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Syntheses and Crystal Structures of Heteroleptic Stannylenes and Germylenes

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Two novel, monomeric heteroleptic derivatives of divalent Sn [Sn(2-{$(Me_3Si)_2C$}-C_5H_4N)R] [R = $Sn(SiMe_3)_3$ (**1**) or $Si(SiMe_3)_3$ (**2**)] and divalent Ge [Ge(2-{$(Me_3Si)_2C$}-C_5H_4N)R] [R = Cl (**3**) or $CH(PPh_2)_2$ (**4**)] have been prepared and characterized, and their molecular structures were determined by single-crystal X-ray diffraction. The stannylenes **1** and **2** were prepared from the corresponding heteroleptic chloro-analogue, [Sn(2-{$(Me_3Si)_2C$}-C_5H_4N)Cl]; **1** is the first structurally characterized compound to contain a bond between divalent Sn and tetravalent Sn and **2** is only the second structurally characterized example of a silyl-substituted heteroleptic stannylene. The Ge analogue of [Sn(2-{$(Me_3Si)_2C$}-C_5H_4N)Cl] (**3**) has been prepared and its utility as a precursor to further examples of heteroleptic germylenes demonstrated by the preparation and characterization of [Ge(2-{$(Me_3Si)_2C$}-C_5H_4N)$CH(PPh_2)_2$] (**4**).

Introduction

The organometallic chemistry of the heavier divalent group 14 element carbene analogues, ER_2, is now an active area of research, with structural data available for an increasingly wide range of compounds ($E = Sn > Ge \gg Pb > Si$; R = alkyl, aryl, amide, silyl).[1,2] This is due in part to the rich variety of reactivity and coordination chemistry encountered,[3] but also to the now wide availability of techniques such as $^{29}Si\{^1H\}$, $^{119}Sn\{^1H\}$, and $^{207}Pb\{^1H\}$ NMR spectroscopies for the direct, in situ study of non-hydrogen/carbon nuclei. There is a great deal of interest in thermally or photolytically generated Si and Ge carbene analogues,[4,5] however, it is the Sn analogues which have afforded by far the greatest number of stable, structurally characterized (and monomeric) examples.[6−20] This is a reflection on (i) the broad range of divalent precursors available, e.g. SnX_2 (X = halide or amide), (ii) the robust nature of SnR_2 (in comparison, for example, with the Pb analogues which have weaker Pb−ligand bonds, a tendency to disproportionate,[21] and are often light and/or thermally sensitive), and (iii) the $I = {}^1/_2$, ca. 9% abundant, ^{119}Sn nucleus.

We have recently made several reports on the preparation and characterization of organometallic derivatives of divalent Sn.[2,22] For example, the additional intramolecular N-atom coordination provided by 2-{$(Me_3Si)_2C$}-C_5H_4N permitted the preparation of a range of novel heteroleptic compounds by providing stabilization with respect to ligand redistribution and/or oligomerization. [Sn(2-{$(Me_3Si)_2C$}-C_5H_4N){$CH(PPh_2)_2$}][2] (**5**) was of interest inter alia as the homoleptic Sn(II) and Pb(II) analogues [E{$CH(PPh_2)_2$}$_2$] (E = Sn, Pb) have been shown to possess two different bonding modes (η^1, C-bound and η^2, P-bound) within the same molecule. [Sn(2-{$(Me_3Si)_2C$}-C_5H_4N)(C_6H_2-2,4,6-Pr^i_3)][2] (**6**), prepared by the reaction of [Sn(2-{$(Me_3Si)_2C$}-C_5H_4N)Cl][23] with $Li(Et_2O)\cdot C_6H_2$-2,4,6-Pr^i_3, is stable in solution at

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Table 1. Comparison of Seleted NMR Chemical Shift Data for Pertinent $CH(PPh_2)_2$- and 2-$\{(Me_3Si)_2C\}$-C_5H_4N-Containing Compounds (298 K, 5.872 T)

	$CH(PPh_2)_2$, δ		2-$\{(Me_3Si)_2HC\}$-C_5H_4N, δ			
compound	^1H	^{13}C	^{31}P	^1H	^{13}C	solvent
$CH_2(PPh_2)_2$	2.78, t, $^2J(^{31}P-^1H)$ 4 Hz	28.85, t, $^1J(^{31}P-^{13}C)$ 48 Hz	−21.0	–	–	C_6D_6
$Li(Et_2O)\cdot CH(PPh_2)_2$	2.16, bs	18.14, bs	−2.9	–	–	C_6D_6
4	3.81[b], d, $^2J(^{31}P-^1H)$ 6 Hz	22.80, t, $^1J(^{31}P-^{13}C)$ 105 Hz	1.1, −11.0	–	38.10	C_6D_6
	–	24.61, t, $^1J(^{31}P-^{13}C)$ 104 Hz	−0.1, −11.1	–	39.69	C_4D_8O
5[a]	3.44[b], d, $^2J(^{31}P-^1H)$ – Hz[c]	26.79, t, $^1J(^{31}P-^{13}C)$ 114 Hz	−0.4, −10.7	–	28.70[d]	C_6D_6
2-$\{(Me_3Si)_2HC\}$-C_5H_4N	–	–	–	1.70	33.30	C_6D_6

[a] Reference 2. [b] Internally referenced to minor $CH_2(PPh)_2$ impurity. [c] Barely resolvable doublet. [d] C_4D_8O, 245 K, 9.395 T.

ambient temperature: the homoleptic bis-aryl analogue $Sn(C_6H_2\text{-}2,4,6\text{-}Pr^i_3)_2$ trimerizes in solution above −30 °C to yield the structurally characterized cyclic trimer $[Sn(C_6H_2\text{-}2,4,6\text{-}Pr^i_3)_2]$ **7**,[2,24] crystals of which have been shown to undergo a solid-state phase transition from orthorhombic, space group $Pna2_1$ at 220 K to monoclinic, space group $P2_1/c$ for the same crystals at 298 K. Building on the work presented in our earlier communication,[22] we now report in full the preparation, characterization and crystal structure of [Sn(2-$\{(Me_3Si)_2C\}$-C_5H_4N)$\{Sn(SiMe_3)_3\}$] (**1**) and its novel, isostructural Si analogue, [Sn(2-$\{(Me_3Si)_2C\}$-C_5H_4N)$\{Si(SiMe_3)_3\}$] (**2**). **1** is the first structurally characterized compound to contain a bond between divalent Sn and tetravalent Sn.[25] Its $^{119}Sn\{^1H\}$ NMR spectrum permits the first measurement of ^1J coupling between Sn atoms of different valence. Compound **2** is only the second structurally characterized heteroleptic stannylene containing a silyl substituent and is of particular interest since the central divalent Sn is bound to an element more electropositive than carbon: the other example, [Sn$\{C_6H_3\text{-}2,6\text{-}(NMe_2)_2\}$(Si$\{(\text{-}NCH_2Bu^t)_2\text{-}1,2\text{-}C_6H_4\}\{C_6H_3\text{-}2,6\text{-}(NMe_2)_2\}$)], obtained in good yield by the treatment of [Si$\{(\text{-}NCH_2Bu^t)_2\text{-}1,2\text{-}C_6H_4\}$][26] with [Sn$\{C_6H_3\text{-}2,6\text{-}(NMe_2)_2\}_2$][27] was very recently reported.[28] Continuing our program of study into the versatility of group 14 element carbene analogues in the preparation of heterometallic (group 14/group 8) clusters, we have now begun to explore the utility of Ge(II) species. Thus, we now report the preparation, characterization, and molecular structure of the heteroleptic germylene [Ge(2-$\{(Me_3Si)_2C\}$-C_5H_4N)Cl] (**3**) and demonstrate its utility as a precursor to further heteroleptic compounds of Ge(II) by presenting its dialkyl derivative, [Ge(2-$\{(Me_3Si)_2C\}$-C_5H_4N)$\{CH(PPh_2)_2\}$] (**4**). The preparation and molecular structure of [Sn(2-$\{(Me_3Si)_2C\}$-C_5H_4N)R] (R = Cl) was first reported in a preliminary communication a decade ago and along with the R = $N(SiMe_3)_2$ or 2-$\{(Me_3Si)_2C\}$-C_5H_4N derivatives, was among the first heteroleptic mononuclear Sn(II) compounds to be reported.[23,29] However, also reported were unsuccessful attempts at the preparation of both [Ge(2-$\{(Me_3Si)_2C\}$-$C_5H_4N)_2$] and [Ge(2-$\{(Me_3Si)_2C\}$-C_5H_4N)Cl] (**3**).[23] In our laboratory, we have succeded in preparing both of these materials in high yield, although the preparation and molecular structure of the former, dialkyl Ge(II) derivative has since been reported by others.[30]

Experimental Section

Equipment. All experiments were carried out under an atmosphere of argon. All chemical manipulations were performed, either using standard Schlenk line techniques employing a dual manifold vacuum/argon line fitted exclusively with Young's type greaseless taps, or in a Miller-Howe glovebox under an atmosphere of dinitrogen operating at <1 ppm O_2 and <5 ppm H_2O. Solvents were predried by distillation over the appropriate drying agent under an atmosphere of dinitrogen for 72 h prior to use, freeze−thaw degassed, and stored in ampules under dinitrogen or argon, either in the presence of a potassium mirror (C_6D_6, toluene, Et_2O and hexane) or a sodium mirror (thf).

Multinuclear NMR Spectroscopy. ^1H, $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$, $^{31}P\{^1H\}$, and $^{119}Sn\{^1H\}$ NMR spectra were recorded using a Bruker DPX instrument (operating at a field strength of 5.872 T) with observational frequencies of 250.00, 62.86, 49.662, 101.202, and 93.181 MHz, respectively. ^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ spectra were referenced externally to $SiMe_4$, $^{31}P\{^1H\}$ spectra were referenced externally to 85% H_3PO_4 solution, and $^{119}Sn\{^1H\}$ spectra were referenced externally to $SnMe_4$. Low resolution CI mass spectra were recorded on a Fisons "Autospec" double focusing mass spectrometer.

X-ray Crystallography. A crystal of **1** was mounted at the end of a glass fiber under Perfluorpolyether RS 3000 and quickly placed in a cryostream at 160 K. The intensities were collected using synchrotron radiation (λ = 0.6879) and a Siemens SMART CCD area detector system at the SRS, station 9.8, Daresbury. The structure was solved by direct methods using SHELXL 97. Data were corrected for adsorption using SADABS. Hydrogen atoms were included in the calculated positions for final refinement cycles. All non-hydrogen atoms were refined anisotropically. The structures of **2**−**4** were determined from image plate X-ray diffraction data from a Mar 180 cm plate using ambient temperature data, capillary-mounted crystals and Mo $K\alpha$ sealed tube radiation with a graphite monochromator (λ = 0.710 73 Å). 95 images having a 2° rotation per image were collected using a data collection time of 5 min per frame and a crystal-to-plate distance of 75 mm. The XDS program[31] was used for data processing and merged together with MARSCALE, the MarResearch version of XSCALE.[31] Final cell constants were determined using the GLOREF routine within XDS, using refined diffraction spots

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Table 2. Summary of Crystal Data and Intensity Collection Parameters for 1 and 2

	1	**2**
empirical formula	$C_{21}H_{49}NSi_5Sn_2$	$C_{21}H_{49}NSi_6Sn$
M	693.44	602.84
temperature/K	160(2)	293(2)
habit	red needles	red needles
cryst syst	orthorhombic	monoclinic
space group	*Pbca*	$P2_1/n$
unit cell dimens		
a/Å	17.064(3)	11.795(5)
b/Å	17.759(5)	9.344(4)
c/Å	21.585(3)	31.394(8)
α/deg	90	90
β/deg	90	91.84
γ/deg	90	90
volume/Å^3	6541(2)	3458(3)
Z	8	4
D_c/Mg m^{-3}	1.408	1.158
μ/mm^{-1}	1.720	0.956
F(000)	2816	1264
data collection		
θ range/deg	1.83 to 27.13	2.54 to 23.19
index ranges, *hkl*	−17 to 16, −23 to 5, −26 to 26	0 to 11, 0 to 10, −34 to 34
no. of reflcns collcd	22087	10547
no. of indep reflcns	6241 [R(int) = 0.0523]	3767 [R(int) = 0.0345]
structure refinement	full-matrix least-squares on all F^2	full-matrix least-squares on all F^2
no. of params refined	263	263
final *R*, *R′* indices (observed data)	0.0308, 0.0866	0.0448, 0.1158
Goodness-of-fit on F^2	0.648	1.093

Table 3. Atom Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for 1

	x	*y*	*z*	*U*(eq)
Sn(1)	1241(1)	452(1)	3745(1)	26(1)
Sn(2)	1893(1)	1663(1)	4457(1)	23(1)
Si(1)	932(1)	−74(1)	2281(1)	30(1)
Si(2)	2257(1)	1164(1)	2450(1)	29(1)
Si(3)	1166(1)	1223(1)	5438(1)	31(1)
Si(4)	1616(1)	3087(1)	4344(1)	30(1)
Si(5)	3356(1)	1531(1)	4690(1)	30(1)
N(1)	316(2)	1257(1)	3358(1)	27(1)
C(1)	−309(2)	1674(2)	3510(1)	34(1)
C(2)	−622(2)	2182(2)	3108(1)	39(1)
C(3)	−285(2)	2259(2)	2530(1)	36(1)
C(4)	344(2)	1817(2)	2369(1)	31(1)
C(5)	643(2)	1311(1)	2791(1)	24(1)
C(6)	1299(2)	776(1)	2712(1)	23(1)
C(7)	1715(2)	−799(2)	2212(2)	53(1)
C(8)	562(3)	164(2)	1492(2)	52(1)
C(9)	80(2)	−515(2)	2684(2)	43(1)
C(10)	3064(2)	594(2)	2790(2)	45(1)
C(11)	2381(2)	1170(2)	1590(1)	45(1)
C(12)	2363(2)	2162(2)	2698(1)	34(1)
C(13)	3596(3)	2002(2)	5443(2)	53(1)
C(14)	3661(2)	528(2)	4751(2)	51(1)
C(15)	3966(2)	1970(2)	4069(2)	40(1)
C(16)	2537(3)	3621(2)	4326(4)	127(3)
C(17)	1026(3)	3406(2)	5014(2)	73(2)
C(18)	1041(4)	3358(2)	3653(2)	89(2)
C(19)	1329(3)	1805(2)	6151(2)	57(1)
C(20)	101(2)	1215(2)	5262(2)	47(1)
C(21)	1459(3)	239(2)	5632(2)	52(1)

Table 4. Atom Coordinates (× 10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for 2

	x	*y*	*z*	*U*(eq)
Sn	9384(1)	4486(1)	1108(1)	47(1)
Si(1)	11527(2)	5416(2)	1790(1)	53(1)
Si(4)	7644(2)	2644(2)	929(1)	43(1)
Si(3)	7515(2)	3404(2)	204(1)	63(1)
Si(2)	9652(2)	3432(2)	2213(1)	59(1)
Si(5)	5937(2)	3418(2)	1237(1)	61(1)
Si(6)	7656(2)	98(2)	895(1)	67(1)
C(3)	12224(8)	636(8)	1378(3)	86(3)
N	10765(4)	2707(5)	1061(1)	48(1)
C(0)	10456(6)	3875(6)	1723(2)	42(2)
C(6)	7165(10)	536(9)	169(3)	110(4)
C(1)	11022(5)	2684(6)	1488(2)	43(2)
C(9)	5686(8)	2467(11)	1756(3)	107(3)
C(4)	11972(8)	704(9)	948(3)	90(3)
C(7)	5943(8)	5402(8)	1347(3)	91(3)
C(8)	10473(8)	3647(9)	2737(2)	84(3)
C(5)	11233(7)	1736(8)	797(2)	71(2)
C(10)	8922(8)	3154(12)	−43(2)	105(3)
C(11)	12802(7)	4864(9)	2129(3)	82(2)
C(2)	11770(7)	1632(7)	1650(2)	67(2)
C(13)	6184(11)	−562(10)	748(5)	159(6)
C(14)	8398(8)	4676(11)	2242(3)	105(3)
C(15)	10823(8)	7023(8)	2033(3)	90(3)
C(16)	12132(8)	5999(9)	1266(2)	82(3)
C(17)	6395(8)	2424(11)	−142(2)	100(3)
C(18)	9141(8)	1533(9)	2190(3)	92(3)
C(19)	4649(7)	3060(12)	872(3)	108(3)
C(20)	8564(13)	−542(11)	452(5)	182(7)
C(21)	8075(19)	−838(10)	1394(4)	244(12)

collected over 190° of rotation. The structure was solved using the direct methods routine in SHELXS and refined using the SHELX96 version of SHELXL. Hydrogen atoms were placed in calculated positions and the final cycles of refinement were full-covariance least squares. Data collection and structure refinement parameters are shown in Table 2 (**1** and **2**) and Table 7 (**3** and **4**). The lower precision of **4** is due to crystal decay during data collection, corrected for by the scaling in the CORRECT step of XDS. Atomic coordinates for **1**−**4** are shown in Tables 3, 4, 8, and 9, respectively. Important intramolecular distances and angles for **1**−**4** are shown in Tables 5, 6, 10, and 11, respectively. The structure plots (Figure 1, Figure 2, Figure 3, and Figure 4) were drawn using the *ORTEP-3 for Windows* program.[32]

Materials. LiBu^n (2.5 mol dm^{-3} in hexane), 2-MeC$_5$H$_4$N, CH$_2$(PPh$_2$)$_2$, SiMe$_3$Cl, SiCl$_4$, GeCl$_4$, SnHBu$^n{}_3$, SnCl$_2$ (97%), SnCl$_4$, and Li wire were purchased from Aldrich Chemical Co. and used as received. The Li reagents, [Li(tmeda)·(2-{(Me$_3$Si)$_2$C}-C$_5$H$_4$N)],[33] [Li(thf)$_3$·Sn(SiMe$_3$)$_3$],[34] [Li(thf)$_3$·Si-

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[32] *ORTEP-3 for Windows* (32-bit version, 1.04*β*, build date 05-01-98) supplied by Dr L. J. Farrugia, University of Glasgow (louis@chem.gla.ac.uk).

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Table 5. Selected Distances (Å) and Angles (deg) for 1 [Estimated Standard Deviations (Esds) in Parentheses]

Distances			
Sn(1)−N(1)	2.288(2)	Sn(2)−Si(3)	2.5770(8)
Sn(1)−C(6)	2.304(2)	Sn(2)−Si(4)	2.5833(10)
Sn(1)−Sn(2)	2.8689(5)	Sn(2)−Si(5)	2.5585(10)
Angles			
N(1)−Sn(1)−C(6)	61.36(9)	Si(3)−Sn(2)−Si(4)	106.63(3)
N(1)−Sn(1)−Sn(2)	89.68(6)	Si(3)−Sn(2)−Si(5)	106.25(3)
C(6)−Sn(1)−Sn(2)	108.29(6)	Si(4)−Sn(2)−Si(5)	106.71(3)
Sn(1)−Sn(2)−Si(3)	91.50(2)	Sn(1)−Sn(2)−Si(4)	127.76(2)
Sn(1)−Sn(2)−Si(5)	114.54(2)	C(6)−C(5)−N(1)	111.8(2)

Table 6. Selected Distances (Å) and Angles (deg) for 2 [Estimated Standard Deviations (Esds) in Parentheses]

Distances			
Sn−N	2.335(5)	Si(4)−Si(3)	2.386(2)
Sn−C	2.345(6)	Si(4)−Si(5)	2.374(3)
Sn−Si(4)	2.7236(18)	Si(4)−Si(6)	2.381(2)
Angles			
N−Sn−C	61.36(18)	Sn−Si(4)−Si(3)	91.88(7)
N−Sn−Si(4)	93.43(13)	Sn−Si(4)−Si(5)	111.53(8)
C−Sn−Si(4)	113.49(15)	Sn−Si(4)−Si(6)	129.43(10)
Si(3)−Si(4)−Sn	91.88(7)	Si(5)−Si(4)−Sn	111.53(8)
Si(6)−Si(4)−Sn	129.43(10)	C−C(1)−N	112.5(5)

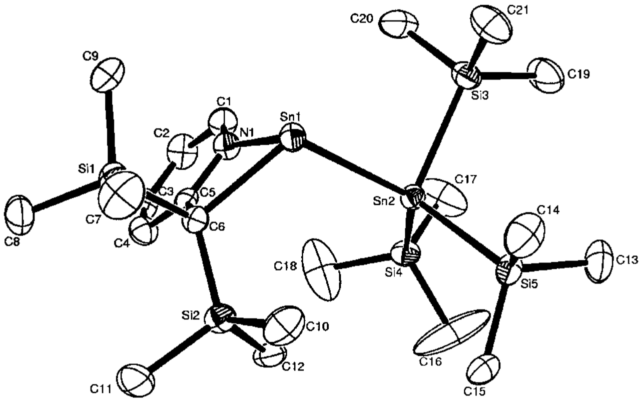

Figure 1. Molecular structure of [Sn(2-{$(Me_3Si)_2C$}-C_5H_4N){$Sn(SiMe_3)_3$}] (**1**) (thermal ellipsoids drawn at the 50% probability level).

$(SiMe_3)_3$],[35,36] and $Li(Et_2O)\cdot CH(PPh_2)_2$,[37] were prepared according to literature methods as was the Sn(II) precursor [Sn(2-{$(Me_3Si)_2C$}-C_5H_4N)Cl].[23] [Ge(2-{$(Me_3Si)_2C$}-$C_5H_4N)_2$] can be prepared according to published methods also.[30]

Synthesis of [$GeCl_2\cdot$diox]. To a Schlenk tube containing $GeCl_4$ (16.00 mL, 30.00 g, 139.93 mmol), Et_2O (90 mL), hexane (90 mL), 1,4-dioxane (30 mL), and a stir-bar was added a solution of $SnHBu^n_3$ (38.00 mL, 40.73 g, 139.93 mmol) in Et_2O (50 mL) over a 20 min period; a white precipitate formed. The mixture was stirred overnight and then refluxed for 48 h. The solution was filtered, and remaining white microcrystalline material washed with hexane (2 × 60 mL) and then dried in vacuo. Yield 18.38 g (79.36 mmol, 57%).

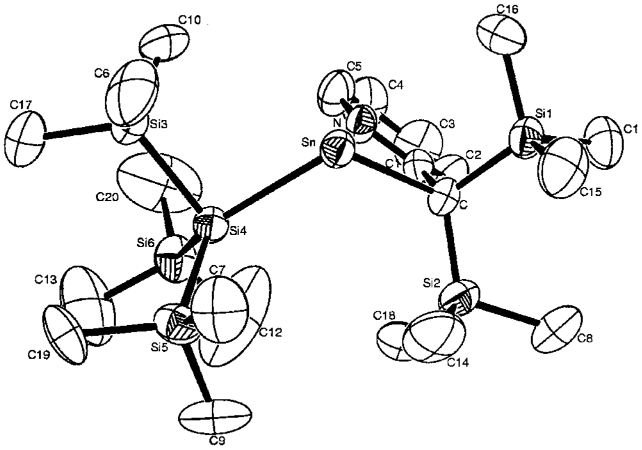

Figure 2. Molecular structure of [Sn(2-{$(Me_3Si)_2C$}-C_5H_4N){$Si(SiMe_3)_3$}] (**2**) (thermal ellipsoids drawn at the 50% probability level).

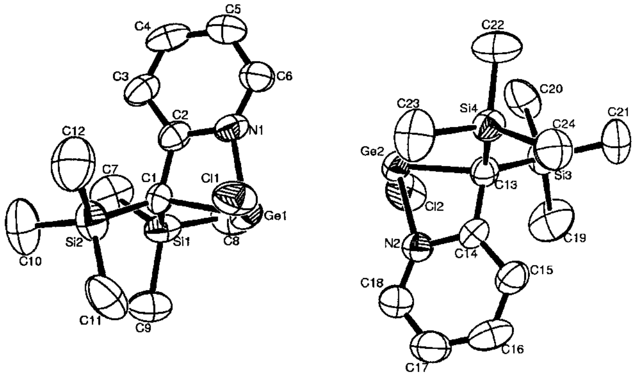

Figure 3. Molecular structure of [Ge(2-{$(Me_3Si)_2C$}-C_5H_4N)Cl] (**3**) showing the two independent molecules (thermal ellipsoids drawn at the 50% probability level).

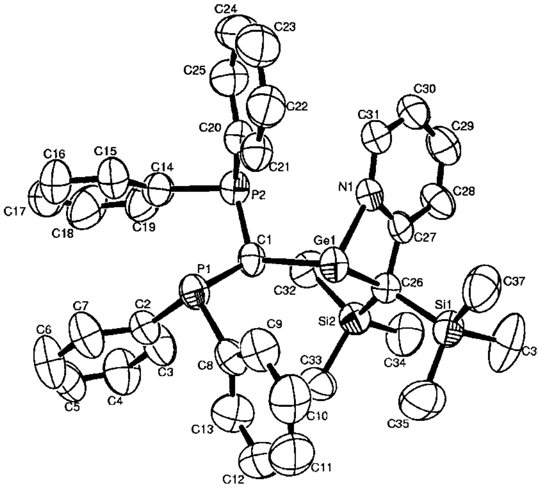

Figure 4. Molecular structure of [Ge(2-{$(Me_3Si)_2C$}-C_5H_4N){$CH(PPh_2)_2$}] (**4**) (thermal ellipsoids drawn at the 50% probability level).

Syntheses of [E(2-{$(Me_3Si)_2C$}-C_5H_4N)R] (1−4). [Sn(2-{$(Me_3Si)_2C$}-C_5H_4N){$Sn(SiMe_3)_3$}] (1). To a Schlenk tube containing [Sn(2-{$(Me_3Si)_2C$}-C_5H_4N)Cl] (3.99 g, 10.21 mmol), a stir-bar, and Et_2O (40 mL) was added with stirring a solution of [$Li(thf)_3\cdot Sn(SiMe_3)_3$][34] (5.73 g, 10.21 mmol) over a 5 min period, resulting in an immediate change from yellow/orange to red. The mixture was stirred for a further 16 h, the Et_2O removed in vacuo, and the product extracted from the LiCl byproduct with hexane (3 × 40 mL). The hexane was removed in vacuo to afford 6.23 g of **1** as a pyrophoric dark red powder (8.99 mmol, 88% yield). Crystals of **1** suitable for an X-ray diffraction study were grown from a saturated hexane solution.

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Table 7. Summary of Crystal Data and Intensity Collection Parameters for 3 and 4

	3	4
empirical formula	$C_{24}H_{44}Ge_2N_2Cl_2Si_4$	$C_{37}H_{43}GeNP_2Si_2$
M	689.05	692.43
temperature/K	293(2)	293(2)
habit	yellow needles	yellow needles
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
unit cell dimens		
a/Å	15.364(5)	10.766(5)
b/Å	14.451(5)	14.338(6)
c/Å	17.309(6)	15.841(6)
α/deg	90	68.83(6)
β/deg	112.73(6)	86.34(6)
γ/deg	90	68.44(6)
volume/Å^3	3544.6	2114
Z	4	2
D_c/Mg m^{-3}	1.291	1.088
μ/mm^{-1}	1.997	0.879
F(000)	1424	724
data collection		
θ range/deg	2.55 to 25.91	3.00 to 23.25
index ranges, *hkl*	0 to 18, 0 to 17, −19 to 18	0 to 11, −14 to 15, −17 to 17
no. of reflcns collcd	9747	8450
no. of indep reflcns	5662 [R(int) = 0.0574]	5484 [R(int) = 0.0677]
structure refinement	full-matrix least-squares on all F^2	full-matrix least-squares on all F^2
no. of params refined	308	388
final *R, R′* indices (observed data)	0.0595, 0.1820	0.0916, 0.3132
Goodness-of-fit on F^2	1.175	1.067

Table 8. Atom Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for 3

	x	*y*	*z*	*U*(eq)
Ge(1)	4953(1)	3968(1)	2308(1)	58(1)
Ge(2)	5206(1)	6557(1)	2990(1)	56(1)
Si(3)	4592(1)	8650(1)	3602(1)	57(1)
Si(4)	3295(1)	7630(1)	1899(1)	54(1)
Cl(1)	3595(1)	3692(1)	1158(1)	73(1)
Si(1)	6958(1)	2985(2)	3146(1)	62(1)
Si(2)	5446(1)	1892(2)	1602(1)	68(1)
Cl(2)	6448(1)	6829(2)	4238(1)	85(1)
N(2)	4358(3)	6038(4)	3575(3)	51(1)
C(13)	4172(3)	7527(4)	3027(3)	47(1)
C(14)	3845(4)	6823(4)	3476(3)	48(1)
N(1)	5616(3)	4535(4)	1572(3)	56(1)
C(1)	5923(4)	3033(4)	2106(4)	51(1)
C(5)	6222(5)	5339(5)	702(4)	66(2)
C(21)	3635(5)	9554(5)	3296(5)	79(2)
C(2)	6100(4)	3758(5)	1565(3)	51(1)
C(6)	5673(4)	5301(5)	1163(4)	62(2)
C(15)	3141(4)	6859(5)	3798(4)	63(2)
C(24)	2089(4)	7974(6)	1816(4)	72(2)
C(4)	6701(4)	4536(6)	667(4)	71(2)
C(3)	6658(4)	3747(5)	1098(4)	64(2)
C(18)	4212(5)	5291(5)	3972(4)	66(2)
C(23)	3132(5)	6459(7)	1374(5)	93(3)
C(16)	2987(5)	6097(7)	4206(5)	81(2)
C(9)	6694(5)	2146(6)	3859(4)	83(2)
C(22)	3749(6)	8450(7)	1316(4)	89(3)
C(17)	3519(5)	5293(6)	4288(4)	77(2)
C(20)	5600(5)	9128(5)	3377(6)	83(2)
C(19)	4977(6)	8458(7)	4758(5)	103(3)
C(7)	8083(4)	2667(7)	3023(4)	87(2)
C(11)	4604(6)	1425(6)	2061(6)	91(3)
C(12)	4820(7)	2009(8)	446(5)	113(3)
C(8)	7145(6)	4155(7)	3642(5)	98(3)
C(10)	6398(6)	1003(7)	1772(7)	115(3)

Data for 1: ^{1}H NMR (C_6D_6, 298 K, 250.00 MHz), δ 7.75 (dd, 1 H), 6.88 (td, 1 H), 6.25 (m, 2 H), 0.49 [s, 27 H, $^3J(^{119,117}Sn-^1H) = 32$ Hz], 0.28 (s, 9 H), 0.23 (s, 9 H); $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K, 62.86 MHz), δ 173.30, 148.23, 136.81, 127.10, 118.70, 35.60, 5.99 [$^2J(^{119,117}Sn-^{13}C) = 38$ Hz] 3.23 [$^1J(^{29}Si-^{13}C) = 48$ Hz], 1.26 [$^1J(^{29}Si-^{13}C) = 46$ Hz]; $^{29}Si\{^1H\}$ NMR (C_6D_6, 298 K, 49.662 MHz), δ 0.2 [$^2J(^{119,117}Sn-^{29}Si) = 21$ Hz], −3.5 [$^2J(^{119,117}Sn-^{29}Si) = 13$ Hz], −4.7 [$^1J(^{119}Sn-^{29}Si) = 208$ Hz, $^1J(^{117}Sn-^{29}Si) = 199$ Hz]; $^{119}Sn\{^1H\}$ NMR (C_6D_6, 298 K, 93.18 MHz), δ 897 [$^1J(^{119}Sn-^{119}Sn) = 6746$ Hz, $^1J(^{117}Sn-^{119}Sn) = 6448$ Hz], −502 [$^1J(^{119}Sn-^{119}Sn) = 6765$ Hz, $^1J(^{117}Sn-^{119}Sn) = 6467$ Hz]. Elem. Anal. for $C_{21}H_{49}Si_5NSn_2$, found (calcd): C, 36.63 (36.37); H, 6.92 (7.12); N, 2.13 (2.02).[38]

[Sn(2-{(Me$_3$Si)$_2$C}-C$_5$H$_4$N){Si(SiMe$_3$)$_3$}] (2). To a Schlenk tube containing [Sn(2-{(Me$_3$Si)$_2$C}-C$_5$H$_4$N)Cl] (4.70 g, 12.03 mmol), a stir-bar, and Et$_2$O (80 mL), cooled to −78 °C using a dry ice/acetone slush bath, was added a stirred slurry of [Li(thf)$_3$·Si(SiMe$_3$)$_3$] (5.79 g, 12.30 mmol) over a 30 min period. The red mixture was allowed to warm slowly to ambient temperature (ca. 8 h) and stirred for a further 16 h. The Et$_2$O was removed in vacuo, the product extracted with hexane (1 × 80 mL). Concentration of the hexane solution in vacuo followed by cooling with liquid N$_2$ and filtration afforded 4.17 g of **2** as a red pyrophoric powder (6.92 mmol, 56% yield). Red needles of **2** were grown from a concentrated Et$_2$O solution.

Data for 2: ^{1}H NMR (C_6D_6, 298 K, 250.00 MHz), δ 7.85 (d, 1 H), 6.86 (t, 1 H), 6.32 (d, 1 H), 6.23 (t, 1 H), 0.44 (s, 27 H), 0.29 (s, 9 H), 0.24 (s, 9 H); $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K, 62.86 MHz), δ 173.40, 147.82, 137.17, 127.01, 118.54, 38.95 [*C*{Si(CH$_3$)$_3$}$_2$], 4.99 [Si{Si(*C*H$_3$)$_3$}$_3$], 3.50 [C{Si(*C*H$_3$)$_3$}$_2$], 1.63 [C{Si(*C*H$_3$)$_3$}$_2$]; $^{119}Sn\{^1H\}$ NMR (C_6D_6, 298 K, 93.18 MHz), δ 876. MS (CI, 70 eV) *m*/*z* 603 $M^{+\cdot}$, 588 $M^{\bullet+}$ − Me, 356 $M^{\bullet+}$ − Si(SiMe$_3$)$_3$. Elem. Anal. for $C_{21}H_{49}Si_6NSn$, found (calcd): C, 41.11 (41.84); H, 8.14 (8.19); N, 2.84 (2.32).[38]

[Ge(2-{(Me$_3$Si)$_2$C}-C$_5$H$_4$N)Cl] (3). To a Schlenk tube containing [GeCl$_2$·diox] (4.10 g, 17.70 mmol), a stir-bar and Et$_2$O (50 mL), cooled to −78 °C using a dry ice/acetone slush bath, was added a stirred slurry of [Ge(2-{(Me$_3$Si)$_2$C}-C$_5$H$_4$N)$_2$] (9.55 g, 17.51 mmol) also in Et$_2$O (70 mL) over a 45 min period. After complete addition of the [Ge(2-{(Me$_3$Si)$_2$C}-C$_5$H$_4$N)$_2$], the thick pale yellow slurry was allowed to warm slowly to ambient temperature (ca. 8 h) and stir overnight. The Et$_2$O was removed in vacuo, and the product was extracted with warm hexane (3 × 60 mL). As the solution was filtered, large yellow crystals of **3** were seen to form and these were isolated (4.22 g, 12.25 mmol) by removing the hexane solution into the second Schlenk tube via cannula. The hexane was removed in vacuo

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[38] Similarly poor elemental analysis values for N were found for [Sn(2-{(Me$_3$Si)$_2$C}-C$_5$H$_4$N)R] {R = (2-{(Me$_3$Si)$_2$C}-C$_5$H$_4$N) or Cl}: 5.2 (4.7) or 4.1 (4.7) and 3.4 (3.6) or 4.0 (3.6), respectively. Jolly, B. S.; Lappert, M. F.; Engelhardt, L. M.; White, A. H.; Raston, C. L. *J. Chem. Soc., Dalton Trans.* **1993**, 2653.

Table 9. Atom Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for 4

	x	*y*	*z*	*U*(eq)
Ge(1)	7191(1)	7938(1)	6333(1)	55(1)
P(1)	5249(2)	6529(2)	6791(2)	55(1)
P(2)	8082(2)	5565(2)	6177(2)	57(1)
C(1)	7048(9)	6417(7)	6784(6)	52(2)
Si(1)	8272(3)	9192(2)	7211(2)	66(1)
Si(2)	9344(3)	6647(2)	8333(2)	61(1)
C(26)	8761(9)	7786(7)	7197(6)	54(2)
N(1)	9068(7)	7548(6)	5813(5)	55(2)
C(27)	9661(10)	7653(7)	6459(6)	58(2)
C(20)	7465(10)	6309(8)	4970(7)	61(2)
C(14)	7489(11)	4444(8)	6465(7)	65(2)
C(2)	5218(9)	5396(7)	7817(6)	59(2)
C(32)	10105(12)	5308(8)	8176(8)	79(3)
C(8)	4371(9)	7688(8)	7151(7)	59(2)
C(21)	6486(10)	7330(8)	4611(7)	63(2)
C(30)	10987(12)	7366(9)	4978(8)	75(3)
C(28)	11013(10)	7568(9)	6390(7)	70(3)
C(31)	9679(11)	7440(8)	5066(7)	67(3)
C(15)	6402(11)	4464(9)	6014(9)	77(3)
C(19)	8190(13)	3500(8)	7184(8)	82(3)
C(25)	8149(12)	5822(10)	4358(8)	78(3)
C(29)	11645(11)	7429(9)	5656(8)	77(3)
C(13)	4201(12)	7619(9)	8044(9)	81(3)
C(9)	3821(11)	8689(9)	6470(9)	76(3)
C(4)	5978(15)	4044(10)	9344(9)	95(4)
C(3)	6090(12)	4889(10)	8559(8)	82(3)
C(34)	10716(15)	6685(12)	8992(10)	102(4)
C(22)	6216(13)	7872(10)	3683(8)	81(3)
C(5)	4946(14)	3718(10)	9335(10)	92(4)
C(24)	7844(16)	6406(14)	3418(10)	101(4)
C(16)	5978(14)	3598(11)	6282(10)	93(4)
C(33)	7905(14)	6664(10)	9070(8)	87(3)
C(7)	4214(11)	5011(9)	7809(9)	83(3)
C(6)	4094(14)	4174(10)	8565(11)	101(4)
C(37)	7831(18)	10196(10)	6030(9)	104(5)
C(10)	3131(12)	9600(9)	6663(11)	89(4)
C(18)	7700(20)	2659(11)	7467(11)	113(5)
C(23)	6902(16)	7413(12)	3097(9)	98(4)
C(17)	6677(18)	2696(12)	7041(12)	104(5)
C(12)	3519(15)	8520(12)	8237(12)	102(4)
C(35)	6747(16)	9498(11)	7844(11)	110(5)
C(36)	9592(18)	9420(13)	7732(15)	136(7)
C(11)	3004(14)	9524(12)	7540(13)	104(4)

Table 10. Selected Distances (Å) and Angles (deg) for 3 [Estimated Standard Deviations (Esds) in Parentheses]

Distances			
Ge(1)−N(1)	2.082(4)	Ge(2)−N(2)	2.075(4)
Ge(1)−C(1)	2.138(5)	Ge(2)−C(13)	2.138(5)
Ge(1)−Cl(1)	2.2948(19)	Ge(2)−Cl(2)	2.2962(19)
Angles			
N(1)−Ge(1)−C(1)	67.1(2)	N(2)−Ge(2)−C(13)	66.9(2)
N(1)−Ge(1)−Cl(1)	91.89(14)	N(2)−Ge(2)−Cl(2)	93.06(14)
C(1)−Ge(1)−Cl(1)	101.86(17)	C(13)−Ge(2)−Cl(2)	102.52(15)
C(1)−C(2)−N(1)	110.0(4)	C(13)−C(14)−N(2)	110.0(4)

to afford **3** as an O_2- and H_2O-sensitive, yellow powder (7.35 g, 21.34 mmol) which was then washed with freezing-cold hexane (1 × 40 mL). Combined yield of crystalline/washed **1**, 9.63 g (27.95 mmol, 80%).

Data for 3: ^{1}H NMR (C_6D_6, 298 K), δ 7.45 (bs, 1 H), 7.03 (dt, 1 H), 6.54 (bs, 1 H), 6.40 (bt, 1 H), 0.32 (s, 18 H); $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K), δ 174.54 (b, C_5H_4N), 143.95 (b, C_5H_4N), 139.66 (C_5H_4N), 126.10 (C_5H_4N), 119.65 (C_5H_4N), 39.24 [b, $\mathit{C}\{Si(CH_3)_3\}_2$], 1.61 [b, $C\{Si(\mathit{C}H_3)_3\}_2$]; $^{29}Si\{^1H\}$ NMR (C_6D_6, 298 K), δ 0. Elem. Anal. for $C_{12}H_{22}Si_2NGeCl$, found (calcd): C, 39.97(41.83); H, 6.30 (6.44), N, 4.50 (4.06).[38]

[Ge(2-{$(Me_3Si)_2C$}-C_5H_4N){$CH(PPh_2)_2$}] (4). To a Schlenk tube containing [Ge(2-{$(Me_3Si)_2C$}-C_5H_4N)Cl] (**3**) (1.30 g, 3.77 mmol), a stir-bar, and Et_2O (50 mL) was added a stirred slurry of $Li(Et_2O)\cdot CH(PPh_2)_2$ (1.53 g, 3.30 mmol), also in Et_2O, over a 30 min period. Stirring overnight resulted in an orange solution and the formation of a substantial yellow precipitate. The Et_2O was removed in vacuo and the resulting intensely yellow solid washed with freezing-cold hexane (2 × 60 mL). **4** was separated from the LiCl byproduct with hot toluene (50 mL) and isolated as an intensely yellow solid by removal of the toluene in vacuo. Yield 1.72 g (2.48 mmol, 75%). Redissolution in hot toluene afforded upon cooling, **4** as large intensely yellow, X-ray quality needles which could be handled in air for a number of minutes without any visible signs of decomposition.

Table 11. Selected Distances (Å) and Angles (deg) for 4 [Estimated Standard Deviations (Esds) in Parentheses]

Distances			
P(1)−C(1)	1.883(9)	P(2)−C(1)	1.836(9)
P(1)−C(2)	1.846(9)	P(2)−C(14)	1.841(9)
P(1)−C(8)	1.854(10)	P(2)−C(20)	1.845(11)
Ge(1)−N(1)	2.089(7)	Ge(1)−C(26)	2.142(9)
Ge(1)−C(1)	2.097(8)		
Angles			
N(1)−Ge(1)−C(1)	98.7(3)	P(2)−C(1)−P(1)	113.3(4)
N(1)−Ge(1)−C(26)	66.6(3)	P(2)−C(1)−Ge(1)	112.7(4)
C(1)−Ge(1)−C(26)	105.8(3)	P(1)−C(1)−Ge(1)	111.4(4)
C(2)−P(1)−C(8)	101.1(4)	C(14)−P(2)−C(20)	101.5(4)
C(2)−P(1)−C(1)	104.4(4)	C(1)−P(2)−C(14)	104.9(4)
C(8)−P(1)−C(1)	103.8(4)	C(1)−P(2)−C(20)	105.6(4)
C(26)−C(27)−N(1)	111.4(8)		

Data for 4: ^{1}H NMR (C_6D_6, 298 K), δ 8.15−6.06 [$P(C_6\mathit{H}_5)$ and $C_5\mathit{H}_4N$, 24 H; 6.51, d, $C_5\mathit{H}_4N$; 6.06, t, $C_5\mathit{H}_4N$], 3.81 [d, 1H, $CH(PPh_2)_2$], 0.43 and 0.02 [s, 9H, $C\{Si(C\mathit{H}_3)_3\}_2$]; $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K), δ 171.89 (C_5H_4N), 146.45 (C_5H_4N), 141.50−125.64 [$P(\mathit{C}_6H_5)$ and C_5H_4N], 124.71 (C_5H_4N), 118.44 (C_5H_4N), 38.10 [$\mathit{C}\{Si(CH_3)_3\}_2$], 22.80 [$\mathit{C}H(PPh_2)_2$, t, $^1J(^{31}P-^{13}C) = 105$ Hz], 4.07 and 1.57 [$C\{Si(\mathit{C}H_3)_3\}_2$]; $^{13}C\{^1H\}$ NMR (C_4D_8O, 298 K), δ 173.70 (C_5H_4N), 148.33 (C_5H_4N), 141.74−129.67 [$P(\mathit{C}_6H_5)$ and C_5H_4N], 127.16 (C_5H_4N), 120.81 (C_5H_4N), 39.69 [$\mathit{C}\{Si(CH_3)_3\}_2$], 24.61 [$\mathit{C}H(PPh_2)_2$, t, $^1J(^{31}P-^{13}C) = 104$ Hz], 5.52 and 3.03 [$C\{Si(\mathit{C}H_3)_3\}_2$]; $^{29}Si\{^1H\}$ NMR (C_6D_6, 298 K), δ −0.3; $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K), δ 1.1 (s, 1 P), −11.0 (s, 1 P). MS (CI, NH_3) *m/z* 694 $M^{+\cdot}$, 457 $M^{\bullet +}$ − (2-{$(Me_3Si)_2C$}-C_5H_4N), 384 $CH_2(PPh_2)_2$, 310 $M^{\bullet +}$ − {2-$CH(PPh_2)_2$, 238 2-{$(Me_3Si)_2CH$}-C_5H_4N. Elem. Anal. for $C_{37}H_{42}Si_2NP_2Ge$, found (calcd): C, 63.90 (64.27); H, 6.21 (6.12); N, 2.18 (2.02).[38]

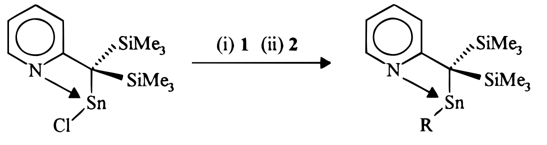
Results and Discussion

The precursor to **1** and **2**, [Sn(2-{$(Me_3Si)_2C$}-C_5H_4N)Cl], was prepared in high yield (ca. 70%) according to the literature method. Reaction of 2 equiv of [Li(tmeda)·(2-{$(Me_3Si)_2C$}-C_5H_4N)][33] with $SnCl_2$ in Et_2O at ambient temperature yields [Sn(2-{$(Me_3Si)_2C$}-$C_5H_4N)_2$], which undergoes ligand redistribution with 1 equiv of $SnCl_2$ to to afford 2 equiv of the desired material.[23]

Syntheses of [E(2-{$(Me_3Si)_2C$}-C_5H_4N)R] (1−4). [Sn(2-{$(Me_3Si)_2C$}-C_5H_4N)(C_6H_2-2,4,6-Pr^i_3)] (1). Compound **1** was prepared by the treatment of a stirred solution of [Sn(2-{$(Me_3Si)_2C$}-C_5H_4N)Cl] in Et_2O at −78 °C with a solution of 1 equiv of [$Li(thf)_3$.{$Sn(SiMe_3)_3$}], also in Et_2O (Scheme 1) and was obtained as a dark red pyrophoric powder in 88% yield. Recrystallization from a very concentrated hexane solution produced small dark red needles of suitable quality for crystallographic analysis.

[Sn(2-{$(Me_3Si)_2C$}-C_5H_4N){$Si(SiMe_3)_3$}] (2). Compound **2** was prepared in a manner analogous to that for **1** but using [$Li(thf)_3$·{$Si(SiMe_3)_3$}] (Scheme 1) and was obtained as a red pyrophoric powder in 56% yield.

Scheme 1. Preparation of [Sn(2-{$(Me_3Si)_2C$}-C_5H_4N)R] [R = $Sn(SiMe_3)_3$ (1) or $Si(SiMe_3)_3$ (2)]



R = $Sn(SiMe_3)_3$ **1**, 88 %
R = $Si(SiMe_3)_3$ **2**, 56 %

Reagents and conditions

(i) Et_2O, LiR, hexane extraction. Recrystallisation from hexane.

(ii) Et_2O, -78 °C, LiR, hexane extraction. Recrystallisation from Et_2O at -30 °C.

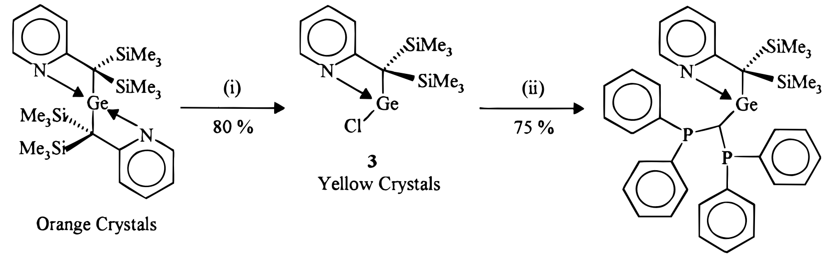
Cooling of an Et_2O solution of **2** to −30 °C afforded dark red needles suitable for crystallographic analysis.

[Ge(2-{$(Me_3Si)_2C$}-C_5H_4N)Cl] (3). Compound **3** was prepared in high yield (80%) from the reaction of [Ge(2-{$(Me_3Si)_2C$}-C_5H_4N)$_2$] with 1 equiv of [$GeCl_2$·diox] (ca. 1% excess) in Et_2O at ambient temperature (Scheme 2). This route is identical to the preferred preparation of the Sn analogue,[23] however, during extraction of **3** from residual [$GeCl_2$·diox] using hot hexane, small amounts of a white precipitate were observed: ^1H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectra of the crude **3** extract (i.e., before washing with hexane at just above its freezing point) revealed the presence of 2-{$(Me_3Si)_2HC$}-C_5H_4N. Thus, **3** appears to be less thermally robust in solution than its Sn analogue.

[Ge(2-{$(Me_3Si)_2C$}-C_5H_4N){$CH(PPh_2)_2$}] (4). Compound **4** was prepared by the treatment of a stirred solution of [Ge(2-{$(Me_3Si)_2C$}-C_5H_4N)Cl] (ca. 14% excess) in Et_2O at ambient temperature with a stirred slurry of Li(Et_2O)·$CH(PPh_2)_2$, also in Et_2O and was obtained as an intensely yellow powder in 75% yield (Scheme 2). [As was found for **5**, a small amount of “free” $CH_2(PPh_2)_2$ was shown to be present by ^1H and $^{31}P\{^1H\}$ NMR spectroscopies]. Redissolution of this solid in hot toluene afforded upon cooling **4** as intensely yellow needles which did not show any visible signs of decomposition upon exposure to air for a period of minutes.

Multinuclear NMR Spectroscopic Data for [E(2-{$(Me_3Si)_2C$}-C_5H_4N)R] (1−4). [Sn(2-{$(Me_3Si)_2C$}-C_5H_4N){$Sn(SiMe_3)_3$}] (1). The ^1H NMR spectrum of **1** in C_6D_6 at ambient temperature exhibits resonances with characteristic chemical shifts and integral values for both ligands. The resonances corresponding to the aromatic ^1H environments of 2-{$(Me_3Si)_2C$}-C_5H_4N are observed at δ 7.85, 6.98, 6.68, and 6.36. The observation of two chemically distinct $SiMe_3$ ^1H environments for this ligand, at δ 0.33 and 0.04, indicates the persistence of the formally coordinate N−Sn bond in solution (at ambient temperature) thereby preventing rotation of the bidentate ligand about the C−Sn bond which would render the two $SiMe_3$ groups equivalent. Additionally, it is presumably the longer $(Me_3Si)_3Sn$−Sn bond (allowing free rotation) compared with the corresponding $(Me_3Si)_2N$−Sn bond in [Sn(2-{$(Me_3Si)_2C$}-C_5H_4N)-{$N(SiMe_3)_2$}] that results in the equivalence of the $Sn(SiMe_3)_3$ ligand ^1H (and ^{13}C) environments in **1** at ambient temperature. In agreement with the ^1H NMR spectrum, two distinct ^{13}C resonances are observed for the $SiMe_3$ groups of the 2-{$(Me_3Si)_2C$}-C_5H_4N ligand, at δ 2.49 and 2.30. The $^{29}Si\{^1H\}$ NMR spectrum exhibits three resonances. The resonance at δ −4.7 is assigned, on the basis of its $^1J(^{119}Sn-^{29}Si)$ and $^1J(^{117}Sn-^{29}Si)$ satellites (208 and 199 Hz respectively) and its greater intensity, to the $SiMe_3$ groups of the $Sn(SiMe_3)_3$ ligand. The two resonances at δ 0.2 and −3.5, with $^2J(^{119,117}Sn-^{29}Si)$ satellites of 21 and 13 Hz respectively, are assigned to the chemically distinct $SiMe_3$ groups of the 2-{$(Me_3Si)_2C$}-C_5H_4N ligand. The $^{119}Sn\{^1H\}$ NMR spectrum of **2** comprises two sharp singlet resonances, at δ 897 and −502. The high-frequency resonance is to higher frequency compared with the corresponding resonances for other derivatives of divalent Sn for which ^{119}Sn NMR chemical shift data have been reported, e.g. [Sn(2-{$(Me_3Si)_2C$}-C_5H_4N){$CH(PPh_2)_2$}] at δ 397 and [Sn(2-{$(Me_3Si)_2C$}-C_5H_4N)(C_6H_2-2,4,6-$Pr^i{}_3$)] at δ 474.[2] Similarly, the other resonance is to much higher frequency than that for the Li precursor **1** (C_6D_6, δ −878).[34] Both resonances exhibit well-resolved $^1J(^{119}Sn-^{119}Sn)$ and $^1J(^{117}Sn-^{119}Sn)$ satellites, unsymmetrically positioned about the ^{119}Sn resonance being observed. This is a result of isotope shifts (the satellite nuclei are bound to the Sn isotopes ^{117}Sn and ^{119}Sn and the central resonance corresponds to those bound to nonmagnetic nuclei) and is obvious in this instance owing to the large couplings involved. Thus, the resonance at δ 896.53 has ^{119}Sn satellites with a ^1J coupling of 6746 Hz and chemical shift of δ 897.44, and ^{117}Sn satellites with a ^1J coupling of 6448 Hz and chemical shift of δ 896.64. The corresponding values for the resonance at δ −501.84 are 6765 Hz and δ −501.68, 6467 Hz and δ −500.71, respectively.

Scheme 2. Preparation of [Ge(2-{$(Me_3Si)_2C$}-C_5H_4N)R] [R = Cl (3) or $CH(PPh_2)_2$ (4)]



Orange Crystals

3
Yellow Crystals

4
Yellow Crystals

Reagents and conditions

(i) Et_2O, $GeCl_2$.diox, hexane extraction, hexane wash/crystallisation.

(ii) Et_2O, Li(Et_2O).$CH(PPh_2)_2$, toluene extraction. Recrystallisation from hot toluene.

[Sn(2-{(Me$_3$Si)$_2$C}-C$_5$H$_4$N){Si(SiMe$_3$)$_3$}] (2). The ^{1}H and ^{13}C{^{1}H} NMR spectra of **2** in C$_6$D$_6$ at ambient temperature are essentially the same as those for **1** and thus the notion that the formally coordinate N−Sn bond persists in solution at ambient temperature for **2** also is confirmed: similarly, resonances confirming only single ^{1}H and ^{13}C environments for the Si(Si*Me*$_3$)$_3$ ligand were observed. The resonance corresponding to the C atom of the 2-{(Me$_3$Si)$_2$C} moiety appears at δ 38.95, to higher frequency compared with that for **1** (δ 35.60), but to lower frequency compared with that for the parent chloro-species (δ 43.34). The ^{29}Si{^{1}H} NMR spectrum exhibits only three resonances: these are assigned on the basis of their integral values and by analogy with the assignments made for **1**. The resonance at δ −5.8, with $^1J(^{29}\mathrm{Si}-^{29}\mathrm{Si})$ and $^2J(^{119,117}\mathrm{Sn}-^{29}\mathrm{Si})$ satellites of 43 and 36 Hz respectively, corresponds to the SiMe$_3$ groups of the Si(SiMe$_3$)$_3$ ligand with a chemical shift extremely similar to that of its Li salt, [Li(thf)$_3$·Si(SiMe$_3$)$_3$] (δ −5.2).[36] The resonances at δ −0.3 and −3.3, the former with $^2J(^{119,117}\mathrm{Sn}-^{29}\mathrm{Si})$ satellites of 33 Hz, are assigned to the chemically distinct SiMe$_3$ groups of the 2-{(Me$_3$Si)$_2$C}-C$_5$H$_4$N ligand. That the $^2J(^{119,117}\mathrm{Sn}-^{29}\mathrm{Si})$ coupling on the resonance at δ −3.3 is not fully resolved at 5.872 T and that the corresponding values in **1** (21 and 13 Hz) are also different from each other is at present not understood, but is presumably a reflection on the position of the two Si atoms with respect to the lone pair at the central divalent Sn. Furthermore, the resonance corresponding to the central ^{29}Si atom of the Si(SiMe$_3$)$_3$ ligand was not observed: the ^{119}Sn chemical shift of the Sn(SiMe$_3$)$_3$ ligand in **1** is to considerably higher frequency in comparison with that of its Li salt, [Li(thf)$_3$·Sn(SiMe$_3$)$_3$] (δ −502 vs −878).[34] Thus, it is possible that the ^{29}Si resonance of the central Si atom for **2** occurs to higher frequency compared with that of its Li salt [δ −189.4; a 1:1:1:1 quartet with $^1J(^7\mathrm{Li}-^{29}\mathrm{Si})$ 39 Hz][36] also, but that it is masked by the broad peak in the ^{29}Si{^{1}H} spectrum that appears at ca. δ 100−130 and which corresponds to the glass insert of the NMR probe. The ^{119}Sn{^{1}H} NMR spectrum in C$_6$D$_6$ at ambient temperature exhibits a single resonance at δ 876 which does not exhibit any resolvable $^nJ(^{29}\mathrm{Si}-^{119}\mathrm{Sn})$ satellites (n = 1 or 2) and is only ca. 20 ppm different from that for **1**.

[Ge(2-{(Me$_3$Si)$_2$C}-C$_5$H$_4$N)Cl] (3). The ^{1}H NMR spectrum of **3** in C$_6$D$_6$ at ambient temperature exhibits resonances with characteristic chemical shifts and integral values, very similar to those observed for its Sn analogue[23] though considerably broader. This suggests that the formally cordinate N−Ge bond, though not persistent in solution, is much stronger than the corresponding bond in [Sn(2-{(Me$_3$Si)$_2$C}-C$_5$H$_4$N)Cl] for which the ^{1}H and ^{13}C{^{1}H} NMR spectra exhibit sharp resonances. In the ^{13}C{^{1}H} NMR spectrum, resonances for the aromatic ^{13}C environments of the 2-{(Me$_3$Si)$_2$C}-C$_5$H$_4$N ligand are observed at δ 174.54, 143.95, 139.66, 126.10, and 119.65. The resonance for the quaternary ^{13}C environment of the 2-{(Me$_3$Si)$_2$C} moiety is observed at δ 39.24, several ppm to lower frequency compared with that for [Sn{2-[(Me$_3$Si)$_2$C]-C$_5$H$_4$N}Cl] (δ 43.34). In agreement with the ^{1}H NMR spectrum, only one (albeit broad) ^{13}C resonances is observed for the SiMe$_3$ groups, at δ 1.61. The ^{29}Si{^{1}H} NMR spectrum exhibits a single broad resonance at δ 0.

[Ge(2-{(Me$_3$Si)$_2$C}-C$_5$H$_4$N){CH(PPh$_2$)$_2$}] (4). The ^{1}H NMR spectrum of **4** in C$_6$D$_6$ at ambient temperature exhibits reasonably sharp resonances with chemical shifts and integral values characteristic of the two ligands. Table 1 contains a comparison of selected NMR chemical shift data for pertinent CH(PPh$_2$)$_2$- and 2-{(Me$_3$Si)$_2$C}-C$_5$H$_4$N-containing compounds. The doublet at δ 3.81 [$^2J(^{31}\mathrm{P}-^1\mathrm{H})$ = 6 Hz] is similar to that observed for its Sn analogue **5**[2] (though is very much sharper) with both resonances to much higher frequency compared with CH$_2$(PPh$_2$)$_2$ and Li(Et$_2$O)·CH(PPh$_2$)$_2$ (δ 2.78 and 2.16, respectively): a doublet (presumably two unresolved, overlapping doublets) rather than a triplet is observed as a result of the two distinct ^{31}P environments (vide infra). Contrasting that for **3**, but as found for [Sn(2-{(Me$_3$Si)$_2$C}-C$_5$H$_4$N){CH(PPh$_2$)$_2$}],[2] **1**, and **2**, two distinct resonances corresponding to the SiMe$_3$ ^{1}H environments are observed, indicating that the N−Ge bond persists in solution at ambient temperature. The ^{13}C{^{1}H} NMR spectrum of **4** in C$_6$D$_6$ at ambient temperature, in contrast to that for **5**, exhibits only sharp resonances. The sharpness and number of distinct resonances in the ^{13}C{^{1}H} NMR spectrum suggest that the coalescence point corresponding to unrestricted rotation about the E−CH(PPh$_2$)$_2$ bond which is being closely approached at ambient temperature for **5** (E = Sn), is energetically much further away for **4** (E = Ge). This is in agreement with the shorter E−CH(PPh$_2$)$_2$ bond for E = Ge vs Sn (vide infra). In agreement with the ^{1}H NMR spectrum and further supporting the persistence of the formally coordinate N−Ge bond of **4** in solution at ambient temperature, resonances corresponding to two distinct SiMe$_3$ ^{13}C environments are observed (δ 4.07 and 1.57). The resonance corresponding to the C atom of the 2-{(Me$_3$Si)$_2$C} moiety appears at δ 38.10. The resonance corresponding to the central C atom of the CH(PPh$_2$)$_2$ ligand appears at δ 22.80 as an apparent triplet with $^1J(^{31}\mathrm{P}-^{13}\mathrm{C})$ 105 Hz: on the basis of the observed doublet in the ^{1}H NMR spectrum [E−C*H*(PPh$_2$)$_2$, δ 3.81, $^2J(^{31}\mathrm{P}-^1\mathrm{H})$ = 6 Hz] and by analogy with the discussion presented for **5**,[2] it is likely that this triplet is in fact an overlapping pair of doublets. This chemical shift is slightly to lower frequency with respect to that for “free” bis(diphenylphosphino)methane [C$_6$D$_6$, δ 28.86, $^1J(^{31}\mathrm{P}-^{13}\mathrm{C})$ = 48 Hz] and **5** [C$_6$D$_6$, δ 26.79, $^1J(^{31}\mathrm{P}-^{13}\mathrm{C})$ = 114 Hz] but to significantly higher frequency than the corresponding resonances for Li(Et$_2$O)·CH(PPh$_2$)$_2$ (C$_6$D$_6$, δ 18.14). This suggests therefore that in solution, the CH(PPh$_2$)$_2$ ligand of **4** is bound to the central Ge atom η^1, via the central C atom. The ^{31}P{^{1}H} NMR spectrum of **4** in C$_6$D$_6$ at ambient temperature, like that for **3**, exhibited two resonances with equal integral values and similar intensities (δ 1.1 and −11.0). The ^{29}Si{^{1}H} NMR spectrum of **4** was also recorded in C$_6$D$_6$ at ambient temprature and exhibits a single and slightly broad resonance at δ 0. (The ambient temperature ^{29}Si{^{1}H} NMR spectrum of **5** exhibited a single resonance, while at 245 K in C$_4$D$_8$O, exhibited two just resolvable resonances, centered at δ 2).[2]

Crystal Structures of [E(2-{(Me$_3$Si)$_2$C}-C$_5$H$_4$N)R] (1−4). The molecular structures of **1-4** are presented in Figures 1−4, respectively. Table 2 contains a summary of cell constants and data collection parameters for **1** and **2**, respectively. Table 3 and Table 4 contain atom coordinates (× 10^4) and temperature factors ($Å^2 \times 10^3$) for **1** and **2** respectively. Important intramolecular distances and angles for compounds **1** and **2** are listed in Tables 5 and 6, respectively. Table 7 contains a summary of cell constants and data collection parameters for **3** and **4** respectively. Tables 8 and 9 contain atom coordinates (×10^4) and temperature factors ($Å^2 \times 10^3$) for **3** and **4** respectively. Important intramolecular distances and angles for compounds **3** and **4** are listed in Tables 10 and 11, respectively.

[Sn(2-{$(Me_3Si)_2C$}-C_5H_4N){Sn($SiMe_3)_3$}] (1). The molecular structure of **1** illustrated in Figure 1 shows it to be monomeric with a distorted trigonal pyramidal geometry about the central, three coordinate divalent Sn atom, Sn(1), typical of heteroleptic 2-{$(Me_3Si)_2C$}-C_5H_4N derivatives of Sn(II).[2,23] The Sn(1) atom is bonded to the 2-{$(Me_3Si)_2C$}-C_5H_4N ligand via the C atom of the 2-{$(Me_3Si)_2C$} substituent [C(6)] and by a formally coordinate bond with the N atom of the C_5H_4N ring. The Sn(1)−C(6) bond length of 2.304(2) Å is marginally shorter than that found in the related, covalent [Sn(2-{$(Me_3Si)_2C$}-C_5H_4N)R] [R = Cl, 2.32(2) Å (both molecules); R = 2-{$(Me_3Si)_2C$}-C_5H_4N, 2.334(6), 2.346(6) and 2.377(7) Å; R = N$(SiMe_3)_2$, 2.356(8) Å],[23] a result of the longer Sn(1)−R bond when R = Sn$(SiMe_3)_3$, reducing the steric congestion about the Sn(1) center. The Sn(1) and Sn(2) atoms are bound by a single bond, 2.8689(5) Å in length; this is the first structurally authenticated measurement of a bond between divalent Sn and tetravalent Sn. The C_5H_4N ring of the 2-{$(Me_3Si)_2C$}-C_5H_4N ligand shows values typical for an aromatic system.

[Sn(2-{$(Me_3Si)_2C$}-C_5H_4N){Si($SiMe_3)_3$}] (2). The molecular structure of compound **2** is presented in Figure 2. It can be seen that it is monomeric in the solid state and that the central divalent Sn atom is three-coordinate, bound η^1 to the Si$(SiMe_3)_3$ ligand and η^2 to the 2-{$(Me_3Si)_2C$}-C_5H_4N ligand; thus **2** is isostructural with **1**. The 2-{$(Me_3Si)_2C$}-C_5H_4N ligand is bound to the central Sn atom through the central C atom of the 2-{$(Me_3Si)_2C$} substituent and the N atom of the C_5H_4N ring [Sn−C, 2.345(6); Sn−N, 2.335(5) Å; Table 6]. The Sn−Si bond length of 2.7236(18) Å is significantly longer than the corresponding distances in [(Sn{Si$(SiMe_3)_3$}$_2$)$_2$] [2.6667(11) and 2.6781(11) Å],[39] [Sn{Si$(SiMe_3)_3$}$_2$(μ-Cl)Li(thf)$_3$] [2.681(2) Å][40] and [Sn{C_6H_3-2,6-$(NMe_2)_2$}(Si{(-NCH_2Bu^t)$_2$-1,2-C_6H_4}{C_6H_3-2,6-$(NMe_2)_2$})] [2.636(2) Å].[28] The geometry about the central Si atom of the Si$(SiMe_3)_3$ ligand is distorted tetrahedral [Sn−Si(4)−Si(3), 91.88(7); Sn−Si(4)−Si(5), 111.53(8); Sn−Si(4)−Si(6), 129.43(10)°], as is found for the two corresponding Si environments in the bis{Si$(SiMe_3)_3$} derivative: the angles about one Si atom are similar to those in **2** [99.78(5), 106.19(5), and 131.88(6)°] while the angles about the second Si atom are much less distorted from ideal [112.06(5), 112.35(5), and 115.51(5)°].

[Ge(2-{$(Me_3Si)_2C$}-C_5H_4N)Cl] (3). The molecular structure of compound **3** is presented in Figure 3. Like **1** and **2**, **3** is monomeric in the solid state and the central divalent group 14 element is three-coordinate, bound η^1 to the R (Cl) ligand and η^2 to the 2-{$(Me_3Si)_2C$}-C_5H_4N ligand. However, there are two crystallographically independent molecules in the unit cell, the geometries of which differ only very slightly; **3** is isostructural with [Sn(2-{$(Me_3Si)_2C$}-C_5H_4N)Cl]. The 2-{$(Me_3Si)_2C$}-C_5H_4N ligand is bound to the Ge atom through the central C atom of the 2-{$(Me_3Si)_2C$} substituent and the N atom of the C_5H_4N ring [Ge(1,2)−C(1,13), 2.138(5), 2.138(5); Ge(1,2)−N(1,2), 2.082(4), 2.075(4) Å; Table 10]: the Ge(1,2)−Cl(1,2) bond lengths are 2.2948(19) and 2.2962(19) Å. These Ge−C and Ge−Cl distances are are very much longer than those in dimeric [(Ge{C_6H_3-2,6-(C_6H_2-2,4,6-Me_3)$_2$}Cl)$_2$] which has a Ge−Ge bond of 2.443(2) Å and terminal Cl atoms [Ge−C, 2.000(6); Ge−Cl, 2.120(2) Å]: the Sn analogue is dimeric also, but possesses two bridging Cl atoms and no metal−metal interaction.[1] The C(1,13)−Ge(1,2)−Cl(1,2) and N(1,2)−Ge(1,2)−Cl(1,2) angles of 101.86(17), 102.52(15), 91.89(14), and 93.06(14) are very close to the corresponding angles in [Sn(2-{$(Me_3Si)_2C$}-C_5H_4N)Cl], while the much larger N(1,2)−Ge(1,2)−C(1,13) angles [67.1(2) and 66.9(2) vs 61.4(6) and 61.7(6)°] are a consequence of the shorter Ge−ligand C, N bond lengths in **3**. These angles are also slightly larger than that observed for the four-coordinate homoleptic analogue, [Ge(2-{$(Me_3Si)_2C$}-C_5H_4N)$_2$] [64.8(3)°] but are very similar to those for the five-coordinate derivatives, [Ge(2-{$(Me_3Si)_2C$}-C_5H_4N)$_2$Se] [67.16(13) and 67.40(13)°] and [Ge(2-{$(Me_3Si)_2C$}-C_5H_4N)$_2$Te] [67.12(8)°].[30]

[Ge(2-{$(Me_3Si)_2C$}-C_5H_4N){CH$(PPh_2)_2$}] (4). An examination of the molecular structure presented in Figure 4 reveals compound **4** to be monomeric in the solid state also. The central Ge atom is η^2-bound to the 2-{$(Me_3Si)_2C$}-C_5H_4N ligand through the C atom of the 2-{$(Me_3Si)_2C$} substituent and the N atom of the C_5H_4N ring [Ge(1)−C(26), 2.142(9), Ge(1)−N(1), 2.089(7) Å] and η^1 bound to the CH$(PPh_2)_2$ ligand through its central C atom, C(1) [Ge(1)−C(1) 2.097(8) Å]. The molecular structures of [E{CH$(PPh_2)_2$}$_2$] (E = Sn, Pb)[41] and [Sn(2-{$(Me_3Si)_2C$}-C_5H_4N){CH$(PPh_2)_2$}] **(5)** have been reported,[2] but **4** is the first structurally characterized germylene employing the CH$(PPh_2)_2$ ligand. The Ge−ligand C, N bond lengths (Ge(1)−C(26), 2.142(9) and Ge(1)−N(1), 2.089(7) Å) are not significantly different from those in **3**; the Ge(1)−C(26) distance and the Ge-*C*H$(PPh_2)_2$ [Ge(1)−C(1), 2.097(8) Å] distance are also not significantly different.

Conclusions

We have prepared and structurally characterized two novel, monomeric heteroleptic derivatives of divalent Sn, the stannylenes **1** and **2**. We envisage that these will play an important role in the development of compounds containing bonds between low-valent group 14 elements. Additionally, we have prepared and structurally characterized two monomeric heteroleptic derivatives of divalent Ge, germylenes **3** and **4**, demonstrating the utility of [Ge(2-{$(Me_3Si)_2C$}-C_5H_4N)Cl] (**3**) as a precursor to further novel divalent Ge compounds by the preparation of the CH(PPh_2)-containing [Ge(2-{$(Me_3Si)_2C$}-C_5H_4N){CH$(PPh_2)_2$}] (**4**). As illustrated for their Sn

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analogues,[2,23] the ^{1}H NMR spectra of **3** and **4** reveal the persistence of the formally coordinate N−E bond in solution at ambient temperature for **4** only. With regards to the chemistry of compounds containing bonds between main group elements and tranistion metals, we predict that the heteroleptic nature of **1**−**4** will give rise to interesting reactivity in their coupling with transition metal clusters.

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Supporting Information Available: Tables of X-ray data, positional and thermal parameters, bond distances and angles, least-squares planes, ^{29}Si{^{1}H} and ^{119}Sn{^{1}H} NMR spectra for **1** (25 pages). Ordering information is given on any current masthead page.

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