[2.2.2]*m,p,p*- and [2.2.2]*m,m,p*-Cyclophane-Ag-triflate: new π-prismand complexes†

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L e t t e r

The 17- and 16-membered [2.2.2]*m,p,p*- and [2.2.2]*m,m,p*-cyclophane form crystalline 1 : 1 Ag-triflate π-prismand complexes surprisingly similar to the well-known 18-membered *p,p,p*-isomer.

It is known that π-prismands and certain hydrocarbon cyclophanes are capable of forming π-complexes with small metal cations, where benzene rings act as π-donors for the complex.[1] This fascinating complexation behaviour is especially effective for [2.2.2]paracyclophane and related structures.[2,3] Pierre *et al.*[3] reported the preparation of the Ag-triflate complex of [2.2.2]paracyclophane and claimed that it was the first member of a new class of compounds; owing to the complexation properties they proposed the name π-prismand for such hydrocarbon cyclophanes. Further studies revealed that in the π-prismand–Ag$^+$ complex the silver ion is bonded not to the centre of the benzene ring but to the edge of the cavity owing to a specific interaction with one carbon–carbon double bond in each phenyl moiety.[4] It has been shown that concave hydrocarbon cyclophanes can extract certain metal ions from an aqueous phase into a non-polar phase.[5] Vögtle *et al.* have tested these hydrocarbons as ionophores and showed that PVC–[2.2.2]paracyclophane membranes demonstrate remarkable sensitivity towards silver above alkali metals, alkaline earth metals and thallium ions.[5]

The synthesis of [2.2.2]*m,p,p*- (**9**) and [2.2.2]*m,m,p*-cyclophane (**10**) is based on well-known cyclophane methodology where sulfide cyclisation is done under high dilution followed by oxidation and sulfone pyrolysis.[6,7] The key reactions are the high dilution cyclisations of the 1,2-bis[4-(bromomethyl)phenyl]ethane (**1**) or 1,2-bis[3-(bromomethyl)phenyl]ethane (**2**) with 1,3-di(thiomethyl)benzene (**3**) or 1,4-di(thiomethyl)benzene (**4**) to form 1,10-dithia[3.3.2]*m,p,p*-cyclophane (**5**) or 1,10-dithia[3.3.2]*p,m,m*-cyclophane (**6**), respectively, using toluene as a solvent (Scheme 1). The cyclisation to **5** gave 44% yield and to **6** 81% yield. The cyclic disulfides **5** and **6** were oxidized by H$_2$O$_2$ under reflux to 1,10-dithiatetroxide[3.3.2]*m,p,p*-cyclophane (**7**) and to 1,10-dithiatetroxide[3.3.2]*p,m,m*-cyclophane (**8**). The disulfones **7** and **8** were identified by IR spectrometry which showed strong absorption at the —SO$_2$— band (1100–1330 cm^{-1}). The yields for the oxidation reactions were 85% and 64% for **7** and **8**, respectively. The disulfones **7** and **8** were pyrolysed to the desired cyclophanes, namely [2.2.2]*m,p,p*-cyclophane (**9**) and to [2.2.2]*m,m,p*-cyclophane (**10**) by using the ring oven pyrolysis apparatus[6] at 600 °C and 1 × 10^{-5} torr. The yield after isolation was 69% for **9** and 56% for **10** (no — SO$_2$ absorption was detected in the IR spectra; the analysis of the compounds gave satisfactory

results‡). The complexation abilities of the cyclophanes **9** and **10** were tested by the same procedure used by Pierre *et al.* for the preparation of the Ag-triflate complex of [2.2.2]*p,p,p*-cyclophane.[3] The complexation was done by mixing equimolecular amounts of free ligand (**9** or **10**) in dichloromethane and silver triflate in tetrahydrofuran. The mixture was stirred and allowed to evaporate very slowly to dryness in darkness at room temperature. The complexation was verified by the changed NMR spectra,‡ thus giving complexes **11** and **12** (Scheme 1). Since X-ray diffraction has previously been used successfully to verify the structures of the structurally similar π-complexes, we aimed to produce crystals suitable for X-ray analysis§ of **11** and **12**. The crude complex **11** was dissolved in

‡ Spectroscopy. **9**. ^{1}H NMR (CDCl$_3$): δ 2.80–2.89 (m, 8H), 2.94 (s, 4H), 6.22 (s, 1H), 6.67 (s, 8H), 7.06 (dd, 2H), 7.24 (t, 1H); ^{13}C NMR (CDCl$_3$): δ 35.00, 35.92, 36.30, 125.47, 127.80, 127.94, 128.87, 132.31, 137.12, 137.14, 140.24; HRMS *m/z* (M$^+$, C$_{24}$H$_{24}$): calcd 312.187 80, obsd 312.187 77, mp 108 °C. **10**. ^{1}H NMR (CDCl$_3$): δ 2.80–2.86 (m, 8H), 2.88 (s, 4H), 6.18 (s, 2H), 6.58 (s, 4H), 6.97 (d, 2H), 7.05 (d, 2H), 7.18 (t, 2H); and ^{13}C NMR (CDCl$_3$): δ 34.09, 36.90, 37.70, 125.63, 125.74, 127.91, 128.34, 129.99, 137.62, 140.08, 140.43; HRMS *m/z* (M$^+$, C$_{24}$H$_{24}$): calcd 312.187 80, obsd 312.187 73. **11**. ^{1}H NMR (CDCl$_3$): δ 2.86 (s, 4H), 2.94 (s, 4H), 3.08 (s, 4H), 6.02 (s, 1H), 6.98 (s, 4H), 7.05 (s, 4H), 7.29 (s, 2H), 7.65 (s, 1H); ^{13}C NMR: δ 33.97, 35.11, 35.91, 123.44, 124.76, 127.41, 128.84, 131.97, 137.62, 138.82, 139.52, mp 158 °C. **12**. ^{1}H NMR (CDCl$_3$): δ 2.94 (s, 8H), 2.97 (s, 4H), 6.31 (s, 2H), 6.94 (s, 4H), 7.26 (d, 2H), 7.30 (d, 2H), 7.58 (t, 2H); ^{13}C NMR: δ 32.97, 36.68, 37.41, 123.26, 126.54, 126.81, 128.28, 132.10, 134.77, 139.66, 141.82.

§ X-ray crystal structure analysis. **11**. C$_{24}$H$_{24}$AgO$_3$SCF$_3$, M = 569.37, orthorhombic, a = 8.736(1), b = 20.272(2), c = 26.112(2) Å, V = 4624.3(8) Å^3, space group *Pbca* (no. 61), μ(MoKα) = 1.011 mm^{-1}, Z = 8, D_c = 1.636 g cm^{-3}, $F(000)$ = 2304, T = 296 ± 1 K. Enraf-Nonius CAD4 diffractometer, 4258 collected reflections, 4066 unique reflections [2636 $I > 2σ(I)$] were used for refinement. *Lp* correction, absorption correction, (T_{max} 74.16%, T_{min} 71.24%). Structure solution by direct methods (SIR92[9]) and refinement on F^2 (SHELXL-97[10]). The final R values were R = 0.0348, wR^2 = 0.0936 [$I > 2σ(I)$], R = 0.0680, wR^2 = 0.1016 (all data) for 298 parameters. A final difference map displayed no electron density higher than 0.62 e Å^{-3}. **12**. C$_{24}$H$_{24}$AgO$_3$SCF$_3$, M = 569.37, monoclinic, a = 14.233(2), b = 10.134(1), c = 15.885(4) Å, β = 97.293(2)°, V = 2272.6(7) Å^3, space group *P2$_1$/c* (no. 14), μ(MoKα) = 1.029 mm^{-1}, Z = 4, D_c = 1.664 g cm^{-3}, $F(000)$ = 1152, T = 173 ± 2 K. Enraf-Nonius CAD4 diffractometer, 4161 collected reflections, 3990 unique reflections [2581 $I > 2σ(I)$] were used for refinement. *Lp* correction, absorption correction (T_{max} 81.65%, T_{min} 75.02%). Structure solution by direct methods (SIR92[9]) and refinement on F^2 (SHELXL-97[10]). The final R values were R = 0.0377, wR^2 = 0.0760 [$I > 2σ(I)$], R = 0.0816, wR^2 = 0.0838 (all data) for 298 parameters. A final difference map displayed no electron density higher than 0.52 e Å^{-3}. Atomic coordinates, bond lengths, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 440/037.

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† triflate = trifluoromethanesulfonate.
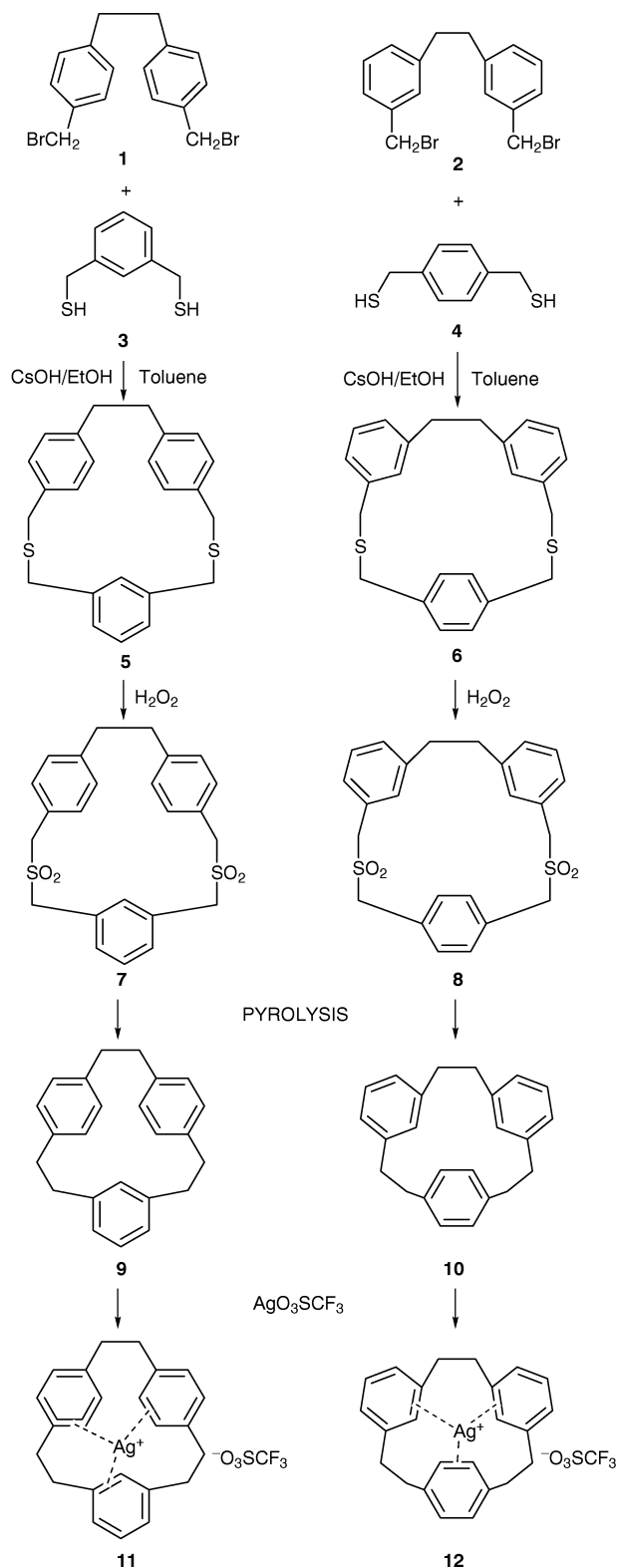
Scheme 1

hexane–dichloromethane, and crude complex **12** in dichloromethane–diethyl ether. Both were allowed to evaporate very slowly in the darkness, the former at room temperature and the latter in a refrigerator, giving nicely defined small well-diffracting crystals.

The molecular structures of **11** and **12** compared with the [2.2.2]*p,p,p*-cyclophane-Ag-triflate[3] are shown in Fig. 1.

The structures of the complexes are remarkably similar, keeping in mind that the [2.2.2]*p,p,p*-cyclophane has an 18-membered ring[8] the new *m,p,p*-cyclophane a 17-membered and the *m,m,p*-cyclophane only a 16-membered ring. The reduction of the ring size is caused by the change of the spatial connections inside the isomeric $C_{24}H_{24}$ skeleton. Although the formal ring size is reduced from the *ppp*- to the *mmp*-isomer, the cavities or clefts in all three isomers are nearly equal in size. The size of the complexing cleft is defined by the non-bonded contact distances between the carbon atoms that are closest (bonded) to the silver ion. For the [2.2.2]*p,p,p*-cyclophane-Ag-triflate these distances are 3.69, 3.71 and 3.56 Å for C4···C23, C5···C16 and C15···C24, respectively. In **11** the similarly defined distances between C4···C24, C5···C15 and C14···C19 are 4.02, 4.13 and 3.15 Å and in **12** are 3.89, 3.18, and 3.82 Å for C8···C23, C7···C11 and C16···C24, respectively. The different spatial orientation of the phenyl rings in each isomer can readily be seen from the torsion angles of the $-CH_2-CH_2-$ bridging bonds which are -62 (C23—C1—C2—C3), 37 (C6—C9—C10—C11) and 65° (C14—C17—C18—C19) for **11**, 63 (C22—C1—C2—C3), 65 (C7—C9—C10—C11) and $-61°$ (C15—C17—C18—C19) for **12** and 23 (C22—C1—C2—C3), 52 (C6—C9—C10—C11), 49° (C14—C17—C18—C19) for the [2.2.2]*p,p,p*-cyclophane-Ag-triflate.

In all of the Ag complexes the silver ion is located in the cleft or pocket created by the three phenyl rings. The interaction (bonding) between the silver and the cyclophane is accomplished by the π-bonding with one of the double bonds in each phenyl ring. The coordination sphere around the silver ion is supplemented by the O atom of the triflate anion with slightly shorter bond lengths as for the carbons (Fig. 1). The bonding distances are remarkably similar (Fig. 1) in spite of the ring size reduction. Due to the conformational and symmetry differences the bonding in **11** (the less symmetrical phane) is slightly different, showing three shorter and three longer bonds between silver and carbon atoms. These results confirm that the silver ion is indeed not bonded to the centre of the benzene rings and the ring size reduction and conformational isomerism do not exclude the π-complex formation between the title cyclophanes and silver ions.

Owing to the very small amounts of the prepared cyclophanes **9** and **10** (*ca.* 20–30 mg), we are currently developing the synthesis in order to produce different isomers (particularly the *mmm*-isomer) and more material for complexation, extraction and dynamic NMR studies.
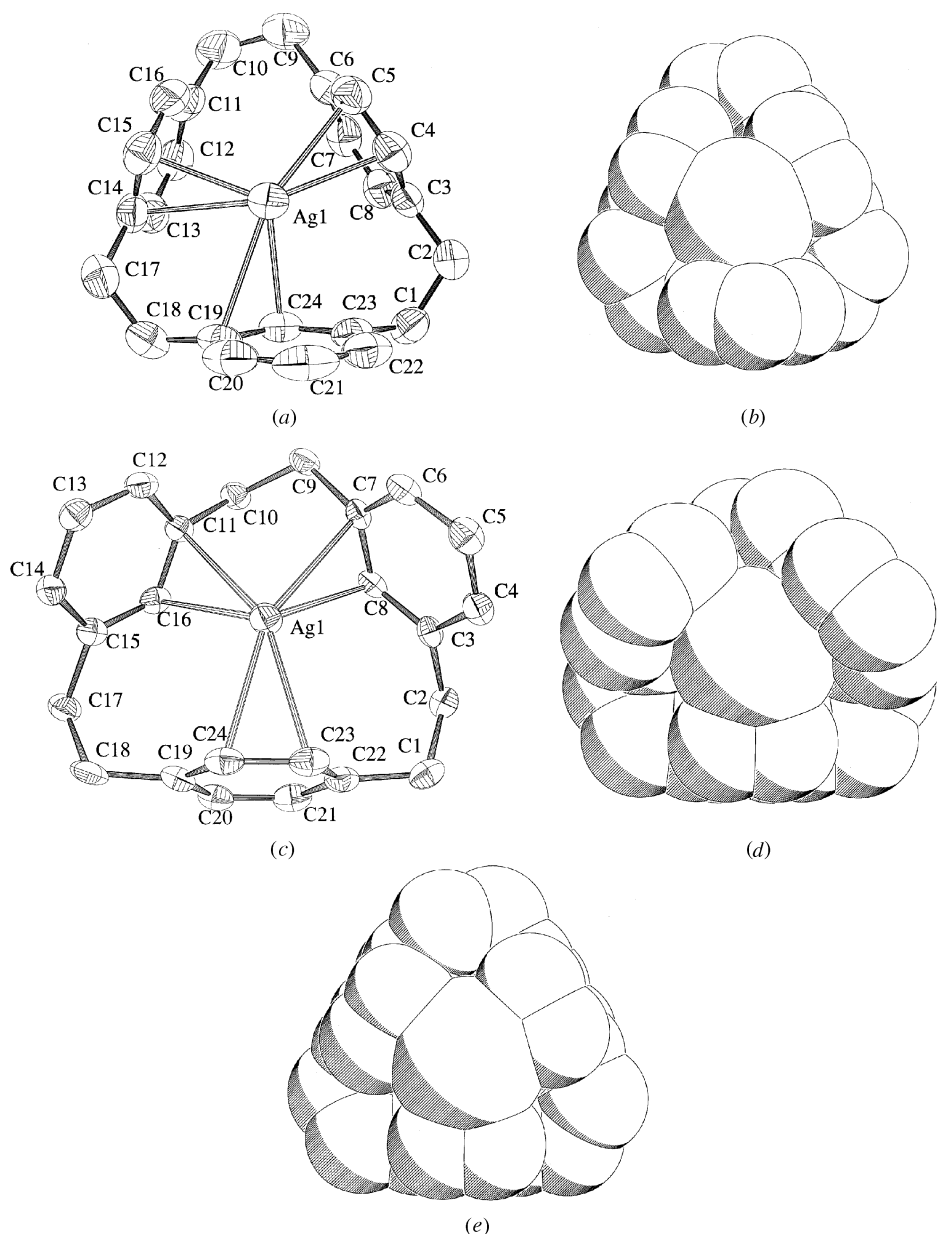
Acknowledgements

Fig. 1 ORTEP[11]/SCHAKAL[12] plots with labelling/space-filling model for **11** [(*a*) and (*b*)] and **12** [(*c*) and (*d*)] and [2.2.2]*p,p,p*-cyclophane-Ag-triflate[3] (*e*). Bond distances (in Å) around the silver ion: **11**, Ag1—C4 2.57, Ag1—C5 2.78, Ag1—C14 2.80, Ag1—C15 2.54, Ag1—C19 2.78, Ag1—C24 2.59 and Ag1—O1 2.43; **12**, Ag1—C7 2.67, Ag1—C8 2.56, Ag1—C11 2.65, Ag1—C16 2.61, Ag1—C23 2.57, Ag1—C24 2.58, Ag1—O1 2.35; [2.2.2]*p,p,p*-Cyclophane-Ag-triflate [the same numbering as for (*a*)], Ag1—C4 2.56, Ag1—C5 2.63, Ag1—C15 2.70, Ag1—C16 2.55, Ag1—C23 2.63, Ag1—C24 2.62 and Ag1—O1 2.32. The coordinated triflate anion and H atoms have been omitted for clarity.

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