A Convenient Synthesis and Some Characteristic Reactions of Novel Propiolamidinium Salts

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Abstract: Starting from *N*,*N*,*N*′,*N*′,*N*″,*N*″-hexaalkylguanidinium chlorides and terminal alkynes, a series of new orthoamide derivatives of alkynecarboxylic acids were prepared. The orthoamides were converted into propiolamidinium chlorides by reaction with benzoyl chloride and into propiolamidinium triflates by reaction with triethylsilyl trifluoromethanesulfonate. Propiolamidinium salts undergo conjugate addition reactions with *sec*-amines and thiols. Treatment of terminal alkyne chlorides with silver(I) oxide afforded a silver complex, which can apparently adopt the composition of either a bisalkynyl silver complex $[Ag(CCC(NMe_2)_2)_2]AgCl_2$ or a monoalkynyl silver complex $[ClAgCCC(NMe_2)_2]$.

Key words: alkynes, amidinium salts, orthoamides, hexamethylguanidinium chloride, silyl triflates

Acetylenic iminium (**1**), amidium (**2**), and amidinium (**3**) salts combine in one organic cation two reactive functional groups (Figure 1). It can be expected that due to the electron-deficient C≡C triple bond and to a susceptibility of the ambident functionality toward nucleophilic reagents, these salts are potentially useful building blocks in organic synthesis. In fact, a variety of chemical transformations have been reported for acetylenic iminium salts **1**.[1,2] Amidium salts **2**, although readily obtained by O-alkylation of alkynecarboxylic acid amides, have been explored to a much lesser extent,[3] and very little is known about the chemistry of alkynyl amidinium salts (also called propiolamidinium salts) **3**.

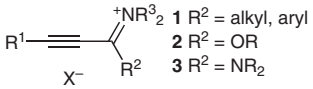


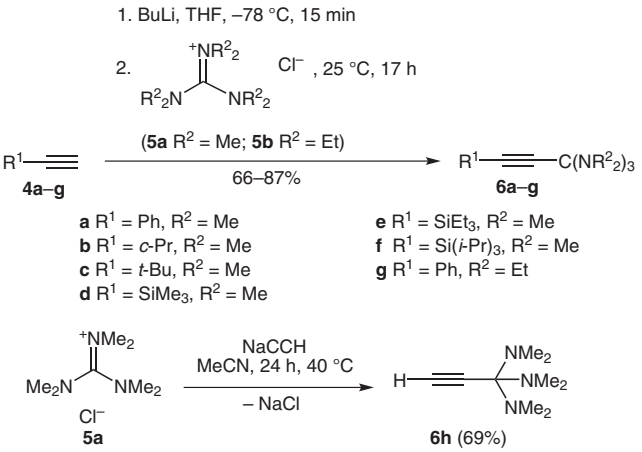
Figure 1

Even reports on the synthesis of propiolamidinium salts are scarce. An obvious approach would be the N-alkylation of propiolamidines, $R^1C{\equiv}CC(=NR)(NR_2)$. However, Viehe and Baum have found this transformation not to be proficient, in contrast to the N-protonation using perchloric acid. The reaction of *N*,*N*-dimethyl-*N*′-methylpropiolamidine and methyl iodide was sluggish and gave *N*,*N*′-tetramethylphenylpropiolamidinium iodide in very low yield; stronger alkylation reagents, including methyl triflate, did not produce better results.[4]

Kantlehner and coworkers took another approach, namely electrophile-induced deamination of a propiolic acid orthoamide. However, their synthesis of propiolamidinium chloride **3a**-Cl (see Scheme 2 below) from benzoyl chloride and 3,3,3-tris(dimethylamino)-1-phenylprop-1-yne remains the only example of this method so far reported.[5]

We explored another approach to salts **3** without success: the reaction of alkynyl lithium or alkynyl Grignard compounds with chlorotetramethylformamidinium chloride[6] did not afford the desired propiolamidinium salts. In this context, it must be remembered that the reaction of phenyl lithium and higher alkyl lithium compounds with this chloroformamidinium salt also did not take the expected addition/substitution pathway, but instead gave products derived from radical intermediates.[7] Coupling of the chloroformamidinium salt with terminal alkynes under Sonogashira conditions was also unsuccessful.

We returned, therefore, to alkynyl orthoamides as potential precursors of propiolamidinium salts **3**. It has been reported that terminal alkynes can be converted into alkynyl orthoamides by subsequent treatment with sodium hydride (80% in mineral oil) and hexamethylguanidinium chloride (HMG-Cl; **5a**) in tetrahydrofuran.[8] As we were facing low yields in some cases and it appeared that the



Scheme 1 Synthesis of alkynyl orthoamides **6a–h**

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quality of sodium hydride in mineral oil affected the yields, we switched from sodium to lithium acetylides.

Terminal alkynes **4** were lithiated quantitatively with *n*-butyllithium in tetrahydrofuran and immediately converted into the corresponding alkynyl orthoamides **6a–g** with the hexaalkylguanidinium salts **5a** and **5b** (Scheme 1 and Table 1). Similar reactions of organolithium compounds with **5a** have been described previously.[9] The lithium acetylides are soluble in tetrahydrofuran and react at an acceptable rate with guanidinium salts **5** suspended in tetrahydrofuran. In contrast, sodium acetylides are formed slowly due to the low solubility of sodium hydride in tetrahydrofuran and subsequently react slowly with guanidinium salts **5**, suspended in tetrahydrofuran, to afford orthoamides **6**.

The terminal alkynyl orthoamide **6h** could not be prepared effectively in the same way because the (mono)lithium acetylide readily underwent irreversible disproportionation in tetrahydrofuran at 0 °C to form the insoluble, less reactive dilithium acetylide and acetylene.[10] As the main product, we isolated the bis(orthoamide) derivative of acetylenedicarboxylic acid (see Kantlehner et al.[8]). Hence, we made use of sodium acetylide, but the reaction was carried out in acetonitrile as a dipolar solvent to increase the solubility of both starting materials.

The ester-substituted alkyne orthoamide **6i** (see Scheme 4 below) could also not be prepared in this way because of polymerization of the lithiated propiolic ester. Therefore, **6i** was synthesized as published from tris(dimethylamino)ethoxymethane and ethyl propiolate.[11]

The orthoamides **6b**, **6c**, and **6h** were successfully converted into the novel propiolamidinium chlorides **3b**, **3c**, and **3h**-Cl by treatment with benzoyl chloride, following the procedure established for **3a**-Cl (Scheme 2 and Table 2).[5] Because the propiolamidinium chloride salts **3**-Cl are hygroscopic, they were converted into the more stable propiolamidinium tetraphenylborate salts **3**-BPh_4 by an anion-exchange reaction.

Unfortunately, the benzoyl chloride method was not applicable to trialkylsilyl-substituted alkynyl orthoamides

Table 1 Alkynyl Orthoamides **6a–h**

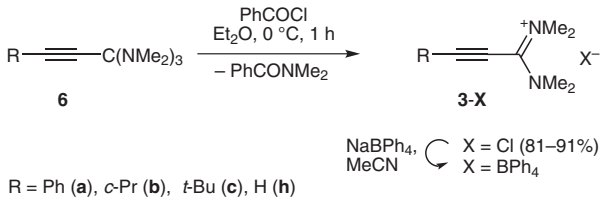
Product	Molecular formula[a]	Yield (%)	Bp[b] (°C/mbar)	^{1}H NMR (δ)[c]	^{13}C{^{1}H} NMR (δ)[d]	IR (cm^{-1})[e] $\nu_{C\equiv C}$
6a	$C_{15}H_{23}N_3$ (245.36)	79	105/0.05[f]	2.55 (s, 18 H, NCH_3), 7.29–7.32 (m, 3 H, PhH), 7.49–7.51 (m, 2 H, PhH)	40.0 (NCH_3), 85.2, 85.8 (C≡C), 94.2 (*C*N(CH_3)$_2$), 113.2, 128.0, 128.2, 131.9 (C_{Ph})	2218
6b	$C_{12}H_{23}N_3$ (209.33)	75	95/0.3	0.68–0.80 (m, 4 H, CH_2 cp), 1.29–1.36 (m, 1 H, CH cp), 2.44 (s, 18 H, NCH_3)	–0.6 (CH cp), 8.6 (CH_2 cp), 39.9 (NCH_3), 70.7 (NC*C*≡C), 89.3 (NCC≡*C*), 93.6 (*C*N(CH_3)$_2$)	2231
6c	$C_{13}H_{27}N_3$ (225.37)	78	90/0.2	1.28 (s, 9 H, CH_3), 2.44 (s, 18 H, NCH_3)	27.5 (*C*(CH_3)$_3$), 31.4 (C(*C*H_3)$_3$), 39.9 (NCH_3), 73.8 (NC*C*≡C), 93.4 (*C*N(CH_3)$_2$), 94.8 (NCC≡*C*)	2235
6d	$C_{12}H_{27}N_3Si$ (241.45)	82	95/0.1	0.19 (s, 9 H, Si(CH_3)$_3$), 2.44 (s, 18 H, NCH_3)	0.2 ($SiCH_3$), 39.8 (NCH_3), 89.5 (Si*C*≡C), 93.7 (*C*N(CH_3)$_2$), 100.7 (NC*C*≡C)	2161
6e	$C_{15}H_{33}N_3Si$ (283.53)	87	105/0.1	0.63 (q, *J* = 7.9 Hz, 6 H, Si*C*$H_2$$CH_3$), 1.02 (t, *J* = 7.9 Hz, 9 H, CH_2C*H*$_3$), 2.46 (s, 18 H, 6 NCH_3)	4.6 ($SiCH_2$*C*H_3), 7.3 ($SiCH_2$), 39.8 (NCH_3), 86.9 (Si*C*≡C), 93.9 (*C*N(CH_3)$_2$), 101.8 (NC*C*≡C)	2160
6f	$C_{18}H_{39}N_3Si$ (325.61)	71	135/0.01	1.10–1.12 (m, 21 H, Si(*i*-Pr)), 2.47 (s, 18 H, NCH_3)	11.4 (Si*C*HCH_3), 18.8 (CH*C*H_3), 39.9 (NCH_3), 85.7 (Si*C*≡C), 94.0 (*C*N(CH_3)$_2$), 102.7 (NC*C*≡C)	2160
6g	$C_{21}H_{35}N_3$ (329.52)	66	160/0.01	1.09 (t, *J* = 7.1 Hz, 18 H, CH_2C*H*$_3$), 2.91 (q, *J* = 7.1 Hz, 12 H, NC*H*$_2$$CH_3$), 7.26–7.28 (m, 3 H, PhH), 7.40–7.42 (m, 2 H, PhH)	16.0 (CH_2*C*H_3), 43.9 (N*C*$H_2$$CH_3$), 83.8 (NC*C*≡C), 89.7 (NCC≡*C*), 96.0 (*C*N(CH_3)$_2$), 123.9, 127.6, 128.7, 131.4 (C_{Ph})	2221
6h	$C_9H_{19}N_3$ (169.27)	69	65/5	2.12 (s, 1 H, C≡CH), 2.48 (s, 18 H, NCH_3)[c]	40.3 (NCH_3), 73.7 ($^1J_{C,H}$ = 263 Hz, C≡*C*H), 79.7 (NC*C*≡C), 94.2 (*C*N(CH_3)$_2$)[d]	2280, 3304 (≡CH)

[a] Since the orthoamides are rather moisture-sensitive oily compounds, no combustion analysis was carried out.
[b] Kugelrohr distillation.
[c] Carried out at 400.13 MHz in $CDCl_3$ (**6h**: in C_6D_6); cp = cyclopropyl.
[d] Carried out at 100.61 MHz in $CDCl_3$ (**6h**: in C_6D_6); cp = cyclopropyl; assignments were made on the basis of HMBC experiments.
[e] Film.
[f] Oily **6a** slowly crystallized as off-white needles (mp 28–30 °C).

Table 2 Propiolamidinium Salts **3**

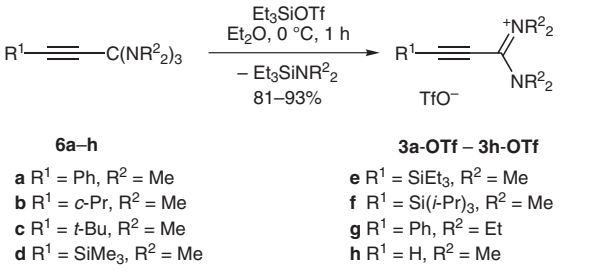
Product	Molecular formula	Yield (%)	CHN		Mp (°C)	^{1}H NMR (δ)[a]	^{13}C{^{1}H} NMR (δ)[b]	IR (cm^{-1})[c]
			Calcd	Found				C≡C C=N$^+$
3b-Cl	$C_{10}H_{17}ClN_2$ (200.71)	85	–[d]	–	>121 (dec.)	0.90–0.94 (m, 2 H, CH_2 cp), 1.07–1.12 (m, 2 H, CH_2 cp), 1.50–1.57 (m, 1 H, CH cp), 3.38 (s, 12 H, $^+NCH_3$)	0.4 (CH cp), 10.7 (CH_2 cp), 44.0 (NCH_3), 64.9 (NC*C*≡C), 116.1 (NCC≡*C*), 152.3 (*C*$^+$(N(CH_3)$_2$)$_2$)	2223 1614
3c-Cl	$C_{11}H_{21}ClN_2$ (216.75)	87	–[d]	–	>177 (dec.)	1.13 (s, 9 H, CH_3), 3.52 (s, 12 H, $^+NCH_3$)	28.9 (*C*(CH_3)$_3$), 29.7 (C(*C*H_3)$_3$), 44.2 (NCH_3), 69.7 (NC*C*≡C), 118.8 (NCC≡*C*), 152.3 (*C*$^+$(N(CH_3)$_2$)$_2$)	2224 1619
3h-Cl	$C_7H_{13}ClN_2$ (160.64)	84	–[d]	–	> 93 (dec.)	3.31 (s, 12 H, $^+NCH_3$), 5.24 (s, 1 H, C≡CH)	44.6 (NCH_3), 71.4 (NC*C*≡C), 99.7 (H*C*≡C), 153.0 (*C*$^+$(N(CH_3)$_2$)$_2$)	2090 1619
3a-OTf	$C_{14}H_{17}F_3N_2O_3S$ (350.36)	89	C, 47.99; H, 4.89; N, 8.00	C, 47.83; H, 5.15; N, 8.00	125–126	3.47 (s, 12 H, $^+NCH_3$), 7.44–7.48 (m, 2 H, PhH), 7.55–7.63 (m, 3 H, PhH)	44.4 (NCH_3), 77.3 (NC*C*≡C), 107.6 (NCC≡*C*), 117.8, 129.1, 132.2, 132.7 (C_{Ph}), 152.3 (*C*$^+$(N(CH_3)$_2$)$_2$)	2219 1615
3b-OTf	$C_{11}H_{17}F_3N_2O_3S$ (314.32)	85	C, 42.03; H, 5.45; N, 8.91	–[e]	yellow oil	1.02–1.05 (m, 2 H, CH_2 cp), 1.14–1.18 (m, 2 H, CH_2 cp), 1.57–1.64 (m, 1 H, CH cp), 3.34 (s, 12 H, $^+NCH_3$)	0.3 (CH cp), 10.5 (CH_2 cp), 43.4 (NCH_3), 64.8 (NC*C*≡C), 116.5 (NCC≡*C*), 152.7 (*C*$^+$(N(CH_3)$_2$)$_2$)	2221 1616
3c-OTf	$C_{12}H_{21}F_3N_2O_3S$ (330.37)	80	C, 43.63; H, 6.41; N, 8.48	C, 43.55; H, 6.39; N, 8.39	66–67	1.34 (s, 9 H, CH_3), 3.35 (s, 12 H, $^+NCH_3$)	28.9 (*C*(CH_3)$_3$), 29.6 (C(*C*H_3)$_3$), 43.7 (NCH_3), 68.7 (NC*C*≡C), 119.4 (NCC≡*C*), 152.8 (*C*$^+$(N(CH_3)$_2$)$_2$)	2230 1622
3d-OTf	$C_{11}H_{21}F_3N_2O_3SSi$ (346.44)	82	C, 38.14; H, 6.11; N, 8.09	C, 38.07; H, 6.04; N, 7.84	71–73	0.32 (s, 9 H, $SiCH_3$), 3.40 (s, 12 H, $^+NCH_3$)	–1.1 ($SiCH_3$), 43.8 (NCH_3), 90.2 (NC*C*≡C), 117.9 (NCC≡*C*), 151.6 (*C*$^+$(N(CH_3)$_2$)$_2$)	2169 1627
3e-OTf	$C_{14}H_{27}F_3N_2O_3SSi$ (388.52)	86	C, 43.28; H, 7.00; N, 7.21	C, 43.13; H, 7.09; N, 7.15	80–82	0.75 (q, *J* = 7.9 Hz, 6 H, Si*C*$H_2$$CH_3$), 1.03 (t, *J* = 7.9 Hz, 9 H, $SiCH_2$*C*H_3), 3.43 (s, 12 H, $^+NCH_3$)	3.5 ($SiCH_2$), 7.3 (CH_2*C*H_3), 43.9 (NCH_3), 91.2 (NC*C*≡C), 116.7 (NCC≡*C*), 151.6 (*C*$^+$(N(CH_3)$_2$)$_2$)	2170 1627
3f-OTf	$C_{17}H_{33}F_3N_2O_3SSi$ (430.60)	81	C, 47.42; H, 7.72; N, 6.51	C, 47.24; H, 7.79; N, 6.69	103–105	1.11–1.12 (m, 18 H, CHCH_3), 1.16–1.24 (m, 3 H, SiC*H*CH_3), 3.42 (s, 12 H, $^+NCH_3$)	10.9 (SiCH), 18.5 (CH*C*H_3), 44.0 (NCH_3), 92.1 (NC*C*≡C), 116.2 (NCC≡*C*), 151.5 (*C*$^+$(N(CH_3)$_2$)$_2$)	2165 1627
3g-OTf	$C_{18}H_{25}F_3N_2O_3S$ (406.46)	88	C, 53.19; H, 6.20; N, 6.89	C, 53.08; H, 6.32; N, 6.69	46–47	1.44 (t, *J* = 7.2 Hz, 12 H, CH_2C*H*$_3$), 3.81 (q, *J* = 7.2 Hz, 8 H, ^+NC*H*$_2CH_3$), 7.46–7.56 (m, 2 H, PhH), 7.58–7.62 (m, 3 H, PhH)	13.3 (CH_3), 48.6 (NCH_2), 77.7 (NC*C*≡C), 105.0 (NCC≡*C*), 118.0, 129.1, 132.4, 132.8 (C_{Ph}), 151.3 (*C*$^+$(N(CH_3)$_2$)$_2$)	2217 1586
3h-OTf	$C_8H_{13}F_3N_2O_3S$ (274.26)	82	C, 35.03; H, 4.48; N, 10.21	–[e]	red oil	3.45 (s, 12 H, $^+NCH_3$), 4.33 (s, 1 H, C≡CH)	44.0 (NCH_3), 70.6 (NC*C*≡C), 97.0 (H*C*≡C), 151.5 (*C*$^+$(N(CH_3)$_2$)$_2$)	2115 1627

[a] Carried out at 400.13 MHz in $CDCl_3$ (**3h**-Cl: in CD_3CN); cp = cyclopropyl.
[b] Carried out at 100.61 MHz in $CDCl_3$ (**3h**-Cl: in CD_3CN); δ (CF_3) = 120.8 (q, $^1J_{C,F}$ = 319 Hz); NMR assignments were confirmed by 2D correlation spectra.
[c] Neat (ATR measurement).
[d] The hygroscopic chlorides **3b**, **3c**, and **3h**-Cl were converted into tetraphenylborates **3b**, **3c**, and **3h**-BPh_4 for elemental analysis (see experimental section).
[e] Elemental analyses of oils **3b** and **3h**-OTf were not successful; the composition was confirmed by mass spectrometry (CI): **3b**-OTf: *m*/*z* = 165 $[M_{cat}]^+$; **3h**-OTf: *m*/*z* = 125 $[M_{cat}]^+$.



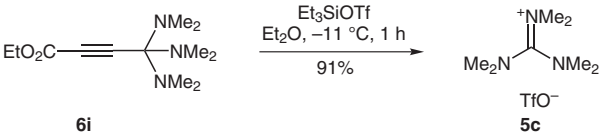
Scheme 2 Synthesis of novel propiolamidinium chlorides **3**-Cl and tetraphenylborates **3**-BPh_4

6d–f, which suffered unspecific decomposition. We were pleased to find that orthoamides **6a–h** all underwent clean deamination upon treatment with triethylsilyl trifluoromethanesulfonate (triflate), and alkynyl amidinium triflates **3a–h**-OTf were obtained in high yields (Scheme 3, Table 2). During work-up, the by-product, (dimethylamino)triethylsilane, was easily removed in vacuo. Triethylsilyl triflate is to be preferred over trimethylsilyl triflate (vide infra), because the latter unavoidably contains traces of triflic acid, which give rise to the formation of the dialkylammonium triflate that is hard to separate from the amidinium salt.



Scheme 3 Synthesis of propiolamidinium triflates **3a–h**-OTf

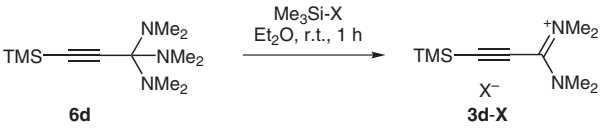
Under the same reaction conditions, orthoamide **6i** was cleaved at the C_{alkyne}–C_N bond, and hexamethylguanidinium triflate (**5c**) was isolated in high yield (Scheme 4). The reason for this different behavior is not yet known.



Scheme 4 Et_3SiOTf-induced cleavage of alkynyl orthoamide **6i**

The highly electrophilic silyl triflates were found to be the best reagents for effective deamination of orthoamides **6a–h**. A comparison of the TMS triflate with the TMS halides was made for the transformation of the trimethylsilyl-substituted alkynyl orthoamide **6d** (Table 3). It was evident that the yield diminished with decreasing silylating power of the reagent. Silyl halides could be used to prepare the bromide and iodide salts, however, the chloride salts could not be isolated. The bromide and iodide salts were obtained as oils. We were also unable to provide analytically pure bromides or chlorides by recrystallization. When Me_3SiOTf was added slowly to a solution

Table 3 Reaction of Orthamide **6d** with Trimethylsilyl Halides and Triflate



X	Yield of **3d**-X (%)[a]
Cl	n/a[b]
Br	47
I	67
OTf	77

[a] The crude product was recrystallized from Et_2O/CH_2Cl_2 at –20 °C.
[b] The formation of the propiolamidinium chloride was observed as an off-white precipitate, which slowly decomposed.

of **6d** in tetrahydrofuran, the propiolamidinium salt **3d**-OTf immediately precipitated as a brown powder.

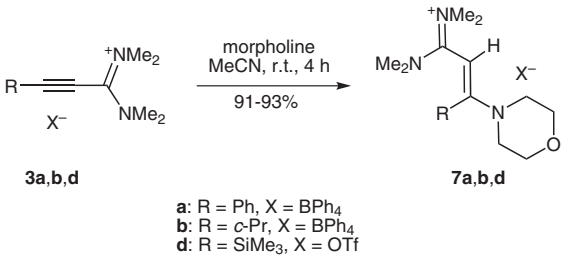
It should be added that the stability of the propiolamidinium salts derived from **6d** was closely related to the anion used, with the chloride salt showing the lowest stability. However, the electrophile was also important, since an analogous reaction with benzoyl triflate was not successful.

As found in previous studies,[4,5] propiolamidinium salts **3** appear to be very reluctant to undergo common cycloaddition reactions. They did not participate in Diels–Alder reactions with cyclopentadiene (even under heating in acetonitrile), and were not amenable to 1,3-dipolar cycloaddition reactions with ethyl diazoacetate or oxazolium mesoionic reagents.

On the other hand, the propiolamidinium salts underwent diastereoselective Michael-type nucleophilic addition with *sec*-amines. As an example, the reaction of salts **3** with morpholine afforded the β-morpholino-propeneamidinium salts **7** in high yields (Scheme 5), with *syn*-addition being observed exclusively (the configuration was established by NOE NMR experiments). Whereas *syn*-addition is the rule for Michael additions of this kind, it must also be kept in mind that the cations of salts **7** represent vinamidinium systems, which, due to the push-pull substitution of the enaminic double bond, can easily assume the most stable configuration irrespective of the geometry of the addition step.

Such an addition reaction was previously reported by Weingarten,[12] whereby, 3-phenylpropiolamidinium acetate, which resulted from the reaction of acetic acid with orthoamide **6a**, was trapped in situ by conjugate addition of dimethylamine. Other synthetic routes to propeneamidinium salts have been based on condensation reactions.[13]

Propiolamidinium salts **3** also reacted with thiols through conjugate addition. Examples with cyclohexylmercaptan (**8a**) and benzenethiol (**8b**) are shown in Scheme 6. The reaction with propiolamidinium chloride **3a**-Cl afforded a mixture of *E*/*Z*-isomeric salts **9a** and **10a**, respectively. In

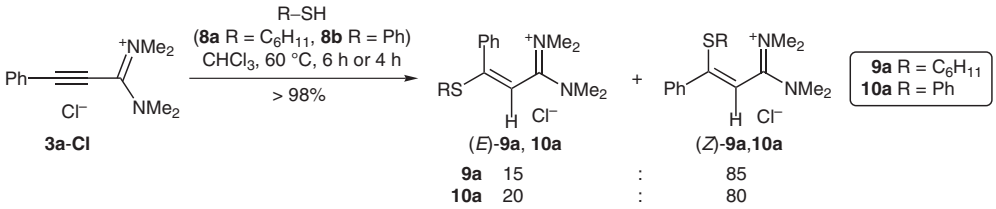


Scheme 5 Conjugate addition of morpholine to propiolamidinium salts **3a**-BPh_4, **3b**-BPh_4 and **3d**-OTf

contrast to salts **7**, formation of the *Z*-isomer predominated in both cases. For the isomeric 3-cyclohexylthiopropeneamidinium chlorides **9a**, the configurational assignment was accomplished by selective NOE experiments, which revealed perturbation effects between the olefinic proton and the neighboring ^{1}H nuclei. For example, irradiation at δ = 6.32 ppm [2-H for the major isomer (*Z*)-**9a**] resulted in through-space interactions with the signals at δ = 3.36 [$N(CH_3)_2$] and 7.47 ppm (PhH).

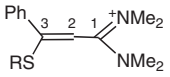
Assignment of the *E*- or *Z*-configuration of propeneamidinium salts **10a** by NOE experiments was not reliable due to the presence of closely spaced ^{1}H signals of the phenyl and the phenylthio groups. However, the similarity of the ^{1}H and ^{13}C NMR chemical shifts compared with (*E*)- and (*Z*)-**9a** (Table 4) allowed us to assume the same configuration for the major vs. the minor isomers in both cases. It should also be mentioned that the relevant ^{1}H and ^{13}C NMR data assigned to the two diastereomers of **10a** are, in all details, analogous to those of a related propeneiminium salt, 4-(1-methyl-3-phenyl-3-phenylthio-2-propen-ylidene)morpholinium triflate.[14] Additionally, we were able to assign characteristic NMR chemical shifts of (*E*)- and (*Z*)-**10a** based upon computationally calculated molecular structures of (*E*)- and (*Z*)-**9a** (see the Supporting Information).

The terminal alkyne **3h** offered the opportunity to metalate the acetylenic C–H bond, paving the way to other alkynyl amidinium salts that are substituted or functionalized at the remote acetylenic carbon atom. Bertrand and



Scheme 6 Conjugate addition of cyclohexylmercaptan (**8a**) and benzenethiol (**8b**) to propiolamidinium chloride **3a**-Cl

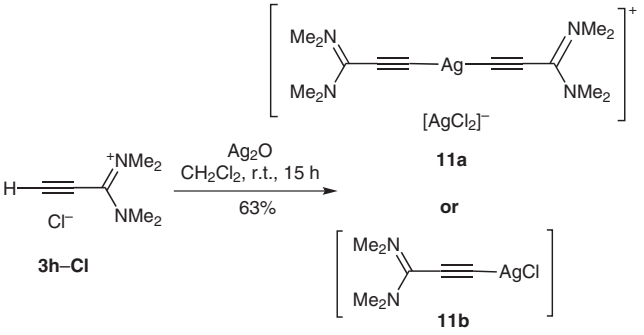
Table 4 ^{1}H and ^{13}C NMR Data of Salts **9a** and **10a**[a]



Compd	^{1}H NMR δ (ppm)				^{13}C NMR δ (ppm)				
	2-H	NCH_3	PhH	R	C-1	C-2	C-3	NCH_3	Other signals
(*E*)-**9a**	6.05	3.05			167.1	109.2	162.3		25.3, 25.4, 32.3 (CH_2); 45.2 (SCH); 127.8, 129.2, 131.0, 136.3 (C_{Ph})
			7.42–7.49	1.02–1.71 (5 CH_2) 2.70–2.81 (SCH)				42.8–43.7[b]	
(*Z*)-**9a**	6.32	3.36			166.6	118.0	156.2		25.0, 25.6, 33.8 (CH_2); 45.5 (SCH); 127.7, 129.0, 130.4, 136.4 (C_{Ph})
(*E*)-**10a**	5.29	3.04, 3.15[c]			166.2	109.2	164.2		127.7, 128.7, 129.3, 130.4, 130.7, 131.3, 134.9 (C_{Ph})[d]
			7.14–7.63 (Ph, SPh)					42.3–43.2[b]	
(*Z*)-**10a**	6.72	3.43			166.0	118.4	154.8		128.2, 128.5, 128.6, 129.2, 130.5, 130.7, 131.1, 135.7 (C_{Ph})

[a] Recorded in $CDCl_3$ with TMS as internal standard. NMR data for **9a** were recorded with a Bruker DRX 400, data for **10a** were recorded with an AMX 500 spectrometer.
[b] The NCH_3 signals were strongly broadened due to coalescence.
[c] Two broadened, symmetrical NCH_3 signals.
[d] One ^{13}C signal for C_{Ph} in (*E*)-**10a** coincides with a signal of (*Z*)-**10a**.

co-workers[15] have just reported that 2-ethynyl-1,3-dimethylimidazolium iodide, which can be considered as a special type of an alkynyl amidinium salt, is readily metalated with silver oxide to give the complex [(1,3-Me_2ImC≡C)$_2$Ag]I, which was characterized by an X-ray crystal structure analysis and used for transmetalation reactions.



Scheme 7 Conversion of ethynyl orthoamide **7h** into silver complex **11a** and/or **11b**

By partial analogy, we found that salt **3h**-Cl reacts smoothly with silver(I) oxide to give the stable silver(I) bisacetylide complex **11** (Scheme 7). The proposed structure, a linear $[Ag(CCC(NMe_2)_2)_2]^+$ cation and an $[AgCl_2]^-$ anion, which should be associated through an Ag–Ag interaction (see Wang and Lin;[16] silver alkynyl complexes forming metallic clusters are also known[17]), is in agreement with elemental analysis and mass spectra. To our surprise, however, a single-crystal X-ray structure analysis revealed the structure of monoacetylide silver complex **11b** (note that **11a** and **11b** have the same relative elemental composition). In the crystal structure, two symmetry-related molecules of **11b** form a dimer with a four-membered cyclic Ag–Cl···Ag–Cl core. It appears, therefore, that in solution an equilibrium exists between complexes **11a** and **11b**[16] and that the ESI(+) mass spectrum reveals only the cation of complex **11a**. Further studies on this issue, as well as on metalation and transmetalation reactions, are underway.[18]

In summary, we have developed a novel method to prepare propiolamidinium triflates **3a**–**g**-OTf, including an improved procedure for the preparation of alkynyl orthoamides from terminal alkynes and hexaalkylguanidinium chlorides. These alkynyl orthoamides are versatile synthetic building blocks in their own right.[9b,19] It is hoped that propiolamidinium salts **3** will prove to be useful substrates for further transformations.

All reactions were carried out in rigorously dried glassware under an atmosphere of argon, making use of Schlenk techniques, and taking into account the moisture-sensitivity of the orthoamides and amidinium salts. Solvents were dried by established procedures and stored over molecular sieves (4 Å for Et_2O, CH_2Cl_2, pentane, and THF, 3 Å for EtOAc and acetonitrile). Trimethyl and triethylsilyl triflate were freshly distilled prior to use. NMR spectra were recorded with a Bruker DRX 400 spectrometer operating at 400.1 MHz for ^{1}H and 100.6 MHz for ^{13}C. NOE experiments and 2D NMR spectra were recorded with an AMX 500 spectrometer operating at 500.1 MHz for ^{1}H and 125.7 MHz for ^{13}C. The solvent signals served as internal standard for NMR spectroscopic measurements. IR spectra were obtained with a Bruker Vector 22 FT-IR spectrophotometer using a Harrick Scientific MVP ATR unit equipped with a ZnSe crystal. Melting points were determined with a Büchi Melting Point B-540 apparatus and are uncorrected. Elemental analyses were performed with an Elemental Vario Micro Cube. The HRMS spectrum for **11** was recorded with a Bruker Daltonics micrOTOF-Q instrument (ESI).

Hexamethylguanidinium chloride (**5a**) and hexaethylguanidinium chloride (**5b**) were prepared according to the literature procedure[20] and dried over P_2O_5 for 3 d at 165 °C in vacuo (0.01 mbar).

Sodium acetylide (NaCCH) was purchased as an 18% slurry in xylene from Acros Organics, the xylene was removed in vacuo. The crude sodium acetylide was washed several times with anhydrous hexane, filtered off through a sintered glass filter and dried at 60 °C in vacuo (0.5 mbar) for 3 h.

Triethylsilyl- and triisopropylsilylacetylene (**4e** and **4f**) were synthesized according to a slightly modified literature procedure.[21] To form the reactive mono-lithium acetylide species, a solution of *n*-BuLi (1 M in Et_2O, 0.25 mol, 250 mL) was slowly added to a saturated solution of acetylene in THF (50 mL containing approx. 2.5 equiv of acetylene) through a double-ended needle at –78 °C.

Cylohexylmercaptan (**8a**) and benzenethiol (**8b**) were dried with $CaCl_2$, and distilled at 40 mm pressure in a stream of argon.

All other reagents were purchased from commercial suppliers and used without further purification.

Alkynyl Orthoamides 6; Typical Procedure

To a solution of an alkyne **4** (12.0 mmol) in THF (12 mL) cooled to –78 °C was slowly added BuLi (2.5 M in hexane, 4.80 mL) via a syringe. The reaction mixture was kept for 15 min at –78 °C and then allowed to warm to r.t. Hexamethyl- or hexaethylguanidinium chloride (**5a** or **5b**, 11.5 mmol) was swiftly added, and the suspension was vigorously stirred at ambient temperature for 17 h. The precipitated LiCl was filtered through a sintered glass filter under an argon atmosphere, and the solvent was then removed at 40 °C/175 mbar. The residue was carefully distilled in a Kugelrohr apparatus to afford colorless or light-yellow oils. Alkynyl orthoamides can be stored in Schlenk tubes under an argon atmosphere in a freezer at –20 °C. For yields, physical and spectroscopic data, see Table 1.

3,3,3-Tris(dimethylamino)propyne (6h)

Sodium acetylide (1.87 g, 39 mmol) was suspended in anhydrous MeCN (20 mL). HMG-Cl (6.00 g, 33 mmol) was added, and the slurry was stirred for 1 d at 40 °C. The precipitated NaCl was filtered off through a sintered glass filter under an argon atmosphere and the MeCN was quickly removed at 40 °C/80 mbar. The residue was distilled in a Kugelrohr apparatus (65 °C/5 mbar) to afford a highly hygroscopic yellow oil, which quickly crystallized as off-white needles.

Yield: 3.85 g (69%); mp 24–26 °C.

Propiolamidinium Chlorides 3-Cl; Typical Procedure

To a solution of alkynyl orthoamide **6a**–**c** or **6h** (4.0 mmol) in Et_2O (25 mL) was slowly added a solution of freshly distilled benzoyl chloride (0.48 mL, 4.1 mmol) in Et_2O (8 mL) at 0 °C. The reaction mixture was stirred for 40 min, during which time a white powdery precipitate formed. The liquid phase was removed by pipette, and the precipitate was washed several times with Et_2O. The light-brown solid was dried and recrystallized from CH_2Cl_2/Et_2O to afford propiolamidinium chlorides **3** as off-white powders (see Table 2). The synthesis of **3a**-Cl by this method has already been described.[5] For elemental analysis, the propiolamidinium chlorides

3-Cl were converted into non-hygroscopic tetraphenylborate salts **3**-BPh_4 (vide infra).

Propiolamidinium Tetraphenylborates 3; Typical Procedure
Propiolamidinium chloride **3a–c** or **3h**-Cl (4.0 mmol) was dissolved in an adequate quantity of MeCN. A solution of sodium tetraphenylborate (1.37 g, 4.0 mmol) in MeCN (5 mL) was added and the mixture was stirred for 15 min at 60 °C. The precipitated NaCl was hot-filtered off, the filtrate was evaporated in vacuo, and the crude product was recrystallized from MeCN to afford the tetraphenylborate.

3a-BPh_4
Yield: 1.89 g (91%); mp 172–173 °C.

Anal. Calcd for $C_{37}H_{37}BN_2$ (520.51): C, 85.38; H, 7.16; N, 5.38. Found: C, 85.12; H, 7.18; N, 5.28.

3b-BPh_4
Yield: 1.69 g (87%); mp 140–141 °C.

Anal. Calcd for $C_{34}H_{37}BN_2$ (484.48): C, 84.29; H, 7.70; N, 5.78. Found: C, 84.09; H, 7.71; N, 5.65.

3c-BPh_4
Yield: 1.78 g (89%); mp 157–158 °C.

Anal. Calcd for $C_{35}H_{41}BN_2$ (500.52): C, 83.99; H, 8.26; N, 5.60. Found: C, 83.70; H, 8.19; N, 5.43.

3h-BPh_4
Yield: 1.49 g (84%); mp >183 °C (dec.).

Anal. Calcd for $C_{31}H_{33}BN_2$ (444.42): C, 83.78; H, 7.48; N, 6.30. Found: C, 83.64; H, 7.52; N, 6.27.

Propiolamidinium Triflates 3; Typical Procedure
To a cooled solution (0 °C) of triethylsilyl trifluoromethanesulfonate (0.91 mL, 4.0 mmol) in pentane (12 mL) was slowly added a solution of alkynyl orthoamide **6a–h** (4.0 mmol) in Et_2O (5 mL) from a cooled dropping funnel.

3a-OTf and 3c–g-OTf
A yellow oil separated from the above Et_2O–pentane solution, and the mixture was kept stirring for 30 min at 0 °C. The supernatant phase was decanted, and the residual oil was solidified by anhydrous Et_2O trituration and by scratching the inner wall of the flask with a glass rod. The crude solid product was taken up in CH_2Cl_2 and again slowly precipitated by addition of Et_2O. The solid was dried in vacuo to afford the salts as tan-colored powders.

3b-OTf and 3h-OTf
A deeply colored oil separated from the organic phase, and the mixture was kept stirring at 0 °C for 15 min. The supernatant organic phase was thoroughly removed by pipette and the residual oil was triturated several times with anhydrous pentane in an ultrasonic bath. For yields, physical and spectroscopic data, see Table 2.

Compound 6i
In the case of orthoamide **6i**, *N*,*N*,*N*′,*N*′,*N*″,*N*″-hexamethylguanidinium triflate (**5c**) was isolated as a white powder, which was recrystallized from MeCN and dried for 6 h at 60 °C in vacuo (0.01 mbar).

Yield: 1.07 g (91%); mp 177–178 °C.

IR (ATR): 2919, 1597, 1479, 1409, 1280, 1222, 1164, 1025, 897 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 3.01 (NCH_3).

^{13}C NMR (DMSO-d_6): δ = 39.4 (NCH_3), 120.6 (q, $^1J_{C-F}$ = 322 Hz, CF_3), 162.3 {$C^+[N(CH_3)_2]_3$}.

MS (CI): *m*/*z* (%) = 144 (100) $[M_{cat}]^+$, 145 (8) $[M_{cat} + H]^+$.

Anal. Calcd for $C_8H_{18}F_3N_3O_3S$ (293.31): C, 32.76; H, 6.19; N, 14.33. Found: C, 32.75; H, 6.00; N, 14.13.

***N*,*N*,*N*′,*N*′-Tetramethyl(3-morpholino-3-phenylprop-2-yne)amidinium Tetraphenylborate (7a)**
To a solution of tetraphenylborate salt **3a**-BPh_4 (1.04 g, 2.0 mmol) in MeCN (14.0 mL) was slowly added dried morpholine (0.175 mL, 2.0 mmol), and the mixture was stirred for 4 h at ambient temperature. The solution was concentrated in vacuo, and the white precipitate was filtered off and recrystallized form EtOAc to afford **7a** as white crystals.

Yield: 1.13 g (93%); mp 181–182 °C.

IR (ATR): 3056, 2957, 2865, 1585, 1553, 1480, 1447, 1397, 1343, 1265, 1242, 1220, 1154, 1118, 1062, 1032, 903, 821 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 2.71 (s, 12 H, $^+NCH_3$), 3.23–3.25 (m, 4 H, CH_2 morpholino), 3.69–3.71 (m, 4 H, CH_2 morpholino), 4.86 (s, 1 H, C=CH), 6.77–6.79 (m, 4 H, PhH), 6.91–6.94 (m, 8 H, PhH), 7.17–7.18 (m, 8 H, PhH), 7.35–7.33 (m, 2 H, PhH), 7.55–7.52 (m, 3 H, PhH).

^{13}C NMR (DMSO-d_6): δ = 41.5 (NCH_3), 49.2 (NCH_2), 65.6 (OCH_2), 88.8 (C=*C*H), 121.5, 125.2 (q, $^3J_{B,C}$ = 2.7 Hz, B*C*$_{Ph}$), 128.9, 129.0, 130.8, 134.1, 135.5 (C_{Ph}), 164.3 (q, $^1J_{B,C}$ = 49.5 Hz, BC_{Ph}), 167.1 {$C^+[N(CH_3)_2]_2$}, 169.4 (*C*=CH).

Anal. Calcd for $C_{41}H_{46}BN_3O$ (607.63): C, 81.04; H, 7.63; N, 6.92. Found: C, 80.36; H, 7.80; N, 6.92.

***N*,*N*,*N*′,*N*′-Tetramethyl(3-morpholino-3-cyclopropylprop-2-yne)amidinium Tetraphenylborate (7b)**
Prepared as for **7a**.

Yield: 1.04 g (91%); mp 171–172 °C.

IR (ATR): 3052, 2983, 2888, 2853, 1573, 1532, 1441, 1421, 1399, 1372, 1267, 1238, 1150, 1121, 1060, 1025, 953, 906, 876 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 0.34–0.37 (m, 2 H, CH_2 cp), 0.93–0.97 (m, 2 H, CH_2 cp), 1.52–1.57 (m, 1 H, CH cp), 2.97 (s, 12 H, NCH_3), 3.55–3.57 (m, 4 H, CH_2 morpholino), 3.66–3.68 (m, 4 H, CH_2 morpholino), 4.46 (s, 1 H, C=CH), 6.77–6.80 (m, 4 H, PhH), 6.91–6.94 (m, 8 H, PhH), 7.17–7.18 (m, 8 H, PhH).

^{13}C NMR (DMSO-d_6): δ = 6.9 (CH_2 cp), 12.6 (CH cp), 41.4 (NCH_3), 47.5 (NCH_2), 65.7 (OCH_2), 83.1 (C=*C*H), 121.5, 125.3 (q, $^3J_{B,C}$ = 2.7 Hz, B*C*$_{Ph}$), 135.5 (C_{Ph}), 164.3 (q, $^1J_{B,C}$ = 49.5 Hz, BC_{Ph}), 167.1 {$C^+[N(CH_3)_2]_2$}, 169.4 (*C*=CH).

Anal. Calcd for $C_{38}H_{46}BN_3O$ (571.60): C, 79.85; H, 8.11; N, 7.35. Found: C, 79.63; H, 8.24; N, 7.29.

***N*,*N*,*N*′,*N*′-Tetramethyl(3-morpholino-3-trimethylsilylprop-2-yne)amidinium Trifluoromethanesulfonate (7d)**
Yield: 0.77 g (87%); mp 121–122 °C.

IR (ATR): 2966, 2910, 2864, 1582, 1521, 1399, 1255, 1222, 1140, 1116, 1030, 952, 914, 829 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.33 (s, 9 H, $SiCH_3$), 3.09–3.12 (m, 12 H, NCH_3), 3.33–3.55 (m, 4 H, CH_2 morpholino), 3.74–3.77 (m, 4 H, CH_2 morpholino), 4.38 (s, 1 H, C=CH).

^{13}C NMR ($CDCl_3$): δ = 0.1 ($SiCH_3$), 42.1 (NCH_3), 51.2 (NCH_2), 67.0 (OCH_2), 89.9 (C=*C*H), 120.9 (q, $^1J_{C-F}$ = 319 Hz, CF_3), 168.2 {$C^+[N(CH_3)_2]_2$}, 174.0 (*C*=CH).

Anal. Calcd for $C_{15}H_{30}F_3N_3O_4SSi$ (433.56): C, 41.55; H, 6.97; N, 9.69. Found: C, 41.60; H, 6.88; N, 9.65.

N,N,N′,N′-Tetramethyl(3-cyclohexylthio-3-phenylprop-2-yne)amidinium Chloride (*E*/*Z*-9a)

To a solution of **3a**-Cl (710 mg, 3.0 mmol) in $CHCl_3$ (2.0 mL) was added cyclohexylmercaptan (**8a**) (370 μL, 3.0 mmol), and the mixture was stirred for 4 h at 60 °C. The solution was concentrated in vacuo, and the yellow crude product was triturated several times with Et_2O in an ultrasonic bath to afford **9a** as a yellow sticky oil (isomeric mixture, *Z*/*E* = 85:15).

Yield: 943 mg (99%). For spectroscopic data, see Table 4.

For elemental analysis, the chloride salts *E*/*Z*-**9a** were converted into the tetraphenylborate salts (see procedure above), which were recrystallized from $CHCl_3$.

Anal. Calcd for $C_{43}H_{49}BN_2S$ (636.74): C, 81.11; H, 7.76; N, 4.40. Found: C, 81.08; H, 7.70; N, 4.47.

N,N,N′,N′-Tetramethyl(3-phenyl-3-phenylthioprop-2-yne)amidinium Chloride (*E*/*Z*-10a)

To a solution of **3a**-Cl (710 mg, 3.0 mmol) in $CHCl_3$ (2.0 mL) was added benzenethiol (**8b**; 310 μL, 3.0 mmol) and the mixture was stirred for 6 h at 60 °C. The solution was concentrated in vacuo, and the residual yellow oil was triturated several times with Et_2O in an ultrasonic bath to afford **10a** as a bright yellow solid (isomeric mixture, *Z*/*E* = 80:20).

Yield: 1.02 g (98%). For spectroscopic data, see Table 4.

For elemental analysis, chloride salts *E*/*Z*-**10a** were converted into the tetraphenylborate salts (see procedure above), which were recrystallized from $CHCl_3$.

Anal. Calcd for $C_{43}H_{43}BN_2S$ (630.69): C, 81.89; H, 6.87; N, 4.44. Found: C, 81.82; H, 6.82; N, 4.43.

Complex 11

Salt **3h**-Cl (870 mg, 5.4 mmol) was dissolved in CH_2Cl_2 (25 mL), and silver(I) oxide (625 mg, 2.7 mmol) was added. The mixture was stirred for 15 h and then reduced to three-quarter of its volume. The gray-brown crude solid was collected and dissolved in refluxing anhydrous $CHCl_3$ (125 mL). The solution was filtered hot, allowed to cool and placed in a refrigerator at – 32 °C to precipitate **11** as an off-white powder.

Yield: 910 mg (63%); mp >159 °C (dec.).

IR (ATR): 2934, 2079, 1597, 1471, 1408, 1394, 1285, 1172, 1025, 886 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 3.22 (s, NCH_3).

^{13}C NMR (DMSO-d_6): δ = 42.8 (NCH_3), 94.2 (*C*CAg), 151.9 {*C*[$N(CH_3)_2$]$_2$}; *C*Ag not observed.

HRMS (ESI, +): *m*/*z* calcd for $C_{14}H_{24}AgN_4^+$: 355.1052; found: 355.1046.

Anal. Calcd for $C_{14}H_{24}Ag_2Cl_2N_4$ (535.01): C, 31.43; H, 4.52; N, 10.47. Found: C, 31.61; H 4.56; N, 10.52.

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