Articles

Bridged Silver(I) Complexes of the Polycyclic Aromatic Compounds Tetraphenylethylene and 1,1,4,4-Tetraphenyl-1,3-butadiene

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For the purpose of investigating the coordination behavior of the sterically congested alkenes and exploring the possibility of cofacial complexation in the polycyclic aromatic system for formation of extended polymeric networks, tetraphenylethylene (tphe) and 1,1,4,4-tetraphenyl-1,3-butadiene (tphb) have been studied with regard to their complexation with a silver(I) ion. The crystal structures of [Ag(tphe)(CIO₄)(*p*-xylene)], [Ag₂(tphe)(CIO₄)₂], [Ag₄(tphe)(CF₃SO₃)₄], [Ag₂(tphb)(CIO₄)₂], and [Ag₂(tphb)(CF₃SO₃)₂], together with the metal-free ligands tphe and tphb, have been determined by single-crystal X-ray diffraction. The π -electron-rich cleft in organic components is found to offer a potential site for complexation, which can be utilized to generate an interesting array of organometallic compounds with one- and two-dimensional frameworks.

Introduction

Transition-metal π complexes of polycyclic aromatic hydrocarbons exhibit stereochemical features of exceptional interest; examples are the conformational variability in silver complexes of planar aromatic compounds with a vast range of open frameworks and layered materials in which the ionic inorganic species is occluded within an organic framework.¹ It is the overall planarity of the organic components and the extended delocalized π system that have caused the current interest in the elaboration of the synthetic chemistry of metal ion-aromatic π -donor-acceptor complexes with possible applications in electrical conductors and photosensitive devices.²⁻⁴

Our interest in these compounds stems from the work involving transition-metal derivatives of highly anellated arenes such as pyrene,⁵ perylene,⁵ coronene,⁶ benzo[*ghi*]perylene,⁷ and

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naphtho[2,3-*a*]pyrene⁸ for their unique shape, size, and a number of closely spaced molecular orbitals. These organic species exhibit extraordinary abilities, combining good ligating property and perfect planarity concurrently interacting with metal ions above and below rings. We therefore wished to synthesize silver-(I) complexes of phenylated alkenes to explore the possibility of cofacial complexation of the cation– π complexes and to examine any unusual coordination and reactivity which these organic ligands might induce. For simplicity we have limited our initial work to the synthesis of silver derivatives of tetraphenylethylene (tphe) and 1,1,4,4-tetraphenyl-1,3-butadiene (tphb). The results of our study are reported herein.

Experimental Section

General Methods. All reactions and manipulations were carried out under an argon atmosphere by using usual Schlenk techniques. Solvents were dried and distilled by using standard methods prior to use. Highpurity argon was used to deoxygenate solvents. Reagent grade tphe and tphb were purchased from Tokyo Chemical Industry Co., Ltd., whereas silver(I) perchlorate and silver(I) trifluoromethanesulfonate were purchased from Aldrich. All other chemicals were purchased from Wako Pure Chemical, Inc. and used as received. The IR spectra were recorded as KBr disks on a JASCO FT-IR-8000 spectrometer, and ESR spectra, on a JEOL JES-TE200 ESR spectrometer.

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Table 1. Crystallographic Data for tphe, tphb, and Complexes 1-5

	tphe	tphb	1	2	3	4	5
formula	$C_{26}H_{20}$	$C_{28}H_{22}$	C ₃₄ H ₃₀ AgClO ₄	$C_{26}H_{20}Ag_2Cl_2O_8$	$C_{30}H_{20}Ag_4S_4F_{12}O_{12}\\$	$C_{28}H_{22}Ag_2Cl_2O_8$	$C_{30}H_{22}Ag_{2}S_{2}F_{6}O_{6}$
fw	332.44	358.48	645.93	747.08	1360.17	773.12	872.35
space	$P2_1$	$\overline{P1}$	$P2_1/n$	Pccn	C2/c	P1	C2/c
group							
<i>a</i> , Å	9.8234(8)	10.110(1)	12.345(3)	18.7791(6)	20.527(5)	8.220(2)	19.534(2)
b, Å	9.5014(9)	10.851(2)	9.253(3)	9.322(2)	10.028(1)	8.9164(2)	5.0005(7)
<i>c</i> , Å	10.7065(3)	9.820(2)	25.376(1)	14.8669(1)	18.905(1)	10.396(2)	30.962(1)
α, deg		103.64(1)				108.185(2)	
β , deg	107.0892(9)	94.95(1)	98.719(1)		94.257(1)	93.824(2)	91.861(1)
γ , deg		99.31(1)				112.033(5)	
$V, Å^3$	955.2(1)	1024.3(3)	2865.2(8)	2602.5(4)	3880.8(8)	656.3(2)	3022.8(5)
Ζ	2	2	4	4	4	1	4
T, °C	22	23	22	22	22	22	-150
λ(Mo Kα), Å	0.71069	0.71069	0.71069	0.71069	0.71069	0.71069	0.71069
ρ , g/cm ³	1.156	1.162	1.497	1.907	2.328	1.956	1.917
μ , cm ⁻¹	0.65	0.65	8.32	17.55	23.17	17.43	15.11
R_1^a	0.050	0.047	0.055	0.055	0.064	0.035	0.036
wR_2^b	0.161	0.138	0.090	0.166	0.162	0.068	0.10

 ${}^{a} \sum (|F_{o}| - |F_{c}|) / \sum |F_{o}|. {}^{b} [\sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o}^{2})^{2}]^{1/2}.$

Safety Note. Perchlorate salts of metal complexes with organic ligands are potentially explosive! Only small amounts of materials should be prepared, and these should be handled with great caution.

Synthesis of [Ag(tphe)(ClO₄)(*p***-xylene)] (1). To a** *p***-xylene solution (5 mL) containing silver perchlorate (20.7 mg, 0.1 mmol) was added tphe (33.2 mg, 0.1 mmol). The mixture was stirred for 10 min and filtered. A portion of the filtrate (3 mL) was transferred to a 7 mm diameter glass tube and gently layered with 3 mL of** *n***-pentane as a diffusion solvent. The glass tube, sealed under Ar and wrapped with aluminum foil, was left standing at room temperature for 2 weeks; colorless brick crystals of 1** were obtained (30 mg, 46%). Anal. Calcd for $C_{30}H_{25}AgClO_4$ (the formula with half solvent molecule): C, 60.78; H, 4.22. Found: C, 60.54; H, 4.20. Main IR bands (cm⁻¹): 3070(m), 1956(w), 1888(w), 1599(m), 1480(s), 1442(s), 1111(s), 680(s), 626-(s).

[Ag₂(tphe)(ClO₄)₂] (2). This compound was synthesized in a manner similar to that for 1 with 1,3,5-trimethylbenzene in place of *p*-xylene as the solvent. The yield was 43% (16 mg). Anal. Calcd for $C_{26}H_{20}$ -Ag₂Cl₂O₈: C, 41.76; H, 2.68. Found: C, 41.72; H, 2.71. Main IR bands (cm⁻¹): 3074(m), 2015(w), 1956(w), 1597(m), 1486(s), 1442(s), 1118-(s), 690(s), 630(s).

[Ag₄(tphe)(CF₃SO₃)₄] (3). To a 1,3,5-trimethylbenzene solution (10 mL) containing silver trifluoromethanesulfonate (51.4 mg, 0.2 mmol) was added tphe (33.2 mg, 0.1 mmol). The mixture was stirred for 10 min and filtered. A portion of the filtrate (3 mL) was transferred to a glass tube and layered with *n*-hexane as a diffusion solvent. The glass tube, sealed under Ar and wrapped with Al-foil, was left standing at room temperature for 2 weeks; colorless brick crystals of **3** were obtained (31 mg, 46%). Anal. Calcd for $C_{30}H_{20}Ag_4S_4F_{12}O_{12}$: C, 26.49; H, 1.47. Found: C, 26.53; H, 1.48. Main IR bands (cm⁻¹): 3076(m), 1956(w), 1894(w), 1599(m), 1480(s), 1442(s), 1269(s), 1182(s), 1035-(s), 695(s), 636(s).

[Ag₂(tphb)(ClO₄)₂] (4). To a solution of tphb (17.9 mg, 0.05 mmol) in 5 mL of 1,3,5-trimethylbenzene was added 20.7 mg of silver perchlorate (0.1 mmol). The mixture was stirred and filtered. A portion of the filtrate (3 mL) was transferred to a 7 mm diameter glass tube and layered with 3 mL of *n*-hexane as a diffusion solvent. The tube was sealed under Ar and wrapped with Al-foil, and after standing for 2 weeks at room temperature, yellow plate crystals of **4** were obtained (18 mg, 47%). Anal. Calcd for C₂₈H₂₂Ag₂Cl₂O₈: C, 43.50; H, 2.85. Found: C, 43.21; H, 2.56. Main IR bands (cm⁻¹): 3053(m), 1597(m), 1478(m), 1350(m), 1107(s), 730(s), 628(s).

[Ag₂(tphb)(CF₃SO₃)₂] (5). Yellow needle single crystals of 5 were synthesized in a manner similar to that for 4 with silver triflate in place of silver perchlorate. The yield was 60% (26 mg). Anal. Calcd for $C_{30}H_{22}Ag_2S_2F_6O_6$: C, 41.30; H, 2.52. Found: C, 41.04; H, 2.52. Main IR bands (cm⁻¹): 3053(m), 1599(m), 1436(w), 1352(m), 1265(s), 1142-(s), 1035(s), 698(s), 642(s).

X-ray Data Collection and Structure Solutions and Refinements. A suitable single crystal was mounted on a glass fiber, and diffraction data were collected at -150 °C for **5** and at room temperature for the rest on a Quantum charge-coupled device area detector coupled with a Rigaku AFC7 diffractometer with graphite monochromated Mo K α radiation. The $\omega/2\theta$ scan mode was employed, and stationary background counts were recorded on each side of the reflection, the ratio of peak counting time vs background counting time being 2:1. Weak reflections ($I < 10.0\sigma(I)$) were rescanned up to three times and counts accumulated to improve counting statistics. The intensities of three reflections were monitored regularly after measurement of 150 reflections and indicated crystal stability in all cases. Azimuthal scans of several reflections for each compound indicated no need for an absorption correction. All intensity data were corrected for Lorentz polarization effects.

The structures were solved by direct methods (MITHRIL⁹) followed by subsequent Fourier-difference calculation and refined by a full-matrix least-squares analysis on F^2 , using the TEXSAN package.¹⁰ All of the full-occupancy non-hydrogen atoms were refined anisotropically. Hydrogen atoms of all of the structures were introduced in their calculated positions; they were included, but not refined, in the refinement. The counteranions CIO_4^- were found to have high thermal motions in **1**, **2**, and **4**. Details of the X-ray experiments and crystal data are summarized in Table 1. Selected bond lengths and bond angles are given in Table 2.

Results

Crystal Structures of tphe and tphb. To gain an insight into cation— π interactions, the crystal structures of the metalfree ligands tphe and tphb were determined by X-ray analysis. Single crystals for both compounds were obtained by recrystallization of the sample in *n*-pentane. The infrared bands of tphe appear at 3074 cm⁻¹ (ν_{C-H}) and 1498 cm⁻¹ ($\nu_{C=C}$), whereas the corresponding bands for tphb fall into 3078 and 1450 cm⁻¹, respectively. Structure determination revealed that tphe possesses two sets of face-to-face or cofacial benzene rings around the central C=C bond, with dihedral angles between phenyl groups of 54.84 and 55.58°. For tphb, all of the four phenyl rings are twisted against the plane defined by the butadiene moiety with dihedral angles of 43.1, 47.3, 47.5, and 48.5°. We do not deal with any detailed structures here because their structural data are presented as Supporting Information. However, these

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes $1\!-\!5$

complex 1								
Ag-O(1)	2.394(7)	Ag-C(2)	2.519(5)					
Ag-C(3) Ag-C(27)	2.702(6) 2.533(6)	Ag = C(15) Ag = C(28)	2.602(5) 2.571(5)					
O(1)-Ag- $C(2)$	115.4(3)	O(1) - Ag - C(3)	87.8(3)					
O(1) - Ag - C(15)	83.2(3)	O(1) - Ag - C(27)	100.5(2)					
O(1) - Ag - C(28) C(2) - Ag - C(15)	122.3(2)	C(2) - Ag - C(3) C(2) - Ag - C(27)	30.5(2)					
C(2) - Ag - C(13) C(2) - Ag - C(28)	124.1(2) 111.6(2)	C(2) = Ag - C(27) C(3) = Ag - C(15)	108.8(2) 137.1(2)					
C(3) - Ag - C(27)	103.7(2)	C(3) - Ag - C(28)	122.8(2)					
C(15) - Ag - C(27) C(27) - Ag - C(28)	119.2(2) 31.4(2)	C(15) - Ag - C(28)	96.9(2)					
complex 2								
$A\sigma - O(1)$	2 389(6)	$A\sigma = O(3)$	2,536(8)					
Ag-C(1)	2.672(4)	Ag-C(2)	2.464(5)					
Ag-C(13)	2.506(5)							
O(1) - Ag - O(3)	78.6(2)	O(1) - Ag - C(1)	144.4(2)					
C(1)-Ag- $C(2)O(3)$ -Ag- $C(1)$	114.6(2) 113.7(1)	O(1) - Ag - C(13) O(3) - Ag - C(2)	99.3(2) 106.9(2)					
O(3) - Ag - C(13)	106.6(2)	C(1) - Ag - C(2)	30.9(1)					
C(1) - Ag - C(13)	107.9(2)	C(2) - Ag - C(13)	135.9(2)					
Complex 3								
Ag(1)-O(1)	2.343(4)	Ag(1) - O(3)	2.573(5)					
Ag(1) - O(4) Ag(1) - C(2)	2.470(5)	Ag(1) = O(5) Ag(1) = C(2)	2.570(4) 2.481(6)					
Ag(2) - O(2)	2.375(4)	Ag(2) - O(3)	2.587(5)					
Ag(2) - O(4)	2.521(5)	Ag(2) - O(6)	2.498(4)					
Ag(2) = C(8)	2.571(5)	Ag(2) = C(9)	2.442(6)					
O(1) - Ag(1) - O(3) O(1) - Ag(1) - O(5)	86.0(2)	O(1) - Ag(1) - O(4) O(1) - Ag(1) - C(1)	134.5(1)					
O(1) - Ag(1) - C(2)	129.6(2)	O(3) - Ag(1) - O(4)	75.2(2)					
O(3) - Ag(1) - O(5) O(3) - Ag(1) - C(2)	73.1(1)	O(3) - Ag(1) - C(1) O(4) - Ag(1) - O(5)	92.0(2) 126.9(2)					
O(3) Ag(1) C(2) O(4) - Ag(1) - C(1)	135.7(2)	O(4) - Ag(1) - O(3) O(4) - Ag(1) - C(2)	120.9(2)					
O(5) - Ag(1) - C(1)	86.9(2)	O(5) - Ag(1) - C(2)	119.8(2)					
C(1) - Ag(1) - C(2) O(2) - Ag(2) - O(4)	32.8(2) 81.9(2)	O(2) - Ag(2) - O(3) O(2) - Ag(2) - O(6)	129.0(1) 82.3(2)					
O(2) - Ag(2) - C(8)	123.2(2)	O(2) - Ag(2) - C(9)	130.0(2)					
O(3) - Ag(2) - O(4) O(3) - Ag(2) - C(8)	74.1(2)	O(3) - Ag(2) - O(6) O(3) - Ag(2) - C(0)	80.4(1)					
O(3) - Ag(2) - C(8) O(4) - Ag(2) - O(6)	103.9(1) 130.4(2)	O(3) - Ag(2) - C(3) O(4) - Ag(2) - C(8)	102.7(2)					
O(4) - Ag(2) - C(9)	131.5(2)	O(6) - Ag(2) - C(8)	125.1(2)					
O(6) - Ag(2) - C(9)	93.5(2)	C(8) - Ag(2) - C(9)	31.8(2)					
complex 4								
Ag-O(1) Ag-C(1)	2.358(3) 2.551(3)	$Ag=O(1^{\circ})$ Ag=C(2)	2.489(3) 2.447(3)					
Ag-C(10)	2.526(3)	Ag-C(11)	2.626(3)					
O(1)-Ag-O(1')	71.0(1)	O(1)-Ag-C(1)	112.3(1)					
O(1) - Ag - C(2)	106.0(1)	O(1) - Ag - C(10)	113.8(1)					
O(1) = Ag = C(11) O(1') = Ag = C(2)	143.2(1) 152.6(1)	O(1) - Ag - C(1) O(1') - Ag - C(10)	83.8(1)					
O(1') - Ag - C(11)	97.3(1)	C(1)-Ag- $C(2)$	32.72(9)					
C(1) - Ag - C(10)	132.59(9)	C(1) - Ag - C(11)	101.71(10)					
C(2) = Ag = C(10) C(10) = Ag = C(11)	31.46(10)	C(2) = Ag = C(11)	96.6(1)					
Ag-O(1)	2.418(3)	Ag-O(2)	2.417(3)					
Ag-O(3)	2.503(3)	Ag-O(3')	2.524(3)					
Ag-C(5)	2.413(3)	Ag-C(6)	2.598(4)					
O(1) - Ag - O(2) O(1) - Ag - O(3')	83.36(9) 128.33(0)	O(1) - Ag - O(3) O(1) - Ag - O(5)	78.22(9)					
O(1) - Ag - C(6)	132.2(1)	O(2) - Ag - O(3)	130.07(9)					
O(2)-Ag-O(3')	80.61(9)	O(2) - Ag - C(5)	127.1(1)					
O(2)-Ag-C(6) O(3)-Ag-C(5)	95.6(1) 101.8(1)	O(3) - Ag - O(3') O(3) - Ag - C(6)	75.7(1) 130.6(1)					
O(3') - Ag - C(5)	106.7(1)	O(3') - Ag - C(6)	98.2(1)					
C(5) - Ag - C(6)	32.1(1)							



Figure 1. Molecular structure and atom numbering of 1.

features are crucial in determining the overall structures of their metal complexes as presented below.

Characterization of the tphe Complexes 1, 2, and 3. Silver-(I) complexes of tphe-**1, 2,** and **3**—were prepared by the reaction of the appropriate starting material, $AgClO_4$ or $AgCF_3$ -SO₃, with tphe in *p*-xylene or 1,3,5-trimethylbenzene. All of the complexes were air-stable white crystals and found to be mildly light sensitive as solids and more sensitive in solution, thus samples were stored in the aluminum foil wrapped containers in a freezer.

The crystallographic studies revealed that 1 exists in the solid state as a simple mononuclear complex, albeit one with some unusual features. An ORTEP drawing of 1 with the atom numbering scheme is shown in Figure 1, which shows the tetrahedrally coordinated Ag(I) ion bonded to one tphe moiety, one *p*-xylene solvent molecule, and one perchlorate anion. The tphe interacts with the metal center in an η^1/η^2 fashion, and as anticipated, the silver ion is found in the cleft between the two phenyl rings, at Ag-C distances of 2.602(5), 2.519(5), and 2.702(6) Å, respectively. The coordination of *p*-xylene deserves some comment. Previously, the coordination of silver(I) toward m-xylene and o-xylene was reported by Amma and coworkers,11,12 and both complexes are found to be reasonably stable in the air and show an oxygen-bridged dimeric structure of bis(xylene)silver perchlorate. This work presents the first example of *p*-xylene coordinated to a metal ion in an η^2 , rather than η^1 , fashion as observed in the *m*- or *o*-xylene system. Although the Ag–C distances of 2.533(6) and 2.571(5) Å found in *p*-xylene are comparable with those in the other two xylene complexes, it should be noted that the coordinated *p*-xylene entities are gradually liberated in the absence of sufficient solvent vapor pressure primarily because of the volatility of the solvent. This gives rise to a little deviation of the elemental analysis from the calculated data (in fact, the measured C and H percentages are consistent with the calculated data on the basis of the formula having half of the *p*-xylene molecules).

By using 1,3,5-trimethylbenzene to replace *p*-xylene in the above reaction, a polynuclear complex **2** was isolated, whose molecular structure is given in Figure 2. In contrast with the coordination of *p*-xylene in **1**, the solvent molecule 1,3,5-trimethylbenzene does not have effective interaction with the metal ion in **2** presumably because of the three bulky methyl groups that block the metal ion from approaching the π electrons of the benzene rings. The structure of **2** features an ionic sheet

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⁽¹²⁾ Taylor, I. F., Jr.; Amma, E. L. Chem. Commun. 1970, 1442.



Figure 2. Molecular structure and atom numbering of 2.



Figure 3. Two-dimensional sheet structure and the schematic view of 2.

made up of Ag–OClO₂O–Ag chains separated by the aromatic groups as shown in Figure 3. The zigzag chains may be viewed as an alternating tetrahedral of the ClO₄⁻ ions and the four-coordinate Ag(I) ion sharing a common oxygen vertex, propagating along the *a* axis. Each aromatic group bridges two adjacent ionic chains by chelating one Ag in each cleft, giving a two-dimensional sheet network. Each silver atom acquires its usual coordination number of four by forming bonds with the π orbitals of two η^1/η^2 phenyl groups and two oxygen atoms of the different perchlorate anions. The Ag–C bond distances and bond angles are normal, Table 2, which do not deserve further comment.

Complex **3** was synthesized by the similar reaction to that for **2**, with AgCF₃SO₃ in place of AgClO₄ as the starting material. As in **2**, 1,3,5-trimethylbenzene is not involved in coordination with the metal ion. Despite similar reaction conditions and the same solvent employed, these two complexes exhibit significantly different crystallographic and structural features originated from the different bonding nature of the counterions. In **3**, there exist two crystallographically independent Ag(I) ions, Figure 4. The ionic sheet made up of Ag– CF₃SO₃–Ag chains is still maintained, in which the triflate ions involve an unusual tetradentate bonding fashion linking four metal ions, with Ag–O bond lengths ranging from 2.343(4) to 2.587(5) Å. Each silver atom in turn is coordinated to one phenyl group of the organic ligand and one oxygen atom of the four different tetradentate CF₃SO₃⁻ ions in a distorted square pyramid



Figure 4. Molecular structure and atom numbering of 3.



Figure 5. Two-dimensional sheet structure and the schematic view of 3.

geometry, with four oxygen atoms forming the base plane and the π interaction occupying the apex position. As a result, the Ag(1) and Ag(2) ions are bridged by four triflates to give a dinuclear unit with an Ag···Ag separation of 3.284 Å, Figure 5. Complex **3** is unusual in the sense that each tphe is interacting with four metal centers with each phenyl group η^2 -bonded to one metal ion, rather than cofacially binding the metal center in the cleft as observed in **1** and **2**.

IR spectroscopy indicated the presence of the appropriate counterion and the presence of ligands within the complexes. Typically, aromatic hydrocarbons in their transition-metal complexes can form charge-transfer species or even organic radicals depending on the degree of charge transfer in the ground state. At room temperature, no strong ESR spectrum was observed for **1** and **2**. On the contrary, **3** exhibited a well-resolved intense resonance at g = 2.0063, typical of aromatic hydrocarbon radicals.¹³ However, the spin density for the organic radicals, estimated from the comparison with the DPPH (diphenylpic-

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Figure 6. Molecular structure (a) and perspective view of infinite chain structure (b) in 4. Noncoordinating oxygen atoms of the perchlorate ions are omitted for clarity.

rylhydrazyl) standard, was less than 0.1%, so low that the ESR signal could be easily associated with an impurity. The attribution of the observed ESR signal is not immediately known.

Characterization of the tphb Complexes 4 and 5. Silver-(I) complexes of tphb, **4** and **5**, were prepared by the reaction of tphb with 2 molar equiv of appropriate metal salt in 1,3,5trimethylbenzene. Compounds **4** and **5** were both air stable yellow crystals and mildly light sensitive in the solid state. IR spectroscopy indicated the presence of the appropriate counterion and the presence of ligands within the complexes. At room temperature, no strong ESR spectrum was observed in either case.

The crystallographic studies revealed that complex **4** exists in the solid state as a one-dimensional polymer of silver(I) dimers. Figure 6 depicts a perspective view with atom numbering of the molecule. Each ClO_4^- anion bridges between two metal centers at Ag–O distances of 2.358(3) and 2.489(3) Å. The double-bridged dinuclear core Ag₂O₂ is thus formed with an Ag•••Ag separation of 3.946 Å. The polyhedron of metal coordination is completed to four by further interaction with π electrons of one phenyl group of two different tphb entities; in other words, each ligand group bridges between two adjacent ionic dinuclear cores with each phenyl ring η^2 -interacting with one metal center, giving rise to an alternate Ag₂O₂–aromatic– Ag₂O₂ sequential arrangement running along the *c* axis.

Figure 7 indicates a portion of the molecular structure of **5**, in which each silver(I) ion is coordinated to one oxygen atom of four separate triflates and one phenyl group of the tphb in a distorted square-based pyramidal geometry. As observed in **3**, each triflate ion is bonded to four metal centers, with Ag–O bond lengths ranging from 2.417(3) to 2.524(3) Å. The four O atoms defining the basal plane around the Ag ion deviates significantly from the mean plane by 0.28 Å. The apical coordination site is occupied by π electrons from one phenyl ring of the tphb at Ag–C bond distances of 2.413(3) and 2.598-(4) Å. Each tphb group uses only two of its four phenyl rings to link the nearby ionic chains, leading to a two-dimensional array of the metal ions. It is interesting to note that the two phenyl groups bound to Ag are almost coplanar to the butadiene moiety.



Figure 7. Molecular structure (a), perspective view of two-dimensional sheet structure (b), and the schematic view (c) in 5.

Discussion

Silver(I) complexes of tphe and tphb are easily prepared without elaborate syntheses, suggesting that the cation $-\pi$ interactions are favorable in most cases. However, the reactivity and the topology of the ensuing coordination networks are found to depend strongly on the counterion, solvent, and ligand geometry.¹⁴ Thus, understanding how these considerations affect metal coordination and influence crystal packing is at the heart of controlling coordination network assembly.

We have systematically studied the reactivity of silver(I) salts with tphe in different solvents. Benzene and its methylsubstituted species have long been suggested as the ideal media for preparation of the silver(I)– π complexes.^{1,5–8,11,12} However, our attempt to obtain silver(I) complexes of tphe in benzene or toluene failed because of the competitive complexation of the solvent molecule to Ag(I) ions over tphe.¹⁵ When such a reaction was carried out in *p*-xylene as discussed in the Experimental Section, a mononuclear 1:1 metal-to-tphe complex of **1** was isolated, which includes weakly bound solvent molecule. To explore the coordination network based on the ionic species and the sterically congested alkenes without involvement of the

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Scheme 1



solvent molecule, 1,3,5-trimethylbenzene was selected as the reaction media in the preparation of **2**–**5**. As we had proposed, 1,3,5-trimethylbenzene did not coordinate to Ag(I) because of the steric hindrance of the methyl groups, and the synthesized products turned out to be our expected alkene-based polymeric organometallic compounds. We infer from this result that the cation– π interaction in silver–tphe and silver–tphb systems is quite weak, and the related reactivity in solution is solvent dependent.

From the examples given, it becomes clear that large coordinating oxyanions such as NO_3^- , CIO_4^- , and $CF_3SO_3^-$ play a crucial role in stabilizing the silver(I) complexes and in the construction of the extended polynuclear system.^{1,16-19} In this work, silver perchlorate and silver triflate feature prominently as ionic chains or columns in silver– π networks, and in particular, the perchlorate coordinates in a variety of ways to the silver, such as terminal bonding to one metal as observed in **1** or bridging two metal centers by two or even one oxygen atom of the ion in **2** and **4**. The bonding diversity of the counterion leads to the final products as, respectively, a simple mononuclear, two-dimensional sheet, and one-dimensional infinite chain structures with different stoichiometries.

We have also used the triflate ion to argue the importance of a counterion in building silver $-\pi$ frameworks. Among the silver salts in hand, AgCF₃SO₃ is the most accessible, safe, and stable. The coordinative properties of the triflate ions have been reviewed.²⁰ The inertness and low nucleophilicity of the anion suggest that it can have a useful role as both indifferent anions and a relatively labile leaving group in inorganic chemistry. Apart from the purely ionic state there are several possible modes of bonding available to $CF_3SO_3^-$ in related silver(I) complexes. Scheme 1. It often acts as an uncoordinated or unidentate group,¹⁷ but sometimes shows bidentate behavior.^{18,19} The tridentate bridging of the triflate ion is rare but occurred in the silver(I) complex of naphtho [2,3-a] pyrene.⁸ This work presents the first example of a silver(I) complex involving tetradentate-bridging triflate ions. The average Ag-O bond distances of 2.49 and 2.47 Å found in 3 and 5, respectively, are normal and comparable with the documented data.8,17-19 The remarkable feature of the tetradentate bonding of CF₃SO₃⁻ observed in this work is that the ionic column of Ag-SO₃ generates an extended channel network consisting of alternating inner squares and outer octagons as shown in Figure 8. The

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Figure 8. Tetradentate bridging of four Ag ions by one triflate in 3 and 5 and created channel network consisting of inner squares and outer octagons.

Scheme 2



formation of such an ionic channel network may have profound influence on the stability of the synthesized products and on the packing of the organic components with particular conformation.

The final structures resulting from connection of the ionic chains by the aromatic groups also strongly depends on the detailed geometry and conformation of the hydrocarbons. Despite intensive interest in cation $-\pi$ interactions, only very few π complexes of the sterically congested alkenes have been reported in the literature.²¹ In previous studies of the silver(I) complexes of aromatics, attention was devoted to the planar, 1,5-7nonplanar,22 and linear hydrocarbons.8 They feature two aromatic planes sandwiching the ionic chain on both sides resulting in layered structures or act as linear bidentate ligands interacting with metal ions alternately in an infinite-chain fashion. In this work, we have examined the coordination chemistry of the phenylated alkenes. In sharp contrast with our recently reported silver(I) complex of 2,5-norbornadiene in which the aromatic moiety interacts with two metal centers via two double bonds of the olefin,²² the complexation of the central double bond is found to be prevented in tphe because of the steric hindrance of the four phenyl groups despite the expectation that it should be normally regarded as a preferred site of interaction. Schemes 2 and 3 illustrate the complexation sites and the least-squares plane calculation of tphe and tphb observed in complexes 1-5.

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Scheme 3



In fact, both tphe and tphb can offer opportunities for a wide variety of donor-acceptor interactions by twisting the benzene rings around the central C=C bond(s). They feature four equivalent benzene rings mutually or individually inclined to approach the metal centers. The least-squares plane calculation indicates that half of the tphe moiety is twisted against the other by 10.10° for the metal-free ligand. As the number of benzene rings bound to Ag increases from 1 to 3, the C=C twisting angles decreases to 8.35, 4.73, and 4.49°, respectively. The dihedral angles between phenyl groups in 1 (53.46 and 57.92°) and 2 (52.15°) are only slightly changed compared with the corresponding angles of 54.84 and 55.58° observed in the coordination-free tphe, indicating that the cleft formed by the two benzene rings in tphe is sterically suitable for chelating one metal ion. By contrast, the two dihedral angles of the tphe differ widely in 3 because of the absence of a cofacial interaction

with the silver atom. A similar case was observed in the tphb complexes 4 and 5, where each benzene ring π -interacts with one metal ion, and the dihedral angles between the butadiene and phenyl groups also differ significantly from those of the free ligand. This result is important in that it suggests that the π -electron-rich clefts in both tphe and tphb offer several complexation sites depending upon the countrions employed.

Conclusions

This work was part of the general research effort aimed at extending the range of cation $-\pi$ complexes by (i) designing and using new hydrocarbons, (ii) altering the reaction media, and (iii) changing the nature of the counterion in the organic/ inorganic hybrid networks. To establish whether the phenylated alkenes tphe and tphb did adopt extended frameworks as we had proposed, single-crystal X-ray diffraction studies were undertaken on certain examples. The structural characterization of five unprecedented organosilver(I) complexes shows that both organic compounds bind the metal ion through phenyl- π interactions rather than the olefin moiety. It also demonstrates the consequences of bringing aromatic rings into close range upon complexation of metal ions, that is, the extreme coordinative flexibility and variety. Nevertheless, the precise structural features of the cation $-\pi$ complexes formed are subtly dependent upon the ligand geometry and the conformation, solvent, and nature of the anion used. This finding is an interesting parallel to the recently reported coordination chemistry of silver(I) toward nitrogen donor ligands.^{14,16}

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determination of tphe, tphb, and 1-5. This material is available free of charge via the Internet at http://pubs.acs.org.

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