Molecular and Crystal Structure of Chlorido[2-(*N*,*N*,*N′*,*N′*-tetramethylamidinio)ethynido]silver

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Dedicated to Professor Heinrich Nöth on the occasion of his 85th birthday

The solid-state structure of chlorido[2-(*N*,*N*,*N′*,*N′*-tetramethylamidinio)ethynido]silver (**3**), obtained by *C*(*sp*)-metalation of *N*,*N*,*N′*,*N′*-tetramethyl-propiolamidinium chloride with silver(I) oxide, has been determined by X-ray diffraction analysis. A comparison of bond lengths in the propiolamidinium moiety with those of the two genuine propiolamidinium salts **4** and **5**, as well as with data for the isolated *N*,*N*,*N′*,*N′*-tetramethyl-propiolamidinium cation obtained by quantum-chemical calculations, has been made. It can be concluded that complex **3** is better described as a (tetramethylamidinio)ethynyl than as a 3,3-bis(dimethylamino)allenylidene silver complex.

Key words: Acetylenic Amidinium Salts, Alkynyl Silver Compound, 3,3-Diaminoallenylidene Silver Complex

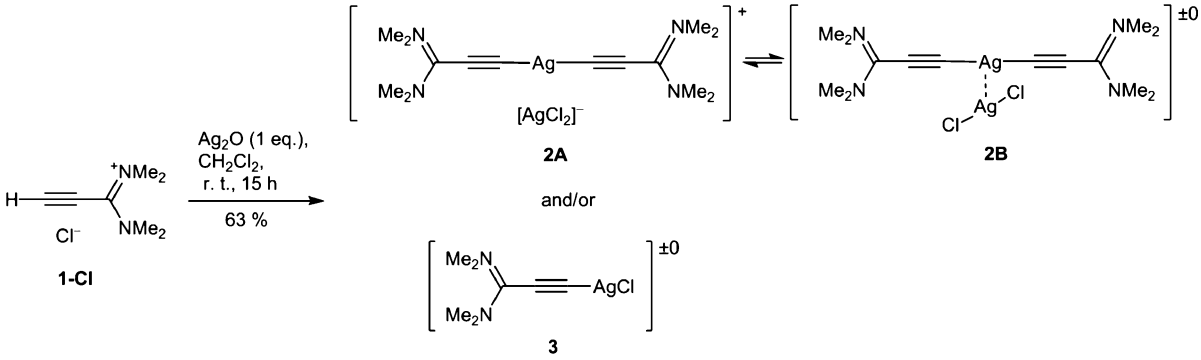
Introduction

Alkyn-1-yl silver compounds represent an emerging class of organometallic reagents [1]. They have been employed for various alkynylation reactions (*e. g.* acylation, alkylation, halogenation) and transmetalation reactions [2 – 5] and constitute intermediates in various silver assisted *C*(*sp*),*C*(*sp*^{2})-cross coupling reactions [1, 6 – 8]. On the other hand, the exact structure of alkynyl silver compounds is often not known. Organyl silver compounds in general are subject to a broad structural variation [9]; this was documented again in a recent survey of NHC-silver complexes (NHC = *N*-heterocyclic carbene) [10]. Alkyn-1-yl complexes of silver can form polymers [11, 12], aggregates with low nuclearity [12, 13], cage compounds with Ag_n clusters [14 – 16], and 2D and 3D organometallic networks [17 – 20]. Solid-state structures with discrete alkynyl silver units appear to be rare [3, 21].

In a recent publication, we have reported on the successful C(*sp*)-metalation of the propiolamidinium salt **1-Cl** [22]. Different results have been obtained concerning the exact structure of the obtained silver complex. In particular, we have found evidence that the structure of the species observed by ESI mass spectrometry was not the same as the solid-state structure. Here, we present the structure obtained by single-crystal X-ray diffraction analysis and discuss the bond description of the organic moiety in this complex.

Results and Discussion

Treatment of the propiolamidinium salt **1-Cl** with solid silver(I) oxide in dichloromethane furnished a silver complex, the elemental analysis of which was in agreement with the molecular formula $(C_7H_{12}AgClN_2)_n$, *i. e.* a 1 : 1 composition of the deprotonated propiolamidinium moiety and AgCl [22]. An (+)-ESI high-resolution mass spectrum clearly showed the molecular ion peak at $m/z = 355.1052$, corresponding to $C_{14}H_{24}{}^{107}AgN_4^+$, and the accompanying ^{109}Ag isotope peak. The only other major peak corresponded to $[Ag(CCC(NMe_2)_2)]^+$. These data suggested to us the molecular structure **2** (Scheme 1), composed of an $[Ag(CCC(NMe_2)_2)_2]^+$ cation and an $[AgCl_2]^-$ anion. The molecular conductivity of a 10^{-3}–10^{-4} M solution of the complex in acetonitrile was determined



Scheme 1. Reaction of salt **1-Cl** with Ag_2O.

as 56 – 62 S mol^{-1} cm^2, which is much lower than the value of 120 – 160 S mol^{-1} cm^2 expected for 1 : 1 electrolytes [23]. This points to a balanced solution equilibrium between salt **2A** and one or more ion-paired species; one such species could be **2B**, which features an Ag(I)–Ag(I) interaction.

To our surprise, however, an X-ray crystal structure determination of the product obtained from **1-Cl** and Ag_2O revealed the presence of the simple σ-alkynyl silver complex **3** (molecular formula $C_7H_{12}AgClN_2$) (*vide infra*). NHC complexes of the type $[(NHC)_2Ag]^+[AgHal_2]^-$ have appeared in the literature, but their structure was not always proven rigorously [10, 24]. Nolan and coworkers [25] have reported the structure of $[(IMes)_2Ag]^+[AgCl_2]^-$ (IMes = 1,3-dimesitylimidazolylidene), which shows separate cations and anions with no Ag(I)-Ag(I) interactions. In the crystal structure of another complex, an $[(NHC)_2Ag]^+$ unit bound to an $[(NHC)Ag–(\mu Cl)_2–AgCl]^-$ unit was observed, which supported the authors' view of a dynamic equilibrium between (NHC) AgCl and $[(NHC)_2Ag]^+[AgCl_2]^-$ in solution [25]. Wang and Lin [26] have synthesized the silver(I)-carbene complex $[Ag(Et_2\text{-Bimy})_2][AgBr_2]$ (Et_2-Bimy = 1,3-diethylbenzimidazol-2-ylidene), which in the solid state is composed of an $[Ag(Et_2\text{-Bimy})_2]^+$ cation associated with an $[AgBr_2]^-$ anion through an Ag(I)···Ag(I) interaction (d = 2.954(4) Å). In the same study, a solution equilibrium of the complex has been suggested in which the ion pair, the separated ions and a 1 : 1 complex analogous to **3** participate. Conductivity measurements gave similar results as those reported above. We therefore assume that analogous equilibria exist in both cases; however, while in our study the 1 : 1 complex **3** was found in the solid state, a 2 : 2 ion-pair complex analogous to **2B** was obtained in the reported case [26].

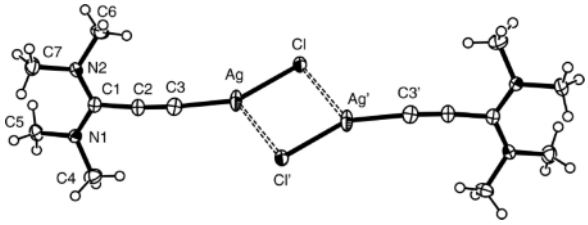


Fig. 1. Structure of compound **3** in the crystal, with 50 % probability displacement ellipsoids. Bond lengths (Å) and angles (deg): Ag–C(3) 2.052(4), Ag–Cl 2.429 (1), Ag–Cl′ 2.764 (1), Cl–Ag′ 2.764(1), N(1)–C(1) 1.332(4), N(1)–C(4) 1.461(5), N(1)–C(5) 1.467(4), N(2)–C(1) 1.331(5), N(2)–C(7) 1.463(5), N(2)–C(6) 1.467(4), C(1)–C(2) 1.435(5), C(2)–C(3) 1.204(5); C(3)–Ag–Cl 152.82(12), C(3)–Ag–Cl′ 121.44(12), Cl–Ag–Cl′ 85.68(4), Ag–Cl–Ag′ 94.32(4), C(1)–N(1)–C(4) 121.8(3), C(1)–N(1)–C(5) 123.5(3), C(4)–N(1)–C(5) 114.5(3), C(1)–N(2)–C(7) 124.2(3), C(1)–N(2)–C(6) 120.8(3), C(7)–N(2)–C(6) 114.4(3), N(2)–C(1)–N(1) 123.1(3), N(2)–C(1)–C(2) 118.1(3), N(1)–C(1)–C(2) 118.8(3), C(1)–C(2)–C(3) 174.5(4), C(2)–C(3)–Ag 175.3(4). Symmetry transformation used to generate equivalent atoms (Cl′, Ag′): $-x+1, -y+2, -z+1$.

The structure of complex **3** in the solid state is shown in Fig. 1. The mononuclear silver complex forms a centrosymmetric coordination dimer through weak Ag···Cl′ contacts (d(Ag–Cl) = 2.429 Å, d(Ag–Cl′ = 2.764 Å) giving rise to a planar trapezoid Ag_2Cl_2 core (angles: Cl–Ag–Cl′ 85.68(4)°, Ag–Cl–Ag′ 94.32(4)°). The Ag···Ag′ distance (3.815 Å) is much longer than the van der Waals distance, so that an argentophilic interaction can be excluded. The two NCN planes of this dimer are almost coplanar, and their least-squares plane and the Ag_2Cl_2 plane form an angle of 56.0°.

Scheme 2. Resonance structures of the acetylenic ligand in complex **3**.

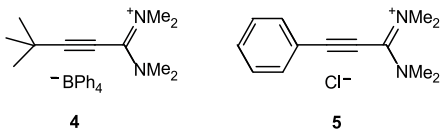
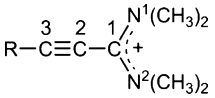


Fig. 2. Propiolamidinium salts **4** and **5**.

At this point the question had to be answered, how much the bond geometry in the acetylenic ligand of complex **3** deviates from that in genuine propiolamidinium cations. In principle, the state of bonding of this ligand can be described as a resonance hybrid of an amidinioethynide and a bis(dimethylamino)allenylidene (Scheme 2).

The requisite data came from the X-ray diffraction analysis of salt **4** (Figs. 2 and 3), which we had at hand [22], and of salt **5** (Fig. 2) [27], which was described while this work was in progress. In addition, we determined the structure of the isolated *N*,*N*,*N′*,*N′*-tetramethylpropiolamidinium cation (**1**, without anion) by quantum-chemical calculations. The relevant bond lengths and angles are compiled in Table 1. It can be seen that most of the data for **3**–**5** are very similar. While the C1–C2 distances are equal within the error limits, a small variation in the C2–C3 distances can be seen. The observed C2–C3 bond lengths are all in the upper part of the typical experimental range for C,C triple bonds; a value of 1.170(8) Å has been reported for a related propyne iminium salt [28]. Re-

Table 1. Selected bond lengths (Å) and angles (deg) for the propiolamidinium moieties of **3**, **4**, **5** (all from X-ray diffraction data) and **1** (calculated gas-phase structure) with estimated standard deviations in parentheses.



	3	**4**	**5**[a]	**1**[b]
Distances				
C1–C2	1.435(5)	1.434(3)	1.430(2)	1.432
C2–C3	1.204(5)	1.187(3)	1.197(2)	1.211
C1–N	1.331(5), 1.332(5)	1.321(3), 1.334(3)	1.325(2), 1.330(2)	1.343, 1.343
N–CH_3	1.461(5) – 1.467(4)	1.459(3) – 1.469(4)	1.462(2) – 1.465(2)	
Angles				
C1–C2–C3	174.5(4)	176.3(3)	176.3(1)	
C2–C3–(Ag or C)	175.3(4)	178.6(3)	178.4(1)	
Sum of valence angles at N1, N2	359.8, 359.4	359.9, 359.3	359.5, 359.7	
Torsion angles				
C2-C1-N1-C9	17.6	13.3	19.5(2)	15.6
C2-C2-N2-C10	17.6	14.6	18.2(2)	15.8

[a] Data taken from ref. [27]; [b] calculated for the isolated cation at the B3LYP/6-311+G** level of theory [32].

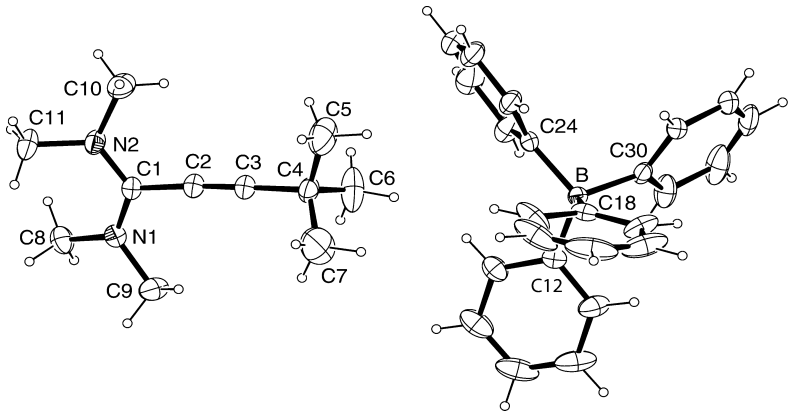
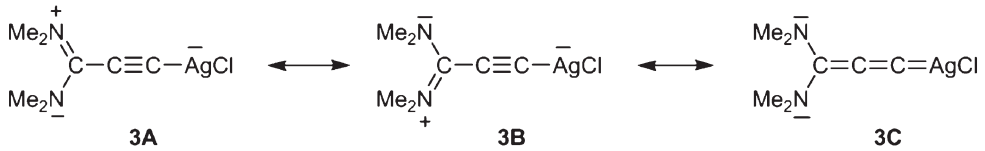
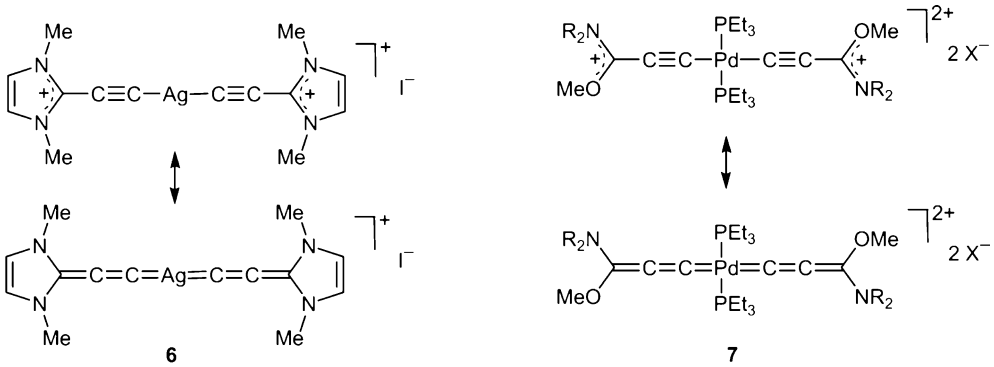


Fig. 3. Structure of compound **4** in the crystal, with 50% probability displacement ellipsoids. Selected bond lengths (Å) and angles (deg): N(1)–C(1) 1.321(3), N1–C8 1.461(3), N1 –C9 1.462(3), N2–C1 1.334(3), N2–C11 1.459(3), N2–C(10) 1.469(4), C1–C2 1.434(3), C2–C3 1.187(3), C3–C4 1.469(3), C4–C5 1.499(5), C4–C6 1.516(5), C4–C7 1.476(5), B–C 1.635(3) – 1.649(3); C1–N1–C8 125.0(2), C1–N1–C9 121.1(2), C8–N1–C9 113.8(2), C1–N2–C11 124.6(2), C1–N2–C10 120.5(2), C11–N2–C10 114.2(2), N1–C1–N2 125.2(2), N1–C1–C2 117.3(2), N2–C1–C2 117.5(2), C1–C2–C3 176.3(3), C2–C3–C4 178.6(3).



Scheme 3. Bond resonance structures in complex **3**.



Scheme 4. Limiting structures of complexes **6** and **7**.

markably, the calculated C2–C3 bond length for the gas-phase structure of **1** is distinctly larger than these values (1.211 Å). A natural localized molecular orbital (NLMO) analysis [29 – 31] of cation **1**, using the B3LYP functional, indicated a bond order of 2.7 for the acetylenic bond. In all cations, the C1–N bond lengths and the sum of bond angles at the nitrogen atoms have values that are compatible with a completely delocalized π bond in the amidinium $(NCN)^+$ unit. The Ag–C bond length (2.052(4) Å) is at the lower end of the range of silver-carbon σ bond lengths (2.05 – 2.21 Å) [10, 26, 33].

The bond geometry in the propiolamidinium part of silver complex **3** barely differs from that in salts **4** and **5**. The moderate elongation of the acetylenic bond C2–C3 to a value of 1.204(5) Å is not accompanied by other significant changes in bond lengths that would allow to assume a large degree of electron delocalization between the metal and the amidinium moiety toward the bond structure of a [bis(dimethylamino)allenylidene]silver complex **3C** (Scheme 3). IR-spectroscopic data seem to support this view, since the wavenumber of the ν(C≡C) absorption is not much smaller in complex **3** than in propiolamidinium cation **1**; in the ATR-IR spectra it appears at 2090 cm^{-1} for **1-Cl**, at 2115 cm^{-1} for **1-OTf** and at 2079 cm^{-1} for **3** [22].

In a related study, Bertrand and coworkers [3] have obtained the silver complex **6** (Scheme 4) by metalation of 2-ethynyl-1,3-dimethylimidazolium iodide with Ag_2O. The relevant bond lengths (C1–C2 1.408(15), C2–C3 1.235(15), C1–N 1.343(12) and 1.351(13), Ag–C3 2.026(10) Å) indicate a stronger contribution of the diaminoallenylidene resonance structure to the bonding in the ligands than in the case of **3**. It appears that the imidazolium ring acts as a better π-electron acceptor for the acetylenic π system than the acyclic tetramethylcarbamidinium unit.

In another related study, Fischer and coworkers [4] have prepared Pd(II) complexes **7** with two 3-alkoxy-3-dialkylaminoallenylidene ligands (or zwitterions $^-C{\equiv}C{-}C^+(OR)(NR_2)$, depending on the point of view). Based on certain NMR and IR data, these authors have emphasized the strong contribution of the alkynyl-type resonance form to the bonding in these so-called bis(allenylidene) complexes. In particular, the observation of a rather high barrier to rotation around the C-NR_2 bond points to the iminium character of this unit and thus to the prevalence of the amidinium-type resonance structure. The same criterion cannot be applied in the case of complex **3**, since the rotation around the two C–N partial bonds of the amidinium unit is fast on the NMR time scale in both **3** and in the precursor compound **1–Cl**.

Conclusion

Complex **3** is one of the few alkynylsilver compounds known so far which are not parts of an oligomeric or polymeric ensemble in the solid state. It exists as a discrete molecule of the type RC≡C–Ag–Cl, which forms a centrosymmetric dimer across the Ag–Cl bond. Several different solid-state structures have been reported for (NHC)AgHal complexes, including monomeric and dimeric ones as in the case of **3** [25, 34, 35], while (Ph_3P)AgCl forms a cubane-like tetrameric aggregate [36].

A comparison of the relevant bond lengths of **3** with those of the precursor propiolamidinium ion **1** shows no significant changes on metalation, except for a small increase of the C≡C bond length. This brings us to conclude that the (tetramethylamidinio)ethynide moiety upon σ coordination to AgCl does not undergo a significant electron delocalization toward a pronounced bis(dimethylamino)allenylidene character. This is in some contrast to the related (imidazolio)ethynide moiety in silver complex **6** [3].

Experimental Section

The syntheses of silver complex **3** and of *N*,*N*,*N*′,*N*′-tetramethyl-(4,4-dimethylbut-1-yne)amidinium tetraphenylborate (**4**) have been reported [22].

X-Ray structure determination

Suitable crystals were obtained by crystallization from chloroform (for **3**) or ethyl acetate (for **4**). Data collection was performed with a Stoe IPDS diffractometer for **3** and an Oxford Diffraction instrument (SuperNova, Dual Source, Atlas CCD) for **4**. Software for structure solution and refinement: SHELXS/L-97 [37, 38]; molecule plots: ORTEP-3 [39–41]. In the refinement procedure, the hydrogen atoms of the methyl groups were allowed to rotate with a fixed angle around the C–C bond to best fit the experimental electron density, with d(C–H) = 0.98 Å and U(H) set to 1.5 U_{eq}(C). Further details are provided in Table 2.

Table 2. Crystal structure data for **3** and **4**.

	3	**4**
Formula	$C_7H_{12}AgClN_2$	$C_{35}H_{41}BN_2$
M_r	267.51	500.51
Crystal size, mm^3	0.23 × 0.19 × 0.08	0.22 × 0.20 × 0.04
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	*Pbca*
a, Å	10.833(3)	12.9391(2)
b, Å	7.3350(13)	13.8851(4)
c, Å	12.052(3)	34.3742(6)
β, deg	98.36(3)	90
V, Å^3	947.5(4)	6175.7(2)
Z	4	8
D_{calcd}, g cm^{-3}	1.88	1.08
μ(Mo K_α), mm^{-1}	2.4	0.5
F(000), e	528	2160
Radiation	Mo K_α	Cu K_α
Temperature, K	193(2)	260(2)
hkl range	$-13 \le h \le 13$	$-8 \le h \le 15$
	$-9 \le k \le 8$	$-16 \le k \le 12$
	$-14 \le l \le 14$	$-33 \le l \le 41$
θ range, deg	2.36 – 26.10	3.42 – 73.54
Refl. measured	12696	12383
Refl. unique	1857	5295
R_{int}	0.0807	0.0173
Param. refined / restraints	104 / 0	350 / 0
$R(F)$ / $wR(F^2)$[a] [$I > 2\sigma(I)$]	0.0292 / 0.0590	0.0673 / 0.1866
$R(F)$ / $wR(F^2)$[a] (all refls.)	0.0533 / 0.0633	0.0816 / 0.2029
GoF (F^2)[b]	0.854	1.055
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.37 / −0.92	0.36 / −0.24

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; [b] $\mathrm{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

CCDC 923836 (**3**) and 923837 (**4**) 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.

Acknowledgement

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