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Adduct Formation or Metathesis Reactions of Silver Complexes Containing the Fluorinated Ligands $[HB(3,5-(CF_3)_2Pz)_3]^-$ and $[CF_3SO_3]^-$: Formation of Silver Adducts Containing Unsupported Silver−Germanium Bonds

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A mixture of $[HB(3,5-(CF_3)_2Pz)_3]Ag(\eta^2$-toluene) and $[(Me)_2ATI]GeCl$ in CH_2Cl_2, rather than undergoing metathesis, formed a 1:1 adduct $[HB(3,5-(CF_3)_2Pz)_3]Ag\leftarrow GeCl[(Me)_2ATI]$ (**1**, where $[HB(3,5-(CF_3)_2Pz)_3]$ = hydrotris(3,5-bis(trifluoromethyl)pyrazolyl)borate and $[(Me)_2ATI]$ = *N*-methyl-2-(methylamino)troponiminate) featuring a silver−germanium bond. Solutions of **1** (in CH_2Cl_2 or toluene) did not precipitate AgCl even after several days. However, it easily underwent metathesis with CF_3SO_3Ag, leading to the chloride-free product $[HB(3,5-(CF_3)_2Pz)_3]Ag\leftarrow Ge(OSO_2CF_3)[(Me)_2ATI]$ (**2**). Compounds **1** and **2** were characterized by X-ray crystallography. The Ag−Ge bond distances of **1** and **2** are 2.4215(9) and 2.4116(10) Å, respectively.

Introduction

Silver salt metathesis is the most widely used method of introducing weakly coordinating anions to a metal ion.[1−3] It requires a metal halide and a silver derivative of a weakly coordinating ligand as starting materials. The product formation is driven by the silver halide precipitation. Silver salt metathesis reaction proceeds smoothly for a large number of ligand−metal combinations. However, there are instances where this method completely fails or proceeds very slowly.[1,3] Such situations are usually encountered when large, weakly coordinating anions are used in the reaction. On rare occasions, these mixtures produce long-lived, isolable intermediates. Two such examples are $CpFe(CO)_2I\rightarrow Ag(B_{11}CH_{12})$[2] and $(PPh_3)_2(CO)(Cl)Ir\rightarrow Ag(B_{11}CH_{12})$.[4] These species are very important because they provide valuable clues about the mechanism of the silver salt metathesis process, which is complex and has not been well understood for inorganic systems.[2,5,6]

An area of interest to us concerns the chemistry of two-coordinate, cationic group 14 species such as $\{[(i\text{-}Pr)_2ATI]Ge\}^+$ and $\{[(i\text{-}Pr)_2ATI]Sn\}^+$ (where $[(i\text{-}Pr)_2ATI]$ = *N*-isopropyl-2-(isopropylamino)troponiminate).[7−9] The halide abstraction from the appropriate starting material is the most convenient approach to their synthesis. For example, the treatment of $[(i\text{-}Pr)_2ATI]GeCl$ or $[(Me)_2ATI]GeCl$ with CF_3SO_3Ag in CH_2Cl_2 leads to rapid chloride/$CF_3SO_3^-$ metathesis and the formation of the expected product $[(i\text{-}Pr)_2ATI]GeOSO_2CF_3$ or $[(Me)_2ATI]GeOSO_2CF_3$, respectively (Figure 1).[7] We have also investigated the effects of counterion on the properties of the cationic germanium species. Some weakly coordinating anions, e.g., $[(\eta^5\text{-}C_5H_5)ZrCl_2(\mu\text{-}Cl)_3ZrCl_2(\eta^5\text{-}C_5H_5)]^-$, serve well as counterions to cationic germanium species, while others like BPh_4^- react with the Ge^+ ion, leading to various products, e.g., $[(Me)_2ATI]GePh\cdot BPh_3$.[7]

Highly fluorinated tris(pyrazolyl)borates such as $[HB(3,5-(CF_3)_2Pz)_3]^-$ (where $[HB(3,5-(CF_3)_2Pz)_3]$ = hydrotris(3,5-bis(trifluoromethyl)pyrazolyl)borate) are an interesting group of anions with weak donor properties.[10−15] It is even possible to isolate compounds featuring a "naked" $[HB(3,5-(CF_3)_2Pz)_3]^-$ ion.[13] Thus, they may be useful as weakly coordinating counterions in various applications. In this paper, we report results from a study that involves the use of $[(Me)_2ATI]GeCl$ and $[HB(3,5-(CF_3)_2Pz)_3]Ag$ salts[16,17] to generate cationic germanium compounds containing the $[HB(3,5-(CF_3)_2Pz)_3]^-$ counterion.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of purified nitrogen either using standard Schlenk techniques or in a Vacuum Atmospheres single-station drybox equipped with a −25 °C refrigerator. Solvents were purchased from commercial sources and distilled from conventional drying agents prior to use. Glassware was oven-dried at 150 °C overnight. The NMR spectra were recorded at 25 °C on a Bruker MSL-300 spectrometer (^1H, 300.15 MHz; ^{13}C, 75.47 MHz; ^{19}F, 282.36 MHz). Proton and carbon chemical shifts are

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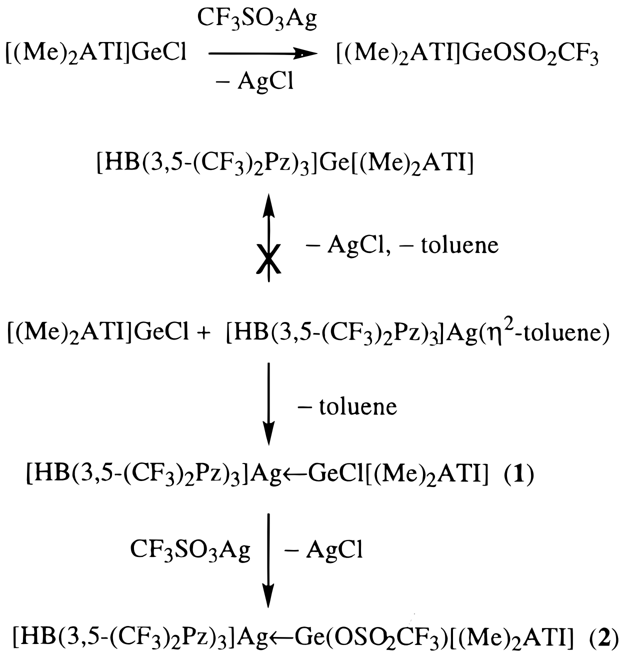

Figure 1. Reactivity of $[(Me)_2ATI]GeCl$ toward silver salts of $[HB(3,5-(CF_3)_2Pz)_3]^-$ and $[CF_3SO_3]^-$.

reported in parts per million versus Me_4Si. ^{19}F NMR chemical shifts were referenced relative to an external $CFCl_3$ standard. Infrared spectra were recorded on a BioRad 40S spectrometer. Melting points were obtained on a Mel-Temp II apparatus and were not corrected. Elemental analyses were performed at the University of Texas at Arlington using a Perkin-Elmer Model 2400 CHN analyzer. Syntheses of $[(Me)_2ATI]GeCl$ and $[HB(3,5-(CF_3)_2Pz)_3]Ag(\eta^2$-toluene) were carried out as reported previously.[7,17]

$[HB(3,5-(CF_3)_2Pz)_3]Ag{\leftarrow}GeCl[(Me)_2ATI]$ (1). $[(Me)_2ATI]GeCl$ (300 mg, 1.18 mmol) and $[HB(3,5-(CF_3)_2Pz)_3]Ag(\eta^2$-toluene) (97 mg, 1.18 mmol) were mixed in dichloromethane (15 mL) at room temperature. The solution was stirred overnight and filtered through a bed of Celite. The filtrate was concentrated, mixed with a small amount of toluene, and kept at −25 °C. Yellow crystals of **1** were obtained in 90% yield. Mp: 172−174 °C. ^1H NMR ($CDCl_3$): δ 3.35 (s, 6H, CH_3), 6.89 (s, 3H, Pz-CH), 7.00 (d, 1H, $J = 11.3$ Hz), 7.02 (t, 2H, $J = 9.7$ Hz), 7.57 (dd, 2H, $J = 9.7, 11.3$ Hz). ^{19}F NMR ($CDCl_3$): δ −58.9 (d, ^5J(F,H) = 3.2 Hz), −61.1 (d, ^4J(F,Ag) = 1.9 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 31.5 (CH_3), 106.3 (CH), 116.9, 119.3 (q, ^1J(C,F) = 270 Hz, CF_3), 120.4 (q, ^1J(C,F) = 270 Hz, CF_3), 125.6, 138.8, 140.0 (q, ^2J(C,F) = 42.6 Hz, CCF_3), 143.4 (q, ^2J(C,F) = 38.3 Hz, CCF_3), 158.6. IR (Nujol mull), cm^{-1}: 2631 (B-H). Anal. Calcd for $C_{24}H_{15}F_{18}N_8BAgGeCl{\cdot}CH_2Cl_2$: C, 28.09; H, 1.60; N, 10.48. Found: C, 28.09; H, 1.13; N, 9.98.

$[HB(3,5-(CF_3)_2Pz)_3]Ag{\leftarrow}Ge(OSO_2CF_3)[(Me)_2ATI]$ (2). $[HB(3,5-(CF_3)_2Pz)_3]Ag{\leftarrow}GeCl[(Me)_2ATI]$ (300 mg, 0.28 mmol) and CF_3SO_3Ag (7 mg, 0.28 mmol) were mixed in dichloromethane (15 mL) at room temperature. The solution was stirred overnight and filtered through a bed of Celite. The filtrate was concentrated, mixed with a small amount of toluene, and kept at −25 °C. Yellow crystals of **2** were obtained in 93% yield. Mp: at ~120 °C, the color of the sample changed to brown, and then the sample melted at 200−201 °C. ^1H NMR ($CDCl_3$): δ 3.53 (s, 6H, CH_3), 6.92 (s, 3H, CH), 7.36 (d, 1H, $J = 11.3$ Hz), 7.38 (t, 2H, $J = 9.5$ Hz), 7.85 (t, 2H, $J = 10.4$ Hz). ^{19}F NMR ($CDCl_3$): δ −58.9 (d, ^5J(F,H) = 2.7 Hz, CF_3), −61.1 (CF_3), −78.2 (SO_3CF_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 32.1 (CH_3), 106.3 (CH), 118.7, 119.0 (q, ^1J(C,F) = 332 Hz, SO_3CF_3), 119.2 (q, ^1J(C,F) = 270 Hz, CF_3), 120.3 (q, ^1J(C,F) = 270 Hz, CF_3), 128.8, 139.3 (q, ^2J(C,F) = 32.0 Hz, CCF_3), 139.5, 143.6 (q, ^2J(C,F) = 37.7 Hz, CCF_3), 159.8. IR (Nujol mull), cm^{-1}: 2631 (B-H). Anal. Calcd for $C_{25}H_{15}F_{21}N_8BO_3SAgGe{\cdot}CH_2Cl_2$: C, 26.41; H, 1.45; N, 9.47. Found: C, 27.10; H, 1.52; N, 9.18.

Table 1. Crystal Data for $[HB(3,5-(CF_3)_2Pz)_3]Ag{\leftarrow}GeCl[(Me)_2ATI]$ (**1**) and $[HB(3,5-(CF_3)_2Pz)_3]Ag{\leftarrow}Ge(OSO_2CF_3)[(Me)_2ATI]$ (**2**)

compound	**1**·CH_2Cl_2	**2**
formula	$C_{25}H_{17}AgBCl_3F_{18}GeN_8$	$C_{25}H_{15}AgBF_{21}GeN_8O_3S$
fw	1069.09	1097.78
T, K	183(2)	183(2)
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a, Å	14.148(2)	18.279(3)
b, Å	17.524(2)	9.142(2)
c, Å	16.006(3)	23.008(4)
α, deg	90	90
β, deg	114.120(12)	108.248(8)
γ, deg	90	90
V, Å^3	3622.1(11)	3651.5(13)
Z	4	4
λ (Mo Kα), Å	0.710 73	0.710 73
D_c, Mg/m^3	1.960	1.997
μ (Mo Kα), mm^{-1}	1.719	1.568
GOF (on F^2)	1.068	1.045
R1, wR2 ($I > 2\sigma(I)$)^a	0.0393, 0.0837	0.0527, 0.1311
R1, wR2 (all data)^a	0.0564, 0.0905	0.0682, 0.1434

^{a} $R1 = [\Sigma||F_o| - |F_c||]/[\Sigma|F_o|]$ and $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/[\Sigma[w(F_o^2)^2]]^{1/2}$.

X-ray Structure Determination. A suitable crystal covered with a layer of hydrocarbon oil was selected and attached to a glass fiber and immediately placed in the low-temperature nitrogen stream. Data collections were carried out at low temperature on a Siemens P4 diffractometer equipped with a LT-2A device for low-temperature work and graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The unit cell parameters of **1** and **2** were determined by least-squares refinement of 26 and 37 reflections, respectively. Structures were solved by direct methods, followed by successive cycles of full-matrix least-squares refinement on F^2 and difference Fourier analysis. All the non-hydrogen atoms were refined anisotropically. The H atoms on boron were located from the difference map. The remaining hydrogens were included at calculated positions. They were treated as riding atoms with isotropic displacement parameters fixed at 1.2 or 1.5 times the values refined for the respective host atom. Compound **1** crystallizes with a molecule of CH_2Cl_2 in the asymmetric unit. In compound **2**, a rotational disorder (over two sites) was observed for the CF_3 fluorines of C16 and C26, and this disorder was modeled successfully. Software programs and the sources of scattering factors are contained in the Bruker SHELXTL 5.1 software package provided by the Bruker Analytical X-ray Instruments, Inc. Some details of data collection and refinements are given in Table 1. Selected bond distances and angles are given in Tables 2 and 3.

Results and Discussion

Germanium(II) compounds $[(R)_2ATI]GeOSO_2CF_3$ (where R = Me, *n*-Pr, *i*-Pr) can be synthesized easily from a metathesis reaction between the corresponding chloro adducts $[(R)_2ATI]GeCl$ and CF_3SO_3Ag.[7,18] However, a mixture of $[HB(3,5-(CF_3)_2Pz)_3]Ag(\eta^2$-toluene)[17] and $[(Me)_2ATI]GeCl$[7] in CH_2Cl_2, rather than undergoing metathesis, produced a very interesting 1:1 adduct $[HB(3,5-(CF_3)_2Pz)_3]Ag{\leftarrow}GeCl[(Me)_2ATI]$ (**1**) featuring a silver−germanium bond. Compound **1** has been isolated as a yellow crystalline solid in 90% yield. Results of the X-ray crystallographic study established that the silver complex **1** contains an Ag−Ge bond rather than an Ag−Cl linkage (Figure 2). The silver−germanium bond distance of **1** is 2.4215(9) Å. Compound **1** is a rare structurally characterized molecule with an unsupported silver−germanium bond.[19,20] Structures and

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag$\leftarrow$GeCl[(Me)$_2$ATI] (**1**)

Ag−N(32)	2.375(4)	N(31)−B	1.556(8)
Ag−N(22)	2.400(4)	N(1)−C(2)	1.332(7)
Ag−Ge	2.4215(9)	N(1)−C(10)	1.465(7)
Ag−N(12)	2.431(4)	N(9)−C(8)	1.351(7)
Ge−N(1)	1.885(5)	N(9)−C(11)	1.461(7)
Ge−N(9)	1.896(5)	C(2)−C(3)	1.414(8)
Ge−Cl(1)	2.2573(18)	C(2)−C(8)	1.460(8)
N(11)−N(12)	1.354(6)	C(3)−C(4)	1.378(9)
N(11)−B	1.563(8)	C(4)−C(5)	1.374(10)
N(21)−N(22)	1.358(6)	C(5)−C(6)	1.373(10)
N(21)−B	1.552(8)	C(6)−C(7)	1.381(9)
N(31)−N(32)	1.360(6)	C(7)−C(8)	1.396(8)
N(32)−Ag−N(22)	82.17(15)	N(21)−B−N(11)	109.3(5)
N(32)−Ag−Ge	134.88(10)	N(31)−B−N(11)	109.5(4)
N(22)−Ag−Ge	126.60(11)	C(2)−N(1)−C(10)	122.4(5)
N(32)−Ag−N(12)	78.48(14)	C(2)−N(1)−Ge	115.8(4)
N(22)−Ag−N(12)	79.96(14)	C(10)−N(1)−Ge	121.7(4)
Ge−Ag−N(12)	134.23(10)	C(8)−N(9)−C(11)	122.5(5)
N(1)−Ge−N(9)	82.7(2)	C(8)−N(9)−Ge	115.1(4)
N(1)−Ge−Cl(1)	99.80(16)	C(11)−N(9)−Ge	121.9(4)
N(9)−Ge−Cl(1)	97.80(15)	N(1)−C(2)−C(3)	121.9(6)
N(1)−Ge−Ag	122.10(14)	N(1)−C(2)−C(8)	113.2(5)
N(9)−Ge−Ag	130.47(15)	N(9)−C(8)−C(7)	121.1(6)
Cl(1)−Ge−Ag	116.14(5)	N(9)−C(8)−C(2)	112.3(5)
N(21)−B−N(31)	109.9(4)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag$\leftarrow$Ge(OSO$_2$CF$_3$)[(Me)$_2$ATI] (**2**)

Ag−N(32)	2.367(6)	N(1)−C(2)	1.339(9)
Ag−N(22)	2.373(6)	N(9)−C(8)	1.311(9)
Ag−N(12)	2.397(6)	C(2)−C(3)	1.403(11)
Ag−Ge	2.4116(10)	C(2)−C(8)	1.461(11)
Ge−N(1)	1.865(6)	C(3)−C(4)	1.367(12)
Ge−N(9)	1.883(6)	C(4)−C(5)	1.366(13)
Ge−O(1)	2.020(5)	C(5)−C(6)	1.384(12)
N(11)−N(12)	1.358(8)	C(6)−C(7)	1.358(11)
N(11)−B	1.550(10)	C(7)−C(8)	1.416(11)
N(21)−N(22)	1.361(8)	C(12)−S	1.825(12)
N(21)−B	1.558(11)	S−O(3)	1.398(7)
N(31)−N(32)	1.367(8)	S−O(2)	1.407(7)
N(31)−B	1.556(10)	S−O(1)	1.464(6)
N(32)−C(33)	1.317(9)		
N(32)−Ag−N(22)	81.4(2)	N(11)−B−N(31)	109.3(6)
N(32)−Ag−N(12)	77.82(19)	N(11)−B−N(21)	110.2(6)
N(22)−Ag−N(12)	81.8(2)	N(31)−B−N(21)	110.4(6)
N(32)−Ag−Ge	135.03(14)	N(1)−C(2)−C(3)	122.9(7)
N(22)−Ag−Ge	136.07(15)	N(1)−C(2)−C(8)	112.1(6)
N(12)−Ag−Ge	123.12(15)	N(9)−C(8)−C(7)	122.1(7)
N(1)−Ge−N(9)	83.4(3)	N(9)−C(8)−C(2)	113.7(6)
N(1)−Ge−O(1)	95.3(2)	O(3)−S−O(2)	118.2(5)
N(9)−Ge−O(1)	93.6(2)	O(3)−S−O(1)	113.0(4)
N(1)−Ge−Ag	129.54(18)	O(2)−S−O(1)	111.1(4)
N(9)−Ge−Ag	126.68(19)	O(3)−S−C(12)	105.7(6)
O(1)−Ge−Ag	118.22(14)	O(2)−S−C(12)	103.7(5)
C(2)−N(1)−Ge	115.6(5)	O(1)−S−C(12)	103.5(4)
C(8)−N(9)−Ge	115.1(5)	S−O(1)−Ge	129.3(3)

bonding of such compounds with transition metal−main group element bonds are also of significant current interest.[21−23]

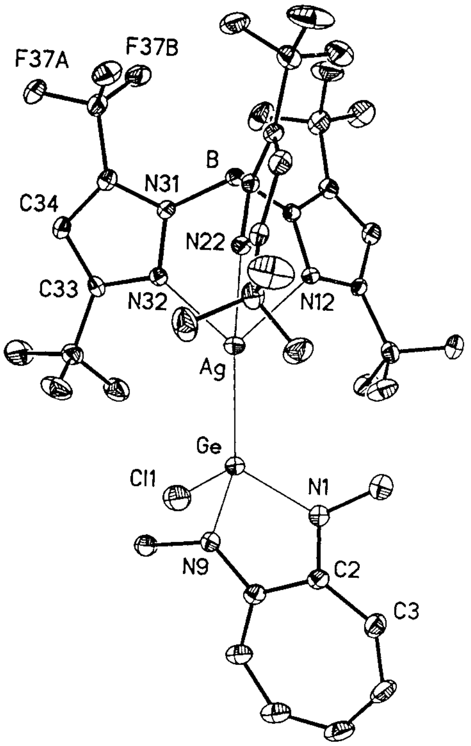

Figure 2. Molecular structure of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag$\leftarrow$GeCl[(Me)$_2$ATI] (**1**); hydrogen atoms have been omitted for clarity.

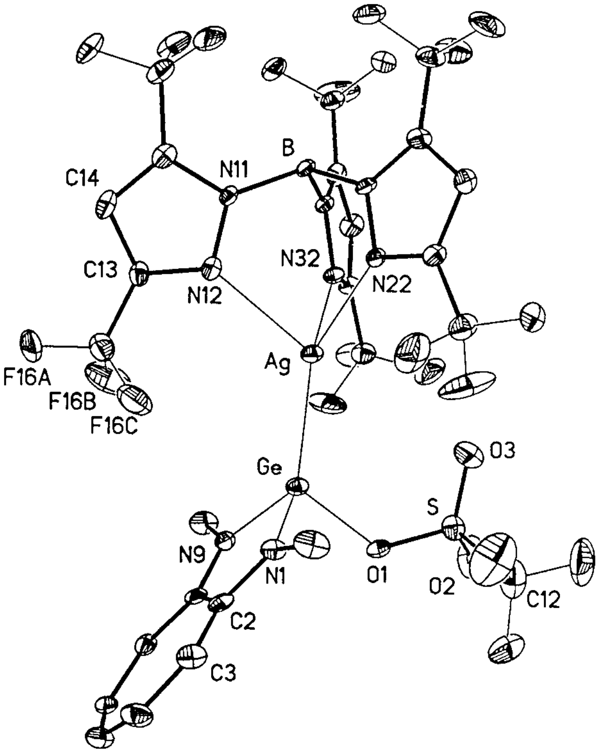

Figure 3. Molecular structure of [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag$\leftarrow$Ge(OSO$_2$CF$_3$)[(Me)$_2$ATI] (**2**); hydrogen atoms have been omitted for clarity.

Solutions of **1** (in CH$_2$Cl$_2$ or toluene) did not precipitate AgCl even after several days. However, it easily underwent metathesis with CF$_3$SO$_3$Ag, leading to the chloride-free product [HB(3,5-(CF$_3$)$_2$Pz)$_3$]Ag$\leftarrow$Ge(OSO$_2$CF$_3$)[(Me)$_2$ATI] (**2**) and AgCl in

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(19) *Cambridge Structural Database*; Cambridge Crystallographic Data Centre: Cambridge, England, 1999.

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quantitative yield (Figure 1). Compound **2** also features an unsupported silver−germanium bond (Figure 3). The Ag−Ge bond of **2** (2.4116(10) Å) is slightly shorter than that of **1** (2.4215(9) Å). The coordination geometry of Ag(I) and Ge(II) ions of **1** and **2** may be described as pseudotetrahedral. The average Ge−N bond distances of **1** (1.891(5) Å) and **2** (1.874(6) Å) are shorter than the corresponding bond length of the three-coordinate starting material $[(Me)_2ATI]GeCl$ (1.937(3) Å).[7] This is probably a result of an increased s-character of the Ge−N bond due to silver ion coordination to the germanium atom. The N−Ge−N angle of **1** or **2** is about 3° larger than that of $[(Me)_2ATI]GeCl$ (80.1(1)°).

The fact that $[(Me)_2ATI]GeCl$ undergoes metathesis with CF_3SO_3Ag[24] but not with $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(\eta^2\text{-toluene})$ suggests that weakly coordinating anions play an active role in these reactions. However, we have successfully used silver salts of $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ in metathesis reactions involving various metal and metalloid halides, e.g., Au(CO)Cl, $Mn(CO)_5Br$, InCl, and GaI.[14,16,25,26] Thus, the nature of the metal/metalloid−halide interaction is also important.

Overall, results from this paper and a few previous studies suggest that the success of halide abstraction by the silver ion depends on several factors, including the nature of the metalloid/metal−halide bond, the anion, and the solvent.[1−5] The mechanism also appears to be diverse, as evident from the isolable intermediates such as $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag\leftarrow GeCl[(Me)_2ATI]$ and $CpFe(CO)_2I\rightarrow Ag(B_{11}CH_{12})$. Considering the growing importance of weakly donating ligands in various applications,[3,27] we believe that more efforts are clearly warranted to understand the mechanism of the silver salt metathesis, the most common method of their introduction to metals.[1] We are currently studying the effects of metalloid and halide ions on $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag$ metathesis chemistry.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag\leftarrow GeCl[(Me)_2ATI]$ and $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag\leftarrow Ge(OSO_2CF_3)[(Me)_2ATI]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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