## Hydrocarbon Molecules with Novel Structure: a Dehydroannulene with Silver(I)-Complexing Ability and a Double C<sub>60</sub> Adduct of Pentacene

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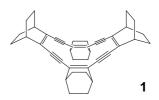
The first silver(I) complexes of tetradehydro[16]annulene fused with four bicyclo[2.2.2]octene units were synthesized, and the incorporation of the silver atom into the cavity center was shown by X-ray crystallography. The degree of complexation was affected by the counteranion. In contrast to the AgOTf complex, the AgSbF<sub>6</sub> complex was found to be more strongly coordinated to the dehydroannulene ligand. On the other hand, the solid-state reaction using high-speed vibration milling technique was applied to cycloaddition of fullerene C<sub>60</sub> to pentacene. There was obtained a new C<sub>60</sub> double adduct as a unique product for the solid-state reaction.

Keywords: dehydroannulene / silver complex / C<sub>60</sub> / cycloaddition / mechanochemistry

# **1.** A Dehydroannulene with Silver(I)-Complexing Ability [1].

Dehydroannulene is a macrocyclic conjugated  $\pi$ -system containing acetylene linkage(s). Previously we reported the synthesis of a series of dehydroannulenes fused with bicyclo[2.2.2]octene frameworks [2]. The heightening of the HOMO of the  $\pi$ -systems due to the  $\sigma$ - $\pi$  conjugation with the  $\sigma$ -bonds in rigid bicyclic frameworks has been demonstrated by electrochemical measurements.

The electron donation from the HOMO of the  $\pi$ -system should work favorably for complexation of a metal ion in the cavity of the cyclic  $\pi$ -system. Thus, when



tetradehydro[16]annulene **1** was allowed to react with an equimolar amount of either  $AgSbF_6$  or AgOTf, the corresponding silver complexes were obtained as red crystals in 92 or 84% yield. The results of X-ray crystallography indicated that the silver ion is encapsulated in the middle of the cavity of the  $\pi$ -system, and is more strongly coordinated by the ligand for  $1 \cdot AgSbF_6$  than for  $1 \cdot AgOTf$ .

### ORGANIC MATERIALS CHEMISTRY —High-Pressure Organic Chemistry—

#### Scope of Research

Fundamental studies are being made for creation of new functional materials with novel structures and properties and for utilization of high pressure in organic synthesis. The major subjects are: synthetic and structural studies on novel cyclic  $\pi$ -systems; chemical transformation of fullerene  $C_{60}$ ; utilization of carbon monoxide and dioxide for organic synthesis under the transition-metal catalysis.

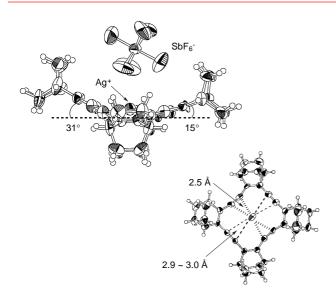


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**Figure 1.** Molecular structure of  $1 \cdot \text{SbF}_6$  determined by X-ray crystallography. A side view and a top view (with  $\text{SbF}_6$  eliminated for clarity).

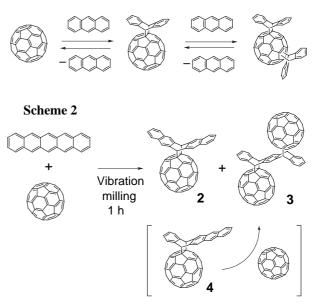
The Ag-C(alkyne) distance of 1·AgOTf varies only from 2.714(7) Å to 2.863(7) Å, indicating almost equal coordination with the four acetylene units whereas the ligand of  $1 \cdot \text{SbF}_6$  is slightly deformed due to the stronger coordination with a pair of acetylene units which are opposite with each other. The Ag-C distance at the stronger coordination site is 2.52(1)–2.54(1) Å as shown in Figure 1.

These results are in good agreement with the Mulliken charge calculated at the HF/STO-3G level for the silver atoms of AgSbF<sub>6</sub> and AgOTf using the X-ray structures. Apparently the annulene-type ligand in the present work is reducing the positive charge on the silver atom and the extent of this reduction is larger for the case of AgSbF<sub>6</sub>. This type of coordination is presumed to be principally due to the interaction between the HOMO of the ligand and the LUMO of the metal, and the annelation with the bicyclic frameworks, which raises the HOMO level of the  $\pi$ -system, has strengthened this interaction as expected.

#### 2. A Double C<sub>60</sub> Adduct of Pentacene.

The mechanochemical solid-state reaction of fullerene  $C_{60}$  using a technique of high-speed vibration milling has been successfully utilized in our group in the nucleophilic addition of organozinc reagent [3] and the selective dimerization of  $C_{60}$  to give the first fullerene dimer  $C_{120}$  [4].

When this technique was applied to the [4+2] cycloaddition of  $C_{60}$  with anthracene, it was found that an apparent equilibrium state can be established within Scheme 1



about 30 minutes in spite of the heterogeneous solidstate reaction conditions (Scheme 1).

The similar high-speed vibration milling of  $C_{60}$  with pentacene was found to afford not only the symmetrical monoadduct 2 but the double  $C_{60}$  adduct 3 as shown in Scheme 2. Adduct 3 was not obtained by the reaction in solution in toluene, and is supposed to be formed by highly selective trapping of the non-symmetrical monoadduct 4 from the anti-face by the second  $C_{60}$ molecule, which exists abundantly in the surroundings of 4 under the present solvent-free conditions. Thus, in this particular case, the present reaction conditions appear to be favorable for the trapping of the kinetic product.

The electrochemical measurement on the double  $C_{60}$  adduct **3** indicated that there is no appreciable through-space interaction between the two  $C_{60}$  cages within the molecule.

#### References

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