Synthesis, Characterization and Reactivity of Dinuclear and Trinuclear Aluminum-Bridged Ferrocenophanes

Bernd Wrackmeyer,*^[a] Elena V. Klimkina,^[a] and Wolfgang Milius^[a]

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Ferrocene derivatives bearing substituents with aluminum in the 1,1'-positions, in the absence of donor ligands, possess rather unusual structural features. Starting from various dipyridine adducts of such 1,1'-disubstituted ferrocene derivatives, it proved possible to trap the pyridine as the adducts $R_3Al(py)$ and monitor the formation of dinuclear and trinuclear aluminum-bridged ferrocenophanes in solution by NMR spectroscopy. For the first time, the dynamic behaviour of such complexes was studied and a complete set of NMR spectroscopic data has been reported. The dinuclear complex $[Fe(\eta^5-C_5H_4)_2]_2Al_3Et_5$ was characterized by X-ray structural analysis.

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Introduction

The chemistry of ferrocene derivatives bearing aluminum in the 1,1'-positions appears to be complex and fairly unpredictable in the absence of donors. In previous work,^[1] we successfully introduced rational synthetic methods to prepare dipyridine adducts **1**, **2** and **3** (Scheme 1), which, in contrast to their gallium congeners,^[2–5] had not been known. Interestingly, other attempts in this field, in the absence of pyridine, have produced compounds such as **4**^[6] and **5**^[7] (Scheme 1), in which at least the central aluminum atoms possess rather unusual surroundings. Although the molecular structures of **4a** and **5b** were determined by Xray structural analysis,^[6,7] their solution-state structures were not studied in detail, as the reported NMR spectroscopic data sets were incomplete and some data were probably misinterpreted. In the present work, we have taken advantage of our experience with pyridine adducts of ferrocenylaluminum compounds as well as dipyridine adducts $1-3^{[1]}$ to find alternative routes to compounds of type 4 and 5. Indeed, these dinuclear and trinuclear complexes should be somehow related to species 2 and 3. Their formation in equilibria is feasible, if it proves possible to offer another suitable acceptor for the pyridine ligands. It will be shown that AlMe₃ or AlEt₃ can play this role.

Results and Discussion

We studied the reactivity of starting materials $1-3^{[1]}$ towards AlMe₃ and AlEt₃, respectively, in order to form the pyridine adducts AlR₃(py) and monitor the fate of the pyridine-free ferrocenediylaluminum compounds. The most



Scheme 1. Some known 1,1'-disubstituted ferrocene derivatives with aluminum, as dipyridine adducts $1-3^{[1]}$ and as pyridine-free compounds $4^{[6]}$ and 5.^[7]

- [a] Anorganische Chemie II, Universität Bayreuth, 95440 Bayreuth, Germany Fax: +49-921-552157 E-mail: b.wrack@uni-bayreuth.de
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important results are summarized in Scheme 2. Independent of starting material 1, 2 or 3, the use of $AlMe_3$ or $AlEt_3$ resulted in the formation of 4a or 4b as the final products in solution. Compounds 4a and 4b could be isolated as crystalline solids. The molecular structure of 4a has





Scheme 2. Three different routes to the dinuclear, threefold-aluminum-bridged ferrocenophane of type 4, of which 4a has been isolated previously by treatment of $AlMe_2Cl$ with 1,1'-dilithioferrocene.^[6]

already been described, and that of **4b** was determined in the present work (vide infra). Compounds **4** are stable in $[D_8]$ toluene under an atmosphere of argon for prolonged periods of time at -20 °C and decompose slowly in CD_2Cl_2 .

Clearly, the pyridine ligands are caught by the trialkylaluminum, as shown by NMR spectra of the reaction mixtures (see Table 1 for NMR spectroscopic data of pure compounds **4a,b**). The formation of **4** is the result of complex rearrangements in the equilibrated mixtures in order to reduce electron deficiency and coordinative unsaturation of the aluminum atoms. The presence of slow dynamic equilibria is illustrated in Figure 1 by ${}^{1}H{-}{}^{1}H$ NOE difference spectra, which, in addition to NOE, also give rise to numerous intensities caused by inter- and intramolecular exchange processes. In contrast, as shown in Figure 2, for pure compound **4b** (isolated and redissolved crystalline sample), the analogous experiments reveal solely intramolecular exchange between the AlEt(a,b) groups.

The bonding of the central aluminum atom in **4** is of major interest, as the structure in the solid state shows markedly different Al–C(ferrocene) distances, two shorter and two longer ones, which therefore may imply a coordina-

Table 1. ¹³C NMR spectroscopic data^[a,b,c] of compounds 4 and 5.

	4a			4b			5a		5b	
	R = Me		R = Et			R = Me		R = Et		
	[D ₈]toluene	$C_6 D_6^{[d]}$	CD_2Cl_2	[D ₈]toluene	CD_2Cl_2		[D ₈]toluene	CD_2Cl_2	[D ₈]toluene	CD_2Cl_2
$\delta^{13}C(\text{fc-}C^1)$	56.6 [br.]	56.9 [br.]	56.6 [br.]	55.8 [br.]	55.8 [br.]	$\delta^{13}C(\text{fc-}C^1)$	58.5 [br.]	58.9 [br.]	56.8 [br.]	n.o.
						$\delta^{13}C(\text{fc-C}^6)$	86.0 [br.]	86.0 [br.]	85.7 [br.]	
$\delta^{13}C(\text{fc-}C^2)$	82.0	82.5	82.0	81.7	81.7	$\delta^{13}C(\text{fc-}C^{2,5})$	80.4 (br.)	80.4 (br.)	80.2 (br.)	80.3 (br.)
δ^{13} C(fc-C ⁵)	82.3	82.7	82.4	82.0	82.1	$\delta^{13}C(\text{fc-} C^{7,10})$	80.0 (br.)	79.9 (br.)	79.9 (br.)	79.8 (br.)
$\delta^{13}C(\text{fc-C}^3)$	78.5	78.9	78.9	78.4	78.7	$\delta^{13}C(\text{fc-C}^{3,4})$	76.1 (br.)	76.5 (br.)	76.2 (br.)	76.4 (br.)
$\delta^{13}C(\text{fc-}C^4)$	77.4	77.9	78.0	77.4	77.8	$\delta^{13}C(\text{fc-C}^{8,9})$				
δ^{13} C: R(a)	-4.2 [br.]	-3.8 [br.]	-4.9 [br.]	5.7 [br.], 10.2	5.2 [br.], 9.7 (br.)	δ^{13} C: AlR ₂	-4.8 [br.]	-5.1 [br.]	n.o., 9.9	3.5 [br.], 8.7
δ^{13} C: R(b)	-5.3 [br.]	-4.8 [br.]	-5.3 [br.]	3.6 [br.], 9.9	3.2 [br.], 9.4 (br.)	δ^{13} C: AlR	-2.8 [br.]	-3.5 [br.]	n.o., 10.0	3.5 [br.], 9.1
δ^{13} C: R(c)	-5.7 [br.]	-5.1 [br.]	-5.8 [br.]	5.1 [br.], 11.1	4.4 [br.], 10.8					

[a] The assignment of the NMR signals is based on ¹H{¹H} NOESY^[9] and 2D ¹H–¹³C gHSQC^[10] experiments. [b] [br.] denotes broad ¹³C resonances of aluminum-bonded atoms; (br.) denotes broad ¹³C resonances due to dynamic effects. [c] n.o. = not observed. [d] NMR spectroscopic data from ref.^[6] ¹³C NMR (75.46 MHz, C₆D₆): δ = –8.0, –4.8, –2.8, 68.2, 77.5, 82.0, 82.3 ppm. ¹H NMR (300.13 MHz, C₆D₆): δ = –0.69 (s, 3 H), –0.67 (s, 6 H), –0.40 (s, 6 H), 4.21, 4.37 (m, 8 H), 4.49 (m, 8 H) ppm. Some of these data correspond to those found here for **5a**.



Figure 1. 399.8 MHz ¹H{¹H} NOE difference spectra (gradient enhanced^[9]) of the reaction mixture containing 4b, AlEt₃ and Et₃-Al(py) (in [D₈]toluene at 23 °C, relaxation delay 2.0 s, mixing time 0.6 s). The irradiated resonance signals (arrows) give rise to intensities (NOE or Exchange) as indicated. (A) Normal ¹H NMR spectrum. (B) Irradiation of ¹H[AlCH₂(b)]; response: magnetization transfer^[11] between AlCH₂ groups of AlEt(a), AlEt(b) and AlEt₃, whereas NOE is observed for ¹H(AlCH₂) of AlEt(c), ¹H(Me) of AlEt(b), AlEt(a) and AlEt(c) groups, and (fc)¹H⁵ and (fc)¹H². (C) Irradiation of ¹H(Me) of AlEt(a); response: magnetization transfer between Me of AlEt(a), AlEt(b) and AlEt₃. (D) Irradiation of (fc) ${}^{1}\text{H}^{5}$; response: magnetization transfer between (fc) ${}^{1}\text{H}^{5}$ and (fc) ${}^{1}\text{H}^{2}$, whereas NOE is observed for (fc)¹H^{3,4}, ¹H(AlCH₂) and ¹H(Me) of AlEt(a) and AlEt(b). (E) Irradiation of (fc)¹H²; response: magnetization transfer between (fc)¹H⁵ and (fc)¹H², whereas NOE is observed for (fc)¹H^{3,4}, ¹H(AlCH₂) and ¹H(Me) of AlEt(c), and for ¹H(AlCH₂) of AlEt(a) and AlEt(b).

tion number of three for the aluminum. The reported NMR spectroscopic data set^[6] is incomplete and inconclusive in this respect. The ¹³C NMR spectra of **4a**,**b** (see Figure 3 for **4b**) show all expected ¹³C NMR signals in agreement with the proposed structure.

Broad ¹³C NMR signals are expected for ¹³C nuclei linked to aluminum owing to partially relaxed scalar ²⁷Al– ¹³C spin–spin coupling as a result of efficient scalar nuclear relaxation [short values $T_2^{SC}(^{13}C)$] of the second kind. However, there is only one broad ¹³C(fc)–Al NMR signal. This is in the region typical of bridging Al–C(fc)–Al



Figure 2. 399.8 MHz ¹H{¹H} NOE difference spectra (gradient enhanced^[9]) of **4b** (in [D₈]toluene at 23 °C, relaxation delay 2.0 s, mixing time 0.6 s). The irradiated resonance signals (arrows) give rise to the indicated respective intensities (NOE or Exchange). (A) Normal ¹H NMR spectrum. (B) Irradiation of ¹H[AlCH₂(a)]: response: magnetization transfer^[11] between AlCH₂(a) and AlCH₂(b), whereas NOE is observed for (fc)¹H⁵ and (fc)¹H², and ¹H(Me) of AlEt(a). (C) Irradiation of ¹H(Me) of AlEt(c); response: (fc)¹H², ¹H(AlCH₂) of AlEt(c). (D) Irradiation of (fc)¹H⁵; response: (fc)¹H², ¹H^{3,4}, and weaker for ¹H(AlCH₂) of the AlEt(a) and AlEt(b). (E) Irradiation of (fc)¹H²; response: ¹H^{3,4} and ¹H(Me) and ¹H(AlCH₂) of AlEt(c), and weaker for ¹H(AlCH₂) of AlEt(a) and AlEt(b). (F) Irradiation of (fc)¹H^{3,4}; response: (fc)¹H⁵ and (fc)¹H².

groups.^[8] Hence, this strongly supports fast exchange of the central aluminum between all four $C^1(fc)$ carbon atoms in order to relieve this aluminum atom from electronic and coordinative strain, as indicated in the formula for **4**.





Figure 3. 125.8 MHz ${}^{13}C{H}$ NMR spectrum of **4b** (in [D₈]toluene at 23 °C). Note the broad ${}^{13}C(Al)$ NMR signals; there are three for ${}^{13}C(Et)Al$ and only one ${}^{13}C(fc)Al$.

Considering the solution-state structure of **4**, it was tempting to offer another nucleophile such as a carbanion to the central aluminum. Thus, the reactions of **4b** with EtLi in benzene/cyclohexane were studied. Mixtures containing **4b** and small amounts of $Et_3Al(py)$ reacted smoothly with EtLi (Scheme 3). The formation of **6b** together with Li[AlEt₄] follows conclusively from the NMR spectra (see Table 2), in particular from ²⁷Al NMR spectroscopy.

Having isolated compounds **4**, it was of interest to study their reactivity towards pyridine (Scheme 4). Addition of pyridine opens the ferrocenophane systems to give **7a**,**b**, as shown by the NMR spectra (see Table 2) of the reaction mixtures (see Figure 4 for **7b**). These equilibria are finally driven to **1a**,**b** in the presence of $R_3Al(py)$. Therefore, compounds **7a**,**b** may also be of importance in the formation of **4** following Scheme 2.

When the reactions of **3** with AlR₃ (Scheme 2) were carefully monitored by using ¹H and ¹³C NMR spectroscopy, the intermediate formation of another species was observed. These intermediates are most likely compounds $5^{[7]}$ (NMR spectroscopic data of **5a,b** are included in Table 1), and we propose Scheme 5 to explain their formation. Thus, AlR₃ does not only abstract the pyridine ligands from **3**, it also exchanges its alkyl groups with the aluminum atoms in **3** to give trinuclear complexes **5**. Therefore, complexes **5**

Table 2. 13 C NMR spectroscopic data^[a,b,c] of compounds **6b** and **7**.

	6b ^[d] R = Et [D ₂]toluene, pv	7a R = Me [D _s]toluene	7b R = Et
$\delta^{13}C(\text{fc-}C^1)$	n.o.	72.3 [br.]	71.8 [br.]
$\delta^{13}C(\text{fc-C}^6)$		73.2 [br.]	72.6 [br.]
$\delta^{13}C(\text{fc-}C^{2,5})$	76.3 (br.)	76.2	76.5
$\delta^{13}C(\text{fc-C}^{3,4})$	72.2 (br.)	71.0	71.0
$\delta^{13}C(\text{fc-C}^{7,10})$	_	76.1	76.3
$\delta^{13}C(\text{fc-C}^{8,9})$	_	71.6	71.6
δ^{13} C: AlR ₂	3.2 (br.), 12.1 (br.)	–9.1 [br.]	1.3 [br.], 10.87
AlR		-8.2 [br.]	2.5 [br.], 10.94
$\delta^{13}C(py)$	124.3 (C _β)	123.8 (C _β)	124.1 (С _в)
	136.8 (C_{γ})	137.5 (C_{γ})	136.6 (C_{γ})
	149.8 (C _a)	150.1 (C _α)	149.2 (C _a)

[a] The assignment of the NMR signals is based on ¹H{¹H} NOESY^[9] and 2D ¹H–¹³C gHSQC^[10] experiments. [b] [br.] denotes broad ¹³C resonances of aluminum-bonded atoms; (br.) denotes broad ¹³C resonances due to dynamic effects. [c] n.o. = not observed. [d] δ^{27} Al{¹H} 165 ($h_{1/2} \approx 1000$ Hz).

must be considered as intermediates prior to the formation of **4**. Schemes 2, 4 and 5 emphasize the complex behaviour of 1,1'-aluminum-substituted ferrocene derivatives.

Although the NMR signals of 5 were rather weak relative to those of 4, their regular appearance for R = Me, Et and



Scheme 3. Reaction of 4b with EtLi and pyridine.



Scheme 4. Reactivity of 4 towards pyridine and shifting the equilibria by addition of AlR₃.



Figure 4. Parts of the 399.8 MHz ¹H{¹H} NOE difference spectra (gradient enhanced^[9]) of a reaction mixture, in which 4b was converted into 7b with Et₃Al(py) (in [D₈]toluene at 23 °C, relaxation delay 1.0 s, mixing time 0.4 s). The irradiated transitions (arrows) gave rise to intensities (NOE) as indicated. (A) Normal ¹H NMR spectrum. (B) Irradiation of AlCH₂ of AlEt; response: ¹H(Me) of the AlEt, and (fc)¹H^{7,10}, (fc)¹H^{2,5} and (fc)¹H^{8,9}. (C) Irradiation of ¹H(Me) of AlEt; response: ¹H(AlCH₂) of AlEt, and (fc)¹H^{2,5} and (fc)¹H^{8,9}. (D) Irradiation of (fc)¹H^{8,9}; response: (fc)¹H^{7,10}, (fc)¹H^{2,5}, and ¹H(Me) and ¹H(AlCH₂) of AlEt. (È) Irradiation of (fc)¹H^{3,4}; response: $(fc)^{1}H^{7,10}$, $(fc)^{1}H^{2,5}$, and ${}^{1}H(Me)$ and ${}^{1}H(AlCH_{2})$ of AlEt₂.

their peculiar somewhat broad features were striking. An example is shown for the ¹³C NMR spectra in Figure 5, which also shows the inverse ¹H-¹³C heteronuclear shift



Scheme 5. Formation of trinuclear ferrocenophane 5 by abstracting the pyridine ligands from 3 with the use of a slight excess amount of AlR₃.

correlation for the CH(fc) region. There are four different CH(fc) units clearly evident from the ¹H NMR spectra, of which two corresponding signals overlap in the ¹³C NMR spectra. There can be no doubt about the structure of 5b in the solid state,^[7] proving the presence of a three-coordinate central aluminum and two terminal different four-coordinate aluminum atoms bearing one and two ethyl groups, respectively. Meaningful and conclusive NMR spectroscopic data of **5b** were not reported.^[7]

Assuming a rigid structure of 5 in solution, many more signals than those observed (Figure 5) were expected. However, dynamic processes (Scheme 6) involving exchange of the alkyl groups accompanied by exchange of the bonds between the terminal aluminum atoms Al(1,3) and the ferrocenediyl groups simplifies the situation. Then, the required four CH(fc) units with slightly exchange-broadened signals fit to the dynamic structure of 5. Moreover, the dynamic structure requires on average two broad ¹³C(fc)Al NMR signals at any time, one in the region for bridging Al(1)-C(fc)-Al(2) and Al(2)-C(fc)-Al(3) units and the other one for terminal C(fc)-Al(1) and C(fc)-Al(3) bonds. These weak broad signals are observed. Unfortunately, the limited solubility of compounds 5 did not allow their NMR spectra to be recorded at low temperature.



Figure 5. 100.5 MHz ${}^{13}C{}^{1}H$ NMR spectrum and contour plot of part of the 400 MHz 2D ${}^{1}H{}^{-13}C$ -correlated spectrum [recorded by the gradient-selected (gs-)HSQC method^[10]] of a mixture **4a/5a** (in CD₂Cl₂ at 23 °C).



Scheme 6. Dynamic processes in 5. The exchange of the R groups and of the ferrocenedial groups is indicated by arrows.

X-ray Structure Analysis of Aluminum-Bridged Ferrocenophane 4b

The molecular structure of **4b** is shown in Figure 6 and selected structural data are given in Table 3 and compared with those reported for **4a**.^[6] The AlEt₂ units are linked unsymmetrically to the ferrocenediyl groups. The surroundings of the central aluminum atom appears to be close to trigonal planar { $\Sigma[\angle Al(2)] = 357.5^{\circ}$ }, and the distances to the next ferrocenediyl carbon atoms are rather long (351.6, 253.6 pm). Major differences between the structures of **4b** and **4a** may be found in the exact positions of the central aluminum atom Al(2). This may be due to different steric effects exerted by methyl (**4a**) and ethyl groups (**4b**). Otherwise, the important structural features are comparable. Table 3 lists the α , β and τ angles ^[12,13] for **4b**, describing the distortions of the ferrocene geometry. Typically, the α

angles are small, whereas the β angles are larger because of the bridging nature of the carbon atoms linked to aluminum. The arrangement of the three aluminum atoms in **4b** enforce considerable twist angles $\tau^{[13]}$ (39.8 and 22.8°) of the cyclopentadienyl rings against an eclipsed structure.

Experimental Section

General: All preparative work as well as handling of the samples was carried out with precautions to exclude trace amounts of air and moisture. Carefully dried solvents and oven-dried glassware were used throughout. The deuterated solvent CD_2Cl_2 was distilled from CaH_2 under an atmosphere of argon. All other solvents were distilled from Na metal under an atmosphere of argon. Starting materials such as Me₃Al (2.0 M in hexanes), Et₃Al (1.0 M in hexanes), pyridine (anhydrous, 99.8%), EtLi (0.5 M in benzene/cyclohexane, 90:10) (all from Aldrich) were commercial products and



Figure 6. Molecular structure of **4b** (ORTEP plot, 30% probabilities; hydrogen atoms are omitted for clarity); see Table 3 for structural parameters. The methyl carbon of the ethyl group [C(23)– C(24)] is statistically disordered. (The relatively large space requirement of the disordered methyl carbon atoms of the ethyl substituents in **4b** may also be seen by the difference of the unit cell volumes in **4a** and **4b**. By taking into account Z = 2 in **4b** and Z = 4 in **4a** there is a difference of about 450 Å³ for five methyl C atoms).

used as received. Compounds **1b**, **2b** and **3** were prepared by literature procedures.^[1] Owing to the extreme sensitivity of the new organoaluminum compounds, elemental analysis did not give reliable results. Attempts to measure mass spectra (EI MS, 70 eV) did not reveal the respective molecular ions. Instead, the pattern of diferrocene (CpFeC₅H₄)₂ was observed. NMR measurements: Varian INOVA 400: ¹H, ¹³C, ²⁷Al NMR; Bruker DRX 500: ¹H, ¹³C, ²⁷Al NMR; chemical shifts are given with respect to SiMe₄ [δ^{1} H (CHDCl₂) = 5.31 ppm, δ^{1} H (C₆D₅CD₂H) = 2.08 ppm; δ^{13} C (CD₂Cl₂) = 53.8 ppm, δ^{13} C(C₆D₅CD₃) = 20.4 ppm]; external 1.1 M Al(NO₃)₃ in D₂O [δ^{27} Al = 0 ppm for Ξ (²⁷Al) = 26.056890 MHz]. The melting points (uncorrected) were determined by using a Büchi 510 melting point apparatus.

$[Fe(\eta^5\text{-}C_5H_4)_2]_2Al_3R_5$ (4) from 1,1'-Bis(dialkylalanyl)ferrocene Dipyridine Adduct 1b

4a ($\mathbf{R} = \mathbf{Me}$): To a solution of the dipyridine adduct of 1,1'-bis(diethylalanyl)ferrocene (1b; 200 mg, 0.39 mmol) in [D₈]toluene (1 mL) cooled to -40 °C was added Me₃Al (2.0 M in hexanes, 2.0 mL, 4.0 mmol). The reaction mixture was allowed to reach ambient temperature and then stirred for 1 h. Readily volatile materials were removed in vacuo. The resulting mixture contained 4a together with Me₃Al, Me₃Al(py), Et₃Al(py) and several unidentified side products (¹H and ¹³C NMR). The brown oil thus obtained was washed with hexane (2 mL), the residue oil after removal of the hexane was dried in vacuo to give 73 mg (72%) of 4a (about 95%) (together with Me₃Al(py) and several unidentified side products). Data for 4a: ¹H NMR (399.8 MHz, [D₈]toluene, 23 °C): δ = -0.88 [s, 6 H, CH₃(a)Al], -0.25 [s, 6 H, CH₃(b)Al], 0.21 [s, 3 H, CH₃(c)Al], 4.02 (m, 4 H, H⁵), 4.16 (m, 4 H, H²), 4.36 (m, 8 H, H^{3,4}) ppm. ¹H NMR (399.8 MHz, C₆D₆, 23 °C): δ = -0.78 [s, 6 H, CH₃(a)Al], -0.16 [s, 6 H, CH₃(b)Al], 0.29 [s, 3 H, CH₃(c)Al], 4.08 (m, 4 H, H⁵), 4.21 (m, 4 H, H²), 4.36 (m, 8 H, H^{3,4}) ppm. ¹H NMR (399.8 MHz, CD_2Cl_2 , 23 °C): $\delta = -1.29$ [br. s, 6 H, $CH_3(a)Al$], -0.65 [br. s, 6 H, CH₃(b)Al], 0.07 [s, 3 H, CH₃(c)Al], 4.36 (m, 4 H, H⁵), 4.40 (m, 4 H, H²), 4.87 (m, 4 H, H⁴), 4.91 (m, 4 H, H³) ppm. Data for Me₃Al: ¹H NMR (399.8 MHz, $[D_8]$ toluene, 23 °C): $\delta = -0.40$

Table 3. Selected bond lengths [pm] and angles $[\circ]^{[a]}$ of ferrocenophanes **4b** and **4a**^[6] for comparison.

	4b		4 a
Al(1)-C(1)	218.6(6)	Al(3)-C(31)	215.1(2)
Al(3)-C(11)	219.2(6)	Al(1)-C(21)	216.0(2)
Al(1)-C(16)	199.4(7)	Al(3)-C(11)	198.6(3)
Al(3)-C(6)	203.6(6)	Al(1)-C(41)	203.8(2)
Al(2)-C(1)	205.5(6)	Al(2)-C(31)	203.3(2)
Al(2)-C(11)	201.8(6)	Al(2)-C(21)	201.5(2)
Al(2)C(16)	321.6	Al(2)C(11)	326.2
Al(2)C(6)	253.6	Al(2)C(41)	244.4(3)
Al(1)-C(21)	198.3(7)	Al(3)–C(5)	196.6(5)
Al(1)-C(23)	197.8(8)	Al(3)-C(4)	197.0(3)
Al(3)-C(27)	196.2(8)	Al(1)-C(1)	197.7(3)
Al(3)-C(29)	199.0(8)	Al(1)-C(2)	196.3(3)
Al(2)C(25)	196.6(7)	Al(2)-C(3)	193.8(2)
Al(1)Al(2)	312.4	Al(3)Al(2)	288.0
Al(2)···Al(3)	284.5(3)	Al(2)···Al(1)	297
Al(1)···Al(3)	589.9	Al(1)•••Al(3)	587
C(1)C(11)	364.7	C(31)···C(21)	360.8
C(16)···C(6)	556.9	C(11)···C(41)	554.7
Al(2)Fe(1)	270.8(2)	Al(2)Fe(2)	261.7
Al(2)Fe(2)	314.0	Al(2)Fe(1)	
Al(1)-Al(2)-Al(3)	162.4	Al(3)-Al(2)-Al(1)	162.3
Al(1)-C(1)-Al(2)	94.8(2)		
Al(3)C(11)Al(2)	84.9(2)		
Al(1)C(16)Al(2)	69.2		
Al(3)-C(6)-Al(2)	76.0		
C(1)-Al(1)-C(16)	103.6(2)	C(31)-Al(3)-C(11)	103.63(9)
C(1)-Al(1)-C(21)	103.2(3)	C(31)-Al(3)-C(5)	100.52(11)
C(1)-Al(1)-C(23)	109.3(3)	C(31)-Al(3)-C(4)	
C(16)-Al(1)-C(21)	110.9(3)	C(11)-Al(3)-C(5)	110.34(12)
C(16)-Al(1)-C(23)	116.0(3)	C(11)-Al(3)-C(4)	
C(21)-Al(1)-C(23)	112.6(3)	C(5)-Al(3)-C(4)	115.30(13)
C(11)-Al(3)-C(6)	97.2(2)	C(21)-Al(1)-C(41)	97.03(9)
C(11)-AI(3)-C(27)	105.9(3)	C(21)-AI(1)-C(1)	107.49(1)
C(11)-AI(3)-C(29)	108.5(3)	C(21)-AI(1)-C(2)	
C(6) - AI(3) - C(27)	110.3(3)	C(41) - AI(1) - C(1)	
C(6) - AI(3) - C(29)	116.9(3)	C(41) - AI(1) - C(2)	105 22(0)
C(27) - AI(3) - C(29)	115.8(4)	C(1) = AI(1) = C(2)	105.33(9)
C(1) = AI(2) = C(11)	127.2(3)	C(31) - AI(2) - C(21)	120.09(9)
C(1) = AI(2) = C(25) C(11) = AI(2) = C(25)	113.4(3) 116.0(2)	C(31) - AI(2) - C(3)	110.02(11) 112.46(11)
$\nabla (11) - AI(2) - C(23)$	110.9(5)	C(21) = AI(2) = C(3)	112.40(11)
$\frac{\mathcal{L}[\mathcal{L} Al(2)]}{\mathcal{L}(1) + \mathcal{L}(2) + \mathcal{L}(1)}$	557.5 72 5	Z[ZAI(Z)]	555.2
C(1) - AI(2) - C(10) C(1) - AI(2) - C(6)	05.2		
C(1) = A1(2) = C(0) C(11) = A1(2) = C(6)	95.2 87.5		
C(11) = A1(2) = C(16)	78.9		
C(16) - A1(2) - C(25)	105.4		
C(6) - A1(2) - C(25)	104.0		
$C_{c} / C_{c} (\alpha_{c}) [\text{Fe}(1)]$	40		
$C_5 / C_5 (\alpha_1) [Fe(1)]$	59		
$C_5 [C(6)]/A[(3) (B_1)]$	25.4		
$C_{5} [C(16)]/ Al(1) (B_{2})$	11.1		
$C_5 [C(1)]/A](1) (B_2)$	55.6		
$C_5 [C(1)]/Al(2) (B_4)$	49.5		
$C_5 [C(11)]/Al(3) (B_5)$	66.2		
$C_5 [C(11)]/ Al(2) (\beta_6)$	32.4		
C_5 / C_5 (twist) (τ_1) Fe(1)	39.8		
C_5 / C_5 (twist) (τ_2) Fe(2)	22.8		

[a] See Ref.^[12,13] for the definition of the angles α , β and τ .

(s, CH₃Al) ppm. ¹³C NMR (100.5 MHz, [D₈]toluene, 25 °C): $\delta = -7.3$ [br., CH₃Al] ppm.

4b ($\mathbf{R} = \mathbf{E}\mathbf{t}$): The synthesis was carried out as described for **4a**, starting from **1b** (205 mg, 0.40 mmol) in [D₈]toluene (1 mL) and a solution of Et₃Al (1.0 M in hexane, 2.5 mL, 2.5 mmol). The re-

sulting mixture contained 4b together with Et₃Al, Et₃Al(py) and several unidentified side products (¹H and ¹³C NMR). The brown oil thus obtained was washed with hexane (2 mL), and the orange solid after removal of the hexane was dried in vacuo to give 108 mg of **4b** (about 50%) together with Et₃Al(py) and Et₃Al (¹H and ¹³C NMR). Single orange crystals of 4b for X-ray analysis were grown from a [D₈]toluene solution after 2 d at -24 °C. M.p. 145-150 °C. Data for **4b**: ¹H NMR (399.8 MHz, [D₈]toluene, 23 °C): $\delta = -0.28$ [q, 4 H, CH₂(a)Al], 0.45 [q, 4 H, CH₂(b)Al], 0.87 [q, 2 H, CH₂(c)-All, 0.93 [t, 6 H, CH₃(b)], 1.30 [t, 6 H, CH₃(a)], 1.59 [t, 3 H, $CH_3(c)$], 3.99 (m, 4 H, H⁵), 4.23 (m, 4 H, H²), 4.36 (m, 8 H, H^{3,4}) ppm. ¹H NMR (399.8 MHz, CD₂Cl₂, 23 °C): $\delta = -0.60$ [br., 4 H, CH₂(a)Al], 0.53 [br., 4 H, CH₂(b)Al], 0.80 [q, 2 H, CH₂(c)Al], 0.96 [br., 12 H, CH₃(a), CH₃(b)], 1.44 [t, 3 H, CH₃(c)], 4.35 (m, 4 H, H⁵), 4.40 (m, 4 H, H²), 4.89 (m, 4 H, H⁴), 4.91 (m, 4 H, H³) ppm. Data for Et₃Al(py): ¹H NMR (399.8 MHz, [D₈]toluene, 23 °C): δ = 0.27 (q, 6 H, CH₂Al), 1.32 (t, 9 H, CH₃), 6.52 (m, py-H_{β}), 6.87 (m, py-H_{γ}), 8.17 (m, py-H_{α}) ppm. ¹³C NMR (100.5 MHz, [D₈]toluene, 25 °C): δ = 0.5 [br., CH₂Al], 10.3 (CH₃), 124.8 (py-C₆), 137.5 $(py-C_{\gamma})$, 147.4 $(py-C_{\alpha})$ ppm. Data for Et₃Al: ¹H NMR (399.8 MHz, $[D_8]$ toluene, 23 °C): $\delta = 0.39$ (q, 6 H, CH₂Al), 1.17 (t, 9 H, CH₃) ppm. ¹³C NMR (100.5 MHz, [D₈]toluene, 25 °C): $\delta = 0.6$ (br., CH₂Al), 8.7 (CH₃) ppm.

[Fe(η^5 -C₅H₄)₂]₂Al₃Et₅ (4b) from Bis(µ-ferrocene-1,1'-diyl)bis]ethyl-(*N*-pyridine)aluminum] (2b): To a suspension of 2b (25 mg; 0.039 mmol) in [D₈]toluene (0.5 mL) cooled to -20 °C was added a solution of Et₃Al (1.0 M in hexane, 0.1 mL, 0.1 mmol). This suspension was stirred for 2 h. The resulting solution contained 4b, Et₃Al, Et₃Al(py) and several unidentified side products (¹H and ¹³C NMR).

Reaction of Tris(μ -ferrocene-1,1'-diyl)bis[N-pyridine]aluminum (3) with R₃Al

4a/5a (R = Me): To a suspension of 3 (140 mg, 0.18 mmol) in $[D_8]$ toluene (1.2 mL) cooled to -20 °C was added Me₃Al (2.0 M in hexanes, 1.25 mL, 2.5 mmol). After stirring the reaction mixture for 5 h at ambient temperature, readily volatile materials were removed in vacuo and the remaining oil was dissolved in [D8]toluene (1.5 mL). Solid materials were separated by centrifugation, the supernatant liquid phase was collected and volatile materials were removed in vacuo. The resulting mixture (160 mg) contained 4a together with Me₃Al, Me₃Al(py), FcH and several unidentified side products (¹H and ¹³C NMR). The orange-brown oil thus obtained was washed with hexane (2 mL), the orange solid after removal of the hexane was dried in vacuo to give 98 mg of 4a (about 60%) together with Me₃Al(py) (25%) and 5a (15%) (¹H and ¹³C NMR). Data for 5a: ¹H NMR (399.8 MHz, [D₈]toluene, 23 °C): $\delta = -0.84$ (s, 3 H, CH₃), -0.81 (s, 6 H, 2 CH₃), 4.19 (br. m, 6 H, H^{2,5}), 4.32 (br. m, 6 H, H^{7,10}), 4.49 (br. m, m, 6 H, 6 H, H^{3,4}, H^{8,9}) ppm. ¹H NMR (399.8 MHz, CD₂Cl₂, 23 °C): δ = -1.24 (s, 3 H, CH₃), -1.22 (s, 6 H, 2 CH₃), 4.41 (m, 6 H, H^{2,5}), 4.49 (br. m, 6 H, H^{7,10}), 4.80 (br. m, 6 H, H^{8,9}), 4.83 (br. m, 6 H, H^{3,4}) ppm. Data for Me₃Al(py): ¹H NMR (399.8 MHz, [D₈]toluene, 23 °C): $\delta = -0.35$ (s, CH₃Al), 6.46 (m, py-H_{β}), 6.86 (m, py-H_{γ}), 8.16 (m, py-H_{α}) ppm. ¹H NMR (399.8 MHz, C_6D_6 , 23 °C): $\delta = -0.31$ (s, CH_3Al), 6.35 (m, py- H_β), 6.72 (m, py-H_{γ}), 8.11 (m, py-H_{α}) ppm. ¹³C NMR (100.5 MHz, $[D_8]$ toluene, 25 °C): $\delta = -7.7$ (br., CH₃Al), 124.8 (py-C_{β}), 137.5 (py- C_{γ}), 147.1 (py- C_{α}) ppm.

4b/5b (**R** = **Et**): The synthesis was carried out as described for 4a, starting from 3 (100 mg, 0.13 mmol) in $[D_8]$ toluene (1.2 mL) and a solution of Et₃Al (1.0 M in hexane, 1.31 mL, 1.31 mmol). The orange-brown oil thus obtained was washed with hexane (1.5 mL), and the orange solid after removal of the hexane was dried in vacuo

to give 114 mg of **4b** (about 45%) together with **5b** (7%) and Et₃. Al(py) (47%) (¹H and ¹³C NMR). The solid was washed with hexane (0.5 mL) and dried under high vacuum to leave an orange powder (75 mg), containing about 95% of **4b** together with Et₃Al(py) (¹H NMR). Data for **5b**: ¹H NMR (399.8 MHz, [D₈]toluene, 23 °C): $\delta = -0.25$ (q, 2 H, CH₂Al), -0.16 (q, 4 H, 2 CH₂Al), 0.89 (t, 3 H, CH₃), 0.93 (t, 6 H, 2 CH₃), 4.17 (br. m, 6 H, H^{2.5}), 4.31 (br. m, 6 H, H^{7,10}), 4.48 (m, 6 H, H^{8.9}), 4.49 (m, 6 H, 6 H, H^{3.4}) ppm. ¹H NMR (399.8 MHz, CD₂Cl₂, 23 °C): $\delta = -0.62$ (q, 2 H, CH₂Al), -0.52 (q, 4 H, 2 CH₂Al), 0.48 (t, 3 H, CH₃), 0.56 (t, 6 H, 2 CH₃), 4.41 (m, 6 H, H^{2.5}), 4.48 (br. m, 6 H, H^{7,10}), 4.80 (m, 6 H, H^{8.9}), 4.84 (m, 6 H, H^{3.4}) ppm.

$[Fe(\eta^5\text{-}C_5H_4)_2]_3Al_3R_3$ (5) from $Tris(\mu\text{-}ferrocene\text{-}1,1'\text{-}diyl)bis[\textit{N}\text{-}pyr-idine]aluminum$ (3)

5a (**R** = **Me**): To a suspension of **3** (53 mg, 0.069 mmol) in CD_2Cl_2 (1.5 mL) cooled to -50 °C was added Me₃Al (2.0 M in hexanes, 0.07 mL, 0.14 mmol). After stirring the reaction mixture for 30 min at ambient temperature, readily volatile materials were removed in vacuo, and the remaining oil was dissolved in [D₈]toluene (1.5 mL). Solid materials were separated by centrifugation, and the supernatant liquid phase was collected. The resulting mixture contained **5a** (about 60%, which, in our hands, could not be further purified) together with Me₃Al(py), FcH and several unidentified side products (¹H NMR).

5b (**R** = **Et**):^[7] The synthesis was carried out as described for **5a** (vide supra), starting from **3** (40 mg, 0.052 mmol) in CD₂Cl₂ (1.5 mL) and a solution of Et₃Al (1.0 M in hexane, 0.11 mL, 0.11 mmol). The resulting mixture contained **5b/4b** (\approx 1:2) together with Et₃Al(py) and FcH (¹H NMR).

$[Fe(\eta^{5}\text{-}C_{5}H_{4})_{2}]_{3}Al_{3}R_{3}$ (5) from 4 and 3

5a (**R** = **Me**): A mixture containing **4a**/[Me₃Al(py),Me₃Al] (80 mg; from **3** and Me₃Al, vide supra) was dissolved in [D₈]toluene (2 mL) and **3** (38 mg, 0.050 mmol) was added; this suspension was stirred for 20 h. After centrifugation from **3**, the supernatant liquid phase was decanted and volatile materials were evaporated. The residue was washed with hexane to leave an orange-red solid (95 mg) containing about 70% of **5a** [together with Me₃Al(py), ferrocene and several unidentified side products. ¹H NMR].

5b (**R** = **Et**): The synthesis was carried out as described for **5a**, starting from a mixture containing **4b**/Et₃Al(py) (104 mg; from **3** and Et₃Al, vide supra) in [D₈]toluene (2 mL) and **3** (36 mg, 0.047 mmol). The orange-brown oil thus obtained was washed with hexane (1.5 mL), and the orange solid obtained after removal of the hexane was dried in vacuo to give 94 mg of **5b**^[7] (\approx 80%) together with Et₃Al(py), ferrocene and several unidentified side products (¹H NMR).

Dilithium 1,1'-Bis[triethyl(ferrocenyl)]alanate (6b) and Lithium Tetra(ethyl)alanate: To a mixture containing 4b/Et₃Al(py) (223 mg, vide supra) dissolved in [D₈]toluene (1 mL) cooled to -50 °C was added LiEt (0.5 m in benzene/cyclohexane, 90:10; 2.25 mL; 1.13 mmol]. The mixture was warmed to room temperature, stirred for 1 h and the volatile materials were then removed in vacuo. The remaining solid was dissolved in [D₈]toluene (0.5 mL), and a layer of brown-black oil was formed at the bottom. The oil after removal of [D₈]toluene was dissolved in pyridine (0.3 mL) at 5 °C. Then, [D₈]toluene (0.1 mL) was added. The solution thus obtained contained **6b**(*x* py) and Li(*x* py)AlEt₄. Data for **6b** (*x* py; $x \ge 8$): ¹H NMR (500.1 MHz, [D₈]toluene, 23 °C): $\delta = 0.39$ (br. q, 8 H, CH₂Al), 1.70 (br. t, 12 H, CH₃), 4.49 (br. m, 8 H, H^{2.3,4,5}), 6.90 (m, py-H_β), 7.25 (m, py-H_γ), 8.42 (m, py-H_a) ppm. ²⁷Al{¹H} NMR (130.3 MHz, [D₈]toluene, 23 °C): $\delta = 165$ ($h_{1/2} \approx 1000$ Hz) ppm.



Data for LiAlEt₄ (*x* py; $x \ge 4$): ¹H NMR (500.1 MHz, [D₈]toluene, 23 °C): $\delta = 0.39$ (br. q, 8 H, CH₂Al), 1.44 (br. t, 12 H, CH₃), 6.90 (m, py-H_β), 7.25 (m, py-H_γ), 8.42 (m, py-H_a) ppm. ¹³C NMR (125.8 MHz, [D₈]toluene, 23 °C): $\delta = 3.3 [{}^{1}J({}^{27}Al, {}^{13}C) = 73$ Hz, AlCH₂], 12.0 (CH₃), 124.3 (py-C_β), 136.7 (py-C_γ), 149.8 (py-C_a) ppm. ²⁷Al{}¹H} NMR (130.3 MHz, [D₈]toluene, 23 °C): $\delta = 169$ ($h_{1/2} = 12$ Hz) ppm.

1,1-Bis{1-[1'-dialkyl(pyridine)aluminum]ferrocenyl}-1-alkylaluminum Pyridine Adduct (7)

7a (Alkyl = Me): Pyridine (0.04 mL, ≈5 equiv.) was added to a reaction mixture containing **4a**/Me₃Al(py) (50 mg, from **3** and Me₃Al) in [D₈]toluene at 0 °C. The solution was stirred for 0.5 h. The resulting mixture contained about 80% of **7a** together with Me₃Al(py), FcH, FcAlMe₂(py) and several unidentified side products (¹H and ¹³C NMR). Product **7a** decomposes at room temperature to give **1a** (≈60% after 1 d), FcAlMe₂(py) and FcH. Data for **7a**: ¹H NMR (399.8 MHz, [D₈]toluene, 23 °C): δ = −0.13 (t, 12 H, CH₃), 0.17 (t, 3 H, CH₃), 4.27 (m, 4 H, H^{7,10}), 4.45 (m, 4 H, H^{2,5}), 4.64 (m, 4 H, H^{8,9}), 4.69 (m, 4 H, H^{3.4}), 6.79 (m, py-H_β), 7.12 (m, py-H_γ), 8.51 (m, py-H_α) ppm. ¹H NMR (399.8 MHz, C₆D₆, 23 °C): δ = −0.11 (t, 12 H, CH₃), 0.19 (t, 3 H, CH₃), 4.30 (m, 4 H, H^{7,10}), 4.48 (m, 4 H, H^{2.5}), 4.68 (m, 4 H, H^{8,9}), 4.72 (m, 4 H, H^{3.4}), 6.70 (m, py-H_β), 7.03 (m, py-H_γ), 8.52 (m, py-H_α) ppm.

7b (Alkyl = Et): The procedure was analogous to that described for **7a**, starting from a mixture containing **4b**/Et₃Al(py) (55 mg, from **1b** and Et₃Al) and pyridine (0.04 mL). The resulting mixture contained about 80% of **7b** together with Et₃Al(py) (¹H and ¹³C

Table 4. Crystallographic data of dialuma[1.1]ferrocenophane 4b.

	4b
Formula	C ₃₀ H ₄₁ Al ₃ Fe ₂
Crystal	red-orange prism
Dimensions [mm]	$0.28 \times 0.22 \times 0.18$
Crystal system	triclinic
Space group	$P\overline{1}$
a [pm]	1042.1(2)
b [pm]	1104.6(2)
c [pm]	1370.6(3)
a [°]	75.11(3)
β [°]	73.44(3)
γ [°]	77.90(3)
Z	2
$\mu [{ m mm}^{-1}]$	1.112
Measuring range (θ) [°]	1.9-26.0
Reflections collected	9976
Independent reflections $[I > 2\sigma(I)]$	5191
Absorption correction	none ^[a]
Refined parameters	316
$wR_2/R_1 [I > 2\sigma(I)]$	0.175/0.066
Max./min. res. e^- dens. $[10^{-6} \times e \text{ pm}^{-3}]$	0.879 / -0.445

[a] Absorption correction did not improve the data set.

NMR). Product **7b** decomposes slowly at room temperature to give **1b** (\approx 70% after 5 d), FcAlEt₂(py) and FcH. Data for **7b**: ¹H NMR (399.8 MHz, [D₈]toluene, 23 °C): δ = 0.54 (q, 8 H, CH₂Al), 0.81 (q, 2 H, CH₂Al), 1.45 (t, 12 H, CH₃), 1.56 (t, 3 H, CH₃), 4.29 (m, 4 H, H^{7,10}), 4.50 (m, 4 H, H^{2,5}), 4.63 (m, 4 H, H^{8,9}), 4.72 (m, 4 H, H^{3,4}), 6.73 (m, py-H_β), 7.08 (m, py-H_γ), 8.48 (m, py-H_α) ppm.

Crystal Structure Determination of Complex 4b: Data were collected with a STOE IPDS I diffractometer with graphite monochromated Mo- K_{α} ($\lambda = 71.073$ pm) radiation. All other details pertinent to the crystal structure determinations are listed in Table 4.^[14] A crystal of appropriate size was sealed under an atmosphere of argon in a Lindemann capillary. The data collection was carried out at 293 K.

Supporting Information (see footnote on the first page of this article): ¹H NMR spectrum of **4a** is given.

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- B. Wrackmeyer, E. V. Klimkina, W. Milius, *Eur. J. Inorg. Chem.* 2009, 3155–3162, preceding publication.
- [2] A. Althoff, P. Jutzi, N. Lenze, B. Neumann, A. Stammler, H.-G. Stammler, *Organometallics* 2002, 21, 3018–3022.
- [3] A. Althoff, P. Jutzi, N. Lenze, B. Neumann, A. Stammler, H.-G. Stammler, *Organometallics* 2003, 22, 2766–2774.
- [4] P. Jutzi, N. Lenze, B. Neumann, H.-G. Stammler, Angew. Chem. 2001, 113, 1469–1473; Angew. Chem. Int. Ed. 2001, 40, 1424–1427.
- [5] A. Althoff, D. Eisner, P. Jutzi, N. Lenze, B. Neumann, W. W. Schoeller, H.-G. Stammler, *Chem. Eur. J.* 2006, 12, 5471–5480.
- [6] H. Braunschweig, G. K. B. Clentsmith, S. Hess, T. Kupfer, K. Radacki, *Inorg. Chim. Acta* 2007, 360, 1274–1277.
- [7] H. Braunschweig, C. Burschka, G. K. B. Clentsmith, T. Kupfer, K. Radacki, *Inorg. Chem.* 2005, 44, 4906–4908.
- [8] B. Wrackmeyer, E. V. Klimkina, T. Ackermann, W. Milius, Inorg. Chem. Commun. 2007, 10, 743–747.
- [9] K. Stott, J. Keeler, Q. N. Van, A. J. Shaka, J. Magn. Reson. 1997, 125, 302–324.
- [10] T. Parella, J. Magn. Reson. 2004, 167, 266-272.
- [11] A. E. Derome, Modern NMR Techniques for Chemistry Research, Pergamon, Oxford, 1987, pp. 188–190.
- [12] M. Herberhold, Angew. Chem. 1995, 107, 1985–1987; Angew. Chem. Int. Ed. Engl. 1995, 34, 1837–1839.
- [13] B. Wrackmeyer, E. V. Klimkina, H. E. Maisel, O. L. Tok, M. Herberhold, *Magn. Reson. Chem.* 2008, 46, S30–S35.
- [14] CCDC-723413 [for 4b at 293 K] 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.

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