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Synthesis and Properties of Cryptands with a Thioether Bridge and π-Donors – Silver(I) and Copper(I)-Complexes

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Keywords: Cage compounds / Alkynes / Silver / Copper

The syntheses of seven bridgehead diazabicycloalkanes are reported. The bridges are represented by either a thioether chain and two 3-hexyne units (**4** and **6**–**8**), one selenoether chain and two 3-hexyne units (**5**), or one dithioether chain and two 4,4′-diethylbiphenyl units (**9**, **10**). X-ray investigations reveal for **4**–**10** the *in*/*in* conformation at the bridgehead nitrogen atoms. Reactions with Cu^I triflate yield the endohedral Cu^I complexes of **4**–**6**. Endohedral complexes of **6**, **7**, and **10** were isolated with silver triflate. X-ray investigations and spectroscopic studies on the metal complexes reveal interactions between the metal ion and the nitrogen-, chalcogen-, and π-units. In addition to the bicyclic systems **4**–**10** we synthesized the tripodal systems **28**–**33** in a one-pot reaction. In the cases of **28** and **33** we were able to isolate the corresponding Ag^I complexes. X-ray studies show an interaction between the metal ion and the nitrogen atom and one double bond of each of the three adjacent phenyl rings.

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Introduction

After the seminal papers of Pedersen[1] on crown ethers and Lehn et al.[2] on cryptands these types of compounds were in the focus of chemists. Quite some time had to pass until crown thioethers participated in this development[3] because safe and high-yield routes to these species were lacking. Advances in synthetic methodology[4] and safe and general, high-yield routes[5] resulted in strong activity in this field.[5] Reports on the corresponding podands[6] and cryptands[7] with thioether bridges such as **1** are sparse, probably because a method that provides them in high yields is still missing.

The starting point of the research reported in this manuscript was a simple one-pot synthesis of the bridgehead diazabicycloalkanes **2** and **3**[8,9] with alkyne and phenyl units in the bridges (Figure 1). The two species were able to form isolable complexes with Cu^+ and Ag^+ (**2**) and Ag^+ (**3**), respectively. In both cases the metal ion does not only interact with the nitrogen atoms but also with the π-units. In order to extend the variety of ligands for transition metals it was of interest to have easy access to bicyclic ligands with at least one thioether bridge and further alkyne or phenyl ligands. In this paper we report a one-pot synthesis of the bicyclic cryptands **4**–**10** and their complexing properties with silver and/or copper(I) ions.

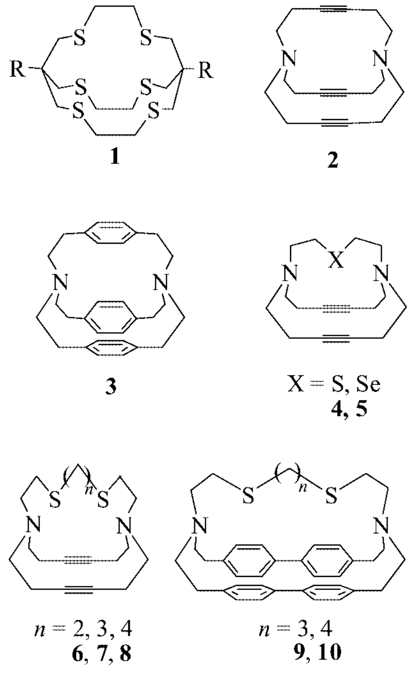

Figure 1. Bicyclic cryptands **1**–**10**.

Results

(a) Synthesis and Structures of 4–8

To synthesize our target molecules we adopted a one-pot synthesis developed for bridgehead diazabicycloalkanes.[10] The preparation of **4**–**8** was achieved in a three-component cyclization from an α,ω-diamine (**11**) and an α,ω-dibromide

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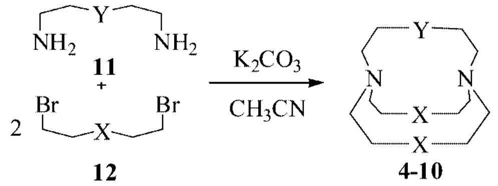
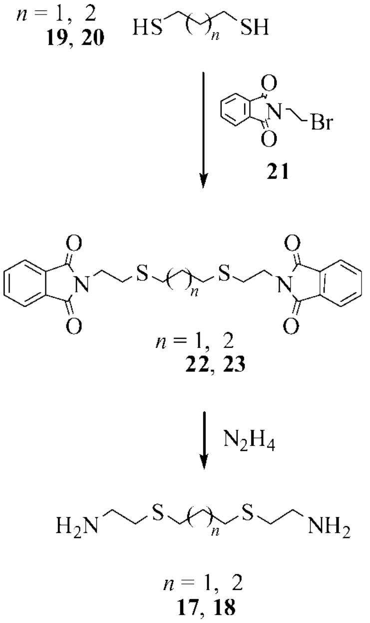
(**12**) as shown in Scheme 1. The components were heated in acetonitrile under reflux. The yields varied between 33% (**5**) and 53% (**7**). From the starting materials 1,5-diamino-3-thiapentane (**13**),[11] 1,5-diamino-3-selenapentane (**14**),[12] 1,8-diamino-3,6-dithiaoctane (**15**),[13] as well as 1,6-dibromohex-3-yne (**16**)[14] were prepared according to literature procedures.



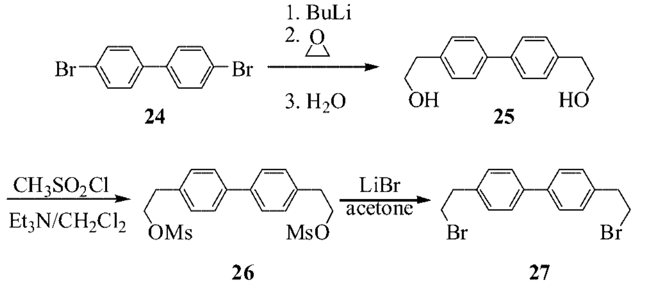
Scheme 1.

The synthesis of 1,9-diamino-3,7-dithianonane (**17**) and 1,10-diamino-3,8-dithiadecane (**18**) followed those procedures[13] used for **13**–**15** and is summarized in Scheme 2. The dianions of the α,ω-dithiols **19** and **20** were reacted with *N*-(2-bromoethyl)phthalimide (**21**) to the α,ω-diphthalimidodithianes **22** and **23**. The protecting groups were removed by heating of **22** and **23**, respectively, with hydrazine in ethanol to afford **17** and **18** in good yields.



Scheme 2.

The preparation of 4,4′-bis(2-hydroxyethyl)biphenyl (**25**) (Scheme 3) was described in the literature from biphenyl and ethylene oxide under Lewis acid catalysis.[15] This procedure gave us a mixture of the 4-(2-hydroxyethyl)biphenyl and **25** which was difficult to separate. Therefore, a different path as shown in Scheme 3 was used. The starting point was the commercially available 4,4′-dibromobiphenyl (**24**), which was treated with an excess of *n*-butyllithium and ethylene oxide to afford **25** in 92% yield. The diol **25** was converted via the dimesylate **26** into the dibromide **27** in a straight forward way (Scheme 3).



Scheme 3.

With regard to the silver(I) complexes of **3**, **9**, and **10** we also prepared the tripodal systems **28**–**33** listed in Figure 2. The synthesis follows that given in Scheme 1 by applying a one-pot reaction of (2-bromoethyl)benzene[15] or 4-(2-bromoethyl)biphenyl[16] with the corresponding amines such as (2-aminoethyl)benzene which was commercially available, 4-(2-aminoethyl)biphenyl,[17] or 1-aminobut-3-yne.[18,19] The components were heated in acetonitrile under reflux with an excess of potassium carbonate.

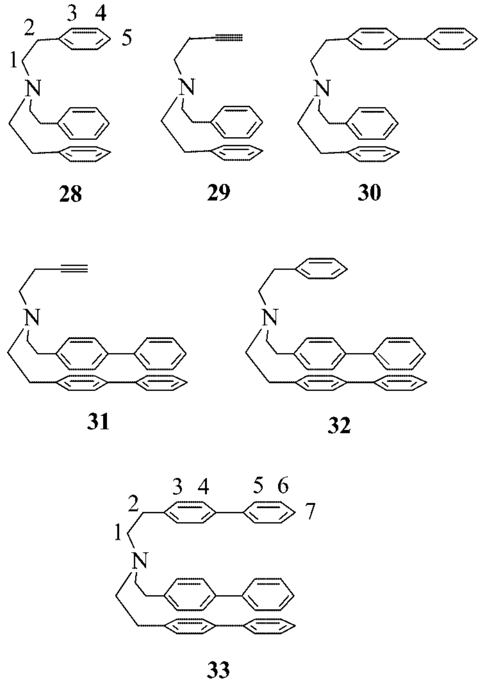


Figure 2. Tripodal systems **28**–**33**.

(b) Spectroscopic and Structural Properties

In Table 1 we list the ^{13}C chemical shift of the sp centers of **4**–**8** as well as the wave numbers for the C,C stretching mode of the triple bonds derived by Raman spectroscopy. It is seen that the δ values for the sp centers vary only slightly between 79.5 and 81 ppm indicating hardly any strain in these systems. This view is supported by the wave numbers for the stretching vibration of the triple bonds. For **7** and **8** we encountered dynamic processes in the ^1H NMR spectra which led to a line broadening at room temperature.

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Table 1. Comparison of the chemical shift of the sp carbon atoms (δ) and the alkyne wave numbers of **4**–**8**.

Compound	**4**	**5**	**6**	**7**	**8**
δ(sp) [ppm]	80.6[b]	80.6[b]	79.5[a]	79.9[a]	80.2[a]
$\tilde{\nu}$ [cm^{-1}][c]	2228	2227	2236	2231	2237
	2291	2289	2300	2293	2297

[a] $CDCl_3$. [b] CD_2Cl_2. [c] Raman spectroscopic data.

For **4**–**10** we grew single crystals which allowed a comparison of the geometrical parameters. In Figure 3 we show the structures of **4**, **6**, **7**, and **10**. In all cases we find the *in*/*in* conformation at the bridgehead positions. A single nearly planar nitrogen atom is only seen in **4**. The heteroatoms of the bridges point outwards and do not seem very well suited for the complexation of a cation in the inside of the cages. In Table 2 we list the distances between the bridgeheads (N···N), the sum of the bonding angles ($\Sigma_{\omega N}$), and the distance between the centers of the π-systems, either triple bonds (**4**–**8**) or aromatic rings (**9**, **10**). In the latter case each biphenyl ring provides two centers. It is interesting to note that the N···N distance of **4** is larger than that of **5**. We ascribe this difference to the larger C–S–C angle (99°) of **4** as compared to the C–Se–C angle (97°) of **5**. In all cases the triple bonds are not oriented parallel to each other. In the biphenyl-bridged cages the N···N distances amount to nearly 10 Å.

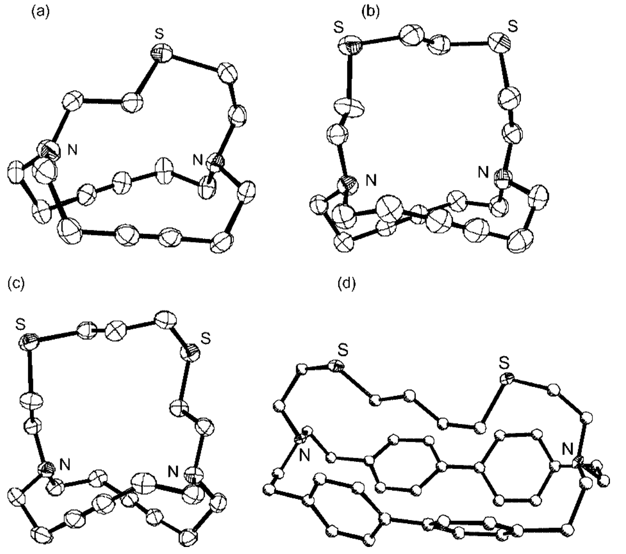

Figure 3. Molecular structures of **4** (a), **6** (b), **7** (c) and **10** (d).

Table 2. Selected distances and angles (degrees) of **4**–**10**.

Compound	**4**	**5**	**6**[d]		**7**	**8**	**9**	**10**
N···N [Å]	4.72	4.31	4.87	4.79	4.90	5.20	9.79	9.94
($\Sigma_{\omega N}$)[a]	344	(329)[c]	342	335	338	343	328	328
	357	343	342	336	342	344	343	330
π···π (sp)(Å)[b]	3.84	4.30	3.87	4.17	3.92	3.77		

[a] Sum of the C–N–C angles at nitrogen centers. [b] Transannular distances between centers of π-systems. [c] Unreliable due to partial disorder. [d] Two independent molecules in the unit cell.

(c) Formation of Metal Complexes

The reactions of **28** and **33** with silver triflate afforded the 1:1 complexes. For **29**, **30**, and **32** the corresponding 1:1 silver complexed ions were only detected in the mass spectrum (FAB+). In Figure 4 we show the molecular structures of **28**·Ag^+ and **33**·Ag^+ in a front and side view. In **28**·Ag^+ the distance between the nitrogen center and silver atom amounts to 2.41 Å. This distance is closer than that found in the silver complex of **3** (2.47 Å).[10] The interaction between the silver ion and the aromatic rings is evident from the change of the NMR shifts. In the uncomplexed species (**28**) the protons at the sp^3 centers (positions 1 and 2 in **28**) show two close lying multiplets at 2.75–2.81 and 2.84–2.90 ppm. Similarly, the aromatic protons resonate at 7.21–7.24 and 7.32 ppm. In the silver complex the CH_2 protons give rise to two pronounced triplets at δ = 2.70 and 2.94 ppm. In the aromatic region two protons of each C_6H_5 ring give rise to a doublet at δ = 6.84 ppm. These spectroscopic data are in line with the observation that the silver ion shows a much closer contact with the *ortho* carbon atoms (position 3 in **28**) of the benzene rings as compared to the other sp^2 centers. For the three phenyl rings in **28**·Ag^+ we observe a tilting of the aromatic rings in a conrotatory fashion parallel to the C_3 axis. This brings one carbon atom per ring close to the metal center. The distance between these carbon atoms of the phenyl rings and the metal ion (average 2.47 Å, see Table 3) are similar to that found for various silver complexes of [2.2.2]- and [2.2.1]cyclophanes.[20–25] For **33**·Ag^+ we observe in the ^{1}H NMR spectrum two triplets at δ = 2.83 and 2.99 ppm for the hydrogen atoms at centers 1 and 2 (see Figure 2). Six of the aromatic hydrogen atoms are shifted towards higher field due to the complexation and give rise to a doublet at δ = 6.96 ppm. The other 21 aromatic hydrogen atoms show up at 7.35–7.44 ppm. These results suggest a similar situation for the silver atom as in **28**·Ag^+. Indeed, the molecular structure of **33**·Ag^+ reveals that the metal ion is situated close to the nitrogen atom. The N–Ag^+ distance amounts to 2.37 Å (Table 3). The view along the N···Ag axis of **33**·Ag^+ shows that the aromatic rings are twisted in a conrotatory way similar to that found in **28**·Ag^+. This orientation allows a closer interaction between the metal atom and C3 than to the other sp^2 centers (average 2.43 Å, Table 3).

For **4**–**10** we infer from the downfield shift of the signals for the aliphatic hydrogen atoms in the ^{1}H NMR spectra and from the mass spectrometric data the inclusion of silver and/or copper(I) ions into the cavities of these species. In all cases except for **9** this result was confirmed by the isolation of single crystals which allowed a detailed study of the molecular structure. For **4** and **5** we were able to isolate only complexes with copper(I) triflate. The reaction of **6** with silver or copper triflate gave complexes with one metal ion in the cavity. For all the other cryptates, only silver complexes could be characterized. In the case of **10** even two silver ions were incorporated in the cavity. In Figure 5 we show the molecular structures of **4**·$Cu(CF_3SO_3)$, **8**·$Ag(CF_3SO_3)$, and **10**·2[$Ag(CF_3SO_3)_2$].

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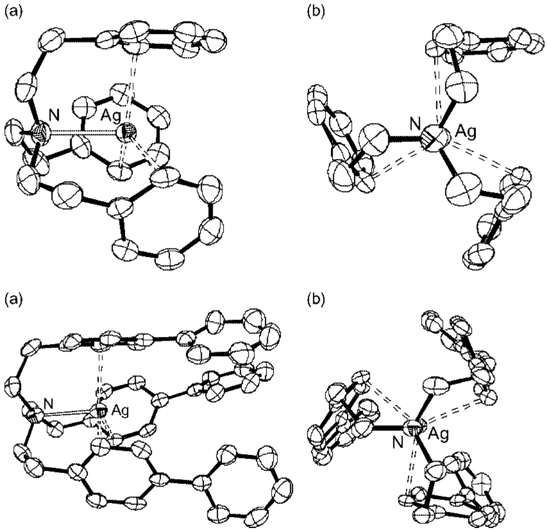

Figure 4. Molecular structures of **28**·Ag$^+$ (top) and **33**·Ag$^+$ in a front view (a) and a view along the N–Ag axis (b).

Table 3. Selected distances [Å] of Ag^I triflates of **28** and **33**.

	28·Ag$^+$	**33·Ag$^+$**
N···Ag	2.409	2.371
π···Ag	2.47[a,b]	2.43[a,b]
π···π	3.72[a,b]	3.72[a,b]

[a] Average value. [b] Closest atom of C_6 units.

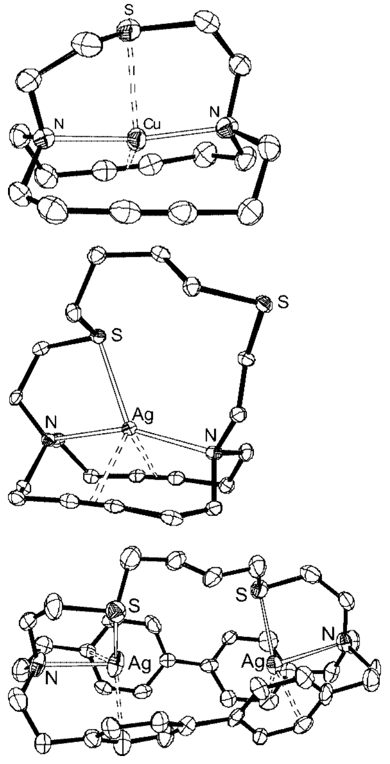

Figure 5. Molecular structures of **4**·Cu$^+$ (top), **8**·Ag$^+$ and **10**·2(Ag$^+$) (bottom).

In Table 4 we collected the most relevant distances and angles of the metal complexes of **4**–**8** and **10**. The copper complex of **4** shows a considerable change in the conformation of the ligand. The N···N distance is substantially shortened from 4.72 Å (free ligand) to 4.20 Å (complex) (see Figure 3 and Figure 5). As a result of this change the triple bonds are oriented almost parallel and the chalcogen center of the bridge is turned towards the metal. This change allows almost equal distances to both nitrogen centers (2.10 and 2.16 Å) but close contact to only one triple bond (2.13 Å), whereas the distance to the other (2.71 Å) is considerably longer. The copper–nitrogen distances are expanded with regard to copper(I) amine complexes (average value 2.18 Å)[26] but comparable to those reported for **2**·Cu$^+$ (2.11 Å).[9] The distance Cu–S (2.52 Å) is longer than those reported in other thioether-Cu^I complexes (2.25–2.30 Å).[27]

The molecular structure of **5**·Cu$^+$ is isomorphous to that of **4**·Cu$^+$. The N···N distance in the complex (4.21 Å) is about as long as that in **4**·Cu$^+$ (4.20 Å). The same holds for the N–Cu distances and the N–M–N angle, 160.5° in **4**·Cu$^+$ and 161.6° for **5**·Cu$^+$. Also both triple bonds are almost oriented parallel to each other in contrast to the free ligand. The selenium atom is bent sideways to interact with the copper ion (Cu–Se = 2.62 Å). The complex shows one close contact to one triple bond (2.16 Å) only.

Table 4. Selected distances [Å] and angles (degrees) of Ag^I or Cu^I triflates of **4**–**8** and **10**.

Compound	**4·Cu$^+$**	**5·Cu$^+$**	**6·Ag$^+$**	**6·Cu$^+$**	**7·Ag$^+$**	**8·Ag$^+$**	**10·2(Ag$^+$)**
N···N	4.200	4.209	4.830	5.077	5.129	4.739	9.951
N···M	2.101	2.098	2.435	2.150	2.646	2.368	2.429
	2.160	2.166	2.450	3.150	2.678	2.468	2.444
X···M[a]	2.520	2.620	2.757	2.275	2.754	2.574	2.500
			2.876	2.562	2.773	5.043	2.564
M···π	2.134	2.157	2.609	2.093	2.640	2.656	2.53[b,d,e]
	2.705	2.733	2.664	3.015	2.721	2.745	2.47[c,d,e]
N···M···N[f]	160.5	161.6	197.3	214.0	211.6	203.2	
π···π	4.335	4.363	4.286	3.751	4.011	4.304	3.611[d,e]
$\tilde{\nu}_{(C\equiv C)}$ [cm^{-1}][g]					2206	2204	
					2281	2266	

[a] X = S for **4**, **7**–**9**, **11**; X = Se for **5**; X = O for **6**. [b] Average value for Ag1. [c] Average value for Ag2. [d] Average value. [e] Closest atom of C_6 units. [f] For comparison with the other structures we define the N–metal–N angle as greater than 180° if the metal deviates from the N···N axis in the direction of the thioether bridge and smaller than 180° if it deviates towards the π-system. [g] Raman spectroscopic data.

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The molecular structures of **6**·Ag^+ and **6**·Cu^+ are shown in Figure 6. In the case of **6**·Ag^+ we are not dealing with a purely endohedral complex between ligand and metal. The unit cell does not only show the endohedral metal ion but also exohedral metal ions between the thioether groups (see Figure 6) that lead to a coordination polymer. In the endohedral complex the metal ion deviates from the N···N axis in the direction of the thioether bridge N···Ag···N (197.3°). This deviation is due to a interaction between the silver ion and the sulfur centers. The Ag···S distances found (Table 4; 2.76 Å and 2.88 Å) compare well with other thioether–silver distances.[28,29] The distances between the exohedral silver centers and the thioether groups amount to 2.49 Å and 2.50 Å. The average Ag···N distance (2.45 Å) is longer than the one reported for **2**·Ag (2.31 Å).[8] The distances between the endohedral silver ions and the triple bonds (2.61, 2.66 Å) are still within the reach of a weak metal–π-bond. Raman studies on **6**·Ag^+ failed due to a fast decomposition of the complex during the Raman experiment. Our studies show that the large silver ion prefers a coordination number of 6.

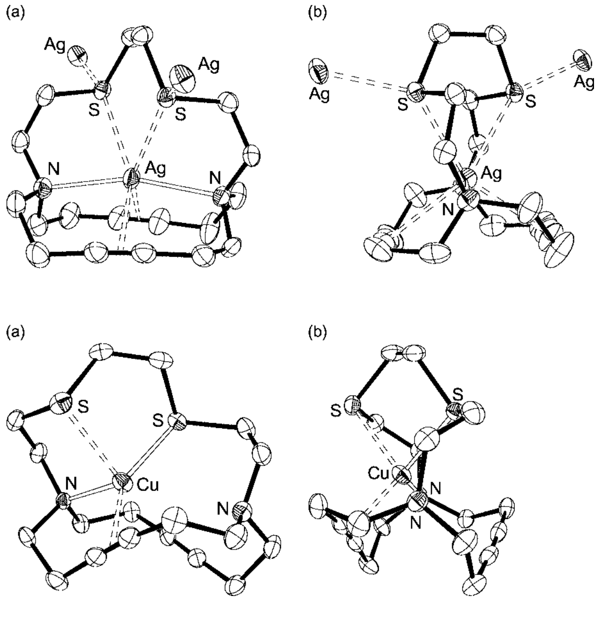

Figure 6. Molecular structure of **6**·Ag^+ (top) and **6**·Cu^+ (bottom) in a front view (a) and a view along the N–N axis (b). The hydrogen atoms are omitted for the sake of clarity.

The structure of **6**·Cu^+ (Figure 6) is remarkably different from that of **6**·Ag^+. The position of the metal is shifted towards one nitrogen center and one triple bond. The distance to the nitrogen center amounts to 2.15 Å and to the triple bond to 2.09 Å. The distances to the second nitrogen center and to the second triple bond in **6**·Cu^+ exceed 3 Å (Table 4). As a consequence both triple bonds in **6**·Cu^+ are not oriented parallel (Figure 6). Furthermore, the metal ion coordinates to both thioether groups (2.28, 2.56 Å). This establishes a coordination number of 4 for the metal in **6**·Cu^+.

The inclusion of Ag^I in the cavity of **7** does not change the tilting of the triple bonds, but changes the conformation of the 3,7-dithiononane bridge in so far as the sulfur centers are turned inward to interact with the metal ion. The N···N distance is even increased as compared to the free ligand. The silver ion is shifted considerably out of the N···N axis towards the sulfur atoms (N–Ag–N angle 211.6°). In line with this, the distances between the triple bonds and the silver ion amount to 2.64 and 2.72 Å. These values are about 0.2 Å larger than those reported for **2**·Ag^+.[9] In the case of **7**·Ag^+ it was possible to measure the wave number for the stretching vibration of the triple bond ($\tilde{\nu}$ = 2281 and 2206 cm^{-1}). These values are shifted towards lower energy as compared to the free ligand ($\tilde{\nu}$ = 2293 and 2231 cm^{-1}) which is evidence for an interaction between the metal and the triple bonds. The distances between the sulfur centers and the metal atom amount to 2.75 and 2.77 Å. These values are close to those reported for thioether-silver distances (2.6–2.8 Å).[28,29]

The molecular structure of **8**·Ag^+ (Figure 5) is quite different from that of **7**·Ag^+ in so far as only one sulfur atom of the flexible dithia bridge interacts with the silver center. The other sulfur atom points outwards. The Ag–S distance (2.57 Å) is rather close compared to the other values. The N···N distance is shortened by about 0.5 Å compared to the uncomplexed system. The N–Ag distances (2.37 and 2.47 Å) are much shorter than for **7**·Ag^+ (see Table 4) and the two triple bonds are oriented parallel to each other. The interaction between the silver ion and the triple bonds is evident not only from the distances (2.66 and 2.75 Å) but also in the lowering of the wave numbers for the stretching vibration ($\tilde{\nu}$ = 2266 and 2204 cm^{-1}) as compared to **8** ($\tilde{\nu}$ = 2297 and 2237 cm^{-1}). The reaction of **9** with silver(I) triflate afforded a 1:1 complex as evidenced by HR-FAB^+ data. The comparison between the ^1H NMR spectroscopic data of **9**·Ag^+ with those of **9** shows a downfield shift of the signals for the protons.

The reaction of **10** with silver(I) triflate afforded single crystals which could be investigated by means of the X-ray technique. It turned out that the cavity of **10** is large enough to house two silver ions (Figure 5). The incorporation of the two metal ions causes only a small change in the length of the cavity but a large one in the conformation of the thioether chain. The sulfur atoms are now turned inwards (see also Figure 3). The distance between the two silver ions in **10**·2(Ag^+) was found to be 5.18 Å. This value is clearly larger than the sum of the van der Waals radii of Ag^+ (3.1–3.2 Å).[30,31] The average distance to the nitrogen atoms was found to be 2.44 Å which compares well with those recorded for **6**·Ag^+ and **8**·Ag^+ (Table 4). A closer look at the Ag···phenyl interaction reveals a situation very similar to that encountered for **28**·$Ag^+$and **33**·Ag^+ as well as for various [2.2.2] and [2.2.1]cyclophanes.[20–25] One carbon atom per ring is much closer to the silver ion than the other sp^2 centers. For three phenyl rings this is a *ortho* carbon (average distance 2.48 Å), only in one case is the silver ion closest to the *ipso*-carbon (2.50 Å). This coordination does not affect the planarity of the aromatic rings. The Ag–S distance of 2.50 Å is similar to that found in **8**·Ag^+ and shorter than in **6**·Ag^+ and **7**·Ag^+ (see Figure 6).

Concluding Remarks

Our main goal to find a simple procedure for the preparation of N-bridgehead diazabicyclo-cages with one thioether bridge and π units in the other two was achieved. Like in crown thioethers the sulfur atoms adopt the exodentate orientation. However, when a metal ion was in the cavity this unfavorable position was changed to a more favorable one, mostly to the endodentate one. The prepared cage systems afforded endohedral complexes with silver or copper ions. It could be shown that the metal ions try to interact with a maximum of *n*-donors (N, S, Se) and π-donors (triple bonds or phenyl rings).

Experimental Section

General Methods: All melting points are uncorrected. Elemental analyses were carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg. UV/Vis absorption data were recorded with a Hewlett-Packard HP 8452A Diode Array-spectrometer, IR spectra were recorded with a Bruker Vector 22 FT-IR instrument. The NMR spectra were measured with a Bruker WH 300 or Avance 500 spectrometer (^{1}H NMR at 300 or 500 MHz and ^{13}C NMR at 75 or 125 MHz), using the solvent as an internal standard (δ). FAB mass spectra refer to data from a JEOL JMS-700 instrument. As matrix for the FAB experiments, *m*-nitrobenzyl alcohol was used. All reactions were carried out in dried glassware under argon using dried and oxygen-free solvents. Starting materials were prepared according to literature procedures. From the starting materials 1,5-diamino-3-thiapentane,[11] 1,5-diamino-3-selenapentane,[12] 1,8-diamino-3,6-dithiaoctane,[13] 1,6-dibromohex-3-yne,[14] (2-bromoethyl)benzene,[15] 4-(2-bromoethyl)biphenyl,[16] 4-(2-aminoethyl)biphenyl[17], and 1-aminobut-3-yne[18,19] were prepared according to literature procedures. 2-Aminoethylbenzene and 4,4′dibromobiphenyl were commercially available.

X-ray Crystallographic Study: Data were collected with a Bruker Smart CCD diffractometer at 200 K for **4**, **6**, **7**, **4**·Cu$^+$, **5**·Cu$^+$, **6**·Cu$^+$, **6**·Ag$^+$, **7**·Ag$^+$, **10**·2(Ag$^+$), **28**·Ag$^+$, **33**·Ag$^+$, and with a Bruker APEX diffractometer at 100 K for **5**, **8**, **9**, **10**, and **8**·Ag$^+$. Mo-K_α radiation was used in all cases and the intensities were corrected for Lorentz, polarization, and absorption effects. Relevant crystal and data collection parameters are given in Tables 5, 6, 7, 8 and 9. The structures were solved by direct methods and refined against F^2 with a full-matrix least square algorithm by using the SHELXTL software package.[32] Hydrogen atoms were refined isotropically for **8**, in all other cases they were considered at calculated positions and refined using appropriate riding models. In **10**, **10**·2(Ag$^+$), and **6**·Ag$^+$ some solvent molecules or anions had to be treated as disordered, in **4**·Cu$^+$ and **5**·Cu$^+$ on one side of the cage the three methylene groups next to the nitrogen atom occur in two alternative positions, in **9** an ethylene unit of the thioether bridge is affected by disorder. In **4**·Cu$^+$ and **5**·Cu$^+$ the copper position is not fully occupied. The charge balance is maintained by partial replacement of the metal ion by a proton, which could be refined isotropically with an occupation of about 30% in both cases. CCDC-279304 (for **4**), -279305 (for **5**), -279306 (for **6**), -279307 (for **7**), -279308 (for **8**), -279309 (for **9**), -279310 (for **10**), -279311 (for **4**·Cu$^+$), -279312 (for **5**·Cu$^+$), -279313 (for **6**·Cu$^+$), -279314 (for **6**·Ag$^+$), -279315 (for **7**·Ag$^+$), -279316 (for **8**·Ag$^+$), -279317 [for **10**·2(Ag$^+$)], -279318 (for **28**·Ag$^+$), and -279319 (for **33**·Ag$^+$) 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.

1,9-Diphthalimido-3,7-dithiononane (22): To a solution of 1,3-propane dithiole (4.2 g, 39 mmol) in dry toluene (250 mL) cooled to –30 °C, was added dropwise *n*BuLi in hexane (51 mL). After 30 min

Table 5. Crystal data and structural refinement for **4**–**7**.

	4	**5**	**6**	**7**
Empirical formula	$C_{16}H_{24}N_2S$	$C_{16}H_{24}N_2Se$	$C_{18}H_{28}N_2S_2$	$C_{19}H_{30}N_2S_2$
Formula weight [g/mol]	276.43	323.33	336.54	350.57
Temperature [K]	200(2)	200(2)	200(2)	200(2)
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
Z	4	2	4	4
a	13.9024(4)	8.7619(9)	9.5652(2)	13.6724(2)
b	12.1766(4)	9.3813(10)	13.0918(3)	9.6549(1)
c	9.4685(3)	10.0202(11)	15.9324(3)	15.3467(2)
α	90	74.661(2)	102.849 (1)	90
β	107.952(1)	79.285(2)	93.051(1)	102.995(1)
γ	90	84.656(2)	100.820(1)	90
V [Å^3]	1524.83(8)	779.61(14)	1901.9(7)	1973.97(4)
$D_{\text{calcd.}}$ [g/cm^3]	1.204	1.377	1.176	1.180
Abs. coeff. [mm^{-1}]	0.202	2.398	0.279	0.272
Max. / min. transmission	0.97 / 0.95	0.80 / 0.67	0.95 / 0.73	0.97 / 0.92
Crystal shape	polyhedron	polyhedron	polyhedron	polyhedron
Crystal size [mm^3]	$0.24 \times 0.16 \times 0.14$	$0.18 \times 0.11 \times 0.10$	$0.37 \times 0.29 \times 0.24$	$0.30 \times 0.20 \times 0.10$
Θ range [°]	1.54 to 26.36	2.14 to 28.38	1.84 to 27.44	1.53 to 27.49
Reflections collected	14360	8130	19809	19923
Indep. reflections [R(int)]	3112 (0.0428)	3870 (0.0344)	8624 (0.0255)	4535 (0.0356)
Obsd. reflections [$I > 2\sigma(I)$]	2310	2878	6308	3568
Data / restraints / parameters	3112 / 0 / 172	3870 / 74 / 191	8624 / 0 / 397	4535 / 0 / 208
GOF(F^2)	1.02	1.04	1.07	1.04
$R(F)$	0.037	0.045	0.039	0.033
$R_w(F^2)$	0.083	0.103	0.097	0.078
$(\Delta\rho)_{\max}$, $(\Delta\rho)_{\min}$ [e·Å^{-3}]	0.18 and –0.25	0.60 and –0.51	0.39 and –0.44	0.22 and –0.23

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Table 6. Crystal data and structural refinement for **8**–**10**.

	8	**9**	**10**
Empirical formula	$C_{20}H_{32}N_2S_2$	$C_{39}H_{46}N_2S_2$	$C_{40}H_{48}N_2S_2 \cdot 1.5\ CH_2Cl_2$
Formula weight	364.60	606.90	748.31
Temperature [K]	100(2)	200(2)	100(2)
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_1/c$	$\mathrm{P}2_12_12$
Z	4	4	4
a	7.2802(6)	14.392(2)	14.648(2)
b	14.149(1)	16.697(2)	29.035(4)
c	19.870(2)	15.492(2)	8.950(1)
α	90	90	90
β	93.587(2)	117.506(3)	90
γ	90	90	90
V [Å^3]	2042.7(3)	3301.9(7)	3806.6(9)
$D_{\text{calcd.}}$ [g/cm^3]	1.186	1.22	1.306
Abs. coeff. [mm^{-1}]	0.265	0.19	0.383
Max. / min. transmission	0.98 / 0.92	0.99 / 0.93	0.98 / 0.89
Crystal shape	irregular	irregular	irregular
Crystal size [mm^3]	0.30 × 0.07 × 0.07	0.38 × 0.07 × 0.04	0.32 × 0.26 × 0.06
Θ range [°]	1.77 to 24.71	2.01 to 21.97	1.56 to 28.32
Reflections collected	15874	19853	39939
Indep. reflections [R(int)]	3486 (0.0789)	4021 (0.0725)	9449 (0.1470)
Obsd. reflections [$I > 2\sigma(I)$]	2937	3227	6525
Data / restraints / parameters	3486 / 0 / 345	4021 / 0 / 574	9449 / 12 / 436
GOF(F^2)	1.25	1.19	1.10
$R(F)$	0.071	0.058	0.134
$R_w(F^2)$	0.122	0.104	0.311
$(\Delta\rho)_{\max}$, $(\Delta\rho)_{\min}$ [e·Å^{-3}]	0.37 and –0.33	0.20 and –0.20	0.83 and –0.71

Table 7. Crystal data and structural refinement for **6·Ag$^+$**, **7·Ag$^+$**, and **8·Ag$^+$**.

	6·Ag$^+$	**7·Ag$^+$**	**8·Ag$^+$**
Empirical formula	$C_{20}H_{28}Ag_2F_6N_2O_6S_4$	$C_{20}H_{30}AgF_3N_2O_3S_3$	$C_{21}H_{32}AgF_3N_2O_3S_3$
Formula weight	850.42	607.51	621.54
Temperature [K]	200(2)	200(2)	200(2)
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
Z	4	4	2
a	11.3822(1)	10.5359(1)	9.846(1)
b	13.6579(1)	15.1706(3)	9.918(1)
c	19.1305(1)	15.0937(3)	13.103(1)
α	90	90	96.383(2)
β	93.208(1)	93.805(1)	106.648(2)
γ	90	90	92.734(29)
V [Å^3]	2969.31(4)	2407.20(7)	1214.0(2)
$D_{\text{calcd.}}$ [g/cm^3]	1.902	1.676	1.700
Abs. coeff. [mm^{-1}]	1.676	1.146	1.138
Max. / min. transmission	0.7638 / 0.5538	0.89 / 0.80	0.97 / 0.83
Crystal shape	polyhedron	polyhedron	irregular
Crystal size [mm^3]	0.40 × 0.21 × 0.17	0.20 × 0.12 × 0.10	0.17 × 0.17 × 0.03
Θ range [°]	1.79 to 27.48	1.91 to 27.46	1.64 to 28.36
Reflections collected	30222	16273	12638
Indep. reflections [R(int)]	6807 0.0253	5420 0.0422	5974 0.0314
Obsd. reflections [$I > 2\sigma(I)$]	5876	3979	4803
Data / restraints / parameters	6807 / 91 / 434	5420 / 0 / 289	5974 / 0 / 426
GOF(F^2)	1.07	1.03	1.00
$R(F)$	0.025	0.032	0.034
$R_w(F^2)$	0.061	0.068	0.068
$(\Delta\rho)_{\max}$, $(\Delta\rho)_{\min}$ [e·Å^{-3}]	0.89 and –0.82	0.52 and –0.77	1.06 and –0.89

of mechanical stirring at –30 °C a solution of *N*-2-bromoethylphthalimid (20 g, 78.7 mmol) in dry toluene (250 mL) was added dropwise over a period of 1 h so that the temperature was maintained below 0 °C. After mechanical stirring overnight at room temperature the suspension was finally refluxed for 1 h. To workup water (100 mL) was added and the organic layer was washed a further 2× with water. After drying with magnesium sulfate and removal of the solvent, pure **22** (13.2 g, 75%) was obtained by crystallization from acetone as a white solid, m.p. 106 °C. ^{1}H NMR (500 MHz, C_6D_6): δ = 1.59 (q, ^3J = 7.1 Hz, 2 H, CH_2), 2.36 (t, ^3J

Table 8. Crystal data and structural refinement for **10·2(Ag^+)**, **28·Ag^+**, and **33·Ag^+**.

	10·2(Ag^+)	**28·Ag^+**	**33·Ag^+**
Empirical formula	$C_{42}H_{48}Ag_2F_6N_2O_{6.5}S_4$	$C_{26}H_{29}AgCl_2F_3NO_3S$	$C_{44}H_{41}AgCl_2F_3NO_3S$
Formula weight	1142.80	671.33	899.61
Temperature [K]	200(2)	200(2)	200(2)
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$C2$	$P2_12_12_1$	Cc
Z	4	4	4
a	49.5268(10)	13.6160(2)	30.3342(5)
b	8.3859(2)	13.8719(2)	9.0243(2)
c	11.1401(1)	14.8042(3)	15.2387(3)
α	90	90	90
β	102.566(1)	90	103.637(1)
γ	90	90	90
V [Å^3]	4516.32(15)	2796.21(8)	4053.92(14)
$D_{calcd.}$ [g/cm^3]	1.681	1.595	1.474
Abs. coeff. [mm^{-1}]	1.127	1.035	0.735
Max. / min. transmission	0.96 / 0.81	0.95 / 0.62	0.96 / 0.77
Crystal shape	polyhedron	polyhedron	polyhedron
Crystal size [mm^3]	0.20 × 0.04 × 0.04	0.52 × 0.28 × 0.05	0.38 × 0.24 × 0.06
Θ range [°]	0.84 to 22.99	2.01 to 24.09	1.38 to 25.34
Reflections collected	16130	22138	17041
Indep. reflections [R(int)]	6290 (0.0591)	4431 (0.0493)	7344 (0.0484)
Obsd. reflections [$I>2\sigma(I)$]	4918	3867	5788
Data / restraints / parameters	6290 / 264 / 637	4431 / 0 / 334	7344 / 2 / 496
GOF (F^2)	1.04	1.02	0.99
R (F)	0.042	0.031	0.040
$R_w(F^2)$	0.076	0.064	0.062
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ [e·Å^{-3}]	0.63 and –0.44	0.49 and –0.36	0.42 and –0.47

Table 9. Crystal data and structural refinement for **4·Cu^+**, **5·Cu^+**, and **6·Cu^+**.

	4·Cu^+	**5·Cu^+**	**6·Cu^+**
Empirical formula	$C_{17}H_{24}CuF_3N_2O_3S_2$	$C_{17}H_{24}CuF_3N_2O_3SSe$	$C_{19}H_{28}CuF_3N_2O_3S_3$
Formula weight	489.04	535.94	549.15
Temperature [K]	200(2)	201(2)	200(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1$
Z	4	4	2
a	9.7328(1)	9.7680(1)	9.0166(1)
b	10.5468(2)	10.6242(2)	9.7697(1)
c	18.9631(3)	18.9135(1)	13.6670(2)
α	90	90	90
β	93.159(1)	92.897(1)	108.306(1)
γ	90	90	90
V [Å^3]	1943.60(5)	1960.28	1142.99(2)
$D_{calcd.}$ [g/cm^3]	1.671	1.816	1.596
Abs. coeff. [mm^{-1}]	1.388	3.127	1.278
Max. / min. transmission	0.77 / 0.67	0.71 / 0.41	0.88 / 0.57
Crystal shape	polyhedron	polyhedron	polyhedron
Crystal size [mm^3]	0.32 × 0.30 × 0.20	0.36 × 0.24 × 0.12	0.49 × 0.29 × 0.10
Θ range [°]	2.10 to 27.47	2.09 to 27.48	1.57 to 27.48
Reflections collected	19753	19922	11787
Indep. reflections [R(int)]	4451 (0.0283)	4494 (0.0298)	5192 (0.0227)
Obsd. reflections [$I > 2\sigma(I)$]	3799	3961	4853
Data / restraints / parameters	4451 / 92 / 285	4494 / 92 / 285	5192 / 1 / 280
GOF (F^2)	1.04	1.05	1.04
R (F)	0.027	0.024	0.025
$R_w(F^2)$	0.068	0.055	0.064
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ [e·Å^{-3}]	0.34 and –0.42	0.28 and –0.35	0.35 and –0.41

= 7.2 Hz, 4 H, CH_2), 2.55 (t, ^3J = 7.0 Hz, 4 H, CH_2), 3.60 (t, ^3J = 7.0 Hz, 4 H, CH_2), 6.81–6.85 (m, 4 H, C$_{ar}H$), 7.36–7.41 (m, 4 H, C$_{ar}H$) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 29.2 (s, CH_2), 30.0 (s, CH_2), 30.4 (s, CH_2), 37.2 (s, CH_2), 123.1 (t, C_{ar}), 132.6 (q, C_{ar}), 133.6 (t, C_{ar}), 167.9 (q, CO) ppm. IR (KBr): $\tilde{\nu}$ = 3459, 3053, 2964, 2929, 2850, 1773, 1714, 1465, 1449, 1442, 1419 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 294 (4.5) nm. HRMS (FAB) calcd. for $C_{23}H_{22}N_2O_4S_2$, 455.1099; found 455.1073. $C_{23}H_{22}N_2O_4S_2$ (455.11): calcd. C 60.77, H 4.88, N 6.16, S 14.11; found C 60.49, H 4.96, N 6.13, S 14.08.

1,10-Diphthalimido-3,8-dithiodecane (23): To a solution of 1,3-propanedithiol (4.8 g, 39 mmol) in dry toluene (250 mL), cooled to –30 °C was added dropwise *n*BuLi in hexane (51 mL). After 30 min of mechanical stirring at –30 °C a solution of *N*-2-bromoethylphthalimide (20 g, 78.7 mmol) in dry toluene (250 mL) was added dropwise over a period of 1 h so that the temperature was maintained below 0 °C. After mechanical stirring overnight at room temperature the suspension was finally refluxed for 1 h. To workup water (100 mL) was added and the organic layer was washed further 2× with water. After drying with magnesium sulfate and removal of the solvent, pure **23** (12.1 g, 66%) was obtained by crystallization from acetone as a white solid, m.p. 100 °C. ^{1}H NMR (500 MHz, C_6D_6): δ = 1.39 (s, 4 H, CH_2), 2.27 (s, 4 H, CH_2), 2.57 (t, ^3J = 7.1 Hz, 4 H, CH_2), 3.62 (t, ^3J = 7.0 Hz, 4 H, CH_2), 6.82–6.86 (m, 4 H, $C_{ar}H$), 7.38–7.42 (m, 4 H, $C_{ar}H$) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 28.6 (s, CH_2), 30.1 (s, CH_2), 31.2 (s, CH_2), 37.2 (s, CH_2), 123.1 (t, C_{ar}), 132.6 (q, C_{ar}), 133.6 (t, C_{ar}), 167.9 (q, CO) ppm. IR (KBr): $\tilde{\nu}$ = 3460, 3102, 3048, 3018, 2945, 2923, 2865, 1774, 1699, 1613, 1578, 1464, 1433, 1417 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 294 (3.5) nm. HRMS (FAB) calcd. for $C_{24}H_{24}N_2O_4S_2$ 469.1256; found 469.1263. $C_{24}H_{24}N_2O_4S_2$ (469.13): calcd. C 61.52, H 5.16, N 5.98, S 13.68; found C 61.26, H 5.15, N 6.01, S 13.56.

1,9-Diamino-3,7-dithiononane·Dihydrochloride (17·2HCl): To a solution of **22** (13.2 g, 29.1 mmol) in dry ethanol (50 mL) was added dropwise a solution of hydrazine (3.1 g, 61.1 mmol) in water (5 mL). After temporary clearance of the solution a solid precipitate commenced to separate. The whole mixture was heated at reflux for 2 h then concentrated hydrochloric acid (12 mL) was added slowly and the obtained clear solution was stirred for a further 30 min. The alcohol was removed by evaporation and the suspension was dissolved in water. The solid was filtered off and washed with water. The water was removed by evaporation and the raw material was crystallized from methanol to obtain **17·2HCl** (7.5 g, 96%) as a white solid, m.p. 192 °C. ^{1}H NMR (300 MHz, CD_3OD): δ = 1.86–1.96 (m, 2 H, CH_2), 2.72 (t, ^3J = 7.1 Hz, 4 H, CH_2), 2.86 (t, ^3J = 6.9 Hz, 4 H, CH_2), 3.16 (t, ^3J = 6.7 Hz, 4 H, CH_2), 4.84 (s, 6 H, NH_3Cl) ppm. ^{13}C NMR (75 MHz, CD_3OD): δ = 29.7 (s, CH_2), 30.3 (s, CH_2), 31.1 (s, CH_2), 40.2 (s, CH_2) ppm. IR (KBr): $\tilde{\nu}$ = 3440, 3023, 2040, 1718, 1628, 1459, 1412 cm^{-1}. $C_7H_{20}Cl_2N_2S_2$ (267.29): calcd. C 31.46, H 7.54, N 10.48, S 23.99, Cl 26.53; found C 31.61, H 7.52, Cl 26.42, N 10.34, S 23.71.

1,10-Diamino-3,8-dithiodecane·Dihydrochloride (18·2HCl): To a solution of **23** (5.5 g, 11.7 mmol) in dry ethanol (25 mL) was added dropwise a solution of hydrazine (1.23 g, 24.6 mmol) in water (2 mL). After temporary clearance of the solution a solid precipitate commenced to separate. The whole mixture was heated at reflux for 2 h then concentrated hydrochloric acid (12 mL) was added slowly and the obtained clear solution was stirred for further 30 min. The alcohol was removed by evaporation and the suspension was dissolved in water. The solid was filtered off and washed with water. The water was removed by evaporation and the raw material was crystallized from methanol to obtain **18·2HCl** (2.7 g, 83%) as a white solid, m.p. 203 °C. ^{1}H NMR (300 MHz, CD_3OD): δ = 1.71–1.76 (m, 4 H, CH_2), 2.63 (t, ^3J = 7.1 Hz, 4 H, CH_2), 2.83 (t, ^3J = 6.9 Hz, 4 H, CH_2), 3.15 (t, ^3J = 6.8 Hz, 4 H, CH_2), 4.83 (s, 6 H, NH_3Cl) ppm. ^{13}C NMR (75 MHz, CD_3OD): δ = 29.4 (s, CH_2), 29.7 (s, CH_2), 31.9 (s, CH_2), 40.0 (s, CH_2) ppm. IR (KBr): $\tilde{\nu}$ = 3440, 2999, 2045, 2059, 1582, 1508, 1463 cm^{-1}. $C_8H_{22}Cl_2N_2S_2$ (281.31): calcd. C 34.16, H 7.88, N 9.96, S 22.79, Cl 25.21; found C 34.31, H 7.85, Cl 25.27, N 9.90, S 22.83.

4,4′-Bis(2-hydroxyethyl)biphenyl (25): To a suspension of 4,4′-dibromobiphenyl (30.00 g, 96 mmol) in dry hexane (1200 mL) was added a solution of 10 M *n*BuLi in hexane (42 mL, 420 mmol). The mixture was heated at reflux for 12 h. To this suspension dry THF (500 mL) was added and cooled to –40 °C. Subsequently ethylene oxide (31 mL, 617 mmol) was added. After 36 h of mechanical stirring at –35 °C water (500 mL) was added. Subsequently the mixture was stirred for a further 30 min. The white precipitate was then filtered off and dried with silica gel and finally crystallized from hexane to yield **25** (21 g, 92%), m.p. 183 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.45 (t, ^3J = 5.8 Hz, 2 H, OH), 2.87 (t, ^3J = 6.6 Hz, 4 H, CH_2), 3.85 (t, ^3J = 6.6 Hz, 4 H, CH_2), 7.29 (d, ^3J = 8.1 Hz, 4 H, $C_{ar}H$), 7.53 (d, ^3J = 8.1 Hz, 4 H, $C_{ar}H$) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 38.8 (s, CH_2), 63.44 (s, CH_2), 126.9 (t, C_{ar}), 129.4 (t, C_{ar}), 137.9 (q, C_{ar}), 138.9 (q, C_{ar}) ppm. IR (KBr): $\tilde{\nu}$ = 3420, 3030, 2942, 2878, 2049, 1911, 1633, 1500, 1476 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 258 (4.3) nm. HRMS (FAB) calcd. for $C_{16}H_{18}O_2$ 242.1307; found 242.1323. $C_{16}H_{18}O_2$ (242.13): calcd. C 79.31, H 7.49; found C 79.17, H 7.31.

4,4′-Bis(2-methylsulfonylethyl)biphenyl (26): To a solution of **25** (21.4 g, 88.3 mmol) in dichloromethane (350 mL) was added by cooling to –20 °C triethylamine (28.8 g, 285 mmol). Subsequently methanesulfonyl chloride (24.5 g, 213.8 mmol) was added to the mixture at such a rate that the temperature was maintained below –10 °C. After the addition was completed the suspension was stirred for 2 h. For workup water (100 mL) was added and the organic layer was washed with 10% hydrogen chloride solution, followed by saturated sodium hydrogen carbonate solution and again by saturated sodium chloride solution and water. The organic layer was dried with magnesium sulfate and the solvent evaporated. Purification by column chromatography (alumina; cyclohexane/ethyl acetate, 4:1) afforded **26** (29.0 g, 82%) as a white solid, m.p. 82 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 2.87 (s, 6 H, CH_3), 3.09 (t, ^3J = 6.8 Hz, 4 H, CH_2), 4.43 (t, ^3J = 6.8 Hz, 4 H, CH_2), 7.32 (d, ^3J = 8.2 Hz, 4 H, $C_{ar}H$), 7.56 (d, ^3J = 8.2 Hz, 4 H, $C_{ar}H$) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 35.6 (s, CH_2), 37.6 (CH_3), 70.9 (s, CH_2), 127.5 (t, C_{ar}), 129.9 (t, C_{ar}), 136.2 (q, C_{ar}), 139.7 (q, C_{ar}) ppm. IR (KBr):$\tilde{\nu}$ = 3434, 3027, 2942, 1913, 1500, 1428, 1401 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 258 (4.4) nm. HRMS (FAB) calcd. for $C_{18}H_{22}O_6S_2$ 398.0858; found 398.0850. $C_{18}H_{22}O_6S_2$ (398.09): calcd. C 54.25, H 5.56, S 16.09; found C 54.61, H 5.54, S 15.85.

4,4′-Bis(2-bromoethyl)biphenyl (27): A solution of **26** (20 g, 50.2 mmol) in acetone (800 mL) was refluxed with LiBr (26 g, 301.1 mmol) overnight. Water was added to dissolve the precipitated salt and the acetone was removed by evaporation. The aqueous layer was extracted 5× with dichloromethane, and the combined organic layers were dried with magnesium sulfate. After evaporation of the solvent pure **27** (14.3 g, 81%) was obtained by column chromatography (alumina; hexane/diethyl ether, 5:1) as a white solid, m.p. 107 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 3.20 (t, ^3J = 7.5 Hz, 4 H, CH_2), 3.63 (t, ^3J = 7.4 Hz, 4 H, CH_2), 7.30 (d, ^3J = 8.1 Hz, 4 H, $C_{ar}H$), 7.56 (d, ^3J = 8.2 Hz, 4 H, $C_{ar}H$) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 33.5 (s, CH_2), 39.2 (s, CH_2), 127.3 (t, C_{ar}), 129.5 (t, C_{ar}), 138.4 (q, C_{ar}), 139.6 (q, C_{ar}) ppm. IR (KBr): $\tilde{\nu}$ = 3444, 3052, 3026, 2959, 2930, 2051, 1633, 1493, 1447 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 260 (4.4) nm. HRMS (FAB) calcd. for $C_{16}H_{16}Br_2$ 367.9599; found 367.9607. $C_{16}H_{16}Br_2$ (367.96): calcd. C 52.21, H 4.38, Br 43.41; found C 52.35, H 4.44, Br 43.19.

General Procedure for the Condensation of Primary Amines with Terminal Bromo Compounds to the Tertiary Amines 28–33: A primary amine (5 mmol) and a terminal bromo-compound (10 mmol) were added together to a suspension of finely powdered potassium carbonate (4.9 g, 35 mmol) in acetonitrile (200 mL). The mixture was stirred intensively and refluxed for 2 d until the starting material was consumed. The mixture was filtered and the solvent evaporated. The residue was purified by column chromatography on alumina.

Tris(2-phenylethyl)amine (28): 945 mg (58%); m.p. 31 °C; cyclohexane/ethyl acetate, 50:1. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 2.75–2.81 (m, 6 H, CH_2), 2.84–2.90 (m, 6 H, CH_2), 7.21–7.24 (m, 9 H, $C_{ar}H$), 7.32 (t, ^3J = 7.2 Hz, 6 H, $C_{ar}H$) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 34.2 (s, CH_2), 56.4 (s, CH_2), 126.2 (t, C_{ar}), 128.7 (t, C_{ar}), 129.2 (t, C_{ar}), 141.4 (q, C_{ar}) ppm. IR (KBr): $\tilde{\nu}$ = 3480, 3086, 3028, 2957, 2933, 2864, 2798, 1946, 1873, 1809, 1751, 1600, 1491, 1452 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 258 (3.0) nm. HRMS (FAB) calcd. for $C_{24}H_{28}N$ 330.2221; found 330.2207. $C_{24}H_{27}N$ (330.22): calcd. C 87.49, H 8.26, N 4.25; found C 87.44, H 8.22, N 4.40.

(But-3-ynyl)bis(2-phenylethyl)amine (29): 305 mg (22%) colorless liquid; hexane/diethyl ether, 10:1. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 2.01 (m, 1 H, $\equiv CH$), 2.30 (m, 2 H, CH_2), 2.72–2.84 (m, 10 H, CH_2), 7.15–7.21 (m, 4 H, $C_{ar}H$), 7.25–7.31 (m, 6 H, $C_{ar}H$) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 17.7 (s, CH_2), 34.4 (s, CH_2), 53.2 (s, CH_2), 56.3 (s, CH_2), 69.1 (t, $\equiv CH$), 83.6 (q, $\equiv C$), 126.3 (t, C_{ar}), 128.7 (t, C_{ar}), 129.2 (t, C_{ar}), 141.2 (q, C_{ar}) ppm. IR (KBr): $\tilde{\nu}$ = 3294, 3026, 2948, 2860, 2812, 2117, 1946, 1868, 1805, 1742, 1602, 1496, 1453 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 260 (2.5) nm. HRMS (FAB) calcd. for $C_{20}H_{23}N$ 278.1909; found 278.1918. $C_{20}H_{23}N$ (278.19): calcd. C 86.59, H 8.36, N 5.05; found C 86.64, H 8.33, N 5.27.

[2-(Biphenyl-4-yl)ethyl]bis(2-phenylethyl)amine (30): 940 mg (47%); m.p. 54 °C; hexane/diethyl ether, 10:1. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 2.74–2.87 (m, 12 H, CH_2), 7.18 (d, ^3J = 8.0 Hz, 6 H, $C_{ar}H$), 7.26 (m, 6 H, $C_{ar}H$), 7.31–7.34 (m, 1 H, $C_{ar}H$), 7.43 (t, ^3J = 7.7 Hz, 2 H, $C_{ar}H$), 7.53 (d, ^3J = 8.0 Hz, 2 H, $C_{ar}H$), 7.60 (d, ^3J = 7.5 Hz, 2 H, $C_{ar}H$) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 33.7 (s, CH_2), 34.1 (s, CH_2), 56.1 (s, CH_2), 56.2 (s, CH_2), 126.1 (t, C_{ar}), 127.2 (t, C_{ar}), 127.2 (t, C_{ar}), 127.3 (t, C_{ar}), 128.5 (t, C_{ar}), 129.0 (t, C_{ar}), 129.1 (t, C_{ar}), 129.6 (t, C_{ar}), 139.0 (q, C_{ar}), 140.5 (q, C_{ar}), 141.3 (q, C_{ar}) ppm. IR (KBr): $\tilde{\nu}$ = 3025, 2946, 1597, 1495, 1486, 1453 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 256 (4.4) nm. HRMS (EI+) calcd. for $C_{30}H_{31}N$ 405.2457; found 405.2448. $C_{30}H_{31}N$ (405.24): calcd. C 88.84, H 7.70, N 3.45; found C 88.44, H 7.84, N 3.57.

Bis[2-(biphenyl-4-yl)ethyl]but-3-ynylamine (31): 553 mg (25%) colorless oil; hexane/diethyl ether, 10:1. ^{1}H NMR: (500 MHz, CD_2Cl_2): δ = 2.04 (t, ^4J = 2.6 Hz, 1 H, $\equiv CH$), 2.37 (dt, ^3J = 4.8, ^4J = 2.6 Hz, 2 H, $C\equiv CCH_2$), 2.82–2.87 (m, 10 H, CH_2), 7.29 (d, ^3J = 8.1 Hz, 4 H, $C_{ar}H$), 7.34 (pt, ^3J = 7.4 Hz, 2 H, $C_{ar}H$), 7.44 (pt, ^3J = 7.7 Hz, 4 H, $C_{ar}H$), 7.54 (d, ^3J = 8.1 Hz, 4 H, $C_{ar}H$), 7.61 (d, ^3J = 7.2 Hz, 4 H) ppm. ^{13}C NMR: (125 MHz, CD_2Cl_2): δ = 17.6 (s, CH_2), 33.9 (s, CH_2), 53.10 (s, CH_2), 56.1 (s, CH_2), 69.10 (t, $\equiv CH$), 83.6 (q, $\equiv C$), 127.2 (t, C_{ar}), 127.3 (t, C_{ar}), 127.4 (t, C_{ar}), 129.1 (t, C_{ar}), 129.6 (t, C_{ar}), 139.1 (q, C_{ar}), 140.3 (q, C_{ar}), 141.3 (q, C_{ar}) ppm. IR (KBr): $\tilde{\nu}$ = 3441, 3307, 3055, 3026, 1487, 1449, 1407 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 258 (4.6) nm. HRMS (FAB) calcd. for $C_{32}H_{31}N$ 430.2534; found 430.2534. $C_{32}H_{31}N$ (430.25): calcd. C 89.47, H 7.27, N 3.26; found C 89.08, H 7.25, N 3.32.

Bis[2-(biphenyl-4-yl)ethyl](2-phenylethyl)amine (32): 566 mg (56%); m.p. 82 °C; hexane/diethyl ether, 10:1. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 2.78–2.92 (m, 12 H, CH_2), 7.20 (d, ^3J = 7.6 Hz, 3 H, $C_{ar}H$), 7.26 (d, ^3J = 8.2 Hz, 6 H, $C_{ar}H$), 7.31–7.36 (m, 2 H, $C_{ar}H$),7.44 (t, ^3J = 8.0 Hz, 4 H, $C_{ar}H$), 7.53 (d, ^3J = 8.2 Hz, 4 H, $C_{ar}H$), 7.60 (d, ^3J = 8.5 Hz, 4 H, $C_{ar}H$) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 33.9 (s, CH_2), 34.2 (s, CH_2), 56.2 (s, CH_2), 56.3 (s, CH_2), 126.2 (t, C_{ar}), 127.3 (t, C_{ar}), 127.3 (t, C_{ar}), 127.5 (t, C_{ar}), 128.7 (t, C_{ar}), 129.1 (t, C_{ar}), 129.2 (t, C_{ar}), 129.7 (t, C_{ar}), 135.4 (q, C_{ar}), 139.1 (q, C_{ar}), 140.6 (q, C_{ar}), 141.4 (q, C_{ar}) ppm. IR (KBr): $\tilde{\nu}$ = 3440, 3057, 3027, 2943, 2859, 2808, 1486, 1452, 1408 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 258 (4.6) nm. HRMS (FAB) calcd. for $C_{36}H_{36}N$ 482.2848; found 482.2881. $C_{36}H_{35}N$ (482.28): calcd. C 89.77, H 7.32, N 2.91; found C 89.54, H 7.39, N 3.03.

Tris[2-(biphenyl-4-yl)ethyl]amine (33): 405 mg (15%); m.p. 75 °C; hexane/diethyl ether, 20:1. ^{1}H NMR: (300 MHz, CD_2Cl_2): δ = 2.79–2.85 (m, 6 H, CH_2), 2.88–2.93 (m, 6 H, CH_2), 7.26 (d, ^3J = 8.1 Hz, 6 H, $C_{ar}H$), 7.30–7.35 (m, 3 H, $C_{ar}H$), 7.43 (t, ^3J = 7.5 Hz, 6 H, $C_{ar}H$), 7.52 (d, ^3J = 8.1 Hz, 6 H, $C_{ar}H$), 7.59 (d, ^3J = 7.6 Hz, 6 H, $C_{ar}H$) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 33.8 (s, CH_2), 56.2 (s, CH_2), 127.3 (t, C_{ar}), 127.3 (t, C_{ar}), 127.4 (t, C_{ar}), 129.1 (t, C_{ar}), 129.7 (t, C_{ar}), 139.0 (q, C_{ar}), 140.6 (q, C_{ar}), 141.4 (q, C_{ar}) ppm. IR (KBr): $\tilde{\nu}$ = 3440, 3027, 2924, 2854, 1486, 1461, 1450 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 258 (4.7) nm. HRMS (FAB) calcd. for $C_{42}H_{40}N$ 558.3160; found 558.3134. $C_{42}H_{39}N$ (558.32): calcd. C 90.44, H 7.05, N 2.51; found C 90.09, H 7.32, N 2.65.

General Procedure for the Cyclization of α,ω-Diamines with 1,6-Dibromo-3-hexyne (16) to the Bicyclic Diynes 4–8: 1,6-Dibromo-3-hexyne (**17**) (1.5 g, 6.25 mmol) and the corresponding α,ω-diamines (2 mmol) were added together to a suspension of finely powdered potassium carbonate (4.5 g, 33 mmol) in acetonitrile (125 mL). The mixture was stirred intensively and refluxed for 3 d until the starting material was consumed. The mixture was filtered and the solvent evaporated. The residue was purified by column chromatography on alumina.

4-Thia-1,7-diazabicyclo[5.6.6]nonadeca-10,16-diyne (4): Yield: 227 mg of **4** (41%), column chromatography with cyclohexane/ethyl acetate, 20:1, m.p. 69 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 2.24–2.35 (m, 8 H, CH_2), 2.52–2.56 (m, 8 H, CH_2), 2.76 (t, ^3J = 6.0 Hz, 4 H, CH_2), 2.98 (t, ^3J = 6.0 Hz, 4 H, CH_2) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 19.5 (s, CH_2), 30.6 (s, CH_2), 53.4 (s, CH_2), 56.5 (s, CH_2), 80.6 (q, C_{alkyne}) ppm. IR (KBr): $\tilde{\nu}$ = 3447, 2900, 2835, 2801, 2781, 2731, 1449, 1432 cm^{-1}. Raman: $\tilde{\nu}$ = 2228, 2291 cm^{-1}. HRMS (FAB) calcd. for $C_{16}H_{25}N_2S$ 277.1738; found 277.1731. $C_{16}H_{24}N_2S$ (272.17): calcd. C 69.52, H 8.75, N 10.13, S 11.60; found C 69.31, H 8.77, N 10.04, S 11.43.

4-Selena-1,7-diazabicyclo[5.6.6]nonadeca-10,16-diyne (5): Yield: 212 mg of **5** (33%), column chromatography with cyclohexane/ethyl acetate, 20:1, m.p. 107 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 2.26–2.33 (m, 8 H, CH_2), 2.52–2.56 (m, 8 H, CH_2), 2.89 (t, ^3J = 6.1 Hz, 4 H, CH_2), 3.01 (t, ^3J = 6.1 Hz, 4 H, CH_2) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 19.5 (s, CH_2), 22.2 (s, CH_2), 53.3 (s, CH_2), 57.4 (s, CH_2), 80.6 (q, C_{alkyne}) ppm. IR: (KBr): $\tilde{\nu}$ = 3445, 2951, 2903, 2790, 2728, 1453, 1428 cm^{-1}. Raman: $\tilde{\nu}$ = 22278, 22891 cm^{-1}. HRMS (FAB) calcd. for $C_{16}H_{25}N_2{}^{82}Se$ 327.1184; found 327.1144. $C_{16}H_{24}N_2Se$ (327.12): calcd. C 59.43, H 7.48, N 8.66; found C 59.28, H 7.55, N 8.58.

4,7-Dithia-1,10-diazabicyclo[8.6.6]docosa-13,19-diyne (6): Yield: 291 mg of **6** (43%), column chromatography with cyclohexane/ethyl acetate, 50:1, m.p. 134 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 2.26 (mt, 8 H, CH_2), 2.44–2.48 (m, 8 H, CH_2), 2.61–2.65 (m, 8 H, CH_2), 2.74 (s, 4 H, SCH_2CH_2S) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.7 (s, CH_2), 30.4 (s, CH_2), 31.8 (s, CH_2), 53.2 (s, CH_2), 54.3 (s, CH_2), 79. 5 (q, C_{alkyne}) ppm. IR (KBr): $\tilde{\nu}$ = 3440, 2956, 2900, 2801, 2730, 1630, 1455, 1421 cm^{-1}. Raman: $\tilde{\nu}$ = 22368, 2300 cm^{-1}. HRMS (FAB) calcd. for $C_{18}H_{29}N_2S_2$ 337.1772; found 337.1735.

$C_{18}H_{28}N_2S_2$ (337.18): calcd. C 64.24, H 8.39, N 8.32, S 19.05; found C 64.25, H 8.33, N 8.26, S 19.21.

4,8-Dithia-1,11-diazabicyclo[9.6.6]tricosa-14,20-diyne (7): Yield 360 mg of **7** (53%), column chromatography with cyclohexane/ethyl acetate, 50:1, m.p. 89 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.91–2.00 (q, ^3J = 7.1 Hz, 2 H, $\mathrm{C}H_2$), 2.29 (br. s, 8 H, $\mathrm{C}H_2$), 2.57 (br. s, 12 H, $\mathrm{C}H_2$), 2.71 (t, ^3J = 7.0 Hz, 8 H, $\mathrm{S C}H_2\mathrm{CH_2C}H_2\mathrm{S}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.3 (s, $C\mathrm{H}_2$), 28.2 (s, $C\mathrm{H}_2$), 29.2 (s, $C\mathrm{H}_2$), 30.0 (s, $C\mathrm{H}_2$), 53.7 (s, $C\mathrm{H}_2$), 54.5 (s, $C\mathrm{H}_2$), 79.9 (q, C_alkyne) ppm. IR (KBr): $\tilde{\nu}$ = 3446, 2943, 2924, 2901, 2821, 2745, 2725, 1458, 1434, 1424 cm^{-1}. Raman: $\tilde{\nu}$ = 2231, 2293 cm^{-1}. HRMS (FAB) calcd. for $C_{19}H_{31}N_2S_2$ 351.1928; found 351.1920. $C_{19}H_{30}N_2S_2$ (351.19): calcd. C 65.09, H 8.62, N 7.99, S 18.29; found C 64.71, H 8.52, N 7.94, S 18.38.

4,9-Dithia-1,12-diazabicyclo[10.6.6]tetracosa-15,21-diyne (8): Yield: 275 mg of **8** (39%), column chromatography with cyclohexane/ethyl acetate, 50:1, m.p. 72 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.79–1.83 (m, 4 H, $\mathrm{C}H_2$), 2.32 (s, 8 H, $\mathrm{C}H_2$), 2.62–2.70 (m, 20 H, $\mathrm{C}H_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.3 (s, $C\mathrm{H}_2$), 28.7 (s, $C\mathrm{H}_2$), 31.0 (s, $C\mathrm{H}_2$), 31.8 (s, $C\mathrm{H}_2$), 53.89 (s, $C\mathrm{H}_2$), 55.4 (s, $C\mathrm{H}_2$), 80.2 (q, C_alkyne) ppm. IR (KBr): $\tilde{\nu}$ = 3440, 2939, 2900, 2819, 2744, 1628, 1456, 1422, 1422 cm^{-1}. Raman: $\tilde{\nu}$ = 2237, 2297 cm^{-1}. HRMS (FAB) calcd. for $C_{20}H_{32}N_2S_2$ 365.2095; found 365.2056. $C_{20}H_{32}N_2S_2$ (365.21): calcd. C 65.88, H 8.85, N 7.68, S 17.59; found C 65.70, H 8.84, N 7.65, S 17.30.

General Procedure for the Cyclization of α,ω-Diamines with 4,4′-Bis(2-bromoethyl)biphenyl (27): To the bicyclic compounds **9** and **10** 4,4′-bis(2-dibromoethyl)biphenyl (**27**) (6.7 g, 10 mmol) and the diamines **17** and **18** (4 mmol), respectively, were added together to a suspension of finely powdered potassium carbonate (8.5 g, 61 mmol) in acetonitrile (400 mL). The mixture was stirred intensively and refluxed for 5 d until the starting material was consumed. The mixture was filtered and the solvent evaporated. The residue was purified by column chromatography on alumina.

4,8-Dithia-14,15,20,21-tetrabenzena-1,11-diazabicyclo[9.6.6]tricosaphane (9): 476 mg (20%); hexane/diethyl ether, 20:1, m.p. 180 °C (decomp.). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.49–0.54 (q, ^3J = 7.4 Hz, 2 H, $\mathrm{SCH_2C}H_2$), 1.13 (t, ^3J = 7.1 Hz, 4 H, $\mathrm{C}H_2$), 1.30 (t, ^3J = 7.4 Hz, 4 H, $\mathrm{SC}H_2\mathrm{CH_2C}H_2\mathrm{S}$), 2.21 (t, ^3J = 7.1 Hz, 4 H, $\mathrm{C}H_2$), 2.51–2.55 (m, 4 H, $\mathrm{C}H_2$), 2.72–2.77 (m, 4 H, $\mathrm{C}H_2$), 2.89–2.94 (m, 4 H, $\mathrm{C}H_2$), 2.97–3.02 (m, 4 H, $\mathrm{C}H_2$), 7.22 (d, ^3J = 8.1 Hz, 8 H, $\mathrm{C_{ar}}H$), 7.45 (d, ^3J = 8.1 Hz, 8 H, $\mathrm{C_{ar}}H$) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 30.6 (s, $C\mathrm{H}_2$), 30.8 (s, $C\mathrm{H}_2$), 31.9 (s, $C\mathrm{H}_2$), 33.6 (s, $C\mathrm{H}_2$), 53.7 (s, $C\mathrm{H}_2$), 53.9 (s, $C\mathrm{H}_2$), 126.3 (t, C_ar), 130.5 (t, C_ar), 138.3 (q, C_ar), 139.5 (t, C_ar) ppm. IR (KBr): $\tilde{\nu}$ = 3439, 2910, 2849, 2788, 1733, 1499, 1457, 1422 cm^{-1}. UV/Vis (CH_2Cl_2): λ_max (lg ε) = 260 (4.8) nm. HRMS (FAB) calcd. for $C_{39}H_{47}N_2S_2$ 607.3181; found 607.3166. $C_{39}H_{46}N_2S_2$ (607.32): calcd. C 77.18, H 7.64, N 4.62, S 10.57; found C 77.04, H 7.65, N 4.65, S 10.77.

4,9-Dithia-15,16,21,22-tetrabenzena-1,12-diazabicyclo[10.6.6]tetracosaphane (10): Yield: 384 mg of **10** (16%), column chromatography with hexane/diethyl ether, 10:1, m.p. 189 °C (decomp.). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.67 (m, 4 H, $\mathrm{SCH_2C}H_2$), 1.53–1.54 (pd, ^3J = 8.9 Hz, 4 H, $\mathrm{C}H_2$), 1.70 (t, ^3J = 6.6 Hz, 4 H, $\mathrm{C}H_2$), 2.36 (t, ^3J = 6.6 Hz, 4 H, $\mathrm{C}H_2$), 2.54–2.59 (m, 4 H, $\mathrm{C}H_2$), 2.73–2.78 (m, 4 H, $\mathrm{C}H_2$), 2.87–2.94 (m, 8 H, $\mathrm{C}H_2$), 7.16 (d, ^3J = 8.0 Hz, 8 H, $\mathrm{C_{ar}}H$), 7.32 (d, ^3J = 8.0 Hz, 8 H, $\mathrm{C_{ar}}H$) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 30.0 (s, $C\mathrm{H}_2$), 31.0 (s, $C\mathrm{H}_2$), 31.1 (s, $C\mathrm{H}_2$), 33.1 (s, $C\mathrm{H}_2$), 54.2 (s, $C\mathrm{H}_2$), 55.2 (s, $C\mathrm{H}_2$), 126.5 (t, C_ar), 130.2 (t, C_ar), 138.6 (q, C_ar), 139.3 (q, C_ar) ppm. IR (KBr): $\tilde{\nu}$ = 3440, 3022, 2963, 2908, 2855, 2783, 2729, 1738, 1632, 1500, 1456, 1448, 1402 cm^{-1}. UV/Vis (CH_2Cl_2): λ_max (lg ε) = 258 (4.5) nm. HRMS (FAB) calcd. for $C_{40}H_{49}N_2S_2$ 621.3337; found 621.3317. $C_{40}H_{48}N_2S_2$ (621.33): calcd. C 77.37, H 7.79, N 4.51, S 10.33; found C 77.01, H 7.75, N 4.60, S 10.43.

General Procedure for the Synthesis of Copper(I) Complexes [4·Cu$^+$][CF_3SO_3] and [5·Cu$^+$][CF_3SO_3]: To a solution of the copper(I) triflate toluene complex (61 mg, 0.2 mmol) in anhydrous dichloromethane (5 mL) was added in the absence of light a solution of the corresponding cryptand (0.1 mmol) in anhydrous dichloromethane (5 mL). After stirring for 1 h the mixture was filtered and evaporation of the solvent gave the corresponding copper(I) complex in quantitative yield.

Complex [4·Cu$^+$][$CF_3SO_3^-$]: ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 2.71 (t, ^3J = 5.6 Hz, 8 H, $\mathrm{C}H_2$), 2.69–2.72 (m, 4 H, $\mathrm{C}H_2$), 2.75–2.77 (m, 4 H, $\mathrm{C}H_2$), 2.84–2.88 (m, 4 H, $\mathrm{C}H_2$), 2.95 (s, 4 H, $\mathrm{C}H_2$) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 19.8 (s, $C\mathrm{H}_2$), 30.9 (s, $C\mathrm{H}_2$), 37.8 (s, $C\mathrm{H}_2$), 54.2 (s, $C\mathrm{H}_2$), 55. 5 (q, OTf$^-$), 80.2 (q, C_alkyne) ppm. IR (KBr): $\tilde{\nu}$ = 3444, 2924, 2906, 2839, 1634, 1457, 1426 cm^{-1}. Raman: $\tilde{\nu}$ = 2231 cm^{-1}. HRMS (FAB) calcd. for $C_{16}H_{24}CuN_2S$ 341.0939; found 341.0938.

Complex [5·Cu$^+$][$CF_3SO_3^-$]: ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 2.64 (t, ^3J = 6.0 Hz, 8 H, $\mathrm{C}H_2$), 2.71–2.78 (m, 8 H, $\mathrm{C}H_2$), 2.86–2.91 (m, ^3J = 6.0 Hz, 4 H, $\mathrm{C}H_2$), 2.98 (t, ^3J = 5.3 Hz, 4 H, $\mathrm{C}H_2$), 2.95 (s, 4 H, $\mathrm{C}H_2$) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 18.9 (s, $C\mathrm{H}_2$), 30.9 (s, $C\mathrm{H}_2$), 53.9 (s, $C\mathrm{H}_2$), 56.4 (s, $C\mathrm{H}_2$), 80.0 (q, C_alkyne) ppm. IR (KBr): $\tilde{\nu}$ = 3441, 2922, 2868, 1630, 1460, 1427 cm^{-1}. HRMS (FAB) calcd. for $C_{16}H_{24}CuN_2Se$ 387.0400; found 387.0406.

General Procedure for the Synthesis of Silver Complexes [6·Ag$^+$][$CF_3SO_3^-$], [10·2(Ag$^+$)][$CF_3SO_3^-$]$_2$, [28·Ag$^+$][$CF_3SO_3^-$], and [33·Ag$^+$][$CF_3SO_3^-$]: To a solution of silver triflate (53 mg, 0.2 mmol) in anhydrous dichloromethane (5 mL) was added in the absence of light a solution of the corresponding cryptand (0.1 mmol) in anhydrous dichloromethane (5 mL). After stirring for 1 h the mixture was filtered and evaporation of the solvent gave the corresponding silver complex in quantitative yield.

Complex [6·Ag$^+$][$CF_3SO_3^-$]: ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 2.46–2.61 (m, 16 H, $\mathrm{C}H_2$), 2.69–2.73 (m, 4 H, $\mathrm{C}H_2$), 2.77–2.81 (m, 4 H, $\mathrm{C}H_2$), 2.93 (s, 4 H, $\mathrm{SC}H_2\mathrm{C}H_2\mathrm{S}$) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 18.6 (s, $C\mathrm{H}_2$), 29.3 (s, $C\mathrm{H}_2$), 30.7 (s, $C\mathrm{H}_2$), 53.0 (s, $C\mathrm{H}_2$), 53.1 (s, $C\mathrm{H}_2$), 79.3 (q, C_alkyne) ppm. IR (KBr): $\tilde{\nu}$ = 3444, 2963, 2920, 2849, 1461, 1434 cm^{-1}. HRMS (FAB) calcd. For $C_{18}H_{28}AgN_2S_2$ 445.0741; found 445.0701.

Complex [7·Ag$^+$][$CF_3SO_3^-$]: ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.79 (t, ^3J = 6.6 Hz, 4 H, $\mathrm{C}H_2$), 2.13–2.22 (m, 2 H, $\mathrm{C}H_2$), 2.47–2.54 (m, 8 H, $\mathrm{C}H_2$), 2.61 (m, 4 H, $\mathrm{C}H_2$), 2.74 (t, ^3J = 5.5 Hz, 4 H, $\mathrm{C}H_2$), 2.86–2.93 (m, 8 H, $\mathrm{C}H_2$), 2.63–3.68 (m, 4 H, $\mathrm{C}H_2$) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 19.4 (s, $C\mathrm{H}_2$), 25.9 (s, $C\mathrm{H}_2$), 31.6 (s, $C\mathrm{H}_2$), 32.3 (s, $C\mathrm{H}_2$), 53.3 (s, $C\mathrm{H}_2$), 53.7 (s, $C\mathrm{H}_2$), 68.0 (q, OTf$^-$), 79.7 (q, C_alkyne) ppm. IR (KBr): $\tilde{\nu}$ = 3441, 2963, 2916, 2840, 2823, 1629, 1459, 1446, 1433, 1418 cm^{-1}. Raman: $\tilde{\nu}$ = 2206, 2281 cm^{-1}. HRMS (FAB) calcd. for $C_{19}H_{30}AgN_2S_2$ 459.0898; found 459.0888.

Complex [8·Ag$^+$][$CF_3SO_3^-$]: ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.92 (s, 4 H, $\mathrm{C}H_2$), 2.53–2.66 (m, 16 H, $\mathrm{C}H_2$), 2.76 (t, ^3J = 6.5 Hz, 4 H, $\mathrm{C}H_2$), 2.91 (s, 4 H, $\mathrm{C}H_2$), 2.98 (t, ^3J = 6.5 Hz, 4 H, $\mathrm{C}H_2$) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 18.5 (s, $C\mathrm{H}_2$), 26.4 (s, $C\mathrm{H}_2$), 31.4 (s, $C\mathrm{H}_2$), 32.2 (s, $C\mathrm{H}_2$), 53.4 (s, $C\mathrm{H}_2$), 60.9 (q, OTf$^-$), 78.9 (q, C_alkyne) ppm. IR (KBr):$\tilde{\nu}$ = 3443, 2924, 2846, 1629, 1457, 1439 cm^{-1}. HRMS (FAB) calcd. for $C_{20}H_{32}AgN_2S_2$ 471.1058; found 471.1075.

Complex [9·Ag$^+$][$CF_3SO_3^-$]: ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.77 (s, 2 H, $\mathrm{C}H_2$), 1.63 (s, 4 H, $\mathrm{C}H_2$), 2.27 (t, ^3J = 6.8 Hz, 4 H, $\mathrm{C}H_2$), 2.62–2.67 (m, 4 H, CH_2), 2.84–2.89 (m, 4 H, CH_2), 3.00–3.05 (m, 4 H, CH_2), 3.11–3.17 (m, 4 H, CH_2), 7.39 (d, ${}^3J$ = 7.6 Hz, 8 H, $C_{ar}H$), 7.55 (d, ${}^3J$ = 7.6 Hz, 8 H, $C_{ar}H$) ppm. IR: (KBr): $\tilde{\nu}$ = 3449, 3022, 2941, 2915, 2795, 2736, 1626, 1499, 1450, 1425, 1407 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 270 (3.4) nm. HRMS (FAB) calcd. for $C_{39}H_{46}AgN_2S_2$ 715.2150; found 715.2158.

Complex $[10\cdot2(Ag^+)][CF_3SO_3^-]_2$: ${}^1H$ NMR (300 MHz, CD_2Cl_2): δ = 1.01 (s, 4 H, CH_2), 2.44 (s, 4 H, CH_2), 2.51 (br. s, 4 H, CH_2), 2.75 (br. s, 4 H, CH_2), 2.80–2.88 (m, 4 H, CH_2), 2.95–3.05 (m, 4 H, CH_2), 3.09–3.21 (m, 8 H, CH_2), 7.56 (d, ${}^3J$ = 7.8 Hz, 8 H, $C_{ar}H$), 7.68 (d, ${}^3J$ = 7.1 Hz, 8 H, $C_{ar}H$) ppm. ${}^{13}C$ NMR (75 MHz, CD_2Cl_2): δ = 27.4 (s, CH_2), 31.8 (s, CH_2), 33.3 (s, CH_2), 34.6 (s, CH_2), 49.6 (s, CH_2), 53.7 (s, CH_2), 54.1 (s, CH_2), 54.4 (s, CH_2), 67.9 (q, OTf$^-$), 124.7 (t, C_{ar}), 125.8 (t, C_{ar}), 127.3 (t, C_{ar}), 138.0 (q, C_{ar}), 139.0 (q, C_{ar}) ppm. IR (KBr): $\tilde{\nu}$ = 3444, 2926, 2792, 1627, 1500, 1451 cm^{-1}. HRMS (FAB) calcd. for $C_{40}H_{47}Ag_2N_2S_2$ 835.1279; found 835.1303. $C_{42}H_{48}Ag_2F_6N_2O_6S_4$ (863.88): calcd. C 44.54, H 4.26, N 2.47; found C 44.84, H 4.60, N 2.57.

Complex $[28\cdot Ag^+][CF_3SO_3^-]$: Colorless crystals, soluble in dichloromethane or chloroform, m.p. 145 °C (decomp.). ${}^1H$ NMR (500 MHz, CD_2Cl_2): δ = 2.70 (t, ${}^3J$ = 6.0 Hz, 6 H, CH_2), 2.94 (t, ${}^3J$ = 6.0 Hz, 6 H, CH_2), 6.84 (d, ${}^3J$ = 7.0 Hz, 6 H, $C_{ar}H$), 7.30–7.37 (m, 9 H, $C_{ar}H$) ppm. ${}^{13}C$ NMR (125 MHz, CD_2Cl_2): δ = 33.0 (s, CH_2), 57.6 (s, CH_2), 124.2 (t, C_{ar}), 127.7 (t, C_{ar}), 130.6 (t, C_{ar}), 139.2 (q, C_{ar}) ppm. IR (KBr): $\tilde{\nu}$ = 3441, 3085, 3061, 3026, 2951, 2861, 2799, 1627, 1603, 1495, 1453 cm^{-1}. HRMS (FAB) calcd. for $C_{24}H_{27}{}^{109}AgN$ 438.1191; found 438.1229. $C_{25}H_{27}AgF_3NO_3S$ (586.42)·0.75 CH_2Cl_2: calcd. C 47.57, H 4.42, N 2.15, S 4.93; found C 47.50, H 4.42, N 2.31, S 5.10.

Complex $[33\cdot Ag^+][CF_3SO_3^-]$: Colorless, light-sensitive crystals, soluble in dichloromethane or chloroform, m.p. 173 °C (decomp.). ${}^1H$ NMR (500 MHz, CD_2Cl_2): δ = 2.83 (t, ${}^3J$ = 5.8 Hz, 6 H, CH_2), 2.99 (t, ${}^3J$ = 5.8 Hz, 6 H, CH_2), 6.96 (d, ${}^3J$ = 7.9 Hz, 6 H, $C_{ar}H$), 7.43 (d, ${}^3J$ = 8.0 Hz, 6 H, $C_{ar}H$) ppm. ${}^{13}C$ NMR (125 MHz, CD_2Cl_2): δ = 32.4 (s, CH_2), 57.1 (s, CH_2), 124.6 (t, C_{ar}), 126.9 (t, C_{ar}), 127.9 (t, C_{ar}), 128.7 (t, C_{ar}), 129.6 (t, $_{Car}$), 138.1 (q, C_{ar}), 138.6 (q, C_{ar}), 140.2 (q, C_{ar}) ppm. IR (KBr): $\tilde{\nu}$ = 3441, 3028, 2929, 1625, 1519, 1487, 1458, 1407 cm^{-1}. HRMS (FAB) calcd. for $C_{43}H_{39}{}^{109}AgN$ 666.2130; found 666.2112. $C_{43}H_{29}AgF_3NO_3S$ (804.64): calcd. C 63.39, H 4.82, N 1.71, S 3.94; found C 63.28, H 4.89, N 2.04, S 4.28.

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