Quaternary 4-Amino-1,2,4-triazolium Salts: Crystal Structures of Ionic Liquids and *N*-Heterocyclic Carbene (NHC) Complexes

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Z. Naturforsch. **2009**, *64b,* 603 – 616; received April 15, 2009

Dedicated to Professor Gerhard Maas on the occasion of his 60th birthday

Quaternary salts were prepared by reaction of 4-amino-1,2,4-triazole and 4-amino-3,5-dialkyl-1,2,4-triazoles (alkyl = Me, Et) with dimethyl and diethyl sulfate at ambient temperature. Subsequent ion metathesis gave hexafluorophosphates and bis(trifluoromethylsulfonyl)imides as crystalline derivatives or ionic liquids. Methylation at 100 °C gave the 4-(dimethylamino)-1-methyl-1,2,4-triazolium salt, a precursor for a new carbene ligand which was incorporated into Ag and Rh complexes. The synthesis of 5-bromo-4-(dimethylamino)-1-methyl-1,2,4-triazolium hexafluorophosphate is also reported. Crystal structures of fourteen compounds have been determined by X-ray diffraction.

Key words: Carbene, Ionic Liquid, NHC, Rhodium, Silver, Triazolium

Introduction

Azolium salts have attracted significant attention in several different fields of application. Early imidazolium and triazolium salts were pursued for their bioactivity [1 – 4]. To date, countless salts with low melting points (ionic liquids, ILs), to a large part of the imidazolium but also triazolium type, have been prepared. This area has achieved tremendous importance in the course of the last decades. ILs have been proposed for numerous potential applications [5], and the number of original publications on this topic has soared. In a more recent development, protic ionic liquids (PILs) [6 – 8] are obtained either by protonation of the corresponding bases [9] or by employment of quaternary salts containing additional functional groups, such as *N*-amino groups [10]. Thus, low-melting salts of 4-amino-1,2,4-triazole have been prepared with nitric, perchloric, and dinitramidic acids [11]. Due to their relatively high nitrogen content they have been termed 'energetic compounds'. These nitrogen-rich compounds constitute another field of current interest [12, 13]. Furthermore, quaternary 3-alkyl-1-amino-1,2,3-triazolium halides [14] and nitrates [15], and 1-alkyl-4-amino-1,2,4-triazolium bromides [16], nitrates [16, 17], and perchlorates [17, 18] have been characterized. The salts with oxygen-containing anions have been investigated as propellants and explosives. In yet another field of research, azolium cations are valuable precursors of carbenes which themselves are of importance in catalysis [19]. General routes to *N*-heterocyclic carbene (NHC) complexes include deprotonation of an azolium salt in the presence of a metal cation, oxidative insertion of zero-valent metals into the C–Hal bond of an azolium salt, and transmetallation from a preformed complex [20]. Often imidazolium salts are used, but recently more and more triazole-derived carbenes have been reported. Thus, syntheses and structures of 1,2,4-triazol-5-ylidene transition metal complexes [21, 22], even di-NHC complexes derived from the 1,2,4-trimethyl-1,2,4-triazolium dica-

0932–0776 / 09 / 0600–0603 $ 06.00

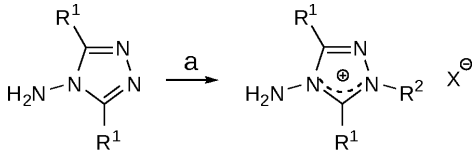
tion [23], have been published. Only a few examples of heteroatom *N*-substituted triazole-based carbenes are known, such as *N*-alkyloxy-1,2,4-triazol-5-ylidene [24] and *N*-dialkylamino-1,2,4-triazol-5-ylidene [25] systems. However, the required triazolium salts had to be prepared by elaborate *de novo* syntheses from acyclic precursors.

One objective of this work was to examine PILs with protic functional groups using an inexpensive starting material. Commercial 4-amino-1,2,4-triazole was a self-evident choice. The respective 4-amino-3,5-dialkyl-1,2,4-triazoles are also readily available from carboxylic acids and hydrazine [26]. We further intended to discover new quaternary salts of 4-amino-1,2,4-triazole suitable as ligand precursors for NHC complexes. Finally, we planned to study the solid-state structures of these salts by crystallography, in continuation of our earlier work on fundamental *N*-aminoazolium chlorides [27].

Results and Discussion

4-Amino-1,2,4-triazoles are primarily alkylated at the N-1 position of the heterocycle despite the presence of the amino group [28]. Selective monomethylation was achieved using inexpensive dialkylsulfates (alkyl = Me, Et) at r. t. yielding the quaternary alkylsulfates **1a** – **5a**, preferably in a solvent such as acetonitrile (Scheme 1). Mixtures of hydrogensulfate and alkylsulfate were obtained when the exothermic reaction was carried out without a solvent. Regardless of the anion, these crude mixtures were perfectly suitable for the preparation of other salts by ion metathesis (Scheme 1). The methylsulfates are also prone to hydrolysis, as demonstrated by the isolation of the crystalline hydrogensulfate **2d** after prolonged exposure of the methylsulfate **2a** to the atmosphere. As expected, methanol was detected by NMR in the mother liquor.

It seemed to be interesting to study new salts of these known cations with respect to their crystal structures. Consequently, hexafluorophosphates **2b** – **6b** were prepared in order to get crystals, and bis(trifluoromethylsulfonyl)imides ('triflimides') **1c** – **6c**, for anticipated ILs. Unfortunately, no crystalline hexafluorophosphate of the 4-amino-1-methyl-1,2,4-triazolium cation could be isolated due to its high solubility in water. The tetraphenylborate **1b** was prepared instead. Some of the salts (**3b**, **3c**, **5b**, **6c**) do qualify as ILs with a melting point below 100 °C. The triflimide **1c** remained liquid at r. t.



1a- 5a

b

1b, c- 5b, c

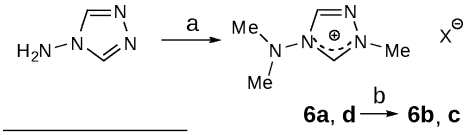
a) $(R^2O)_2SO_2$; b) ion metathesis

	R^1	R^2	X
1a	H	Me	$MeOSO_3$
1b	H	Me	Ph_4B
1c	H	Me	Tf_2N
2a	Me	Me	$MeOSO_3$
2b	Me	Me	PF_6
2c	Me	Me	Tf_2N
2d	Me	Me	$HOSO_3$
3a	Me	Et	$EtOSO_3$
3b	Me	Et	PF_6
3c	Me	Et	Tf_2N
4a	Et	Me	$MeOSO_3$
4b	Et	Me	PF_6
4c	Et	Me	Tf_2N
5a	Et	Et	$EtOSO_3$
5b	Et	Et	PF_6
5c	Et	Et	Tf_2N

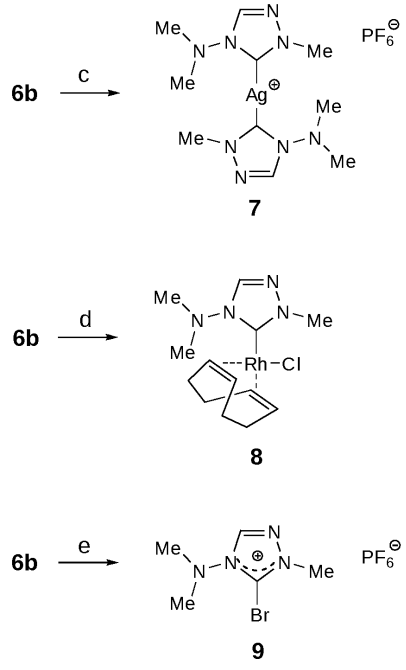
Scheme 1.

When the methylation was conducted at higher temperature and without solvent, the new 4-(dialkylamino) derivative **6a** was obtained (Scheme 2). The transient mono-alkylamino compound was not observed under these conditions. The synthesis of 4-alkylamino-1,2,4-triazoles by base-induced rearrangement of 4-amino-1-alkyl-1,2,4-triazolium salts has been described previously [29], and the products have later been claimed in patents as herbicides and fungicides [30, 31]. Another known pathway to 4-alkylamino-1,2,4-triazoles is by reduction of the corresponding imines [32]. However, no direct alkylation of the 4-amino group has been described so far.

At least theoretically, the number of equivalents of alkylating agent in conjunction with reaction time and temperature determines not only the degree of methylation but also the type of the anion present in the product. Depending on the conditions, three methylation products (**1a**, **6a** and **6d**) are accessible from 4-amino-1,2,4-triazole. Practically, there are limitations due to conflicting requirements. Thus, 4-amino-1-methyl-1,2,4-triazolium hydrogensulfate could not be prepared by a simple methylation because the high tempera-



	X
6a	$MeOSO_3$
6b	PF_6
6c	Tf_2N
6d	$HOSO_3$



a) $(MeO)_2SO_2$; b) ion metathesis; c) Ag_2O; d) $[ClRh(cod)]_2$, Et_3N; e) Br_2, Na_2CO_3

Scheme 2.

ture required for utilization of both methyl groups of the dimethyl sulfate would lead to permethylation; on the other hand, at the low temperature necessary for monomethylation, the reaction does not proceed from methylsulfate to hydrogensulfate, even when only half an equivalent of dimethyl sulfate is used.

Peralkylation of 4-amino-1,2,4-triazole has never been observed with other common alkylating agents such as alkyl halides. Interestingly, the reaction of 1-methyl-1,2,4-triazole with Me_3O^+ BF_4^- under forceful conditions is known to produce 1,2,4-trimethyl-1,2,4-triazolium dications [33]. Preliminary experiments with Me_3O^+ BF_4^- in dichloromethane showed that 4-amino-1,2,4-triazole gave mixtures of at least mono-, di- and trimethylated products of not yet fully known constitution. Further work is currently in progress.

In order to demonstrate the potential of **6b** as a carbene precursor, a crystalline silver-carbene complex **7** was readily prepared from **6b** and silver oxide in methanol (Scheme 2). This compound may prove to be useful for transmetallation reactions [34 – 36]. In addition, the rhodium(I) complex **8** was synthesized (Scheme 2) in analogy to a published procedure [24, 25]. Finally, the 5-bromo derivative **9** was obtained in a straight-forward manner by the action of bromine and sodium carbonate on **6b** (Scheme 2). It is noteworthy that the bromination did not occur at all in pure methanol but gave a satisfactory yield when a mixture of methanol and water was employed. NMR spectra in DMSO appeared to indicate the presence of hydrolyzed material in the product. However, a solution in acetone gave excellent spectra. The hydrolysis did not occcur in a mixture of acetonitrile and water, either. Obviously, partial hydrolysis occurred in the DMSO solution. In order to validate this observation, the DMSO solution was allowed to stand for a week after addition of a drop of D_2O. The spectrum then showed complete conversion to the presumed product of hydrolysis, namely 4-(dimethylamino)-1-methyl-1,2,4-triazolin-5-one. Details of this reaction and of the product will be communicated later. It should also be noted that preliminary experiments of oxidative insertion of palladium(0) with **9**, in analogy to previous work [37], were not successful but yielded only unchanged starting materials.

Crystal structures

The cations described by Scheme 1 contain amino groups as potential H bond donor sites. Consequently, their interaction with suitable acceptor (A) groups of the counterion X will be a potent directing force in the aggregation of cationic and anionic components in the solid state. Thus, the following discussion of those crystal structures where is X is either PF_6 (**2b**, **3b**, **4b**), Tf_2N (**2c**, **3c**, **4c**, **5c**) or $HOSO_3$ (**2d**) will focus on this particular kind of (cation)NH···A(anion) interactions (Table 2).

Compound **1b** (space group $P2_12_12_1$) is a special case in this respect since Ph_4B does not have a suitable H bond acceptor function. Additionally, tetraphenylborate is relatively large compared to the size of the cation, so that the latter merely occupies voids in a framework of Ph_4B units (Fig. 1b). Moreover,

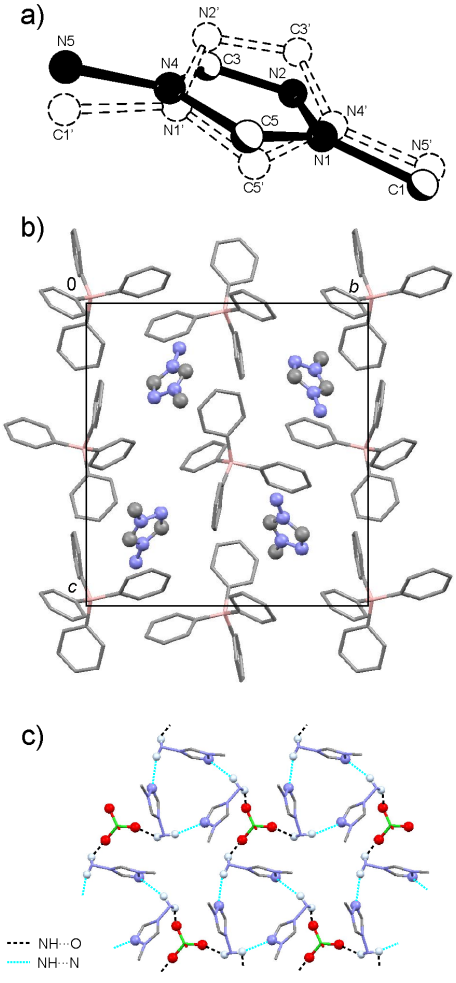


Fig. 1. Crystal structure of **1b**. (a) Positional disorder of the cation moiety: the major component is represented by full lines, and all H atoms are omitted for clarity. (b) Crystal packing viewed along the *a* axis. Cations occupy the voids in a framework composed of tetraphenylborate moieties. Hydrogen atoms are omitted for clarity, and the atoms of the cation are drawn as balls. (c) Portion of a trigonal 2D H-bonded sheet found in the perchlorate analog of **1b** [17]. Three NH···N-bonded cations form an $R_3^3(15)$ ring, and each of the cations is further linked to two other cations *via* NH···OClO···HN bridges. Atoms engaged in hydrogen bonding are drawn as balls, and all other H atoms are omitted for clarity.

the cation is even able to adopt two alternative positions (Fig. 1a) without a noticeable effect on its Ph_4B environment. It is also worth noting that the aggregation in the crystal structure of the perchlorate analog of **1b** [17] is driven by H bonding which leads to a fundamentally different result. There, NH···N-bonded cations form an $R_3^3(15)$ ring [38], and each of

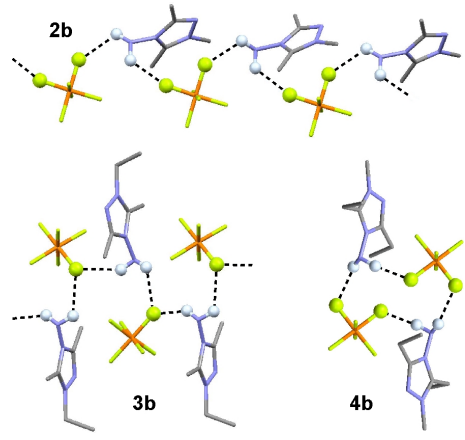


Fig. 2. Hydrogen bonding motifs with PF_6 anions in the crystal structures of **2b**, **3b**, and **4b**. H and F atoms engaged in hydrogen bonding are drawn as balls, and all other H atoms are omitted for clarity.

the cations is further linked to two more cations by NH···OClO···HN bridges *via* one ClO_4 unit. Fig. 1c shows that an extended 2D H-bonded sheet, exhibiting trigonal symmetry, is formed due to these interactions.

Fig. 2 illustrates the three distinct NH···F-bonded motifs observed in crystal structures with X = PF_6, *i. e.* **2b**, **3b** and **4b**. In the case of **2b** (space group *Cc*) there are two independent NH···F bonds which involve two different F atoms. The 1D infinite chain formed as a consequence of this interaction propagates parallel to the crystallographic *c* axis and exhibits glide symmetry. Chains adjacent to one another in this crystal structure are related by translational symmetry. A somewhat different situation is found in the crystal structure of **3b** (space group $P2_1/n$, $Z' = 2$). Again, there are two independent NH···F bonds per chain, but in this case the same F site is employed twice (see Fig. 2). A helical H-bonded chain with 2_1 symmetry results from these interactions. It has a crankshaft shape and propagates parallel to the crystallographic *b* axis. There are two formula units in the asymmetric unit of **3b**, so that this crystal structure contains two independent H-bonded chains. By contrast, the crystal structure of **4b** (space group $P2_1/n$) exhibits discrete NH···F-bonded units composed of two cations and two PF_6 anions, and two distinct F sites engage in H bonding, which results in the centrosymmetric $R_4^4(12)$ ring shown in Fig. 2.

An overview of the NH···O-bonded patterns present in crystal structures where X = Tf_2N, *i. e.* **2c**, **3c**, **4c** and **5c**, is given in Fig. 3. It is a recurring feature in all these structures that one of the two Tf_2N sul-

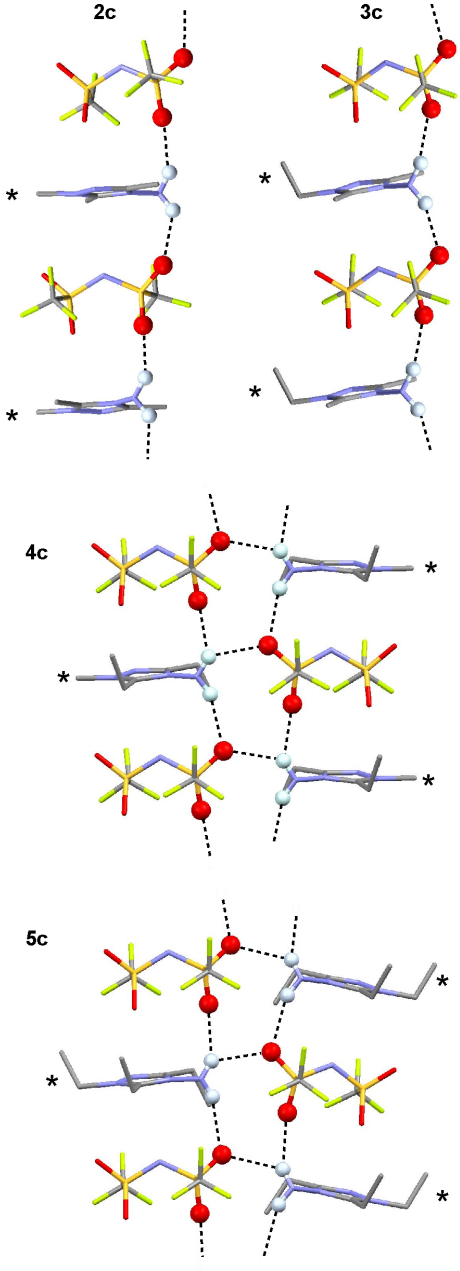


Fig. 3. 1D Hydrogen bonding motifs with triflimide anions in the crystal structures of **2c**, **3c**, **4c**, and **5c**. O and H atoms engaged in hydrogen bonding are drawn as balls, all other H atoms are omitted for clarity, and the cations are marked with asterisks.

fonyl groups acts as an NH···O=S=O···HN bridge between two cation moieties. In the crystal structure of **2c** (space group $P2_1/n$), this interaction links cations and Tf_2N moieties together in a single-stranded chain.

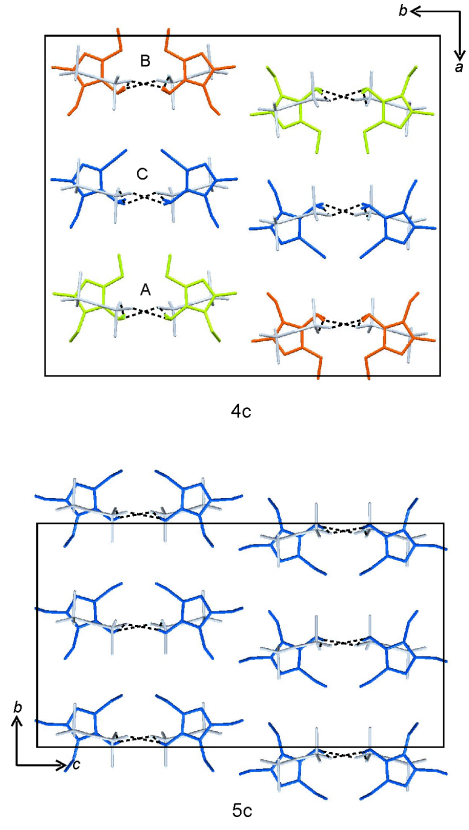
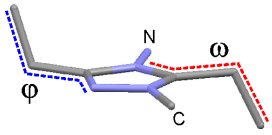


Fig. 4. Comparison of the crystal packing of **4c** ($P2_1/c$, $Z' = 3$) and **5c** (*Pbca*). Each structure is viewed parallel to the translation of the NH···O-bonded chain, *i. e.* along the *c* (**4c**) or *a* axis (**5c**). Tf_2N ions are colored grey, and all F atoms are omitted for clarity. The orthorhombic packing of **5c** is largely maintained in the crystal structure of **4c** whose three independent cations A, B and C adopt different conformations.

This 1D extended structure propagates in [101] direction, and exhibits glide symmetry. It can be seen from Fig. 3 that the same single-stranded chain motif is also present in the crystal structure of **3c** (space group $P\bar{1}$). In this case, however, the extended 1D structure, which runs parallel to the crystallographic *a* axis, contains no symmetry elements apart from translation. Furthermore, a somewhat more complex double-stranded motif is present in the structures of **5c** (space group *Pbca*) and **4c** ($P2_1/c$ with $Z' = 3$). It is obtained by joining two adjacent single strands together by one additional NH···O bond, so that one H and one O site act as two-fold H bond donor and acceptor, respectively, and the two individual strands are related to one another by glide symmetry. The extended 1D structure is composed of fused $R_3^3(8)$ rings in which two cation



Compound/molecule	φ	ω
4b	96.6	−94.5
4c / A	3.2	−103.1
4c / B	−6.7	−110.3
4c / B[a]	−49.5	−110.3
4c / C	95.0	−99.1
5c	97.5	−99.9

[a] Minor component of disorder.

Fig. 5. Torsion angles φ and ω describing the rotation angles of the two ethyl groups relative to the triazole ring in compounds with R^1 = Et (see Scheme 1).

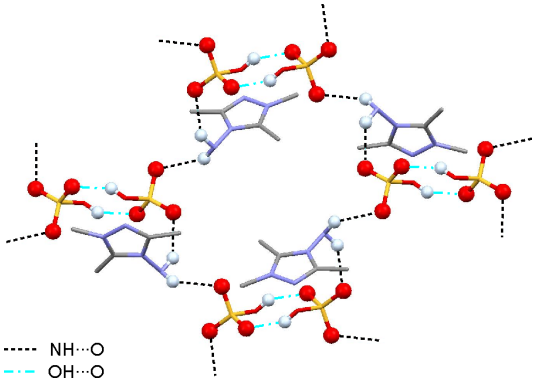


Fig. 6. Portion of the 2D H-bonded network in the crystal structure of **2d** showing a central $R_{10}^{10}(32)$ ring composed of four cations and six hydrogensulfate moieties. H and O atoms engaged in hydrogen bonding are drawn as balls, and all other H atoms are omitted for clarity.

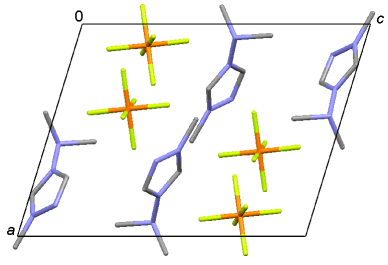


Fig. 7. Arrangement of the molecules of **6b** in the crystal. For clarity, H atoms are omitted.

and two anion moieties are joined together. Moreover, a comparison with the program XPAC [39] reveals that, despite different space group symmetries, the entire crystal packing arrangements of **4c** and **5c** are the same in principle, and this similarity is illustrated in Fig. 4. However, there are three independent H-bonded

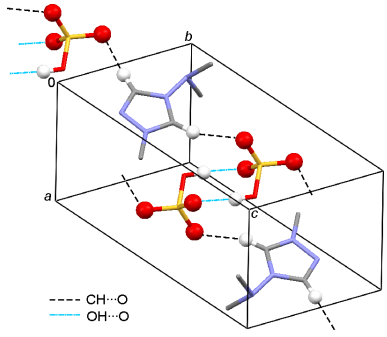


Fig. 8. Arrangement of the molecules of **6d** in the crystal. H and O atoms engaged in hydrogen bonding are drawn as balls, and all other H atoms are omitted for clarity.

double-stranded chains in **4c**, but just one in **5c**. The described similarity relationship dictates that the unit cell parameters of **4c** (a', b', c') and **5c** (a, b, c) correspond closely to one another in the following manner: $a' \approx 1.5\ b$, $b' \approx c$, $c' \approx a$ (see also Table 1 and Fig. 4).

Using the torsion angles φ and ω, as defined in Fig. 5, which describe the rotation angles of the two ethyl groups relative to the triazole ring, we have analyzed the cation conformation for those compounds where R^1 = Et, *i. e.* **4b**, **5c** and **4c**. These parameters are listed in Fig. 5. For **4b**, **5c** and molecule C of **4c**, they indicate that both ethyl groups lie approximately perpendicular to the plane of the triazole ring. In the remaining two independent molecules A and B of **4c** this geometry is, by contrast, adopted by just one ethyl group while the other lies approximately in the plane of the triazole ring. It is interesting to note that the minor disorder component of molecule B has an intermediate geometry.

In the crystal structure of **2d**, the cation is NH···O-bonded to two $HOSO_3$ units, and in addition, the hydrogensulfate anions form centrosymmetric OH···O-bonded dimers. Fig. 6 shows a portion of the extended 2D hydrogen-bonded network which results from these interactions. It lies parallel to the (101) plane and is composed of fused $R_{10}^{10}(32)$ rings which are centrosymmetric and link four cations and six $HOSO_3$ moieties together.

In contrast, the 4-(dimethylamino)-1-methyl-1,2,4-triazolium cation does not contain potential H donors. Hence, there is a complete lack of strong interactions in compound **6b** (Fig. 7). In the crystal structure of **6d**, again a dimeric hydrogensulfate is formed, but only weak CH···O interactions (Table 2) are observed between the anion and the cation (Fig. 8). In the silver-NHC complex **7**, the Ag atoms are arranged in layers

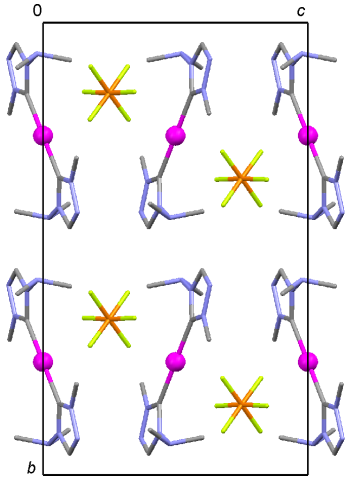


Fig. 9. Arrangement of the molecules of **7** in the crystal. For clarity, H atoms are omitted.

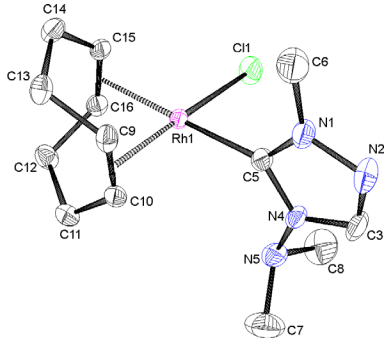


Fig. 10. ORTEP plot of complex **8**. For clarity, H atoms are omitted.

parallel to the (001) plane (Fig. 9), and the Ag–C bond length of 2.093(4) Å is in the usual range. Weak Ag···F1 contacts with a distance of 3.123(7) Å were found. The rhodium complex **8** shows the expected square-planar geometry (Fig. 10), and the Rh–C bond length of 2.019(3) Å is unremarkable. The molecules are linked by weak CH···Cl interactions (Table 2). The crystal structure of the 5-bromo derivative **9** revealed a C–Br bond length of 1.816(5) Å. Again, no strong interactions were detected (Fig. 11).

Conclusion

Simple and inexpensive transformations have yielded new ionic liquids and interesting crystalline solids. Permethylation of 4-amino-1,2,4-triazole affords a new fundamental carbene precursor. It can be perceived that a revival of well-known systems may

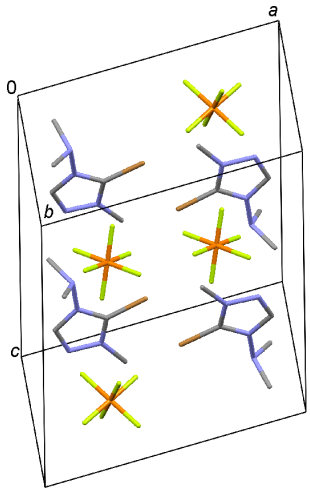


Fig. 11. Arrangement of the molecules of **9** in the crystal.

turn into a beneficial stimulus for new chemistry. We believe that the new functionalized ligand has potential and warrants further research.

Experimental Section

4-Amino-3,5-dialkyl-1,2,4-triazoles were prepared according to known procedures [26]. NMR spectra were recorded using Bruker AC 300 and Avance II+ 600 spectrometers. IR spectra were obtained with a Nicolet 5700 FT spectrometer in ATR mode. X-Ray diffraction data were collected on Oxford Diffraction Gemini-R Ultra, Stoe IPDS 2, and Nonius Kappa CCD diffractometers using MoK_α or CuK_α radiation.

*General procedure for the preparation of compounds **1a**, **2a**, **3a**, **4a**, and **5a***

A solution of 4-amino-3,5-dialkyl-1,2,4-triazole (5 g, 59 mmol) and dialkylsulfate (71 mmol, 1.2 equivalents) in CH_3CN (250 mL) was stirred at ambient temperature for 24 h. The solvent was evaporated and the residue washed with Et_2O (3 × 50 mL) to give the crude product as a clear oil which was dried in vacuum to constant weight.

*General procedure for the preparation of compounds **2b**, **3b**, **4b**, and **5b***

A mixture of the respective 1-alkyl-4-amino-3,5-dialkyl-1,2,4-triazolium alkylsulfate **2a** – **5a** (2 g) and NH_4PF_6 (1.05 equivalents) was ultrasonicated for 2 h. The precipitate was collected by filtration, washed with H_2O (10 mL) and Et_2O (20 mL), and dried. Suitable crystals were obtained by slow evaporation of MeOH solutions.

Table 1. Crystal data and structure refinement details.

Compound	**1b**	**2b**	**2c**	**2d**	**3b**
CCDC no.	726933	726934	726935	726936	726937
Chemical formula	$C_{24}H_{20}B{\cdot}C_3H_7N_4$	$C_5H_{11}N_4{\cdot}F_6P$	$C_5H_{11}N_4{\cdot}C_2F_6NO_4S_2$	$C_5H_{12}N_4O_4S$	$C_6H_{13}N_4{\cdot}F_6P$
M_r	418.34	272.13	407.32	224.25	286.17
Crystal shape, color	plate, colorless	isometric fragment, colorless	prismatic fragment, colorless	prism, colorless	prismatic fragment, colorless
Crystal size, mm^3	$0.3\times0.2\times0.1$	$0.4\times0.4\times0.4$	$0.36\times0.32\times0.28$	$0.4\times0.3\times0.2$	$0.4\times0.16\times0.16$
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_12_12_1$	Cc	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	9.0749(18)	13.5070(9)	8.4779(4)	8.3995(3)	16.8185(2)
b, Å	15.269(3)	7.4379(5)	12.8127(7)	11.0918(3)	7.73610(10)
c, Å	16.447(3)	12.4612(8)	14.0342(7)	11.0203(3)	18.3294(2)
β, deg	90	121.156(5)	90.734(4)	109.274(2)	94.9760(10)
V, Å^3	2279.0(8)	1071.32(13)	1524.34(13)	969.17(5)	2375.84(5)
Z	4	4	4	4	8
D_x, g cm^{-3}	1.22	1.69	1.78	1.54	1.60
μ, mm^{-1}	0.07	0.32	0.44	0.33	2.73
$F(000)$, e	888	552	824	472	1168
Diffractometer	Oxford Diffraction Gemini-R Ultra	Stoe IPDS 2	Stoe IPDS 2	Nonius KappaCCD	Oxford Diffraction Gemini-R Ultra
Radiation type	MoK_α	MoK_α	MoK_α	MoK_α	CuK_α
Data collection method	ω scans	rotation method	rotation method	ϕ and ω scans	ω scans
Temperature, K	173(2)	173(2)	173(2)	233(2)	100(2)
θ_{max}, deg	25.0	25.1	25.1	25.0	66.9
h, k, l range	±10, $-18\rightarrow17$, $-19\rightarrow15$	$-15\rightarrow16$, ±8, ±14	±10, $-13\rightarrow15$, ±16	±9, $-13\rightarrow12$, ±13	±19, $-8\rightarrow9$, $-17\rightarrow21$
Absorption correction	multi-scan	none	none	none	multi-scan
Measured reflections	14256	6693	9636	5385	19239
Independent reflections	2291 (R_{int} = 0.025)	1881 (R_{int} = 0.036)	2642 (R_{int} = 0.033)	1680 (R_{int} = 0.016)	4160 (R_{int} = 0.027)
Observed reflections [$I\geq2\sigma(I)$]	2130	1815	2139	1587	3830
Refinement on	F^2	F^2	F^2	F^2	F^2
Data/restraints/parameters	2291/0/280	1881/2/155	2642/0/227	1680/2/178	4160/0/325
R_1/wR_2 [$I\geq2\sigma(I)$]	0.065/0.117	0.050/0.134	0.033/0.082	0.030/0.083	0.047/0.127
R_1/wR_2 (all data)	0.070/0.119	0.052/0.136	0.045/0.086	0.032/0.084	0.045/0.129
Goodness of fit	1.17	1.07	1.03	1.02	1.10
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.34/−0.32	0.66/−0.45	0.27/−0.28	0.16/−0.28	0.95/−0.51

*General procedure for the preparation of compounds **1c**, **2c**, **3c**, **4c**, and **5c***

The metathesis of the respective 1-alkyl-4-amino-3,5-dialkyl-1,2,4-triazolium alkylsulfate **1a**–**5a** (2 g) and $LiTf_2N$ (1.05 equivalents) in H_2O resulted in the formation of a second dense liquid phase. Compound **1c** was washed with small volumes of H_2O and Et_2O, and the volatiles were removed in vacuum to give a clear liquid. The compounds **2c**, **3c**, **4c** and **5c** crystallized on standing and were collected by filtration, washed with H_2O and Et_2O, and dried. Single crystals were obtained by slow evaporation of MeOH solutions.

*4-Amino-1-methyl-1,2,4-triazolium methylsulfate (**1a**)*

Yield: 12.4 g (99 %). – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 3.36 (s, 3H), 4.04 (s, 3H), 6.7 (br s, 2H), 9.14 (s, 1H), 10.05 (s, 1H). – ^{13}C NMR (150 MHz, [D$_6$]DMSO): δ = 39.3, 53.4, 143.5, 145.5. – IR (neat): ν = 3295, 3080, 2951, 1634, 1574, 1455, 1207, 1057, 996, 743, 609, 579, 554 cm^{-1}.

*4-Amino-1-methyl-1,2,4-triazolium tetraphenylborate (**1b**)*

From **1a** and sodium tetraphenylborate in the minimum amount of H_2O. Yield: 720 mg (72 %). Single crystals from MeOH. M. p. 195 – 196 °C. – ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 4.02 (s, 3H), 6.80 (m, 4H), 6.94 (m, 8H), 7.19 (m, 8H), 9.16 (s, 1H), 10.05 (s, 1H). – ^{13}C NMR (150 MHz, [D$_6$]DMSO): δ = 39.3, 122.0, 125.8, 136.0, 143.4, 145.5, 163.8 (q, J_{C-B} = 49 Hz). – IR (neat): ν = 3349, 3256, 3055, 2999, 1604, 1576, 1478, 1426, 1148, 1068, 1030, 907, 852, 738, 705, 605 cm^{-1}.

*4-Amino-1-methyl-1,2,4-triazolium triflimide (**1c**)*

Yield: 1.7 g (47 %). Colorless liquid, $[n]_D^{20}$ = 1.4281. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 4.01 (s, 3H), 6.9 (br

Table 1 (continued).

Compound	**3c**	**4b**	**4c**	**5c**	**6b**
CCDC no.	726938	726939	726940	726941	726942
Chemical formula	$C_6H_{13}N_4{\cdot}C_2F_6NO_4S_2$	$C_7H_{15}N_4{\cdot}F_6P$	$C_7H_{15}N_4{\cdot}C_2F_6NO_4S_2$	$C_8H_{17}N_4{\cdot}C_2F_6NO_4S_2$	$C_5H_{11}N_4{\cdot}F_6P$
M_r	421.35	300.2	435.38	449.41	272.15
Crystal shape, color	thin plate, colorless	plate, colorless	platy fragment, colorless	plate, colorless	fragment of a lath, colorless
Crystal size, mm^3	$0.20\times0.16\times0.02$	$0.40\times0.36\times0.12$	$0.40\times0.40\times0.22$	$0.48\times0.28\times0.08$	$0.2\times0.16\times0.16$
Crystal system	triclinic	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$Pbca$	$P2_1/n$
a, Å	8.1283(13)	7.4927(2)	23.7133 (2)	8.20470(10)	8.9534(3)
b, Å	8.3875(15)	14.8605(3)	27.6050 (3)	15.7263(3)	10.6379(3)
c, Å	14.031(3)	11.6146(3)	8.08214 (7)	28.5497(5)	11.6021(4)
α, deg	97.409(15)	90	90	90	90
β, deg	96.302(15)	106.685(3)	89.999(1)	90	106.968(4)
γ, deg	118.535(18)	90	90	90	90
V, Å^3	817.1(3)	1238.78(6)	5287.32(8)	3683.76(11)	1056.94(6)
Z	2	4	12	8	4
D_x, g cm^{-3}	1.71	1.61	1.64	1.62	1.71
μ, mm^{-1}	3.85	0.29	3.59	0.38	0.33
$F(000)$, e	428	616	2664	1840	552
Diffractometer	Oxford Diffraction Gemini-R Ultra	Oxford Diffraction Gemini-R Ultra	Oxford Diffraction Gemini-R Ultra	Oxford Diffraction Gemini-R Ultra	Oxford Diffraction Gemini-R Ultra
Radiation type	CuK_α	MoK_α	CuK_α	MoK_α	MoK_α
Data collection method	ω scans	ω scans	ω scans	ω scans	ω scans
Temperature, K	173(2)	100(2)	100(2)	100(2)	100(2)
θ_{max}, deg	67.4	25.4	67.3	25.3	25.4
h, k, l range	±9, $-9\rightarrow8$, $-15\rightarrow16$	$-8\rightarrow9$, $-17\rightarrow15$, ±13	$-28\rightarrow27$, ±32, ±9	$-8\rightarrow9$, ±18, ±34	±10, $-12\rightarrow10$, ±13
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Measured reflections	6646	9398	44137	25053	6604
Independent reflections	2849 (R_{int}=0.041)	2261 (R_{int}=0.027)	9244 (R_{int}=0.028)	3350 (R_{int}=0.027)	1922 (R_{int}=0.030)
Observed reflections [$I\geq2\sigma(I)$]	2182	1966	8838	3072	1548
Refinement on	F^2	F^2	F^2	F^2	F^2
Data/restraints/parameters	2849/2/235	2261/0/174	9244/9/742	3350/0/255	1922/0/148
R_1/wR_2 [$I\geq2\sigma(I)$]	0.057/0.165	0.034/0.076	0.068/0.158	0.031/0.073	0.032/0.066
R_1/wR_2 (all data)	0.076/0.185	0.042/0.079	0.070/0.159	0.036/0.075	0.050/0.070
Goodness of fit	1.12	1.10	1.21	1.10	1.04
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.35/−0.54	0.21/−0.28	1.19/−0.68	0.45/−0.32	0.25/−0.29

s, 2H), 9.14 (s, 1H), 10.06 (s, 1H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 38.9, 119.5 (q, J_{C-F} = 322 Hz, 2C), 143.0, 145.0. – IR (neat): ν = 3358, 3305, 3251, 3149, 3106, 1635, 1574, 1345, 1326, 1177, 1128, 1049, 978, 880, 790, 741, 654, 610, 598, 569, 509 cm^{-1}.

*4-Amino-1,3,5-trimethyl-1,2,4-triazolium methylsulfate (**2a**)*

Yield: 10.4 g (98 %). – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.44 (s, 3H), 2.61 (s, 3H), 3.35 (s, 3H), 3.89 (s, 3H), 6.4 (br s, 2H). – IR (neat): ν = 3331, 3196, 1639, 1593, 1422, 1397, 1166, 1036, 852, 578 cm^{-1}.

*4-Amino-1,3,5-trimethyl-1,2,4-triazolium hexafluorophosphate (**2b**)*

Yield: 1.7 g (74 %). M. p. 144 – 145 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.45 (s, 3H), 2.61 (s, 3H), 3.89 (s, 3H), 6.4 (br s, 2H). – IR (neat): ν = 3395, 3316, 1621, 1579, 1403, 1290, 824, 735, 555 cm^{-1}.

*4-Amino-1,3,5-trimethyl-1,2,4-triazolium triflimide (**2c**)*

Yield: 2.3 g (67 %). M. p. 105 – 106 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.45 (s, 3H), 2.61 (s, 3H), 3.89 (s, 3H), 6.4 (br s, 2H). – ^{13}C NMR (150 MHz, [D$_6$]DMSO): δ = 9.4, 9.7, 37.9, 120.0 (q, J_{C-F} = 317 Hz, 2C), 152.8, 153.2. – IR (neat): ν = 3381, 1639, 1594, 1398, 1347, 1328, 1224, 1181, 1132, 1050, 933, 842, 797, 740, 612, 569, 514 cm^{-1}.

*4-Amino-1,3,5-trimethyl-1,2,4-triazolium hydrogensulfate (**2d**)*

The product crystallized after months from the liquid methylsulfate **2a**, obviously due to hydrolysis. M. p. 122 –

Table 1 (continued).

Compound	**6d**	**7**	**8**	**9**
CCDC no.	726943	726944	726945	726946
Chemical formula	$C_5H_{11}N_4 \cdot HO_4S$	$C_{10}H_{20}AgN_8 \cdot F_6P$	$C_{13}H_{22}ClN_4Rh$	$C_5H_{10}BrN_4 \cdot F_6P$
M_r	224.25	505.18	372.71	351.05
Crystal shape, color	platy fragment, colorless	platy fragment, colorless	prism, colorless	platy fragment, colorless
Crystal size, mm^3	$0.28 \times 0.2 \times 0.12$	$0.24 \times 0.20 \times 0.16$	$0.25 \times 0.05 \times 0.03$	$0.36 \times 0.24 \times 0.04$
Crystal system	triclinic	monoclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$	$C2/c$	$Pbca$	$P2_1/c$
a, Å	6.9323(5)	8.3357(4)	12.0356(3)	11.1600(5)
b, Å	8.2263(6)	19.5051(9)	13.4939(3)	7.8657(3)
c, Å	9.8309(7)	11.9259(5)	19.2428(4)	14.5840(6)
α, deg	68.529(7)	90	90	90
β, deg	72.599(7)	106.238(5)	90	104.791(4)
γ, deg	71.073(7)	90	90	90
V, Å^3	483.05(7)	1861.67(15)	3125.17(12)	1237.79(9)
Z	2	4	8	4
D_x, g cm^{-3}	1.54	1.802	1.584	1.884
μ, mm^{-1}	0.33	1.24	1.26	3.51
$F(000)$, e	236	1008	1520	688
Diffractometer	Oxford Diffraction Gemini-R Ultra	Oxford Diffraction Gemini-R Ultra	Nonius KappaCCD	Oxford Diffraction Gemini-R Ultra
Radiation type	MoK_α	MoK_α	MoK_α	MoK_α
Data collection method	ω scans	ω scans	ϕ and ω scans	ω scans
Temperature, K	173(2)	173(2)	233(2)	173(2)
θ_{max}, deg	25.4	25.3	25.0	25.4
h, k, l range	$\pm 8, \pm 9, -11 \rightarrow 9$	$-8 \rightarrow 10, -18 \rightarrow 23, -14 \rightarrow 13$	$\pm 14, \pm 16, -22 \rightarrow 19$	$-13 \rightarrow 10, -7 \rightarrow 9, -15 \rightarrow 17$
Absorption correction	none	multi-scan	none	multi-scan
Measured reflections	3705	5841	18494	4722
Independent reflections	1756 ($R_{int} = 0.027$)	1701 ($R_{int} = 0.031$)	2746 ($R_{int} = 0.039$)	2263 ($R_{int} = 0.039$)
Observed reflections $[I \geq 2\sigma(I)]$	1475	1420	2180	1504
Refinement on	F^2	F^2	F^2	F^2
Data/restraints/parameters	1756/0/131	1701/0/123	2746/4/191	2263/0/157
R_1/wR_2 $[I \geq 2\sigma(I)]$	0.034/0.085	0.040/0.108	0.029/0.064	0.040/0.097
R_1/wR_2 (all data)	0.043/0.087	0.048/0.112	0.041/0.068	0.066/0.102
Goodness of fit	1.07	1.05	1.04	0.91
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.19/−0.37	1.40/−0.75	0.67/−0.62	0.56/−0.36

123 °C. – ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 2.45 (s, 3H), 2.63 (s, 3H), 3.88 (s, 3H), 5.7 (br s, 3H). – ^{13}C NMR (150 MHz, [D$_6$]DMSO): δ = 9.4, 9.7, 37.8, 152.9, 153.3. – IR (neat): ν = 3329, 2933, 1635, 1586, 1439, 1416, 1396, 1306, 1228, 1153, 1048, 840, 578, 561 cm^{-1}.

*4-Amino-1-ethyl-3,5-dimethyl-1,2,4-triazolium ethylsulfate (**3a**)*

Yield: 10.8 g (91 %). – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.08 (t, J = 7.2 Hz, 3H), 1.36 (t, J = 7.3 Hz, 3H), 2.46 (s, 3H), 2.65 (s, 3H), 3.71 (q, J = 7.2 Hz, 2H), 4.24 (q, J = 7.3 Hz, 2H), 6.4 (br s, 2H). – ^{13}C NMR (150 MHz, [D$_6$]DMSO): δ = 9.2, 9.8, 13.9, 15.5, 45.8, 61.8, 152.3, 153.5. – IR (neat): ν = 3292, 3182, 2982, 2942, 2902, 1639, 1578, 1445, 1388, 1208, 1047, 1012, 912, 766, 620, 579 cm^{-1}.

*4-Amino-1-ethyl-3,5-dimethyl-1,2,4-triazolium hexafluorophosphate (**3b**)*

Yield: 0.8 g (37 %). M. p. 94 – 95 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.37 (t, J = 7.3 Hz, 3H), 2.46 (s, 3H), 2.64 (s, 3H), 4.25 (q, J = 7.3 Hz, 2H), 6.4 (br s, 2H). – ^{13}C NMR (150 MHz, [D$_6$]DMSO): δ = 9.2, 9.8, 13.9, 45.9, 152.2, 153.5. – IR (neat): ν = 3400, 3330, 1625, 1578, 1396, 925, 822, 555 cm^{-1}. – $C_6H_{13}F_6N_4P$ (286.16): calcd. C 25.18, H 4.58, N 19.58; found C 25.24, H 4.29, N 19.27.

*4-Amino-1-ethyl-3,5-dimethyl-1,2,4-triazolium triflimide (**3c**)*

Yield: 2.2 g (70 %). M. p. 65 – 66 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.37 (t, J = 7.3 Hz, 3H), 2.46 (s, 3H), 2.65 (s, 3H), 4.25 (q, J = 7.3 Hz, 2H), 6.4 (br s, 2H). –

Table 2. Hydrogen bonding geometries (Å, deg).

Compound	Interaction	H···*A*	*D*···*A*	*D*–H···*A*	Symmetry code (*A*)
2b	N5–Ha···F4	2.50	3.076	122	$1/2+x, -1/2+y, z$
	N5–Hb···F2	2.63	3.288	126	–
2c	N5–Ha···O3	2.38	3.080	135	$1/2+x, 1/2-y, 1/2+z$
	N5–Hb···O4	2.16	2.965	147	–
2d	N5–Ha···O2	2.30	2.864	122	–
	N5–Ha···O2a	2.27	3.052	147	–
	N5–Hb···O3	2.24	3.000	143	$1/2-x, -1/2+y, 3/2-z$
	N5–Hb···O3a	2.24	2.999	144	$1/2-x, -1/2+y, 3/2-z$
	O1–H···O4	1.83	2.574	148	$-x, 1-y, 2-z$
3b	N5–Ha···F3	2.34	2.893	122	$3/2-x, -1/2+y, 1/2-z$
	N5–Hb···F3	2.26	2.986	144	$x, -1+y, z$
	N55–Ha···F8	2.18	3.016	160	$x, 1+y, z$
	N55–Hb···F8	2.34	3.035	138	$3/2-x, 1/2+y, 3/2-z$
3c	N5–Ha···O3	2.22	3.143	160	–
	N5–Hb···O4	2.23	3.117	154	$1+x, y, z$
4b	N5–Ha···F4	2.29	3.057	151	$-1/2+x, 1/2-y, -1/2+z$
	N5–Hb···F6	2.25	3.147	167	$1/2-x, 1/2+y, 1/2-z$
4c	N5A–Ha1···O11	2.34	3.096	144	$x, y, 1+z$
	N5A–Ha2···O12	2.55	3.093	120	$x, 1/2-y, 1/2+z$
	N5A–Ha2···O12	2.26	3.125	166	–
	N5B–Hb1···O24	2.37	3.093	139	–
	N5B–Hb1···O23	2.42	3.099	135	$x, 3/2-y, -1/2+z$
	N5B–Hb2···O23	2.37	3.192	155	$x, y, -1+z$
	N5C–Hc1···O33	2.28	3.104	156	–
	N5C–Hc2···O34	2.47	3.090	128	$x, y, -1+z$
	N5C–Hc2···O33	2.46	3.068	126	$x, 3/2-y, -1/2+z$
5c	N5–Ha···O4	2.45	3.070	132	$-1/2+x, y, 1/2-z$
	N5–Ha···O3	2.37	3.115	148	–
	N5–Hb···O4	2.31	3.117	156	$1+x, y, z$
6d	C3–H···O3	2.30	3.241	172	$1-x, 1-y, -z$
	C5–H···O2	2.21	3.119	159	$1-x, 1-y, 1-z$
	O1–H···O4	1.79	2.626	172	$1-x, 1-y, 1-z$
7	C3–H···F2	2.25	3.070	144	$1-x, -y, 1-z$
8	C3–H···Cl1	2.56	3.492	172	$1/2+x, y, 1/2-z$

IR (neat): ν = 3373, 3000, 1639, 1585, 1350, 1321, 1183, 1130, 1047, 918, 824, 798, 742, 609, 569, 515 cm^{-1}.

*4-Amino-3,5-diethyl-1-methyl-1,2,4-triazolium methylsulfate (**4a**)*

Yield: 9.2 g (97 %). – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.21 (t, *J* = 7.5 Hz, 3H), 1.25 (t, *J* = 7.5 Hz, 3H), 2.84 (q, *J* = 7.5 Hz, 2H), 3.06 (q, *J* = 7.5 Hz, 2H), 3.34 (s, 3H), 3.95 (s, 3H), 6.5 (br s, 2H). – ^{13}C NMR (150 MHz, [D$_6$]DMSO): δ = 10.0, 10.4, 16.4, 17.3, 37.9, 53.4, 155.8, 157.3. – IR (neat): ν = 3310, 2986, 2948, 1634, 1582, 1460, 1171, 1044, 999, 845, 754, 575 cm^{-1}.

*4-Amino-3,5-diethyl-1-methyl-1,2,4-triazolium hexafluorophosphate (**4b**)*

Yield: 0.5 g (22 %). M. p. 120 – 121 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.21 (t, *J* = 7.5 Hz, 3H), 1.25 (t, *J* = 7.5 Hz, 3H), 2.84 (q, *J* = 7.5 Hz, 2H), 3.05 (q, *J* = 7.5 Hz, 2H), 3.95 (s, 3H), 6.5 (br s, 2H). – ^{13}C NMR (150 MHz, [D$_6$]DMSO): δ = 10.1, 10.4, 16.4, 17.3, 37.9, 155.8, 157.1. – IR (neat): ν = 3392, 3323, 2996, 2950, 1634, 1583, 1459, 1246, 1060, 956, 823, 741, 555 cm^{-1}.

*4-Amino-3,5-diethyl-1-methyl-1,2,4-triazolium triflimide (**4c**)*

Yield: 2.4 g (73 %). M. p. 109 – 110 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.21 (t, *J* = 7.5 Hz, 3H), 1.25 (t, *J* = 7.5 Hz, 3H), 2.84 (q, *J* = 7.5 Hz, 2H), 3.05 (q, *J* = 7.5 Hz, 2H), 3.95 (s, 3H), 6.5 (br s, 2H). – IR (neat): ν = 3362, 2998, 2951, 1642, 1587, 1462, 1348, 1184, 1131, 1046, 960, 840, 796, 740, 611, 568, 514 cm^{-1}.

*4-Amino-1,3,5-triethyl-1,2,4-triazolium ethylsulfate (**5a**)*

Yield: 9.9 g (94 %). – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.08 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.6 Hz, 3H), 1.26

(t, J = 7.5 Hz, 3H), 1.38 (t, J = 7.2 Hz, 3H), 2.85 (q, J = 7.5 Hz, 2H), 3.08 (q, J = 7.6 Hz, 2H), 3.71 (q, J = 7.1 Hz, 2H), 4.30 (q, J = 7.2 Hz, 2H), 6.5 (br s, 2H). – ^{13}C NMR (150 MHz, [D$_6$]DMSO): δ = 10.0, 11.0, 14.4, 15.5, 16.3, 17.4, 45.8, 61.7, 155.4, 157.5. – IR (neat): ν = 3298, 3179, 2984, 2946, 1638, 1571, 1460, 1386, 1192, 1045, 1005, 915, 846, 745, 577 cm^{-1}.

*4-Amino-1,3,5-triethyl-1,2,4-triazolium hexafluorophosphate (**5b**)*

Yield: 1.1 g (52 %). M. p. 81 – 82 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.22 (t, J = 7.5 Hz, 3H), 1.26 (t, J = 7.5 Hz, 3H), 1.39 (t, J = 7.2 Hz, 3H), 2.85 (q, J = 7.5 Hz, 2H), 3.08 (q, J = 7.5 Hz, 2H), 4.30 (q, J = 7.2 Hz, 2H), 6.5 (br s, 2H). – IR (neat): ν = 3392, 3323, 2997, 2951, 1634, 1576, 1458, 1391, 943, 822, 741, 555 cm^{-1}. – $C_8H_{17}F_6N_4P$ (314.21): calcd. C 30.58, H 5.45, N 17.83; found C 30.50, H 5.10, N 17.52.

*4-Amino-1,3,5-triethyl-1,2,4-triazolium triflimide (**5c**)*

Yield: 2.4 g (79 %). M. p. 106 – 107 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.22 (t, J = 7.5 Hz, 3H), 1.26 (t, J = 7.5 Hz, 3H), 1.39 (t, J = 7.3 Hz, 3H), 2.85 (q, J = 7.5 Hz, 2H), 3.08 (q, J = 7.5 Hz, 2H), 4.30 (q, J = 7.3 Hz, 2H), 6.5 (br s, 2H). – ^{13}C NMR (150 MHz, [D$_6$]DMSO): δ = 10.1, 11.0, 14.4, 16.3, 17.4, 45.8, 120.0 (q, J_{C-F} = 321 Hz, 2C), 155.4, 157.5. – IR (neat): ν = 3361, 3000, 2952, 1639, 1573, 1463, 1346, 1193, 1132, 1035, 965, 825, 795, 742, 611, 568, 514 cm^{-1}.

*4-(Dimethylamino)-1-methyl-1,2,4-triazolium methylsulfate (**6a**)*

A mixture of 4-amino-1,2,4-triazole (5 g, 59 mmol) and dimethyl sulfate (17 mL, 178 mmol, 3 equivalents) was heated at 100 °C for 5 h. After cooling the viscous oil was stirred with Et$_2$O (3 × 20 mL), the solvent was discarded, and the residue was dried in vacuum. Yield: 2.7 g (95 %). – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.91 (s, 6H), 3.36 (s, 3H), 3.99 (s, 3H), 9.55 (s, 1H), 10.37 (s, 1H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 40.1, 47.9 (2C), 53.3, 142.5 (2C).

*4-(Dimethylamino)-1-methyl-1,2,4-triazolium hexafluorophosphate (**6b**)*

A mixture of 4-amino-1,2,4-triazole (5 g, 59 mmol) and dimethyl sulfate (10 mL, 105 mmol, 1.8 equivalents) was heated at 100 °C for 24 h. After cooling the viscous oil was stirred with Et$_2$O (3 × 20 mL), and the solvent was discarded. The oil was dissolved in H$_2$O (30 mL), and a solution of NH_4PF_6 (10.7 g, 65 mmol) in H$_2$O (30 mL) was added with stirring. The precipitate was filtered, washed with H$_2$O (10 mL) and sucked dry. The crude product was recrystallized from a hot mixture of MeOH (30 mL) and H$_2$O (30 mL), filtered, washed with MeOH/H$_2$O (10 mL) and Et$_2$O (2 × 10 mL), and dried to give **6b** as colorless needles. Yield: 12.0 g (74 %). M. p. 141 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.94 (s, 6H), 4.01 (s, 3H), 9.61 (s, 1H), 10.44 (s, 1H). – ^{13}C NMR (150 MHz, [D$_6$]acetone): δ = 39.1, 47.6 (2C), 142.2, 142.3. – IR (neat): ν = 3161, 3127, 1581, 1458, 1135, 1063, 1020, 983, 884, 820, 742, 706, 669, 642, 591, 555, 489, 459 cm^{-1}.

*4-(Dimethylamino)-1-methyl-1,2,4-triazolium triflimide (**6c**)*

A mixture of 4-amino-1,2,4-triazole (1.0 g, 12 mmol) and dimethyl sulfate (2 mL, 21 mmol, 1.8 equivalents) was heated at 100 °C for 24 h. After cooling the viscous oil was stirred with Et$_2$O (3 × 5 mL), and the solvent was discarded. The oil was dissolved in H$_2$O (10 mL), and a solution of $LiTf_2N$ (3.6 g, 12 mmol) in H$_2$O (50 mL) was added with stirring. The resulting second dense phase was separated, washed with H$_2$O, and dried in vacuum. The product crystallized overnight. Yield: 3.4 g (70 %). M. p. 78 – 80 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.94 (s, 6H), 4.01 (s, 3H), 9.61 (s, 1H), 10.44 (s, 1H). – ^{13}C NMR (150 MHz, [D$_6$]DMSO): δ = 39.4, 48.2 (2C), 120.0 (q, J_{C-F} = 317 Hz, 2C), 142.8 (2C). – IR (neat): ν = 3141, 1574, 1466, 1346, 1181, 1138, 1050, 914, 837, 790, 740, 671, 612, 569, 512 cm^{-1}. – $C_7H_{11}F_6N_5O_4S_2$ (407.31): calcd. C 20.64, H 2.72, N 17.19, S 15.74; found C 21.01, H 2.83, N 16.80, S 15.37.

*4-(Dimethylamino)-1-methyl-1,2,4-triazolium hydrogensulfate (**6d**)*

A mixture of 4-amino-1,2,4-triazole (5 g, 59 mmol) and dimethyl sulfate (8.5 mL, 89 mmol) was heated at 100 °C for 24 h. After cooling the viscous oil was stirred with Et$_2$O (3 × 20 mL), and the solvent was discarded. Volatiles were removed in vacuum, and part of the resulting oil crystallized overnight. The hygroscopic solid was collected by filtration and dried. Yield: 1.1 g (8 %). M. p. 105 – 110 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.94 (s, 6H), 4.02 (s, 3H), 6.0 (br s, 1H), 9.61 (s, 1H), 10.47 (s, 1H). – IR (neat): ν = 3099, 3063, 1567, 1460, 1331, 1233, 1160, 1143, 1049, 832, 577 cm^{-1}.

*Bis[4-(dimethylamino)-1-methyl-1,2,4-triazolin-5-ylidene]silver(I) hexafluorophosphate (**7**)*

A suspension of 4-(dimethylamino)-1-methyl-1,2,4-triazolium hexafluorophosphate (**6b**) (1.0 g, 3.7 mmol) and Ag_2O (0.42 g, 1.8 mmol) in MeOH (20 mL) was stirred in the dark for 18 h at r. t. The colorless precipitate was

collected by filtration, washed with MeOH (1 mL) and Et_2O (10 mL), and dried. Yield: 0.82 g (88 %). M. p. 183 – 184 °C (dec). – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.98 (s, 6H), 4.07 (s, 3H), 9.20 (s, 1H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 41.3, 48.1, 142.3, 178.4 (br). – IR (neat): ν = 3160, 2965, 2870, 2835, 2790, 1471, 1451, 1405, 1374, 1230, 1057, 1028, 960, 927, 880, 826, 741, 677, 657, 593, 556, 517 cm^{-1}.

*Chloro(η^4-1,5-cyclooctadiene)[4-(dimethylamino)-1-methyl-1,2,4-triazolin-5-ylidene]rhodium(I) (**8**)*

To a solution of 4-(dimethylamino)-1-methyl-1,2,4-triazolium hexafluorophosphate (**6b**) (100 mg, 0.37 mmol) and [RhCl(cod)]$_2$ (90 mg, 0.18 mmol) in dry THF (2 mL) Et_3N (50 μL, 0.37 mmol) was added, and the mixture was stirred under Ar for 24 h at r. t. The solvent was removed and the residue treated with *iso*-pentane (2×1 mL). Then the residue was extracted with Et_2O (3 × 2 mL) and the solvent evaporated to yield 50 mg (37 %) of **8** as a yellow oil. Single crystals were obtained by diffusion of *iso*-pentane into a solution of **8** in Et_2O. M. p. 158 – 159 °C. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.95 (m, 4H), 2.41 (m, 4H), 3.16 (s, 6H), 3.46 (m, 2H), 4.30 (s, 3H), 5.06 (m, 2H), 8.02 (s, 1H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.0 (br s), 29.4 (br s), 32.6 (br s), 33.5 (br s), 41.6, 49.1 (2C), 68.8 (br s), 70.2 (br s), 98.1 (br s), 99.2 (br s), 140.8, 184.7 (d, J_{C-Rh} = 51 Hz). – IR (neat): ν = 3089, 3029, 2993, 2918, 2867, 2831, 2787, 1526, 1456, 1430, 1328, 1236, 1217, 1162, 1100, 1053, 1022, 990, 957, 923, 862, 818, 739, 705, 657, 604, 524, 492, 448 cm^{-1}.

*5-Bromo-4-(dimethylamino)-1-methyl-1,2,4-triazolium hexafluorophosphate (**9**)*

To a suspension of 4-(dimethylamino)-1-methyl-1,2,4-triazolium hexafluorophosphate (**6b**) (1.0 g, 3.7 mmol) in MeOH (3 mL) and H_2O (3 mL) bromine (0.19 mL, 3.7 mmol) and Na_2CO_3 (0.39 g, 3.7 mmol) were added. The mixture was stirred for 5 h at r. t. The precipitate was collected by filtration, washed with H_2O (2 mL) and Et_2O (10 mL) and dried. The crude product was stirred with acetone (9 mL). Insoluble matter was removed by filtration, and the product was precipitated by addition of Et_2O (9 mL), filtered and dried to yield 0.91 g (71 %) of pure **9** as colorless needles. M. p. 198 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.92 (s, 6H), 4.00 (s, 3H), 9.94 (s, 1H). – ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 3.14 (s, 6H), 4.21 (s, 3H), 9.76 (s, 1H). – ^{13}C NMR (75 MHz, [D$_6$]acetone): δ = 40.7, 48.2 (2C), 135.2, 144.1. – IR (neat): ν = 3154, 1532, 1466, 1414, 1331, 1240, 1185, 1082, 1020, 992, 872, 823, 731, 682, 657, 606, 556, 527 cm^{-1}.

X-Ray structure determination

In the crystal structure of **1b**, the whole cation was found to be statistically disordered over two positions. Each component of the disorder was treated as a rigid fragment (FRAG in SHELXL [40]), and the geometry used was that of the previously reported perchlorate analog [17]. The site occupancy of the main component was fixed at 0.6 in the final cycles of refinement. As illustrated in Fig. 1a, the mean planes of the two disordered fragments are tilted against one another by 28.0°, and the positions of their respective NH_2 and Me substituents are approximately interchanged.

Although the lattice of the structure of **4c** has an almost perfect orthorhombic geometry, solving it in the orthorhombic system proved to be impossible. Instead, a solution was obtained for $Z' = 3$ in the monoclinic space group $P2_1/c$, and consequently a pseudo-merohedral twin with equal contributions from the two twin domains was refined. A detailed analysis of the final structure model confirmed that the choice of space group symmetry was indeed correct. The terminal C atom of one ethyl group of one cation is statistically disordered over two positions. Geometrical restraints were applied for chemically equivalent C–C distances affected by this disorder, and the final occupancy of the main disorder fragment was 0.65(3).

Crystal data and structure refinement details are summarized in Table 1. CCDC 726933 – 726946 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.

Acknowledgements

A. S. is grateful for FWF grant SFB-F2107. T. G. is grateful for Lise-Meitner program M1135-N17.

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