# 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

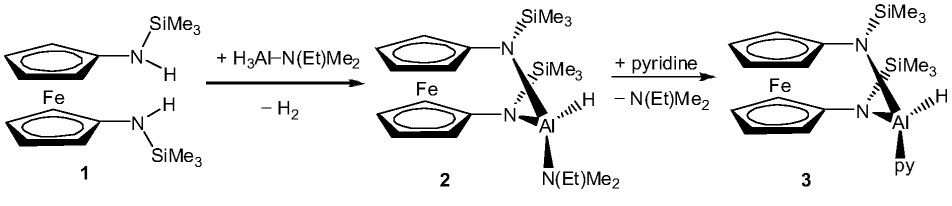
With a few exceptions [1] the aluminum atom in aluminum amides prefers the coordination number 4 and achieves it either by dimerization [2] or by accepting a suitable donor ligand. The latter coordination can take place in an intra- [3] or intermolecular way [4]. Nevertheless, such aluminum amides remain 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 $H_3Al$–$NEtMe_2$ [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 $Me_3Si$–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.

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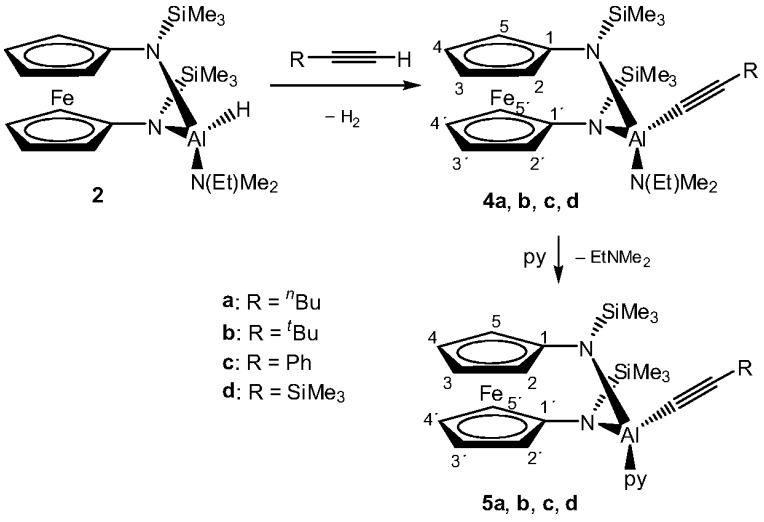
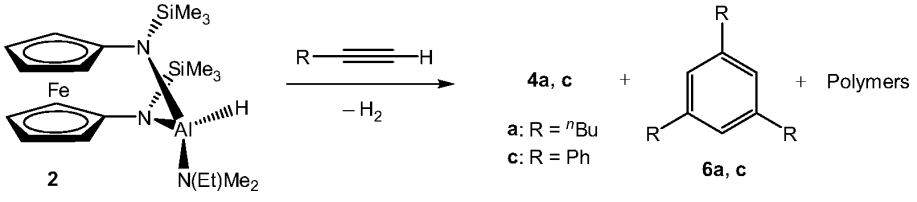



Scheme 2. Conversion of the Al–H function into the Al–C≡C–R function.




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 $Me_3Si$–C≡C–H. In the latter cases, heating to 75 °C (for $^{t}$Bu–C≡C–H) and 60 °C (for $Me_3Si$–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 crystalline 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-

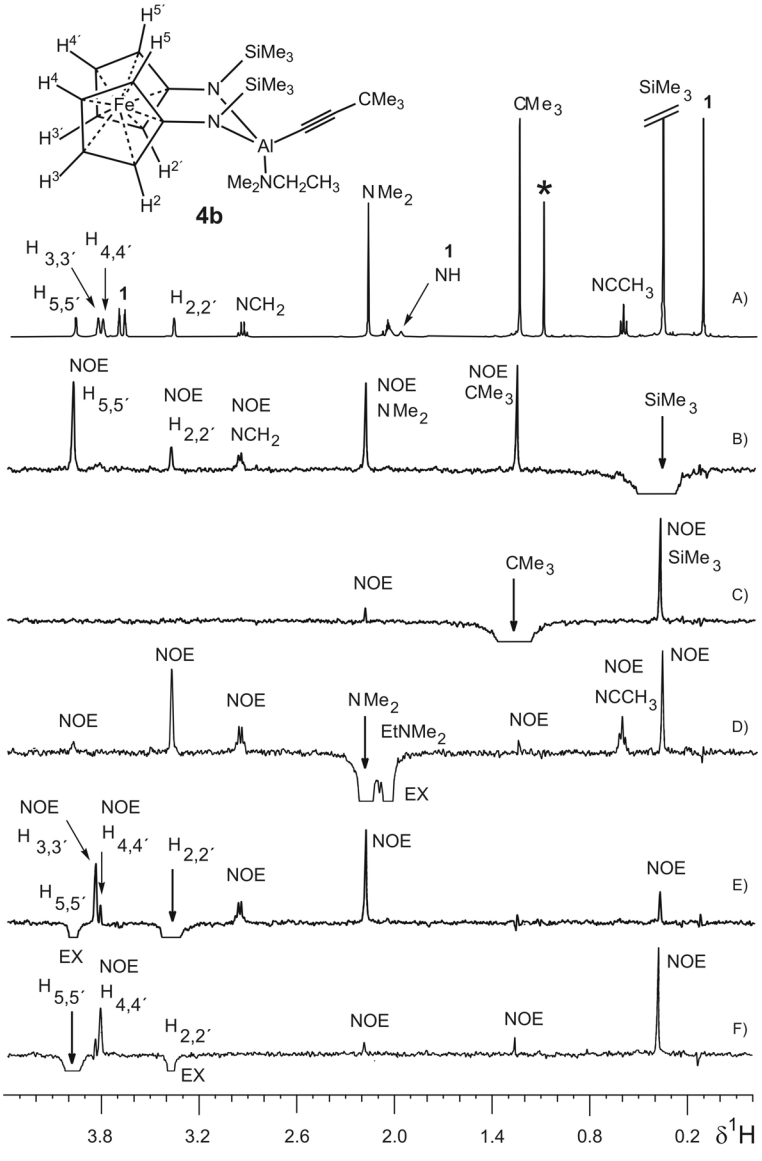



Fig. 1. 400 MHz $^1H\{^1H\}$ NOE difference spectra (gradient enhanced [12]) of **4b** (10 % in $[D_8]$toluene at 23 °C; relaxation delay 1.5 s; mixing time 0.8 s; 24 min of spectrometer time). The irradiated resonance signals are marked by arrows; the resulting intensities arising from NOE or EXchange are marked. (A) Normal $^1H$ 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**, intramolecular 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 $^1H$ 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 |
| $\delta^{13}$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) |
| $\delta^{13}$C(fc-C$^1$) | 106.9 | 106.3 | 106.8 | 106.7 | 106.6 | 106.5 | 106.3 | 106.1 | 106.0 |
| $\delta^{13}$C(fc-C$^2$) | 67.1 | 66.3 | 66.9 | 66.7 | 67.2 | 66.9 | 68.1 (br) | 67.8 | 68.2 (br) |
| $\delta^{13}$C(fc-C$^5$) | 69.0 | 69.0 | 69.7 | 69.5 | 69.9 | 69.7 | | | |
| $\delta^{13}$C(fc-C$^3$) | 64.8 | 64.0 | 65.1 | 65.1 | 65.0 | 65.2 | 64.8 | 64.6 | 298 K |
| $\delta^{13}$C(fc-C$^4$) | 64.1 | 63.3 | 64.5 | 64.5 | 64.3 | 64.6 | | | |
| $\delta^{13}$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) | |
| $\delta^{13}$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) |
| $\delta^{13}$C(R) | 13.8 (*C*H$_3$) | 13.4 | 31.2 (CH$_3$) | 31.0 (CH$_3$) | 125.8 (C$_i$) | 0.1 (55.9) | 31.3 (CH$_3$) | 31.0 (CH$_3$) | 0.2 (55.6) |
| | 20.2 (*C*H$_2$(CH$_2$)$_2$CH$_3$) | 19.5 | 28.5 (*C*Me$_3$) | 28.3 (*C*Me$_3$) | 127.7 (C$_p$) | | 28.5 (*C*Me$_3$) | 28.4 (*C*Me$_3$) | |
| | 22.5 (*C*H$_2$CH$_3$) | 21.9 | | | 125.5 (C$_m$) | | | | |
| | 31.4 (*C*H$_2$CH$_2$CH$_3$) | 30.5 | | | 131.5 (C$_o$) | | | | |
| $\delta^{13}$C | 52.1, 5.9 (NCH$_2$CH$_3$) | 50.5, 4.9 | 52.0, 5.6 | 51.2, 5.0 | 52.3, 6.0 | 52.0, 5.4 | 124.3 (C$_\beta$) (br) | 124.1 (C$_\beta$) (br) | 124.4 (C$_\beta$) (br) |
| (EtNMe$_2$ or | 43.7 (NCH$_3$) | 42.2 | 43.3 | 42.5 | 43.8 | 43.2 | 137.0 (C$_\gamma$) (br) | 137.0 (C$_\gamma$) (br) | 136.8 (C$_\gamma$) (br) |
| pyridine) | | | | | | | 149.6 (C$_\alpha$) (br) | 149.0 (C$_\alpha$) (br) | 148.2 (C$_\alpha$) (br) |
| $\delta^{27}$Al | 120 | | 123 | | – | 105 | 120 | | 105 |
| ($h_{1/2}$, Hz) | (3000 Hz, | | (3000 Hz, | | | (4600 Hz, | (4000 Hz, | | (4600 Hz, |
| | ±500 Hz) | | ±500 Hz) | | | ±500 Hz) | ±500 Hz) | | ±500 Hz) |
| $\delta^{29}$Si | 4.0 (56.2) | 3.9 | 4.1 (56.2) | | 4.0 (56.2) | 4.4 (56.2) | 3.8 (55.8) | | 3.9 (55.6) |
| | | | | | | (NSiMe$_3$) | | | (NSiMe$_3$) |
| | | | | | | −21.9 | | | −21.9 (55.6) |
| | | | | | | (CSiMe$_3$) | | | (CSiMe$_3$) |

[a] In $CD_2Cl_2$ (**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.

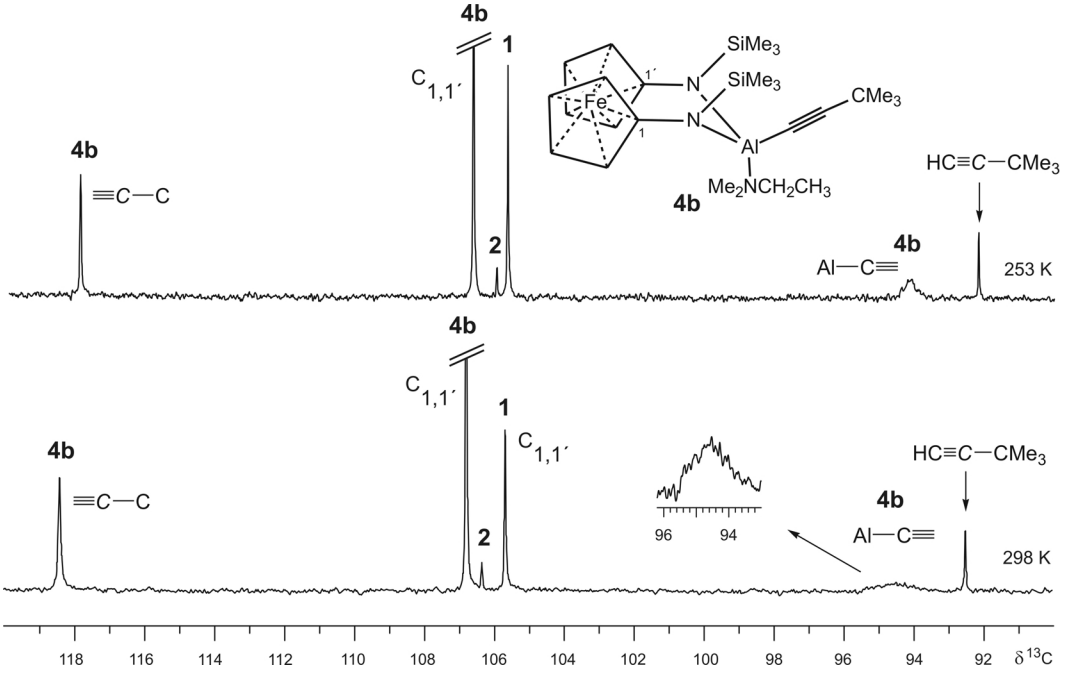



Fig. 2. Parts of the low temperature (upper trace, 62.9 MHz) and r. t. (lower trace, 100.5 MHz) $^{13}C\{^1H\}$ NMR spectra of the ferrocenophane **4b** containing some **1**, formed during the reaction, **2** and $^t$Bu–C≡C–H ([$D_8$]toluene). The $^{13}C$(Al–C≡) NMR signal sharpens considerably at lower temperature owing to "quadrupole decoupling" [18].

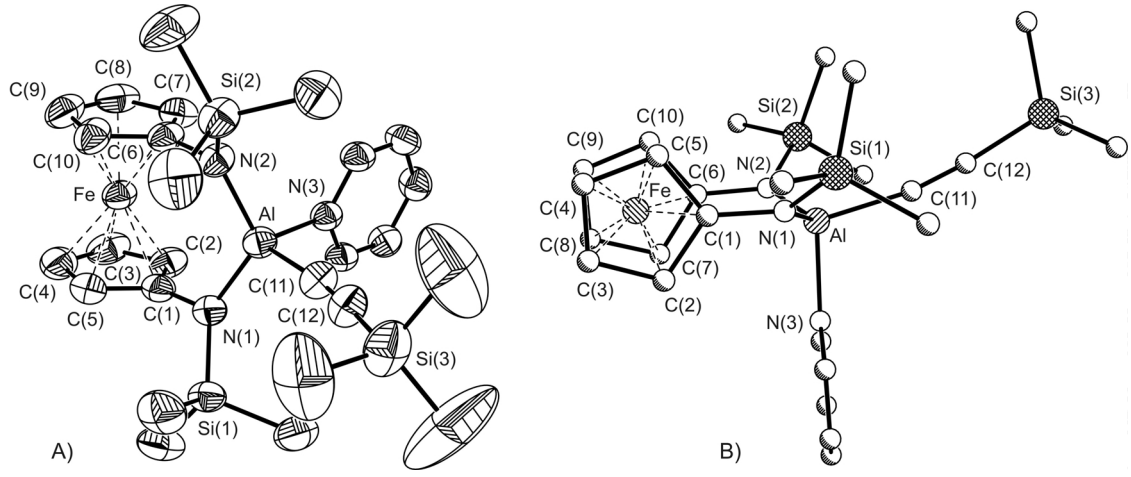



Fig. 3. Molecular structure of **5d** (A) (ORTEP plot, displacement ellipsoids at the 40 % probability level) and (B) (ball and stick model); hydrogen atoms are omitted for clarity, see Table 2 for structural parameters.

temperatures $< -20$ °C both in $[D_8]$toluene and $CD_2Cl_2$.

$^{13}$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(2) |
| 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 Fe–C(1)–N(1)–N(2)–C(6)[c] | 50.0 | 51.8 |
| $C_5$ / $C_5$ ($\alpha$) | 2.9 | 2.3 |
| $C_5$ / N(1) ($\beta_1$) | 0.3 towards iron | 1.6 towards iron |
| $C_5$ / N(2) ($\beta_2$) | 1.4 towards iron | 0.2 towards iron |
| $C_5$–Fe–$C_5$ ($\gamma$) | 176.6 | 176.7 |
| $C_5$ / $C_5$ (twist) ($\tau$) | 2.8 | 5.1 |
| Fe–$C_5$ (center) | 164.2 | 164.3 |
| | 164.5 | 164.5 |

[a] The definition of the angles $\alpha$, $\beta$, $\gamma$ and $\tau$ 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 $CD_2Cl_2$ 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-diazaalumina-[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: $^1H$, $^{13}C$, $^{27}Al$, and $^{29}Si$ NMR (refocused INEPT [21] based on $^2J(^{29}Si,^1H)$ = 7 Hz); Varian INOVA 400: $^1H$, $^{13}C$ NMR; chemical shifts are given with respect to $Me_4Si$ [$\delta^1H$ ($CHDCl_2$) = 5.33, $\delta^1H$ ($C_6D_5CD_2H$) = 2.08; $\delta^{13}C$ ($CD_2Cl_2$) = 53.8, $\delta^{13}C$ ([$D_8$]toluene) = 20.4; $\delta^{29}Si$ = 0 for $\Xi(^{29}Si)$ = 19.867184 MHz]; external 1.1 M $Al(NO_3)_3$ in $D_2O$ [$\delta^{27}Al$ = 0 for $\Xi(^{27}Al)$ = 26.056890 MHz]. Assignments of $^1H$ and $^{13}C$ NMR signals are based on $^1H/^1H$-NOE difference, and 2D $^1H/^{13}C$-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 $CD_2Cl_2$ (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** ($^1H$, $^{13}C$ and $^{29}Si$ NMR). **4a**: $^1H$ NMR (399.8 MHz; $CD_2Cl_2$, 298 K): $\delta$ = 0.10 (s, 18H, $Me_3Si$), 0.85, 0.90 (t,t, 3H, 3H, $CH_2CH_3$), 1.19 (m, 2H, $CCH_2CH_3$), 1.47 (m, 2H, $CH_2CH_2CH_3$), 2.17 (m, 2H, $CH_2(CH_2)_2CH_3$), 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 ($^1H$, $^{13}C$ and $^{29}Si$ NMR). **4b**: $^1H$ NMR (399.8 MHz; [$D_8$]toluene; 298 K): $\delta$ = 0.38 (s, 18H, $Me_3Si$), 0.62 (t, 3H, $CH_2CH_3$, $J$ = 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=$CH_2$: $^1H$ 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 ($^1H$, $^{13}C$ and $^{29}Si$ NMR). **4c**: $^1H$ NMR (399.8 MHz; $CD_2Cl_2$, 298 K): $\delta$ = 0.17 (s, 18H, $Me_3Si$), 1.23 (t, 3H, $CH_2CH_3$, $J$ = 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 ($^1H$, $^{13}C$ and $^{29}Si$ NMR). **4d**: $^1H$ NMR (399.8 MHz; [$D_8$]toluene; 298 K): $\delta$ = 0.24 (s, 9H, $Me_3SiC$), 0.38 (s, 18H, $Me_3SiN$), 0.60 (t, 3H, $CH_2CH_3$, $J$ = 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) |
| $\alpha$, deg | 100.62(3) |
| $\beta$, deg | 101.75(3) |
| $\gamma$, deg | 108.61(3) |
| $Z$ | 2 |
| Absorption coefficient $\mu$ (mm$^{-1}$) | 0.624 |
| Diffractometer | Stoe IPDS I (Mo$K_\alpha$ radiation, $\lambda$ = 71.073 pm), graphite monochromator |
| Measuring range ($\vartheta$, °) | 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): $\delta$ = 2.5 ($Me_3Si$), 14.0 ($CH_3$), 19.8 ($CH_2(CH_2)_2CH_3$), 23.0 ($CH_2CH_3$), 31.5 ($CH_2CH_2CH_3$), 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): $\delta$ = 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): $\delta$ = 0.29 (s, 18H, $Me_3Si$), 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): $\delta$ = 2.7 ($Me_3Si$), 68.3 (br) ($C^{2,2',5,5'}$), 65.0 ($C^{3,3',4,4'}$), 106.0 ($C^{1,1'}$), 109.2 (br) (≡*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): $\delta$ = 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): $\delta$ = 0.25 (s, 9H, $Me_3SiC$), 0.36 (s, 18H, $Me_3SiN$), 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.