

## A Neutral, Monomeric Germanium(I) Radical

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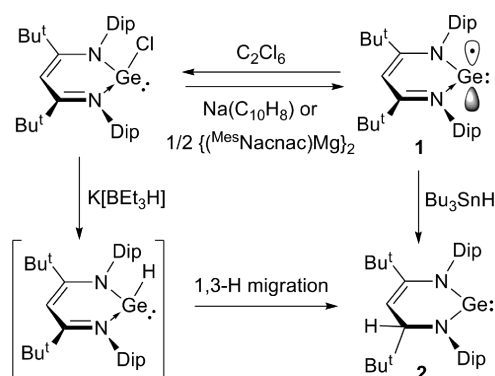
## Supporting Information

**ABSTRACT:** Stoichiometric reduction of the bulky  $\beta$ -diketiminato germanium(II) chloride complex  $[(^{\text{Bu}^t}\text{Nacnac})\text{GeCl}]$  ( $^{\text{Bu}^t}\text{Nacnac} = [\{\text{N}(\text{Dip})\text{C}(\text{Bu}^t)\}_2\text{CH}]^-$ ,  $\text{Dip} = \text{C}_6\text{H}_3\text{Pr}^{i-2,6}$ ) with either sodium naphthalenide or the magnesium(I) dimer  $[\{(^{\text{Mes}}\text{Nacnac})\text{Mg}\}_2]$  ( $^{\text{Mes}}\text{Nacnac} = [(\text{MesNCMe})_2\text{CH}]^-$ ,  $\text{Mes} = \text{mesityl}$ ) afforded the radical complex  $[(^{\text{Bu}^t}\text{Nacnac})\text{Ge}]^\bullet$  in moderate yields. X-ray crystallographic, EPR/ENDOR spectroscopic, computational, and reactivity studies revealed this to be the first authenticated monomeric, neutral germanium(I) radical.

Some of the most significant advances in p-block chemistry over the past decade have stemmed from the realization that the frontier electronic properties and reactivity of heavier main-group systems can resemble those of d-block complexes.<sup>1</sup> This has led, in part, to the recent rapid development of the chemistry of stable, heavier main-group radical complexes.<sup>2</sup> In view of the unquestioned importance of related “open-shell” transition-metal complexes in numerous areas of synthesis, catalysis, small-molecule activation, etc.,<sup>3</sup> it is clear that a greater understanding of p-block radicals would greatly benefit the progression of the emerging “transition-metal-like” reactivity of low oxidation state main-group compounds.

Although neutral heavier group-14 radicals are becoming well-established, a number of important challenges remain unfulfilled in this area. For example, while a variety of heavier “Gomberg”-type radicals  $[\text{E}^{\text{III}}\text{R}_3]^\bullet$  ( $\text{E} = \text{Si}, \text{Ge}, \text{Sn}$ ;  $\text{R} = \text{alkyl}, \text{aryl}, \text{silyl}, \text{amide}$ , etc.)<sup>2</sup> have been reported and shown to display interesting redox chemistry, no related neutral element(I) radicals  $[:\text{E}^{\text{I}}\text{R}]^\bullet$  have been isolated.<sup>4</sup> This is perhaps not surprising, as such species would be expected to be extremely susceptible to dimerization and other reactivity. Indeed, radicals of this type are the likely intermediates in the formation of a range of heavier alkyne analogues REER ( $\text{R} = \text{bulky terphenyl}, \text{amidinate}$  etc.) from the reduction of higher oxidation state precursors REX or  $\text{RSiCl}_3$  ( $\text{X} = \text{halide}, \text{H}$ ).<sup>5</sup> These reactive systems are fast becoming valuable reagents for the “transition-metal-like” activation of small molecules (e.g.,  $\text{H}_2$ ,  $\text{NH}_3$ ,  $\text{CO}$ ,  $\text{C}_2\text{H}_4$ , etc.).<sup>1,5</sup> In order to electronically and kinetically stabilize radicals of the type  $[:\text{E}^{\text{I}}\text{R}]^\bullet$ , we reasoned that utilizing ligands  $\text{R}$  that both chelate and provide

**Scheme 1. Syntheses of Compounds 1 and 2 (Byproducts Omitted; Dip =  $\text{C}_6\text{H}_3\text{Pr}^{i-2,6}$ )**



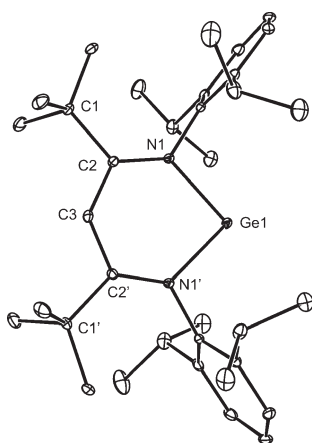
considerable steric shielding to E would be required. In this respect, we recently reported the potentially suitable precursor complexes  $[(^{\text{Bu}^t}\text{Nacnac})\text{ECl}]$  ( $\text{E} = \text{Ge}, \text{Sn}$ ;  $^{\text{Bu}^t}\text{Nacnac} = [\{\text{N}(\text{Dip})\text{C}(\text{Bu}^t)\}_2\text{CH}]^-$ ,  $\text{Dip} = \text{C}_6\text{H}_3\text{Pr}^{i-2,6}$ ),<sup>6</sup> which incorporate an extremely bulky  $\beta$ -diketiminato ligand. Initial attempts to reduce these complexes with excess elemental potassium or lithium did not yield element(I) compounds but instead gave rise to products derived from reductive ligand contraction reactions.<sup>6</sup> In contrast, employing stoichiometric amounts of soluble reducing agents in related reactions has allowed access to the first neutral, monomeric germanium(I) radical, which is described herein.

The reaction of  $[(^{\text{Bu}^t}\text{Nacnac})\text{GeCl}]$  with 1 equiv of sodium naphthalenide in THF or 0.5 equiv of the magnesium(I) dimer  $[\{(^{\text{Mes}}\text{Nacnac})\text{Mg}\}_2]$  ( $^{\text{Mes}}\text{Nacnac} = [(\text{MesNCMe})_2\text{CH}]^-$ ,  $\text{Mes} = \text{mesityl}$ )<sup>7</sup> in toluene afforded the extremely air-sensitive purple-red compound **1** in 36 or 38% yield, respectively, after recrystallization from hexane (Scheme 1).<sup>8</sup> Similar reduction reactions were carried out with the tin(II) complexes  $[(^{\text{Bu}^t}\text{Nacnac})\text{SnCl}]$  and  $[(^{\text{Bu}^t}\text{Nacnac})\text{Sn}(\text{O}_3\text{SCF}_3)]$ , but these led only to the deposition of tin metal and the formation of the known azabutadiene  $\text{DipN}=\text{C}(\text{Bu}^t)\text{C}(\text{H})=\text{C}(\text{H})\text{Bu}^t$ .<sup>9</sup>

Compound **1** is stable for months in the solid state at ambient temperature. Its molecular structure (Figure 1) reveals it to

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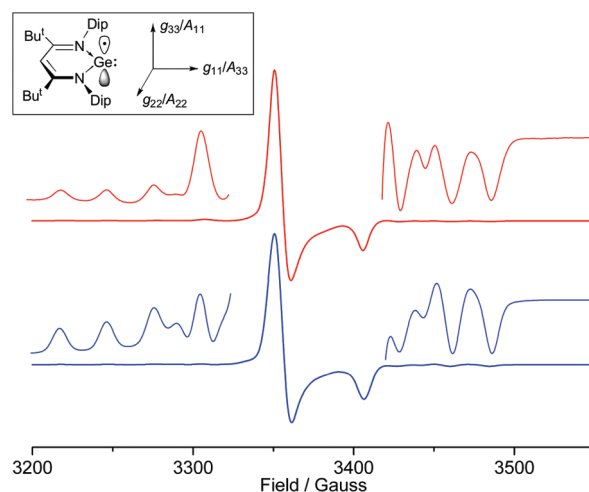
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**Figure 1.** Thermal ellipsoid plot (20% probability surface) of the molecular structure of  $[(\text{Bu}^t\text{Nacnac})\text{Ge}]^+$  (**1**). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): N1–Ge1, 1.9988(11); N1–C2, 1.3251(18); C2–C3, 1.4074(16); N1–Ge1–N1', 91.97(7); C2–N1–Ge1, 127.38(10); C2'–C3–C2, 131.73(19). Primes (') denote the symmetry operation  $-x, y, -z + 1/2$ .

possess a planar heterocyclic core and an apparently delocalized  $\text{NC}_3\text{N}$  ligand backbone. The N–Ge distances and N–Ge–N angle in the heterocycle are comparable to those in the precursor complex  $[(\text{Bu}^t\text{Nacnac})\text{GeCl}]$  (mean 1.988 Å and  $91.99(8)^\circ$ , respectively)<sup>6</sup> but greater and more acute, respectively, than those in the related two-coordinate cation  $[(\text{Dip}^t\text{Nacnac})\text{Ge}]^+$  ( $\text{Dip}^t\text{Nacnac} = [\text{N}(\text{Dip})\text{C}(\text{Me})_2\text{CH}]^+$ ) [1.894(2) Å;  $93.0(1)^\circ$ ].<sup>10</sup> It is clear that significant kinetic protection is provided to the Ge center in **1** by the flanking Dip groups, which is enhanced by their buttressing of the backbone *tert*-butyl substituents. There is no crystallographic evidence for the presence of a hydride ligand on Ge1.

In solution, compound **1** is not indefinitely stable at ambient temperature and gradually decomposes ( $t_{1/2} \approx 5$  h at  $20^\circ\text{C}$ )<sup>11</sup> to yield  $\text{DipN}=\text{C}(\text{Bu}^t)\text{C}(\text{H})=\text{C}(\text{H})\text{Bu}^t$  as the only product identifiable by  $^1\text{H}$  NMR spectroscopy.<sup>9</sup> The radical nature of **1** is evidenced by the fact that in  $\text{C}_6\text{D}_6$  solutions it is effectively NMR-silent. A simulation of its continuous-wave (CW) X-band EPR spectrum (Figure 2) showed it to have slightly rhombic symmetry with  $g_{11} = 1.968$ ,  $g_{22} = 1.997$ ,  $g_{33} = 2.001$ , and  $g_{\text{iso}} = 1.988$ , in excellent agreement with those predicted by theory (see below; Table 1). The spectrum is consistent with a one-electron  $\pi$ -based radical in that the “out-of-plane” component,  $g_{33}$ , is close to the free-spin value (2.0023). It is of note that hyperfine couplings (hfc's) to the  $^{73}\text{Ge}$  nucleus ( $I = 9/2$ , 7.8% abundance) were observed in the spectrum and satisfactorily simulated using the values  $A_{11} = \pm 82.5$  MHz,  $A_{22} = \pm 37.5$  MHz, and  $A_{33} = \pm 42.0$  MHz. The largest coupling gives rise to a decet of lines centered on  $g_{33}$ , as would be expected for a  $\pi$  radical. However, for a pure  $\pi$  radical, the other two couplings (centered on  $g_{11}$  and  $g_{22}$ ) should be very small. The magnitude of these couplings for **1** could imply some degree of spin delocalization onto the ligand. That said, although  $A_{\text{iso}}$  could not be experimentally determined for **1** because of the low resolution of its room-temperature EPR spectrum, the magnitudes of its  $^{73}\text{Ge}$  hfc's are on the same order as  $A_{\text{iso}}$  for other planar, monomeric Ge-centered  $\pi$  radicals (e.g.,  $[\text{Ge}\{\text{CH}(\text{SiMe}_3)_2\}_2]^+$ , 35 MHz;<sup>12</sup>  $[\text{Ge}(\text{SiMe}_2\text{Bu}^t)_3]^+$ , 56 MHz<sup>13</sup>) but considerably less than those observed for pyramidal radicals (e.g.,  $[\text{Ge}\{\text{N}(\text{SiMe}_3)_2\}_3]^+$ , 479 MHz<sup>14</sup>).



**Figure 2.** CW X-band EPR spectrum (80 K) of **1** (red = experimental, blue = simulation). The inset shows the axes and  $g/A$  labels used for the EPR/ENDOR discussion.

**Table 1.** Computed and Experimental hfc Tensors (top) and  $g$  tensors (bottom) for **1a** and **1**, respectively

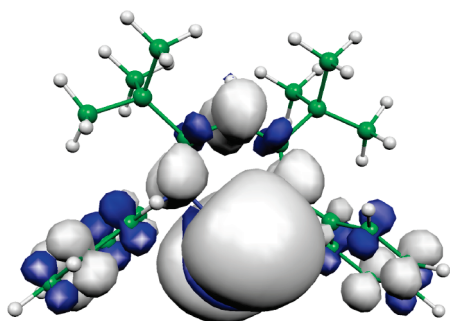
	hfc Tensor Components (MHz)			
	$^{73}\text{Ge}$			$^1\text{H}_{(\text{on C3})}$
	$A_{\text{iso}}$	$A_{11}, A_{22}, A_{33}$	$A_{\text{iso}}$	$A_{11}, A_{22}, A_{33}$
BHLYP	7.80	−71.2, 43.9, 50.7	−5.15	−8.43, −5.53, −1.48
exptl	—	$\pm 82.5, \pm 37.5, \pm 42.0$	−4.40	−6.80, −4.10, −2.30

	$g$ Tensor Components			
	$g_{\text{iso}}$	$g_{11}$	$g_{22}$	$g_{33}$
BHLYP	1.9850	1.9593	1.9928	2.0029
exptl	1.988	1.968	1.997	2.001

Davies and Mims pulsed ENDOR spectra of a frozen toluene solution of **1** were recorded at 10 K to ascertain the extent of spin delocalization onto the ligand (see Figure S5 in the Supporting Information). The largest  $^1\text{H}$  coupling ( $A_{11} = -6.8$  MHz,  $A_{22} = -4.1$  MHz,  $A_{33} = -2.3$  MHz;  $A_{\text{iso}} = -4.4$  MHz) was assigned to the ligand-backbone proton (i.e., that on C3 in the crystal structure), and its components compare well with those predicted by calculations on a model of **1** (see below; Table 1). For sake of comparison, these couplings are significantly smaller than hfc's to ligand-backbone protons reported for five-membered N-heterocyclic germanium radicals (e.g.,  $A_{\text{iso}} \approx 15$  MHz for  $\text{RGe}\{\text{N}(\text{Bu}^t)\text{C}(\text{H})\}_2$ , R = alkyl, silyl, etc.),<sup>15</sup> in which the spin density is largely delocalized over the unsaturated NCCN ligand fragment. Accordingly, it is apparent that the ligand spin delocalization in **1** is not well developed.

Although  $\beta$ -diketiminates have been widely employed to stabilize very low oxidation state metal centers from across the periodic table,<sup>5a,16</sup> evidence is beginning to emerge that they are not completely redox innocent ligands.<sup>17</sup> To assess the degree of spin delocalization (i.e., reduction) on the  $\text{Bu}^t\text{Nacnac}$  ligand in **1**, calculations were carried out on a model complex, **1a**, in which the isopropyl groups were replaced with hydrogen atoms. The optimized geometry of **1a** (RI-BP86/TZVP) was close to that of



**Figure 3.** Spin density distribution for the model system **1a** (BHYLP/IGLO-II; isosurface = 0.0005 au).

the experimental compound, but the Ge–N bond lengths were slightly overestimated (by  $\sim 2.6\%$ ). The optimized structure of **1a** was used for subsequent single-point calculations employing several different functionals with varying amounts of exact (Hartree–Fock) exchange admixture.

We found that calculations carried out with the hybrid BHYLP (50% exact exchange) functional in combination with an IGLO-II basis set for all atoms yielded the best agreement with the EPR/ENDOR experimental data (see Table 1). However, regardless of the functional used, the calculations indicated that the spin density on **1a** (Figure 3) is predominantly centered on Ge (BHYLP, 91.2%; B3LYP, 87.3%; BP86, 84.9%) with little delocalization on to the NCCCN backbone of the ligand. Moreover, the spin density at Ge clearly resembles that of a  $\pi$ -type radical involving a Ge  $4p_\pi$  orbital, which according to the calculations almost exclusively constitutes the  $\alpha$ -SOMO of the compound. Its HOMO and LUMO are ligand-based (see Figure S8), while the Ge lone pair is associated with HOMO–2 and has very high  $s$  character (91.2%), as determined by an analysis of the natural localized molecular orbitals (NLMOs). The full weight of the available crystallographic, spectroscopic, and theoretical evidence is compatible with the formulation of **1** as a neutral, monomeric germanium(I)  $\pi$  radical.

Consistent with the view of **1** as a Ge-centered radical is the result of its reaction with the mild chlorinating agent  $\text{C}_2\text{Cl}_6$  in benzene- $d_6$  at  $20^\circ\text{C}$  (Scheme 1). This led to essentially quantitative formation of the  $\text{Ge}^{\text{II}}$  precursor complex  $[(^{\text{Bu}^t}\text{Nacnac})\text{GeCl}]$  in less than 30 s (as determined by NMR spectroscopy). In light of this result, the reaction of **1** with the potential hydrogen source  $\text{Bu}^n_3\text{SnH}$  was carried out. Instead of the expected germanium(II) hydride product  $[(^{\text{Bu}^t}\text{Nacnac})\text{GeH}]$  (cf.  $[(^{\text{Dip}}\text{Nacnac})\text{GeH}]$ ),<sup>18</sup> the reaction afforded a mixture of compounds (including  $\text{Sn}_2\text{Bu}^n_6$ ) from which the novel cyclic diamidogermylene  $[(^{\text{Bu}^t}\text{NacnacH})\text{Ge}]$  (**2**) (Scheme 1) was isolated in low yield ( $<10\%$ ). Although the formation of **2** could suggest significant spin delocalization on the ligand of **1**, a subsequent attempt to prepare  $[(^{\text{Bu}^t}\text{Nacnac})\text{GeH}]$  via the reaction of  $[(^{\text{Bu}^t}\text{Nacnac})\text{GeCl}]$  with  $\text{K}[\text{BEt}_3\text{H}]$  (cf. the preparation of  $[(^{\text{Dip}}\text{Nacnac})\text{GeH}]$ ),<sup>18</sup> also gave **2** in 22% isolated yield with no evidence for the formation of  $[(^{\text{Bu}^t}\text{Nacnac})\text{GeH}]$ . This implies that  $[(^{\text{Bu}^t}\text{Nacnac})\text{GeH}]$  is an unstable intermediate in the reaction that rapidly undergoes a hydride migration reaction to form **2**. Notably, an almost identical process has been proposed for the rearrangement of unstable  $[(^{\text{Bu}^t}\text{Nacnac})\text{Sc}(\text{H})\text{Cl}]$  to  $[(^{\text{Bu}^t}\text{NacnacH})\text{ScCl}]$ , which is itself unstable and decomposes via C–N cleavage to give  $\text{DipN}=\text{C}(\text{Bu}^t)\text{C}(\text{H})=\text{C}(\text{H})\text{Bu}^t$ .<sup>9</sup> Similarly, **2** decomposes over 48 h in benzene solutions to give a high yield of the same azabutadiene ( $>70\%$ ) as the only identifiable

product. The apparent lower stability of  $[(^{\text{Bu}^t}\text{Nacnac})\text{GeH}]$  relative to its less hindered analogue  $[(^{\text{Dip}}\text{Nacnac})\text{GeH}]$  (decomp.  $170^\circ\text{C}$ )<sup>18</sup> is likely due to the greater steric bulk of the former, leading to greater distortion of its  $\text{GeN}_2\text{C}_3$  heterocycle from planarity and hence to significantly less electron delocalization within the chelate ring than is the case for the latter compound (cf.  $[(^{\text{Dip}}\text{Nacnac})\text{GeCl}]$ <sup>19</sup> vs  $[(^{\text{Bu}^t}\text{Nacnac})\text{GeCl}]$ <sup>6</sup>). This in turn would be expected to make the imine carbon center of  $[(^{\text{Bu}^t}\text{Nacnac})\text{GeH}]$  very susceptible to intramolecular nucleophilic attack from its hydride ligand. The X-ray crystallographic and spectroscopic data for **2** are fully consistent with its formulation as a localized, N-heterocyclic diamidogermylene (see the Supporting Information).

In summary, the stoichiometric reduction of a bulky  $\beta$ -diketiminato germanium(II) chloride complex has yielded a radical complex that crystallographic, spectroscopic, computational, and reactivity studies have shown to be a monomeric, neutral germanium(I) radical. We continue to explore the stabilization of very low oxidation state “open-shell” main-group complexes, with a view to developing their “transition-metal-like” reactivity.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Synthesis details and characterization data for **1**, **2**, and  $[(^{\text{Bu}^t}\text{Nacnac})\text{Sn}(\text{O}_3\text{SCF}_3)]$ ; full details and references for the EPR/ENDOR experiments and computational studies; ORTEP diagrams for **2**,  $[(^{\text{Bu}^t}\text{Nacnac})\text{Sn}(\text{O}_3\text{SCF}_3)]$ , and  $[\{\text{N}(\text{Mes})\text{C}(\text{Me})\text{C}(\text{H})\text{C}(\text{Me})\}\text{Ge}\{\text{N}(\text{Mes})\}\{[(^{\text{Mes}}\text{Nacnac})\text{Mg}]_2(\mu\text{-Cl})\}]$ ; and crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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