1,3,2-Diazaalumina-[3]ferrocenophanes with Alkyn-1-yl Substituents at Aluminum

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The 1,3,2-diazaalumina-[3]ferrocenophane-ethyl(dimethyl)amine adduct **2**, containing an Al–H function, reacts with terminal alkynes R–C≡C–H [R = ^{n}Bu (**a**), ^{t}Bu (**b**), Ph (**c**), SiMe$_3$ (**d**)] by elimination of H$_2$ to the amine adducts **4a** – **d** containing an Al–C≡C–R function. Addition of pyridine leads to the corresponding pyridine adducts **5a** – **d**, of which the molecular structure of **5d** could be determined by single crystal X-ray diffraction. The formation of **4** is accompanied by side reactions such as trimerization of the alkynes to the 1,3,5-trisubstituted benzene derivatives **6a, c**, and some polymerization of the alkynes. The solution-state structures of **4** and **5** were confirmed by multinuclear magnetic resonance spectroscopy (^{1}H, ^{13}C, ^{27}Al, ^{29}Si NMR). Structural features and molecular dynamics were investigated by appropriate ^{1}H/^{1}H NOE and magnetization transfer experiments, and particular attention was paid to the correct assignment of ^{13}C(Al–C≡C–R) NMR signals.

Key words: Aluminum, Ferrocenophane, Alkynes, NMR, X-Ray

Introduction

With a few exceptions [1] the aluminum atom in aluminum amides prefers the coordination number 4 and achieves it either by dimerization [2] or by accepting a suitable donor ligand. The latter coordination can take place in an intra- [3] or intermolecular way [4]. Nevertheless, such aluminum amides remain reactive; in particular if they bear at least one halide or hydride function at the aluminum atom in addition to amido groups. Recently, we have shown that 1,3,2-diazaalumina-[3]ferrocenophanes **2** and **3** are readily accessible [5] by the reaction of 1,1′-bis(trimethylsilylamino)ferrocene **1** with H$_3$Al–NEtMe$_2$ [6a] (Scheme 1), in which an Al–H bond is present, inviting a study of further transformations.

Aluminum hydrides are well known to undergo hydroalumination reactions with alkynes or alkenes [7]. However, this behavior is less evident if the aluminum atom is coordinated to fairly strong donors such as amines [8]. On the other hand, aluminum hydrides, in general in the presence of transition metal complexes, can catalyze cyclotrimerization of alkynes [9], polymerization of alkynes [10], and of course the widely studied polymerization of olefins [11]. In the light of these properties of aluminum hydrides, we have studied the reactivity of the hydride **2** towards four representative terminal alkynes R–C≡C–H [R = ^{n}Bu (**a**), ^{t}Bu (**b**), Ph (**c**), SiMe$_3$ (**d**)].

Results and Discussion

In all cases studied (Scheme 2), we noted elimination of H$_2$ as soon as the alkyne was added to the solution containing the aluminum hydride **2**. In the case of ^{n}Bu–C≡C–H, an insoluble polymer was formed at the same time. This is also true for Ph–C≡C–H, whereas in the cases of ^{t}Bu–C≡C–H and Me$_3$Si–C≡C–H, polymerization appears to be negligible.
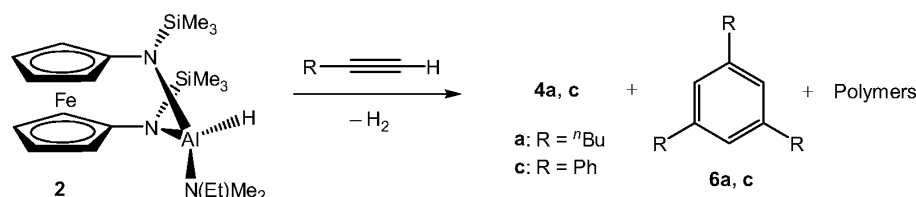
Monitoring of the reactions by NMR spectroscopy (^{1}H, ^{13}C and ^{29}Si NMR) has shown that the concentration of **2** decreases fast in the cases of ^{n}Bu–C≡C–H
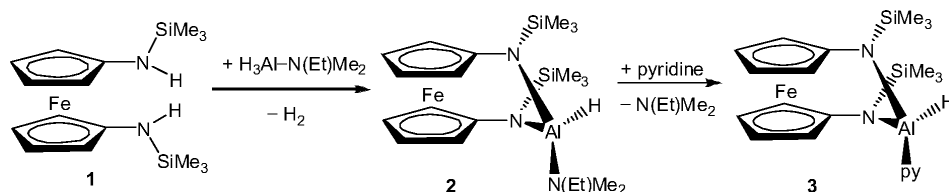
Scheme 1. Synthesis of 1,3,2-diazaalumina-[3] ferrocenophane adducts containing an Al–H function.
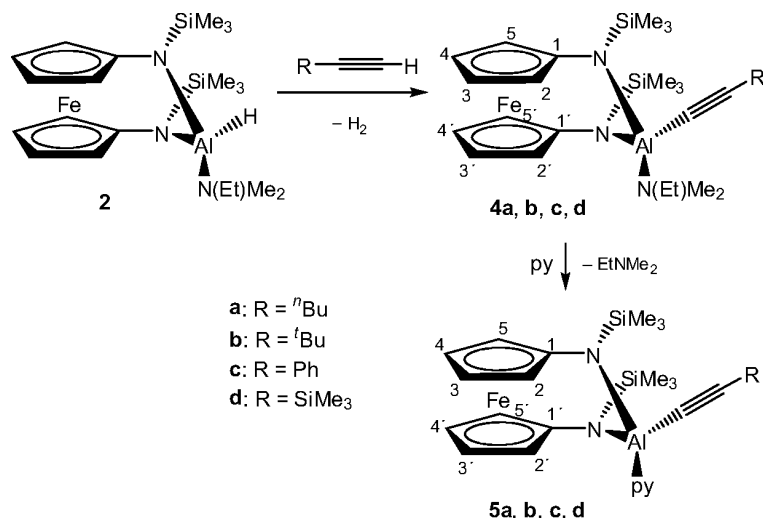
Scheme 2. Conversion of the Al–H function into the Al–C≡C–R function.

a: R = ^{n}Bu
b: R = ^{t}Bu
c: R = Ph
d: R = SiMe$_3$

Scheme 3. The formation of the Al–C≡C–R function is accompanied by cyclotrimerization and polymerization in the cases of the alkynes ^{n}Bu–C≡C–H and Ph–C≡C–H.

and Ph–C≡C–H, and rather slowly for ^{t}Bu–C≡C–H and Me$_3$Si–C≡C–H. In the latter cases, heating to 75 °C (for ^{t}Bu–C≡C–H) and 60 °C (for Me$_3$Si–C≡C–H) for several hours was necessary in order to accelerate and complete the reactions.

Primary products of hydroalumination were not observed. However, the reaction mixture containing **2**, ^{t}Bu–C≡C–H and **4b** also contained a small amount of ^{t}Bu–CH=CH$_2$, most likely the result of hydroalumination followed by protolytic cleavage of the Al–C= bond [8d]. More complex reactions involving hydroalumination are indicated by the formation of the 1,3,5-trisubstituted benzene derivatives **6a, c** as side products. They were identified in the reaction mixtures by their characteristic ^{13}C NMR data, and in the cases of **6a, c**, the formation of the trimers is accompanied by that of polymers (Scheme 3).

In any case, the main products, as far as the aluminum compounds are concerned, are the alkyn-1-yl derivatives **4a–d** which are converted, upon addition of pyridine, into the respective pyridine adducts **5a–d**. All compounds **4** and **5** are extremely sensitive to hydrolysis, and in spite of all precautions the reaction mixtures also contain variable amounts of **1**. The pyridine adduct **5d** could be isolated as crys-

talline material suitable for X-ray structural analysis (*vide infra*).

NMR spectroscopic studies in solution

The solution-state structures of the new compounds **4** and **5** are based on a consistent set of NMR data given in Table 1 and in the Experimental Section. The findings are in agreement with the results for the solid-state structure of **5d** (*vide infra*).

For the solutions, the most important structural properties were revealed by ^{1}H/^{1}H-NOE experiments which, in the present cases, are most conveniently carried out in 1D mode (Fig. 1). These phase-sensitive pulsed gradient enhanced experiments [12] served to prove the mutual neighborhood of the various groups within the molecule, and they have provided evidence for intra- and intermolecular exchange processes. Thus, the normal ^{1}H NMR spectra of the compounds **4** can be explained by proposing either a structure with a planar or a non-planar arrangement of the heterocycle consisting of the atoms Fe,C(1),N,Al,N,C(1′), and there is no evidence for any significant exchange with the small amount of excess of the amine N(Et)Me$_2$ always present in solution. However, Fig. 1 shows clearly that two dynamic processes have to be con-
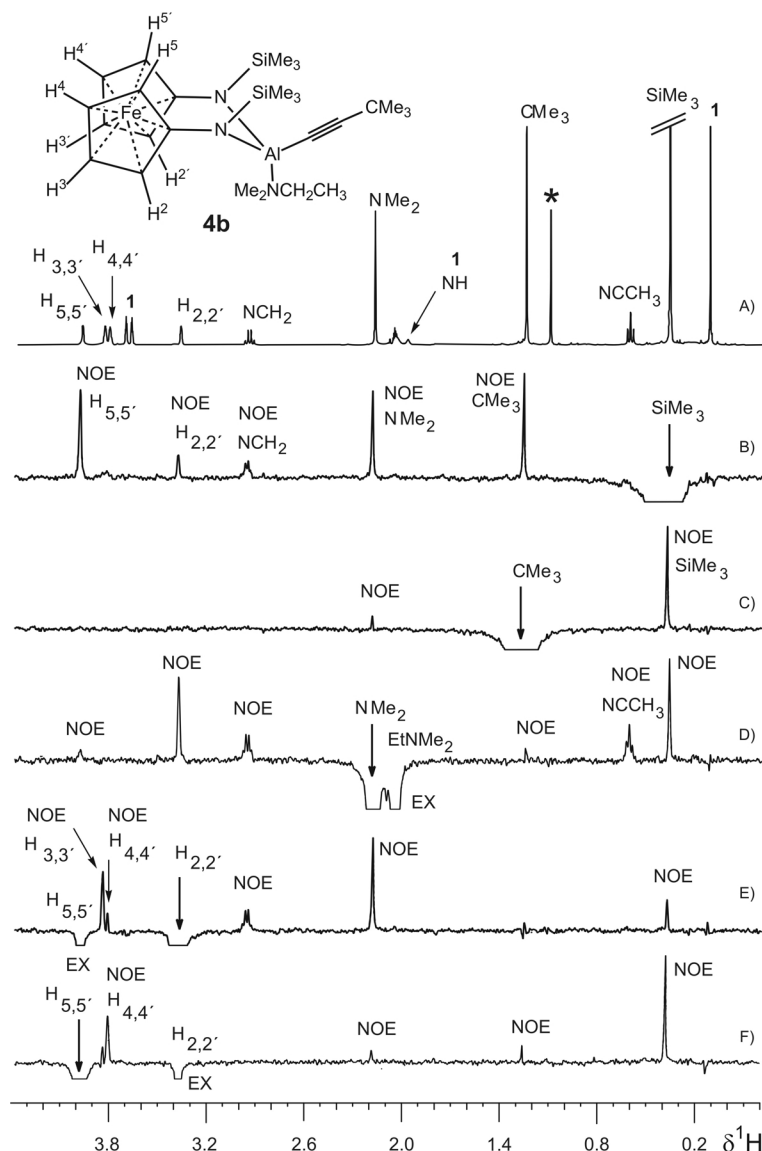
Fig. 1. 400 MHz ^{1}H{^{1}H} NOE difference spectra (gradient enhanced [12]) of **4b** (10 % in [D$_8$]toluene at 23 °C; relaxation delay 1.5 s; mixing time 0.8 s; 24 min of spectrometer time). The irradiated resonance signals are marked by arrows; the resulting intensities arising from NOE or EXchange are marked. (A) Normal ^{1}H NMR spectrum. The mixture contained **4b**, some **1**, formed during the reaction, ^{t}Bu–C≡C–H (marked by asterisks), and a small amount of N(Et)Me$_2$. (B) The NSiMe$_3$-resonance was irradiated and response is shown: H$^{5,5'}$ (+++) and H$^{2,2'}$ (++) of the cyclopentadienyl groups, NCH$_2$ and NMe$_2$ of the dimethyl(ethyl)amine ligand, and the CMe$_3$ group. (C) The CMe$_3$-resonance was irradiated and response is shown: NMe$_2$ (+) of the N(Et)Me$_2$ ligand, the SiMe$_3$ (+++) group. (D) The NMe$_2$-resonance of the N(Et)Me$_2$ ligand was irradiated and response is shown: H$^{5,5'}$ (+) and H$^{2,2'}$ (+++) of the cyclopentadienyl groups, NEt (+++) of the N(Et)Me$_2$ ligand, the CMe$_3$ (+) and the SiMe$_3$ (+++) group. Magnetization transfer [13] takes place between NMe$_2$ of the N(Et)Me$_2$ ligand and NMe$_2$ of the free N(Et)Me$_2$, indicating slow exchange. (E) The H$^{2,2'}$-resonance of the cyclopentadienyl groups was irradiated and response is shown: magnetization transfer takes place between H$^{2,2'}$ and H$^{5,5'}$, whereas NOE is observed for H$^{4,4'}$ (+) and H$^{3,3'}$ (+++) of the cyclopentadienyl groups, NCH$_2$ (++) and NMe$_2$ (+++) of the N(Et)Me$_2$ ligand, the SiMe$_3$ (++) group. (F) The H$^{5,5'}$-resonance of the cyclopentadienyl groups was irradiated and response is shown: magnetization transfer takes place between H$^{5,5'}$ and H$^{2,2'}$, whereas NOE is observed for H$^{4,4'}$ (+++) and H$^{3,3'}$ (+++) of the cyclopentadienyl groups, and the CMe$_3$ (+) and SiMe$_3$ (+++) group.

sidered: (i) ring inversion taking place slowly (*e. g.* exchange (EX) signals as a result of magnetization transfer [13] for H$^{2,2'}$ and H$^{5,5'}$), proving a non-planar arrangement of the Fe,C(1),N,Al,N,C(1') atoms, and (ii) intermolecular exchange taking place between coordinated and non-coordinated amine. The NOE experiments indicate that the N–Si bond vectors point into the same direction as the C≡C–R group, and in this arrangement repulsive interactions between the SiMe$_3$ groups and the bulky amine are avoided.

Since the pyridine ligand in compounds **5** is less bulky than the tertiary amine in compounds **4**, in-tramolecular dynamic processes (ring inversion) in **5** are faster than for **4**. Furthermore, even a very small amount of pyridine in excess (difficult to prevent owing to traces of decomposition of **5** in solution) causes faster exchange than the tertiary amine. This gives rise to dynamically broadened ^{1}H and ^{13}C NMR signals at r. t. As observed for **3** [5] or comparable Al-alkyl derivatives [14], these signals would become sharper at lower temperature. However, in the case of **5**, this is difficult to observe in an undisturbed way, since the pyridine adducts **5** tend to become increasingly insoluble at

Table 1. ^{13}C, ^{29}Si, and ^{27}Al NMR data[a] of the compounds **4a – d** and **5b, d**.

Compound	**4a**		**4b**		**4c**	**4d**	**5b**		**5d**
R	R = ^{n}Bu		R = ^{t}Bu		R = Ph	R = SiMe$_3$	R = ^{t}Bu		R = SiMe$_3$
T (K)	298	233	298	253	298	298	298	253	298
δ^{13}C(SiMe$_3$)	3.2 (56.3)	2.2	3.7 (56.2)	3.7	3.2 (56.2)	3.7 (56.3)	2.9 (55.8)	3.1	2.8 (55.6)
δ^{13}C(fc-C^1)	106.9	106.3	106.8	106.7	106.6	106.5	106.3	106.1	106.0
δ^{13}C(fc-C^2)	67.1	66.3	66.9	66.7	67.2	66.9	68.1 (br)	67.8	68.2 (br)
δ^{13}C(fc-C^5)	69.0	69.0	69.7	69.5	69.9	69.7			
δ^{13}C(fc-C^3)	64.8	64.0	65.1	65.1	65.0	65.2	64.8	64.6	298 K
δ^{13}C(fc-C^4)	64.1	63.3	64.5	64.5	64.3	64.6			
δ^{13}C(Al-C≡)	94.5 [br]	95.0 [br]	94.6 [br]	94.2 [br]	n. o.[b]	n. o.[b]	94.2 [br]	94.5 [br]	n. o.[b]
($h_{1/2}$, Hz)	(≈ 70 Hz)	(35 Hz)	(≈ 100 Hz)	(30 Hz)			(≈ 120 Hz)	(25 Hz)	
δ^{13}C(≡C–R)	110.6 (br)	109.3	118.4 (br)	118.0	108.8 (br)	117.8 (br)	118.5 (br)	118.0	117.3 (br)
($h_{1/2}$, Hz)	(8 Hz)	(4 Hz)	(8 Hz)	(2.5 Hz)	(15 Hz)	(5 Hz)	(6 Hz)	(5 Hz)	(7 Hz)
δ^{13}C(R)	13.8 (CH$_3$) 20.2 (CH$_2$(CH$_2$)$_2$CH$_3$) 22.5 (CH$_2$CH$_3$) 31.4 (CH$_2$CH$_2$CH$_3$)	13.4 19.5 21.9 30.5	31.2 (CH$_3$) 28.5 (CMe$_3$)	31.0 (CH$_3$) 28.3 (CMe$_3$)	125.8 (C$_i$) 127.7 (C$_p$) 125.5 (C$_m$) 131.5 (C$_o$)	0.1 (55.9)	31.3 (CH$_3$) 28.5 (CMe$_3$)	31.0 (CH$_3$) 28.4 (CMe$_3$)	0.2 (55.6)
δ^{13}C (EtNMe$_2$ or pyridine)	52.1, 5.9 (NCH$_2$CH$_3$) 43.7 (NCH$_3$)	50.5, 4.9 42.2	52.0, 5.6 43.3	51.2, 5.0 42.5	52.3, 6.0 43.8	52.0, 5.4 43.2	124.3 (C$_\beta$) (br) 137.0 (C$_\gamma$) (br) 149.6 (C$_\alpha$) (br)	124.1 (C$_\beta$) (br) 137.0 (C$_\gamma$) (br) 149.0 (C$_\alpha$) (br)	124.4 (C$_\beta$) (br) 136.8 (C$_\gamma$) (br) 148.2 (C$_\alpha$) (br)
δ^{27}Al	120		123		–	105	120		105
($h_{1/2}$, Hz)	(3000 Hz, ±500 Hz)		(3000 Hz, ±500 Hz)			(4600 Hz, ±500 Hz)	(4000 Hz, ±500 Hz)		(4600 Hz, ±500 Hz)
δ^{29}Si	4.0 (56.2)	3.9	4.1 (56.2)		4.0 (56.2)	4.4 (56.2) (NSiMe$_3$) −21.9 (CSiMe$_3$)	3.8 (55.8)		3.9 (55.6) (NSiMe$_3$) −21.9 (55.6) (CSiMe$_3$)

[a] In CD$_2$Cl$_2$ (**4a**, **4c**), [D$_8$]toluene (**4b**, **4d**, **5b**, **5d**); coupling constants (±0.5 Hz) $^1J(^{29}$Si,^{13}C) are given in parentheses; [br] denotes broad ^{13}C resonances of aluminum-bonded atoms; (br) denotes broad ^{13}C resonances due to dynamic effects; [b] n. o. = not observed.
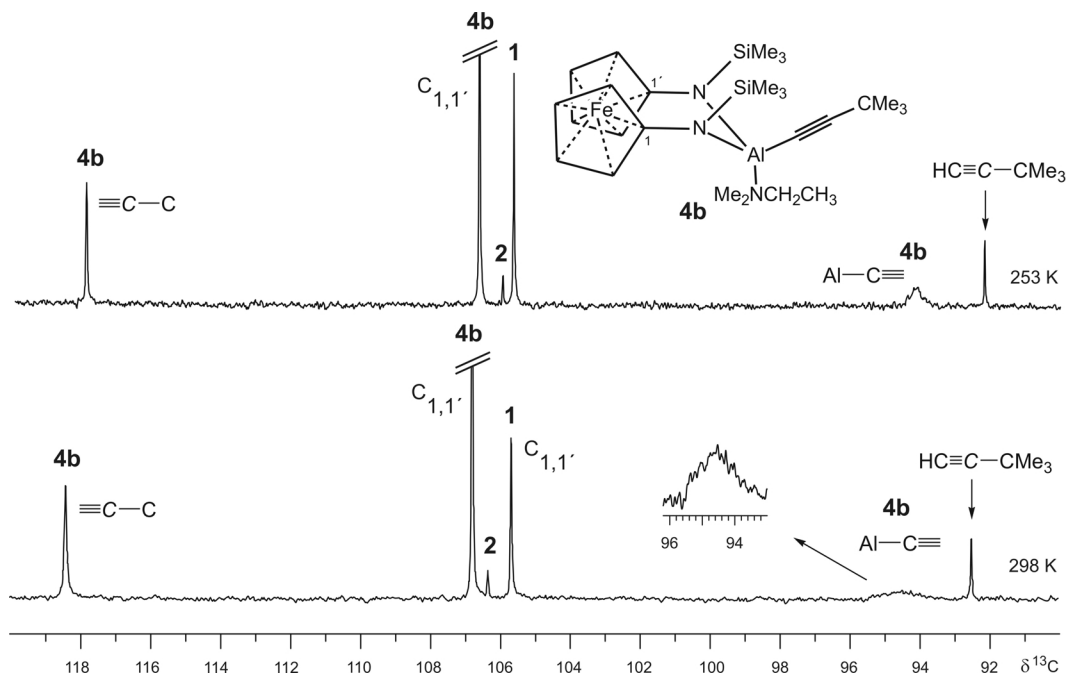

Fig. 2. Parts of the low temperature (upper trace, 62.9 MHz) and r. t. (lower trace, 100.5 MHz) ^{13}C{^{1}H} NMR spectra of the ferrocenophane **4b** containing some **1**, formed during the reaction, **2** and ^{t}Bu–C≡C–H ([D$_8$]toluene). The ^{13}C(Al–C≡) NMR signal sharpens considerably at lower temperature owing to "quadrupole decoupling" [18].
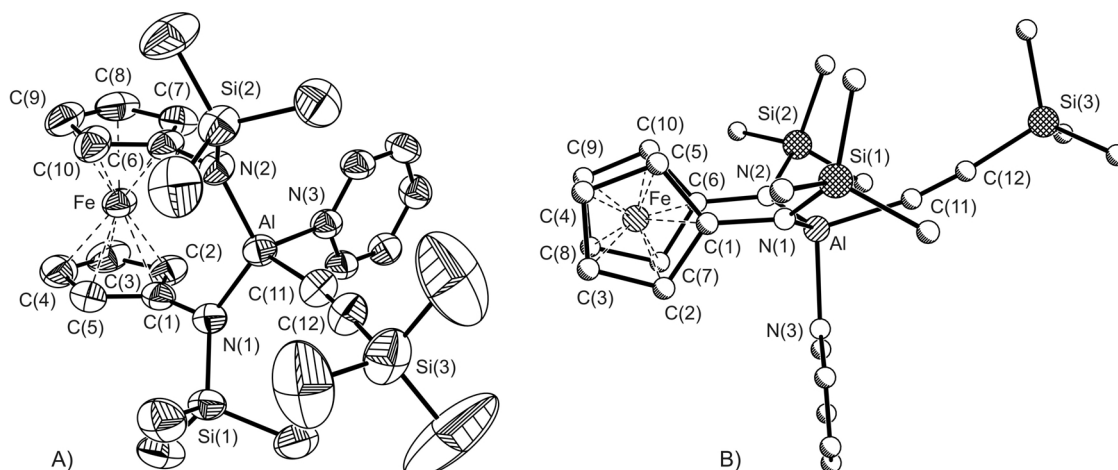
Fig. 3. Molecular structure of **5d** (A) (ORTEP plot, displacement ellipsoids at the 40 % probability level) and (B) (ball and stick model); hydrogen atoms are omitted for clarity, see Table 2 for structural parameters.

temperatures < -20 °C both in [D$_8$]toluene and CD$_2$Cl$_2$.

^{13}C NMR data of some aluminum-nitrogen compounds with terminal Al–C≡C–R functions have been reported [15–17]. Unfortunately, the assignment of the ^{13}C(alkyne) NMR signals appears to be incorrect in many cases [15]. Frequently the assignment of the ^{13}C(Al–C≡) NMR signal appears to be erroneous considering the reported chemical shifts [16], or the more readily observed slightly broadened ^{13}C(≡C–R) NMR signal was mistaken for that of ^{13}C(Al–C≡). There are also examples, where ^{13}C NMR signals belonging undoubtedly to the terminal alkyne R–C≡C–H itself (see *e. g.* [15b]) were wrongly assigned to the Al–C≡C–R unit. This confusion prompted us to look carefully for the ^{13}C(alkyne) NMR signals in the case of compounds **4** and **5**. It turned out indeed that the ^{13}C(Al–C≡) NMR signals are expectedly rather broad ($h_{1/2} > 80$ Hz at 23 °C) and difficult to observe owing to fairly long relaxation times $T_1(^{13}$C) and efficient scalar relaxation of the second kind [18, 19] (short $T_2(^{13}$C)). Therefore, we show the ^{13}C(Al–C≡C) NMR signals of **4b** as an example (Fig. 2) which may give a sort of guidance for related studies in the field of alkyn-1-ylaluminum chemistry.

Single crystal X-ray diffraction of the ferrocenophane **5d**

The molecular structure of **5d** is shown in Fig. 3, and selected structural parameters, in comparison with those for the hydride **3**, are given in Table 2. Intermolecular interactions for **5d** in the solid state appear to be negligible. The major structural properties of the

Table 2. Selected bond lengths (pm) and angles (deg)[a] of the [3]ferrocenophanes **5d** (Fig. 3) and **3** [5] for comparison.

	5d	**3**[b]
Al–N(1)	184.1(2)	183.7(4)
Al–N(2)	183.3(3)	184.0(4)
Al–N(3) (from py)	199.5(2)	199.7(4)
Al–C(11)	195.7(3)	–
N(1)–Si(1)	173.8(2)	173.9(4)
N(2)–Si(2)	174.7(2)	173.4(4)
C(11)–C(12)		–
Si(3)–C(12)		–
N(1)···N(2)	318.1	316.7
C(1)···C(6)	324.5	324.3
Fe···Al	350.2	351.1
N(1)–Al–N(2) (*endo*)	119.9(1)	118.9(2)
N(1)–Al–C(11)	110.9(1)	–
N(2)–Al–C(11)	110.2(1)	
N(3)–Al–C(11)	104.5(1)	
N(1)–Al–N(3) (from py)	104.8(1)	104.2(2)
N(2)–Al–N(3) (from py)	105.1(1)	105.3(2)
C(1)–N(1)–Si(1)	116.6(2)	119.1(3)
C(6)–N(2)–Si(2)	117.1(2)	116.5(3)
Al–N(1)–C(1)	116.0(2)	116.3(3)
Al–N(2)–C(6)	116.5(2)	116.7(3)
Al–N(1)–Si(1)	125.3(1)	122.4(2)
Al–N(2)–Si(2)	124.6(1)	124.3(2)
Al–C(11)–C(12)		–
C(11)–C(12)–Si(3)		–
Fe–C(1)–N(1)–Al–N(2)–C(6)[c]	12.4	12.8
Distance of Al from the plane	50.0	51.8
Fe–C(1)–N(1)–N(2)–C(6)[c]		
C$_5$ / C$_5$ (α)	2.9	2.3
C$_5$ / N(1) (β_1)	0.3 towards iron	1.6 towards iron
C$_5$ / N(2) (β_2)	1.4 towards iron	0.2 towards iron
C$_5$–Fe–C$_5$ (γ)	176.6	176.7
C$_5$ / C$_5$ (twist) (τ)	2.8	5.1
Fe–C$_5$ (center)	164.2	164.3
	164.5	164.5

[a] The definition of the angles α, β, γ and τ is given in ref. [20]; [b] ref. [5]; [c] mean deviation from plane in pm.

1,3,2-diazaalumina-[3]ferrocenophane unit are almost unchanged when the Al–H function in **3** is replaced by the Al–C≡C–SiMe$_3$ function in **5d**, and the solid-state structure corresponds closely to the findings from solution-state NMR spectra. In both **5d** and **3**, the surroundings of the nitrogen atoms are not exactly planar (sum of bond angles 357.9° and 357.8°). Deviations from linearity in the Al–C≡C–SiMe$_3$ unit are expectedly small, and the length of the C≡C bond is well inside the known range. Interestingly, the bond length Al–C(11) (195.7(3) pm) in **5d** is almost identical with that reported for Al–C(Me) (196.4(5) pm) and Al–C(Et) (196.5(7) pm) of the analogous pyridine adducts containing the Al-Me or Al-Et functions [14].

Experimental Section

General

All syntheses and the handling of the samples were carried out observing necessary precautions to exclude traces of air and moisture. Carefully dried solvents and oven-dried glassware were used throughout. The deuteriated solvent CD$_2$Cl$_2$ was distilled over CaH$_2$ in an atmosphere of Ar. All other solvents were distilled from Na metal in an atmosphere of Ar. 1,1′-Diaminoferrocene [6b], 1,1′-bis(trimethylsilylamino)ferrocene **1** [6a] and the dimethyl-(ethyl)amine adduct of the 1,3-bis(trimethylsilyl)-1,3,2-di-azaalumina-[3]ferrocenophane **2** [5] were prepared as described. 1-Hexyne, 3,3-dimethyl-1-butyne, ethynylbenzene, and ethynyl(trimethyl)silane were commercial products and distilled prior to use. NMR measurements: Bruker ARX 250: ^{1}H, ^{13}C, ^{27}Al, and ^{29}Si NMR (refocused INEPT [21] based on $^2J(^{29}Si,^1H) = 7$ Hz); Varian INOVA 400: ^{1}H, ^{13}C NMR; chemical shifts are given with respect to Me$_4$Si [δ^1H (CHDCl$_2$) = 5.33, δ^1H (C$_6$D$_5$CD$_2$H) = 2.08; δ^{13}C (CD$_2$Cl$_2$) = 53.8, δ^{13}C ([D$_8$]toluene) = 20.4; δ^{29}Si = 0 for $\Xi(^{29}Si) = 19.867184$ MHz]; external 1.1 M Al(NO$_3$)$_3$ in D$_2$O [δ^{27}Al = 0 for $\Xi(^{27}Al) = 26.056890$ MHz]. Assignments of ^{1}H and ^{13}C NMR signals are based on ^{1}H/^{1}H-NOE difference, and 2D ^{1}H/^{13}C-HETCOR experiments. The melting points (uncorrected) were determined using a Büchi 510 apparatus.

2-(Alkyn-1-yl)-1,3-bis(trimethylsilyl)-2-dimethyl(ethyl)-amine-1,3,2-diazaalumina-[3]ferrocenophanes 4

Hexyn-1-yl derivative 4a

A solution of the dimethyl(ethyl)amine adduct of 1,3-bis(trimethylsilyl)-1,3,2-diazaalumina-[3]ferrocenophane **2** (120 mg, 0.26 mmol) in toluene (5 mL) was cooled to 0 °C, and 1-hexyne (22 mg, 0.03 mL, 0.26 mmol) was added. The reaction mixture was allowed to reach ambient temperature and stirring was continued for 20 h. Volatile materials were

removed *in vacuo*, and the remaining yellow-brown oil was dissolved in CD$_2$Cl$_2$ (1 mL). After separation from insoluble polymers, the resulting mixture contained the adducts **4a** (*ca.* 40 %) and **2** (*ca.* 30 %) together with **1** and 1,3,5-tributylbenzene **6a** (^{1}H, ^{13}C and ^{29}Si NMR). **4a**: ^{1}H NMR (399.8 MHz; CD$_2$Cl$_2$, 298 K): $\delta = 0.10$ (s, 18H, Me$_3$Si), 0.85, 0.90 (t,t, 3H, 3H, CH$_2$C*H$_3$*), 1.19 (m, 2H, CC*H$_2$*CH$_3$), 1.47 (m, 2H, C*H$_2$*CH$_2$CH$_3$), 2.17 (m, 2H, C*H$_2$*(CH$_2$)$_2$CH$_3$), 2.63 (s, 6H, NCH$_3$), 3.23 (q, 2H, NCH$_2$), 3.45 (m, 2H, H$^{2,2'}$), 3.76 (m, 4H, H$^{4,4',3,3'}$), 3.88 (m, 2H, H$^{5,5'}$).

3,3-Dimethylbutin-1-yl derivative 4b

3,3-Dimethyl-1-butyne (16 mg, 0.024 mL, 0.19 mmol) was added in excess to a solution of **2** (46 mg, 0.10 mmol) in [D$_8$]toluene (1 mL). The reaction mixture was kept stirring at 70–75 °C for 10 h. The resulting mixture contained the adducts **4b** (*ca.* 70 %) together with 3,3-dimethylbut-1-yne (20 %), **1**, and free dimethyl(ethyl)amine (^{1}H, ^{13}C and ^{29}Si NMR). **4b**: ^{1}H NMR (399.8 MHz; [D$_8$]toluene; 298 K): $\delta = 0.38$ (s, 18H, Me$_3$Si), 0.62 (t, 3H, CH$_2$C*H$_3$*, $J = 7.6$ Hz), 1.27 (s, 9H, C(CH$_3$)$_3$), 2.20 (s, 6H, NCH$_3$), 2.97 (q, 2H, NCH$_2$), 3.40 (m, 2H, H$^{2,2'}$), 3.83 (m, 2H, H$^{4,4'}$), 3.86 (m, 2H, H$^{3,3'}$), 4.00 (m, 2H, H$^{5,5'}$).

^{t}Bu–CH=CH$_2$: ^{1}H NMR (399.8 MHz; [D$_8$]toluene; 298 K): $\delta = 0.95$ (s, 9H, C(CH$_3$)$_3$), 4.83 (dd, 1H, =CH$_2$, $^2J(^1H,^1H) = 1.5$ Hz, $^3J(^1H,^1H)_{cis} = 10.6$ Hz), 4.90 (dd, 1H, =CH$_2$, $^2J(^1H,^1H) = 1.5$ Hz, $^3J(^1H,^1H)_{trans} = 17.4$ Hz), 5.77 (dd, 1H, =CH, $^3J(^1H,^1H) = 10.6$ Hz, 17.4 Hz). – ^{13}C NMR (62.9 MHz, [D$_8$]toluene, 298 K): $\delta = 28.9$ (CH$_3$), 109.2 (=CH$_2$), 149.7 (=CH).

Phenylethynyl derivative 4c

The synthesis was carried out as described for **4a**, starting from 120 mg (0.26 mmol) of **2** in [D$_8$]toluene (1.5 mL) and ethynylbenzene (55 mg, 0.059 mL, 0.54 mmol). The resulting mixture contained the adducts **4c** (*ca.* 70 %) together with phenylacetylene (15 %), **1**, and a small amount of unidentified olefins (^{1}H, ^{13}C and ^{29}Si NMR). **4c**: ^{1}H NMR (399.8 MHz; CD$_2$Cl$_2$, 298 K): $\delta = 0.17$ (s, 18H, Me$_3$Si), 1.23 (t, 3H, CH$_2$C*H$_3$*, $J = 7.2$ Hz), 2.71 (s, 6H, NCH$_3$), 2.30 (q, 2H, NCH$_2$), 3.51 (m, 2H, H$^{2,2'}$), 3.70 (m, 2H, H$^{4,4'}$), 3.80 (m, 2H, H$^{3,3'}$), 3.94 (m, 2H, H$^{5,5'}$), 7.25–7.50 (m, 5H, Ph).

Trimethylsilylethynyl derivative 4d

The synthesis was carried out as described for **4b**, starting from 100 mg (0.22 mmol) of **2** in [D$_8$]toluene (1.5 mL) and trimethylsilylacetylene (32 mg, 0.046 mL, 0.33 mmol). The reaction mixture was kept stirring at 60 °C for 28 h. The resulting mixture contained the adduct **4d** (*ca.* 70 %) together with **1**, trimethylsilylacetylene (10 %) and free dimethyl(ethyl)amine (^{1}H, ^{13}C and ^{29}Si NMR). **4d**: ^{1}H NMR (399.8 MHz; [D$_8$]toluene; 298 K): $\delta = 0.24$ (s, 9H, Me$_3$SiC), 0.38 (s, 18H, Me$_3$SiN), 0.60 (t, 3H, CH$_2$C*H$_3$*, $J = 7.2$ Hz),

Table 3. Crystallographic data of the [3]ferrocenophane **5d**.

	5d
Formula	$C_{26}H_{40}AlFeN_3Si_3$
Crystal	yellow orange prism
Dimensions, mm^3	$0.22 \times 0.17 \times 0.15$
Crystal system	triclinic
Space group	$P\bar{1}$
a, pm	1038.0(2)
b, pm	1154.2(2)
c, pm	1505.3(3)
α, deg	100.62(3)
β, deg	101.75(3)
γ, deg	108.61(3)
Z	2
Absorption coefficient μ (mm^{-1})	0.624
Diffractometer	Stoe IPDS I (MoK_α radiation, $\lambda = 71.073$ pm), graphite monochromator
Measuring range (ϑ, °)	2.1 – 26.0
Reflections collected	11845
Independent reflections [$I \geq 2\sigma(I)$]	5810
Absorption correction[a]	None
Refined parameters	307
wR2/R1 [$I \geq 2\sigma(I)$]	0.117/0.049
Max./min. residual electron density ($e\,pm^{-3} \times 10^{-6}$)	0.56/−0.21

[a] Absorption corrections did not improve the parameter set.

2.19 (s, 6H, NCH$_3$), 2.96 (q, 2H, NCH$_2$), 3.38 (m, 2H, H$^{2,2'}$), 3.83 (m, 2H, H$^{4,4'}$), 3.85 (m, 2H, H$^{3,3'}$), 4.00 (m, 2H, H$^{5,5'}$).

2-(Alkyn-1-yl)-1,3-bis(trimethylsilyl)-2-pyridine-1,3,2-diazaalumina-[3]ferrocenophanes 5

Hexyn-1-yl derivative *5a*

A solution of **4a** (*ca.* 60 mg, 0.11 mmol) in [D$_8$]toluene (1 mL) was cooled to 0 °C, and pyridine (0.008 mL, 0.10 mmol) was added. The mixture was stirred for 1 h and centrifuged. The resulting mixture contained *ca.* 40 % of the adduct **5a** together with **1**. **5a**: ^{13}C NMR (62.9 MHz, [D$_8$]toluene, 298 K): δ = 2.5 (Me$_3$Si), 14.0 (CH$_3$), 19.8 (*C*H$_2$(CH$_2$)$_2$CH$_3$), 23.0 (*C*H$_2$CH$_3$), 31.5 (*C*H$_2$CH$_2$CH$_3$), 68.0 (br) (C$^{2,2',5,5'}$), 64.7 (C$^{3,3',4,4'}$), 105.9 (C$^{1,1'}$). – ^{29}Si NMR (49.7 MHz, [D$_8$]toluene, 298 K): δ = 3.5.

3,3-Dimethylbutyn-1-yl derivative *5b*

The synthesis was carried out as described for **5a**, starting from *ca.* 54 mg (0.10 mmol) of **4b** and pyridine (0.008 mL, 0.10 mmol), to give 51 mg of **5b** (93 %). – ^{1}H NMR (399.8 MHz; [D$_8$]toluene; 298 K): δ = 0.29 (s, 18H, Me$_3$Si), 1.22 (s, 9H, C(CH$_3$)$_3$), 3.64 (br) (m, 4H, H$^{2,2',5,5'}$), 3.77 (m, 4H, H$^{3,3',4,4'}$), 6.62 (br) (m, 2H, H$_\beta$), 6.89 (br) (m, 1H, H$_\gamma$), 8.70 (br) (m, 2H, H$_\alpha$).

Phenylethynyl derivative *5c*

The synthesis was carried out as described for **5a**, starting from *ca.* 55 mg (0.10 mmol) of **4c** and pyridine (0.008 mL, 0.10 mmol) to give a mixture containing **5c** (*ca.* 30 %) and **1**. **5c**: ^{13}C NMR (62.9 MHz, [D$_8$]toluene, 298 K): δ = 2.7 (Me$_3$Si), 68.3 (br) (C$^{2,2',5,5'}$), 65.0 (C$^{3,3',4,4'}$), 106.0 (C$^{1,1'}$), 109.2 (br) ($\equiv$*C*–Ph, $h_{1/2} \approx 15$ Hz), 126.0 (C$_m$), 127.4 (C$_p$), 131.8 (C$_o$). – ^{29}Si NMR (49.7 MHz, [D$_8$]toluene, 298 K): δ = 3.7.

Trimethylsilylethynyl derivative *5d*

The synthesis was carried out as described for **5a**, starting from *ca.* 61 mg (0.11 mmol) of **4b** and pyridine (0.009 mL, 0.11 mmol) to give 56 mg of **5b** (90 %). Crystallization from [D$_8$]toluene, after 4 d at −30 °C, gave orange crystals of **5b**; m. p. 155 – 165 °C. – ^{1}H NMR (250.1 MHz; [D$_8$]toluene; 298 K): δ = 0.25 (s, 9H, Me$_3$SiC), 0.36 (s, 18H, Me$_3$SiN), 3.72 (br) (m, 4H, H$^{2,2',5,5'}$), 3.84 (m, 4H, H$^{3,3',4,4'}$), 6.58 (br) (m, 2H, H$_\beta$), 6.81 (br) (m, 1H, H$_\gamma$), 8.95 (br) (m, 2H, H$_\alpha$).

Crystal structure determination of the [3]ferrocenophane *5d*

Details pertinent to the crystal structure determination are listed in Table 3. Crystals of appropriate size were sealed under argon in a Lindemann capillary, and the data collection was carried out at 20 °C [22].

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[22] CCDC 647385 (**5d**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.