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Synthesis of Pentafluorophenyl Silver by Means of Lewis Acid Catalysis: Structure of Silver Solvent Complexes[§]

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The synthesis and structure of lithium and silver tetrakis(pentafluorophenyl)borate salts have been studied in different solvents ranging from polar (CH_2Cl_2, diethyl ether) to nonpolar (toluene, pentane). While $Li[B(C_6F_5)_4]$ is stable in all studied solvents and crystallizes with four ether molecules from ether and with two toluene molecules from toluene, the silver salt is only stable when the Ag^+ ion is strongly coordinated such as in $[Ag(toluene)_3][B(C_6F_5)_4]$ or $[Ag(Et_2O)_3][B(C_6F_5)_4]$. In weakly coordinating solvents such as CH_2Cl_2 $Ag[B(C_6F_5)_4]$ decomposes, yielding AgC_6F_5 and $B(C_6F_5)_3$. The overall process of the AgC_6F_5 synthesis starting from $B(C_6F_5)_3$ and LiC_6F_5 can formally be regarded as a $B(C_6F_5)_3$-catalyzed reaction. The salt $[Ag(toluene)_3][B(C_6F_5)_4]$ presents an easily accessible, ether-free, stable silver salt of the $[B(C_6F_5)_4]^-$ anion. All compounds have been fully characterized.

1. Introduction

As early as 1970,[1] pentafluorophenylsilver, AgC_6F_5, was synthesized in the reaction of $Ag[CF_3COO]$ and LiC_6F_5 or $Ag((CF_3)_2CF)$ and C_6F_5Br (Chart 1).[2−4] Ever since several synthetic routes to pentafluorophenylsilver have been published as summarized in Chart 1.[5] While most reactions gave AgC_6F_5 in good yields, they have in common that either they are rather inconvenient to handle or toxic compounds are involved. The best synthetic route to AgC_6F_5 so far seems to be the reaction of AgF with $Me_3Si(C_6F_5)$ in propionitrile, EtCN. The major drawback of this reaction is the necessary preparation of $Me_3Si(C_6F_5)$ from Me_3SiCl and C_6F_5MgBr.[5,6]

AgC_6F_5 was shown to be an excellent transfer reagent for pentafluorophenyl groups in synthetic metal- and nonmetal organic chemistry, although moisture and oxygen sensitive.[5,7−14] By heating (> 276 °C) and exposure to light, AgC_6F_5 is easily converted into perfluorobiphenyl and silver metal.[1,5]

A few 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, $Me_2C_6H_3$, $(MeO)_2C_6H_3$), $AgC_6F_5 \cdot L$ (L = EtCN), and $Ag_2R_2 \cdot L$ have been reported.[15−19] However, examples of structurally characterized organosilver(I) complexes are still rare, appearing mostly as monomeric or tetrameric species in the solid state.[2,20−23] Diarylargentate complexes are composed of separated ion pairs.[24]

Recently, we studied the generation and stability of silver and lithium salts containing new weakly coordinating anions,[25]

[§] Dedicated to Prof. Dr. Uwe Rosenthal on the occasion of his 60th birthday.

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(1) Miller, W. T.; Sun, K. K. *J. Am. Chem. Soc.* **1970**, *92*, 6985.

(2) Smith, V. B.; Massey, A. G. *J. Organomet. Chem.* **1970**, *23*, C9.

(3) Uson, R.; Laguna, A.; Abad, J. A. *J. Organomet. Chem.* **1983**, *246*, 341.

(4) Fernandez, E. J.; Laguna, A.; Mendigrave, A. *Inorg. Chim. Acta* **1994**, *223*, 161.

(5) Tyrra, W.; Wickleder, M. S. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1841.

(6) Respess, W. L.; Tamborski, C. *J. Organomet. Chem.* **1969**, *18*, 263.

(7) Naumann, D.; Tyrra, W.; Herrmann, R.; Pantenburg, I.; Wickleder, M. S. *Z. Anorg. Allg. Chem.* **2002**, *628*, 833.

(8) Doucette, W. J.; Kim, J.; Kautz, J. A.; Gipson, S. L. *Inorg. Chim. Acta* **2000**, *304*, 237.

(9) Garcia, M. P.; Jimenez, M. V.; Lahoz, F. J.; Oro, L. A. *Inorg. Chem.* **1995**, *34*, 2153.

(10) Danopoulos, A. A.; Wilkinson, G.; Sweet, T. K. N.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1994**, 1037.

(11) Laguna, A.; Fernandez, E. J.; Mendia, A.; Ruiz-Romero, M. E.; Jones, P. G. *J. Organomet. Chem.* **1989**, *365*, 201.

(12) Yagupolskii, Yu. L.; Gerus, I. I.; Yagupolskii, L. M. *Zh. Org. Khim.* **1981**, *17*, 2512.

(13) Bennett, R. L.; Bruce, M. I.; Gardner, R. C. F. *J. Chem. Soc., Dalton Trans.* **1973**, 2653.

(14) Bennett, R. L.; Bruce, M. I.; Goodfellow, R. J. *J. Fluorine Chem.* **1973**, *2*, 447.

(15) van Koten, G.; Noltes, G. *Comprehensive Organometallic Chemistry*, Vol. *2*; Pergamon: Oxford, 1982; p 709.

(16) Uson, R.; Laguna, A.; Abad, J. A. *J. Organomet. Chem.* **1983**, *246*, 341.

(17) Lingnau, R.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 436.

(18) Uson, R.; Luguna, A.; Uson, A.; Jones, P. G.; Meyer-Bäse, K. *J. Chem. Soc., Dalton Trans.* **1988**, 341.

(19) Fernandez, E. J.; Laguna, A.; Mendia, A. *Inorg. Chim. Acta* **1994**, *223*, 161.

(20) Gambarotta, S.; Floriani, C.; Chiesa-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1983**, 1087.

(21) Meyer, E. M.; Gambarotta, S.; Floriani, C.; Chiesa-Villa, A.; Guastini, C. *Organometallics* **1989**, *8*, 1067.

(22) Edwards, D. A.; Harker, R. M.; Mahon, M. F.; Molloy, K. C. *J. Chem. Soc., Dalton Trans.* **1997**, 3509.

(23) Voelker, H.; Labahn, D.; Bohnen, F. M.; Herbst-Irmer, R.; Roesky, H. W.; Stalke, D.; Edelmann, F. T. *New J. Chem.* **1999**, *23*, 905.

(24) Hwang, C.-S.; Power, P. P. *J. Organomet. Chem.* **1999**, *589*, 234.

(25) Bernsdorf, A.; Brand, H.; Hellmann, R.; Köckerling, M.; Schulz, A.; Villinger, A.; Voss, K. *J. Am. Chem. Soc.* **2009**, *131*, 8958.

Chart 1. Synthetic Routes to AgC_6F_5[a]

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

[a] M = e.g., Cd, Zn.

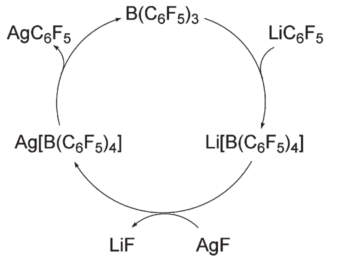
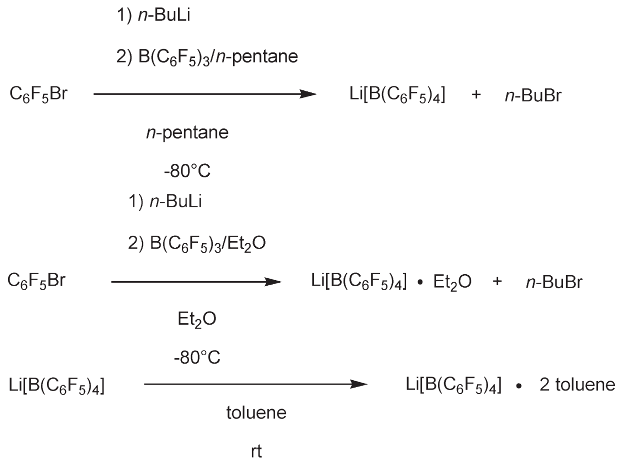


Figure 1. Formal catalytic cycle with $B(C_6F_5)_3$ as catalyst in the generation of AgC_6F_5.

Chart 2. Synthesis of $Li[B(C_6F_5)_4]$ and Its Solvent Complexes



in comparison with the known chemically robust tetrakis(pentafluorophenyl)borate, $[B(C_6F_5)_4]^-$. During this study, we realized that pure solvent-free $Ag[B(C_6F_5)_4]$ is labile with respect to decomposition into AgC_6F_5 and $B(C_6F_5)_3$, which finally led to a new synthetic approach to AgC_6F_5. Here we report on a new synthetic route to AgC_6F_5 in a facile two-step reaction (Figure 1), which formally uses tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, as catalytic reagent. Moreover, the structures of several lithium and silver tetrakis(pentafluorophenyl)borate solvent complexes are discussed.

2. Results and Discussion

Synthesis of Lithium and Silver Tetrakis(pentafluorophenyl)borate Solvent Complexes. The stabilization of highly electrophilic metal cations such as Li^+ or Ag^+ or as solvent (Lewis acid base) complexes is commonly achieved by replacing the small and strongly coordinating counterion by a large and weakly coordinating anion (wca) such as tetrakis(pentafluorophenyl)borate, $[B(C_6F_5)_4]^-$.[26]

Solvent-free lithium tetrakis(pentafluorophenyl)borate is easily prepared in the reaction of *n*-BuLi with tris(pentafluorophenyl)borane in pentane,[27] while the reaction in donor solvents such as diethyl ether (σ donor) and toluene (π donor) yields the corresponding solvent complex salts $Li[B(C_6F_5)_4]\cdot Et_2O$ and $Li[B(C_6F_5)_4]\cdot 2$ toluene, respectively, as shown in Chart 2. A closer look at the reaction in diethyl ether revealed that at first $Li[B(C_6F_5)_4]\cdot 4Et_2O$ (crystallizes at −80 °C) was formed, which releases readily 1.5 Et_2O at ambient temperatures and 10^{-3} Torr to give $Li[B(C_6F_5)_4]\cdot 2.5Et_2O$ with a melting point of 120 °C (cf. $Li[B(C_6F_5)_4]$: mp 253 °C). Constant heating at this temperature *in vacuo* finally affords $Li[B(C_6F_5)_4]\cdot Et_2O$ with a melting point of 184 °C. The last diethyl ether molecule cannot be removed thermally, which is a major drawback, when for example diethyl ether free salts are needed.

We studied two synthetic routes to silver tetrakis(pentafluorophenyl)borate (Chart 3): (i) $Li[B(C_6F_5)_4]\cdot Et_2O$ was treated with $AgNO_3$,[27] which gave after separation from $LiNO_3$ and recrystallization from dichloromethane crystalline $Ag[B(C_6F_5)_4]\cdot Et_2O$, while (ii) recrystallization of $Ag[B(C_6F_5)_4]\cdot Et_2O$ from toluene over three hours at 50 °C resulted in the formation of $Ag[B(C_6F_5)_4]\cdot 2$ toluene (decomposition above 94 °C). Starting from $Li[B(C_6F_5)_4]\cdot Et_2O$, we did not succeed in preparing solvent-free $Ag[B(C_6F_5)_4]$ by means of recrystallization. A closer look at the reaction in diethyl ether and toluene revealed, depending on the reaction condition, that in diethyl ether first $Ag[B(C_6F_5)_4]\cdot 3Et_2O$ crystallizes at ambient temperatures, while in toluene $Ag[B(C_6F_5)_4]\cdot 3$ toluene (= $[Ag(toluene)_3][B(C_6F_5)_4]$, see section X-ray Crystallography) is formed. Stepwise release of up to two Et_2O molecules or one toluene molecule, respectively, readily occurs at slightly elevated temperatures (50−60 °C) and reduced pressure (10^{-3} Torr) to give $Ag[B(C_6F_5)_4]\cdot Et_2O$ with a melting point of 117 °C (decomposition) and $Ag[B(C_6F_5)_4]\cdot 2$ toluene with a melting point of 94 °C (decomposition). The last diethyl ether/toluene molecules cannot be removed thermally. The $Ag[B(C_6F_5)_4]\cdot 2$ toluene complex is thermally stable at ambient temperatures, can be prepared in high yields, and displays an ether-free species, which makes this silver toluene complex interesting for salt metathesis reaction in low nucleophilicity solvents, where diethyl ether molecules remain attached to the cations.

Synthesis of Pentafluorophenylsilver by Means of Formal $B(C_6F_5)_3$ Catalysis. Since Li^+/Ag^+ cation exchange reactions starting from $Li[B(C_6F_5)_4]\cdot Et_2O$ to obtain ether-free Ag^+ salts were not successful, solvent-free $Li[B(C_6F_5)_4]$ was reacted with AgF in CH_2Cl_2 at 30−60 °C under ultrasonic irradiation for eight hours, a methods that has been introduced by Krossing et al. and successfully been applied in the synthesis of $AgAl(OR^F)_4$ (e.g., R^F = $-CH(CF_3)_2$, $-C(CH_3)(CF_3)_2$, $-C(CF_3)_3$).[28] Surprisingly, in the analogous reaction (with AgF and $Li[B(C_6F_5)_4]$) solvent-free pentafluorophenylsilver, AgC_6F_5, was obtained in high yields (90%) besides free $B(C_6F_5)_3$ and LiF (Chart 4). Separation of LiF was achieved by filtration, while $B(C_6F_5)_3$ was removed by repeatedly washing with *n*-hexane. Almost three-fourths of the utilized Lewis acid $B(C_6F_5)_3$ can be

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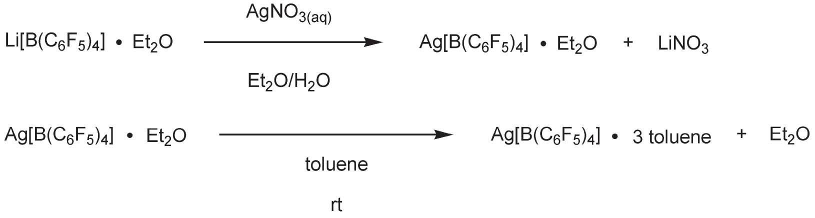
[26] Reviews: (a) Krossing, I.; Raabe, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2066. (b) Reed, C. *Acc. Chem. Res.* **1998**, *31*, 133. (c) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927, and references therein.

[27] Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245.

[28] Krossing, I. *Chem.—Eur. J.* **2001**, *7*, 490.

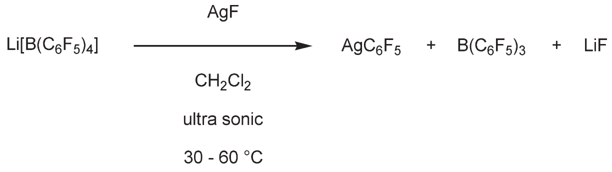
Chart 3. Synthesis of $Ag[B(C_6F_5)_4]$ and Its Solvent Complexes



$$Li[B(C_6F_5)_4] \cdot Et_2O \xrightarrow[Et_2O/H_2O]{AgNO_{3(aq)}} Ag[B(C_6F_5)_4] \cdot Et_2O + LiNO_3$$

$$Ag[B(C_6F_5)_4] \cdot Et_2O \xrightarrow[\text{toluene, rt}]{} Ag[B(C_6F_5)_4] \cdot 3\ \text{toluene} + Et_2O$$

Chart 4. Synthesis of AgC_6F_5



$$Li[B(C_6F_5)_4] \xrightarrow[\substack{CH_2Cl_2 \\ \text{ultra sonic} \\ 30-60\ °C}]{AgF} AgC_6F_5 + B(C_6F_5)_3 + LiF$$

Table 1. Crystallographic Details of $[Li(Et_2O)_4][B(C_6F_5)_4$, $[Li(Et_2O)][B(C_6F_5)_4]\cdot CH_2Cl_2$, and $[Li(toluene)][B(C_6F_5)_4]\cdot$toluene

	$[Li(Et_2O)_4]$-$[B(C_6F_5)_4$	$[Li(Et_2O)$-$][B(C_6F_5)_4]\cdot CH_2Cl_2$	$[Li(toluene)]$-$[B(C_6F_5)_4]\cdot$toluene
chem formula	$C_{40}H_{40}$-$BF_{20}LiO_4$	$C_{28.50}H_{11}$-$BClF_{20}LiO$	$C_{38}H_{16}BF_{20}Li$
fw [g mol^{-1}]	982.47	802.57	870.26
color	colorless	colorless	colorless
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a [Å]	11.15(1)	10.909(7)	9.981(5)
b [Å]	11.18(1)	13.662(9)	13.158(7)
c [Å]	17.84(2)	19.69(1)	14.992(8)
α [deg]	78.19(2)	90.00	107.899(8)
β [deg]	85.85(2)	95.36(2)	96.979(9)
γ [deg]	89.76(2)	90.00	108.65(1)
V [Å^3]	2170(3)	2921(3)	1722(2)
Z	2	4	2
$\rho_{calc.}$ [g cm^{-3}]	1.503	1.825	1.679
μ [mm^{-1}]	0.152	0.285	0.173
$\lambda_{Mo\ K\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173(2)	173(2)	173(2)
measd reflns	18 964	26 944	32 497
indep reflns	5548	6643	8256
reflns with $I > 2\sigma(I)$	4127	5006	6010
$R_{int.}$	0.0332	0.0284	0.0303
$F(000)$	1000	1580	864
R_1 ($R[F^2 > 2\sigma(F^2)]$)	0.0406	0.0351	0.0387
wR_2 (F^2)	0.1105	0.0909	0.1061
GooF	1.097	1.064	1.068
parameters	659	565	543
CCDC #	757606	757607	757608

Table 2. Crystallographic Details of $[Ag(toluene)_3][B(C_6F_5)_4]$ and $Ag(C_6F_5)(CH_3CN)$

	$[Ag(toluene)_3]$-$[B(C_6F_5)_4]$	$AgC_6F_5\cdot CH_3CN$
chem formula	$C_{45}H_{24}AgBF_{20}$	$C_8H_3AgF_5N$
fw [g mol^{-1}]	1063.32	315.98
color	colorless	colorless
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$
a [Å]	10.898(5)	22.159(9)
b [Å]	13.413(7)	10.009(4)
c [Å]	14.514(8)	9.140(5)
α [deg]	77.47(2)	90.00
β [deg]	87.50(2)	113.57(1)
γ [deg]	76.42(1)	90.00
V [Å^3]	2013(2)	1858(1)
Z	2	8
ρ_{calcd} [g cm^{-3}]	1.754	2.259
μ [mm^{-1}]	0.629	2.209
$\lambda_{Mo\ K\alpha}$ [Å]	0.71073	0.71073
T [K]	173(2)	173(2)
measd reflns	40 833	12 262
indep reflns	10 612	3354
reflections with $I > 2\sigma(I)$	8101	3028
$R_{int.}$	0.0393	0.0339
$F(000)$	1052	1200
R_1 ($R[F^2 > 2\sigma(F^2)]$)	0.0361	0.0197
wR_2 (F^2)	0.0968	0.0488
GooF	1.056	1.077
parameters	617	139
CCDC #	757609	757610

recovered in high purity by subsequent sublimation at 110 °C for six hours. The driving force of the 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 significant donor–acceptor interactions as in $Ag[B(C_6F_5)_4]\cdot n$ toluene (n = 2, 3) or $Ag[B(C_6F_5)_4]\cdot nEt_2O$ (n = 1–3), Ag^+ seems to be the stronger Lewis acid, resulting in the abstraction of $C_6F_5^-$ from the $[B(C_6F_5)_4]^-$ ion, yielding AgC_6F_5 and $B(C_6F_5)_3$. Since $B(C_6F_5)_3$ can be recovered, the overall process, as shown in Figure 1, can formally be regarded as a Lewis acid-catalyzed synthesis of AgC_6F_5. Bochmann et al. demonstrated the degradation of the $[B(C_6F_5)_4]^-$ ion in the reaction of $[Ph_3C]^+[B(C_6F_5)_4]^-$ with $AlMe_3$ in which the *in situ*-generated $[AlMe_2]^+[B(C_6F_5)_4]^-$ immediately decomposes to $B(C_6F_5)_3$ and $AlMe_2(C_6F_5)$. The authors assumed cations such as $[AlMe_2]^+$ are too electrophilic to be stabilized even by $[B(C_6F_5)_4]^-$ and immediately react with abstraction of $[C_6F_5]^-$.[29,30]

A similar Lewis acid/Lewis base reaction is assumed for weakly coordinating anions of the type $[Al(OR^F)_4]^-$ in the presence of very electrophilic cations, where the decomposition is initiated either by ligand (R^FO^-) or fluoride ion abstraction, finally leading to $[(R^FO)_3Al{-}F{-}Al(OR^F)_3]^-$.[31]

X-ray Crystallography. The structures of $[Li(Et_2O)_4][B(C_6F_5)_4]$, $[Li(toluene)][B(C_6F_5)_4]\cdot$toluene, $[Li(Et_2O)_2][B(C_6F_5)_4]\cdot CH_2Cl_2$, $[Ag(Et_2O)_3][B(C_6F_5)_4]$, $[Ag(toluene)_3][B(C_6F_5)_4]$, and $AgC_6F_5\cdot CH_3CN$ have been determined. Tables 1 and 2 present the X-ray crystallographic data. The molecular structures and coordination spheres of the cations along with selected molecular parameters are depicted in Figures 2–6 and S1–S3 (see Supporting Information).

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(29) Bochmann, M.; Sarsfield, M. J. *Organometallics* **1998**, *17*, 5908.

(30) See also: Korolev, A. V.; Ihara, E.; Guzei, I. A.; Young, V. G.; JordanR., F. *J. Am. Chem. Soc.* **2001**, *123*, 8291.

(31) (a) Krossing, I.; Reisinger, A. *Coord. Chem. Rev.* **2006**, *250*, 2721. (b) Gonsior, M.; Krossing, I.; Müller, L.; Raabe, I.; Jansen, M.; Van Wullen, L. *Chem.—Eur. J.* **2002**, *8*, 4475. (c) Krossing, I. *Dalton Trans.* **2002**, *4*, 500. (d) Krossing, I.; Raabe, I. *Chem.—Eur. J.* **2004**, *10*, 5017.

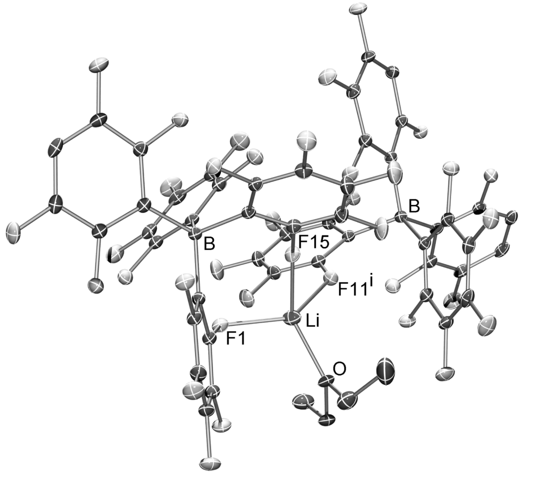

Figure 2. ORTEP drawing of the tetrahedral coordination around the Li$^+$ in the crystal of $[Li(Et_2O)][B(C_6F_5)_4]\cdot CH_2Cl_2$. Thermal ellipsoids are shown with 50% probability at 173 K. Selected distances in Å, angles in deg: Li−O1 1.946(6), Li−F11^i 1.996(3), Li−F15 2.003(3), Li−F1 2.020(3), Li−F12^i 2.489(4); O1−Li−F12^i 129.1(2), O1−Li−F15 122.2(2), F11^i−Li−F1 135.3(2), F11^i−Li−F15 86.7(1), F15−Li−F1 88.8(1). Symmetry code: i $-x+1/2$, $y-1/2$, $-z+3/2$.

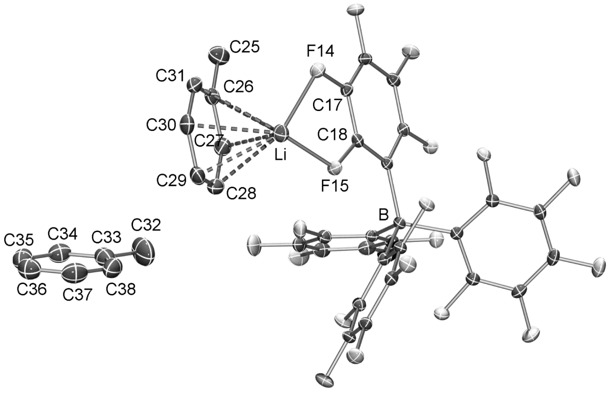

Figure 3. ORTEP drawing of the molecular structure of **3** (only one of the two independent molecules is shown) in the crystal. Thermal ellipsoids are shown with 50% probability at 228 K. Selected distances in Å, angles in deg: C25−C26 1.497(3), C26−C31 1.388(3), C26−C27 1.392(3), C27−C28 1.394(3), C28−C29 1.386(3), C29−C30 1.377(3), C30−C31 1.390(3), C32−C33 1.487(4), C33−C34 1.367(3), C33−C38 1.421(4), C34−C35 1.365(3), C35−C36 1.345(3), C36−C37 1.345(4), C37−C38 1.364(4); C31−C26−C27 118.5(2), C31−C26−C25 120.7(2), C27−C26−C25 120.8(2), C29−C28−C27 119.7(2), C30−C29−C28 119.8(2), C29−C30−C31 120.5(2), C34−C33−C38 115.7(2), C34−C33−C32 122.6(3), C38−C33−C32 121.7(3), C35−C34−C33 122.8(2) .

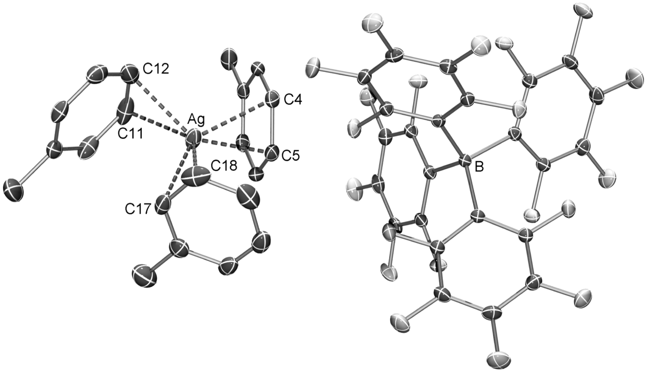

Figure 4. ORTEP drawing of the asymmetric unit of $[Ag(toluene)_3][B(C_6F_5)_4]$ in the crystal. Thermal ellipsoids are shown with 50% probability at 173 K.

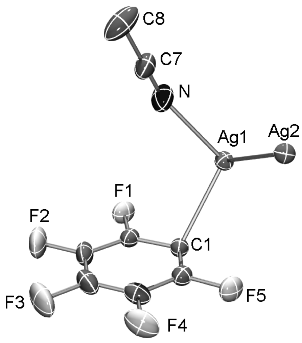

Figure 5. ORTEP drawing of the molecular structure of $Ag(C_6F_5)(CH_3CN)$ (the asymmetric unit is shown) in the crystal. Thermal ellipsoids are shown at 50% probability at 173 K.

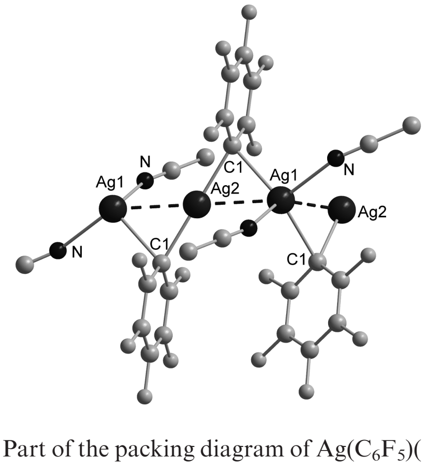

Figure 6. Part of the packing diagram of $Ag(C_6F_5)(CH_3CN)$ in the crystal. Thermal ellipsoids are shown with 50% probability at 228 K. Selected distances in Å, angles in deg: Ag1−C1^i 2.381(2), Ag1−N1 2.392(2), Ag1−Ag2 2.802(1), Ag2−C1^i 2.147(2); C1i−Ag1−C1 138.70(7), C1^i−Ag1−N1 105.33(6), C1−Ag1−N1 101.91(6), N1−Ag1−N1^i 96.24(9), C1^i−Ag1−Ag2 48.11(4), C1−Ag1−Ag2 105.05(4), N1−Ag1−Ag2 85.39(5), N1^i−Ag1−Ag2 148.52(4). Symmetry codes: (i) $-x$, y, $-z+1/2$; (ii) x, $-y$, $z-1/2$; (iii) $-x$, $-y$, $-z$.

$[Li(Et_2O)_4][B(C_6F_5)_4]$ crystallizes in the triclinic space group $P\bar{1}$ with two formula units per cell. The structure consists of separated Li$^+$(diethyl ether)$_4$ and tetrakis(pentafluorophenyl)borate units ($[B(C_6F_5)_4]^-$) with no significant cation···anion contacts. Only weak (ether)C−H···F−C(aryl) interactions are found. The crystallographic asymmetric unit contains one ion pair, [Li$^+$(diethyl ether)$_4$]-$[B(C_6F_5)_4]^-$ (Figure S1, see Supprting Information). The Li$^+$ ion is bonded to each oxygen atom of the four diethyl ether molecules, forming a tetrahedral coordination environment around the cation with Li−O distances between 1.952(5) and 1.970(5) Å. Two of the diethyl ether molecules are disordered.

The central boron atom of the $[B(C_6F_5)_4]^-$ anion is tetracoordinated. The average length of the B−C(aryl) linkage amounts to 1.649 Å (between 1.643 and 1.655 Å). The coordination geometry around boron in the BC$_4$ core is slightly distorted, with the smallest angle of 104.4(2)° and the largest 115.5(2)°.

[Li(Et$_2$O)][B(C$_6$F$_5$)$_4$]$\cdot$CH$_2$Cl$_2$ crystallizes in the monoclinic space group $P2_1/n$ with four formula units per cell. The asymmetric unit consists of one [Li(Et$_2$O)]$^+$ and [B(C$_6$F$_5$)$_4$]$^-$, as well as one CH$_2$Cl$_2$ molecule. Both the CH$_2$Cl$_2$ and the ether molecule are disordered. While the CH$_2$Cl$_2$ fills only the voids in the unit cell, the Et$_2$O molecules coordinate via the oxygen atom (d(Li−O) = 1.946(6) Å). Furthermore, three F$\cdots$Li$^+$ contacts are observed, resulting in a strongly distorted tetrahedral Li$^+$ coordination geometry with F−Li−F and F−Li−O bonding angles of 135.3(2)°, 88.8(1)°, 86.7(1)° and 109.8(2)°, 110.2(2)°, 122.2(2)°, respectively, as depicted in Figure 2. Two types of coordination modes are found for the three F$\cdots$Li$^+$ contacts: (i) monodentate via F11^i atom (d(Li−F11^i) = 1.996(6) Å); (ii and iii) bidentate via two F atoms (d(Li−F1) = 2.020(2), d(Li−F15) = 2.003(3) Å) of another adjacent [B(C$_6$F$_5$)$_4$]$^-$ ion. The sum of van der Waals radii for lithium and fluorine is 3.3 Å.[32] Taking this value into consideration, an additional weak F$\cdots$Li$^+$ contact is found (d(Li−F12^i) 2.489(4) Å), so that the coordination around the Li$^+$ ion is best described as a 4+1 coordination. Such weak F$\cdots$Li$^+$ contacts (with distances of 2.3−3.3 Å) were already observed by Strauss in lithium salts of the type Li[Al{OCH(CF$_3$)$_2$}$_4$] and Li[Al{OCH(CF$_3$)$_2$}$_4$].[33]

[Li(toluene)][B(C$_6$F$_5$)$_4$]$\cdot$toluene crystallizes in the triclinic space group $P\bar{1}$ with two formula units per cell. The asymmetric unit consists of one [Li(toluene)]$^+$ and [B(C$_6$F$_5$)$_4$]$^-$, as well as one noncoordinating toluene molecule (Figure 3). The most interesting structural feature is the coordination of the Li$^+$ ion, which coordinates to nine atoms (Figure S2, see Supporting Information). Besides one strongly interacting toluene molecule, which coordinates via all six ring carbon atoms in a η^6 fashion with Li−C distances of 2.515(4)−2.731(4) Å (cf. 2.533(16)−2.751(11) Å in [Li(benzene)][B(C$_6$F$_5$)$_4$]$\cdot$benzene),[34] four F$\cdots$Li$^+$ contacts with three different [B(C$_6$F$_5$)$_4$]$^-$ ions are observed, resulting in a strongly distorted pseudo-square-pyramidal Li$^+$ coordination geometry (toluene considered as one donor). Among these four F$\cdots$Li$^+$ contacts are one bidentate (d(Li−F14) = 2.210(3) and d(Li−F15) = 2.052(3) Å) and two monodentate coordination modes (d(Li−F9^i) = 2.038(3) and d(Li−F18^{ii} = 2.151(3) Å; cf. $\sum r_{\mathrm{ion}}(\mathrm{Li^+F^-})$ = 1.90 (CN = 4) and 2.09 (CN = 6) Å).[35] The known [Li(benzene)][B(C$_6$F$_5$)$_4$]$\cdot$benzene compound crystallizes isotypically as centrosymmetric dimers, also with two η^6-coordinated and two uncoordinated molecules of benzene per dimer.[34] Similar to [Li(toluene)][B(C$_6$F$_5$)$_4$]$\cdot$toluene, each Li$^+$ cation is linked by two [B(C$_6$F$_5$)$_4$] anions via short Li$\cdots$F contacts to form a centrosymmetric dimer. In addition, the Li$^+$ cation displays a short contact to an F atom of a neighboring [[B(C$_6$F$_5$)$_4$]$^-$ anion.

Comparison of the (C−C)$_{\mathrm{toluene}}$ bond lengths in the η^6-coordinated toluene molecule with those in the noncoordinating toluene molecule indicates that the coordinated (C−C)$_{\mathrm{toluene}}$ bonds are slightly affected upon coordination in the [Li(toluene)]$^+$ ion, leading to slightly longer bonds on average (Figure 4).

[Ag(Et$_2$O)$_3$][B(C$_6$F$_5$)$_4$] crystallizes in the triclinic space group $P\bar{1}$ with two formula units per cell. The silver cation is coordinated by three oxygen atoms of the diethyl ether molecules at significantly different distances. The local coordination environment, however, is almost planar. These fairly different Ag−O structural parameters can be attributed to steric repulsion between the ethyl groups. It should be noted that only a poor data set was obtained, which do not allow a detailed discussion of structural parameters but are good enough to prove unambiguously the existence of the [Ag(Et$_2$O)$_3$]$^+$ ion and the structural motif, in accord with structural data, published recently for [Ag(Et$_2$O)$_3$][N(CN)$_2\cdot$2B(C$_6$F$_5$)$_3$].[25] In agreement with these experimental observations, theoretical results by Feller and Dixon obtained for the gas-phase species [Ag(Me$_2$O)$_n$]$^+$ (n = 1−4, Me$_2$O = dimethyl ether) show the same picture.[36] The synthesis of [Ag(Et$_2$O)$_3$][BF$_4$] has already been reported but without any structural data,[37] and in agreement with our observation this salt loses the ether molecules at room temperature. Weakly coordinating anions such as [B(C$_6$F$_5$)$_4$]$^-$ and [N(CN)$_2\cdot$2B(C$_6$F$_5$)$_3$]$^-$ seem to stabilize this unusual tricoordination and lead to a larger thermal stability.

[Ag(toluene)$_3$][B(C$_6$F$_5$)$_4$] also crystallizes in the triclinic space group $P\bar{1}$ with two formula units per cell. The asymmetric unit consists of one independent [Ag(toluene)$_3$]$^+$ and one [B(C$_6$F$_5$)$_4$]$^-$ ion (Figure 4). No significant cation$\cdots$anion contacts are found (besides small F$_{\mathrm{aryl}}\cdots$H$_{\mathrm{toluene}}$ contacts, > 2.4 Å, and one Ag$\cdots$F contact < 4.0 Å at 3.415 Å, cf. $\sum r_{\mathrm{vdW}}(\mathrm{Ag\cdots F})$ = 3.2 Å).[35] The silver cation is coordinated by two carbon atoms (d(Ag−C) < 2.89 Å) of each of the three toluene molecules in an η^2 fashion (Figure S3, see Supporting Information), resulting in a coordination number of six. Each toluene molecule forms a short (d(Ag1−C17) = 2.413(2), d(Ag−C5) = 2.419(2), d(Ag−C12) = 2.440(2) Å) and a slightly longer bond (d(Ag−C4) = 2.552(2), d(Ag−C11) = 2.559(3), d(Ag1−C18) = 2.630(3) Å). The remaining four Ag−C$_{\mathrm{toluene}}$ distances are in the range 2.89−3.80 Å (Figure S3) and can be considered to be weak van der Waals interactions (cf. $\sum r_{\mathrm{cov}}(\mathrm{Ag{-}C})$ = 2.215 and $\sum r_{\mathrm{vdW}}(\mathrm{Ag\cdots C})$ = 3.4 Å).[35] The observed Ag−C distances are in good agreement with other Ag−C bonds in silver complexes; for example, in [Ag(toluene)$_2${Al(OR$^{\mathrm{F}}$)$_4$}] (R$^{\mathrm{F}}$ = CH(CF$_3$)$_2$) Ag−C bonds in the range 2.363(5)−2.647(6) Å are found.[28] In the latter complex besides the η^2 coordination of the two toluene molecules, two strong Ag−O and two weak Ag$\cdots$F interactions with the alkoxy anion are observed, while in [Ag(toluene)$_3$][B(C$_6$F$_5$)$_4$] no strong stabilizing Ag$\cdots$anion contacts are found.

The local silver coordination environment is slightly distorted pseudo trigonal planar with C$_{\mathrm{short}}$−Ag−C$_{\mathrm{short}}$ angles of 111.91°, 118.67°, and 128.81° (angle sum 359.39°). The distortion from perfect planarity can be attributed to packing effects. Recently, it was shown that weakly coordinating

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(32) (a) Pauling, L. *The Nature of Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960. (b) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(33) Ivanova, S. M.; Nolan, B. G.; Kobayashi, Y.; Miller, S. M.; Anderson, O. P.; Strauss, S. H. *Chem.—Eur. J.* **2001**, *7*, 503.

(34) Bolte, M.; Ruderfer, A.; Müller, T. *Acta Crystallogr.* **2005**, *E61*, m1581.

(35) Holleman, A. F.; Wiberg, E. N. *Lehrbuch der Anorganischen Chemie*, 102 ed.; Walter de Gruyter: Berlin, 2007; p 2002.

(36) Feller, D.; Dixon, D. *J. Phys. Chem. A* **2002**, *106*, 5136.

(37) Meerwein, H.; Hederich, V.; Wunderlich, K. *Ber. Deutsch. Pharm. Ges.* **1958**, *291*, 541.

anions[26] stabilize unusual tricoordination at Ag^+ as shown in $[Ag(Et_2O)_3][N[(CN) \cdot B(C_6F_5)_3]_2$ and $[Ag(\eta^2\text{-}C_2H_4)_3][Al\{OC(CF_3)_3\}_4]$, respectively.[25,38] Especially the $[Ag(\eta^2\text{-}C_2H_4)_3]^+$ ion, prepared by Krossing et al., and $[Ag(benzene)_3][B(C_6F_5)_4]$, prepared by Kitagawa, Komatsu, et al.,[39] strongly resemble the $[Ag(toluene)_3]^+$ ion with respect to structure and bonding. In all cases the key to formation of these complexes is the utilization of weakly coordinating ions, which formally generate pseudo-gas-phase conditions.[26a,40] Like $[Ag(toluene)_3]^+$ in $[Ag(toluene)_3][B(C_6F_5)_4]$, the $[Ag(\eta^2\text{-}C_2H_4)_3]^+$ ion forms an almost trigonal-planar, spokewheel arrangement. Furthermore, also no significant $(C{-}C)_{coordinated}$ bond elongation was found. The $(C{-}C)_{toluene}$ bond lengths compare well to those in uncoordinated toluene (cf. *d*(C4−C5) = 1.389(3), *d*(C11−C12) = 1.365(4), *d*(C17−C18) = 1.400(4), vs $d(C{-}C)_{uncoordinated}$ 1.327−1.391 Å in Figure S3 (see Supporting Information); in *d*(C−C) = 1.363−1.393 Å in pure toluene),[41] indicating that the coordinated $(C{-}C)_{toluene}$ bond is unaffected upon coordination in the $[Ag(toluene)_3]^+$ ion.

In comparison with the $[Ag(benzene)_3]^+$ ion it was found that the difference between the smaller and the longer Ag−C bonds (see above) is significantly smaller in $[Ag(toluene)_3]^+$ (average difference 0.284 vs 0.156 Å). Hence, in the case of $[Ag(benzene)_3]^+$ the authors concluded a nearly η^1 coordination, while in $[Ag(toluene)_3]^+$ an η^2 coordination like in $[Ag(\eta^2\text{-}C_2H_4)_3]^+$ can be assumed.

Examples of structurally characterized silver(I) compounds are still rare because of inter- and intramolecular exchange equilibria exhibiting a diverse complexity. Hence, the $[Ag(toluene)_3][B(C_6F_5)_4]$ fills this gap and represents an interesting extension to the $[Ag(\eta^2\text{-}C_2H_4)_3]^+$ and $[Ag(benzene)_3][B(C_6F_5)_4]$ ions. The first structural report on a "tris-benzene" Ag^+ complex, $[Ag(C_6D_6)_3][BF_4]$, was obtained by accident in the reaction of $[(dppe)RhCl]_2$ with EtCl in C_6D_6 and $AgBF_4$ as facilitator.[42] However, here the silver ion coordinates only one benzene-d_6 in a η^2 fashion, while the other two are coordinated in a η^1 fashion. The overall environment of the Ag^+ is trigonal-bipyramidal with one apical position occupied by a fluorine atom (*d*(Ag−F) = 2.488(8) Å).

$AgC_6F_5 \cdot CH_3CN$ crystallizes in the monoclinic space group *C*2/*c* with eight formula units per cell, which is isotypic to the related $AgC_6F_5 \cdot C_2H_5CN$ compound.[5] The asymmetric unit consists of an $Ag_2(C_6F_5)$ unit attached to one CH_3CN molecule (Figure 5). In the unit cell two crystallographically different Ag ions, Ag1 and Ag2, are present (Figures 5 and 6), with Ag2 in linear coordination (*d*(Ag2−C) = 2.147(2), cf. 2.128(5) Å in $AgC_6F_5 \cdot C_2H_5CN$) with two carbon atoms ($\angle(C1^i{-}Ag2{-}C1^{ii}) = 180.00(7)°$) of two bridging phenyl groups, while a bent $C1{-}Ag{-}C1^i$ moiety is found ($d(Ag1{-}C1^i) = 2.387(5)$, cf. 2.128(5) Å in $AgC_6F_5 \cdot C_2H_5CN$).[5,24,18] The acetonitrile molecule coordinates only to Ag1 at a distance of 2.392(2) Å,[22] which results in a distorted tetrahedral coordination.

Usually arylsilver[20−23] and perfluoroalkenylsilver[43] are tetrameric in the solid state, while diaryl argentates are built up from separated ion pairs.[24] Due to the existence of C_6F_5 bridges in $AgC_6F_5 \cdot CH_3CN$, infinite chains are formed in the unit cell as depicted in Figure 6. While most silver compounds with a bridging aryl ligand form polynuclear complexes,[5,16−18,20−22] the first reported example, exhibiting an infinite chain, was the $AgC_6F_5 \cdot C_2H_5CN$ compound.[5]

3. Experimental Section

General Information. All manipulations were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk or drybox techniques.

Dichloromethane was purified according to a literature procedure,[44] dried over P_4O_{10}, and freshly distilled prior to use. *n*-Hexane and *n*-pentane were dried over Na/benzophenone/tetraglyme and freshly distilled prior to use. Acetonitrile was dried over P_4O_{10} and freshly distilled prior to use. Toluene was dried over Na/K/benzophenone and freshly distilled prior to use. Bromopentafluorobenzene (99%, Alfa Aesar) was freshly distilled prior to use. Boron trichloride (99.9%, Aldrich) was recondensed prior to use. Silver fluoride (Aldrich, 99%) and *n*-BuLi (2.5 M, in hexanes, Acros) were used as received. Tris(pentafluorophenyl)borane $B(C_6F_5)_3$,[27] lithium tetrakis(pentafluorophenyl)borate diethyl etherate, $Li[B(C_6F_5)_4] \cdot Et_2O$,[27] and silver tetrakis(pentafluorophenyl)borate diethyl etherate, $Ag[B(C_6F_5)_4] \cdot Et_2O$,[45,46] have been reported previously, but were prepared according to modified procedures.

NMR. $^{19}F\{^1H\}$, $^{13}C\{^1H\}$, ^{13}C-DEPT, $^{11}B\{^1H\}$, and ^1H NMR spectra were obtained on a Bruker AVANCE 250 or 300 spectrometer and were referenced internally to the deuterated solvent (^{13}C, CD_2Cl_2: $\delta_{reference}$ = 54 ppm, CD_3CN: $\delta_{reference}$ = 118.1 ppm, C_6D_6: $\delta_{reference}$ = 128 ppm) or to protic impurities in the deuterated solvent (^1H, $CDHCl_2$: $\delta_{reference}$ = 5.31 ppm, C_6D_5H: $\delta_{reference}$ = 7.16 ppm). CD_2Cl_2 and CD_3CN were dried over P_4O_{10}; C_6D_6 was dried over Na/benzophenone. IR: Nicolet 380 FT-IR with Smart Orbit ATR device was used. Raman: Bruker VERTEX 70 FT-IR with RAM II FT-Raman module, equipped with a Nd:YAG laser (1064 nm) was used.[47] CHN analyses: Analysator Flash EA 1112 from Thermo Quest or C/H/N/S-Mikronalysator TruSpec-932 from Leco was used. Melting points are uncorrected (EZ-Melt, Stanford Research Systems). Heating rate 20 °C/min (clearing points are reported). DSC: DSC 823e from Mettler-Toledo, heating rate 5 °C/min, was used.

For details concerning X-ray structure determination see Supporting Information.

Synthesis of Lithium Tetrakis(pentafluorophenyl)borate, $Li[B(C_6F_5)_4]$. To a stirred solution of C_6F_5Br (4.939 g, 20 mmol) in *n*-pentane (80 mL) is added dropwise *n*-BuLi (2.5 M, 8.2 mL, 20.5 mmol) at −80 °C over a period of 5 min. The resulting colorless suspension is stirred for 30 min at this temperature. A suspension of finely ground $B(C_6F_5)_3$ (10.75 g, 21 mmol) in *n*-pentane (40 mL) is then added in one portion. The resulting colorless suspension is stirred for a further 5 min at this temperature and is then slowly warmed to ambient temperatures over a period of one hour. The resulting colorless suspension is filtered (F4) and washed three times by repeated back distillations of solvent. Removal of solvent and drying *in vacuo* at 110 °C for 10 hours

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(38) (a) Krossing, I.; Reisinger, A. *Angew. Chem.* **2003**, *115*, 5903; *Angew. Chem., Int. Ed.* **2003**, *42*, 5725. (b) Reisinger, A.; Trapp, N.; Krossing, I.; Altmannshofer, S.; Herz, V.; Presnitz, M.; Scherer, W. *Angew. Chem.* **2007**, *119*, 8445; *Angew. Chem., Int. Ed.* **2007**, *46*, 8295.

(39) Ogawa, K.; Kitagawa, T.; Ishida, S.; Komatsu, K. *Organomet.* **2005**, *24*, 4842.

(40) Cameron, T. S.; Decken, A.; Dionne, I.; Fang, M.; Krossing, I.; Passmore, J. *Chem.—Eur. J.* **2002**, *8*, 3386.

(41) Anderson, M.; Bosio, L.; Bruneaux-Poulle, J.; Fourme, R. *J. Chim. Phys. Phys.-Chim. Biol.* **1977**, 68.

(42) Batsanov, A. S.; Crabtree, S. P.; Howard, J. A. K.; Lehmann, Ch. W.; Kilner, M. *J. Organomet. Chem.* **1998**, *550*, 59.

(43) Jeffries, P. M.; Wilson, S. R.; Girolami, G. S. *J. Organomet. Chem.* **1993**, *449*, 203.

(44) Fischer, C. B.; Xu, S.; Zipse, H. *Chem.—Eur. J.* **2006**, *12*, 5779.

(45) Mukaiyama, T.; Maeshima, H.; Jona, H. *Chem. Lett.* **2001**, 388.

(46) Hayashi, Y.; Rohde, J. J.; Corey, E. J. *J. Am. Chem. Soc.* **1996**, *118*, 5502.

(47) Raman and IR data are given in the Supporting Information.

yields 9.199 g (13.4 mmol, 67%) of $Li[B(C_6F_5)_4]$ as a colorless solid. Mp: 253 °C (dec). Anal. Calcd (found): C, 42.02 (41.58); H, 0.00 (0.11). ^{11}B NMR (25 °C, C_6D_6, 96.3 MHz): δ −16.4. $^{13}C\{^1H\}$ NMR (25 °C, C_6D_6, 75.5 MHz): δ 123 (br, *ipso-C*), 137.3 (dm, *m-C*F, $^1J(^{13}C-^{19}F)$ = 246 Hz), 139.2 (dm, *p-C*F, $^1J(^{13}C-^{19}F)$ = 251 Hz), 148.6 (dm, *o-C*F, $^1J(^{13}C-^{19}F)$ = 238 Hz). $^{19}F\{^1H\}$ NMR (25 °C, C_6D_6, 282.4 MHz): δ −164.1 (m, *m*-C*F*, $^1J(^{13}C-^{19}F)$ = 246 Hz), −158.7 (dm, *p*-C*F*, $^1J(^{13}C-^{19}F)$ = 251 Hz), −134.9 (dm, *o*-C*F*, $^1J(^{13}C-^{19}F)$ = 238 Hz). Recrystallization from toluene gives $Li[B(C_6F_5)_4]\cdot 2$ toluene. Prolonged exposure to vacuum at elevated temperatures leads to a complete loss of the two toluene molecules.

Synthesis of Lithium Tetrakis(pentafluorophenyl)borate Diethyletherate, $Li[B(C_6F_5)_4]\cdot Et_2O$. To a stirred solution of C_6F_5Br (10.13 g, 41 mmol) in diethyl ether (200 mL) is added dropwise *n*-BuLi (2.5M, 16.4 mL, 41 mmol) at −80 °C over a period of 5 min. The resulting colorless suspension is stirred for 30 min at this temperature. A suspension of $B(C_6F_5)_3$ (20.48 g, 40 mmol) in diethyl ether (100 mL) is then added by means of PTFE tubing in one portion. The resulting colorless suspension is stirred for a further 10 min at this temperature and is then slowly warmed to ambient temperatures over a period of one hour. The solvent is removed *in vacuo*, resulting in a colorless, crystalline residue, which is washed two times with 100 mL portions of *n*-pentane and dried *in vacuo* (this crude product contains about 2.5 molecules of diethyl ether and shows a melting point of 120 °C). The crystalline residue is then slowly heated to 120 °C *in vacuo*, which yields 29.92 g (39.4 mmol, 98%) of $Li[B(C_6F_5)_4]\cdot Et_2O$ as a colorless solid. Mp: 184 °C. Anal. Calcd (found): C, 44.24 (44.06); H, 1.33 (1.47). ^1H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ 1.17 (t, 6H, C*H*$_3$, $^3J(^1H-^1H)$ = 7.1 Hz), 3.64 (q, 4H, C*H*$_2$, $^3J(^1H-^1H)$ = 7.1 Hz). ^{11}B NMR (25 °C, CD_2Cl_2, 80.3 MHz): δ −16.6. $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 62.9 MHz): δ 14.4 (s, *C*H$_3$), 67.5 (s, *C*H$_2$), 123.1 (br, *ipso-C*), 137.4 (dm, *m-C*F, $^1J(^{13}C-^{19}F)$ = 244 Hz), 139.3 (dm, *p-C*F, $^1J(^{13}C-^{19}F)$ = 249 Hz), 148.8 (dm, *o-C*F, $^1J(^{13}C-^{19}F)$ = 239 Hz). $^{19}F\{^1H\}$ NMR (25 °C, CD_2Cl_2, 282.4 MHz): δ −165.7 (m, *m*-C*F*, $^1J(^{13}C-^{19}F)$ = 244 Hz), −160.8 (dm, *p*-C*F*, $^1J(^{13}C-^{19}F)$ = 249 Hz), −135.5 (dm, *o*-C*F*, $^1J(^{13}C-^{19}F)$ = 239 Hz). The residual equivalent of diethyl ether may be removed by dissolution of $Li[B(C_6F_5)_4]\cdot Et_2O$ in excess toluene, removal of solvent, and drying for five hours at 60 °C *in vacuo*.

Synthesis of Silver Tetrakis(pentafluorophenyl)borate Diethyl Etherate, $Ag[B(C_6F_5)_4]\cdot Et_2O$. To a stirred solution of lithium tetrakis(pentafluorophenyl)borate diethyl etherate, $Li[B(C_6F_5)_4]\cdot Et_2O$ (7.601 g, 10 mmol), in diethyl ether (80 mL) is added ddropwise a solution of $AgNO_3$ (3.397 g, 20 mmol) in H_2O (20 mL, acidified with a few drops of HNO_3(conc)) at ambient temperatures, resulting in a colorless, clear aqueous layer and a colorless, clear diethyl ether layer. The mixture is shaken in a separation funnel and the ethereal layer is separated and washed again with H_2O (10 mL). The solvent is removed *in vacuo*, resulting in a pale brown residue, which is dried at 60 °C for two hours *in vacuo*. The resulting brownish solid is dissolved in dichloromethane (10 mL) and filtered (F4), resulting in a clear, colorless solution. Removal of solvent and drying *in vacuo* for three hours at 50 °C yields 8.206 g (9.53 mmol, 95%) of $Ag[B(C_6F_5)_4]\cdot Et_2O$ as a colorless microcrystalline solid. Mp: 117 °C (dec). Anal. Calcd (found): C, 39.06 (39.77); H, 1.17 (1.80). ^1H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ 1.30 (t, 6H, C*H*$_3$, $^3J(^1H-^1H)$ = 7.0 Hz, $^1J(^{13}C-^1H)$ = 126.4 Hz), 3.69 (q, 4H, C*H*$_2$, $^3J(^1H-^1H)$ = 7.0 Hz, $^1J(^{13}C-^1H)$ = 144.0 Hz). ^{11}B NMR (25 °C, CD_2Cl_2, 96.3 MHz): δ −14.7. $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ 16.0 (s, *C*H$_3$), 68.2 (s, *C*H$_2$), 124.8 (br, *ipso-C*), 136.9 (dm, *m-C*F, $^1J(^{13}C-^{19}F)$ = 245 Hz), 138.8 (dm, *p-C*F, $^1J(^{13}C-^{19}F)$ = 247 Hz), 148.7 (dm, *o-C*F, $^1J(^{13}C-^{19}F)$ = 239 Hz). $^{19}F\{^1H\}$ NMR (25 °C, CD_2Cl_2, 282.4 MHz): δ −165.7 (m, *m*-C*F*, $^1J(^{13}C-^{19}F)$ = 245 Hz), −161.8 (dm, *p*-C*F*, $^1J(^{13}C-^{19}F)$ = 247 Hz), −131.2 (dm, *o*-C*F*, $^1J(^{13}C-^{19}F)$ = 239 Hz).

Synthesis of Silver Tetrakis(pentafluorophenyl)borate Toluene Solvate, $Ag[B(C_6F_5)_4]\cdot 2$ Toluene. Silver tetrakis(pentafluorophenyl)borate diethyl etherate, $Ag[B(C_6F_5)_4]\cdot Et_2O$ (1.722 g, 2 mmol), is dissolved in toluene (20 mL) at ambient temperatures, resulting in a colorless, oily outer layer and a colorless, clear upper layer. Removal of solvent results in a colorless solid, which is dried *in vacuo* for five hours at 50 °C. The resulting residue is dissolved in a minimum of hot toluene and cooled to ambient temperature over a period of 10 hours, resulting in the deposition of colorless crystals. The supernatant is removed, and the crystalline residue is washed with *n*-pentane (5 mL) and dried *in vacuo* for five hours at 50 °C, which yields 1.616 g (1.66 mmol, 83%) of $Ag[B(C_6F_5)_4]\cdot 2$ toluene as a microcrystalline solid. Mp: 94 °C (dec). Anal. Calcd (found): C, 47.00 (46.46); H, 1.66 (1.73). ^1H NMR (25 °C, CD_2Cl_2, 250.13 MHz): δ 2.39 (s, 3H, C*H*$_3$), 6.8−7.7 (m, 5H, C*H*-aryl). $^{11}B\{^1H\}$ NMR (25 °C, CD_2Cl_2, 80.3 MHz): δ −16.6. $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 62.9 MHz): δ 21.8 (s, *C*H$_3$, toluene), 123.1 (s, *p-C*H, toluene), 124 (br, *ipso-C*), 127.2 (s, *C*H, toluene), 129.8 (s, *C*H, toluene), 136.9 (dm, *m-C*F, $^1J(^{13}C-^{19}F)$ = 244 Hz), 138.9 (dm, *p-C*F, $^1J(^{13}C-^{19}F)$ = 244 Hz), 114.5 (s, *ipso-C*, toluene), 148.8 (dm, *o-C*F, $^1J(^{13}C-^{19}F)$ = 236 Hz). $^{19}F\{^1H\}$ NMR (25 °C, CD_2Cl_2, 282.4 MHz): δ −167.4 (m, *m*-C*F*, $^1J(^{13}C-^{19}F)$ = 244 Hz), −163.4 (dm, *p*-C*F*, $^1J(^{13}C-^{19}F)$ = 244 Hz), −133.3 (dm, *o*-C*F*, $^1J(^{13}C-^{19}F)$ = 236 Hz).

Synthesis of Pentafluorophenyl Silver, AgC_6F_5. Lithium tetrakis(pentafluorophenyl)borate, $Li[B(C_6F_5)_4]$ (6.859 g, 10 mmol), and silver fluoride (1.649 g, 13 mmol) were combined and suspended in dichloromethane (60 mL). The resulting orange-colored suspension was sonicated in an ultrasonic bath at 40−60 °C for eight hours. The resulting grayish suspension is filtered (F5), resulting in a brownish, clear solution. The solvent is removed *in vacuo*, and the resulting pale brownish solid is redissolved in *n*-hexane (30 mL), filtered (F4), and washed four times by repeated back distillations of solvent. Removal of solvent and drying *in vacuo* yields 2.461 g (8.95 mmol, 90%) of pure $Ag[B(C_6F_5)_4]$ as an off-white solid. Mp: 276 °C. Anal. Calcd (found): C, 26.21 (25.89); H, 0.00 (0.00). $^{13}C\{^1H\}$ NMR (25 °C, CD_3CN, 62.9 MHz): δ 121.7 (br, *ipso-C*), 137.0 (dm, *m-C*F, $^1J(^{13}C-^{19}F)$ = 252 Hz), 140.1 (dm, *p-C*F, $^1J(^{13}C-^{19}F)$ = 244 Hz), 150.0 (dm, *o-C*F, $^1J(^{13}C-^{19}F)$ = 221 Hz). $^{19}F\{^1H\}$ NMR (25 °C, CD_3CN, 282.4 MHz): δ −163.1 (m, *m*-C*F*), −159.1 (dm, *p*-C*F*), −106.5 (dm, *o*-C*F*). $^{19}F\{^1H\}$ NMR (25 °C, CD_2Cl_2, 282.4 MHz): δ −158.3 (m, *m*-C*F*), −143.8 (br, *p*-C*F*), −100.4 (dm, *o*-C*F*). Recrystallization from CH_3CN gives $AgC_6F_5\cdot(CH_3CN)$.

Recovering of $B(C_6F_5)_3$. The washing solutions from the synthesis of $Li[B(C_6F_5)_4]$ and AgC_6F_5 contain mainly $B(C_6F_5)_3$, which is recovered by sublimation at 110 °C for six hours (cf. 3.2). This procedure yields about 73% of the possible quantity of $B(C_6F_5)_3$ as a colorless solid, which can directly be used for further syntheses.

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Supporting Information Available: Crystallographic data in CIF data format. The CIF files are also available online from the Cambridge Crystallographic Data Centre (CCDC Nos. 757606−757610). This material is available free of charge via the Internet at http://pubs.acs.org.