

N-Heterocyclic Germylidenide and Stannylidenide Anions: Group 14 Metal(II) Cyclopentadienide Analogues

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The reaction of a sterically bulky β -diketiminato lithium complex [Li(^{But}Nacnac)] (^{But}Nacnac = [{N(Dip)C(Bu^t)}₂CH]⁻, Dip = C₆H₃Prⁱ₂-2,6) with GeCl₂·dioxane has given the germanium(II) chloride complex [(^{But}Nacnac)GeCl] (**3**). Both it and its known tin analogue, [(^{But}Nacnac)SnCl] (**4**), were crystallographically characterized and found to be monomeric in the solid state. The reduction of both complexes with elemental lithium in THF led to lithium complexes of N-heterocyclic germylidenide and stannylidenide anions, viz., [(THF)Li{ η^5 -EC(Bu^t)C(H)C(Bu^t)N(Dip)}] (E = Ge, **5**; Sn, **6**). The reduction of the germanium(II) precursor, **3**, also afforded the germanium(II) amide complex [(^{But}Nacnac)Ge{N(H)(Dip)}] (**7**). The mechanisms of formation of the complexes are thought to involve a number of steps, including reductive ring contraction reactions. The crystallographic and spectroscopic data for [(THF)Li{ η^5 -EC(Bu^t)C(H)C(Bu^t)N(Dip)}] indicate a significant degree of aromatic π -delocalization within their heterocycles.

Introduction

Cyclopentadienides (Cp⁻) are aromatic 6π -electron ligands that have been utilized in the preparation of complexes with nearly every metal in the periodic table. The diverse array of applications that such complexes have found in the past 50 years (e.g., in catalysis, materials science, asymmetric synthesis) has led to their unquestionable importance to chemistry.¹ In more recent times, considerable efforts have been made to prepare analogues of Cp⁻ that incorporate the heavier group 14 elements, which could potentially be used as ligands in the formation of transition metal complexes. Considerable progress has been made in this direction with the preparation of structurally characterized examples of alkali metal salts of silole and germole anions and dianions.² Both experimental and theoretical evidence have shown the dianionc forms of these heterocycles, e.g., $[EC_4Ph_4]^{2-1}$ $(E = Si^3 \text{ or } Ge^4)$, to have considerable aromatic character.

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In contrast, the monoanions, e.g., $[{R_3Si}EC_4Me_4]^-$, display aromatic delocalization only when η^5 -coordinated to transition metal fragments.⁵ It was not until 2005 that considerable aromaticity in a crystallographically authenticated dianionic stannole complex, viz., $[(\mu-\eta^5-SnC_4Ph_4){Li(OEt_2)}_2]$, was demonstrated.^{6,7} Impressively, in 2010, a dianionic plumbole analogue of this system, $[Li(DME)_3][(DME)Li(\eta^5-PbC_4Ph_4)]$, was reported to contain the first example of an aromatic lead heterocycle.⁸

Although the intracyclic bonding in the above-mentioned aromatic dianionic heterocycles can be represented by significant contributions from resonance forms with tetrelene character,² they are best described as having tetravalent group 14 centers. To the best of our knowledge, the only known low-valent heavier group 14 element Cp^- analogue is found in the N-heterocyclic germylidenide complex 1 (Chart 1).

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This was reported by Driess et al. to result from the potassium reduction of the β -diketiminato germanium(II) chloride compound [(^{Dip}Nacnac)GeCI] (^{Dip}Nacnac = [{N(Dip)C(Me)}₂-CH]⁻, Dip = C₆H₃Prⁱ₂-2,6). The mechanism of its formation was suggested to involve several reductive processes including a ring contraction of the germanium heterocycle. Experimental spectroscopic and structural data for 1 implied it to be aromatic, a situation that was verified by the calculated negative nuclear independent chemical shift (NICS) values obtained for the heterocycle (NICS(1) = -7.4 ppm, NICS(2) = -7.7 ppm).⁹ In contrast, the KC₈ reduction of [(^{Dip}Nacnac)SnCI] has been reported to generate tin metal and small amounts of the homoleptic complex [Sn(^{Dip}Nacnac)₂] presumably via a disproportionation process.¹⁰

The reductions of $[(^{Dip}Nacnac)ECI](E = Ge \text{ or } Sn)$ can be compared to the potassium reductions of the closely related bulky guanidinato and amidinato germanium(II) chloride complexes [LGeCl] ($L = [{N(Dip)}_2CR]^-, R = NPr_2^i$ (Priso), Bu^t (Piso)). Dissimilar to the ring contraction reaction that gave 1, these afforded the germanium(I) dimers 2 via reductive coupling processes.^{11,12} Compounds **2** can be considered as intramolecularly base stabilized examples of digermynes, RGeGeR, the remarkable further chemistry of which is rapidly developing.¹³ Given that we have previously shown the coordinating and stabilizing properties of bulky guanidinates and amidinates to closely mimic those of β -diketiminates,¹⁴ we were motivated to prepare other examples of group 14 metal(I) dimers, but incorporating the latter ligands. It was reasoned that the use of β -diketiminates bulkier than DipNacnac might circumvent ring contraction and/or disproportionation reactions from occurring during the reduction of suitable metal(II) precursors. Although this proved not to be the case, the study has led to the first example of an N-heterocyclic stannylidenide anion and its germanium counterpart (cf. 1), both of which display characteristics of aromatic systems.



Figure 1. Thermal ellipsoid plot (25% probability surface) of the molecular structure of $[(^{But}Nacnac)GeCl]$ (3). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) for 3: Ge(1)–N(1) 1.9394(19), Ge(1)–N(2) 2.036(2), Ge(1)–Cl(1) 2.2942(8), N(1)–C(2) 1.374(3), N(2)–C(4) 1.328(3), C(2)–C(3) 1.368(4), C(3)–C(4) 1.432(3), N(1)–Ge(1)–N(2) 91.99(8), N(1)–Ge(1)–Cl(1) 95.39(6), N(2)–Ge(1)–Cl(1) 93.70(6). Selected bond lengths (Å) and angles (deg) for 4: Sn(1)–N(2) 2.136(3), Sn(1)–N(1) 2.223(3), Sn(1)–Cl(1) 2.4466(13), N(1)–C(2) 1.322(5), N(2)–C(4) 1.361(5), C(2)–C(3) 1.419(5), C(3)–C(4) 1.389(5), N(2)–Sn(1)–N(1) 87.60(12), N(2)–Sn(1)–Cl(1) 91.82(10), N(1)–Sn(1)–Cl(1) 92.55(9).

Results and Discussion

The β -diketiminate ligand that was chosen for this study was ^{But}/Nacnac ([{N(Dip)C(Bu^t)}₂CH]⁻), which has previously been shown to be substantially more sterically imposing toward N,N'-chelated metal centers than ^{Dip}Nacnac.¹⁵ The monomeric germanium(II) precursor complex [(^{But}/Nacnac)GeCl] (**3**) was prepared in good yield by the reaction of *in situ* generated [Li(^{But}/Nacnac)] with GeCl₂·dioxane in diethyl ether.¹⁶ A variation of the literature procedure¹⁷ was used to synthesize its tin(II) analogue, [(^{But}/Nacnac)SnCl] (**4**). Attempts to prepare the lead counterpart of **3** and **4** by reaction of [Li(^{But}/Nacnac)] with PbCl₂ were not successful and afforded no identifiable products.¹⁸ Similarly, the reaction of [Li(^{But}/Nacnac)] with one equivalent of SiBr₄ in the presence of tmeda did not give the intended product, [(^{But}/Nacnac)SiBr₃],¹⁹ but instead yielded

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a complex mixture of products, from which a few crystals of the unusual lithium β -diketiminate adduct complex [(^{Bu}/Nacnac)Li{BrLi(tmeda)}₂] were isolated (see Supporting Information).

The spectroscopic data for 3 are comparable with those for the known tin complex 4.¹⁷ Both complexes were crystallographically characterized, and the molecular structure of 3 can be found in Figure 1 (see Supporting Information for the ORTEP diagram of 4). The compounds are isostructural with each other and have similar geometries to the previously reported systems [$(^{Dip}Nacnac)ECI$] (E = Ge or Sn).¹⁰ However, the bond lengths within the NC₃N backbones of 3 and 4 suggest a significantly reduced level of electronic delocalization than in [(^{Dip}Nacnac)ECl]. This undoubtedly results from a considerably greater distortion of the ligand backbones from planarity in the more hindered compounds. An indication of the increased steric protection afforded by the metal centers in the bulkier systems 3 and 4 can be gauged by comparing the CNC angles in those compounds (3, 124.3° mean; 4, 124.9° mean) with the same angles in [(^{Dip}Nacnac)GeCl] (120.5° mean) and [(^{Dip}Nacnac)SnCl] (121.8° mean).¹⁰

Early attempts to reduce 3 and 4 with elemental potassium were not encouraging, as they yielded intractable product mixtures. As a result, attention was turned to the milder reductant lithium, which was reacted with the two precursors in THF to give moderate to high yields of yellow 5 and deep green 6 (Scheme 1). A moderate yield of the orange germanium(II) amide complex 7 was also isolated from the reaction that afforded 5. The analogous tin amide, 8, could not be crystallized from the mixture that gave 6, though an ¹H NMR spectroscopic analysis of that mixture was consistent with its presence. It is notable that the previously reported reduction of [(DipNacnac)GeCl] generated significant quantities of a complex analogous to 7, viz., [(^{Dip}Nacnac)Ge{N(H)(Dip)}].⁹ Therefore, it is apparent that the mechanisms of formation of 5, and by implication 6, are similar to that for 1. We suggest these involve transient lithium germylidenide or stannylidenide salts, 9, which undergo ring contraction reactions to give the amide complexes, 10. These then undergo salt elimination reactions with either 3 or 4 to give 11, which are further reduced, yielding the isolated complexes 5 and 6 and the transient lithium amide complexes 12. The latter could participate in solvent hydrogen abstraction reactions, yielding 7 and 8. It is noteworthy that several closely related reductive ring contraction reactions have been documented as arising from the



Figure 2. Thermal ellipsoid plot (25% probability surface) of the molecular structure of $[(\text{THF})\text{Li}\{\eta^5-\text{SnC}(\text{Bu}^{t})\text{C}(\text{H})\text{C}-(\text{Bu}^{t})\text{N}(\text{Dip})\}]$ (6); hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) for 6: Sn(1)–C(4) 2.0981(19), Sn(1)–N(1) 2.1907(16), N(1)–C(2) 1.400(2), C-(2)–C(3) 1.394(3), C(3)–C(4) 1.415(3), Sn(1)–Li(1) 2.759(4), N(1)–Li(1) 2.208(4), C(2)–Li(1) 2.184(4), C(3)–Li(1) 2.175(4), C(4)–Li(1) 2.316(4), O(1)–Li(1) 1.866(4), C(4)–Sn(1)–N(1) 77.12(7). Selected bond lengths (Å) and angles (deg) for 5: Ge(1)–C(4) 1.896(2), Ge(1)–N(1) 1.9660(16), N(1)–C(2) 1.404(2), C(2)–C(3) 1.387(3), C(3)–C(4) 1.421(3), Ge(1)–Li(1) 2.596(4), N(1)–Li(1) 2.215(4), C(2)–Li(1) 2.225(4), C(3)–Li(1) 2.204(4), C(4)–Li(1) 2.303(4), C(4)–Ge(1)–N(1) 83.13(8).

alkali metal reduction of, for example, $[(^{But}Nacnac)TiCl_2]^{20}$ or $[(^{But}Nacnac)ZrCl_3]$.²¹ Although **5** is stable in solution and the solid state for long periods under an inert atmosphere, its tin counterpart decomposes over several hours in solution at ambient temperature, depositing tin metal. This process generates, among other products, significant amounts of the enamine (Dip)N=C(Bu^t)C(H)=C(H)(Bu^t).²² In addition, **6** also slowly decomposes in the solid state at 20 °C and should, therefore, be stored in the freezer.

Both compounds 5 and 6 were crystallographically characterized and found to be isostructural monomers (cf. dimeric 1). As a result, only the molecular structure of 6 is depicted in Figure 2 (see Supporting Information for the ORTEP diagram of 5). In both 5 and 6, the Li(THF) fragment is coordinated to an essentially planar heterocycle in an η^{5} -fashion with Li–Ge and Li–Sn distances that are slightly shorter than in the aromatic dianionic tetrelole complexes $[(\mu - \eta^5 - \text{GeC}_4\text{Ph}_4) \{\text{Li}(\text{dioxane})_2\}_2] (2.70 \text{ Å mean})^{4b}$ and $[(\mu - \eta^5 - \text{SnC}_4 \text{Ph}_4) \{ \text{Li}(\text{OEt}_2) \}_2]$ (2.76 Å mean),⁶ respectively. Likewise, the Li–C distances in 5 and 6 are of the same order as those in the dianionic complexes (2.28-2.43 A and 2.19–2.41 Å, respectively). The intracyclic bond lengths for 5 are close to those reported for 1 (Ge-N 1.944(2) Å, Ge-C 1.887(2) Å, N-C 1.382(3) Å, C-C 1.371(3) and 1.411(3) Å)⁹ and, thus, are strongly suggestive of appreciable π -resonance stabilization within the heterocycle. Although

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Figure 3. Thermal ellipsoid plot (25% probability surface) of the molecular structure of $[(^{But}Nacnac)Ge\{N(H)(Dip)\}]$ (7); hydrogen atoms (except H(3)) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)–N(3) 1.9097(12), Ge(1)–N(1) 1.9963(11), Ge(1)–N(2) 2.0377(11), N(1)–C(2) 1.3603(17), N(2)–C(4) 1.3173(17), C(2)–C(3) 1.3755(19), C(3)–C(4) 1.4300(19), N(3)–Ge(1)–N(1) 99.31(5), N(3)–Ge(1)–N(2) 98.60(5), N(1)–Ge(1)–N(2) 92.18(4).

there are no stannylidenide anions to compare with that in 6, the magnitude of the bond lengths within the NC₃ fragment of the stannacycle implies a similar level of delocalization to that in 1 and 5. Consistent with this is the Sn-C distance of the compound, which is considerably shorter than those in the aromatic stannole dianion $[(\mu - \eta^5 - \text{SnC}_4\text{Ph}_4)\{\text{Li}(\text{OEt}_2)\}_2]$ (2.16 Å mean)⁶ and the tetravalent precursor to this complex, $[Ph_2SnC_4Ph_4]$ (2.13 Å mean).²³ Slightly at odds with the proposed delocalization over the stannacycle is its Sn-N separation, which is comparable with those in 4, but longer than such bonds in neutral N-heterocyclic stannylenes (known range 2.051-2.189 Å).²⁴ That said, the tin centers in those heterocycles have a lower coordination number than that in 6. Moreover, the Sn-N distance in 6 is considerably shorter than those between localized imine fragments and divalent Sn atoms, e.g., 2.278 Å in [{(SiMe₃)₂N}Sn{ κ^2 -N, $N'-N(Bu^{t})=C(H)C(H)_{2}N(Bu^{t})]^{25}$

The molecular structure of 7 is portrayed in Figure 3 and is essentially isostructural to $[(^{Dip}Nacnac)Ge\{N(H)(Dip)\}],^9$ with a puckered heterocycle that is reminiscent of the heterocycle in 3. As was the case for $[(^{Dip}Nacnac)Ge\{N(H)(Dip)\}]$, the exocyclic Ge–N distance in 7 is significantly shorter than both of its endocyclic interactions. The acuteness of the angles about the germanium(II) center (93.4° mean) of the complex indicates a high degree of s-character to its lone pair.

The solution-state ¹H and ¹³C NMR spectra of 7 signify that it retains its solid-state structure in solution. Contrastingly, the NMR data for 5 and 6 correspond to the compounds possessing C_s symmetry in solution. It seems plausible that this is a result of an intermolecular exchange and/or intramolecular migration of their Li(THF) fragments, which is rapid on the NMR time scale. Cooling d_8 toluene solutions of each compound to $-30 \,^{\circ}\text{C}$ (i.e., close to their solubility limits) did not result in resolution of their spectra. Consistent with the proposed π -delocalization within the heterocycles are the signals for their backbone protons, which appear at δ 7.08 ppm (5) and δ 7.78 ppm (6), i.e., considerably downfield from the corresponding signals in the precursor molecules **3** (δ 6.41 ppm) and **4** (δ 6.14 ppm).¹⁷ Furthermore, the downfield chemical shifts of the α -carbon centers of the anions (5, δ 194.7 ppm; 6, δ 226.9 ppm) are not dissimilar to those normally observed for germole and stannole dianions.^{2,4,6,7} Perhaps, more illuminating are the high-field resonances observed in the ⁷Li NMR spectra of 5 $(\delta - 5.31 \text{ ppm})$ and **6** $(\delta - 4.66 \text{ ppm})$. These are at comparable chemical shifts to those reported for germole and stannole dianionic complexes (e.g., δ –4.36 ppm for [(μ - η ⁵-SnC₄Ph₄)- ${\rm Li(OEt_2)}_2$].⁶ The high-field positions of the signals for such complexes are thought to arise from strong shielding of their lithium centers by diatropic ring currents above and below the aromatic 6π -electron heterocycles.²⁶ Delocalization of the π -system within the stannacycle of **6** is also indicated by the remarkable downfield chemical shift of the signal in its ¹¹⁹Sn NMR spectrum (δ 524.2 ppm). This lies more than 770 ppm to lower field than the signal for the precursor complex, 4 (δ -252.0 ppm),¹⁷ and is markedly downfield of resonances reported for isoelectronic stannole dianions (e.g., $[(\mu - \eta^5 - \text{SnC}_4\text{Ph}_4) \{\text{Li}(\text{OEt}_2)\}_2], \delta 163.3 \text{ ppm})^6$ and neutral N-heterocyclic stannylenes (e.g., [:Sn{N(Mes)C-(H)}₂] (Mes=mesityl), δ 259 ppm).²⁷ That said, such comparisons should be treated with some caution, as ¹¹⁹Sn NMR chemical shifts for tin(II) compounds are very sensitive to the coordination number of the metal and the nature of the atoms bonded to it. Indeed, they can range over more than 2000 ppm.²⁸ What is clear, however, is that there is a significant delocalization of the negative charge on the heterocycle in 6 away from the tin atom.

Conclusions

In summary, germanium(II) and tin(II) chloride complexes incorporating a very bulky β -diketiminate ligand have been prepared and structurally characterized. Their reduction with elemental lithium has afforded anionic N-heterocyclic germylidenide and stannylidenide complexes, the latter of which has no precedent in the literature. The X-ray crystallographic and spectroscopic data for these compounds indicate significant aromatic π -delocalization over their heterocycles. Accordingly, the systems can be viewed as group 14 metal(II) cyclopentadienide analogues. Work is ongoing in our groups to explore the possibility of using the complexes as transfer reagents in the formation of novel d-block metal sandwich and half-sandwich complexes.

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Table 1. Summary of	f Crystallographic Da	ta for Compounds 3–7
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	3	4	5	6	7
empirical formula	C ₃₅ H ₅₃ ClGeN ₂	C35H53ClN2Sn	C ₂₇ H ₄₄ GeLiNO	C27H44LiNOSn	C47H71GeN3
fw	609.83	655.93	478.16	524.26	750.66
cryst syst	monoclinic	monoclinic	triclinic	triclinic	orthorhombic
space group	$P2_1/n$	$P2_1/n$	$P\overline{1}$	$P\overline{1}$	Pbca
a (Å)	12.625(3)	12.5810(6)	9.3348(3)	9.4259(2)	14.437(3)
$b(\mathbf{A})$	18.369(4)	18.6731(7)	10.7638(3)	9.9475(3)	20.288(4)
c(A)	15.562(3)	15.7415(6)	14.9412(5)	15.6200(4)	29.679(6)
α (deg)	90	90	92.791(2)	78.139(2)	90
β (deg)	110.27(3)	111.903(5)	107.011(3)	78.782(2)	90
γ (deg)	90	90	108.743(3)	75.844(2)	90
vol (Å ³)	3385.5(12)	3431.2(2)	1342.46(7)	1373.64(6)	8693(3)
Ζ	4	4	2	2	8
ρ (calcd) (g cm ⁻³)	1.196	1.270	1.183	1.268	1.147
$\mu (\text{mm}^{-1})$	1.008	0.847	1.158	0.947	0.738
<i>F</i> (000)	1304	1376	512	548	3248
cryst size (mm)	$0.25 \times 0.20 \times 0.15$	$0.25 \times 0.20 \times 0.12$	$0.20 \times 0.15 \times 0.10$	$0.20 \times 0.20 \times 0.10$	0.50 imes 0.45 imes 0.30
θ range (deg)	2.94 to 25.34	2.90 to 25.24	3.11 to 26.99	3.15 to 27.00	3.00 to 28.00
reflns collected	11 442	32 845	12920	14847	20 008
R _{int}	0.0449	0.1005	0.0276	0.0171	0.0215
unique reflns	6079	6190	5827	5974	10470
goodness of fit	1.014	1.050	0.990	1.068	1.023
temp (K)	150(2)	173(2)	173(2)	173(2)	123(2)
R1 indices $[I > 2\sigma(I)]$	0.0386	0.0580	0.0368	0.0271	0.0306
wR2 indices (all data)	0.0858	0.0778	0.0818	0.0661	0.0774

Experimental Section

General Methods. All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of high-purity dinitrogen or argon. THF and hexane were distilled over potassium, while diethyl ether was distilled over Na/K alloy. ¹H and ¹³C{¹H} NMR spectra were recorded on either Bruker DXP300 or DPX400 spectrometers and were referenced to the resonances of the solvent used. $^{7}Li{^{1}H}$ and 119 Sn{ 1 H} NMR spectra were recorded on a Bruker Avance 400 spectrometer and were referenced to external 1 M aqueous LiCl and SnMe₄, respectively. Mass spectra were obtained from the EPSRC National Mass Spectrometric Service at Swansea University. IR spectra were recorded using a Nicolet 510 FT-IR spectrometer as Nujol mulls between NaCl plates. Microanalyses were carried out by Campbell Microanalytical, Ottago. A reproducible microanalyses could not be obtained for 6 due to its thermal instability at ambient temperature in the solid state. Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected. The compounds ^{But}NacnacH²⁹ and [(^{But}Nacnac)SnCl]¹⁷ were prepared by variations of literature procedures. All other reagents were used as received.

Preparation of [(^{Bur}Nacnac)GeCI] (3). A solution of 1.6 M BuⁿLi in hexane (0.63 mL, 1.0 mmol) was added to a solution of ^{Bur}NacnacH (0.50 g, 1.0 mmol) in diethyl ether (15 mL) at -80 °C over 5 min. The solution was warmed to ambient temperature and stirred for 2 h, after which time it was cooled to -80 °C and a suspension of GeCl₂·dioxane (0.23 g, 1.0 mmol) in diethyl ether (15 mL) at -80 °C was added to it. The reaction mixture was warmed to room temperature and stirred for 2 h, where-upon volatiles were removed *in vacuo*. The residue was extracted into hexane (40 mL), and the extract filtered and stored at -30 °C overnight to yield yellow crystals of **3** (0.37 g, 61%): mp 231–233 °C; ¹H NMR (300 MHz, C₆D₆, 298 K) δ 1.05 (d, ³J_{HH} = 6.9 Hz, 6 H, CH(CH₃)₂), 1.11 (s, 18 H, C(CH₃)₃), 1.17 (d, ³J_{HH} = 6.9 Hz, 6 H, CH(CH₃)₂), 1.30 (d, ³J_{HH} = 6.9 Hz, 6 H, CH(CH₃)₂), 4.05 (sept, ³J_{HH} = 6.9 Hz, 2 H, CH(CH₃)₂), 4.05 (sept, ³J_{HH} = 6.9 Hz, 2 H, CH(CH₃)₂), 6.41 (s, 1 H, NCCHCN); ¹³C NMR (75 MHz, C₆D₆, 298 K) δ 24.3, 24.5, 26.3, 28.3 (CH(CH₃)₂), 28.4, 28.5 (CH(CH₃)₂), 31.9 (C(CH₃)₃), 41.9 (C(CH₃)₃), 105.6 (NCCCN),

123.9, 125.1, 127.3, 141.6, 144.5, 146.3 (Ar-C), 173.2 (CBu^t); IR ν/cm^{-1} (Nujol) 1548w, 1378s, 1359m, 1312m, 1260m, 1130m, 1098m, 798m, 785m; MS (EI 70 eV), m/z (%) 610.3 (M⁺, 25), 575.3 (M⁺ - Cl, 15), 244.1 (DipNCCBu^tH⁺, 100). Anal. Calcd for C₃₅H₅₃ClGeN₂: C 68.93, H 8.76, N 4.59. Found: C 68.94, H 8.63, N 4.61.

Preparation of $[(THF)Li\{\eta^5-GeC(Bu^t)C(H)C(Bu^t)N(Dip)\}]$ (5) and [(^{But}Nacnac)Ge{N(H)(Dip)}] (7). To a slurry of lithium powder (40 mg, 5.7 mmol) in THF (40 mL) at -80 °C was added a solution of 3 (0.15 g, 0.25 mmol) in THF (40 mL) over 5 min. The mixture was warmed to 20 °C and stirred overnight. All volatiles were subsequently removed in vacuo, and the residue was extracted into hexane (15 mL). The extract was filtered and stored at -30 °C overnight to yield yellow crystals of 5 (0.05 g, 83%). The mother liquor was concentrated to ca. 7 mL and stored at -30 °C overnight to yield orange crystals of 7 (0.035 g. 37%). Data for **5**: mp 137–139 °C; ¹H NMR (300 MHz, C_6D_6 , 298 K) δ 1.20 (d, ${}^{3}J_{\text{HH}} = 6.9$ Hz, 6 H, CH(CH₃)₂), 1.23 (br m, 4 H, THF-CH₂), 1.26 (s, 9 H, NCC(CH₃)₃), 1.48 (d, ${}^{3}J_{\text{HH}} = 6.9$ Hz, 6 H, CH(CH₃)₂), 1.65 (s, 9 H, GeCC(CH₃)₃), 2.64 (sept, ${}^{3}J_{\text{HH}} = 6.9 \text{ Hz}, 2 \text{ H}, CH(CH_{3})_{2}), 3.37 \text{ (br m, 4 H, THF-OCH}_{2}),$ 7.08 (s, 1 H, NCCH), 7.12–7.34 (m, 3 H, Ar-H); ¹³C{¹H} NMR (75 MHz, C₆D₆, 300 K) δ 22.6 (CH(CH₃)₂), 23.0 (CH(CH₃)₂), 25.3 (THF-CH₂), 28.5 (CH(CH₃)₂), 33.2 (NCC(CH₃)₃), 35.1 (GeCC(CH₃)₃), 37.4 (NCC(CH₃)₃), 37.8 (GeCC(CH₃)₃), 68.7 (THF-OCH₂), 112.5 (NCCH), 123.1, 125.8, 132.0, 146.4 (Ar-C), 147.5 (NCC), 194.7 (GeCC); ⁷Li{¹H} NMR (155.4 MHz, C₆D₆, 300 K) δ -5.31; IR ν/cm^{-1} (Nujol) 1664w, 1546w, 1466 m, 1245s, 1190m, 1135m, 985m, 801m, 758m, 719w; MS (EI 70 eV), m/z (%) 328.3 (DipNC(Bu^t)C(H)C(Bu^t)H⁺, 10), 270.2 (DipNC(Bu^t)C(H)CH⁺, 100). Anal. Calcd for C₂₇H₄₄GeLiNO: C 67.82, H 9.27, N 2.93. Found: C 67.61, H 9.01, N 2.86. Data for 7: mp 155–160 °C (dec); ¹H NMR (300 MHz, C₆D₆, 298 K) δ 1.01, 1.13, 1.20, 1.22, 1.23, 1.33 (6*d*, ${}^{3}J_{\text{HH}} = 6.9$ Hz, 36 H, CH(CH₃)₂), 1.13 (s, 18 H, C(CH₃)₃), 2.83 (sept, ${}^{3}J_{HH} = 6.9$ Hz, 1 H, $CH(CH_3)_2$), 3.18 (sept, ${}^{3}J_{HH} = 6.9$ Hz, 2 H, $CH(CH_3)_2$), 3.24 (sept, ${}^{3}J_{HH} = 6.9$ Hz, 2 H, CH(CH₃)₂), 3.24 (sept, ${}^{3}J_{HH} = 6.9$ Hz, 1 H, $CH(CH_3)_2$), 4.85 (s, 1 H, NH), 6.15 (s, 1 H, NCCHCN), 6.86–7.13 (m, 9 H, Ar-H); ¹³C{¹H} NMR (75 MHz, C₆D₆, 300 K) δ 23.1, 23.9, 25.2, 26.6, 26.8, 27.4 (6 × CH(CH₃)₂), 28.6, 28.7, 28.8, 29.1 (4 × $CH(CH_3)_2$), 32.3 (C(CH_3)₃), 42.5 ($C(CH_3)_3$), 101.3 (NCCCN), 117.8, 121.8, 124.1, 124.7, 125.6, 126.8, 135.2, 137.5, 143.4, 144.1, 145.7, 146.0 (Ar-*C*), 174.1 (*C*Bu^t); IR *v*/cm⁻¹

⁽²⁹⁾ Budzelaar, P. H. M.; van Oort, A. B.; Orpen, A. G. Eur. J. Inorg. Chem. 1998, 1485.

(Nujol) 1547m, 1489m, 1388m, 1362m, 1260s, 1155m, 1129m, 800m, 782m, 750m; MS (EI 70 eV), m/z (%) 751.5 (M⁺, 3), 575.3 (M⁺ – DipNH, 100). Anal. Calcd for C₄₇H₇₁GeN₃: C 75.20, H 9.53, N 5.60. Found: C 74.89, H 9.32, N 5.41.

N.B. The quoted yields of **5** and **7** assume the mechanism proposed for their formation (see Scheme 1) is in operation.

Preparation of $[(THF)Li\{\eta^5-SnC(Bu^t)C(H)C(Bu^t)N(Dip)\}]$ (6). To a slurry of lithium powder (40 mg, 5.7 mmol) in THF (30 mL) at $-80 \text{ }^{\circ}\text{C}$ was added a solution of 4 (0.15 g, 0.23 mmol)in THF (30 mL) over 5 min. The mixture was warmed to 0 °C and stirred for 6 h, yielding a deep red solution. All volatiles were subsequently removed in vacuo, and the deep green residue was extracted into hexane (15 mL). The extract was filtered and stored at -30 °C overnight to yield deep green crystals of 6 (0.04 g, 52%): mp 137–139 °C; ¹H NMR (300 MHz, C₆D₆, 298 K) δ $1.25 (d, {}^{3}J_{HH} = 6.9 Hz, 6 H, CH(CH_{3})_{2}), 1.23 (br m, 4 H, THF CH_2$), 1.27 (s, 9 H, NCC(CH_3)₃), 1.46 (d, ${}^{3}J_{HH} = 6.9$ Hz, 6 H, $CH(CH_3)_2$, 1.58 (s, 9 H, SnCC(CH₃)₃), 2.77 (sept, ${}^{3}J_{HH} = 6.9$ Hz, 2 H, C*H*(CH₃)₂), 3.40 (br m, 4 H, THF-OCH₂), 7.16–7.33 (m, 3 H, Ar-*H*), 7.78 (s, 1 H, NCC*H*); ¹³C{¹H} NMR (75 MHz, C₆D₆, 300 K) δ 23.0 (CH(CH₃)₂), 23.4 (CH(CH₃)₂), 25.2 (THF-CH₂), 28.6 (CH(CH₃)₂), 33.4 (NCC(CH₃)₃), 35.1 (SnCC(CH₃)₃), 39.6 (NCC(CH₃)₃), 40.2 (SnCC(CH₃)₃), 67.9 (THF-OCH₂), 116.6 (NCCH), 122.7, 124.7, 131.6, 147.7 (Ar-C), 156.6 (NCC), 226.9 (Sn*CC*); ⁷Li{¹H} NMR (155.4 MHz, C₆D₆, 300 K) δ –4.66; ¹¹⁹Sn{¹H} NMR (149.1 MHz, C₆D₆, 300 K) δ 524.2 (p.w. at 1/2 height = 44 Hz); IR ν /cm⁻¹ (Nujol) 1663w, 1546w, 1464m, 1245s, 1191m, 1136m, 985m, 804m, 757m; MS (EI 70 eV), m/z (%) 328.3 (DipNC(Bu^t)C(H)C(Bu^t)H⁺, 20), 178.1 (DipNH₂⁺, 100).

N.B. The quoted yield of **6** assumes the mechanism proposed for its formation (see Scheme 1) is in operation.

(30) Sheldrick, G. M. SHELX-97; University of Göttingen, 1997.

X-ray Crystallography. Crystals of 3–7, [(^{Bu}/Nacnac)Li(OEt₂)], and [(^{Bu}/Nacnac)Li{BrLi(tmeda)}₂] suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using a Nonius Kappa CCD diffractometer using a graphite monochromator with Mo K α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined on F^2 by full matrix least-squares (SHELX97³⁰) using all unique data. All non-hydrogen atoms are anisotropic with hydrogen atoms (except the amino proton of 7) included in calculated positions (riding model). Crystal data and details of data collections and refinement are given in Table 1. CCDC numbers: 7811154– 7811160.

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Supporting Information Available: Crystallographic data as CIF files for 3–7, [(^{But}Nacnac)Li(OEt₂)], and [(^{But}Nacnac)Li{BrLi(tmeda)}₂]; ORTEP diagrams for 4, 5, [(^{But}Nacnac)Li(OEt₂)], and [(^{But}Nacnac)Li{BrLi(tmeda)}₂]; details of the crystallographic experiments and selected metrical parameters for [(^{But}Nacnac)Li(OEt₂)] and [(^{But}Nacnac)Li{BrLi(tmeda)}₂]. This material is available free of charge via the Internet at http:// pubs.acs.org.