

# Germanium-Containing Heterobicyclic 10- $\pi$ -Electron Ring Systems. Synthesis and Characterization of Neutral and Cationic Germanium(II) Derivatives of Aminotroponimines

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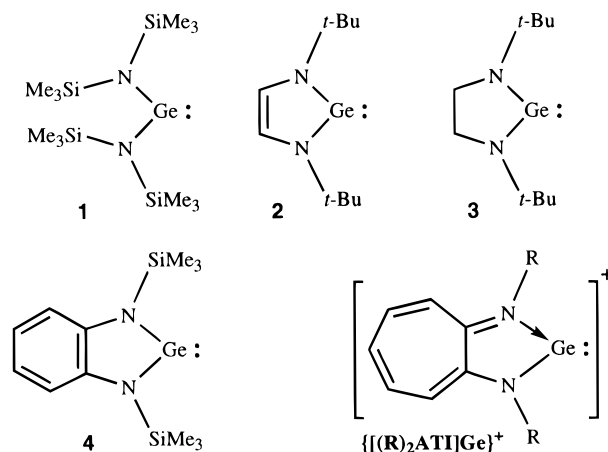
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**Abstract:** The neutral and cationic aminotroponimine derivatives of germanium(II) have been investigated. The treatment of  $\text{GeCl}_2 \cdot (1,4\text{-dioxane})$  with  $[(i\text{-Pr})_2\text{ATI}]\text{Li}$  or  $[(\text{Me})_2\text{ATI}]\text{Li}$  in a 1:1 molar ratio gave the corresponding monochloro germanium(II) complex. Substitution of the chloride ion of  $[(i\text{-Pr})_2\text{ATI}]\text{GeCl}$  with weakly coordinating anions  $[\text{CF}_3\text{SO}_3]^-$  and  $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2(\mu\text{-Cl})_3\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_5)]^-$  led to cationic germanium(II) species containing  $\{[(i\text{-Pr})_2\text{ATI}]\text{Ge}\}^+$  ion. Although NMR data of the cationic species show notable differences relative to their neutral analog, the solid state data show only minor changes in the  $\text{C}_7\text{N}_2\text{Ge}$  moiety. The Ge–N bond distances of the cations are not indicative of significant Ge–N  $\pi$ -bonding. These compounds feature some of the smallest N–Ge–N angles known for Ge(II) compounds. Attempted synthesis of the tetraphenylborate salt of  $\{[(\text{Me})_2\text{ATI}]\text{Ge}\}^+$  led to a phenyl group transfer product  $[(\text{Me})_2\text{ATI}]\text{GePh} \cdot \text{BPh}_3$  with a Ge(II)–B bond. Details of the  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectroscopy and X-ray crystal structures of all these compounds are described.

## Introduction

In the last two decades the chemistry of thermally stable bivalent compounds of germanium has developed into an active area of research.<sup>1–8</sup> Ligands with nitrogen donors have particularly been useful in the synthesis of these systems. Compounds **1–4** represent a group of monomeric germynes (germanium analogs of carbene) with good thermal stability.<sup>9–12</sup> They display two-coordinate, V-shaped geometry at the germanium center. Sterically demanding substituents are necessary to prevent the aggregation of these species. For example, the *N*-isopropyl analog of **3** forms dimers in the solid state.<sup>13</sup> Compound **2** is significantly more stable than the closely related **3**.<sup>11</sup> This and the results from several other studies suggest that the conjugated ligand backbones may also play an important role in improving the stability.<sup>2,14,15</sup> In fact, it is even possible to isolate carbon<sup>16–18</sup> and silicon<sup>19</sup> analogs of **2** (carbenes and silylenes) in stable crystalline form.<sup>2</sup> Some of the germynes

serve as good precursors (e.g., **3**) for the chemical vapor deposition of germanium<sup>11,13</sup> or as starting material (e.g., **1**) for the synthesis of various germanium derivatives.<sup>7,8,20–23</sup>



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In contrast to the neutral germynes (e.g., **1–4**), related cationic germanium(II) complexes are rare.<sup>1</sup> A small number of such species having cyclopentadienyl ligands (e.g.,  $\{[\eta^5\text{-C}_5\text{Me}_5]\text{Ge}\}\text{X}$ , where  $\text{X} = [\text{BF}_4]$ ,  $[\text{CF}_3\text{SO}_3]$ , and  $[\text{AlCl}_4]$ ;<sup>24,25</sup>

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{ $[\eta^2\text{-Me}_4\text{C}_5\text{H}]\text{Me}_2\text{Si}[\eta^5\text{-Me}_4\text{C}_5]\text{Ge}][\text{GeCl}_3]$ },<sup>26,27</sup> arenes (e.g., [ $(p\text{-C}_6\text{H}_4\text{CH}_2\text{CH}_2)_3\text{GeCl}_2$ ] $[\text{Al}_4\text{O}_2\text{Cl}_{10}]$ ),<sup>28</sup> and nitrogen donors (e.g., [ $\text{Ge}_2(3,5\text{-}(\text{CH}_3)_2\text{Pz})_3][\text{GeCl}_3]$ )<sup>29</sup> and {[HB(3,5- $(\text{CH}_3)_2\text{Pz})_3\text{-Ge}]\text{I}$ }<sup>30</sup> have been reported in the literature.

One area of focus in our laboratory is the chemistry of *N*-alkyl-2-(alkylamino)troponimate ( $[(\text{R})_2\text{ATI}]^-$ ) derivatives of main group elements.<sup>31–33</sup> This ligand  $[(\text{R})_2\text{ATI}]^-$ , which features a delocalized 10- $\pi$ -electron ligand backbone, has not been used widely in the main group chemistry.<sup>31–35</sup> Considering the current level of interest in the main group heterocyclic  $\pi$ -systems,<sup>2,11,12,14–16,18,19,36–43</sup> and the importance of germynes<sup>1–8</sup> and the germanium centered cations,<sup>1,24,44–46</sup> we have decided to investigate the neutral and cationic  $[(\text{R})_2\text{ATI}]^-$  derivatives of germanium(II). We were particularly interested in investigating the role the two nitrogen donors and the cyclic  $\pi$ -system in  $[(\text{R})_2\text{ATI}]^-$  may play in stabilizing species such as  $\{[(\text{R})_2\text{ATI}]\text{Ge}\}^+$  in the monomeric form.

In this paper we report the synthesis and characterization of germanium(II) derivatives of aminotroponimate ligands  $[(i\text{-Pr})_2\text{ATI}]^-$  and  $[(\text{Me})_2\text{ATI}]^-$ . They include a novel cationic species  $\{[(i\text{-Pr})_2\text{ATI}]\text{Ge}\}[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2(\mu\text{-Cl})_3\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_5)]$  and a triphenylboron adduct  $[(\text{Me})_2\text{ATI}]\text{GePh}\cdot\text{BPh}_3$ . Synthesis of  $[(\text{Me})_2\text{ATI}]\text{GePh}\cdot\text{BPh}_3$  involves a phenyl group transfer from a  $\text{BPh}_4^-$  anion.

## Experimental Section

All manipulations were carried out under an atmosphere of purified nitrogen with standard Schlenk techniques or in a Vacuum Atmospheres single station drybox equipped with a  $-25^\circ\text{C}$  refrigerator. Solvents were distilled from conventional drying agents and degassed twice prior to use. Glassware was oven-dried at  $150^\circ\text{C}$  overnight.  $[(i\text{-Pr})_2\text{ATI}]\text{H}$ ,<sup>31</sup>  $[(\text{Me})_2\text{ATI}]\text{H}$ ,<sup>33</sup> and  $\text{GeCl}_2\cdot(1,4\text{-dioxane})$  were prepared according to the previously reported methods. *n*-BuLi (1.6 M solution in hexane),  $(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_3$ ,  $\text{CF}_3\text{SO}_3\text{Ag}$ , and  $\text{NaBPh}_4$  were obtained from commercial sources and used as received. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at room temperature on a Bruker MSL-300 spectrometer ( $^1\text{H}$ , 300.13 MHz;  $^{13}\text{C}$ , 75.47 MHz) or a Nicolet NT-200 spectrometer ( $^1\text{H}$ , 200.07 MHz;  $^{13}\text{C}$ , 50.31 MHz), unless otherwise noted. Chemical shifts for  $^1\text{H}$  NMR spectra are relative to internal  $\text{Me}_4\text{Si}$ . The  $^{13}\text{C}$  NMR

spectra were run with  $^1\text{H}$  decoupling and the chemical shifts are reported in ppm vs  $\text{Me}_4\text{Si}$ . 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 on a Perkin Elmer 2400 CHN analyzer.

**Synthesis of  $[(i\text{-Pr})_2\text{ATI}]\text{GeCl}$  (5).** A diethyl ether solution (20 mL) of  $[(i\text{-Pr})_2\text{ATI}]\text{H}$  (500 mg, 2.45 mmol) was treated with *n*-BuLi (1.53 mL, 1.6 M hexane solution) at  $0^\circ\text{C}$ . This mixture was then stirred for 0.5 h and slowly added to  $\text{GeCl}_2\cdot(1,4\text{-dioxane})$  (570 mg, 2.45 mmol) in diethyl ether (15 mL) at  $-78^\circ\text{C}$ . The mixture immediately became cloudy. After an hour, the mixture was allowed to warm to room temperature and stirred overnight. The resulting reddish solution was filtered through a bed of Celite, and the volatile materials were removed from the filtrate under reduced pressure to obtain the product as an orange red solid (92% yield, 0.70 mg). Recrystallization from toluene–hexane at  $-20^\circ\text{C}$  gave orange crystals of  $[(i\text{-Pr})_2\text{ATI}]\text{GeCl}$ . Mp  $108\text{--}110^\circ\text{C}$ ;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  1.32 (d, 6H,  $J = 6.2$  Hz,  $\text{CH}_3$ ), 1.52 (d, 6H,  $J = 6.2$  Hz,  $\text{CH}_3$ ), 3.67 (septet, 2H,  $J = 6.2$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 6.29 (t, 1H,  $J = 9.4$  Hz,  $\text{H}_5$ ), 6.34 (d, 2H,  $J = 11.4$  Hz,  $\text{H}_{3,7}$ ), 6.76 (t, 2H,  $J = 10.2$  Hz,  $\text{H}_{4,6}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  22.7 ( $\text{CH}_3$ ), 23.7 ( $\text{CH}_3$ ), 49.3 ( $\text{CH}(\text{CH}_3)_2$ ), 115.5 ( $\text{C}_5$ ), 122.0 ( $\text{C}_{3,7}$ ), 136.6 ( $\text{C}_{4,6}$ ), 160.6 ( $\text{C}_{2,8}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.63 (d, 12H,  $J = 6.3$  Hz,  $\text{CH}_3$ ), 4.26 (septet, 2H,  $J = 6.3$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 6.74 (t, 1H,  $J = 9.3$  Hz,  $\text{H}_5$ ), 6.92 (d, 2H,  $J = 11.2$  Hz,  $\text{H}_{3,7}$ ), 7.33 (t, 2H,  $J = 10.4$  Hz,  $\text{H}_{4,6}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  23.8 (br s,  $\text{CH}_3$ ), 49.3 ( $\text{CH}(\text{CH}_3)_2$ ), 115.7 ( $\text{C}_5$ ), 123.0 ( $\text{C}_{3,7}$ ), 136.8 ( $\text{C}_{4,6}$ ), 160.5 ( $\text{C}_{2,8}$ ). Anal. Calcd for  $\text{C}_{13}\text{H}_{19}\text{N}_2\text{ClGe}$ : C, 50.15; H, 6.15; N, 9.0. Found: C, 50.18; H, 6.26; N, 8.73.

**Synthesis of  $\{[(i\text{-Pr})_2\text{ATI}]\text{Ge}\}[\text{CF}_3\text{SO}_3]$  (6).**  $[(i\text{-Pr})_2\text{ATI}]\text{GeCl}$  (100 mg, 0.32 mmol) and  $\text{CF}_3\text{SO}_3\text{Ag}$  (80 mg, 0.32 mmol) were mixed in dichloromethane (10 mL) at room temperature. The mixture immediately became cloudy yellow and was then stirred overnight and filtered through a bed of Celite. The filtrate was concentrated and kept at  $-20^\circ\text{C}$  to obtain **6** as a yellow solid in 86% yield. X-ray quality crystals were obtained from a dichloromethane–hexane solution. Mp  $111\text{--}113^\circ\text{C}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.68 (d, 6H,  $J = 6.2$  Hz,  $\text{CH}_3$ ), 4.40 (septet, 2H,  $J = 6.2$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 7.15 (t, 1H,  $J = 9.5$  Hz,  $\text{H}_5$ ), 7.29 (d, 2H,  $J = 11.3$  Hz,  $\text{H}_{3,7}$ ), 7.64 (dd, 2H,  $J = 11.2, 11.8$  Hz,  $\text{H}_{4,6}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  23.9 ( $\text{CH}_3$ ), 49.4 ( $\text{CH}(\text{CH}_3)_2$ ), 117.6 ( $\text{C}_5$ ), 119.5 (q,  $\text{CF}_3$ ,  $J(\text{C},\text{F}) = 320$  Hz), 127.3 ( $\text{C}_{3,7}$ ), 137.4 ( $\text{C}_{4,6}$ ), 160.2 ( $\text{C}_{2,8}$ );  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  1.39 (d, 6H,  $J = 6.6$  Hz,  $\text{CH}_3$ ), 3.66 (septet, 2H,  $J = 6.6$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 6.46 (t, 1H,  $J = 9.5$  Hz,  $\text{H}_5$ ), 6.52 (d, 2H,  $J = 11.6$  Hz,  $\text{H}_{3,7}$ ), 6.68 (dd, 2H,  $J = 11.0, 9.0$  Hz,  $\text{H}_{4,6}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  23.5 ( $\text{CH}_3$ ), 49.3 ( $\text{CH}(\text{CH}_3)_2$ ), 117.2 ( $\text{C}_5$ ), 120.7 (q,  $\text{CF}_3$ ,  $J(\text{C},\text{F}) = 318$  Hz), 126.1 ( $\text{C}_{3,7}$ ), 137.1 ( $\text{C}_{4,6}$ ), 160.1 ( $\text{C}_{2,8}$ ). Anal. Calcd for  $\text{C}_{14}\text{H}_{19}\text{F}_3\text{N}_2\text{O}_3\text{SGe}$ : C, 39.57; H, 4.51; N, 6.59. Found: C, 39.11; H, 4.51; N, 6.59.

**Synthesis of  $\{[(i\text{-Pr})_2\text{ATI}]\text{Ge}\}[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2(\mu\text{-Cl})_3\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_5)]$  (7).**  $[(i\text{-Pr})_2\text{ATI}]\text{GeCl}$  (100 mg, 0.32 mmol) and  $(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_3$  (169 mg, 0.64 mmol) were mixed in dichloromethane (15 mL) at room temperature. This mixture was then stirred overnight and filtered through a bed of Celite. The filtrate was collected and the volatile materials were removed under reduced pressure to obtain a yellow solid. Recrystallization from dichloromethane–hexanes at  $-20^\circ\text{C}$  gave yellow crystals of **7**. Mp  $187\text{--}189^\circ\text{C}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.67 (d, 12H,  $J = 6.6$  Hz,  $\text{CH}_3$ ), 4.46 (septet, 2H,  $J = 6.6$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 6.55 (s, 5H, CH), 7.30 (t, 1H,  $J = 9.4$  Hz,  $\text{H}_5$ ), 7.42 (d, 2H,  $J = 11.3$  Hz,  $\text{H}_{3,7}$ ), 7.73 (t, 2H,  $J = 10.3$  Hz,  $\text{H}_{4,6}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  24.2 ( $\text{CH}_3$ ), 50.6 ( $\text{CH}(\text{CH}_3)_2$ ), 118.5 ( $\text{C}_5$ ), 120.5 ( $\text{C}_3$ ), 124.7, 137.4 ( $\text{C}_{4,6}$ ), 160.2 ( $\text{C}_{2,8}$ ). Anal. Calcd for  $\text{C}_{23}\text{H}_{29}\text{N}_2\text{Cl}_7\text{GeZr}\cdot 1.1\text{CH}_2\text{Cl}_2$ : C, 31.12; H, 3.38; N, 3.01. Found: C, 31.52; H, 3.54; N, 2.41.

**Synthesis of  $[(\text{Me})_2\text{ATI}]\text{GeCl}$  (8).** A THF solution (20 mL) of  $[(\text{Me})_2\text{ATI}]\text{H}$  (500 mg, 3.37 mmol) was treated with *n*-BuLi (2.11 mL, 3.37 mmol, 1.6 M hexane solution) at  $0^\circ\text{C}$ . This mixture was then stirred for 0.5 h and slowly added to  $\text{GeCl}_2\cdot(1,4\text{-dioxane})$  (780 mg, 3.37 mmol) in THF (20 mL) at  $0^\circ\text{C}$ . After being stirred for an additional 1 h, the mixture was allowed to warm to room temperature and stirred overnight. The volatiles were removed under vacuum, and the solid residue was extracted into toluene. The solution was filtered through a bed of Celite, and the filtrate was concentrated and cooled to  $-25^\circ\text{C}$  to obtain **8** in 65% yield. X-ray quality crystals were obtained from a mixture of toluene–dichloromethane at  $-20^\circ\text{C}$ . Mp

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**Table 1.** Crystal Data and Summary of Data Collection and Refinement

	5	6	7	8	9
formula	C <sub>13</sub> H <sub>19</sub> ClN <sub>2</sub> Ge	C <sub>14</sub> H <sub>19</sub> F <sub>3</sub> GeN <sub>2</sub> O <sub>3</sub> S	C <sub>23</sub> H <sub>29</sub> Cl <sub>7</sub> GeN <sub>2</sub> Zr <sub>2</sub>	C <sub>9</sub> H <sub>11</sub> ClN <sub>2</sub> Ge	C <sub>33</sub> H <sub>31</sub> BN <sub>2</sub> Ge
fw	311.34	424.96	836.66	255.24	539.00
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> , Å	16.398(2)	7.8359(14)	10.043(1)	9.825(3)	8.378(1)
<i>b</i> , Å	9.745(2)	13.562(2)	21.372(3)	11.664(2)	16.677(1)
<i>c</i> , Å	36.510(5)	16.994(2)	14.888(2)	10.110(2)	19.026(2)
α, deg	90	90	90	90	90
β, deg	99.496(10)	97.04(1)	104.084(13)	118.22(2)	90.76(1)
γ, deg	90	90	90	90	90
vol, Å <sup>3</sup>	5754.6(14)	1792.3(5)	3099.4(8)	1020.9(4)	2657.9(5)
<i>Z</i>	16	4	4	4	4
<i>T</i> , K	183(2)	183(2)	183(2)	183(2)	183(2)
λ(Mo Kα), Å	0.71073	0.71073	0.71073	0.71073	0.71073
density (calc), g/cm <sup>3</sup>	1.437	1.575	1.793	1.661	1.346
absorpn coeff, mm <sup>-1</sup>	2.296	1.869	2.244	3.216	1.177
R1, wR2 [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	0.0389, 0.0719	0.0274, 0.0668	0.0390, 0.0998	0.0253, 0.0545	0.0315, 0.0706
R1, wR2 [all data] <sup>a</sup>	0.0693, 0.0853	0.0344, 0.0710	0.0551, 0.1099	0.0335, 0.0575	0.0456, 0.0763

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

**Table 2.** Selected Bond Distances (Å) and Angles (deg) (L = [(*i*-Pr)<sub>2</sub>ATI]; M = Ge or Sn; X = Cl or O)

	LGeCl <sup>a</sup>	LSnCl	[(Me) <sub>2</sub> ATI]GeCl	LGeOTf	{LGe} <sup>+</sup>	{LSn} <sup>+</sup>
M–N	1.956(4)	2.164(5)	1.937(3)	1.910(2)	1.901(5)	2.153(3)
		2.164(5)	1.938(3)	1.916(2)	1.917(5)	2.142(3)
M–X	2.368(2)	2.542(2)	2.377(1)	2.255(2)		
N–C <sub>ring</sub>	1.341(6)	1.332(7)	1.342(4)	1.354(3)	1.347(8)	1.335(5)
		1.331(7)	1.342(4)	1.352(3)	1.346(8)	1.341(5)
N–M–N	80.3(2)	73.9(2)	80.1(1)	81.79(8)	81.7(2)	74.48(12)
N–M–X	96.6(1)	92.43(13)	96.28(8)	89.63(8)		
		94.13(12)	97.30(8)	88.74(8)		

<sup>a</sup> Averages of four independent molecules in the asymmetric unit.

145–148 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.30 (s, 6H, CH<sub>3</sub>), 6.82 (m, 3H), 7.39 (t, 2H, *J* = 9 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ 2.37 (s, 6H, CH<sub>3</sub>), 115.8 (C<sub>5</sub>), 123.6 (C<sub>3,7</sub>), 137.3 (C<sub>4,6</sub>), 160.8 (C<sub>2,8</sub>). Anal. Calcd for C<sub>9</sub>H<sub>11</sub>N<sub>2</sub>GeCl: C, 42.35; H, 4.34; N, 10.98. Found: C, 41.59; H, 4.28; N, 9.70.

**Synthesis of [(Me)<sub>2</sub>ATI]GePh-BPh<sub>3</sub> (9).** [(Me)<sub>2</sub>ATI]GeCl (150 mg, 0.59 mmol) and NaBPh<sub>4</sub> (201 mg, 0.59 mmol) were mixed in dichloromethane (15 mL) at room temperature. The mixture gradually turned bright red and was then stirred overnight and filtered through a bed of Celite. The filtrate was concentrated and kept at –20 °C. Dark red-orange crystals of **9** were obtained from dichloromethane–hexane in 84% yield. Mp 210–215 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.37 (s, 6H, CH<sub>3</sub>), 6.30 (d, *J* = 11.2 Hz), 6.52 (t, *J* = 9.4 Hz), 7.11–7.30 (m, br); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ 32.8 (CH<sub>3</sub>), 114.5, 122.0, 125.7 (br), 127.1, 130.0, 135.0, 136.4, 138.9, 142.2, 161.2. Anal. Calcd for C<sub>33</sub>H<sub>31</sub>BN<sub>2</sub>Ge: C, 73.53; H, 5.80; N, 5.20. Found: C, 73.23; H, 5.56; N, 4.56.

**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.<sup>47</sup> Data collections were carried out at –90 °C on a Siemens P4 diffractometer equipped with a LT-2A device for low-temperature work and graphite monochromated Mo Kα radiation (λ = 0.710 73 Å). The unit cell parameters of **5**, **6**, **7**, **8**, and **9** were determined by least-squares refinement of 33, 30, 30, 30, and 66 reflections, respectively. Three standard reflections were measured at every 97 data points to check for crystal deterioration and/or misalignment. No significant deterioration in intensity was observed. Data were corrected for Lorentz, polarization, and absorption (using ψ scans) effects. Structures were solved by direct methods followed by successive cycles of full-matrix least-squares refinement on *F*<sup>2</sup> and difference Fourier analysis. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at calculated positions. They were treated as riding atoms with isotropic displacement parameters fixed 1.2 or 1.5 times the value refined for the respective host atom. Software programs and the sources of scattering factors are contained in the SHELXTL (PC

version 5 based on SHELXL-93) software package<sup>48</sup> provided by the Siemens 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 Table 2. Further details of the crystal structures are presented in the Supporting Information.

## Results and Discussion

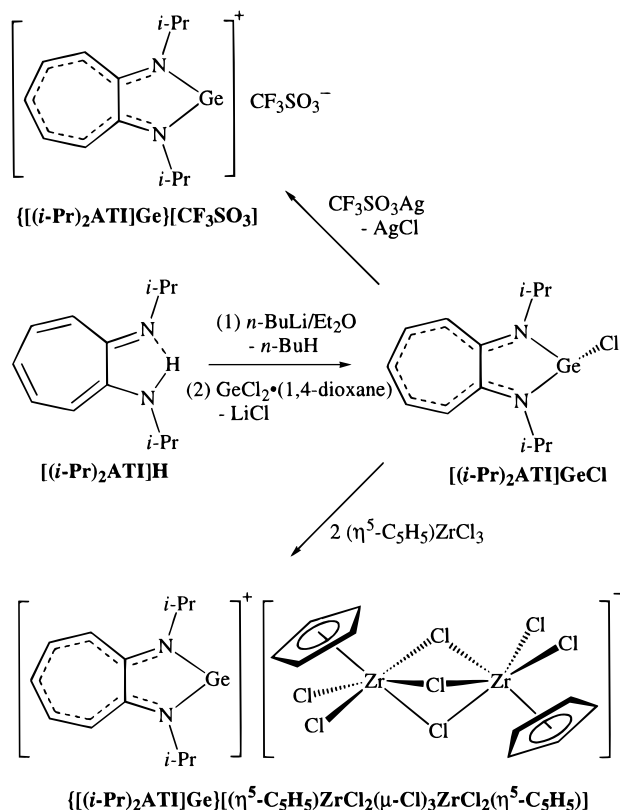
Synthesis of the germanium(II) chlorides [(*i*-Pr)<sub>2</sub>ATI]GeCl (**5**) and [(Me)<sub>2</sub>ATI]GeCl (**8**) was achieved by the treatment of GeCl<sub>2</sub>·(1,4-dioxane) with [(*i*-Pr)<sub>2</sub>ATI]Li or [(Me)<sub>2</sub>ATI]Li in a 1:1 molar ratio in Et<sub>2</sub>O or THF. The products were isolated as orange solids in excellent yields (Schemes 1 and 2) and characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and by X-ray diffraction. The <sup>1</sup>H NMR spectrum of **5** taken in CDCl<sub>3</sub> shows three well-separated multiplets which correspond to H(5), H(3,7), and H(4,6). The <sup>13</sup>C NMR spectrum displayed four resonances for the ring carbons. A nearly identical four-signal pattern was observed for **8** in the aromatic region of the <sup>13</sup>C NMR spectrum. Interestingly, methyls of the isopropyl substituents of **5** appear as two sets of doublets in the <sup>1</sup>H NMR spectrum recorded in C<sub>6</sub>D<sub>6</sub>, suggesting two different environments for the –CH<sub>3</sub> moieties. This is perhaps due to the asymmetry caused by the Cl group on the germanium center. Likewise, they appear as two signals in the <sup>13</sup>C NMR spectrum. However, in CDCl<sub>3</sub>, methyl groups appear only as a doublet in the <sup>1</sup>H NMR spectrum and as a broad singlet in the <sup>13</sup>C spectrum. A similar solvent effect was observed in the tin analog [(*i*-Pr)<sub>2</sub>ATI]SnCl.

The X-ray crystal structure of **5** and the atom numbering scheme are shown in Figure 1. The asymmetric unit contains four chemically similar but crystallographically different molecules of **5**. One of them is notably different from the rest due to the orientation of methyls of the isopropyl groups as illustrated

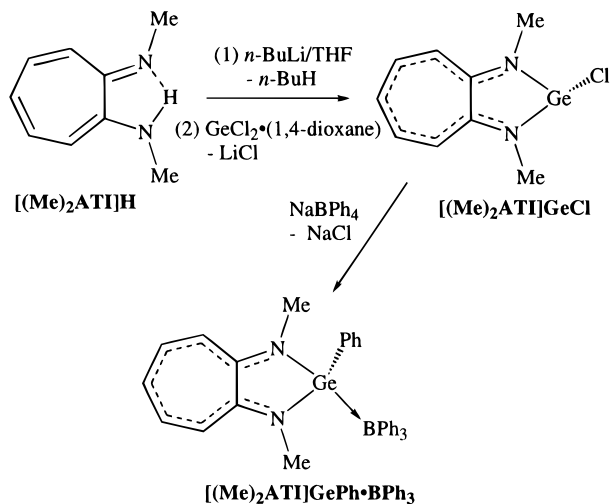
(47) Hope, H. In *Experimental Organometallic Chemistry*; ACS Symposium Series, No. 357; Wayda, A. L., Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; p 257.

(48) SHELXTL (PC Version 5.0); Siemens Industrial Automation, Inc.: Madison, WI, 1994.

## Scheme 1

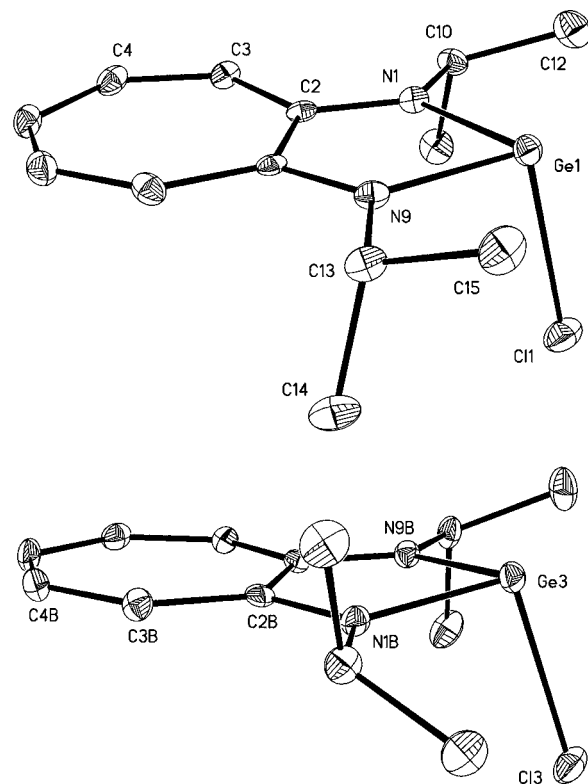


## Scheme 2

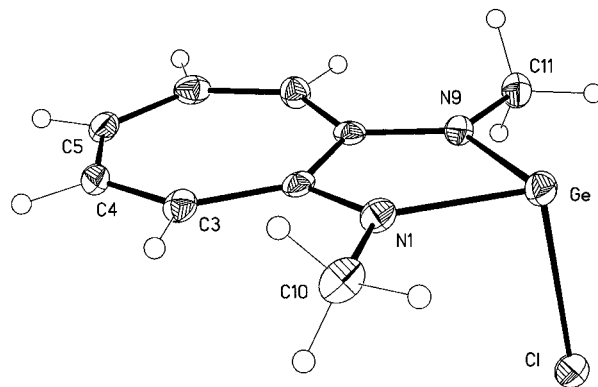


in Figure 1. The germanium center adopts a pyramidal geometry that is fairly common in Ge(II) chemistry. The average Ge–Cl and Ge–N distances are 2.368(2) and 1.956(4) Å, respectively. The X-ray crystal structure of **8**, which contains a sterically less demanding  $[(\text{Me})_2\text{ATI}]^-$  ligand, is illustrated in Figure 2. The Ge–Cl (2.3774(10) Å) and Ge–N (1.937(3) and 1.938(3) Å) bond distances are essentially similar to those of **5**. As evident from the data presented in Table 2, the Ge–N distances are significantly shorter and the N–Ge–N angles are several degrees larger than the corresponding structural parameter in  $[(i\text{-Pr})_2\text{ATI}]\text{SnCl}$ . These germanium compounds do not show intermolecular  $\text{Ge} \cdots \text{Cl}$  contacts whereas the tin complex displays weak  $\text{Sn} \cdots \text{Cl}$  interactions.<sup>32</sup>

In order to generate cationic  $\{[(R)_2\text{ATI}]\text{Ge}\}^+$  species, we have attempted the substitution of the chloride group of **5** or **8** with various weakly coordinating anions. The treatment of  $[(i\text{-Pr})_2\text{ATI}]\text{GeCl}$  with  $\text{CF}_3\text{SO}_3\text{Ag}$  led to  $\{[(i\text{-Pr})_2\text{ATI}]\text{Ge}\}^+[\text{CF}_3\text{SO}_3]^-$  (**6**)



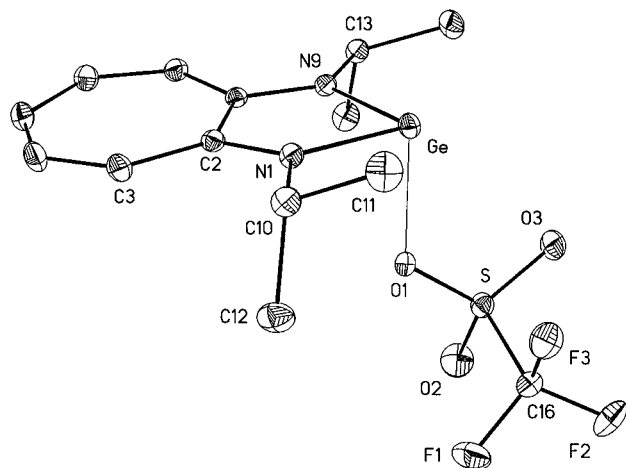
**Figure 1.** Structures and atom numbering schemes of two crystallographically different molecules of  $[(i\text{-Pr})_2\text{ATI}]\text{GeCl}$  (**5**).



**Figure 2.** Structure and atom numbering scheme for  $[(\text{Me})_2\text{ATI}]\text{GeCl}$  (**8**).

in good yield. The room temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR data indicate the presence of magnetically equivalent methyl groups. For example,  $-\text{CH}_3$  groups of **6** give rise to a doublet in the  $^1\text{H}$  NMR spectrum taken in  $\text{C}_6\text{D}_6$ . Note that in **5** two sets of doublets were observed for the corresponding protons. These data agree with the removal of chloride from the germanium center leading to a relatively less crowded environment around germanium. The  $^1\text{H}$  NMR resonances of the ring protons of **6** ( $\delta$  7.15, 7.29, and 7.64 in  $\text{CDCl}_3$ ) show a downfield shift relative to those of **5** ( $\delta$  6.74, 6.92, and 7.33). This may be an indication of the increased positive charge on the ligand backbone.

The X-ray crystallographic data of **6** do not show complete anion/cation separation (Figure 3). The  $\text{CF}_3\text{SO}_3^-$  group binds weakly to the germanium center with a Ge–O distance of 2.255(2) Å (cf. sum of the covalent radii of Ge and O = 1.95 Å). In addition, the packing diagram shows that there is a very long intermolecular contact between germanium and oxygen atoms ( $\text{Ge} \cdots \text{O}$ , 3.87 Å;  $\text{O} \cdots \text{Ge}$ ,  $152^\circ$ ) forming a chain structure. The Ge–N distances are slightly shorter than those of the chloro analogs **5** and **8** (Table 2).

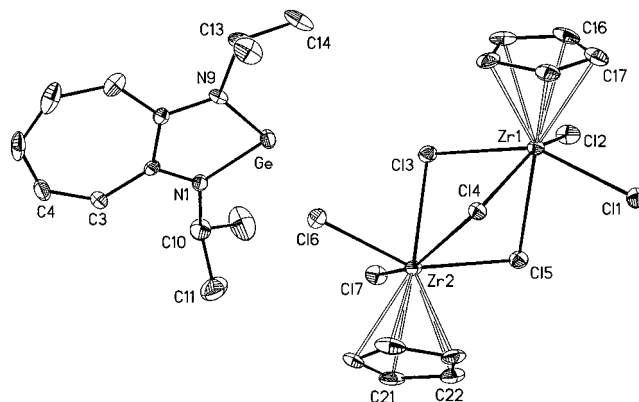


**Figure 3.** Structure and atom numbering scheme for  $\{[(i\text{-Pr})_2\text{ATI}]\text{Ge}\}^+[\text{CF}_3\text{SO}_3]^-$  (**6**).

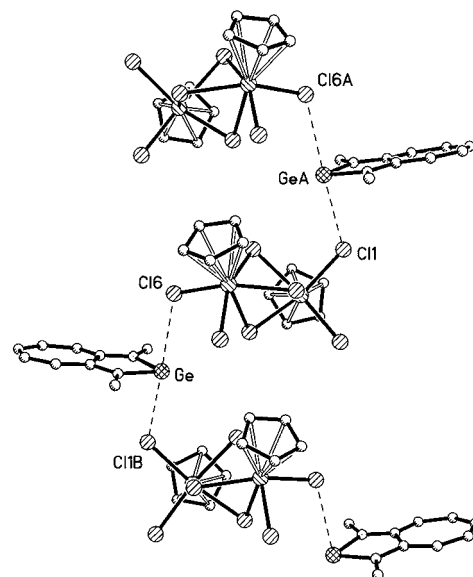
We have reported earlier the synthesis of a cationic Sn(II) species using the  $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2(\mu\text{-Cl})_3\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_5)]^-$  anion.<sup>32</sup> It is also possible to prepare the analogous Ge(II) complex  $\{[(i\text{-Pr})_2\text{ATI}]\text{Ge}\}[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2(\mu\text{-Cl})_3\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_5)]^-$  (**7**). This was obtained by treating **5** with 2 equiv of  $(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_3$  in  $\text{CH}_2\text{Cl}_2$  (Scheme 1). The  $(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_3$  serves as a chloride abstracting agent in this reaction. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic data of the crude mixture indicate the formation of **7** with some unidentified impurities. Compound **7** can be crystallized from  $\text{CH}_2\text{Cl}_2$ –hexane. It is an air- and moisture-sensitive yellow solid that shows moderate solubility in  $\text{CHCl}_3$  or  $\text{CH}_2\text{Cl}_2$ . The solubility of **7** is very poor in hydrocarbon solvents such as toluene.

Both the  $^1\text{H}$  and  $^{13}\text{C}$  NMR data corresponding to the  $\{[(i\text{-Pr})_2\text{ATI}]\text{Ge}\}^+$  unit are very similar between **6** and **7**. The ring protons of **7** show a small downfield shift compared to the corresponding  $^1\text{H}$  resonances of  $\{[(i\text{-Pr})_2\text{ATI}]\text{Sn}\}[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2(\mu\text{-Cl})_3\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_5)]^-$ . Apart from that, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **7** are similar to those of the tin analog. The  $^{119}\text{Sn}$  NMR spectroscopic data of  $\{[(i\text{-Pr})_2\text{ATI}]\text{Sn}\}[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2(\mu\text{-Cl})_3\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_5)]^-$  suggested the presence of two coordinate Sn(II) species.<sup>32</sup> Therefore, it is reasonable to expect that the Ge(II) species **7** (and **6**) would also show similar ion separation in solution. The NMR data of **7** can also be compared to those of the free ligand  $[(i\text{-Pr})_2\text{ATI}]\text{H}$ .<sup>31</sup> Compared to  $[(i\text{-Pr})_2\text{ATI}]\text{H}$ , all the corresponding resonances due to protons of **7** appear at significantly downfield positions. Some of the  $^{13}\text{C}$  NMR chemical shifts are also notably different. For example, the peak due to C(2,8) of **7** appears around  $\delta$  160 whereas in the free ligand it was observed at 151 ppm.

The solid state structure of **7** is depicted in Figure 4. Compound **7** consists of the cationic  $\{[(i\text{-Pr})_2\text{ATI}]\text{Ge}\}^+$  moiety and the chloride bridged  $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2(\mu\text{-Cl})_3\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_5)]^-$  anion. Features of the anionic  $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2(\mu\text{-Cl})_3\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_5)]^-$  unit are described elsewhere.<sup>32</sup> The germanium center adopts a V-shaped geometry with a N–Ge–N angle of  $81.7(2)^\circ$ . The  $\text{C}_7\text{N}_2\text{Ge}$  moiety is essentially planar. The Ge–N bond distances in the cation are 1.901(5) and 1.917(5) Å. In addition to these two bonds, there are two weak interactions between the germanium ion of the cation and terminal chloride atoms (Cl6 and Cl1A) of the  $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2(\mu\text{-Cl})_3\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_5)]^-$  anions. This gives rise to a zigzag chain structure shown in Figure 5. Similar interactions in the Sn(II) cation lead to centrosymmetric dimers.<sup>32</sup> These Ge $\cdots$ Cl separations of 3.123 and 3.115 Å are considerably long compared to the typical Ge–Cl single-bond distances. They can be compared to covalently bound Ge–Cl distances of **5** (av. 2.368(2) Å) and



**Figure 4.** Structure and atom numbering scheme for  $\{[(i\text{-Pr})_2\text{ATI}]\text{Ge}\}^+[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2(\mu\text{-Cl})_3\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_5)]^-$  (**7**).

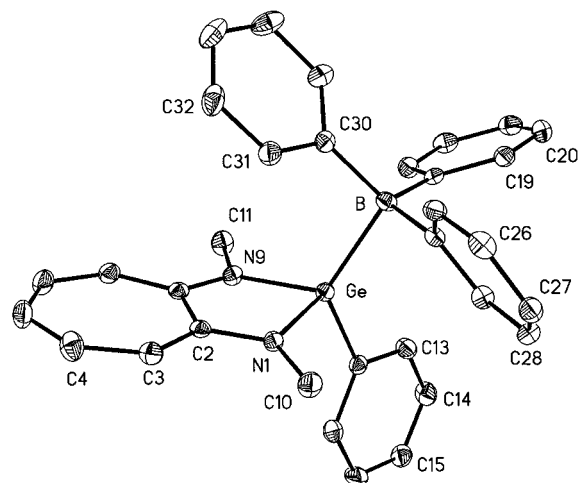


**Figure 5.** Diagram of **7** showing weak Ge $\cdots$ Cl interactions.

**8** (2.377(1) Å) or to the weak Ge $\cdots$ Cl contacts (3.235(6) and 3.394(6) Å) of  $\{[\eta^2\text{-Me}_4\text{C}_5\text{H}]\text{Me}_2\text{Si}[\eta^5\text{-Me}_4\text{C}_5]\text{Ge}\}[\text{GeCl}_3]$ .<sup>26</sup> The Cl6 $\cdots$ Ge $\cdots$ Cl1A angle is  $169.8^\circ$ . It is also noteworthy that the Ge $\cdots$ Cl contacts of **7** are even longer than the Sn $\cdots$ Cl separations of the tin analog (2.979 and 3.070 Å).

Interestingly, the key structural parameters of the cationic  $\{[(i\text{-Pr})_2\text{ATI}]\text{Ge}\}^+$  moiety are only slightly different from neutral germanium complexes such as **5** or **8** (see Table 2). The Ge–N bond lengths are marginally smaller and the N–Ge–N angles are  $>2^\circ$  wider in the cationic species. The Ge–N distances and N–Ge–N angles of **7** can also be compared to those of **1** (Ge–N, 1.878(5), 1.873(5) Å; N–Ge–N,  $107.1(2)^\circ$ ),<sup>9</sup> **2** (Ge–N, 1.856(1) Å; N–Ge–N,  $84.8(1)^\circ$ ),<sup>11</sup> **3** (Ge–N, 1.833(2) Å; N–Ge–N,  $88.0(1)^\circ$ ),<sup>11</sup> **4** (Ge–N, 1.861(8), 1.866(9) Å; N–Ge–N,  $87.2(4)^\circ$ ),<sup>12</sup> and the interesting cyclic species  $[\text{Ge}(\text{NC}_6\text{H}_2\text{Bu}^i\text{-}2,4,6)_2]_2$  (Ge–N, 1.844(3), 1.855(3) Å; N–Ge–N,  $86.3(1)^\circ$ ),<sup>49</sup> and  $[\text{Ge}(\text{NC}_6\text{H}_3\text{Pr}^i\text{-}2,6)_3]_3$  (Ge–N, av 1.859(2) Å; N–Ge–N, av  $101.8(1)^\circ$ ).<sup>22,23</sup> A typical Ge=N bond is about 1.691–1.703 Å long.<sup>1</sup> In general, these Ge–N distances are shorter than the corresponding interatomic distances of **6** and **7**. This is perhaps due to the difference between diamido donors (e.g., in **2**) and the amido/imido donor combination (e.g., in **7**). As mentioned earlier, a few structurally characterized cationic germanium compounds are also known, e.g.,  $[\text{Ge}_2(3,5\text{-(CH}_3)_2\text{Pz})_3][\text{GeCl}_3]$ <sup>29</sup> and  $\{[\text{HB}(3,5\text{-(CH}_3)_2\text{Pz})_3]\text{Ge}\}^+$ .<sup>30</sup> The Ge–N dis-

(49) Hitchcock, P. B.; Lappert, M. F.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1587.



**Figure 6.** Structure and atom numbering scheme for  $[(\text{Me})_2\text{ATI}]\text{GePh}\cdot\text{BPh}_3$  (**9**).

tances and N–Ge–N angles of these three coordinate germanium(II) species are 1.971 Å, 90.5° and 2.03 Å, 86.9°, respectively. They are significantly larger than the corresponding structural parameters of **6** and **7**. Overall, compounds **5**–**8** feature some of the smallest N–Ge–N angles observed in Ge(II) chemistry.<sup>2</sup>

In order to isolate a two-coordinate Ge(II) cation free of even weak cation/anion interactions, we have attempted to replace  $\text{Cl}^-$  of **5** with  $\text{BPh}_4^-$  anions. Unfortunately, the reaction between **5** and  $\text{NaBPh}_4$  resulted in a complicated mixture of products. The analogous reaction between  $\text{NaBPh}_4$  and **8** was much cleaner and afforded a red solid. The NMR data of this product, however, did not point to the formation of expected  $\{[(\text{Me})_2\text{ATI}]\text{Ge}\}[\text{BPh}_4]$ . For example, the aromatic region of the  $^{13}\text{C}$  NMR spectrum showed eleven well-separated signals. Fortunately, this compound produced excellent X-ray quality crystals, and the finding of the X-ray diffraction study is illustrated in Figure 6 and indicates the formation of  $[(\text{Me})_2\text{ATI}]\text{GePh}\cdot\text{BPh}_3$  (**9**) rather than the cationic Ge(II) species. Although the exact mechanism is uncertain, the formation of  $[(\text{Me})_2\text{ATI}]\text{GePh}\cdot\text{BPh}_3$  may involve a phenyl group migration from  $\text{BPh}_4^-$  anion to the cationic germanium(II) center followed by the association of the two resulting fragments  $\text{BPh}_3$  and  $[(\text{Me})_2\text{ATI}]\text{GePh}$ . The phenyl group transfer from  $\text{BPh}_4^-$  to metal centers is well-known.<sup>50</sup> However, we are unaware of such instances involving germanium(II) cations.

The germanium atom of **9** adopts a tetrahedral geometry with Ge–N bond lengths of 1.913(2) and 1.920(2) Å. These distances are not very different when compared to the corresponding bond lengths of **8**. Structurally authenticated mol-

ecules containing Ge–B bonds are mostly limited to the carborane family.<sup>51</sup> Nevertheless, the Ge–B distance of 2.156(4) Å can be compared to Ge<sup>II</sup>–B (2.265(6), 2.243(6), and 2.250(6) Å) and Ge<sup>IV</sup>–B (1.995(6) distances of *closo*-1-Ge<sup>II</sup>-2,3-(Me<sub>3</sub>Si)<sub>2</sub>-5-(Ge<sup>IV</sup>Cl<sub>3</sub>)-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>3</sub>.<sup>52</sup> The N–Ge–N angle of 81.69(10)° is similar to that observed in the cationic derivatives.

One of the interesting features of aminotroponiminato derivatives of germanium(II) is the planar, bicyclic 10- $\pi$ -electron ring system. In contrast to the neutral adducts such as **5** or **8**, the germanium center of the  $\{[(i\text{-Pr})_2\text{ATI}]\text{Ge}\}^+$  cation has an empty out-of-plane p-orbital that is capable of interacting with the ligand  $\pi$ -electron system. Such  $\pi$ -interaction would lead to a somewhat shorter Ge–N bond distance. Theoretical studies predict that in  $\text{Ge}(\text{NH}_2)_2$  the  $p_\pi$ – $p_\pi$  delocalization would shorten the Ge–N distance by about 0.06–0.07 Å.<sup>14</sup> A comparison of structural data between  $[(i\text{-Pr})_2\text{ATI}]\text{GeCl}$  and  $\{[(i\text{-Pr})_2\text{ATI}]\text{Ge}\}^+$  indeed shows a reduction (about 0.047 Å). However, the magnitude of shortening, particularly when considered along with possible steric effects and experimental uncertainties, is not indicative of a significant change in the Ge–N bond order. The presence of non-bonded contacts between the cationic germanium center and anions also points to the relatively weak nature of this  $p_\pi$ – $p_\pi$  bonding.

In summary, neutral and cationic germanium(II) derivatives of aminotroponiminate ligand can be isolated in stable, crystalline form. These compounds feature heterobicyclic  $\text{C}_7\text{N}_2\text{Ge}$  ring systems. The NMR data of the cationic species suggest the delocalization of positive charge over the  $\text{C}_7\text{N}_2\text{Ge}$  ring. However, this does not accompany a significant increase in the Ge–N  $\pi$ -bonding. Attempted synthesis of the tetraphenylborate salt of  $\{[(\text{Me})_2\text{ATI}]\text{Ge}\}^+$  led to a novel phenyl group transfer product with a Ge<sup>II</sup>–B bond.

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**Supporting Information Available:** Tables of crystallographic data, atomic coordinates, thermal parameters, and complete bond distances and angles for **5**, **6**, **7**, **8**, and **9** (28 pages). See any current masthead page for ordering and Internet access instructions.

JA970196B

(51) *Cambridge Structural Database*; Cambridge, England, January, 1996.

(52) Siriwardane, U.; Islam, M. S.; Maguire, J. A.; Hosmane, N. S. *Organometallics* **1988**, *7*, 1893.

(50) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927 and the references therein.