DOI: 10.1002/ejic.200900272

1,1′-Disubstituted Ferrocenes with Aluminum: Dinuclear and Trinuclear Dialumina[1.1]ferrocenophanes as Pyridine Adducts

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

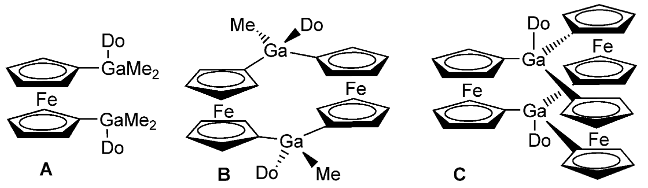
Keywords: Metallocenes / Aluminum / Ferrocenophane / Nitrogen heterocycles / Structure elucidation

Ferrocenes bearing dialkylaluminum substituents in the 1,1′-positions were characterized as their dipyridine adducts, and it was shown that they can be transformed into dinuclear alkylaluminum-bridged [1.1]ferrocenophanes and finally into the trinuclear aluminum-bridged ferrocenophane, both as dipyridine adducts. The synthesis of the latter compound was optimized and found to be most efficient (>40 % yield) through the reaction of 1,1′-dilithioferrocene with $MeAlCl_2$. The molecular structures of the dinuclear and trinuclear complexes were determined by X-ray crystallography. The solution-state structures of the new compounds were studied by multinuclear magnetic resonance methods, including ^1H–^1H NOE difference experiments.

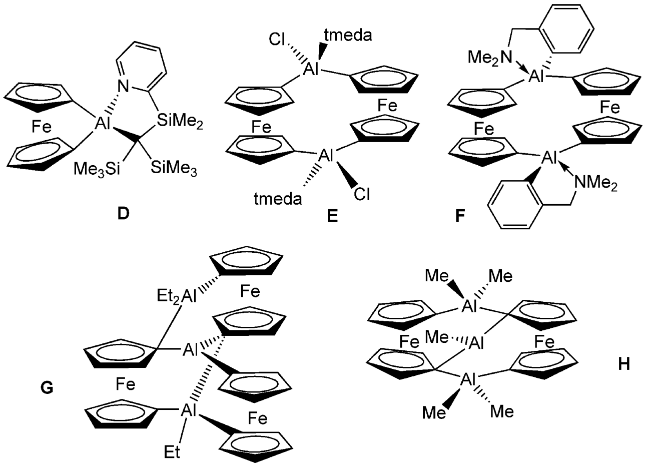
Introduction

The labile character of the polar Al–C bonds in organoaluminum compounds provides challenges with respect to straightforward preparative procedures and studying the structure and reactivity of many of these reactive species.[1–4] Although numerous trialkylaluminum compounds are well studied and have found widespread applications,[5–7] much information is still lacking on other triorganoalanes. In this context, ferrocenylaluminum compounds have also been somewhat neglected.[8] Thus, the first dialkyl(ferrocenyl)alanes, $(Fc\text{-}AlR_2)_2$, were described only recently, and the molecular structure was determined for $(Fc\text{-}AlMe_2)_2$.[9] This is also true for tri(ferrocenyl)aluminum, Fc_3Al, which was isolated and characterized as its pyridine adduct.[10] Ferrocene invites the synthesis of 1,1′-disubstituted derivatives, and this was attempted with aluminum to give a few expected[11–13] and some rather unexpected products.[14–16] Indeed, it appears that the corresponding gallium chemistry is more predictable,[17–19] as shown by compounds **A**, **B** and **C** in Scheme 1, whereas the aluminum chemistry holds surprises (Scheme 2). Compounds **E** and **F** are related to **B**, although the substitution at the aluminum atom is rather different, whereas compounds **G**[15] and **H**[16] have no relatives in gallium chemistry.

In the present work, we have set out to prepare the hitherto unknown aluminum analogues of the ferrocenylgallium compounds **A**, **B** and **C**.



Scheme 1. Typical gallium compounds derived from 1,1′-disubstituted ferrocene; **A**,[17] **B**,[18a] **C**[19] (Do is, for example, pyridine or dmso).



Scheme 2. Some aluminum compounds derived from 1,1′-disubstituted ferrocene; **D**,[11] **E**,[12a] **F**,[12b,15] **G**,[15] **H**.[16]

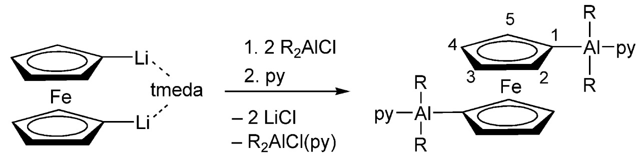
Results and Discussion

Considering the successful strategy leading to dialkyl(ferrocenyl)aluminum compounds,[9] when we prepared the pyridine adducts $FcAlR_2(py)$,[9,10] we optimized the condi-

---

[a] Anorganische Chemie II, Universität Bayreuth,
95440 Bayreuth, Germany
Fax: +49-921-552157
E-mail: b.wrack@uni-bayreuth.de

tions for the reaction of 1,1′-dilithioferrocene(tmeda)[20] with dialkylaluminum chlorides R_2AlCl [R = Me (**a**), Et (**b**)] in the presence of pyridine to obtain the desired 1,1′-ferrocenediyl derivatives $fc(AlR_2)_2(py)_2$ **1a** and **1b** (Scheme 3). Apparently, these reactions depend critically on conditions, as, for example, **G**[15] and **H**[16] were obtained from the same starting materials, however, without pyridine under different conditions.

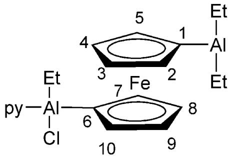


1a,b

a: R = Me
b: R = Et

Scheme 3. Synthesis of the 1,1′-bis(dialkylalanyl)ferrocenes as dipyridine adducts [the stoichiometry of $fcLi_2(tmeda)$ is ill defined. Therefore, a slight excess amount of R_2AlCl was used].

Dipyridine adducts **1a**,**b** could be isolated in ≥90% purity, containing a variable amount of ferrocene, trace amounts of $FcAlR_2(py)$ **5a**,**b** as decomposition products (depending on the time of storage and the solvent) and a small amount of another compound, which was subsequently prepared, isolated and characterized as **4**, the aluminum analogue of **C**. In the case of **1b**, there was also a small amount of **2b** present, in particular when the reaction was carried out in thf, indicating the property of the $AlEt_2$ group to undergo facile exchange reactions in spite of the presence of pyridine. The structures of **1a**,**b** are supported by their NMR spectroscopic data (Table 1), their purity is evident from the ^1H NMR spectra and the NOE difference experiments help with the assignment (Figures 1 and 2).



2b

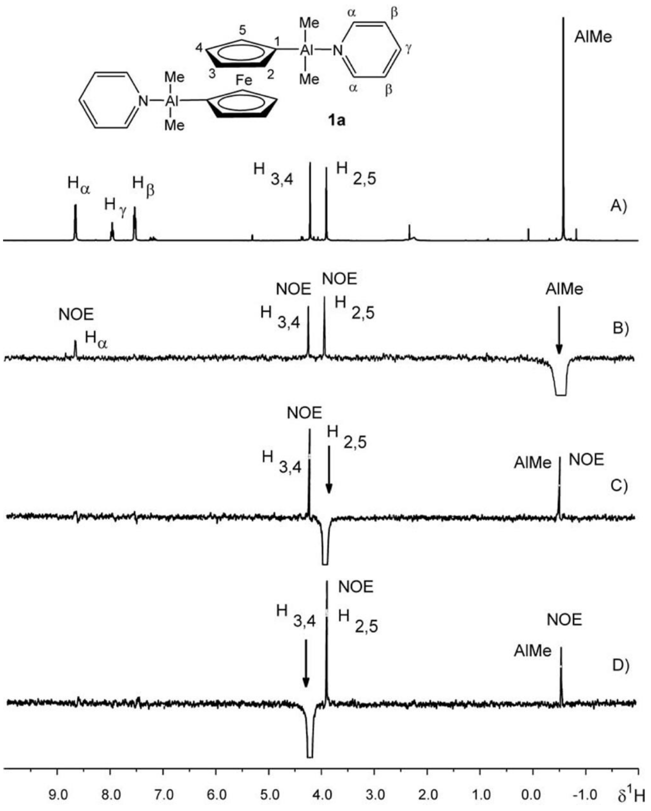


Figure 1. 400 MHz ^1H–^1H gradient enhanced NOE difference spectra[21] of **1a** (in CD_2Cl_2 at 23 °C; relaxation delay 1.5 s; mixing time 0.8 s). Irradiated transitions are marked by arrows; the resulting intensities arising from NOE are indicated. The observed NOE for $^1H^{3,4}$ upon irradiation of the $^1H(AlMe_2)$ transitions indicate that the structure shown for **1a** is the preferred conformation. A) Normal ^1H NMR spectrum. B) Irradiation: $^1H(AlMe_2)$; response: $^1H^{2,5}$ (larger) and $^1H^{3,4}$ (smaller) and $^1H(H_\alpha\text{-py})$. C) Irradiation: $^1H^{2,5}$; response: $^1H^{3,4}$ and $^1H(AlCH_3)$ of the Me_2Al group. D) Irradiation: $^1H^{3,4}$; response: $^1H^{2,5}$ and $^1H(AlCH_3)$ of the Me_2Al group.

The potential of the exchange reactions encouraged us to take a closer look at the mixtures containing **1b** and **2b**, as they might open a way to the aluminum analogue of **B** (Scheme 1) with AlEt units (Scheme 4) instead of GaMe.

Table 1. ^{13}C and ^{27}Al NMR spectroscopic data[a,b,c] of compounds **1**, **2b** and **4**.

Compound	**1a**, R = Me			**1b**, R = Et		**2b**, R = Et		**4**	
	298 K CD_2Cl_2	233 K CD_2Cl_2	298 K $[D_8]$toluene	298 K CD_2Cl_2	298 K $[D_8]$toluene	298 K CD_2Cl_2	298 K $[D_8]$toluene	298 K CD_2Cl_2	298 K $[D_8]$toluene
$\delta^{13}C(fc\text{-}C^1)$	72.8 (br.)	71.6	72.8 (br.)	72.2 (br.)	72.5 (br.)	72.5 (br.) 72.8 (br.)	n.o.	71.4 (br.)	n.o.
$\delta^{13}C(fc\text{-}C^{2,5})$	75.7	74.9	76.1	75.9	76.3	75.5, 76.2 ($fc\text{-}C^{2,5,7,10}$)	75.9, 76.6	76.4	76.6
$\delta^{13}C(fc\text{-}C^{3,4})$	70.9	70.2	71.5	70.7	71.3	71.1, 71.3 ($fc\text{-}C^{3,4,8,9}$)	71.9, 72.0	70.5	70.9
$\delta^{13}C(R)$	–9.6 (br., CH_3)	–10.2	–8.8 (br.)	0.7 (br., CH_2) 10.2 (CH_3)	1.2 (br.) 10.9	0.7 (br., 2 CH_2) 1.5 (br., CH_2) 10.2 (2 CH_3) 9.2 (CH_3)	1.2 (br.) 1.3(br.) 10.8 9.8	–	–
$\delta^{13}C(py)$	125.6 (C_β) 140.5 (C_γ) 147.9 (C_α)	124.8 139.3 147.2	124.4 138.4 147.9	125.8 141.0 147.8	124.7 139.5 147.5	125.8 141.0 147.8	124.7 139.5 147.5	125.1 139.9 147.9	124.5 140.1 152.7
$\delta^{27}Al$, $h_{1/2}$ / Hz	170 (6500 ± 500)			165 (6500 ± 500)		n.o.		n.o.	

[a] The assignment of the NMR signals is based on $^1H\{^1H\}$ NOESY[21] and 2D ^1H–^{13}C gHSQC[22] experiments. [b] br. = broad ^{13}C resonances of aluminum-bonded atoms. [c] n.o. = not observed.

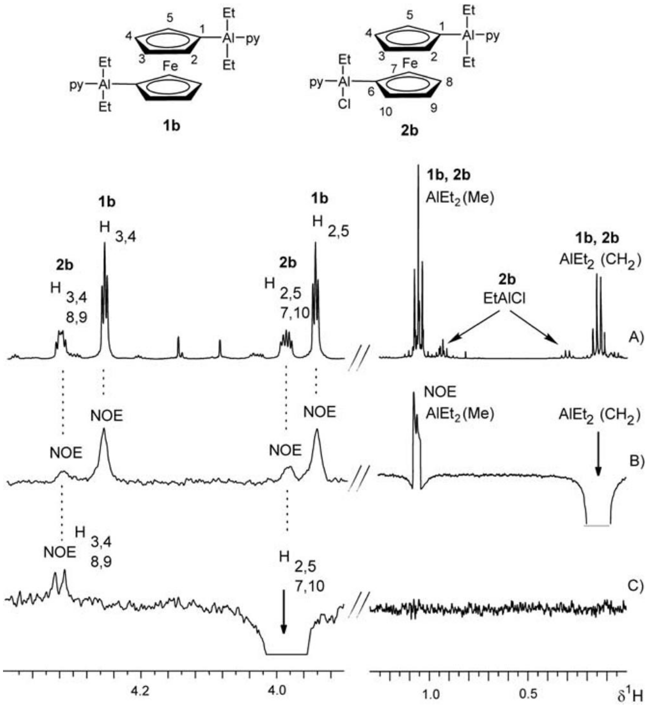
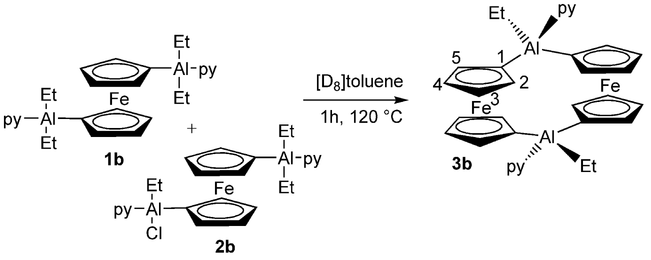


Figure 2. 400 MHz ^{1}H–^{1}H gradient enhanced NOE difference spectra[21] of a mixture of **1b** and **2b** (in CD_2Cl_2 at 23 °C; relaxation delay 2.0 s; mixing time 0.6 s). The irradiated transitions are marked by arrows; the resulting intensities arising from NOE are indicated. The preferred solution-state conformations of **1b** and **2b** are shown. A) Normal ^{1}H NMR spectrum. B) Irradiation: $AlCH_2$ group of AlEt; response: $^1H^{2,5}$ and $^1H^{3,4}$ from **1b** and $^1H^{2,5,7,10}$ and $^1H^{3,4,8,9}$ from **2b**. C) Irradiation: $^1H^{2,5,7,10}$ from **2b**; response: $^1H^{3,4,8,9}$ from **2b**.

Heating of these mixtures in toluene at 120 °C for 1 h afforded $AlEt_3$(py) and a crystalline, rather insoluble material that could be analyzed by ^{1}H NMR spectroscopy and X-ray structural analysis (vide infra) as the dinuclear ethylaluminum-bridged [1.1]ferrocenophane **3b**. In the absence of **2b**, the formation of **3b** in an appreciable amount was not observed (however, see Scheme 5).



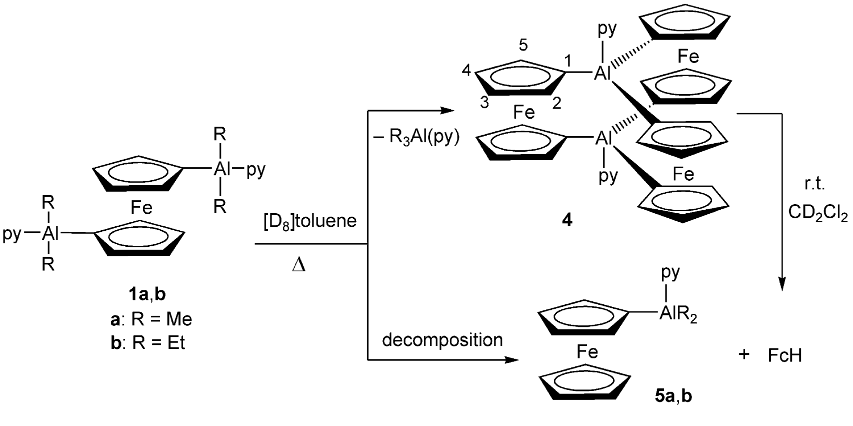
Scheme 4. Synthesis of ethylaluminum-bridged [1.1]ferrocenophane **3b**.

In contrast with gallium compound **B**,[18a] [1.1]ferrocenophane **3b** appears to be nonfluxional in solution, as there are four ^{1}H(ferrocene) NMR signals resolved, typical of a rigid structure. Moreover, the ^{1}H NMR spectra show that the exchange between free pyridine and pyridine linked to aluminum must be slow on the NMR timescale. Most likely, the coordinative N(py)–Al bond in **3b** is stronger than the N(py)–Ga bond in **B**.

Now the route to the dipyridine adduct of trinuclear aluminum-bridged ferrocenophane **4**, the analogue of **C**, seemed to be open. NMR signals of low intensity for this compound were observed in the reaction solutions containing **1a**,**b**. Therefore, we tried to optimize conditions to increase the amount of **4** in the respective mixtures. The problems are indicated in Scheme 5. The formation of **4** starting from **1a**,**b** is accompanied by extensive decomposition to leave **5a**,**b** (identified by their NMR spectroscopic data given in Table 2) and ferrocene, along with other unidentified products (partial hydrolysis cannot be excluded). In CD_2Cl_2, after isolating a small amount of **4**, decomposition takes place to give ferrocene.

When we used **1a** in the presence of 2,2′-bipyridine, a significant amount of **4** was formed together with **5a**, as could be monitored by ^{1}H and ^{13}C NMR spectroscopy (Figure 3). However, it proved extremely difficult to isolate **4** from these complex mixtures.

Therefore, we had to change the approach (Scheme 6) and decided to use the reaction of fcLi$_2$(tmeda) with aluminum trichloride. The result was disappointing; although the



Scheme 5. Attempted synthesis of **4** and its decomposition.

Table 2. ^{13}C NMR spectroscopic data[a,b,c] of compound **5**.

Compound	**5a**, R = Me 298 K CD_2Cl_2	 298 K [D_8]toluene	**5b**, R = Et 298 K CD_2Cl_2	 298 K [D_8]toluene
δ^{13}C(Fc-C^1)	n.o.	73.6 (br.)	n.o.	n.o.
δ^{13}C(Fc-C^{2,5})	76.3	76.5	76.6	76.6
δ^{13}C(Fc-C^{3,4})	71.2	71.6	71.1	71.4
δ^{13}C(Fc-Cp)	67.7	67.9	67.8	67.9
δ^{13}C(R)	–8.4 (br., CH_3)	–9.1 (br.)	0.8 (br., CH_2) 10.2 (CH_3)	1.0 (br.) 10.6
δ^{13}C(py)	125.6 (C_β) 140.5 (C_γ) 148.6 (C_α)	124.6 138.5 148.1	126.1 141.5 147.6	125.3 140.2 147.0

[a] The assignment of the NMR signals is based on ^{1}H{^{1}H} NOESY[21] and 2D ^{1}H–^{13}C gHSQC[22] experiments. [b] br. = broad ^{13}C resonances of aluminum-bonded atoms. [c] n.o. = not observed.

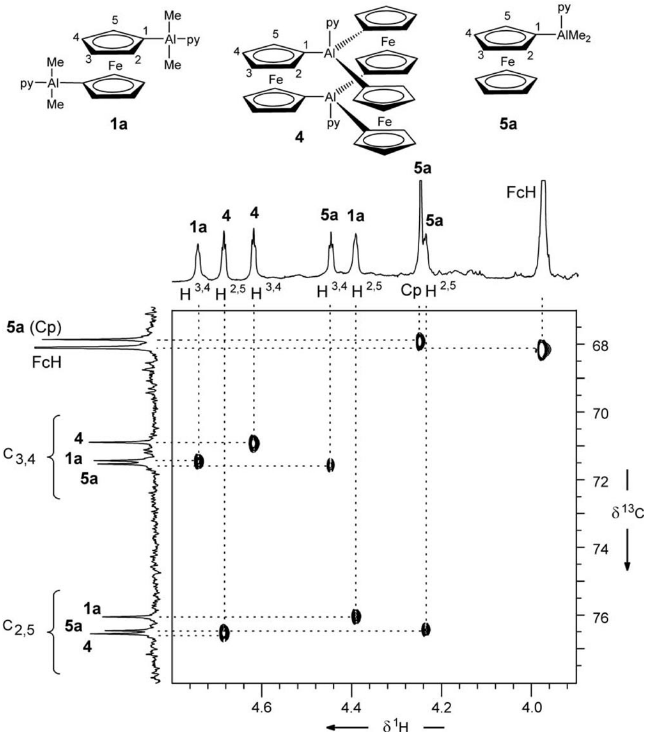
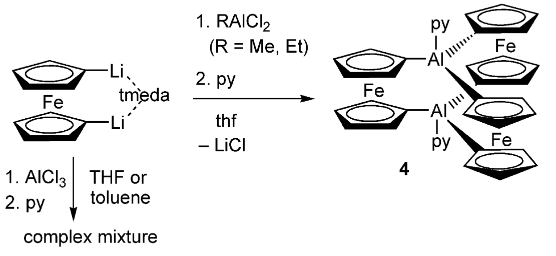


Figure 3. Contour plot of part of the 400 MHz 2D ^{1}H–^{13}C-correlated spectrum (in [D_8]toluene at 23 °C) of a mixture containing **1a**, **4**, **5a** and ferrocene (after heating **1a** with 2,2′-bipyridine for 2.5 h at 100 °C in [D_8]toluene) recorded by the gradient-selected gHSQC method.[22]



Scheme 6. Optimized synthesis of the trinuclear aluminum-bridged ferrocenophane **4** [best with $MeAlCl_2$; in the case of $EtAlCl_2$, the formation of **3b** was also observed (in repeated experiments with ca. 5–20%)].

complex mixtures resulting from these reactions may have contained trace amounts of **4**. In the final experiments, the alkylaluminum dichlorides $RAlCl_2$ (R = Me, Et) were used in the presence of pyridine. Indeed, this route afforded **4** in reasonable yields (≈40%) and proceeded most efficiently with the use of $MeAlCl_2$. The use of $EtAlCl_2$ afforded mixtures containing mainly **4** and a small amount of **3b**.

Compound **4** was isolated as an air- and moisture-sensitive orange-coloured powder, slightly soluble in toluene and in CD_2Cl_2. In the latter solvent, slow decomposition occurred (Scheme 5). However, crystals of **4**, suitable for X-ray structural analysis, could be collected from saturated solutions of **4** in CD_2Cl_2 (vide infra).

X-ray Structure Analyses of Ferrocenophanes 3b and 4

The molecular structures of **3b** and **4** are shown in Figures 4 and 5, respectively, and structural parameters are listed in Table 3, together with the corresponding data of gallium analogues **B** and **C**. As can be seen, the main structural features of **3b** and **4** agree with those determined for **B** and **C**. In **3b**, the ethyl groups are in the *trans* position, showing statistical disorder for the CH_3 groups. Crystals of **4** contained solvent molecules of CD_2Cl_2 when the crystals were grown by slow evaporation of a solution at ambient temperature; thus, the crystals were of lower quality and only the low-temperature X-ray diffraction study gave useful results.

As in the case of Ga in **C**, the ferrocenyl groups are twisted owing to the pyramidal surroundings of Al in **4**, giving rise to the presence of enantiomers in the crystal lattice, which according to ^{1}H and ^{13}C NMR spectra readily interconvert in solution. The arrangement of the molecules

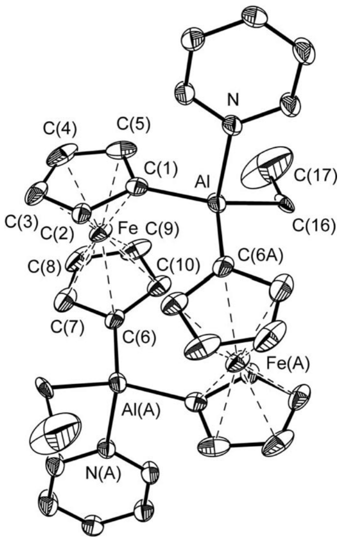


Figure 4. Molecular structure of **3b** (ORTEP plot, 30% probabilities; hydrogen atoms are omitted for clarity; see Table 3 for structural parameters). The methyl carbon atoms of the ethyl groups are statistically disordered. This can be seen by the unusually large temperature coefficients (due to this disorder, the relevant C–C distances are too long).

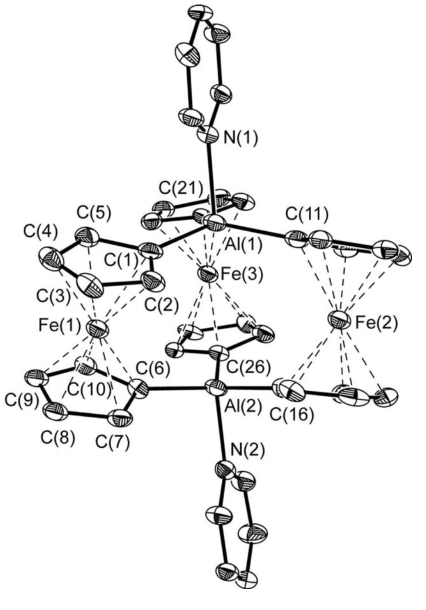


Figure 5. Molecular structure of **4** (ORTEP plot, 30% probabilities; hydrogen atoms are omitted for clarity; the CD_2Cl_2 molecules found in the crystal lattice are not shown; see Table 3 for structural parameters).

of **4** in the crystal lattice is shown in Figure 6. The enantiomers, labelled A and B, are not in separate layers as in the case of gallium analogue **C**. Because crystals of **4** contain CD_2Cl_2, whereas crystals of **C** contain toluene, it is possible that the solvent controls the respective arrangement of the enantiomers in the lattice.

Conclusions

The use of pyridine adducts of organoaluminum compounds opens the way to species that have not been obtained before, but these species are analogous to the comparable gallium compounds. Having achieved the synthesis of the trinuclear aluminum bridged ferrocenophane **4** as its dipyridine adduct, the next steps in synthesis will have to deal with attempts to remove the pyridine in **4**.

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

Table 3. Selected bond lengths [pm] and angles [°][a] of dialumina[1.1]ferrocenophane pyridine adducts **3b** and **4** and those of digalla[1.1] ferrocenophane pyridine adducts **3**[GaMe] and **4**[Ga].

	3b		**3**[GaMe][b]		**4** (CD_2Cl_2)		**4**[Ga] [c]
Al–C(1)	196.0(4)	Ga(1)–C(1)	198.1(6)	Al(1)–C(1)	196.8(11)	Ga(1)–C(1)	196.8(19)
				Al(2)–C(6)	196.3(10)		
Al–C(6A)	196.8(5)	Ga(1)–C(6A)	195.7(6)	Al(1)–C(11)	197.9(12)	Ga(1)–C(16)	196.5(17)
				Al(2)–C(16)	195.3(12)		
Al–C(16)	203.0(4)	Ga(1)–C(11)	197.6(7)	Al(1)–C(21)	195.1(13)	Ga(1)–C(21)	197.3(17)
				Al(2)–C(26)	196.2(12)		
Al–N	203.7(3)	Ga(1)–N	214.4(5)	Al(1)–N(1)	205.7(9)	Ga(1)–N(1)	214.3(14)
				Al(2)–N(2)	204.8(9)		
Al–Al(A)	480.3	Ga(1)–Ga(1A)	476.8	Al(1)–Al(2)	391.4	Ga(1)–Ga(2)	387
C(1)–Al–C(6A)	115.91(18)	C(1)–Ga(1)–C(6A)	115.6(2)	C(1)–Al(1)–C(11)	116.4(5)	C(1)–Ga(1)–C(16)	117.9(8)
				C(6)–Al(2)–C(16)	117.7(5)		
C(1)–Al–C(16)	119.91(19)	C(1)–Ga(1)–C(11)	117.9(3)	C(1)–Al(1)–C(21)	121.1(5)	C(1)–Ga(1)–C(21)	116.8(7)
				C(6)–Al(2)–C(26)	114.4(5)		
C(6A)–Al–C(16)	113.28(18)	C(6A)–Ga(1)–C(11)	118.3(3)	C(11)–Al(1)–C(21)	116.0(5)	C(16)–Ga(1)–C(21)	120.6(8)
				C(16)–Al(2)–C(26)	121.8(4)		
C(1)–Al–N	100.17(15)	C(1)–Ga(1)–N	97.5(2)	C(1)–Al(1)–N(1)	95.8(4)	C(1)–Ga(1)–N(1)	98.1(7)
				C(6)–Al(2)–N(2)	102.4(4)		
C(6A)–Al–N	100.02(15)	C(6A)–Ga(1)–N	100.0(2)	C(11)–Al(1)–N(1)	100.4(4)	C(16)–Ga(1)–N(1)	95.0(6)
				C(16)–Al(2)–N(2)	95.5(4)		
C(16)–Al–N	103.12(14)	C(11)–Ga(1)–N	101.2(2)	C(21)–Al(1)–N(1)	99.4(4)	C(21)–Ga(1)–N(1)	98.8(7)
				C(26)–Al(2)–N(2)	97.2(4)		
C_5/C_5 (α)	3.3	C_5/C_5 (α)	3	C_5/C_5 (α_1) [Fe(1)]	2.7	C_5/C_5 (α)	4
				C_5/C_5 (α_2) [Fe(2)]	4.0		
				C_5/C_5 (α_3) (Fe(3))	2.7		
C_5/Al (β_1)	4.3 (towards Fe)	C_5/Ga	1	C_5 [Fe(1)]/Al(1) (β_1)	9.2	C_5/Ga (β)	4
				C_5 [Fe(2)]/Al(1) (β_2)	4.2		
				C_5 [Fe(3)]/Al(1) (β_3)	5.3 (bent away from Fe)		
C_5/Al(A) (β_2)	2.7 (bent away from Fe)			C_5 [Fe(1)]/Al(2) (β_4)	2.6		
				C_5 [Fe(2)]/Al(2) (β_5)	4.5		
				C_5 [Fe(3)]/Al(2) (β_6)	8.6 (bent away from Fe)		
C_5/C_5 (twist) (τ)	62.3	C_5/C_5 (twist) (τ)	62	C_5/C_5 (twist) (τ_1) Fe(1)	13.5	C_5/C_5 (twist) (τ)	11
				C_5/C_5 (twist) (τ_2) Fe(2)	14.8		
				C_5/C_5 (twist) (τ_3) Fe(3)	22.4		

[a] See Ref.[23] for the definition of the angles α, β and τ. [b] Ref.[18a] [c] Ref.[19]

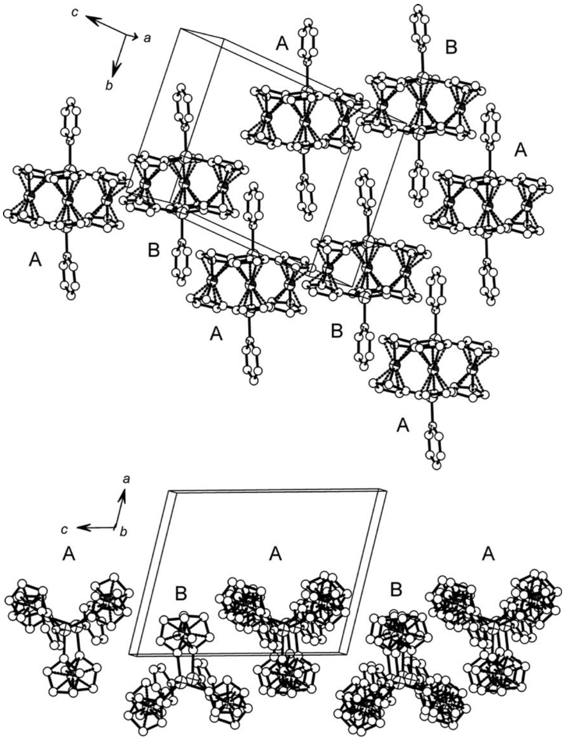


Figure 6. Two different views (see the axes systems) of the arrangements of the enantiomers A and B of **4** in the crystal lattice (the CD_2Cl_2 molecules are not shown).

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 BuLi (1.6 M in hexane), aluminum trichloride (anhydrous, powder 99.999% metal basis), Me_2AlCl (1.0 M in hexanes), $MeAlCl_2$ (1.0 M solution in hexanes), $EtAlCl_2$ (1.8 M solution in toluene) (all from Aldrich), Et_2AlCl (1.0 M in hexane) (Acros), pyridine (anhydrous, 99.8%) (Aldrich) were commercial products and used as received. The compound $fcLi_2$(tmeda)[20] was prepared by literature procedures. NMR measurements: Bruker ARX 250: ^1H, ^{13}C, ^{27}Al NMR; Varian INOVA 400: ^1H, ^{13}C, ^{27}Al NMR; chemical shifts are given with respect to $SiMe_4$ [$\delta^1H(CHDCl_2)$ = 5.33 ppm, $\delta^1H(C_6D_5CD_2H)$ = 2.08 ppm; $\delta^{13}C(CD_2Cl_2)$ = 53.8 ppm, $\delta^{13}C(C_6D_5\mathit{C}D_3)$ = 20.4 ppm]; external 1.1 M $Al(NO_3)_3$ in D_2O [$\delta^{27}Al$ = 0 for $\delta(^{27}Al)$ = 26.056890 MHz]. The melting points (uncorrected) were determined by using a Büchi 510 melting point apparatus. Owing to the extreme sensitivity of the new compounds to air and moisture, a notorious property of organoaluminum compounds, elemental analysis did not give reliable results. Attempts to measure mass spectra (MS, EI, 70 eV) did not reveal the respective molecular ions. Instead, the pattern of diferrocene $(CpFeC_5H_4)_2$ was observed.

1,1′-Bis(dialkylalanyl)ferrocene Dipyridine Adducts 1

1a (Alkyl = Me): Freshly prepared $fcLi_2$(tmeda) (1092 mg, 3.48 mmol) was taken up in toluene (30 mL); the suspension was cooled to –15 °C and Me_2AlCl (1.0 M in heptane, 7.0 mL, 7.0 mmol) was added dropwise. The reaction mixture was stirred at –15 °C for 1 h and pyridine (1.0 mL, 12.4 mmol) was added at 0 °C. Then, the mixture was allowed to reach ambient temperature whilst stirring for 20 h. After centrifugation, the supernatant liquid phase was carefully decanted and volatile materials were evaporated. The remaining oil was washed with pentane, dissolved in toluene (20 mL) and pyridine (1.0 mL, 12.4 mmol) was then added. After stirring the mixture for 2 h, insoluble materials were separated by centrifugation, and the clear liquid was collected. Volatile materials were removed in vacuo to leave an oil that was washed with pentane and evaporated again to give an orange-yellow residue (720 mg) containing about 90% of **1a** together with **5a** and ferrocene (^1H and ^{13}C NMR). Washing with hexane dissolved most of the ferrocene and **5a** to give **1a** (552 mg, >95%; see Figure 1). Data for **1a**: M.p. 230–240 °C. ^1H NMR (399.8 MHz, CD_2Cl_2, 23 °C): δ = –0.58 (s, 12 H, CH_3Al), 3.91 (m, 4 H, $H^{2,5}$), 4.22 (m, 4 H, $H^{3,4}$), 7.53 (m, py-H_β), 7.96 (m, py-H_γ), 8.66 (m, py-H_α) ppm. ^1H NMR (250.1 MHz, CD_2Cl_2, –40 °C): δ = –0.62 (s, 12 H, CH_3Al), 3.90 (m, 4 H, $H^{2,5}$), 4.21 (m, 4 H, $H^{3,4}$), 7.52 (m, py-H_β), 7.95 (m, py-H_γ), 8.59 (m, py-H_α) ppm. ^1H NMR (399.8 MHz, [D_8]toluene, 23 °C): δ = –0.07 (s, 12 H, CH_3Al), 4.40 (m, 4 H, $H^{2,5}$), 4.75 (m, 4 H, $H^{3,4}$), 6.37 (m, py-H_β), 6.73 (m, py-H_γ), 8.32 (m, py-H_α) ppm. ^1H NMR (399.8 MHz, [D_8]toluene, 80 °C): δ = –0.18 (s, 12 H, CH_3Al), 4.26 (m, 4 H, $H^{2,5}$), 4.60 (m, 4 H, $H^{3,4}$), 6.56 (m, py-H_β), 6.91 (m, py-H_γ), 8.39 (m, py-H_α) ppm. Data for **5a**: ^1H NMR (399.8 MHz, CD_2Cl_2, 23 °C): δ = –0.57 (s, 6 H, CH_3Al), 4.01 (m, 2 H, $H^{2,5}$), 4.08 (s, 5 H, Cp), 4.30 (m, 2 H, $H^{3,4}$), 7.53 (m, py-H_β), 7.96 (m, py-H_γ), 8.66 (m, py-H_α) ppm. ^1H NMR (400.1 MHz, [D_8]toluene, 23 °C): δ = –0.18 (s, 6 H, CH_3Al), 4.24 (m, 2 H, $H^{2,5}$), 4.25 (s, 5 H, Cp), 4.45 (m, 2 H, $H^{3,4}$), 6.47 (m, py-H_β), 6.81 (m, py-H_γ), 8.33 (m, py-H_α) ppm. ^1H NMR (399.8 MHz, [D_8]toluene, 80 °C): δ = –0.27 (s, 6 H, CH_3Al), 4.15 (m, 2 H, $H^{2,5}$), 4.17 (s, 5 H, Cp), 4.39 (m, 2 H, $H^{3,4}$), 6.57 (m, py-H_β), 6.91 (m, py-H_γ), 8.39 (m, py-H_α) ppm.

1b (Alkyl = Et): Freshly prepared $fcLi_2$(tmeda) (1454 mg, 4.63 mmol) was taken up in hexane (40 mL); the suspension was cooled to –10 °C and Et_2AlCl (1.0 M in hexane, 9.3 mL, 9.3 mmol) was added dropwise. The reaction mixture was stirred at 20 °C for 3 h, cooled to –20 °C and pyridine (1.50 mL; 18.54 mmol) was added. The mixture was kept stirring at room temperature for 20 h. After centrifugation, the supernatant liquid phase was carefully decanted and volatile materials were evaporated. The resulting oil was dissolved in toluene (30 mL), and from the clear liquid phase after centrifugation and evaporation an oily residue was left. This was washed with pentane to leave an orange-red residue (955 mg) containing about 90% of **1b** (together with **2b**, **4**, **5b** and ferrocene, about 10%; ^1H and ^{13}C NMR). Data for **1b**: ^1H NMR (399.8 MHz, CD_2Cl_2, 23 °C): δ = 0.16 (q, J = 8.2 Hz, 8 H, CH_2Al), 1.11 (t, J = 8.2 Hz, 12 H, CH_3), 3.95 (m, 4 H, $H^{2,5}$), 4.26 (m, 4 H, $H^{3,4}$), 7.58 (m, py-H_β), 8.01 (m, py-H_γ), 8.66 (m, py-H_α) ppm. ^1H NMR (399.8 MHz, [D_8]toluene, 23 °C): δ = 0.59 (q, J = 8.2 Hz, 8 H, CH_2Al), 1.48 (t, J = 7.2 Hz, 12 H, CH_3), 4.38 (m, 4 H, $H^{2,5}$), 4.74 (m, 4 H, $H^{3,4}$), 6.40 (m, py-H_β), 6.77 (m, py-H_γ), 8.33 (m, py-H_α) ppm. ^1H NMR (399.8 MHz, [D_8]toluene, 90 °C): δ = 0.49 (q, J = 8.2 Hz, 8 H, CH_2Al), 1.39 (t, J = 8.2 Hz, 12 H, CH_3), 4.24 (m, 4 H, $H^{2,5}$), 4.58 (m, 4 H, $H^{3,4}$), 6.56 (m, py-H_β), 6.95 (m, py-H_γ), 8.44 (m, py-H_α) ppm. Data for **5b**: ^1H NMR (399.8 MHz, CD_2Cl_2, 23 °C): δ = 0.18 (q, J = 8.2 Hz, 4 H, CH_2Al), 1.12 (t, J = 8.2 Hz, 6 H, CH_3), 4.05 (m, 2 H, $H^{2,5}$), 4.10 (s, 5 H, Cp), 4.32 (m, 2 H, $H^{3,4}$), 7.65 (m, py-H_β), 8.06 (m, py-H_γ), 8.62 (m, py-H_α) ppm. ^1H NMR (399.8 MHz, [D_8]toluene, 23 °C): δ = 0.42 (q, J = 8.2 Hz, 4 H, CH_2Al), 1.36 (t, J = 8.2 Hz, 6 H, CH_3), 4.19 (s, 5 H, Cp), 4.21 (m, 2 H, $H^{2,5}$), 4.42 (m, 2 H, $H^{3,4}$), 6.54 (m, py-H_β), 6.92 (m, py-H_γ), 8.29 (d, py-H_α) ppm.

1,1′-Bis(diethylalanyl)ferrocene Dipyridine Adduct 1b and 1-Diethylalanyl-1′-chloro(ethyl)alanylferrocene Dipyridine Adduct 2b: Freshly prepared fcLi$_2$(tmeda) (1424 mg, 4.53 mmol) was taken up in thf (15 mL); the suspension was cooled to –20 °C and Et$_2$AlCl (1.0 M in hexane, 10.3 mL, 10.3 mmol) was added dropwise. The mixture was allowed to reach ambient temperature and was stirred for 20 h. Volatile materials were removed in vacuo, and the remaining oil was dissolved in toluene (30 mL). Solid materials were separated by centrifugation, and the supernatant liquid phase was collected, cooled to 0 °C and pyridine (1.1 mL, 13.68 mmol) was added, and the mixture was stirred for 20 h. After another centrifugation all volatile materials were removed in vacuo from the liquid phase to leave an oil. This was washed with hexane (50 mL), and the solid obtained after drying in vacuo was dissolved in Et$_2$O (30 mL). Insoluble materials were filtered off, the solvent was removed in vacuo and an orange-red residue was left (1715 mg) containing about 80% of **1b** and 20% of **2b** (together with **4** and ferrocene, <5%; ^{1}H and ^{13}C NMR). Data for **2b**: ^{1}H NMR (399.8 MHz, CD$_2$Cl$_2$, 23 °C): δ = 0.17 (q, J = 8.2 Hz, 4 H, CH$_2$Al), 0.32 (q, J = 8.2 Hz, 2 H, CH$_2$Al), 0.99 (t, J = 8.2 Hz, 3 H, CH$_3$), 1.11 (t, J = 8.2 Hz, 6 H, CH$_3$), 3.98 (m, 4 H, H^{2,5,7,10}), 4.32 (m, 4 H, H^{3,4,7,8}), 7.58 (m, py-H$_\beta$), 8.01 (m, py-H$_\gamma$), 8.66 (m, py-H$_\alpha$) ppm. ^{1}H NMR (399.8 MHz, [D$_8$]toluene, 23 °C): δ = 0.60 (q, J = 8.2 Hz, 4 H, CH$_2$Al), 0.66 (q, J = 8.2 Hz, 2 H, CH$_2$Al), 1.42 (t, J = 8.2 Hz, 3 H, CH$_3$), 1.48 (t, J = 8.2 Hz, 6 H, CH$_3$), 4.43, 4.44 (m, m, 2 H, 2 H, H^{2,5}, H^{7,10}), 4.88 (m, 4 H, H^{3,4,7,8}), 6.33 (m, py-H$_\beta$), 6.70 (m, py-H$_\gamma$), 8.33 (m, py-H$_\alpha$) ppm.

Bis(μ-ferrocene-1,1′-diyl)bis[ethyl(*N*-pyridine)aluminum] (3b): In repeated experiments, a mixture of **1b/2b** (4:1, 64 mg) was dissolved in [D$_8$]toluene (1 mL) in an NMR tube and heated at 120 °C (oil bath) for 1 h. Single red-orange crystals of **3b** (16 mg) suitable for X-ray analysis were growing after 1 d. The supernatant solution contained mainly **1b** along with **2b**, **5b**, ferrocene and several other unidentified products. (In thf, the analogous reaction at 70 °C also gave **3b**). Data for **3b**: M.p. >210 °C (decomp.). ^{1}H NMR (399.8 MHz, CD$_2$Cl$_2$, 23 °C): δ = 0.44 (q, J = 8.2 Hz, 4 H, CH$_2$Al), 1.19 (t, J = 8.2 Hz, 6 H, CH$_3$), 4.10, 4.53 (m, m, 4 H, 4 H, H^2, H^5), 4.30 (m, 8 H, H^{3,4}), 7.0 (m, 4 H, py-H$_\beta$), 7.85 (m, 2 H, py-H$_\gamma$), 8.52 (m, 4 H, py-H$_\alpha$) ppm.

Reaction of fcLi$_2$(tmeda) with RAlCl$_2$ and Pyridine

Synthesis of Tris(μ-ferrocene-1,1′-diyl)bis[*N*-pyridine]aluminum (4)

Alkyl = Me: To freshly prepared fcLi$_2$(tmeda) (1525 mg, 4.85 mmol) cooled to –30 °C was added thf (30 mL). MeAlCl$_2$ (1.0 M in hexane, 5.5 mL, 5.5 mmol) was added dropwise. The mixture was warmed to ambient temperature, stirred for 48 h, concentrated to 15 mL and cooled to 0 °C. Pyridine (0.75 mL, 9.33 mmol) was then added and stirring was continued for 20 h. The formation of a red-orange precipitate was observed. After centrifugation, the supernatant liquid phase was decanted. Et$_2$O (5 mL) and pyridine (0.2 mL) were added to the solid. This suspension was stirred for 1 h, and the liquid phase was again separated by centrifugation. The remaining solid was washed with hexane (5 mL) and dried under high vacuum to give **4** (487 mg, 43%) as an orange powder. Single orange crystals of **4** for X-ray analysis were grown from a CD$_2$Cl$_2$ solution after 1 week at room temperature. Product **4** decomposes slowly in CD$_2$Cl$_2$ under an atmosphere of argon at room temperature. M.p. >300 °C (decomp.). ^{1}H NMR (399.8 MHz, CD$_2$Cl$_2$, 23 °C): δ = 4.34 (m, 12 H, H^{2,5}), 4.37 (m, 12 H, H^{3,4}), 7.21 (m, 4 H, py-H$_\beta$), 7.69 (m, 2 H, py-H$_\gamma$), 8.26 (m, 4 H, py-H$_\alpha$) ppm. ^{1}H NMR (399.8 MHz, [D$_8$]toluene, 23 °C): δ = 4.63 (m, 12 H, H^{3,4}), 4.69 (m, 12 H, H^{2,5}), 5.97 (m, py-H$_\beta$), 6.35 (m, py-H$_\gamma$), 8.21 (m, py-H$_\alpha$) ppm.

Alkyl = Et: To freshly prepared fcLi$_2$(tmeda) (1525 mg, 4.86 mmol) cooled to –20 °C was added thf (30 mL). Then, EtAlCl$_2$ (1.8 M in toluene, 3.10 mL, 5.58 mmol) was added dropwise. The mixture was allowed to reach ambient temperature, stirred for 20 h and then concentrated to 15 mL. The mixture was cooled to 0 °C and pyridine (0.6 mL; 7.46 mmol) was added; the mixture was stirred for 40 h. The formation of a red-orange precipitate was observed. Following centrifugation, the supernatant liquid phase was decanted, thf (5 mL) and pyridine (0.5 mL) were added to the solid, the suspension was stirred for 1 h and the solid material was again separated by centrifugation. The solid was washed with hexane (5 mL) and dried under high vacuum to leave an orange powder (754 mg) containing about 80% of **4** together with **3b** (5–20%; ^{1}H NMR).

Preparation of 4 from 1b (or 1a)

Method A: Compound **1b** (or **1a**; 40–60 mg) was dissolved in [D$_8$]-toluene (0.6 mL; concentrated solution) in a tightly closed NMR tube that was heated at 130 °C (oil bath) for 3 h. An orange solid formed, and the supernatant liquid was decanted. The solid was washed with hexane and identified as **4** by NMR spectroscopy. The supernatant solution contained mainly **1b**, along with **5b**, ferrocene and several unidentified side products.

Method B: To a solution of **1a** (50 mg) dissolved in [D$_8$]toluene (0.6 mL) was added 2,2′-bipyridine (7 mg), and the mixture was transferred into an NMR tube, which was tightly closed. The mixture was heated at 100 °C (oil bath) for 2.5 h. The solution thus obtained contained **1a**, **4**, **5a**, ferrocene (see Figure 3) and 2,2′-bipyridine.

Crystal Structure Determination of Complexes 3b and 4: Details pertinent to the crystal structure determinations are listed in Table 4.[24] Crystals of appropriate size were sealed under an atmosphere of argon in Lindemann capillaries. The data collections were carried out at 133 K for **3b** and for **4** by using a STOE IPDS II diffractometer with graphite monochromated Mo-K_α (λ = 71.073 pm) radiation.

Table 4. Crystallographic data of dialuma[1.1]ferrocenophane **3b** and **4**.

	3b	4
Formula	$C_{34}H_{36}Al_2Fe_2N_2$	$C_{40}H_{34}Al_2Fe_3N_2 \cdot CD_2Cl_2$
Crystal	red-orange prism	orange prism
Temperature [K]	133(2)	133(2)
Dimensions [mm]	0.35 × 0.22 × 0.18	0.35 × 0.18 × 0.16
Crystal system	Monoclinic	Triclinic
Space group	*C*2/*c*	$P\bar{1}$
Lattice parameters		
a [pm]	1971.5(4)	1110.5(2)
b [pm]	1338.8(3)	1199.1(2)
c [pm]	1120.2(2)	1402.6(3)
α [°]		96.38(3)
β [°]	102.82(3)	104.00(3)
γ [°]		90.23(3)
Z	4	2
μ [mm^{-1}]	1.095	1.424
Measuring range (ϑ) [°]	1.9–25.7	1.51–25.97
Reflections collected	18777	21954
Independent reflections [$I > 2\sigma(I)$]	2735	6763
Absorption correction	none[a]	none[a]
Refined parameters	181	451
wR_2/R_1 [$I > 2\sigma(I)$]	0.143/0.056	0.225/0.096
Max./min. electron density [e pm^{-3} × 10^{-6}]	0.796/–0.719	1.208/–0.622

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

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft.

---

[1] T. Mole, E. A. Jeffery, *Organoaluminum Compounds*, Elsevier, New York, **1972**, p. 465 pp.

[2] a) E. Negishi in *Organometallics in Organic Synthesis 1*, Wiley, New York, **1980**, p. 286; b) J. J. Eisch in *Comprehensive Organometallic Chemistry 1* (Eds.: G. Wilkinson, G. G. A. Stone, E. W. Abel), Pergamon Press, Oxford, **1982**, pp. 555–577.

[3] H. Yamamoto in *Organometallics in Synthesis: A Manual* (Ed.: M. Schlosser), 2nd ed., Wiley, New York, **2002**, pp. 535–577.

[4] M. Oishi in *Science of Synthesis Vol. 7: Compounds of Groups 13 and 2 (Al, Ga, In, Tl, Be … Ba)* (Ed.: H. Yamamoto), Thieme, Stuttgart, **2004**, pp. 261–385.

[5] J. Boor, *Ziegler–Natta Catalysts and Polymerizations*, Academic Press, New York, **1979**, p. 656.

[6] G. Zweifel, J. A. Miller, *Organic Reaction* **1984**, *32*, 375–517.

[7] M. Witt, H. W. Roesky, *Curr. Sci.* **2000**, *78*, 410–430.

[8] a) G. H. Robinson, S. G. Bott, J. L. Atwood, *J. Coord. Chem.* **1987**, *16*, 219–224; b) R. D. Rogers, W. J. Cook, J. L. Atwood, *Inorg. Chem.* **1979**, *18*, 279–282; c) J. L. Atwood, B. L. Bailey, B. L. Kindberg, W. J. Cook, *Aust. J. Chem.* **1973**, *26*, 2297–2298.

[9] B. Wrackmeyer, E. V. Klimkina, T. Ackermann, W. Milius, *Inorg. Chem. Commun.* **2007**, *10*, 743–747.

[10] B. Wrackmeyer, E. V. Klimkina, T. Ackermann, W. Milius, *Inorg. Chim. Acta* **2009**, in press.

[11] a) J. A. Schachner, C. L. Lund, J. W. Quail, J. Müller, *Organometallics* **2005**, *24*, 785–787; b) C. L. Lund, J. A. Schachner, J. W. Quail, J. Müller, *Organometallics* **2006**, *25*, 5817–5823.

[12] a) J. A. Schachner, C. L. Lund, J. W. Quail, J. Müller, *Acta Crystallogr., Sect. E* **2005**, *61*, m682–m684; b) J. A. Schachner, G. A. Orlowski, J. W. Quail, H.-B. Kraatz, J. Müller, *Inorg. Chem.* **2006**, *45*, 454–459.

[13] K. Knabel, I. Krossing, H. Nöth, H. Schwenk-Kircher, M. Schmidt-Amelunxen, T. Seifert, *Eur. J. Inorg. Chem.* **1998**, 1095–1114.

[14] J. L. Atwood, A. L. Shoemaker, *J. Chem. Soc., Chem. Commun.* **1976**, 536–537.

[15] H. Braunschweig, C. Burschka, G. K. B. Clentsmith, T. Kupfer, K. Radacki, *Inorg. Chem.* **2005**, *44*, 4906–4908.

[16] H. Braunschweig, G. K. B. Clentsmith, S. Hess, T. Kupfer, K. Radacki, *Inorg. Chim. Acta* **2007**, *360*, 1274–1277.

[17] A. Althoff, P. Jutzi, N. Lenze, B. Neumann, A. Stammler, H.-G. Stammler, *Organometallics* **2002**, *21*, 3018–3022.

[18] a) A. Althoff, P. Jutzi, N. Lenze, B. Neumann, A. Stammler, H.-G. Stammler, *Organometallics* **2003**, *22*, 2766–2774; b) W. Uhl, I. Hahn, A. Jantschak, T. Spies, *J. Organomet. Chem.* **2001**, *637–639*, 300–303.

[19] a) P. Jutzi, N. Lenze, B. Neumann, H.-G. Stammler, *Angew. Chem.* **2001**, *113*, 1469–1473; *Angew. Chem. Int. Ed.* **2001**, *40*, 1424–1427; b) A. Althoff, D. Eisner, P. Jutzi, N. Lenze, B. Neumann, W. W. Schoeller, H.-G. Stammler, *Chem. Eur. J.* **2006**, *12*, 5471–5480.

[20] M. Herberhold, A. Ayazi, W. Milius, B. Wrackmeyer, *J. Organomet. Chem.* **2002**, *656*, 71–80.

[21] K. Stott, J. Keeler, Q. N. Van, A. J. Shaka, *J. Magn. Reson.* **1997**, *125*, 302–324.

[22] T. Parella, *J. Magn. Reson.* **2004**, *167*, 266–272.

[23] M. Herberhold, *Angew. Chem.* **1995**, *107*, 1985–1987; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1837–1839.

[24] CCDC-723411 (for **3b**) and -723412 (for **4**) contain 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.

Received: March 22, 2009