

Synthesis and structural characterization of novel silver(I) complexes of tetrahydro[16]annulene annelated with bicyclo[2.2.2]octene units

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The first silver(I) complexes of tetrahydro[16]annulene annelated with bicyclo[2.2.2]octene units were prepared and the incorporation of a silver atom into the cavity center was shown by X-ray crystallography.

The versatility of tribenzotrithydro[12]annulene (**1**) as a ligand in metal complexes was demonstrated by Youngs *et al.*¹ The cavity size of ligand **1** was shown to be suitable for the incorporation of first row transition metals into the cavity center, while the size is too small for a second row transition metal. For example, silver gave only a sandwich complex.¹ Even for a higher homologue, tetrabenzotetrahydro[16]annulene (**2**), there has been no example of incorporation of a second or third row transition metal within its cavity. Only a dicobalt complex has been reported, in which two of the triple bonds are coordinated from the outer side.²

Recently we synthesized a series of dehydroannulenes annelated with bicyclo[2.2.2]octene (abbreviated as BCO) including tetrahydro[16]annulene (**3**),³ which are characterized by a rather low oxidation potential indicative of a raised HOMO level by the annelation of the BCO units.³ The raised HOMO level should be effective for an interaction between the occupied 2p orbital of the ligand and empty 5s orbital of the silver,⁴ which would strengthen the coordination bond by donation from the ligand to the metal.⁵ Here we report the synthesis of novel silver-dehydro[16]annulene **3** complexes prepared based on such a rationale.

Annulene **3** was stirred with 1 equiv. of silver(I) triflate (AgOTf) or silver(I) hexafluoroantimonate (AgSbF₆) in THF at room temperature for a few days. After concentration of the solution, hexane was added to give precipitates of silver complex **4** (**3**·AgOTf) or **5** (**3**·AgSbF₆) both as red powders in 84% or 92% yield respectively. These complexes are stable to air, moisture, and light, in contrast to many silver-alkene, -alkyne, and -arene complexes which are essentially light- or air-sensitive.^{6,7}

Single crystals of **4** containing 0.5 equiv. hexane and of **5** containing 1 equiv. dichloromethane were obtained and examined by X-ray crystallography.[†] As shown in Fig. 1, the silver atom is present in the center of the cavity for both complexes and the counter anions are located above the silver atom. The structure of the central ring of the ligand is still tub-like but the folding angles are smaller compared with the X-ray structure of **3**.³ The shortest distances between the silver and the counter anions, *i.e.* Ag–O in **4** and Ag–F in **5**, were 2.31(1) and 2.67(1) Å respectively. The Ag–O distance is shorter than those (2.36–2.53 Å) in nine reported complexes of AgOTf with arenyl or alkynyl ligands,^{7–10} whereas the Ag–F distance is longer than

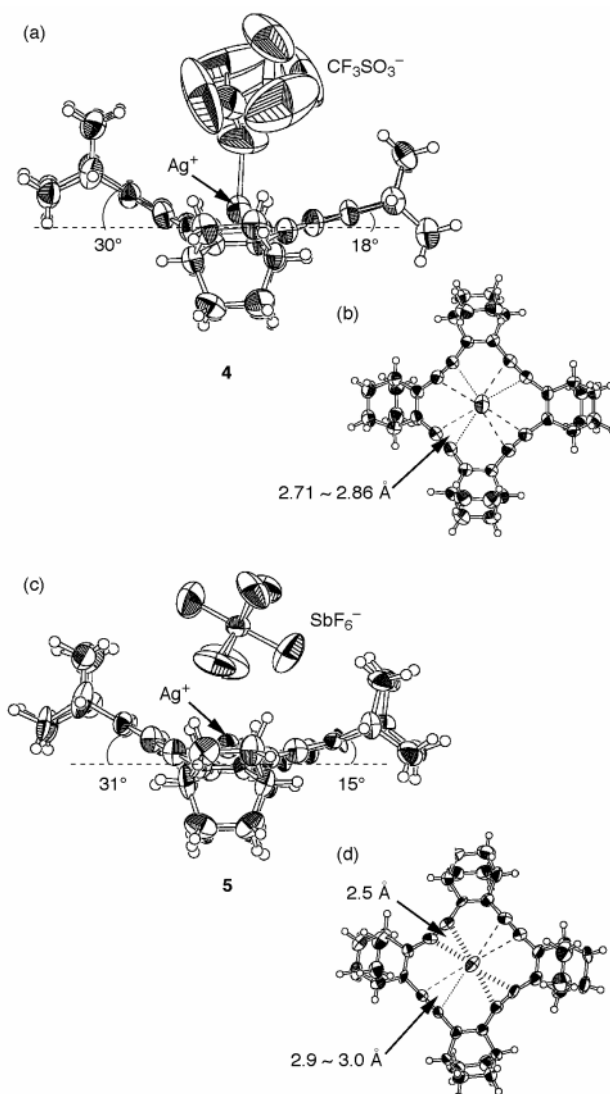
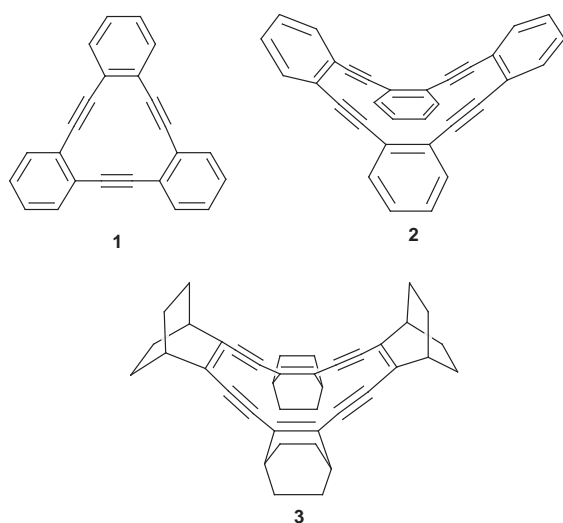


Fig. 1 ORTEP drawing showing (a), (c) side views and (b), (d) top views of **4** and **5**. The counter anions are omitted in the top views for clarity.

Table 1 ^1H and ^{13}C NMR spectra for **3–5**

Compd.	^1H NMR, δ		^{13}C NMR, δ			
	CH	CH ₂	C=C	C \equiv C	CH	CH ₂
3^a	2.47	1.47 (32H)	132.8	95.4	37.2	25.3
3^b	2.49	1.54 (16H) 1.44 (16H)	132.5	95.0	36.9	24.9
4^a	2.61	1.55 (32H)	133.4	97.4	36.7	25.1
5^b	2.64	1.65 (16H) 1.44 (16H)	133.4	98.3	36.5	24.7

^a In CDCl₃, ^b In CD₂Cl₂.

the average (2.63 Å) of those (2.54–2.71 Å) in three reported complexes of AgSbF₆ with arenyl ligands.¹¹

These Ag–anion distances are reflected in the modes of coordination with ligands. The Ag–C(alkyne) distance of complex **4** varies only from 2.714(7) Å to 2.863(7) Å, indicating almost equal coordination with the four acetylene units. On the other hand, the ligand of complex **5** is deformed due to the stronger coordination with a pair of acetylene units which are opposite to each other. The Ag–C distance at the stronger coordination site is 2.52(1)–2.54(1) Å whereas that at the other site is 2.85(2)–3.05(2) Å. Accordingly, the C \equiv C–C angle for **4** varies only from 170.0(8)° to 174.1(8)°, whereas for **5** the C \equiv C–C angle is 164(1)–170(1)° at the more strongly coordinated site and 174(1)–178(1)° at the other site.

In order to compare the degree of coordination in **4** and **5**, the Mulliken charge was calculated at the HF/STO-3G level for the silver atoms of AgOTf and AgSbF₆ using the X-ray structures with and without the ligand. The charge of silver in the structure with the ligand was calculated to be +0.20 for AgOTf and +0.29 for AgSbF₆, while that for the structure without the ligand was +0.50 for AgOTf and +0.77 for AgSbF₆. These results indicate that this annulene-type ligand reduces the positive charge on the silver atom and the extent of this reduction is larger for the case of AgSbF₆. This type of coordination is presumed to be principally due to the electron donation from the HOMO of the ligand to the LUMO of the metal, and the annelation of the BCO units which raises the HOMO level of the π -system would strengthen this coordination.

The IR spectrum of complex **4** showed that the energy of the C \equiv C stretching band became weak [2155 cm⁻¹ (br)] compared with the free ligand **3** (2251, 2173 cm⁻¹), while the absorption for **5** was too weak to observe. As shown in Table 1, both the ^1H and ^{13}C NMR spectra for **4** and **5** also showed slight changes from those of the free ligand. Particularly noteworthy is the downfield shift for the NMR signal for the acetylenic carbon. For the methylene carbon of complexes **4** and **5**, only one NMR signal was observed, indicating that the central ring of the ligand was inverting rapidly on the NMR time scale, like the free ligand **3**.

In summary, we prepared a novel silver complex of tetradecahydro[16]annulene annelated with BCO units. This

[16]annulene-type ligand was found to have a cavity size suitable for the incorporation of second-row metals, *i.e.* silver, into the center of the ring. Calculated Mulliken charges for the complexes of **4** and **5** indicated that there is considerable electron donation from the ligand to the silver atom.

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Notes and References

† *Crystal data for 4-0.5(C₆H₁₄): C₄₄H₄₇AgF₃O₃S, $M = 820.78$, monoclinic, space group $P2_1/c$, $a = 11.780(5)$, $b = 14.766(3)$, $c = 22.502(2)$ Å, $\beta = 98.79(2)^\circ$, $V = 3868(1)$ Å³, $Z = 4$, $\mu(\text{Cu-K}\alpha) = 51.20$ cm⁻¹, $T = 293$ K, for 4265 observed reflections within $2\theta = 120.1^\circ$ and $I > 3.00\sigma(I)$. Data were corrected for absorption (Ψ scan; min., max. correction factors 0.56, 1.00) and Lorentz polarization effects. There is disorder in the trifluoromethyl moiety and two oxygen atoms not directly contacted to the silver atom. The final R value was $R = 0.080$. For **5-CH₂Cl₂**: C₄₁H₄₂AgCl₂F₆Sb, $M = 949.30$, triclinic, space group $P\bar{1}$, $a = 12.381(3)$, $b = 15.412(4)$, $c = 12.067(3)$ Å, $\alpha = 109.78(2)$, $\beta = 117.45(2)$, $\gamma = 84.00(2)^\circ$, $V = 1919.1(10)$ Å³, $Z = 2$, $\mu(\text{Cu-K}\alpha) = 114.32$ cm⁻¹, $T = 293$ K, for 2617 observed reflections within $2\theta = 120.1^\circ$ and $I > 3.00\sigma(I)$. Data were corrected for Lorentz polarization effects. The final R value was $R = 0.055$. CCDC 182/1014.*

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