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Terminal Acetylenic Iminium Salts: Cycloaddition Reactions with Azides leading to 1,2,3-Triazoles and Bicyclic 1,2,3-Triazolium Salts

Michael Keim[a] and Gerhard Maas*[a]

Abstract: Terminal acetylenic iminium triflate salts [HC≡C-C(R)=N$^+$Me$_2$ TfO$^-$] represent very potent dipolarophiles which undergo [3+2] cycloadditions with aryl and benzyl azides at very mild and uncatalyzed conditions, yielding 1,4-disubstituted 1,2,3-triazoles with complete regioselectivity. Addition of nucleophiles at the iminium group of the cycloadducts leads to diverse 1-aryl-(or benzyl-)-4-dimethylaminomethyl-1,2,3-triazoles. The first formed cycloaddition adducts subsequently react with a second molecule of the acetylenic iminium salt by a consecutive Michael addition/1,5-cyclization to form 2,4-dihydropyrrolo[1,2-*c*][1,2,3]triazol-7-ium triflates. Further transformations of the latter salts are described, among them the conversion into a mesoionic carbene, isolated as a monomeric silver(I) complex.

Introduction

The synthesis and potential applications of 1,2,3-triazoles have attracted much attention during the last two decades. In particular, these five-membered heterocycles own a rigid and chemically rather stable scaffold, which renders substituted and functionalized 1,2,3-triazoles as molecular entities of interest in bioorganic and medicinal, supramolecular and material chemistry. Among other things, they have been and still are research objects as bioactive compounds[1,2] and drug-like candidates.[1,3]

The 1,2,3-triazole ring system can be assembled by various metal-free cycloaddition routes,[4] among them the now classical Huisgen reaction from alkynes and azides.[5,6] Although this [3+2] cycloaddition reaction can be completely atom-economic, the regioselectivity is often not satisfactory and the kinetics strongly depend on the electronic properties of the reaction partners. For example, phenyl azide reacts quickly with ynamines[7] and enamines (which can serve as masked ynamines on the way to 1,2,3-triazoles[4d,8]), but only at significant thermal activation with electron-deficient or unactivated alkynes.[9–11] These drawbacks can be overcome by metal-catalyzed azide–alkyne cycloadditions, which have been developed by the Meldal, Sharpless and Fokin groups. The copper-catalyzed (CuAAC)[12,13] and the ruthenium(II)-catalyzed (RuAAC)[14] versions of these "click" reactions are nowadays widely used in the chemical community because of their regioselectivity, mild reaction conditions, efficiency, and tolerance of various functional groups. While the CuAAC reaction is applicable to terminal alkynes only, Ru-catalysis also accelerates the cycloaddition to internal alkynes. The control of regioselectivity in these reactions is remarkable: copper-catalyzed cycloadditions of azides and terminal alkynes provide 1,4-disubstituted 1,2,3-triazoles, while ruthenium catalysis leads to 1,5-disubstituted triazoles.

Given the ongoing interest in functionalized 1,2,3-triazoles, we set out to study the preparation of iminium-substituted triazoles by a [3+2] cycloaddition method. Acetylenic iminium salts are expected to react more rapidly with sufficiently electron-rich organoazides than related electron-deficient dipolarophiles such as acetylenic esters and carboxamides; in terms of the frontier orbital concept applied to these cycloadditions, an iminium group lowers the acetylenic LUMO compared with a carbonyl function. In fact, triazole formation by [3+2] cycloaddition reactions of benzyl azide with *N*,*N*-dimethyl-propiolcarboxamidinium[15] and acetylene-1,2-bis(carboxamidinium)[16] salts have been reported and a certain acceleration as compared to corresponding carboxamides was noted. On the other hand, we have just reported that terminal acetylenic iminium salts HC≡C-C(R)=N$^+$Me$_2$·TfO$^-$ (R = aryl, H) are extremely reactive dienophiles in [4+2] cycloaddition (Diels-Alder) reactions,[17] by far better than related acetylenic iminium salts with an internal C,C triple bond.[18] This high reactivity is considered to result from the synergy of electronic factors (lowered $HOMO_{dipole}$–$LUMO_{dipolarophile}$ gap, polar effects) and steric factors (less steric hindrance in the transition state).

It can be expected that terminal acetylenic iminium salts are not only excellent electron-deficient dienophiles for [4+2] cycloaddition reactions, but also highly reactive dipolarophiles in [3+2] cycloaddition reactions with sufficiently electron-rich 1,3-dipoles. This is confirmed by their reactions with organoazides leading to 1,2,3-triazol-4-yl iminium and bicyclic triazolium salts, which we present in this paper.

Results and Discussion

The 1,3-dipolar cycloaddition of phenyl azide and propyne iminium triflate **1a** was investigated first and furnished an unexpected result (Scheme 1). Remarkably enough, the reaction took place already at room temperature with a moderate rate. With a slight excess of the azide, a product mixture was obtained, the ^{1}H NMR spectra of which suggested the presence

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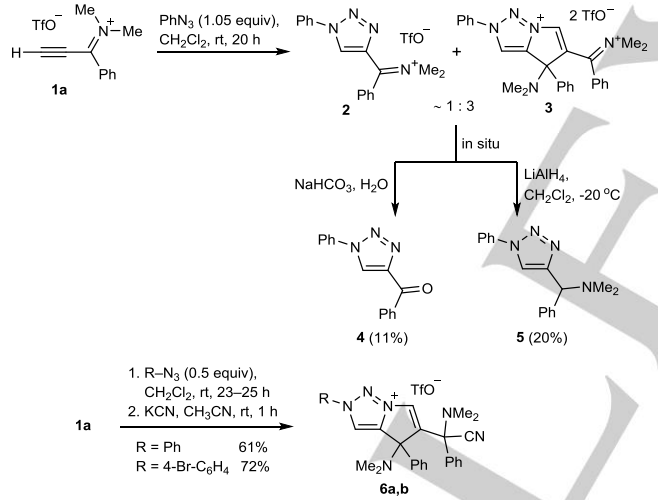
of two iminium salts (δ(NMe) between 3.4 and 4.2 ppm). The minor component of that mixture was the expected (1,2,3-triazol-4-yl)methaniminium salt **2**, which was confirmed by alkaline hydrolysis yielding triazolyl ketone **4** and by hydride reduction with lithium alanate yielding (triazolylmethyl)amine **5**, both in low yield. The major component of the product mixture could be enriched by partial extractive removal of **2** with chloroform, but due to its extreme lability toward hydrolysis, it could not be isolated in pure form. Based on the assumption that the unknown compound was still an iminium salt, potassium cyanide was added to obtain a monocationic species with an α-dimethylaminonitrile moiety. An ESI mass spectrum showed a basis peak corresponding to $[C_{29}H_{29}N_6]^+$, in agreement with an adduct of two acetylene, one azide and one cyanide units. Efforts to crystallize the salt were unsuccessful and an anion exchange, tetraphenylborate for triflate, was also in vain. The structure of this salt as a bicyclic 2,4-dihydro-pyrrolo[1,2-*c*][1,2,3]triazol-7-ium triflate was finally established, when single crystals of **6b** suited for an XRD analysis were obtained by replacing phenyl azide with 4-bromophenyl azide (Figure 1). Thus, the formerly unknown product **3** is the 2:1 addition product of acetylenic iminium salt **1a** and phenyl azide, which results from a [3+2] cycloaddition/Michael addition/1,5-cyclization cascade. When the 2:1 stoichiometry of the reactants was applied, salt **3** could be produced indeed selectively at the expense of the 1:1 cycloaddition product **2**.



Scheme 1. Cycloadducts and their derivatives obtained from propyne iminium salt **1a** and aryl azides.

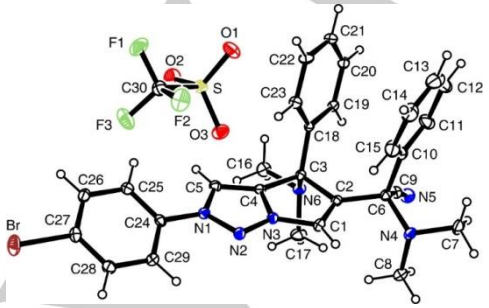
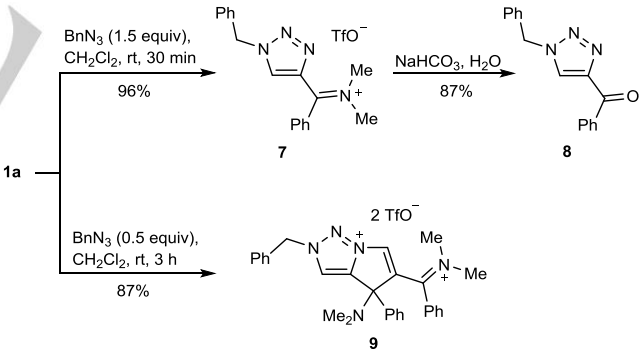


Figure 1. Molecular structure of triazolium salt **6b** in the solid state (ORTEP plot). The numbering scheme is arbitrary. Bond distances (Å): N1–N2 1.335(3), N2–N3 1.319(3), N3–C4 1.361(3), N3–C1 1.414(3), C4–C5 1.369(4), C5–N1 1.370(3).

The following structural aspects of triazolium salts **6a,b** are of interest: a) According to the NMR spectra, only one of two possible diastereomers was formed, the relative configuration of which can be seen in Figure 1. b) The ^{1}H NMR spectra (500 MHz) indicate that the molecule is in the coalescence region at ambient temperature; the slow exchange regime is observed at ≤-40 °C (see Figure 2, Supporting Information). It is obvious that the dynamics are caused by hindered rotation around bonds at the two closely positioned and sterically overloaded chiral centers.

Benzyl azide, as anticipated, adds to terminal acetylenic iminium salts faster than phenyl azide, but again, the final result depends on the stoichiometry of the reactants (Scheme 2). With a 1:1 molar ratio, the cycloaddition was complete after 30 minutes and yielded the 1,4-disubstituted triazole **7** almost quantitatively beside traces of triazolium salt **9**. When a 2:1 molar ratio and an extended reaction time were applied, the product ratios were reversed and **9** was obtained in high yield. This very moisture-sensitive salt could be isolated in pure form and fully characterized by its NMR and HRMS data.

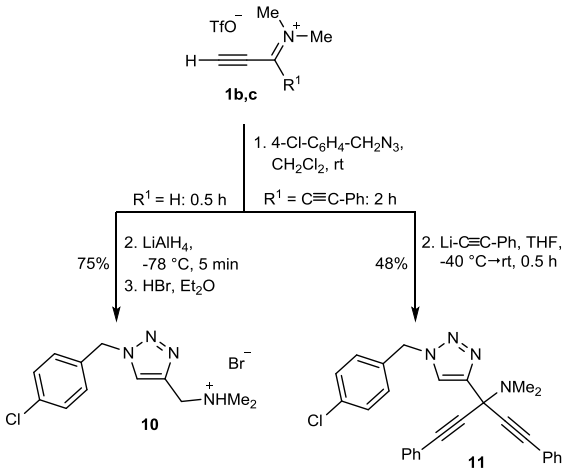
Alkaline hydrolysis of triazolyl-methaniminium salt **7** yielded the 1,4-disubstituted triazolyl ketone **8** in good yield. This result clearly highlights the effect of the iminium activation of the acetylenic bond, since the direct [3+2] cycloaddition of benzyl azide to the corresponding alkynyl ketone requires harsh conditions and yields **8** in moderate yield and with low regioselectivity (refluxing benzene, 40 hours, 48% yield, 69:31 ratio of 1,4- and 1,5-regioisomers).[19] On the other hand, ketone **8** and similar acyltriazoles can be prepared regioselectively and in good yields by CuAAC reactions.[20,21] Under optimized conditions (catalyst, additives), mild reaction conditions (r.t., 5 h) could be achieved.[21]



Scheme 2. Reactions of acetylenic iminium salt **1a** with benzyl azide.

As it was described above for the cycloaddition products obtained from aryl azides (see Scheme 1), triazoles such as **7** and the bicyclic triazolium salt **9** can be submitted to further transformations without isolation in a two-step one-pot reaction sequence. By variation of the propyne iminium salt, the organoazide and the nucleophile that adds to the iminium unit, diverse 1,4-disubstituted 1,2,3-triazoles are readily accessible. Two examples are shown in Scheme 3. The acetylenic aldiminium salt **1b** underwent a very fast 1,3-dipolar cycloaddition with 4-chlorobenzyl azide at room temperature; the resulting iminium-substituted triazole was converted in situ by very mild hydride reduction into a (1,2,3-triazol-4-yl-methyl)amine, which was isolated as the hydrobromide **10**. In a

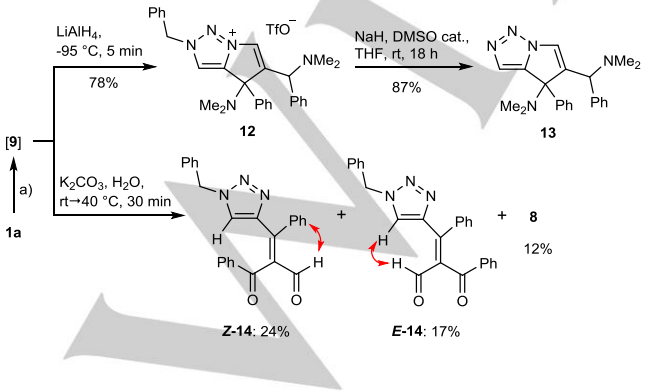
similar manner, bis(phenylethynyl)iminium salt **1c** could be converted into triazole **11** with phenylethynyl lithium as the nucleophile.



Scheme 3. Triazoles **10** and **11** obtained from propyne iminium salts **1b,c** in a two-step one-pot reaction.

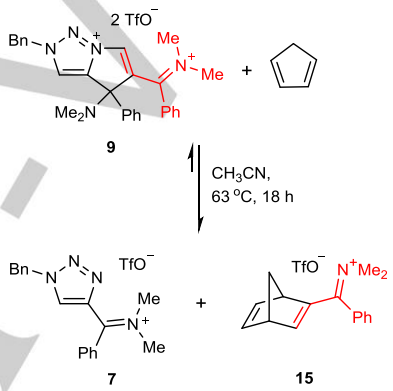
In a similar manner, salt **9** was generated from propyne iminium salt **1a** and benzyl azide in a 1:(0.42–0.45) molar ratio and was transformed in situ as shown in Scheme 4. Hydride reduction with $LiAlH_4$ leading to the monocationic salt **12** had to be performed at very low temperature, in order to avoid the complete decomposition which was observed at "harsher" conditions. *N*-debenzylation of **12** with NaH/DMSO provided the neutral pyrrolo[1,2-*c*]triazole **13**.

Hydrolysis of **9** with aqueous potassium carbonate unexpectedly led to a product mixture, from which triazolyl ketone **8** and the β-ketoaldehydes ***Z*-14** and ***E*-14** could be isolated separately by HPLC. The double bond configuration could be assigned by NOESY NMR spectra (see Scheme 4). We assume that the latter compounds, which at first glance could be regarded as Knoevenagel products derived from ketone **8** and 3-phenyl-3-oxopropanal or a synthetic equivalent thereof, are formed by a somewhat complex mechanism, which starts with a rupture of the bicyclic structure of **9**, triggered by Michael addition of OH^- at the olefinic iminium unit (see the Supporting Information for a formula scheme).



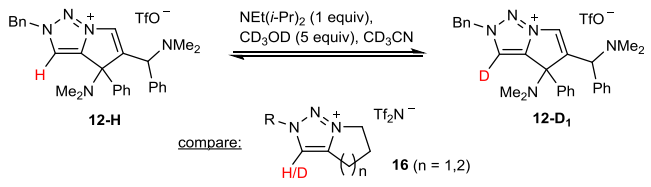
Scheme 4. In-situ derivatization of the bicyclic triazolium salt **9** the arrows indicate strong NOE interactions (irradiation at the CHO proton resonance for both isomers of **14**). a) See Scheme 2.

The thermal stability of the bicyclic triazolium salts reported in this study is only moderate. As Scheme 5 shows, triazolium salt **9** and cyclopentadiene underwent a slow reaction when heated at a moderately elevated temperature; ^{1}H NMR spectra indicated the selective formation of triazole **7** and norbornadienyl iminium salt **15**[17] in a 1.0:0.9 ratio beside small amounts of side products. Obviously, the formation of **9** from triazole **7** and propyne iminium ion **1a** by a formal [3+2] cycloaddition is reversible, i.e., **9** is thermally cleaved into its components, of which triazole **7** is observed directly and alkyne **1a** is trapped by cyclopentadiene in a fast Diels-Alder reaction. The cyclo-reversion reaction of the cation could also be observed in an ESI mass spectrum.



Scheme 5. Transfer of a propyne iminium unit (**1a**) from bicyclic dication salt **9** to cyclopentadiene. Bn = $PhCH_2$.

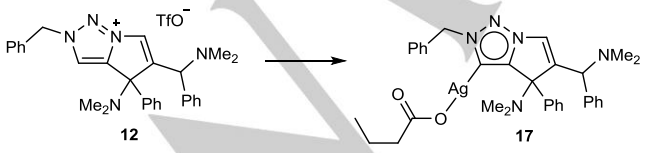
In contrast to the large number of known 1,3-disubstituted and 1,3,4- or 1,3,5-trisubstituted 1,2,3-triazolium salts, *C*,*N*-annelated congeners are still rare. They can be synthesized by an intramolecular *N*-alkylation of appropriate 1,2,3-triazoles.[22] In one paper, salts **16** were presented which showed some potential for the nucleophilic organocatalysis of the base-assisted oxidative esterification of certain aldehydes.[22c] It is obvious that these triazolium salts are precursors of catalytically active mesoionic 1,2,3-triazolyl-5-ylidenes, as was evidenced by proving the relative acidity of the triazolium C–H bond in a H/D exchange experiment. In accordance with lit. 22c, we were able to observe the deuterium incorporation by ^{1}H NMR monitoring of the triazolium 5-H proton (δ = 9.18 ppm) under the conditions given in Scheme 6. The exchange reaction turned out to be relatively slow; a steady equilibrium was reached within two days (the integration of triazolium-H was 0.78 after 2 hours, 0.73 after 2 days).



Scheme 6. H/D exchange in triazolium salt **12**.

1,2,3-Triazolylidenes belong to the family of “abnormal” or “mesoionic” carbenes;[23] they have been isolated in pure form[24] and have recently become quite popular as novel nucleophilic heterocyclic carbene (NHC) ligands in late-transition metal complexes, some of which proved useful catalysts for diverse chemical transformations.[25,26] Ag–NHC complexes have been widely used for transmetalation reactions to obtain other transition metal–NHC complexes.[25,26] For this purpose, they are typically generated in situ by treating the azolium salt with basic silver compounds such as Ag_2O or Ag_2CO_3 or from preformed free NHCs.[27] Only a few (1,2,3-triazolylidene)silver complexes have been characterized structurally and spectroscopically, and the diversity of coordination motifs became evident.[25] Very recently, two monomolecular complexes of the type (trz)AgX (X = CN, I), derived from a monocyclic 1,3,4-trisubstituted-1,2,3-triazolium ion, have been described.[28] With all these facts in mind, we briefly checked the possibility to obtain a stable (bicyclic 1,2,3-triazolylidene)silver complex (“Ag(btrz)”) derived from the bicyclic triazolium salt **12**.

When triazolium triflate **12** was allowed to react with Ag_2O in CH_3CN, NMR spectra showed the disappearance of the triazolium-H signal, but a pure product could not be isolated. On the other hand, when **12** was treated briefly with potassium butoxide in THF followed by addition of AgOTf, monitoring of the reaction indicated complete conversion after 18 h and formation of a major product (^{1}H NMR). However, this product could not be obtained in pure form, because most efforts (chromatography, precipitation, selective crystallization) ended in decomposition and formation of undefined product mixtures. However, when the crude reaction product was dissolved in warm di-*n*-butyl ether/chloroform and the mixture was brought back to room temperature, a dark-grey, sticky oil separated, which was at most sparingly soluble in common organic solvents and appeared to contain elemental silver. The organic phase contained at least three compounds: unconsumed triazolium salt **12**, an unknown compound (^{1}H NMR: broad signals, no triazolium proton) and a silver complex which could be isolated in low yield by crystallization. These crystals were identified as the (1,2,3-triazol-5-ylidene)silver complex **17**, [(btrz)Ag(C_3H_7COO)], by X-ray diffraction analysis (Scheme 7, Figure 3). Notably, a butyrate ligand is present, which must result from cleavage of an ether C–O bond and oxidation. Further studies are necessary in order to clarify the mechanism of this transformation, which seems to involve a novel oxidative cleavage of an ether C–O bond. Interestingly, a MALDI mass spectrum of **17** showed prominent peaks which can be assigned to $[Ag(btrz)_2]^+$ and $[btrz + H]^+$ (see Experimental Section).



Scheme 7. Formation of the (1,2,3-triazolylidene)silver complex **17**. Conditions: 1. KO-*t*-Bu, THF, 0 °C, 5 min; 2. AgOTf, rt, 18 h, 3. Crystallization: (*n*-Bu)$_2$O, $CHCl_3$, 70 °C, 45 min, then pentane; yield: ~6%.

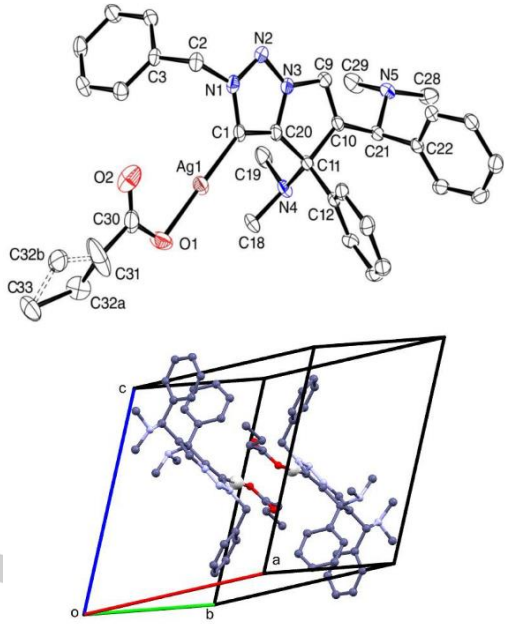


Figure 3. Molecular structure (top ORTEP presentation) and unit cell content of silver complex **17** in the crystal. The numbering scheme is arbitrary. The n-butyl chain is disordered. Selected bond distances (Å) and angles (deg): Ag1–C1 2.054(3), Ag1–O1 2.095(3), C30–O1 1.267(6), C30–O2 1.209(6), C1–Ag1–O1 178.9(1), C30–O1–Ag1 109.1(3).

The molecular structure of **17** exhibits an almost planar arrangement of bicyclic triazolylidene–Ag–OOC and a linear geometry which is typical for dicoordinated silver complexes. Notably, the carboxylate ligand is monocoordinated to the silver atom, whereas silver(I) carboxylates frequently form dimeric, oligomeric and polymeric structures with the general formula $[Ag_2(carboxylato\text{-}O,O')_2]_n$ featuring bridging carboxylate ligands.[29] Obviously, the presence of an NHC ligand breaks down the common coordination pattern of Ag(I) carboxylates. This has been noted before for PR_3 ligands. Thus, the complex [Ag(P(*n*-Bu)$_3$)(C(CH_3)$_3$COO)] forms a dimer made up from two monomers in which the carboxylate ligand is unsymmetrically dicoordinated to the silver atom.[30] Furthermore, the compound [Ag(P(C_6H_4-2-CH_2NMe_2)$_3$)(CF_3COO)] is a tricoordinated, T-shaped monomeric complex containing a monocoordinated trifluoroacetato ligand.[31] The Ag–O and C–O bond lengths in the latter complex [Ag–O1 2.183(2), C–O1 1.222(3), C–O2 1.206(3) Å] show significant differences compared to **17**: the Ag–O distance is much longer than in **17** and the C–O single and double bonds are less localized. The bond length Ag–C_{btrz} (2.054(3) Å) in **17** is at the lower side of the so far known range (2.064–2.105 Å[25]); specifically, it is shorter than in comparable structures [2.087 Å in (trz)AgX (X = CN, I);[28] 2.084 Å in a (1,2,4-trisubstituted 1,2,3-triazol-5-ylidene)AgCl complex, a “normal NHC” complex[32]]. In the crystal, the unit cell of **17** contains two centrosymmetrically related molecules. With a distance of 4.661 Å for Ag···Ag(1-*x*, 1-*y*,1-*z*), an argentophilic interaction[33] can be excluded.

Conclusions

Terminal acetylenic iminium salts are not only among the most reactive electron-deficient dienophiles in Diels-Alder reactions, as we have reported earlier, but perform equally well as dipolarophiles in [3+2] cycloaddition reactions with sufficiently electron-rich organoazides. With (ring-substituted) phenyl and benzyl azide, the 1,3-dipolar cycloaddition leading to 1,4-disubstituted 1,2,3-triazoles is considerably faster than with neutral acetylenic carbonyl compounds, high-yielding, completely regioselective, and does not require metal catalysis. The high electrophilicity of the propyne iminium ion unit paves the way to little known bicyclic 1,2,3-triazolium salts in a [3+2] cycloaddition/Michael addition/1,5-cyclization cascade. The presence of the iminium function in the triazole and triazolium products allows for further transformation into neutral products, as is exemplified by hydride reduction, addition of carbon nucleophiles (cyanide, phenylacetylenide), and alkaline ring-opening reaction of a bicyclic triazolium salt. Finally, bicyclic triazolium salts **12** are ligand precursors for transition metal complexes, as was demonstrated by the formation of an isolable Ag–NHC complex.

Experimental Section

Methods and materials. All reactions involving moisture-sensitive compounds were carried out in rigorously dried glassware under an argon atmosphere. Solvents were dried by established procedures and stored over molecular sieves (4 Å; 3 Å for acetonitrile). All chemicals, except where stated, were purchased from commercial sources and used without further purification. Propyne iminium salts **1a–c**[17] were prepared by published methods. Melting points were determined in open capillaries with a Büchi B-540 instrument at a heating rate of 2 °C/min. IR spectra of solid samples prepared as KBr pellets or oils between NaCl plates were recorded on a Bruker Vector 22 FT-IR instrument. NMR spectra were recorded on a Bruker DRX 400 spectrometer operating at 400.13 MHz for ^{1}H and 100.61 MHz for ^{13}C and on a Bruker AMX 500 spectrometer operating at 500.14 MHz for ^{1}H and 125.79 MHz for ^{13}C and were referenced to the residual proton signal of the solvent. If necessary, ^{13}C signals were assigned by means of DEPT-135, HMBC and HSQC experiments. Mass spectra were recorded with the following instruments: Finnigan-MAT SSQ-7000 (CI, 100 eV) and SolariX (HRMS, ESI). Elemental analyses were carried out with an elementar Hanau vario MICRO cube analyser. Column chromatography was performed on silica gel (Silica 60, Macherey-Nagel, 63-200 mesh).

Phenyl(1-phenyl-1*H*-1,2,3-triazol-4-yl)methanone (4): To a solution of propyne iminium salt **1a** (1.64 g, 5.34 mmol) in CH_2Cl_2 (8 mL), phenyl azide (635 mg, 5.34 mmol) was added, and the mixture was stirred for 20 h. Thereafter aqueous $NaHCO_3$ was added, the organic layer was separated, dried (Na_2SO_4), and the volatiles were removed at 800 mbar/40 °C. The black residue was purified via column chromatography (SiO_2, cyclohexane/EtOAc = 5:1, R_f = 0.38) which gave **4** (150 mg, 0.602 mmol, 11%) as a colorless solid. M.p. 128.7–130.1 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.47–7.57 (m, 5 H, H_{Ph}), 7.61–7.65 (m, 1 H, H_{Ph}), 7.79–7.82 (m, 2 H, H_{Ph}), 8.46–8.49 (m, 2 H, H_{Ph}), 8.73 (s, 1 H, 5-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 120.85, 126.50, 128.53, 129.59, 130.04, 130.72, 133.52, 136.43 (all C_{Ph}); 136.50 (C_{Trz}), 148.61 (C-5), 185.60 (C=O). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3139 (m), 1643 (s), 1597 (m), 1574 (m), 1525 (s), 1347 (m), 1268 (s), 991 (m), 905 (m), 760 (m), 719 (s), 685 (s). MS (CI, 100 eV): *m/z* (%) = 277 (100) [M + C_2H_4]$^+$. $C_{15}H_{11}N_3O$ (249.27 g/mol): calcd. C 72.28, H 4.45, N 16.86; found C 72.21, H 4.51, N 16.89.

***N*,*N*-Dimethyl-1-phenyl-1-(1-phenyl-1*H*-1,2,3-triazol-4-yl)methanamine (5):** To a solution of propyne iminium salt **1a** (628 mg, 2.04 mmol) in CH_2Cl_2 (4.5 mL), phenyl azide (255 mg, 2.15 mmol) was added and the mixture was stirred for 20 h. Thereafter $LiAlH_4$ (2.5 mL, 6.0 mmol, 2.4 M in THF) was added at -20 °C and stirring was continued for 1 h. The reaction was quenched with EtOAc and extracted wich 1 N HCl. The aqueous phase was separated and $NaOH_{aq}$ was added (pH 12). After extraction with EtOAc, the organic layer was separated, dried (Na_2SO_4), and the volatiles were removed at 200 mbar/40 °C. The black residue was purified via column chromatography (SiO_2, cyclo-hexane/EtOAc/NEt_3 = 1:3:0.05, R_f = 0.52) which gave **5** (113 mg, 0.41 mmol, 20%) as an orange oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 2.29 (s, 6 H, N(CH_3)$_2$), 4.66 (s, 1 H, CH), 7.25–7.29 (m, 1 H, H_{Ph}), 7.33–7.37 (m, 2 H, H_{Ph}), 7.39–7.43 (m, 1 H, H_{Ph}), 7.48–7.53 (m, 4 H, H_{Ph}), 7.70–7.72 (m, 2 H, H_{Ph}), 7.91 (s, 1 H, 5-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 44.16 (N(CH_3)$_2$), 68.71 (Ph*C*H), 119.97, 120.53, 127.68, 128.29, 128.76, 129.81, 137.22, 140.97, 150.36. IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3061 (m), 2987 (m), 2951 (m), 2864 (m), 2820 (m), 2775 (s), 1599 (s), 1502 (s), 1453 (s), 1258 (m), 1231 (s), 1178 (m), 1076 (m), 1039 (s), 803 (m), 756 (s), 695 (s). MS ((+)-ESI): *m/z* (%) = 279.1589 (calcd. 279.16097 for $C_{17}H_{19}N_4^+$, [M + H]$^+$). $C_{17}H_{18}N_4$ (278.36 g/mol): calcd. C 73.35, H 6.52, N 20.13; found C 72.66, H 6.72, N 18.53. The elemental analysis could not be improved.

5-(Cyano(dimethylamino)(phenyl)methyl)-4-(dimethylamino)-2,4-diphenyl-2,4-dihydropyrrolo[1,2-*c*][1,2,3]triazol-7-ium Triflate (6a): To a solution of propyne iminium salt **1a** (1.64 g, 5.34 mmol) in CH_2Cl_2 (8 mL), phenyl azide (318 mg, 2.67 mmol, 0.5 equiv.) was added and the mixture was stirred for 23 h. The volatile components were removed at 0.02 mbar, and the residue was dissolved in CH_3CN (2 mL) and added dropwise to a suspension of KCN (452 mg, 6.94 mmol, 1.3 equiv.) in CH_3CN (20 mL). After complete addition stirring was continued for 1 h. Then Et_2O and *n*-pentane were added, until a purple oil separated. The upper layer was collected by decantation (the purple residue was discarded), the solvents were evaporated and the residue was dissolved in CH_2Cl_2 (4 mL) and filtered. To the filtrate Et_2O was added until the solution became turbid. *n*-Pentane was added whereupon an oil separated. Decantation, washing of the residue with Et_2O and drying at 0.01 mbar gave **6a** (998 mg, 1.63 mmol, 61%) as a dark violet solid (decomposition starting at 102 °C). ^{1}H NMR (CD_2Cl_2, 500 MHz, 220 K): δ [ppm] = 1.73, 2.27, 2.45, 2.59 (each s, 3H, NMe); 5.96 (d, *J* = 8.3 Hz, 1 H, H_{Ph}), 6.48 (td, *J* = 7.7, 1.4 Hz, 1 H, H_{Ph}), 6.81 (td, *J* = 7.7, 1.5 Hz, 1 H, H_{Ph}), 6.90 (d, *J* = 8.5 Hz, 1 H, H_{Ph}), 7.27 (td, *J* = 7.8, 1.4 Hz, 1 H, H_{Ph}), 7.58–7.63 (m, 3 H, H_{Ph}), 8.01 (d, *J* = 8.1 Hz, 1 H, H_{Ph}), 8.05–8.07 (m, 2 H, H_{Ph}), 8.36 (s, 1 H, C=CH), 9.17 (s, 1 H, 3-H). ^{13}C NMR (CD_2Cl_2, 125 MHz, 220 K): δ [ppm] = 40.25 (2 NMe), 42.19 (NMe), 42.23 (NMe) 70.08 (C_{sp3}), 78.94 (*C*-CN), 111.94 (CN), 120.53 (q, $^1J_{C,F}$ = 320.2 Hz, TfO^-), 121.53 (C_{Ph}), 123.85 (HC_{Trz}), 124.28 (*HC*=C), 124.94–135.14 (15 C_{Ph}), 144.64 (C_{Trz}), 151.99 (HC=*C*). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3066 (m), 3004 (m), 2963 (m), 2877 (m), 2836 (m), 2793 (m), 1632 (m), 1596 (m), 1564 (m), 1496 (s), 1452 (s), 1388 (m), 1260 (s), 1223 (s), 1154 (s), 1031 (s), 1002 (m), 830 (m), 764 (m), 747 (m), 696 (s), 636 (s). HRMS ((+)-ESI): *m/z* = 461.24497 (calcd. 461.24482 for $C_{29}H_{29}N_6^+$, [M - OTf]$^+$). $C_{30}H_{29}F_3N_6O_3S$ (610.66 g/mol): calcd. C 59.01, H 4.79, N 13.76; found C 59.00, H 4.88, N 13.46.

2-(4-Bromophenyl)-5-(cyano(dimethylamino)(phenyl)methyl)-4-(dimethylamino)-4-phenyl-2,4-dihydropyrrolo[1,2-*c*][1,2,3]triazol-7-ium Triflate (6b): Prepared from **1a** (1.28 g, 4.17 mmol) and 4-bromophenyl azide (413 mg, 2.09 mmol) according to **6a**. Yield: 1.04 g (1.51 mmol, 72%), beige solid (decomposition starting at 122 °C). ^{1}H NMR (CD_2Cl_2, 500 MHz, 220 K): δ [ppm] = 1.73, 2.27, 2.45, 2.59 (each s, 3 H, NMe), 5.95 (d, *J* = 7.8 Hz, 1 H, H_{Ph}), 6.47 (t, *J* = 7.6 Hz, 1 H, H_{Ph}), 6.81 (t, *J* = 7.5 Hz, 1 H, H_{Ph}), 6.90 (d, *J* = 7.9 Hz, 1 H, H_{Ph}), 6.96 (d, *J* = 7.6 Hz, 1 H, H_{Ph}), 6.99 (d, *J* = 7.9 Hz, 1 H, H_{Ph}), 7.04 (t, *J* = 7.6 Hz, 1 H, H_{Ph}), 7.20 (d, *J* = 7.9 Hz, 1 H, H_{Ph}), 7.27 (t, *J* = 7.7 Hz, 1 H, H_{Ph}), 7.74 (d, *J* = 8.8 Hz, 2 H, H_{Ph}), 7.98–8.02 (m, 3 H, H_{Ph}), 8.32 (s, 1 H, C=CH), 9.18 (s, 1 H, H_{Trz}). ^{13}C NMR (CD_2Cl_2, 125 MHz, 220 K): δ [ppm] = 40.28 (2

NMe), 42.19 (NMe), 42.28 (NMe), 70.11 (C_{sp3}), 79.00 (*C*-CN), 111.91 (CN), 120.48 (q, $^1J_{C,F}$ = 320.1 Hz, TfO^-), 123.16 (C_{Ph}), 123.93 (HC_{Trz}), 124.16 (H*C*=C), 124.89–134.74 (14 C_{Ph} signals), 144.81 (C_{Trz}), 152.45 (HC=*C*). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3067 (m), 3004 (m), 2963 (m), 2876 (m), 2836 (m), 2793 (m), 1632 (m), 1564 (m), 1493 (s), 1452 (s), 1403 (m), 1260 (s), 1223 (s), 1070 (m), 1032 (s), 997 (m), 832 (m), 750 (m), 712 (m), 697 (m), 637 (s). HRMS ((+)-ESI): *m/z* = 541.15309 (calcd. 541.15329 for $C_{29}H_{28}{}^{81}BrN_6{}^+$), 539.15513 (calcd. 539.15533 for $C_{29}H_{28}{}^{79}BrN_6{}^+$, [M - OTf]$^+$). $C_{30}H_{28}BrF_3N_6O_3S$ (689.55 g/mol): calcd. C 52.26, H 4.09, N 12.19; found C 52.77, H 4.42, N 11.97; $C_{30}H_{28}BrF_3N_6O_3S{\cdot}0.35\ Et_2O$ (689.55 + 0.35×74.12 g/mol): calcd. C 52.71, H 4.44, N 11.75.

***N*-((1-Benzyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methylene)-*N*-methylmethanaminium Triflate (7):** To a solution of propyne iminium salt **1a** (885 mg, 2.88 mmol) in CH_2Cl_2 (8 mL), benzyl azide (539 µL, 4.32 mmol, 1.5 equiv.) was added. After stirring for 0.5 h at ambient temperature, the solvent was evaporated at 0.02 mbar and the residue was washed with several portions of ether. Drying of the residue at 0.02 mbar gave **7** (1.22 g, 2.76 mmol, 96%) as a brownish solid, which was slighly contaminated with triazolium salt **9**. M.p. 93 °C (decomposition starting at 70 °C). ^{1}H NMR (CD_3CN, 500 MHz): δ [ppm] = 3.51 (s, 3 H, NMe), 4.12 (s, 3 H, NMe), 5.63 (s, 2 H, PhCH_2), 7.35–7.40 (m, 5 H, H_{Ph}), 7.52–7.53 (m, 2 H, H_{Ph}), 7.64–7.67 (m, 2 H, H_{Ph}), 7.74–7.77 (m, 1 H, H_{Ph}), 8.19 (s, 1 H, H_{Trz}). ^{13}C NMR (CD_3CN, 125 MHz): δ [ppm] = 48.18 (NMe), 48.71 (NMe), 54.80 (C_{benzyl}), 121.81 (q, $^1J_{C,F}$ = 321.0 Hz, TfO^-); 129.05, 129.50, 129.53, 129.71, 129.90, 132.58 133.46, 135.06 (all C_{Ph}); 136.55 (C_{Trz}), 142.04 (C_{Trz}), 169.91 (C=N). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3130 (m), 1641 (m), 1537 (m), 1263 (s), 1224 (m), 1154 (s), 1031 (s), 771 (m), 733 (m), 637 (s). HRMS ((+)-ESI): *m/z* = 291.16056 (calcd. 291.16042 for $C_{18}H_{19}N_4$, [M - OTf]$^+$). $C_{19}H_{19}F_3N_4O_3S$ (440.44 g/mol): calcd. C 51.81, H 4.35, N 12.72; found C 51.89, H 4.41, N 12.73.

(1-Benzyl-1*H*-1,2,3-triazol-4-yl)(phenyl)methanone (8): To a solution of propyne iminium salt **1a** (420 mg, 1.37 mmol) in CH_2Cl_2 (8 mL), benzyl azide (364 mg, 2.73 mmol, 2.0 equiv.) was added. After stirring for 1 h at ambient temperature *n*-pentane was added, whereupon an orange oil separated. The upper layer was removed and the residue was washed with several portions of ether, then dissolved in CH_2Cl_2, and saturated aqueous $NaHCO_3$ was added. After stirring for 5 min, the mixture was extracted with ether and brine, the organic layer was dried over Na_2SO_4, and the volatiles were evaporated. The residue was taken up in *n*-hexane/$CHCl_3$ (9:1) and the mixture was filtered through silica gel. Solvent evaporation furnished **8** (313 mg, 1.19 mmol, 87%) as a white solid; m.p. 114.3–115.2 °C. (lit.[19]: 115–116 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 5.60 (s, 2 H, $PhCH_2$), 7.32–7.35 (m, 2 H, H_{Ph}), 7.37–7.43 (m, 3 H, H_{Ph}), 7.48–7.53 (m, 2 H, H_{Ph}), 7.58–7.62 (m, 1 H, H_{Ph}), 8.17 (s, 1 H, H_{Trz}), 8.40–8.42 (m, 2 H, H_{Ph}). ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 54.55 (PhCH_2); 128.39, 128.48, 129.26, 129.42, 130.67, 133.37, 133.79 (all C_{Ph}); 136.57 (C_{Trz}), 148.44 (C_{Trz}), 185.75 (C=O). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3119 (s), 1635 (s), 1598 (m), 1573 (m), 1518 (s), 1346 (m), 1232 (s), 1048 (m), 901 (s), 713 (s), 692 (s). HRMS ((+)-ESI): *m/z* = 549.20044 (calcd. 549.20095 for $C_{32}H_{26}N_6NaO_2{}^+$, [2M + Na]$^+$), 286.09492 (calcd. 286.09508 for $C_{16}H_{13}N_3NaO^+$, [M + Na]$^+$). $C_{16}H_{13}N_3O$ (263.30 g/mol): calcd. C 72.99, H 4.98, N 15.96; found C 72.93, H 4.99, N 16.09.

2-Benzyl-4-(dimethylamino)-5-((dimethyliminio)(phenyl)methyl)-4-phenyl-2,4-dihydropyrrolo[1,2-*c*][1,2,3]triazol-7-ium Triflate (9): To a solution of propyne iminium salt **1a** (450 mg, 1.46 mmol) in CH_2Cl_2 (8 mL), benzyl azide (97.5 mg, 0.732 mmol, 0.5 equiv.) was added. After stirring for 3 h at ambient temperature, ether was added whereupon an oil precipitated. The upper layer was decanted and the oily residue was washed with several portions of ether and dried at 0.02 mbar. The resulting brown solid was dissolved in a minimum amount of CH_2Cl_2, cooled to -78 °C, and ether was added until a solid precipitated. Filtration under argon and washing with cold $CHCl_3$ gave **9** (478 mg, 0.639 mmol, 87%) as a colorless, very hygroscopic, solid; m.p. 144 °C (dec.). ^{1}H NMR (CD_3CN, 500 MHz): δ [ppm] = 1.76 (s, 6 H, NMe), 2.80 (s, 3 H, NMe), 3.52 (s, 3 H, NMe), 5.98 (s, 2 H, PhCH_2), 7.35 (d, *J* = 7.2 Hz, 2 H, H_{Ph}), 7.53–7.57 (m, 5 H, H_{Ph}), 7.59–7.63 (m, 3 H, H_{Ph}), 7.69–7.73 (m, 2 H, H_{Ph}), 7.76–7.79 (m, 3 H, H_{Ph}), 8.45 (s, 1 H, C=CH), 8.80 (s, 1 H, H_{Trz}). ^{13}C NMR (CD_3CN, 125 MHz): δ [ppm] = 40.54 (NMe), 47.49 (NMe), 48.56 (NMe), 59.53 ($PhCH_2$), 84.22 (C-4), 122.04 (q, $^1J_{CF}$ = 320.8 Hz, TfO^-), 127.90 (HC=C), 128.84 (HC_{Trz}); 130.09, 130.36, 130.44, 130.53, 130.90, 131.48, 132.04, 132.36, 132.57, 134.63 (all C_{Ph}); 139.25 (HC=*C*), 142.42 ($C_{q,Trz}$), 176.27 (C=N). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3091 (m), 1658 (m), 1454 (m), 1283 (s), 1258 (s), 1225 (s), 1161 (s), 1030 (s), 752 (m), 700 (m), 638 (s). HRMS ((+)-ESI): *m/z* = 1345.40641 (calcd. 1345.37142 for $C_{61}H_{62}F_9N_{10}O_9S_3{}^+$, [2M - OTf]$^+$), 598.21645 (calcd. 598.20942 for $C_{30}H_{31}F_3N_5O_3S^+$, [M - OTf]$^+$), 421.20663 (calcd. 421.20229 for $C_{27}H_{25}N_4O^+$, [M + H_2O - H_2NMe_2OTf]$^+$), 291.16099 (calcd. 291.16042 for $C_{18}H_{19}N_4{}^+$, [cation of **7**]$^+$). $C_{31}H_{31}F_6N_5O_6S_2$ (747.73 g/mol): calcd. C 49.80, H 4.18, N 9.37; found C 49.28, H 4.22, N 9.33; $C_{31}H_{31}F_6N_5O_6S_2{\cdot}0.43\ H_2O$ (689.55 + 0.43×18.02 g/mol): calcd. C 49.28, H 4.25, N 9.27.

1-(1-(4-Chlorobenzyl)-1*H*-1,2,3-triazol-4-yl)-*N*,*N*-dimethylmethanaminium bromide (10): To a solution of propyne iminium salt **1b** (326 mg, 1.41 mmol) in CH_2Cl_2 (8 mL) and CH_3CN (2 mL), 4-Chlorobenzyl azide (354 mg, 2.12 mmol, 1.5 equiv.) was added and the mixture was stirred for 0.5 h. Thereafter the solution was cooled to -78 °C and $LiAlH_4$ (588 µL, 1.41 mmol, 2.4 M in THF) was added dropwise. After stirring for 5 min the reaction was quenched at this temperature by adding acetone followed by extraction with ether and brine. The organic layer was dried (Na_2SO_4) and the volatile components were evaporated. The residue was dissolved in EtOAc/MeOH (10:1) and filtered through flash silica gel. The filtrate was collected, the solvents were removed, and the residue was dissolved in ether. Conc. HBr was added dropwise until pH 1 was reached. The resulting oil was separated, washed with ether and dried at 0.02 mbar to obtain **10** (351 mg, 1.06 mmol, 75%) as a yellow oil, which could not be purified further. ^{1}H NMR (CD_3CN, 400 MHz): δ [ppm] = 2.72 (d, *J* = 5.2 Hz, 6 H, $N(CH_3)_2$), 4.32 (d, *J* = 4.9 Hz, 2 H, NCH_2), 5.59 (s, 2 H, PhCH_2), 7.31–7.33 (m, 2 H, H_{Ph}), 7.39–7.41 (m, 2 H, H_{Ph}), 8.26 (s, 1 H, H_{Trz}), 10.84 (s, br, 1 H, NH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 42.91 ($N(CH_3)_2$), 49.53 (NCH_2), 55.72 (PhCH_2), 129.99 (C_{Ph}), 131.05 (HC_{Trz}), 131.59 (C_{Ph}), 133.07 (C_{Ph}), 134.89 (C_{Ph}), 135.47 (C_{Trz}). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2954 (s), 2680 (s), 2469 (m), 1624 (m), 1492 (s), 1469 (s), 1438 (m), 1411 (m), 1275 (s), 1230 (m), 1162 (m), 1053 (m), 1030 (m), 1015 (m), 951 (m), 812 (m), 639 (m). HRMS ((+)-ESI): *m/z* = 251.10613 (calcd. 251.10580 for $C_{12}H_{16}ClN_4{}^+$, [M – Br]$^+$). $C_{12}H_{16}BrClN_4$ (331.64 g/mol).

3-(1-(4-Chlorobenzyl)-1*H*-1,2,3-triazol-4-yl)-*N*,*N*-dimethyl-1,5-diphenylpenta-1,4-diyn-3-amine (11): To a solution of propyne iminium salt **1c** (617 mg, 1.86 mmol) in CH_2Cl_2 (30 mL), 4-chlorobenzyl azide (467 mg, 2.79 mmol, 1.5 equiv.) was added. After stirring for 2 h at ambient temperature, the mixture was cooled to -40 °C and phenylethynyl lithium [prepared from phenylacetylene (300 mg, 2.94 mmol) and *n*-BuLi (1.18 mL, 2.94 mmol, 2.5 M in hexane) in THF (10 mL) at -40 °C] was added dropwise. After stirring for 0.5 h at ambient temperature the reaction was quenched by addition of water followed by extraction with ether. The organic layer was dried (Na_2SO_4) and the volatile components were evaporated. The residue was dissolved in EtOAc and filtered through flash silica gel. The filtrate was submitted to HPLC (cyclohexane/EtOAc) which gave **11** (403 mg, 0.89 mmol, 48%) as an orange oil, which could not be fully purified. ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 2.47 (s, 6 H, $N(CH_3)_2$), 5.50 (s, 2 H, PhCH_2), 7.20–7.22 (m, 2 H, H_{Ph}), 7.27–7.34 (m, 8 H, H_{Ph}), 7.48–7.50 (m, 4 H, H_{Ph}), 7.68 (s, 1 H, 5-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 40.13 ($N(CH_3)_2$), 53.26 (PhCH_2), 56.36 (C_q), 85.03 and 122.01 (C≡C), 122.47 (C-5); 128.00, 128.40, 129.08, 129.17, 131.72, 132.81, 134.52 (all C_{Ph}); 148.97 (C_{Trz}). IR (NaCl): $\tilde{\nu}$ [cm^{-1}] = 2953 (s), 2864 (m), 1491 (s), 1447 (m), 1211 (m), 1044 (m), 1012 (m), 757 (s), 692 (s). HRMS ((+)-ESI): *m/z* = 901.33451 (calcd. 901.32953 for $C_{56}H_{47}Cl_2N_8{}^+$, [2M + H]$^+$), 451.16993 (calcd. 451.16840 for $C_{28}H_{24}ClN_4{}^+$, [M + H]$^+$), 406.1115 (calcd. 406.11055 for $C_{26}H_{17}ClN_3{}^+$, [M - NMe_2]$^+$). $C_{28}H_{23}ClN_4$ (450.97 g/mol).

2-Benzyl-4-(dimethylamino)-5-((dimethylamino)(phenyl)methyl)-4-phenyl-2,4-dihydropyrrolo[1,2-*c*][1,2,3]triazol-7-ium Triflate (12): To a solution of propyne iminium salt **1a** (460 mg, 1.50 mmol) in CH_2Cl_2 (8 mL), benzyl azide (85 mg, 0.64 mmol, 0.42 equiv.) was added. After stirring for 4 h at ambient temperature, the solution was cooled to -95 °C and $LiAlH_4$ (310 µL, 0.745 mmol, 2.4 M in THF, 0.5 equiv.) was added dropwise. After 5 min the reaction was quenched at this temperature by addition of acetone, the suspension was warmed to ambient temperature and water was added. The mixture was extracted with ether and brine, the organic layer was dried (Na_2SO_4), and the volatile components were removed at 800 mbar/40 °C. The resulting brownish solid was dissolved in a minimum amount of CH_2Cl_2 and ether, and *n*-pentane was added until the solution became turbid. Then the mixture was cooled to -78 °C, whereupon a voluminous precipitate appeared. Filtration and washing with ether gave **12** (299 mg, 0.49 mmol, 78%) as a slightly violet solid; m.p. 159.3–160.5 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ [ppm] = 2.14 (s, 6 H, NMe), 2.27 (s, 6 H, NMe), 4.20 (d, J = 1.1 Hz, 1 H, CH), 6.02 (d, J = 14.3 Hz, 1 H, PhC*H*), 6.08 (d, J = 14.3 Hz, 1 H, PhC*H*), 6.68–6.70 (m, 2 H, H_{Ph}), 6.76–6.79 (m, 4 H, H_{Ph}), 6.83–6.87 (m, 3 H, H_{Ph}), 6.90–6.93 (m, 1 H, H_{Ph}), 7.40–7.45 (m, 3 H, H_{Ph}), 7.62–7.64 (m, 2 H, H_{Ph}), 7.76 (s, 1 H, HC=C), 9.09 (s, 1 H, H_{Trz}). ^{13}C NMR ($CDCl_3$, 125 MHz): δ [ppm] = 40.76 (NMe), 44.25 (NMe), 58.19 (Ph*C*H$_2$), 67.60 (CH), 79.58 ($C_{sp3,\ ring}$), 120.81 (q, $^1J_{CF}$ = 320.2 Hz, TfO^-), 121.21 (H*C*=C), 126.97 (C_{Ph}), 127.06 (HC_{Trz}); 127.57, 127.88, 128.67, 128.93, 129.18, 129.54, 129.77, 129.93, 132.10, 133.03, 135.90 (all C_{Ph}); 143.59 ($C_{q,\ Trz}$), 157.80 (HC=*C*). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 1455 (m), 1276 (s), 1259 (s), 1225 (m), 1154 (s), 1031 (s), 702 (m), 637 (s). HRMS ((+)-ESI): *m/z* = 450.26480 (calcd. 450.26522 for $C_{29}H_{32}N_5^+$, [M - OTf]$^+$). $C_{30}H_{32}F_3N_5O_3S$ (599.67 g/mol): calcd. C 60.09, H 5.38, N 11.68; found C 60.27, H 5.41, N 11.67.

5-((Dimethylamino)(phenyl)methyl)-*N*,*N*-dimethyl-4-phenyl-4*H*-pyrrolo[1,2-*c*][1,2,3]triazol-4-amine (13): To a solution of triazolium salt **12** (136 mg, 0.227 mmol) in THF (5 mL), NaH (6.8 mg, 0.227 mmol, 80% in mineral oil, 1.0 equiv.) and DMSO (0.5 µL, 7.2 µmol, 0.03 equiv.) was added. After stirring for 18 h at ambient temperature, the volatile components were evaporated. The residue was dissolved in EtOAc and filtered through flash silica gel. The filtrate was collected and evaporated to dryness to obtain **13** (71 mg, 0.197 mmol, 87%) as a slightly violet solid; m.p. 173.8–174.5 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 2.20 (s, 6 H, HC-N(C*H*$_3$)$_2$), 2.24 (s, 6 H, N(CH$_3$)$_2$), 4.12 (d, J = 1.4 Hz, 1 H, PhC*H*), 6.75–6.92 (m, 10 H, H_{Ph}), 7.53 (d, J = 0.7 Hz, 1 H, H_{Trz}), 7.71–7.72 (m, 1 H, C=CH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 40.54 (NMe$_2$), 44.39 (HC-N*Me*$_2$), 67.38 (Ph*C*H), 76.15 (C-4), 122.39 (H*C*=C); 126.96, 127.49, 127.55, 127.91, 127.98, 129.07 (all C_{Ph}); 129.73 (HC_{Trz}), 136.77 (C_{Ph}), 137.65 (C_{Ph}), 140.60 (C_{Trz}), 147.77 HC=*C*). IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3091 (s), 2938 (m), 2862 (m), 2826 (m), 2786 (s), 1641 (m), 1490 (m), 1452 (s), 1431 (m), 1199 (m), 1183 (m), 1041 (s), 1017 (m), 835 (m), 724 (m), 699 (s), 633 (m). HRMS ((+)-ESI): *m/z* = 719.43920 (calcd. 719.42927 for $C_{44}H_{51}N_{10}^+$, [2M + H]$^+$), 360.21923 (calcd. 360.21827 for $C_{22}H_{25}N_5^+$, [M + H]$^+$), 287.15576 (calcd. 287.15428 for $C_{20}H_{19}N_2^+$, [M - NMe$_2$ - N$_2$]$^+$). $C_{22}H_{25}N_5$ (359.48 g/mol): C 73.51, H 7.01, N 19.48. A correct elemental analysis could not be obtained.

2-Benzoyl-3-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-3-phenylacrylaldehyde (14): To a solution of propyne iminium salt **1a** (484 mg, 1.58 mmol) in CH_2Cl_2 (8 mL), benzyl azide (95 mg, 0.71 mmol, 0.45 equiv.) was added. After stirring for 4 h at ambient temperature, saturated aqueous K_2CO_3 (400 µL) was added and the mixture was wamed to 40 °C for some minutes. Na_2SO_4 was added to bind residual water, and after filtration the volatiles were evaporated. The residue was dissolved in $CHCl_3$ and filtered through a pad of silica gel. The filtrate was submitted to HPLC (*n*-hexane/$CHCl_3$) which furnished **8** (51 mg, 0.19 mmol, 12%) as a colorless solid, followed by ***Z*-14** (69 mg, 0.18 mmol, 24%) and ***E*-14** (47 mg, 0.12 mmol, 17%) as yellow solids. M.p. ***Z*-14**: 73.8–76.2 °C; m.p. ***E*-14**: 66.1–70.1 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): ***Z*-14**: δ [ppm] = 5.34 (s, 2 H, PhC*H*$_2$), 7.03–7.05 (m, 2 H, H_{Ph}), 7.25–7.29 (m, 3 H, H_{Ph}), 7.31 (s, 1 H, H_{Trz}), 7.38 (t, J = 7.6 Hz, 2 H, H_{Ph}), 7.46–7.53 (m, 6 H, H_{Ph}), 7.90–7.92 (m, 2 H, H_{Ph}), 9.58 (s, 1 H, CHO); ***E*-14**: δ [ppm] = 5.56 (s, 2 H, PhC*H*$_2$), 7.13–7.21 (m, 5 H, H_{Ph}), 7.25–7.29 (m, 4 H, H_{Ph}), 7.35–7.42 (m, 5 H, H_{Ph} and H_{Trz}), 7.74–7.76 (m, 2 H, H_{Ph}), 10.41 (s, 1 H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz): ***Z*-14**: δ [ppm] = 54.17 (Ph*C*H$_2$), 126.47 (HC_{Trz}); 127.86, 128.74, 128.79, 128.88, 129.12, 129.17, 130.42, 130.68, 133.49, 133.99, 134.42, 136.63 (all C_{Ph}), 137.54 (C=*C*-CHO), 145.65 ($C_{q,\ Trz}$), 147.84 (C=C-CHO), 191.18 (CHO), 196.11 (C=O); ***E*-14**: δ [ppm] = 54.60 (PhCH$_2$), 126.94 (HC_{Trz}); 128.14–137.34 (12 C_{Ph}), 139.61 (C=*C*-CHO), 145.99 ($C_{q,\ Trz}$), 146.24 (*C*=C-CHO), 191.73 (CHO), 195.94 (C=O). IR (KBr): ***Z*-14**: $\tilde{\nu}$ [cm^{-1}] = 1681 (s), 1653 (s), 1593 (s), 1450 (m), 1377 (m), 1270 (s), 1240 (m), 1165 (m), 1050 (m), 966 (m), 911 (m), 782 (m), 730 (s); ***E*-14**: $\tilde{\nu}$ [cm^{-1}] = 1678 (s), 1653 (s), 1593 (s), 1450 (m), 1368 (m), 1315 (m), 1266 (m), 1233 (m), 1166 (m), 1052 (m), 963 (m), 912 (m), 728 (s), 695 (s). HRMS ((+)-ESI): ***Z*-14**: *m/z* = 809.28419 (calcd. 809.28467 for $C_{50}H_{38}N_6NaO_4^+$, [2M + Na]$^+$), 416.13683 (calcd. 416.13695 for $C_{25}H_{19}N_3NaO_2^+$, [M + Na]$^+$); ***E*-14**: *m/z* = 809.28444 (calcd. 809.28467 for $C_{50}H_{38}N_6NaO_4^+$, [2M + Na]$^+$), 416.13694 (calcd. 416.13695 for $C_{25}H_{19}N_3NaO_2^+$, [M + Na]$^+$).

(2-Benzyl-4-(dimethylamino)-5-((dimethylamino)(phenyl)methyl)-4-phenyl-2,4-dihydropyrrolo[1,2-*c*][1,2,3]triazol-7-ium-3-yl)(butyryloxy)argentate(I) (17): To a solution of triazolium salt **12** (565 mg, 0.94 mmol) in THF (15 mL), potassium *tert*-butoxide (108 mg, 0.96 mmol, 1.02 equiv.) was added at -20 °C. After stirring for 5 min, AgOTf (242 mg, 0.94 mmol, 1.0 equiv.) was added and stirring was continued for 18 h at ambient temperature. The volatile components were evaporated at 0.01 mbar, and the residue was dissolved in a minimum amount of CH_2Cl_2 and filtered through a paper filter under an argon atmosphere. The filtrate was collected and the solvent was removed. The solid residue was dissolved in *n*-butyl ether/$CHCl_3$ at 60 °C. After cooling to ambient temperature a dark-grey, sticky oil separated. The supernatant solution was poured into *n*-pentane, whereupon a colorless solid precipitated, which was filtered off to obtain 280 mg of a mixture of **12** and an unknown species (0.43:1). Further separation and identification of the main species failed. By slow evaporation of the mother liquor, crystals of **17** (35 mg, 54 µmol, 6%) were obtained. ^{1}H NMR ($CDCl_3$, 500 MHz): δ [ppm] = 0.92 (t, J = 7.4 Hz, 3 H, CH_3), 1.61–1.67 (m, 2 H, CH_2), 2.18 (s, 6 H, N(CH$_3$)$_2$), 2.26 (t, J = 7.5 Hz, 2 H, CH_2), 2.41 (s, 6 H, N(CH$_3$)$_2$), 4.29 (s, 1 H, CH), 5.81 (s, 2 H, PhC*H*$_2$), 6.71–6.84 (m, 7 H, H_{Ph}), 6.86–6.89 (m, 2 H, H_{Ph}), 6.92–6.95 (m, 1 H, H_{Ph}), 7.38–7.43 (m, 3 H, H_{Ph}), 7.58–7.59 (m, 2 H, H_{Ph}), 7.61 (s, 1 H, C=CH). ^{13}C NMR ($CDCl_3$, 125 MHz): δ [ppm] = 14.39 (CH_3), 20.21 (CH_2), 38.82 (CH_2), 41.23 (N(CH$_3$)$_2$), 44.37 (CH-(N(CH$_3$)$_2$), 60.50 (Ph*C*H$_2$), 77.94 ($C_{q,sp3}$), 120.55 (C=*C*H, ring); 127.33, 127.70, 127.74, 128.24, 128.46, 128.92, 129.07, 129.13, 129.28, 134.80, 135.10, 136.82 (all C_{Ph}); 149.84 (C_{Trz}), 155.76 (*C*=CH, ring), 161.44 (C–Ag), 181.04 (C=O). HRMS (MALDI): *m/z* = 1007.41841 and 1005.41823 (calcd. 1007.42010 and 1005.42044 for $[C_{58}H_{64}{}^{107/109}AgN_{10}]^+$, [Ag(btrz)$_2$]$^+$), 450.26476 (calcd. 450.26522 for $C_{29}H_{32}N_5^+$, [btrzH]$^+$); btrz = bicyclic 1,2,3-triazolylidene. $C_{33}H_{38}AgN_5O_2$ (644.57 g/mol): calcd. C 61.49, H 5.94, N 10.87.

X-ray Crystallography

Data collection was performed on an Oxford Diffraction Rigaku instrument for **6b** (SuperNova, Dual Source, Atlas CCD, Mo K_α radiation) and a Bruker D8 Quest diffractometer (Mo K_α) for **17**; T = 150 K. Structure solution: SHELXT;[34] structure refinement: SHELXL-2014/7.[35] Molecule plots: ORTEP-3 for Windows[36] and Mercury, version 3.10.1.[37]

Selected data for **6b**: Diffusion crystallization from CH_2Cl_2 and diethylether/pentane. ($C_{29}H_{28}BrN_6$)(CF_3SO_3), M_w = 689.55. Monoclinic space group $P2_1/c$, a = 9.3632(2), b = 33.3632(5), c = 11.4279(2) Å, b = 109.754(2)°, V = 3359.84(2) Å^3; Z = 4, D_x = 1.363 g cm^{-3}, μ = 1.34 mm^{-1}. R = 0.0442 (5397 reflexions with $I > 2\sigma(I)$), $wR2$ = 0.1221 (all 6376 data). Residual electron densities between 1.38 (close to Br) and -1.19 e Å^{-3}.

Selected data for **17**: Crystals were obtained by slow evaporation of a solution in $CHCl_3$/di(n-butyl)ether and pentane. $C_{33}H_{38}AgN_5O_2$, M_w =

644.55. Triclinic space group *P*-1, *a* = 11.2877(7), *b* = 11.5726(7), *c* = 13.8670(7) Å, α = 69.899(2), β = 70.185 (2), γ = 66.664(2)°; *Z* = 2, D_x = 1.410 g cm^{-3}, μ = 0.70 mm^{-1}. *R* = 0.0456 (5772 reflexions with $I > 2\sigma(I)$), *wR*2 = 0.1393 (all 7573 data). Maximal residual electron densities were 1.01 (close to C32a) and 0.88 Å^{-3} (close to Ag1). Due to disorder of the alkyl chain, the two hydrogen atoms at C31 were not included and restraints were imposed on the distances in the C31–C32A/B–C33 fragment.

CCDC 1880079 (**6b**) 1880080 (**17**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: alkynes • azides • cycloaddition • iminium salts • triazoles • mesoionic carbenes

Supporting Information

^{1}H and ^{13}C NMR spectra of all new compounds, temperature-dependent ^{1}H NMR spectra of **6a**, mechanistic proposal for **9** → **14**, full titles for lit. 2 and 3.

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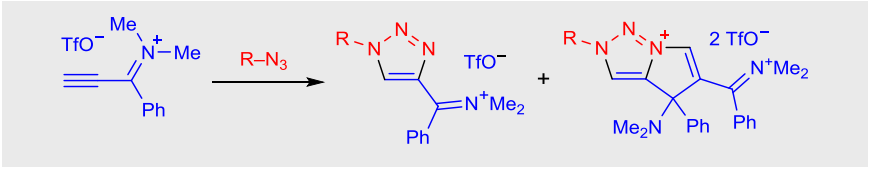

Terminal acetylenic iminium triflates are excellent dipolarophiles for [3+2] cyclo-additions with (ring-substituted) benzyl and phenyl azide, yielding novel 1,2,3-triazol-4-yl)methaniminium salts. The latter are readily converted into 2:1 adducts, dicationic bicyclic 1,2,3-triazolium salts, which can be transformed into some interesting compounds, among them a mesoionic carbene and a Ag(I) complex thereof.

1,2,3-Triazoles

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Terminal Acetylenic Iminium Salts: 1,3-Dipolar Cycloaddition Reactions with Azides leading to 1,2,3-Triazoles and Bicyclic 1,2,3-Triazolium Salts