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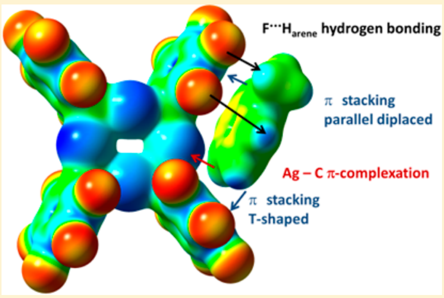
Pentafluorophenyl Silver: Structure and Bonding of Arene Solvates

Muhammad Farooq Ibad,[†] Axel Schulz,*[,†,‡] and Alexander Villinger[†]

[†]Institut für Chemie, Abteilung Anorganische Chemie, Universität Rostock, Albert-Einstein-Strasse 3a, 18059 Rostock, Germany
[‡]Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Strasse 29a, 18059 Rostock, Germany

S *Supporting Information*

ABSTRACT: The synthesis and full characterization of a series of AgC_6F_5·arene complexes (arene = RC_6H_5 with R = Me, Et; $R_2C_6H_4$, $R_3C_6H_3$, $R_4C_6H_2$, and R_5C_6H with R = Me) are presented. The structure and bonding are discussed on the basis of X-ray and theoretical studies with respect to the substitution pattern at the arene. Additionally, the structure of neat AgC_6F_5 and a facile way to generate crystals of pure AgC_6F_5 are reported.



INTRODUCTION

Pentafluorophenylsilver, AgC_6F_5, is a valuable starting material, e.g., for the introduction of a C_6F_5 group.[1−6] AgC_6F_5 was first isolated by Miller and Sun in 1970, when they treated silver trifluoroacetate, $AgCF_3COO$, with pentafluorophenyl lithium, LiC_6F_5 (Scheme 1).[1,7−9] Alternatively, AgC_6F_5 was obtained from the reaction of pentafluorophenyl bromide, C_6F_5Br, and perfluoroisopropylsilver, $Ag(CF_3)_2CF$.[1] Since acetonitrile was used in all these reactions, either as solvent or for recrystallization, it can be assumed that only the acetonitrile solvate was finally isolated, as was shown later by Tyrra and our group.[3,5] Another elegant approach for isolating AgC_6F_5 is the reaction of AgF with $Me_3Si(C_6F_5)$ again in donor solvents such as nitriles (Scheme 1), however, with the disadvantage of preparing $Me_3Si(C_6F_5)$ prior to that. Usually, AgC_6F_5 is isolated as an 1:1 adduct from nitriles. These adducts lose their donor at approximately 80−100 °C, and finally neat AgC_6F_5 decomposes at 274 °C.[3,5] As AgC_6F_5 dissolves only in polar solvents and is usually obtained from reactions in polar solvents, the structure of neat AgC_6F_5 is unknown. Already Tyrra speculated about the structure in 2002: "... polymeric especially tetrameric units can be assumed for donor-free AgC_6F_5."[3]

Scheme 1. Synthetic Routes to AgC_6F_5

(1) $Li(C_6F_5) + Ag(CF_3COO) \longrightarrow Ag(C_6F_5) + Li(CF_3COO)$

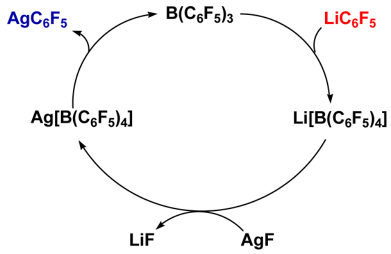
(2) $C_6F_5Br + Ag(CF(CF_3)_2) \longrightarrow Ag(C_6F_5) + (CF_3)_2CFBr$

(3) $NBu_4Ag(C_6F_5)_2 + AgClO_4 \longrightarrow 2\ Ag(C_6F_5) + NBu_4ClO_4$

(4) $M(C_6F_5)_2 + 2\ AgNO_3 \longrightarrow 2\ Ag(C_6F_5) + M(NO_3)_2$

(5) $AgF + Me_3Si(C_6F_5) \longrightarrow Ag(C_6F_5) + Me_3SiF$

Scheme 2. Formal Catalytic Cycle with $B(C_6F_5)_3$ as Catalyst in the Generation of AgC_6F_5



Recently, we reported on a two-step formal $B(C_6F_5)_3$-catalyzed reaction generating neat AgC_6F_5 in weakly coordinating solvents such as CH_2Cl_2 as illustrated in Scheme 2. It was shown that salt metathesis reaction of AgF and $Li[B(C_6F_5)_4]$ in CH_2Cl_2 under ultrasonic irradiation yielded in situ neat $Ag[B(C_6F_5)_4]$, which decomposed rapidly into AgC_6F_5 and $B(C_6F_5)_3$. The driving force of AgC_6F_5 formation is the instability of the solvent-free $Ag[B(C_6F_5)_4]$ intermediate. If the Ag^+ ion is not stabilized by a donor solvent as in easily accessible $Ag[B(C_6F_5)_4]\cdot n$ toluene ($n = 2, 3$) or $Ag[B(C_6F_5)_4]\cdot n Et_2O$ ($n = 1−3$), Ag^+ is a very strong Lewis acid, resulting in the abstraction of $C_6F_5^-$ from the $[B(C_6F_5)_4]^-$ ion, yielding AgC_6F_5 and $B(C_6F_5)_3$.[5]

The coordination chemistry of mono- and polynuclear arylsilver(I) complexes of the type AgR (e.g., R = C_6H_5, C_6F_5, C_6Cl_5, MeC_6H_4, $Me_2C_6H_3$, $(MeO)_2C_6H_3$), AgC_6F_5·L (L = EtCN), and Ag_2R_2·L has been studied;[8−16] however, examples of structurally characterized organosilver(I) complexes are still rare, appearing mostly as monomeric or tetrameric species in the solid state.[11,14−17] Diarylargentate complexes form monomeric ion pairs,[18] while $[AgC_6F_5]\cdot RCN$ (R = Me, Et) is the first example exhibiting an infinite chain.[3,5]

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A similar structural motif was found for the mixed silver−gold compound $[Ag(C_5H_5N)_3][Au(C_6F_5)_2]\cdot C_5H_5N$.[19]

Herein we report the synthesis and full characterization of a series of $[AgC_6F_5]\cdot$arene complexes (arene = RC_6H_5 with R = Me, Et; $R_2C_6H_4$, $R_3C_6H_3$, $R_4C_6H_2$, and R_5C_6H with R = Me). Additionally, we present the unprecedented solid-state structure of AgC_6F_5 and a facile way to generate crystals of neat AgC_6F_5.

■ RESULTS AND DISCUSSION

1. Synthesis. *Neat AgC_6F_5.* As illustrated in Scheme 2,[5] solvent-free, pure AgC_6F_5 was obtained from $Li[B(C_6F_5)_4]$ and AgF, which were first combined and suspended in dichloromethane prior to sonification in an ultrasonic bath at 40−60 °C for 8 h. The resulting grayish suspension was filtered, resulting in a clear, brownish solution. Removal of CH_2Cl_2 followed by extraction of $B(C_6F_5)_3$ by washing with *n*-hexane yielded an off-white solid AgC_6F_5 (yield: 90%, T_{dec} = 276 °C). With pure AgC_6F_5 in hand, we were able to study the solvation of AgC_6F_5 in differently substituted arenes (arene = benzene (**b**), toluene (**tol**), ethylbenzene (**eb**), 1,2-dimethylbenzene (**12dm**), 1,3-dimethylbenzene (**13dm**), 1,4-dimethylbenzene (**14dm**), 1,2,3-trimethylbenzene (**123tm**), 1,2,4-trimethylbenzene (**124tm**), 1,3,5-trimethylbenzene (**135tm**), 1,2,3,5-tetramethylbenzene (**1235tem**), 1,2,4,5-tetramethylbenzene (**1245tem**), 1,2,3,4,5-pentamethylbenzene (**12345 pm**).

$(AgC_6F_5)_4\cdot n$ arene. Neat pentafluorophenylsilver, AgC_6F_5, was suspended in a minimum of the corresponding benzene derivative (see above) at ambient temperatures (Scheme 3). The mixture was stirred for 30 min, followed by gently heating to 80 °C, until a clear, colorless solution was obtained. Slow cooling to ambient temperatures over a period of 1 h resulted in the deposition of colorless crystals or a precipitate (in the case of benzene and toluene). Removal of excess arene by decantation and drying in vacuo gave the corresponding tetrakis(pentafluorophenylsilver) arene adduct, $(AgC_6F_5)_4\cdot n$ arene (n = 1, 2, or 4; arene = toluene, ethylbenzene, 1,2-dimethylbenzene, 1,3-dimethylbenzene, 1,4-dimethylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene), as a colorless solid in good yields (40−80%). For the tetra- and pentamethylbenzenes (arene = 1,2,3,5-tetramethylbenzene, 1,2,4,5-tetramethylbenzene, 1,2,3,4,5-pentamethylbenzene), a slightly different procedure was applied. Neat AgC_6F_5 was also suspended and stirred in the corresponding arene, however for 3 h at 60−80 °C, under reduced pressure (10^{-3} mbar). The mixture was slowly cooled to ambient temperature over a period of 30 min. The resulting solid was filtered and washed three times by repeated back distillation with *n*-hexane.

Scheme 3. Synthesis of Tetrameric $(AgC_6F_5)_4\cdot n$arene Solvates

$$4\ AgC_6F_5 \xrightarrow[\substack{\text{r.t. to 80°C} \\ n\,=\,1,\,2,\,4}]{\text{excess arene}} (AgC_6F_5)_4\cdot n\ \text{arene}$$

Interestingly, both synthetical protocols did not work for the preparation of the arene adducts $(AgC_6F_5)_4\cdot n$ arene (arene = *n*-propyl benzene, isopropyl benzene, hexamethylbenzene). In all these cases no adduct formation was observed since only the starting material, pure AgC_6F_5, could be crystallized. To our surprise, these reactions can be utilized to generate colorless single crystals of AgC_6F_5 (40−80% yield) suitable for X-ray elucidation (see below).

Once the crystalline material is isolated from the solvent, all $(AgC_6F_5)_4\cdot n$ arene adducts tend to easily lose solvent molecules, which can be enhanced by drying under reduced pressure. For this reason, all investigated materials were dried to mass constancy to obtain correct elemental analysis data and melting points or decomposition points. By this procedure, $(AgC_6F_5)_4\cdot 2$ arene (arene = benzene, toluene, ethylbenzene, 1,3-dimethylbenzene, 1,2,3,4,5-pentamethylbenzene) lose one solvent molecule, or $(AgC_6F_5)_4\cdot 4$ arene (arene = 1,2 dimethylbenzene, 1,2,4-trimethylbenzene) even lose two solvent molecules. Solvent-free polymeric AgC_6F_5 decomposes at 276 °C, while tetrameric $(AgC_6F_5)_4\cdot n$ arene adducts melt and/or decompose between 77 and 155 °C (see the SI), clearly displaying a smaller thermal stability.

Table 1. Selected NMR and Structural Data of $(AgC_6F_5)_4\cdot$arene Complexes (δ in ppm, d in Å) along with Computed Charges (in e)[a]

	$\Delta\delta[^1H]_{av}$[b]	$\Delta\delta[^{13}C]_{av}$[b]	$\eta(\pi)$[g]	$d_s(Ag-C_{arene})$[d]	$d_{av}(Ag-C_{arene})$[d]	$d_{av}(Ag-Ag)$[d]	$q_{av}(Ag)$[c]	$Q_{ct,arene}$[c]
$(AgC_6F_5)_n$						2.806		
$[Ag]_4\cdot$**2b**	0.28	0.3	[e]	[e]	[e]	[e]	[e]	[e]
$[Ag]_4\cdot$**2tol**	0.13	0.1	2	2.934(5)	3.707	2.771	0.586	0.026
$[Ag]_4\cdot$**2eb**	0.22	0.3	2, 3	2.962(1)	3.672	2.766	0.592	0.023
$[Ag]_4\cdot$**412dm**	0.25	0.3	3	2.665(2)	3.512	2.768	0.026	0.027
$[Ag]_4\cdot$**213dm**	0.28	0.6	3	2.751(2)	3.462	2.771	0.600	0.028
$[Ag]_4\cdot$**214dm**	0.26	0.3	2	2.946(2)	3.560	2.767	0.594	0.027
$[Ag]_4\cdot$**4123tm**	0.21	0.3	2, 3	2.591(3)	3.512	2.776	0.600	0.030
$[Ag]_4\cdot$**2124tm** (A)	0.15	0.3	3	2.76(1)	3.406	2.798	0.597	0.027
$[Ag]_4\cdot$**4124tm** (B)	0.15	0.3	3	2.776(3)	3.527	2.775	0.595	0.027
$[Ag]_4\cdot$ **2135tm**	0.25	0.3	2	2.746(2)	3.533	2.777	0.629	0.024
$[Ag]_4\cdot$**21235tem**	0.02	0.2	3	2.780(2)	3.503	2.788	0.600	0.039
$[Ag]_4\cdot$**1245tem**	−0.01	0.0	[e]	[e]	[e]	[e]	[e]	[e]
$[Ag]_4\cdot$**212345 pm**[f]	0.16	0.0	3	2.454(3)	3.177	2.761	0.622	0.029

[a] $[Ag]_4 = (AgC_6F_5)_4$, dm = dimethyl, tm = trimethyl, tem = tetramethyl, pm = pentamethyl. [b] $\Delta\delta = \delta$(neat arene) − δ(complex) in ppm, av = average values, exact values are given in Table S19 of the SI. [c] q and Q_{CT} in e. [d] s = shortest, av = average, exact values in Tables S17 and S18. [e] Crystalline material was obtained, however not suitable for X-ray elucidation. [f] *n*-Hexane solvate. [g] $\eta(\pi)$ = number of all $d(Ag-C_{arene})$ < 3.5 Å (cf. $\sum r_{vdW}(Ag\cdots C)$ = 3.42 Å).

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Solution ^{1}H and ^{13}C NMR data revealed for $(AgC_6F_5)_4{\cdot}n$ arene (up to triple substitution at the arene) stable adducts (with bound arenes) even in CD_2Cl_2 solution as illustrated by the $\Delta\delta = \delta$(free arene) − δ(bound arene) values in Table 1 (see also Table S19), while for the 4- and 5-fold-substituted arenes only very weak arene interactions were detected.

2. Structure and Bonding. Crystals suitable for X-ray crystallographic analysis were obtained either directly from the saturated solution of AgC_6F_5 dissolved in the corresponding arene at low temperature (usually 5 °C) or by cooling a saturated dichloromethane solution to 5 °C. In the case of 1,2,3,4,5-pentamethylbenzene, crystals suitable for X-ray crystallographic analysis were obtained from the saturated reaction solution after addition of *n*-hexane, leading to $(AgC_6F_5)_4{\cdot}2$ (1,2,3,4,5-pentamethylbenzene) *n*-hexane solvate. Astonishingly, when AgC_6F_5 was treated with 1,2,4-trimethylbenzene, depending on the crystallization conditions, either crystals of $(AgC_6F_5)_4{\cdot}4$(1,2,4,-trimethylbenzene) or the disolvate $(AgC_6F_5)_4{\cdot}2$(1,2,4-trimethylbenzene) could be obtained; that is, formation of the disolvate is favored at higher temperatures and concentration. All crystals were selected in Fomblin YR-1800 perfluoroether at ambient temperature. The samples were cooled to 173(2) K during measurement.

Structure of Neat AgC_6F_5. $^{1}_{\infty}\{AgC_6F_5\}$[20] crystallizes in the orthorhombic space group *Cmcm* with four formula units per cell. Each Ag^+ ion is surrounded by two bridging $C_6F_5^-$ ligands with μ_2-bound carbon atoms in a linear arrangement as displayed by the C1−Ag1−C1′ angle of 180.0°, in contrast to the situation found in $^{1}_{\infty}\{AgC_6F_5{\cdot}CH_3CN\}$ with alternating bent (138.7°) and linear arrangements.[3,5] As depicted in Figure 1, a one-dimensional infinite Ag−C zigzag chain[21] is formed in the crystal along the *c*-axis with bent Ag−C−Ag′ (79.4°) moieties and equal Ag−C bond lengths of 2.195(3) Å (cf. 2.147(2) and 2.128(5) Å in $AgC_6F_5{\cdot}RCN$, R = Me, Et).[3,5] Looking along the *c*-axis, all C_6F_5 rings are found eclipsed to each other, and a straight chain of equidistantly arranged Ag^+ ions with Ag···Ag distances of 2.8058(2) Å (cf. 2.89 Å in Ag metal) is recognized. Hence, in addition to the Ag−C coordination, as depicted in Figure 1, Ag···Ag ($d^{10}-d^{10}$) interactions[22] must be considered, as the Ag···Ag distances are significantly shorter than the sum of van der Waals radii of two silver atoms (cf. $\sum r_{vdW}$(Ag···Ag) = 3.44 Å)[23] and are comparable to those found in other structurally characterized Ag complexes.[24] Commonly, arylsilver and perfluoroalkenylsilver are tetrameric in the solid state, while diaryl argentates are build up from separated ion pairs.[21,22,25−39] With bridging C_6F_5 units, infinite chains were also observed in the unit cell of $AgC_6F_5{\cdot}RCN$ (R = Me, Et),[3,5] although most silver compounds with a bridging aryl ligand prefer to form polynuclear complexes. Interestingly, a molecular $Ag_4(C_6F_5)_4$ moiety with a Ag_4 zigzag chain (Ag−Ag distances: 2.7264(5), 3.0627(7) Å) was observed by Fu and Zhu et al. embedded between two germylene units.[40] In contrast to AgC_6F_5, the lighter congener base-free CuC_6F_5 forms a tetramer with bridging C_6F_5 moieties and short Cu···Cu distances.[41] Strong Ag···π_{arene} as well as Ag···Ag interactions have also been observed in a series of trinuclear silver(I) complexes of fluorinated pyrazolates displaying extended columnar structures.[42−44] Trinuclear mercury complexes with extensive π_{arene} interactions are also known.[45,46]

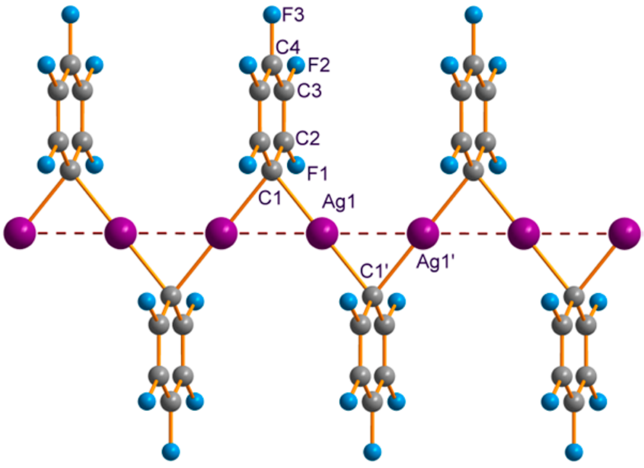


Figure 1. Ag−C zigzag chains along the *c*-axis in the crystal of $^{1}_{\infty}\{AgC_6F_5\}$ (view along the *a*-axis). Selected distances in Å, angles in deg: Ag1−C1 2.195(3), Ag1−C1′ 2.195(3), Ag1···Ag1′ 2.8058(2); C1′−Ag1−C1 180.0(1), C1−Ag1−Ag1′ 129.72(6), Ag1′−Ag1−Ag1″ 180.0, Ag1−C1′−Ag1′ 79.5(1).

Structure of $(AgC_6F_5)_4{\cdot}n$ arene Adducts. With respect to the space groups, number of formula units, and bonding situation of the arene, there are no clear trends to be detected (see Tables S17 and S18). However, in contrast to neat $^{1}_{\infty}\{AgC_6F_5\}$, upon coordination of arene molecules, no one-dimensional Ag−C zigzag chains are formed but in all cases tetrameric $(AgC_6F_5)_4{\cdot}n$ arene molecular units as depicted in Figure 2. Interestingly, Ag^+-C_{arene} π-complexation[47,48] of all arene molecules is not observed in all cases. For example, in $(AgC_6F_5)_4{\cdot}2$ toluene only one toluene molecule is bound to one Ag^+ center in a formal η^2-coordination mode (Figure 2), while the other one can be regarded as crystal solvent without significantly interacting with Ag^+ ions (all $d(Ag-C_{arene}) > 3.5$ Å). A similar situation is found in $(AgC_6F_5)_4{\cdot}2$ arene (arene = ethylbenzene and 1,4-dimethylbenzene, Figure 3). Since it is rather difficult to give correct connectivities (hapticities) of asymmetrically coordinated arenes, we have used the number of $d(Ag-C_{arene}) < 3.5$ Å contacts as criterion (cf. $\sum r_{vdW}$(Ag···C) = 3.42 Å), leading to hapticity values ranging between 2 and 3 (Table 1).[49] It seems to be interesting to have a look at the trends of the shortest and average distances, $d_s(Ag{\cdots}C_{arene})$ and $d_{av}(Ag{\cdots}C_{arene})$, respectively (Table 1). As can be derived from these data, the larger the degree of substitution, the shorter the $d_s(Ag{\cdots}C_{arene})$ value, ranging from 2.45 (1,2,3,4,5-pentamethylbenzene) to 2.96 Å (ethylbenzene), and the average $d_{av}(Ag{\cdots}C_{arene})$ value is from 3.17 to 3.71 Å, respectively. Interestingly, the average Ag···Ag distances, ranging between 2.76 and 2.79 Å are not sensitive to the number of coordinated arenes nor the degree of substitution, but they are significantly shortened compared to the value of 2.806 Å in neat $^{1}_{\infty}\{AgC_6F_5\}$ (vide supra).

As illustrated in Figures 2−4, there are different ways to divide and classify the $(AgC_6F_5)_4{\cdot}n$ arene adducts discussed here: (i) With respect to the number of π-coordinated arene molecules, we observed mono, double, and 4-fold adduct formation. Interestingly, for **124tm** we found double and 4-fold adduct formation (species A and B, Figures 2 and 3, Table 1). In the case of double adduct formation, the arene always forms adduct bonds with opposite Ag^+ ions of the tetrameric unit (Ag1 and Ag3 complexation). (ii) The arene can feature one donor−acceptor interaction to one Ag^+ ion of one tetrameric unit or can even act as a bridging ligand between two tetrameric units, leading to (−Ag_4−arene−Ag_4−) chains in the crystal (Figure 3). The latter is often the case when only one arene

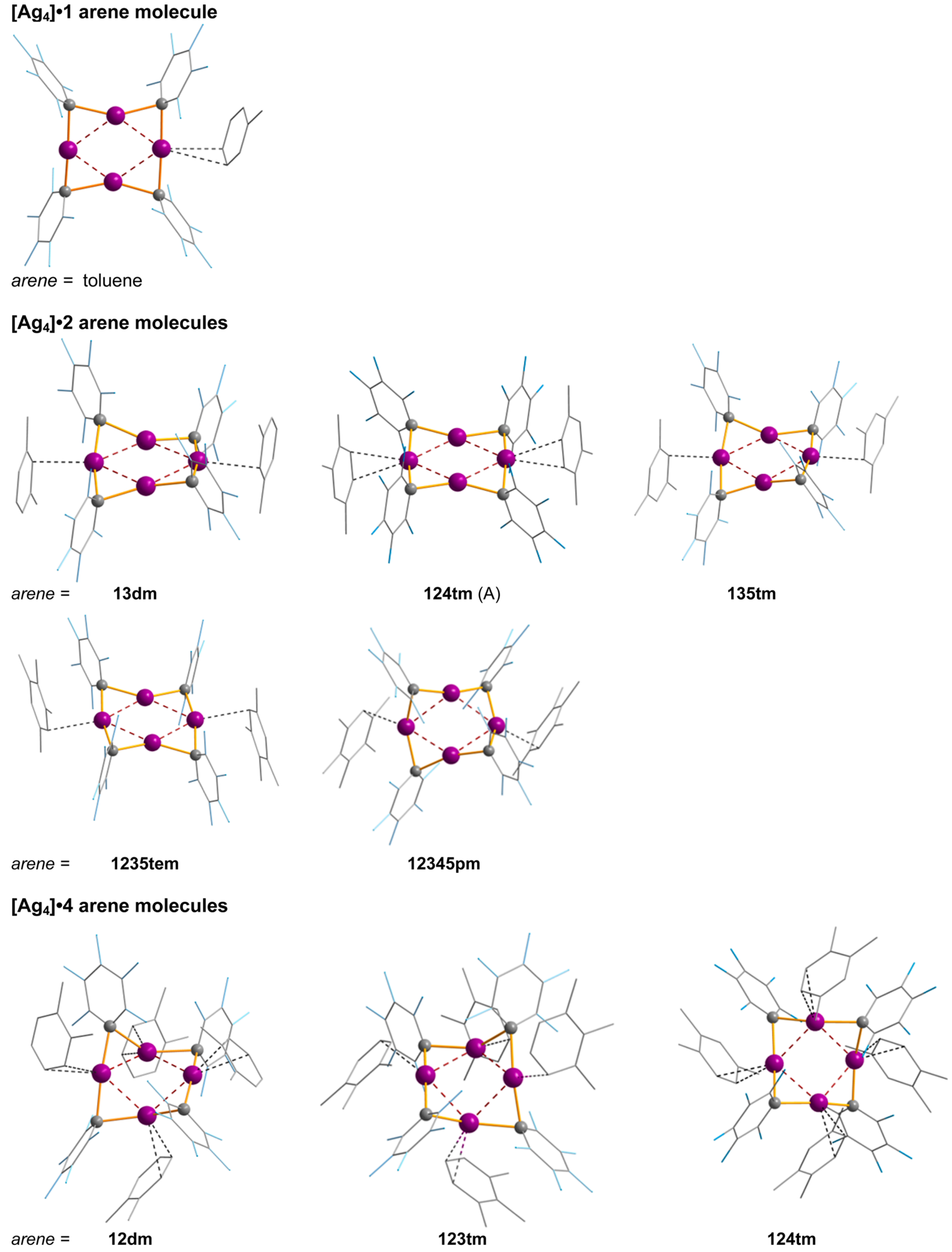
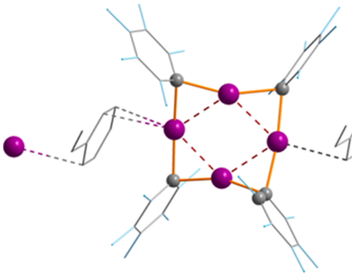
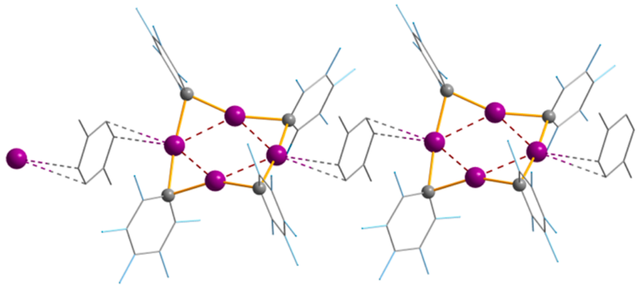


Figure 2. Molecular structures of $(AgC_6F_5)_4 \cdot n$ arene adducts with molecular units (Ag violet, C gray).

molecule acts as a donor solvent (arene = **eb**, **14dm**) with relatively small Ag···C distances (<3.42 Å). In these cases, the second arene molecule always serves as crystal solvent species with distances to the tetramer considerably larger than the sum



arene = **eb**



arene = **14dme**

Figure 3. Molecular structures of $(AgC_6F_5)_4{\cdot}n$ arene adducts with one-dimensional ($-Ag_4-$arene$-Ag_4-$) chains in the crystals (Ag violet, C gray).

of the van der Waals radii (cf. $\sum r_{vdW}(Ag{\cdots}C)$ = 3.42 Å). It should be noted that these solvent molecules are easily released, e.g., under reduced pressure or with time outside the solvent under normal pressure. Such ($-M_4-$arene$-M_4-$) chains have also been observed by Jäkle et al. for the lighter congener copper with arenes such as naphthalene or 2,2′-bithiophene displaying $Cu{\cdots}\pi_{arene}$ and Cu⋯S interactions.[50] (iii) The most prominent structural motif is the eight-membered Ag_4C_4 heterocycle of the tetrameric unit (Figures 2–4), which, however, can feature three different structural modifications with respect to the planarity of the Ag_4 and/or C_4 moiety (Figure 4). A planar Ag_4C_4 ring is formed for adducts of **tol**, **124tm** (structure A) and **1235tem** with planar Ag_4 and C_4 units, while for $(AgC_6F_5)_4{\cdot}n$ arene (arene = **eb**, **13dm**, **14dm**, and **135tm**) it forms a folded C_4 ring, whereas the Ag_4 ring remains planar. Finally, a puckered eight-membered Ag_4C_4 ring is observed for arene = **12dm**, **123tm**, **124** (structure B), and **12345 pm**. There seems to be no clear correlation between the planarity/nonplanarity of the eight-membered ring and the degree of substitution or the substitution pattern. Moreover, the Ag_4C_4 eight-membered ring is highly flexible with respect to the arrangement of the C_6F_5 rings, especially if van der Waals interactions with arene molecules can be formed (vide infra, Figures 4 and S2).

It should be noted that computations at the B3LYP/6-31G(d,p)[51] level of theory for $(AgC_6F_5)_4$ (without arene solvate molecules) display only the planar eight-membered ring as a minimum structure at a very flat (with respect to nonplanarity) potential energy surface. Thus, it can be assumed that small changes in the environment of the tetrameric unit can result in a large effect on the arrangement of the Ag_4C_4 heterocycle in accord with experimental observations.

Let us finally tackle the question of why upon coordination of arene molecules in ${}^1_\infty\{AgC_6F_5\}$ the one-dimensional Ag–C zigzag chains are transformed into tetrameric $(AgC_6F_5)_4{\cdot}n$ arene molecular units. Obviously, lots of weak interactions of the arenes with the AgC_6F_5 moieties favor the formation of tetramers rather than chains. A closer look at these weak interactions revealed a large number of different types of van der Waals interactions: (i) Ag^+-C_{arene} π-complexation, (ii) π-stacking between $C_6F_5^-$ and the arene (parallel displaced and T-shaped arrangements),[47,52−54] and (iii) $F{\cdots}H_{arene}$ hydrogen bonding (Figure 5). For example, the electrostatic potential (ESP) mapped onto the electron density of $(AgC_6F_5)_4{\cdot}$toluene nicely illustrates the electrostatically favorable arrangement of one toluene molecule allowing strong van der Waals interaction between one Ag^+ center and $C_{toluene}$ centers (shortest Ag⋯C 2.934 Å). Additionally, two types of rather weak F⋯H hydrogen bonds might be discussed between F atoms of the $C_6F_5^-$ ion and protons of the methyl group ($F{\cdots}H_{methyl,toluene}$ 2.85 Å) and protons of the aryl ring ($F{\cdots}H_{aryl,toluene}$ 2.78 Å). In the latter case, protons of the toluene species can interact with

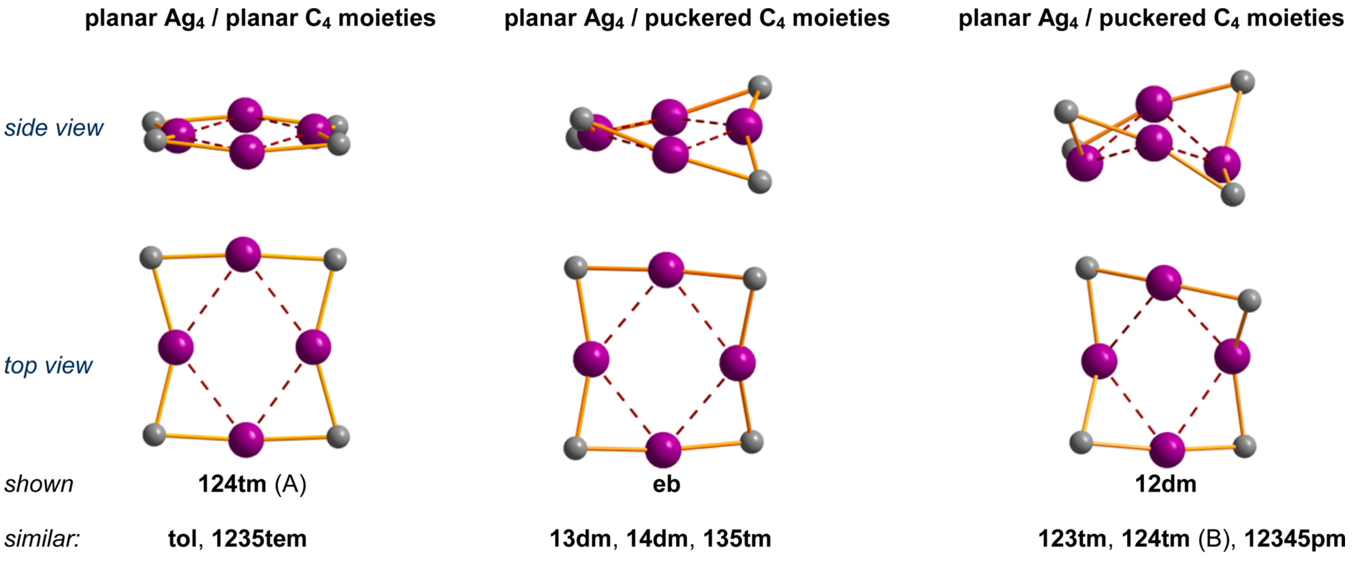


Figure 4. Molecular structures of Ag_4 and C_4 moieties within an eight-membered Ag_4C_4 ring in $(AgC_6F_5)_4{\cdot}n$ arene adducts (Ag violet, C gray).

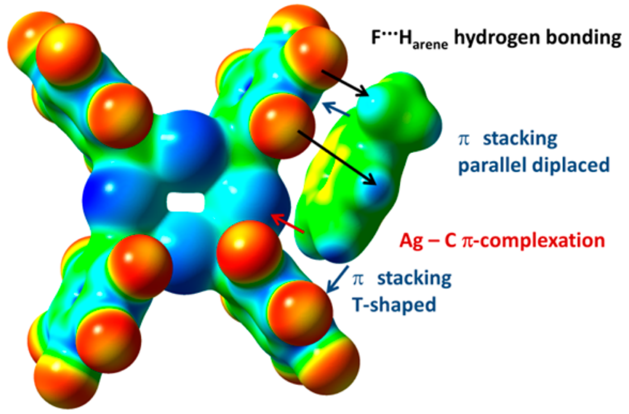


Figure 5. Computed charge density isosurface plot for X-ray structural data of $(AgC_6F_5)_4 \cdot 2$ toluene (one toluene solvate molecule omitted for clarity). The isosurface has been colored according to the electrostatic potential (red: most negative regions; blue: most positive regions).

fluorine atoms of two adjacent $C_6F_5^-$ rings, since the toluene lies parallelly displaced[55] to one and almost perpendicular (T-shaped)[56] to the second $C_6F_5^-$ ring with one $C-H_{aryl,toluene}$ bond pointing directly to the perpendicular $C_6F_5^-$ ring center.[57] These are known arrangements discussed in cases of π-stacking interactions. A second example is as follows: For the chain-like $(-Ag_4-\text{arene}-Ag_4-)$ units in $(AgC_6F_5)_4 \cdot n$ arene species (arene = **eb**, **1.2dm**, Figure 3) the pocket formed by the two Ag_4C_4 units generates exactly the space needed to host one arene molecule (Figure 6). In the case of the $(AgC_6F_5 \cdot \text{arene})_4$ species, the ESPs nicely illustrate solvated Ag_4C_4 units leading to ball-shaped moieties with all F atoms and the methyl groups at the surface of these balls, as depicted in Figure S3. So depending on the energy gain by all above-discussed small interactions (Figure 5), pocket formation in chain-like structures (utilizing one molecule) of formal monoadducts or double/4-fold adduct formation within one molecular tetrameric Ag_4C_4 unit is favored (Figure S3). In summary, it can be assumed that Ag−C π-complexation,[47] π-stacking[52] between the arene and $C_6F_5^-$ rings, and weak F···H hydrogen bond interactions, which are observed in *all* considered, structurally highly flexible arene adducts (see Figure S3), considerably stabilize the four-membered ring system rather than allowing a chain-like structure as found in neat ${}^1_\infty\{AgC_6F_5\}$.

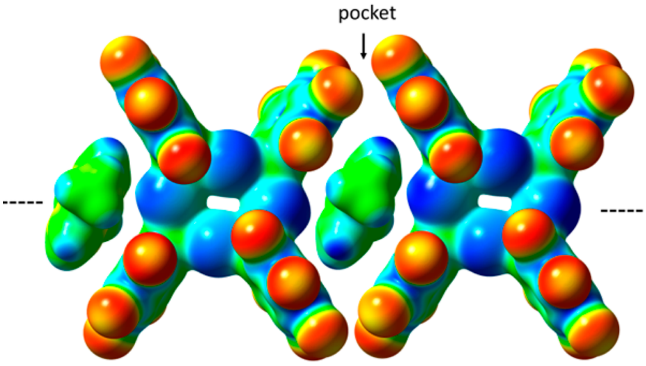


Figure 6. ESP plotted onto a charge density isosurface for X-ray structural data of a section of the chainlike structure in the crystal structure of $(AgC_6F_5)_4 \cdot 2$ 1,4-dimethylbenzene (one solvate molecule omitted for clarity). Shown is one pocket between two Ag_4C_4 units hosting one 1,4-dimethylbenzene.

In agreement with these weak interactions, the computed charge transfer from the arenes to the silver centers is rather small, with 0.02−0.04*e* per arene molecule according to NBO[58−60] analysis (NBO = natural bond analysis, Table 1). Hence, these interactions can be considered purely electrostatic in nature. The computed partial charges of the formal Ag^+ ions amount to +0.59 to +0.63*e*, indicating some covalency between the formal Ag^+ and $C_6F_5^-$ ions. Actually, NBO analysis finds highly polar $Ag-C_{C6F5}$ bonds, which, however, are almost 90% localized at the carbon center.

3. CONCLUSION

The isolation of crystalline AgC_6F_5 was achieved by recrystallization of amorphous AgC_6F_5 from arenes with bulky substituents or a high degree of substitution at the arene. The solid-state structure revealed Ag−C zigzag chains along the *c*-axis in the crystal. Hence crystalline AgC_6F_5 should be better denoted as polymeric ${}^1_\infty\{AgC_6F_5\}$. With less bulky arene ${}^1_\infty\{AgC_6F_5\}$ forms a series of different types of tetrameric $(AgC_6F_5)_4 \cdot n$ arene adducts (n = 1, 2, 4). Molecular tetrameric $(AgC_6F_5)_4$ units are favored over a chain-like structure as found in neat ${}^1_\infty\{AgC_6F_5\}$ due to a multitude of Ag−C π-complexation, π-stacking, and F···H hydrogen bond interactions. Furthermore, it should be stressed that different structures from the ones reported may form under other crystallization conditions, for example when using non-coordinating solvents with different amounts of the arenes present.

■ EXPERIMENTAL SECTION

General Information. All manipulations were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk or drybox techniques. *Note:* Since $(AgC_6F_5)_4 \cdot n$ arene adducts are highly labile solvates, it is simply impossible to obtain more accurate elemental analysis (EA). These are highly labile species that easily lose their solvent molecules even under standard conditions. So whenever these species are removed from the mother liquor, the substance releases solvent, which was not taken into account in the EA.

General Procedure for the Synthesis of Tetrakis(pentafluorophenylsilver) Arene Adducts $(AgC_6F_5)_4 \cdot n$ arene. *Procedure 1.* Arene = benzene, toluene, ethylbenzene, 1,2-dimethylbenzene, 1,3-dimethylbenzene, 1,4-dimethylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 1,2,3,5-tetramethylbenzene. Neat pentafluorophenylsilver AgC_6F_5 (0.100 g, 0.36 mmol) was suspended in a minimum of the corresponding arene (3−5 mL) at ambient temperatures. The mixture was stirred for 30 min, followed by gently heating to 60 °C, until a clear, colorless solution was obtained. Slow cooling to ambient temperature over a period of 1 h resulted in the deposition of colorless crystals or a precipitate (in the case of benzene and toluene). Removal of excess arene by decantation and drying in vacuo gave the corresponding tetrakis(pentafluorophenylsilver) arene adduct $(AgC_6F_5)_4 \cdot n$ arene (n = 1, 2; arene = toluene, ethylbenzene, 1,2-dimethylbenzene, 1,3-dimethylbenzene, 1,4-dimethylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene) as a colorless solid in good yields (40−80%).

Procedure 2. Arene = 1,2,3,5-tetramethylbenzene, 1,2,4,5-tetramethylbenzene, 1,2,3,4,5-pentamethylbenzene. Neat pentafluorophenylsilver, AgC_6F_5 (0.100 g, 0.36 mmol), was suspended and stirred in the corresponding arene (about 5 g) for 3 h at 60−80 °C, at a reduced pressure of 1^{-3} mbar. The mixture was slowly cooled to ambient temperature over a period of 30 min. The resulting solid was separated by filtration (F4) and washed three times by repeated back distillation with *n*-hexane. Drying in vacuo with gentle heating gave the corresponding tetrakis(pentafluorophenylsilver) arene adduct

$(AgC_6F_5)_4\cdot n$ arene (1,2,3,5-tetramethylbenzene, 1,2,4,5-tetramethylbenzene) as a colorless solid in good yields (40–80%). In the case of 1,2,3,4,5-pentamethylbenzene, the filtrate (instead of the residue) was used to obtain crystals of the corresponding tetrakis(pentafluorophenylsilver) arene adduct $(AgC_6F_5)_4\cdot n$ arene (yield: 15–20%, see below).

$(AgC_6F_5)_4\cdot 2$ benzene. Mp: 154.60 °C, 223.33 °C (dec). Anal. Calcd for $(AgC_6F_5)_4\cdot C_6H_6$, % (found): C 30.59 (29.02); H 0.51 (1.06). ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 7.35 (s, 6H, ArC*H*). ^{13}C{^{1}H} NMR (25 °C, CD_2Cl_2, 75.47 MHz): δ = 102.0 (br, *ipso*-C), 128.9 (s, 6CH, benzene), 137.7 (dm, *m*-CF, $^1J(^{13}C{-}^{19}F)$ = 259 Hz), 144.7 (dm, *p*-CF, $^1J(^{13}C{-}^{19}F)$ = 259 Hz), 153.8 (dm, *o*-CF, $^1J(^{13}C{-}^{19}F)$ = 236 Hz). ^{19}F{^{1}H} NMR (25 °C, CD_2Cl_2, 282.4 MHz): δ = −158.2 (m, *m*-CF, $^1J(^{13}C{-}^{19}F)$ = 259 Hz), −144.1 (dm, *p*-CF, $^1J(^{13}C{-}^{19}F)$ = 259 Hz), −100.4 (dm, *o*-CF, $^1J(^{13}C{-}^{19}F)$ = 236 Hz). IR (ATR, 16 scans): 1631 (m), 1602 (w), 1557 (w), 1537 (w), 1504 (s), 1463 (w), 1440 (s), 1427 (s), 1379 (m), 1333 (m), 1265 (m), 1131 (w), 1110 (w), 1073 (m), 1056 (s), 1009 (w), 980 (w), 949 (s), 769 (w), 747 (m), 717 (w), 687 (m), 662 (w), 597 (m). MS (CI$^+$, isobutane): 1101 $[Ag_4(C_6F_5)_4 + H]^+$, 1100 $[Ag_4(C_6F_5)_4]^+$, 353 $[AgC_6F_5\cdot C_6H_6 + H]^+$, 335 $[C_6F_5 - C_6F_5 + H]^+$, 334 $[C_6F_5 - C_6F_5]^+$, 224 $[C_6F_5 - C_4H_9]^+$, 206 $[C_6F_5 - C_3H_3]^+$, 117 $[C_6H_6 + C_3H_3]^+$, 79 $[C_6H_6 + H]^+$.

$(AgC_6F_5)_4\cdot 2$ toluene. Mp: 124.43 °C. Anal. Calcd for $(AgC_6F_5)_4\cdot C_7H_8$, % (found): C 31.24 (30.08); H 0.68 (0.88). ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 2.33 (s, 3H, ArC*H*$_3$), 7.10–7.26 (m, 5H, ArC*H*). ^{13}C{^{1}H} NMR (25 °C, CD_2Cl_2, 75.47 MHz): δ = 21.7 (s, CH_3, toluene), 102.8 (br, *ipso*-C), 125.7 (s, CH, toluene), 128.7 (s, 2CH, toluene), 129.6 (s, 2CH, toluene), 137.6 (dm, *m*-CF, $^1J(^{13}C{-}^{19}F)$ = 259 Hz), 138.6 (s, C, toluene), 144.8 (dm, *p*-CF, $^1J(^{13}C{-}^{19}F)$ = 259 Hz), 153.8 (dm, *o*-CF, $^1J(^{13}C{-}^{19}F)$ = 236 Hz). ^{19}F{^{1}H} NMR (25 °C, CD_2Cl_2, 282.4 MHz): δ = −158.2 (m, *m*-CF, $^1J(^{13}C{-}^{19}F)$ = 259 Hz), −144.1 (dm, *p*-CF, $^1J(^{13}C{-}^{19}F)$ = 259 Hz), −100.4 (dm, *o*-CF, $^1J(^{13}C{-}^{19}F)$ = 236 Hz). IR (ATR, 16 scans): 1631 (m), 1603 (w), 1586 (w), 1562 (w), 1557 (w), 1538 (w), 1504 (s), 1469 (w), 1441 (s), 1427 (s), 1379 (m), 1333 (m), 1265 (m), 1195 (w), 1131 (w), 1112 (w), 1073 (s), 1056 (s), 1007 (w), 982 (w), 949 (s), 740 (m), 718 (m), 697 (m), 661 (w), 620 (w), 596 (m), 542 (w). MS (CI$^+$, isobutane): 1101 $[Ag_4(C_6F_5)_4 + H]^+$, 353 $[AgC_6F_5\cdot C_6H_6 + H]^+$, 335 $[C_6F_5 - C_6F_5 + H]^+$, 334 $[C_6F_5 - C_6F_5]^+$, 224 $[C_6F_5 - C_4H_9]^+$, 206 $[C_6F_5 - C_3H_3]^+$, 135 $[C_7H_8 + C_3H_7]^+$, 93 $[C_7H_8 + H]^+$. Crystals suitable for X-ray crystallographic analysis were obtained by cooling a saturated dichloromethane solution to 5 °C.

$(AgC_6F_5)_4\cdot 2$ ethylbenzene. Mp: 77.20 °C (dec). Anal. Calcd for $(AgC_6F_5)_4\cdot C_8H_{10}$, % (found): C 31.87 (28.24); H 0.84 (0.77). ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 1.21 (t, 3H, C*H*$_3$, ^3J (^{1}H–^{1}H) = 7.6 Hz), 2.63 (q, 2H, C*H*$_2$, ^3J (^{1}H–^{1}H) = 7.6 Hz), 7.11–7.30 (m, 5H, ArC*H*). ^{13}C{^{1}H} NMR (25 °C, CD_2Cl_2, 75.47 MHz): δ = 16.0 (s, CH_3, ethylbenzene), 29.4 (s, CH_2, ethylbenzene), 102.8 (br, *ipso*-C), 126.0 (s, CH, ethylbenzene), 128.4 (s, 2CH, ethylbenzene), 128.8 (s, 2CH, ethylbenzene), 137.6 (dm, *m*-CF, $^1J(^{13}C{-}^{19}F)$ = 259 Hz), 145 (s, C, ethylbenzene), 144.8 (dm, *p*-CF, $^1J(^{13}C{-}^{19}F)$ = 259 Hz), 153.6 (dm, *o*-CF, $^1J(^{13}C{-}^{19}F)$ = 234 Hz). ^{19}F{^{1}H} NMR (25 °C, CD_2Cl_2, 282.4 MHz): δ = −158.2 (m, *m*-CF, $^1J(^{13}C{-}^{19}F)$ = 259 Hz), −144.1 (dm, *p*-CF, $^1J(^{13}C{-}^{19}F)$ = 259 Hz), −100.4 (dm, *o*-CF, $^1J(^{13}C{-}^{19}F)$ = 234 Hz). IR (ATR, 16 scans): 1630 (m), 1604 (w), 1583 (w), 1557 (w), 1537 (w), 1501 (s), 1447 (s), 1434 (s), 1380 (m), 1341 (m), 1307 (m), 1258 (s), 1232 (s), 1201 (m), 1149 (m), 1133 (m), 1072 (s), 1055 (s), 998 (w), 982 (m), 954 (s), 908 (w), 808 (w), 790 (w), 775 (w), 748 (m), 718 (w), 684 (w), 661 (w), 640 (w), 597 (m), 554 (w). MS (CI$^+$, isobutane): 335 $[C_6F_5 - C_6F_5 + H]^+$, 334 $[C_6F_5 - C_6F_5]^+$, 168 $[C_6F_5H]^+$, 119 $[C_9H_{11}]^+$. Crystals suitable for X-ray crystallographic analysis were obtained directly from the above reaction solution.

$(AgC_6F_5)_4\cdot 4$ (1,2-dimethylbenzene). Mp: 89.5 °C (dec). Anal. Calcd for $(AgC_6F_5)_4\cdot 2C_8H_{10}$, % (found): C 36.62 (36.23); H 1.54 (1.58). ^{1}H NMR (25 °C, CD_2Cl_2, 250.13 MHz): δ = 2.25 (s, 6H, ArC*H*$_3$), 7.03–7.14 (m, 4H, ArC*H*). ^{13}C{^{1}H} NMR (25 °C, CD_2Cl_2, 125.75 MHz): δ = 20.0 (s, 2CH_3, *1,2-dimethylbenzene*), 101.9 (br, *ipso*-C), 125.7 (s, 2CH, *1,2-dimethylbenzene*), 130.0 (s, 2CH, *1,2-dimethylbenzene*), 137.6 (s, 2C, *1,2-dimethylbenzene*), 137.7 (dm, *m*-CF, $^1J(^{13}C{-}^{19}F)$ = 259 Hz), 144.9 (dm, *p*-CF, $^1J(^{13}C{-}^{19}F)$ = 259 Hz), 153.8 (dm, *o*-CF, $^1J(^{13}C{-}^{19}F)$ = 234 Hz). ^{19}F{^{1}H} NMR (25 °C, CD_2Cl_2, 282.4 MHz): δ = −158.2 (m, *m*-CF, $^1J(^{13}C{-}^{19}F)$ = 259 Hz), −144.1 (dm, *p*-CF, $^1J(^{13}C{-}^{19}F)$ = 259 Hz), −100.4 (dm, *o*-CF, $^1J(^{13}C{-}^{19}F)$ = 234 Hz). IR (ATR, 16 scans): 2930 (w), 2861 (w), 1631 (m), 1602 (w), 1554 (w), 1536 (w), 1502 (s), 1447 (s), 1432 (s), 1387 (m), 1377 (m), 1338 (m), 1259 (m), 1187 (w), 1159 (w), 1132 (w), 1118 (w), 1073 (m), 1057 (s), 1022 (w), 954 (s), 870 (w), 760 (m), 746 (m), 716 (w), 664 (w), 595 (m), 581 (w). MS (CI$^+$, isobutane): 1101 $[(AgC_6F_5)_4 + H]^+$, 937, 936, 935 933 $[Ag_4^{isotopic}(C_6F_5)_3 + H]^+$, 383, 382, 381 $[AgC_6F_5\cdot C_8H_{10} + H]^+$, 382, 381, 380 $[AgC_6F_5\cdot C_8H_{10}]^+$, 109, 107 $[Ag^{isotopic}]^+$, 107 $[C_8H_{10} + H]^+$. Crystals suitable for X-ray crystallographic analysis were obtained directly from the above reaction solution.

$(AgC_6F_5)_4\cdot 2$ (1,3-dimethylbenzene). Mp: 85.59 °C (dec). Anal. Calcd for $(AgC_6F_5)_4\cdot C_8H_{10}$, % (found): C 31.87 (31.53); H 0.84 (1.22). ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 2.29 (s, 6H, ArC*H*$_3$), 6.93–7.04 (m, 3H, ArC*H*), 7.08–7.13 (m, 1H, ArC*H*). ^{13}C{^{1}H} NMR (25 °C, CD_2Cl_2, 75.47 MHz): δ = 21.6 (s, CH_3, 1,3-dimethylbenzene), 101.2 (br, *ipso*-C), 126.4 (s, CH, 1,3-dimethylbenzene), 128.4 (s, CH, 1,3-dimethylbenzene), 130.4 (s, 2CH, 1,3-dimethylbenzene), 138.5 (dm, *m*-CF, $^1J(^{13}C{-}^{19}F)$ = 258 Hz), 138.5 (s, 2C, 1,3-dimethylbenzene), 144.8 (dm, *p*-CF, $^1J(^{13}C{-}^{19}F)$ = 258 Hz), 153.7 (dm, *o*-CF, $^1J(^{13}C{-}^{19}F)$ = 234 Hz). ^{19}F{^{1}H} NMR (25 °C, CD_2Cl_2, 282.4 MHz): δ = −158.2 (m, *m*-CF, $^1J(^{13}C{-}^{19}F)$ = 258 Hz), −144.1 (dm, *p*-CF, $^1J(^{13}C{-}^{19}F)$ = 258 Hz), −100.4 (dm, *o*-CF, $^1J(^{13}C{-}^{19}F)$ = 234 Hz). IR (ATR, 16 scans): 1631 (m), 1603 (w), 1586 (w), 1562 (w), 1557 (w), 1538 (w), 1504 (s), 1469 (w), 1441 (s), 1427 (s), 1379 (m), 1333 (m), 1265 (m), 1195 (w), 1131 (w), 1112 (w), 1073 (s), 1056 (s), 1007 (w), 982 (w), 949 (s), 740 (m), 718 (m), 697 (m), 661 (w), 620 (w), 596 (m), 542 (w). MS (CI$^+$, isobutane): 1100 $[Ag_4(C_6F_5)_4]^+$, 933 $[Ag_4(C_6F_5)_3]^+$, 334 $[C_6F_5 - C_6F_5]^+$, 223 $[C_6F_5 - C_4H_8]^+$, 168 $[C_6F_5 - H]^+$, 147 $[C_8H_{10} + C_3H_5]$, 107 $[Ag]^+$, 107 $[C_8H_{10} + H]^+$, 106 $[C_8H_{10}]^+$, 91 $[C_7H_7]^+$. Crystals suitable for X-ray crystallographic analysis were obtained directly from the above reaction solution by storage at 5 °C.

$(AgC_6F_5)_4\cdot 2$ (1,4-dimethylbenzene). Mp: 109.17 °C (dec). Anal. Calcd for $(AgC_6F_5)_4\cdot 2\ C_8H_{10}$, % (found): C36.62 (36.95); H 1.54 (1.81). ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 2.29 (s, 6H, ArC*H*$_3$), 7.05 (s, 4H, ArC*H*). ^{13}C{^{1}H} NMR (25 °C, CD_2Cl_2, 62.89 MHz): δ = 21.0 (s, 2CH_3, 1,4-dimethylbenzene), 101.9 (br, *ipso*-C), 129.1 (s, 4CH, 1,4-dimethylbenzene), 135.6 (s, 2C, 1,4-dimethylbenzene), 137.7 (dm, *m*-CF, $^1J(^{13}C{-}^{19}F)$ = 259 Hz), 144.8 (dm, *p*-CF, $^1J(^{13}C{-}^{19}F)$ = 259 Hz), 153.8 (dm, *o*-CF, $^1J(^{13}C{-}^{19}F)$ = 234 Hz). ^{19}F{^{1}H} NMR (25 °C, CD_2Cl_2, 282.4 MHz): δ = −158.2 (m, *m*-CF, $^1J(^{13}C{-}^{19}F)$ = 259 Hz), −144.1 (dm, *p*-CF, $^1J(^{13}C{-}^{19}F)$ = 259 Hz), −100.4 (dm, *o*-CF, $^1J(^{13}C{-}^{19}F)$ = 234 Hz). IR (ATR, 16 scans): 2929 (w), 2873 (w), 1650 (w), 1644 (m), 1631 (m), 1603 (w), 1557 (w), 1502 (s), 1447 (s), 1435 (s), 1383 (s), 1375 (s), 1338 (s), 1299 (w), 1262 (m), 1226 (m), 1198 (w), 1180 (w), 1075 (s), 1057 (s), 977 (s), 956 (s), 900 (m), 860 (w), 812 (m), 791 (m), 774 (m), 755 (m), 748 (m), 726 (w), 717 (w), 683 (m), 661 (m), 644 (w), 610 (w), 597 (m), 573 (m), 540 (w). MS (CI$^+$, isobutane): 1100 $[Ag_4(C_6F_5)_4]^+$, 933 $[Ag_4(C_6F_5)_3]^+$, 334 $[C_6F_5 - C_6F_5]^+$, 223 $[C_6F_5 - C_4H_8]^+$, 168 $[C_6F_5 - H]^+$, 147 $[C_8H_{10} + C_3H_5]^+$, 107 $[Ag]^+$, 107 $[C_8H_{10} + H]^+$, 106 $[C_8H_{10}]^+$, 91 $[C_7H_7]^+$. Crystals suitable for X-ray crystallographic analysis were obtained directly from the above reaction solution.

$(AgC_6F_5)_4\cdot 4$ (1,2,3-trimethylbenzene). Mp: 123 °C (dec). Anal. Calcd for $(AgC_6F_5)_4\cdot 2.5\ C_9H_{12}$, % (found): C 39.89 (38.46); H 2.16 (2.45). ^{1}H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ = 2.17 (s, 3H, ArC*H*$_3$), 2.27 (s, 6H, ArC*H*$_3$), 6.97–7.89 (m, 3H, ArC*H*). ^{13}C{^{1}H} NMR (25 °C, CD_2Cl_2, 75.47 MHz): δ = 15.6 (s, CH_3, 1,2,3-trimethylbenzene), 20.8 (s, 2CH_3, 1,2,3-trimethylbenzene), 101.7 (br, *ipso*-C), 124.7 (s, CH, 1,2,3-trimethylbenzene), 127.6 (s, 2CH, 1,2,3-trimethylbenzene), 136.1 (s, C, 1,2,3-trimethylbenzene), 137.3 (s, 2C, 1,2,3-trimethylbenzene), 137.7 (dm, *m*-CF, $^1J(^{13}C{-}^{19}F)$ = 258 Hz), 144.8 (dm, *p*-CF, $^1J(^{13}C{-}^{19}F)$ = 258 Hz), 153.8 (dm, *o*-CF,

$^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 234 Hz). $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR (25 °C, $\mathrm{CD_2Cl_2}$, 282.4 MHz): $\delta = -158.2$ (m, *m*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 258 Hz), −144.1 (dm, *p*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 258 Hz), −100.4 (dm, *o*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 234 Hz). IR (ATR, 16 scans): 1630 (m), 1603 (w), 1574 (w), 1556 (w), 1537 (w), 1532 (w), 1503 (s), 1499 (s), 1444 (s), 1429 (s), 1383 (m), 1373 (m), 1338 (m), 1373 (m), 1338 (m), 1331 (m), 1262 (m), 1253 (m), 1185 (w), 1161 (w), 1127 (m), 1110 (m), 1085 (m), 1070 (m), 1053 (s), 999 (w), 980 (m), 953 (s), 894 (m), 789 (s), 757 (m), 739 (m), 710 (m), 684 (m), 660 (m), 611 (w), 590 (m), 532 (w). MS ($\mathrm{CI^+}$, isobutane): 1100 $[\mathrm{Ag_4(C_6F_5)_4}]^+$, 933 $[\mathrm{Ag_4(C_6F_5)_3}]^+$, 334 $[\mathrm{C_6F_5-C_6F_5}]^+$, 223 $[\mathrm{C_6F_5-C_4H_8}]^+$, 135 $[\mathrm{C_{10}H_{14}+H}]$, 133 $[\mathrm{C_{10}H_{13}}]^+$, 121 $[\mathrm{C_9H_{12}+H}]^+$, 120 $[\mathrm{C_9H_{12}}]^+$, 119 $[\mathrm{C_9H_{11}}]^+$, 105 $[\mathrm{C_8H_9}]^+$. Crystals suitable for X-ray crystallographic analysis were obtained from a saturated solution of dichloromethane and 1,2,3-trimethylbenzene.

$(\mathrm{AgC_6F_5})_4\cdot 2$ (1,2,4-trimethylbenzene). Mp: 103.15 °C (dec). Anal. Calcd for $(\mathrm{AgC_6F_5})_4\cdot 2\mathrm{C_9H_{12}}$, % (found): C 37.64 (37.76); H 1.81 (1.80). ^{1}H NMR (25 °C, $\mathrm{CD_2Cl_2}$, 250.13 MHz): δ = 2.20 (s, 3H, ArC*H*$_3$), 2.24 (s, 3H, ArC*H*$_3$), 2.25 (s, 3H, ArC*H*$_3$), 6.86 (d, 1H, $^3J(^1\mathrm{H}-^1\mathrm{H})$ = 7.7 Hz, ArC*H*), 6.96 (s, 1H, ArC*H*), 6.98 (d, 1H, $^3J(^1\mathrm{H}-^1\mathrm{H})$ = 7.7 Hz, ArC*H*). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (25 °C, $\mathrm{CD_2Cl_2}$, 62.89 MHz): δ = 19.5 (s, *C*H$_3$, 1,2,4-trimethylbenzene), 19.9 (s, *C*H$_3$, 1,2,4-trimethylbenzene), 21.1 (s, *C*H$_3$, 1,2,4-trimethylbenzene), 102.0 (br, *ipso*-C), 126.1 (s, CH, 1,2,4-trimethylbenzene), 129.3 (s, CH, 1,2,4-trimethylbenzene), 130.9 (s, CH, 1,2,4-trimethylbenzene), 134.1 (s, *C*, 1,2,4-trimethylbenzene), 135.9 (s, *C*, 1,2,4-trimethylbenzene), 137.2 (s, *C*, 1,2,4-trimethylbenzene), 137.4 (dm, *m*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 259 Hz), 144.8 (dm, *p*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 259 Hz), 153.7 (dm, *o*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 234 Hz). $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR (25 °C, $\mathrm{CD_2Cl_2}$, 282.4 MHz): δ = −158.2 (m, *m*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 259 Hz), −144.1 (dm, *p*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 259 Hz), −100.4 (dm, *o*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 234 Hz). $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR (25 °C, $\mathrm{C_6D_6}$, 282.4 MHz): δ = −157.6 (m, *m*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 259 Hz), −145.1 (dm, *p*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 259 Hz), −100.4 (dm, *o*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 234 Hz). IR (ATR, 16 scans): 2925 (w), 1644 (w), 1631 (m), 1603 (w), 1557 (w), 1537 (w), 1503 (s), 1447 (s), 1435 (s), 1385 (m), 1379 (m), 1338 (m), 1260 (m), 1152 (w), 1132 (w), 1113 (w), 1074 (m), 1055 (s), 1021 (w), 1001 (w), 979 (w), 956 (s), 892 (w), 882 (w), 821 (m), 775 (w), 755 (w), 745 (m), 716 (w), 703 (w), 684 (m), 660 (w), 644 (w), 594 (m), 573 (w), 542 (m). MS ($\mathrm{CI^+}$, isobutane): 1101 $[\mathrm{Ag_4(C_6F_5)_4+H}]^+$, 933 $[\mathrm{Ag_4(C_6F_5)_3}]^+$, 334 $[\mathrm{C_6F_5-C_6F_5}]^+$, 121 $[\mathrm{C_9H_{12}+H}]^+$, 120 $[\mathrm{C_9H_{12}}]^+$. Crystals suitable for X-ray crystallographic analysis were obtained directly from the above reaction solution.

$(\mathrm{AgC_6F_5})4\cdot 2$ (1,3,5-trimethylbenzene). Mp: 83 °C (dec). Anal. Calcd for $(\mathrm{AgC_6F_5})_4\cdot 2\mathrm{C_9H_{12}}$, % (found): C 37.64 (37.47); H 1.81 (2.10). ^{1}H NMR (25 °C, $\mathrm{CD_2Cl_2}$, 250.13 MHz): δ = 2.25 (s, 9H, ArC*H*$_3$), 6.77−6.79 (m, 3H, ArC*H*). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (25 °C, $\mathrm{CD_2Cl_2}$, 62.89 MHz): δ = 21.5 (s, 3*C*H$_3$, 1,3,5-trimethylbenzene), 101.5 (br, *ipso*-C), 127.2 (s, 3CH, 1,3,5-trimethylbenzene), 137.5 (dm, *m*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 259 Hz), 138.4 (s, 3*C*, 1,2,3-trimethylbenzene), 144.8 (dm, *p*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 259 Hz), 153.6 (dm, *o*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 234 Hz). $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR (25 °C, $\mathrm{CD_2Cl_2}$, 282.4 MHz): δ = −158.2 (m, *m*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 259 Hz), −144.1 (dm, *p*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 259 Hz), −100.4 (dm, *o*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 234 Hz). IR (ATR, 16 scans): 2929 (w), 1630 (m), 1603 (w), 1557 (w), 1537 (w), 1532 (w), 1502 (s), 1446 (s), 1434 (s), 1378 (m), 1342 (m), 1336 (m), 1260 (m), 1199 (w), 1131 (w), 1094 (m), 1072 (s), 1053 (s), 1007 (w), 979 (m), 955 (s), 882 (w), 839 (m), 775 (s), 745 (m), 713 (w), 690 (m), 661 (w), 640 (w), 594 (m), 574 (m). MS ($\mathrm{CI^+}$, isobutane): 1100 $[\mathrm{Ag_4(C_6F_5)_4}]^+$, 933 $[\mathrm{Ag_4(C_6F_5)_3}]^+$, 334 $[\mathrm{C_6F_5-C_6F_5}]^+$, 223 $[\mathrm{C_6F_5-C_4H_8}]^+$, 135 $[\mathrm{C_{10}H_{14}+H}]$, 133 $[\mathrm{C_{10}H_{13}}]^+$, 121 $[\mathrm{C_9H_{12}+H}]^+$, 120 $[\mathrm{C_9H_{12}}]^+$, 119 $[\mathrm{C_9H_{11}}]^+$, 105 $[\mathrm{C_8H_9}]^+$. Crystals suitable for X-ray crystallographic analysis were obtained directly from the above reaction solution by storage at ambient temperature.

$(\mathrm{AgC_6F_5})_4\cdot 2$ (1,2,3,5-tetramethylbenzene). Mp: 96.98 °C. Anal. Calcd for $(\mathrm{AgC_6F_5})_4\cdot 2\mathrm{C_{10}H_{14}}$, % (found): C 38.63 (38.27); H 2.06 (2.38). ^{1}H NMR (25 °C, $\mathrm{CD_2Cl_2}$, 300.13 MHz): δ = 2.12 (s, 3H, ArC*H*$_3$), 2.21 (s, 3H, ArC*H*$_3$), 2.23 (s, 6H, 2ArC*H*$_3$), 6.80 (s, 2H, 2ArC*H*). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (25 °C, $\mathrm{CD_2Cl_2}$, 75.47 MHz): δ = 15.2 (s, *C*H$_3$, 1,2,3,5-tetramethylbenzene), 20.8 (s, 2*C*H$_3$, 1,2,3,5-tetramethylbenzene), 21.1 (s, *C*H$_3$, 1,2,3,5-tetramethylbenzene), 102.0 (br, *ipso*-C), 127.9 (s, 2*C*H, 1,2,3,5-tetramethylbenzene), 132.8 (s, *C*, 1,2,3,5-tetramethylbenzene), 135.0 (s, *C*, 1,2,3,5-tetramethylbenzene), 137.2 (s, 2*C*, 1,2,3,5-tetramethylbenzene), 137.4 (dm, *m*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 259 Hz), 144.8 (dm, *p*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 259 Hz), 153.7 (dm, *o*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 234 Hz). $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR (25 °C, $\mathrm{CD_2Cl_2}$, 282.4 MHz): −158.2 (m, *m*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 259 Hz), −144.1 (dm, *p*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 259 Hz), −100.4 (dm, *o*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 234 Hz). $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR (25 °C, $\mathrm{C_6D_6}$, 282.4 MHz): δ = −158.2 (m, *m*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 259 Hz), −144.1 (dm, *p*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 259 Hz), −100.4 (dm, *o*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 234 Hz). IR (ATR, 16 scans): 2953 (w), 2925 (w), 2861(w), 1644 (w), 1634 (m), 1601 (w), 1557 (w), 1510 (m), 1505 (m), 1462 (s), 1450 (s), 1379 (m), 1338 (m), 1275 (m), 1260 (m), 1083 (s), 1056 (m), 977 (s), 955 (s), 891 (w), 862 (m), 797 (w), 775 (w), 768 (w), 755 (m), 746 (w), 726 (w), 709 (w), 684 (m), 660 (m), 610 (w), 602 (w), 573 (m), 555 (w), 522 (w), 475 (w), 448 (w), 426 (w), 408 (w). MS ($\mathrm{CI^+}$, isobutane): 334 $[\mathrm{C_6F_5-C_6F_5}]^+$, 223 $[\mathrm{C_6F_5-C_4H_8}]^+$, 135 $[\mathrm{C_{10}H_{14}+H}]$, 134 $[\mathrm{C_{10}H_{14}}]^+$, 133 $[\mathrm{C_{10}H_{13}}]^+$. Crystals suitable for X-ray crystallographic analysis were obtained from a saturated solution of dichloromethane and 1,2,3,5-tetramethylbenzene.

$(\mathrm{AgC_6F_5})_4\cdot$1,2,4,5-tetramethylbenzene. Mp: 105.89 °C (dec). Anal. Calcd for $(\mathrm{AgC_6F_5})_4\cdot 0.5\mathrm{C_{10}H_{14}}$, % (found): C 29.85 (30.39); H 0.60 (0.46). ^{1}H NMR (25 °C, $\mathrm{CD_2Cl_2}$, 300.13 MHz): δ = 2.19 (s, 12H, 4ArC*H*$_3$), 6.91 (s, 2H, 2ArC*H*). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (25 °C, $\mathrm{CD_2Cl_2}$, 62.89 MHz): δ = 19.46 (s, 4*C*H$_3$, 1,2,4,5-tetramethylbenzene), 102.0 (br, *ipso*-C), 130.3 (s, 2*C*H, 1,2,4,5-tetramethylbenzene), 134.7 (s, 4*C*, 1,2,4,5-tetramethylbenzene), 137.7 (dm, *m*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 259 Hz), 144.8 (dm, *p*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 259 Hz), 153.2 (dm, *o*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 234 Hz). $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR (25 °C, $\mathrm{CD_2Cl_2}$, 282.4 MHz): δ = −158.2 (m, *m*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 259 Hz), −144.1 (dm, *p*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 259 Hz), −100.4 (dm, *o*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 234 Hz). IR (ATR, 16 scans): 2953 (w), 2925 (w), 2861(w), 1644 (w), 1634 (m), 1601 (w), 1557 (w), 1510 (m), 1505 (m), 1462 (s), 1450 (s), 1379 (m), 1338 (m), 1275 (m), 1260 (m), 1083 (s), 1056 (m), 977 (s), 955 (s), 891 (w), 862 (m), 797 (w), 775 (w), 768 (w), 755 (m), 746 (w), 726 (w), 709 (w), 684 (m), 660 (m), 610 (w), 602 (w), 573 (m), 555 (w), 522 (w), 475 (w), 448 (w), 426 (w), 408 (w). MS ($\mathrm{EI^+}$): 1105, 1103, 1101, $[\mathrm{Ag_4(C_6F_5)_4}^{\mathrm{isotopic}}]^+$, 937, 936, 935, 933 $[\mathrm{Ag_4(C_6F_5)_3}^{\mathrm{isotopic}}]^+$, 383, 382, 381 $[\mathrm{AgC_6F_5\cdot C_8H_{10}+H}]^+$, 382, 381, 380 $[\mathrm{AgC_6F_5\cdot C_8H_{10}}]^+$, 335, 334 $[\mathrm{C_6F_5-C_6F_5}^{\mathrm{isotopic}}]^+$, 168, 167 $[\mathrm{C_6F_5}^{\mathrm{isotopic}}]^+$, 134 $[\mathrm{C_{10}H_{14}}]^+$, 109, 107 $[\mathrm{Ag}^{\mathrm{isotopic}}]^+$.

$(\mathrm{AgC_6F_5})_4\cdot 2$ (1,2,3,4,5-pentamethylbenzene) n-hexane solvate. Mp: 117.8 °C. Anal. Calcd for $(\mathrm{AgC_6F_5})_4\cdot \mathrm{C_{11}H_{16}}\cdot 0.5\ \mathrm{C_6H_{14}}$ (elemental analysis was performed with the dried *n*-hexane solvate), % (found): C 35.32 (36.46); H 1.87 (1.60). ^{1}H NMR (25 °C, $\mathrm{CD_2Cl_2}$, 250.13 MHz): δ = 2.14 (s, 6H, 2ArC*H*$_3$), 2.18 (s, 3H, ArC*H*$_3$), 2.19 (s, 6H, 2ArC*H*$_3$), 6.77 (s, 1H, ArC*H*). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (25 °C, $\mathrm{CD_2Cl_2}$, 62.89 MHz): δ = 16.15 (s, 2*C*H$_3$, pentamethylbenzene), 16.52 (s, *C*H$_3$, pentamethylbenzene), 20.81 (s, 2*C*H$_3$, pentamethylbenzene), 101.5 (br, *ipso*-C), 129.28 (s, CH, pentamethylbenzene), 132.68 (s, 2*C*, pentamethylbenzene), 133.65 (s, 2*C*, pentamethylbenzene), 135.25 (s, *C*, pentamethylbenzene), 137.9 (dm, *m*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 253 Hz), 144.7 (dm, *p*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 250 Hz), 153.8 (dm, *o*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 226 Hz). $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR (25 °C, $\mathrm{CD_2Cl_2}$, 282.4 MHz): δ = −158.2 (m, *m*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 259 Hz), −144.1 (dm, *p*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 259 Hz), −100.4 (dm, *o*-CF, $^1J(^{13}\mathrm{C}-^{19}\mathrm{F})$ = 234 Hz). IR (ATR, 16 scans): 3003 (w), 2921 (w), 2867 (w), 1630 (m), 1603 (m), 1558 (w), 1533 (w), 1500 (s), 1442 (s), 1428 (s), 1386 (m), 1372 (m), 1335 (m), 1289 (w), 1256 (m), 1130 (w), 1111 (w), 1071 (m), 1052 (s), 1010 (m), 952 (s), 895 (w), 866 (m), 798 (w), 743 (m), 714 (w), 683 (w), 667 (w), 589 (m), 534 (w). MS ($\mathrm{EI^+}$): 1105, 1103, 1101, 1099 $[\mathrm{Ag_4(C_6F_5)_4}^{\mathrm{isotopic}}]^+$, 937, 936, 935, 933 $[\mathrm{Ag_4(C_6F_5)_3}^{\mathrm{isotopic}}]^+$, 383, 382, 381 $[\mathrm{AgC_6F_5\cdot C_8H_{10}}]^+$, 335, 334 $[\mathrm{C_6F_5-C_6F_5}^{\mathrm{isotopic}}]^+$, 382, 381, 380 $[\mathrm{AgC_6F_5\cdot C_8H_{10}}]^+$, 168, 167 $[\mathrm{C_6F_5}^{\mathrm{isotopic}}]^+$, 149, 148 $[\mathrm{C_{11}H_{16}}^{\mathrm{isotopic}}]^+$, 148 $[\mathrm{C_{11}H_{16}}]^+$, 109, 107 $[\mathrm{Ag}^{\mathrm{isotopic}}]^+$. Crystals suitable for X-ray crystallographic analysis were obtained from the filtered, saturated reaction solution after addition of *n*-hexane.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, and tables giving synthetic and characterization data, computational procedures, and X-ray data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00492.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: axel.schulz@uni-rostock.de.

Notes

The authors declare no competing financial interest.

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