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Synthesis and Structure of a New Tetrakis(pentafluorophenyl)borate Salt of the Silver(I) Cation with Novel Trigonal Planar Tris(benzene) Coordination

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Summary: A new, analytically pure silver(I) salt, $Ag(C_6H_6)_3^+B(C_6F_5)_4^-$ *(**1**), was prepared, and its structure determined by single-crystal X-ray crystallography. The geometry around the silver atom in salt **1** is trigonal planar, which represents a novel coordination mode for a silver(I) coordinated with three independent arene molecules. The three benzene molecules are bound to the silver atom with estimated hapticities of* $\eta^{1.36}$, $\eta^{1.31}$, *and* $\eta^{1.44}$. *No contact was found between the silver cation and the* $B(C_6F_5)_4^-$ *anion.*

Introduction

Silver(I) and thallium(I) salts of a weakly coordinating anion[1] such as the tetrakis(pentafluorophenyl)borate anion ($TPFPB^-$),[2] as well as the carborane anion ($CB_{11}H_{12}^-$) and its derivatives,[3] are useful for generating reactive cationic species via halide-ion abstraction. While Tl^+TPFPB^- has recently been reported as a stable salt and has been shown to be useful for metathesis reactions,[4] Ag^+TPFPB^- is more difficult to handle without aromatic molecules coordinated to the silver ion. Thus, except for patents,[5] reports of Ag^+TPFPB^- are quite limited. To the best of our knowledge, this Ag^+ salt has been reported as a catalyst only in glycosylation[6] or Friedel−Crafts reactions,[7] and no X-ray structures of Ag^+TPFPB^- with aromatic ligands have been reported.[8] Here we report on the preparation of the $TPFPB^-$ salt of a new silver(I) complex, $Ag(C_6H_6)_3^+$-$TPFPB^-$ (**1**), and its X-ray structure, clearly demonstrating the presence of a silver ion coordinated with three benzene molecules in a trigonal planar fashion.

Results and Discussion

Treatment of Li^+TPFPB^- in diethyl ether with aqueous $AgNO_3$ at room temperature in the dark resulted in the formation of Ag^+TPFPB^-, which was isolated from the organic layer as a highly light-sensitive colorless solid. This solid was recrystallized from benzene to afford analytically pure $Ag(C_6H_6)_3^+TPFPB^-$ (**1**) in 83% yield as colorless crystals. The crystalline solid is nonhygroscopic and thermally stable at temperatures up to 138 °C and can be handled under air without any special precautions. It is also stable in the presence of ordinary light. The salt is moderately soluble in organic solvents such as diethyl ether, tetrahydrofuran, toluene, dichloromethane, and chloroform, while it is insoluble in hexane. No benzene molecule is released from the silver ion under reduced pressure (1×10^{-4} Torr, 24 h at room temperature), unlike $Ag^+CB_{11}H_{12}^-{\cdot}2C_6H_6$[9] and $Ag(C_6D_6)_3^+BF_4^-$.[10]

The molecular structure of **1**, determined by X-ray crystallography, is shown in Figure 1. The silver atom is bonded to three benzene molecules through one carbon atom of each benzene ring. The geometry around the silver atom is trigonal planar, as demonstrated by the C−Ag−C angles [C1−Ag−C7 = 119.7(2)°, C1−Ag−C13 = 122.4(2)°, and C7−Ag−C13 = 117.9(2)°], which are close to 120° and the sum of which is 360.0°. No significant distortion in the complexed benzene rings was observed [ΔR(C−C) < 0.045 Å, the sum of the internal angles = 720.0°]. The slight deviation from an equilateral hexagon can be attributed to packing effects, which are shown by a weak C−H···F contact (2.394 Å) between one of the coordinating benzene molecules and the anion. In contrast, the closest distance between the silver and fluorine atoms in $TPFPB^-$ is 3.70 Å, indicating the absence of any bonding interactions; for reference, the sum of the van der Waals radii of Ag and F is 3.19 Å.[11] The nearest Ag−C distances, 2.391(6) (Ag−

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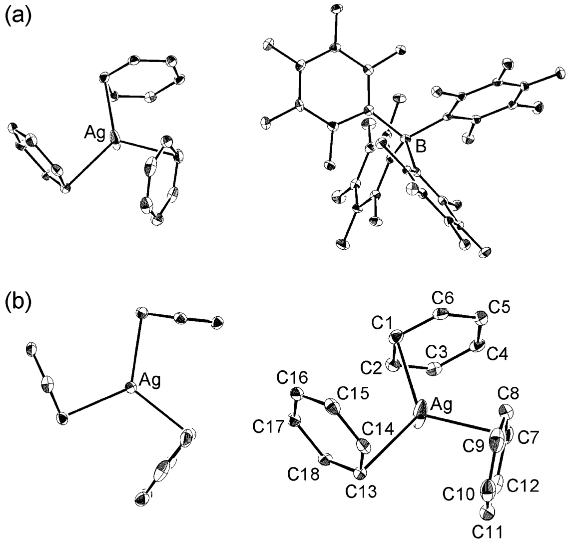

Figure 1. (a) ORTEP drawing of $Ag(C_6H_6)_3{}^+TPFPB^-$ (**1**). Hydrogen atoms are omitted for clarity. (b) Two additional views of the cation moiety. Selected bond lengths (Å): Ag−C1 = 2.391(6), Ag−C2 = 2.660(6), Ag−C7 = 2.398(7), Ag−C8 = 2.737(8), Ag−C13 = 2.400(6), Ag−C14 = 2.646(6). Selected angles (deg): C1−Ag−C7 = 119.7(2), C1−Ag−C13 = 122.4(2), C7−Ag−C13 = 117.9(2), C2−C1−Ag = 84.8(4), C6−C1−Ag = 93.1(4), C12−C7−Ag = 91.7(4), C8−C7−Ag = 88.2(4), C14−C13−Ag = 83.9(4), C18−C13−Ag = 92.2(4).

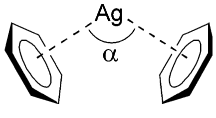

Figure 2. General representation of the "grab angle" α, which is defined as the angle between the normals to the planes of the benzene rings.

C1), 2.398(7) (Ag−C7), and 2.400(6) Å (Ag−C13), are compatible with that observed [2.400(7) Å] in the X-ray crystal structure of $Ag^+CB_{11}H_{12}{}^-\cdot 2C_6H_6$, which was reported as the first example of the η^1-coordination of carbon to silver.[9] The next closest Ag−C distances are 2.660(6) (Ag−C2), 2.737(8) (Ag−C8), and 2.646(6) Å (Ag−C14). The C2−C1−Ag, C8−C7−Ag, and C14−C13−Ag angles, 84.8(4)°, 88.2(4)°, and 83.9(4)°, respectively, are somewhat less than 90°, which would be expected for an ideal η^1-coordination. If the hapticity of coordination is estimated as η^x; $x = 1 + 2(d_1{}^2 - D^2)^{1/2}/[(d_1{}^2 - D^2)^{1/2} + (d_2{}^2 - D^2)^{1/2}]$,[12] where d_1 and d_2 are the closest and second closest Ag−C distances, respectively, and D is the distance between Ag and the mean plane of the benzene ring, the three coordinations are represented as $\eta^{1.36}$, $\eta^{1.31}$, and $\eta^{1.44}$, respectively.

On the basis of structural data for 40 examples of Ag(arene)$_2{}^+$ or Ag(arene)$_3{}^+$ complexes that have no chemical linkage between the coordinating arene molecules, Kochi et al. reported that the "grab angle" α (Figure 2) falls into three classes, 95°, 130°, and 155° (±3°), corresponding to the octahedral, tetrahedral, and linear hybridization of silver, respectively.[13] The α values observed for **1**, i.e., 119.2°, 121.4°, and 119.5°, belong to none of these classifications and are rather similar to the angles (∼120°) observed in Ag-cyclic polyarene complexes,[14] in which the silver atom adopts a trigonal pyramidal geometry. It is not usual for Ag^+ to form a trigonal planar complex.[15] Polymeric $Ag(CHPh_3)^+MeCB_{11}F_{11}{}^-$ is the only known example of such a complex that is coordinated with three aromatic rings,[15] and to our knowledge, **1** is the first reported trigonal planar Ag complex with three independent arene ligands.[16] This is in contrast to the reported structure of $Ag(C_6D_6)_3{}^+BF_4{}^-$, in which Ag^+ is coordinated in a tetrahedral fashion with three C_6D_6 molecules and one of the fluorine atoms of the $BF_4{}^-$ anion.[10]

Theoretical calculations[17] indicated that the differences in binding energy between the η^1- and η^2-coordinations are quite small (<0.5 kcal mol^{-1}) in silver-benzene complexes and that the silver ion can migrate on the entire π plane of benzene with virtually no activation barrier. Experimentally, η^1- and η^2-coordinations frequently coexist in the same crystal[13] and are sometimes observed even for the same silver atom.[10,18] In the present case, however, the silver atom is located above one of the carbon atoms of each benzene ring in a nearly η^1-fashion, where the electron density is the highest.[19] An η^2-type coordination was not observed, indicating the absence of π-back-donation from a filled d orbital of the silver atom to the π^* orbital of the arene. These results can be interpreted to indicate that the silver atom behaves simply as an electron acceptor, since the counteranion ($TPFPB^-$) has negligible electron-donating ability.

According to the theoretical considerations, it appears to be possible that the silver atom shows a fluxional behavior around the benzene ring in solution. In ^1H and ^{13}C NMR spectra of **1** in CD_2Cl_2, the benzene exhibited a single peak at δ 7.43 and 128.3,[20] respectively, at ambient temperature, indicating the very rapid migration of the silver atom through an η^1−η^2-type exchange or reversible dissociation. This interconversion is so fast that no signal splitting or line broadening was observed in spectra taken at −90 °C.

In conclusion, the facile synthesis and X-ray crystal structure of a silver(I) salt of $TPFPB^-$, **1**, is described. The silver ion has a trigonal planar geometry coordinated with three benzene molecules in a nearly η^1-fashion, which has not been reported to date. This salt is quite stable under air, and its distinct formula weight permits its use in accurate molar quantities in reactions. This suggests the utility of **1** as an excellent reagent for metatheses and for one-electron oxidations to form cationic species with a $TPFPB^-$ counteranion.[21,22]

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[20] ^1H and ^{13}C chemical shifts for benzene, under the same conditions, are δ 7.36 and 128.9, respectively.

Experimental Section

General Procedures. Commercially available reagents were of reagent-grade quality and were used as received. ^{1}H and ^{13}C NMR spectra were recorded using CD_2Cl_2 as the solvent at ambient temperature on a Varian Mercury-300 spectrometer and at −90 °C on a JEOL JNM-AL400 spectrometer.

Preparation of $Ag(C_6H_6)_3{}^+TPFPB^-$ (1). All procedures were carried out in the dark. To a stirred solution of $Li^+TPFPB^-\cdot(Et_2O)_{3.7}$[23] (0.170 g, 0.177 mmol) (Tokyo Chemical Industry Co., Ltd.) in diethyl ether (3 mL) was added dropwise a solution of $AgNO_3$ (71.8 mg, 0.42 mmol) in H_2O (5 mL) dropwise. After stirring the reaction mixture at room temperature for 15 min, the organic layer was separated and dried ($MgSO_4$), and the solvent was evaporated under vacuum. The resulting colorless solid was recrystallized from hot benzene (1.5 mL). The solution was let stand at room temperature for 24 h to give $Ag(C_6H_6)_3{}^+TPFPB^-$ (0.150 g, 0.147 mmol, 83%) as colorless crystals: mp 138 °C (dec); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.43 (s); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 148.8 (d, $^1J_{CF}$ = 243 Hz, C_{ortho}), 138.8 (d, $^1J_{CF}$ = 246 Hz, C_{para}), 136.9 (d, $^1J_{CF}$ = 241 Hz, C_{meta}), 128.3 (CH), 124.0 (C_{ipso}); IR (KBr, cm^{-1}) 1642, 1515, 1462, 1374, 1279, 1090, 979, 774, 770, 705, 684, 662. Anal. Calcd for $C_{42}H_{18}AgBF_{20}$: C, 49.40; H, 1.78. Found: C, 49.38; H, 1.73.

X-ray Crystallography. Intensity data were collected at 100 K on a Bruker SMART APEX diffractometer with Mo Kα radiation and a graphite monochromator. The structure was solved by direct methods (SHELXTL) and refined by full-matrix least-squares on F^2 (SHELXL-97). All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed using AFIX instructions. Crystal data for **1**: MF = $C_{42}H_{18}AgBF_{20}$: M_w = 1021.24, 0.2 × 0.2 × 0.2 mm^3, monoclinic, $C2/c$, a = 30.205(5) Å, b = 11.0645(19) Å, c = 23.910(4) Å, β = 113.694(3)°, Z = 8, V = 7317(2) Å^3, D_{calcd} = 1.854 g/cm^3, $2\theta_{max}$ = 50°, reflections: 18 648 collected, 6444 independent (R_{int} = 0.0485), 6444 observed, 631 parameters, R_1 = 0.0714, wR_2 = 0.1325, GOF = 1.031, largest difference peak and hole 2.695 and −3.926 e Å^{-3}, respectively (around Ag atom).

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra and complete details of the X-ray crystallographic studies of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Studies of the use of **1** in generating some unstable cations and radical cations are currently underway in our laboratory.

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