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Cooperative activation of azides by an Al/N-based active Lewis pair – unexpected insertion of nitrogen atoms into C–Si bonds and formation of $AlCN_3$ heterocycles

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Abstract: The active Lewis pairs (ALPs) 2,6-$Me_2H_8C_5N$–C(H) = C($SiMe_3$)–AlR_2 (**1a:** R = ^{t}Bu, **1b**, R = ^{i}Bu) have strained AlC_2N heterocycles and relatively weak Al–N bonds. They react readily with a series of organic azides R′N_3 [R′ = Ph, $CH_2C_6H_4$(4-^{t}Bu), ^{t}Bu, $SiMe_3$, CH_2Ph] by cleavage of the heterocycles and addition of the azides with their α-N atoms to the Al atom. The Al–N interactions result in an activation of the azide groups which insert into the C–Si bonds of the vinyl groups with their terminal γ-N atoms. Compounds with approximately planar five-membered $AlCN_3$ heterocycles and intact N_3 groups are formed in highly selective reactions.

Keywords: active Lewis pair; aluminum; azides; heterocycles; substrate activation.

Dedicated to: Professor Arndt Simon on the occasion of his 80th birthday.

1 Introduction

Investigations into the reactivity of frustrated Lewis pairs (FLPs) are an important topic in current research. FLPs have coordinatively unsaturated Lewis acidic and basic centers, and caused by this specific functionality they show a unique cooperative behaviour in stoichiometric and catalytic transformations. These highly promising materials are considered as attractive alternatives or complements for transition metal catalysts. The majority of FLPs is based on systems with B and P atoms as Lewis acids and Lewis bases [1–4], but it has recently been shown that Al/P based systems are also highly efficient in various transformations [5–10]. Al atoms possess an inherently high Lewis acidity, which makes an activation by electron-withdrawing substituents, as required in B based systems, unnecessary. A class of compounds closely related to the Al/P FLPs contain Al or Ga and N atoms. Weak bonding interactions between the Lewis acidic metal and the Lewis basic N atoms result in strained four- [11–14] or three-membered heterocyles [15–18]. Cleavage of the relatively weak donor-acceptor bonds in the presence of suitable substrates results in a reactivity similar to that of FLPs. Due to the lack of frustration these compounds were named active Lewis pairs (ALPs) [11]. The exceptional and variable reactivity of these ALPs has been demonstrated by their reactions with isocyanates, nitriles, terminal alkynes, carbon dioxide, carbodiimide and other substrates [11–18]. Particularly noteworthy is their capability to oligomerize suitable monomeric starting materials such as cyanamides [12]. Typical examples of Al/N based active Lewis pairs are shown in Scheme 1 (**1**, **A**).

Organic azides, R′N_3, represent a particularly interesting class of substrates, which react with monomolecular B/P or Al/P FLPs to yield heterocycles with one (**B**) [9, 19–22], two (**C**) [23] or three (**D**) [24] N atoms of the azide groups included in the rings (Scheme 1). A related reaction of $[Ph_3C][B(C_6F_5)_4]$ and $F_5C_6N_3$ led in the presence of P(*o*-tol)$_3$ and Ph_3SiH to $[(Ph_3Si)(F_5C_6)N{-}N{=}N{-}P(o\text{-tol})_3][B(C_6F_5)_4]$ as an acyclic analogue of compound **D** [25]. Organic azides are highly reactive species that are frequently explosive but of importance for the synthesis of nitrogen containing heterocycles and amines [26–29]. They loose dinitrogen when exposed to higher temperatures, light, pressure or in the presence of transition metal catalysts. The highly reactive six-electron nitrene species formed as intermediates found application for the synthesis of amines [26–29]. Some FLP azide adducts were similarly found to release dinitrogen at elevated temperatures or after irradiation with UV light, but the reactive nitrenes could not be utilised synthetically and were usually trapped instead by the FLPs to form thermally stable adducts (**E**, Scheme 1) [21–23]. A B/P FLP

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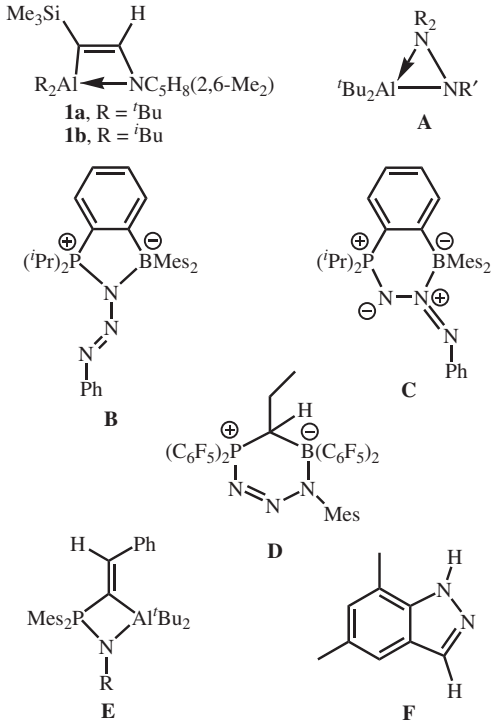


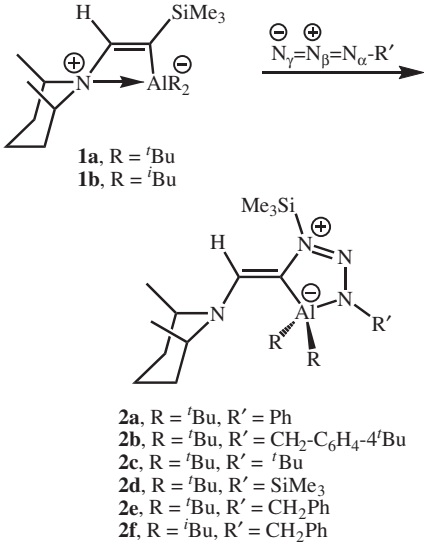
Scheme 1: Al/N based active Lewis pair molecules and products of their reactions with azides. (A) $NR_2 = NC_5H_8$, R′ adamantyl; (E) $R = C_6H_4$(4-Cl).

was reported to show an anomalous Staudinger reaction upon treatment with $MesN_3$, which by C–H bond activation was converted into the indazole derivative **F** [19]. In the absence of Lewis bases 9-borafluorenes react with azides $R'N_3$ by ring expansion [30]. This manuscript reports on investigations into the reactions of a range of organic azides with the ALP agent **1**.

2 Results and discussion

The active Lewis pairs **1a** and **1b** are readily accessible by hydroalumination of the trimethylsilyl-alkynylamine 2,6-$Me_2C_5H_8N$–C≡C–$SiMe_3$ with R_2Al–H (R = ^{t}Bu, ^{i}Bu) [11]. The *trans* addition of the Al–H bonds to the alkynyl groups is in these cases favoured by an intramolecular Al–N interaction which results in the formation of strained four-membered AlC_2N heterocycles with relatively long Al–N bonds and acute C=C–Al angles of about 90°. Treatment of the ALPs **1** with a range of alkyl and aryl azides afforded in moderate (**2a**, 56%) to good yields (**2b–f**, >72%) the insertion products **2** as colourless solids (Scheme 2). The constitution of the products is unexpected, and in contrast to reactions of previously investigated FLPs (see Introduction) the Lewis basic N atoms of the ALPs are not involved in coordination of the azide molecules, which may be caused by the relatively unfavourable formation of N–N bonds. Instead five-membered $AlCN_3$ heterocycles are selectively formed in which the α-N atom of the azide is bound to the Al atom while the γ-N atom has been inserted into the Si–C bond of the vinyl group of the ALP. The reactions proceeded smoothly at room temperature and surprisingly showed no dependence on the steric demand and electronic properties of the azide substituents (aryl, alkyl or silyl groups) or on the substituents at the Al atoms.

The NMR spectra of compounds **2** in solution resemble those of the starting materials with characteristic chemical shifts in the downfield region of the ^{1}H NMR spectra for the vinylic H atoms at $\delta = 7.1$ ppm on average. Shifts for the ^{t}Bu groups between $\delta = 1.30$ and 1.36 ppm confirm the presence of four-coordinate Al atoms. The most significant differences between compounds **1** and **2** with respect to the ALP part of the molecules are downfield shifts in the ^{29}Si NMR spectra from $\delta \approx -10$ ppm for **1** with Si–C(vinyl) [11] to $\delta = +17.4$ (**2f**) to +21.1 ppm (**2a**) for compounds **2** having Si–N bonds. The resonances of the endocyclic vinylic C atoms in the ^{13}C NMR spectra (Al*C*=CH) are shifted to a higher field from about $\delta = 161$ to $\delta = 133.1$ ppm on average in **2**. The signals of the N atoms of the azide groups in the ^{15}N NMR spectra (HN-HMBC, referenced to liq. NH_3) are characterised by a downfield shift of more than 150 ppm from values below $\delta = 100$ (α-N) and 250 ppm (β-N) in the free azides [31–34] to values in the range of $\delta = 265$ and 435 ppm, respectively, in the heterocycles. By contrast, the shifts



Scheme 2: Reactions of the active Lewis pair molecules **1a, b** with various azides $R'N_3$.

of the signals for the γ-N atoms ($\delta = 247$ ppm) do not change significantly relative to those of the starting materials. The downfield shifts of the NC*H*Me protons ($\delta = 3.38$–3.60 ppm) of the piperidyl substituents of **2** are consistent with an equatorial arrangement of the NC*H* protons and an axial arrangement of the methyl groups in solution [35–41]. This suggestion is supported by the relatively small linewidth of the respective multiplets with values below 30 Hz (distances between the outer lines of the multiplets ≈27 Hz), which excludes the presence of the usually large $^3J_{H(ax)H(ax)}$ coupling constant which would be characteristic of an axial arrangement of the NC*H*Me proton. The assigned configuration was confirmed by crystal structure determination (Fig. 1). This situation may be compared with the position of the methyl groups in the starting materials which according to the results of crystal structure determinations is axial in case of bulky ^{t}Bu substituents (**1a**, $\delta = 3.36$ ppm, line width ca. 27 Hz), but equatorial for the sterically less demanding ^{i}Bu groups [**1b**, $\delta = 2.13$ ppm, line width (*pseudo*-quintet) ca. 40 Hz] [11]. The IR spectra of compounds **2** do not show a distinctive change compared to the starting materials. The EI mass spectra show peaks (*m/z*, 100%) which could be assigned to the molecular ion minus a ^{t}Bu or ^{i}Bu group.

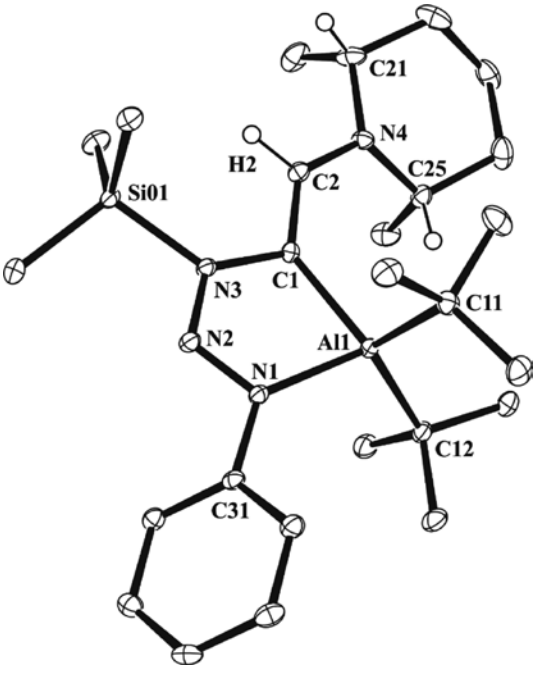


Fig. 1: Molecular structure and numbering scheme of compound **2a**. The structures of compounds **2b–f** are similar. Displacement ellipsoids are drawn at the 40% probability level. H atoms (except H2, H21 and H25, arbitrary radius) have been omitted.

The molecular structure of compound **2a** is shown in Fig. 1, those of compounds **2b–f** are similar. They feature essentially planar $AlCN_3$ heterocycles (largest deviation from average plane: C1, 4–6 pm). The only exception is compound **2b** whose structure is more distorted (largest deviation from average plane: N1, 13 pm) and may be better viewed as adopting an envelope conformation with Al in the apical position and a flap angle of 18°. The Al atoms have a distorted tetrahedral environment with alkyl substituents above and below the molecular plane. The piperidyl rings are *cis* to the Al atoms and adopt a chair conformation with Me groups in axial positions. These results for the solid state confirm the NMR spectroscopic findings for solutions. The bonding parameters of all compounds are essentially identical with endocyclic angles within the $AlCN_3$ heterocycle ranging from about 81° at the Al, 107° at the vinylic C and about 115° at the N_β atoms (Table 1). The comparatively small angle of the sp^2-hybridised vinylic C atom may be due to the considerable ionic character of the Al–C bond. All Al–C bond lengths are with ca. 201 pm very similar and comparable to those of the starting materials. By contrast, the Al–N bond lengths of molecules **2** are with around 196 pm much shorter than in compounds **1** [**1a:** 214.5(1); **1b:** 210.3(3) pm] and in the typical range of four-coordinate Al atoms [42–45]. Both N–N bond lengths of the azide groups are with 130–132 pm in a narrow range and between standard values for N–N single (142 pm) and N–N double bonds (128 pm). They indicate delocalisation of π-electron density between the three atoms. The endocyclic N–C distances to the vinylic C atoms correspond with ca. 144 pm to typical N–C single bonds. The $AlCN_3$ heterocycle found in compounds **2** is a unique structural motif and to the best of our knowledge for the first time observed for an Al compound. The heterocycles are surprisingly stable, and compound **2e** can be heated in benzene solution for 3 days to 100°C without apparent decomposition, while compound **2a** in contrast decomposed under similar conditions slowly to an unidentified product.

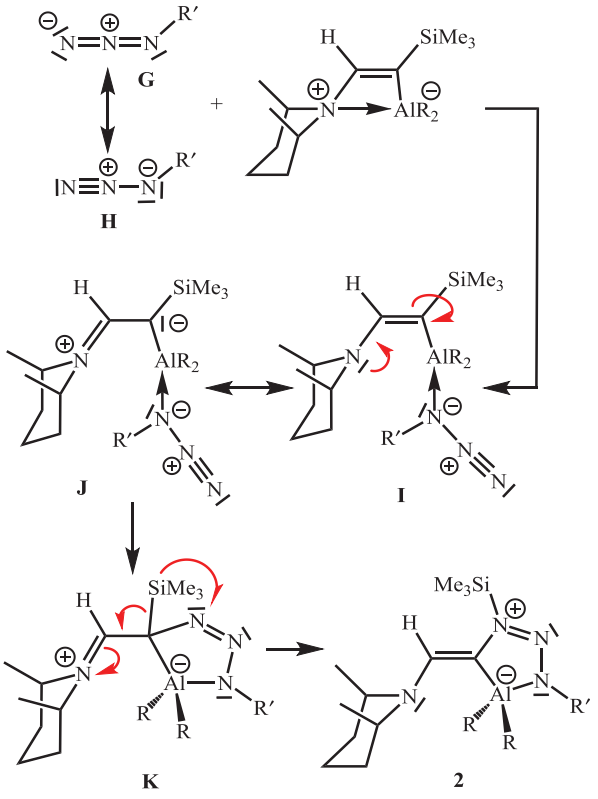
The formation of compounds **2** represents a completely new type of reactions in Al/P-based FLP or Al/N-based ALP chemistry. Usually the O or N atoms of substrates (carbonyl compounds, imines) approach the Lewis acidic Al atoms of the FLPs or ALPs as the initiating step of the respective transformation. By the interaction with the metal atom the polarity of the C=O or C=N bonds and the electrophilicity of the C atoms increase and facilitate the nucleophilic attack of the Lewis basic ALP or FLP centers at this position by ring closure [7, 8] or by initiating another secondary reaction such as an insertion

Table 1: Important bond lengths (pm) and angles (deg) of compounds **2a–f**.

Parameter	2a	2b	2c	2d[a]	2e	2f
Al–R	201.9 (av.)	201.2 (av.)	202.1 (av.)	202.1 (av.)	200.6 (av.)	199.1 (av.)
Al–C(C=C)	201.4(2)	200.1(2)	201.3(1)	201.6 (av.)	200.0(2)	199.5(1)
Al–N	195.5(1)	196.0(1)	197.7(1)	195.1 (av.)	194.3(2)	195.0(1)
(Al)N–N	132.0(2)	130.3(2)	130.3(2)	132.4 (av.)	130.4(2)	130.5(1)
N–NR_2	131.0(2)	131.9(2)	131.1(1)	131.4 (av.)	132.2(2)	131.8(1)
(Al)C–N	143.3(2)	145.5(2)	144.8(2)	143.8 (av.)	144.6(3)	144.5(1)
C=C	137.0(2)	136.0(2)	136.4(2)	136.7 (av.)	136.5(3)	136.0(2)
N–Al–C	80.82(5)	80.93(6)	81.47(5)	82.51 (av.)	81.30(8)	80.94(4)
Al–N–N	116.44(9)	115.28(9)	115.23(8)	114.57 (av.)	117.6(1)	117.06(7)
N–N–N	115.0(1)	114.8(1)	116.4(1)	116.53 (av.)	114.4(2)	114.97(9)
N–N–C	119.4(1)	118.9(1)	119.5(1)	119.56 (av.)	119.3(2)	118.53(8)
N–C–Al	107.57(9)	105.93(9)	106.95(8)	106.42 (av.)	107.4(1)	108.07(7)

[a]Average of two independent molecules.

into a M–C bond [12, 13, 16]. Azides with a homonuclear N_3 group react with Al/P-based FLPs by coordination of the terminal N atom to the Lewis acidic and basic atoms (see Introduction). The reactions of azides with the Al/N-based ALPs **1** follow another pathway, and we suggest the following mechanism in accordance with observations reported in the literature (Scheme 3). The bonding situation in organo substituted azides is described by two resonance structures (**G** and **H**), which result in average bond orders of 1,5 and 2,5 for the N–N bonds. The first step of the reactions with **1** may comprise adduct formation between the strongly polarizing Al atoms and the α-N atoms of the azides, which are bound to the alkyl or silyl substituents and bear a partial negative charge. Such complexes are well-known in transition metal [46–49] or main group element chemistry [50–53] and are in support of the resonance structure with a N–N single and a N≡N triple bond. Experimental (NMR spectroscopy) and theoretical studies with protonated hydrazoic azide $[H_2N–N≡N]^+$ [54–60] gave evidence for a partial positive charge at the terminal γ-N atom of such complexes. Coordination of the azide to Al results in ring cleavage in the ALP backbone by opening of the endocyclic Al–N donor-acceptor bond. The piperidyl N atom becomes three-coordinate and its lone pair is delocalized into the C=C π bond, which results in an increased electron density and nucleophilicity of the trimethylsilyl bound vinylic C atom (resonance structures **I** and **J**; Scheme 3). This electron-rich C atom may attack the γ-N atom of the azide to form a five-membered heterocyclic intermediate (**K**). 1,2-Shift of the trimethylsilyl group from C to N is well documented in the literature [61–67] and results finally in the formation of compounds **2**. As recently published, treatment of $(F_5C_6)_2B–C≡C$-Ph with $(F_5C_6)_2B$-N_3 leads in a related reaction via C–H bond activation of the aromatic solvent and H migration to an analogous BCN_3 heterocycle [68].



Scheme 3: Proposed mechanism for the formation of **2**. R = ^{i}Bu, ^{t}Bu; R′ = Ph, CH_2-C_6H_4-4^{t}Bu, ^{t}Bu, $SiMe_3$, CH_2Ph.

3 Conclusion

The Al/N-based active Lewis pairs **1** are obtained on a facile route by hydroalumination of ynamines. They have

strained four-membered AlC_2N heterocycles, and cleavage of the relatively weak endocyclic Al–N donor-acceptor bonds causes their unique reactivity. Reactions with various azides are reported in this article, which afforded unexpected products and yielded independently of the steric and electronic properties of the substituents at the azide groups selectively a new type of compounds (**2**). The endocyclic Al–N donor-acceptor bond of **1** is cleaved, the α-N atom of the azide is instead coordinated to the Al atom, while the γ-N atom is inserted into the C–Si bond of a vinylic C atom to form an unprecedented five-membered AlN_3C heterocycle. A mechanism is suggested in which the azido group is activated by coordination to the Al atom. Cleavage of the endocyclic Al–N bonds of the ALPs results in delocalization of electron density into the C=C π bonds and an increased nucleophilicity of the silyl bound vinylic C atoms which facilitates the attack at the γ-N atoms of the azides to form AlN_3C rings. The well-known 1,2-shift of the $SiMe_3$ groups from C to N represents the last step of these reactions and leads to the formation of products **2**. This reaction pathway represents a remarkable example for the influence of cooperativity on the behaviour of ALPs and the importance of the opposite functionalities of Lewis acidic and basic centres for their unusual chemical properties.

4 Experimental section

All procedures were carried out under an atmosphere of purified argon in dried solvents (*n*-hexane, with $LiAlH_4$; 1,2-difluorobenzene, pentafluorobenzene and α,α,α-trifluorotoluene with molecular sieves). NMR spectra were recorded in C_6D_6 at ambient probe temperature using the following Bruker instruments: Avance I (^{1}H, 400.13 MHz; ^{13}C, 100.62 MHz; ^{29}Si 79.49 MHz, ^{15}N 40.55 MHz) or Avance III (^{1}H, 400.03 MHz; ^{13}C, 100.59 MHz, ^{29}Si, 79.47 MHz; ^{15}N, 40.54 MHz) and referenced internally to residual solvent resonances (^{1}H, ^{13}C; chemical shift data δ in ppm) or to liquid NH_3 in case of ^{15}N. ^{13}C NMR spectra were all proton-decoupled. Elemental analyses were determined by the microanalytic laboratory of the Westfälische Wilhelms Universität Münster. IR spectra were recorded as KBr pellets on a Shimadzu Prestige 21 spectrometer, electron impact mass spectra on a Finnigan MAT95 mass spectrometer. The azide starting materials except ^{t}BuN$_3$ are commercially available as neat liquids or as solutions in inert solvents and were used as purchased without further purification. ^{t}BuN$_3$ [69] and $C_5H_8(2,6\text{-}Me_2)N\text{–}C(H)=C(SiMe_3)AlR_2$ (**1a**, R = ^{t}Bu; **1b**, R = ^{i}Bu) [11] were synthesised according to literature procedures. The assignment of NMR spectra is based on HSQC, HMBC, DEPT135, HN-HMBC and H,H-ROESY data.

4.1 Compound 2a

PhN_3 (1.88 mL, 0.94 mmol, 0.5 M in MeO^{t}Bu) was added to a solution of **1a** (0.33 g, 0.94 mmol) in *n*-hexane (20 mL) at $T = -30$°C. The mixture was warmed to room temperature and stirred overnight. All volatiles were removed *in vacuo* (1×10^{-3} mbar), and the residue was recrystallized from pentafluorobenzene (2 mL) at –30°C to yield colourless crystals of **2a**. Yield: 0.25 g (56%); m. p. (argon, sealed capillary): 86°C (dec). – IR (KBr pellet): ν = 3069 vw, 3034 vw, 2984 s, 2932 vs, 2862 s, 2808 vs, 2754 m, 2722 vw, 2689 m ν(CH); 1954 vw, 1938 vw, 1778 vw, 1736 vw, 1564 vs, br. ν(N=N), ν(C=C), phenyl; 1489 s, 1462 s, 1389 vs, 1373 s, 1344 s, 1327 vs, 1308 m, 1292 s, 1256 vs, 1236 sh δ(CH); 1194 vs, 1144 m, 1105 vs, 1076 vs, 1051 s, 1026 m, 999 w ν(CC), ν(CN), ν(NN); 976 w, 957 w, 935 vw, 893 m, 847 vs, 806 s, 762 vs, 731 w $\rho(CH_3Si)$; 694 s, 681 sh, 631 s ν(SiC); 590 m, 563 s, 505 s, 424 s ν(AlC), ν(AlN), δ(CC) cm^{-1}. – ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ = 7.73 (d, $^3J_{HH}$ = 7.6 Hz, 2 H, *o*-H), 7.24 (*pseudo*-t, $^3J_{HH}$ = 7.5 Hz, 2 H, *m*-H), 7.23 (s, 1 H, C=C*H*), 6.98 (t, $^3J_{HH}$ = 7.4 Hz, 1 H, *p*-H), 3.58 (m, 2 H, NC*H*Me), 1.60 (m, 2 H, NCHCH_2), 1.46 (s, 1 H, NCHCH$_2$CH_2), 1.36 (s, 18 H, Al^{t}Bu), 1.25 (m, 2 H, NCHCH_2), 1.19 (m, 1 H, NCHCH$_2$CH_2), 1.08 (d, $^3J_{HH}$ = 7.0 Hz, 6 H, NCH*Me*), 0.32 (s, 9 H, $SiMe_3$). – ^{13}C NMR (100.6 MHz, C_6D_6, 300 K): δ = 148.2 (*ipso*-C), 148.0 (AlC=*C*H), 134.0 (br., Al*C*=CH), 129.2 (*m*-C), 125.1 (*p*-C), 121.2 (*o*-C), 52.2 (N*C*HMe), 32.4 (AlC*Me*$_3$), 30.1 (NCH*C*H$_2$), 20.7 (NCH*Me*), 17.5 (br., Al*C*Me$_3$), 14.1 (NCHCH$_2$*C*H$_2$], 1.6 ($SiMe_3$). – ^{29}Si NMR (79.5 MHz, C_6D_6, 300 K): δ = 21.1. – ^{15}N NMR (40.5 MHz, C_6D_6, 300 K): δ = 423 (N*N*N), 255 (NPh), 251 ($NSiMe_3$), 96 (NCHMe). – MS (EI; 20 EV; 318 K): *m*/*z* (%) = 413 (100) [M–^{t}Bu]$^+$. – $C_{26}H_{47}AlN_4Si$ (470.8): calcd. C 66.3, H 10.1, N 11.9; found C 65.9, H 9.5, N 12.0.

4.2 Compound 2b

Compound **2b** was synthesised according to the general procedure (see **2a**) from 4-*t*-butylbenzyl azide, 4-^{t}Bu-$C_6H_4CH_2N_3$, (0.15 mL, 0.16 g, 0.85 mmol) and **1a** (0.30 g, 0.85 mmol) in *n*-hexane (10 mL). Recrystallisation of the residue from α,α,α-triflourotoluene at $T = -20$°C yielded compound **2b** as colourless crystals. Yield: 0.40 g (87%); m. p. (argon, sealed capillary): 117°C (dec). – IR (KBr pellet): ν = 3092 vw, 3055 vw, 3028 vw, 2965 vs, 2938 vs, 2866 vs, 2818 vs, 2756 w, 2718 vw, 2686 w ν(CH); 1900 vw, 1766 vw, 1578 vs, br., 1512 m ν(N=N), ν(C=C), phenyl;

1466 vs, 1437 m, 1410 s, 1369 vs, 1354 s, 1319 vs, 1308 vs, 1269 s, 1254 vs δ(CH); 1233 m, 1211 w, 1194 s, 1152 s, 1142 vs, 1113 vs, 1090 w, 1057 vs, 1030 s, 997 w ν(CC), ν(CN), ν(NN); 974 m, 949 w, 939 vw, 899 s, 878 m, 849 vs, 829 vs, 800 s, 760 m, 745 vw, 731 m ρ(CH_3Si); 689 s, 673 m, 625 vs ν(SiC); 598 s, 581 s, 552 s, 529 m, 521 m, 492 s, 473 s, 463 m, 430 s, 401 s ν(AlC), ν(AlN), δ(CC) cm^{-1}. – ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ = 7.32 (d, $^3J_{HH}$ = 8.4 Hz, 2 H, *o*-H), 7.26 (d, $^3J_{HH}$ = 8.4 Hz, 2 H, *m*-H), 7.02 (s, 1 H, NC=C*H*), 4.97 (s, 2 H, NCH_2Aryl), 3.52 (m, 2 H, NC*H*Me), 1.59 (m, 2 H, NCHCH_2), 1.49 (s, 1 H, NCHCH$_2$CH_2), 1.31 (s, 18 H, Al^{t}Bu), 1.20 (s, 9 H, Aryl^{t}Bu), 1.28 (m, 2 H, NCHCH_2), 1.21 (m, 1 H, NCHCH$_2$CH_2), 1.10 (d, $^3J_{HH}$ = 6.9 Hz, 6 H, NCH*Me*), 0.27 (s, 9 H, $SiMe_3$). – ^{13}C NMR (100.6 MHz, C_6D_6, 300 K): δ = 150.0 (*p*-C), 146.0 (AlC=*C*H), 136.6 (*ipso*-C), 132.1 (br., Al*C*=CH), 128.9 (*o*-C), 125.4 (*m*-C), 57.8 (NCH_2), 52.0 (N*C*H), 34.5 (Aryl-C*Me*$_3$), 32.0 (AlC*Me*$_3$), 31.5 (Ar*C*Me$_3$), 30.4 (NCH*C*H$_2$), 20.6 (NCH*Me*), 17.1 (br., Al*C*Me$_3$), 14.6 (NCHCH$_2$*C*H$_2$), 1.5 ($SiMe_3$). – ^{29}Si NMR (79.5 MHz, C_6D_6, 300 K): δ = 18.3. – ^{15}N NMR (40.5 MHz, C_6D_6, 300 K): δ = 442 (N*N*N), 242 (NSiMe$_3$), 92 (NCHMe), NCH_2 n.o. – MS (EI; 20 EV; 323 K): *m*/*z* (%) = 483 (100) [M–^{t}Bu]$^+$. – $C_{31}H_{57}AlN_4Si$ (540.9): calcd. C 68.8, H 10.6, N 10.4; found C 68.8, H 10.4, N 10.3.

4.3 Compound 2c

Compound **2c** was synthesised according to the general procedure (see **2a**) from ^{t}BuN$_3$ (2.88 mL, 0.43 mmol, 0.15 M in *n*-hexane) and **1a** (0.15 g, 0.43 mmol) in *n*-hexane (20 mL). Recrystallisation of the residue from 1,2-difluorobenzene (2 mL) at *T* = –30°C yielded compound **2c**. Yield: 0.18 g (93%); m. p. (argon, sealed capillary): 90°C (dec). – IR (KBr pellet): ν = 2961 vs, 2940 vs, 2914 vs, 2866 vs, 2812 vs, 2750 w, 2720 vw, 2689 w ν(CH); 1973 vw, 1884 vw, 1761 vw, 1570 vs ν(N=N), ν(C=C); 1479 m, 1468 vs, 1396 vs, 1377 vs, 1360 vs, 1348 vs, 1335 vs, 1323 vs, 1306 m, 1296 w, 1281 vs, 1267 m, 1252 vs δ(CH); 1233 s, 1225 s 1204 vs, 1155 w, 1144 w, 1111 vs, 1084 vs, 1055 vs, 1024 w, 1005 w ν(CC), ν(CN), ν(NN); 999 w, 976 m, 947 vw, 937 vw, 930 vw, 881 vs, br., 833 vs, 808 vs, 760 m, 731 m ρ(CH_3Si); 694 w, 681 s, 635 vs ν(SiC); 598 vs, 575 vs, 565 s, 548 s, 521 vw, 509 s, 482 m, 428 s, 415 m, 401 s ν(AlC), ν(AlN), δ(CC) cm^{-1}. – ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ = 6.91 (s, 1 H, NC=C*H*), 3.38 (m, 2 H, NCH), 1.62 (m, 2 H, NCHCH_2), 1.50 (s, 1 H, NCHCH$_2$CH_2), 1.42 (s, 9 H, N^{t}Bu) 1.35 (s, 18 H, Al^{t}Bu), 1.28 (m, 2 H, NCHCH_2), 1.22 (m, 1 H, NCHCH$_2$CH_2), 1.11 (d, $^3J_{HH}$ = 6.9 Hz, 6 H, NCH*Me*), 0.31 (s, 9 H, $SiMe_3$). – ^{13}C NMR (100.6 MHz, C_6D_6, 300 K): δ = 146.1 (AlC=*C*H), 135.9 (br., Al*C*=CH), 59.1 (N*C*Me$_3$), 53.2 (N*C*HMe), 32.6 (AlC*Me*$_3$), 30.7 (NCH*C*H$_2$), 30.4 (NC*Me*$_3$), 20.7 (NCH*Me*), 16.9 (br., Al*C*Me$_3$), 15.7 (NCHCH$_2$*C*H$_2$), 1.6 ($SiMe_3$). – ^{29}Si NMR (79.5 MHz, C_6D_6, 300 K): δ = 18.1. – ^{15}N NMR (40.5 MHz, C_6D_6, 300 K): δ = 280 (NCMe$_3$), 237 (NSiMe$_3$), 89 (NCHMe), N*N*N n.o. – MS (EI; 20 EV; 298 K): *m*/*z* (%) = 493 (100) [M–^{t}Bu]$^+$. – $C_{24}H_{51}AlN_4Si$ (450.8): calcd. C 63.9, H 11.4, N 12.4; found C 64.0, H 11.3, N 12.4.

4.4 Compound 2d

Me_3SiN_3 (0.06 mL, 0.057 g, 0.50 mmol) was added at room temperature to a solution of **1a** (0.17 g, 0.48 mmol) in *n*-hexane (10 mL). The mixture was heated to *T* = 50°C and stirred for 5 d. All volatiles were removed *in vacuo*, and the residue was recrystallised from 1,2-difluorobenzene (2 mL) at *T* = –30°C to yield compound **2d** as colourless crystals. Yield: 0.18 g (79%); m. p. (argon, sealed capillary): 104°C (dec). – IR (KBr pellet): ν = 2988 s, 2941 vs, 2926 vs, 2903 sh, 2864 s, 2814 vs, 2749 w, 2718 vw, 2685 w ν(CH); 1568 vs, br. ν(N=N), ν(C=C); 1464 s, 1443 vw, 1400 vs, 1373 m, 1354 w, 1339 w, 1325 s, 1308 vs, 1288 vs, 1271 m, 1254 vs δ(CH); 1184 vs, 1144 s, 1132 m, 1111 vs, 1086 m, 1053 vs, 1032 vw, 1013 vw, 1003 vw ν(CC), ν(CN), ν(NN); 961 vs, 935 w, 885 m, 845 vs, 833 vs, br., 808 vs, 756 s, 731 vw ρ(CH_3Si); 696 vw, 679 m, 629 s ν(SiC); 588 s, 575 s, 559 m, 540 m, 511 m, 482 s, 430 s, 417 w, 401 s ν(AlC), ν(AlN), ν(SiN), δ(CC) cm^{-1}. – ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ = 7.18 (s, 1 H, NC=C*H*), 3.58 (m, 2 H, NCH), 1.61 (m, 2 H, NCHCH_2), 1.47 (s, 1 H, NCHCH$_2$CH_2), 1.32 (s, 18 H, Al^{t}Bu), 1.26 (m, 2 H, NCHCH_2), 1.19 (m, 1 H, NCHCH$_2$CH_2), 1.09 (d, $^3J_{HH}$ = 6.9 Hz, 6 H, NCH*Me*), 0.43 (s, 9 H, AlNSiMe_3), 0.30 (s, 9 H, CNSi*Me*$_3$). – ^{13}C NMR (100.6 MHz, C_6D_6, 300 K): δ = 147.4 (AlC=*C*H), 133.3 (br., Al*C*=CH), 52.0 (N*C*H), 32.5 (AlC*Me*$_3$), 30.2 (NCH*C*H$_2$), 20.7 (NCH*Me*), 16.8 (br., Al*C*Me$_3$), 14.3 (NCHCH$_2$*C*H$_2$), 1.6 (CNSi*Me*$_3$), 1.2 (AlNSiMe_3). – ^{29}Si NMR (79.5 MHz, C_6D_6, 300 K): δ = 19.5 (CNSiMe_3), 11.3 (AlNSiMe_3). – ^{15}N NMR (40.5 MHz, C_6D_6, 300 K): δ = 268 (CNSiMe$_3$), 261 (AlNSiMe$_3$), 93 (NCHMe), N*N*N n.o. – MS (EI; 20 EV; 326 K): *m*/*z* (%) = 409 (100) [M–^{t}Bu]$^+$. – $C_{23}H_{51}AlN_4Si_2$ (466.8): calcd. C 59.2, H 11.0, N 12.0; found C 59.1, H 11.0, N 11.8.

4.5 Compound 2e

Compound **2e** was synthesised according to the general procedure (see **2a**) from $PhCH_2N_3$ (0.51 g, 0.38 mmol, 0.76 mL of a 0.5 M solution in CH_2Cl_2) and compound **1a** (0.13 g, 0.37 mmol) in *n*-hexane (10 mL). Recrystallisation of the residue from pentafluorobenzene (2 mL) at *T* = –40°C yielded compound **2e** as yellow crystals. Yield: 0.17 g (95%); m. p. (argon, sealed capillary): 80°C (dec). – IR (KBr pellet): ν = 3063 vw, 3028 w, 2938 vs, 2864 s, 2816 vs,

2752 w, 2689 w ν(CH); 1572 vs, br. ν(N=N), ν(C=C), phenyl; 1495 w, 1462 s, 1377 vs, 1325 vs, 1306 s, 1254 vs δ(CH); 1227 m, 1207 vw, 1186 m, 1144 m, 1111 s, 1055 s, 1026 m, 1001 w ν(CC), ν(CN), ν(NN); 976 w, 943 w, 878 m, 847 vs, 808 s, 752 m, 737 sh ρ(CH_3Si); 698 s, 637 m, 621 w ν(SiC); 596 s, 579 m, 554 w, 507 w, 496 w, 478 m, 464 w ν(AlC), ν(AlN), δ(CC) cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ = 7.31 (d, $^3J_{HH}$ = 7.6 Hz, 2 H, *o*-H), 7.16 (*pseudo*-t, $^3J_{HH}$ = 7.5 Hz, 2 H, *m*-H), 7.06 (t, $^3J_{HH}$ = 7.4 Hz, 1 H, *p*-H), 7.03 (s, 1 H, NC=C*H*), 4.94 (s, 2 H, NCH_2), 3.52 (m, 2 H, NC*H*Me], 1.60 (m, 2 H, NCHCH_2), 1.48 (s, 1 H, NCHCH_2CH_2), 1.30 (s, 18 H, Al^{t}Bu), 1.27 (m, 2 H, NCHCH_2), 1.20 (m, 1 H, NCHCH_2CH_2), 1.09 (d, $^3J_{HH}$ = 7.0 Hz, 6 H, NCH*Me*), 0.26 (s, 9 H, $SiMe_3$). – ^{13}C NMR (100.6 MHz, C_6D_6, 300 K): δ = 146.1 (AlC = *C*H), 139.6 (*ipso*-C), 132.0 (br., Al*C* = CH), 129.0 (*o*-C), 128.5 (*m*-C), 127.3 (*p*-C), 58.1 (NCH_2), 52.0 (N*C*HMe), 32.0 (AlC*Me*$_3$), 30.4 (NCH*C*H_2), 20.6 (NCH*Me*), 17.1 (br., Al*C*Me_3), 14.5 (NCHCH$_2$*C*H_2), 1.5 ($SiMe_3$). – ^{29}Si NMR (79.5 MHz, C_6D_6, 300 K): δ = 18.5. – ^{15}N NMR (40.5 MHz, C_6D_6, 300 K): δ = 442 (N*N*N), 244 ($NSiMe_3$), 93 (NCHMe), NCH_2 n.o. – MS (EI; 20 EV; 300 K): *m*/*z* (%) = 427 (100) [M–^{t}Bu]$^+$. – $C_{27}H_{49}AlN_4Si$ (484.8): calcd. C 66.9, H 10.2, N 11.6; found C 66.2, H 9.8, N 11.1.

4.6 Compound 2f

Compound **1b** was synthesised *in situ* by hydroalumination of (2,6-Me_2)C_5H_8N–C≡C–$SiMe_3$ (0.25 mL, 0.21 g, 1.00 mmol) with ^{i}Bu$_2$Al–H (0.18 mL, 0.14 g, 1.00 mmol) in *n*-hexane (20 mL) [11]. $PhCH_2N_3$ (0.13 g, 1.00 mmol, 2.00 mL of a 0.5 M solution in CH_2Cl_2) was added at room temperature. The mixture was stirred for 1 h, all volatiles were removed *in vacuo*, and the residue was recrystallized from pentafluorobenzene (2 mL) at *T* = –30°C to yield **2f** as colourless crystals. Yield: 0.35 g (72%); m. p. (argon, sealed capillary): 55°C (dec). – IR (KBr pellet): ν = 3086 w, 3065 w, 3028 m, 2997 m, 2980 s, 2941 vs, 2884 vs, 2855 vs, 2764 m ν(CH); 1965 vw, 1948 w, 1881 vw, 1773 w, 1628 s, 1574 vs, br., 1533 m ν(N=N), ν(C=C), phenyl; 1495 s, 1466 s, 1465 s, 1443 s, 1406 vs, 1381 vs, 1364 vs, 1327 vs, 1315 vs, 1300 vs, 1275 s, 1254 vs, 1234 s δ(CH); 1188 vs, 1165 vs, 1150 vs, 1115 vs, 1078 s, 1061 vs, 1053 vs, 1026 s, 1011 w, 1001 w ν(CC), ν(CN), ν(NN); 978 m, 953 w, 941 m, 916 vw, 895 s, 883 s, 837 vs, 810 m, 733 m, 718 vw, 700 vs ρ(CH_3Si); 687 s, 660 vs, 644 s, 633 vs, 611 vs ν(SiC); 590 m, 563 vw, 521 s, 500 s, 480 s, 453 vs ν(AlC), ν(AlN), δ(CC) cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ = 7.36 (d, $^3J_{HH}$ = 7.2 Hz, 2 H, *o*-H), 7.18 (*pseudo*-t, $^3J_{HH}$ = 7.2 Hz, 2 H, *m*-H), 7.09 (t, $^3J_{HH}$ = 7.4 Hz, 1 H, *p*-H), 7.00 (s, 1 H, NC=C*H*), 4.85 (s, 2 H, NCH_2), 3.60 (m, 2 H, NC*H*Me), 1.93 (m, $^3J_{HH}$ = 6.6 Hz, 2 H, C*H*Me_2), 1.53 (m, 3 H, NCHCH_2 and NCHCH$_2$CH_2), 1.28 (m, 2 H, NCHCH_2), 1.18 (m, 1 H, NCHCH$_2$CH_2), 1.18 and 1.10 (each d, $^3J_{HH}$ = 6.5 Hz, 6 H, CHMe_2), 1.13 (d, $^3J_{HH}$ = 7.1 Hz, 6 H, NCH*Me*), 0.32 (s, 9 H, $SiMe_3$), 0.30 (d overlap, 4 H, $AlCH_2$). – ^{13}C NMR (100.6 MHz, C_6D_6, 300 K): δ = 144.4 (AlC=*C*H), 138.6 (*ipso*-C), 131.4 (br., Al*C*=CH), 129.7 (*o*-C), 128.7 (*m*-C), 127.7 (*p*-C), 58.5 (NCH_2), 52.0 (N*C*HMe), 30.5 (NCH*C*H_2), 28.6 and 28.5 (CH*Me*$_2$), 27.4 (*C*HMe_2), 23.2 (br., $AlCH_2$), 20.7 (NCH*Me*), 14.7 (NCHCH$_2$*C*H_2), 1.3 ($SiMe_3$). – ^{29}Si NMR (79.5 MHz, C_6D_6, 300 K): δ = 17.4. – ^{15}N NMR (40.5 MHz, C_6D_6, 300 K): δ = 435 (N*N*N), 239 ($NSiMe_3$), 94 (NCHMe), NCH_2 n.o. – MS (EI; 20 EV; 318 K): *m*/*z* (%) = 485 (2), [M + H]$^+$, 427 (100) [M–^{i}Bu]$^+$. – $C_{27}H_{49}AlN_4Si$ (484.8): calcd. C 66.9, H 10.2, N 11.6; found C 66.6, H 9.8, N 11.3.

4.7 Crystallographic data

Single crystals suitable for X-ray crystallography were obtained by crystallization from 1,2-difluorobenzene (**2d**), pentafluorobenzene (**2a**, **2c**, **2e**, **2f**) or α,α,α-trifluorotoluene (**2b**). Intensity data was collected on a Bruker D8 Venture diffractometer with multilayer optics and Mo$K\alpha$ radiation. The collection method involved ω scans. Data reduction was carried out using the program SAINT+ [70, 71]. The crystal structures were solved by Direct Methods using SHELXTL [72–74]. Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculations based on F^2 using SHELXTL [72–74]. H atoms were positioned geometrically and allowed to ride on their respective parent atoms. Compound **2c** cocrystallised with one molecule of pentafluorobenzene per unit cell which was disordered across the inversion centre. Compound **2d** had two independent molecules in the asymmetric unit.

CCDC 19475544 (**2a**), 1947545 (**2b**), 1947546 (**2c**), 1947547 (**2d**), 1947548 (**2e**) and 1947549 (**2f**) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

5 Supporting information

The crystal structure data including atomic coordinates and displacement parameters for **2a–f** are also given as supplementary material available online (DOI: 10.1515/znb-2019-0138).

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