

1,2,4-Triazolium-5-ylidene and 1,2,4-triazol-3,5-diylidene as new ligands for transition metals

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Abstract

Ab initio calculations show the 1,2,4-triazolium-5-ylidene (**3a**) and 1,2,4-triazol-3,5-diylidene (**4a**) are true minima on the potential surface. As expected, **4a** is much higher in energy than its triazole isomers **5a**, **6a** and **8a** and the 1,2,4-triazol-3-ylidene (**7a**). Sodium methoxy adds to the diquatery salt of 1,2,4-triazoles (**9b,c**) to give the corresponding monocationic heterocycles **10b,c** in 70 and 50% yield, respectively. One equivalent of silver(I) acetate reacts with **9b** leading to the bis(1,2,4-triazolium-5-ylidene)silver(I) complex (**11b**) in 80% yield. Under the same experimental conditions, but using two equivalents of silver(I) acetate, solid-state one-dimensional polymers **12b,c** featuring the coplanar 1,2,4-triazol-3,5-diylidene ligands coordinated to silver(I) are obtained in 90% yield. **12c** has been fully characterized including a single-crystal X-ray diffraction study. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Carbene; Organometallic polymers; Silver complexes; Aromaticity

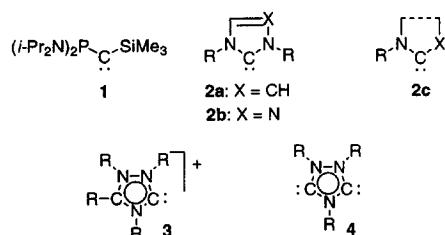
1. Introduction

In 1988 we reported the synthesis and reactivity of the stable (phosphino)(silyl)carbene (**1**) [1] and in 1991, Arduengo et al. reported the synthesis and X-ray crystal structure of an imidazol-2-ylidene of type (**2a**) [2]. Recently, other stable nitrogen-substituted cyclic or

non-cyclic carbenes **2b–c** have been prepared [3] (Scheme 1). In contrast to carbenes of type **1**, cyclic aminocarbenes **2a,b** have proved to be excellent ligands for transition metals, and the resulting complexes appeared to feature some interesting catalytic activities [3a,c].

Independent calculations by the groups of Frenking [4a], Apeloig [4b], and Enders [4c] demonstrated that carbenes of types **2a** and **2b** feature some aromatic character, which explains, at least in part, their remarkable stability. It was therefore tempting to try synthesizing 1,2,4-triazolium-5-ylidene (**3**) and 1,2,4-triazol-3,5-diylidene (**4**) as potential candidates for new families of stable carbenes [5] (Scheme 1). Indeed, such heterocyclic carbene-cations **3** and biscarbenes **4** have a conjugated six- π -electron system, and hence obey the Hückel rule [6].

Here we report theoretical and experimental results concerning the synthesis, stability and ligand properties of a 1,2,4-triazolium-5-ylidene (**3**) and 1,2,4-triazol-3,5-diylidene (**4**).



Scheme 1.

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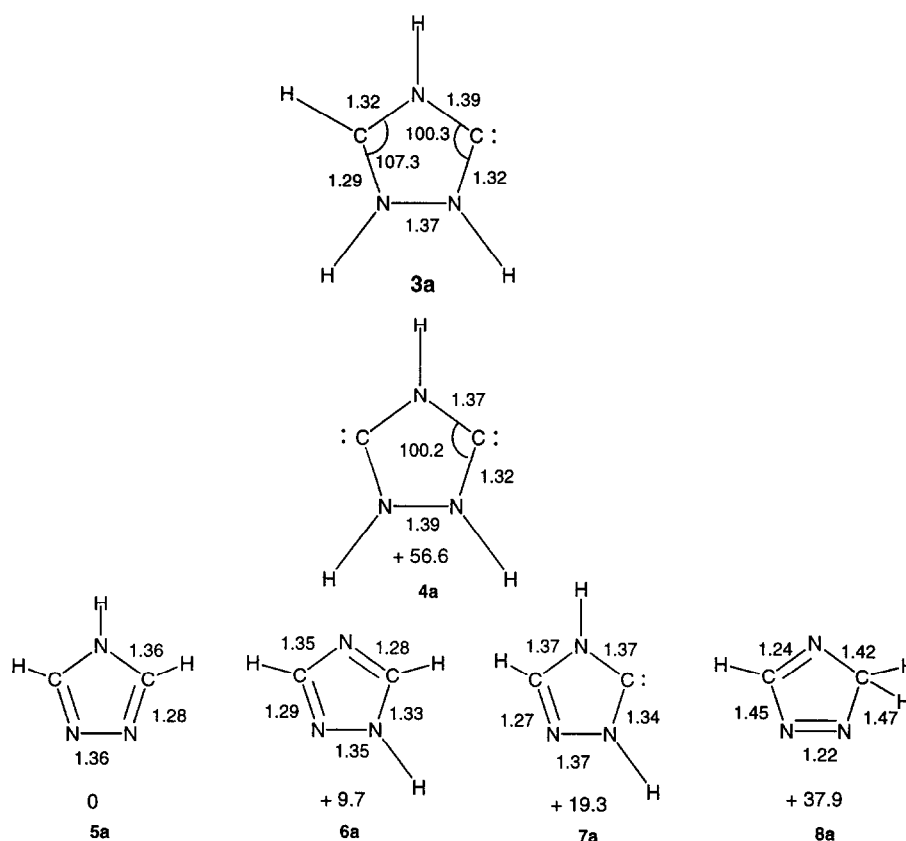


Fig. 1. Selected calculated bond lengths (Å) and angles (°) for compounds **3a**–**8a** and relative energies (kcal mol⁻¹) for **4a**–**8a**.

2. Results and discussion

To check that carbene cations and biscarbenes of type **3** and **4**, respectively, are rigid π -conjugated systems, we carried out calculations on the parent compounds **3a** and **4a** as well as on **5a**–**8a**, which are the known isomers of **4a**. Calculations were performed at the RHF-SCF-DZP level for the geometry optimizations. On each minimum, correlation effects were estimated through MP4 calculations (HONDO-8 program from the MO-TECC-89 package [7]). The 1,2,4-triazol-3,5-diylidene (**4a**) is a true minimum on the potential surface, although as expected, is much higher in energy than its triazole isomers **5a**, **6a** and **8a** and 1,2,4-triazol-3-ylidene (**7a**) (Fig. 1). **4a** has a C_{2v} symmetry (all hydrogens are located in the plane of the ring) with the two carbenic lone pairs lying in the same plane and pointing in directions that form an angle of about 143° (vide infra). All the endocyclic bond lengths are halfway between those for single and double bonds. The angle at the carbenic centers is 100.2°, which confirms that **4a** belongs to the family of carbenes like imidazol-2-ylidenes (**2a**) and triazol-5-ylidenes (**2b**), for which aromaticity has been well established [4]. Of interest, according to Bird's indices [8], **4a** exhibits 72% of the aromaticity of the cyclopentadienyl anion. The carbene cation **3a** is also a minimum on the potential

surface and as expected, the molecule is calculated to be planar. The nitrogen–carbocation bond lengths are slightly shorter than the nitrogen–carbene bond distances, and the bond angle at the carbocation wider than that at the carbene center (107.3 and 100.3°, respectively). According to Bird's indices, **3a** is less aromatic than **4a** with 63% of the aromaticity of the cyclopentadienyl anion.

The obvious potential precursor for both the carbene cations **3** and bis(carbenes) **4** are the diquaternary salts of 1,2,4-triazoles, i.e. the heterocycles **9b,c**. A single-crystal X-ray diffraction study of **9b** reveals that all the substituents lie in the plane of the ring (maximum deviation 0.13 Å), and that the carbon–nitrogen and nitrogen–nitrogen bond lengths are half-way between those for single and double bonds (Fig. 2). The experimentally observed geometric parameters for **9b** are similar to those calculated for the parent compound **9a** (Fig. 2) and are consistent with their aromatic character. Interestingly, according to Bird's indices, the dication **9a** would be even more aromatic than **3a** and **4a** with some 75% of the aromaticity of the cyclopentadienyl anion.

So far, all attempts to generate a stable free carbene cation or biscarbene from **9b,c** failed. For example, using Enders' synthetic strategy [9], sodium methoxide reacts with **9b,c** to afford the corresponding monoca-

tionic heterocycles **10b,c** in 70 and 50% yield, respectively, but attempted thermolysis under vacuum at various temperatures failed (Scheme 2).

Thus we chose to investigate the possibility of using the 1,2,4-triazolium-5-ylidene (**3**) as a ligand for metals. By analogy with Wanzlick's synthetic strategy [10], one equivalent of silver(I) acetate was treated with a suspension of **9b** in refluxing THF for 2 h, affording complex **11b**, which was isolated as a yellow oil in 80% yield (Scheme 3). The unsymmetrical nature of the heterocyclic ligand of **11b** was first apparent from the presence of three ^1H - and ^{13}C -NMR signals for the three N–Me groups. The carbenic carbon appeared at 189.2 ppm, as expected by comparison with the ^{13}C -NMR data observed for the analogous imidazol-2-ylidene sil-

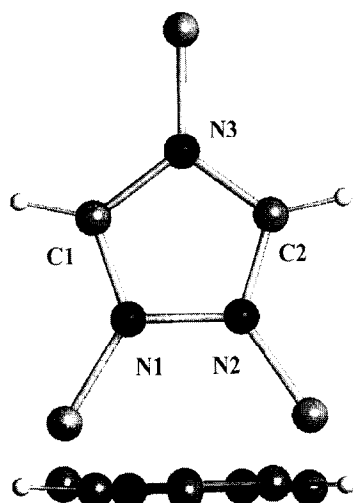
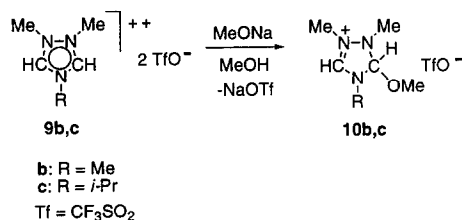
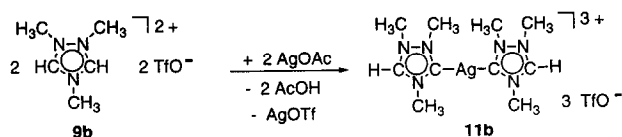


Fig. 2. Ball and stick views of the crystal structure of **9b**. Selected bond lengths (Å) and angles ($^\circ$): N1–C1, 1.296(7); N1–N2, 1.370(5); N2–C2, 1.305(6); C1–N3, 1.326(6); C2–N3, 1.337(6); C1–N1–N2, 107.5(4); C2–N2–N1, 107.3(4); N1–C1–N3, 109.1(5); N2–C2–N3, 108.4(4); C1–N3–C2, 107.7(5). For comparison, the calculated geometric parameters for **9a** are as follows: N1–C1, 1.30; N1–N2, 1.35; C1–N3, 1.24; N1–C1–N3, 107.0.



Scheme 2.



Scheme 3.

ver complex [11]. The CH carbon appeared at 144.8 ppm and the CH hydrogen at 9.7 ppm, in the range observed for the starting material **9b**.

Although transition-metal carbene complexes have been studied widely [12], carbene–metal-type polymers have never been explored. Therefore, it was of interest to try use 1,2,4-triazole-3,5-diylidenes (**4**) as building blocks for organometallic polymer synthesis.

Dicationic heterocycles **9b,c** were treated with two equivalents of AgOAc in refluxing THF for 2 h. After filtration, an extremely light-sensitive white powder was obtained (90% yield). Elemental analyses showed a 2:1 silver triflate/bis(carbene) ratio in agreement with the ratio of reagents used. The ^1H - and ^{13}C -NMR spectra of the solution obtained from **9b** and **9c** revealed the presence of a methyl and an isopropyl group, respectively, bound to nitrogen and two equivalent N–Me groups, which suggested the presence of the bis(carbene) fragment. The signal for the two equivalent carbenic carbons appeared at 185.0 (**12b**) and 182.9 ppm (**12c**), very close to that observed for the imidazol-2-ylidene-silver complex [183.6, $J(\text{AgC}) = 188.0$ and 208.6 Hz [11]], but no silver–carbon coupling constant was observed, even at low temperatures. However, when the ^{13}C -NMR spectrum was performed in *dmf-d*₇ or acetone-*d*₆ at 193 K, in the presence of Cl[−] (from KCl), the signal for the carbene–carbon atoms was split into two broad signals [$J(\text{AgC}) = 200$ Hz], while the other signals remained unchanged. These results collectively suggest that the silver–bis(carbene)–silver unit is present in solution, but as already observed for other silver complexes [13], rapid exchange occurs. The exchange process is slowed down in the presence of a coordinating anion such as Cl[−].

Interestingly, single crystals of **12c**, suitable for an X-ray diffraction study were obtained at -30°C from an acetonitrile–ether solution. The view of the solid-state structure (Fig. 3) shows the polymeric nature of **12c**. The five-membered rings are planar (maximum deviation 0.07 Å), and all the bond lengths in the ring are half-way between those for single and double bonds, and are very close to those of the calculated free bis(carbene) **4a**. There is no interaction between the metal and the anion (nearest distance: Ag(2)–F(2) = 3.18 Å). The silver atoms are essentially linearly coordinated with a C–Ag–C bond angle of 175–180°. The Ag–C bond lengths [2.086(4)–2.090(4) Å] and the N–C–N angles [103.9(3) $^\circ$] are very similar to those observed for the imidazol-2-ylidene-silver complex [2.067(4)–2.078(4) Å; 103.6(4)–104.8(4) $^\circ$] [11]. The rings in the polymer are absolutely coplanar and due to the alternation in the orientation of the rings (two rings with the *i*-Pr group on one side of the chain and two rings with the *i*-Pr group on the other side), **12c** is a one-dimensional metal–bis(carbene) polymer. Interestingly, in agreement with the calculations on the 1,2,4-

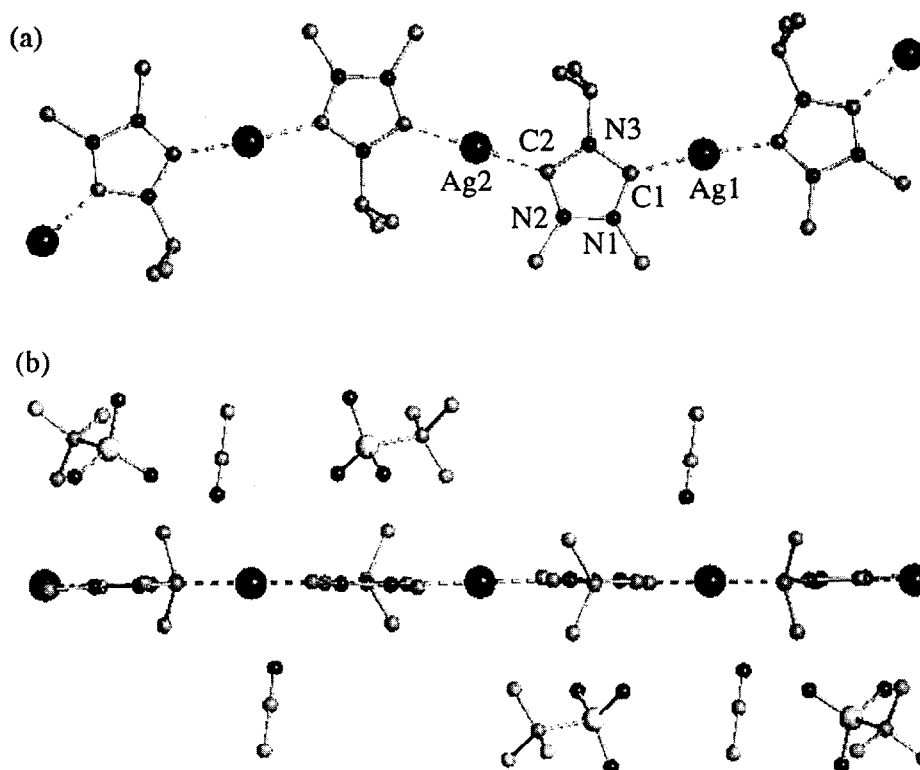


Fig. 3. (a) Ball and stick view showing the polymeric nature of **12'c**. (b) Ball and stick view showing the planarity of **12'c**, the counteranions and the solvent molecules. Selected bond lengths (Å) and angles (°): Ag1–C1, 2.086(4); Ag2–C2, 2.090(4); N1–C1, 1.320(5); C1–N3, 1.370(5); N1–N2, 1.373(5); N2–N3, 1.368(5); C2–N2, 1.318(5); C1–Ag1–C1A, 174.7(2); C2–Ag2–C2A, 180.0(1); N1–C1–Ag1, 126.0(3); N3–C1–Ag1, 130.1(3); N2–C2–Ag2, 126.8(3); N3–C2–Ag2, 129.1(3); N1–C1–N3, 103.9(3); C1–N1–N2, 109.9(3); N2–C2–N3, 104.0(3); C2–N2–N1, 110.0(3); C2–N3–C1, 112.2(3).

triazol-3,5-diyldene (**4a**), which predicted that the two lone pairs point in directions that form an angle of about 143° , the two Ag–C directions in **12'c** form a 146.8° angle.

Note that in contrast to the 2:1 silvca. triflate–bis(carbene) ratio found in the bulk material (**12c**), the crystal of **12'c** analyzed by X-ray diffraction study showed a 1:1 ratio. Moreover, it appeared that the crystal of **12'c** was totally insoluble in acetonitrile. However, addition of a small amount of silver triflate to the suspension of **12'c** in the same solvent gave a homogeneous solution, which showed the same NMR data as those of the acetonitrile solution of the bulk material **12c**. Therefore, the bulk material **12c** either is a 1:1 mixture of more or less polymeric **12'c** and silver triflate or, alternatively, has a structure such as TfO–Ag–bis(carbene)–Ag–OTf.

3. Conclusions

When compared to the imidazol-2-ylidenes (**2a**) and 1,2,4-triazol-3-ylidenes (**2b**), heterocycles of type **3** feature, besides the carbene moiety, a second functional

group that could be used for further reactions, and also as a consequence of its cationic nature, ligands of type **3** could be useful for the preparation of water soluble complexes. Since carbon-rich organometallics containing rigid π -conjugated chains are currently attracting interest [14], the properties of **12** and related polymers are under active investigation. Finally, the availability of free stable cationic carbenes **3** and biscarbenes **4** should expand the range of transition metal complexes that can be prepared considerably.

4. Experimental

4.1. Methods and instrumentation

All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques. Dry, oxygen-free solvents were employed. ^1H - and ^{13}C -NMR spectra were recorded on Bruker AC80, AC200, WM250 or AMX400 spectrometers. ^1H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as the external standard. Mass spectra were obtained on a Ribermag R10 10E instrument.

4.2. Synthesis and single-crystal X-ray diffraction study of dicationic heterocycle **9b**

Heterocycle **9b** has been prepared as reported by Curphey and Prasad [15], but replacing trimethyloxonium tetrafluoroborate by methyl trifluoromethanesulfonate. m.p. 160–162°C. ¹H-NMR (DMSO-*d*₆): δ 4.22 (s, 3H, NCH₃), 4.50 (s, 6H, NCH₃), 10.79 (s, 2H, CH); ¹³C[¹H]-NMR (CD₃CN): δ 38.7 (NCH₃), 38.9 (NCH₃), 120.3 (q, ¹J_{C-F} = 320.1 Hz, CF₃), 147.7 (CH). Recrystallization in acetonitrile at –30°C afforded single crystals suitable for an X-ray diffraction study. Crystal data for **9b**, C₇H₁₁F₆N₃O₆S₂, *M* = 411.31, triclinic, *P* $\bar{1}$, *a* = 6.373(2), *b* = 10.385(3), *c* = 13.158(4) Å, α = 76.44(2), β = 76.18(2), γ = 82.04(3)°, *V* = 819.0(4) Å³, *Z* = 2, ρ_{calc.} = 1.668 Mg m⁻³, *F*(000) = 416, λ = 0.71073 Å, *T* = 293(2) K, μ(Mo-Kα) = 0.419 mm⁻¹, crystal size 0.2 × 0.1 × 0.1 mm³, 4.6 < 2θ < 48.5°, 4796 reflections collected, 2441 independent (*R*_{int} = 0.044), refinement of 312 parameters using 151 restraints, largest electron density residue: 0.429 e Å⁻³, *R*₁ (for *F* > 2σ(*F*)) = 0.057 and *wR*₂ = 0.166 (all data) with *R*₁ = Σ||*F*_o| – |*F*_c||/Σ|*F*_o| and *wR*₂ = (Σ *w*(*F*_o² – *F*_c²)²/Σ *w*(*F*_o²)^{0.5}). The data were collected on a STOE-IPDS diffractometer. The structure was solved by direct methods (SHELXS-96) [18] and refined using the least-square method on *F*² [19].

4.3. Synthesis of dicationic heterocycle **9c**

To a dichloromethane solution of 1*H*-1,2,4-methyltriazole [16] (8.3 g, 0.1 mol) was added at room temperature (r.t.) one equivalent of isopropyl trifluoromethanesulfonate (19.2 g, 0.1 mol) prepared as described previously [17]. The solution was stirred under reflux for 3 h, and after evaporation of the solvent, the triazolium was obtained as a yellow oil (24.7 g, 90% yield) and used for the second step without further purification.

To a 1,2-dichloroethane solution (20 ml) of the triazolium (5.0 g, 20 mmol) was added 2.5 ml of methyl trifluoromethanesulfonate (22 mmol). The solution was stirred under reflux for 24 h. A brown precipitate was formed, filtered, and washed several times with 1,2-dichloroethane. The dicationic heterocycle **9c** was obtained as a white powder (5.8 g, 73% yield). m.p. 170–172°C. ¹H-NMR (CD₃CN): δ 1.65 (d, ³J_{H-H} = 6.6 Hz, 6H, CH(CH₃)₂), 4.34 (s, 6H, NCH₃), 5.03 (sept, ³J_{H-H} = 6.6 Hz, 1H, NCH(CH₃)₂), 10.22 (s, 2H, CH); ¹³C[¹H]-NMR (CD₃CN): δ 21.5 (CH(CH₃)₂), 38.7 (NCH₃), 58.9 (NCH(CH₃)₂), 121.1 (q, ¹J_{C-F} = 320.1 Hz, CF₃), 145.2 (CH).

4.4. Synthesis of cationic heterocycles **10b,c**

To a methanol solution (20 ml) of dicationic heterocycle **9b** or **9c** (3 g) was added a methanol solution (20 ml) of sodium methoxide (1.2 equivalents). The solution was stirred for 2 h at r.t. After evaporation of the solvent, the residue was washed with ether and then extracted with dichloromethane. Heterocycles **10b** and **10c** were obtained as yellow oils. **10b**: 70% yield, ¹H-NMR (CDCl₃): δ 2.59 (s, 3H, OCH₃), 2.97 (s, 6H, NCH₃), 3.14 (s, 3H, NCH₃), 5.74 (s, 1H, CHOCH₃), 9.31 (s, 1H, CH). ¹³C[¹H]-NMR (CDCl₃): δ 31.1 (NCH₃), 33.9 (NCH₃), 39.6 (NCH₃), 49.3 (OCH₃), 105.2 (CHOCH₃), 120.3 (q, ¹J_{C-F} = 320.1 Hz, CF₃), 149.2 (CH). **10c**: 50% yield, ¹H-NMR (CDCl₃): δ 1.54 (d, ³J_{H-H} = 6.5 Hz, 3H, CH(CH₃)₂), 1.61 (d, ³J_{H-H} = 6.5 Hz, 3H, CH(CH₃)₂), 3.00 (s, 3H, OCH₃), 3.42 (s, 3H, NCH₃), 3.64 (s, 3H, NCH₃), 4.10 (sept, ³J_{H-H} = 6.5 Hz, 1H, NCH(CH₃)₂), 6.11 (s, 1H, CHOCH₃), 9.00 (s, 1H, CH). ¹³C[¹H]-NMR (CDCl₃): δ 21.0 (CH(CH₃)₂), 21.5 (CH(CH₃)₂), 34.3 (NCH₃), 40.0 (NCH₃), 49.2 (NCH(CH₃)₂), 50.0 (OCH₃), 104.2 (CHOCH₃), 121.3 (q, ¹J_{C-F} = 320.1 Hz, CF₃), 147.9 (CH).

4.5. Synthesis of the bis(1,2,4-triazolium-5-ylidene)-silver complex (**11b**)

One equivalent of silver acetate were added to a suspension of dicationic heterocycle **9b** in THF. The resulting mixture was stirred under reflux for 3 h and a white powder precipitated. After several washes with THF, the white powder was dissolved in CD₃CN and analyzed by NMR spectroscopy. ¹H-NMR (CD₃CN): δ 4.01 (s, 3H, NCH₃), 4.19 (s, 3H, CH₃N–NCH₃), 4.22 (s, 3H, CH₃N–NCH₃), 9.72 (s, 1H, CH). ¹³C[¹H]-NMR (CD₃CN): δ 37.2, 38.5 and 38.6 (NCH₃), 121.1 (q, ¹J_{C-F} = 320.1 Hz, CF₃), 144.8 (CH), 189.2 (C_{Ag}).

4.6. Reaction of the dicationic heterocycles **9b,c** with two equivalents of AgOAc

Two equivalents of silver acetate were added to a suspension of dicationic heterocycle **9b** or **9c** in THF. The resulting mixture was stirred under reflux for 3 h and a white powder precipitated. After several washes with THF, the white powder was dissolved in CD₃CN and analyzed by NMR spectroscopy. **12b**: ¹H-NMR (CD₃CN): δ 4.07 (s, 3H, NCH₃), 4.20 (s, 6H, CH₃N–NCH₃). ¹³C[¹H]-NMR (CD₃CN): δ 38.3 (CH₃N–NCH₃), 41.2 (NCH₃), 121.1 (q, ¹J_{C-F} = 320.1 Hz, CF₃), 185.0 (C_{Ag}, no silver–carbon coupling constant was observed). **12c**: ¹H-NMR (CD₃CN): δ 1.60 (d, ³J_{H-H} = 6.85 Hz, 6H, CH(CH₃)₂), 4.14 (s, 6H, NCH₃), 4.83 (sept, ³J_{H-H} = 6.6 Hz, 1H, NCH(CH₃)₂). ¹³C[¹H]-NMR (CD₃CN): δ 24.1 (CH(CH₃)₂), 38.9 (NCH₃), 56.8 (NCH(CH₃)₂), 121.1 (q, ¹J_{C-F} = 320.1

Hz, CF₃), 182.9 (C_{Ag}, no silver–carbon coupling constant was observed).

Potassium chloride was added to a dmf-*d*₇ or acetone-*d*₆ solution of **12b** and the resulting mixture was analyzed by NMR spectroscopy. At r.t., the ¹³C[¹H]- and ¹H-NMR spectra were identical to those obtained before addition of KCl. However, at 193 K, the following spectra were observed. ¹H-NMR (dmf-*d*₇): δ 4.24 (s, 3H, NCH₃), 4.93 (s, 6H, CH₃N–NCH₃). ¹³C[¹H]-NMR (dmf-*d*₇): δ 38.9 (CH₃N–NCH₃), 41.9 (NCH₃), 121.1 (q, ¹J_{C–F} = 320.1 Hz, CF₃), 185.5 (broad d, ¹J_{Ag–C} = 197 Hz, C_{Ag}, the signal is too broad to differentiate between ¹J_{107Ag–C} and ¹J_{109Ag–C}).

The white powder of **12b** or **12c** was dissolved in an acetonitrile–ether solution and white crystals of **12b** (m.p. (dec.) 145°C) and **12c** (m.p. (dec.) 154°C) were obtained at –30°C. Only crystals of **12c** suitable for a single-crystal X-ray diffraction study were obtained. Crystal data for **12c**, C₈H₁₃AgF₃N₃O₃S (CH₃CN), *M* = 437.20, orthorhombic, *Pnma*, *a* = 16.737(3), *b* = 24.393(4), *c* = 7.911(1) Å, *V* = 3229.8(9) Å³, *Z* = 8, ρ_{calc.} = 1.798 Mg m^{–3}, *F*(000) = 1744, λ = 0.71073 Å, *T* = 133(2) K, μ(Mo–K_α) = 1.424 mm^{–1}, crystal size 0.25 × 0.25 × 0.15 mm³, 4.8 < 2θ < 50.5°, 30 981 reflections collected, 2931 independent (*R*_{int} = 0.051), refinement of 215 parameters using 33 restraints, largest electron density residue: 1.433 e Å^{–3}, *R*₁ (for *F* > 2σ(*F*)) = 0.039 and *wR*₂ = 0.103 (all data) with *R*₁ = Σ||*F*_o| – |*F*_c||/Σ|*F*_o| and *wR*₂ = (Σ *w*(*F*_o² – *F*_c²)²/Σ *w*(*F*_o²)^{0.5}). The data were collected on a Stoe–Siemens–Huber four-circle diffractometer. The intensities of a cooled crystal in an oil drop were measured with a Siemens CCD-area detector. The structure was solved by direct methods (SHELXS-96) [18] and refined using the least-squares method on *F*² [19].

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures of **12c** and **9b** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 141143 and 141142, respectively. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-

1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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