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# Reactivity of a Super-Electron-Rich Olefin Derived from Cyclam

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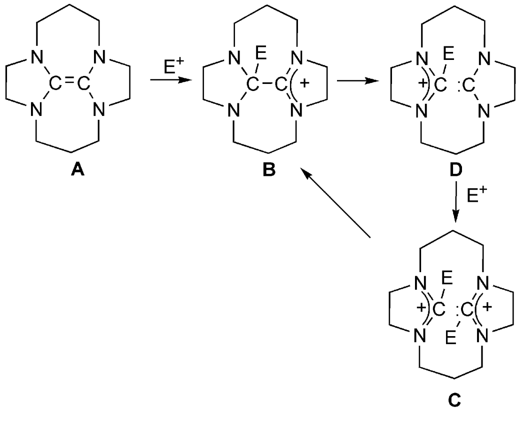
A series of new compounds has been synthesised from an electron-rich olefin derived from cyclam (**A**). Thus, **A** reacts with oxygen gas to give the *syn*-bis(urea) **1** and with sulfur to yield the *anti*-bis(thiourea) **2**. The reaction of **A** with triflic acid furnishes the bis(imidazolium) triflate **3**, which gives the monoprotonated imidazolium salt **4** upon treatment with sodium tetraphenylborate in water. Theoretical calculations (DFT) predict the diprotonated species to be energetically disfavoured, thus demonstrating the importance of hydrogen-bonding interactions. Treatment of compound **3** with silver oxide affords the di- and monoprotonated cationic salts **5a** and **5b** in THF and dichloromethane, respectively. The molecular structures of compounds **1**, **2**, **3**, **4**, **5a** and **5b** have been established by X-ray diffraction.

## Introduction

Enetetramines or electron-rich olefins (EROs) have been used as precursors for a large number of (N-heterocyclic carbene)metal (NHC–metal) complexes.[1] Their electron-richness confers on them a very high reactivity as strong nucleophiles, which assists in the preparation of numerous products by reaction, amongst others, with dioxygen, sulfur, water, aldehydes, alcohols and other protic compounds.[2] EROs have therefore been labelled as organic super-electron donors.[3] In this context, the first ionisation potential of $C_2(NMe_2)_4$ or $[C\{N(Me)CH_2\}_2]_2$ is around 6 eV (cf. $C_2H_4$: 10.5 eV).[4]

Imidazolium salts are convenient precursors for NHC–metal complexes as they can often be used under milder conditions than EROs. Such salts, which are also good sources of NHCs or NHC–Ag complexes, can be treated with $O_2$ or sulfur to yield ureas or thioureas, respectively.[5] These salts may form part of bi- or polydentate ligand–metal catalysts,[6] but they can also be effective as metal-free catalysts for processes including Diels–Alder or epoxide ring-opening reactions.[7]

The ERO **A** (Scheme 1), which is derived from cyclam (1,4,8,11-tetraazacyclotetradecane), can act not only as a neutral compound but also as a *C*,*C*′-chelating ligand (formally by insertion of a metal atom into the C=C bond).[8] Furthermore, it is a precursor for numerous cyclam derivatives of great value.[9] For example, in a preliminary communication, reference was made to the bis(urea) **1** (Scheme 2) and its 1:1 adduct with $ZnCl_2$.[8a]



Scheme 1.

The unimolecular dissociation of an ERO into two diaminocarbenes (e.g., imidazolidin-2-ylidenes) is unfavourable (but not impossible[10]), contrary to the situation with those EROs which have a certain degree of "aromaticity". To account for the reaction of an ERO with an electrophile ($E^+$), it has been proposed[11] (Scheme 1) that the reaction proceeds by attack of $E^+$ on the C–C bond of the ERO,

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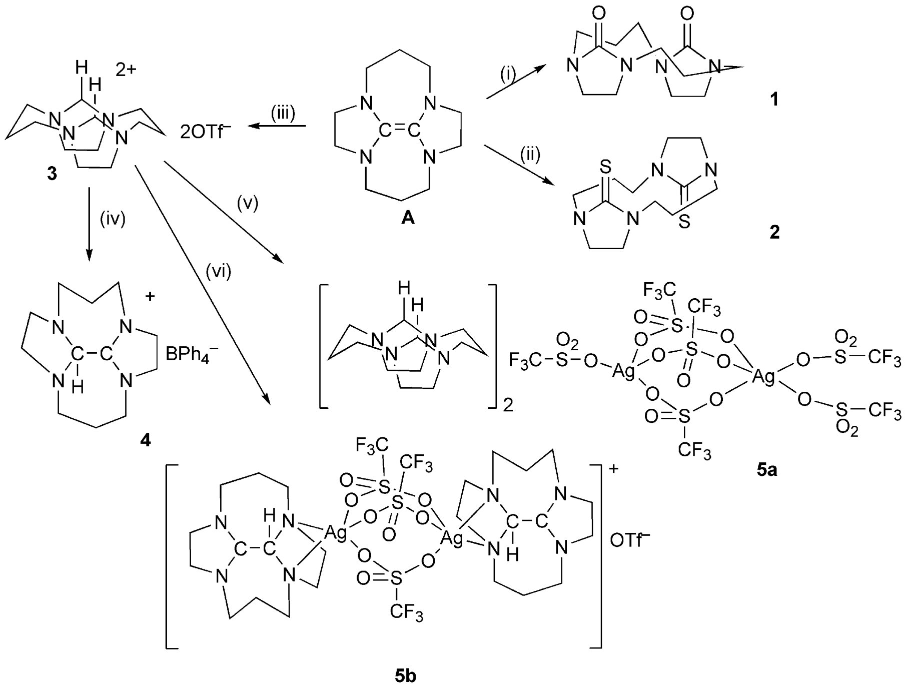


Scheme 2. Synthesis of compounds **1**–**5**. Reagents and conditions: (i) pentane, $O_2$, 25 °C; (ii) pentane, $S_8$, 25 °C; (iii) pentane, 2 equiv. HOTf, 25 °C; (iv) $H_2O$, $NaBPh_4$, 25 °C; (v) thf, $Ag_2O$, 25 °C, then reflux; (vi) dichloromethane, $Ag_2O$, 25 °C.

followed by C–C dissociation and further attack of $E^+$ on the dissociated carbene moiety. This is shown in Scheme 1 for **A** as the ERO.

## Results and Discussion

The aim of this work was to study the chemistry of the macrocyclic ERO **A** in more detail (cf. ref.[7a]) in order to exploit its potential as both a powerful electron donor and a precursor for a bis(carbene) ligand. Oxidative reactions of **A** leading to the derivatives **1**–**5** are depicted in Scheme 2.

Exposure of a pentane solution of **A** to dioxygen [(i) in Scheme 2] produced a yellow luminescence, which faded upon precipitation of the colourless bis(urea) **1**. Such behaviour is typical of the reaction of an ERO with air[12] and has been proposed as being due to the initial formation of an oxetane intermediate and its subsequent fragmentation. The crystalline compound **1**, which was obtained in excellent yield, was characterised by satisfactory microanalysis, IR [including the strong ν(C=O) absorption at 1713 $cm^{-1}$] and NMR spectroscopy (the $^1H$ spectrum shows the geminal methylene protons to be inequivalent), and finally by single-crystal X-ray diffraction.

The molecular structure of **1** is shown in Figure 1, and selected geometrical parameters are listed in Table 1. The C(1)=O(1) and C(7)=O(2) bonds are arranged in a *syn* configuration, and the O(1)···O(2) and C(1)···C(7) distances are 2.967(2) and 3.131(2) Å, respectively. The almost parallel five-membered rings [dihedral angle: 16.53(7)°] are not eclipsed, possibly due to O/O repulsion,[13] which may also be responsible for this compound not inverting to the *anti* isomer. However, the latter was obtained by carbonylative cyclisation from cyclam; this reaction afforded the five- and six-membered cyclic urea units bridged through nitrogen atoms by two and three methylene units, respectively. Computational studies have concluded that the macrocycles containing two five-membered urea units are 4.7 kcal$mol^{-1}$ more stable and that the *syn* isomer is only about 1 kcal$mol^{-1}$ less stable than the *anti* isomer, with an activation energy of 32.7 kcal $mol^{-1}$ for the *syn* → *anti* conversion.[14]

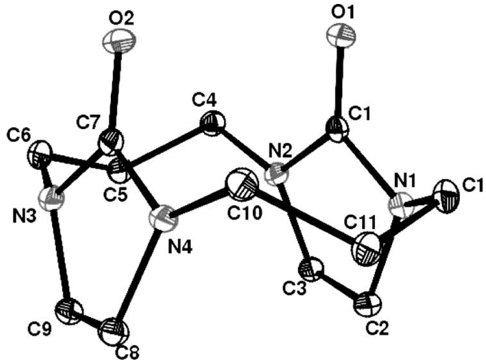


Figure 1. ORTEP drawing of bis(urea) **1** with thermal ellipsoids shown at 30% probability.

Imidazolidin-2-thiones are of interest because of their numerous potential applications and also as a source of NHCs upon reductive desulfurisation. They are generally prepared from EROs or NHCs,[15] imidazolium halides,[5b] cyclic formaldehyde aminals,[16] and NHC–Ag complexes. Consistent with the unsaturated nature of EROs and their high nucleophilicity, **A** reacts instantly with sulfur in toluene to afford the bis(thiourea) **2** [(ii) in Scheme 2]. Crystal-

Table 1. Selected bond lengths [Å] and angles [°] for **1** and **2**.[a]

| 1 | | 2 | |
|---|---|---|---|
| Bond lengths | | | |
| O1–C1 | 1.226(2) | S1–C1 | 1.671(3) |
| O2–C7 | 1.226(2) | | |
| N1–C1 | 1.386(2) | N1–C1 | 1.348(3) |
| N2–C1 | 1.365(2) | N2–C1 | 1.349(3) |
| N3–C7 | 1.378(2) | | |
| N4–C7 | 1.367(2) | | |
| N1–C2 | 1.462(2) | N1–C3 | 1.449(3) |
| N2–C3 | 1.457(2) | N2–C2 | 1.455(3) |
| N3–C9 | 1.462(2) | | |
| N4–C8 | 1.459(2) | | |
| C2–C3 | 1.521(2) | C2–C3 | 1.520(4) |
| C8–C9 | 1.526(2) | | |
| O1–O2 | 2.967(2) | | |
| C4–C5 | 1.530(2) | C4–C5 | 1.519(4) |
| C5–C6 | 1.531(2) | C5–C6 | 1.539(4) |
| C4–N2 | 1.453(2) | C4–N1 | 1.459(3) |
| C6–N3 | 1.459(2) | C6–N2$^{a}$ | 1.451(3) |
| C11–C12 | 1.527(2) | | |
| C11–C10 | 1.527(2) | | |
| C10–N4 | 1.453(2) | | |
| C12–N1 | 1.459(2) | | |
| Bond angles | | | |
| N1–C1–N2 | 108.3(1) | N1–C1–N2 | 108.2(2) |
| C1–N1–C2 | 109.3(1) | C1–N1–C3 | 112.6(2) |
| C1–N2–C3 | 110.1(1) | C1–N2–C2 | 112.7(2) |
| N1–C2–C3 | 102.5(1) | N1–C3–C2 | 103.0(2) |
| N2–C3–C2 | 101.3(1) | N2–C2–C3 | 103.2(2) |
| N3–C7–N4 | 108.5(1) | C1–N1–C4 | 125.4(2) |
| C7–N3–C9 | 109.8(1) | C4–C5–C6 | 118.8(2) |
| C7–N4–C8 | 110.3(1) | N2$^{a}$–C6–C5 | 112.7(2) |
| N3–C9–C8 | 102.5(1) | C1–N2–C6$^{a}$ | 126.1(2) |
| N4–C8–C9 | 101.6(1) | C1–N1–C4 | 125.4(2) |
| C4–C5–C6 | 116.5(1) | | |
| C5–C4–N2 | 113.1(1) | | |
| C10–C11–C12 | 117.4(1) | | |
| C11–C10–N4 | 113.3(1) | | |

[a] Symmetry transformations used to generate equivalent atoms: $^{a}$: $-x$, $-y$, $-z + 1$.

line, colourless **2** was obtained in good yield and was characterised by satisfactory microanalysis, IR and NMR spectroscopy (the $^{1}H$ NMR spectrum shows the geminal methylene protons to be inequivalent), and ultimately by single-crystal X-ray diffraction.

The molecular structure of the crystalline centrosymmetric bis(thiourea) **2** is illustrated in Figure 2, and selected geometrical parameters are listed in Table 1. The mutually parallel five-membered ring thioureas are arranged in an *anti* orientation, and the C1–S1, C1–N1, and C1–N2 distances are appropriate for a thiourea.[17]

Treatment of a pentane solution of **A** with triflic acid eventually furnished the bis(dihydroimidazolium) triflate **3** in excellent yield [(iii) in Scheme 2]. It was crystallised from dichloromethane/hexane and characterised by satisfactory microanalysis, IR (cf. ref.[18] for [OTf]$^{-}$ data) and NMR spectroscopy (including a resonance at $\delta$ = 5.49 ppm, assigned to the iminium protons), and finally by single-crystal X-ray diffraction.

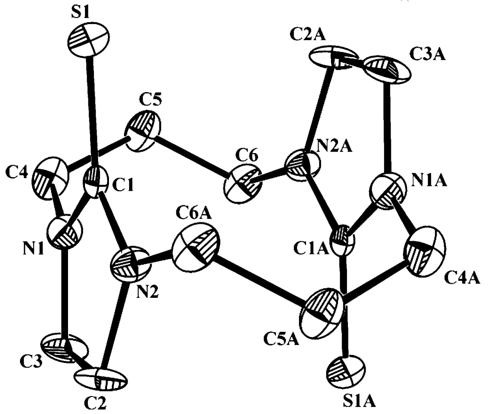


Figure 2. ORTEP drawing of bis(thiourea) **2** with thermal ellipsoids shown at 30% probability.

The molecular structure of the cation of **3** is shown in Figure 3, and selected geometrical parameters are listed in Table 2. The two almost eclipsed (dihedral angle: 27.90°) dihydroimidazolium rings are bridged through their nitrogen atoms by a pair of $(CH_2)_3$ units, and are aligned in a *syn* arrangement [evidently the *syn* → *anti* inversion is not favoured, as in the bis(benzoimidazolium) analogues[13]]. The endocyclic N–C–N angles are unexceptional for dihydroimidazolium rings, and the corresponding average C–N (1.31 Å) and C–C (1.515 Å) bond lengths are appropriate for their C–N multiple- and C–C single-bond character, respectively.

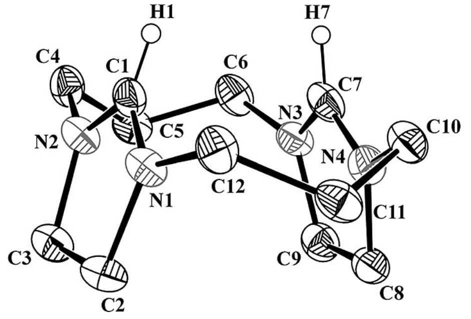


Figure 3. ORTEP drawing of bis(imidazolium) triflate **3** with thermal ellipsoids shown at 30% probability.

Addition of an excess of an aqueous solution of sodium tetraphenylborate to compound **3** instantly led to the precipitation of colourless tetrahydrobis(imidazolium) tetraphenylborate (**4**) in good yield [(iv) in Scheme 2]. Crystallisation from acetone/diethyl ether produced X-ray quality crystals. The isolation of the monocationic salt **4** is of interest as it provides, for the case where the ERO is **A**, evidence for the formerly only postulated[19] initially formed product of electrophilic attack at an ERO (cf. Scheme 1). Whereas this reaction is unusual, it has previously been suggested that a salt containing a $[BPh_4]$ anion might react with a protic compound with elimination of $BPh_3$ and $C_6H_6$.[20] In the present experiment, no attempt was made to determine whether these were the co-products of **4**. Compound **4** gave satisfactory microanalysis and IR and NMR spectra.

Table 2. Selected bond lengths [Å] and angles [°] for **3** and **4**.

| 3 | | 4 | |
|---|---|---|---|
| Bond lengths | | | |
| N1–C1 | 1.287(9) | N3–C7 | 1.322(5) |
| N2–C1 | 1.334(8) | N4–C7 | 1.333(5) |
| N3–C7 | 1.300(8) | N1–C1 | 1.461(5) |
| N4–C7 | 1.291(9) | N2–C1 | 1.436(5) |
| N1–C2 | 1.486(7) | N3–C8 | 1.477(5) |
| N2–C3 | 1.472(8) | N4–C9 | 1.468(4) |
| N4–C8 | 1.476(8) | N1–C2 | 1.470(5) |
| N3–C9 | 1.473(8) | N2–C3 | 1.467(5) |
| C2–C3 | 1.539(9) | C8–C9 | 1.513(6) |
| C8–C9 | 1.532(9) | C2–C3 | 1.474(7) |
| C11–C10 | 1.527(8) | C1–C7 | 1.520(5) |
| C11–C12 | 1.545(9) | | |
| N1–C12 | 1.463(7) | | |
| N4–C10 | 1.471(7) | | |
| C5–C4 | 1.535(9) | | |
| C5–C6 | 1.530(9) | | |
| N2–C4 | 1.458(8) | | |
| N3–C6 | 1.457(9) | | |
| Bond angles | | | |
| N1–C1–N2 | 114.9(7) | C7–N3–C8 | 111.4(3) |
| C1–N2–C3 | 108.9(6) | C7–N4–C9 | 111.1(3) |
| C1–N1–C2 | 109.7(5) | N3–C8–C9 | 102.8(3) |
| N1–C2–C3 | 102.9(5) | N4–C9–C8 | 103.4(3) |
| N2–C3–C2 | 103.1(5) | N1–C1–N2 | 105.0(3) |
| N3–C7–N4 | 117.1(7) | C1–N1–C2 | 105.9(4) |
| C7–N3–C9 | 107.9(6) | C1–N2–C3 | 107.0(3) |
| C7–N4–C8 | 108.3(5) | N1–C2–C3 | 106.7(4) |
| N3–C9–C8 | 103.6(5) | N2–C3–C2 | 105.9(4) |
| N4–C8–C9 | 103.0(5) | C1–N2–C4 | 114.6(3) |
| C7–N3–C6 | 127.8(7) | C1–N1–C12 | 113.7(3) |
| N4–C10–C11 | 112.7(5) | N2–C4–C5 | 112.0(3) |
| C10–C11–C12 | 115.4(6) | C4–C5–C6 | 112.7(3) |
| C1–N1–C12 | 125.6(6) | C5–C6–N4 | 113.4(4) |
| C3–N2–C4 | 123.3(5) | C7–N4–C6 | 129.5(3) |
| C6–N3–C9 | 123.4(5) | C7–C1–N2 | 109.8(4) |
| N3–C7–N4 | 110.9(3) | C7–N3–C10 | 128.5(4) |

The molecular structure of the cation of crystalline **4** is shown in Figure 4, and selected geometrical parameters are listed in Table 2. The most significant feature is the presence (unlike in its dianionic precursor **3**) of a transannular C–C single bond [C1–C7 1.500(5) Å] joining the two five-membered rings. The average C–N endocyclic five-membered ring bond lengths are 1.448 and 1.327 Å for the C1-hydrogenated ring and its C7 cationic neighbour, respectively, whereas the endocyclic N–C–N bond angles are 105.1° at C1 and 110.9° at C7. The torsion angle between the two rings is 140.8(2)°.

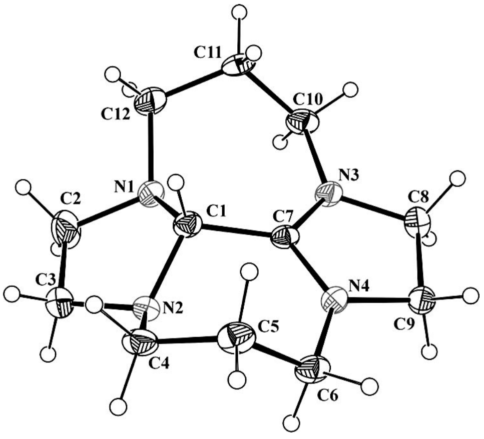
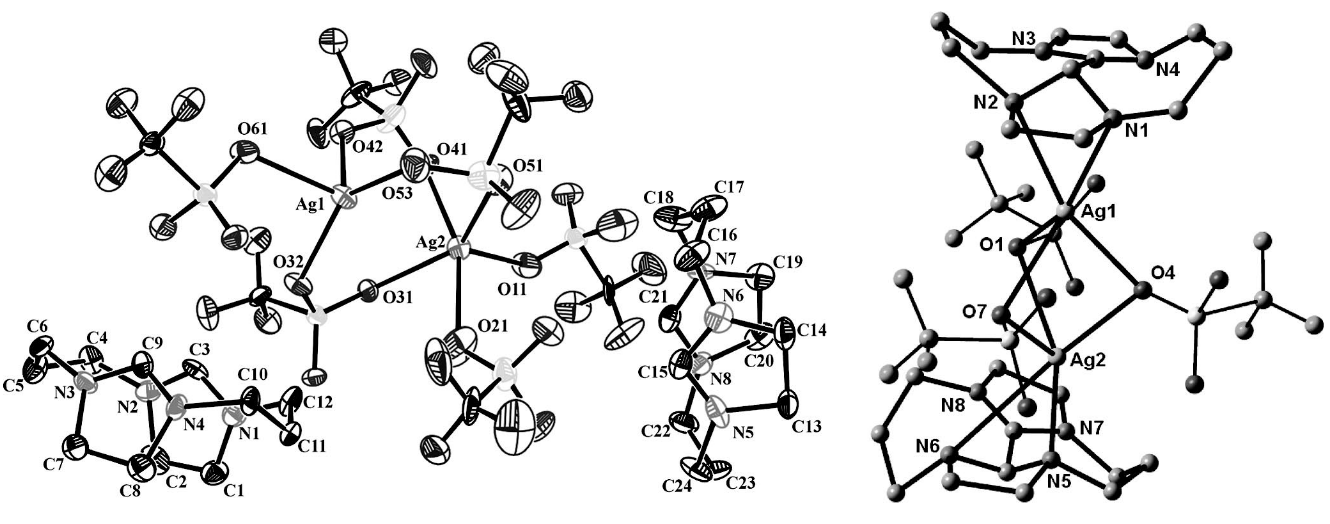


Figure 4. ORTEP drawing of the imidazolium tetraphenylborate **4** with thermal ellipsoids shown at 30% probability.

The crystalline, light-sensitive complex bis[bis(dihydroimidazolium) hexa(trifluoromethylsulfonato)]diargentate (**5a**) was prepared from **3** and $Ag_2O$ by heating under reflux in THF and crystallisation from THF/hexane [(v) in Scheme 2]. It failed to give satisfactory C, H, N microanalysis, but subsequent characterisation by IR and NMR spec-



(a) (b)

Figure 5. (a) ORTEP drawing of bis(imidazolinium) $[Ag_2(OTf)_6]^{4-}$ **5a** with thermal ellipsoids shown at 30% probability. (b) Molecular diagram of the cation of **5b**.

troscopy and finally by single-crystal X-ray diffraction confirmed its structure. The formation of **5a** was particularly unexpected, since earlier studies on the reaction of an imidazolium (such as permethylimidazolium or 1,3-diethyl-4,5-benzimidazolium) hexafluorophosphate with $Ag_2O$ yielded the corresponding NHC salt $[Ag(NHC)_2][PF_6]$.[6a,21] The molecular structure of **5a** (illustrated in Figure 5) consists of two bis(imidazolinium) cations and the anion $[Ag_2(OTf)_6]^{4-}$, in which two inequivalent silver atoms with one and two $\kappa^1$-$O_3SCF_3$ ligands respectively, are bridged by three $\mu^2$-$\kappa^3$-triflate groups. Some selected geometric data are found in Table 3.

Table 3. Selected bond lengths [Å] and angles [°] for **5a**.

| Bond lengths | | | |
|---|---|---|---|
| N1–C3 | 1.31(2) | Ag1–Ag2 | 3.364(2) |
| N2–C3 | 1.30(2) | Ag1–O61 | 2.48(1) |
| N1–C1 | 1.42(2) | Ag1–O32 | 2.313(8) |
| N2–C2 | 1.51(2) | Ag1–O53 | 2.27(1) |
| C1–C2 | 1.42(2) | Ag1–O42 | 2.392(9) |
| N3–C9 | 1.29(2) | Ag2–O11 | 2.34(1) |
| N4–C9 | 1.26(2) | Ag2–O21 | 2.57(2) |
| N3–C7 | 1.44(2) | Ag2–O31 | 2.426(9) |
| N4–C8 | 1.42(2) | Ag2–O41 | 2.47(1) |
| C7–C8 | 1.52(2) | Ag2–O51 | 2.38(1) |
| N1–C12 | 1.45(2) | | |
| C11–C12 | 1.55(2) | | |
| C10–C11 | 1.49(2) | | |
| N4–C10 | 1.52(2) | | |
| N2–C4 | 1.46(2) | | |
| C4–C5 | 1.52(2) | | |
| C5–C6 | 1.49(2) | | |
| N3–C6 | 1.45(2) | | |
| **Bond angles** | | | |
| N1–C3–N2 | 111(1) | C8–N4–C9 | 111(1) |
| C3–N2–C2 | 107(1) | C3–N2–C4 | 127(1) |
| N2–C2–C1 | 105(1) | N2–C4–C5 | 118(1) |
| C2–C1–N1 | 103(1) | C5–C6–N3 | 117(1) |
| N3–C9–N4 | 117(1) | C6–N3–C9 | 128(1) |
| C9–N3–C7 | 105(1) | O11–Ag2–O21 | 103.5(5) |
| N3–C7–C8 | 106(1) | | |
| N4–C8–C7 | 100(1) | | |

As the nature of (carbene)silver complexes[22] is sometimes dependent on the solvent used in their synthesis,[22b] the preparation of **5** was carried out in different solvents. Performing the reaction in dichloromethane at room temperature [(vi) in Scheme 2] afforded a colourless, light-sensitive crystalline solid (**5b**) in excellent yield (80%), which was characterised by satisfactory microanalysis, IR and NMR spectroscopy, and by single-crystal X-ray diffraction. The molecular structure of the cation of **5b** is depicted in Figure 5b. The formation of **5b** is also (like that of **5a**) unusual, and instead of being a (carbene)silver compound, two silver atoms, bridged by three bidentate triflate ligands, are coordinated to two nitrogen atoms of the "protonated five-membered ring" of the bis(imidazolium) cation with a nonbonding silver–silver distance of 3.416 Å.[23] The charge of the monocationic entity is complemented by the solvent-separated triflate ion.

## Computational Study

In order to rationalise the varied reactivity patterns that led to the isolation of the mono- or diprotonated compounds under different reaction conditions, as well as to try to ascertain the feasibility of the carbenic intermediate proposed in the Wanzlick reaction scheme (Scheme 1), we undertook a computational study of species **A**–**D** with $E^+ = H^+$, based on density functional theory (DFT). The results of this study are presented below.

### *Geometry Optimisation of A, B and C*

These three species were found to correspond to energy minima on the potential energy surface; the corresponding atomic coordinates are provided as Supporting Information. The optimised structure of **B** is very similar to those of the cations in the experimental structures of **4** and **5b**. Similarly, the optimized geometry of **C** is very close to the experimental structures of **3** and **5a**. In both cases, the tricoordinated carbon atoms appear in perfectly planar conformations, as appropriate for the diazaallyl nature of the $N_2C$ fragment(s). The central C–C bond length in **B** (1.54 Å) is in good agreement with the experimental value in **4** and indicative of its single-bond character. It should also be noted that the added positive charge in the monoprotonated form **B** is transferred mostly (57%) to the allylic NCN group, according to the qualitative expectations of the Lewis structure **B** (Scheme 1).

The structure of ERO **A**, which has not so far been experimentally determined, is shown in Figure 6, and the most relevant bonding parameters are given in Table 4. It should be noted that the central carbon atoms are in a perfectly planar environment, the sum of their bond angles being 360°. The C=C and C–N bond lengths of the central unit [1.34(2) and 1.43(2) Å, respectively] are in excellent agreement with the experimental values in related com-

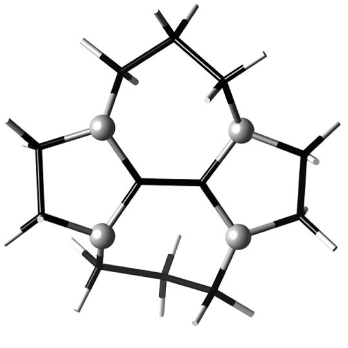


Figure 6. Optimized structure of the electron-rich olefin **A**.

Table 4. Selected bonding parameters for the optimised structure of **A**.

| Bond lengths [Å] | | Bond angles [°] | | Torsion angle [°] | |
|---|---|---|---|---|---|
| C=C | 1.348 | C–C–N | 125.8 | N–C–C–N | 0.7 |
| C–N | 1.432 | N–C–N | 108.5 | | |

pounds having a 2,2′-bis(imidazolidinylidene) unit [i.e., **A** devoid of the $(CH_2)_3$ bridges between the nitrogen atoms].[24]

Attempts to optimise the carbene structure **D** were unsuccessful, and we were unable to characterise that species either as an intermediate or as a transition state. Attempts to optimise it starting from the geometry of **C** with one deprotonated carbon atom gave the form **B**, both in the singlet and triplet states (with the triplet some 69 kcal mol$^{-1}$ higher in energy).

### *Energetics of the Protonation Reactions*

To understand the formation of the mono- and diprotonated species it is necessary to consider the acid/base reactions shown in Equations (1), (2), and (3). Because of the charge separation in these reactions, the cation–anion interactions are expected to strongly favour the reverse reactions, as actually found in our calculations for the gas phase when BaseH = triflic acid. Such calculations taking into account the presence of polar solvents (dichloromethane, THF or water) yielded stable ionic forms and gave negative reaction enthalpies for the first protonation step [Equation (1)]. However, the second protonation step [Equation (2)] was found to be energetically uphill (by roughly 1 kcal mol$^{-1}$ in THF and by 70 kcal mol$^{-1}$ in an alkane), in apparent disagreement with the fact that species **C** has been isolated in pentane as the salt **3** and that no monoprotonated species was formed in that solvent.

$$\mathbf{A} + \text{BaseH} \rightarrow \mathbf{A}\text{H}^+ + \text{Base}^- \quad (1)$$

$$\mathbf{A}\text{H}^+ + \text{BaseH} \rightarrow \mathbf{A}\text{H}_2^{2+} + \text{Base}^- \quad (2)$$

$$\mathbf{A} + 2\ \text{BaseH} \rightarrow \mathbf{A}\text{H}_2^{2+} + 2\ \text{Base}^- \quad (3)$$

This inconsistency suggests that the cation–anion interaction, which is neglected in our calculations, could be playing a non-negligible role in stabilising the dication **C**. A closer inspection of the crystal structure of compound **3** revealed the presence of hydrogen-bonding interactions between the cation **C** and the triflate anions (Figure 7). Thus, two oxygen atoms of one of the neighbouring triflate anions form O···H–C hydrogen bonds (2.47 Å). The second triflate ion forms O···H–C interactions between one oxygen atom and two imidazolidinyl hydrogen atoms (2.34 and 2.56 Å). If the formation of any of these two ionic pairs is taken into account in the calculations, the formation reaction of the dicationic species **C** [Equation (3)] is found to be exothermic in the gas phase as well as in a non-polar solvent (by more than 80 kcal mol$^{-1}$), in agreement with its isolation under the experimental conditions of reaction (iii) in Scheme 2, even if these interactions are overestimated because of the shorter intermolecular distances in the optimised structures compared to the experimental ones. If the ionic interaction of the dication with a triflate anion is a driving force for the stabilisation of such a species, it is likely that these hydrogen bonds are also present in **5a**. Revisiting that structure, we find that one triflate ion indeed has two short C–H···O contacts (2.32 and 2.39 Å; Figure 8).

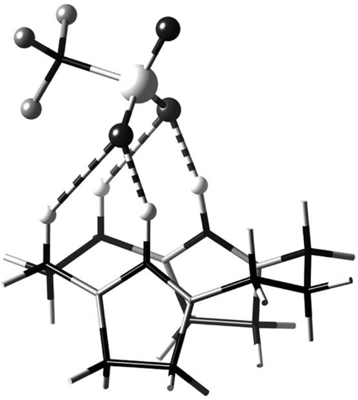


Figure 8. Optimised structure of a **C** triflate ion pair showing the two short C–H···O hydrogen bonds (dotted lines).

## Conclusions

The reaction of an electron-rich olefin derived from cyclam with HOTf has led to the isolation of bis(imidazolium) derivatives **3** and **5a**. The monoprotonated cation was isolated as **4** with tetraphenylborate as counterion. Our DFT

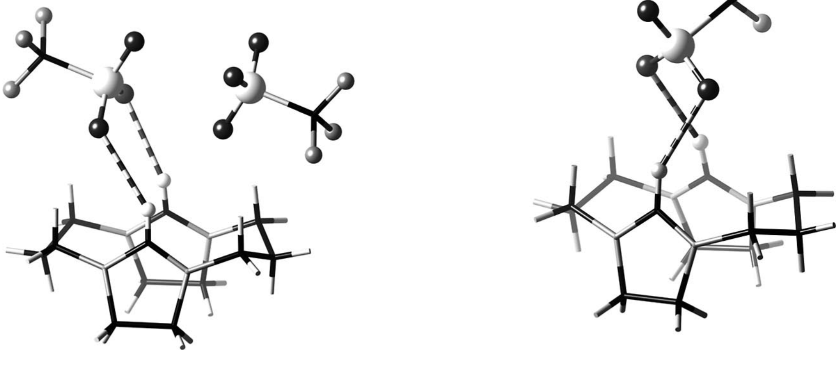


Figure 7. Hydrogen-bonding interactions (dotted lines) between dication **C** and the triflate anions in the crystal structure of compounds **3** (left) and **5a** (right).

calculations do not support the existence of a monoprotonated intermediate or transition state with a carbene function. Calculations also indicate that protonation of the electron-rich olefin is disfavoured in apolar solvents. However, the dicarbocationic species was isolated as **3** from alkane solutions due to C–H···O hydrogen-bonding interactions with the triflate counterion. Reaction of the bis(imidazolium) derivative with silver oxide led to the isolation of two different silver triflate complexes (**5a** and **5b**) depending on the nature of the solvent.

## Experimental Section

**General Procedures:** The preparation and handling of the compounds described here was performed with rigorous exclusion of air and moisture under dinitrogen by using standard vacuum-line and Schlenk techniques. All solvents were dried and distilled under dinitrogen. The ERO **A** was prepared according to a literature procedure.[8a] The commercially available compounds cyclam, $Ag_2O$, HOTf and $NaBPh_4$ were used as received from Aldrich. IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer as KBr pellets. $^1H$ and $^{13}C$ NMR spectra were recorded with a Varian Mercury 200 or a Bruker Avance 400 Fourier spectrometer. Trace amounts of protonated solvents were used as references, and chemical shifts ($\delta$) are reported in units of parts per million relative to $SiMe_4$.

**Synthesis of 1:** Dry dioxygen was bubbled through a solution of **A** (0.205 g, 0.926 mmol) in pentane (20 mL) for about 5 min. After the initial yellow chemiluminescence had faded, a white precipitate appeared. The mixture was stirred at room temperature for 30 min, then the mixture was filtered to afford the white solid **1** (0.200 g, 85%), which was crystallised from dichloromethane and ethanol. IR (KBr): $\tilde{\nu}$ = 2948 (m), 2914 (m), 2845 (m), 1713 (vs), 1668 (s), 1498 (s), 1454 (s), 1435 (s), 1263 (vs), 1207 (m), 1042 (s), 768 (w), 742 (m) $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 293 K): $\delta$ = 1.28 (m, 2 H, $CH_2$), 2.08 (m, 2 H, $CH_2$), 2.84 (m, 2 H, $CH_2N$), 2.91 (m, 2 H, $CH_2N$), 3.11 (m, 4 H, $CH_2N$), 3.40 (m, 4 H, $CH_2N$), 4.13 (m, 4 H, $CH_2N$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): $\delta$ = 21.9 (s, $CH_2$), 41.8 (s, $CH_2N$), 43.5 (s, $CH_2N$), 160.6 (s, $C$=O) ppm. $C_{12}H_{20}N_4O_2$ (252.32): calcd. C 57.12, H 7.99, N 22.20; found C 55.9, H 8.06, N 21.55.

**Synthesis of 2:** A suspension of sulfur (0.016 g, 0.486 mmol) in toluene was added to a solution of **A** (0.052 g, 0.243 mmol) in toluene (5 mL). A dark pink precipitate was inmediately formed. The suspension was stirred at room temperature for 2 h, then concentrated to dryness, and dichloromethane (10 mL) was added. The mixture was then filtered. Addition of hexane (3 mL) to the filtrate and cooling to –30 °C gave the white crystalline solid **2** (0.040 g, 60%). IR (KBr): $\tilde{\nu}$ = 2973 (vw), 2936 (vw), 2917 (m), 2876 (m), 2847 (w), 1508 (vs), 1489 (vs), 1453 (s), 1418 (s), 1373 (m), 1353 (m), 1326 (s), 1301 (s), 1284 (s), 1258 (s), 1232 (m), 1097 (m), 966 (w), 625 (m) 537 (w) $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 293 K): $\delta$ = 2.25 (m, 4 H, $CH_2$), 3.06 (m, 4 H, $CH_2N$), 3.34 (m, 4 H, $CH_2N$), 4.31 (m, 4 H, $CH_2N$), 4.51 (m, 4 H, $CH_2N$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): $\delta$ = 21.3 (s, $CH_2$), 45.6 (s, $CH_2N$), 48.5 (s, $CH_2N$), 182.8 (s, $C$=S) ppm. $C_{12}H_{20}N_4S_2$ (284.44): calcd. C 50.67, H 7.08, N 19.69, S 22.54; found C 50.5, H 7.08, N 19.67, S 22.03.

**Synthesis of 3:** Triflic acid (0.0157 mL, 1.78 mmol) was added to a solution of **A** (0.198 g, 0.891 mmol) in pentane (5 mL). A gelatinous precipitate was formed. The suspension was stirred at room temperature for 2 h, then concentrated to dryness. Addition of diethyl ether (20 mL) gave a white solid, which was partially dissolved in dichloromethane. Addition of hexane to the filtrate yielded white crystals of **3** (0.371 g, 80%), which were filtered off, washed with hexane and dried under vacuum. The sparingly soluble white solid was very hygroscopic. IR (KBr): $\tilde{\nu}$ = 2957 (vw), 2881 (vw), 2812 (vw), 1612 (s), 1295 (s), 1268 (vs), 1223 (m), 1156 (s), 1143 (s), 1032 (s), 638 (s) 516 (w) $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 293 K): $\delta$ = 2.24 (m, 2 H, $CH_2$), 2.30 (m, 2 H, $CH_2$), 3.35 (m, 2 H, $CH_2N$), 3.49 (m, 4 H, $CH_2N$), 3.73 (m, 2 H, $CH_2N$), 3.80 (m, 2 H, $CH_2N$), 3.87 (m, 2 H, $CH_2N$), 4.05 (m, 2 H, $CH_2N$), 4.22 (m, 2 H, $CH_2N$), 5.49 (s, 1 H, CH), 8.29 (br., 1 H, HOTf) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): $\delta$ = 24.3 (s, $CH_2$), 46.3 (s, $CH_2N$), 52.2 (s, $CH_2N$), 78.7 (s, CH), 120.3 (q, $^1J_{C,F}$ = 319.2 Hz, $CF_3$), 160.1 (s, CH$C$N) ppm. $C_{14}H_{22}F_6N_4O_6S_2$ (520.47): calcd. C 32.3, H 4.26, N 10.76; found C 32.4, H 4.38, N 11.02.

**Synthesis of 4:** A solution of $NaBPh_4$ (0.150 g, o.436 mmol) in water (15 mL) was added to a solution of **3** (0.0873 g, 0.167 mmol) in water (3 mL). A precipitate formed immediately, then the suspension was stirred at room temperature for 1 h and filtered. The white precipitate of **4** (0.077 g, 85%) was washed with water and dried under vacuum. An acetone/diethyl ether solution of **4** at –30 °C afforded white crystals suitable for an X-ray diffraction study. IR (KBr): $\tilde{\nu}$ = 3052 (m), 3009 (m), 2996 (m) 2930 (w), 2834 (w), 1661 (w), 1602 (s), 1579 (m), 1559 (w), 1477 (m), 1423 (w), 1296 (m), 1223 (w), 733 (s), 706 (vs), 612 (m) $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 293 K): $\delta$ = 1.69 (m, 2 H, $CH_2$), 1.99 (m, 2 H, $CH_2$), 2.68 (m, 4 H, $CH_2N$), 2.90 (m, 2 H, $CH_2N$), 3.01 (m, 2 H, $CH_2N$), 3.11 (m, 2 H, $CH_2N$), 3.25 (m, 4 H, $CH_2N$), 3.39 (m, 2 H, $CH_2N$), 3.86 (s, 1 H, CH), 6.92 (m, 4 H, Ar), 7.06 (m, 8 H, Ar), 7.38 (m, 8 H, Ar) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): $\delta$ = 26.5 (s, $CH_2$), 47.2 (s, $CH_2N$), 51.1 (s, $CH_2N$), 51.6 (s, $CH_2N$), 52.4 (s, $CH_2N$), 78.3 (s, CH), 121.8 (s, Ar), 125.7 (s, Ar), 135.9 (s, Ar), 163.9 ($^1J_{C,B}$ = 49.31 Hz, $Ar_{ipso}$), 167.3 (s, CH$C$N) ppm. $C_{36}H_{41}BN_4$ (540.56): calcd. C 79.99, H 7.64, N 10.36; found C 79.2, H 7.72, N 9.88.

**Synthesis of 5a:** $Ag_2O$ (0.094 g, 0.405 mmol) was added to a solution of **3** (0.2092 g, 0.402 mmol) in THF (30 mL). The suspension, protected from light, was refluxed for 2 h, then filtered. The volume of the filtrate was reduced to about 10 mL, and hexane (3 mL) was added. Upon cooling the solution to –30 °C, white crystals of **5a** (0.083 g, 40%) were obtained. IR (KBr): $\tilde{\nu}$ = 2950 (vw), 2835 (vw), 1712 (w), 1663 (w), 1610 (m), 1505 (vw), 1463 (vw), 1261 (vs), 1233 (s, sh), 1167 (s), 1032 (s), 657 (m, sh), 639 (s), 575 (w), 518 (w) $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 293 K): $\delta$ = 2.13 (m, 4 H, $CH_2$), 2.93 (m, 2 H, $CH_2N$), 3.26 (m, 4 H, $CH_2N$), 3.60 (m, 4 H, $CH_2N$), 3.98 (m, 2 H, $CH_2N$), 4.15 (m, 4 H, $CH_2N$), 11.13 (s, 2 H, CHN) ppm. $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 293 K): $\delta$ = 28.7 (s, $CH_2$), 43.1 (s, $CH_2N$), 45.0 (s, $CH_2N$), 49.5 (s), 54.8 (s), 83.5 (s, CH), 122.4 (q, $^1J_{C,F}$ = 319.7 Hz, $CF_3$), 163.4 (s, CHN), 168.7 (s) ppm. $C_{30}H_{44}Ag_2F_{18}N_8O_{18}S_6$ (1554.8): calcd. C 23.17, H 2.85, N 7.20.

**Synthesis of 5b:** $Ag_2O$ (0.134 g, 0.578 mmol) was added to a solution of **3** (0.299 g, 0.574 mmol) in dichloromethane (20 mL). The suspension, protected from light, was stirred for 24 h, then the resulting black-brown solid was filtered off. The volume of the colourless filtrate was reduced to about 10 mL, then hexane (10 mL) was added. Upon cooling at –30 °C, white crystals of **5b** (0.270 g, 75%) were obtained. IR (KBr): $\tilde{\nu}$ = 2950 (vw), 2835 (vw), 1663 (w), 1609 (m), 1456 (vw), 1265 (vs), 1226 (s, sh), 1161 (s), 1146 (s, sh), 1032 (s), 638 (m, sh), 573 (w), 518 (w) $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 293 K): $\delta$ = 2.07 (m, 2 H, $CH_2$), 2.17 (m, 2 H, $CH_2$), 2.87 (m, 4 H, $CH_2N$), 3.28 (m, 2 H, $CH_2N$), 3.46 (m, 2 H, $CH_2N$), 3.66 (m, 2 H, $CH_2N$), 3.78 (m, 2 H, $CH_2N$), 3.90 (m, 2 H, $CH_2N$), 4.15 (m, 2 H, $CH_2N$), 4.21 (s, 1 H, CH) ppm. $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 293 K): $\delta$ = 26.7 (s, $CH_2$), 47.6 (s, $CH_2N$), 52.0 (s, $CH_2N$), 81.0

Table 5. Crystal data and structure refinement for **1**–**4** and **5a**.

| | **1** | **2** | **3** | **4** | **5a** |
|---|---|---|---|---|---|
| Empirical formula | $C_{12}H_{20}N_4O_2$ | $C_{12}H_{20}N_4S_2$ | $C_{14}H_{22}F_6N_4O_6S_2$ | $C_{36}H_{41}BN_4$ | $C_{15}H_{22}AgF_9N_4O_9S_3$ |
| Formula mass | 252.32 | 284.44 | 520.47 | 540.56 | 777.40 |
| $T$ [K] | 160(2) | 250(2) | 180(2) | 180(2) | 180(2) |
| $\lambda$ [Å] | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | monoclinic | monoclinic | triclinic | triclinic | orthorhombic |
| Space group | $P2_1/c$ | $P2_1/c$ | $P\bar{1}$ | $P\bar{1}$ | $P2_12_12_1$ |
| $a$ [Å] | 7.6941(9) | 6.923(2) | 8.180(3) | 11.472(4) | 12.203(2) |
| $b$ [Å] | 13.256(1) | 11.263(4) | 11.485(4) | 12.029(4) | 12.905(2) |
| $c$ [Å] | 11.988(1) | 8.676(3) | 12.069(4) | 12.338(4) | 33.656(5) |
| $\alpha$ [°] | | | 104.297(4) | 73.504(5) | |
| $\beta$ [°] | 94.272(2) | 104.067(5) | 98.176(5) | 67.543(5) | |
| $\gamma$ [°] | | | 104.441(4) | 71.521(5) | |
| $V$ [Å$^3$] | 1219.2(2) | 656.2(4) | 1038.7(6) | 1466.2(8) | 5300(1) |
| $Z$ | 4 | 2 | 2 | 2 | 8 |
| $\rho_{\text{calcd.}}$ [g/cm$^3$] | 1.375 | 1.440 | 1.664 | 1.224 | 1.948 |
| μ [mm]$^{-1}$ | 0.096 | 0.394 | 0.351 | 0.072 | 1.113 |
| $F$(000) | 544 | 304 | 536 | 580 | 3104 |
| Crystal size [mm] | 0.40 × 0.13 × 0.13 | 0.45 × 0.40 × 0.33 | 0.32 × 0.23 × 0.20 | 0.31 × 0.24 × 0.08 | 0.43 × 0.37 × 0.29 |
| $\theta$ range for data collection [°] | 2.29–25.00 | 3.02–25.08 | 1.78–25.00 | 1.82–25.00 | 1.78–25.00 |
| Index ranges | $-7 \le h \le 9$<br>$-15 \le k \le 15$<br>$-14 \le l \le 14$ | $-8 \le h \le 8$<br>$-13 \le k \le 13$<br>$-10 \le l \le 10$ | $-9 \le h \le 9$<br>$-13 \le k \le 13$<br>$-14 \le l \le 14$ | $-13 \le h \le 13$<br>$-14 \le k \le 13$<br>$-14 \le l \le 14$ | $-14 \le h \le 12$<br>$-15 \le k \le 13$<br>$-38 \le l \le 36$ |
| Reflections collected | 6439 | 2373 | 6623 | 8330 | 24129 |
| Independent reflections | 2098<br>[$R$(int) = 0.0304] | 1124<br>[$R$(int) = 0.0820] | 3570<br>[$R$(int) = 0.0673] | 5103<br>[$R$(int) = 0.1288] | 9124<br>[$R$(int) = 0.0790] |
| Data/restraints/parameters | 2098/0/163 | 1124/0/83 | 3570/0/298 | 5103/0/370 | 9124/0/739 |
| Goodness-of-fit on $F^2$ | 1.038 | 0.873 | 0.919 | 0.705 | 0.972 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R1 = 0.0398$<br>$wR_2 = 0.0963$ | $R1 = 0.0378$<br>$wR_2 = 0.0891$ | $R1 = 0.0705$<br>$wR_2 = 0.1777$ | $R1 = 0.0573$<br>$wR_2 = 0.1273$ | $R1 = 0.0750$<br>$wR_2 = 0.1797$ |
| $R$ indices (all data) | $R1 = 0.0486$<br>$wR_2 = 0.1015$ | $R1 = 0.0509$<br>$wR_2 = 0.0938$ | $R1 = 0.1570$<br>$wR_2 = 0.2486$ | $R1 = 0.1224$<br>$wR_2 = 0.1783$ | $R1 = 0.1541$<br>$wR_2 = 0.2181$ |
| Largest difference peak/hole [e Å$^{-3}$] | 0.186/–0.224 | 0.310/–0.184 | 0.433/–0.725 | 0.193/–0.283 | 1.152/–0.921 |

(s, CH), 120.6 (q, $^1J_{C,F}$ = 319.1 Hz, $CF_3$), 167.1 (s, CH*C*N) ppm. $C_{28}H_{42}Ag_2F_{12}N_8O_{12}S_4$ (1254.7): calcd. C 26.80, H 3.37, N 8.93, S 10.22; found C 27.7, H 3.45, N 9.29, S 10.52.

**X-ray Crystallography:** A summary of crystal data and refinement parameters for compounds **1**, **2**, **3**, **4** and **5a** is given in Table 5. The single crystals were mounted on a glass fibre and transferred to a Bruker X8 APEX II CCD-based diffractometer equipped with a graphite-monochromated Mo-$K_\alpha$ radiation source ($\lambda$ = 0.71073 Å). Data were integrated by using the SAINT[25] program, and an absorption correction was performed with the program SADABS.[26] The software package SHELXTL version 6.12[27] was used for space-group determination; structure solution and refinement was carried out by full-matrix least-squares methods based on $F^2$. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed by using a riding model and included in the refinement at calculated positions. Special features/exceptions: Single crystals of **5b** were obtained by crystallisation from dichloromethane/hexane. Despite measuring several crystals, each of them proved to be of very poor quality and was only weakly diffracting (ratio observed/unique reflections 13%), therefore only a partial structural solution was obtained. Nevertheless, the results obtained were sufficient to adequately establish the atom connectivity. CCDC-708124 (for **1**), -708125 (for **2**), -708126 (for **3**), -708127 (for **4**), -708128 (for **5a**), and -708129 (for **5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via http://www.ccdc.cam.uk/data_request/cif.

**Computational Details:** Density functional calculations were carried out by using the GAUSSIAN03 package[28] and the hybrid density functional B3LYP.[29] A split-valence basis set (6-31G**) was used, with polarization functions for all main group elements.[30] Geometry optimizations were carried out on the full potential energy surface, without symmetry restrictions, and they were confirmed as minima by a vibrational analysis. Solvent effects were taken into account through the PCM algorithm[31] by using standard options of PCM and cavity keywords and calculating the energies with water, tetrahydrofuran, dichloromethane and heptane as a solvent at the geometries optimized for the gas phase (single-point calculations).

**Supporting Information** (see also the footnote on the first page of this article): Atomic coordinates for the optimized structures of species **A**–**C**, for the two ion pairs formed by the dication **C** and one triflate anion and for the trio formed by **C** and two triflate anions.

## Acknowledgments

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