

Preparation, Characterization, and Theoretical Analysis of Group 14 Element(I) Dimers: A Case Study of Magnesium(I) Compounds as Reducing Agents in Inorganic Synthesis

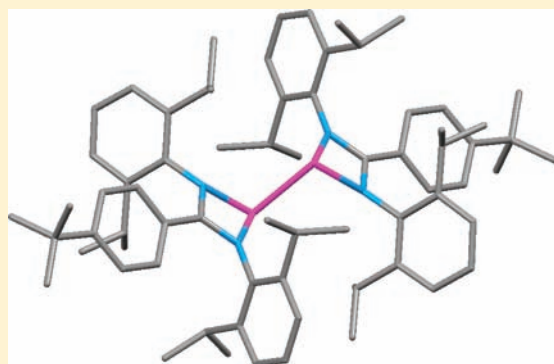
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S Supporting Information

ABSTRACT: A synthetic route to the new amidine (DipNH)(DipN)-C(C₆H₄Bu^t-4) (ButisoH; Dip = C₆H₃Prⁱ-2,6) has been developed. Its deprotonation with either LiBuⁿ or KN(SiMe₃)₂ yields the amidinate complexes [M(Butiso)] (M = Li or K). Their reactions with group 14 element halides/pseudohalides afford the heteroleptic group 14 complexes [(Butiso)SiCl₃], [(Butiso)ECl] (E = Ge or Sn), and [{"(Butiso)-Pb(μ-O₃SCF₃)(THF)}_∞], all of which have been crystallographically characterized. In addition, the synthesis and spectroscopic characterization of the homoleptic complex [Pb(Butiso)₂] is reported. Reductions of the heteroleptic complexes with a soluble magnesium(I) dimer, [{"^{Mes}Nacnac}Mg]₂ (^{Mes}Nacnac = [(MesNCMe)₂CH]⁻; Mes = mesityl), have given moderate-to-high yields of the group 14 element(I) dimers [{"(Butiso)E}₂] (E = Si, Ge, or Sn), the X-ray crystallographic studies of which reveal trans-bent structures. The corresponding lead(I) complex could not be prepared. Comprehensive spectroscopic and theoretical analyses of [{"(Butiso)E}₂] have allowed their properties to be compared. All complexes possess E–E single bonds and can be considered as intramolecularly base-stabilized examples of ditetrelynes, REER. Taken as a whole, this study highlights the synthetic utility of soluble and easy to prepare magnesium(I) dimers as valuable alternatives to the harsh, and often insoluble, alkali-metal reducing agents that are currently widely employed in the synthesis of low-oxidation-state organometallic/inorganic complexes.



INTRODUCTION

In 2007, the syntheses of the first room-temperature-stable magnesium(I) complexes [LMgMgL] (L = [(DipN)₂CNPrⁱ]₂⁻, Priso⁻, or [(DipNCMe)₂CH]⁻, ^{Dip}Nacnac⁻; Dip = C₆H₃Prⁱ-2,6), were reported.¹ Since that time, a variety of related dimers have been forthcoming, and their further chemistry has begun to develop.^{2–4} This work has revealed that perhaps the greatest application potential that these “bottleable” magnesium(I) species hold is as selective reducing agents for organic and organometallic synthesis.^{2,3} In this respect, they possess a number of properties that can make them appealing alternatives to the “traditional” reducing agents (e.g., alkali metals, magnesium, KC₈, SmI₂, etc.) that are widely employed by synthetic chemists. For example, they are very thermally stable (decomposition > 300 °C in some cases), are only moderately air- and moisture-sensitive, are soluble in a wide range of organic solvents, can be prepared in high yields on gram scales, and do not present any significant fire or toxicity hazards.

These properties are especially advantageous for the synthesis of low-oxidation-state p-block compounds, the chemistry of which has rapidly developed over the past 2 decades.⁵ Despite the emerging importance of such compounds, their preparation

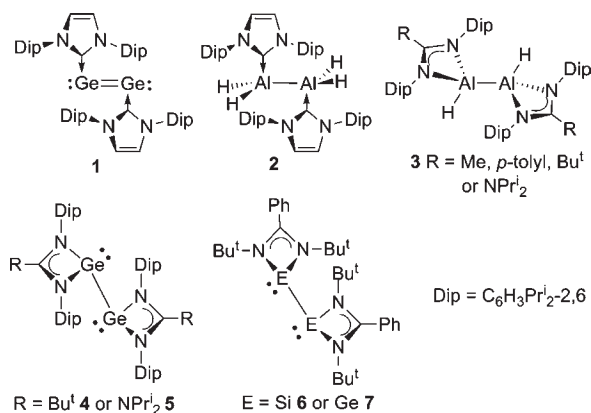
via the reduction of “normal oxidation state” precursor complexes can be problematic. These syntheses generally involve insoluble, and sometimes harsh, reducing agents, e.g., Li(s), Na(s), K(s), KC₈, and Mg(s), which can be difficult to use stoichiometrically and which often lead to “over-reduction” of the precursor complex and/or the occurrence of other side reactions.^{5,6} Recently, the solubility and moderate reducing nature of magnesium(I) dimers have lent them to use as stoichiometric reagents for the syntheses of species that so far have not been accessible by other routes. These include the N-heterocyclic carbene (NHC) stabilized digermanium(0) complex, **1** (via reduction of an NHC adduct of GeCl₂),^{2d,7} and the first examples of stable, neutral aluminum(II) hydride complexes, **2** and **3** (via reduction of aluminum(III) hydride precursors).^{2g,7}

In order to further demonstrate the synthetic utility of magnesium(I) dimers, we chose to investigate their use in the preparation of a series of novel amidinato-coordinated group 14 element(I) dimers as a case study. The first example of such a complex, trans-bent **4** (and a guanidinato-coordinated analogue, **5**),

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Chart 1

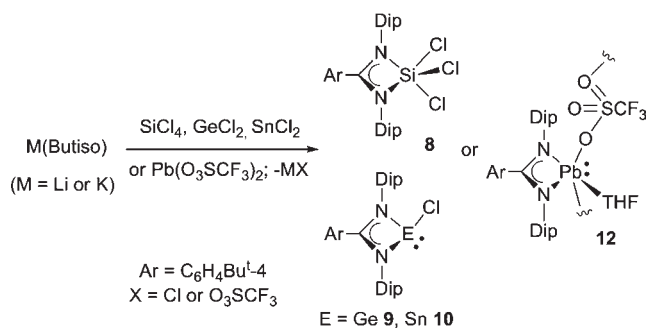


was reported by us in 2006.⁸ Subsequently, Roesky et al. described the related gauche-bent silicon(I) and germanium(I) dimers, **6**⁹ and **7**,¹⁰ respectively (Chart 1).¹¹ Compounds **4–7** can be considered as intramolecularly base-stabilized examples of the doubly or triply bonded trans-bent heavier group 14 alkyne analogues, RGe=GeR and RSi≡SiR (R = bulky terphenyl, aryl, or silyl), the chemistry of which has been extensively explored by the groups of Power, Sekiguchi, and others.¹² Similarly, Roesky et al.'s 1,2-ditretlenes, **6** and **7**, have begun to show their synthetic worth, especially toward the activation of small molecules.¹³ Despite this, the preparations of **4–7** via the reduction of amidinato element(II or IV) chloride precursors with potassium metal or K₂C₈ are quite low-yielding (**4**, 16%; **5**, 13%; cf. **6**, 5%; **7**, 35%), a situation that will no doubt hamper the future expansion of their chemistry. It seemed to us that using magnesium(I) dimers as alternative reducing agents in similar reactions might allow us access to higher yields of related silicon(I) and germanium(I) dimers. Moreover, because tin(I) and lead(I) analogues of **4–7** are currently unknown, these were seen as worthwhile synthetic targets because their properties and reactivity could be compared to those of their lighter group 14 counterparts and to those of previously prepared distannyne and diplumbyne complexes, REER (E = Sn or Pb).¹² Our efforts in this direction are reported herein.

RESULTS AND DISCUSSION

The amidinate ligand used in this study, [(DipN)₂C(C₆H₄-Bu^t-4)]⁻ (Butiso⁻), was chosen for its steric bulk, which could potentially impart significant kinetic stability to low-valent group 14 compounds incorporating it, and because we have previously found that complexes of Butiso⁻ readily crystallize from non-coordinating solvents.¹⁴ The conjugate acid of the ligand, ButisoH, was prepared in good yield by the reaction of 4-*tert*-butylphenyllithium with the carbodiimide DipN=C=NDip, followed by an aqueous workup. The solution NMR spectra of ButisoH show the compound to exist as more than one isomer/tautomer in solution, as is common for amidines and guanidines.¹⁵ In the solid state, an X-ray crystal structure of the compound (see the Supporting Information) revealed it to cocrystallize as a mixture of its (*Z*)-anti and (*E*)-syn isomeric forms. The amidine can be readily deprotonated with LiBuⁿ or KN(SiMe₃)₂ to give alkali-metal amidinate complexes, [M(Butiso)] (M = Li or K), which can be used as transfer reagents in subsequent reactions without purification. It is of note that on one occasion the lithium

Scheme 1



complex crystallized from hexane and its X-ray crystal structure was determined (see the Supporting Information). This showed the complex to be dimeric, [Li{Li(κ²-N,N'-Butiso)₂}], with two different lithium coordination environments, one chelated by two localized Butiso⁻ ligands and one chelated by one N center from each amidinate. This structural motif had been previously displayed by a closely related lithium guanidinate complex, [Li{Li(κ²-N,N'-Giso)₂}] (Giso⁻ = [(DipN)₂CN(C₆H₁₁)₂]⁻).^{15a}

The preparation of the amidinato group 14 element chloride complexes that were to be used as precursors to the target element(I) dimers was achieved by the reaction of either SiCl₄, GeCl₂·dioxane or SnCl₂ with 1 equiv of the lithium or potassium salt of Butiso⁻ in tetrahydrofuran (THF) or diethyl ether. The products of these reactions, **8–10**, were all obtained as colorless crystalline solids in moderate yields (Scheme 1). Attempts to form the analogous lead(II) complex [(Butiso)PbCl], via a similar 1:1 reaction in THF, were not successful and instead led to the homoleptic complex [Pb(Butiso)₂] (**11**) and unreacted PbCl₂. Compound **11** probably originates from the initially generated [(Butiso)PbCl], which, because of its greater solubility than PbCl₂, reacts further with [Li(Butiso)] to give **11**. In order to access a heteroleptic precursor complex related to [(Butiso)PbCl], 1 equiv of [K(Butiso)] was added to a THF solution of [Pb(O₃SCF₃)₂]. This afforded the polymeric complex [{(Butiso)Pb(μ-O₃SCF₃)(THF)}_∞] (**12**) in low isolated yield.

The solution-state NMR spectra of **8–10** are largely consistent with their proposed structures. In the case of **8**, a singlet resonance was observed in its ²⁹Si{¹H} NMR spectrum at δ = -89.4 ppm, which is in the normal region for five-coordinate silicon complexes (cf. δ = -98.9 ppm for [(PhC(NBu^t)₂){SiCl₃}]₁₆). That said, the ¹H and ¹³C{¹H} NMR spectra of **8** are suggestive of the compound possessing one chemically equivalent set of methine protons and two sets of isopropylmethyl protons. This is not what would be expected if the compound retained a rigid trigonal-bipyramidal structure with axial and equatorial N centers in solution (vide infra) and implies that a fluxional process, which is rapid on the NMR time scale, is in operation. This likely involves a scrambling of the coordinated N and Cl atoms of the complex between its axial and equatorial sites, via an intermediate square-pyramidal structure. Clearly, in solution, compound **12** does not retain its polymeric structure; however, its NMR spectra are compatible with the Butiso⁻ ligand chelating its Pb center in an N,N' fashion, as is the case in the solid state (vide infra).

All complexes **8–10** and **12** were crystallographically characterized, and the molecular structures of **8**, **9**, and **12** are depicted in Figure 1 (see also Table 1). Because the structure of compound **10** is isomorphous to that of **9**, its molecular

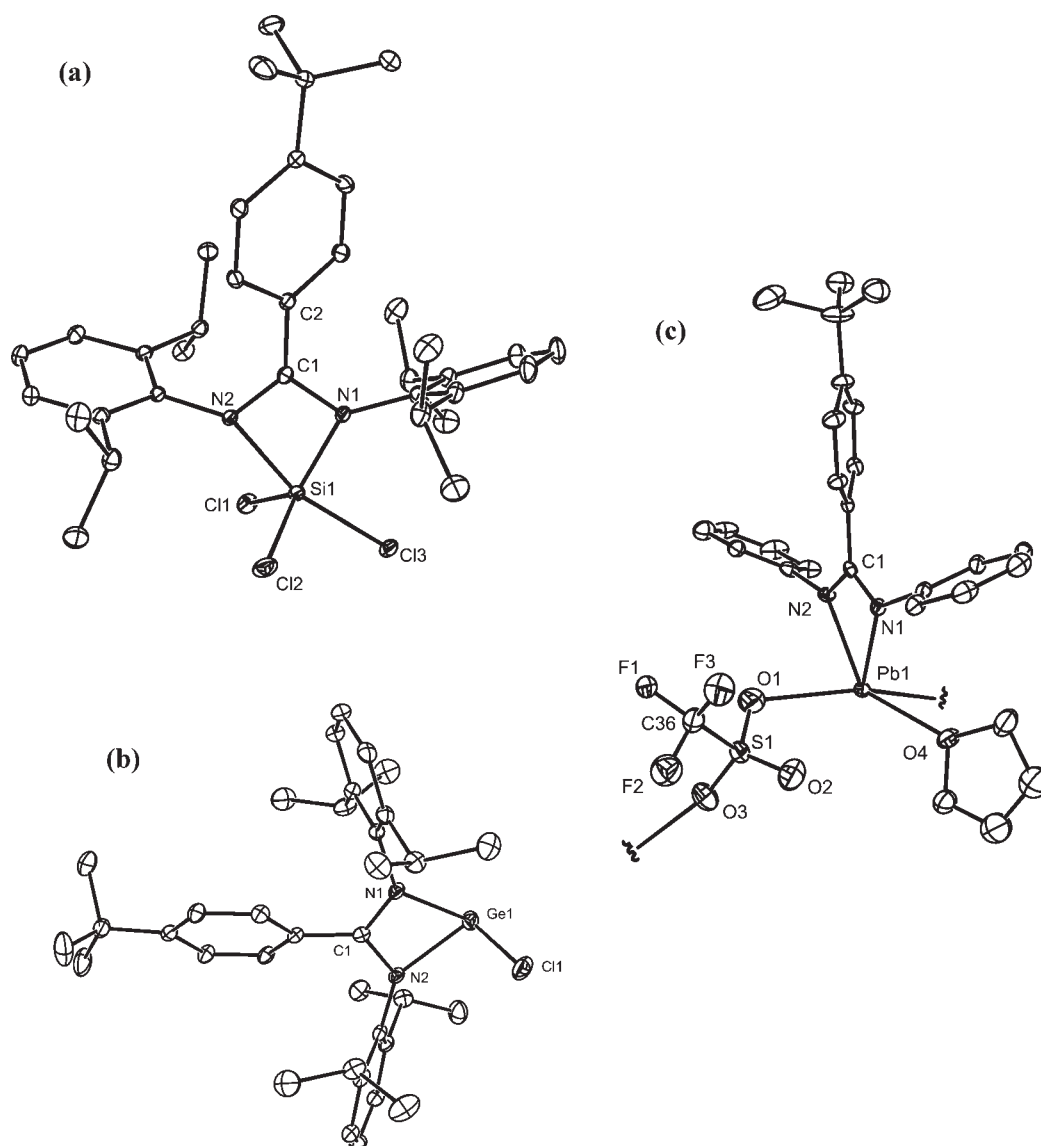


Figure 1. Thermal ellipsoid plots (25% probability surface) of the molecular structures of (a) **8**, (b) **9**, and (c) **12**. The H atoms of all structures and the isopropyl groups of **12** are omitted. Select metrical parameters for these compounds and for **10** are given in Table 1.

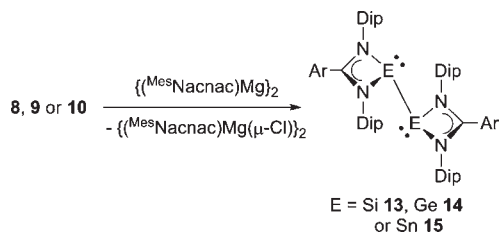
Table 1. Selected Interatomic Distances (Å) and Angles (deg) for **8–10** and **12**

	8	9	10	12
E–N1	1.7693(14)	2.074(3)	2.229(2)	2.289(7)
E–N2	1.9912(14)	2.071(3)	2.243(3)	2.427(7)
E–X ^a	2.0427(6) (Cl1)	2.249(3)	2.4059(19)	2.595(12) (O1)
	2.0526(7) (Cl2)			2.727(7) (O3) ^b
	2.1293(6) (Cl3)			2.700(8) (O4)
C1–N1	1.362(2)	1.332(5)	1.338(4)	1.338(11)
C1–N2	1.309(2)	1.342(5)	1.333(4)	1.315(11)
N–E–N	68.62(6)	63.32(12)	59.06(8)	56.2(2)
N–C–N	105.57(14)	108.9(3)	111.2(3)	113.9(8)

^a X = Cl or O; where more than one value is given, the relevant atom label is presented after the bond length. ^b Symmetry operation: $x', -x + 1/2, y - 1/2, -z + 1/2$.

structure (and that of a different structural modification of **8**) can be found in the Supporting Information. Complex **8** is monomeric and exhibits a trigonal-bipyramidal silicon coordination geometry, with N1 and N2 taking up equatorial and axial sites, respectively [$\text{N2–Si1–Cl1} = 162.52(8)^\circ$]. The NCN fragment of the amidinate ligand appears to be only partially delocalized, and the overall structure of the complex is very similar to that of $[\{\text{PhC}(\text{NBU}^+)_2\}\text{SiCl}_3]$.¹⁷ Complexes **9** and **10** are also monomeric with distorted pyramidal Ge or Sn centers, the geometries of which [Σ angles = 257.3° (**9**), 249.5° (**10**)] indicate that they possess high-*s*-character lone pairs. These structures are closely related to previously reported amidinato and guanidinato complexes, e.g., $[(\text{Giso})\text{ECl}]$ and $[(\text{Piso})\text{ECl}]$ (E = Ge or Sn; $\text{Piso}^- = [(\text{DipN})_2\text{CBu}^+]^-$).^{8,18} Compound **12** forms one-dimensional polymeric strands in the solid state, with each five-coordinate Pb center being ligated by O atoms from two bridging triflate anions, one N,N'-chelating Butiso⁻ ligand, and one molecule of THF. The structure is similar to that of the four-coordinate triflate-bridged polymer $[\{(\text{DipNacnac})\text{Pb}(\mu\text{-O}_3\text{SCF}_3)\}_\infty]$,¹⁹ and its

Scheme 2



Pb—O distances are in the normal ranges for lead—triflate and Pb—THF interactions.²⁰ There is only one structurally characterized heteroleptic amidinato lead complex in the literature to compare with **12**, and in that dimeric, four-coordinate complex, $[\{(\text{Piso})\text{Pb}(\mu\text{-Cl})\}_2]$,²¹ the two crystallographically independent Pb—N distances [2.330(4) and 2.326(4) Å] are identical. This is not the case for **12**, in which the Pb1—N2 separation is considerably greater than the Pb1—N1 distance.

The magnesium(I) reducing agent that was chosen for this study was $[\{(\text{MesNacnac})\text{Mg}\}_2]$ ($\text{MesNacnac} = [(\text{MesNCMe})_2\text{-CH}]^-$; Mes = mesityl),^{2c} because we previously showed this to have a greater reactivity than more sterically hindered dimers, e.g., $[\{(\text{Dip})\text{Nacnac}\}\text{Mg}\}_2]$.² The reaction of the silicon(IV) complex **8** with 1.5 equiv of $[\{(\text{MesNacnac})\text{Mg}\}_2]$ in toluene led to the formation of a deep-blue solution and a colorless precipitate of $[\{(\text{MesNacnac})\text{Mg}(\mu\text{-Cl})\}_2]$. Workup of this reaction mixture afforded a high isolated yield (91%) of the deep-blue silicon(I) dimer **13** after its recrystallization from pentane (Scheme 2). Similarly, the related reaction between the group 14 element(II) precursor **9** or **10** with 0.5 equiv of $[\{(\text{MesNacnac})\text{Mg}\}_2]$ gave red-purple **14** and dichroic orange—green **15** in isolated crystalline yields of 71% and 36%, respectively. An attempt to form the lead(I) analogues of **13–15** via the treatment of **12** with $[\{(\text{MesNacnac})\text{Mg}\}_2]$ resulted in the deposition of lead metal and the formation of the amidine ButisoH. It is of note that reacting **8** with 1 equiv of $[\{(\text{MesNacnac})\text{Mg}\}_2]$ did not generate a silicon(II) compound, $[(\text{Butiso})\text{SiCl}]$, but instead yielded a mixture of **13** and unreacted **8**. This contrasts with Roesky et al.'s treatment of $[\{\text{PhC}(\text{NBu}^t)_2\}\text{SiCl}_3]$ with 2 equiv of potassium metal, which gave $[\{\text{PhC}(\text{NBu}^t)_2\}\text{SiCl}]$, albeit in very low yield (10%).¹⁶

In order to compare the efficacy of $[\{(\text{MesNacnac})\text{Mg}\}_2]$ to that of other reducing agents, the silicon(IV) complex **8** was reacted with an excess of lithium metal, 3 equiv of lithium naphthalenide, or 1.5 equiv of $[(\text{THF})_3\text{Mg}(\text{anthracene})]$. The first reaction led to a blue solution at -50°C , but upon warming to 20°C , this color was lost and $[\text{Li}(\text{Butiso})]$ was recovered from the reaction mixture. Therefore, “over-reduction” of **8** by the excess lithium metal had almost certainly occurred. The other two reactions did yield persistent blue solutions at 20°C , but during their workup, it proved very difficult to remove the generated naphthalene or anthracene, and only low yields of impure **13** could be recovered from the mixtures.

The isolation of **13–15** allowed us to compare the physical and spectroscopic properties of this series of compounds. For example, although all are extremely air- and moisture-sensitive, their thermal stability decreases with an increase in the size of the group 14 element, presumably because of a concomitant decrease in the E—E bond strength as the group is descended. This is reflected in their Raman spectra, an analysis of which allowed the tentative assignment of bands due to E—E stretching modes

at ν 388 cm^{-1} (**13**), 192 cm^{-1} (**14**), and 165 cm^{-1} (**15**). Although the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the compounds are similar and consistent with their proposed structures, some revealing information could be gained from multinuclear NMR spectroscopic studies on **13** and **15**. The ^{29}Si NMR spectrum of **13** exhibits a singlet resonance at low field ($\delta = 96.9$ ppm), as might be expected for a three-coordinate silicon complex. This value is comparable with that for the related complex **6** ($\delta = 76.3$ ppm)⁹ but is significantly downfield from the signals observed for Robinson's silicon(I) chloride—NHC complex, $[(\text{IPr})\text{Si}(\text{Cl})\text{-Si}(\text{Cl})(\text{IPr})]$ ($\delta = 38.4$ ppm; $\text{IPr} = \text{:C}\{\text{N}(\text{Dip})\text{C}(\text{H})\}_2$),^{11a} and a recently reported intramolecularly base-stabilized disilyne, $[\{\kappa^2\text{-}N,P\text{-}(\text{C}_7\text{H}_8)\text{P}(\text{Bu}^t)_2\text{N}(\text{Dip})\}\text{Si}\}_2]$ ($\delta = -18.5$ ppm).^{11b} In this respect, it is noteworthy that ^{29}Si NMR chemical shifts for related two-coordinate disilynes, $\text{RSi}\equiv\text{SiR}$, can vary in the field by more than 70 ppm.¹² The ^{119}Sn NMR spectrum of **15** displays a resonance at $\delta = 777.7$ ppm (N.B.: no ^{117}Sn satellites were detected), which is downfield of the value for the base-stabilized distannynes, $[\{\kappa^3\text{-}C,N,N'\text{-}C_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-}2,6\}\text{Sn}\}_2]$ (four-coordinate, $\delta = 612$ ppm)^{11c} and $[\text{Ar}'(\text{RN}\equiv\text{C})\text{SnSn}(\text{C}\equiv\text{NR})\text{Ar}']$ (three-coordinate, $\text{R} = \text{Bu}^t$, $\delta = 181$ ppm; $\text{R} = \text{Mes}$, $\delta = 381$ ppm; $\text{Ar}' = \text{C}_6\text{H}_3(\text{C}_6\text{H}_3\text{Pr}^i_{3-2,4,6})_2\text{-}2,6$).²² To the best of our knowledge, the only reported ^{119}Sn NMR chemical shifts for two-coordinate distannynes are $\delta = 335$ and -36 ppm from the solid-state spectra of $[\text{Ar}'\text{SnSnAr}']$ and $[\text{Ar}^*\text{SnSnAr}^*]$ ($\text{Ar}^* = \text{C}_6\text{H}_3(\text{C}_6\text{H}_3\text{Pr}^i_{3-2,4,6})_2\text{-}2,6$), respectively.²³ It is clear that drawing any comparisons from these data should be treated with some caution because ^{119}Sn NMR chemical shifts are well-known to be very sensitive to the coordination number of the metal and the nature of the atoms bonded to it.²⁴

The electronic spectra of the intensely colored complexes **13–15** were obtained, and all showed a moderately strong absorption band in the visible region {toluene solutions, λ_{max} [nm] (ϵ [$\text{L mol}^{-1}\text{cm}^{-1}$]): **13**, 629 (7520); **14**, 502 (6030); **15**, 388 (2100)}. It is interesting that there is a decrease in the wavelength of this absorption on going from the lighter to the heavier group 14 elements in these complexes. This is the opposite of what is normally observed for multiply bonded group 14 element(I) dimers (lowest energy transition: $\pi \rightarrow \pi^*$),²⁵ which suggests that the E—E bonds of **13–15** have little π character. At this stage, one cannot be certain as to what electronic transitions give rise to the colors of these complexes, but the energies of these transitions are comparable with the few previously reported for related singly bonded element(I) dimers. Pertinent examples here include the tin(I) dimer $[\{\kappa^3\text{-}C,N,N'\text{-}C_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-}2,6\}\text{Sn}\}_2]$ [$\lambda_{\text{max}} = 367$ nm (4300)],^{11c} the germanium(I) dimer $[(\text{Dip})\text{Nacnac}\text{GeGe}\{\text{C}(\text{Me})\text{C}(\text{H})\text{C}(\text{Me})\text{-N}(\text{Dip})\}]$ [$\lambda_{\text{max}} = 501$ nm (2600)],^{11c} and the silicon(I) dimer $[(\text{IPr})\text{Si}(\text{Cl})\text{-Si}(\text{Cl})(\text{IPr})]$ ($\lambda_{\text{max}} = 510$ nm).^{11a}

The X-ray crystal structures of **13–15** were obtained, and all were found to be isostructural, while **13** and **14** are also isomorphous. As a result, only the molecular structure of **13** is depicted in Figure 2, although relevant geometric parameters for all complexes can be found in Table 2. It is clear that all complexes are dimeric and possess trans-bent structures similar to that of **4** but different from the gauche-bent structures of the less sterically hindered species, **6** and **7**. In the case of **7**, density functional theory (DFT) calculations implied that the gauche-bent form of the complex is favored by ca. 3.5 kcal mol^{-1} over its trans-bent isomer.¹⁰ The E—E distances in the compounds are fully consistent with singly bonded interactions and increase with heavier E. Indeed, these bonds are similar in length to other

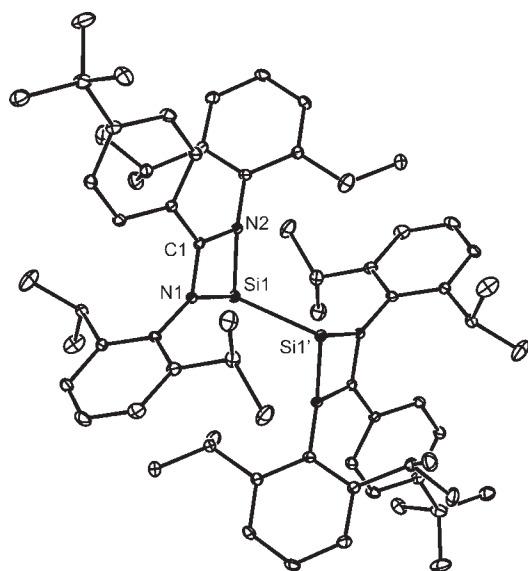


Figure 2. Thermal ellipsoid plot (25% probability surface) of the molecular structure of **13**. H atoms are omitted. Symmetry operation: $\bar{1}$, $-x$, $-y$, $-z$. Select metrical parameters for **13–15** are given in Table 2.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for **13–15**^a

	13	14	15
E–E	2.4885(15)	2.6136(9)	3.0141(8)
E–N	1.872(2)	2.025(2)	2.243(3)
	1.877(2)	2.028(3)	2.237(3)
			2.240(3)
			2.244(3)
C–N	1.346(3)	1.338(4)	1.338(5)
	1.360(3)	1.350(4)	1.328(5)
			1.332(5)
			1.338(5)
N–E–N	69.36(10)	64.68(10)	59.04(12)
			58.84(12)
N–C–N	104.0(2)	107.5(3)	111.8(3)
			111.2(3)

^a Where more than one value is given, the order follows the numbering scheme for N atoms. Compound **15** does not sit on a crystallographic center of inversion and therefore possesses two crystallographically independent Sn atoms and four N centers (see the Supporting Information for the ORTEP drawing).

singly bonded element(I) dimers in the literature, e.g., 2.413(2) Å for **6**,⁹ 2.6380(8) Å for **4**,⁸ and 2.9712(12) Å for $[\{\kappa^3\text{-C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}\}\text{Sn}]_2$.^{11c} In line with the E–E single bonds in **13–15** is the pyramidal coordination geometry of their E centers, which indicates that they each possess a lone pair of electrons. As the degree of pyramidalization increases for heavier E [Σ angles about E = 267.5° (**13**), 254.9° (**14**), 248.8° (mean; **15**)], it can be assumed that the s character of the lone pair also increases, in line with what would be expected from the inert pair effect.²⁶ Concomitantly, the degree of trans bending for the compounds increases down the group [$\text{C}_{(\text{backbone})}\text{EE}$ angle: 103.9° (**13**), 98.5° (**14**), 97.0° (mean; **15**)], as is well-known

for ditetrelynes, REER.¹² The bond lengths within the NCN fragments of the amidinate ligands in all complexes indicate that they are delocalized.

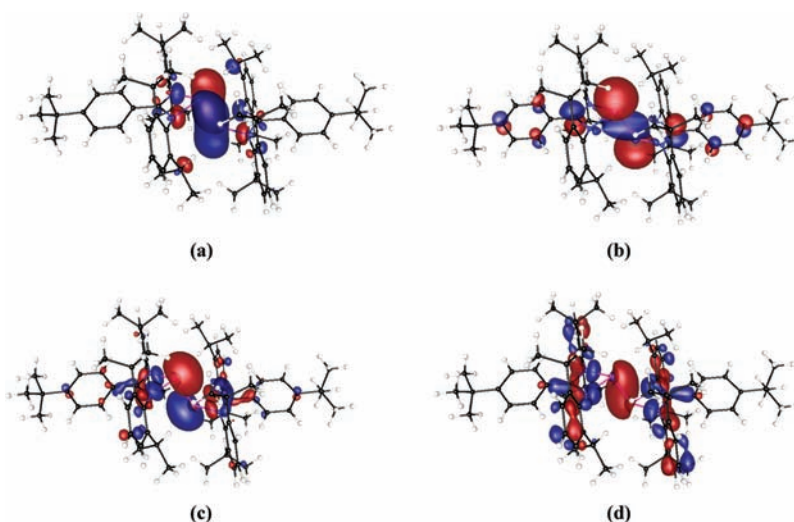
In order to shed light on the nature of the bonding in **13–15** and their synthetically inaccessible lead analogue, $[\{(\text{Butiso})\text{Pb}\}_2]$ (**16**), DFT calculations (RI-BP86/def2-TZVPP) were carried out on the full molecules in the gas phase (**13a–16a**). Similar calculations were carried out on the sterically condensed molecules, $[\{\text{PhC}(\text{NPh})_2\text{E}\}_2]$ (**13b–16b**), in which substituted aryl groups were replaced by phenyl substituents. The geometry optimization of all molecules yielded trans-bent structures (see Figure S4 in the Supporting Information) similar to those experimentally observed but different from the gauche-bent structure previously calculated for **7**.¹⁰ There is general agreement between the calculated (Table 3) and experimental geometrical parameters for the compounds, except for the E–E distances of **13a–15a**, which are ca. 0.1 Å longer than the values measured for **13–15** in the solid state. In contrast, the calculated E–E bonds of the model compounds **13b–15b**, which are shorter than those in **13a–15a**, agree quite well with the experimental data. This may be partly caused by fortuitous error cancellation because the experimental E–E distances given by X-ray structure analyses can be affected by crystal packing forces, which tend to shorten long and weak bonds.²⁷ It is thus conceivable that the calculated values for **13a–15a** are a faithful representation of the free molecules, while **13b–15b** better mimic the E–E bonding situation in the solid state. As a component of this theoretical study, the vibrational frequencies for the E–E stretching modes of **13a–16a** were calculated using the harmonic approximation, and the values obtained [ν 358.5 cm⁻¹ (**13a**), 193.8 cm⁻¹ (**14a**), 131.5 cm⁻¹ (**15a**), 102.5 cm⁻¹ (**16a**)] were found to be close to the available experimentally observed anharmonic frequencies for **13–15** mentioned above [N.B.: the calculated values for the “cut-down” model systems, **13b–16b**, are only slightly higher; ν 380.9 cm⁻¹ (**13b**), 197.2 cm⁻¹ (**14a**), 144.3 cm⁻¹ (**15a**), 108.5 cm⁻¹ (**16a**)].

The electronic structure of the calculated molecules was examined and found to be similar for all compounds. Therefore, only the molecular orbitals (MOs) of **13a** that are most closely associated with its Si–Si bond are depicted in Figure 3. The highest occupied molecular orbital (HOMO) is clearly a σ -type Si–Si bonding orbital, which is largely derived from the overlap of two Si-centered p orbitals. An natural bond order (NBO) analysis of **13a** supported this proposition and showed the σ bond to have 88.7% p character and 11.1% s character. Not surprisingly, the p character of the E–E bonds of **13a–16a** increases down the group (**14a**, 90.0%; **15a**, 92.5%; **16a**, 96.4%). The HOMO–1 and HOMO–16 of **13a** represent the plus and minus combinations of the σ -type lone-pair MOs at Si, and these are high in s character (NBO: 72.6%). Moreover, the percentage of s character of the lone-pair orbital of the E centers in **13a–16a** increases with heavier E (**14a**, 81.7%; **15a**, 88.0%; **16a**, 94.0%). While the lowest unoccupied molecular orbital (LUMO) and LUMO+1 for **13a** are predominantly ligand-based orbitals, LUMO+2 is essentially a π -type Si–Si bonding orbital. The nature and ordering of the frontier orbitals for the germanium(I) dimer **14a** are equivalent, although the empty π -type E–E bonding orbitals of the heavier species **15a** and **16a** are associated with their LUMOs.

The frontier orbitals of **13a–16a** are strikingly similar to those previously calculated for a model of the germanium(I) dimer **4**⁸ and are plainly consistent with the compounds having E–E single bonds with negligible π character. In this respect, the

Table 3. Select Bond Lengths (Å), Angles/Torsion Angles (deg), and Calculated E–E BDEs D_e (kcal mol⁻¹) for the Optimized Geometries of 13a–16a and 13b–16b (RI-BP86/def2-TZVPP)

E	Si		Ge		Sn		Pb	
	13a	13b	14a	14b	15a	15b	16a	16b
E–E	2.560	2.515	2.731	2.657	3.111	3.038	3.240	3.176
E–N	1.880–1.893	1.900–1.903	2.044–2.075	2.055	2.265–2.278	2.265–2.267	2.383–2.400	2.383–2.385
N–C	1.364–1.371	1.355–1.360	1.347–1.358	1.348–1.350	1.344–1.351	1.345–1.347	1.342–1.348	1.343–1.344
N–E–N	69.6	68.7	64.5	64.0	58.9	58.6	56.0	55.9
N–C–N	103.9	104.5	108.6	107.7	111.9	111.0	113.2	112.6
C–E–E	108.8	98.5–98.6	102.6	93.3	99.4	91.1–91.2	98.5	90.6–90.8
C–E–E–C	180.0	180.0	180.0	180.0	180.0	179.9	179.9	179.9
N–E–E–N	108.4	110.8–110.9	114.7–114.8	115.9	120.7	121.3–121.5	123.6	124.0–124.2
D_e	16.6	30.7	18.1	31.8	19.9	29.7	19.5	28.9

**Figure 3.** (a) LUMO+2, (b) HOMO, (c) HOMO–1, and (d) HOMO–16 of 13a.

experimental compounds **13–15** are different to the trans-bent, two-coordinate ditetrelynes, REER (E = Si, Ge, or Sn), which have been calculated to have E–E multiple bonds with orders ranging from ca. 2 for E = Ge or Sn to ca. 3 for E = Si.^{12,25,28} That said, it is now clear that the potential energy surface relating to the trans bending of distannynes is very shallow, and such systems with relatively acute C–Sn–Sn angles (ca. 98°) and long Sn–Sn single bonds (ca. 3.08 Å) are synthetically accessible.²⁵ These singly bonded distannynes, and their diplumbyne analogues, RPbPbR, which are invariably void of multiple bond character, are therefore directly comparable with **13–15**. It should be noted that although two-coordinate disilynes and digermynes always possess considerable multiple bond character, several recent reports have shown that when they form adducts with isonitriles, their bond orders are reduced to unity.²⁹ Consequently, they are also related to **13–15**, which can be considered to be intramolecularly base-stabilized ditetrelynes.

The high p character of the E–E bonds of **13a–16a** indicates that these interactions may be weaker than generally expected for E–E single bonds. We calculated the bond dissociation energies (BDEs) of each compound, yielding two (Butiso)E fragments in the electronic doublet state. The BDEs of the model compounds

13b–16b (yielding two [PhC(NPh)₂]E fragments) were also calculated. The theoretically predicted BDE (D_e) values are shown in Table 3. For **13a–16a**, these lie between 16.6 and 19.9 kcal mol⁻¹, thus suggesting that their E–E bonds are indeed rather weak. Remembering that the calculated E–E bond lengths for **13a–15a** were overestimated by ~0.1 Å, it might be expected that their calculated BDEs would be smaller than the BDEs of the experimental compounds **13–15**. Considering that the E–E bond lengths of the model “cut-down” compounds **13b–15b** are in much better agreement with the experimental values for **13–15**, their E–E BDEs may be better suited for predictions of the BDEs in the experimental compounds in the solid state. Table 3 shows that the BDEs of the E–E bonds in **13b–16b** are between 28.9 and 31.8 kcal mol⁻¹, i.e., considerably greater than those for **13a–16a**. All of these values may be compared with the calculated BDEs of the unsupported E–E single bonds in the parent systems HEEH (E = Si–Pb), which possess planar trans-bent structures with H–E–E angles of ca. 90°. ^{28a} The π orbitals in these two-coordinate species are empty, and the atoms, E, carry σ lone-pair orbitals. The BDEs of these compounds, calculated at a level of theory (BP86/QZ4P) similar to that used here, are 40.3 (Si), 37.2 (Ge), 33.0 (Sn), and 31.0 (Pb)

kcal mol⁻¹.^{28a} A comparison of these values with the data in Table 3 shows that the E–E bonds in three-coordinate **13a**–**16a** and **13b**–**16b** are somewhat weaker than those in the unsupported two-coordinate parent systems. It is noteworthy that all of these BDEs are significantly lower and more uniform than those reported for the molecules H₃E–EH₃.³⁰ Their calculated BDEs (BP86/TZ2P) are 72.4 (Si), 67.5 (Ge), 57.4 (Sn), and 46.8 (Pb) kcal mol⁻¹. The percentages of s character of the E^{III}–E^{III} bonds in H₃E–EH₃ were calculated to be considerably higher than those for the E^I–E^I bonds of the molecules described herein. A full analysis of the factors that determine the comparative strengths of E^I–E^I and E^{III}–E^{III} single bonds will form the basis of a forthcoming theoretical study by us.

CONCLUSIONS

In summary, the utility of a dimeric magnesium(I) compound as a soluble and stoichiometric reducing agent for inorganic synthesis has been demonstrated by its use in the facile preparation of a series of amidinato coordinated group 14 element(I) dimers. These include the first tin(I) example of such species. Access to these compounds has allowed a detailed comparison of their properties using a variety of spectroscopic, crystallographic, and theoretical techniques. Given the emerging importance of group 14 element(I) dimers to small-molecule activation, etc., there is much scope to examine the further chemistry of the compounds prepared in this study. Moreover, we believe that the advantageous properties of easy to prepare magnesium(I) compounds will lead to them finding widespread use as more selective alternatives to the harsh and often insoluble alkali-metal reducing agents that are commonly used in the preparation of low-oxidation-state p-block systems. We continue to explore the reactivity of magnesium(I) compounds and will report on this in a series of forthcoming publications.

EXPERIMENTAL SECTION

General Methods. All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of high-purity dinitrogen. THF, hexane, pentane, and toluene were distilled over potassium, while diethyl ether was distilled over a Na/K alloy. ¹H and ¹³C{¹H} NMR spectra were recorded on either Bruker DPX300 or AvanceIII 400 spectrometers and were referenced to the resonances of the solvent used. ²⁹Si{¹H} and ¹¹⁹Sn{¹H} NMR spectra were recorded on a Bruker AvanceIII 400 spectrometer and were referenced to external SiMe₄ and SnMe₄, respectively. Mass spectra were obtained from the EPSRC National Mass Spectrometric Service at Swansea University (Swansea, Wales, U.K.). IR spectra were recorded using a Perkin-Elmer RX1 FT-IR spectrometer as Nujol mulls between NaCl plates. UV–vis spectra were recorded on a Cary 1E spectrometer. Microanalyses were carried out by Campbell Microanalytical Laboratory, University of Otago (Dunedin, New Zealand). Raman spectra were recorded on crystalline samples of **13**–**15** sealed in glass capillaries under dinitrogen using a Renishaw RM2000 micro-Raman spectrometer with 514 nm excitation from a diode laser. Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected. The compounds Pb(O₃SCF₃)₂³¹ and [({^{Me}Snacnac})Mg]₂^{2e} were prepared by variations of the literature procedures. [K(Butiso)] was prepared by treating a toluene solution of ButisoH with KN(SiMe₃)₂. The resultant reaction mixture was then filtered, volatiles were removed in vacuo, and [K(Butiso)] was used without further purification. All other reagents were used as received.

Preparation of ButisoH. A solution of 1-bromo-4-*tert*-butylbenzene (3.39 g, 15.9 mmol) in diethyl ether (20 mL) was added slowly to a slurry of lithium powder (200 mg, 28.9 mmol) and diethyl ether (40 mL), which was heated at reflux. After the addition, the solution was heated at reflux for an additional 1 h. The purple/red mixture was subsequently filtered into a solution of the carbodiimide DipN=C=N-Dip (5.80 g, 16.0 mmol) in diethyl ether (40 mL) at –50 °C. The resultant solution was subsequently warmed to room temperature and stirred for 1 h. The reaction mixture was quenched with H₂O (15 mL) and the organic layer collected. The aqueous layer was extracted with dichloromethane (2 × 30 mL), and the combined organic layers were dried over MgSO₄. Volatiles were removed in vacuo, and the residue was washed with hexane (8 mL), leaving ButisoH as a colorless solid (5.05 g, 70%). Mp: 162–164 °C. ¹H NMR (400 MHz, 298 K, C₆D₆): main isomer, δ 0.89 (d, ³J_{H,H} = 6.8 Hz, 6H, CH(CH₃)₂), 0.92 (d, ³J_{H,H} = 6.8 Hz, 6H, CH(CH₃)₂), 1.05 (s, 9H, C(CH₃)₃), 1.39 (d, ³J_{H,H} = 6.8 Hz, 6H, CH(CH₃)₂), 1.40 (d, ³J_{H,H} = 6.8 Hz, 6H, CH(CH₃)₂), 3.30 (sept, ³J_{H,H} = 6.8 Hz, 2H, CH(CH₃)₂), 3.50 (sept, ³J_{H,H} = 6.8 Hz, 2H, CH(CH₃)₂), 5.92 (s, 1H, NH), 6.93 (d, ³J_{H,H} = 8.0 Hz, 2H, ArH), 6.99–7.30 (m, 6H, ArH), 7.64 (d, ³J_{H,H} = 8.0 Hz, 2H, ArH); minor isomer, δ 0.65 (br, 6H, CH(CH₃)₂), 0.97 (br, 6H, CH(CH₃)₂), 1.05 (s, 9H, C(CH₃)₃), 1.11 (br, 6H, CH(CH₃)₂), 1.24 (vbr, 6H, CH(CH₃)₂), 3.31 (vbr, 2H, CH(CH₃)₂), 3.58 (vbr, 2H, CH(CH₃)₂), 5.68 (s, 1H, NH), 7.01–7.31 (m, 10H, ArH). ¹³C{¹H} NMR (100 MHz, 298 K, C₆D₆): main isomer, δ 21.1 (CH(CH₃)₂), 21.6 (CH(CH₃)₂), 23.2 (CH(CH₃)₂), 23.5 (CH(CH₃)₂), 27.4 (CH(CH₃)₂), 27.8 (CH(CH₃)₂), 29.7 (C(CH₃)₃), 33.2 (C(CH₃)₃), 122.0 (ArC), 122.4 (ArC), 122.6 (ArC), 123.4 (ArC), 127.9 (ArC), 131.3 (ArC), 133.7 (ArC), 137.9 (ArC), 143.6 (ArC), 143.7 (ArC), 151.2 (ArC), 151.3 (ArC), CN₂ resonance not observed. IR (Nujol, cm⁻¹): ν 3424s (NH), 3360s (NH), 1651s, 1621s, 1587s, 1563m, 1407m, 1326m, 1298m, 1269m, 1105m, 1081m, 936m, 848m, 826m, 780m, 760s. MS (ES, 35 eV): *m/z* 497.3 (MH⁺, 100%).

N.B.: In C₆D₆ solutions, ButisoH exists as two isomeric forms in an approximate ratio of 1:2. Only the ¹H NMR spectroscopic data are given for both isomers.

Preparation of [(Butiso)SiCl₃] (8). LiBuⁿ (1.76 mL, 2.83 mmol, 1.6 M solution in hexane) was added to a solution of ButisoH (1.33 g, 2.83 mmol) in diethyl ether (40 mL) at –78 °C. The resultant solution was warmed to room temperature, whereupon it was cooled again to –78 °C. To this was added SiCl₄ (0.34 mL, 2.83 mmol) over 2 min. The mixture was warmed to room temperature and stirred for 1 h, and volatiles were removed in vacuo. The pale-yellow residue was extracted into hexane (25 mL), and the extract was concentrated to ca. 15 mL and cooled to –30 °C overnight to give colorless crystals of **8** (775 mg, 43%). Mp: 180–182 °C (melts, no visible decomposition up to 300 °C). ¹H NMR (400 MHz, 298 K, C₆D₆): δ 0.74 (s, 9H, C(CH₃)₃), 0.95 (d, ³J_{H,H} = 6.8 Hz, 12H, CH(CH₃)₂), 1.43 (d, ³J_{H,H} = 6.8 Hz, 12H, CH(CH₃)₂), 3.75 (sept, ³J_{H,H} = 6.8 Hz, 4H, CH(CH₃)₂), 6.81 (d, ³J_{H,H} = 8.8 Hz, 2H, ArH), 7.02–7.15 (m, 6H, ArH), 7.34 (d, ³J_{H,H} = 8.8 Hz, 2H, ArH). ¹³C{¹H} NMR (100 MHz, 298 K, C₆D₆): δ 22.6 (CH(CH₃)₂), 23.9 (CH(CH₃)₂), 28.0 (CH(CH₃)₂), 29.0 (C(CH₃)₃), 33.5 (C(CH₃)₃), 121.1 (ArC), 123.6 (ArC), 124.1 (ArC), 127.4 (ArC), 130.1 (ArC), 133.6 (ArC), 145.1 (ArC), 156.6 (ArC), 169.7 (CN₂). ²⁹Si NMR (80 MHz, 298 K, C₆D₆): δ –89.4. IR (Nujol, cm⁻¹): ν 1664m, 1609s, 1570m, 1543m, 1501m, 1421s, 1379s, 1261s, 1204m, 1178m, 1097s, 934m, 862m, 792s. MS (EI, 70 eV): *m/z* 628.3 (M⁺, 15%), 585.2 (M⁺·Prⁱ, 25%), 496.3 (ButisoH⁺, 5%), 453.3 (ButisoH⁺·Prⁱ, 5%), 320.2 (Butiso⁺·NDip, 100%). HREL Acc. mass calcd for C₃₃H₄₇Cl₃N₂Si: *m/z* 628.2569. Found: *m/z* 628.2565. Anal. Calcd for C₃₃H₄₇Cl₃N₂Si: C, 66.70; H, 7.52; N, 4.45. Found: C, 66.42; H, 7.79; N, 4.28.

Preparation of [(Butiso)GeCl] (9). A solution of [Li(Butiso)] (0.300 g, 0.60 mmol) in THF (20 mL) was added to a solution of GeCl₂·dioxane (0.138 g, 0.60 mmol) in THF (40 mL) at –78 °C. The

resultant mixture was slowly warmed to room temperature and stirred overnight. Volatiles were removed in vacuo, and the residue was extracted into pentane (30 mL). The extract was concentrated to 15 mL and cooled to $-30\text{ }^{\circ}\text{C}$ overnight to give colorless crystals of **9** (0.134 g, 37%). Mp: $197\text{--}199\text{ }^{\circ}\text{C}$ (dec). ^1H NMR (400 MHz, 298 K , C_6D_6): δ 0.79 (s, 9H, $\text{C}(\text{CH}_3)_3$), 0.98 (d, $^3J_{\text{H,H}} = 6.8\text{ Hz}$, 6H, $\text{CH}(\text{CH}_3)_2$), 1.02 (d, $^3J_{\text{H,H}} = 6.8\text{ Hz}$, 6H, $\text{CH}(\text{CH}_3)_2$), 1.19 (d, $^3J_{\text{H,H}} = 6.8\text{ Hz}$, 6H, $\text{CH}(\text{CH}_3)_2$), 1.46 (d, $^3J_{\text{H,H}} = 6.8\text{ Hz}$, 6H, $\text{CH}(\text{CH}_3)_2$), 3.62 (sept, $^3J_{\text{H,H}} = 6.8\text{ Hz}$, 2H, $\text{CH}(\text{CH}_3)_2$), 4.05 (sept, $^3J_{\text{H,H}} = 6.8\text{ Hz}$, 2H, $\text{CH}(\text{CH}_3)_2$), 6.81 (d, $^3J_{\text{H,H}} = 8.8\text{ Hz}$, 2H, ArH), 6.95–7.15 (m, 6H, ArH), 7.20 (d, $^3J_{\text{H,H}} = 8.8\text{ Hz}$, 2H, ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, 298 K , C_6D_6): δ 21.5 ($\text{CH}(\text{CH}_3)_2$), 21.7 ($\text{CH}(\text{CH}_3)_2$), 25.0 ($\text{CH}(\text{CH}_3)_2$), 25.1 ($\text{CH}(\text{CH}_3)_2$), 27.5 ($\text{CH}(\text{CH}_3)_2$), 28.0 ($\text{CH}(\text{CH}_3)_2$), 29.2 ($\text{C}(\text{CH}_3)_3$), 33.3 ($\text{C}(\text{CH}_3)_3$), 122.5 (ArC), 123.3 (ArC), 123.9 (ArC), 125.6 (ArC), 125.7 (ArC), 128.6 (ArC), 136.0 (ArC), 142.3 (ArC), 144.6 (ArC), 154.0 (ArC), 169.9 (CN_2). IR (Nujol, cm^{-1}): ν 1651m, 1610m, 1463m, 1456m, 1435w, 1402w, 1261s, 1099s (br), 1020s (br), 864m, 847w, 803s. MS (EI, 70 eV): m/z 604.3 (M^+ , 10%), 561.2 ($\text{M}^+ - \text{Pr}^i$, 5%), 496.3 (ButisoH $^+$, 8%), 453.3 (ButisoH $^+ - \text{Pr}^i$, 43%), 320.2 (Butiso $^+ - \text{NDip}$, 100%). HREI. Acc. mass calcd for $\text{C}_{35}\text{H}_{47}\text{Cl}^{70}\text{GeN}_2$: m/z 600.2665. Found: m/z 600.2662. Anal. Calcd for $\text{C}_{35}\text{H}_{47}\text{ClGeN}_2$: C, 69.62; H, 7.85; N, 4.64. Found: C, 69.05; H, 7.92; N, 4.69.

Preparation of [(Butiso)SnCl] (10). A solution of [K(Butiso)] (0.550 g, 1.03 mmol) in THF (20 mL) was added to a slurry of SnCl $_2$ (0.196 g, 1.03 mmol) in THF (40 mL) at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was slowly warmed to room temperature and stirred overnight. Volatiles were removed in vacuo, and the residue was extracted into pentane (30 mL). The extract was concentrated to 15 mL and placed at $-30\text{ }^{\circ}\text{C}$ overnight to yield colorless crystals of **10** (0.456 g, 68%). Mp: $199\text{--}201\text{ }^{\circ}\text{C}$ (melts, no visible decomposition up to $300\text{ }^{\circ}\text{C}$). ^1H NMR (400 MHz, 298 K , C_6D_6): δ 0.82 (s, 9H, $\text{C}(\text{CH}_3)_3$), 0.96–1.06 (m of overlapping d, br, 12H, $\text{CH}(\text{CH}_3)_2$), 1.12 (d, br, 6H, $\text{CH}(\text{CH}_3)_2$), 1.48 (d, br, 6H, $\text{CH}(\text{CH}_3)_2$), 3.55 (sept, br, 2H, $\text{CH}(\text{CH}_3)_2$), 4.08 (sept, br, 2H, $\text{CH}(\text{CH}_3)_2$), 6.84 (d, $^3J_{\text{H,H}} = 8.8\text{ Hz}$, 2H, ArH), 6.90–7.12 (m, 6H, ArH), 7.14 (d, $^3J_{\text{H,H}} = 8.8\text{ Hz}$, 2H, ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, 298 K , C_6D_6): δ 21.4 ($\text{CH}(\text{CH}_3)_2$), 21.7 ($\text{CH}(\text{CH}_3)_2$), 24.9 ($\text{CH}(\text{CH}_3)_2$), 25.6 ($\text{CH}(\text{CH}_3)_2$), 27.5 ($\text{CH}(\text{CH}_3)_2$), 27.8 ($\text{CH}(\text{CH}_3)_2$), 29.3 ($\text{C}(\text{CH}_3)_3$), 33.2 ($\text{C}(\text{CH}_3)_3$), 122.1 (ArC), 122.6 (ArC), 123.2 (ArC), 123.5 (ArC), 125.0 (ArC), 128.5 (ArC), 137.5 (ArC), 141.7 (ArC), 143.9 (ArC), 153.0 (ArC), 172.4 (CN_2). ^{119}Sn NMR (150 MHz, 298 K , C_6D_6): δ 28.4. IR (Nujol, cm^{-1}): ν 1651m, 1619s, 1586m, 1364s, 1322s, 1281s, 1261m, 1098m, 1054m, 1016m, 968m, 934m, 827m, 802m, 776s. MS (EI, 70 eV): m/z 650.3 (M^+ , 2%), 496.4 (ButisoH $^+$, 15%), 453.4 (ButisoH $^+ - \text{Pr}^i$, 18%), 320.2 (Butiso $^+ - \text{NDip}$, 100%). HREI. Acc. mass calcd for $\text{C}_{35}\text{H}_{47}\text{Cl}^{116}\text{SnN}_2$: m/z 646.2440. Found: m/z 646.2441.

Preparation of [Pb(Butiso) $_2$] (11). A solution of [Li(Butiso)] (0.500 g, 0.99 mmol) in THF (20 mL) was added to a slurry of PbCl $_2$ (0.350 g, 1.26 mmol) in THF (20 mL) at room temperature over 5 min. The mixture was stirred overnight before volatiles were removed in vacuo. The residue was extracted into hexane (30 mL) and the extract concentrated to 15 mL. Cooling the solution to $-30\text{ }^{\circ}\text{C}$ overnight yielded pale-yellow crystals of **11** (0.45 g, 75% based on Butiso). Mp: $137\text{--}139\text{ }^{\circ}\text{C}$ (dec). ^1H NMR (400 MHz, 298 K , C_6D_6): δ 0.60–1.60 (v br, 48H, $\text{CH}(\text{CH}_3)_2$), 0.84 (s, 18H, $\text{C}(\text{CH}_3)_3$), 3.10–4.10 (v br, 8H, $\text{CH}(\text{CH}_3)_2$), 6.88 (d, $^3J_{\text{H,H}} = 8.8\text{ Hz}$, 4H, ArH), 6.82–7.16 (m, 12H, ArH), 7.14 (d, $^3J_{\text{H,H}} = 8.8\text{ Hz}$, 4H, ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, 298 K , C_6D_6): δ 23.1 (v br, $\text{CH}(\text{CH}_3)_2$), 28.3 (v br, $\text{CH}(\text{CH}_3)_2$), 30.7 ($\text{C}(\text{CH}_3)_3$), 34.2 ($\text{C}(\text{CH}_3)_3$), 123.0 (br, ArC), 123.9 (ArC), 124.9 (br, ArC), 125.5 (br, ArC), 130.6 (ArC), 135.8 (ArC), 142.3 (br, ArC), 143.4 (br, ArC), 144.4 (br, ArC), 151.9 (ArC), 167.8 (CN_2). IR (Nujol, cm^{-1}): ν 1636m, 1619s, 1609m, 1588m, 1563m, 1398s, 1380s, 1265m, 1178m, 1104m, 1018m, 947m, 935m, 844m, 824m, 801m. MS (EI, 70 eV): m/z 1198.8 (M^+ , 1%), 703.3 ($\text{M}^+ - \text{Butiso}$, 21%), 496.3 (ButisoH $^+$, 16%), 453.3 (ButisoH $^+ - \text{Pr}^i$, 20%), 320.2 (Butiso $^+ - \text{NDip}$, 100%).

Preparation of [K(Butiso)] [K(Butiso)] (0.400 g, 0.75 mmol) in THF (20 mL) was added to a solution of Pb(O $_3\text{SCF}_3$) $_2$ (0.430 g, 0.85 mmol) in THF (20 mL) at $-78\text{ }^{\circ}\text{C}$. The mixture was slowly warmed to room temperature and stirred overnight. Volatiles were removed in vacuo, and the residue was extracted into pentane ($2 \times 15\text{ mL}$). The pale-yellow extract was concentrated to 10 mL and placed at $-30\text{ }^{\circ}\text{C}$ overnight to give yellow crystals of **12 (0.154 g, 24%). Mp: $124\text{--}126\text{ }^{\circ}\text{C}$. ^1H NMR (400 MHz, 298 K , C_6D_6): δ 0.83 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.01 (d, $^3J_{\text{H,H}} = 6.8\text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 1.39 (d, $^3J_{\text{H,H}} = 6.8\text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 1.41–1.47 (m, 4H, $\text{O}(\text{CH}_2\text{CH}_2)_2$), 3.51–3.57 (m, 4H, $\text{O}(\text{CH}_2\text{CH}_2)_2$), 3.64 (sept, $^3J_{\text{H,H}} = 6.8\text{ Hz}$, 4H, $\text{CH}(\text{CH}_3)_2$), 6.80–7.14 (m, 10H, ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, 298 K , C_6D_6): δ 22.0 ($\text{CH}(\text{CH}_3)_2$), 24.3 ($\text{CH}(\text{CH}_3)_2$), 25.0 ($\text{O}(\text{CH}_2\text{CH}_2)_2$), 27.2 ($\text{CH}(\text{CH}_3)_2$), 29.3 ($\text{C}(\text{CH}_3)_3$), 33.1 ($\text{C}(\text{CH}_3)_3$), 66.8 ($\text{O}(\text{CH}_2\text{CH}_2)_2$), 121.9 (ArC), 123.4 (ArC), 125.0 (ArC), 128.8 (ArC), 137.0 (ArC), 138.2 (ArC), 142.9 (ArC), 152.4 (ArC), 171.7 (CN_2). ^{19}F NMR (377 MHz, 298 K , C_6D_6): δ -77.4 . IR (Nujol, cm^{-1}): ν 1650m, 1619s, 1609s, 1587m, 1414s, 1362vs, 1316s, 1200s, 1056s, 1017vs, 873m, 846s, 824s, 804s, 775s. MS (EI, 35 eV): m/z 497.7 (ButisoH $_2^+$, 100%).**

Preparation of [K(Butiso)Si] $_2$ (13). A solution of [K(Butiso)Mg] $_2$ (0.350 g, 0.49 mmol) in toluene (20 mL) was added to a solution of **8** (0.200 g, 0.32 mmol) in toluene (20 mL) at $20\text{ }^{\circ}\text{C}$. The mixture was stirred for 1 h, during which time it gradually changed from yellow to deep blue. Volatiles were removed in vacuo, and the residue was extracted into pentane (30 mL). The extract was concentrated to 20 mL and placed at $-30\text{ }^{\circ}\text{C}$ overnight to give deep-blue crystals of **13** (0.151 g, 91%). Mp: $235\text{--}237\text{ }^{\circ}\text{C}$ (dec). ^1H NMR (400 MHz, 298 K , C_6D_6): δ 0.86 (s, 18H, $\text{C}(\text{CH}_3)_3$), 0.99 (d, br, 12H, $\text{CH}(\text{CH}_3)_2$), 1.08 (d, br, 12H, $\text{CH}(\text{CH}_3)_2$), 1.16 (v tr of two overlapping d, br, 24H, $\text{CH}(\text{CH}_3)_2$), 3.82 (sept, br, 4H, $\text{CH}(\text{CH}_3)_2$), 3.87 (sept, br, 4H, $\text{CH}(\text{CH}_3)_2$), 6.77 (d, $^3J_{\text{H,H}} = 8.8\text{ Hz}$, 4H, ArH), 7.00–7.16 (m, 16H, ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, 298 K , C_6D_6): δ 21.6 ($\text{CH}(\text{CH}_3)_2$), 22.5 ($\text{CH}(\text{CH}_3)_2$), 22.7 ($\text{CH}(\text{CH}_3)_2$), 24.4 ($\text{CH}(\text{CH}_3)_2$), 27.4 ($\text{CH}(\text{CH}_3)_2$), 27.8 ($\text{CH}(\text{CH}_3)_2$), 29.4 ($\text{C}(\text{CH}_3)_3$), 33.1 ($\text{C}(\text{CH}_3)_3$), 122.9 (ArC), 123.2 (ArC), 123.7 (ArC), 125.4 (ArC), 127.7 (ArC), 137.2 (ArC), 142.7 (ArC), 143.2 (ArC), 146.9 (ArC), 151.0 (ArC), 159.7 (CN_2). ^{29}Si NMR (80 MHz, 298 K , C_6D_6): δ 96.9. IR (Nujol, cm^{-1}): ν 1651m, 1620m, 1362m, 1261s, 1096s, 1024s, 803s. Raman (solid under N_2 , 514 nm excitation, cm^{-1}): ν 388 (Si–Si str). UV–vis (toluene solution): $\lambda_{\text{max}} = 629\text{ nm}$ ($\epsilon \approx 7520\text{ L mol}^{-1}\text{ cm}^{-1}$). MS (EI, 70 eV): m/z 1046.7 (M^+ , 2%), 523.3 ($[\text{M}/2]^+$, 4%), 496.4 (ButisoH $^+$, 9%), 453.4 (ButisoH $^+ - \text{Pr}^i$, 16%), 320.2 (Butiso $^+ - \text{NDip}$, 100%). HREI. Acc. mass calcd for $\text{C}_{70}\text{H}_{94}\text{N}_4\text{Si}_2$: m/z 1046.7012. Found: m/z 1046.7008.

Preparation of [K(Butiso)Ge] $_2$ (14). A solution of [K(Butiso)Mg] $_2$ (0.119 g, 0.09 mmol) in toluene (20 mL) was added to a solution of **9** (0.100 g, 0.17 mmol) in toluene (20 mL) at $20\text{ }^{\circ}\text{C}$. The mixture was stirred for 1 h, during which time it gradually changed from yellow to red-purple. Volatiles were then removed from the reaction mixture in vacuo, and the residue was extracted into pentane (30 mL). The extract was concentrated to ca. 15 mL and placed at $-30\text{ }^{\circ}\text{C}$ overnight to give red-purple crystals of **14** (0.069 g, 71%). Mp: $178\text{--}179\text{ }^{\circ}\text{C}$ (dec). ^1H NMR (400 MHz, 298 K , C_6D_6): δ 0.84 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.02–1.08 (m of three overlapping d, $^3J_{\text{H,H}} = 6.8\text{ Hz}$, 36H, $\text{CH}(\text{CH}_3)_2$), 1.21 (d, $^3J_{\text{H,H}} = 6.8\text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 3.87 (m of two overlapping sept, $^3J_{\text{H,H}} = 6.8\text{ Hz}$, 8H, $\text{CH}(\text{CH}_3)_2$), 6.81 (d, $^3J_{\text{H,H}} = 8.8\text{ Hz}$, 4H, ArH), 7.00–7.10 (m, 12H, ArH), 7.20 (d, $^3J_{\text{H,H}} = 8.8\text{ Hz}$, 4H, ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, 298 K , C_6D_6): δ 22.9 ($\text{CH}(\text{CH}_3)_2$), 23.4 ($\text{CH}(\text{CH}_3)_2$), 24.1 ($\text{CH}(\text{CH}_3)_2$), 25.7 ($\text{CH}(\text{CH}_3)_2$), 28.4 ($\text{CH}(\text{CH}_3)_2$), 28.6 ($\text{CH}(\text{CH}_3)_2$), 30.5 ($\text{C}(\text{CH}_3)_3$), 34.1 ($\text{C}(\text{CH}_3)_3$), 123.8 (ArC), 123.9 (ArC), 124.5 (ArC), 125.8 (ArC), 129.6 (ArC), 139.8 (ArC), 143.5 (ArC), 143.7 (ArC), 152.5 (ArC), 156.8 (ArC), 170.0 (CN_2). IR (Nujol, cm^{-1}): ν 1653m, 1618m, 1396m, 1364m, 1322m, 1260m, 1177m, 1098s, 1018s, 934m, 830m, 800m, 776m, 744m. Raman (solid under N_2 , 514 nm excitation, cm^{-1}): ν 192 (Ge–Ge str). UV–vis: $\lambda_{\text{max}} = 502\text{ nm}$

Table 4. Summary of Crystallographic Data for Two Structural Modifications of **8**, **9**, **10**, **12**–**15**, ButisoH, and $[\text{Li}\{\text{Li}(\kappa^2\text{-N,N}'\text{-Butiso})_2\}]$

	8	8 ·0.5hexane	9	10	12	13 ·hexane
empirical formula	C ₃₅ H ₄₇ Cl ₃ N ₂ Si	C ₃₈ H ₅₄ Cl ₃ N ₂ Si	C ₃₅ H ₄₇ ClGeN ₂	C ₃₅ H ₄₇ ClN ₂ Sn	C ₄₀ H ₅₅ F ₃ N ₂ O ₄ PbS	C ₇₆ H ₁₀₈ N ₄ Si ₂
fw	630.19	673.27	603.79	649.89	924.11	1133.84
cryst syst	monoclinic	orthorhombic	orthorhombic	orthorhombic	monoclinic	triclinic
space group	<i>P2₁/n</i>	<i>Pbca</i>	<i>Pbcn</i>	<i>Pbcn</i>	<i>C2/c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	10.0389(5)	20.2749(6)	16.414(3)	16.504(3)	29.304(6)	11.9565(7)
<i>b</i> (Å)	20.1943(11)	18.6319(5)	22.426(5)	22.298(5)	12.205(2)	12.0716(7)
<i>c</i> (Å)	17.6677(11)	20.4170(6)	18.926(4)	18.868(4)	27.204(5)	14.1529(8)
α (deg)	90	90	90	90	90	86.468(2)
β (deg)	99.898(3)	90	90	90	94.18(3)	70.557(2)
γ (deg)	90	90	90	90	90	65.810(2)
<i>V</i> (Å ³)	3528.4(3)	7712.7(4)	6966(2)	6944(2)	9704(3)	1750.46(17)
<i>Z</i>	4	8	8	8	8	1
ρ (calcd) (g cm ⁻³)	1.186	1.160	1.151	1.243	1.265	1.076
μ (mm ⁻¹)	0.319	0.296	0.979	0.836	3.566	0.094
<i>F</i> (000)	1344	2888	2560	2704	3728	620
reflns collected	47 702	85 341	17 308	24 616	14 820	22 474
unique reflns	7689	7561	6126	6813	8605	7885
<i>R</i> _{int}	0.0437	0.1265	0.0457	0.0529	0.0456	0.0753
<i>R</i> ₁ indices [<i>I</i> > 2 σ (<i>I</i>)]	0.0387	0.0531	0.0689	0.0448	0.0685	0.0570
w <i>R</i> ₂ indices (all data)	0.1015	0.1400	0.2092	0.1295	0.1923	0.1133
largest peak and hole (e Å ⁻³)	0.33, -0.36	0.41, -0.40	1.64, -0.41	0.66, -0.55	4.42 (near Pb1), -1.36	0.29, -0.24
CCDC no.	816558	816557	816559	816552	816553	816554

	14 ·hexane	15	ButisoH	$[\text{Li}\{\text{Li}(\kappa^2\text{-N,N}'\text{-Butiso})_2\}]$
empirical formula	C ₇₆ H ₁₀₈ Ge ₂ N ₄	C ₇₀ H ₉₄ N ₄ Sn ₂	C ₃₅ H ₄₈ N ₂	C ₇₀ H ₉₄ Li ₂ N ₄
fw	1222.84	1228.87	496.75	1005.37
cryst syst	triclinic	monoclinic	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P2₁/n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	11.968(2)	16.627(3)	9.899(2)	11.698(2)
<i>b</i> (Å)	12.134(2)	19.181(4)	10.533(2)	13.099(3)
<i>c</i> (Å)	14.323(3)	21.647(4)	15.683(3)	24.937(5)
α (deg)	86.60(3)	90	84.35(3)	87.85(3)
β (deg)	70.97(3)	103.36(3)	80.53(3)	76.53(3)
γ (deg)	65.86(3)	90	71.89(3)	65.22(3)
<i>V</i> (Å ³)	1787.9(6)	6717(2)	1531.1(5)	3365.9(12)
<i>Z</i>	1	4	2	2
ρ (calcd) (g cm ⁻³)	1.136	1.215	1.078	0.992
μ (mm ⁻¹)	0.883	0.784	0.062	0.056
<i>F</i> (000)	656	2568	544	1096
reflns collected	13 284	19 653	12 308	17 297
unique reflns	7002	11 808	6652	11 494
<i>R</i> _{int}	0.0348	0.0377	0.0355	0.0333
<i>R</i> ₁ indices [<i>I</i> > 2 σ (<i>I</i>)]	0.0414	0.0446	0.0555	0.0792
w <i>R</i> ₂ indices (all data)	0.0962	0.1061	0.1513	0.2435
largest peak and hole (e Å ⁻³)	0.53, -0.39	1.41, -0.69	0.19, -0.19	0.47, -0.24
CCDC no.	816555	816556	816550	816551

($\varepsilon \approx 6030 \text{ L mol}^{-1} \text{ cm}^{-1}$). MS (EI, 70 eV): *m/z* 496.3 (ButisoH⁺, 10%), 453.4 (ButisoH⁺-Pr⁺, 17%), 320.2 (Butiso⁺-NDip, 100%).

Preparation of $[\{\text{ButisoSn}\}_2]$ (15**).** A solution of $[\{\text{MesNacnac}\}\text{Mg}\}_2]$ (0.119 g, 0.18 mmol) in toluene (20 mL) was added to a solution of **10** (0.230 g, 0.35 mmol) in toluene (20 mL) at 20 °C. The mixture was stirred for 1 h, during which time it gradually changed from yellow to orange-brown. Volatiles were removed in vacuo, and the residue was

extracted into pentane (30 mL). The extract was concentrated to ca. 15 mL and placed at -30 °C to yield dichroic orange–green crystals of **15** (0.080 g, 36%). Mp: 144–146 °C (dec). ¹H NMR (400 MHz, 298 K, C₆D₆): δ 0.81 (d, ³*J*_{H,H} = 6.8 Hz, 12H, CH(CH₃)₂), 0.82 (s, 18H, C(CH₃)₃), 1.00 (d, ³*J*_{H,H} = 6.8 Hz, 12H, CH(CH₃)₂), 1.23 (d, ³*J*_{H,H} = 6.8 Hz, 12H, CH(CH₃)₂), 1.50 (d, ³*J*_{H,H} = 6.8 Hz, 12H, CH(CH₃)₂), 3.99 (sept, ³*J*_{H,H} = 6.8 Hz, 4H, CH(CH₃)₂), 4.13 (sept, ³*J*_{H,H} = 6.8 Hz,

4H, CH(CH₃)₂), 6.87–7.08 (m, 16H, ArH), 7.27 (d, ³J_{H,H} = 8.8 Hz, 4H, ArH). ¹³C{¹H} NMR (100 MHz, 298 K, C₆D₆): δ 22.9 (CH(CH₃)₂), 23.5 (CH(CH₃)₂), 24.5 (CH(CH₃)₂), 26.4 (CH(CH₃)₂), 28.4 (CH(CH₃)₂), 28.9 (CH(CH₃)₂), 30.7 (C(CH₃)₃), 34.3 (C(CH₃)₃), 123.5 (ArC), 123.8 (ArC), 124.3 (ArC), 125.8 (ArC), 130.3 (ArC), 130.4 (ArC), 140.9 (ArC), 143.5 (ArC), 144.1 (ArC), 152.6 (ArC), 162.8 (CN₂). ¹¹⁹Sn NMR (150 MHz, 298 K, C₆D₆): δ 777.7. IR (Nujol, cm⁻¹): ν 1652m, 1620m, 1587m, 1563w, 1360m, 1324m, 1314m, 1262s, 1176m, 1100s, 1019m, 844m, 826m. Raman (solid under N₂, 514 nm excitation, cm⁻¹): ν 165 (Sn–Sn str). UV–vis: λ_{max} = 388 nm (ε ≈ 2100 L mol⁻¹ cm⁻¹). MS (EI, 70 eV): m/z 1110.6 (M⁺–Sn, 1%); 615.3 ([M/2]⁺, 3%), 496.3 (ButisoH⁺, 20%), 453.3 (ButisoH⁺–Pr⁺, 26%), 320.2 (Butiso⁺–NDip, 100%).

X-ray Crystallography. Crystals of two structural modifications of **8**, **9**, **10**, **12–15**, ButisoH, and [Li{Li(κ²-N,N'-Butiso)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 Kα radiation (λ = 0.710 73 Å). The structures were solved by direct methods and refined on F² by full-matrix least squares (SHELX97)³² using all unique data. All non-H atoms are anisotropic with H atoms included in calculated positions (riding model). Crystal data, details of data collection, and refinement are given in Table 4.

Theoretical Studies. Geometry optimizations were carried out using the TurboMole optimizer³³ and gradients at the BP86³⁴/def2-TZVPP³⁵ level of theory. The resolution-of-identity method has been applied.³⁶ Stationary points were characterized as minima by calculating the Hessian matrix analytically at this level of theory. NBO orbital analyses were performed using the program packages Gaussian03³⁷ and NBO 5.0³⁸ at the BP86/def2-TZVPP level.

■ ASSOCIATED CONTENT

Supporting Information. Crystallographic data as CIF files for two structural modifications of **8**, **9**, **10**, **12–15**, ButisoH, and [Li{Li(κ²-N,N'-Butiso)₂}], ORTEP diagrams for **8**·0.5hexane, **10**, **14**, **15**, ButisoH, and [Li{Li(κ²-N,N'-Butiso)₂}], select metrical parameters for ButisoH and [Li{Li(κ²-N,N'-Butiso)₂}], and further details of the calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ REFERENCES

- (1) Green, S. P.; Jones, C.; Stasch, A. *Science* **2007**, *318*, 1754.
- (2) (a) Green, S. P.; Jones, C.; Stasch, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 9079. (b) Overgaard, J.; Jones, C.; Stasch, A.; Iversen, B. B. *J. Am. Chem. Soc.* **2009**, *131*, 4208. (c) Bonyhady, S. J.; Green, S. P.; Jones, C.; Nembenna, S.; Stasch, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 2973. (d) Sidiropoulos, A.; Jones, C.; Stasch, A.; Klein, S.; Frenking, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 9701. (e) Bonyhady, S. J.; Jones, C.; Nembenna, S.; Stasch, A.; Edwards, A. J.; McIntyre, G. J. *Chem.—Eur. J.* **2010**, *16*, 938. (f) Jones, C.; McDyre, L.; Murphy, D. M.; Stasch, A. *Chem. Commun.* **2010**, 46, 1511. (g) Bonyhady, S. J.; Collis, D.; Frenking, G.; Holzmann, N.; Jones, C.; Stasch, A. *Nat. Chem.* **2010**, *2*, 865. (h) Platts, J. A.; Overgaard, J.; Jones, C.; Stasch, A.; Iversen, B. B. *J. Phys. Chem. A* **2011**, *115*, 194.

(3) Reviews: (a) Jones, C. *Coord. Chem. Rev.* **2010**, *254*, 1273. (b) Stasch, A.; Jones, C. *Dalton Trans.* **2011**, *40*, DOI:10.1039/c0dt01831g.

(4) Liu, Y.; Li, S.; Yang, X.-J.; Yang, P.; Wu, B. *J. Am. Chem. Soc.* **2009**, *131*, 4210.

(5) For example, see: (a) Yao, S.; Xiong, Y.; Driess, M. *Organometallics* **2011**, *30*, DOI:org/10.1021/om200017h. (b) Asay, M.; Jones, C.; Driess, M. *Chem. Rev.* **2011**, *111*, 354. (c) Power, P. P. *Nature* **2010**, *463*, 171. (d) Fischer, R. C.; Power, P. P. *Chem. Rev.* **2010**, *110*, 3877. (e) Schnöckel, H. *Chem. Rev.* **2010**, *110*, 4125. (f) Mizuhata, Y.; Sasamori, T.; Tohkitoh, N. *Chem. Rev.* **2009**, *109*, 3479. (g) Nagendran, S.; Roesky, H. W. *Organometallics* **2008**, *27*, 457 and references cited therein.

(6) For example, see: Woodul, W. D.; Richards, A. F.; Stasch, A.; Driess, M.; Jones, C. *Organometallics* **2010**, *29*, 3655 and references cited therein.

(7) N.B.: The silicon(0) and boron(I) analogues of **1** and **2** were previously prepared via the KC₈ reduction of NHC adducts of SiCl₄ and BBr₃, respectively. See: (a) Wang, Y.; Xie, Y.; Wei, P.; King, R. B.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *Science* **2008**, *321*, 1069. (b) Wang, Y.; Quillian, B.; Wei, P.; Wannere, C. S.; Xie, Y.; King, R. B.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *J. Am. Chem. Soc.* **2007**, *129*, 12412.

(8) Green, S. P.; Jones, C.; Junk, P. C.; Lippert, K.-A.; Stasch, A. *Chem. Commun.* **2006**, 3978.

(9) Sen, S. S.; Jana, A.; Roesky, H. W.; Schulzke, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 8536.

(10) Nagendran, S.; Sen, S. S.; Roesky, H. W.; Koley, D.; Grubmüller, H.; Pal, A.; Herbst-Irmer, R. *Organometallics* **2008**, *27*, 5459.

(11) Several related dimeric group 14 element(I) dimers bearing unsupported E–E bonds have been reported. See, for example, E = Si: (a) Reference 7a. (b) Gau, D.; Rodriguez, R.; Kato, T.; Saffron-Merceron, N.; de Cozar, A.; Cossio, F. P.; Baceiredo, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 1092. See E = Ge: (c) Wang, W.; Inoue, S.; Yao, S.; Driess, M. *Chem. Commun.* **2009**, 2661. (d) Leung, W.-P.; Chiu, W.-K.; Chong, K.-H.; Mak, C. W. *Chem. Commun.* **2009**, 6822. See E = Sn: (e) Jambor, R.; Kasna, B.; Kirschner, K. N.; Schürmann, M.; Jurkschat, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 1650.

(12) For recent reviews, see: (a) Power, P. P. *Organometallics* **2007**, *26*, 4362. (b) Sekiguchi, A. *Pure Appl. Chem.* **2008**, *80*, 447. (c) Sasamori, T.; Han, J.-S.; Hironaka, K.; Takagi, N.; Nagase, N.; Tokitoh, N. *Pure Appl. Chem.* **2010**, *82*, 603 and references cited therein.

(13) For example, see: (a) Sen, S. S.; Khan, S.; Roesky, H. W.; Kratzert, D.; Meindl, K.; Henn, J.; Stalke, D.; Demers, J.-P.; Lange, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 2322. (b) Yeong, H.-X.; Xi, H.-W.; Lim, K. H.; So, C.-W. *Chem.—Eur. J.* **2010**, *16*, 12956. (c) Tavcar, G.; Sen, S. S.; Roesky, H. W.; Hey, J.; Kratzert, D.; Stalke, D. *Organometallics* **2010**, *29*, 3930. (d) Sen, S. S.; Roesky, H. W.; Meindl, K.; Stern, D.; Henn, J.; Stueckel, A. C.; Stalke, D. *Chem. Commun.* **2010**, *46*, 5873. (e) Sen, S. S.; Tavcar, G.; Roesky, H. W.; Kratzert, D.; Hey, J.; Stalke, D. *Organometallics* **2010**, *29*, 2343. (f) Yeong, H.-X.; Lau, K.-C.; Xi, H.-W.; Hwa Lim, K.; So, C.-W. *Inorg. Chem.* **2010**, *49*, 371.

(14) Jones, C.; Schulten, C.; Fohlmeister, L.; Stasch, A.; Murray, K. S.; Moubarak, B.; Kohl, S.; Ertem, M. Z.; Gagliardi, L.; Cramer, C. J. *Chem.—Eur. J.* **2011**, *17*, 1294.

(15) (a) Jin, G.; Jones, C.; Junk, P. C.; Lippert, K.-A.; Rose, R. P.; Stasch, A. *New J. Chem.* **2009**, *33*, 64. (b) Coles, M. P. *Dalton Trans.* **2006**, 985.

(16) So, C.-W.; Roesky, H. W.; Magull, J.; Oswald, R. B. *Angew. Chem., Int. Ed.* **2006**, *45*, 3948.

(17) Lu, L.-D.; Li, J.-J.; Yang, W.; Ren, C.-X.; Ding, Y.-Q. *Acta Crystallogr., Sect. E* **2008**, *64*, o870.

(18) (a) Jones, C.; Rose, R. P.; Stasch, A. *Dalton Trans.* **2008**, 2871. (b) Brym, M.; Francis, M. D.; Jin, G.; Jones, C.; Mills, D. P.; Stasch, A.

Organometallics **2006**, *25*, 4799. (c) Nimitsiriwat, N.; Gibson, V. C.; Marshall, E. L.; White, A. J. P.; Dale, S. H.; Elsegood, M. R. *J. Dalton Trans.* **2007**, 4464.

(19) Jana, A.; Sarish, S. P.; Roesky, H. W.; Schulzke, C.; Döring, A.; John, M. *Organometallics* **2009**, *28*, 2563. N.B.: Related polymeric, heteroleptic organolead halide complexes have appeared in the literature. For example, see: Jurkschat, K.; Peveling, K.; Schürmann, M. *Eur. J. Inorg. Chem.* **2003**, 3563. Henn, M.; Deaky, V.; Krabbe, S.; Schürmann, M.; Prosenč, M. H.; Herres-Pawliss, S.; Mahieu, B.; Jurkschat, K. *Z. Anorg. Allg. Chem.* **2011**, 637, 211.

(20) Determined from a survey of the Cambridge Crystallographic Database, Mar 2011.

(21) Stasch, A.; Forsyth, C. M.; Jones, C.; Junk, P. C. *New J. Chem.* **2008**, *32*, 829.

(22) Peng, Y.; Wang, X.; Fetting, J. C.; Power, P. P. *Chem. Commun.* **2010**, 46, 943.

(23) Spikes, G. H.; Giuliani, J. R.; Augustine, M. P.; Nowik, I.; Herber, R. H.; Power, P. P. *Inorg. Chem.* **2006**, *45*, 9132.

(24) (a) Lappert, M. F.; Power, P. P.; Protchenko, A. V.; Seeber, A. L. *Metal Amide Chemistry*; Wiley-VCH: Weinheim, Germany, 2009; Chapter 9. (b) Wrackmeyer, B. In *Tin Chemistry: Fundamentals, Frontiers and Applications*; Davies, A. G., Gielen, M., Pannell, K., Tiekink, E., Eds.; Wiley: Chichester, U.K., 2008.

(25) Peng, Y.; Fischer, R. C.; Merrill, W. A.; Fischer, J.; Pu, L.; Ellis, B. D.; Fetting, J. C.; Herber, R. H.; Power, P. P. *Chem. Sci.* **2010**, *1*, 461.

(26) Drago, R. S. *J. Phys. Chem.* **1958**, *62*, 353.

(27) Jonas, V.; Frenking, G.; Reetz, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 8741.

(28) (a) Lein, M.; Krapp, A.; Frenking, G. *J. Am. Chem. Soc.* **2005**, *127*, 6290. (b) Chen, Y.; Hartmann, M.; Diedenhofen, M.; Frenking, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 2052.

(29) For example, see: (a) Takeuchi, K.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2008**, *130*, 16848. (b) Spikes, G. H.; Power, P. P. *Chem. Commun.* **2007**, 85.

(30) Kovács, A.; Esterhuysen, C.; Frenking, G. *Chem.—Eur. J.* **2005**, *11*, 1813.

(31) Garcia, A. M.; Romero-Salguero, F. J.; Bassani, D. M.; Lehn, J.-M.; Baum, G.; Fenske, D. *Chem.—Eur. J.* **1999**, *5*, 1803.

(32) Sheldrick, G. M. *SHELX-97*; University of Göttingen: Göttingen, Germany, 1997.

(33) Ahlrichs, R.; Baer, M.; Haeser, M.; Horn, H.; Koelmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165.

(34) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(35) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

(36) Eichkorn, K.; Treutler, O.; Ohm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *242*, 652.

(37) Frisch, M. J.; *Gaussian03*, revision B.05; Gaussian, Inc.: Pittsburgh, PA, 2003 (see the Supporting Information for the full reference).

(38) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.