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

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Keywords: Metallocenes / Aluminum / NMR spectroscopy / Structure elucidation / Cyclophanes

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 $[Fe(\eta^5\text{-}C_5H_4)_2]_2Al_3Et_5$ was characterized by X-ray structural analysis.

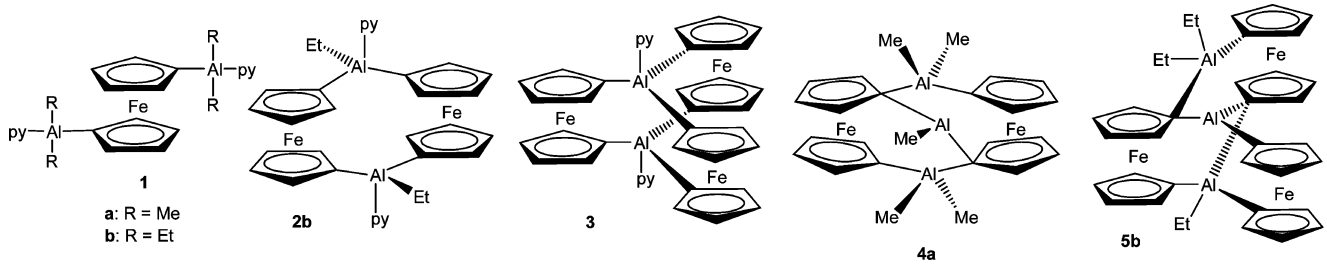
Introduction

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 X-ray 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 $AlMe_3$ or $AlEt_3$ can play this role.

Results and Discussion

We studied the reactivity of starting materials **1**–**3**[1] towards $AlMe_3$ and $AlEt_3$, respectively, in order to form the pyridine adducts $AlR_3(py)$ 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]

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

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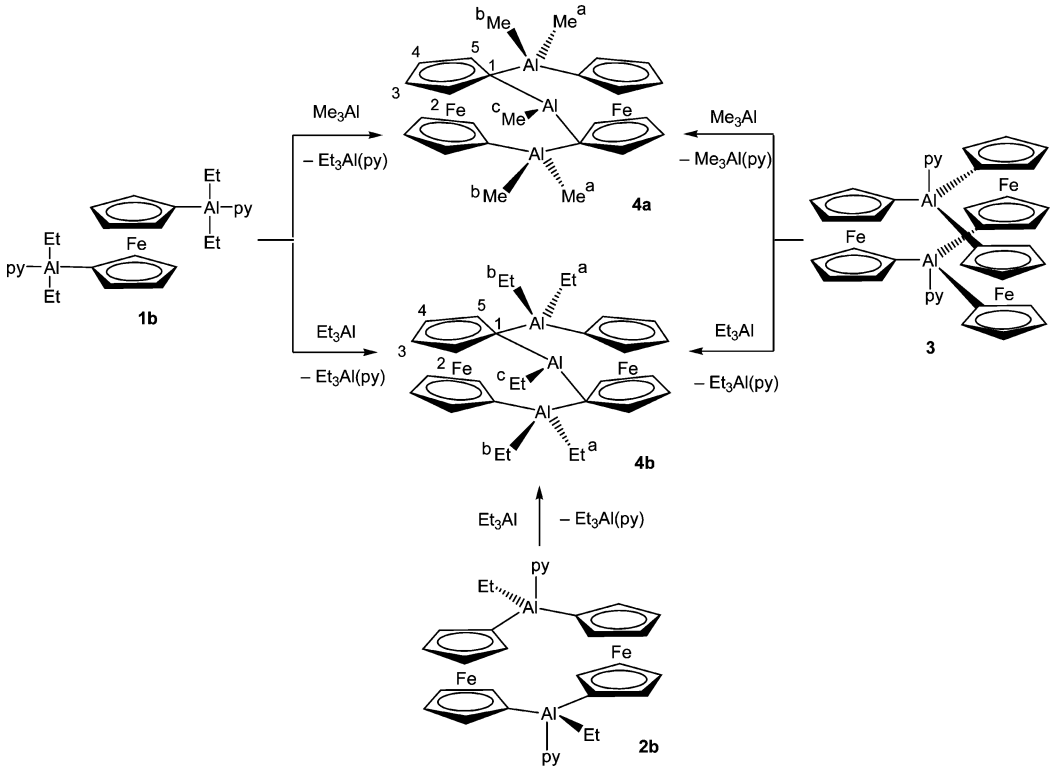


Scheme 2. Three different routes to the dinuclear, threefold-aluminum-bridged ferrocenophane of type **4**, of which **4a** has been isolated previously by treatment of $AlMe_2Cl$ with 1,1′-dilithioferrocene.[6]

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 ^1H–^1H 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. ^{13}C NMR spectroscopic data[a,b,c] of compounds **4** and **5**.

	4a R = Me [D_8]toluene	C_6D_6[d]	CD_2Cl_2	**4b** R = Et [D_8]toluene	CD_2Cl_2		**5a** R = Me [D_8]toluene	CD_2Cl_2	**5b** R = Et [D_8]toluene	CD_2Cl_2
δ^{13}C(fc-C^1)	56.6 [br.]	56.9 [br.]	56.6 [br.]	55.8 [br.]	55.8 [br.]	δ^{13}C(fc-C^1)	58.5 [br.]	58.9 [br.]	56.8 [br.]	n.o.
						δ^{13}C(fc-C^6)	86.0 [br.]	86.0 [br.]	85.7 [br.]	
δ^{13}C(fc-C^2)	82.0	82.5	82.0	81.7	81.7	δ^{13}C(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	δ^{13}C(fc-C^{7,10})	80.0 (br.)	79.9 (br.)	79.9 (br.)	79.8 (br.)
δ^{13}C(fc-C^3)	78.5	78.9	78.9	78.4	78.7	δ^{13}C(fc-C^{3,4})	76.1 (br.)	76.5 (br.)	76.2 (br.)	76.4 (br.)
δ^{13}C(fc-C^4)	77.4	77.9	78.0	77.4	77.8	δ^{13}C(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–^{13}C gHSQC[10] experiments. [b] [br.] denotes broad ^{13}C resonances of aluminum-bonded atoms; (br.) denotes broad ^{13}C resonances due to dynamic effects. [c] n.o. = not observed. [d] NMR spectroscopic data from ref.[6] ^{13}C NMR (75.46 MHz, C_6D_6): δ = –8.0, –4.8, –2.8, 68.2, 77.5, 82.0, 82.3 ppm. ^1H NMR (300.13 MHz, C_6D_6): 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**.

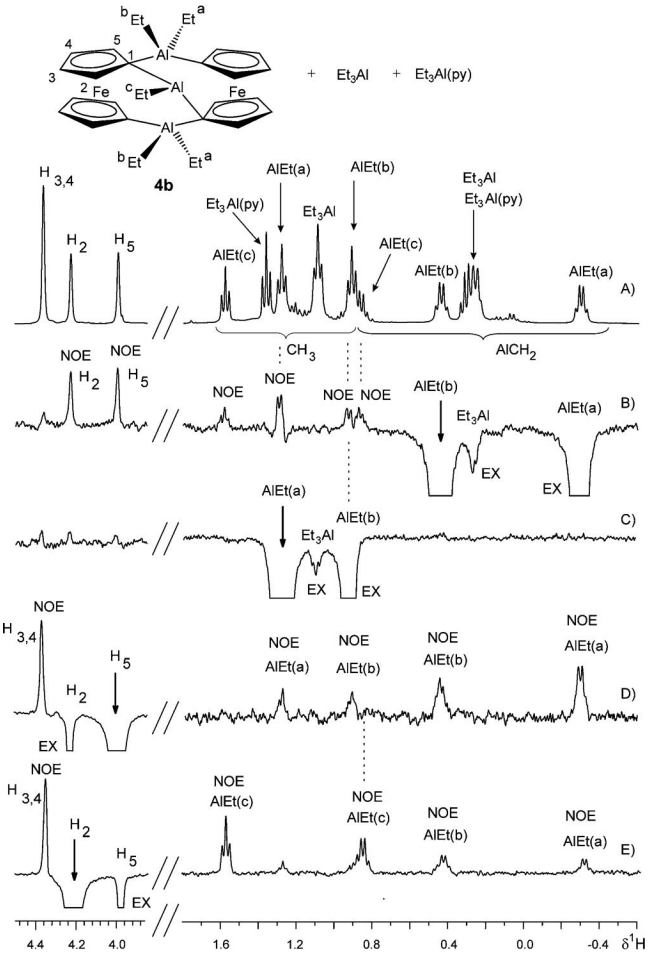


Figure 1. 399.8 MHz $^1H\{^1H\}$ NOE difference spectra (gradient enhanced[9]) of the reaction mixture containing **4b**, $AlEt_3$ and $Et_3Al(py)$ (in $[D_8]$toluene at 23 °C, relaxation delay 2.0 s, mixing time 0.6 s). The irradiated resonance signals (arrows) give rise to intensities (NOE or Exchange) as indicated. (A) Normal ^1H NMR spectrum. (B) Irradiation of $^1H[AlCH_2(b)]$; response: magnetization transfer[11] between $AlCH_2$ groups of AlEt(a), AlEt(b) and $AlEt_3$, whereas NOE is observed for $^1H(AlCH_2)$ of AlEt(c), ^1H(Me) of AlEt(b), AlEt(a) and AlEt(c) groups, and (fc)$^1H^5$ and (fc)$^1H^2$. (C) Irradiation of ^1H(Me) of AlEt(a); response: magnetization transfer between Me of AlEt(a), AlEt(b) and $AlEt_3$. (D) Irradiation of (fc) $^1H^5$; response: magnetization transfer between (fc)$^1H^5$ and (fc)$^1H^2$, whereas NOE is observed for (fc)$^1H^{3,4}$, $^1H(AlCH_2)$ and ^1H(Me) of AlEt(a) and AlEt(b). (E) Irradiation of (fc)$^1H^2$; response: magnetization transfer between (fc)$^1H^5$ and (fc)$^1H^2$, whereas NOE is observed for (fc)$^1H^{3,4}$, $^1H(AlCH_2)$ and ^1H(Me) of AlEt(c), and for $^1H(AlCH_2)$ of AlEt(a) and AlEt(b).

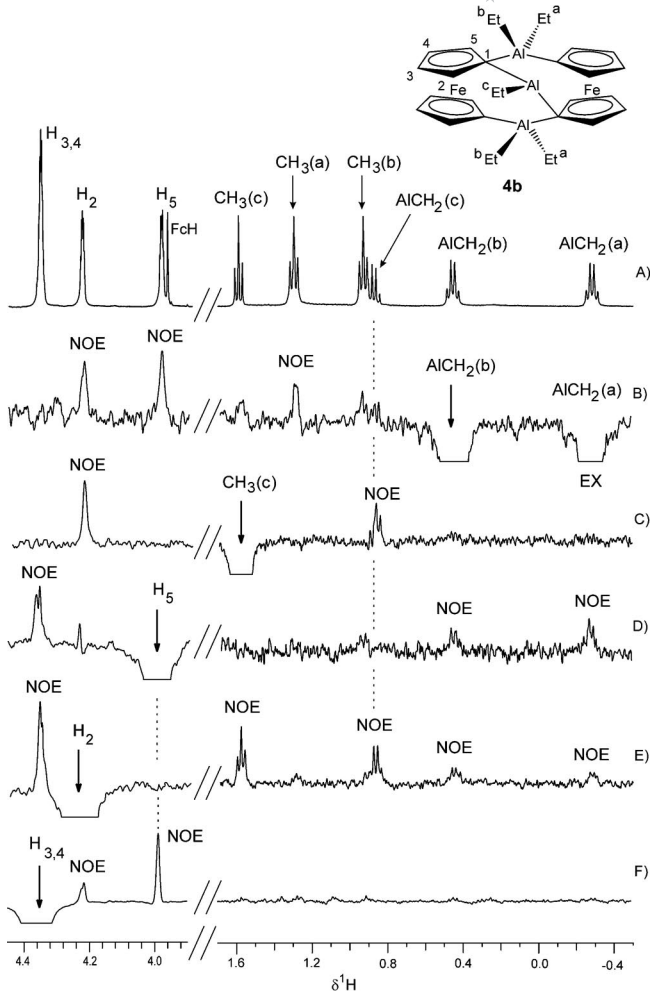
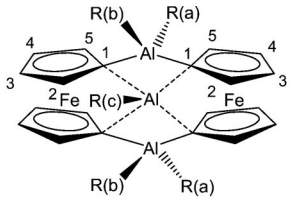


Figure 2. 399.8 MHz $^1H\{^1H\}$ NOE difference spectra (gradient enhanced[9]) of **4b** (in $[D_8]$toluene at 23 °C, relaxation delay 2.0 s, mixing time 0.6 s). The irradiated resonance signals (arrows) give rise to the indicated respective intensities (NOE or Exchange). (A) Normal ^1H NMR spectrum. (B) Irradiation of $^1H[AlCH_2(a)]$: response: magnetization transfer[11] between $AlCH_2(a)$ and $AlCH_2(b)$, whereas NOE is observed for (fc)$^1H^5$ and (fc)$^1H^2$, and ^1H(Me) of AlEt(a). (C) Irradiation of ^1H(Me) of AlEt(c); response: (fc)$^1H^2$, $^1H(AlCH_2)$ of AlEt(c). (D) Irradiation of (fc)$^1H^5$; response: (fc) $^1H^{3,4}$, and weaker for $^1H(AlCH_2)$ of the AlEt(a) and AlEt(b). (E) Irradiation of (fc)$^1H^2$; response: $^1H^{3,4}$ and ^1H(Me) and $^1H(AlCH_2)$ of AlEt(c), and weaker for $^1H(AlCH_2)$ of AlEt(a) and AlEt(b). (F) Irradiation of (fc)$^1H^{3,4}$; response: (fc)$^1H^5$ and (fc)$^1H^2$.

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

Broad ^{13}C NMR signals are expected for ^{13}C nuclei linked to aluminum owing to partially relaxed scalar ^{27}Al–^{13}C 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 ^{13}C(fc)–Al NMR signal. This is in the region typical of bridging Al–C(fc)–Al 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**.



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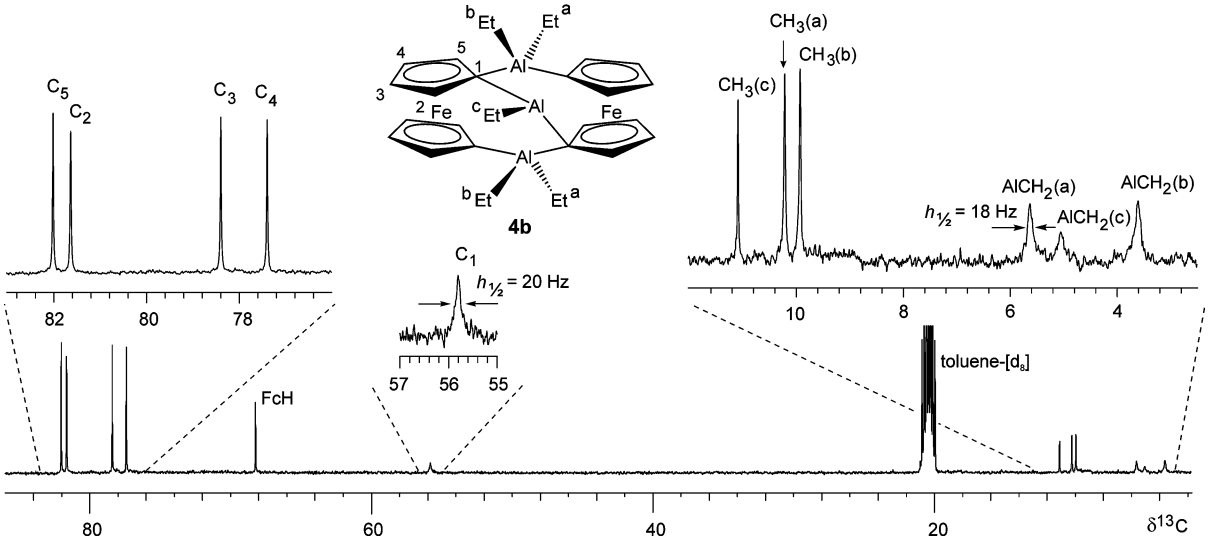


Figure 3. 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum of **4b** (in [D_8]toluene at 23 °C). Note the broad ^{13}C(Al) NMR signals; there are three for ^{13}C(Et)Al and only one ^{13}C(fc)Al.

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[$AlEt_4$] follows conclusively from the NMR spectra (see Table 2), in particular from ^{27}Al 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.

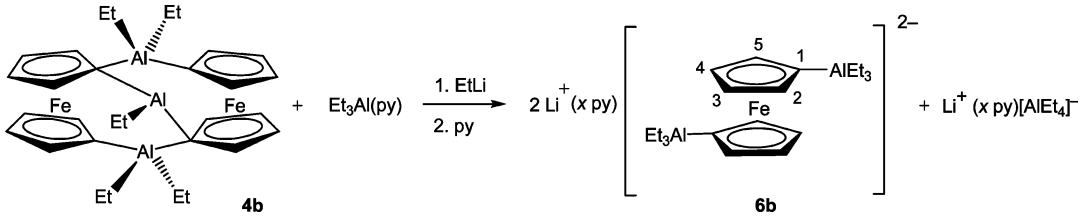
When the reactions of **3** with AlR_3 (Scheme 2) were carefully monitored by using ^1H and ^{13}C NMR spectroscopy, the intermediate formation of another species was observed. These intermediates are most likely compounds **5**[7] (NMR spectroscopic data of **5a**,**b** are included in Table 1), and we propose Scheme 5 to explain their formation. Thus, AlR_3 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** 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.

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

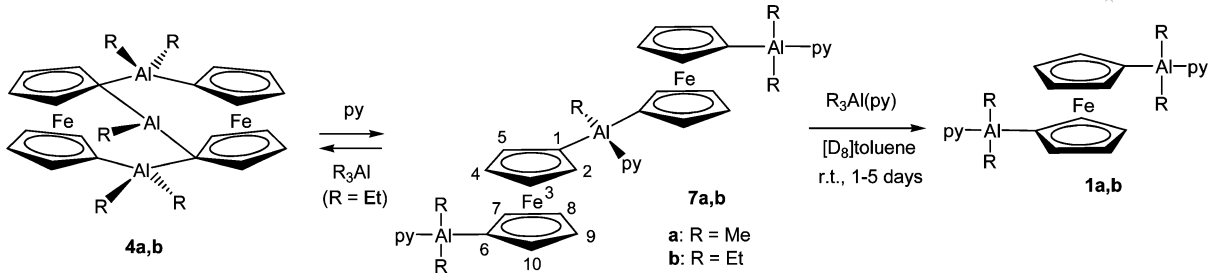
	6b[d] R = Et [D_8]toluene, py	**7a** R = Me [D_8]toluene	**7b** R = Et [D_8]toluene
δ^{13}C(fc-C^1)	n.o.	72.3 [br.]	71.8 [br.]
δ^{13}C(fc-C^6)		73.2 [br.]	72.6 [br.]
δ^{13}C(fc-C^{2,5})	76.3 (br.)	76.2	76.5
δ^{13}C(fc-C^{3,4})	72.2 (br.)	71.0	71.0
δ^{13}C(fc-C^{7,10})	–	76.1	76.3
δ^{13}C(fc-C^{8,9})	–	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
δ^{13}C(py)	124.3 (C_β)	123.8 (C_β)	124.1 (C_β)
	136.8 (C_γ)	137.5 (C_γ)	136.6 (C_γ)
	149.8 (C_α)	150.1 (C_α)	149.2 (C_α)

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

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 AlR_3.

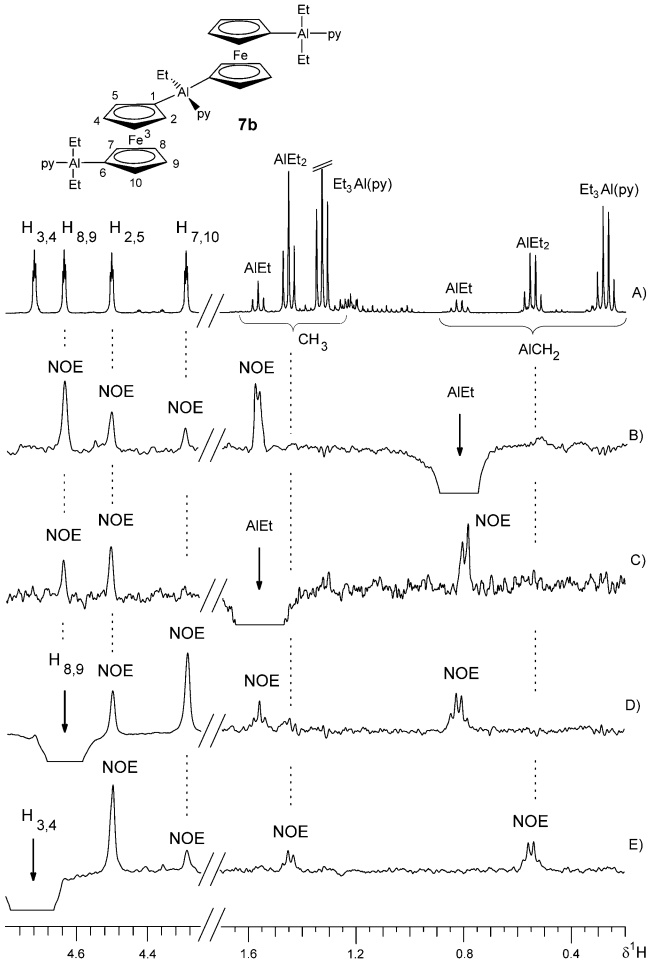
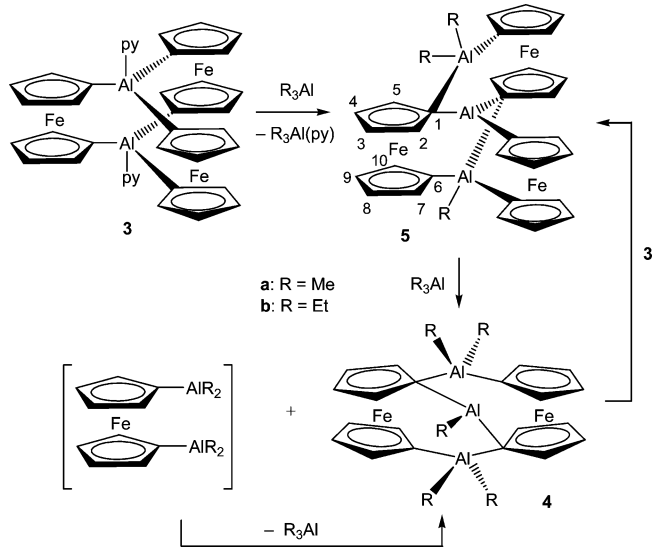


Figure 4. Parts of the 399.8 MHz $^1H\{^1H\}$ NOE difference spectra (gradient enhanced[9]) of a reaction mixture, in which **4b** was converted into **7b** with $Et_3Al(py)$ (in $[D_8]$toluene at 23 °C, relaxation delay 1.0 s, mixing time 0.4 s). The irradiated transitions (arrows) gave rise to intensities (NOE) as indicated. (A) Normal ^1H NMR spectrum. (B) Irradiation of $AlCH_2$ 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: $^1H(AlCH_2)$ 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 $^1H(AlCH_2)$ of AlEt. (E) Irradiation of (fc)$^1H^{3,4}$; response: (fc)$^1H^{7,10}$, (fc)$^1H^{2,5}$, and ^1H(Me) and $^1H(AlCH_2)$ of $AlEt_2$.

their peculiar somewhat broad features were striking. An example is shown for the ^{13}C NMR spectra in Figure 5, which also shows the inverse ^1H–^{13}C 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 AlR_3.

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 ^{13}C 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 ^{13}C(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.

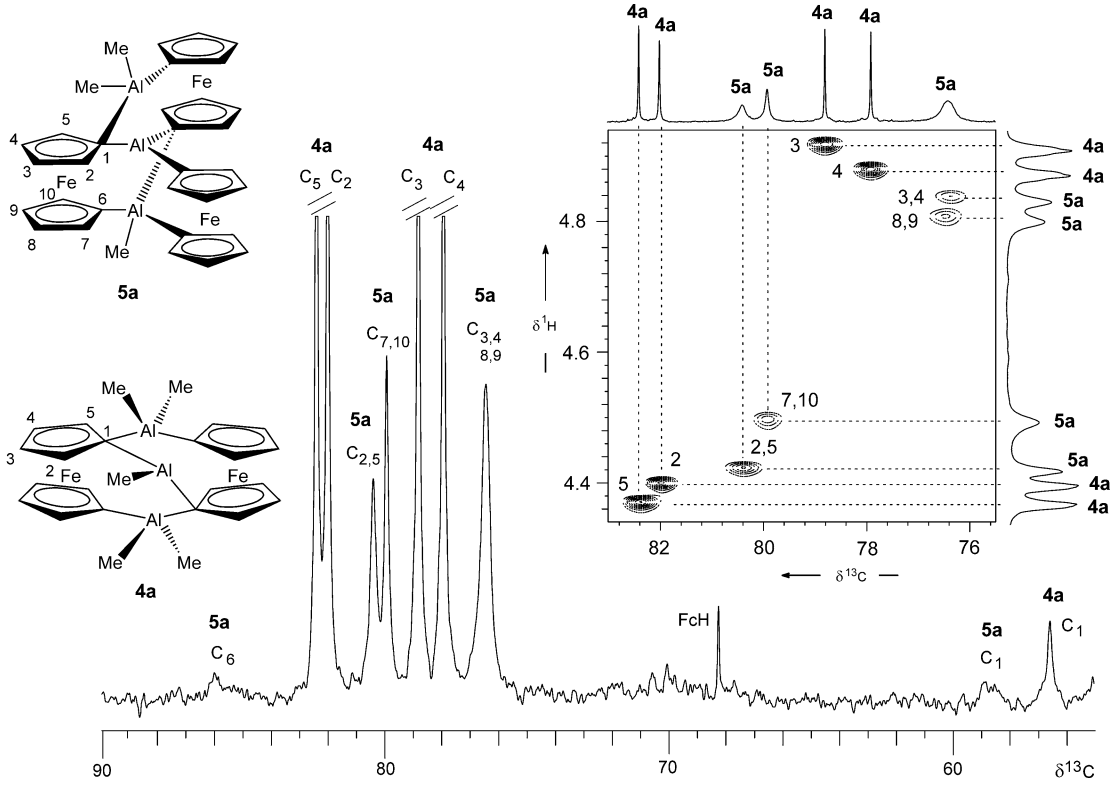
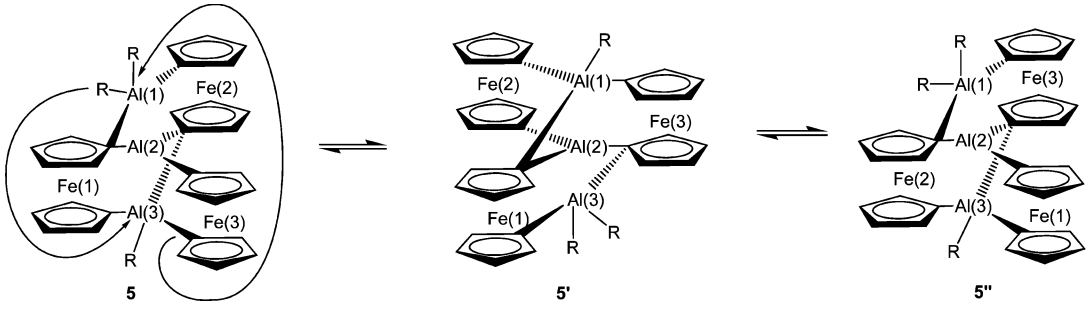


Figure 5. 100.5 MHz $^{13}C\{^1H\}$ NMR spectrum and contour plot of part of the 400 MHz 2D ^1H–^{13}C-correlated spectrum [recorded by the gradient-selected (gs-)HSQC method[10]] of a mixture **4a/5a** (in CD_2Cl_2 at 23 °C).



Scheme 6. Dynamic processes in **5**. The exchange of the R groups and of the ferrocenediyl 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 $AlEt_2$ units are linked unsymmetrically to the ferrocenediyl groups. The surroundings of the central aluminum atom appears to be close to trigonal planar {Σ[∠Al(2)] = 357.5°}, 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 τ[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 Me_3Al (2.0 M in hexanes), Et_3Al (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

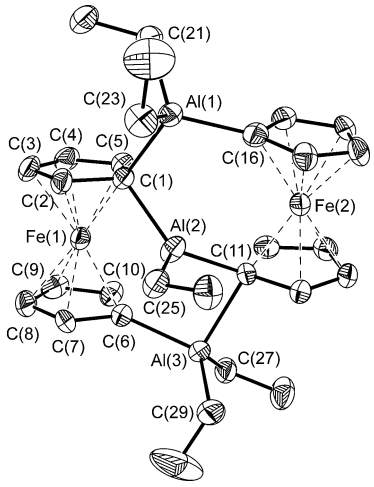


Figure 6. Molecular structure of **4b** (ORTEP plot, 30% probabilities; hydrogen atoms are omitted for clarity); see Table 3 for structural parameters. The methyl carbon of the ethyl group [C(23)–C(24)] is statistically disordered. (The relatively large space requirement of the disordered methyl carbon 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 Å^3 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 $(CpFeC_5H_4)_2$ was observed. NMR measurements: Varian INOVA 400: ^{1}H, ^{13}C, ^{27}Al NMR; Bruker DRX 500: ^{1}H, ^{13}C, ^{27}Al NMR; chemical shifts are given with respect to $SiMe_4$ [δ^1H ($CHDCl_2$) = 5.31 ppm, δ^1H ($C_6D_5CD_2H$) = 2.08 ppm; δ^{13}C (CD_2Cl_2) = 53.8 ppm, $\delta^{13}C(C_6D_5CD_3)$ = 20.4 ppm]; external 1.1 M $Al(NO_3)_3$ in D_2O [δ^{27}Al = 0 ppm for $\Xi(^{27}Al)$ = 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 (R = Me): To a solution of the dipyridine adduct of 1,1′-bis(diethylalanyl)ferrocene (**1b**; 200 mg, 0.39 mmol) in [D_8]toluene (1 mL) cooled to –40 °C was added Me_3Al (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 Me_3Al, Me_3Al(py), Et_3Al(py) and several unidentified side products (^{1}H and ^{13}C 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 Me_3Al(py) and several unidentified side products). Data for **4a**: ^{1}H NMR (399.8 MHz, [D_8]toluene, 23 °C): δ = –0.88 [s, 6 H, CH_3(a)Al], –0.25 [s, 6 H, CH_3(b)Al], 0.21 [s, 3 H, CH_3(c)Al], 4.02 (m, 4 H, H^5), 4.16 (m, 4 H, H^2), 4.36 (m, 8 H, H^{3,4}) ppm. ^{1}H NMR (399.8 MHz, C_6D_6, 23 °C): δ = –0.78 [s, 6 H, CH_3(a)Al], –0.16 [s, 6 H, CH_3(b)Al], 0.29 [s, 3 H, CH_3(c)Al], 4.08 (m, 4 H, H^5), 4.21 (m, 4 H, H^2), 4.36 (m, 8 H, H^{3,4}) ppm. ^{1}H NMR (399.8 MHz, CD_2Cl_2, 23 °C): δ = –1.29 [br. s, 6 H, CH_3(a)Al], –0.65 [br. s, 6 H, CH_3(b)Al], 0.07 [s, 3 H, CH_3(c)Al], 4.36 (m, 4 H, H^5), 4.40 (m, 4 H, H^2), 4.87 (m, 4 H, H^4), 4.91 (m, 4 H, H^3) ppm. Data for Me_3Al: ^{1}H NMR (399.8 MHz, [D_8]toluene, 23 °C): δ = –0.40 (s, CH_3Al) ppm. ^{13}C NMR (100.5 MHz, [D_8]toluene, 25 °C): δ = –7.3 [br., CH_3Al] ppm.

4b (R = Et): The synthesis was carried out as described for **4a**, starting from **1b** (205 mg, 0.40 mmol) in [D_8]toluene (1 mL) and a solution of Et_3Al (1.0 M in hexane, 2.5 mL, 2.5 mmol). The re-

Table 3. Selected bond lengths [pm] and angles [°][a] of ferrocenophanes **4b** and **4a**[6] for comparison.

	4b		**4a**
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)–Al(3)–C(27)	105.9(3)	C(21)–Al(1)–C(1)	107.49(1)
C(11)–Al(3)–C(29)	108.5(3)	C(21)–Al(1)–C(2)	
C(6)–Al(3)–C(27)	110.3(3)	C(41)–Al(1)–C(1)	
C(6)–Al(3)–C(29)	116.9(3)	C(41)–Al(1)–C(2)	
C(27)–Al(3)–C(29)	115.8(4)	C(1)–Al(1)–C(2)	105.33(9)
C(1)–Al(2)–C(11)	127.2(3)	C(31)–Al(2)–C(21)	126.09(9)
C(1)–Al(2)–C(25)	113.4(3)	C(31)–Al(2)–C(3)	116.62(11)
C(11)–Al(2)–C(25)	116.9(3)	C(21)–Al(2)–C(3)	112.46(11)
Σ[∠Al(2)]	357.5	Σ[∠Al(2)]	355.2
C(1)–Al(2)–C(16)	73.5		
C(1)–Al(2)–C(6)	95.2		
C(11)–Al(2)–C(6)	87.5		
C(11)–Al(2)–C(16)	78.9		
C(16)–Al(2)–C(25)	105.4		
C(6)–Al(2)–C(25)	104.0		
C_5 / C_5 (α_1) [Fe(1)]	4.0		
C_5 / C_5 (α_2) [Fe(2)]	5.9		
C_5 [C(6)]/ Al(3) (β_1)	25.4		
C_5 [C(16)]/ Al(1) (β_2)	11.1		
C_5 [C(1)]/ Al(1) (β_3)	55.6		
C_5 [C(1)]/ Al(2) (β_4)	49.5		
C_5 [C(11)]/ Al(3) (β_5)	66.2		
C_5 [C(11)]/ Al(2) (β_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.

sulting mixture contained **4b** together with Et_3Al, Et_3Al(py) and several unidentified side products (^1H and ^{13}C 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 Et_3Al(py) and Et_3Al (^1H and ^{13}C NMR). Single orange crystals of **4b** for X-ray analysis were grown from a [D_8]toluene solution after 2 d at –24 °C. M.p. 145–150 °C. Data for **4b**: ^1H NMR (399.8 MHz, [D_8]toluene, 23 °C): δ = –0.28 [q, 4 H, CH_2(a)Al], 0.45 [q, 4 H, CH_2(b)Al], 0.87 [q, 2 H, CH_2(c)-Al], 0.93 [t, 6 H, CH_3(b)], 1.30 [t, 6 H, CH_3(a)], 1.59 [t, 3 H, CH_3(c)], 3.99 (m, 4 H, H^5), 4.23 (m, 4 H, H^2), 4.36 (m, 8 H, $H^{3,4}$) ppm. ^1H NMR (399.8 MHz, CD_2Cl_2, 23 °C): δ = –0.60 [br., 4 H, CH_2(a)Al], 0.53 [br., 4 H, CH_2(b)Al], 0.80 [q, 2 H, CH_2(c)Al], 0.96 [br., 12 H, CH_3(a), CH_3(b)], 1.44 [t, 3 H, CH_3(c)], 4.35 (m, 4 H, H^5), 4.40 (m, 4 H, H^2), 4.89 (m, 4 H, H^4), 4.91 (m, 4 H, H^3) ppm. Data for Et_3Al(py): ^1H NMR (399.8 MHz, [D_8]toluene, 23 °C): δ = 0.27 (q, 6 H, CH_2Al), 1.32 (t, 9 H, CH_3), 6.52 (m, py-H_β), 6.87 (m, py-H_γ), 8.17 (m, py-H_α) ppm. ^{13}C NMR (100.5 MHz, [D_8]toluene, 25 °C): δ = 0.5 [br., CH_2Al], 10.3 (CH_3), 124.8 (py-C_β), 137.5 (py-C_γ), 147.4 (py-C_α) ppm. Data for Et_3Al: ^1H NMR (399.8 MHz, [D_8]toluene, 23 °C): δ = 0.39 (q, 6 H, CH_2Al), 1.17 (t, 9 H, CH_3) ppm. ^{13}C NMR (100.5 MHz, [D_8]toluene, 25 °C): δ = 0.6 (br., CH_2Al), 8.7 (CH_3) ppm.

[Fe(η^5-C_5H_4)$_2$]$_2$$Al_3Et_5$ (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 [D_8]toluene (0.5 mL) cooled to –20 °C was added a solution of Et_3Al (1.0 M in hexane, 0.1 mL, 0.1 mmol). This suspension was stirred for 2 h. The resulting solution contained **4b**, Et_3Al, Et_3Al(py) and several unidentified side products (^1H and ^{13}C NMR).

Reaction of Tris(μ-ferrocene-1,1′-diyl)bis[*N*-pyridine]aluminum (3) with R_3Al

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 Me_3Al (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 [D_8]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 Me_3Al, Me_3Al(py), FcH and several unidentified side products (^1H and ^{13}C 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 Me_3Al(py) (25%) and **5a** (15%) (^1H and ^{13}C NMR). Data for **5a**: ^1H NMR (399.8 MHz, [D_8]toluene, 23 °C): δ = –0.84 (s, 3 H, CH_3), –0.81 (s, 6 H, 2 CH_3), 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, CD_2Cl_2, 23 °C): δ = –1.24 (s, 3 H, CH_3), –1.22 (s, 6 H, 2 CH_3), 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 Me_3Al(py): ^1H NMR (399.8 MHz, [D_8]toluene, 23 °C): δ = –0.35 (s, CH_3Al), 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): δ = –0.31 (s, CH_3Al), 6.35 (m, py-H_β), 6.72 (m, py-H_γ), 8.11 (m, py-H_α) ppm. ^{13}C NMR (100.5 MHz, [D_8]toluene, 25 °C): δ = –7.7 (br., CH_3Al), 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 Et_3Al (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 Et_3Al(py) (47%) (^1H and ^{13}C 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 Et_3Al(py) (^1H NMR). Data for **5b**: ^1H NMR (399.8 MHz, [D_8]toluene, 23 °C): δ = –0.25 (q, 2 H, CH_2Al), –0.16 (q, 4 H, 2 CH_2Al), 0.89 (t, 3 H, CH_3), 0.93 (t, 6 H, 2 CH_3), 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, CD_2Cl_2, 23 °C): δ = –0.62 (q, 2 H, CH_2Al), –0.52 (q, 4 H, 2 CH_2Al), 0.48 (t, 3 H, CH_3), 0.56 (t, 6 H, 2 CH_3), 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(η^5-C_5H_4)$_2$]$_3$$Al_3R_3$ (5) from Tris(μ-ferrocene-1,1′-diyl)bis[*N*-pyridine]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 Me_3Al (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 [D_8]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 Me_3Al(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 CD_2Cl_2 (1.5 mL) and a solution of Et_3Al (1.0 M in hexane, 0.11 mL, 0.11 mmol). The resulting mixture contained **5b/4b** (≈1:2) together with Et_3Al(py) and FcH (^1H NMR).

[Fe(η^5-C_5H_4)$_2$]$_3$$Al_3R_3$ (5) from 4 and 3

5a (R = Me): A mixture containing **4a/**[Me_3Al(py),Me_3Al] (80 mg; from **3** and Me_3Al, vide supra) was dissolved in [D_8]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 Me_3Al(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**/Et_3Al(py) (104 mg; from **3** and Et_3Al, vide supra) in [D_8]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] (≈80%) together with Et_3Al(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/**Et_3Al(py) (223 mg, vide supra) dissolved in [D_8]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 [D_8]toluene (0.5 mL), and a layer of brown-black oil was formed at the bottom. The oil after removal of [D_8]toluene was dissolved in pyridine (0.3 mL) at 5 °C. Then, [D_8]toluene (0.1 mL) was added. The solution thus obtained contained **6b**(*x* py) and Li(*x* py)$AlEt_4$. Data for **6b** (*x* py; $x \geq 8$): ^1H NMR (500.1 MHz, [D_8]toluene, 23 °C): δ = 0.39 (br. q, 8 H, CH_2Al), 1.70 (br. t, 12 H, CH_3), 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_α) ppm. $^{27}Al\{^1H\}$ NMR (130.3 MHz, [D_8]toluene, 23 °C): δ = 165 ($h_{1/2}$ ≈ 1000 Hz) ppm.

Data for $LiAlEt_4$ (*x* py; $x \geq 4$): ^1H NMR (500.1 MHz, [D$_8$]toluene, 23 °C): δ = 0.39 (br. q, 8 H, CH_2Al), 1.44 (br. t, 12 H, CH_3), 6.90 (m, py-H$_\beta$), 7.25 (m, py-H$_\gamma$), 8.42 (m, py-H$_\alpha$) ppm. ^{13}C NMR (125.8 MHz, [D$_8$]toluene, 23 °C): δ = 3.3 [$^1J(^{27}Al,^{13}C)$ = 73 Hz, $AlCH_2$], 12.0 (CH_3), 124.3 (py-C$_\beta$), 136.7 (py-C$_\gamma$), 149.8 (py-C$_\alpha$) ppm. $^{27}Al\{^1H\}$ NMR (130.3 MHz, [D$_8$]toluene, 23 °C): δ = 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**/Me_3Al(py) (50 mg, from **3** and Me_3Al) in [D$_8$]toluene at 0 °C. The solution was stirred for 0.5 h. The resulting mixture contained about 80% of **7a** together with Me_3Al(py), FcH, $FcAlMe_2$(py) and several unidentified side products (^1H and ^{13}C NMR). Product **7a** decomposes at room temperature to give **1a** (≈60% after 1 d), $FcAlMe_2$(py) and FcH. Data for **7a**: ^1H NMR (399.8 MHz, [D$_8$]toluene, 23 °C): δ = –0.13 (t, 12 H, CH_3), 0.17 (t, 3 H, CH_3), 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$_\beta$), 7.12 (m, py-H$_\gamma$), 8.51 (m, py-H$_\alpha$) ppm. ^1H NMR (399.8 MHz, C_6D_6, 23 °C): δ = –0.11 (t, 12 H, CH_3), 0.19 (t, 3 H, CH_3), 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$_\beta$), 7.03 (m, py-H$_\gamma$), 8.52 (m, py-H$_\alpha$) ppm.

7b (Alkyl = Et): The procedure was analogous to that described for **7a**, starting from a mixture containing **4b**/Et_3Al(py) (55 mg, from **1b** and Et_3Al) and pyridine (0.04 mL). The resulting mixture contained about 80% of **7b** together with Et_3Al(py) (^1H and ^{13}C NMR). Product **7b** decomposes slowly at room temperature to give **1b** (≈70% after 5 d), $FcAlEt_2$(py) and FcH. Data for **7b**: ^1H NMR (399.8 MHz, [D$_8$]toluene, 23 °C): δ = 0.54 (q, 8 H, CH_2Al), 0.81 (q, 2 H, CH_2Al), 1.45 (t, 12 H, CH_3), 1.56 (t, 3 H, CH_3), 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$_\beta$), 7.08 (m, py-H$_\gamma$), 8.48 (m, py-H$_\alpha$) ppm.

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

	4b
Formula	$C_{30}H_{41}Al_3Fe_2$
Crystal	red-orange prism
Dimensions [mm]	0.28 × 0.22 × 0.18
Crystal system	triclinic
Space group	$P\bar{1}$
a [pm]	1042.1(2)
b [pm]	1104.6(2)
c [pm]	1370.6(3)
α [°]	75.11(3)
β [°]	73.44(3)
γ [°]	77.90(3)
Z	2
μ [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 pm^{-3}]	0.879 / –0.445

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

Crystal Structure Determination of Complex 4b: Data were collected with a STOE IPDS I diffractometer with graphite monochromated Mo-K_α (λ = 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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[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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