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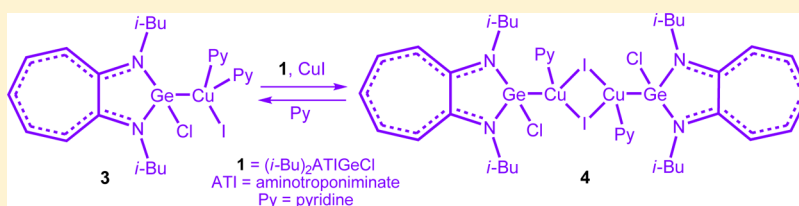
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# Aminotroponiminato(chloro)germylene Stabilized Copper(I) Iodide Complexes: Synthesis and Structure

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## Supporting Information



**ABSTRACT:** Reaction of an aminotroponiminato(chloro)germylene [(i-Bu)<sub>2</sub>ATIGeCl] (1) (ATI = aminotroponimate) with CuI in acetonitrile afforded an aminotroponiminato(chloro)germylene stabilized copper(I) iodide complex [(i-Bu)<sub>2</sub>ATIGeCl]<sub>2</sub>(Cu<sub>4</sub>I<sub>4</sub>)(CH<sub>3</sub>CN)<sub>2</sub> (2) with a tetrameric distorted cubane type Cu<sub>4</sub>I<sub>4</sub> core. The reaction of compound 1 in dichloromethane with CuI in the presence of 2 equiv of pyridine resulted in the first germylene stabilized copper(I) iodide complex [(i-Bu)<sub>2</sub>ATIGeCl](CuI)(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub> (3) with a monomeric CuI core. A reaction of compound 1 with equimolar amounts of CuI and pyridine in dichloromethane resulted in a copper(I) iodide complex [(i-Bu)<sub>2</sub>ATIGeCl]<sub>2</sub>(Cu<sub>2</sub>I<sub>2</sub>)(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub> (4) with a dimeric Cu<sub>2</sub>I<sub>2</sub> core. Interestingly, an interconversion between compounds 3 and 4 and conversion of compound 2 to compounds 3 and 4 under suitable conditions are also reported. The compounds 2–4 have been characterized by multinuclear NMR spectroscopy and single-crystal X-ray diffraction studies. The copper atoms in all these complexes are tetracoordinate, and the Ge(II)–Cu(I) bond lengths in complexes 2, 3, and 4 are 2.341(1), 2.308(1), and 2.345(1) Å, respectively.

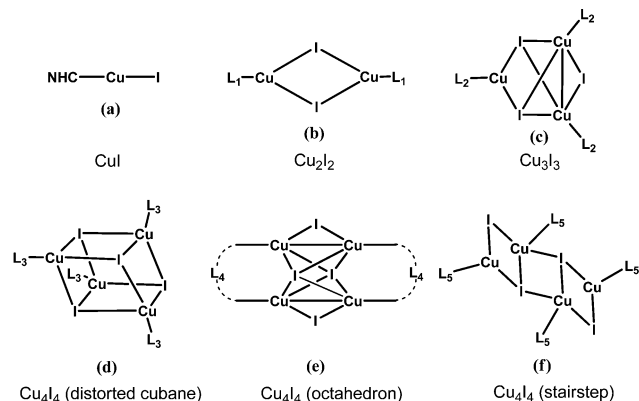
## INTRODUCTION

Copper(I) halide complexes are studied largely for their interesting structural diversity<sup>1</sup> and promising applications in catalysis<sup>2</sup> and materials chemistry<sup>3</sup>. Compounds containing N, P, S, or Se donor atoms and N-heterocyclic carbenes<sup>4</sup> (NHCs) are used as ligands for the synthesis of such complexes (See Chart 1, for representative examples of copper(I) iodide

complexes).<sup>5</sup> The utility of N-heterocyclic germylenes<sup>6</sup> (NHGers), being the heavier analogues of NHCs, for the stabilization of copper(I) halide complexes has also been pursued, but not extensively. To the best of our knowledge, there are only two such reports.<sup>7a,b</sup>

Leung and co-worker's reaction of a pyridyl-1-azaallyl-(chloro)germylene [LGeCl] (L = N(SiMe<sub>3</sub>)C(Ph)C(SiMe<sub>3</sub>)-C<sub>5</sub>H<sub>4</sub>N<sub>2</sub>) with an equimolar amount of CuI resulted in a copper(I) iodide complex [(LGeCl)<sub>4</sub>Cu<sub>4</sub>I<sub>4</sub>] (I),<sup>7a</sup> with a distorted cubane type Cu<sub>4</sub>I<sub>4</sub> core. Recently, Fulton's group reported the synthesis of a copper(I) iodide complex [{(BDI)GeOt-Bu}<sub>2</sub>Cu<sub>2</sub>I<sub>2</sub>] (BDI = {N(2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)C(Me)}<sub>2</sub>CH) (II), with a planar dimeric Cu<sub>2</sub>I<sub>2</sub> core.<sup>7b</sup> Apart from these two cores (Cu<sub>4</sub>I<sub>4</sub> and Cu<sub>2</sub>I<sub>2</sub>), the cores such as CuI,<sup>5a</sup> Cu<sub>3</sub>I<sub>3</sub>,<sup>5c</sup> Cu<sub>6</sub>I<sub>6</sub>,<sup>8</sup> and so forth that are stabilized through other ligand systems, have never been isolated using germylenes. Therefore, to isolate the germylene stabilized copper(I) iodide complexes with the cores such as CuI, Cu<sub>3</sub>I<sub>3</sub>, Cu<sub>6</sub>I<sub>6</sub>, and so forth, we carried out the reaction of aminotroponiminato(chloro)germylene<sup>9a</sup> [(i-Bu)<sub>2</sub>ATIGeCl] (1) with CuI in the absence and presence of pyridine. Accordingly, we report here, the synthesis of aminotroponiminato(chloro)germylene stabilized copper(I) iodide complexes [(i-Bu)<sub>2</sub>ATIGeCl]<sub>2</sub>(Cu<sub>4</sub>I<sub>4</sub>)(CH<sub>3</sub>CN)<sub>2</sub> (2), [(i-Bu)<sub>2</sub>ATIGeCl](CuI)(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub> (3), and [(i-

**Chart 1. Representative Examples of Copper(I) Iodide Complexes**



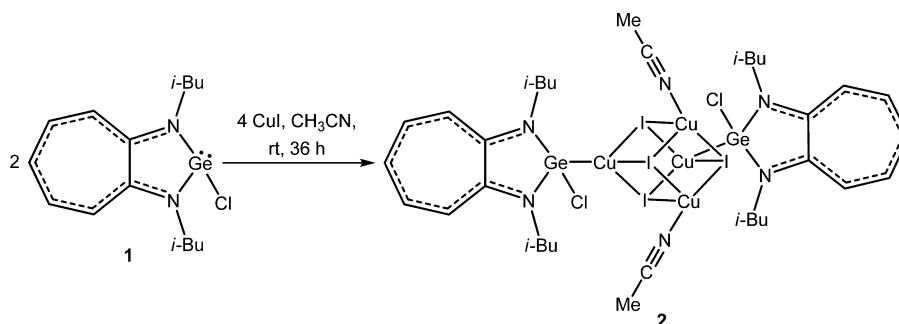
NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; L<sub>1</sub> = 4-(diphenylphosphino)-1,5-diphenyl-1*H*-1,2,3-triazole; L<sub>2</sub> = PH<sub>2</sub>BH<sub>2</sub>NMe<sub>3</sub>; L<sub>3</sub> = methyl(diphenylphosphino); L<sub>4</sub> = 2-(diphenylphosphinomethyl)pyridine; L<sub>5</sub> = triphenylphosphine.

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**Scheme 1.** Synthesis of an Aminotroponiminato(chloro)germylene Stabilized Copper(I) Iodide Complex **2** with a Distorted  $\text{Cu}_4\text{I}_4$  Core



$\text{Bu})_2\text{ATIGeCl}\}_2(\text{Cu}_2\text{I}_2)(\text{C}_5\text{H}_5\text{N})_2]$  (**4**). Interestingly, compound **3** is the first example of a germylene stabilized copper(I) iodide complex with a monomeric  $\text{CuI}$  core. Further, the feasibility to interconvert compounds **3** and **4** and convert compound **2** to compounds **3** and **4** have also been demonstrated for the first time.

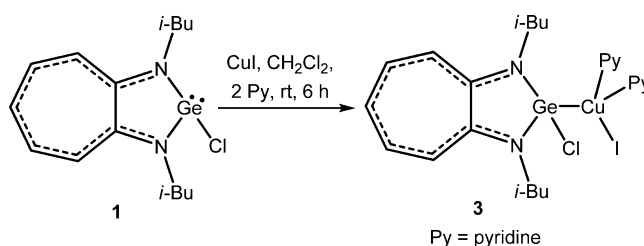
## RESULTS AND DISCUSSION

**Synthesis and Spectra.** Though germylenes are used as donor ligands to stabilize various metal complexes,<sup>6,10</sup> their ability to offer stabilization for the formation of copper(I) halide complexes is not well documented. Therefore, to understand the behavior of aminotroponiminato(chloro)germylene **1** toward  $\text{CuI}$ , its reactions with  $\text{CuI}$  at various stoichiometries were carried out at room temperature in either tetrahydrofuran or dichloromethane. Unfortunately, these reactions resulted in insoluble solids. Anticipating that the insolubility may be due to polymeric products, it was planned to perform these reactions in a much polar and coordinating solvent like acetonitrile. In accordance to our belief, the reaction of compound **1** in acetonitrile with 2 equiv of  $\text{CuI}$  resulted in a freely soluble aminotroponiminato(chloro)germylene stabilized copper(I) iodide complex  $[\{(i\text{-Bu})_2\text{ATIGeCl}\}_2(\text{Cu}_4\text{I}_4)(\text{CH}_3\text{CN})_2]$  (**2**) in about quantitative yields as a yellow solid (Scheme 1). It contains a tetrameric  $\text{Cu}_4\text{I}_4$  core and is soluble in solvents such as dichloromethane, chloroform, acetonitrile, and so forth. In contrast to complex **1** that contains four pyridyl-1-azaallyl(chloro)germylenes to stabilize the distorted  $\text{Cu}_4\text{I}_4$  core, compound **2** has two aminotroponiminato(chloro)germylene and acetonitrile ligands.

In view of the importance of a coordinating ligand like acetonitrile in leading to a soluble product, we intended to carry out the reaction of compound **1** with  $\text{CuI}$  in the presence of pyridine. Accordingly, the reaction of compound **1** with 1 equiv of  $\text{CuI}$  in dichloromethane for 30 min followed by the addition of 2 equiv of pyridine at ambient temperature afforded a novel copper(I) iodide complex  $[\{(i\text{-Bu})_2\text{ATIGeCl}\}(\text{CuI})(\text{C}_5\text{H}_5\text{N})_2]$  (**3**), as an orange solid in about 86% yield (Scheme 2).

Compound **3** contains a monomeric  $\text{CuI}$  core and exhibits good solubility in polar organic solvents like tetrahydrofuran, dichloromethane, toluene, and chloroform. Though NHCs are known to stabilize the copper(I) iodide complexes with a monomeric  $\text{CuI}$  core,<sup>5a</sup> compound **3** is the first example of a germylene stabilized copper(I) iodide complex with a monomeric  $\text{CuI}$  core. To understand further the role of pyridine's stoichiometry in the reaction that afforded

**Scheme 2.** Synthesis of an Aminotroponiminato(chloro)germylene Stabilized Copper(I) Iodide Complex **3** with a Monomeric  $\text{CuI}$  Core



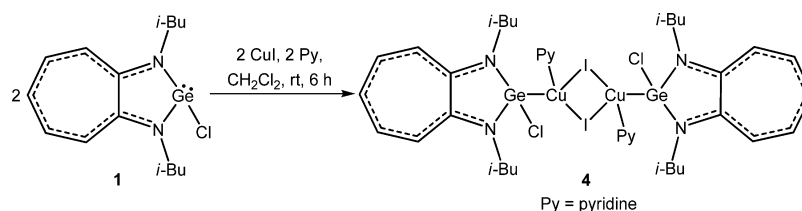
compound **3**, this reaction was carried out with (a) 1 equiv of pyridine and (b) excess of pyridine. The latter reaction resulted only in compound **3**, nevertheless, the former reaction afforded an aminotroponiminato(chloro)germylene stabilized copper(I) iodide complex  $[\{(i\text{-Bu})_2\text{ATIGeCl}\}_2(\text{Cu}_2\text{I}_2)(\text{C}_5\text{H}_5\text{N})_2]$  (**4**), with a dimeric  $\text{Cu}_2\text{I}_2$  core (Scheme 3).

Compound **4** is a yellow solid, obtained in about 94% yield, and is freely soluble in solvents such as chloroform, dichloromethane, and tetrahydrofuran. As the formation of compounds **3** and **4** was dictated by the stoichiometry of pyridine, it was expected that their interconversion would be possible. This idea was tested and found to be true. Accordingly, when the reaction of compound **3** with 1 equiv of compound **1** and  $\text{CuI}$  was carried out in dichloromethane at room temperature, compound **4** was obtained (Scheme 4). Further, the reaction of compound **4** with 2 equiv of pyridine in dichloromethane at room temperature gave compound **3** (Scheme 4).

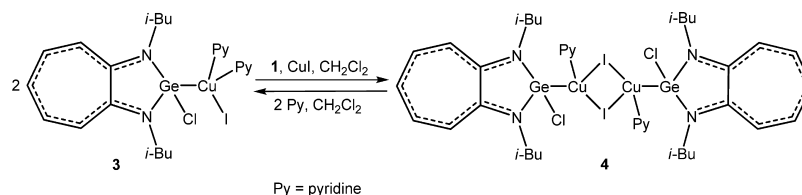
On the basis of successful interconversion between compounds **3** and **4**, the possibility of obtaining these compounds from compound **2** depending on pyridine's stoichiometry was also looked at. The reaction of 1 equiv of compound **2** with 2 equiv of compound **1** and 8 equiv of pyridine in dichloromethane at room temperature afforded compound **3** (Scheme 5). Additionally, the reaction of 1 equiv of compound **2** at room temperature in dichloromethane with 2 equiv of compound **1** and 4 equiv of pyridine resulted in compound **4** (Scheme 5). Thus, these reactions provide alternate routes for the synthesis of compounds **3** and **4**.

The compounds **2–4** are stable at ambient temperature under an inert atmosphere of dry  $\text{N}_2$  for any period of time and characterized in solution through  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic studies. In the  $^1\text{H}$  NMR spectrum of compound **2**, the methyl protons of the isobutyl groups were observed as a doublet (1.05 ppm). The methine and methylene protons of

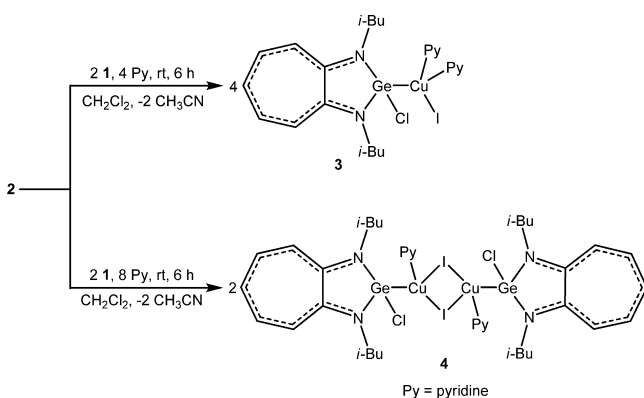
**Scheme 3.** Synthesis of an Aminotroponiminato(chloro)germylene Stabilized Copper(I) Iodide Complex **4** with a Dimeric  $\text{Cu}_2\text{I}_2$  Core



**Scheme 4.** Interconversion Between Compounds **3** and **4**



**Scheme 5.** Conversion of Compound **2** to Compounds **3** and **4**

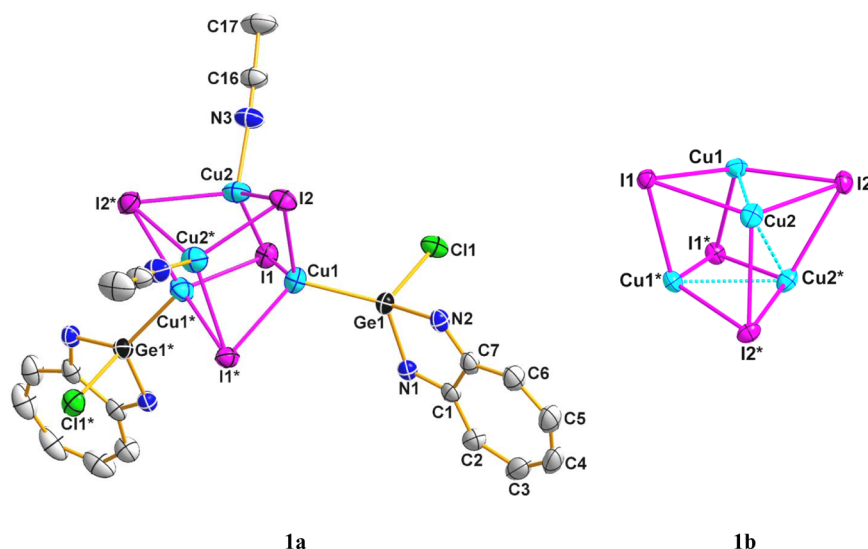


the isobutyl groups appeared as a multiplet (2.31–2.40 ppm) and doublet (3.66 ppm), respectively. Similar spectral pattern was observed for the isobutyl groups of compounds **3** and **4**. A sharp singlet (2.00 ppm) for the methyl protons of acetonitrile ligands in compound **2** was seen in its  $^1\text{H}$  NMR spectrum. The resonances due to the five seven-membered ring protons of compound **2** appeared as a triplet (6.78 ppm), doublet (6.95 ppm), and pseudotriplet (7.32 ppm). These three signals are downfield shifted with respect to the corresponding signals seen in the spectrum of compound **1**.<sup>9a</sup> In line with compound **2**, the triplet and doublet resonances for the seven-membered ring protons of compounds **3** and **4** were seen; nevertheless, the anticipated pseudotriplet resonances merge with the signals due to their pyridine protons and appear as multiplets. In the proton decoupled  $^{13}\text{C}$  NMR spectra of compounds **2** and **4**, nine and ten resonances anticipated for their carbon atoms were observed. But in compound **3**, as one of the pyridine and seven-membered ring carbon resonances overlapped, only nine singlets were seen instead of the anticipated ten signals.

**X-ray Structures of Compounds 2–4.** The structures of compounds **2**, **3**, and **4** were further characterized by single crystal X-ray diffraction studies. Compound **2** crystallized in the monoclinic space group  $P2_1/c$ . Its structure (Figure 1a) clearly reflects the presence of a distorted cubane type  $\text{Cu}_4\text{I}_4$  core stabilized by two aminotroponiminato(chloro)germylene **1** and acetonitrile ligands. The  $\text{Cu}_4\text{I}_4$  core (Figure 1b) can be

visualized as two nonplanar butterfly type  $\text{Cu}_2\text{I}_2$  units ( $\text{Cu1}$ ,  $\text{Cu2}$ ,  $\text{I1}$ ,  $\text{I2}$  and  $\text{Cu1}^*$ ,  $\text{Cu2}^*$ ,  $\text{I1}^*$ ,  $\text{I2}^*$ ) joined together in a staggered conformation by four  $\text{Cu}-\text{I}$  linkages. All the copper atoms are tetracoordinate and possess a distorted tetrahedral geometry around them. The immediate environment around the  $\text{Cu1}$  and  $\text{Cu1}^*$  atoms contains three iodine and one germanium atoms. Nevertheless, the other two copper atoms  $\text{Cu2}$  and  $\text{Cu2}^*$  are surrounded by three iodine and one nitrogen atoms. The germanium atoms also are tetracoordinate and have a distorted tetrahedral geometry provided by two nitrogen, one copper, and one chlorine atoms. All the iodine atoms are  $\mu^3$ -bridged, and each one is attached to three copper atoms. The lengths of the  $\text{Cu}-\text{I}$  bonds range from 2.635(1) to 2.789(1) Å, and this is in agreement with the lengths of the same bonds found in other donor stabilized copper(I) iodide complexes with a  $\text{Cu}_4\text{I}_4$  core.<sup>11</sup> The  $\text{Ge1}-\text{Cu1}$  bond length (2.341(1) Å) is comparable to the corresponding bond length observed in compound **1** (2.359(2) Å). In the other related compounds, that contain  $\text{Ge(II)}-\text{Cu(I)}$  bonds but without any iodine atoms attached to the copper atoms, the  $\text{Ge(II)}-\text{Cu(I)}$  bond lengths range from 2.2138(4) to 2.3563(5) Å.<sup>7c-f</sup> The  $\text{Ge1}-\text{N1}$  and  $\text{Ge1}-\text{N2}$  bond lengths in complex **2** are found to be 1.900(3) and 1.912(3) Å, respectively. These values are slightly shorter than the lengths of the same bonds ( $\text{Ge1}-\text{N1}$  1.933(1) and  $\text{Ge1}-\text{N2}$  1.943(1) Å) in compound **1**.<sup>9a</sup> This may be due to an increased  $\text{N}\rightarrow\text{Ge}$   $\pi$ -donation in compound **2** than in compound **1**.<sup>12</sup> The  $\text{Ge1}-\text{Cl1}$  bond length in compound **2** (2.287(1) Å) is also shorter than the same bond length present in compound **1** (2.3598(5) Å).<sup>9a</sup> The  $\text{Cu2}-\text{N3}$  bond length (1.994(4) Å) in compound **2** is comparable to the length of the  $\text{Cu}-\text{N}_{\text{acetonitrile}}$  bond (1.99(4) Å) in complex  $[\text{Cu}_2\text{I}_2(p\text{-chloroaniline})_2(\text{CH}_3\text{CN})_2]$  with a  $\text{Cu}_4\text{I}_4$  core.<sup>13</sup> The distances between the  $\text{Cu1}$  and  $\text{Cu2}$  atoms and  $\text{Cu2}$  and  $\text{Cu2}^*$  atoms in compound **2** are 2.707(1) and 2.747(1) Å, respectively (Figure 1b). These values are shorter than the sum of the van der Waals radii of copper atoms (2.80 Å) and indicate the cuprophilic interactions between them.<sup>14</sup>

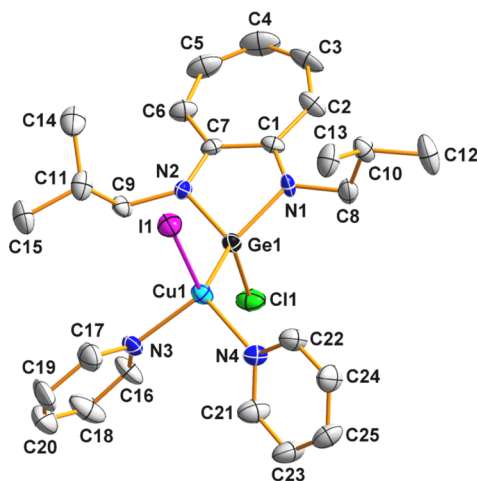
In compound **2**, the  $\text{N}-\text{Ge}-\text{Cl}$  bond angles are almost the same ( $98.7(1)^\circ$ ) and the  $\text{Cl1}-\text{Ge1}-\text{Cu1}$  bond angle is  $115.58(4)^\circ$ . The  $\text{I}-\text{Cu}-\text{I}$  bond angles in this compound range from  $102.17(2)$  to  $121.06(3)^\circ$ . Two of the three  $\text{Ge}-\text{Cu}-\text{I}$  bond angles ( $111.46(2)$  and  $100.90(1)^\circ$ ) are almost equal, but the other one ( $118.04(3)^\circ$ ) differs significantly. The



**Figure 1.** (a) Molecular structure of compound **2**. Thermal ellipsoids are drawn at the 30% probability level. All the isobutyl groups and hydrogen atoms are omitted for clarity. (b)  $\text{Cu}_4\text{I}_4$  core of compound **2** that reveals the cuprophilic interactions. Selected bond lengths (Å) and angles (deg):  $\text{Ge1}-\text{Cu1} = 2.341(1)$ ,  $\text{Cu2}-\text{N3} = 1.994(4)$ ,  $\text{Cu1}-\text{Cu2} = 2.707(1)$ ,  $\text{Cu2}-\text{Cu2}^* = 2.747(1)$ ,  $\text{Cu1}-\text{I1} = 2.789(7)$ ,  $\text{Cu1}-\text{I1}^* = 2.635(7)$ ,  $\text{Cu1}-\text{I2} = 2.711(7)$ ,  $\text{Cu2}-\text{I2} = 2.693(7)$ ,  $\text{Ge1}-\text{Cl1} = 2.287(1)$ ,  $\text{Ge1}-\text{N1} = 1.900(3)$ ,  $\text{Ge1}-\text{N2} = 1.912(3)$ ;  $\text{Cl1}-\text{Ge1}-\text{Cu1} = 115.58(4)$ ,  $\text{Cu1}^*-\text{I1}-\text{Cu2} = 65.63(2)$ ,  $\text{Cu1}^*-\text{I1}-\text{Cu1} = 70.32(2)$ ,  $\text{Cu2}-\text{I1}-\text{Cu1} = 59.54(2)$ ,  $\text{Cu2}-\text{I2}-\text{Cu1} = 60.12(2)$ ,  $\text{Cu2}-\text{I2}-\text{Cu2}^* = 61.03(2)$ ,  $\text{Cu1}-\text{I2}-\text{Cu2}^* = 63.82(2)$ ,  $\text{I1}^*-\text{Cu1}-\text{I2} = 108.31(2)$ ,  $\text{I1}^*-\text{Cu1}-\text{I1} = 102.17(2)$ ,  $\text{I2}-\text{Cu1}-\text{I1} = 115.78(2)$ ,  $\text{I1}-\text{Cu2}-\text{I2}^* = 107.49(2)$ ,  $\text{I2}-\text{Cu2}-\text{I1}^* = 108.74(2)$ ,  $\text{I1}-\text{Cu2}-\text{I2} = 121.06(3)$ ,  $\text{N1}-\text{Ge1}-\text{N2} = 82.3(1)$ ,  $\text{N1}-\text{Ge1}-\text{Cl1} = 98.6(1)$ ,  $\text{N2}-\text{Ge1}-\text{Cl1} = 98.7(1)$ . \*Symmetry transformation used to generate equivalent atoms:  $1-x, y, -z+1/2$ .

$\text{Cu}-\text{I}-\text{Cu}$  bond angles in compound **2** range from  $59.54(2)$  to  $70.32(2)^\circ$ . The germanium centers in this compound lie slightly above ( $0.1697(4)$  Å) the mean planes defined by the respective ATI ligand atoms (two nitrogen and seven ring carbon atoms).

Compound **3** crystallized in the orthorhombic space group  $Pbca$  with one pyridine molecule in the crystal lattice. From its molecular structure (Figure 2), the presence of a  $\text{Ge(II)}-\text{Cu(I)}$

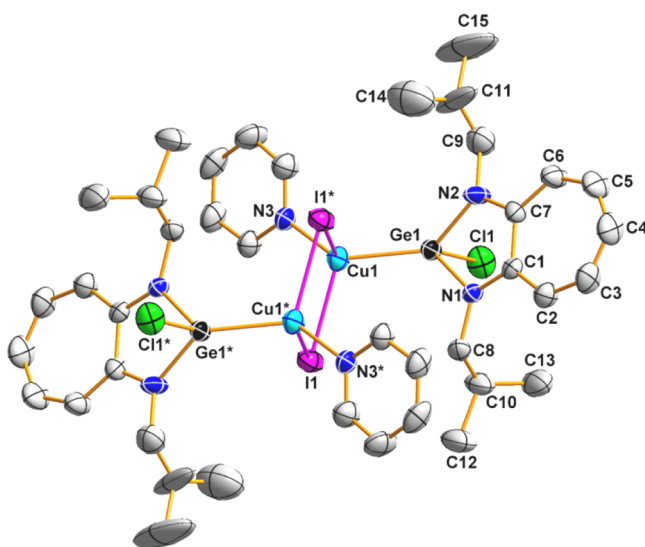


**Figure 2.** Molecular structure of compound **3**. Thermal ellipsoids are drawn at the 30% probability level. Pyridine molecule in the crystal lattice and all the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg):  $\text{Ge1}-\text{Cu1} = 2.308(1)$ ,  $\text{Cu1}-\text{N3} = 2.076(6)$ ,  $\text{Cu1}-\text{N4} = 2.066(6)$ ,  $\text{Cu1}-\text{I1} = 2.622(1)$ ,  $\text{Ge1}-\text{Cl1} = 2.354(2)$ ,  $\text{Ge1}-\text{N1} = 1.890(6)$ ,  $\text{Ge1}-\text{N2} = 1.912(5)$ ;  $\text{Cl1}-\text{Ge1}-\text{Cu1} = 114.65(7)$ ,  $\text{Ge1}-\text{Cu1}-\text{I1} = 111.94(4)$ ,  $\text{N1}-\text{Ge1}-\text{N2} = 82.0(2)$ ,  $\text{N1}-\text{Ge1}-\text{Cl1} = 96.8(2)$ ,  $\text{N2}-\text{Ge1}-\text{Cl1} = 93.7(2)$ ,  $\text{N3}-\text{Cu1}-\text{N4} = 101.1(3)$ .

bond and two pyridine ligands attached to the copper atom can be seen. Both the germanium and the copper atoms have a distorted tetrahedral geometry around them. While the former has an environment of two nitrogen, one copper, and one chlorine atoms, the latter is surrounded by two nitrogen, one germanium, and one iodine atoms. The  $\text{Ge(II)}-\text{Cu(I)}$  bond length ( $2.308(1)$  Å) is slightly shorter than the length of the same bonds ( $2.341(1)$  Å) in compound **2**. The  $\text{Cu1}-\text{I1}$  bond length ( $2.622(1)$  Å) is consistent with that present in other donor stabilized copper(I) iodide complexes with a monomeric  $\text{CuI}$  core and tetrahedral environment for the copper atom.<sup>15</sup> As observed in compound **2**, the  $\text{Ge}-\text{N}$  bond lengths ( $\text{Ge1}-\text{N1}$   $1.890(6)$  and  $\text{Ge1}-\text{N2}$   $1.912(5)$  Å) are shorter than the  $\text{Ge}-\text{N}$  bonds in compound **1** (vide supra). The  $\text{Ge}-\text{Cl}$  bond lengths in compounds **3** ( $2.354(2)$  Å) and **1** ( $2.3598(5)$  Å) are almost the same. The halide atoms ( $\text{I1}$  and  $\text{Cl1}$ ) are nearly *anti* to each other, and it is evident from the  $\text{I1}-\text{Cu1}-\text{Ge1}-\text{Cl1}$  torsion angle of  $172.68(8)^\circ$ . In contrast to compound **2**, the  $\text{N1}-\text{Ge1}-\text{Cl1}$  ( $96.8(2)^\circ$ ) and  $\text{N2}-\text{Ge1}-\text{Cl1}$  ( $93.7(2)^\circ$ ) bond angles in compound **3** are different. But the  $\text{Cl1}-\text{Ge1}-\text{Cu1}$  bond angle in this compound ( $114.65(7)^\circ$ ) is almost comparable to those found in compound **2** ( $115.58(4)^\circ$ ). The  $\text{Ge1}-\text{Cu1}-\text{I1}$  bond angle ( $111.94(4)^\circ$ ) is very close to one of the three such angles found in compound **2** (vide supra). The displacement ( $0.322(1)$  Å) of the germanium atom with respect to the ATI ligand mean plane is higher than that found for compound **2**.

Compound **4** crystallized in the monoclinic space group  $P2_1/n$  and its molecular structure (Figure 3) is centrosymmetric with a rhombic  $\text{Cu}_2\text{I}_2$  core. The copper atoms are tetracoordinate (with two iodine, one germanium, and one nitrogen atoms) and have a distorted tetrahedral geometry. In contrast, the only known germylene stabilized copper(I) iodide complex with a dimeric planar  $\text{Cu}_2\text{I}_2$  core **II** contains tricoordinate copper atoms. The  $\text{Ge(1)}-\text{Cu(1)}$  bond length





**Figure 3.** Molecular structure of compound **4**. Thermal ellipsoids are drawn at the 30% probability level. All the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1–Cu1 = 2.345(1), Cu1–N3 = 2.046(4), Cu1–Cu1\* = 3.020(2), I1–Cu1 = 2.733(1), I1–Cu1\* = 2.651(1), Ge1–N1 = 1.915(4), Ge1–N2 = 1.907(5), Ge1–Cl1 = 2.303(2); Cl1–Ge1–Cu1 = 123.30(5), Cu1–I1–Cu1\* = 68.21(3), I1–Cu1–I1\* = 111.79(3), N1–Ge1–N2 = 81.9(2), N1–Ge1–Cl1 = 98.1(1), N2–Ge1–Cl1 = 93.7(2). \*Symmetry transformation used to generate equivalent atoms:  $-x + 2, -y + 1, -z$ .

(2.345(1) Å) in compound **4** is close to the lengths of the Ge(II)–Cu(I) bonds seen in compounds **2** (2.341(1) Å) and **3** (2.308(1) Å). The Ge–N bond lengths (Ge1–N1 1.915(4) and Ge1–N2 1.907(5) Å) show a similar trend seen in compounds **2** and **3**, as these values are shorter than those present in compound **1**. Similar to compound **2**, the Ge1–Cl1 bond length in compound **4** (2.303(2) Å) is slightly shorter than same bond in compound **1** (2.3598(5) Å). The distance between the copper atoms (3.020(2) Å) in the planar Cu<sub>2</sub>I<sub>2</sub> core is longer than the sum of van der Waals radii of copper atoms (2.80 Å), and this indicates the absence of cuprophilic interaction. Nevertheless, this distance is shorter than the same (3.297(2) Å) in compound **11**. The iodine atoms are  $\mu$ -bridged, and the lengths of the Cu–I bonds in it are 2.651(1) and 2.733(1) Å. These values are consistent with the lengths of the Cu–I bonds present in complex [Cu<sub>2</sub>I<sub>2</sub>(hppH)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (hppH = 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-*a*]pyrimidine) with a rhombic Cu<sub>2</sub>I<sub>2</sub> core.<sup>16</sup> The N1–Ge1–N2 bond angle in compound **4** (81.9(2)°) matches almost with the same angles found in compounds **2** (82.3(1)°) and **3** (82.0(2)°). As in compound **3**, the two N–Ge–Cl bond angles (98.1(1) and 93.7(2)°) in compound **4** are not that close. In comparison to the Cl1–Ge1–Cu1 bond angles in compounds **2** and **3** (vide supra), the same angle in compound **4** is wider (123.30(5)°). The I1–Cu1–I1\* (111.79(3)°) and Cu1–I1–Cu1\* (68.21(3)°) bond angles lie within ranges for the I–Cu–I and Cu–I–Cu bond angles found in compound **2**, respectively. In contrast to compounds **2** and **3**, the germanium atoms of compound **4**, lie almost on the respective ATI ligand mean planes.

## CONCLUSION

In summary, the utility of an aminotroponiminato(chloro)-germylene **1** in stabilizing the copper(I) iodide complexes has been documented for the first time through the synthesis of compounds **2–4**. Interestingly, the first germylene stabilized copper(I) iodide complex **3** having a monomeric CuI core has been isolated. Further, a unique interconversion between compounds **3** and **4** with a monomeric CuI and dimeric Cu<sub>2</sub>I<sub>2</sub> cores, respectively, and conversion of compound **2** to compounds **3** and **4** have also been shown for the first time. Exploiting compound **1** for the stabilization of hitherto unknown copper(I) iodide complexes, checking the catalytic activity of compounds **2–4**, and examination of the photo-physical properties of compounds **2–4**, are currently under progress in our research laboratory.

## EXPERIMENTAL SECTION

All the manipulations that involve air- and moisture-sensitive compounds were performed under a dry N<sub>2</sub> atmosphere using either standard Schlenk or glovebox [Jacomex (GP Concept)-T2 workstation] techniques. CuI and pyridine were purchased from Sigma-Aldrich and Spectrochem chemicals Pvt. Ltd., respectively. Pyridine and dichloromethane were dried over KOH and P<sub>2</sub>O<sub>5</sub>, respectively, and were distilled just before use. Germylene monochloride complex **1** was synthesized according to the literature procedure.<sup>9a</sup> Melting points of the pure compounds were recorded using an Ambassador melting point apparatus by sealing the samples in glass capillaries, and the reported melting points are uncorrected. Elemental analyses were carried out on a Perkin-Elmer CHN analyzer. Multinuclear NMR spectroscopic studies were carried out on a 300 MHz Bruker Topspin NMR spectrometer using anhydrous CDCl<sub>3</sub>. The chemical shifts  $\delta$  are reported in ppm and are referenced internally with respect to the residual solvent (<sup>1</sup>H NMR) and solvent (<sup>13</sup>C NMR) resonances.<sup>17</sup>

**Synthesis of [(*i*-Bu)<sub>2</sub>ATI(GeCl)<sub>2</sub>(CuI)<sub>4</sub>(CH<sub>3</sub>CN)<sub>2</sub>] (**2**).** To a solution of compound **1** (0.50 g, 1.47 mmol) in acetonitrile (40 mL), CuI (0.56 g, 2.94 mmol) was added, and the resultant suspension was stirred for 36 h. All the volatiles were then removed under reduced pressure to yield an orange solid. This solid was dissolved in dichloromethane, filtered through a G-4 frit, and the solvent was removed under reduced pressure. The resultant solid was washed with hexane (5 mL) and dried under reduced pressure to result in an analytically pure sample of compound **2** as a yellow powder. Crystals of compound **2** suitable for single crystal X-ray diffraction studies were grown from its acetonitrile solution by the slow evaporation of the solvent at room temperature. Yield: 1.01 g, 90%. Mp: 67 °C. Anal. Calcd for C<sub>34</sub>H<sub>52</sub>Cl<sub>2</sub>Cu<sub>4</sub>Ge<sub>2</sub>I<sub>4</sub>N<sub>6</sub> (*M* = 1522.80): C, 26.82; H, 3.44; N, 5.52. Found: C, 26.77; H, 3.36; N, 5.48. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.05 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.6 Hz, 24H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.00 (s, 6H, CH<sub>3</sub>), 2.31–2.40 (m, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.66 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.3 Hz, 8H, CH<sub>2</sub>), 6.78 (t, <sup>3</sup>*J*<sub>HH</sub> = 9.0 Hz, 2H, CH), 6.95 (d, <sup>3</sup>*J*<sub>HH</sub> = 11.1 Hz, 4H, CH), 7.32 (t, <sup>3</sup>*J*<sub>HH</sub> = 10.8 Hz, 4H, CH). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  1.92 (CH<sub>3</sub>), 20.68 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.72 (CH(CH<sub>3</sub>)<sub>2</sub>), 54.01 (CH<sub>2</sub>), 116.37 (CN), 116.64 (C<sub>4</sub>), 124.05 (C<sub>2,6</sub>), 137.04 (C<sub>3,5</sub>), 160.47 (C<sub>1,7</sub>).

**Synthesis of [(*i*-Bu)<sub>2</sub>ATI(GeCl)(CuI)(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>] (**3**).** A Schlenk flask was charged with compound **1** (1.00 g, 2.94 mmol), CuI (0.56 g, 2.94 mmol), and dichloromethane (50 mL). This reaction mixture was stirred for 30 min. Then pyridine (0.47 g, 5.88 mmol) was added and the resultant orange red solution was stirred further for 6 h. All the volatiles were then removed under reduced pressure to yield a solid product. It was washed with hexane (5 mL) and dried under reduced pressure to give an analytically pure sample of compound **3** as a yellow solid. Single crystals of compound **3** suitable for X-ray diffraction studies were grown from its pyridine solution by the slow evaporation of pyridine at room temperature. Yield: 1.74 g, 86%. Mp: 101 °C. Anal. Calcd for C<sub>25</sub>H<sub>33</sub>ClCuGeIN<sub>4</sub> (*M* = 688.10): C, 43.64; H, 4.83; N, 8.14. Found: C, 43.57; H, 4.79; N, 8.10. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.93 (d, <sup>3</sup>*J*<sub>HH</sub> = 5.7 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.21–2.28 (m, 2H,

$\text{CH}(\text{CH}_3)_2$ ), 3.59 (d,  $^3J_{\text{HH}} = 6.6$  Hz, 4H,  $\text{CH}_2$ ), 6.76 (t,  $^3J_{\text{HH}} = 9.3$  Hz, 1H, CH), 6.92 (d,  $^3J_{\text{HH}} = 11.1$  Hz, 2H, CH), 7.27–7.33 (m, 6H,  $\text{CH}_{\text{Ar}}$ ), 7.68 (m, 2H, py), 8.80 (m, 4H, py).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.13 ( $\text{CH}(\text{CH}_3)_2$ ), 28.59 ( $\text{CH}(\text{CH}_3)_2$ ), 54.00 ( $\text{CH}_2$ ), 116.65, 124.17, 136.63, 137.08, 150.39, 160.46 (Ar).

**Synthesis of  $[(i\text{-Bu})_2\text{ATI}(\text{GeCl})_2(\text{Cu}_2\text{I}_2)(\text{C}_5\text{H}_5\text{N})_2]$  (4).** To a solution of compound 1 (0.50 g, 1.47 mmol) in dichloromethane (50 mL), CuI (0.28 g, 1.47 mmol) was added and stirred for 30 min. Then pyridine (0.12 g, 1.47 mmol) was added, and the resultant yellow solution was stirred for further 6 h. All the volatiles were then removed under reduced pressure to yield a solid residue. It was washed with hexane (5 mL) and dried under reduced pressure to result in an analytically pure sample of compound 4 as a bright yellow solid. Crystals of compound 4 suitable for single crystal X-ray diffraction studies were grown from its dichloromethane solution by the slow evaporation of the solvent at room temperature. Yield: 0.84 g, 94%. Mp: 121 °C. Anal. Calcd for  $\text{C}_{40}\text{H}_{56}\text{Cl}_2\text{Cu}_2\text{Ge}_2\text{I}_2\text{N}_6$  ( $M = 1218.00$ ): C, 39.44; H, 4.63; N, 6.90. Found: C, 39.39; H, 4.61; N, 6.86.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.01 (d,  $^3J_{\text{HH}} = 6.6$  Hz, 24H,  $\text{CH}(\text{CH}_3)_2$ ), 2.35–2.39 (m, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 3.65 (d,  $^3J_{\text{HH}} = 6.3$  Hz, 8H,  $\text{CH}_2$ ), 6.77 (t,  $^3J_{\text{HH}} = 9.0$  Hz, 2H, CH), 6.93 (d,  $^3J_{\text{HH}} = 11.1$  Hz, 4H, CH), 7.26–7.36 (m, 8H, CH), 7.72 (t,  $^3J_{\text{HH}} = 6.0$  Hz, 2H, py), 8.87 (d,  $^3J_{\text{HH}} = 6.0$  Hz, 4H, py).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.21 ( $\text{CH}(\text{CH}_3)_2$ ), 28.69 ( $\text{CH}(\text{CH}_3)_2$ ), 54.02 ( $\text{CH}_2$ ), 116.59, 124.01, 124.41, 137.04, 137.17, 150.71, 160.47 (Ar).

**Conversion of Compound 3 to 4.** To a solution of compound 3 (0.20 g, 0.29 mmol) in dichloromethane (20 mL), compound 1 (0.10 g, 0.29 mmol) and CuI (0.06 g, 0.29 mmol) were added at room temperature. The resultant mixture was stirred for 6 h to get a clear yellow solution. All the volatiles were then removed under reduced pressure to yield a solid product. This was washed with hexane (5 mL) and dried under vacuum to afford an analytically pure sample of compound 4 as a bright yellow solid. Yield: 0.34 g, 98%.

**Conversion of Compound 4 to 3.** To a solution of compound 4 (0.30 g, 0.24 mmol) in dichloromethane (20 mL), pyridine (0.04 g, 0.48 mmol) was added. The resultant solution was stirred for 6 h, and all the volatiles were then removed under vacuum to get a solid product. This was washed with hexane (5 mL) and dried under reduced pressure to result in an analytically pure sample of compound 3 as a yellow solid. Yield: 0.33 g, 99%.

**Conversion of Compound 2 to 3.** To a solution of compound 2 (0.25 g, 0.16 mmol) in dichloromethane (30 mL), compound 1 (0.11 g, 0.32 mmol) and pyridine (0.10 g, 1.31 mmol) were added at room temperature and stirred. The resultant solution was stirred for additional 6 h. All the volatiles were then removed under reduced pressure to yield a solid product. This was washed with hexane (5 mL) and dried under reduced pressure to result in an analytically pure sample of compound 3 as a yellow solid. Yield: 0.44 g, 98%.

**Conversion of Compound 2 to 4.** To a solution of compound 2 (0.25 g, 0.16 mmol) in dichloromethane (30 mL), compound 1 (0.11 g, 0.32 mmol) and pyridine (0.05 g, 0.65 mmol) were added at room temperature and stirred. The resultant solution was stirred further for 6 h. All the volatiles were then removed under reduced pressure to yield a solid product. This was washed with hexane (5 mL) and dried under vacuum to afford an analytically pure sample of compound 4 as a bright yellow solid. Yield: 0.40 g, 99%.

**X-ray Data Collection for Compounds 2–4.** Single crystals of compounds 2–4 suitable for X-ray diffraction studies were coated with Paratone-N and mounted on a glass fiber. Data were collected at 298 K using a Bruker SMART APEX CCD diffractometer using Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å).<sup>18</sup> The data were integrated using SAINT, and an empirical absorption correction was applied using SADABS.<sup>19</sup> The structures were solved by direct methods and refined by full matrix least-squares on  $F^2$  using SHELXTL software.<sup>20</sup> All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were fixed according to a riding model and were isotropically refined. The important crystallographic data of these compounds are given in Supporting Information, Table S1.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Crystallographic information file (CIF) for compounds 2–4, crystal data and structure refinement parameters for compounds 2–4 (Table S1). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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