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Tetravalent Group 14 Derivatives of a Bulky Aminocarbazole

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Stepwise metalation and metathesis reactions with a bulky aminocarbazole were conducted to prepare derivatives of tetravalent group 14 elements. These were regarded as putatively suitable precursors for the formation of doubly bonded group 14/group 15 molecules such as imino species. Starting from an N-aminocarbazole, deprotonation with benzyl potassium formed the corresponding solvent-free dimeric amide. Metathesis reactions with EBr_4 (E = Si, Ge, Sn) afforded $RN(H)EBr_3$. Deprotonation of $RN(SiMe_3)H$ with benzyl potassium afforded the solvent-free monomeric amide $RN(SiMe_3)K$ which was then treated with $SiCl_4$, $GeBr_4$ and SnI_4. Both obtained series of compounds, $RN(H)EBr_3$ and $RN(SiMe_3)EX_3$, were characterized by multinuclear NMR spectroscopy and SCXRD studies.

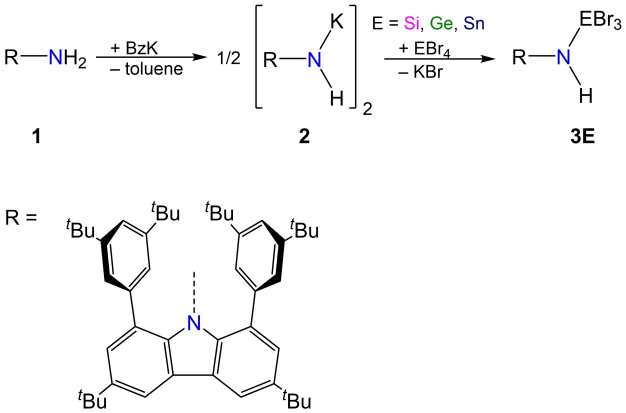
Introduction

Among the multiple bond systems involving heavy group 14 elements, an example for a polar bond is the double bond to nitrogen atoms.[1] Several examples of stable silaimines are known and structurally characterised, but only few methods are known for the synthesis of imino compounds of group 14 elements.

Wiberg and Müller reported on the first silaimine $^tBu_2Si{=}N{-}Si^tBu_3$ which was obtained by metathesis of $^tBu_2SiClN_3$ with $NaSi^tBu_3$ and subsequent elimination of N_2.[2] This method, however, was not extended to other examples. More general access is provided by the reaction of silylenes with organoazides and concomitant elimination of N_2.[3–5] A similar reaction was found by So and coworkers who treated the disilyne $[PhC(N^tBu)_2Si]_2$ with bis(Dipp)carbodiimide (Dipp = 2,6-bis(diisopropyl)phenyl) and obtained the silylenylsilaimine $[PhC(N^tBu)_2Si\{NDipp\}\text{-}Si(N^tBu)_2CPh]$.[6] Recently, Lips induced extrusion of $DippN(SiMe_3)_2$ from $[Dipp(SiMe_3)NSi]_4$ by carbene addition which afforded a cyclic Si_4 unit with both a silylone and silaimine moiety.[7] The seemingly most generally applicable synthetic route to silaimines is salt elimination as reported by Klingebiel who investigated the lithiation of aminofluorosilanes.[8–10]

Examples for the even heavier germaimines and stannaimines are scarce and these studies were spearheaded by Meller. Germaimines could be generated by treatment of $Ge[N(SiMe_3)_2]$ with silyl- and arylazides.[11,12] Just one example of a stannaimine is known which is stable only stable up to −30 °C and was obtained by the reaction of $Sn[N(SiMe_3)_2]$ with $DippN_3$. The reactivity towards a variety of small molecules such as alcohols was studied in detail.[13]

None of the known imino compounds feature two halide substituents on the heavy tetrel, consequently we made it our long-term goal to synthesise such compounds of the general formula $RNEX_2$ (E = Si, Ge, Sn; X = Cl, Br, I; R = bulky carbazole). Conceivable precursors for these compounds would be $RN(H)EX_3$ and $RN(SiMe_3)EX_3$. As certainly some degree of kinetic stabilisation by bulky substituents is required for the imino compounds, we envisaged utilisation of a carbazolyl substituent (R, Scheme 1). This is the logical continuation of work done previously in our group, where transamination reactions of the N-aminocarbazole RNH_2 were studied.[16] Employing a carbazolyl substituent R renders the $RN(H)EX_3$ and $RN(SiMe_3)EX_3$ compounds formal derivatives of hydrazine. Hydrazine derivatives with distinct group 14 substituents, $(Me_3E)_2N{-}N(EMe_3)_2$ (E = C, Si, Ge, Sn), were reported by Wiberg and Veith in 1971, but nothing is known about their suitability for elimination reactions.[14]



Scheme 1. Synthesis of aminocarbazolyl group 14 compounds (R = bulky carbazolyl substituent).

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Results and Discussion

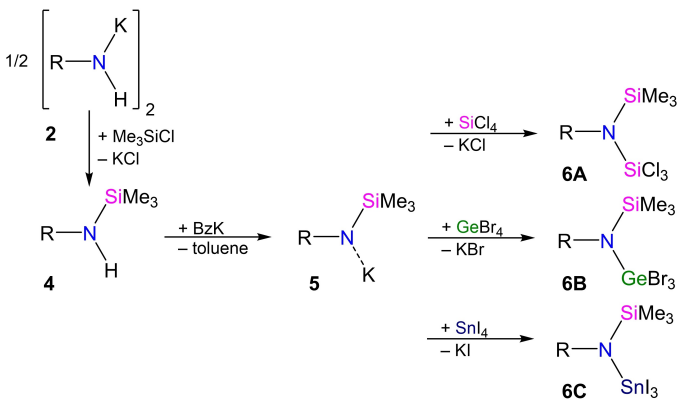
Syntheses

Starting from the N-aminocarbazole RNH_2 (**1**, Scheme 1), stepwise deprotonation and metathesis reactions were planned. As the base of choice, benzyl potassium was employed. The deprotonation of RNH_2 with BzK in toluene afforded $[RN(H)K]_2$ (**2**), which forms an unsymmetric dimer in the solid state with no further solvent molecule coordinated to the potassium atom. The amide **2** was then subjected to metathesis reactions with $SiBr_4$, $GeBr_4$ and $SnBr_4$ in toluene. In all three cases, the reactions proceeded smoothly, and evaporation of all volatiles, extraction with *n*-hexane and recrystallisation afforded the desired compounds $RN(H)EBr_3$ (**3E**, E = Si, Ge, Sn) as colourless, yellow and red compounds, respectively.

All attempted reactions to induce elimination of HBr by addition of metal bases such as ^{t}BuLi, BzK, $Na[N(SiMe_3)_2]$ or organobases such as NHCs or P_4-phosphazene base were unsuccessful in the regard either no abstraction reaction was observed or the N–N bond broke to afford carbazolides. Consequently, a milder approach was studied, aiming to exploit the elimination of Me_3SiX from $RN(SiMe_3)EX_3$.

The amide **2** was again a useful starting material for this path of reactivity (Scheme 2). Metathesis with Me_3SiCl afforded $RN(SiMe_3)H$ (**4**) in good yields as colourless crystalline compound. The subsequent deprotonation requires a coordinating donor solvent such as THF to proceed, and with BzK in toluene no reaction was observed. Similarly, attempts of double deprotonation of RNH_2 (**1**) even in THF never produced RNK_2 but only $[RN(H)K]_2$ (**2**).

The silylated amide $RN(SiMe_3)K$ (**5**) was generated in THF solution, subsequently the solvent was evaporated, and the brown residue was treated with *n*-hexane. Immediately, a yellow powder formed. Again, all volatiles were removed in vacuo and the residue was crystallized from warm *n*-hexane (50 °C). The crystal structure and the NMR spectra confirm that no donor solvent is coordinated to the K atom. This silyl amide was then employed in metathesis reactions with EBr_4 (E = Si, Ge, Sn). Surprisingly, only the reaction with $GeBr_4$ afforded the desired product $RN(SiMe_3)GeBr_3$ (**6A**) as yellow crystalline material, while all efforts with $SiBr_4$ and $SnBr_4$, regardless of drying and degassing the involved chemicals, only afforded quantitative amounts of $RN(SiMe_3)H$. In case of the tin compound, traces of THF were seen as a possible cause as $SnCl_4$ and $SnBr_4$ form sparingly soluble adducts with THF, so in situ (in THF) prepared $RN(SiMe_3)K$ (**5**) had to be avoided. But even though **5** was prepared solvent-free, but still no desired product was observed. However, when SnI_4 was used in toluene, near quantitative formation of $RN(SiMe_3)SnI_3$ (**6C**) was apparent from an ^{1}H NMR spectrum of the reaction mixture. The product could be extracted with *n*-hexane and obtained as dark red crystalline material in moderate yield. A similar problem occurred in case of metathesis of $RN(SiMe_3)K$ with SiX_4, but here no insoluble precipitates are formed. After many variations one experiment was successful: On small scales of 30–40 mg, the reaction of $RN(SiMe_3)K$ with $SiCl_4$ in hexane at 50 °C for 24 h lead to quantitative consumption of $RN(SiMe_3)K$ and only marginal amounts of $RN(SiMe_3)H$. From the champagne coloured reaction mixture, colourless crystals could be isolated, in which approx. 92% $RN(SiMe_3)SiCl_3$ cocrystallised with 8% of the known $RSiCl_3$.[15] These two compounds could not be separated. No other solvents and none of the other silicon halides produced similar results, and larger scaled reactions repeatedly only afforded $RN(SiMe_3)H$.



Scheme 2. Synthesis of silylated aminocarbazolyl group 14 compounds (R = bulky carbazolyl substituent).

NMR spectroscopy

The NMR spectra of the aminocarbazole derivatives reveal that for RN(H)K (**2**), $RN(H)EBr_3$ (**3Si**, **3Ge**, **3Sn**), $RN(SiMe_3)H$ (**4**) and $RN(SiMe_3)K$ (**5**), the rotation around the N–N axis is dynamic on NMR time scale. For instance, in both the ^{1}H and ^{13}C NMR spectra, the tertbutyl groups on the arenes give rise to only one set of resonances with a 2:1 intensity ratio compared to the carbazole tertbutyl groups. In contrast, in the $RN(SiMe_3)EX_3$ molecules (**6A**, **6B**, **6C**), this rotation is hindered and consequently, there are two sets of resonances for the arene tertbutyl groups in both ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR resonance of the N*H* atom of RNH_2 (**1**) shifts from 3.47 to 1.98 upon deprotonation with benzyl potassium in toluene (**2**). Metathesis with group 14 halides then causes a shift to higher field with larger effect the heavier the group 14 element is (**3Si** 4.99, **3Ge** 5.76, **3Sn** 6.48 ppm, Table 1). A similar effect is observed for the ^{1}H NMR resonance of the $SiMe_3$ group of $RN(SiMe_3)H$ (**4**): Upon deprotonation it is shifted from −0.70 ppm to higher energy in **5** −0.42 ppm) and metatheses with the group 14 halides then cause an downfield shift again (**6A** −0.06, **6B** −0.04, **6C** −0.10 ppm). The ^{15}N NMR resonances could provide information about the correlated with the changes in the chemical environment upon introduction of the tetravalent group 14 elements. However, the carbazole-N NMR resonance is only marginally influenced by different substitution of the amino-N and always found in the range of 124 to 147 ppm, with the exception of the amides **2** and **5** (166.9 and 161.5 ppm). The more telling resonance of the amino-N could

Table 1. Selected NMR data. All resonances recorded in C_6D_6, selected computed values are given in italics.

	^{1}H (N*H*)	^{1}H (TMS)	^{15}N (*N*E)	^{15}N (*N*NE)	^{29}Si (*Si*X)	^{29}Si (TMS)	^{119}Sn
1[16]	3.47	–	73.6	128.0	–	–	–
2	1.98	–	142.0	166.9	–	–	–
	1.15		*141*	*185*			
3 Si	4.99	–	89.3	124.1	−63.4	–	–
	3.5		*104*	*137*			
3 Ge	5.76	–	104.7	133.6	–	–	–
	4.3		*118*	*146*			
3 Sn	6.48	–	114.4	140.7	–	–	−383.4
	5.3		*144*	*158*			
4	3.52	−0.70	73.9	131.0	–	8.5	–
	2.2		*79*	*144*		*7*	
5	–	−0.42	130.5	161.5	–	-9.0	–
			121	*173*		*-15*	
6 A	–	−0.06	94.9	132.0	−22.5	17.2	–
			103	*141*	*6*	*16*	
6 B	–	−0.04	112.9	137.2	–	21.6	–
			123	*148*		*20*	
6 C	–	−0.10	n.obs.	147.0	–	23.6	−1141.4
			170	*164*		*23*	

not be observed for **6 C** because of dynamics which influenced the ^{1}H-^{15}N HMBC experiment. The resonance shifts to higher field when heavier group 14 elements are attached to the N atom. This is a trend which is observed both in the RN(H)- and RN($SiMe_3$)-containing series. The ^{29}Si NMR resonance for the $SiBr_3$ moiety of **3 Si** is found slightly downfield shifted compared to $SiBr_4$ but comparable to DippN($SiMe_3$)$SiBr_3$ (**3 Si** −63.4, cf. $SiBr_4$ −92, DippN($SiMe_3$)$SiBr_3$ −63.0 ppm)[17,18] and the corresponding resonance of the $SiCl_3$ moiety in **6 A** (−22.5 ppm) is at nearly the same frequency as in $SiCl_4$ (−20 ppm),[17] DippN($SiMe_3$)$SiCl_3$ (−27.5 ppm)[19] or Ar*N($SiMe_3$)$SiCl_3$ (−26.9 ppm).[20] Similarly, the ^{119}Sn NMR resonance is observed at higher energy for the aminocarbazole derivatives **3 Sn** and **6 C** (**3 Sn** −383.4, **6 C** −1141.4 ppm) compared to the free tetrahalides ($SnBr_4$ −638, SnI_4 −1701 ppm).[21]

IR spectroscopy

The ν(NH) vibrations are found close to the value observed for RNH_2 (**1** 3354 cm^{-1}) for **2** 3355 and **3 Si** 3365 cm^{-1}. For **3 Ge** and **3 Sn** incrementally lower energies were observed (**3 Ge** 3304, **3 Sn** 3253 cm^{-1}).

Crystal structures

The molecular structures of all compounds were determined by single crystal X-ray diffraction (Table 2). As expected for **2** the potassium amide without donor solvents present, there are contacts between K and arene-C atoms between 3.0 and 3.5 Å indicative of π interactions (Figure 1). Within the series of aminocarbazolyl compounds perhaps the most unusual feature is the slightly shortened N−N bond in **3 Si**, **3 Ge** and **3 Sn** (1.400(2), 1.390(5) and 1.397(5) Å), compared to both the other compounds in the series as well as to the sum of covalent radii of 1.42 Å[22] and other main group molecules containing the hydrazine structural motif which display N–N bond lengths in the range of 1.42–1.46 Å,[23–28] even in the instance of the previously reported divalent aminocarbazolyl compounds.[16]

The other bond metrics compare well to known bulky aryl (silyl)amido trihalosilanes, such as DippN($SiMe_3$)$SiCl_3$, DippN($SiMe_3$)$SiBr_3$ and Ar*N($SiMe_3$)$SiCl_3$.[18–20] It is interesting to note that in **6 A** and **6 C** there is no disorder of the $SiMe_3$ and $SiCl_3$ or SnI_3 group with swapped positions. The $SiCl_3$ group of **6 A** points into the cavity formed by the arenes, while in **6 C** the SnI_3 group points out of the cavity (Figure 2). In contrast, in **6 B** the $SiMe_3$ and $GeBr_3$ moiety are disordered with swapped positions. The N–E (E = Si, Ge, Sn) distances fall within the expected ranges.

In the sequence of **3Si**, **3Ge** and **3Sn**, progressively smaller NNE (E = Si, Ge, Sn) angles are observed which is expected when considering the larger EX_3 groups interact more strongly with the flanking arenes and are consequently pushed out of the provided pocket.

Table 2. Structural data (bond lengths in Å, angles in °).

	N–N	N–E(X_3)	N–N–E(X_3)
2	1.418(3)	2.679(2)	150.37(17)
	1.440(3)	2.759(3)	79.55(14)
		2.865(2)	137.09(16)
		2.605(2)	128.22(16)
		2.781(2)	
3 Si	1.400(2)	1.693(2)	125.89(15)
3 Ge	1.390(5)	1.818(4)	121.3(3)
3 Sn	1.397(5)	2.047(4)	117.6(3)
4	1.3968(13)	1.7346(12)	124.11(8)
5	1.423(2)	1.7007(16)	115.87(11)
		2.5670(15)	129.81(11)
6 A	1.439(2)	1.811(2)	115.70(13)
6 B[a]	1.431(2)	1.830(7)	116.8(2)
6 C	1.438(5)	2.055(4)	113.4(3)

[a] $GeBr_3$ and $SiMe_3$ moiety are positionally disordered.

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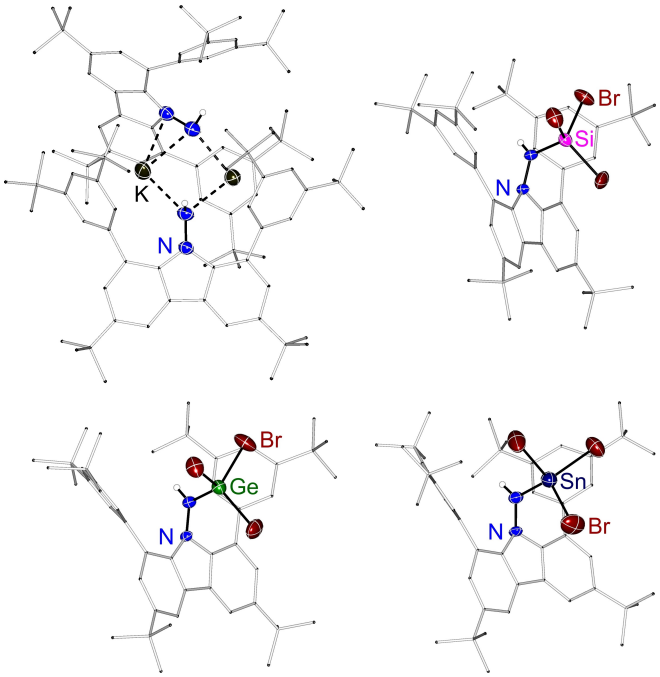

Figure 1. Molecular Structures of $[RN(H)K]_2$ (**2**), $RN(H)SiBr_3$ (**3 Si**), $RN(H)GeBr_3$ (**3 Ge**), and $RN(H)SnBr_3$ (**3 Sn**). Thermal ellipsoids at 50% probability.

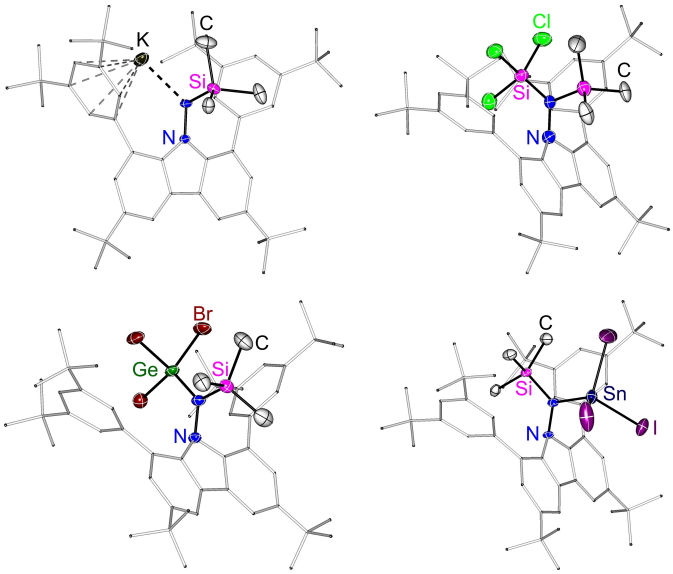

Figure 2. Molecular Structures of $RN(SiMe_3)K$ (**5**), $RN(SiMe_3)SiCl_3$ (**6 A**), $RN(SiMe_3)GeBr_3$ (**6 B**, the $GeBr_3$ and $SiMe_3$ moiety are positionally disordered, of which only one part is displayed), and $RN(SiMe_3)SnI_3$ (**6 C**). Thermal ellipsoids at 50% probability.

Conclusion

We prepared six derivatives $RN(H)EBr_3$ and $RN(SiMe_3)EX_3$ (E = Si, Ge, Sn; X = Cl, Br, I) of a bulky N-aminocarbazole R by stepwise deprotonation and metathesis reactions. These compounds appeared to be suitable precursors for the synthesis of imino compounds of the heavier group 14 elements, $RNEX_2$, but to date all efforts were futile. However, the goal warrants further efforts directed towards facilitating the elimination of HX or Me_3SiX from these formal hydrazine derivatives. Alternatively, other bulky substituents will have to be employed.

Experimental Section

General considerations: NMR spectra were acquired on a Bruker Avance 400 MHz spectrometer. Reported chemical shifts are referenced to the ^1H and ^{13}C NMR resonances of the deuterated solvent.[29] Coupling constants *J* are given in Hertz as positive values regardless of their real individual sign. ^1H, ^{13}C, ^{15}N, ^{29}Si, ^{119}Sn NMR spectra were obtained at 400.1, 100.6, 40.6, 79.5, 149.2 MHz, respectively. IR spectra were recorded on a Bruker Alpha spectrometer using the attenuated total reflection (ATR) technique on powdered samples.

Synthesis of **2**. To a suspension of 21.5 mg BzK (0.159 mmol) in 1 ml toluene, a solution of 105 mg (0.156 mmol) RNH_2 in 1 ml toluene was added. The resulting dark yellow suspension was stirred for 30 min at ambient temperature and then filtered. All volatiles were evaporated in vacuo to give a brown foam. To the foam, 1 ml of hexane was added. The solution was concentrated (approx. 0.25 ml) and left undisturbed for 6 hours, resulting in the deposition of dark yellow crystals. The supernatant was removed via syringe and the crystalline material was dried in vacuo (72 mg, 0.102 mmol, 65%).

^1H NMR (C_6D_6): 1.23 (s, 36 H, Ar^{t}Bu), 1.53 (s, 18 H, Carb^{t}Bu), 1.98 (s, 1 H, **N*H***), 7.22 (s, 2 H, p-C*H*), 7.55 (br s, 6 H, *o*-C*H*, $C^{2,7}H$), 8.46 (d, J_{HH} = 2.0 Hz, 2 H, $C^{4,5}H$). **^{13}C NMR** (C_6D_6): 31.88 (s, Ar-C(CH_3)$_3$), 32.36 (s, Carb-C(CH_3)$_3$), 34.62 (s, Carb-*C*(CH_3)$_3$), 35.02 (s, Ar-*C*(CH_3)$_3$), 115.54 (s, *C*H), 118.63 (s, *C*H), 122.20 (s), 124.97 (br s, $\nu_{1/2}$ = 18.0 Hz, *C*H), 125.28 (s), 128.64 (s, *C*H), 138.86 (s), 139.21 (s), 143.26 (br s, $\nu_{1/2}$ = 6.1 Hz), 149.65 (s). **^{15}N NMR** (C_6D_6): 142.0 (J_{NH} = 50.3 Hz, *N*H), 166.9 (*N*NH). **IR** (ATR, cm^{-1}): 379 (M), 464 (M), 489 (M), 545 (W), 605 (W), 646 (M), 674 (M), 696 (M), 710 (S), 721 (S), 748 (M), 795 (W), 844 (M), 867 (VS), 901 (M), 945 (M), 972 (W), 1026 (W), 1080 (W), 1175 (M), 1202 (M), 1236 (VS), 1274 (M), 1287 (M), 1362 (S), 1376 (M), 1392 (M), 1462 (M), 1477 (S), 1590 (M), 2866 (M), 2903 (M), 2954 (VS), 3059 (W), *3355 (VW, n(NH))*.

Synthesis of **3 Si**. A freshly prepared dark yellow solution of RNHK (546 mg, 0.77 mmol) in 10 ml toluene was added dropwise via syringe to a colourless solution of $SiBr_4$ (296 mg, 0.85 mmol) in 2 ml toluene. The solution quickly turned pale yellowish and turbid. After stirring for 30 min at ambient temperature, the suspension was filtered and the filtrate was evaporated in vacuo. The off-white residue was recrystallised from n-hexane, affording $RNHSiBr_3$ as colourless crystalline material (210 mg, 0.22 mmol, 29%). **^1H NMR** (C_6D_6): 1.39 (s, 36 Hz, Ar^{t}Bu), 1.43 (s, 18 Hz, Carb^{t}Bu), 4.99 (s, J_{HSi} = 23.1 Hz, J_{H15N} = 90.8 Hz, 1 H, N*H*), 7.55 (t, J_{HH} = 1.8 Hz, 2 H, *p*-C*H*), 7.66 (br, $\nu_{1/2}$ = 4.8 Hz, 4 H, *o*-C*H*), 7.75 (d, J_{HH} = 2.0 Hz, 2 H, $C^{2,7}H$), 8.39 (d, J_{HH} = 2.0 Hz, 2 H, $C^{4,5}H$). **^{13}C NMR** (C_6D_6): 31.97 (s, Ar-C(CH_3)$_3$), 32.05 (s, Carb-C(CH_3)$_3$), 34.83 (s, Carb-*C*(CH_3)$_3$), 35.08 (s, Ar-*C*(CH_3)$_3$), 115.69 (s, *C*H), 121.57 (s, *C*H), 124.59 (s), 124.99 (br s, $\nu_{1/2}$ = 19.4 Hz, *C*H), 128.40 (s), 128.83 (s, *C*H), 138.31 (s), 140.30 (s), 144.78 (br s, $\nu_{1/2}$ = 6.1 Hz), 150.60 (s). **^{15}N NMR** (C_6D_6): 89.3 (J_{NH} = 90.7 Hz, *N*H), 124.1 (*N*NH). **^{29}Si NMR** (C_6D_6): −63.4 (s). **IR** (ATR, cm^{-1}): 473 (vs), 486 (w), 517 (s), 644 (w), 719 (w), 865 (m), 982 (m), 1135 (w), 1151 (w), 1203 (w), 1230 (s), 1362 (w), 1592 (w), 2960 (w), *3365 (w, ν(NH))*. **Raman** (1064 nm, cm^{-1}): 7, 21, 29, 39, 47, 87, 108, 127, 182, 204, 552, 797, 825, 1001, 1071, 1202, 1323, 1347, 1366, 1443, 1467, 1600, 2872, 879, 2903, 2930, 2963. **EA** found (calc.): C 62.45 (61.47), H 6.44 (6.99), N 2.99 (2.99).

Synthesis of **3Ge**. To a stirred solution of $GeBr_4$ (78 mg, 0.199 mmol) in toluene (1 ml), a solution of RNHK (138 mg, 0.195 mmol) in 2 ml toluene was added dropwise. The resulting yellow suspension was stirred for 2 hours at ambient temperature and then filtered. The yellow filtrate was evaporated, and the residue was redissolved in 2 ml n-hexane. The solution was concentrated to incipient crystallisation (approx. 0.5 ml) and left undisturbed, resulting in the deposition of yellow crystals. The supernatant was removed via syringe and the crystals were dried in vacuo (141 mg, 0.144 mmol, 74%). **^{1}H NMR** (C_6D_6): 1.40 (s, 36 Hz, Ar^{t}Bu), 1.42 (s, 18 Hz, Carb^{t}Bu), 5.76 (s, J_{H15N} = 84.5 Hz, 1 H, N*H*), 7.57 (t, J_{HH} = 1.7 Hz, 2 H, *p*-C*H*), 7.70 (d, J_{HH} = 1.7 Hz, 4 H, *o*-C*H*), 7.74 (d, J_{HH} = 2.0 Hz, 2 H, $C^{2,7}H$), 8.37 (d, J_{HH} = 2.0 Hz, 2 H, $C^{4,5}H$). **^{13}C NMR** (C_6D_6): 31.94 (s, Ar-C(CH_3)$_3$), 32.00 (s, Carb-C(CH_3)$_3$), 34.86 (s, Carb-C (CH_3)$_3$), 35.11 (s, Ar-*C*(CH_3)$_3$), 115.79 (s, *C*H), 121.76 (s, *C*H), 123.26 (s, *C*H), 124.90 (s), 125.01 (br s, $n_{1/2}$ = 7.5 Hz, *C*H), 128.63 (s), 138.05 (s), 139.94 (s), 145.22 (s), 150.78 (s). **^{15}N NMR** (C_6D_6): 104.7 (J_{NH} = 84.9 Hz, *N*H), 133.6 (*N*NH). **IR** (ATR, cm^{-1}): 414 (m), 645 (s), 716 (s), 865 (vs), 1202 (m), 1223 (m), 1246 (s), 1287 (m), 1362 (vs), 1375 (m), 1392 (m), 1461 (m), 1476 (m), 1590 (s), 2157 (w), 2866 (m), 2903 (m), 2956 (vs), *3304 (w, n(NH))*. **EA** found (calc.+toluene $C_{55}H_{73}N_2GeBr_3$): C 60.67 (61.48), H 6.21 (6.85), N 2.55 (2.61).

Synthesis of **3Sn**. A freshly prepared solution of RNHK in toluene (1050 mg, 1.48 mmol, 20 ml) was added to a solution of $SnBr_4$ (730 mg, 1.67 mmol) in toluene (5 ml) and stirred for 15 h at ambient temperature. The resulting red suspension was filtered and the filtrate was evaporated in vacuo. The red residue was recrystallised from n-hexane, affording $RNHSnBr_3$ (875 mg, 0.85 mmol, 51%). **^{1}H NMR** (C_6D_6): 1.38 (s, 18 H, Carb-^{t}Bu), 1.40 (s, 36 H, Ar-^{t}Bu), 6.48 (s, J_{H119Sn} = 125 Hz, J_{H15N} = 73.6 Hz, 1 H, N*H*), 7.59 (t, J_{HH} = 1.7 Hz, 2 H, *p*-C*H*), 7.70 (d, J_{HH} = 1.8 Hz, 2 H, $C^{2,7}H$), 7.76 (d, J_{HH} = 1.7 Hz, 4 H, *p*-C*H*), 8.27 (d, J_{HH} = 1.8 Hz, 2 H, $C^{4,5}H$). **^{13}C NMR** (C_6D_6): 31.87 (s, Carb-C (CH_3)$_3$), 31.91 (s, Ar-C(CH_3)$_3$), 34.91 (s, Carb-*C*(CH_3)$_3$), 35.16 (s, Ar-*C* (CH_3)$_3$), 116.11 (s, *C*H), 122.19 (s, *C*H), 124.51 (s, *C*H), 125.96 (s), 128.88 (s, *C*H), 129.64 (s), 139.35 (s), 139.51 (s), 146.54 (s), 151.17 (s). **^{15}N NMR** (C_6D_6): 114.4 (*N*H), 140.7 (*N*NH). **^{119}Sn{^{1}H} NMR** (C_6D_6): −383.4 (s). **IR** (ATR, cm^{-1}): 472 (W), 547 (W), 601 (W), 647 (M), 674 (M), 711 (M), 718 (M), 744 (W), 825 (W), 868 (VS), 922 (W), 966 (W), 1024 (W), 1080 (W), 1165 (W), 1182 (W), 1202 (M), 1227 (M), 1244 (S), 1288 (M), 1362 (S), 1392 (M), 1440 (M), 1461 (M), 1475 (M), 1491 (M), 1590 (M), 2866 (M), 2903 (M), 2956 (S), 3059 (VW), *3253 (VW, n (NH))*. **EA** found (calc.): C 56.43 (56.06), H 5.79 (6.37), N 2.52 (2.72).

Synthesis of **4**. In a Schlenk flask, 2.09 g RNH_2 (3.11 mmol) and 0.420 g benzyl potassium (3.11 mmol, 1.00 Äq) were combined. To the solid mixture, 25 mL of toluene were added and the brownish suspension was stirred until no red powder was visible any more. Then, 0.7 ml chlorotrimethylsilane (0.598 g; 5.41 mmol) were added and stirring continued until the solution turned colourless again. All volatiles were removed in vacuo, affording an off-white solid. The residue was extracted with 2×25 ml *n*-hexane, filtered and the filtrate was concentrated to approx. 15 ml. Undisturbed storage at 4 °C overnight resulted in the deposition of colourless crystals. The supernatant was removed via syringe and the crystalline material was dried in vacuo (0.935 g, 1.26 mmol, 40%). **^{1}H NMR** (C_6D_6): −0.70 (s, 9 H, $SiMe_3$), 1.39 (s, 36 H, Ar-^{t}Bu), 1.47 (s, 18 H, Carb- ^{t}Bu), 3.52 (s, 1 H, N*H*), 7.53 (t, J_{HH} = 1.9 Hz, 2 H, *p*-C*H*), 7.66 (d, J_{HH} = 1.9 Hz, 4 H, *o*-C*H*), 7.77 (d, J_{HH} = 2.0 Hz, 2 H, $C^{2,7}H$), 8.48 (d, J_{HH} = 2.0 Hz, 2 H, $C^{4,5}H$). **^{13}C NMR** (C_6D_6): −1.20 (s, $SiMe_3$), 31.91 (s, Ar-C(CH_3)$_3$), 32.18 (s, Carb-C(CH_3)$_3$), 35.03 (s, Carb-*C*(CH_3)$_3$), 34.79 (s, Ar-*C*(CH_3)$_3$), 115.50 (s, *C*H), 120.76 (s, *C*H), 123.47 (s, *C*H), 125.21 (s, *C*H), 127.54 (s), 128.72 (s, *C*H), 139.28 (s), 141.35 (s), 142.91 (s), 150.02 (s). **^{15}N NMR** (C_6D_6): 73.9 (*N*H), 131.0 (*N*NH). **^{29}Si NMR** (C_6D_6): 8.5 (s). **IR** (ATR, cm^{-1}): 381 (W), 388 (W), 464 (W), 473 (W), 531 (W), 602 (W), 635 (W), 647 (M), 674 (W), 694 (M), 708 (M), 720 (M), 748 (M), 759 (M), 785 (W), 837 (VS), 868 (VS), 895 (W), 922 (W), 962 (W), 1027 (W), 1074 (W), 1104 (W), 1134 (W), 1182 (W), 1203 (W), 1236 (S), 1247 (S), 1288 (M), 1362 (M), 1376 (W), 1392 (W), 1433 (W), 1461 (M), 1477 (M), 1593 (M), 2866 (W), 2903 (M), 2958 (S), 3054 (VW), 3382 (VWn, *ν(NH)*). **EA** found (calc.): C 83.41 (82.42), H 10.40 (10.04), N 3.89 (3.77).

Synthesis of **5**. In a Schlenk flask, 200 mg RN($SiMe_3$)H (0.269 mmol) and 36 mg benzyl potassium (0.277 mmol) were combined. To the mixture, 5 ml THF were added and the dark red solution was stirred for 15 minutes. The solvent was evaporated and the residue was treated with 3 ml cyclohexane, which was removed by distillation again, affording quantitative amounts of RN($SiMe_3$)K as a yellow powder. Single crystals suitable for X-ray diffraction were obtained by recrystallization from *n*-hexane. **^{1}H NMR** (C_6D_6): −0.42 (s, 9 H, $SiMe_3$); 1.26 (s, 36 H, Ar-^{t}Bu), 1.52 (s, 18 H, Carb-^{t}Bu); 7.29 (s, 2 H, p-C*H*); 7.55 (d, J_{HH} = 1.73 Hz, 2 H, $C^{2,7}H$); 7.67 (s, 4 H, o-C*H*); 8.53 (d, J_{HH} = 1.90 Hz, 2 H, $C^{4,5}H$). **^{13}C NMR** (C_6D_6): 2.92 (s, $SiMe_3$), 31.94 (s, Ar-C(CH_3)$_3$), 32.54 (s, Carb-C(CH_3)$_3$), 34.73 (s, Carb-*C*(CH_3)$_3$), 34.98 (s, Ar-*C* (CH_3)$_3$), 115.54 (s, *C*H), 118.18 (s, *C*H), 122.11 (s), 125.68 (s, *C*H), 126.20 (s, *C*H), 127.12 (s), 138.45 (s), 142.46 (s), 146.35 (s), 148.73 (s). **^{15}N NMR** (C_6D_6): 161.5 (*N*NSi), +130.5 (NSi). **^{29}Si NMR** (C_6D_6): −9.0 (s). **EA** found (calc.): C 77.85 (78.40), H 9.23 (9.42), N 3.25 (3.59).

Synthesis of **6A**. To a suspension of 40 mg RN($SiMe_3$)K (0.051 mmol) in 1 ml *n*-hexane, 20 mg $SiCl_4$ (0.118 mmol) were added via syringe. The yellow suspension was stored in a 50 °C oil bath for 18 hours which resulted in a colour change to champagne. All volatiles were removed in vacuo. The off-white residue was extracted with 1+ 0.5 ml of *n*-hexane and the combined filtrates were slowly evaporated in a conical flask to incipient crystallization. Undisturbed storage overnight afforded crystalline material. The supernatant was decanted and the crystals were dried in vacuo 14 mg (0.016 mmol, 31%). The crystalline material contained 92% RN($SiMe_3$)$SiCl_3$ and 8% $RSiCl_3$. **^{1}H NMR** (C_6D_6): −0.06 (s, 9 H, $SiMe_3$), 1.28 (s, 18 H, ^{t}Bu), 1.34 (s, 18 H, ^{t}Bu), 1.42 (s, 18 H, ^{t}Bu), 7.39 (d, J_{HH} = 2.1 Hz, $C^{2,7}$H), 7.59 (app t, J_{HH} = 1.6 Hz, Ar-C*H*), 7.60 (app t, J_{HH} = 1.6 Hz, Ar-C*H*), 7.63 (app t, J_{HH} = 1.6 Hz, Ar-C*H*), 8.30 (d, J_{HH} = 2.1 Hz, $C^{4,5}$H). **^{13}C NMR** (C_6D_6): 2.29 (s, $SiMe_3$), 31.57 (s, C(CH_3)$_3$), 31.78 (s, C (CH_3)$_3$), 34.55 (s, *C*(CH_3)$_3$), 35.05 (s, *C*(CH_3)$_3$), 35.18 (s, *C*(CH_3)$_3$), 115.43 (s, *C*H), 123.58 (s, *C*H), 124.84 (s, *C*H), 126.79 (s, *C*H), 127.11 (s), 131.45 (s, *C*H), 131.66 (s), 140.64 (s), 142.60 (s), 145.29 (s), 149.92 (s), 150.68 (s). **^{15}N NMR** (C_6D_6): 94.9 (NSi), 132.0 (NNSi). **^{29}Si NMR** (C_6D_6): −22.5 ($SiCl_3$), +17.2 ($SiMe_3$).

Synthesis of **6B**. To a solution of RN($SiMe_3$)K (236 mg, 0.303 mmol) in 5 mL THF, a solution of $GeBr_4$ (199 mg, 0.509 mmol) in 2 mL was added dropwise while stirring. The solution slowly turned yellow within minutes, produced a colourless precipitate and was stirred for 30 minutes. The suspension was filtered and the filtrate was evaporated. The yellow residue was recrystallized from n-hexane, affording yellow crystals. The supernatant was removed via syringe and the crystals were dried in vacuo (141 mg, 0.134 mmol, 44%). **^{1}H NMR** (C_6D_6): −0.04 (s, 9 H, $SiMe_3$), 1.26 (s, 18 H, ^{t}Bu), 1.36 (s, 18 H, ^{t}Bu), 1.41 (s, 18 H, ^{t}Bu), 7.32 (d, J_{HH} = 2.2 Hz, 2 H, $C^{2,7}H$), 7.54 (app t, J_{HH} = 1.7 Hz, 2 H, Ar-C*H*), 7.58 (app t, J_{HH} = 1.8 Hz, 2 H, Ar-C*H*), 7.82 (app t, J_{HH} = 1.6 Hz, 2 H, Ar-C*H*), 8.29 (d, J_{HH} = 2.1 Hz, 2 H, $C^{4,5}H$). **^{13}C NMR** (C_6D_6): 2.87 (s, $SiMe_3$), 31.71 (s, C(CH_3)$_3$), 31.77 (s, C(CH_3)$_3$), 31.89 (s, C(CH_3)$_3$), 34.53 (s, *C*(CH_3)$_3$), 35.11 (s, *C*(CH_3)$_3$), 35.29 (s, *C*(CH_3)$_3$), 115.50 (s, *C*H), 123.65 (s, *C*H), 125.56 (s, *C*H), 126.62 (s, *C*H), 127.27 (s), 131.46 (s), 132.08 (s, *C*H), 141.13 (s), 142.14 (s), 145.38 (s), 150.33 (s), 150.47 (s). **^{15}N NMR** (C_6D_6): 112.9 (*N*Si), 137.2 (*N*NSi). **^{29}Si NMR** (C_6D_6): +21.6 (s). **EA** found (calc.): C 57.45 (58.09), H 6.69 (6.98), N 2.52 (2.66).

Synthesis of **6C**. To a solid mixture of RNTK (180 mg, 0.23 mmol) and SnI_4 (145 mg, 0.23 mmol), 10 ml of precooled (−78 °C) toluene were added at (−78 °C). The mixture was stirred for 30 min at the temperature, then left to warm to room temperature overnight. All volatiles were removed in vacuo and the residue was extracted

with 2×5 ml of hexane. The dark red dark red extract was then concentrated to incipient crystallization (approx. 1.5 ml) and left undisturbed overnight, affording a crop of dark red crystals suitable for SC-XRD. The supernatant was removed via syringe and discarded and the crystals were dried in vacuo (71 mg, 0.059 mmol, 26%). **^{1}H NMR** (C_6D_6): −0.10 (s, $n_{1/2}$ = 35.8 Hz, 9 H, Si(CH_3)$_3$), 1.26 (s, 18 H, Ar-C(CH_3)$_3$), 1.29 (s, 18 H, Ar-C(CH_3)$_3$), 1.51 (s, 18 H, Carb-C (CH_3)$_3$), 7.30 (d, J_{HH} = 2.1 Hz, 2 H, $C^{2,7}$H), 7.43 (app. t, J_{HH} = 1.6 Hz, 2 H, Ar-C*H*), 7.60 (app. t, J_{HH} = 1.6 Hz, 2 H, Ar-C*H*), 8.22 (d, J_{HH} = 2.1 Hz, 2 H, $C^{4,5}$H), 8.24 (app. t, J_{HH} = 1.6 Hz, 2 H, Ar-C*H*). **^{13}C NMR** (C_6D_6): 4.47 (s, $n_{1/2}$ = 26.5 Hz, Si(CH_3)$_3$), 31.56 (s, C(CH_3)$_3$), 31.60 (s, C(CH_3)$_3$), 31.95 (s, C(CH_3)$_3$), 34.72 (s, *C*(CH_3)$_3$), 35.11 (s, *C*(CH_3)$_3$), 35.48 (s, *C*(CH_3)$_3$), 115.89 (s, *C*H), 123.39 (s, *C*H), 125.25 (s, *C*H), 125.76 (s, *C*H), 129.52 (s), 132.60 (s, *C*H), 132.83 (s), 141.49 (s), 143.09 (s), 147.18 (s), 149.62 (s), 151.50 (s). **^{15}N NMR** (C_6D_6): +147.0 (Carb-N), n. obs. (NSi). **^{29}Si NMR** (C_6D_6): +23.6 (s). **^{119}Sn NMR** (C_6D_6): −1141.4 (s, $n_{1/2}$ = 220 Hz). **EA** found (calc.): C 47.83 (49.33), H 5.42 (5.93), N 2.19 (2.26).

Further experimental and computational details are given in the SI.

Deposition Numbers 2031464 (for **2**), 2031465 (for **3 A**), 2031466 (for **3 B**), 2031467 (for **3 C**), 2031468 (for **4**), 2031469 (for **5**), 2031470 (for **6 A**), 2031471 (for **6 B**), and 2031472 (for **6 c**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Conflict of Interest

The authors declare no conflict of interest.

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[1] P. P. Power, *Chem. Rev.* **1999**, *99*, 3463–3504.
[2] N. Wiberg, K. Schurz, G. Reber, G. Müller, *J. Chem. Soc. Chem. Commun.* **1986**, 591–592.
[3] P. P. Samuel, R. Azhakar, R. S. Ghadwal, S. S. Sen, H. W. Roesky, M. Granitzka, J. Matussek, R. Herbst-Irmer, D. Stalke, *Inorg. Chem.* **2012**, *51*, 11049–11054.
[4] K. Yuvaraj, C. Jones, *Dalton Trans.* **2019**, *48*, 11961–11965.
[5] D. Reiter, P. Frisch, D. Wendel, F. M. Hörmann, S. Inoue, *Dalton Trans.* **2020**, *49*, 7060–7068.
[6] S.-H. Zhang, H.-W. Xi, K. H. Lim, Q. Meng, M.-B. Huang, C.-W. So, *Chem. Eur. J.* **2012**, *18*, 4258–4263.
[7] J. Keuter, A. Hepp, C. Mück-Lichtenfeld, F. Lips, *Angew. Chem. Int. Ed.* **2019**, *58*, 4395–4399.
[8] S. Walter, U. Klingebiel, *Coord. Chem. Rev.* **1994**, *130*, 481–508.
[9] J. Niesmann, U. Klingebiel, M. Noltemeyer, R. Boese, *Chem. Commun.* **1997**, *56*, 365–366.
[10] J. Niesmann, U. Klingebiel, M. Schäfer, R. Boese, *Organometallics* **1998**, *17*, 947–953.
[11] J. Pfeiffer, W. Maringgele, M. Noltemeyer, A. Meller, *Chem. Ber.* **1989**, *122*, 245–252.
[12] A. Meller, G. Ossig, W. Maringgele, D. Stalke, R. Herbst-Irmer, S. Freitag, G. M. Sheldrick, *J. Chem. Soc. Chem. Commun.* **1991**, *53*, 1123.
[13] G. Ossig, A. Meller, S. Freitag, R. Herbst-Irmer, G. M. Sheldrick, *Chem. Ber.* **1993**, *126*, 2247–2253.
[14] N. Wiberg, M. Veith, *Chem. Ber.* **1971**, *104*, 3176–3190.
[15] A. Hinz, *Angew. Chem. Int. Ed.* **2020**, *59*, 19065–19069.
[16] A. Hinz, *Chem. Eur. J.* **2019**, *25*, 7843–7846.
[17] U. Niemann, H. C. Marsmann, *Z. Naturforsch. B* **1975**, *30*, 202–206.
[18] A. V. Protchenko, K. H. Birjkumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge, *J. Am. Chem. Soc.* **2012**, *134*, 6500–6503.
[19] N. Winkhofer, A. Voigt, H. Dorn, H. W. Roesky, A. Steiner, D. Stalke, A. Reller, *Angew. Chem. Int. Ed.* **1994**, *33*, 1352–1354; *Angew. Chem.* **1994**, *106*, 1414–1416.
[20] J. Li, A. Stasch, C. Schenk, C. Jones, *Dalton Trans.* **2011**, *40*, 10448.
[21] J. J. Burke, P. C. Lauterbur, *J. Am. Chem. Soc.* **1961**, *83*, 326–331.
[22] P. Pyykkö, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 12770–12779.
[23] N. Götz, S. Herler, P. Mayer, A. Schulz, A. Villinger, J. J. Weigand, *Eur. J. Inorg. Chem.* **2006**, *2006*, 2051–2057.
[24] M. F. Ibad, P. Langer, F. Reiß, A. Schulz, A. Villinger, *J. Am. Chem. Soc.* **2012**, *134*, 17757–17768.
[25] S. Herler, P. Mayer, J. Schmedt auf der Günne, A. Schulz, A. Villinger, J. J. Weigand, *Angew. Chem. Int. Ed.* **2005**, *44*, 7790–7793; *Angew. Chem.* **2005**, *117*, 7968–7971.
[26] A. Schulz, A. Villinger, A. Westenkirchner, *Inorg. Chem.* **2013**, *52*, 11457–11468.
[27] Z. D. Brown, J. D. Guo, S. Nagase, P. P. Power, *Organometallics* **2012**, *31*, 3768–3772.
[28] A. Jana, H. W. Roesky, C. Schulzke, P. P. Samuel, *Organometallics* **2009**, *28*, 6574–6577.
[29] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176–2179.

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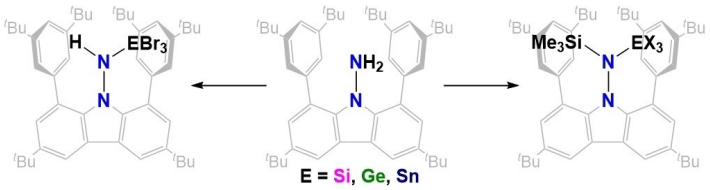

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Novel derivatives of a bulky aminocarbazole featuring tetravalent Si, Ge or Sn atoms were prepared. Deprotonation of the aminocarbazole R-NH_2 or R-N($SiMe_3$)H with benzyl potassium and subsequent metathesis with group 14 halides enables access to a range of molecules featuring the N–N(H)-EX_3 or N–N($SiMe_3$)-EX_3 structural motif (E = Si, Ge, Sn; X = Cl, Br, I).