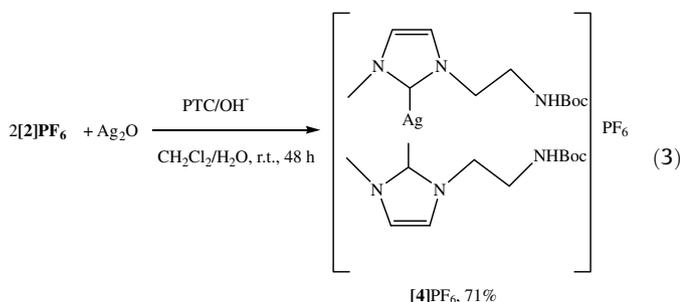


Fig. 2a. ORTEP diagram (30% probability thermal ellipsoids) of **6**.



Complex [**4**] PF_6 was completely characterized (see Section 4). The ^1H and ^{13}C NMR spectra are not significantly different from those of [**4**] $[\text{AgI}_2]$ but unlike this latter the carbene carbon signal at δ 180.3 appears as a broad doublet with $C-^{107/109}\text{Ag}$ coupling constant of 185.4 Hz [19b,27].

Suitable crystals for X-ray diffraction of [**4**] PF_6 have been obtained by slow evaporation from a CDCl_3 solution at room temperature. The crystal packing and structure of [**4**] $\text{PF}_6 \cdot 2\text{CDCl}_3$ are, respectively, shown in Figs. 3 and 4, respectively (selected bonds and angles are indicated in Table 1), and the latter consists of two independent silver biscarbene molecules in a 1:1 enantiomeric mixture. Within the same molecule, the two carbenes coordinated to the same silver atom are absolutely identical and carry the carbamic chain on the same side of the 5-membered ring with respect to the silver position. Furthermore, the *cis* position of the substituents allows the enantiomers to face one another in pairs, with the carbene units not staggered but laying on parallel planes distant about 3.219 Å from each other. The space between the two groups of isomers is filled by the anion and solvent molecules (*vide infra*).

The sterical hindrance caused by the carbamic chains, which are not linear but bent inwards within the same space region, causes the two 5-membered rings to adopt a non-coplanar geometry

and their torsion angle is about 39°. Similarly to what found for **5** and **6**, the 5-membered rings are planar and the bond lengths comparable to those observed for other similar complexes [9e]. The Ag–C bond distances 2.062(7) and 2.088(6) Å are shorter than those found in **6** but comparable with **5** and totally in agreement with what reported for other analogous cationic biscarbene complexes [20a,21]. The C(1)–Ag(1)–C(17) angle is close to linearity with an angle of 177.8(2)°.

We finally studied the reactivity of $[\text{NH}_2\text{CH}_2\text{CH}_2\text{ImMe}]$, [**3**] I toward Ag_2O under a variety of conditions. Our investigations started carrying the reaction between [**3**] I and Ag_2O in a 2:1 ratio in two parallel experiments: (i) in a flask containing anhydrous $\text{DMSO-}d_6$ and 4 Å molecular sieves with the filtered, colourless reaction mixture successively transferred into a NMR tube and (ii) by direct addition of all the reagents in a NMR tube. In both cases the analysis of the NMR spectra indicated that [**3**] I rapidly reacts with Ag_2O to give a single silver-containing product: in the ^1H NMR the peak at δ 9.10 disappears and the resonances of the imidazole CHs backbone are shifted upfield from 7.74 and 7.71 to 7.46 and 7.42, respectively, while nothing can be said on the fate of the NH_2 group, whose resonance is never observed even in the starting proligand. In the ^{13}C NMR spectra the original resonance at δ 136.9 for the NCHN carbon is replaced by a singlet at δ 179.8, analogous to the Ag– $\text{C}_{\text{carbene}}$ found for the silver complexes [**4**] $[\text{AgI}_2]$. However continuous monitoring by NMR showed that this product is rather unstable and rapidly decomposes: the solution turned yellow and a silver mirror together with a brown powdery solid coated the NMR tube whilst the proton and carbon NMR spectra showed that the peaks assigned to the silver adduct weaken in intensity while the resonances of the starting imidazolium salt reappear. When the same reaction was carried in bulk, the black suspension stirred for 2 h was filtered on a celite pad and after addition of acetonitrile a light brown precipitate was obtained.

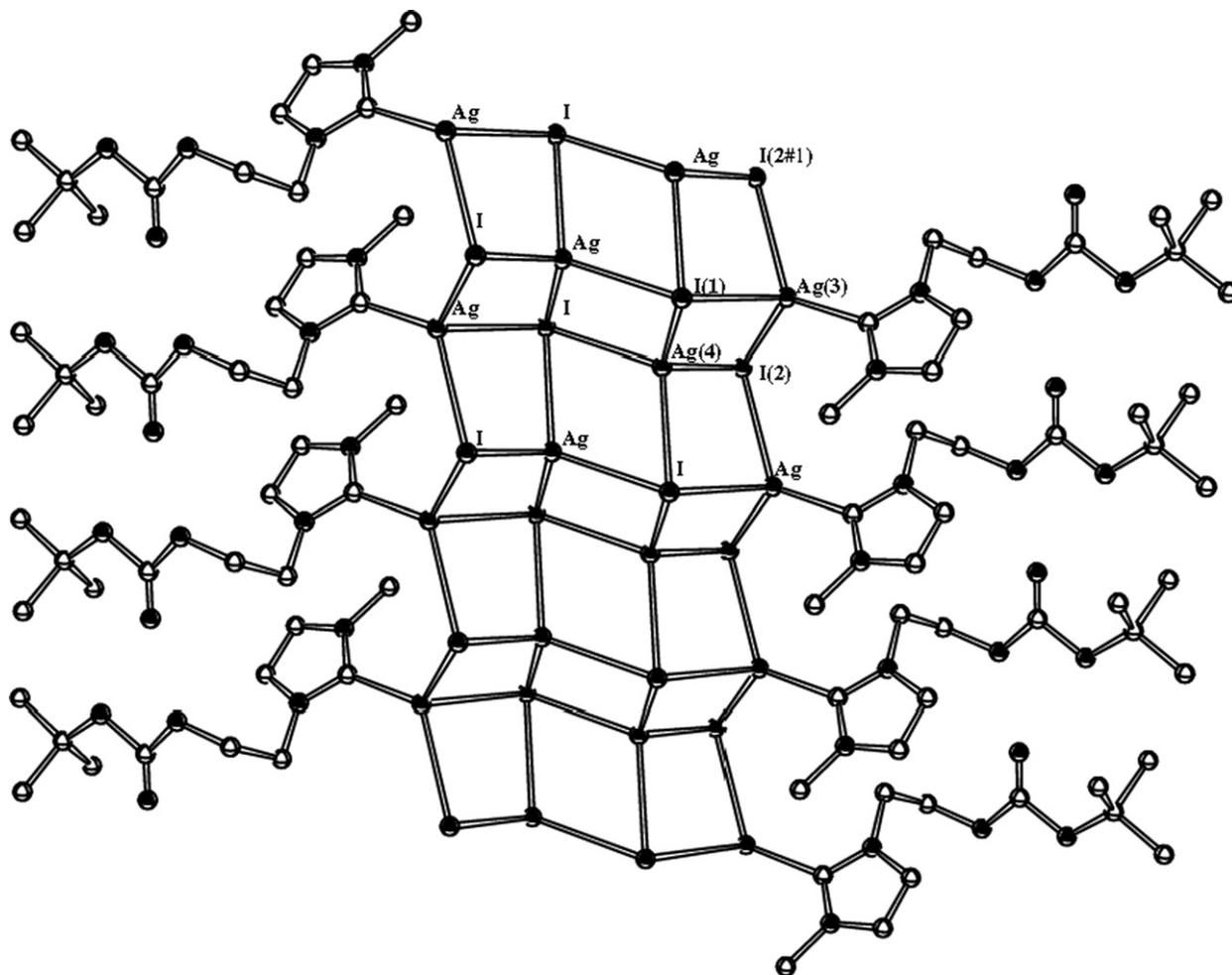


Fig. 2b. ORTEP diagram (30% probability thermal ellipsoids) of **6**. For sake of clarity hydrogen atoms have been omitted.

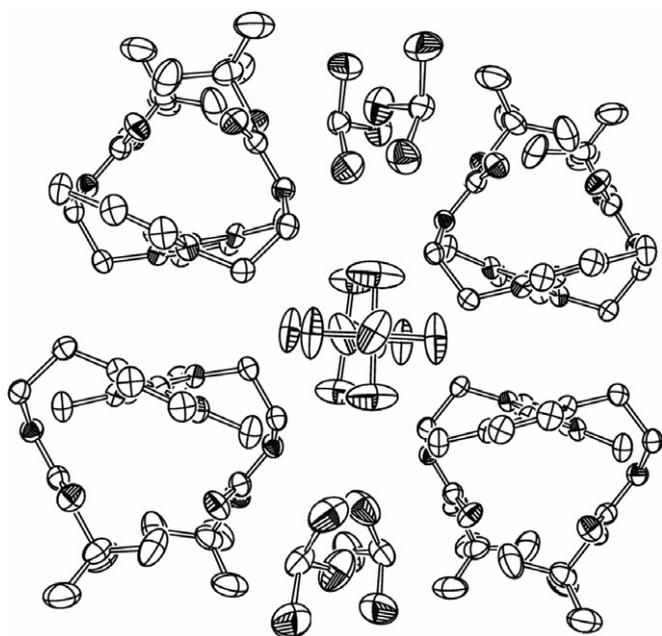


Fig. 3. Crystal packing of **[4]PF₆** (30% probability thermal ellipsoids). For sake of clarity hydrogen atoms have been omitted.

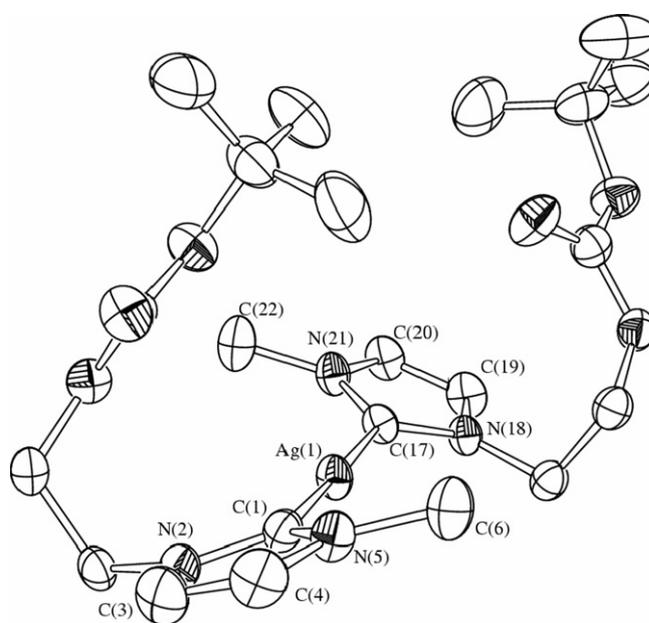


Fig. 4. ORTEP diagram (30% probability thermal ellipsoids) of **[4]PF₆**. For sake of clarity hydrogen atoms have been omitted.

The ESI-MS(+) spectrum of the freshly filtered solution showed peaks for the $[(M+Na)]^+$ cation at 382 (100) and 384 (90) m/z and peaks at 366 (42) 368 (38) m/z that we tentatively attributed to the presence in solution of the neutral species $(NHC-NH_2)AgI$ (**7**, $NHC-NH_2 = 1-(2\text{-aminoethyl})-3\text{-methyl-imidazolin-2-ylidene}$) that in the ESI-MS conditions easily lose the NH_2 fragment.

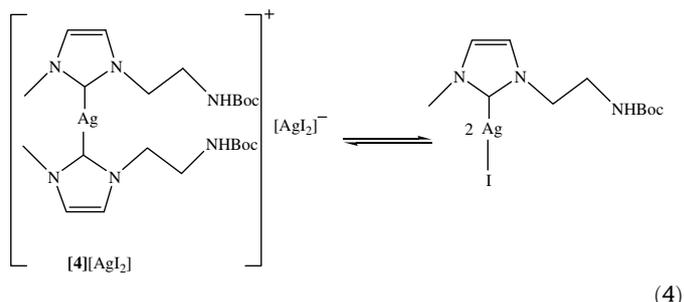
2.3. PGSE and NOE NMR studies

The imidazolium salts **[2]X** ($X = I, PF_6$) and the silver complexes **[4][AgI₂]** and **[4]PF₆** were investigated through NOE and PGSE NMR experiments.

¹H and ¹⁹F-PGSE NMR experiments were carried out for **[2]X**, **[4][AgI₂]** and **[4]PF₆** in CD₂Cl₂, using tetrakis-(trimethylsilyl) silane (TMSS) as internal standard. PGSE measurements allowed the translational self-diffusion coefficients (D_t) for both cationic (D_t^+) and anionic (D_t^-) moieties to be determined (Table 2). From the measured self-diffusion coefficients (D_t), the average hydrodynamic radius (r_H) of the diffusing particles was derived taking advantage of the Stokes–Einstein equation, $D_t = kT/c\pi\eta r_H$, where k is the Boltzman constant, T is the temperature, c is a numerical factor and η is the solution viscosity. D_t data were treated taking all the methodological precautions described in our recent paper [28]. In this regard although the ionic impurity $[NBu_4]^+$ present in **[4]PF₆** do not have any influence in the determination of the counter anion position (vide infra), it certainly does with respect to the self aggregation tendency hence, the hydrodynamic volumes V_H are only reported for the entries 1–5 but not for entries 14–16 as the latter data would represent average V_H values resulting from an ion-pair association among the PF_6^- anion with the two $[NBu_4]^+$ and **[4]**⁺ cations.

From the average hydrodynamic radii of the aggregates, assumed to be spherical, their volumes V_H^+ and V_H^- were obtained. V_H^+ of **[2]PF₆** spans from 421 Å³ (entry 1) to 1394 Å³ (entry 5) while V_H^- is included between 276 and 1242 Å³ (entries 1–5). In **[2]I**, V_H^+ stays in the range of 460–2112 Å³ (entries 6–8). For the silver complex **[4][AgI₂]**, V_H^+ spans from 457 Å³ (entry 9) to 776 Å³ (entry 13). On the other hand the fact that no sensible variation of V_H^+ is observed for complex **[4]PF₆** on varying the concentration (values of 847–960 Å³, entries 14–16) suggests that, as already reported in the literature for analogous studies [28,29] the presence of quadrupolar aggregates is negligible, therefore further confirming that the ionic impurities present do not have any influence with regards to the diffusional data relative to the cation.

The values of V_H^+ measured for **[4][AgI₂]** at low concentration (entry 9) are not consistent with its formulation. It can be noted that V_H^+ is practically identical to that of **[2]I** (entry 6) and about half of that of **[4]PF₆** (entry 14). These observations suggest that the cationic silver iodide **[4][AgI₂]** undergoes a NHC/I exchange between two silver centres (Eq. (4)) leading to the formation of neutral mono-NHC silver iodide in diluted solution via a mechanism similar to that suggested by Wang and Lin [19b].



In order to have an idea of the level of aggregation, V_H^+ and V_H^- can be compared with the volume of the ion pair (V_H^0) obtaining the cationic (N^+) and anionic (N^-) aggregation numbers (Table 2) [29]. We have recently shown that only for molecules not having inlets V_H^0 is well-described by the van der Waals volume (V_{vdw}) of the ion pair, easily obtainable from X-ray or theoretical data [30]. In other cases, it is preferable to use the hydrodynamic volume measured at very low concentration or extrapolated at infinite dilution (V_H^0). This procedure, requiring time-consuming PGSE experiments, can be avoided combining diffusion NMR and conductometric measurements or even by a single diffusion measurement if the volume of one ionic fragment is known or can be well-described by V_{vdw} [31]. Imposing $V_{vdw} = 62 \text{ \AA}^3$ for PF_6^- in **[2]PF₆**, a volume of 392 Å³ was determined for **[2]**⁺ from the PGSE measurement at the lowest concentration (Table 2, entry 1). Consequently, V_H^0 of **[2]PF₆**, derived by adding the volumes of the single ions, was 454 Å³ (entry 1). V_H^0 of **[2]I**, **[4][AgI₂]** and **[4]PF₆** were properly obtained combining V_{vdw} of I^- , Ag^+ , and PF_6^- with the volume of **[2]**⁺. It is important to outline that for **[2]I** and **[4]PF₆** the observed V_H^0 s for the most diluted solutions are consistent with the V_H^0 s calculated according to the procedure above-described (entries 6 and 14).

The aggregation tendency of compounds can be evaluated looking at the trends of N^+ and N^- (Table 2) or V_H^+ with the concentra-

Table 2

Diffusion coefficients ($10^{10}D_t$, $m^2 s^{-1}$), hydrodynamic radii (r_H , Å), hydrodynamic volumes (V_H , Å³) and aggregation number for cation (N^+) and anion (N^-) of compounds **[2]X** ($X = I, PF_6$), **[4][AgI₂]** and **[4]PF₆** in CD₂Cl₂ as a function of concentration (C, mM)

		D_t^+	D_t^-	r_H^+	r_H^-	V_H^+	V_H^-	N^+	N^-	C
1	[2]PF₆ ($V^0 = 454 \text{ \AA}^3$)	12.6	15.3	4.65	4.04	421	276	0.9	0.6	0.14
2		11.3	11.5	4.79	4.72	460	440	1.0	1.0	2.3
3		10.9	11.1	4.92	4.82	499	469	1.1	1.0	8.7
4		7.10	7.37	6.43	6.23	1113	1012	2.4	2.2	126
5		5.58	5.84	6.93	6.67	1394	1242	3.1	2.7	237
6	[2]I ($V^0 = 426 \text{ \AA}^3$)	11.6	–	4.79	–	460	–	1.1	–	1.0
7		10.4	–	5.11	–	560	–	1.3	–	14
8		2.64	–	7.96	–	2112	–	5.0	–	458
9	[4][AgI₂] ($V^0 = 441 \text{ \AA}^3$)	11.6	–	4.78	–	457	–	^b	–	0.01
10		11.4	–	4.83	–	471	–	^b	–	0.08
11		11.1	–	4.90	–	492	–	^b	–	0.72
12		10.6	–	4.98	–	517	–	^b	–	2.3
13		9.5	–	5.70	–	776	–	^b	–	10.5 ^a
14	[4]PF₆ ($V^0 = 853 \text{ \AA}^3$) ^c	9.29	–	5.87	–	847	–	1.0	–	2.3
15		8.68	–	5.92	–	869	–	1.0	–	22.4
16		7.41	–	6.12	–	960	–	1.1	–	120.5

^a Saturated solution.

^b Since compound **[4][AgI₂]** undergoes the equilibrium described in Eq. (4) (vide infra), N cannot be properly defined.

^c Contaminated with $[NBu_4]PF_6$.

tion: as expected, $N^{+/-}$ and V_H^+ increase with the concentration. Ion pairing is the main aggregative process below 14 mM (N^+ little deviates from 1) for **[2]**PF₆ and **[2]**I salts whereas at higher concentration, aggregation of ion pairs occurs: at ca. 100 mM, **[2]**PF₆ is prevalently present as ion quadruples (entry 4), at ca. 250 mM, it forms hexapoles (entry 5), finally **[2]**I at still higher concentration (ca. 450 mM) appears to form decapoles (entry 9). On the other hand, the silver complex **[4]**PF₆ does not exhibit any tendency to form aggregates higher than ion pairs also at the highest concentration investigated (entry 16) [32].

The anion–cation relative orientation in solution for **[2]**PF₆ and **[4]**PF₆ was determined by detecting dipolar interionic interactions in the ¹⁹F, ¹H-HOESY NMR spectra (Figs. 5 and 6). NOE data were treated taking into account that the volumes of the cross peaks are proportional to $(n_I n_S / n_I + n_S)$ where n_I and n_S are the number of equivalent I and S nuclei, respectively (Table 3) [33]. In the ¹⁹F, ¹H-HOESY NMR spectrum of **[2]**PF₆, strong contacts were observed between F-atoms of the counterion and H(1) and H(7) protons. Medium contacts were detected with H(2), H(5) and H(6) resonances while the anion did not show any interaction with protons H(3) and H(4) of the imidazolium ring. This pattern of NOE contacts indicates that PF₆⁻ is mainly located close to the H(1) of the imidazolium ring. From this position the anion has the possibility to interact with H(2) methyl protons and H(5) and H(6) methylene protons. The presence of a strong interaction between the anion and the acidic NH proton (Table 3) indicates the establishment of a hydrogen bond between a fluorine of the anion and the proton H(7) (Fig. 5). An analogous relative anion–cation orientation was deduced for 2-pyridylmethyl imidazolium salts from computational and NOE experiments [14].

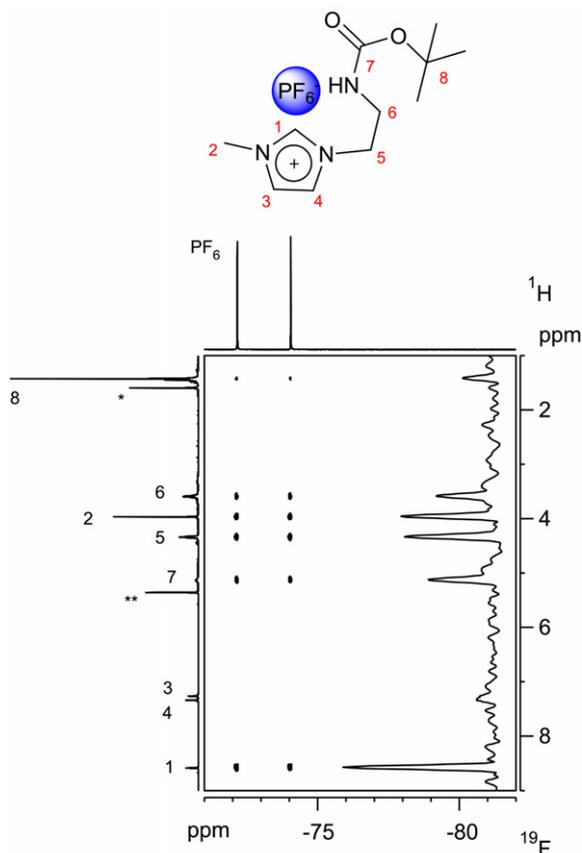


Fig. 5. ¹⁹F, ¹H-HOESY NMR spectrum (376.65 MHz, 296 K, CD₂Cl₂) of **[2]**PF₆. On the right the column projection is reported. * Denotes the H₂O resonance. ** Denotes the residue of non-deuterated solvent.

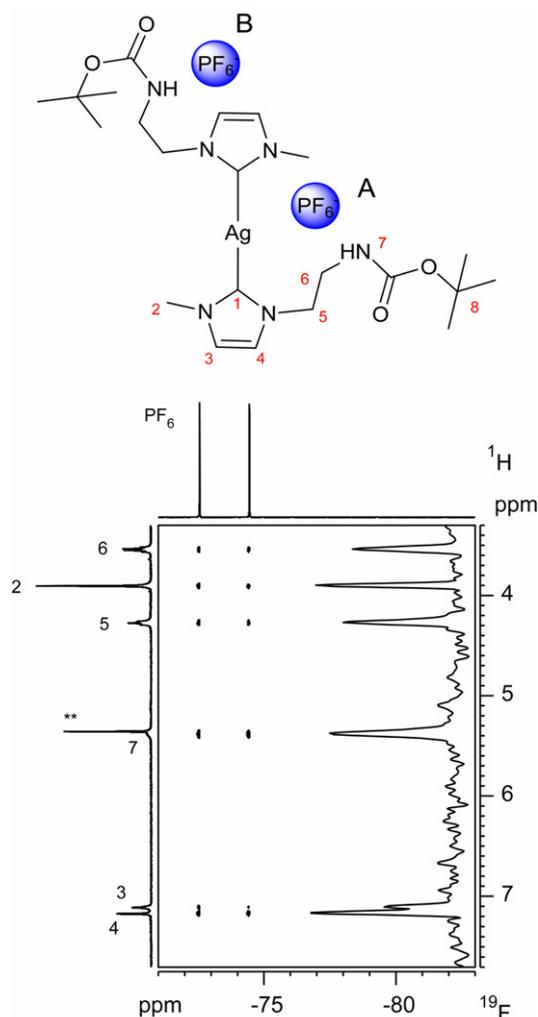


Fig. 6. A section of ¹⁹F, ¹H-HOESY NMR spectrum (376.65 MHz, 296 K, CD₂Cl₂) of **[4]**PF₆. On the right the column projection is reported. ** Denotes the residue of non-deuterated solvent.

Table 3

Relative NOE intensities treated taking into account that the volumes of the NOE cross peaks are proportional to $(n_I n_S / n_I + n_S)$ and determined by arbitrarily fixing at 1 the intensity of the NOE(s) between the anion resonances and H(2) resonances

	[2] PF ₆	[4] PF ₆
H(1)	3.56	–
H(2)	1	1
H(3)	–	1.22
H(4)	–	2.84
H(5)	1.22	1.53
H(6)	1.04	1.31
H(7)	1.94	4.20
H(8)	0.16	0.31

Differently from what observed for the related imidazolium salt, the ¹⁹F, ¹H-HOESY NMR spectrum of **[4]**PF₆ indicates that the counterion interacts with all protons of the cationic moieties (Fig. 6 and Table 3). In particular, the anion strongly interacts with NH and H(4) imidazolium ring protons. Medium intensity contacts are detected with H(3), H(5) and H(6) resonances while the anion shows weak interactions with H(8) protons of the Boc group. The quantitative NOE analysis does not allow a single anion–cation orientation explaining all the data found. In the solid state, four anion–cation orientations are present (Fig. 7); in two of them the

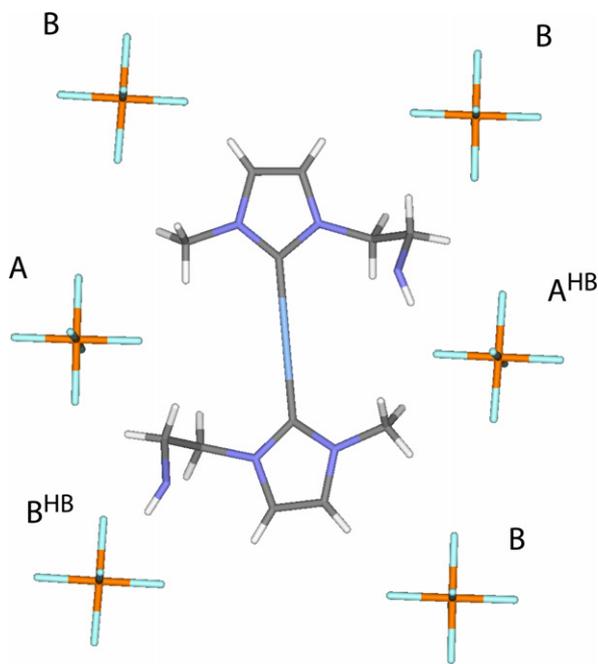


Fig. 7. A view of four anion position (A^{HB} , A , B and B^{HB}) present in the solid state for compound **[4]**PF₆. The Boc groups is omitted for clarity.

anion stays close to the Ag atom (A and A^{HB} , Ag–P distances ranging around 5.6 Å) whereas in the other two, the anion locates close to imidazolium ring (B and B^{HB} , Ag–P distances ranging around 7.8 Å). In A^{HB} and B^{HB} positions an hydrogen bond between the fluorine of the counterion and the NH groups is present (N–F distances ranging around 3.2 Å). The observation of strong PF₆⁻/NH and PF₆⁻/H(4) NOEs in the ¹⁹F, ¹H-HOESY NMR spectrum (Fig. 6) suggests that A^{HB} and B^{HB} orientations are prevalently present in solution (Fig. 7).

3. Conclusions

We have developed a simple and selective method for the preparation of the Boc-protected [BocNHCH₂CH₂ImMe]X **[2]**X, (X = I, PF₆) and its straightforward transformation into the unprotected 1-(2-aminoethyl)-3-methylimidazolium salts [NH₂CH₂CH₂ImMe]X, **[3]**X. The reaction of **[2]**X with Ag₂O led to the silver complexes **4–6** whose structures in the solid state and in solution confirmed the fascinating structural diversity of NHC–silver complexes and the importance of the role played by the counterion. NMR studies indicate that also in solution the latter has a key role: with a weakly coordinating anion (X = PF₆) the biscarbene salt [(NHC–NHBoc)₂Ag]PF₆, **[4]**PF₆, forms whereas when X = I an equilibrium between a similar complex having AgI₂⁻ as counterion and a mono-carbene silver iodide (NHC–NHBoc)AgI establishes.

Studies on the chemistry of the reported silver complexes as carbene transfer reagents are currently in progress and will be reported at a later date.

4. Experimental

4.1. Materials and procedures

All reactions were carried out under Argon using standard Schlenk techniques. Solvents were dried and distilled under nitrogen prior to use, dimethyl sulfoxide was dried over CaH₂ and distilled under reduced pressure; the deuterated solvents used after

being appropriately dried and degassed were stored in ampoules under argon on 4 Å molecular sieves. The prepared derivatives were characterized by elemental analysis and spectroscopic methods. The IR spectra were recorded with a FT-IR spectrometer Perkin–Elmer Spectrum 2000. The IR spectra on the crystals were recorded with a Nexus 470 instrument configured with a Nicolet Continuum microscope and a MCT liquid nitrogen cooled detector; the spectra were collected in the Near Normal-Reflection-Absorption mode. The NMR spectra were recorded using Varian Gemini XL 300 (¹H, 300.1; ¹³C, 75.5 MHz), Varian MercuryPlus VX 400 (¹H, 399.9; ¹³C, 100.6 MHz), Varian Inova 600 (¹H, 599.7, ¹³C, 150.8 MHz) instruments. The spectra were referenced internally to residual solvent resonances, and were recorded at 298 K for characterization purposes; full ¹H and ¹³C NMR assignments were done, when necessary, by gCOSY, gHSQC and HMBC NMR experiments using standard Varian pulse sequences. ESI-MS analysis were performed by direct injection of methanol solutions of the metal complexes using a WATERS ZQ 4000 mass spectrometer. Elemental analyses were performed on a ThermoQuest Flash 1112 Series EA Instrument. The reagents 1-methylimidazole, 2-bromoethylamine hydrobromide, imidazole (ImH), Ag₂O were used as purchased from Aldrich; MeI was distilled under argon and stored on molecular sieves; NaH (60% dispersion in mineral oil, Aldrich) was washed several time with petroleum ether and the resulting free-flow white powder was stored under Argon; 2-*t*-Boc-aminoethylbromide [carbamic acid 2-bromoethyl-*t*-butyl ester] was prepared according to literature procedures [34]; sodium imidazolid (Nalm) was prepared in large quantities by reacting imidazole with NaH in THF. Petroleum ether (Etp) refers to a fraction of b.p. 60–80 °C. Column chromatography were carried out on silica gel previously heated at about 200 °C while a slow stream of a dry nitrogen was passed through it [35]. Melting points were taken with a Stuart Scientific Melting point apparatus SMP3 and were uncorrected.

4.2. Reaction between 1-methylimidazole and 2-bromoethylamine hydrobromide

According to literature procedure [16] a mixture of 1-methylimidazole (2.00 g, 0.024 mol) and 2-bromoethylamine hydrobromide (5.00 g, 0.024 mol) in 15 mL of acetonitrile was heated with stirring at 80 °C for 4 h. After removal of the solvent under vacuum the residue was recrystallized from ethanol to afford a white solid. The NMR and ESI-MS analyses carried out on (i) the crude material before recrystallization from ethanol, (ii) the ethanol mother liquors and (iii) the crystallized white solid, revealed the presence of 3-methylimidazolium bromide **A** (soluble in ethanol, 72.5% NMR), the target molecule **B** (20.5%) together with **C** (6.5%) and **D** (0.5%) (see Scheme 1). Characterization of **A**: ¹H NMR (399.9 MHz, D₂O): δ = 8.68 (s, 1H, NCHN), 7.50 (s, 2H, CH_{imid}), 3.95 (s, 3H, NCH₃), NH not observed; ESI-MS (MeOH, *m/z*): 83 (100) [M]⁺; 79 (100), 81 (97) [M]⁻. Characterization of **B**, **C**, **D**: ¹H NMR (399.9 MHz, D₂O): δ = 8.94, 8.89, 8.84 (NCHN), 7.66, 7.57, 7.48 (CH_{imid}), 3.96, 3.94 (NCH₃), 4.70–4.30 (m, CH₂), 3.80–2.80 (m, CH₂); ESI-MS (MeOH, *m/z*): 126 (100) [CH₃ImCH₂CH₂NH₂]⁺, 169 (88) [CH₃ImCH₂CH₂NHCH₂CH₂NH₂]⁺, 212 (20) [CH₃ImCH₂CH₂NHCH₂CH₂NHCH₂CH₂NH₂]⁺; 79 (100), 81 (97) [M]⁻.

4.3. Synthesis of BocNHCH₂CH₂Im (1)

This product was synthesized using a modified literature method [17]. In a 250 mL flask 2.53 g (0.028 mol) of Nalm was reacted with 6.25 g (0.028 mol) of *N*-Boc-bromoethylamine in THF (ca. 50 mL). The reaction suspension was stirred overnight at room temperature and the precipitated NaBr removed by filtration. Purification of the crude material by column chromatography on silica

gel (eluting with CH₂Cl₂:MeOH:NH₄OH 100:5:1–100:5:2) gave a white solid identified as **1** (2.21 g, 37%). ¹H NMR (399.9 MHz, CDCl₃): δ 7.45 (s, 1H, NCHN), 7.06 (s, 1H, CH_{imid}), 6.91 (s, 1H, CH_{imid}), 4.62 (br s, 1H, NH), 4.07 (t, 2H, ³J_{H,H} = 6.0 Hz, NCH₂), 3.42 (m, 2H, CH₂NHBoc), 1.42 (s, 9H, CH₃). ¹³C-{¹H}NMR (100.6 MHz, CDCl₃): δ 155.8 (C=O), 137.1 (NCHN, Im), 129.2 (CH_{imid}), 118.8 (CH_{imid}), 79.6 (Cq, *t*-Bu), 46.4 (NCH₂), 41.3 (CH₂NHBoc), 28.1 (CH₃). IR (THF, cm⁻¹) 1714 (vs, ν_{CO}). ESI-MS (MeOH, *m/z*): 234 (100) [M+Na]⁺.

4.4. Synthesis of 1-(2-BocNH-ethyl)-3-methylimidazolium iodide [2]I

To a solution of **1** (0.380 g, 1.80 mmol) dissolved in THF (ca. 10 mL) an excess of MeI (0.5 mL) was added. The reaction was stirred overnight and the solvent removed under vacuum to yield 0.623 g (98%) of a yellow oil identified as [2]I. ¹H NMR (399.9 MHz, CDCl₃): δ 9.70 (s, 1H, NCHN), 7.45 (s, 1H, CH_{imid}), 7.39 (s, 1H, CH_{imid}), 5.78 (t, 1H, ³J_{H,H} = 5.8 Hz, NH), 4.55 (t, 2H, ³J_{H,H} = 5.6 Hz, NCH₂), 4.07 (s, 3H, NCH₃), 3.68 (m, 2H, CH₂NHBoc), 1.40 (s, 9H, CH₃). ¹³C-{¹H}NMR (100.6 MHz, CDCl₃): δ 156.2 (C=O), 137.0 (CH, NCHN), 123.1 (2CH, CH_{imid}), 79.9 (Cq, *t*-Bu), 46.7 (NCH₂), 40.2 (CH₂NH), 37.2 (NCH₃), 28.6 (CH₃, *t*-Bu). ¹H NMR (399.9 MHz, CD₃CN): δ 8.70 (s, 1H, NCHN), 7.42 (s, 1H, CH_{imid}), 7.37 (s, 1H, CH_{imid}), 5.78 (br s, 1H, NH), 4.25 (t, 2H, ³J_{H,H} = 5.6 Hz, NCH₂), 3.85 (s, 3H, NCH₃), 3.45 (m, 2H, CH₂NHBoc), 1.36 (s, 9H, CH₃). ¹H NMR (399.9 MHz, D₂O): δ 7.52 (s, 1H, CH_{imid}), 7.48 (s, 1H, CH_{imid}), 4.30 (t, 2H, ³J_{H,H} = 6.0 Hz, NCH₂), 3.92 (s, 3H, NCH₃), 3.54 (m, 2H, CH₂NHBoc), 1.39 (s, 9H, CH₃). IR (THF, cm⁻¹) 1708 (vs, ν_{CO}). ESI-MS (MeOH, *m/z*): 226 (100) [M]⁺, 127 (100) [M]⁻. Anal. Calc. for C₁₁H₂₀N₃O₂: C, 37.40; H, 5.70; N, 11.90. Found: C, 37.80; H, 5.90; N, 12.20%.

4.5. Synthesis of 1-(2-BocNH-ethyl)-3-methylimidazolium hexafluorophosphate [2]PF₆

In a 100 mL two-neck flask 0.162 g (0.46 mmol) of [2]I were dissolved in 5 mL of CH₂Cl₂. Solid AgPF₆ (0.127 g, 0.50 mmol) was added and after stirring the reaction mixture for 4 h the AgI formed was separated by filtration on a celite pad. The solvent was removed under vacuum to give 0.160 g (94%) of [2]PF₆ as a colourless oil. ¹H NMR (399.9 MHz, CDCl₃): δ 8.70 (s, 1H, NCHN), 7.26 (s, 1H, CH_{imid}), 7.20 (s, 1H, CH_{imid}), 5.35 (br s, 1H, NH), 4.31 (t, 2H, ³J_{H,H} = 5.6 Hz, NCH₂), 3.93 (s, 3H, NCH₃), 3.55 (m, 2H, CH₂NHBoc), 1.39 (s, 9H, CH₃). ¹³C-{¹H}NMR (100.6 MHz, CDCl₃): δ 156.4 (C=O), 136.6 (CH, NCHN), 123.0 (2CH, CH_{imid}), 79.7 (Cq, *t*-Bu), 49.8 (NCH₂), 40.3 (CH₂NH), 36.4 (NCH₃), 28.2 (CH₃). IR (THF, cm⁻¹) 1714 (vs, ν_{CO}). ESI-MS (MeOH, *m/z*): 226 (100) [M]⁺, 145 (100) [M]⁻. Anal. Calc. for C₁₁H₂₀F₆N₃O₂P: C, 35.58; H, 5.40; N, 11.32. Found: C, 35.60; H, 5.70; N, 11.55%.

4.6. Synthesis of 1-(2-aminoethyl)-3-methylimidazolium iodide [3]I

Neat 1-(2-BocNH-ethyl)-3-methylimidazolium iodide [2]I 0.220 g (0.62 mmol) was heated under Argon at 185 °C for 30 min. The oil changed colour from pale yellow to dark orange to yield 0.157 g (quantitative yield) of [3]I. ¹H NMR (399.9 MHz, D₂O): δ 7.58 (s, 1H, CH_{imid}), 7.53 (s, 1H, CH_{imid}), 4.47 (t, 2H, ³J_{H,H} = 6.0 Hz, NCH₂), 3.95 (s, 3H, NCH₃), 3.38 (t, 2H, ³J_{H,H} = 6.0 Hz, CH₂NH₂). ¹H NMR (399.9 MHz, DMSO-*d*₆): δ 9.10 (s, 1H, NCHN), 7.74 (dd, 1H, ³J_{H,H} = 2.0 Hz, ⁴J_{H,H} = 1.6 Hz, CH_{imid}), 7.71 (dd, 1H, ³J_{H,H} = 2.0 Hz, ⁴J_{H,H} = 1.6 Hz, CH_{imid}), 4.24 (t, 2H, ³J_{H,H} = 5.2 Hz, ImCH₂), 3.85 (s, 3H, NCH₃), 3.07 (t, 2H, ³J_{H,H} = 5.6 Hz, CH₂NH₂). ¹³C-{¹H}NMR (100.6 MHz, DMSO-*d*₆): δ 136.9 (CH, NCHN), 123.5 (CH_{imid}), 122.5 (CH_{imid}), 49.6 (NCH₂), 40.1 (CH₂NH₂), 35.8 (NCH₃). ESI-MS (MeOH, *m/z*): 126 (100) [M]⁺, 127 (100) [M]⁻. Anal. Calc.

for C₆H₁₂N₃: C, 28.46; H, 4.74; N, 16.60. Found: C, 28.50; H, 4.77; N, 16.90%.

4.7. Synthesis of 1-(2-aminoethyl)-3-methylimidazolium hexafluorophosphate [3]PF₆

Neat 1-(2-BocNH-ethyl)-3-methylimidazolium hexafluorophosphate [2]PF₆ 0.150 g (0.40 mmol) was heated under Argon at 210 °C for 3 h. The oil changed from colourless to orange to yield 0.108 g of [3]PF₆ in quantitative yield. ¹H NMR (399.9 MHz, D₂O): δ 8.91 (s, 1H, NCHN), 7.63 (s, 1H, CH_{imid}), 7.55 (s, 1H, CH_{imid}), 4.62 (m, 2H, ImCH₂), 3.95 (s, 3H, NCH₃), 3.59 (m, 2H, CH₂NH₂). ESI-MS (MeOH, *m/z*): 126 (100) [M]⁺, 145 (100) [M]⁻. Anal. Calc. (%) for C₆H₁₂F₆N₃P: C, 26.57; H, 4.46; N, 15.50. Found: C, 26.95; H, 4.77; N, 15.79%.

4.8. 1-(2-BocNH-ethyl)-3-methyl-imidazol-2-ylidene silver iodides [4][AgI₂], **5**, **6**

To a solution of [2]I 0.467 g (1.32 mmol) in CH₂Cl₂ (ca. 10 mL) stirred in a Schlenck, Ag₂O 0.158 g (0.68 mmol) was added. The suspension was stirred for 2 h, filtered and the solvent removed under vacuum to give 0.600 g of a white solid identified as [4][AgI₂]. ¹H NMR of **4** (399.9 MHz, CDCl₃): δ 7.00 (s, 1H, CH_{imid}), 6.91 (s, 1H, CH_{imid}), 4.34 (t, 2H, ³J_{H,H} = 6.0 Hz, NCH₂), 3.89 (s, 3H, NCH₃), 3.56 (t, 2H, ³J_{H,H} = 6.0 Hz, CH₂NH), 1.40 (s, 9H, CH₃), the resonance for the NH proton was not observed. ¹³C-{¹H}NMR (100.6 MHz, CDCl₃): δ 184.9 (C–Ag), 157.0 (C=O), 121.7 (CH_{imid}), 121.4 (CH_{imid}), 79.8 (Cq, *t*-Bu), 50.9 (NCH₂), 41.4 (CH₂NH), 39.0 (NCH₃), 28.4 (CH₃). IR (THF, cm⁻¹) 1716 (vs, ν_{CO}); IR (refl./abs., cm⁻¹): 3339 (s, ν_{NH}), 3160, 3134, 3119, 3098 (m, =CH), 3001, 2976, 2930 (broad vs, –CH), 1701 (vs, ν_{CO}). ESI-MS (MeOH, *m/z*): 557 (100), 558 (27), 559 (97), 560 (25) [C₂₂H₃₈AgN₆O₄]⁺; 361 (100), 363 (90) [AgI₂]⁻. M.p. = 189 °C dec. Colourless, suitable crystals for X-ray diffraction corresponding to **5** have been obtained from a double layer acetone/hexane at –20 °C.

During the re-crystallization phases we noticed the formation of increasing amounts of an insoluble white product soluble in hot CDCl₃. The ¹H NMR presented two sets of signals: one attributed to [4][AgI₂] and one to a new complex **6**. ¹H NMR of **6** (399.9 MHz, CDCl₃, 313 K): δ 7.37 (s, 1H, CH_{imid}), 7.30 (s, 1H, CH_{imid}), 4.56 (t, 2H, ³J_{H,H} = 5.6 Hz, NCH₂), 4.04 (s, 3H, NCH₃), 3.66 (t, 2H, ³J_{H,H} = 5.6 Hz, CH₂NH), 1.38 (s, 9H, CH₃), the resonance for the NH proton was not observed. Attempts to run an overnight ¹³C-{¹H}NMR spectra at 313 K led to decomposition of the silver complex. Complex **6** (colourless crystals obtained from a double layer acetone/hexane at –20 °C) was also characterized by X-ray diffraction. The elemental analyses of [4][AgI₂] on the bulk material always gave erratic results probably due the presence of trace amounts of **6**.

4.9. Synthesis of bis[1-(2-BocNH-ethyl)-3-methyl-imidazol-2-ylidene]silver hexafluorophosphate [4]PF₆

A mixture of 0.132 g (0.36 mmol) of [2]PF₆ in 5 mL of dichloromethane, 0.042 g (0.18 mmol) of Ag₂O, 100 mg (2.5 mmol) of NaOH in 3 mL of H₂O (1.8 M) and 23 mg (0.06 mmol) of [NBu₄]PF₆ as a phase transfer catalyst was stirred for 48 h. The organic layer was separated from the aqueous layer and filtered to remove solid by-products. Addition of hexane precipitated the crude product, however despite repeated purifications by recrystallization from dichloromethane/hexane the silver complex [4]PF₆ resulted always contaminated by the phase transfer catalyst. After four crystallizations 0.101 g of a mixture composed of [4]PF₆ (0.13 mmol, Y = 71%, calculated from the NMR spectra) and [NBu₄]⁻ (0.03 mmol) was obtained. ¹H NMR (399.9 MHz, CDCl₃): δ 7.13 (s,

¹H, CH_{imid}), 7.02 (s, 1H, CH_{imid}), 5.42 (br s, 1H, NH), 4.23 (t, 2H, ³J_{H,H} = 6.0 Hz, NCH₂), 3.86 (s, 3H, NCH₃), 3.50 (m, 2H, CH₂NH), 1.35 (s, 9H, CH₃). ¹³C-{¹H}NMR (100.6 MHz, CDCl₃): δ 180.0 (br d, ¹J_{C-107/109Ag} = 185.4 Hz), 156.2 (C=O), 122.5 (CH_{imid}), 122.0 (CH_{imid}), 79.4 (Cq, *t*-Bu), 51.4 (NCH₂), 41.5 (CH₂NH), 38.6 (NCH₃), 28.3 (CH₃). IR (CH₂Cl₂, cm⁻¹) 1712 (vs, ν_{CO}); IR (refl./abs., cm⁻¹): 3304 (s, NH), 2966 (broad vs, CH), 1680 (vs, ν_{CO}). ESI-MS (MeOH, *m/z*): 557 (100), 558 (27), 559 (97), 560 (25) [M]⁺; 145 (100) [M]⁻. Colourless, suitable crystals for X-ray diffraction have been obtained by slow evaporation from a CDCl₃ solution at room temperature. The crystals were removed from the vial with a small amount of mother liquor and immediately coated with silicon grease.

4.10. Reaction of [3]I with Ag₂O

[DMSO-*d*₆]: (a) An NMR tube was charged with [3]I (35.0 mg, 0.14 mmol), Ag₂O (18.0 mg, 0.077 mmol) and DMSO-*d*₆ (0.6 mL). The tube was sealed under argon and the resulting suspension was monitored at room temperature by an NMR spectrometer. The ¹H NMR spectrum showed the existence of a silver complex after 5 min. – ¹H NMR (399.9 MHz, DMSO-*d*₆): δ 7.46 (s, 1H, CH_{imid}), 7.42 (s, 1H, CH_{imid}), 4.09 (t, 2H, ³J_{H,H} = 5.6 Hz, NCH₂), 3.81 (s, 3H, NCH₃), 2.90 (t, 2H, ³J_{H,H} = 5.6 Hz, CH₂NH₂), NH₂ not observed; ¹³C-{¹H}NMR (100.6 MHz, DMSO-*d*₆): δ 179.8 (C–Ag), 123.1 (CH_{imid}), 122.1 (CH_{imid}), 54.1 (NCH₂), 43.1 (CH₂NH₂). (b) In a parallel experiment in a round bottom flask [3]I (104.0 mg, 0.41 mmol) was treated with Ag₂O (53.0 mg, 0.23 mmol), DMSO-*d*₆ (1 mL) and activated 4 Å molecular sieves. After stirring for two hours in the absence of light, part of the solution was transferred with a filtering cannula in a NMR tube. After flame-sealing the tube, the ¹H NMR spectrum showed the resonances described above together with those of the starting [3]I. Moreover as time passed by, a silver mirror together with a brown powdery solid coated the NMR tube whilst the proton and carbon NMR spectra showed that the peaks assigned to the silver adduct weakened in intensity.

[DMSO]. To a solution of [3]I (610 mg, 2.41 mmol) in DMSO (4 mL) stirred in a Schlenk, Ag₂O 308 mg (1.33 mmol) was added. After stirring the reaction mixture for 2 h the black suspension was filtered on a celite pad later washed with 2 × 2 mL of DMSO. The addition of 10 mL of acetonitrile led to the formation of a light brown precipitate that after being further washed with acetonitrile (2 × 5 mL) was dried under vacuum to give 0.650 g of a light brown solid containing an impure silver complex tentatively identified as [1-(2-aminoethyl)-3-methyl-imidazolin-2-ylidene]silver(I) iodide (7). The ESI-MS(+) (MeOH) analysis of the freshly filtered solution showed peaks for the [(C₆H₁₂AgIN₃+Na)]⁺ cation at 382 (100) and 384 (90) *m/z* and peaks at 366 (42) 368 (38) *m/z* for [(C₆H₁₀-AgIN₂+Na)]⁺ (no peaks were observed in the ESI-MS(-) spectrum).

4.11. Single-crystal X-ray diffraction studies of 5, 6 and [4]PF₆

Crystal data and collection details for 5, 6 and [4]PF₆ · 2CDCl₃ are reported in Table 4. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector operating at 50 kV and 30 mA, using Mo K_α radiation. An empirical correction was applied using SADABS [36]. The structure was solved by direct methods and refined by full-matrix least squares on *F*² using SHELXL97 [37]. The non-hydrogen atoms were subjected to anisotropic refinement, the disordered ones were split in two positions using distance and anisotropic displacement parameter restraints. Hydrogen atoms were added in calculated positions, which were not refined but continuously updated with respect to their carbon atoms, and were given a fixed isotropic thermal parameters.

4.12. NOE measurements

The ¹H-NOESY [38] NMR experiments were acquired by the standard three-pulse sequence or by the PFG version [39]. Two-dimensional ¹⁹F-¹H-HOESY NMR experiments were acquired using

Table 4
Crystal Data for 5, 6 and [4]PF₆ · 2CDCl₃

Compound	5	6	[4]PF ₆ · 2CDCl ₃
Formula	C ₁₄ H ₇₆ Ag ₄ I ₄ N ₁₂ O ₈	C ₂₂ H ₃₈ Ag ₄ I ₄ N ₆ O ₄	C ₁₈ H ₇₈ D ₂ Ag ₂ Cl ₁₂ F ₁₂ N ₁₂ O ₈ P ₂
Formula weight	1840.25	1389.66	1884.32
<i>T</i> (K)	296(2)	298(2)	298(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> 2(1)/ <i>n</i>
<i>a</i> (Å)	9.3688(15)	46.28(2)	12.2213(14)
<i>b</i> (Å)	10.5290(17)	4.513(2)	33.636(4)
<i>c</i> (Å)	16.916(3)	18.828(10)	19.440(2)
α (°)	101.691(2)	90	90
β (°)	91.257(2)	92.872(6)	90.113(2)
γ (°)	93.741(2)	90	90
Cell volume (Å ³)	1629.5(5)	3927(4)	7991.3(16)
<i>Z</i>	1	4	4
<i>D</i> _{calc} (g cm ⁻³)	1.875	2.350	1.566
μ (mm ⁻¹)	3.130	5.142	1.011
<i>F</i> (000)	888	2576	3808
Crystal size (mm)	0.15 × 0.10 × 0.08	0.12 × 0.12 × 0.08	0.25 × 0.25 × 0.10
θ Limits (°)	1.98–25.00	2.17–25.00	1.21–25.00
Index ranges	–11 ≤ <i>h</i> ≤ 11, –12 ≤ <i>k</i> ≤ 12, –20 ≤ <i>l</i> ≤ 20	–54 ≤ <i>h</i> ≤ 54, –5 ≤ <i>k</i> ≤ 5, –22 ≤ <i>l</i> ≤ 22	–14 ≤ <i>h</i> ≤ 14, –40 ≤ <i>k</i> ≤ 40, –23 ≤ <i>l</i> ≤ 23
Reflections collected	15604	17109	75615
Independent reflections [<i>R</i> _{int}]	5718 [0.0462]	3471 [0.0973]	14082 [0.0759]
Completeness to θ = 25.00° (%)	99.6	99.9	99.9
Data/restraints/parameters	5718/0/333	3474/216/264	14082/384/866
Goodness-of-fit on <i>F</i> ²	1.002	1.037	1.073
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.0441	0.0810	0.0549
<i>wR</i> ₂ (all data)	0.0900	0.2284	0.1695
Largest difference in peak and hole (e Å ⁻³)	0.684 and –0.611	1.805 and –1.570	0.855 and –0.696

the standard four-pulse sequence or the modified version [40]. The number of transients and the number of data points were chosen according to the sample concentration and to the desired final digital resolution. Semi-quantitative spectra were acquired using a 2 s relaxation delay and 800 ms mixing times.

4.13. PGSE measurements

All the PGSE NMR measurements were performed by using the standard stimulated echo pulse sequence [41] on a Bruker AVANCE DRX 400 spectrometer equipped with a GREAT 1/10 gradient unit and a QNP probe with a Z-gradient coil, at 296 K without spinning.

The dependence of the resonance intensity (I) on a constant waiting time and on a varied gradient strength (G) is described by Eq. (5):

$$\ln \frac{I}{I_0} = -(\gamma\delta)^2 D_t \left(\Delta - \frac{\delta}{3} \right) G^2 \quad (5)$$

where I = intensity of the observed spin echo, I_0 = intensity of the spin echo without gradients, D_t = diffusion coefficient, Δ = delay between the midpoints of the gradients, δ = length of the gradient pulse, and γ = magnetogyric ratio.

The shape of the gradients was rectangular, their duration (δ) was 4–5 ms, and their strength (G) was varied during the experiments. The semi-logarithmic plots of $\ln(I/I_0)$ versus G^2 were fitted using a standard linear regression algorithm and an R factor better than 0.99 was always obtained. Different values of Δ , “nt” (number of transients) and number of different gradient strengths (G) were used for different samples. The self-diffusion coefficient D_t , that is directly proportional to the slope of the regression line obtained by plotting $\ln(I/I_0)$ versus G^2 (Eq. (5)), was estimated by measuring the proportionality constant, using a sample of HDO (5%) in D_2O (known diffusion coefficient in the range 274–318 K) [42] in the same exact condition as the sample of interest using TMSS as internal standard. D_t data were treated as described in the literature [28]. The measurement uncertainty was estimated by determining the standard deviation of m by performing experiments with different Δ values. Standard propagation of error analysis yielded a standard deviation of approximately 3–4% in the hydrodynamic radius and 10% in the hydrodynamic volumes and aggregation numbers.

5. Supplementary material

CCDC 682762, 650792 and 650793 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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