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Communication

Silver(I) complex of 5,6,11,12-tetradehydrodibenzo[*a*,*e*]cyclooctene

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Abstract

The reaction of 5,6,11,12-tetradehydrodibenzo[*a*,*e*]cyclooctene with silver(I)triflate yielded a 1:2 complex. X-ray investigations revealed that each silver ion is tetrahedrally coordinated to one triple bond and three oxygen atoms of the triflate anion.

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1. Introduction

Examples of interactions of silver ions with olefinic π-systems are legion [1]. Much less data were available until 1980 for alkyne–silver(I) interactions [2]. Only very recently a number of studies broadened our knowledge of silver–alkyne complexes by applying ^{13}C NMR spectroscopy, IR- and Raman spectroscopy as well as X-ray investigations on single crystals [3–8]. The spectroscopic investigations indicated weak interactions between the metal and the triple bonds as evidenced by small high field shifts of the ^{13}C NMR data ($\Delta\delta \cong 1$–7 ppm) and a lowering of the stretching frequency of the triple bond by about 50–60 cm^{-1}.

In connection with our recent studies on silver triflates of cyclic and bicyclic diynes such as 1,6-cyclodecadiyne [4], 1,8-diazabicyclo[6,6,6]eicosa-4,11,17-triyne [7] and various 1,8-bridged 1,8-diazabicyclododeca-4,11-diynes [8] as well as investigations by Schulte and Behrens on seven membered cycloheptynes [6] we were interested to test the reaction of a highly strained diyne, 5,6,11,12-tetradehydrodibenzo[*a*,*e*]cyclooctene (**1**), with silver(I)triflate.

The diyne (**1**) was prepared according to Otera et al. [9] stirring a solution of **1** and silver(I) triflate in dry degassed tetrahydrofuran over a short period yielded a pale yellow powder (Scheme 1).

The analytical data show that a complex between **1** and 2 equiv. of silver(I) triflate was formed (Scheme 1). The ^{13}C NMR data revealed a small shift of the sp centers of **2** ($\delta = 104.5$ ppm) as compared to **1** ($\delta = 109.5$ ppm). The Raman frequency of the triple bonds changed from 2152 cm^{-1} (**1**) to 2057 cm^{-1} (**2**).

Single crystals of **2** could be obtained by recrystallization from acetone. In Table 1 we compare the most relevant bond lengths and bond angles of **2** with those of **1**.

In Fig. 1 we show the molecular unit of **2** and its ensemble in the solid state.

The comparison between **1** and **2** (Table 1) reveals a slight elongation of the triple bonds in the complex. The bond angles C(sp)–C(sp)–C(sp^2) in **2** decrease slightly. This indicates a weak complexation as reported in other cases [4–8]. The measured distance between the silver ion and the center of the triple bond (2.159(3) Å) is close to those distances reported for strained cyclic monoynes (2.10–2.20 Å) [6] and shorter than for nonstrained systems (2.30–2.70 Å) [3–5,7,8]. A lowering of the stretching vibration of the triple bond in **2** as compared to **1** is also another evidence for this interpretation.

In the solid state the silver(I) ions are coordinated tetrahedrally by three oxygen atoms and one triple bond [11]. Each trifluoromethanesulfonate anion coordinates three silver(I) ions with its three oxygen atoms. The silver

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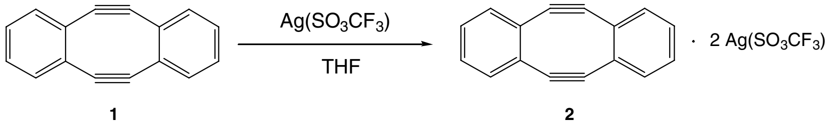

Scheme 1.

Table 1
Comparison between the most relevant bond distances (Å) and bond angles (°) of **1** and **2**

	1 [10]	**2**
C(sp)–C(sp)	1.202(2)	1.224(4)
C(sp)–C(sp^2)	1.445(2)	1.441(4)
Ag-π[a]		2.159(3)
Ag–O		2.307(2)
C(sp)–C(sp)–C(sp^2)	155.77(17)	155.6(3)

[a] Center of triple bond.

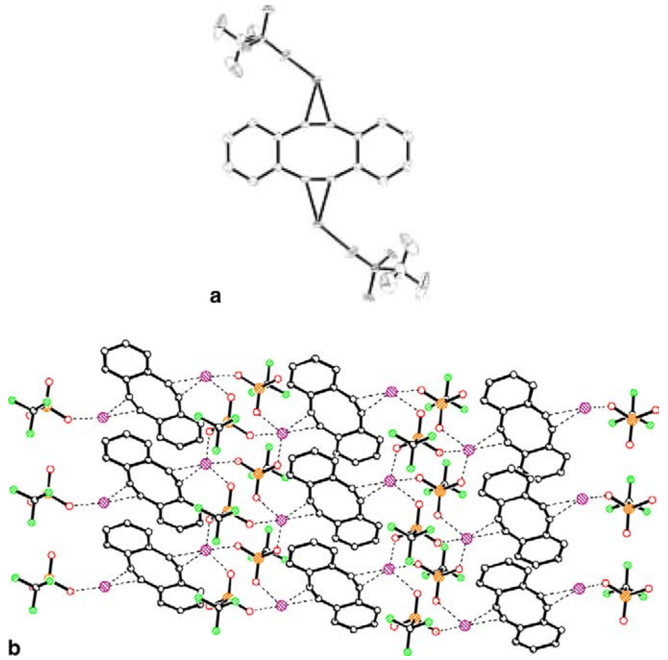

Fig. 1. (a) X-ray crystal structure of **2** (ORTEP-plot). The hydrogen atoms are omitted for the sake of clarity. (b) Section of the solid state structure of **2** (ORTEP-plot). The hydrogen atoms are omitted for the sake of clarity.

coordination results in one dimensional polymeric chains which are linked in *c*-direction to a two dimensional structure via the two triple bonds of the diynes.

2. Experimental

The reaction was carried out under argon in predried glassware using Schlenk techniques. THF was distilled over sodium and was transferred under argon. 5,6,11,12-Tetradehydrodibenzo[*a*,*e*]cyclooctene (**1**) was synthesized in four steps as published by Otera et al. [9]. Silver(I)trifluoromethanesulfonate was purchased from Acros. ^{1}H and ^{13}C NMR: Bruker Avance 500 (^{1}H at 500 MHz and ^{13}C at 125.77 MHz) using the solvent as internal standard. IR: Bruker Vector 22 FT-IR. UV: Hewlett-Packard HP 8452A. The elemental analysis was carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg.

2.1. Preparation of **2**

A 25-mL Schlenk flask was charged under argon with **1** (50 mg, 0.25 mmol) and degassed THF (15 mL). Silver(I)trifluoromethanesulfonate (65 mg, 0.25 mmol) was then added. While the mixture was stirred at room temperature under exclusion of light for 1 h, a pale yellow precipitate was slowly formed. The solvent was removed by filtration, the residue was washed three times with petrolether 30/40 and dried under vacuum yielding 79 mg of a pale yellow solid (44%) m.p. 248 °C (decomp.). ^{1}H NMR (500 MHz, acetone-d_6): $\delta = 6.95$–7.02 (m, 4H, H_{arom}), 7.15–7.21 (m, 4H, H_{arom}); ^{13}C NMR (125 MHz, acetone-d_6): $\delta = 104.5$ (C_{alkyne}), 128.5 (C_{arom}), 129.5 (C_{arom}), 130.8 (C_{arom}); IR (KBr): $\nu_{max} = 3450$, 3058, 2148, 1687, 1621, 1445, 1262, 1176, 1036 cm^{-1}; Raman: $\nu_{max} = 2057$, 1595 cm^{-1}; UV–Vis (ethanol): $\lambda_{max} = 226$ (log ε 3.97), 244 (log ε 3.87), 256 (log ε 4.37), 264 (log ε 4.37), 270 (log ε 4.77) nm. Anal. Calc. for $C_{18}H_8Ag_2F_6O_6S_2$: C, 30.28; H, 1.13; S, 8.98. Found: C, 30.74; H, 1.40; S, 9.09%.

Acknowledgements

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[11] Crystal Structure of **2**: dimensions $0.32 \times 0.12 \times 0.02\ \mathrm{mm}^3$, crystal system triclinic, space group $P\bar{1}$, $Z = 1$, $a = 5.1176(2)$ Å, $b = 10.7009(5)$ Å, $c = 10.8881(4)$ Å, $\alpha = 62.922(1)°$, $\beta = 86.174(1)°$, $\gamma = 87.051(1)°$, $V = 529.57(4)$ Å^3, $\rho = 2.239\ \mathrm{g\ cm}^{-3}$; $T = 200(2)$ K, $\theta_{\max} = 27.48°$, radiation Mo Kα, $\lambda = 0.71073$ Å, 0.3° omega-scans with CCD area detector, covering a whole sphere in reciprocal space; 5497 reflections measured, 2409 unique ($R_{\mathrm{int}} = 0.0298$), 2068 observed ($I > 2\sigma(I)$); intensities were corrected for Lorentz and polarization effects; an empirical absorption correction was applied using SADABS [12] based on the Laue symmetry of the reciprocal space, $\mu = 2.13\ \mathrm{mm}^{-1}$; structure solved by direct methods and refined against F^2 with a full-matrix least-squares algorithm using the SHELXTL-PLUS (5.10) software package [13]; 154 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.06 for observed reflections, final residual values $R_1(F) = 0.026$, $wR\ (F^2) = 0.060$ for observed reflections, residual electron density -0.51 to 0.93 e Å^{-3}. CCDC 284626 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrievin.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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