Synthesis and Structural Characterization of Tin Analogues of *N*-Heterocyclic Carbenes

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The synthesis and X-ray crystal structures of five *N*-heterocyclic stannylenes are reported. These compounds, containing a variety of backbones, were prepared by the salt metathesis of the appropriate dilithiated diamide with SnCl₂ and show a high degree of thermal stability compared to the corresponding species with unsaturated backbones. If bulky di*iso*propylphenyl groups are attached to the nitrogen centers then the structures are monomeric, but when the less bulky mesityl groups are employed the solid-state structure was shown to be dimeric.

Introduction

The quest for isolable carbenes has come to form part of chemical folklore.^{1,2} The best known example of this class of compound is based on the imidazol-2-ylidene framework (Chart 1, type A, E = C) which was first reported by Arduengo et al. in 1991 using imidazolium salts as precursors.³ This stimulated considerable interest in the preparation of similar species, and shortly after, carbenes derived from benzimidazole (Chart 1, type C, E = C) and acyclic representatives were added to the group.⁴ These N-heterocyclic carbenes (NHCs) and their acyclic counterparts derive their remarkable stability from the strong N-C carbene π -donation that leads to a largely filled $p(\pi)$ orbital at the carbene carbon atom. It is no coincidence that most applications of stable carbenes involve the Arduengo-type imidazole-based carbenes as they are much more stable than the benzimidazole- based or acyclic representatives.⁵ These applications, particularly the distinctive performance of NHC- supported complexes in catalytic reactions,¹ have been another driving force in the development of this area.

An alternative strategy to modification of this class of compound is to alter the various components of the heterocyclic ring framework. One commonly explored route has been to probe the versions of these ligands with saturated backbones, 4,5-dihydroimidazol-2-ylidenes (Chart 1, type **B**, E = C), which have been found to be less stable as free carbenes and are more strongly basic than their unsaturated analogues.⁶ In addition, several elegant studies have sought to vary the groups directly adjacent to the divalent carbon center. For example, the *P*-heterocyclic carbenes (PHCs)⁷ and cyclic (alkyl)(amino)carbenes (CAAC) systems⁸ developed by Bertrand and co-workers have been shown to have rather different properties compared to the parent NHCs.^{8,9}

A more commonly explored approach is to substitute the carbene center with an isovalent p-block atom. Examples of analogues of the Arduengo-type carbene have been successfully synthesized for many elements from groups 13 to 16 which requires the formal adjustment of charge to give formally anionic (group 13),¹⁰ neutral (group 14),^{11–13} cationic (group 15),¹⁴ or dicationic (group 16)¹⁵ species. In each case, the main-group center is two coordinate and

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 a E = C, Si, Ge, Sn, Pb.

formally possesses a lone pair of electrons. To complement these synthetic studies, molecular orbital calculations have been employed to probe the similarities and differences between the electronic structures of the various members of this class of compounds.^{11,13,16,17} Within the more specific class of neutral compounds that are the group 14 analogues of NHCs which are the direct subject of this paper, most attention has focused on the lighter elements Si^{11,17,18} and Ge,^{13,19–22} and several structurally characterized examples of these have been reported containing both saturated and unsaturated backbones. Furthermore, several of the compounds proved to be preparable on a sufficient scale to enable their reactivity, in particular regarding their use as ligands

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toward transition metals, to be investigated.^{18,21,23,24} In contrast, NHC analogues of the heaviest group 14 elements tin and lead are relatively sparse, despite the well-known inert pair effect which suggests that the divalent group 14 species should become more stable upon descending the group. Lead analogues of NHCs have recently been reported by us and others.^{25–27} Only recently have tin analogues of Arduengo-type carbenes and their benzannulated derivatives been described.^{22,27-30} The chemistry of related tin(II) amides has expanded considerably in the last few decades following the pioneering studies of Lappert and co-workers,³¹ and we believe N-heterocyclic stannylenes to be particularly attractive in extending the heavier group 14 analogues of such compounds and eventually exploring their catalytic chemistry. It is also noteworthy that simple Sn(II) halides already have important applications as promoters for Ptcatalyzed hydroformylation.³² In this paper we report the synthesis and X-ray crystal structures of five examples of N-heterocyclic stannylenes.

Results and Discussion

Synthesis. The stannylenes 1-5 (Chart 2) were readily synthesized using a salt metathesis procedure similar to those that have previously proved successful for other tin(II)

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Chart 2^a



^{*a*} Dipp = $2,6^{-i}Pr_2C_6H_3$, Mes = $2,4,6^{-}Me_3C_6H_2$.

amides,^{33,34} that is, by the addition of equimolar quantities of the dilithium salts of the appropriate diamide with $SnCl_2$ in diethylether at -78 °C followed by gradual warming to room temperature and stirring for approximately 2 h.

The low temperatures at which the reactions were carried out were found to be essential as shown by the attempted synthesis of **1** at room temperature which gave a large mixture of products (¹H NMR spectroscopy) and negligible quantities of the desired product. All the products were isolated by extraction into *n*-hexane followed by filtration of the byproduct; highly air- and moisture-sensitive single crystals of **1**–**5** were produced by storage of concentrated *n*-hexane solutions at -18 °C for 16 h. The crystalline yields of **1**–**5** varied widely between 15 and 81%, which, given that the ¹H NMR spectra of the solutions showed evidence for only the desired product and the free diamine in each case, suggests that the isolated crystalline yield is a consequence of the high air and moisture sensitivity of the product and the high solubility of some of the complexes in *n*-hexane.

Compounds 1-5 have either a yellow (3 and 4) or orange (1, 2, and 5) coloration. Moreover, 3 and 5 are thermochromic; upon heating, 3 changed from yellow to red coloration and 5 changed from an orange to red coloration. Similar temperature-dependent color changes have been noted for other low valent tin amides.^{30,33,35}

The ¹H NMR spectra of 1, 2 and 4 show two doublets for pairs of CH₃ moieties of the diisopropyl groups (each coupling to the CH), yet one septet for the CH proton. This is a commonly encountered feature of complexes of this bulky ligand due to restricted rotation around the N-aryl bond, which leads to different environments for the methyl groups within each CHMe₂ unit, with one pointing relatively toward the tin atom, and one pointing in the direction of the backbone carbon atoms. In contrast, complex 5, which has less steric congestion as a result of the smaller central fourmembered SnN₂Si ring, exhibits magnetically equivalent isopropyl groups, presumably on account of rotation about the C-N bond being relatively fast on the ¹H NMR time scale. No ^{117/119}Sn satellites could be discerned in the ¹H spectra of 1-5, presumably as a result of interaction through the quadrupolar amide nitrogen centers.

Further information on the identities of the species was gleaned from ¹¹⁹Sn NMR spectroscopy (in C₆D₆, see Figure 1), which showed a distinctive range of chemical shifts $\{\delta = 499 \ (5), 386 \ (3), 366 \ (1), 291 \ (2) \text{ and } 172 \ (4) \text{ ppm}\}.$ The chemical shifts for 1, 2, 3, and 5 are all consistent with two-coordinate tin centers and are of a similar order of magnitude to those previously observed for benzannellated tin(II) amides;²⁹ these values are at higher frequencies than the closely related 1,3,2 λ^2 -diazastannoles (type A, E = Sn these are the analogues of 1 and 3 containing unsaturated backbones; for *tert*-butyl substituents on N, $\delta = 237$ ppm and for mesityl groups, $\delta = 259$ ppm),²⁸ which originates from the greater shielding of the Sn(II) center in the latter from π -conjugation. The lower frequency resonance for 4 suggests a higher coordination number at the tin center which is unsurprising given the O-donor atom present in the ligand backbone (vide infra). The formulation and structure of 4 is closely related to a stannylene containing an N-donor atom in the backbone.36

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Figure 1. ¹¹⁹Sn NMR spectra of 1-5 in C₆D₆.

In contrast to some Sn(II) complexes, 1-5 are photolytically stable; thus, toluene solutions of 1-5 can be stored under anaerobic conditions for many weeks without any sign of deterioration of the sample. In addition, complexes 1-5all show a relatively high degree of thermal stability, decomposing between 115 and 250 °C, in marked contrast to compounds of type A (E = Sn) which decompose at 60 °C via chelotropic fragmentation to yield diazadienes and elemental tin.²⁸ Furthermore, a solution of 1 in C₆D₆ was heated to 60 °C for 6 days without any sign of decomposition. The relative thermal stability of the N-heterocyclic stannylene with a saturated backbone compared to an unsaturated backbone is in stark contrast to the corresponding N-heterocyclic carbenes for which the species with unsaturated backbones show far higher stability. This interesting difference is presumably a consequence of the much lower aromatic stabilization of Sn analogues of Arduengo-type carbenes which thus favors the chelotropic decomposition pathway.

Solid State Structures. X-ray diffraction experiments were performed on suitable single crystals of each of the compounds 1-5 and their molecular structures are shown in Figures 2–6. Key bond lengths and angles are summarized in the legends of the respective figures, and a ready comparison of some significant bond dimensions are collated

in Table 1; data relating to the structures and collection parameters are shown in Table 2.

Complexes 1, 2, 4, and 5 which contain the bulky diisopropylphenyl ligand are essentially monomeric, whereas 3, which contains the less bulky 2,4,6-trimethylphenyl (mesityl) ligand, forms a dimer. In 1, 2 and 5, the tin(II) center is two-coordinate, being bonded to two planar N-centers and forming part of nonplanar five- (1), six- (2), or planar four- (5) membered heterocyclic rings. In complex 4, the oxygen atom in the ligand backbone forms a contact with the tin center {Sn-O 2.437(1) Å, cf. 2.527(5) Å in $SnCl_2 \cdot 1, 4$ -dioxane}, which renders the tin center formally three-coordinate, an observation which is consistent with the ¹¹⁹Sn chemical shift of this species. The di*iso*propylphenyl groups align essentially perpendicular to the N-heterocyclic stannylene ring in each case. The Sn atoms bond essentially symmetrically to both N centers, although there are minor variances which in some cases fall just outside of experimental error.

Far more significant are the variations of Sn–N bond lengths between compounds, for which the Sn–N distances increase in the order 1 (av. 1.989 Å), 2 (av. 2.034 Å), 4 (av. 2.075 Å), and 5 (av. 2.090 Å). These distances compare to average Sn–N bond lengths of 2.093 Å in Gudat's tin analogue of an Arduengo-type carbene,²⁸ and 2.059 and 2.082 Å observed in the two structurally characterized examples of monomeric annulated *N*-heterocyclic stan-

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Figure 2. Molecular structure of **1** showing the monomer (top) and aggregation through long-range Sn…aryl interactions (bottom). The molecule was disordered over two sites that were related by a 2-fold rotation axis oriented through the N1–N1A vector; thus atoms Sn, C(13) and C(14) are disordered over two positions (with 50% occupancy); only one position of the tin atom and carbon atoms in the ligand backbone are shown. Thermal ellipsoids are at 50% probability and all hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°) for **1**: Sn(1)–N(1) 1.973(2), Sn(1)–N(1A) 2.004(2), N(1)–C(13) 1.548(6), C(13)–C(14) 1.542(11), N(1A)–C(14) 1.543(6), N(1)–Sn(1)–N(1A) 84.15(8), C(1)–N(1)–Sn(1) 130.6(2), C(1)–N(1)–C(13) 112.5(3), C(13)–N(1)–Sn(1) 113.8(3), C(1A)–N(1A)–Sn(1) 132.9(2), C(1A)–N(1A)–C(14A) 111.7(3), C(14)–N(1a)–Sn(1) 113.0(3), Σ angles at N(1) 356.9, Σ angles at N(1A) 357.6, Sn–aryl_entroid 3.51.

nylenes.^{29,30} This comparison serves to highlight the short Sn-N distances within 1 and 2, although the origin of this observation is not readily apparent.

As mentioned above, the use of the smaller mesityl group in **3** compared to the di*iso*propylphenyl group in **1**, **2**, **4**, and **5** leads to aggregation of monomers in the solid state, although the solution ¹¹⁹Sn NMR spectrum is suggestive of a two-coordinate tin center in C₆D₆ solution (vide supra). This fine balance between the formation of monomeric and dimeric structures is further reinforced by comparison of the structures of both **3** and **5** with literature precedents. Whereas **5** is essentially monomeric, closely related species containing SnN₂Si rings show a variety of aggregation; hence, [Me₂Si('BuN)₂Sn] contains a mixture of both monomers and dimers³⁷ in the solid state, whereas [Me₂Si('PrN)₂Sn] is exclusively dimeric;³⁸ similarly imposing silacycloalkyl units on the backbone in [(cyclo)Si('BuN)₂Sn] {cyclo = (CH₂)_n with n = 3-5} realizes dimeric structures.³⁹



Figure 3. Molecular structure of **2**. The thermal ellipsoids are at 50% probability and all hydrogen atoms have been omitted for clarity. The CH₂ group of the backbone is disordered over two sites (SOF = 0.73/0.27) which are shown as C26A and C26B. Selected bond distances (Å) and angles (°) for **2**: Sn(1)-N(1) 2.035(1), Sn(1)-N(2) 2.032(1), N(1)-C(1) 1.435(2), N(1)-C(25A) 1.464(2), N(2)-C(13) 1.435(2), N(2)-C(27A) 1.466(2), C(25A)-C(26A) 1.503(3), C(26A)-C(27A) 1.489(3); N(1)-Sn(1)-N(2) 92.63(6), C(1)-N(1)-Sn(1) 118.1(1), C(1)-N(1)-C(25A) 114.9(1), C(25A)-N(1)-Sn(1) 127.0(1), C(13)-N(2)-Sn(1) 120.1(1), C(13)-N(2)-C(27A) 114.0(1), C(27A)-N(2)-Sn(1) 125.9(1), C(27A)-C(26A)-C(25A) 118.6(2), Σ angles at N(1) 360.0, Σ angles at N(2) 360.0.



Figure 4. Molecular structure of **3**. The thermal ellipsoids are at 50% probability and all hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°) for **3**: Sn(1)–N(1) 2.259(5), Sn(1)–N(2) 2.101(6), Sn(1)–N(1A) 2.366(6), N(1)–C(1) 1.466(8), N(1)–C(19) 1.481(8), N(2)–C(10) 1.423(8), N(2)–C(20) 1.460(8), C(19)–C(20) 1.513(9); N(1)–Sn(1)–N(2) 79.7(2), N(1)–Sn(1)–N(1A) 85.8(2), N(2)–Sn(1)–N(1A) 96.1(2), C(1)–N(1)–Sn(1) 118.6(4), C(1)–N(1)–C(19) 111.0(5), C(19)–N(1)–Sn(1) 106.4(4), C(1)–N(1)–Sn(1A) 117.3(4), C(20)–N(1)–Sn(1A) 107.7(4), Sn(1)–N(1)–Sn(1A) 94.2(2), C(10)–N(2)–Sn(1) 129.1(4), C(10)–N(2)–C(20) 117.5(5), C(20)–N(2)–Sn(1) 113.0(4), Σ angles at N(1) 336.0, Σ angles at N(2) 359.6. Symmetry transformations used to generate equivalent atoms labeled "A" –*x* + 2, –*y* + 1, –*z* + 1.

In a similar vein, the version of **3** (type **A**, E = Sn) containing an unsaturated backbone was found to be a monomer showing no evidence of intermolecular contacts.²⁸ However, the solid-state structure of **3** shows two stannylene units linking through amide moieties to form a dimer, in a similar fashion to that which has been previously observed in the related [R₂Si('BuN)₂Sn] and [1,2-C₆H₄(NMe)₂-Sn]₂.^{29,37,39} The Sn–N bond lengths in **3** fall into three distinct groups: Sn(1)–N(2) and its symmetry equivalent are the shortest as they play no part in intramolecular bonding; the Sn(1)–N(1) and its symmetry equivalent are longer as they are the endocylic Sn–N units which form the base unit in each stannylene ring for dimerization; finally Sn(1)–N(1A)

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Figure 5. Molecular structure of **4**. The thermal ellipsoids are at 50% probability and all hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°) for **1**: Sn(1)–N(1) 2.075(2), Sn(1)–N(2) 2.075(2), Sn(1)–O(1) 2.4369(14), N(1)–C(1) 1.423(3), N(1)–C(25) 1.459(3), N(2)–C(13) 1.419(3), N(2)–C(28) 1.463(3); N(1)–Sn(1)–N(2) 100.55(7), N(1)–Sn(1)–O(1) 73.29(6), N(2)–Sn(1)–O(1) 74.88(6), C(1)–N(1)–Sn(1) 120.29(13), C(1)–N(1)–C(25) 116.72(16), C(25)–N(1)–Sn(1) 122.79(13), C(26)–O(1)–Sn(1) 107.09(12), C(27)–O(1)–Sn(1) 108.15(12), C(13)–N(2)–Sn(1) 121.78(13), C(13)–N(2)–C(28) 118.56(17), C(28)–N(2)–Sn(1) 115.84(13), Σ angles at N(1) 359.8 Σ angles at N(2) 356.2.

and its symmetry equivalent are the longest bonds as these are the intramolecular contacts themselves. The oligomerization is accompanied by a change in geometry at the linking nitrogen centers which become distinctly pyramidal. The Sn–N bond linking separate stannylene units $\{2.366(6) \text{ Å}\}$ is longer than either of those within the individual heterocycle (av. 2.18 Å), but it should be noted that in the heterocycle there is a large difference in the Sn–N bond lengths $\{2.101(6) \text{ and } 2.259(5) \text{ Å}\}.$

Whereas 3 shows strong intermolecular contacts in forming a dimeric structure in the solid state, molecules of 2 and 4 show little or no tendency to associate in their respective solid-state structures. In contrast, complexes 1 and 5 assume an intermediate position and show weak long-range interactions between tin atoms and aryl rings of adjoining molecules. In 1, a quasi-dimeric structure (Figure 1, bottom) is formed by the reciprocal interaction of tin atoms of a stannylene unit with aryl rings of a second molecule, with Sn-aryl_{centroid} distances of 3.51 Å. A rather more complex network of Sn-aryl contacts are seen for 5 where two distinct types of Sn-aryl interactions are evident. The first is an η^2 interaction with one of the phenyl rings of a SiPh₂ unit from the backbone of a neighboring molecule. In addition η^6 interactions with the aryl ring of other diisopropylphenyl groups are evident; the combination of these interactions link individual molecules of 5 into a complex network. It is well established that tin, and indeed most of the low-valent p-block metals, is capable of forming coordination compounds with aromatic hydrocarbons. However, the distances observed in 1 and 5 are much greater than those seen in the well-established examples of Sn $\cdots \eta^6$ -aryl interactions,⁴⁰ where distances as small as 2.53 Å have been observed.⁴¹



Figure 6. Molecular structure of 5 showing the monomer (top) and aggregation through long-range Sn \cdots η^2 -aryl and Sn \cdots η^6 -aryl interactions (bottom). The thermal ellipsoids are at 50% probability and all hydrogen atoms have been omitted for clarity. The unit cell contains two crystallographically independent molecules. Selected bond lengths (Å) and angles (°) are presented for both molecules of 5. first molecule: Sn(1)-N(1)2.100(3), Sn(1)-N(2) 2.071(2), N(1)-C(1) 1.427(4), N(1)-Si(1) 1.726(3), N(2)-C(13) 1.424(4), N(2)-Si(1) 1.733(3), N(1)-Sn(1)-N(2) 74.62(10), C(1)-N(1)-Sn(1) 129.19(19), C(1)-N(1)-Si(1) 133.8(2), Si(1)-N(1)-Sn(1) 95.19(11), C(13)-N(2)-Sn(1) 133.1(2), Si(1)-N(2)-Sn(1) 96.01(11), N(1)-Si(1)-N(2) 93.92(12), Σ angles at N(1) 358.18, Σ angles at N(2) 359.11, av. Sn $-C(\eta^2$ -arene) 3.745; second molecule: Sn(2)-N(3) 2.120(3), Sn(2)-N(4) 2.069(2), N(3)-C(37) 1.411(4), N(3)-Si(2) 1.722(3), N(4)-C(49) 1.425(4), N(4)-Si(2) 1.730(3), N(3)-Sn(2)-N(4) 74.04(10), C(37)-N(3)-Sn(2) 121.70(19), Si(2)-N(3)-Sn(2) 95.11(11), C(49)-N(4)-Sn(2) 132.7(2), C(49)-N(4)-Si(2) 130.2(2), Si(2)-N(4)-Sn(2) 96.75(12), N(3)-Si(2)-N(4) 93.92(12), Σ angles at N(3) 355.81, Σ angles at N(4) 359.65, Sn-arene_{centroid}(η^{6} -) 3.228.

Hence, despite the alignment of monomers hinting at oligomerization in the solid-state structures of 1 and 5, the long intermolecular bond lengths would seem to suggest that these are only very weak interactions.

Compounds 1–3 represent the first structurally characterized examples of *N*-heterocyclic stannylenes possessing saturated organic backbones (type **B**); as noted earlier examples are known for types A^{28} and $C.^{29,30}$ Within the wider context of heavier group 14 element (E) analogues of *N*-heterocyclic carbenes, examples are now known for all the elements although the volume of structural data is relatively limited. For silicon, a handful of examples based on five-membered rings have been reported for all types $A-C;^{24,42}$ the same is true of germanium although examples

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Table 1. Comparison of Significant Bond Lengths and Angles for Compounds 1-5

	1	2	3	4	5 ^{<i>a</i>}	
intermolecular Sn-N	1.973(2)	2.035(1)	2.259(5)	2.075(2)	2.100(3)	2.120(3)
	2.004(2)	2.032(1)	2.101(6)	2.075(2)	2.071(2)	2.069(2)
N–Sn–N	84.15(8)	92.63(6)	79.7(2)	100.52(9)	74.6(1)	74.0(1)
Σ angles at N	356.9	360.0	336.0	359.8	358.2	355.8
	357.6	360.0	359.6	356.2	359.1	359.7

^a There are two independent molecules in the unit cell of 5; each column shows the relevant dimensions for each independent molecule.

Table 2. Selected Crystallographic and Data Collection Parameters for Compounds 1-5

compound	1	2	3	4	5
color, habit	orange plate	yellow block	colorless plate	yellow needle	orange prism
size (mm)	$0.40\times0.25\times0.05$	$0.50\times0.40\times0.10$	$0.40 \times 0.30 \times 0.05$	$0.30\times0.05\times0.05$	$0.45 \times 0.20 \times 0.20$
empirical formula	C26H38N2Sn	$C_{27}H_{40}N_2Sn$	$C_{40}H_{52}N_4Sn_2$	C28H42N2OSn	C36H44N2SiSn
Mw	497.27	511.30	826.28	541.33	651.53
<i>T</i> /K	100	173	100	100	100
crystal system	monoclinic	monoclinic	triclinic	monoclinic	orthorhombic
space group	C2/c	C2/c	$P\overline{1}$	$P2_{1}/c$	Pbca
ρ_{calc} (g cm ⁻³)	1.291	1.267	1.562	1.335	1.318
a/Å	20.165(4)	31.3536(10)	8.828(4)	12.5897(14)	18.014(4)
b/Å	6.5412(13)	11.3904(4)	9.957(4)	17.5722(18)	21.158(4)
c/Å	19.886(4)	17.3236(6)	11.879(5)	12.2886(13)	34.457(7)
α/°	90.00	90.00	66.30(3)	90	90.00
βl°	102.82(3)	119.9150(10)	74.13(3)	97.805(5)	90.00
$\gamma /^{\circ}$	90.00	90.00	68.21(5)	90	90.00
V/A ⁻³	2557.7(9)	5362.5(3)	878.3(7)	2693.4(5)	13133(5)
Ζ	4	8	1	4	16
μ/mm^{-1}	1.012	0.967	1.456	0.97	0.841
reflections: total /independent/R _{int}	13985/2937/0.0178	27821/6151/0.0283	9983/4006/0.0601	34851/6665/0.0408	90410/15070/0.0695
θ range (°)	2.07 to 27.48	1.94 to 27.48	1.89 to 27.48	3.18 to 28.35	1.18 to 27.48
final R1 { $I > 2\sigma(I)$ } and wR2 (all data)	0.0417, 0.0987	0.0234, 0.0627	0.0666, 0.1469	0.0262, 0.0829	0.0434, 0.1171
largest peak, hole	1.151, -0.674	0.293, -0.462	1.926, -3.118	0.429, -0.391	0.917, -0.706

are relatively more common;^{20–22,43} examples for E = Pb are extremely rare.^{25,26} The heterocycle **2** is particularly noteworthy as it represents only the second example of a heavier homologue of a *N*-heterocyclic carbenes as part of a six-membered ring with a saturated organic backbone, the first being our recently reported *N*-heterocyclic plumbylene;²⁶ in this respect, we note examples of analogues for all the heavier group 14 elements save lead involving six-membered rings with unsaturated backbones.⁴⁴

Given such limited structural data, it would be inappropriate to attempt to identify any trends; however, a few observations are pertinent. The heterocycles of type **B** appear to adopt nonplanar geometries in the solid state, and the structures do not show considerable changes upon coordination to a transition metal. Furthermore, the angle subtended at E by the nitrogen centers becomes increasingly acute as the group is descended. Whereas it is tempting to ascribe this to being a consequence of the inert pair effect, it may simply reflect the geometric effect that is a consequence of increasing E-N bond lengths as the group is descended.

Conclusions

In summary, we have shown that tin analogues of *N*-heterocyclic carbenes containing a variety of backbone units may be prepared by salt metathesis of the appropriate dilithiated diamide with SnCl₂. The compounds show a far greater degree of thermal stability than those reported for the corresponding species with unsaturated backbones. When the substituent on the nitrogen centers is the bulky di*iso*-propylphenyl group then the structures are monomeric, but when the less bulky mesityl group is employed then the solid-state structure was shown to be dimeric, although ¹¹⁹Sn NMR spectroscopy suggests a monomeric structure in solution.

Experimental Section

General Experimental. Many of the compounds described herein are extremely air- and moisture-sensitive. All air- and moisture-sensitive materials were weighed out, isolated, and stored in an argon-filled Saffron Beta glovebox. Solvents used were distilled HPLC grade and further dried and degassed using a commercially available solvent purification system (Anhydrous Engineering). All chemicals used were purchased from commercial sources and used as supplied with the exception of the diamine ligand precursors which were synthesized according to established literature procedures.⁴⁵ Melting points were determined by sealing the sample in melting point tubes under argon in a glovebox prior to determination using conventional apparatus. Elemental compositions (C, H and N) were determined by sealing samples in airtight aluminum boats in a glovebox and recorded on a Carlo Erba EA1108 CHN elemental analyzer. Solution NMR spectroscopy

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samples were prepared using dry and degassed deuterated solvent in airtight NMR tubes sealed with a Young's tap; ¹¹⁹Sn and ²⁹Si NMR spectra were run on a Jeol Eclipse and/or Lambda 300 MHz spectrometers and referenced to external samples of SnMe₄ and SiMe₄ respectively. ¹H and ¹³C NMR spectra were referenced to the internal solvent peaks.

General Procedure for the Synthesis of 1–5. The appropriate diamine was dissolved in Et₂O (30 cm³) and 2 equiv of ^{*n*}BuLi (1.6 M in hexane) was added dropwise at 0 °C. The solution was stirred for 2 h and then added to a -78 °C suspension of anhydrous SnCl₂ (0.304 g, 1.6 mmol) in Et₂O (10 cm³). This was allowed to warm to room temperature and then stirred for 2 h before removal of the solvent and extraction into *n*-hexane (40 cm³). The extract was filtered (porosity 3 sinter with celite); the filtrate was reduced in volume in vacuo and storage at -18 °C yielded crystalline product.

Analytical Data for $(CH_2NDipp)_2Sn$ (1). Synthesized using $(CH_2-NH(2,6-iPr_2C_6H_3))_2$ (0.610 g, 1.6 mmol), "BuLi (1.6 M in hexane, 2.0 cm³, 3.2 mmol) and anhydrous SnCl₂ (0.304 g, 1.6 mmol) giving the product as orange crystals.

Yield: 0.48 g, 0.96 mmol, 60%.

Mp: ca. 250 °C (dec).

¹H NMR (300 MHz, C₆D₆): δ 7.25–7.18 (m, 6H, ⁱPr₂C₆H₃), 3.95 (s, 4 H, CH₂N), 3.74 (septet, 4H, ³J_{H-H} = 7.0 Hz, CHMe₂), 1.34 (d, 12H, ³J_{H-H} = 7.0 Hz, MeCHCH₃), 1.27 (d, 12H, ³J_{H-H} = 7.0 Hz, CH₃CHMe) ppm.

¹³C NMR (75.4 MHz, C₆D₆): δ 146.8 (Ar *ipso*-C), 146.2 (Ar *o*-C), 128.0 (Ar *p*-C), 126.2 (Ar *m*-C), 62.2 (CH₂N), 28.3, 26.2, 24.5 (ⁱPr) ppm.

¹¹⁹Sn NMR (111.9 MHz, C₆D₆): δ 366 ppm.

Elemental analysis: Found: C 61.95 H 7.84 N 6.43%. Required: C 62.79 H 7.70 N 5.63%.

Analytical Data for CH₂(CH₂NDipp)₂Sn (2). Synthesized using CH₂(CH₂-NH(2,6-ⁱPr₂C₆H₃))₂ (1.25 g, 3.15 mmol), "BuLi (1.6 M in hexane, 3.9 cm³, 6.3 mmol) and anhydrous SnCl₂ (0.598 g, 3.15 mmol) giving an orange crystalline product.

Yield: 1.30 g, 2.54 mmol, 81%

Mp: 143-149 °C; 248 °C (dec).

¹H NMR (300 MHz, C₆D₆): δ 7.25–7.13 (m, 6H, ⁱPr₂C₆H₃), 3.69 (septet, 4H, ³J_{H-H} = 7.0 Hz, CHMe₂), 3.49 (br. t, 4H, ³J_{H-H} = 5.1 HZ, CH₂(CH₂NDipp)₂), 2.27 (m, 2H, CH₂(CH₂NDipp)₂), 1.34 (d, 12H, ³J_{H-H} = 7.0 Hz, MeCHCH₃), 1.27 (d, 12H, ³J_{H-H} = 7.0 Hz, CH₃CHMe) ppm.

¹³C NMR (75.4 MHz, C₆D₆): δ 147.3 (Ar *ipso*-C), 147.0 (Ar *o*-C), 125.8 (Ar *p*-C), 123.7 (Ar *m*-C), 56.6 (CH₂(CH₂NDipp)₂), 36.6 (CH₂(CH₂NDipp)₂), 27.9, 26.6, 24.7 (ⁱPr) ppm.

¹¹⁹Sn NMR (111.9 MHz, C₆D₆): δ 291 ppm.

Elemental analysis: Found: C 63.84, H 7.90, N 5.66%. Required: C 63.42, H 7.88, N 5.48%.

Analytical Data for $[(CH_2NMes)_2Sn]_2$ (3). Synthesized using $(CH_2-NH(2,4,6-Me_3C_6H_2))_2$ (0.897 g, 3.0 mmol), "BuLi (1.6M, 3.8 cm³, 6.1 mmol) and anhydrous SnCl₂ (0.574 g, 3.0 mmol) yielding the product as yellow crystals.

Yield: 0.184 g, 0.22 mmol, 15%.

Mp: 113–116 °C (turned redder); 120–123 °C (melts); 155 °C (dec).

¹H NMR (300 MHz, C₆D₆): δ 6.95 (s, 4H, C₆H₂Me₃), 3.70 (s, 4H, CH₂NMes), 2.37 (s, 12H, Ar *o*-Me), 2.24 (s, 6H, Ar *p*-Me) ppm.

¹³C NMR (75.4 MHz, C₆D₆): δ (148.4 (Ar *ipso*-C), 134.3 (Ar *o*-C), 132.4 (Ar *p*-C), 129.3 (Ar *m*-C), 59.1 (CH₂NMes), 20.7 (*p*-Me), 19.4 (*o*-Me) ppm.

119Sn NMR (111.9 MHz, C₆D₆): δ 386 ppm.

Elemental analysis: Found: C 58.22 H 6.85 N 7.20%. Required: C 58.14 H 6.34 N 6.78%.

Analytical Data for $O(CH_2CH_2NDipp)_2Sn$ (4). Synthesized using $O(CH_2CH_2N(H)Dipp)_2(0.642 \text{ g}, 1.5 \text{ mmol})$, "BuLi (1.6 M, 1.9 cm³, 3.0 mmol) and anhydrous $SnCl_2$ (0.287 g, 1.5 mmol) yielding the product as yellow crystals.

Yield: 0.380 g, 0.70 mmol, 46%.

Mp: ca 200 °C (dec).

¹H NMR (270.17 MHz, C₆D₆): 7.15–7.09 (m, 6H, ⁱPr₂C₆H₃), 3.75 (septet, 4H, ³J_{H-H} = 6.9 Hz, CHMe₂), 3.48 (br. t, 4H, ³J_{H-H} = 5.3 Hz, OCH₂), 3.28 (br. t, 4H, ³J_{H-H} = 5.3 Hz, NCH₂), 1.27 (d, 12H, ³J_{H-H} = 6.9 Hz, MeCHCH₃), 1.24 (d, 12H, ³J_{H-H} = 6.9 Hz, CH₃CHMe) ppm.

¹³C NMR (75.4 MHz, C₆D₆): δ 148.9 (Ar *ipso*-C), 147.6 (Ar *o*-C), 124.8 (Ar *m*-C), 124.1 (Ar *p*-C), 74.7 (OCH₂), 60.1 (CH₂N), 28.7 (CHMe₂), 25.8 (CH(CH₃)₂) ppm.

¹¹⁹Sn NMR (111.9 MHz, C₆D₆): δ 172 ppm.

Elemental analysis: Found: C 60.89 H 7.78 N 4.99%. Required: C 62.12 H 7.82 N 5.17%.

Analytical Data for Ph₂Si(DippN)₂Sn (5). Synthesized using Ph₂Si(N(H)Dipp)₂ (0.962 g, 1.8 mmol), ^{*n*}BuLi (1.6M, 2.25 cm³, 3.6 mmol) and anhydrous SnCl₂ (0.341 g, 1.8 mmol) yielding the product as orange crystals.

Yield: 0.341 g, 0.52 mmol, 29%.

Mp: 178 °C (turned darker orange); 190–195 °C (melts); 230 °C (dec).

¹H NMR (300 MHz, C₆D₆): δ 7.42–6.99 (collection of m, 16H, Ar–H), 3.83 (septet, 4H, ³J_{H–H} = 6.8 Hz, C**H**Me₂), 1.05 (d, 24H, ³J_{H–H} = 6.8 Hz, CHMe₂) ppm.

¹³C NMR (75.4 MHz, C₆D₆): 144.4, 143.6, 139.1, 134.9, 129.5, 127.5, 123.6, 123.4 (collection of Ar C signals), 28.4 (CHMe₂), 25.6 (CH**Me₂**) ppm.

¹¹⁹Sn NMR (111.9 MHz, C₆D₆): δ 499 ppm.

²⁹Si NMR (59.6 MHz, C₆D₆): δ -14.8 ppm.

Elemental analysis: Found: C 66.00 H 6.94 N 4.31%. Required: C 66.36 H 6.81 N 4.30%.

X-ray Crystallography. Crystals suitable for X-ray diffraction analysis of **1**–**5** were grown from their saturated *n*-hexane solutions, mounted in an inert oil and then transferred to the cold gas stream of the diffractometer. Experiments were performed on **1**, **3**, and **5** using a Bruker-AXS SMART APEX three circle diffractometer;⁴⁶ the corresponding measurements for **2** were made on a Bruker-AXS SMART three circle diffractometer, while the corresponding measurements for **4** were made with a Bruker-AXS Kappa-APEX-II four circle diffractometer.⁴⁷ All diffractometers employed Mo K α radiation ($\lambda = 0.71073$ Å). Intensities were integrated⁴⁸ from several series of exposures, each exposure covering 0.3° in ω . Absorption corrections were applied based on multiple and symmetry-equivalent measurements.⁴⁹ The structures were solved by direct methods and refined by least-squares on weighted F² values

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for all reflections.⁵⁰ All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. Hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters. Refinement proceeded smoothly to give the residuals shown in Table 2. Complex neutral-atom scattering factors were used.⁵¹

As described in the main text, the structure of 1 was disordered with atoms Sn, C21 and C22 disordered over two positions (refined with SOF = 0.5). In addition, the central CH₂ group of the backbone of 2 was disordered over two positions (refined with SOF = 0.73/0.27).

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CCDC reference numbers 706511 (1), 706512 (2) 706513 (3), 706514 (4) and 706515 (5).

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Supporting Information Available: Crystallographic information file is available free of charge via the Internet at http://pubs.acs.org.

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