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Reactivity of Pyridyl-1-azaallyl Germanium(II) Chloride: Synthesis of Novel Lithium Germinate $[\{(PhC{\equiv}C)_3Ge\}_3GeLi(Et_2O)_3]$ and Ge(II)−M(I) (M = Cu and Au) Adducts

Wing-Por Leung,* Cheuk-Wai So, Kim-Hung Chong, Kwok-Wai Kan, Hoi-Shan Chan, and Thomas C. W. Mak

Department of Chemistry, The Chinese University of Hong Kong,
Shatin, New Territories, Hong Kong, China

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The reaction of $[Ge\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}Cl]$ (**1**) with $LiBu^t$ or $LiC{\equiv}CPh$ in Et_2O afforded substituted products $[Ge(R)\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}]$ [R = Bu^t (**2**) or $C{\equiv}CPh$ (**3**)], respectively. However, the one-pot reaction of **1** with $PhC{\equiv}CH$ and Bu^nLi in Et_2O afforded lithium germinate $[\{(PhC{\equiv}C)_3Ge\}_3GeLi(Et_2O)_3]$ (**4**). Compound **1** can also undergo ligand transfer reaction with $LiAlH_4$ to give $[AlH\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}_2]$ (**5**). Treatment of **1** with excess $NaBH_4$ in THF afforded germanium(II) hydride-borane adduct $[Ge(BH_3)\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}H]$ (**6**). The reaction of **1** with MI (M = Cu and Au) gave the first examples of Ge(II)−M(I) adducts $[Ge(CuI)\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}Cl]_4$ (**7**) and $[Ge(AuI)\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}Cl]$ (**8**). Compounds **2**−**8** have been characterized by X-ray analysis.

Introduction

The chemistry of low-valent germanium complexes has attracted much attention in the past decades.[1] It has been realized that this carbene analogue can be stabilized kinetically by using bulky ligands and/or thermodynamically by using electron-donating substituents at the germanium(II) center. Recently, heteroleptic germanium chloride [RGeCl] complexes have been synthesized by metathesis reaction. For example, $[\{HC(CMeNAr)_2\}GeX]$ (Ar = 2,6-$Pr^i_2C_6H_3$, X = H, Me, Bu^n, OH; Ar = Ph, X = I, Me, OMe, OTf),[2] [MamxGeX] [Mamx = methylamino-methyl-*m*-xylyl; X = Me, Bu^n, Bu^t, $C{\equiv}CPh$, OBu^t, N_3, $N(SiMe_3)_2$],[3] $[\{Pr^i_2ATI\}GeX]$ (ATI = aminotroponiminate; X = N_3, OSO_2CF_3),[4] and $[(Bu^t)_3Ge{-}Ge\{C_6H_3\text{-}2,6\text{-}Mes\}]$ (Mes = 2,4,6-trimethylphenyl)[5] have been reported. Recently, the reactivities of heteroleptic germanium(II) chloride toward chalcogen and transition metal complexes have also been investigated.[6] We have reported the synthesis of $[Ge\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}Cl]$ and its reaction with chalcogens.[7] Herein, we report the substitution and ligand transfer reaction of $[Ge\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}Cl]$ and its reaction with group 11 metal iodides.

Results and Discussion

Substitution and Ligand Transfer Reaction. The reaction of **1** with $LiBu^t$ or $LiC{\equiv}CPh$ in Et_2O afforded the substituted products $[Ge(R)\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}]$ [R = Bu^t (**2**) or $C{\equiv}CPh$ (**3**)], respectively (Scheme 1). The products as confirmed by X-ray structure analysis showed that compounds **2** and **3** are heteroleptic germanium(II) complexes with the germanium bonded to a pyridyl-enamido ligand in *N,N′*-chelate fashion and a Bu^t group or ethynyl substituent, respectively.

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* To whom correspondence should be addressed. E-mail: kevinleung@cuhk.edu.hk.

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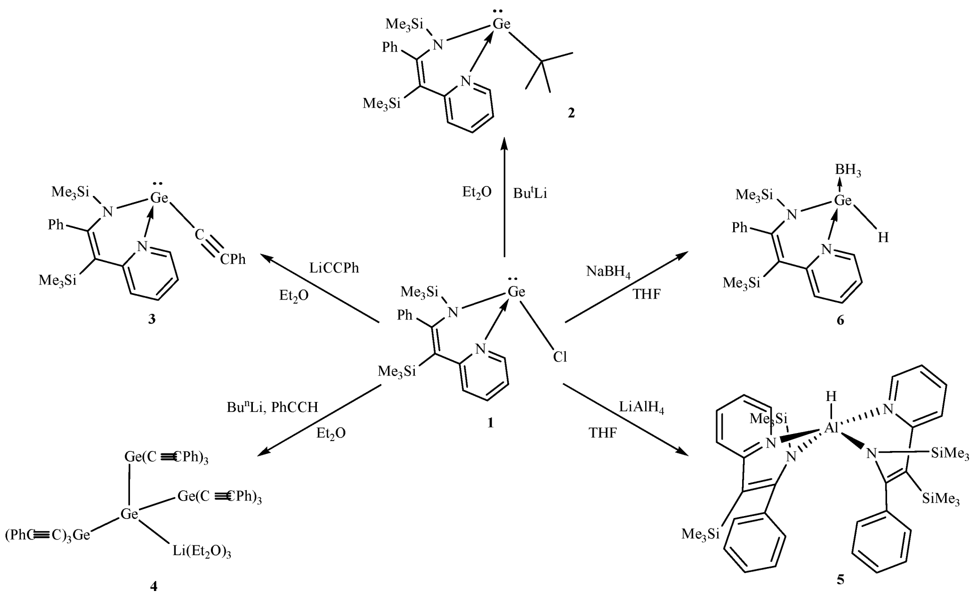
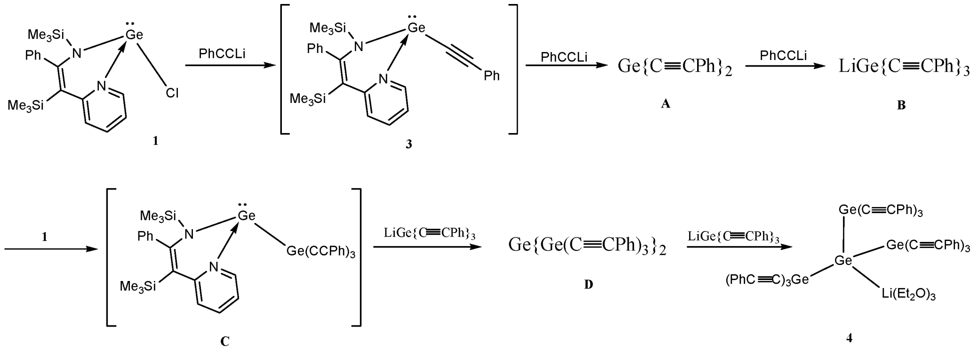
10.1021/om060032g CCC: \$33.50

Scheme 1



Scheme 2

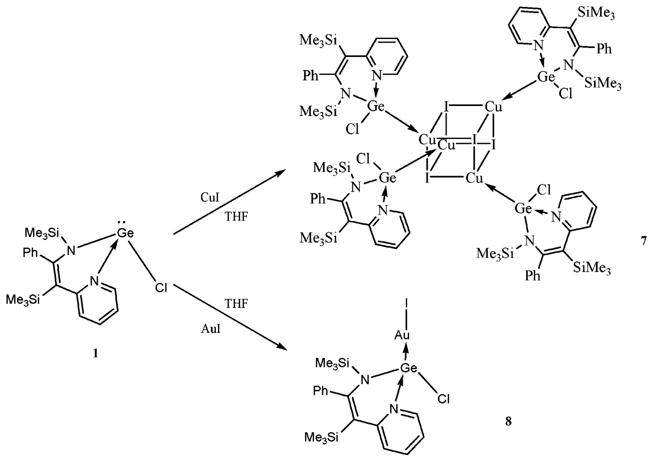


However, one-pot reaction of **1** with PhC≡CH and Bu^{n}Li in Et$_2$O gave [{(PhC≡C)$_3$Ge}$_3$GeLi(Et$_2$O)$_3$] (**4**) instead of **3**. The mechanism for the formation of **4** is proposed in Scheme 2. It is suggested that the intermediate **3** formed underwent a ligand transfer reaction to give **A**. Subsequent addition reaction of **A** with LiC≡CPh formed [LiGe{C≡CPh}$_3$] (**B**) as the intermediate. The lithium germinate **B** then reacted as transfer reagent with **1** to form **C**. Intermediate **C** underwent substitution and addition reaction to afford **4**. Similarly, germyllithium [(Me$_3$Si)$_3$GeLi(THF)$_3$] has been prepared by Stalke and co-workers.[8]

Treatment of **1** with LiAlH$_4$ in THF afforded [AlH{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}$_2$] (**5**), as confirmed by X-ray analysis. The result showed that **1** underwent a ligand transfer reaction with LiAlH$_4$. A similar result has been found in the reaction of [{HC(CMeNAr)$_2$}GeCl] with LiAlH$_4$ to form [{HC(CMeNAr)$_2$}AlH$_2$].[2b] In contrast, the reaction of **1** with excess NaBH$_4$ in THF afforded germanium(II) hydride-borane adduct [Ge(BH$_3$){N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}H] (**6**). Germylene acting as a Lewis base toward borane has been demonstrated in [{Me$_2$ATI}GePh→BPh$_3$] (ATI = aminotroponiminate)[4a] and [Ge{C$_6$H$_3$(NMe$_2$)$_2$-2,6}$_2$BH$_3$].[9]

Reaction with Group 11 Metal Iodides. The reaction of **1** with MI (M = Cu and Au) afforded [Ge(CuI){N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}Cl]$_4$ (**7**) and [Ge(AuI){N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}Cl] (**8**), respectively (Scheme 3). This result demonstrated the Lewis base behavior of **1**. To our knowledge, compounds **7** and **8** are the first examples of a germanium(II)−copper(I) or −gold(I) adduct, although the Lewis base type behavior of germylene toward transition metal complexes has been investigated extensively.[10] Recently, an example of a germanium(II)−silver(I) adduct, [{Me$_2$ATI}GeCl→Ag{(Pz-3,5-(CF$_3$)$_2$)$_3$BH}],[11] has been reported.

Scheme 3



Spectroscopic Properties. Compound **2** is a red crystalline solid, soluble in hydrocarbon solvents. Compounds **3**−**8** are yellow crystalline solids, soluble in THF and sparingly soluble

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in Et_2O and toluene. Compounds **2**−**8** are stable at room temperature under inert atomosphere, but compound **8** is light-sensitive in solution. These compounds have been characterized by NMR spectroscopy and elemental analysis. Compound **6** has also been characterized by IR spectroscopy.

The ^1H NMR spectrum of **2** displayed one set of signals assignable to the pyridyl-1-azaallyl ligand and Bu^t group, respectively. The signals showed an upfield shift when compared with **1**. This is probably due to the electronic effect of the substituents at the germanium.

In the ^{13}C NMR spectrum of **3**, the signals for the acetylenic carbon atoms were observed at δ 112.1 and 115.8 ppm. These signals are comparable to that of δ 109.6 and 111.2 ppm in (Mamx)GeC$\equiv$CPh.[3]

The ^1H spectrum of **4** displayed one set of signals due to the phenyl group and coordinated Et_2O. In the ^{13}C NMR spectrum, the signals for the acetylenic carbon atoms were observed at δ 95.87 and 104.46 ppm, which showed a downfield shift compared to free phenylacetylene (δ 78.6 and 84.6 ppm).[12]

The ^1H NMR of **5** displayed three singlet signals and one broad signal assigned to the two $SiMe_3$ groups. It also showed one set of signals due to the pyridyl and phenyl ring in the normal range, consistent with the solid-state structure. The Al-*H* chemical shift of δ 5.54 ppm in **5** is comparable to that of δ 5.61 ppm in $[\{2,4,6\text{-}Pr^i_3C_6H_2\}_2AlH]_2$[13] and δ 4.72 ppm in $[\{N(SiMe_3)C(Ph)C(SiMe_3)_2\}AlH(\mu\text{-}H)]_2$.[14]

In the ^1H NMR spectrum of **6**, the Ge-*H* chemical shift of δ 6.07 ppm (broad singlet) at 298 K is similar to that of δ 6.70 ppm in $[\{HC(CMeNAr)_2\}GeH(BH_3)]$. However, a broad unresolved doublet of Ge-*H* at 5.95 and 5.96 ppm is observed at 223 K. A broad signal displayed at δ 0.3−1.5 ppm was assigned to the protons of BH_3. The $^{11}B\{^1H\}$ NMR signal of δ −38.88 ppm for **6** is similar to that of $[\{HC(CMeNAr)_2\}GeH(BH_3)]$ (−42 ppm)[2b] and $[Ge\{C_6H_3(NMe_2)_2\text{-}2,6\}_2BH_3]$ (−35 ppm).[9] The ^1H and ^{13}C NMR spectra of **7** and **8** are normal. The IR absorptions at 1897 and 2149 cm^{-1} are indicative of the existence of GeH and BH, respectively.

X-ray Structure. Compound **4** was crystallized as an ether solvate in a stoichiometric ratio of 2:1. Compound **7** cocrystallized with eight independent THF molecules. The molecular structures with the atom-numbering schemes for compounds **2**−**8** are shown in Figures 1−7, respectively. Selected bond distances (Å) and angles (deg) of **2**−**7** are listed in Tables 3−9, respectively.

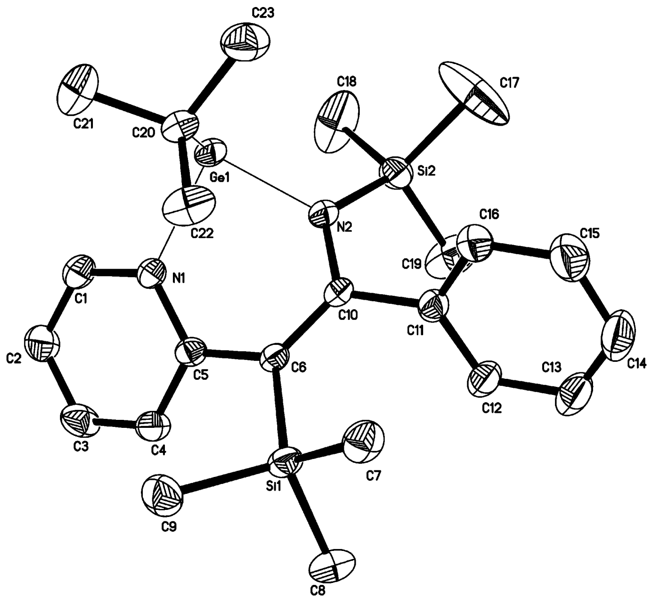

Figure 1. Molecular structure of **2** (ellipsoids are drawn at the 30% probability level).

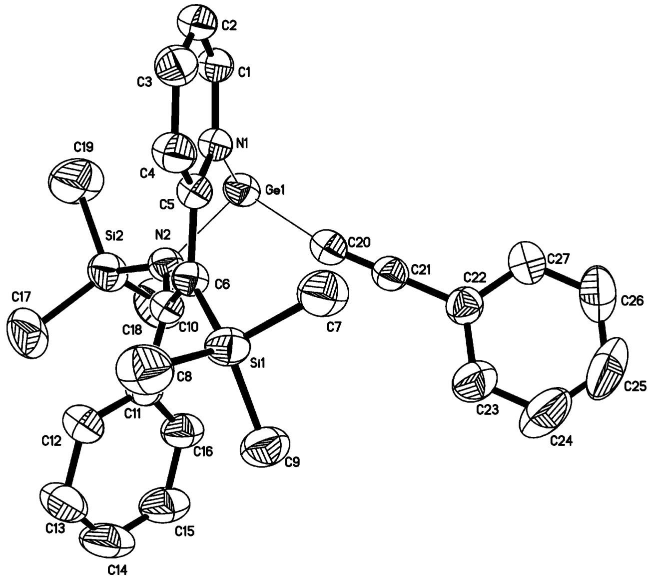

Figure 2. Molecular structure of **3** (ellipsoids are drawn at the 30% probability level).

Compound **2** is a monomeric heteroleptic germylene. The pyridyl-1-azaallyl ligand is bonded in a *N,N′*-chelate fashion to the germanium(II) center. The pyridyl-enamido character of the pyridyl-1-azaallyl ligand was shown by short $M-N_{amide}$, long $N_{amide}-C$, and short C=C bonds as compared with the η^3-1-azaallyl ligand (long M−N, short C−N, and long C=C bonds).[15] The Ge−N(2) bond distance of 1.954(3) Å in **2** is comparable to that in $[Ge\{N(SiMe_3)_2\}_2]$ (2.096(1), 2.088(6) Å)[1b] and $[Ge\{NCMe_2(CH_2)_3CMe_2\}_2]$ (1.90(1), 1.87(1) Å)[11]. The Ge−N distances of 1.954(3) and 2.059(3) Å in **2** are slightly longer than that of 1.920(2) and 2.021(2) Å in **1**. This shows the influence of the substituents at the germanium center (the electron-withdrawing Cl substituent vs the alkyl group). The Ge−C(20) distance of 2.010(3) Å is similar to that of 2.002(4) Å in $[\{CH(CMeNAr)_2\}Ge\text{-}Me]$ and 2.014(3) Å in $[\{CH(CMeNAr)_2\}Ge-(Bu^n)]$.[2a]

The structural features of **3** are similar to those found in **2**. The Ge(1)−C(20) and C(21)−C(22) bond distances of 2.004-

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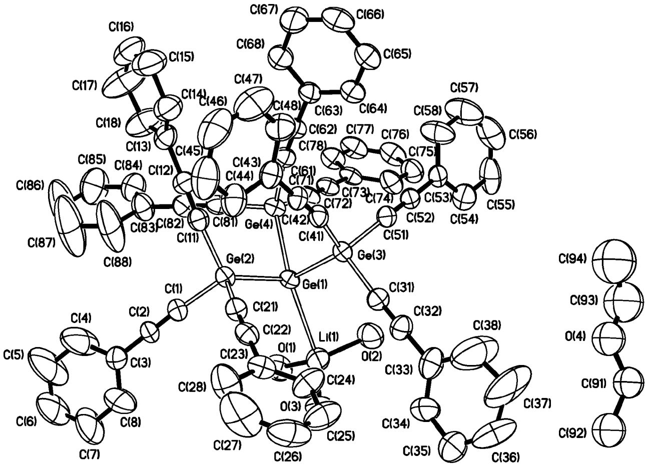

Figure 3. Molecular structure of **4** (ellipsoids are drawn at the 25% probability level).

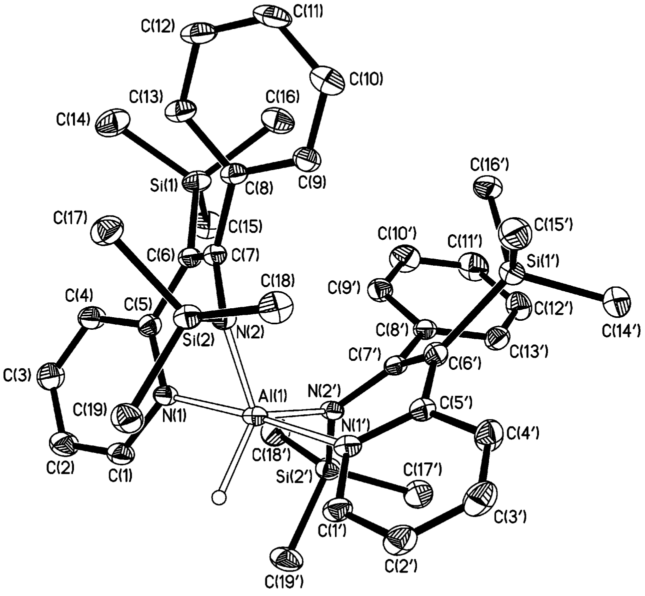

Figure 4. Molecular structure of **5** (ellipsoids are drawn at the 30% probability level).

(4) and 1.213(5) Å are comparable to those in (Mamx)GeC≡CPh [Ge−C$_{ethynl}$ 2.001(4) Å, C≡C 1.209(6) Å].[3]

Compound **4** is a monomeric base-stabilized lithium germinate complex that exhibits two different germanium environments. Ge(2), Ge(3), and Ge(4) are bonded to three phenylacetylenic groups and Ge(1). The four-coordinate Ge(1) is bonded to three germyl atoms and Li(1). Each germanium center displays a distorted tetrahedral geometry. No interaction between C≡C and Li was found. The Ge(1)−Li(1) distance of 3.066(15) Å is the longest among those of the characterized lithiumgermyl compounds such as [(THF)$_2$LiGe{C$_6$H$_4$-2-NMe$_2$}$_3$] and [(THF)LiGe(SiMe$_3$)$_3$] (2.598(9)−2.759(24) Å).[16] This suggests the ionic character of the Ge−Li bond in **4** is more pronounced than the other similar compounds. The angle sum at Ge(II) is 280.6°. This shows that the Ge(1) atom is almost nonhybridized. The lone pair occupies an orbital with high s character, and the σ-bonds to the germyl substituents are formed by using p orbitals at the Ge(1) center. This is consistent with the MO ab initio calculation of [(THF)$_2$LiGe{C$_6$H$_4$-2-NMe$_2$}$_3$].[16a] The average Ge−Ge bond distance is 2.464 Å, which is comparable to those compounds containing Ge−Ge single bond (2.41−2.48 Å).[17] The average Ge−C$_{ethynyl}$ distance of 1.925 Å is similar to that in [(Mamx)GeC≡CPh] (2.001(4) Å) and [(Mamx)GeC≡CH] (1.989(6) Å).[3] The average C≡C distance of 1.167 Å is slightly shorter than the C−C bond length of 1.204 Å in free acetylene.[18]

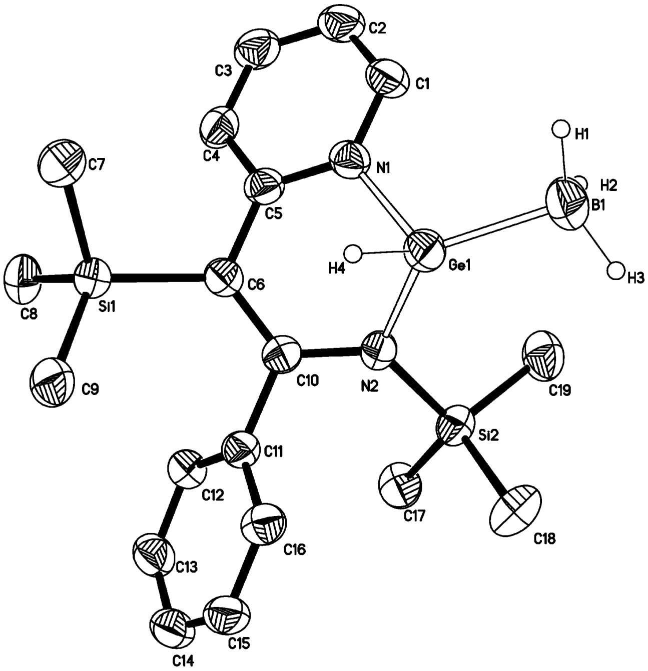

Figure 5. Molecular structure of **6** (ellipsoids are drawn at the 30% probability level).

Compound **5** is a monomeric bis(pyridyl-1-enamido)alane. The pyridyl-1-azaallyl ligand is bonded in an *N*,*N*′-chelate fashion to the aluminum center and displays a trigonal bipyramidal geometry. The Al(1)−H(1) distance of 1.560(3) Å in **5** is similar to that of 1.509 Å in [Al{N(SiMe$_3$)C(Ph)C(SiMe$_3$)$_2$}-(μ-H)H]$_2$[14] and 1.501(12) Å in [(Me$_3$N)HAl{N(H)Dipp}$_2$].[19]

The Ge(1)−B(1) bond distance of 2.064(6) Å in **6** is comparable to that of 2.041(11) Å in [Ge{C$_6$H$_3$(NMe$_2$)$_2$-2,6}$_2$-BH$_3$],[9] but slightly longer than that of 2.015(7) Å in [{HC-(CMeNAr)$_2$}GeH(BH$_3$)][2b].

Compound **7** is a complex with pyridyl-1-azaallyl germanium(II) chloride coordinated to the copper atoms of a distorted Cu$_4$I$_4$ cubane framework. This type of structure can also be found in a CuI complex with a two-electron ligand such as Cu$_4$(μ^3-I)$_4$L (L = NMe$_3$, C$_5$H$_5$N, PPh$_3$, AsPh$_3$).[20] The Ge(1)−Cu(1) bond distance of 2.359(2) Å is longer than the theoretical calculation of the Ge(II)−Cu(I) bond distance (2.250 Å).[21] This may due to the steric repulsion between the pyridyl-1-azaallyl ligand in the cubane structure lengthening the Ge(II)−Cu(I) bond. All the Cu···Cu nonbonding and Cu−I distances in **7** are in the

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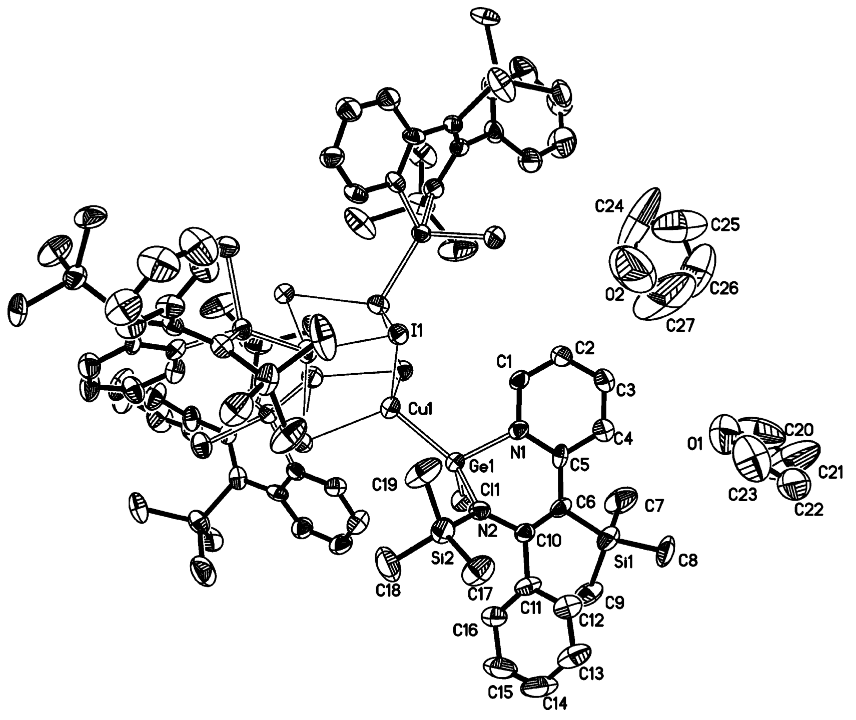

Figure 6. Molecular structure of **7** (ellipsoids are drawn at the 30% probability level).

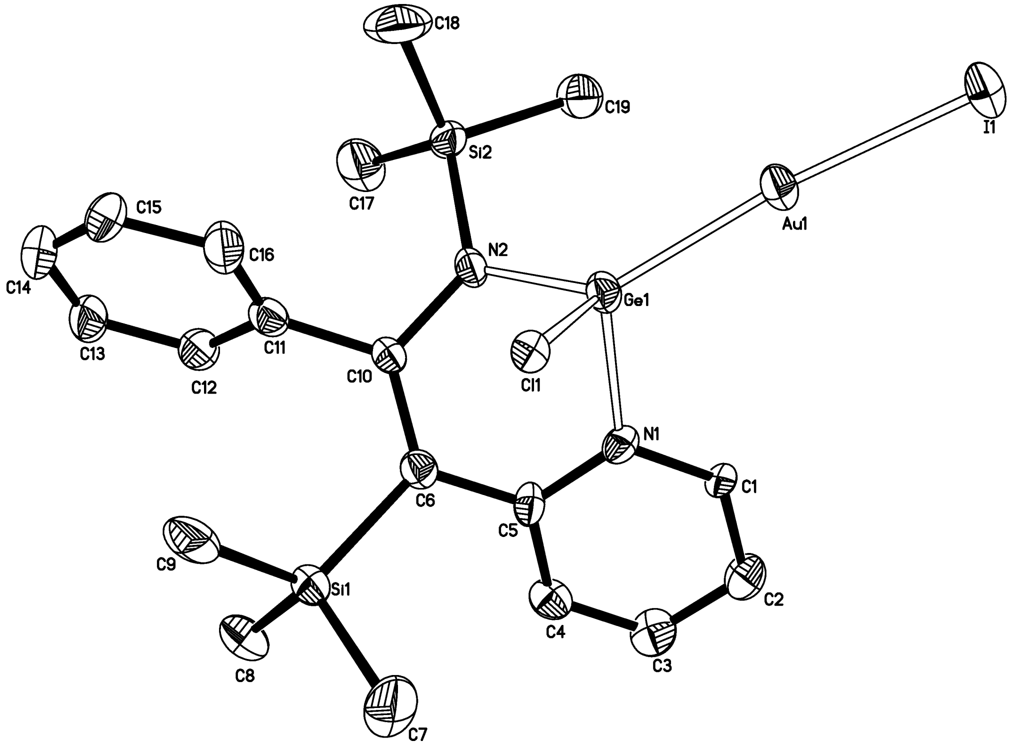

Figure 7. Molecular structure of **8** (ellipsoids are drawn at the 30% probability level).

range of values observed in other Cu(I) iodide cubane systems with a phosphine ligand.[22] In contrast, compound **8** is a monomeric germanium(II)−gold (I) adduct. The Ge(1)−Au(1) bond distance of 2.346(2) Å is similar to the theoretical calculation of 2.349 Å.[21]

The Ge−N_{amide} bond distances of 1.912(3) Å in **6**, 1.888(8) Å in **7**, and 1.884(2) Å in **8** are slighter shorter than that of **1**. It is suggested that the germanium(II) center in **6**−**8** forms a donor−acceptor interaction with the Lewis acid and the electron density around the germanium center is diminished as compared to compound **1**.

Experimental Section

All manipulations were carried out under an inert atmosphere of dinitrogen gas by standard Schlenk techniques. Solvents were dried over and distilled from CaH_2 (hexane) and/or Na (Et_2O, toluene, and THF). [Ge{N($SiMe_3$)C(Ph)C($SiMe_3$)(C_5H_4N-2)}Cl] was prepared by literature procedures.[6] Bu^tLi (1.48 M in hexane), Bu^nLi (1.6M in hexane), LiC≡CPh (1.0 M THF), PhC≡CH,

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Table 1. Crystallographic Data for Compounds 2−5

	2	**3**	**4**	**5**
formula	$C_{23}H_{36}GeN_2Si_2$	$C_{27}H_{32}GeN_2Si_2$	$C_{86}H_{80}Ge_4LiO_{3.5}$	$C_{38}H_{55}AlN_4Si_4$
fw	469.31	513.32	1466.80	707.20
color	red	yellow	yellow	yellow
cryst syst	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a (Å)	9.886(4)	8.3622(17)	15.4011(7)	11.66(1)
b (Å)	13.942(5)	11.227(2)	24.5315(11)	12.74(1)
c (Å)	19.366(7)	16.899(3)	21.9725(10)	14.135(6)
α (deg)	90	107.28(3)	90	90.94(4)
β (deg)	103.139(8)	90.39(3)	90.8000(10)	98.80(3)
γ (deg)	90	100.47(3)	90	94.91(2)
V (Å^3)	2599.3(17)	1486.6(5)	8180.3(6)	2068(3)
Z	4	2	4	2
d_{calcd} (g cm^{-3})	1.199	1.147	1.191	1.136
μ (mm^{-1})	1.281	1.126	1.500	0.195
F(000)	992	536	3020	760
cryst size (mm)	0.68 × 0.47 × 0.44	0.50 × 0.40 × 0.20	1.01 × 0.86 × 0.64	0.25 × 0.22 × 0.20
2θ range (deg)	1.82−28.09	2.53−25.23	1.76−25.00	1.60−24.99
index range	$-13 \le h \le 9$, $-18 \le k \le 17$, $-25 \le l \le 25$	$-9 \le h \le 8$, $0 \le h \le 13$, $-20 \le h \le 19$	$-18 \le h \le 18$, $-29 \le k \le 28$, $-26 \le l \le 22$	$-13 \le h \le 13$, $0 \le k \le 15$, $-16 \le l \le 16$
no. of reflns collected	17 301	4499	43 596	4926
no. of indep reflns	6274	4499	14 397	4926
R1, wR2 ($I > 2(\sigma)I$)	0.0453, 0.1003	0.0524, 0.1413	0.0658, 0.1795	0.0663, 0.1564
R1, wR2 (all data)	0.0953, 0.1130	0.0571, 0.1486	0.1368, 0.2129	0.0903, 0.1700
goodness of fit, F^2	0.878	1.062	0.894	1.073
no. of data/restraints/params	6274/0/253	4499/0/289	14397/583/849	4926/0/429
largest diff peaks (e Å^{-3})	0.636 to −0.498	0.384 to −0.607	0.862 to −0.365	0.295 to −0.361

Table 2. Crystallographic Data for Compounds 6-8

	6	**7**	**8**
formula	$C_{19}H_{31}BGeN_2Si_2$	$C_{108}H_{172}Cl_4Cu_4Ge_4I_4N_8O_8Si_8$	$C_{19}H_{27}AuClGeIN_2Si_2$
fw	427.04	3129.18	771.51
color	colorless	yellow	yellow
cryst syst	monoclinic	tetragonal	triclinic
space group	$P2_1/n$	$P\bar{4}2_1c$	$P\bar{1}$
a (Å)	18.195(4)	22.2933(8)	8.4991(9)
b (Å)	11.688(2)	22.2933(8)	11.1497(12)
c (Å)	11.192(2)	14.1706(7)	14.3709(15)
α (deg)	90	90	80.216(2)
β (deg)	99.29(3)	90	73.291(2)
γ (deg)	90	90	85.197(2)
V (Å^3)	2348.9(8)	7042.7(5)	1284.5(2)
Z	4	2	2
d_{calcd} (g cm^{-3})	1.208	1.476	1.995
μ (mm^{-1})	1.411	2.502	8.281
F(000)	896	3152	728
cryst size (mm)	0.50 × 0.40 × 0.30	0.40 × 0.30 × 0.20	0.50 × 0.40 × 0.20
2θ range (deg)	2.08−25.00	1.29−25.00	1.85−25.00
index range	$-21 \le h \le 21$ $-13 \le k \le 13$ $0 \le l \le 12$	$-26 \le h \le 26$ $-24 \le k \le 26$ $-16 \le l \le 16$	$-9 \le h \le 10$ $-13 \le k \le 13$ $-17 \le l \le 17$
no. of reflns collected	6089	37 635	6860
no. of indep reflns	3568	6217	4472
R1, wR2 ($I > 2(\sigma)I$)	0.0542, 0.1490	0.0429, 0.0901	0.0951, 0.2724
R1, wR2 (all data)	0.0585, 0.1591	0.1110, 0.1223	0.1076, 0.2814
goodness of fit, F^2	1.165	0.915	1.038
no. of data/restraints/params	3568/0/242	6217/0/334	4472/6/244
largest diff peaks (e Å^{-3})	0.480 to −0.726	0.515 to −0.936	4.235 to −3.750

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compound 2

[Ge(Bu^t){N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}] (**2**)			
Ge(1)−N(1)	2.059(3)	N(2)−C(10)	1.398(4)
Ge(1)−N(2)	1.954(3)	C(6)−C(10)	1.372(4)
Ge(1)−C(20)	2.040(3)	C(5)−C(6)	1.471(4)
		N(1)−C(5)	1.363(4)
C(20)−Ge(1)−N(1)	98.3(1)	Ge(1)−N(1)−C(5)	123.5(2)
C(20)−Ge(1)−N(2)	106.0(1)	C(5)−C(6)−C(10)	120.9(3)
N(1)−Ge(1)−N(2)	87.9(1)	C(6)−C(10)−N(2)	123.7(3)
		C(10)−N(2)−Ge(1)	120.0(2)

Table 4. Selected Bond Distances (Å) and Angles (deg) for Compound 3

[Ge(CCPh){N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}] (**3**)			
Ge(1)−C(20)	2.004(4)	Ge(1)−N(1)	2.052(3)
Ge(1)−N(2)	1.966(3)	C(20)−C(21)	1.213(5)
N(1)−C(5)	1.393(5)	C(5)−C(6)	1.494(5)
C(6)−C(10)	1.394(5)	C(10)−N(2)	1.408(5)
C(21)−C(22)	1.455(6)		
N(1)−Ge(1)−N(2)	87.7(1)	N(2)−Ge(1)−C(20)	97.7(1)
C(20)−Ge(1)−N(1)	93.8(1)	Ge(1)−N(1)−C(5)	121.5(2)
N(1)−C(5)−C(6)	120.6(3)	C(5)−C(6)−C(10)	120.1(3)
C(6)−C(10)−N(2)	124.7(3)	C(10)−N(2)−Ge(1)	117.2(2)
Ge(1)−C(20)−C(21)	165.0(4)	C(20)−C(21)−C(22)	179.1(5)

$LiAlH_4$, $NaBH_4$, CuI, and AuI were purchased from Aldrich Chemical Co. and used without purification. The ^1H, ^{13}C, and ^{11}B were recorded on Bruker WM-300 or Varian 400 instruments. All spectra were recorded in C_6D_6 or THF-d_8, and the chemical shifts δ are relative to $SiMe_4$ and $BF_3 \cdot Et_2O$ for ^1H, ^{13}C, and ^{11}B NMR, respectively.

[Ge(Bu^t){N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}] (2). Bu^{t}Li (0.68 mL, 1.00 mmol, 1.48 M in hexane) was added slowly to a solution of [Ge{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}Cl] (**1**) (0.45 g, 1.00 mmol) in Et_2O (50 mL) at 0 °C. The resulting red suspension was raised to ambient temperature and stirred for 17 h. It was filtered and hexane was added to the filtrate and concentrated to yield red crystals of **2**. Yield: 0.33 g (70%). Mp: 125−126 °C. Anal. Found: C, 58.77; H, 7.70; N, 6.12. Calcd for $C_{23}H_{36}GeN_2Si_2$: C,

Table 5. Selected Bond Distances (Å) and Angles (deg) for Compound 4

[{(PhC$\equiv$C)$_3$Ge}$_3$GeLi(Et$_2$O)$_3$]·0.5Et$_2$O (**4**)			
Li(1)−O(1)	1.908(15)	Ge(4)−C(61)	1.907(7)
Li(1)−O(2)	1.915(15)	Ge(4)−C(71)	1.954(7)
Li(1)−O(3)	1.945(14)	Ge(4)−C(81)	1.926(8)
Ge(1)−Li(1)	3.066(15)	C(1)−C(2)	1.180(8)
Ge(1)−Ge(2)	2.463(9)	C(11)−C(12)	1.159(9)
Ge(1)−Ge(3)	2.462(9)	C(21)−C(22)	1.180(8)
Ge(1)−Ge(4)	2.468(9)	C(31)−C(32)	1.147(8)
Ge(2)−C(1)	1.909(7)	C(41)−C(42)	1.150(7)
Ge(2)−C(11)	1.920(8)	C(51)−C(52)	1.175(8)
Ge(2)−C(21)	1.920(7)	C(61)−C(62)	1.186(8)
Ge(3)−C(31)	1.926(7)	C(71)−C(72)	1.171(8)
Ge(3)−C(41)	1.935(6)	C(81)−C(82)	1.156(9)
Ge(3)−C(51)	1.931(7)		
Ge(2)−Ge(1)−Ge(3)	93.1(3)	Ge(1)−Ge(3)−Ge(51)	109.5(2)
Ge(3)−Ge(1)−Ge(4)	94.0(3)	Ge(1)−Ge(3)−C(31)	113.4(2)
Ge(2)−Ge(1)−Ge(4)	93.5(4)	Ge(1)−Ge(3)−C(41)	117.3(2)
Li(1)−Ge(1)−Ge(2)	123.7(3)	Ge(1)−Ge(3)−C(51)	109.5(2)
Li(1)−Ge(1)−Ge(3)	115.1(3)	C(61)−Ge(4)−C(71)	103.0(3)
Li(1)−Ge(1)−Ge(4)	128.8(3)	C(71)−Ge(4)−C(81)	103.8(3)
C(1)−Ge(2)−C(11)	103.8(3)	C(61)−Ge(4)−C(81)	108.0(3)
C(1)−Ge(2)−C(21)	102.2(3)	Ge(1)−Ge(4)−C(61)	117.2(2)
C(11)−Ge(2)−C(21)	107.9(3)	Ge(1)−Ge(4)−C(71)	113.5(2)
Ge(1)−Ge(2)−C(1)	110.7(2)	Ge(1)−Ge(4)−C(81)	110.3(2)
Ge(1)−Ge(2)−C(11)	119.4(2)	O(1)−Li(1)−O(2)	116.2(8)
Ge(1)−Ge(2)−C(21)	111.4(2)	O(1)−Li(1)−O(3)	113.6(8)
C(31)−Ge(3)−C(41)	103.8(3)	O(2)−Li(1)−O(3)	116.9(7)
C(31)−Ge(3)−C(51)	103.1(3)	Ge(1)−Li(1)−O(1)	108.1(6)
C(41)−Ge(3)−C(51)	108.7(3)	Ge(1)−Li(1)−O(2)	94.5(6)
Ge(1)−Ge(3)−C(31)	113.4(2)	Ge(1)−Li(1)−O(3)	104.5(6)
Ge(1)−Ge(3)−C(41)	117.3(2)		

Table 6. Selected Bond Distances (Å) and Angles (deg) for Compound 5

[Al{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}$_2$(H)] (**5**)			
Al(1)−H(1)	1.560(3)	Al(1)−N(1′)	2.070(4)
Al(1)−N(1)	2.060(4)	Al(1)−N(2′)	1.897(4)
Al(1)−N(2)	1.914(4)	N(1′)−C(5′)	1.376(5)
N(1)−C(5)	1.360(6)	C(5′)−C(6′)	1.456(6)
C(5)−C(6)	1.480(7)	C(6′)−C(7′)	1.368(7)
C(6)−C(7)	1.365(6)	C(7′)−N(2′)	1.397(6)
C(7)−N(2)	1.389(5)		
N(2)−Al(1)−N(2′)	118.3(2)	Al(1)−N(1)−C(5)	122.2(3)
N(2)−Al(1)−H(1)	120.0(12)	N(1)−C(5)−C(6)	120.8(4)
N(2′)−Al(1)−H(1)	121.5(12)	C(6)−C(7)−N(2)	127.4(5)
N(1)−Al(1)−N(1′)	175.8(2)	C(7)−N(2)−Al(1)	117.1(3)
N(1)−Al(1)−N(2)	85.8(2)	Al(1)−N(1′)−C(5′)	122.0(3)
N(1)−Al(1)−N(2′)	96.7(2)	N(1′)−C(5′)−C(6′)	120.4(4)
N(1)−Al(1)−H(1)	91.9(13)	C(6′)−C(7′)−N(2′)	126.9(4)
N(1′)−Al(1)−N(2′)	85.8(2)	C(7′)−N(2′)−Al(1)	117.1(3)
N(1′)−Al(1)−N(2)	96.1(2)		
N(1′)−Al(1)−H(1)	83.9(13)		

Table 7. Selected Bond Distances (Å) and Angles (deg) for Compound 6

[Ge(BH$_3$){N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}H] (**6**)			
Ge(1)−jB(1)	2.064(6)	Ge(1)−N(1)	1.994(3)
Ge(1)−N(2)	1.912(3)	N(1)−C(5)	1.369(5)
C(5)−C(6)	1.488(5)	C(6)−C(10)	1.400(5)
C(10)−N(2)	1.402(5)		
N(1)−Ge(1)−N(2)	90.8(1)	N(2)−Ge(1)−B(1)	127.1(2)
B(1)−Ge(1)−N(1)	110.3(2)	Ge(1)−N(1)−C(5)	117.8(2)
N(1)−C(5)−C(6)	121.4(3)	C(5)−C(6)−C(10)	118.8(3)
C(6)−C(10)−N(2)	124.5(3)	C(10)−N(2)−Ge(1)	112.1(2)

58.86; H, 7.73; N, 5.97. ^{1}H NMR (THF-d_8): δ −0.22 (s, 9H, SiMe$_3$), −0.05 (s, 9H, SiMe$_3$), 0.95 (s, 9H, t-Bu), 6.97−7.03 (m, 1H, 5-py), 7.23−7.28 (d, 1H, 3-py), 7.36−7.40 (m, 3H, Ph), 7.45−7.56 (m, 2H, Ph), 7.56−7.66 (m, 1H, 4-py), 8.43−8.48 (d, 1H, 6-py). ^{13}C{^{1}H} NMR (THF-d_8): δ 2.30, 2.44 (SiMe$_3$), 27.49 (*t*-Bu), 105.76 (*C*SiMe$_3$), 119.37, 125.34, 128.30, 129.93, 130.23, 131.44, 136.01, 142.83, 147.70, 161.64 (Ph and Py), 164.37 (N*C*Ph).

Table 8. Selected Bond Distances (Å) and Angles (deg) for Compound 7[a]

[Ge(CuI){N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}Cl]$_4$.8THF (**7**)			
Ge(1)−N(1)	1.984(8)	Ge(1)−N(2)	1.888(8)
Ge(1)−Cl(1)	2.252(3)	Ge(1)−Cu(1)	2.359(2)
Cu(1)−I(1)	2.682(2)	Cu(1)−I(1A)	2.629(2)
Cu(1)−I(1B)	2.756(2)	N(1)−C(5)	1.366(1)
C(5)−C(6)	1.428(1)	C(6)−C(10)	1.370(1)
C(10)−N(2)	1.443(1)	I(1)−Cu(1C)	2.756(2)
N(2)−Ge(1)−N(1)	90.6(3)	N(2)−Ge(1)−Cl(1)	99.5(3)
N(1)−Ge(1)−Cl(1)	96.2(2)	Cu(1)−Ge(1)−N(1)	113.2(2)
Cu(1)−Ge(1)−N(2)	135.6(3)	Cu(1)−Ge(1)−Cl(1)	113.6(9)
Ge(1)−N(1)−C(5)	120.5(7)	N(1)−C(5)−C(6)	123.0(9)
C(5)−C(6)−C(10)	121.1(9)	C(6)−C(10)−N(2)	123.5(9)
C(10)−N(2)−Ge(1)	115.5(6)	Ge(1)−Cu(1)−I(1)	114.0(6)
Ge(1)−Cu(1)−I(1A)	118.0(6)	Ge(1)−Cu(1)−I(1B)	99.4 (5)
Cu(1A)−I(1)−Cu(1)	68.0(5)	Cu(1)−I(1)−Cu(1C)	67.5(4)
Cu(1A)−I(1)−Cu(1C)	68.2(5)		

[a] Symmetry transformations used to generate equivalent atoms: A $-x+2$, $-y+2$, z; B y, $-x+2$, $-z+1$; C $-y+2$, x, $-z+1$

Table 9. Selected Bond Distances (Å) and Angles (deg) for Compound 8

[Ge(AuI){N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}Cl] (**8**)			
Ge(1)−Au(1)	2.346(2)	Au(1)−I(1)	2.561(1)
Ge(1)−N(1)	1.942(1)	Ge(1)−N(2)	1.844(2)
Ge(1)−Cl(1)	2.422(4)	C(10)−N(2)	1.440(2)
C(6)−C(10)	1.400(2)	C(5)−C(6)	1.410(3)
N(1)−C(5)	1.350(2)		
N(2)−Ge(1)−N(1)	93.6(6)	N(2)−Ge(1)−Cl(1)	102.2(5)
N(1)−Ge(1)−Cl(1)	96.7(5)	Au(1)−Ge(1)−Cl(1)	113.9(1)
N(1)−Ge(1)−Au(1)	113.0(5)	N(2)−Ge(1)−Au(1)	130.9(4)
Ge(1)−Au(1)−I(1)	172.8(6)	C(10)−N(2)−Ge(1)	113.9(1)
C(6)−C(10)−N(2)	122.2(2)	C(5)−C(6)−C(10)	122.3(2)
N(1)−C(5)−C(6)	121.7(2)		

[Ge(C$\equiv$CPh){N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}] (3). LiC$\equiv$CPh (1.00 mL, 1.00 mmol, 1 M in THF) was added slowly to a solution of **1** (0.44 g, 0.98 mmol) in Et$_2$O (40 mL) at −90 °C. The resulting yellow suspension was raised to ambient temperature and stirred for 20 h. It was filtered and the filtrate concentrated to give yellow crystals of **3**. Yield: 0.20 g (40%). Mp: 140−142 °C. Anal. Found: C, 63.33; H, 6.19; N, 5.36. Calcd for C$_{27}$H$_{32}$GeN$_2$Si$_2$: C, 63.17; H, 6.28; N, 5.46. ^{1}H NMR (THF-d_8): δ −0.21 (s, 9H, SiMe$_3$), −0.19 (s, 9H, SiMe$_3$), 7.10−7.13 (m, 3H, Ph), 7.20−7.22 (m, 2H, Ph), 7.29 (m, 1H, 5-py), 7.31 (m, 3H, C$_{\text{ethynyl}}$*Ph*), 7.38 (d, 1H, C$_{\text{ethynyl}}$*Ph*), 7.39 (d, 1H, 3-py), 7.61 (m, 1H, C$_{\text{ethynyl}}$*Ph*), 7.88 (t, 1H, 4-py), 8.65−8.66 (d, 1H, 6-py). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 2.28, 3.20 (SiMe$_3$), 103.09 (*C*SiMe$_3$), 112.06 (GeC*C*Ph), 115.80 (Ge*C*CPh), 127.13, 127.32, 129.49, 130.11 (GeCC*Ph*), 118.94, 124.65, 125.89, 131.86, 132.73, 137.97, 144.68, 145.66, 156.56 (Ph & Py), 170.98 (N*C*Ph).

[{(PhC$\equiv$C)$_3$Ge}$_3$GeLi(OEt$_2$)$_3$] (4). Bu^{n}Li (0.46 mL, 0.73 mmol, 1.6 M in hexane) was added to a solution of PhC$\equiv$CH (0.08 mL, 0.73 mmol) in Et$_2$O (30 mL) at 0 °C. The solution was raised to ambient temperature and stirred for 2 h. A solution of **1** (0.31 g, 0.69 mmol) in Et$_2$O (30 mL) was then added slowly to the solution at −90 °C. The resulting yellow suspension was raised to ambient temperature and stirred for 17 h. The reaction mixture was filtered and the filtrate concentrated under reduced pressure to yield yellow crystals of the title compound **4**. Yield: 0.73 g (70%). Mp: 95−96 °C. Anal. Found: C, 70.21; H, 5.07. Calcd for C$_{84}$H$_{75}$Ge$_4$LiO$_3$: C, 70.56; H, 5.29. ^{1}H NMR (THF-d_8): δ 1.09−1.14 (t, 3H, Et$_2$O), 3.35−3.42 (q, 2H, Et$_2$O), 7.01−7.78 (m, 15H, Ph). ^{13}C{^{1}H} NMR (THF-d_8): δ 15.68 (Et$_2$O), 66.32 (Et$_2$O), 95.87 (Ge−C$\equiv$*C*Ph), 104.46 (Ge−*C*$\equiv$CPh), 127.39, 128.21, 128.54, 132.93 (Ph). IR: 2149 cm^{-1} (BH$_3$), 1897 cm^{-1} (GeH).

[Al{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}$_2$(H)] (5). LiAlH$_4$ (0.39 mL, 0.39 mmol, 1 M in THF) was added slowly to a solution of **1** (0.35 g, 0.78 mmol) in THF (50 mL) at −90 °C. The yellow suspension was raised to ambient temperature and stirred for 18 h. A gray, shiny solid was found in the resulting solution. Volatiles were removed under reduced pressure, and the residue was extracted with Et_2O. The mixture was filtered, concentrated, and stored at −30 °C to yield yellow crystals of **5**. Yield: 0.14 g (51%). Mp: 210−211 °C. Anal. Found: C, 64.15; H, 7.33; N, 8.02. Calcd for $C_{38}H_{55}AlN_4Si_4$: C, 64.54; H, 7.84; N, 7.92. ^1H NMR (C_6D_6): δ −0.24 (s, 9H, $SiMe_3$), −0.16 (s, 2H, $SiMe_3$), −0.02 (s, 2H, $SiMe_3$), 0.44−1.41 (br, 5H, $SiMe_3$), 5.54 (s, 1H, AlH), 6.39 (t, 1H, 3-py), 7.03−7.10 (m, 3H, Ph), 7.43−7.47 (m, 2H, Ph), 7.78 (dd, 2H, 4-py and 5-py), 9.39−9.41 (d, 1H, 6-py). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 1.36, 1.67, 2.14, 3.28 ($SiMe_3$), 120.73 (*C*$SiMe_3$), 124.82, 125.42, 129.20, 129.34, 130.64, 137.61, 138.78, 144.48, 145.72, 148.55, 158.74 (Ph and Py), 158.74 (N*C*Ph).

[Ge(BH_3){N($SiMe_3$)C(Ph)C($SiMe_3$)(C_5H_4N-2)}H] (6). A solution of **1** (0.45 g, 1.01 mmol) in THF (30 mL) was added slowly to a stirring suspension of sodium borohydride (0.010 g, 3.70 mmol) in THF (30 mL) at room temperature. The resulting yellow mixture was stirred for 3 days. The solution was filtered and concentrated to yield pale yellow crystals of **6**. Yield: 0.18 g (42%). Mp: 112−115 °C. Anal. Found: C, 53.37; H, 7.28; N, 6.34. Calcd for $C_{19}H_{31}BGeN_2Si_2$: C, 53.43; H, 7.32; N, 6.56. ^1H NMR (THF-d_8): δ −0.20 (s, 9H, $SiMe_3$), −0.18 (s, 9H, $SiMe_3$), 6.07 (br s, 1H, Ge*H*), 7.45−7.51 (m, 5H, Ph), 7.53 (m, 1H, 5-py), 7.68−7.71 (d, 1H, 3-py), 8.08 (t, 1H, 4-py), 8.69 (d, 1H, 6-py). ^1H NMR (THF-d_8, 223 K): δ 5.95, 5.96 (br.d, 1H, Ge*H*). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 2.30, 2.67 ($SiMe_3$), 116.16 (*C*$SiMe_3$), 122.14, 125.78, 128.54, 129.16, 131.19, 131.53, 132.45, 141.42, 144.17, 144.74, 158.39, (Ph & Py), 172.27 (N*C*Ph). $^{11}B\{^1H\}$ NMR (THF-d_8): δ −38.88.

[Ge(CuI){N($SiMe_3$)C(Ph)C($SiMe_3$)(C_5H_4N-2)}Cl(THF)$_2$]$_4$ (7). A solution of **1** (0.45 g, 1.01 mmol) in THF (30 mL) was added slowly to a stirring suspension of copper(I) iodide (0.20 g, 1.05 mmol) in THF (30 mL) at 0 °C. The resulting yellow mixture was raised to ambient temperature and stirred for 18 h. The solution was filtered, and the volatiles were removed under reduced pressure. The residue was extracted with Et_2O, followed by filtration and concentration, to give **35** as yellow crystals. Yield: 0.98 g (38%). Mp: 102−104 °C. Anal. Found: C, 35.41; H, 4.29; N, 4.18. Calcd for $C_{76}H_{108}Cl_4Cu_4Ge_4I_4N_8Si_8$: C, 35.76; H, 4.26; N, 4.39. ^1H NMR (THF-d_8): δ −0.21 (s, 9H, $SiMe_3$), −0.02 (s, 9H, $SiMe_3$), 1.69−1.74 (t, 2H, THF), 3.54−3.56 (d, 2H, THF), 7.34−7.41 (m, 2H, Ph), 7.50 (m, 1H, 5-py), 7.54 (m, 1H, 3-py), 7.63−7.67 (m, 3H, Ph), 7.97−7.99 (t, 1H, 4-py), 9.50 (d, 1H, 6-py). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 1.95, 4.16 ($SiMe_3$), 26.39, 68.23 (THF), 116.09 (*C*$SiMe_3$), 121.50, 126.66, 128.12, 128.99, 130.47, 131.58, 133.12, 141.26, 145.35, 146.55, 156.02 (Ph and Py), 164.74 (N*C*Ph).

[Ge(AuI){N($SiMe_3$)C(Ph)C($SiMe_3$)(C_5H_4N-2)}Cl] (8). A solution of **1** (0.45 g, 1.01 mmol) in THF (30 mL) was added slowly to a stirring suspension of gold(I) iodide (0.35 g, 1.08 mmol) in THF (30 mL) at 0 °C in the absence of light. The resulting yellow mixture was raised to ambient temperature and stirred for 20 h. The solution was filtered, and the volatiles were removed under reduced pressure. The residue was extracted with Et_2O and filtered. The yellow precipitates were separated and dissolved in THF. After filtration, addition of 3 mL of CH_2Cl_2, and concentration of the filtrate, a yellow crystalline solid of **8** was obtained. Yield: 0.25 g (32%). Mp: 95−96 °C. Anal. Found: C, 29.24; H, 3.55; N, 3.51. Calcd for $C_{19}H_{27}AuClGeIN_2Si_2$: C, 29.58; H, 3.53; N, 3.63. ^1H NMR (THF-d_8): δ −0.15 (s, 9H, $SiMe_3$), 0.02 (s, 9H, $SiMe_3$), 7.47−7.53 (m, 5H, Ph), 7.57−7.60 (t, 1H, 5-py), 7.81−84 (d, 1H, 3-py), 8.21−8.23 (t, 1H, 4-py), 9.09 (d, 1H, 6-py). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 1.70, 3.56 ($SiMe_3$), 117.12 (*C*$SiMe_3$), 122.70, 127.87, 128.70, 129.48, 131.51, 131.78, 132.52, 143.29, 144.26, 144.53, 156.86 (Ph and Py), 163.88 (N*C*Ph).

X-ray Crystallography. Single crystals were sealed in Lindemann glass capillaries under nitrogen. X-ray data of **2**−**8** were collected on a Rigaku R-AXIS II imaging plate using graphite-monochromatized Mo Kα radiation ($I = 0.71073$ Å) from a rotating-anode generator operating at 50 kV and 90 mA. Crystal data for **2**−**8** are summarized in Tables 1 and 2. The structures were solved by direct phase determination using the computer program SHELXTL-PC[23] on a PC 486 and refined by full-matrix least squares with anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms were introduced in their idealized positions and included in structure factor calculations with assigned isotropic temperature factor calculations. Full details of the crystallographic analysis of **2**−**8** are given in the Supporting Information.

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Supporting Information Available: Details about the X-ray crystal structures, including ORTEP diagrams and tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **2**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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