Synthesis and Properties of a Germanium(II) Metalloheterocycle Derived from 1,8-Di(isopropylamino)naphthalene. A Novel Ligand Leading to Formation of Ni{Ge[(^{i}PrN)$_2$C$_{10}$H$_6$]}$_4$

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Abstract: A novel mononuclear germylene, Ge[1,8-(^{i}PrN)$_2$C$_{10}$H$_6$] (**1**), was isolated as a stable crystalline solid by the reaction of Li$_2$[1,8-(^{i}PrN)$_2$C$_{10}$H$_6$] with GeCl$_2$(1,4-dioxane). Structural examination of **1** shows that this compound possesses a planar six-membered heterocyclic ring system with a Ge(II) center and that the steric impact of the substituents on the nitrogen centers is greater than that for the related five-membered metalloheterocycles. Compound **1** is readily oxidized with elemental S and Se and the structural details for the dinuclear product [[1,8-(^{i}PrN)$_2$C$_{10}$H$_6$]Ge(μ-S)]$_2$ are reported. Furthermore, the lone pair of electrons on the Ge(II) center in **1** allows this species to function as a novel ligand for the preparation of the unique tetrakis(germylene) complex Ni{Ge[(^{i}PrN)$_2$C$_{10}$H$_6$]}$_4$ (**4**). The structural features of **4** are reported and show that the germylene ligand, when coordinated to the Ni(0) center, now exhibited a twisted (nonplanar) heterometallocycle and a cone angle of 145°.

Introduction

The recent attention aimed at mononuclear, divalent compounds of Ge is propelled by the isolation of stable carbenes and silylenes of the type represented by **I**,[1,2] by the significance of such species from a fundamental perspective, and by the fact that these compounds represent potential building blocks for further synthetic chemistry of this element.[3−8] Nitrogen-based ligands, presumably due to the σ-inductive effect of the electronegative N, have played a pivotal role in the successful isolation of these species with the archetype being Ge(N(SiMe$_3$)$_2$)$_2$.[9] Theoretical and experimental results indicate that ligands exhibiting delocalized heterocyclic π-systems lend improved stability to these compounds.[1b,10−13] For example, (^{t}BuNCHCHN^{t}Bu)Ge (**II**) is significantly more stable than (tBuNCH$_2$CH$_2$NtBu)Ge (**III**).[14] The diaminobenzene-derived compound *o*-C$_6$H$_4$(NSiMe$_3$)$_2$Ge (**IV**)[15] and the aminotroponiminate species [1,2-C$_7$H$_5$(N^{i}Pr)$_2$]Ge$^+$ (**V**)[16] have been prepared and their stability attributed to their 10-π electron systems. In addition to π delocalization, the presence of sterically demanding substituents on the metal-bonded N centers undoubtedly plays an essential role in preventing aggregation of these species.[17] For example, while Ge[N(SiMe$_3$)$_2$]$_2$ is monomeric, Ge(N^{i}Pr$_2$)$_2$ forms dimers in the solid state.[5] A common feature for the reported compounds in this family is the dominance of five-membered heterocyclic ring systems.

One of our general interests, the design and implementation of rigid chelating ligands with delocalized π-electrons, led us to the preparation of a novel diamido ligand that yields a six-membered metalloheterocycle system when coordinated to a metal center.[18] We anticipated that the steric impact exerted by the nitrogen substituents of this ligand would be greater than the five-membered-ring systems of Chart 1 due to the relative geometric constraints of the two cycles. The amido ligand, derived from 1,8-diaminonaphthalene, seemed appealing for stabilization of Ge(II) species and we now report the synthetic and structural details for the new germylene Ge[1,8-(^{i}PrN)$_2$-C$_{10}$H$_6$]. We also report that this compound reacts smoothly with elemental sulfur and selenium via a redox pathway and that the lone pair of electrons on the Ge(II) center permit this species

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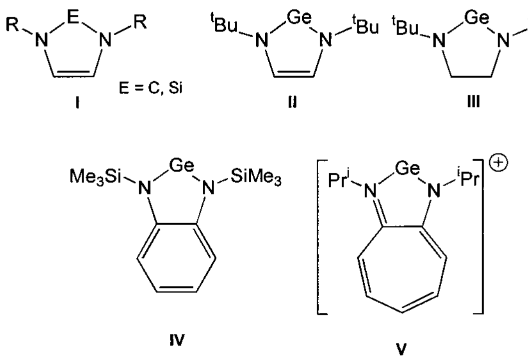
10.1021/ja0100569 CCC: $20.00

Chart 1



to function as a novel ligand for the preparation of a tetrakis(germylene) complex of Ni(0).

Results and Discussion

The metathetical reaction between an equimolar ratio of $Li_2[1,8\text{-}(^iPrN)_2C_{10}H_6]$ and $GeCl_2(dioxane)_2$ in Et_2O successfully provided $Ge[1,8\text{-}(^iPrN)_2C_{10}H_6]$ (**1**) as an orange solid in excellent yield (Scheme 1). An alternative transamination reaction between $Ge(N(SiMe_3)_2)_2$ and $[1,8\text{-}(^iPrNH)_2C_{10}H_6]$ also yields **1**. The first pathway was preferable for isolation of the product.

Compound **1** is soluble in a variety of organic solvents, exhibited a sharp, reversible melting point, and was characterized by NMR spectroscopy, elemental analysis, and X-ray diffraction studies. ^1H and ^{13}C NMR spectroscopy indicate a symmetrical solution structure for **1** with a single set of resonances for the ^iPr substituents and symmetrical naphthalene skeleton.

Single-crystal X-ray diffraction provided details for the level of aggregation and revealed the structural features of **1** (Table 1). Results of this study are displayed in Figure 1 with selected bond distances and angles in Table 2. A clearly distinguishing feature of **1** is that it is a mononuclear species exhibiting a planar six-membered metalloheterocycle. The deviation of the Ge center from the mean plane defined by N(1), C(1), C(6), C(7), and N(2) is only 0.042 Å. Although not present crystallographically, an approximate molecular mirror plane of symmetry passing through the Ge center and bisecting the C(6) and C(5) atoms is consistent with the symmetrical structure deduced from NMR.

The two Ge−N bond lengths in **1** are equivalent within experimental error (1.84 Å) and comparable to those observed for **IV** (range = 1.845(9)−1.868(9) Å)[15] but shorter than those reported for **V** (Ge−N = 1.901−1.92 Å).[16] Further comparison of Ge−N distances can be made with $Ge(N(SiMe_3)_2)$ (1.878(5), 1.873(5) Å),[9] **II** (1.856(1) Å),[14] and **III** (1.833(2) Å).[14] Like the related 1,2 diaminobenzene complex (**IV**) the Ge bonded N atoms (N(1), N(2)) are planar with their lone pairs of electrons aligned for π overlap with the atoms in the six-membered metallocycle ring. Calculations suggest that a true single $Ge^{II}-N$ bond distance for a diaminogermylene should be approximately 1.88 Å and that $p\pi-p\pi$ interactions would shorten the $Ge^{II}-N$ bond by 0.06−0.07 Å.[11] These results suggest some π-stabilizing interaction in **1**.

Except for the N(1)−Ge−N(2) angle of 97.28(7)°, the other angles within the six-membered heterocycle range from 121.00(18)° to 127.53(13)° and approach the ideal angle of 120°. As might be expected, this N−Ge−N angle is smaller than the acyclic species $Ge(N(SiMe_3)_2$ (N−Ge−N 107.1(2)°)[9] but larger than those of the five-membered ring compounds shown in Chart 1 (e.g.: **II**, N−Ge−N = 84.8(1)°;[14] **III**, N−Ge−N = 88.0(1)°;[14] **IV**, N−Ge−N = 87.2(4)°[15]).

As anticipated, the steric impact of the nitrogen substituents is more pronounced in **1** than for the five-membered metalloheterocycles (**II**−**V**). This is demonstrated by the observation that the smallest angle around each of the nitrogen atoms is the one defined by the ^iPr substituent and the Ge(II) center. For example, C(11)−N(1)−Ge and C(14)−N(2)−Ge exhibit values of 115.63(13)° and 115.46(13)°, respectively. For comparison, the analogous angles (Ge−N−Si) for **IV** fall in the range 123.3(5)−124.4(5)°.[15]

Examination of the packing of germylene **1** reveals an ordered antiparallel arrangement between adjacent molecules (Figure 2) and prompts consideration of intermolecular interactions. A similar packing arrangement was observed for $Sn\{o\text{-}C_6H_4[N(CH_2{}^tBu)]_2\}$, which crystallized in bimolecular aggregates due to a weak $\eta^6\text{-}C_6\cdots Sn$ interaction.[19] However, unlike this species, the closest approach between adjacent molecules of **1** is 3.719 Å (Ge and C(7)), a distance that is well beyond any bonding interaction.[20] The absence of extended interactions for compound **1** in the solid state contrasts with the cationic *N*-alkyl-2-(alkylamino)troponiminate derivatives (**V**) which clearly display interactions between the Ge and the counterions.[16]

Germylene **1** is susceptible to oxidation by chalcogens to yield Ge(IV) chalcogenido species (Scheme 2). Reaction of **1** with elemental sulfur or selenium proceeds smoothly with complete conversion (monitored by NMR) to yield species that display ^1H and ^{13}C NMR spectra that are similar to each other and consistent with the formulation of compounds **2** and **3**. However, **1** did not react with the milder oxidizing agent tellurium even after 6 days in the presence of excess Te.

Germanium chalcogenido complexes exhibit a range of aggregation levels that depend on the steric contributions of the supporting ligands and on the presence of other bases that can coordinate to the metal center. Therefore, the structural features of **2** were investigated by single-crystal X-ray diffraction (Table 1). Figure 3 displays the results of this analysis with selected bond distances and angles presented in Table 3. These results show that **2** has a dinuclear structure with bridging sulfido ligands generating a planar $[Ge(\mu\text{-}S)]_2$ unit situated on a crystallographic inversion center. The distorted tetrahedral coordination of the Ge(IV) center is completed by the original diamidonaphthalene ligand. Two molecules of THF cocrystallized in the lattice but display no interaction with **2**.

The Ge atom in **2** deviates to one side of the ligand plane (N(1), C(4), C(9), C(10), N(2)) by 0.251 Å while the methine carbons of the ^iPr groups lie 0.016 Å on the opposite side of this plane. The $Ge^{IV}-N$ bond lengths in **2** of 1.800(3) Å are slightly shorter than those observed for **1**. Other than the N(1)−Ge−N(2) angle, which has increased substantially to 103.91(12)°, the internal angles of the metalloheterocycle are quite similar to those observed in the starting material **1**.

The bond lengths and the internal angles for the germanium sulfido core of **2** are similar to the few reported species exhibiting a $[Ge^{IV}(\mu\text{-}S)]_2$ arrangement which exhibited Ge−S bond lengths in the range 2.226(2)−2.243(8) Å, S−Ge−S angles from 95.2 to 96.7°, and Ge−S−Ge angles from 83.2 to 84.7°.[21−22]

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Scheme 1

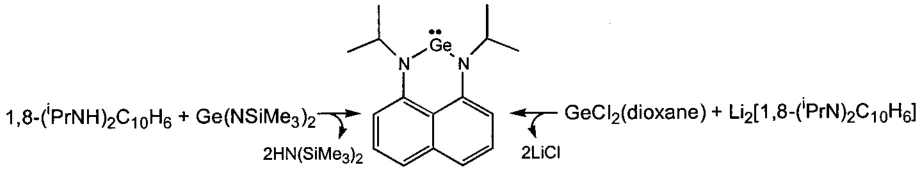

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Table 1. Crystal Data and Structure Refinement for Ge[1,8-(^{i}PrN)$_2$C$_{10}$H$_6$] (**1**), {Ge[1,8-(^{i}PrN)$_2$C$_{10}$H$_6$](μ-S)}$_2$ (**2**), and Ni{Ge[1,8-(^{i}PrN)$_2$C$_{10}$H$_6$]}$_4$ (**4**)

	1	**2**	**4**
empirical formula	$C_{16}H_{20}GeN_2$	$C_{32}H_{40}Ge_2N_4S_2(OC_4H_8)_2$	$C_{64}H_{80}Ge_4N_8Ni(OC_4H_8)_2$
formula weight	312.93	834.19	1454.64
temperature (K)	236(2)	238(2)	203(2)
λ (Å)	0.71073	0.71073	0.71073
space group	*Pbca*	*P*2$_1$/*c*	I-4
unit cell dimensions			
a (Å)	16.191(4)	15.881(2)	24.248(3)
b (Å)	10.877(3)	14.853(2)	24.248(3)
c (Å)	16.398(4)	8.597(1)	11.514(2)
β (deg)		98.974(3)	
volume (Å^3)	2888(1)	2002.9(5)	6770.0(17)
Z	8	2	4
density (Mg/m^3) (calcd)	1.440	1.383	1.427
absorption coeff (mm^{-1})	2.110	1.644	2.080
*R*1^a	0.0342	0.0405	0.0731
w*R*2^b	0.0732	0.0870	0.1700

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

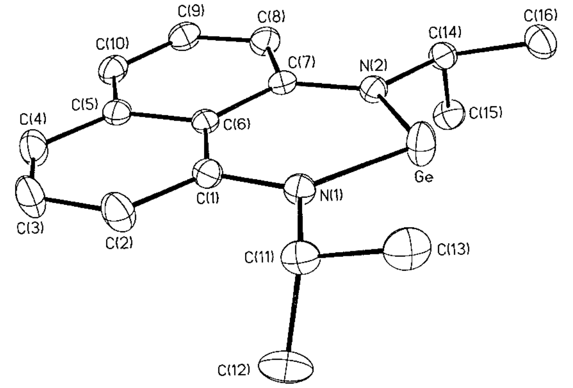

Figure 1. Molecular structure of Ge[1,8-(^{i}PrN)$_2$C$_{10}$H$_6$] (**1**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 30% probability.

Like silylenes and carbenes, germylenes are isolobal with phosphines and may function as ligands to transition metal complexes. Homoleptic silylene Ni complexes were recently reported which exhibit both tetra- and tricoordinate metal atoms.[23] The differences between these coordination environments were attributed to steric bulk of the silylene. To explore the suitability of **1** as a ligand for transition metal complexes the reaction of **1** with bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)$_2$) was investigated. When monitored by ^{1}H NMR spectroscopy in C_6D_6 the reaction between **1** and Ni(COD)$_2$ in a ratio of 4:1 appeared complete and free 1,5-cyclooctadiene was the sole byproduct. The NMR spectroscopic characterization of **4** supports the formation of a single Ge containing product with a single naphthalene environment. These results point to the assignment of a homoleptic germylene as the identity of **4** (Scheme 3).

Table 2. Selected Bond Distances [Å] and Angles [deg] for Ge[1,8-(^{i}PrN)$_2$C$_{10}$H$_6$] (**1**)

	Distances		
Ge−N(1)	1.8417(17)	C(5)−C(10)	1.413(3)
Ge−N(2)	1.8420(16)	C(5)−C(6)	1.443(3)
N(1)−C(1)	1.410(3)	C(6)−C(7)	1.443(3)
N(1)−C(11)	1.487(3)	C(7)−C(8)	1.391(3)
N(2)−C(7)	1.402(2)	C(8)−C(9)	1.392(3)
N(2)−C(14)	1.494(3)	C(9)−C(10)	1.349(3)
C(1)−C(2)	1.387(3)	C(11)−C(12)	1.519(3)
C(1)−C(6)	1.445(3)	C(11)−C(13)	1.524(3)
C(2)−C(3)	1.394(3)	C(14)−C(16)	1.524(3)
C(3)−C(4)	1.359(3)	C(14)−C(15)	1.528(3)
C(4)−C(5)	1.408(3)		
	Angles		
N(1)−Ge−N(2)	97.28(7)	C(5)−C(6)−C(7)	117.42(18)
C(1)−N(1)−C(11)	117.14(16)	C(5)−C(6)−C(1)	116.74(18)
C(1)−N(1)−Ge	127.22(14)	C(7)−C(6)−C(1)	125.84(18)
C(11)−N(1)−Ge	115.63(13)	C(8)−C(7)−N(2)	120.60(18)
C(7)−N(2)−C(14)	116.95(16)	C(8)−C(7)−C(6)	118.35(18)
C(7)−N(2)−Ge	127.53(13)	N(2)−C(7)−C(6)	121.04(17)
C(14)−N(2)−Ge	115.46(13)	C(7)−C(8)−C(9)	122.8(2)
C(2)−C(1)−N(1)	119.80(19)	C(10)−C(9)−C(8)	120.4(2)
C(2)−C(1)−C(6)	119.20(19)	C(9)−C(10)−C(5)	120.4(2)
N(1)−C(1)−C(6)	121.00(18)	N(1)−C(11)−C(12)	111.33(17)
C(3)−C(2)−C(1)	122.3(2)	N(1)−C(11)−C(13)	113.26(18)
C(4)−C(3)−C(2)	120.4(2)	C(12)−C(11)−C(13)	108.9(2)
C(3)−C(4)−C(5)	120.1(2)	N(2)−C(14)−C(16)	113.12(17)
C(4)−C(5)−C(10)	118.2(2)	N(2)−C(14)−C(15)	110.46(17)
C(4)−C(5)−C(6)	121.2(2)	C(16)−C(14)−C(15)	109.13(18)
C(10)−C(5)−C(6)	120.60(19)		

The only other reported homoleptic germylene metal complex, Ni(germylene)$_3$ (germylene = **III**), is not structurally characterized.[14] Structurally characterized Ni germylene complexes are limited to the bis(germylene) complex L$_2$Ni(CO)$_2$ (**A**, L = **III**), the mono(germylene) species LNi(PPh$_3$)$_2$ (L = Ge[N(SiMe$_3$)$_2$] (**B**) or Ge(2,4,6-(CF$_3$)$_3$C$_6$H$_2$)$_2$ (**C**)), and {[(^{t}BuO)(μ-O^{t}Bu)]GeNi-

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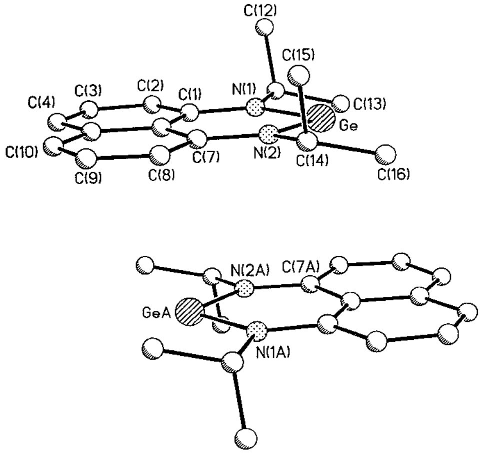


Figure 2. Packing arrangement of Ge[1,8-(^{i}PrN)$_2$C$_{10}$H$_6$] (**1**) showing the relationship between adjacent molecules in the structure.

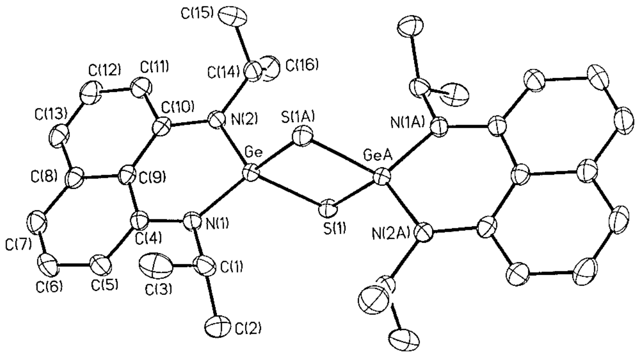
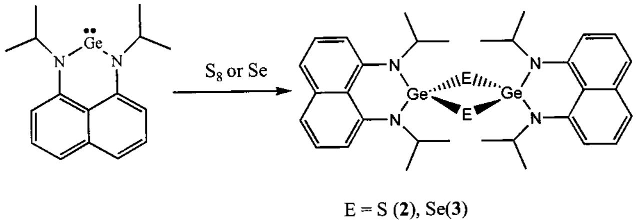


Figure 3. Molecular structure of [[1,8-(^{i}PrN)$_2$C$_{10}$H$_6$]Ge(μ-S)]$_2$ (**3**). Hydrogen atoms and the cocrystallized THF molecules have been omitted for clarity. Thermal ellipsoids are drawn at 30% probability.

Scheme 2

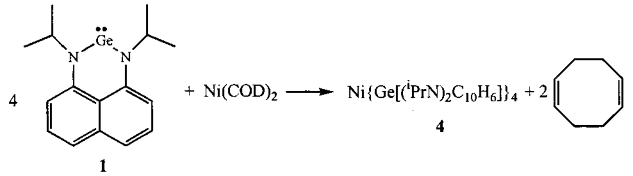


(CO)$_3$}$_2$ (**D**).[14,24,25] Therefore, we chose to carry out a single-crystal X-ray structure determination on **4** (Table 1). This study revealed two independent molecules of the tetrakis(germylene) Ni(0) complex, Ni{Ge[(^{i}PrN)$_2$C$_{10}$H$_6$]}$_4$, with each exhibiting similar structural parameters. One of these is displayed in Figure 4 with selected bond distances and angles provided in Table 4.[26] The Ni center possesses a single crystallographically unique germylene ligand and a coordination environment that is distorted tetrahedral. The Ge−Ni bond length of 2.2400(16) Å is close to the sum of the covalent radii for these elements and similar to the Ge−Ni bond distances observed in **A** and **D**.[14,25] These distances are slightly longer than observed for (Ph$_3$P)$_2$-Ni−Ge[N(SiMe$_3$)$_2$]$_2$ (**B**) with a Ni−Ge distance of 2.206(1) Å and for which some degree of multiple bonding was suggested.[24]

Table 3. Selected Bond Distances [Å] and Angles [deg] for {Ge[1,8-(^{i}PrN)$_2$C$_{10}$H$_6$](μ-S)}$_2$ (**2**)

Distances			
Ge−N(2)	1.800(3)	C(4)−C(9)	1.456(5)
Ge−N(1)	1.800(3)	C(5)−C(6)	1.407(5)
Ge−S(1)#1	2.2230(9)	C(6)−C(7)	1.331(5)
Ge−S(1)	2.2457(9)	C(7)−C(8)	1.415(5)
S(1)−Ge#1	2.2230(9)	C(8)−C(13)	1.407(5)
N(1)−C(4)	1.409(4)	C(8)−C(9)	1.440(4)
N(1)−C(1)	1.479(4)	C(9)−C(10)	1.443(5)
N(2)−C(10)	1.398(4)	C(10)−C(11)	1.378(5)
N(2)−C(14)	1.487(4)	C(11)−C(12)	1.396(5)
C(1)−C(3)	1.527(5)	C(12)−C(13)	1.347(5)
C(1)−C(2)	1.535(5)	C(14)−C(15)	1.517(5)
C(4)−C(5)	1.375(5)	C(14)−C(16)	1.523(6)
Angles			
N(2)−Ge−N(1)	103.91(12)	C(4)−C(5)−C(6)	122.0(4)
N(2)−Ge−S(1)#1	114.23(9)	C(7)−C(6)−C(5)	120.4(4)
N(1)−Ge−S(1)#1	114.58(10)	C(6)−C(7)−C(8)	121.2(4)
N(2)−Ge−S(1)	113.77(10)	C(13)−C(8)−C(7)	118.7(3)
N(1)−Ge−S(1)	115.78(9)	C(13)−C(8)−C(9)	120.8(3)
S(1)#1−Ge−S(1)	95.05(3)	C(7)−C(8)−C(9)	120.5(3)
Ge#1−S(1)−Ge	84.95(3)	C(10)−C(9)−C(8)	116.9(3)
C(4)−N(1)−C(1)	123.1(3)	C(10)−C(9)−C(4)	126.5(3)
C(4)−N(1)−Ge	121.5(2)	C(8)−C(9)−C(4)	116.5(3)
C(1)−N(1)−Ge	115.3(2)	C(11)−C(10)−N(2)	119.4(3)
C(10)−N(2)−C(14)	123.6(3)	C(11)−C(10)−C(9)	118.9(3)
C(10)−N(2)−Ge	122.7(2)	N(2)−C(10)−C(9)	121.8(3)
C(14)−N(2)−Ge	113.8(2)	C(10)−C(11)−C(12)	122.7(4)
N(1)−C(1)−C(3)	113.1(3)	C(13)−C(12)−C(11)	120.1(4)
N(1)−C(1)−C(2)	115.1(3)	C(12)−C(13)−C(8)	120.6(3)
C(3)−C(1)−C(2)	114.1(3)	N(2)−C(14)−C(15)	113.9(3)
C(5)−C(4)−N(1)	119.1(3)	N(2)−C(14)−C(16)	114.1(3)
C(5)−C(4)−C(9)	119.4(3)	C(15)−C(14)−C(16)	114.3(3)
N(1)−C(4)−C(9)	121.5(3)		

Scheme 3



Within the germylene ligands, the Ge−N bond lengths and the N−Ge−N angle are slightly reduced from those of the parent germylene (**1**). Distinct from the planar structure observed for **1**, when bonded to the Ni center the germylene exhibited a substantial twist (Figure 4) as evinced by the torsion angles C(11)−N(1)−C(1)−C(2) = 23.3(13)° and C(14)−N(2)−C(7)−C(8) = 10.4(14)°. This contrasts with the related species **A** and the recently reported homoleptic Ni(silylene)$_3$ complexes.[23] The cone angle observed for the germylene ligand in **4** provides a measure of the steric bulkiness of these ligands when bonded to Ni. Using the space filling diagram shown as the insert in Figure 4 a cone angle of 145° was measured for **1**.

Conclusions

A novel mononuclear germylene is isolated as a stable crystalline solid employing a new *N,N′*-(dialkyl)diaminonaphthalene skeleton. This ligand system forms a planar heterocyclic ring system with the Ge(II) center. Structural characterization of this new compound suggests that the steric impact of the nitrogen substituents on the Ge center is greater for this new six-membered-ring system than for the related five-membered metalloheterocycles. We have established that this compound

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(24) Bender, J. E.; Shusterman, A. J.; Banaszack-Holl, M. M.; Kampf, J. W. *Organometallics* **1999**, *18*, 1547. Litz, K. E.; Bender, J. E.; Kampf, J.; Banaszack-Holl, M. M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 496.

(25) Grenz, M.; Hahn, E.; du Mont, W.-W.; Pickardt, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 61.

(26) Full structural details for both molecules of **4** are provided in the Supporting Information.

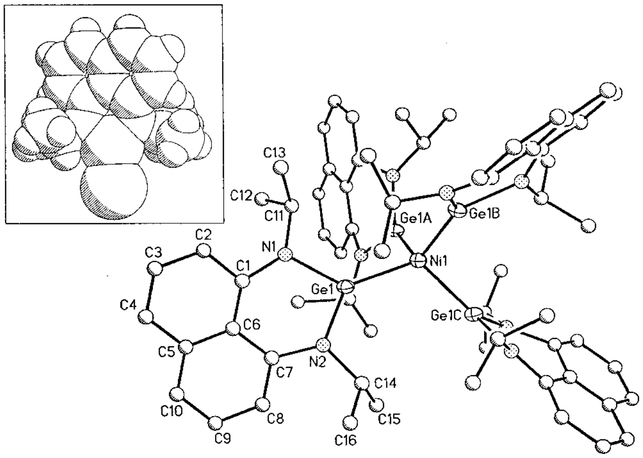

Figure 4. Molecular structure showing one of the two symmetry unique molecules of $\mathrm{Ni\{Ge[(^{i}PrN)_2C_{10}H_6]\}_4}$. Hydrogen atoms and the cocrystallized THF molecules have been omitted for clarity. Thermal ellipsoids are drawn at 30% probability. The inset provides a space filling diagram for one of the two asymmetric units, $\mathrm{NiGe[(^{i}PrN)_2C_{10}H_6]}$ (Ni atom at bottom), of this structure.

Table 4. Selected Bond Distances [Å] and Angles [deg] for $\mathrm{Ni\{Ge[1,8\text{-}(^{\mathit{i}}PrN)_2C_{10}H_6]\}_4}$ (**4**)

	Distances		
Ge(1)−N(2)	1.794(10)	N(1)−C(1)	1.433(12)
Ge(1)−N(1)	1.812(11)	N(1)−C(11)	1.534(17)
Ge(1)−Ni(1)	2.2400(16)	N(2)−C(7)	1.461(12)
Ni(1)−Ge(1)#1	2.2400(16)	N(2)−C(14)	1.490(17)
Ni(1)−Ge(1)#2	2.2400(16)		
Ni(1)−Ge(1)#3	2.2400(16)		
	Angles		
N(2)−Ge(1)−N(1)	96.7(5)	C(7)−N(2)−Ge(1)	122.0(7)
N(2)−Ge(1)−Ni(1)	130.8(3)	C(14)−N(2)−Ge(1)	115.0(8)
N(1)−Ge(1)−Ni(1)	131.6(3)	C(2)−C(1)−C(6)	120.0
Ge(1)−Ni(1)−Ge(1)#1	114.82(5)	C(2)−C(1)−N(1)	115.7(6)
Ge(1)−Ni(1)−Ge(1)#2	99.23(8)	C(6)−C(1)−N(1)	123.5(6)
Ge(1)#1−Ni(1)−Ge(1)#2	114.82(5)	C(8)−C(7)−N(2)	114.5(6)
Ge(1)−Ni(1)−Ge(1)#3	114.82(5)	C(6)−C(7)−N(2)	122.4(6)
Ge(1)#1−Ni(1)−Ge(1)#3	99.23(8)	C(12)−C(11)−N(1)	113.7(12)
Ge(1)#2−Ni(1)−Ge(1)#3	114.82(5)	C(12)−C(11)−C(13)	115.4(13)
C(1)−N(1)−C(11)	122.3(10)	N(1)−C(11)−C(13)	113.2(14)
C(1)−N(1)−Ge(1)	124.5(7)	C(16)−C(14)−N(2)	116.7(14)
C(11)−N(1)−Ge(1)	112.8(8)	C(16)−C(14)−C(15)	112.0(15)
C(7)−N(2)−C(14)	122.6(9)	N(2)−C(14)−C(15)	115.3(14)

can be cleanly oxidized with elemental S and Se. Furthermore, the Ge(II) center in this compound was demonstrated to behave as a Lewis basic center to generate the unique species $\mathrm{Ni\{Ge[(^{i}PrN)_2C_{10}H_6]\}_4}$. Our ongoing investigations are directed at understanding the effects produced by variation of the alkyl substituents and at the potential of germylene **1** as a building block to new germanium compounds as well as its capability as a ligand for transition metal complexes.

Experimental Section

General. All manipulations were carried out in either a nitrogen-filled drybox or under nitrogen following standard Schlenk-line techniques. Unless otherwise noted, solvents were sparged with nitrogen then dried by passage through a column of activated alumina with use of an apparatus purchased from Anhydrous Engineering. Deuterated benzene and toluene were dried by vacuum transfer from potassium. 1,8-Diaminonaphthalene, S_8, Se, Te, MeLi (1.4 M in ether), and bis(1,5-cyclooctadiene)nickel(0) were purchased from Aldrich Chemical Co. and used without further purification. $\mathrm{Ge(N(SiMe_3)_2}$ was prepared according to literature procedures.[9] 1,8-Diisopropyldiaminonaphthalene was prepared by reductive amination of acetone and diaminonaphthalene.[27] ^{1}H NMR spectra were run on either a Gemini 200 MHz or a Bruker 500 MHz spectrometer with deuterated benzene or toluene as a solvent and internal standard. All elemental analyses were run on a Perkin-Elmer PE CHN 4000 elemental analysis system.

^{1}H and ^{13}C NMR spectra were run on a Varian Gemini-200 or a Bruker 500 MHz spectrometer using the residual protons of the deuterated solvent for reference unless otherwise specified.

Preparation of $\mathbf{Li_2[1,8\text{-}(^{i}PrN)_2C_{10}H_6](THF)_4}$. Addition of MeLi (2.5 mL, 1.4 M in ether, 3.5 mmol) to a dark red/purple solution of $\mathrm{1,8\text{-}[HN(^{i}Pr)]_2C_{10}H_6}$ (0.424 g, 1.7 mmol) in ether (ca. 30 mL) led to an immediate color change of the solution to green then brown with gas evolution. The reaction mixture was stirred for 4 h and then all volatiles were removed under vacuum. The crude product (0.440 g, 99%) was then purified by crystallization from THF at −35 °C. The crystals were filtered and dried under vacuum. Product isolated by this method possessed four molecules of THF. ^{1}H NMR ($\mathrm{C_6D_{6,}}$): δ 7.40 (t, 2H, Ar−H), 6.94 (d, 2H, Ar−H), 6.36 (m, 2H, Ar−H), 3.55 (sept, 2H, $\mathrm{CH(Me)_2}$), 3.36 (t, 16H THF), 1.28−1.18 (overlapping signals, 28H, $\mathrm{CH_3}$ and THF).^{13}C NMR ($\mathrm{C_7D_8}$): 127.1 (Ar *C*H), 110.9 (Ar *C*H), 101.3 (Ar *C*H), 68.0 (*C*H$_2$, THF), 47.3 (*C*HMe$_2$), 25.6 (*C*H$_2$, THF), 25.1 (*C*H$_3$). Anal. Calcd for $\mathrm{C_{32}H_{52}N_2O_4Li_2}$: C, 70.83; H, 9.66; N, 5.16. Found: C, 70.48; H, 9.29; N, 5.60.

Preparation of $\mathbf{Ge[1,8\text{-}(^{i}PrN)_2C_{10}H_6]}$ (1) from $\mathbf{GeCl_2}$(dioxane) and $\mathbf{Li_2[1,8\text{-}(^{i}PrN)_2C_{10}H_6]}$. Addition of MeLi (2.86 mL, 1.4 M in ether, 4.0 mmol) to a dark red/purple solution of $\mathrm{1,8\text{-}(N(CH(CH_3)_2)H)C_{10}H_6}$ (0.485 g, 2.0 mmol) in ether (ca. 30 mL) led to a color change to green, then brown with gas evolution. The mixture was stirred for 1 h and solid $\mathrm{GeCl_2{\cdot}dioxane}$ (0.466 g, 2.0 mmol) was then added. The reaction mixture quickly became orange in color and precipitate was formed. After 18 h of stirring the solvent was removed under vacuum and the product was extracted with hexane (ca. 50 mL). Filtration followed by removal of the volatiles yielded **1** (0.50 g, 80%). Compound **1** could be further purified by recrystallization from hexane or ether. ^{1}H NMR ($\mathrm{C_6D_{6,}}$): δ 7.25 (s, 2H, Ar−H), 7.22 (s, 2H, Ar−H), 6.33 (m, 2H, Ar−H), 3.81 (sept, 2H, $\mathrm{CH(Me)_2}$), 1.28 (d, 12H, $\mathrm{CH_3}$).^{13}C NMR ($\mathrm{C_6D_{6,}}$): 144.7 (Ar *C*), 138.6 (Ar *C*), 126.8 (Ar *C*H), 123.9 (Ar *C*), 119.4 (Ar *C*H), 104.5 (Ar *C*H), 51.0 (*C*HMe$_2$), 26.2 (*C*H$_3$). Anal. Calcd for $\mathrm{C_{16}H_{20}N_2Ge}$: C, 61.4; H, 6.44; N, 8.95. Found: C, 61.06; H, 6.78; N, 8.75. Mp 103−105 °C

Preparation of $\mathbf{Ge[1,8\text{-}(^{i}PrN)_2C_{10}H_6]}$ (1) from $\mathbf{Ge[N(SiMe_3)_2]_2}$ and $\mathbf{[1,8\text{-}(^{i}PrNH)_2C_{10}H_6]}$. In a 50-mL round-bottom flask equipped with a magnetic stir bar $\mathrm{Ge[N(SiMe_3)_2]_2}$ (0.316 g, 0.80 mmol) dissolved in 30 mL of hexane was added to a hexane solution of 1,8-diisopropyldiaminonaphthalene (0.195 g, 0.80 mmol). The color of the solution turned from purple to brownish with concomitant formation of precipitate. After being stirred for 18 h the reaction mixture was filtered. The hexane solution was then allowed to stand for one week. An NMR spectrum of the reaction mixture was prepared by removing an aliquot of the mixture, evaporating to dryness, and dissolving in $\mathrm{C_6D_6}$. This indicated that compound **1** along with a small amount of $\mathrm{HN(SiMe_3)_2}$ and unreacted 1,8-diisopropyldiaminonaphthalene were the only constituents. Further purification of **1** from this solution was troublesome due to the high solubility of both products in hexane.

Preparation of $\mathbf{\{[1,8\text{-}(^{i}PrN)_2C_{10}H_6]Ge(\mu\text{-}S)\}_2}$ (2). To a pale orange solution of **1** (0.117 g, 0.36 mmol) in ether (ca. 30 mL) was added solid S_8 (0.047 g, 0.18 mmol). The solution became pale yellow and some unreacted sulfur remained. After 18 h of stirring the reaction mixture was filtered and the solvent was removed under vacuum. The product was recrystallized from THF (0.040 g, 31%). ^{1}H NMR ($\mathrm{C_6D_{6,}}$): δ 7.26 (dd, 2H), 7.18 (t, 2H), 6.88 (dd, 2H), 4.90 (sept, 2H, $\mathrm{CH(Me)_2}$), 1.57 (d, 12H, $\mathrm{CH_3}$). ^{13}C NMR ($\mathrm{C_6D_{6,}}$): 143.0 (Ar *C*), 138.4 (Ar *C*), 126.2 (Ar *C*), 125.7 (Ar *C*H), 120.3 (Ar *C*H), 110.9 (Ar *C*H), 50.6 (*C*HMe$_2$), 20.9 (*C*H$_3$). Anal. Calcd for $\mathrm{C_{16}H_{20}N_2GeS}$: C, 55.70; H, 5.84; N, 8.11. Found: C, 55.85; H, 5.88; N, 8.16. Mp 228 °C dec.

Preparation of $\mathbf{\{[1,8\text{-}(^{i}PrN)_2C_{10}H_6]Ge(\mu\text{-}Se)\}_2}$ (3). In a Teflon-sealed NMR tube, **1** (0.020 g, 63 μmol) was dissolved in approximately 1 mL of $\mathrm{C_6D_6}$. To this pale orange solution was added an excess of solid Se (0.030 g). The solution turned slightly reddish and there remained some solid selenium in the tube. After 6 days the NMR spectra

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(27) Bazinet, P.; Richeson, D. S. Unpublished results.

showed complete conversion of the starting material to **3**. ^{1}H NMR (200 MHz, C_6D_6): δ 7.24 (dd, 2H), 7.19 (t, 2H), 6.87 (dd, 2H), 5.0 (sept, 2H), 1.62 (d, 12H). ^{13}C NMR (200 MHz, $C_6D_{6,}$): 125.7 (2 C), 120.0 (2 C), 110.3 (2 C), 50.9 (2 C), 20.7 (4 C). Mp 237 °C dec.

Preparation of $\{[1,8\text{-}(^i\text{PrN})_2\text{C}_{10}\text{H}_6]\text{Ge}\}_4\text{Ni}$ (4). In a 50-mL round-bottom flask equipped with a magnetic stir bar bis(cyclooctadiene)-nickel (0) (0.050 g, 0.18 mmol) was added to 15 mL of hexane. To the flask was added compound **1** (0.227 g, 0.73 mmol). The pale yellow/green solution rapidly turns orange then, gradually over a few minutes, to a deep burgundy. Precipitation of a red solid was observed after approximately 30 min. The reaction was stirred for an additional 16 h, and product is isolated by filtration (0.190 g, 0.145 mmol, 80%). The product can be further purified by crystallization out of THF at −35 °C. ^{1}H NMR (C_7D_8): δ 7.10 (br, 4H, Ar−H), 6.66 (dd, 2H, Ar−H), 5.17 (sept, 2H, $CH(Me)_2$), 1.41 (d, 12H, CH_3).^{13}C NMR (C_7D_8): 143.4 (Ar *C*), 139.0 (Ar *C*), 127.4 (Ar *C*), 125.8 (Ar *C*H), 120.3 (Ar *C*H), 109.5 (Ar *C*H), 51.5 (*C*HMe$_2$), 22.0 (*C*H$_3$). Anal. Calcd for $C_{64}H_{80}N_8Ge_4Ni$: C, 58.66; H, 6.15; N, 8.55. Found: C, 59.02; H, 5.98; N, 8.26. Mp 193 °C dec.

Structural Determinations for 1, 2, and 4. Single crystals were mounted on thin glass fibers with viscous oil and then cooled to the data collection temperature. Crystal data and details of the measurements are summarized in Table 1. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω-scans at 0, 90, and 180° in ϕ. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.

The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 5.1 program library.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada.

Supporting Information Available: Tables of crystal data structure solutions and refinements, atomic coordinates, bond lengths and angles, and anisoptropic thermal parameters for compounds **1**, **2**, and **4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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