Ag^{I} Cryptates of *N,N′*-Bridged 1,10-Diazacyclooctadeca-5,14-diynes − A Comparison Between the Complexes and the Free Ligands

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Dedicated to Professor Günter Helmchen on the occasion of his 60th birthday

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The bicyclic diaza alkynes **1**–**3** react quantitatively with silver triflate to give the corresponding cryptates **4**–**6**. The solid-state structures of the silver(I) complexes **4** and **6** were determined by means of X-ray diffraction studies. A comparison of the molecular structures of **4** and **6** with those of the uncomplexed ligands **1** and **3** reveals drastic changes in the conformations of the ligands. Evidence for an interaction of the silver ions with alkyne units in **4** and **6** was found from a high-field shift of the ^{13}C signal for the sp carbons in the ^{13}C NMR spectrum.

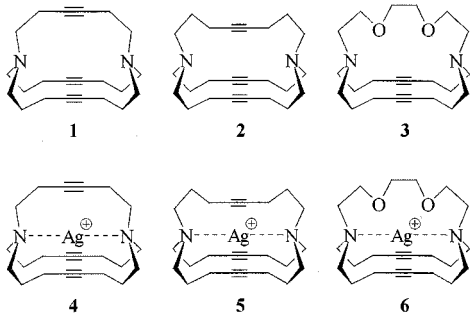
Introduction

Silver complexes of olefins are legion and have been reviewed on several occasions.[1] Less extensive are reports on silver complexes with benzene derivatives and alkynes even though several silver complexes with benzene derivatives[2] and alkynes[3] have been characterized by X-ray investigations. The formation of weak complexes between π-systems and silver ions has also been demonstrated by spectroscopic means[4] and solubility measurements,[5a] and has been used for analytical purposes.[5b]

We have recently synthesized a series of (1,*k*+2)diazabicyclo[*k,l,m*]alkanes[6] in which the bridges contain either alkyne or benzene units. The larger systems incorporate silver(I) and copper(I) ions[6c,6e] and thus provide further examples in which an alkyne or benzene unit is situated in close proximity to a metal ion. The examples shown so far reveal no evidence for an interaction of the metal ion with the π-system; instead, bonding to the amine center(s) is preferred. To contribute further to the question of silver−alkyne interactions we have investigated the silver complexes of the *N,N′*-bridged 1,10-diazacyclooctadeca-5,14-diynes **1**−**3**.[6d] These systems provide a rather flexible cage and thus might respond to a central silver ion with a considerable change of geometry, in such a way that a silver−alkyne interaction might result.

Results and Discussion

The reaction of the bicyclic compounds **1**−**3** with a small excess of silver(I) triflate in dichloromethane leads, in all three cases, to the corresponding cryptates **4**−**6** in quantitative yields (Scheme 1). The colorless crystals are sensitive to light in solution but proved to be stable in the solid state.



Scheme 1

X-ray Analysis

In the cases of **4** and **6**, we were able to grow single crystals by recrystallization from methanol. In Figure 1 and 2 we compare the molecular structures of **1** and **3** with those of **4** and **6**. Table 1 lists the most relevant bond distances in **1**, **3**, **4** and **6**.

A comparison between the congeners **1** and **4**, **3** and **6** reveals considerable conformational changes caused by the silver ion. This shows up in the torsional angle between the triple bonds of the 1,10-diazacyclooctadeca-5,14-diyne units and the N−N distances (Table 1). In compound **1** the bridgeheads adopt the *out/out* conformation with an N−N distance of 5.57 Å. In **4** this distance is reduced to 4.92 Å, while the torsional angle[7] between the triple bonds is enlarged from 23° in **1** to 82° in **4**. In compound **3** the *in/in* conformation is adopted with an N−N distance of 6.12 Å. In **6** the N−N distance is reduced to 4.57 Å. This reduction goes along with a considerable change of the torsional angle between the triple bonds from 20° in **3** to 81° in **6**.

In both silver complexes the metal ion is situated approximately in the center of the cage. The triflate anion no longer participates in the coordination sphere of the metal. Figure 1 and 2 also reveal that, in **4** and **6**, the N−Ag−N

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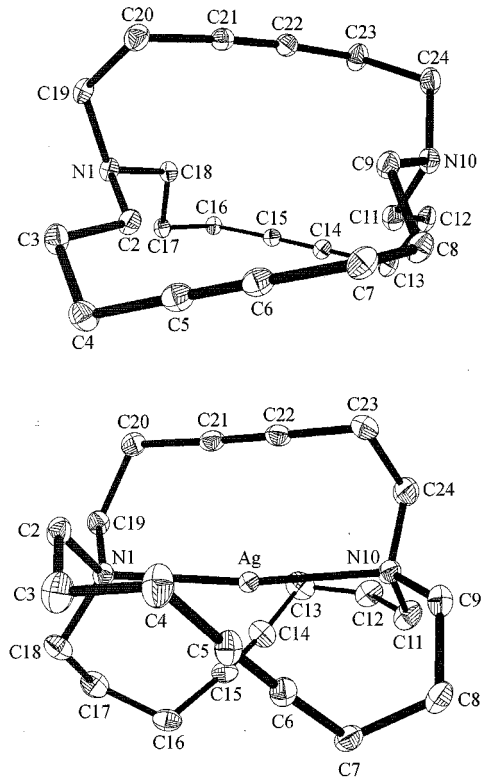

Figure 1. ORTEP plots (25% ellipsoid probability) of the molecular structures of **1** (top) and **4** (bottom)

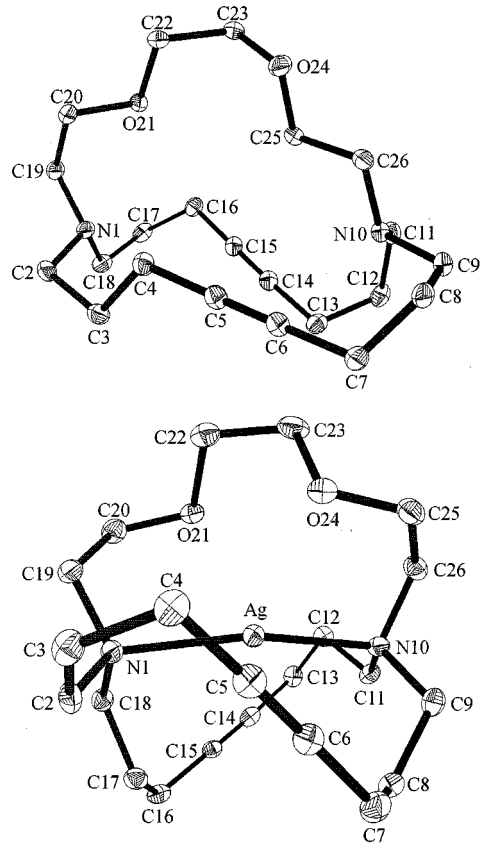

Figure 2. ORTEP plots (25% ellipsoid probability) of the molecular structures of **3** (top) and **6** (bottom)

Table 1. Selected bond lengths [Å] in **1**, **3**, **4** and **6**

	1	**3**	**4**	**6**
N1−N10	5.567(2)	6.122(1)	4.921(3)	4.566(6)/4.566(6)
Ag−N1			2.452(2)	2.323(4)/2.326(4)
Ag−N10			2.479(2)	2.283(4)/2.284(4)
Ag−C5			2.667(3)	2.777(6)/2.774(6)
Ag−C6			2.580(3)	2.921(6)/2.927(6)
C5−C6	1.189(2)	1.193(2)	1.203(4)	1.187(8)/1.207(8)
Ag−C14			2.624(3)	3.951(6)/3.995(6)
Ag−C15			2.588(3)	3.960(5)/3.995(6)
C14−C15	1.186(2)	1.192(2)	1.193(5)	1.190(8)/1.167 (8)
Ag−C21			2.572(3)	
Ag−C22			2.550(3)	
C21−C22	1.185(2)		1.199(4)	
Ag−O21				2.625(4)/2.656(4)
Ag−O24				2.678(4)/2.607 (4)

bonds are not linear but slightly bent: 173° in **4** and 164° in **6**. The Ag−N distances vary between 2.45 Å and 2.48 Å for **4** and 2.32 Å and 2.28 Å for **6**. In both cases they are 0.1 to 0.3 Å longer than those Ag−N distances reported for several $Ag(NH_3)_2^+$ complexes.[8] The values obtained for the Ag−N distances in the cases of **4** and **6** are close to the Ag−N distances reported for the silver complex of 1,8-diazabicyclo[6.6.6]eicosa-4,11,17-triyne.[6c]

To judge the possibility of a metal−alkyne interaction we considered the distances between the triple bonds and the silver ions in **4** and **6** (Table 1). In compound **4** these distances vary between 2.55 Å and 2.67 Å. In compound **6** the variation of the Ag−C(sp) distances is larger and ranges from 2.77 Å to 4.00 Å. A comparison with the Ag−C(sp) distances of other silver alkyne complexes[3,6c] reveals values that are spread between 2.225 Å for a highly strained alkyne[3e] and from 2.85 Å to 3.05 Å in unstrained species.[3d] Based on this comparison we can describe the interaction between the silver ion and the triple bonds in **4** as a bonding one. The same arguments applied to **6** lead to the conclusion that only one triple bond (C5−C6) interacts with the metal. We ascribe this preference to a coordination of the silver ion in **6** with the oxygen atoms. The distances found in the case of **6** [Ag−O21 = 2.656(4) Å and Ag−O24 = 2.607(4) Å] are very similar to those reported for silver complexes of oligo(ethylenoxy)-bridged stilbenes.[9]

^{13}C NMR Investigations

In Figure 3 we have compared the ^{13}C NMR spectra of **1** and **4** (Figure 3a) as well as **3** and **6** (Figure 3b). The comparison between **1** and **4** shows a significant change in the area between δ = 75 and 80 where the sp-hybridized carbon signals are anticipated.

We find for **1** a small signal at δ = 81.8 for the two carbons of the hexyne bridge and at δ = 80.8 a signal of almost double intensity for the four sp carbon atoms of the two octyne bridges. After complexation with Ag^+, the latter signal remains almost unchanged, whereas the smaller signal is shifted upfield by 2.9 ppm.

In the case of the ^{13}C NMR spectrum of **6** at −60 °C we find two signals at δ = 81.1 and δ = 79.2. A comparison with the ^{13}C NMR spectrum of **3** (Figure 3b) suggests the

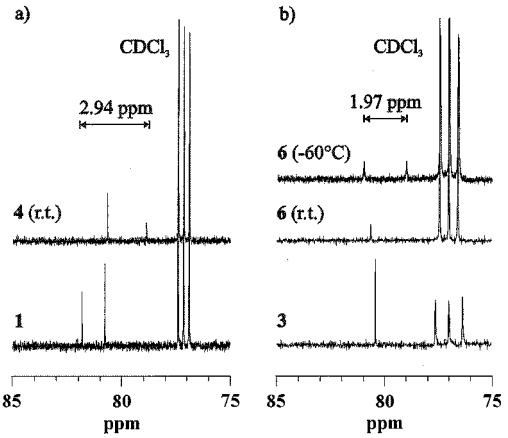

Figure 3. a) Section of the ^{13}C NMR spectrum ($CDCl_3$, 125.76 MHz) of **1** and **4** at room temperature; b) Section of the ^{13}C NMR spectrum ($CDCl_3$, 75.47 MHz) of **3** at room temperature and −60 °C

assignment of the low-field peak to the uncomplexed alkyne unit of **6** while the peak at δ = 79.2 should be assigned to the alkyne unit close to the silver ion.

The observed upfield shift due to complexation with the silver ion is unusual and has so far only been reported for the silver(I) complexes of highly strained thiacycloheptynes[3e] and some alkyne silver(I) hexafluoroacetylacetonato complexes.[3f] In the other silver complexes investigated so far[3] a low-field shift has been encountered. We ascribe the upfield shifts in **4** and **6** due to a close proximity of the metal ion and the triple bond, which is forced by the ligand. The observed upfield shift of the ^{13}C signal upon complexation with Ag^+ implies a better shielding of the sp carbon nuclei and, accordingly, a higher electron density at the coordinated triple bond than at the uncomplexed alkyne group. A possible explanation of this observation is due to the Dewar−Chatt−Duncanson model.[10] It suggests a back donation of electron density from the nitrogen lone pairs through the d orbitals of the silver ion into the antibonding π* orbital of the triple bond.

Conclusions

The incorporation of a silver ion into the cages of **1** and **3** results in drastic changes of the conformations of the ligands. The driving force for this change is a close interaction between the nitrogen centers and the metal. This has been achieved by torsion of both 4-octyne bridges around the N−N axis. As a side effect of these conformational changes we observe close contacts between the silver ion and the triple bonds in the solid state and in solution.

Experimental Section

General Remarks: All reactions were carried out under argon atmosphere with magnetic stirring in dry, degassed CH_2Cl_2. The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ with Bruker WH 300 and Avance 500 instruments, respectively. Mass spectra were obtained with a JEOL JMS 700 spectrometer.

General Procedure for the Complexation: One equivalent of the cryptand (**1**−**3**) was added to 1.1 equivalents of silver(I) triflate in dry degassed CH_2Cl_2 under argon and stirred for one hour with the exclusion of light. The solvent was removed in vacuo and the

Table 2. Crystallographic data for **4** and **6**

	4	**6**
Formula	$C_{23}H_{32}AgF_3N_2O_3S$	$C_{24}H_{36}AgF_3N_2O_6S$
M [g mol^{-1}]	581.44	645.48
Temperature [K]	200(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Z	4	8
a [Å]	12.9234(3)	25.7617(1)
b [Å]	8.9937(2)	8.5768(4)
c [Å]	21.4056(4)	26.0432(1)
α [°]	90	90
β [°]	102.631(1)	105.106(1)
γ [°]	90	90
Volume [Å^3]	2427.74(9)	5555.5(5)
ρ [g cm^{-3}]	1.591	1.54
μ (Mo-K_α) [mm^{-1}]	0.967	0.861
Scan range (θ) [°]	1.6−25.5	1.3−25.6
hkl range	−15/14, −10/10, −22/24	−30/30, −10/10, −30/30
Reflections collected	17586	41817
Independent reflections	4190	9740
	R(int) = 0.0226	R(int) = 0.0517
Observed reflections	3660 [$I > 2\sigma(I)$]	6437 [$I > 2\sigma(I)$]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
max./min. transmission	0.86/0.70	0.96/0.77
data/restraints/parameters	4190 /12/326	9740/0/669
GoF on F^2	1.07	1.06
largest diff. peak and	0.95	1.18
hole [e Å^{-3}]	−0.73	−0.88
final R indices	R_1 = 0.030	R_1 = 0.051
[$I > 2\sigma(I)$]	wR_2 = 0.072	wR_2 = 0.111

remaining white solid recrystallized from methanol yielding colorless crystals in the case of **4** and **6**. For **5** only polymorphic material was obtained.

Ag^I ⊂{1,10-Diazabicyclo[8.8.6]tetracosa-5,14-diyne}trifluoromethanesulfonate (4): FAB-MS: *m/z* (%) = 431.1 [**4** − CF_3SO_3]$^+$ ($^{12}C_{22}{}^1H_{32}{}^{107}Ag^{14}N_2$: 431.2).[11] − ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.79−1.99 (m, 8 H), 2.55 (t, *J* = 6.4 Hz, 8 H), 2.61−2.70 (m, 12 H), 2.72−2.79 (m, 4 H). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.76 MHz) δ = 17.9, 18.5, 25.6, 55.8, 56.2 (CH_2), 78.9, 80.7 (C≡C).

Ag^I⊂{1,10-Diazabicyclo[8.8.8]hexacosa-5,14-diyne}trifluoromethanesulfonate (5): FAB-MS: *m/z* (%) = 459.2 [**5** − CF_3SO_3]$^+$ ($^{12}C_{24}{}^1H_{36}{}^{107}Ag^{14}N_2$: 459.2).[11] − ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.94 (br. s, 12 H), 2.44 (br. s, 12 H), 2.70 (br. s, 12 H). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25.8 MHz) δ = 17.9, 27.4, 55.7 (CH_2), 81.5 (C≡C).

Ag^I⊂{4,7-Dioxa-1,10-diazabicyclo[8.8.8]hexacosa-14,22-diyne}-trifluoromethanesulfonate (6): FAB-MS: *m/z* (%) = 467.1 ($^{12}C_{22}{}^1H_{32}{}^{107}Ag^{14}N_2O_2$: 467.2).[11] − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.81−2.04 (m, 8 H), 2.28−2.42 (m, 8 H), 2.59−2.84 (m, 8 H), 3.69 (s, 4 H), 3.76−3.88 (m, 4 H). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.47 MHz, 25 °C) δ = 17.4, 28.1, 53.0, 55.2, 64.6, 67.4 (CH_2), 80.8 (C≡C); ($CDCl_3$, 75.47 MHz, −60 °C) δ = 15.9, 17.9, 26.8, 29.3, 51.6, 53.5, 55.1, 63.6, 66.6 (CH_2), 79.2, 81.1 (C≡C).

X-ray Crystallographic Study: The measurements on crystals of **4** and **6** were performed on a Bruker SMART CCD X-ray diffractometer using graphite-monochromated Mo-K_a radiation (λ = 0.71073 Å). The SMART software package[12] was used for data collection as well as frame integration. Structure solution was carried out using the SHELXTL V5.10 software package.[13] Intensities were corrected for Lorentz and polarization effects. All structures were solved by direct methods. Full-matrix least-squares refinement was carried out against F^2. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were taken into account at calculated positions. Further details are listed in Table 2. The crystal of **6** contained two independent molecules in the asymmetric unit (see Table 1 and 2).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-138336 (**4**) and 138337 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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