Digermylene Oxide Stabilized Group 11 Metal Iodide Complexes

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S Supporting Information

ABSTRACT: Use of a substituted digermylene oxide as a ligand has been demonstrated through the isolation of a series of group 11 metal(I) iodide complexes. Accordingly, the reactions of digermylene oxide $[\{(i\text{-Bu})_2\text{ATIGe}\}_2\text{O}]$ (ATI = aminotroponiminate) (**1**) with CuI under different conditions afforded $[(\{(i\text{-Bu})_2\text{ATIGe}\}_2\text{O})_2(\text{Cu}_4\text{I}_4)]$ (**2**) with a Cu_4I_4 octahedral core, $[(\{(i\text{-Bu})_2\text{ATIGe}\}_2\text{O})_2(\text{Cu}_3\text{I}_3)]$ (**3**) with a Cu_3I_3 core, and $[\{(i\text{-Bu})_2\text{ATIGe}\}_2\text{O}(\text{Cu}_2\text{I}_2)(\text{C}_5\text{H}_5\text{N})_2]$ (**4**) with a butterfly-type Cu_2I_2 core. The reactions of compound **1** with AgI and AuI produced $[(\{(i\text{-Bu})_2\text{ATIGe}\}_2\text{O})_2(\text{Ag}_4\text{I}_4)]$ (**5**) with a Ag_4I_4 octahedral core and $[\{(i\text{-Bu})_2\text{ATIGe}\}_2\text{O}(\text{Au}_2\text{I}_2)]$ (**6**) with a Au_2I_2 core, respectively. The presence of metallophilic interactions in these compounds is shown through the single-crystal X-ray diffraction and atom-in-molecule (AIM) studies. Preliminary photophysical studies on compound **6** are also carried out.
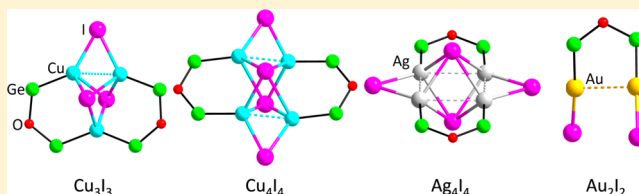
INTRODUCTION

Digermylene oxides $[\text{LGe(II)}-\text{O}-\text{Ge(II)L}]$ (L = bulky monoanionic ligand/substituent) are a class of low-valent germanium compounds where two germylene centers are separated by an oxygen atom (Chart 1).[1] Although a few examples of digermylene oxides are known, the reactivity studies on them are rare. Reported examples include the oxidative addition and Ge−O bond-cleavage reactions that afforded germaacid anhydride complexes with Ge(E)−O−Ge(E) (E = S, Se, Te) moieties and germanium(II) cyanide complex, respectively.[1a,2] Further, it can be anticipated that, due to the presence of a lone pair of electrons on each of the germanium atoms, they can be used as potential ligands.

Though germylenes have been utilized to isolate numerous transition metal complexes,[3] the coordination chemistry of digermylene oxides has never been looked at presumably due to the lack of appropriate precursors. However, it should be mentioned here that there are two reports on the coordination chemistry of disilylene oxides[4] and in situ generated digermylene oxide[5] (Chart 2).

Therefore, we started our investigation using a digermylene oxide, $[\{(i\text{-Bu})_2\text{ATIGe}\}_2\text{O}]$ (**1**),[1a] and report here the examples of digermylene oxide stabilized group 11 metal iodide complexes, $[(\{(i\text{-Bu})_2\text{ATIGe}\}_2\text{O})_2(\text{Cu}_4\text{I}_4)]$ (**2**), $[(\{(i\text{-Bu})_2\text{ATIGe}\}_2\text{O})_2(\text{Cu}_3\text{I}_3)]$ (**3**), $[\{(i\text{-Bu})_2\text{ATIGe}\}_2\text{O}(\text{Cu}_2\text{I}_2)(\text{C}_5\text{H}_5\text{N})_2]$ (**4**), $[(\{(i\text{-Bu})_2\text{ATIGe}\}_2\text{O})_2(\text{Ag}_4\text{I}_4)]$ (**5**), and $[\{(i\text{-Bu})_2\text{ATIGe}\}_2\text{O}(\text{Au}_2\text{I}_2)]$ (**6**) with octahedral Cu_4I_4, Cu_3I_3, butterfly-type Cu_2I_2, octahedral Ag_4I_4, and Au_2I_2 cores, respectively. The structural studies and AIM calculations reveal the presence of metallophilic interactions in all these compounds. Photophysical studies on compound **6** are also performed and compared with compound **1**.

It is noteworthy to state here that germylenes also have stabilized group 11 metal(I) complexes.[6−9,11] For the metal(I) halide complexes, the Dimmer and Wesemann's report of octaanionic cubane type $[\text{Et}_3\text{MeN}]_8[\{\text{AgX}(\text{GeB}_{11}\text{H}_{11})\}_4]$ [X = Cl/Br] obtained by the reactions of germa-*closo*-dodecaborate with silver chloride and silver bromide can be mentioned.[8] For the metal(I) complexes with X substituents on the metal atom, where X is a nonhalide substituent, such as fluorinated tris(pyrazolyl)borate and pentafluorophenyl, the work of Dias and co-workers[6] and Zhu, Fu, and co-workers[7] (Chart 3) can be suggested, respectively.

RESULTS AND DISCUSSION

Synthesis and Spectra. To study the coordination chemistry of digermylene oxides, we investigated the reactions of compound **1** with group 11 metal halides. This is due to the fact that even the use of monodentate germylenes to stabilize group 11 metal halides is limited to copper and gold with only a few examples,[9] despite their very rich coordination chemistry. Accordingly, a reaction of compound $[\{(i\text{-Bu})_2\text{ATIGe}\}_2\text{O}]$ (**1**) and CuI in a 1:2 molar ratio was carried out in tetrahydrofuran at room temperature to produce $[(\{(i\text{-Bu})_2\text{ATIGe}\}_2\text{O})_2(\text{Cu}_4\text{I}_4)]$ (**2**) (Scheme 1) in 92% yield. The reaction of compound **1** and CuI in a 2:3 molar ratio afforded $[(\{(i\text{-Bu})_2\text{ATIGe}\}_2\text{O})_2(\text{Cu}_3\text{I}_3)]$ (**3**) as a unique example of germylene-stabilized trinuclear copper iodide complex in 95% yield (Scheme 2). Further, the role of other donor ligands like pyridine was examined in the reaction of compound **1** with CuI. Accordingly, the reaction of compound **1**, CuI, and

Chart 1. Examples of Digermylene Oxides

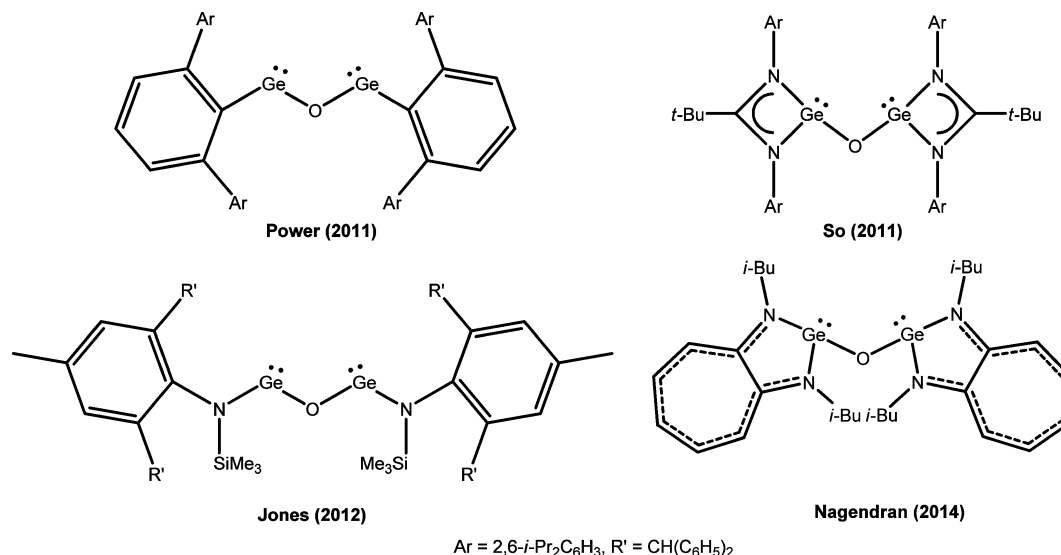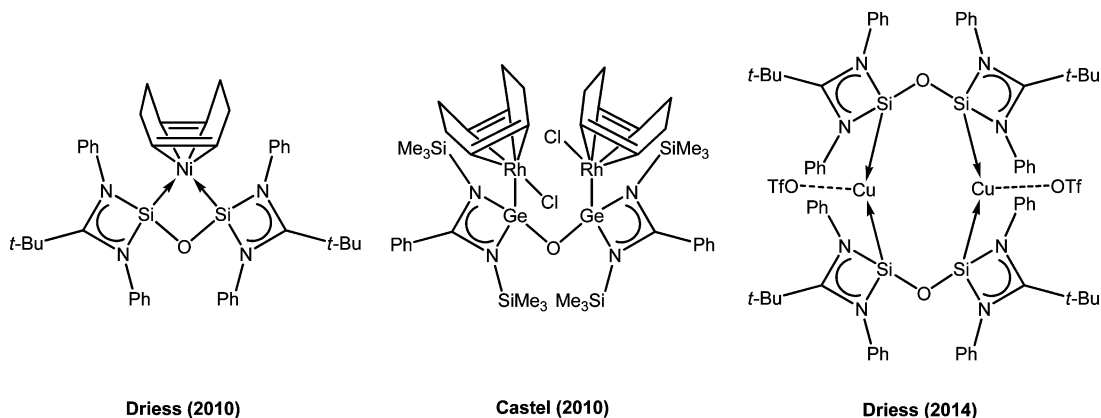Ar = 2,6-i-Pr$_2$C$_6$H$_3$, R' = CH(C$_6$H$_5$)$_2$

Chart 2. Transition Metal Complexes of Disilylene Oxides and In Situ Generated Digermylene Oxide

pyridine in a 1:2:2 stoichiometry in tetrahydrofuran at room temperature resulted in [{(i-Bu)$_2$ATIGe}$_2$O(Cu$_2$I$_2$)(C$_5$H$_5$N)$_2$] (**4**) quantitatively (Scheme 3). Interestingly, in this reaction, an excess amount of pyridine did not change the resultant product and always offered compound **4**. This is in contrast to the reactivity of aminotroponiminato(chloro)germylene complex [(i-Bu)$_2$ATIGeCl] with CuI and pyridine, where the amount of pyridine dictates the structure of the complexes formed.[9a] Compounds **2** and **3** are insoluble in toluene and possess less solubility in tetrahydrofuran and chloroform. Compound **4** shows good solubility in tetrahydrofuran, dichloromethane, and chloroform.
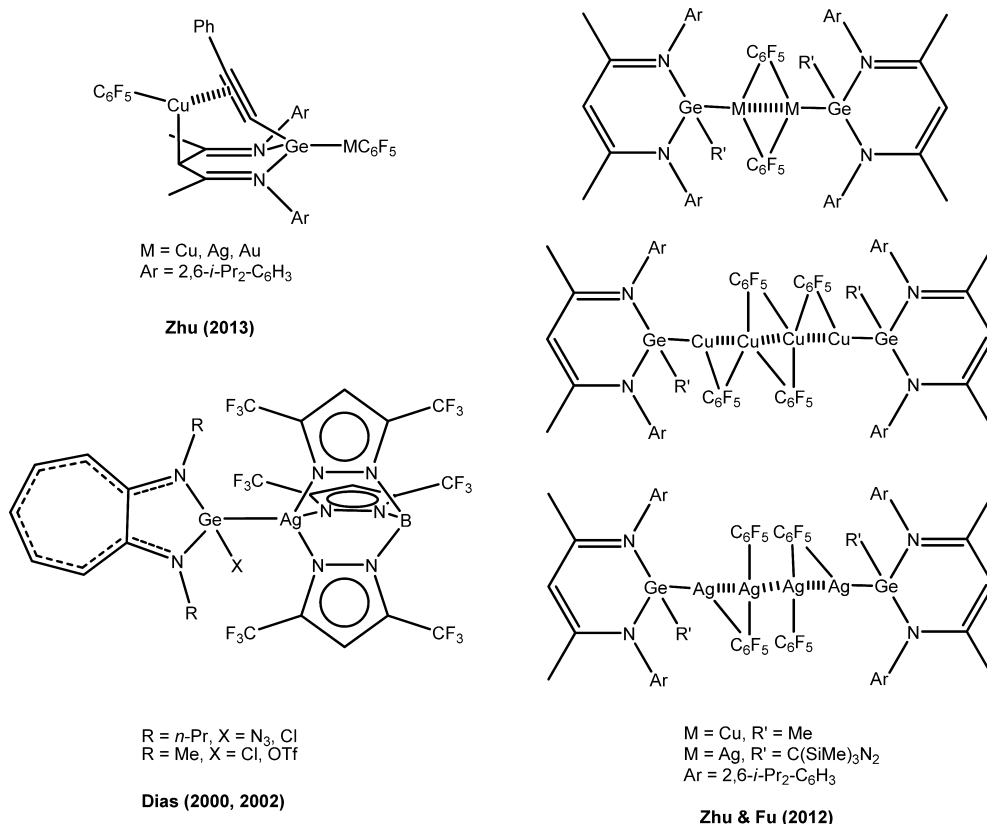
After the successful isolation of digermylene oxide-stabilized copper(I) iodide complexes **2**–**4**, we aimed at the synthesis of digermylene oxide-stabilized silver(I) iodide complexes. Accordingly, the reaction of compound **1** with 2 equiv of AgI in excess pyridine was carried out at room temperature to obtain the germylene-stabilized silver(I) iodide complex [({(i-Bu)$_2$ATIGe}$_2$O)$_2$(Ag$_4$I$_4$)] (**5**) with an Ag$_4$I$_4$ core in 93% yield (Scheme 4). In contrast to the reaction that gave complex **4**, the interesting aspect of this reaction is that, although pyridine is used, it did not get incorporated into the resultant complex **5**. Further, the successful synthesis of compound **5** gains great importance due to the fact that, although there are a number of N-heterocyclic carbene-stabilized silver(I) iodide complexes,

there is no example of a NHGe-stabilized silver(I) iodide complex until now.[10] It is anticipated that the unique bidendate mode of binding of the germanium atoms of the Ge–O–Ge moiety in compound **1** is the key for the successful isolation of compound **5**. It has a limited solubility in polar organic solvents such as tetrahydrofuran and chloroform but reasonable solubility in more polar solvents like dichloromethane, pyridine, and so forth.

To isolate all the group 11 metal(I) halide complexes using the digermylene oxide **1**, we were curious to know about the behavior of compound **1** toward AuI. Reaction of compound **1** with 2 equiv of AuI in excess pyridine for 5 min at room temperature afforded compound [{(i-Bu)$_2$ATIGe}$_2$O(Au$_2$I$_2$)] (**6**) in 91% yield (Scheme 5). It was noticed that the reaction time of 5 min is very crucial, as the formed product started to decompose beyond this time, which was evident through the formation of shiny yellow particles. We anticipate that these particles may be metallic gold formed out of reduction. Compound **6** is fairly soluble in polar solvents like chloroform, dichloromethane, and pyridine.

Further, it was found that the reaction of compound **2** with excess pyridine results in compound **4** quantitatively (Scheme 6). Nevertheless, the reactions carried out to convert (a) compound **2** to compound **3** by adding 0.5 equiv of compound

Chart 3. Examples of Germylene-Stabilized Group 11 Metal Complexes with Non Halogen Substituents on the Metals

M = Cu, Ag, Au
Ar = 2,6-*i*-Pr$_2$-C$_6$H$_3$

Zhu (2013)

R = *n*-Pr, X = N$_3$, Cl
R = Me, X = Cl, OTf

Dias (2000, 2002)

M = Cu, R' = Me
M = Ag, R' = C(SiMe)$_3$N$_2$
Ar = 2,6-*i*-Pr$_2$-C$_6$H$_3$

Zhu & Fu (2012)

Scheme 1. Synthesis of Digermylene Oxide-Stabilized Tetrameric Copper(I) Iodide Complex 2

**1**   **2**
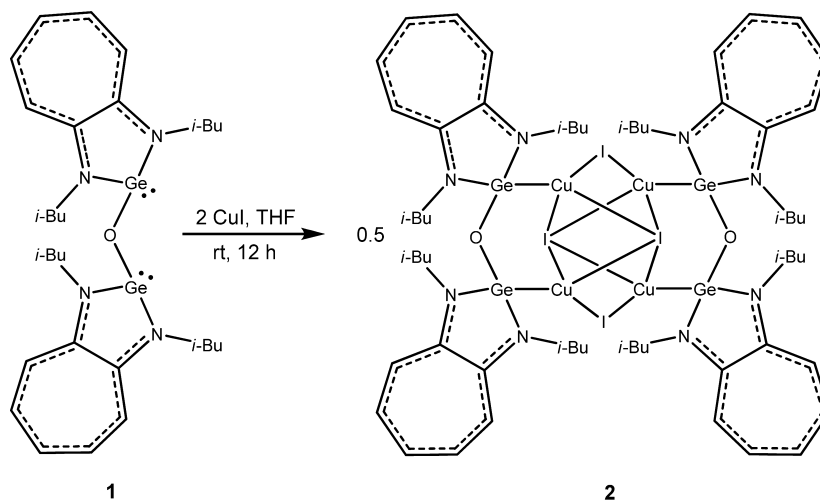
1 and (b) compound **3** to compound **2** by the addition of 1 equiv of CuI did not work.

Compounds **2**–**6** are stable under an atmosphere of dry N$_2$ at ambient temperature and can be shelved for months without decomposition. These compounds were characterized in solution through ^{1}H and ^{13}C NMR spectroscopic studies. In the ^{1}H NMR spectrum of compound **2**, the methyl protons of the isobutyl groups were observed as two doublets (1.08 and 1.15 ppm), while the methine and methylene protons appeared as a multiplet (2.50–2.54 ppm) and doublet (3.61 ppm), respectively. The protons of the seven-membered rings appeared as a triplet (6.54 ppm), a doublet (6.74 ppm), and a pseudotriplet (7.13 ppm). In compound **3**, the signals for the

methyl (1.04–1.11 ppm), methine (2.35–2.43 ppm), methylene (3.60–3.68 ppm), and seven-membered ring protons (6.53–7.53 ppm) appeared as multiplets due to the C1 symmetry of the molecule. In compound **4**, the methyl protons were observed as a multiplet (1.03–1.05 ppm). The methine and methylene protons of the *i*-butyl groups appeared as a broad singlet (2.48 ppm) and multiplet (3.60–3.66 ppm), respectively. Signals due to the seven-membered ring protons appeared as a triplet (6.45 ppm), doublet (6.65 ppm), and pseudotriplet (7.06 ppm) in a 1:2:2 intensity ratio. The pyridine protons were seen as three broad singlets at 7.27, 7.65, and 8.84 ppm. In compound **5**, the methyl, methine, and methylene protons of the isobutyl groups were observed as two
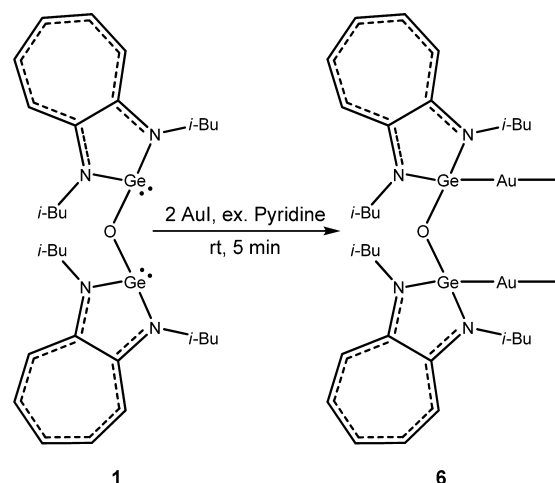
Scheme 2. Synthesis of Digermylene Oxide-Stabilized Trimeric Copper(I) Iodide Complex 3
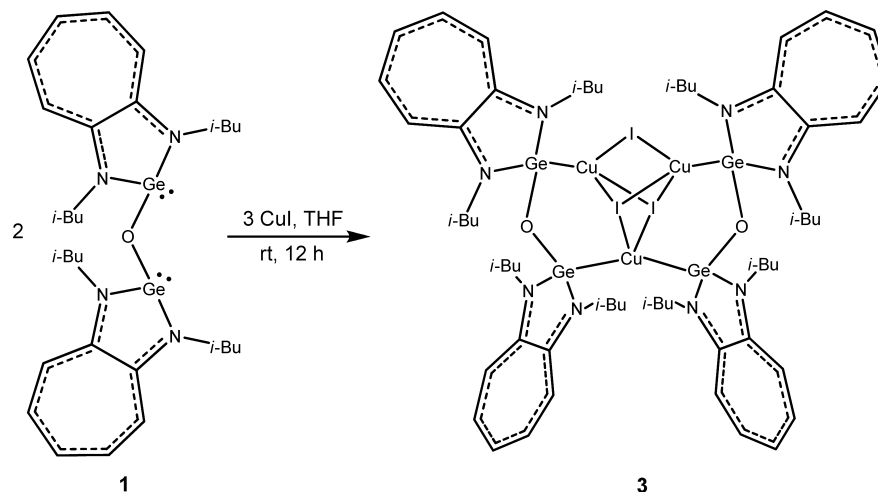
Scheme 3. Synthesis of Digermylene Oxide-Stabilized Dimeric Copper(I) Iodide Complex 4
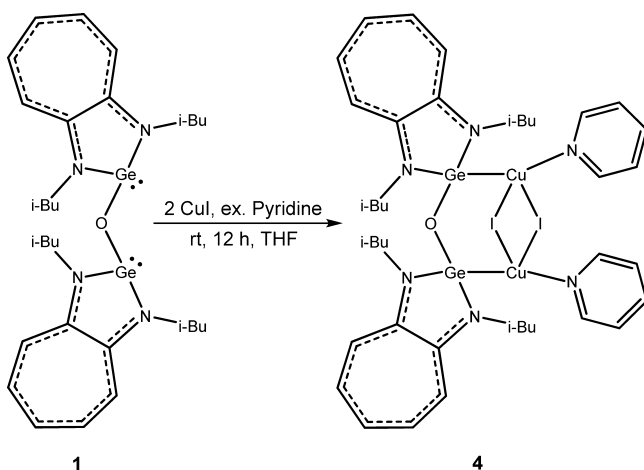

Scheme 5. Synthesis of Digermylene Oxide-Stabilized Gold(I) Iodide Complex 6


doublets (1.08 and 1.11 ppm), a multiplet (2.33−2.46 ppm), and a doublet (3.58 ppm), respectively. Similar to that in compound **2**, the seven-membered ring protons are seen as a triplet (6.66 ppm), doublet (6.81 ppm), and pseudotriplet (7.23 ppm). Like in compound **3**, the protons of the isobutyl

groups (methyl, 1.03−1.11 ppm; methine, 2.26−2.43 ppm; and methylene, 3.54−3.96 ppm) and seven-membered rings (6.83−7.03, 7.36−7.50 ppm) in compound **6** also appeared as multiplets. In the proton decoupled ^{13}C NMR spectra, eight

Scheme 4. Synthesis of Digermylene Oxide-Stabilized Tetrameric Silver(I) Iodide Complex 5
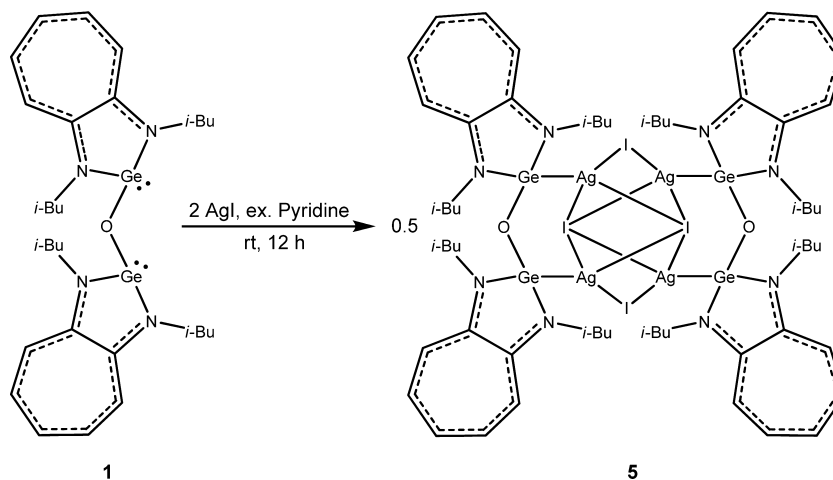
Scheme 6. Conversion of Compound 2 to Compound 4

Figure 2. Emission spectra for compounds **1** and **6** (5 μM solution) in tetrahydrofuran.
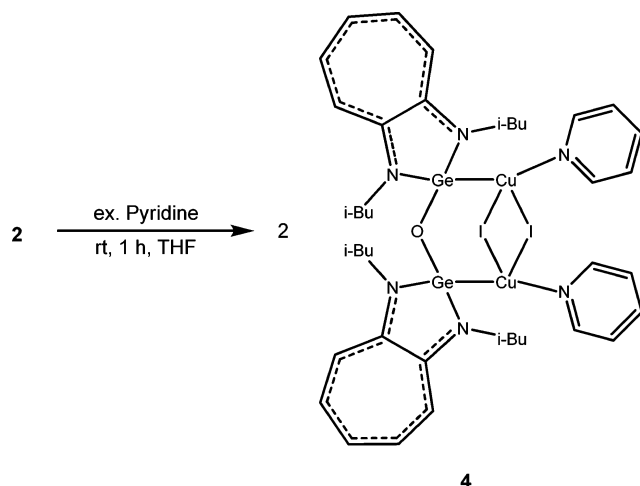
resonances anticipated for compound **2** and **5** were observed. Sixteen signals were observed for compound **3** due to the nonequivalent nature of ligands. For compounds **4** and **6**, 11 and 13 signals were seen, respectively. This reveals that, in compound **6**, the ATI ligands are nonequivalent, and this may be due to the intramolecular aurophilic interaction (vide supra).

Photophysical Studies on Compounds 1 and 6. Photophysical studies were carried out on compounds **1** and **6** at room temperature in tetrahydrofuran. Absorption (compound **6**) and emission (compounds **1** and **6**) spectra are shown in Figures 1 and 2. The UV–vis spectrum of
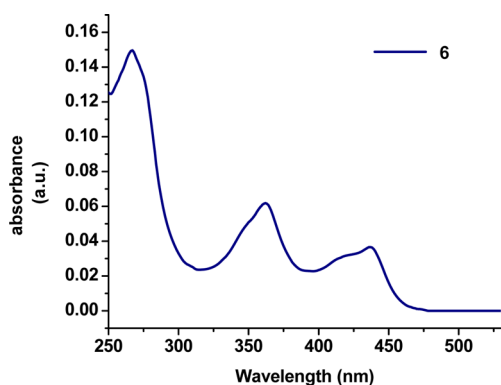

Figure 1. UV–vis spectrum of compound **6** (5 μM solution) in tetrahydrofuran.

compound **6** displays an absorption maxima in the visible region at 438 nm, and this value is slightly blue-shifted (442 nm) to that of compound **1**. Theoretical studies suggest that the excitation from nonbonding p-orbital of iodine (HOMO) to antibonding π-orbital of ATI (LUMO) is mainly responsible for this transition (Table 1). Apart from this, two intense peaks at 266 and 362 nm were observed. These are slightly red-shifted (269 nm) and blue-shifted (367 nm) in comparison to those of compound **1**. The emission spectra of compound **1** displayed two intense peaks at 490 and 486 nm and two other low intensity peaks at 431 and 407 nm (λ_{ex} = 360 nm). In contrast, compound **6** gave four emission peaks of almost equal intensity at 486, 460, 431, and 407 nm (λ_{ex} = 360 nm). Thus, the complexation of gold atoms to the germanium atoms has resulted in an appreciable decrease in the intensity of the
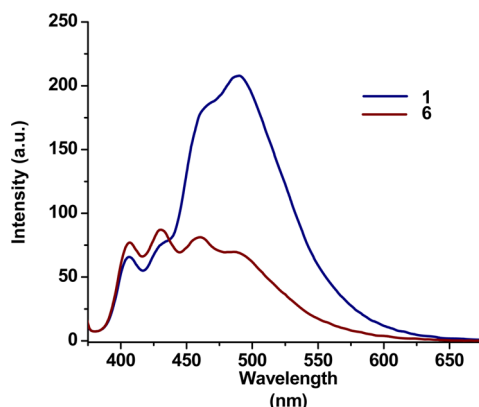
emission peaks at 486 and 460 nm, while the intensities of the other two peaks are almost unaffected.

X-ray Structures of Compounds 2–6. Compounds **2–6** were further characterized by single-crystal X-ray diffraction studies. Compound **2** crystallized in the triclinic space group $P\bar{1}$ (Table S1 in the Supporting Information). Its molecular structure depicts the presence of a Cu_4I_4 octahedral core with tetracoordinate germanium and copper atoms (Figure 3). The core structure can be visualized as a bicapped octahedron constituted using copper and iodine atoms. The iodine atoms are μ_2- and μ_4-bridged. The Ge–Cu bond distances (2.3125(9) and 2.3035(9) Å) match with that seen in other reported germylene copper complexes.[7,9a,11] In comparison to compound **1**, the Ge–O bond distances (1.812(3) and 1.812(4) Å) remain almost unaltered, while the Ge–N bond distances (1.932(4), 1.925(5), 1.927(4), and 1.923(4) Å) show shortening due to the withdrawal of electron density by germanium atoms from the nitrogen atoms.[12] The Cu···Cu separation of 2.573(1) Å (between Cu1 and Cu2*, and Cu2 and Cu1*) is smaller than the sum of van der Waals radii of two copper atoms, and this reveals the presence of cuprophilic interactions.[13] In the simple (monodentate) germylene-stabilized copper iodide complexes, no cuprophilic interaction has been observed.[9d,f] This shows the utility of digermylene oxide **1**. The Cu–I bond distances (2.573(1)–2.7490(8) Å) are in agreement with that seen in the reported copper complexes containing a similar Cu_4I_4 core.[14] The Ge–O–Ge bond angle (117.4(2)°) is considerably less than that found in compound **1** (154.9(3)°), and this shows the ability of digermylene oxide **1** to adjust according to the requirements of the metal atoms during complex formation.[1a]

Compound **3** crystallized in the triclinic space group $P\bar{1}$ (Table S1). Its molecular structure shows the presence of a Cu_3I_3 core stabilized through two digermylene oxide ligands. The Cu_3I_3 core can be visualized as having μ_3-bridged iodine atoms above and below a trigonal plane of three copper atoms and a μ_2-bridged iodine connected to two copper atoms (Figure 4). Two (Cu1 and Cu2) of the three copper atoms have the same coordination environment consisting of a germanium and three iodine atoms. The third copper atom (Cu3) possesses two iodine and two germanium atoms. All the germanium and copper atoms are tetracoordinate and have distorted tetrahedral geometry. The Ge–Cu bond distances (Ge1–Cu1 2.292(1), Ge2–Cu3 2.341(1), Ge3–Cu2 2.291(1), and Ge4–Cu3 2.339(1) Å) are comparable to that found in compound **2**. The Ge–O and Ge–N bond distances also show a trend

Table 1. Observed and Calculated UV-Vis Absorption Maxima for Compound 6

transitions (percentage contribution)[a]	composition of the corresponding orbitals[b]	$\lambda_{max}{}^c$ (ε) (obsd)	λ_{max} (ε) (calcd)
HOMO-1 → LUMO (8)	$p^{nb}{}_{(I)} \rightarrow \pi^*{}_{(ATI)}$	438 (7400)	383.41 (0.0872)
HOMO → LUMO (89)	$p^{nb}{}_{(I)} \rightarrow \pi^*{}_{(ATI)}$		
HOMO → LUMO + 2 (93)	$p^{nb}{}_{(I)} \rightarrow \pi^*{}_{(ATI)}$	362 (12400)	363.45 (0.3102)
HOMO-1 → LUMO + 4 (5)	$p^{nb}{}_{(I)} \rightarrow [p^v{}_{(Ge)} + p^v{}_{(Au)}]$	266 (30400)	266.56 (0.0610)
HOMO-1 → LUMO + 5 (8)	$p^{nb}{}_{(I)} \rightarrow [\sigma^*{}_{(Au-I)} + \sigma^*{}_{(Au-Ge)} + p^v{}_{(Ge)} + p^v{}_{(Au)}]$		
HOMO → LUMO + 6 (73)	$p^{nb}{}_{(I)} \rightarrow [\sigma^*{}_{(Au-I)} + \sigma^*{}_{(Au-Ge)} + p^v{}_{(Ge)} + p^v{}_{(Au)} + s^v{}_{(Au)}]$		

[a]HOMO and HOMO-1 are mainly composed of the nonbonding orbital of the iodine atom. But, a minor d-orbital contribution from the gold atoms is also present. [b]nb = nonbonding, v = virtual. [c]The shoulders near the peaks at 438 and 362 nm in the experimental spectrum (Figure 1) can also be accounted theoretically. Nevertheless, for simplicity, those discussions are not included here, nm (L mol^{-1} cm^{-1}).
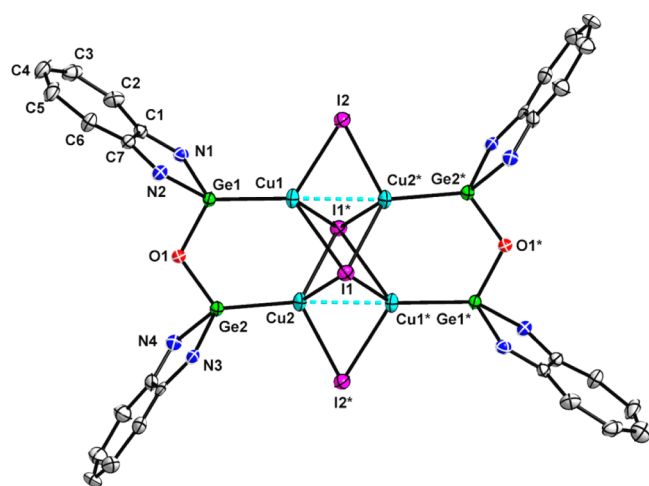
Figure 3. Molecular structure of compound 2. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms and isobutyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1−Cu1 2.3125(9), Ge2−Cu2 2.3035(9), Cu1−Cu2* 2.573(1); Ge1−O1−Ge2 117.4(2), O1−Ge1−Cu1 119.7(1), and O1−Ge2−Cu2 121.5(1). Asterisk indicates symmetry transformations used to generate equivalent atoms: (1) x + 1, −y, −z + 1.
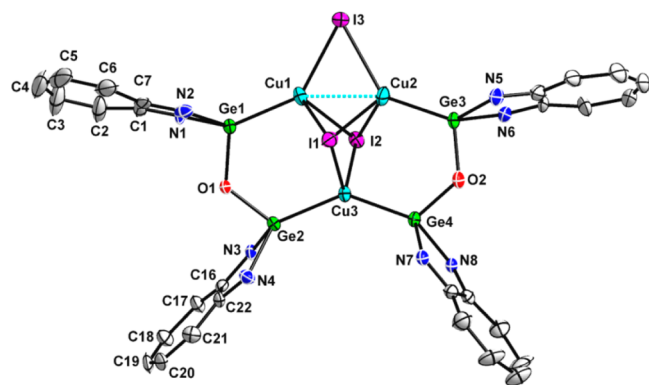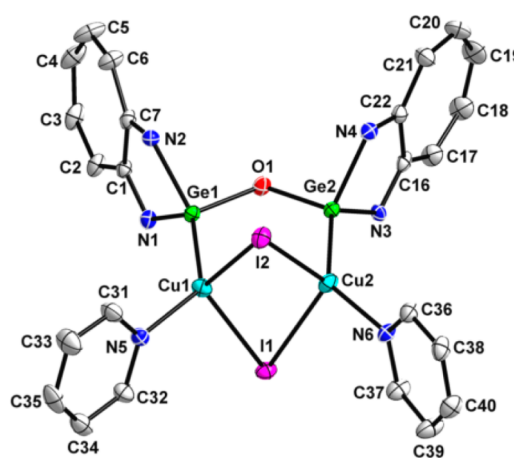

Figure 4. Molecular structure of compound 3. Thermal ellipsoids are drawn at the 40% probability. All hydrogen atoms and isobutyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1−Cu1 2.292(1), Ge2−Cu3 2.341(1), Ge3−Cu2 2.291(1), Ge4−Cu3 2.339(1), Cu2−Cu1 2.500(1); Ge1−O1−Ge2 123.6(3), Ge3−O2−Ge4 122.9(3), O1−Ge1−Cu1 116.9(1), O1−Ge2−Cu3 117.5(1), O2−Ge3−Cu2 115.6(2), O2−Ge4−Cu3 119.8(2).

similar to that seen in compound **2**. The Cu⋯Cu separation of 2.500(1) Å between Cu1 and Cu2 is significantly less than the sum of van der Waals radii of two copper atoms, and this shows

the presence of a cuprophilic interaction. Also, it is slightly shorter than those found in compound **2** (vide supra). The Cu−I bond distances (2.584(1)−2.890(2) Å) and Cu⋯Cu separation are in close agreement with those seen in diphosphine-stabilized copper iodide complexes with Cu$_3$I$_3$ cores.[14b,13,15] Both the Ge−O−Ge bond angles (123.6(3) and 122.9(3)°) are almost equal. In the monodentate germylene-stabilized copper(I) iodide complexes, the cores such as CuI, Cu$_2$I$_2$, and Cu$_4$I$_4$ have been seen and the Cu$_3$I$_3$ core was not found until now.[9a,d,f] Stable isolation of compound **3** using the stabilization offered by a bidentate digermylene oxide ligand **1** has removed that gap.

Compound **4** crystallized in the monoclinic space group P2$_1$/c (Table S1). Its molecular structure (Figure 5) clearly
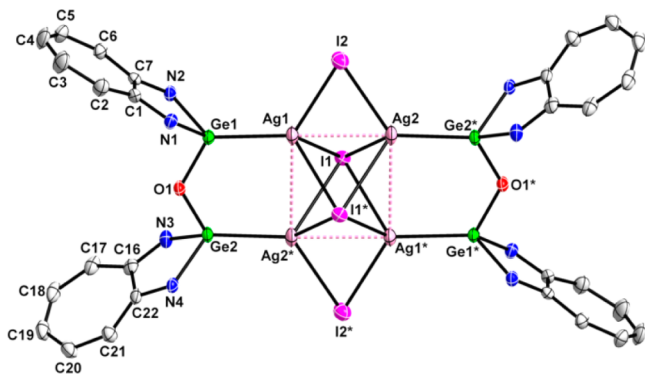

Figure 5. Molecular structure of compound 4. Thermal ellipsoids are drawn at the 40% probability. All hydrogen atoms and isobutyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1−Cu1 2.3146(9), Ge2−Cu2 2.314(1), Cu1−Cu2 2.836(1); O1−Ge1−Cu1 114.8(1), O1−Ge2−Cu2 117.5(1), Ge2−O1−Ge1 119.9(2).

reveals the presence of a butterfly-type Cu$_2$I$_2$ core stabilized through a molecule of digermylene oxide **1** and two pyridine ligands. The germanium atoms are tetracoordinate and have distorted tetrahedral geometries. Both the iodine atoms are μ_2-bridged and each one is connected to two copper atoms. The Ge−N bond lengths (Ge1−N1 1.933(4), Ge1−N2 1.931(4), Ge2−N3 1.943(4), and Ge2−N4 1.946(4) Å) are slightly shorter than that found in compound **1**.[1a] The Cu−I bond lengths (Cu1−I1 2.7336(8), Cu1−I2 2.7351(8), and Cu2−I1 2.8208(8), and Cu2−I2 2.7221(9) Å) reveal the asymmetric positioning of the μ-bridged iodine atoms between the copper

atoms. The Ge−Cu bond lengths (2.3146(9) and 2.314(1) Å) are slightly shorter than that seen in the chlorogermylene-stabilized copper(I) iodide complex [{(i-Bu)₂ATIGeCl}₂(Cu₂I₂)(C₅H₅N)₂] (**I**) (2.345(1) Å) with a planar Cu₂I₂ core.[9a] The Ge−O bond lengths (1.819(3) and 1.807(3) Å) are comparable to the same bond lengths in digermylene oxide **1** (1.807(6) and 1.775(6) Å).[2b] The Cu−I bond distances are comparable to those in the related compounds with tetracoordinate copper atoms in the Cu₂I₂ core.[16] The Cu−N$_{pyridine}$ bond lengths (Cu1−N5 2.033(4) and Cu2−N6 2.036(4) Å) match with the length of the same bonds (2.046(4) Å) in compound **I**. The distance between Cu1 and Cu2 (2.836(1) Å) is close to the sum of the van der Waals radii of two copper atoms (2.80 Å). Therefore, to confirm the presence/absence of cuprophilic interaction between them, AIM studies were performed (vide infra). The Ge−O−Ge bond angle in complex **4** is 119.9(2)°, and this value is greater and smaller than those in compounds **2** and **3**, respectively.

Compound **5** crystallized in the monoclinic space group $P2_1/n$ (Table S1). Its molecular structure is centrosymmetric (Figure 6) and shows the presence of a Ag₄I₄ core stabilized
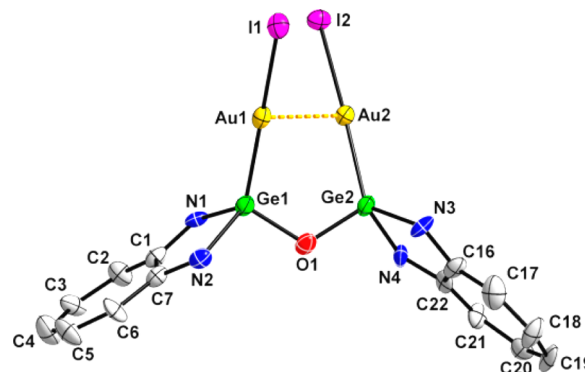

Figure 6. Molecular structure of compound **5**. Thermal ellipsoids are drawn at the 40% probability. All hydrogen atoms and isobutyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1−Ag1 2.4712(7), Ag1−Ag2 2.9221(6), Ag1−Ag2* 3.3049(7); Ge2−O1−Ge1 123.0(2), O1−Ge1−Ag1 119.7(1), O1−Ge2−Ag2* 119.4(1). Asterisk indicates symmetry transformation used to generate equivalent atoms: (1) −x, −y, −z; (2) −x + 1, −y + 1, −z.

through two digermylene oxide ligands. In the Ag₄I₄ core, there is a Ag₄I₂ octahedron with four planar silver atoms and two μ_4-bridged iodine atoms. These iodine atoms are positioned above and below the plane of silver atoms. The other two iodine atoms are μ_2-bridged and lie on the plane that contains the four silver atoms. The compound [Ag₄(μ_3-I)₂(μ_2-I)₂(μ_2-S,C$_{NHC}$)₂] (NHC = 1-(2-(ethylthio)ethyl)-3-mesityl-1H-imidazol-2(3H)-ylidene) (**II**) reported by Fliedel and Braunstein is the only example of a silver halide complex with Ag₄I₄ core where all the silver atoms are in a plane.[17] In compound **5**, all the silver and germanium atoms are tetracoordinate and possess distorted tetrahedral geometries. Interestingly, germanium atoms of the digermylene oxide ligands also lie in the plane of the four silver and two μ_2-bridged iodine atoms. In the silver(I) halide complexes with Ge−Ag but without Ag(I)−X bonds (X = a halogen atom), the Ge−Ag bond lengths range from 2.412(1) to 2.473(1) Å.[6] It is interesting to note that the lengths of the Ge−Ag bonds in compound **5** (2.4712(7) and 2.4706(7) Å) lie within this range. The Ge−O bond lengths (Ge1−O1 1.800(4) and Ge2−O1 1.799(4) Å) are comparable to the same bond

lengths in compound **1**. As in compounds **2**−**4**, the Ge−N bond lengths (1.919(4), 1.925(4), 1.943(5), and 1.918(5) Å) are slightly shorter than those of compound **1**. The Ag−I bond lengths (Ag1−I2 2.8372(6) and Ag2−I2 2.8058(6) Å) are similar to those found in compound **II**. There are four metallophilic interactions between the silver atoms with two different Ag···Ag distances (2.9221(6) and 3.3049(7) Å). These distances are less than the sum of van der Waals radii of two silver atoms (3.40 Å) and suggest the presence of ligand-supported argentophilic interactions.[18] Two Ag···Ag inter-actions between the silver atoms in the Ag−Ge−O−Ge−Ag moieties (2.9221(6) Å) are stronger than the other two Ag···Ag interactions (3.3049(7) Å). The Ge−O−Ge bond angle (123.0(2)°) is greater than those found in compounds **2** and **4**. This may be due to the larger size of the silver atom than the copper atom.

Compound **6** crystallized in the orthorhombic space group *Pbca* (Table S1). The molecular structure of compound **6** (Figure 7) reveals the presence of a digermylene oxide ligand

Figure 7. Molecular structure of compound **6**. Thermal ellipsoid are drawn at the 40% probability. All hydrogen atoms and isobutyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Au1−Ge1 2.347(2), Au2−Ge2 2.345(2), Au1−Au2 3.1562(8); Ge1−O1−Ge2 117.5(6), O1−Ge1−Au1 113.8(4), O1−Ge2−Au2 112.6(3).

stabilized Au₂I₂ core. Both the germanium atoms are tetracoordinate and possess distorted tetrahedral geometries composed by an oxygen, a gold, and two nitrogen atoms. The gold atoms are dicoordinate, and each is connected to a germanium and an iodine atom. The preference of Au(I) for dicoordination limits the structural diversity in gold(I) complexes in comparison to the copper(I) and silver(I) complexes. The Ge−Au bond lengths (2.347(2) and 2.345(2) Å) are in good agreement with those reported for complexes [L¹Ge(CCPh)AuC₆F₅] (2.3683(6) and 2.3641(7) Å), [L¹Ge-(CCPh)(CuC₆F₅)(AuC₆F₅)] (2.3625(4) Å), and [L²GeCl-(AuI)] (2.346(2) Å) (L¹ = HC[C(Me)N-2,6-i-Pr₂C₆H₃]₂; L² = N(SiMe₃)C(Ph)C(SiMe₃)C₅H₄N₂).[7b,9f,19] The Au−I bond lengths (Au1−I1 2.577(1), Au2−I2 2.582(1) Å) are comparable to the Au−I bonds in phosphorus donor-stabilized Au₂I₂ complexes such as [{(o-MeOC₆H₄O)P(1-Nt-Bu)}₂(Au₂I₂)] (2.542(1) and 2.562(2) Å) and [(dppm)(Au₂I₂)] (2.5604(4) Å) (dppm = diphenylphosphinome-thane).[20] The Au···Au distance between the two gold atoms (3.1562(8) Å) is less than the sum of their van der Waals radii (3.3 Å) and indicates the presence of an aurophilic interaction.[21] This interaction between the two gold atoms can be classified as a semisupported aurophilic interaction.[22]

The Ge−Au−I bond angles (172.87(5) and 174.68(6)°) suggest that this moiety is almost linear. The Ge−O−Ge bond angle (117.5(6)°) is comparable with the same bond angle in compound **2** but smaller than those in compounds **3**−**5**. Like in compound **2**, in all other compounds **3**−**6**, the Ge−O−Ge bond angles are considerably smaller than that in compound **1**.

AIM calculations were performed on compounds **2**−**4** and **6** to substantiate the results on metallophilic interactions obtained from structural studies (vide supra). In compounds **2**, **3**, and **6** it confirms the presence of metallophilic interactions. Although structural studies are not conclusive of the metallophilic interaction in compound **4** (vide supra), AIM studies suggest its presence (Table 2). The signs of the

Table 2. Values of Charge Density ($\rho(r_c)$), Laplacian of Charge Density ($\nabla^2\rho(r_c)$), Potential Energy Density ($V(r_c)$), Kinetic Energy Density ($G(r_c)$), and Total Energy Density ($H(r_c)$) at M−M (M = Cu, Au) Bond Critical Points (r_c) in Compounds 2−4 and 6

variables (a.u.)	compound 2	compound 3	compound 4	compound 6
$\rho(r_c)$	0.0233	0.0264	0.0176	0.0164
$\nabla^2\rho(r_c)$	0.0755	0.0935	0.0420	0.0594
$V(r_c)$	−0.0228	−0.0288	−0.0128	−0.0134
$G(r_c)$	0.0208	0.0261	0.0117	0.0141
$H(r_c)$	−0.0020	−0.0027	−0.0011	0.0007

Laplacian of charge density ($\nabla^2\rho(r_c)$) and total energy density ($H(r_c)$) (see Table 2) suggest that these interactions are polar covalent in compounds **2**−**4**, whereas they are noncovalent in compound **6**.

■ CONCLUSION

In conclusion, we have successfully demonstrated the utility of a well-defined digermylene oxide **1** as a ligand through the synthesis of its group 11 metal(I) iodide complexes **2**−**6**. Interestingly, compound **1** forms complexes with all the group 11 metal(I) iodides. On the basis of structural and AIM studies, the presence of metallophilic interactions in compounds **2**−**6** has been shown. Photophysical studies reveal the reduction in the emission intensity upon the coordination of AuI with digermylene oxide **1**.

■ EXPERIMENTAL SECTION

Manipulations that involve air- and moisture-sensitive compounds were performed under a dry N_2 atmosphere using either standard Schlenk or glovebox [Jacomex (GP Concept)-T2 workstation] techniques. Chemicals were purchased from Sigma-Aldrich (CuI, AgI, and AuI) and Spectrochem Chemicals Pvt. Ltd. (pyridine, tetrahydrofuran, and toluene). Pyridine and tetrahydrofuran were dried over KOH and Na/benzophenone, respectively, and were distilled just before use. Compound **1** was synthesized according to the literature procedure.[1a] Melting points of compounds **2**−**6** 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 PerkinElmer CHN analyzer. Multinuclear NMR spectroscopic studies were carried out on a 300 MHz Bruker Topspin NMR spectrometer using anhydrous $CDCl_3$, CD_2Cl_2, and $(CD_3)_2SO$. The chemical shifts δ are reported in ppm and are referenced internally with respect to the residual solvent (^1H NMR) and solvent (^{13}C NMR) resonances.[23] Absorption and emission spectra were recorded on Perkin−Elmer UV−Vis−NIR Lambda 1050 spectrophotometer, SHIMADZU-UV-

2450 UV/vis spectrophotometer, and Perkin−Elmer LS-55 spectrophotometer, respectively.

Synthesis of [{({i-Bu})$_2$ATlGe}$_2$O)$_2$(Cu$_4$I$_4$)] (2). To a solution of compound **1** (0.40 g, 0.64 mmol) in tetrahydrofuran (60 mL), CuI (0.24 g, 1.28 mmol) was added, and the resultant mixture was stirred for 12 h. All the volatiles were removed under reduced pressure to yield an orange solid, which was washed with hexane (10 mL) and dried under reduced pressure to produce an analytically pure sample of compound **2** as an orange powder. Crystals of compound **2** suitable for single-crystal X-ray diffraction studies were grown by the slow evaporation of the solvents at room temperature from its solution in a mixture of dichloromethane and dimethylformamide. Yield: 0.59 g, 92%. Mp: > 230 °C. Anal. Calcd for $C_{60}H_{92}Cu_4Ge_4I_4N_8O_2$ (M = 2009.79): C, 35.86; H, 4.61; N, 5.58. Found: C, 35.84; H, 4.63; N, 5.57. ^1H NMR (300 MHz, CDCl$_3$): δ 1.08 (d, $^3J_{HH}$ = 6.6 Hz, 24H, CH(CH$_3$)$_2$), 1.15 (d, $^3J_{HH}$ = 6.6 Hz, 24H, CH(CH$_3$)$_2$) 2.50−2.54 (m, 8H, CH(CH$_3$)$_2$), 3.61 (d, $^3J_{HH}$ = 7.2 Hz, 16H, CH$_2$), 6.54 (t, $^3J_{HH}$ = 9.3 Hz, 4H, CH), 6.74 (d, $^3J_{HH}$ = 11.4 Hz, 8H, CH), 7.13 (t, $^3J_{HH}$ = 10.5 Hz, 8H, CH). $^{13}C\{^1H\}$ NMR (75 MHz, CDCl$_3$): δ 21.47 (CH(CH$_3$)$_2$), 21.89 (CH(CH$_3$)$_2$), 28.56 (CH(CH$_3$)$_2$), 53.91 (CH$_2$), 115.00, 121.78, 136.61, 159.79 (Ar).

Synthesis of [{({i-Bu})$_2$ATlGe}$_2$O)$_2$(Cu$_3$I$_3$)] (3). To a solution of compound **1** (0.90 g, 1.44 mmol) in tetrahydrofuran (80 mL), CuI (0.41 g, 2.16 mmol) was added in small portions for 30 min, and the resultant mixture was stirred for 12 h. All the volatiles were then removed under reduced pressure to yield an orange solid. It was washed with hexane (10 mL) and dried under reduced pressure to result in an analytically pure sample of compound **3** as an orange powder. Crystals of compound **3** suitable for single-crystal X-ray diffraction studies were grown by very slow cooling of its hot solution prepared in dimethylformamide and toluene. Yield: 1.25 g, 95%. Mp: 178 °C. Anal. Calcd for $C_{60}H_{92}Cu_3Ge_4I_3N_8O_2$ (M = 1819.34): C, 39.61; H, 5.10; N, 6.16. Found: C, 39.58; H, 5.08; N, 6.19. ^1H NMR (300 MHz, CDCl$_3$): δ 1.04−1.11 (m, 48H, CH(CH$_3$)$_2$), 2.35−2.43 (m, 8H, CH(CH$_3$)$_2$), 3.60−3.68 (m, 16H, CH$_2$), 6.53−7.53 (m, 20H, CH). ^1H NMR (300 MHz, (CD$_3$)$_2$SO): δ 0.94−1.12 (m, 48H, CH(CH$_3$)$_2$), 2.30−2.47 (m, 8H, CH(CH$_3$)$_2$), 3.55−4.02 (m, 16H, CH$_2$), 6.74−6.80 (m, 4H, CH), 7.03−7.12 (m, 6H, CH), 7.34−7.41 (m, 6H, CH), 7.66−7.82 (m, 4H, CH). $^{13}C\{^1H\}$ NMR (75 MHz, (CD$_3$)$_2$SO): δ 20.04, 20.28, 20.35, 20.65 (CH(CH$_3$)$_2$), 26.68, 29.25 (CH(CH$_3$)$_2$), 52.05, 52.25, 52.55 (CH$_2$), 114.93, 118.55, 122.33, 136.86, 138.78, 154.14, 158.93 (Ar).

Synthesis of [{({i-Bu})$_2$ATlGe}$_2$O(Cu$_2$I$_2$)(C$_5$H$_5$N)$_2$] (4). To a solution of compound **1** (0.50 g, 0.80 mmol) in tetrahydrofuran (50 mL), CuI (0.30 g, 1.60 mmol) was added, and the resultant mixture was stirred for 30 min. Then pyridine (0.14 g, 1.76 mmol) was added, and this mixture was stirred at room temperature for 12 h. All the volatiles were then removed under reduced pressure to yield an orange solid. It was washed with hexane (5 mL) and dried under reduced pressure to result in an analytically pure sample of compound **4** as an orange powder. Crystals of compound **4** suitable for single-crystal X-ray diffraction studies were grown from its pyridine solution by the slow evaporation of the solvent at room temperature. Yield: 0.89 g, 96%. Mp: 185 °C. Anal. Calcd for $C_{40}H_{56}Cu_2Ge_2I_2N_6O$ (M = 1163.09): C, 41.31; H, 4.85; N, 7.23. Found: C, 41.27; H, 4.82; N, 7.19. ^1H NMR (300 MHz, CDCl$_3$): δ 1.03−1.05 (m, 24H, CH(CH$_3$)$_2$), 2.48 (bs, 4H, CH(CH$_3$)$_2$), 3.60−3.66 (m, 8H, CH$_2$), 6.45 (t, $^3J_{HH}$ = 8.1 Hz, 2H, CH), 6.65 (d, $^3J_{HH}$ = 10.8 Hz, 4H, CH), 7.06 (t, $^3J_{HH}$ = 9.6 Hz, 4H, CH), 7.27 (bs, 4H, Py), 7.65 (bs, 2H, Py), 8.84 (bs, 4H, Py). $^{13}C\{^1H\}$ NMR (75 MHz, CDCl$_3$): δ 21.11 (CH(CH$_3$)$_2$), 21.35 (CH(CH$_3$)$_2$), 28.17 (CH(CH$_3$)$_2$), 53.52 (CH$_2$), 114.58, 121.07, 123.89, 136.24, 136.34, 150.69, 159.75 (Ar).

Synthesis of [{({i-Bu})$_2$ATlGe}$_2$O)$_2$(Ag$_4$I$_4$)] (5). To a solution of compound **1** (0.40 g, 0.64 mmol) in pyridine (20 mL), AgI (0.30 g, 1.28 mmol) was added, and the resultant mixture was stirred at room temperature for 12 h. All the volatiles were then removed under reduced pressure to yield an orange solid. It was dissolved in dichloromethane (50 mL) and filtered through a G-4 frit. The solvent was then removed from the filtrate under reduced pressure to afford an orange solid. This solid was washed with toluene (5 mL) and dried

under reduced pressure to result in an analytically pure sample of compound **5** as an orange powder. Crystals of compound **5** suitable for single-crystal X-ray diffraction studies were grown from its pyridine solution by the slow evaporation of the solvent at room temperature. Yield: 0.65 g, 93%. Mp: 195 °C. Anal. Calcd for $C_{60}H_{92}Ag_4Ge_4I_4N_8O_2$ (M = 2187.08): C, 32.95; H, 4.24; N, 5.12. Found: C, 32.91; H, 4.19; N, 5.10. ^1H NMR (300 MHz, CD_2Cl_2): δ 1.08 (d, $^3J_{HH}$ = 6.0 Hz, 24H, $CH(CH_3)_2$), 1.11 (d, $^3J_{HH}$ = 6.0 Hz, 24H, $CH(CH_3)_2$), 2.33–2.44 (m, 8H, CH), 3.58 (d, 16H, $^3J_{HH}$ = 9.0 Hz, CH_2), 6.66 (t, $^3J_{HH}$ = 9.0 Hz, 4H, CH), 6.81 (d, $^3J_{HH}$ = 12.0 Hz, 8H, CH), 7.23 (t, $^3J_{HH}$ = 9.0 Hz, 8H, CH). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 20.68 ($CH(CH_3)_2$), 21.51 ($CH(CH_3)_2$), 28.03 ($CH(CH_3)_2$), 53.56 (CH_2), 115.37, 122.61, 136.91, 159.39 (Ar).

Synthesis of [{(i-Bu)$_2$ATIGe}$_2$O(Au$_2$I$_2$)] (6). To a solution of compound **1** (0.20 g, 0.32 mmol) in pyridine (20 mL), AuI (0.21 g, 0.64 mmol) was added, and the resultant mixture was stirred at room temperature for 5 min. All the volatiles were then removed under reduced pressure to yield a yellow solid. It was dissolved in dichloromethane (30 mL) and filtered through a G-4 frit. The solvent from the filtrate was removed under reduced pressure to afford a yellow solid. This solid was washed with toluene (5 mL) and dried under reduced pressure to result in an analytically pure sample of compound **6** as an orange powder. Crystals of compound **6** suitable for single-crystal X-ray diffraction studies were grown from its pyridine solution by the slow evaporation of the solvent at room temperature. Yield: 0.37 g, 91%. Mp: 169 °C. Anal. Calcd for $C_{30}H_{46}Au_2Ge_2I_2N_4O$ (M = 1271.73): C, 28.33; H, 3.65; N, 4.41. Found: C, 28.31; H, 3.63; N, 4.39. UV/vis (tetrahydrofuran) λ_{max} (ε) = 266 (30 400 M^{-1} cm^{-1}, br), 362 nm (12 400 M^{-1} cm^{-1}, br), 438 nm (7 400 M^{-1} cm^{-1}, br). ^1H NMR (300 MHz, $CDCl_3$): δ 1.02–1.10 (m, 24H, $CH(CH_3)_2$), 2.28–2.40 (m, 4H, $CH(CH_3)_2$), 3.53–3.87 (m, 8H, CH_2), 6.82–7.03 (m, 6H, CH), 7.36–7.49 (m, 4H, CH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 20.93 ($CH(CH_3)_2$), 27.80 ($CH(CH_3)_2$), 27.94 ($CH(CH_3)_2$), 53.16, 53.77 (CH_2), 117.05, 117.36, 125.01, 125.87, 137.92, 138.43, 158.53, 158.90 (Ar).

Conversion of Compound 2 to Compound 4. To a solution of compound **2** (0.20 g, 0.01 mmol) in tetrahydrofuran, excess pyridine was added at room temperature and stirred for 1 h. Then, the volatiles were remove from the reaction mixture to obtain an analytically pure sample of compound **4** as an orange solid. Yield: 0.23 g, 98%.

X-ray Data Collection for Compounds 2−6. Single crystals of compounds **2−6** suitable for X-ray diffraction studies were coated with a cryoprotectant and mounted on a glass fiber. Data were collected at 150 K using a Bruker SMART APEX CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å).[24] Data integration was performed using the SAINT program. Empirical absorption correction was applied using SADABS.[25] The structures were solved by direct methods and refined by full matrix least-squares on F^2 using SHELXTL software.[26] All the non-hydrogen atoms were refined anisotropically, and positions of hydrogen atoms were fixed according to a riding model. The important crystallographic data of these compounds are summarized in Table S1 (see Supporting Information). In compound **3**, the highly disordered solvent molecules were removed by the Platon/Squeeze program.[27]

Computational Details. DFT calculations were carried out at the B3LYP level of theory using the Gaussian-09 program.[28] The geometry optimization for compound **6** was carried out using 3-21G (C and H), 6-31G* (N and O), and LANL2DZ (Ge, Au, and I) basis sets. The frequency calculation was carried out at the same level of theory to characterize the stationary point as global minima. The time-dependent density functional theory polarizable continuum (TDDFT-PCM) calculations were performed for compound **6** at its optimized geometry to obtain the UV−vis spectrum using tetrahydrofuran as solvent and the aforementioned level of theory and basis sets. AIM calculations were performed on compounds **2−4** and **6** using AIM2000 software.[29] The wave functions required for the AIM calculations on compounds **2−4** and **6** were generated at the B3LYP level of theory using the following basis sets: 3-21G* (C and H), 6-311+G* (N and O), and WTBS (Ge, Cu, Au, and I). The input

coordinates were directly taken from the single-crystal X-ray diffraction studies (to take care of the dispersion interactions).

■ ASSOCIATED CONTENT

ⓈSupporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b01436.

> Crystal data and structure refinement parameters for compounds **2−6**, selected bond lengths and bond angles for compounds **2−6**, molecular graphs of compounds **2−4** and **6** with bond critical points, and coordinates for the optimized geometry of compound **6** (PDF)
> Crystallographic information file for compounds **2−6** (CIF)

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Prof. Takeaki Iwamoto.

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