Stilbene-extended Trithienylmethanophanes: A Novel C_3-Symmetric Cage Molecule Capable of Accommodating an Organic Molecule As Well As Three Silver(I) Ions

Hiroyuki Kurata, Kenji Haruki, and Masaji Oda*
Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043

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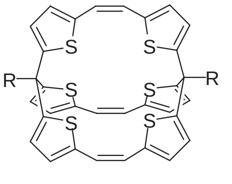
A combination of the Suzuki and the McMurry coupling on tris(5-bromo-2-thienyl)methanes leads to the title compounds which accommodate one *n*-hexane molecule or three silver(I) ions in the cavity.

"Host–Guest Chemistry" as well as "Supramolecular Chemistry" have been keen subjects in current organic chemistry.[1] Although a good number of three-dimensional host or container molecules have been developed,[2] those containing thiophene rings as main component have been rarely known.[3] We have recently reported the synthesis of novel etheno-bridged trithienylmethanophanes **1** that are composed of two tris(2-thienyl)methane units and three *cis*-etheno units.[4,5] X-ray analysis as well as a semi-empirical calculation revealed that the six sulfur atoms direct inside to form a three dimensional cavity surrounded by the sulfur atoms. However, attempted incorporation of metal ions into the cavity has been unsuccessful probably owing to too small cavity-size. Therefore, trithienylmethanophanes of larger sizes have been desired to examine host-ability of trithienylmethanophane systems. Methanophanes **1** were synthesized by a three-fold McMurry coupling of the precursor tris(5-formyl-2-thienyl)methanes. In view of easy functionalization of tris(2-thienyl)methane at 5-positions through lithiation or electrophilic aromatic substitution, this coupling approach would be also applicable to the synthesis of trithienylmethanophanes of larger sizes. Here we wish to report the synthesis of stilbene-extended trithienylmethanophanes **2a** and **2b** that are found to accommodate one *n*-hexane molecule as well as three silver ions in the cavity.



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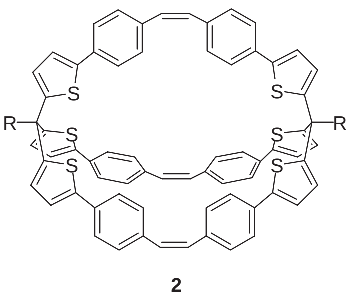

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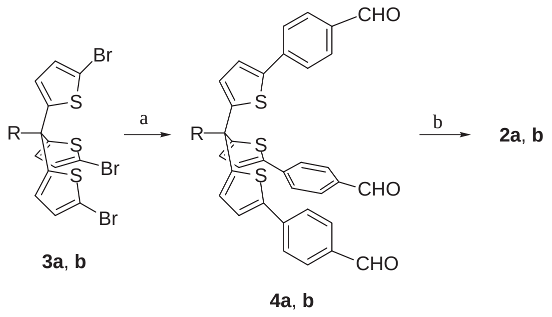
a: R = Me, **b**: R = Hex

Methanophanes **2a** and **2b** were synthesized as shown in Scheme 1 where the Suzuki coupling[6] and the McMurry coupling[7] are key reactions. The Suzuki couplings of tribromide **3a** with 4-formylphenylboronic acid gave trialdehyde **4a** in 93% yield and subsequent the McMurry coupling of **4a** afforded cage molecule **2a** in 17% yield. In similar way, **3b** furnished **2b** in 16% overall yield.



a) 4-formylphenylboronic acid, Pd(PPh_3)$_4$, K_2CO_3aq./DME, reflux, b) $TiCl_4$-Zn, CuI, DME, reflux

Scheme 1.

Both **2a** and **2b** are air-stable, pale yellow, crystalline substances.[8] While **2a** is poorly soluble in organic solvents and rather suitable for obtaining single crystals, **2b** is more soluble and suitable for NMR studies on complex formation. ^{1}H and ^{13}C NMR spectra of **2b** are fairly simple in agreement with D_{3h} symmetry of the molecule, exhibiting five kinds of aromatic and olefinic protons and nine kinds of sp^2 carbons except for the signals of the hexyl groups. The central six etheno protons are observed as a singlet (δ 6.57 in $CDCl_3$) and its ^{13}C satellite signals revealed the relevant coupling constants J(H–H) $= 11.7$ Hz and $J(^{13}\mathrm{C}$–H) $= 157.3$ Hz, the former value indicating all *cis*-geometry of the stilbene uints. Compound **2b** shows a strong but considerably broad absorption at 318 nm ($\log \varepsilon = 5.13$) in CH_2Cl_2 whose tailing reaches as long as 500 nm and is weakly fluorescent exhibiting an emission maximum at 468 nm (quantum yield: $\Phi = 0.03$).

Recrystallization of **2a** from chloroform-hexane afforded single crystals. X-ray crystallographic analysis of this crystal revealed that one hexane molecule is encapsulated in the cavity of every molecule of **2a**.[9] Figure 1a displays the molecular structure of the inclusion complex **2a**•Hex where the included hexane molecule is not very clearly seen owing to either disorder or rotation of hexane in the cavity. In the crystal, the complexes are tightly packed somewhat like three-toothed gears (Figure 1b). This tight packing should make it difficult escape of the included hexane molecule from the cavity and, in fact, the single crystal showed little sign of efflorescence in air at room temperature. Upon dissolution in $CDCl_3$, however, the complex seems to dissociate at least mostly into the components, because ^{1}H signals of the hexane were essentially the same as those of hexane alone in $CDCl_3$.

In addition, thienylmethanophane **2a** and **2b** were found to form complexes with silver(I) ions: for example, upon portionwise addition of silver(I) triflate to a $CDCl_3$ solution of **2b** in a NMR tube, the signals of aromatic and etheno protons continuously move downfield even up to addition of ten molar equivalents (in the presence of **2b**, the triflate dissolves in $CHCl_3$ fairly easily). Single crystals of the complex suitable for X-ray analysis

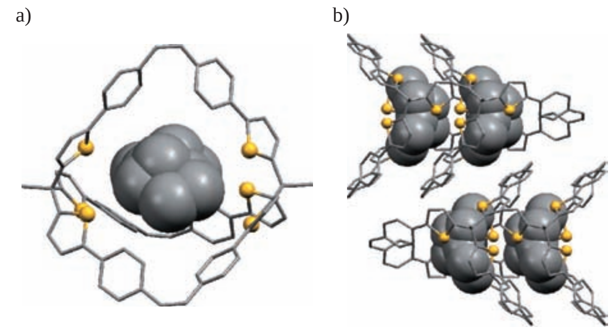


Figure 1. X-ray analysis of **2a**•Hex: a) molecular structure, b) crystal packing viewed along *a* axis. The included hexane molecule is drawn as space filling model, sulfur atoms of the host is represented in a yellow ball model. Hydrogen atoms are omitted for clarity.

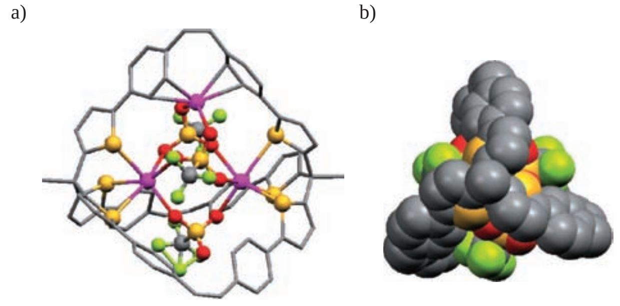


Figure 2. Molecular structure of **2a**•$3Ag^+$: a) side view; pink = Ag, red = O, green = F, yellow = S, gray = C; b) space-filling model viewed along pseudo C_3 axis. Hydrogen atoms are omitted for clarity.

were obtained by recrystallization from chloroform.[10] The crystals thus obtained were efflorescent and X-ray refraction data were collected more successfully on the complex of **2a** at −123 °C.[11] The X-ray analysis revealed that the complex of **2a** accommodates three Ag(I) ions (Figure 2a) and nine chloroform molecules are included in a unit cell. The co-existence of substantially large amount of chloroform made sufficient data collection difficult and therefore the final R-value was rather high value of 13%. Nevertheless, it is clear that there are included three silver(I) ions in the cavity. Two of the three Ag(I) ions seem coordinating to the sulfur atoms of each trithienylmethane units and third one to one of the stilbene units. The cavity size of **2a** is estimated to be approximately 5 × 5 × 5 Å and hence there should be enough room for more than three Ag(I) ions. Figure 2b shows the space filling description of the complex including the triflate ions. The three counter anions are each situated in the clefts between the three bridges of **2a**, which may control the number of included Ag(I) ion to three in spite of the greater room. The continuous down-field shift of ^{1}H NMR signals of **2b** even up to addition of ten molar equivalents of silver triflate may be due to either rather small association constant or complexation of Ag(I) ions also to the outside of host molecule.

Further studies on the host-ability of trithienylmethanopanes **2** and the synthesis of other relating cage molecules are under way.

References and Notes

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8 **2a**: Pale yellow crytals, mp > 330 °C (decomp.); MS (FAB): m/z 1081 $[(M + H)^+]$; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.42 (AA′BB′, 12H), 7.22 (d, $J = 3.8$ Hz, 6H), 7.17 (AA′BB′, 12H), 7.03 (d, $J = 3.8$ Hz, 6H), 6.54 (s, 6H), 2.36 (s, 6H); **2b**: Pale yellow crystals; mp 278–279 °C; MS (FAB) m/z 1222 (M^+); ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.38 (AA′BB′, 12H), 7.17 (d, $J = 3.8$ Hz, 6H), 7.13 (AA′BB′, 12H), 7.03 (d, $J = 3.8$ Hz, 6H), 6.57 (s, 6H), 2.62 (t, 4H), 1.26–1.41 (m, 16H), 0.87 (t, 6H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 152.18, 142.67, 136.13, 132.92, 129.99, 129.21, 126.62, 125.15, 121.95, 50.37, 42.40, 31.66, 29.96, 25.49, 22.74, 14.22; **2b**•$3Ag^+$: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.43 (AA′BB′, 12H), 7.24 (d, $J = 3.8$ Hz, 6H), 7.14 (AA′BB′, 12H), 7.07 (d, $J = 3.8$ Hz, 6H), 6.67 (s, 6H), 2.58 (t, 4H), 1.26–1.67 (m, 16H), 0.87 (t, 6H). (These data are obtained by dissolution of isolated complex in $CDCl_3$ and do not necessarily mean those of 1:3 complex in the solution.)

9 Crystal data: **2a**•Hex; $C_{76}H_{62}S_6$, M_r 1167.72, monoclinic, space group $C2/c$, $a = 26.343(4)$, $b = 11.391(1)$, $c = 20.226(3)$ Å, $\beta = 99.768(7)°$, $V = 5981(1)$ Å^3, $Z = 4$, $D_{calcd} = 1.297$ g/cm^{-3}, Mo Kα radiation ($\lambda = 0.71070$ Å), $T = 150$ K, $2\theta_{max} = 55.0°$, 30186 measured reflections, 6822 unique, $R_{int} = 0.067$, $R = 0.049$ ($I > 2\sigma(I)$), $wR = 0.105$.

10 The single crystals of **2**•$3Ag^+$ were obtained as follows: methanophane **2a** or **2b** were first stirred in THF in the presence of ca. 10 equiv. of silver triflates, the solvent evaporated, chloroform added to the residual white powders, undissolved solids filtered off, the solution concentrated and allowed to stand to deposit almost colorless prisms.

11 Crystal data: **2a**•$3Ag^+$: $C_{155}H_{109}Ag_6Cl_{27}F_{18}O_{18}S_{18}$, M_r 4783.05, triclinic, space group $P\bar{1}$, $a = 17.235(3)$, $b = 21.749(4)$, $c = 24.658(2)$ Å, $\alpha = 82.32(1)$, $\beta = 81.26(2)$, $\gamma = 85.50(1)°$, $V = 9037(2)$ Å^3, $Z = 2$, $D_{calcd} = 1.758$ g/cm^{-3}, Mo Kα radiation ($\lambda = 0.71070$ Å), $T = 150$ K, 40727 measured reflections, 12318 unique, $R_{int} = 0.092$, $R = 0.1304$ ($I > 2\sigma(I)$), $wR = 0.2367$.

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