



Ferrocenylaluminum-pyridine adducts, lithium tetra(ferrocenyl)alanate, and the molecular structure of tri(ferrocenyl)aluminum-pyridine

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ABSTRACT

Aluminum compounds with up to four ferrocenyl groups (Fc) linked to aluminum were prepared and characterized in solution by NMR spectroscopy (^1H , ^{13}C , ^{27}Al NMR), and in one case, tri(ferrocenyl)aluminum-pyridine $\text{Fc}_3\text{Al-py}$ in the solid state by X-ray structural analysis. The attempts to stabilize the unsymmetrical species $\text{R}_2\text{Al-Fc}$ and $\text{RAl}(\text{Fc})_2$ ($\text{R} = \text{Me}, \text{Et}$) as the pyridine adducts were partially successful, although it proved difficult to suppress the formation of species containing Al–Cl functions completely.

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1. Introduction

Although organoaluminum compounds have received enormous attention in organic- and organometallic synthesis as well as in the vast field of homogeneous catalysis [1–4], ferrocenylaluminum compounds are not well presented. Some work has been reported starting from 1,1'-dilithiated ferrocene FcLi_2 and organoaluminum dihalides [5–8]. More simple aluminum compounds were isolated from the reaction of ferrocenylmercury chloride FcHgCl with trimethyl- or triethylaluminum to give mixed dimers **2** [9] (Scheme 1).

Only recently, in a preliminary study, we have reported the first examples of dialkyl(ferrocenyl)aluminum dimers $(\text{R}_2\text{AlFc})_2$ **1** with $\text{R} = \text{Me}$ (**a**), Et (**b**) (Scheme 1), starting from ferrocenyllithium FcLi and the respective dialkylaluminum chlorides. It proved possible to obtain the known mixed dimers **2** (Scheme 1) from $(\text{R}_2\text{AlFc})_2$, and the dimer $(\text{Me}_2\text{AlFc})_2$ **1a** was characterized by X-ray structural analysis [10].

In the present work, we want to give a more detailed account of the preliminary study [10], focusing on pyridine adducts of ferrocenylaluminum compounds, and on complexes in which the aluminum bears two, three and four ferrocenyl groups.

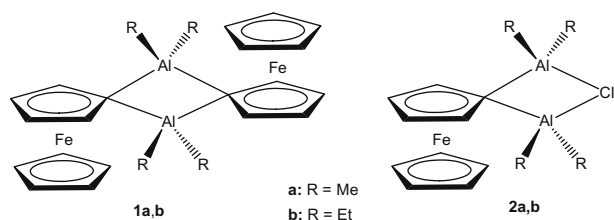
2. Results and discussion

The synthesis of triorganoaluminum compounds of the type $\text{R}_2\text{AlR}'$ is difficult owing to exchange reactions which readily take place leading to mixtures of species such as AlR_3 , $\text{R}_2\text{AlR}'$, $\text{R}'_2\text{AlR}$ and AlR'_3 and the corresponding dimers. The formation of complex mixtures may be suppressed to some extent if the groups R and R' are electronically markedly different, which is the case e.g. for $\text{R} = \text{alkyl}$ (Me, Et) and $\text{R}' = \text{ferrocenyl}$ (Fc). Therefore, it proved possible to prepare and isolate the dimers $(\text{R}_2\text{Al-Fc})_2$ in pure state [10]. Another way to stabilize compounds of the type $\text{R}_2\text{AlR}'$ is conceivable *via* the synthesis of adducts with suitable donors, e.g. with pyridine to give $\text{R}_2\text{AlR}'(\text{py})$. In any case, the Fc-Al bond is labile and readily cleaved and redox reactions may take place. Frequently, this leads to the presence of ferrocene sometimes of biferrocene in the samples studied. Various routes to pyridine adducts of mono-ferrocenylaluminum compounds are shown in the Schemes 2 and 3. The adducts $\text{Fc-AlR}_2(\text{py})$ **3a,b** could be obtained in almost pure state. Depending on the route, the adducts $\text{Fc-AlR}(\text{Cl})(\text{py})$ **4a,b**, containing one Al–Cl function, are also present in mixtures.

Expectedly, the adducts **3** undergo facile exchange reactions with aluminum trichloride, as shown for **3b** (Scheme 3). The reaction of an excess of **3b** with AlCl_3 in the presence of pyridine produces mainly the adduct $\text{Fc-AlEt}(\text{Cl})(\text{py})$ **4b** along with $\text{Et}_2\text{AlCl}(\text{py})$, which is also formed under the same conditions by using an excess of AlCl_3 , if the reaction mixture is worked up after 30 min. Longer reaction times gave mixtures which seem to contain **4b** along with

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Scheme 1. Structurally characterized ferrocenylaluminum compounds.

Fc-AlCl₂(py) **5** as another exchange product. The same mixture is generated by treating **4b** with AlCl₃(py) in toluene at 70 °C for 15 h.

The solution-state structures of the compounds **3–5** follow from their consistent NMR data (Table 1). The assignment of the NMR signals is straightforward (Fig. 1), even in mixtures, as shown for **3b** in the presence of ferrocene, AlEt₃(py) and AlEt₂Cl(py) by ¹H–¹H NOE difference spectra [11].

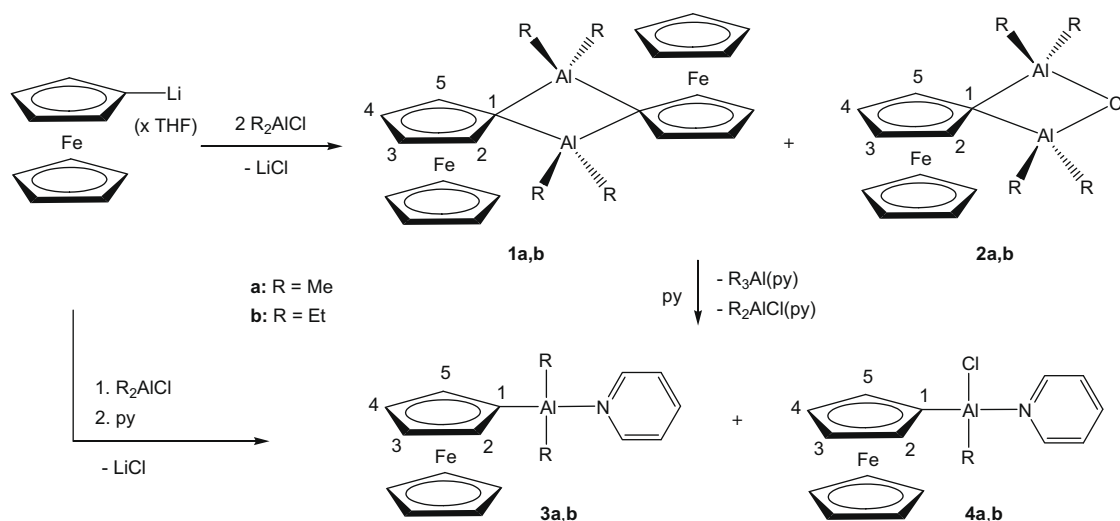
Attempts at the synthesis of alkyl(diferrocenyl)aluminum pyridine adducts **6** gave mixtures containing **6** and Fc-AlR(Cl)(py) **4**, as shown for R = Me in Scheme 4 (see Table 1 for NMR data).

The successful synthesis of the pyridine adduct of tri(ferrocenyl)aluminum **7**(py) depended critically on the amount of FcLi

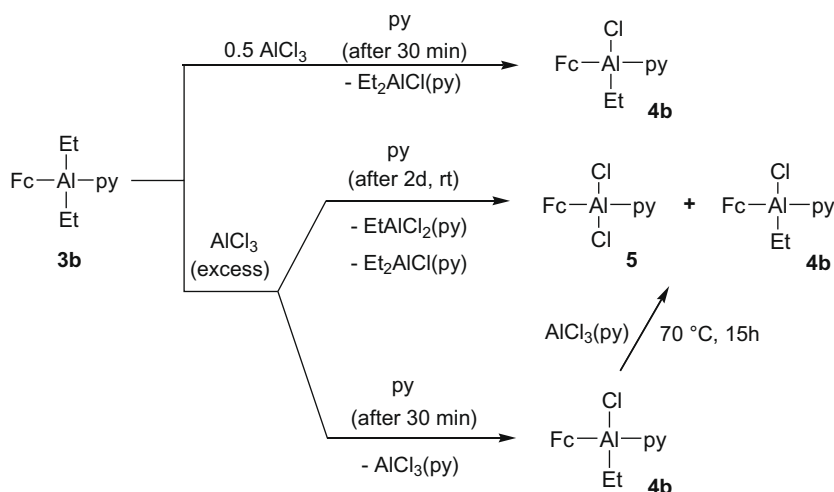
used as well as on the solvent (Scheme 5). Starting from AlCl₃ as a suspension in toluene and adding five equivalents of FcLi(THF) gave first **7**(THF) which, upon addition of pyridine, is easily converted into the desired pyridine adduct **7**(py). The latter could be crystallised and studied by X-ray diffraction (*vide infra*). Using less than five equivalents of FcLi leads to a mixture containing **7**(py) and Fc₂AlCl(py) **8** (see Table 1 for NMR data).

Finally, it was attempted to prepare lithium tetra(ferrocenyl)alunate **9**. The existence of **9** was first noted, when AlCl₃ in THF was treated with six equivalents of FcLi. This produced a mixture containing **7**(THF) and **9**(x THF) (Scheme 5). Then pure **7**(THF) was isolated, and its reaction with one equivalent of FcLi (Scheme 6) gave the pure alunate **9**(x THF).

The formation of the alunate **9** becomes most readily apparent from the ²⁷Al NMR spectra (Fig. 2). Quadrupole-induced ²⁷Al nuclear spin relaxation becomes relatively slow for ²⁹Al nuclei in tetrahedral surroundings [12,13]. Thus, in diluted THF solutions, the line width of the ²⁷Al NMR signal is sufficiently small to allow even for the observation of ¹³C satellites corresponding to ¹J(²⁷Al, ¹³C) = 95 ± 5 Hz. Owing to signal-to-noise problems for such diluted solutions, this parameter could not be determined from ¹³C NMR spectra of **9**. For comparison, a coupling constant ¹J(²⁷Al, ¹³C) = 94 Hz has been measured for Li⁺[AlPh₄]⁻ [14].



Scheme 2. Attempts to prepare the adducts Fc-AlR₂(py) **3a,b**.



Scheme 3. Exchange reactions of Fc-AlEt₂(py) **3b** with aluminum trichloride.

Table 1
¹³C, and ²⁷Al NMR data^{a,b,c} of the compound **3**, **4**, **6–9**.

Compound	AlR	3a R = Me	3b R = Et	4a R = Me	4b R = Et	6a R = Me	7 (py)	7 (THF)	8	9 (x py) excess of py	9 (x py) in THF
7 (K)		298	298 ^d	298	298 ^d	298	298	298	298	298	298
$\delta^{13}\text{C}(\text{Fc}-\text{C}^1)$		73.6 [br]	73.0 [br]	73.3 [br]	73.4 [br]	73.5 [br]	72.8 [br]	72.0 [br]	71.7	73.2 [br]	n.o. ^f
$\delta^{13}\text{C}(\text{Fc}-\text{C}^{2,5})$		76.5	76.6	76.5	76.0	76.4	76.7	76.3	76.2	77.4	77.2
$\delta^{13}\text{C}(\text{Fc}-\text{C}^{3,4})$		71.6	71.8	71.1	71.6	71.2	71.2	71.0	71.0	71.7	68.8
$\delta^{13}\text{C}(\text{Fc}-\text{Cp})$		67.9	68.0	67.8	68.5	67.9	68.1	68.1	68.0	68.1	67.7
$\delta^{13}\text{C}(\text{R})$		-9.1 [br]	-8.8	0.8 [br]	1.0 [br] (CH ₂) 10.6 (CH ₃)	-8.5 [br]	1.9 [br]	68.0	68.0	68.1	68.0
$\delta^{13}\text{C}(\text{py})$ or (THF)		124.8 (C _β) 139.8 (C _γ) 147.0 (C _α)	124.6 125.3 140.2	126.2 141.4 147.6	128.1 141.7 147.9	124.9 140.0 147.3	124.6 140.1 148.1	124.7 67.9 (C _β) 147.5	124.6 140.1 148.1	124.1 136.1 150.3	124.0 135.9 150.4
$\delta^{27}\text{Al}$ <i>h</i> _{1/2} (Hz)		160 (5500 ± 500)	170 (4700 ± 500)	147.6	149.1	150 (7000 ± 500)	145 (4600 ± 500)	150 (4500 ± 500)	155 (60 ± 1)	155 (60 ± 1)	149 (49 ± 1)

^a In toluene-*d*₆] (**3a**, **3b**, **4a**, **4b**, **6a**, **7**(py), **7**(THF), **8**, **9**(x py)), in CD₂Cl₂ (**3b**, **4b**).^b The assignment of the NMR signals is based on ¹H{¹H} NOESY [11], and 2D ¹H/¹³C gHSQC [17] experiments.^c [br] denotes broad ¹³C resonances of aluminum-bonded atoms.^d Measured in toluene-*d*₆].^e Measured in CD₂Cl₂.^f n.o. = not observed.

2.1. X-ray structural analysis of **7**(py)

The molecular structure of **7**(py) is shown in Fig. 3. Intermolecular interactions are negligible. Table 2 contains selected structural parameters, compared with those for the analogous pyridine adduct of the tri(ferrocenyl)silylium cation [Fc₃Si(py)]⁺ [15]. Given for the different central atoms, the structures are well comparable, including the mutual orientations of the ferrocenyl groups around aluminum and silicon, respectively.

3. Conclusions

Pyridine adducts of ferrocenyl(alkyl)aluminum compounds can be prepared and isolated, although they are difficult to obtain in pure state. This is due to the notorious tendency of organoaluminum compounds to undergo exchange reactions. In some cases, it proved difficult to replace the Al–Cl functions completely, and at the same time to avoid the formation of ate-complexes. Expectedly, the most straightforward adduct to be prepared was tri(ferrocenyl)aluminum either with THF or with pyridine as the donor. In this particular case, the straightforward formation of the ate-complex lithium tetra(ferrocenyl)alunate is less favoured for steric reasons, although it can be enforced.

4. Experimental

4.1. General

All preparative work and handling of the samples were carried out observing necessary precautions to exclude traces of air and moisture. Carefully dried solvents and oven-dried glass ware were used throughout. The deuterated solvent CD₂Cl₂ was distilled over CaH₂ in an atmosphere of argon. All other solvents were distilled from Na metal in an atmosphere of argon. Starting materials such as ^tBuLi (1.7 M in pentane), aluminum trichloride (anhydrous, powder 99.999% metal basis), Me₂AlCl (1.0 M in hexanes), MeAlCl₂ (1.0 M in hexanes) (all from Aldrich), Et₂AlCl (1.0 M in hexanes) (Acros), pyridine (anhydrous, 99.8%) (Aldrich) were commercial products. FcLi [16] was prepared by literature procedures. NMR measurements: Bruker ARX 250: ¹H, ¹³C, and ²⁷Al; Varian INOVA 400: ¹H, ¹³C, ²⁷Al NMR; chemical shifts are given relative to Me₄Si [$\delta^1\text{H}$ (CHDCl₂) 5.33, (C₆D₅CD₂H) = 2.08; $\delta^{13}\text{C}$ (CD₂Cl₂) = 53.8, (C₆D₅CD₃) = 20.4; external 1.1 M Al(NO₃)₃ in D₂O [$\delta^{27}\text{Al}$ = 0 for $\Xi(^{27}\text{Al})$ = 26.056890 MHz]. Assignments of ¹H and ¹³C NMR signals are based on ¹H{¹H} NOE difference [11], and 2D ¹H/¹³C gHSQC experiments [17]. The melting points (uncorrected) were determined using a Büchi 510 melting point apparatus.

4.2. Dialkyl(ferrocenyl)aluminum pyridine adduct [(η^5 -C₅H₅)Fe(η^5 -C₅H₄)AlR₂(py)] (**3**)

Alkyl = Me, **3a**: Freshly prepared FcLi (562 mg, 2.93 mmol) was taken up in toluene (25 mL); the suspension was cooled to -78 °C, and Me₂AlCl (2.93 mL of a 1.0 M solution in hexane, 2.93 mmol) was added drop wise. The reaction mixture was stirred at -78 °C for 1 h, then at -50 °C for 30 min, and then it was cooled to -70 °C and pyridine (0.24 mL, 2.93 mmol) was added. This mixture was allowed to reach ambient temperature and was kept stirring for 20 h. Insoluble materials were separated by centrifugation, and the clear liquid was collected. Volatile materials were removed *in vacuo* to leave an orange-yellow residue (853 mg), containing about 80% of **3a** together with FcH and several unidentified side products (¹H and ¹³C NMR).

3a: ¹H NMR (399.8 MHz; toluene-*d*₆]; 25 °C): δ = -0.20 (s, 6H, CH₃Al), 4.20 (s, 5H, Cp), 4.21 (m, 2H, H^{2,5}), 4.43 (m, 2H, H^{3,4}), 6.47 (m, 2H, py-H_β), 6.85 (m, 1H, py-H_γ), 8.23 (d, 2H, py-H_α).

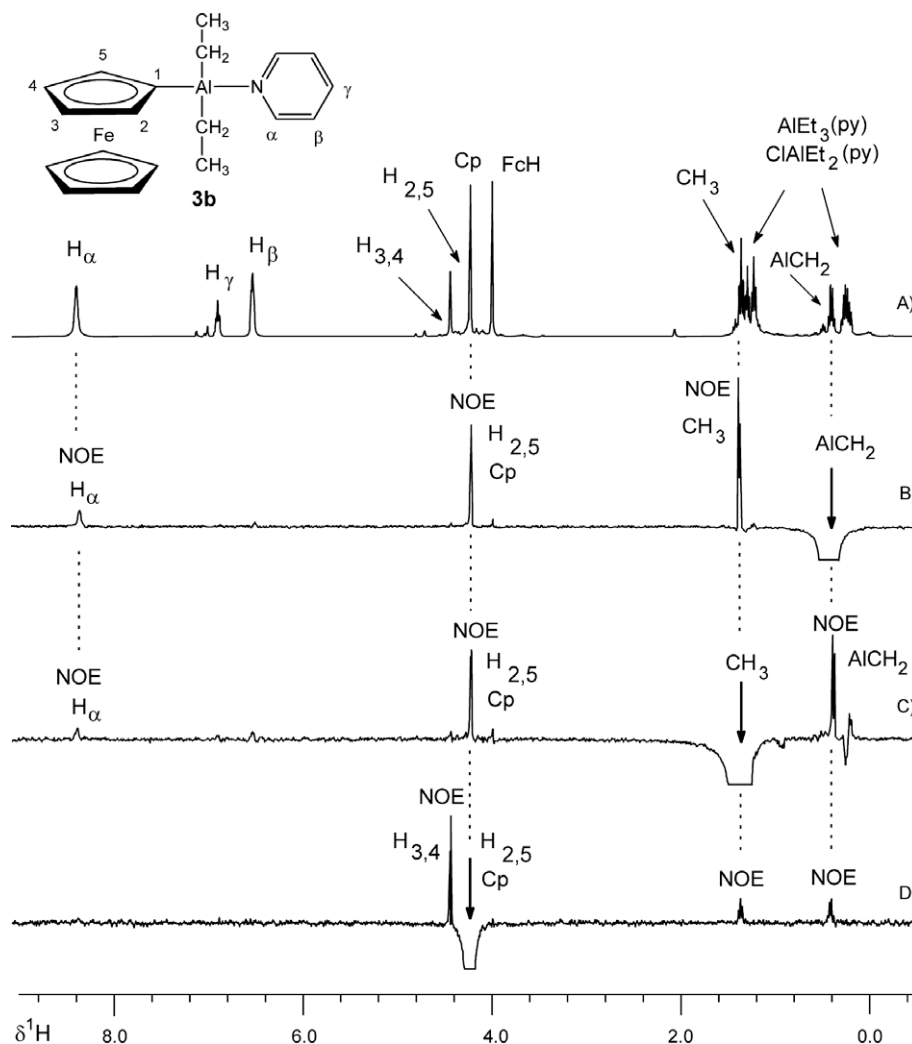


Fig. 1. 399.8 MHz ^1H - ^1H NOE difference spectra (gradient enhanced [11]) of a mixture containing **3b**, FcH, $\text{Et}_3\text{Al}(\text{py})$, and $\text{ClAlEt}_2(\text{py})$ (in toluene- $[\text{d}_8]$, at 23 °C; relaxation delay 2.0 s; mixing time 0.6 s). The irradiated transitions are marked by arrows; the resulting intensities arising from NOE are indicated. (A) Normal ^1H NMR spectrum. (B) Irradiation: $^1\text{H}(\text{AlCH}_2)$ from **3b**; response: $^1\text{H}^{2,5}$ and $^1\text{H}(\text{Cp})$, $^1\text{H}(\text{Me})$ of the EtAl-group, and $^1\text{H}(\text{py-H}_\alpha)$. (C) Irradiation: $^1\text{H}(\text{Me})$ of the EtAl-group from **3b**; response: $^1\text{H}^{2,5}$, $^1\text{H}(\text{Cp})$, $^1\text{H}(\text{AlCH}_2)$ from **3b**, and $^1\text{H}(\text{py-H}_\alpha)$. (D) Irradiation: $^1\text{H}^{2,5}$ and $^1\text{H}(\text{Cp})$; response: $^1\text{H}^{3,4}$, $^1\text{H}(\text{Me})$ and $^1\text{H}(\text{AlCH}_2)$ of the EtAl-group.

Alkyl = Et, **3b**: The synthesis was carried out as described for **3a**, starting from 875 mg (4.56 mmol) of FcLi in toluene (40 mL) and a solution of Et_2AlCl (4.0 mL of a 1.0 M solution in hexane, 4.00 mmol). The reaction mixture was stirred at -78 °C for 1 h, then at -10 °C for 30 min, then cooled to -40 °C, and pyridine (0.50 mL; 6.18 mmol) was added. The red-orange residue (1539 mg) in the end contained about 70% of **3b**, 5% of **4b** together with FcH, $\text{Et}_2\text{AlCl}(\text{py})$, $\text{Et}_3\text{Al}(\text{py})$, and several unidentified side products (^1H and ^{13}C NMR).

3b: ^1H NMR (399.8 MHz; toluene- $[\text{d}_8]$; 25 °C): $\delta = 0.42$ (q, 4H, CH_2Al), 1.36 (t, 6H, CH_3), 4.19 (s, 5H, Cp), 4.21 (m, 2H, $\text{H}^{2,5}$), 4.42 (m, 2H, $\text{H}^{3,4}$), 6.54 (m, py- H_β), 6.92 (m, py- H_γ), 8.29 (d, py- H_α). ^1H NMR (399.8 MHz; CD_2Cl_2 ; 25 °C): $\delta = 0.26$ (q, 4H, CH_2Al), 1.21 (t, 6H, CH_3), 4.14 (m, 2H, $\text{H}^{2,5}$), 4.18 (s, 5H, Cp), 4.41 (m, 2H, $\text{H}^{3,4}$), 7.61 (m, py- H_β), 8.03 (m, py- H_γ), 8.73 (m, py- H_α).

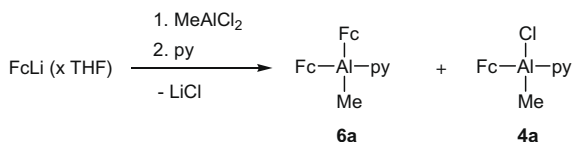
4.3. Dialkyl(ferrocenyl)aluminum pyridine adduct [$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{AlAlk}_2(\text{py})$] (**3**) and alkyl(chloro)(ferrocenyl)aluminum pyridine adduct [$(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{Al}(\text{Cl})\text{Alk}(\text{py})$] (**4**)

Alkyl = Me, **3a** and **4a**: A suspension of freshly prepared FcLi (453 mg, 2.35 mmol) in toluene (20 mL) was cooled to -78 °C, and Me_2AlCl (5 mL of a 1.0 M solution in hexane, 5 mmol) was

added. After stirring the reaction mixture for 1 h at -78 °C and for 20 h at ambient temperature, insoluble materials were separated by centrifugation, and the clear liquid was collected. Volatile materials were removed *in vacuo* to leave 780 mg of a mixture containing **1a** and **2a** (ratio 2:3) together with $\text{Me}_2\text{AlCl}(\text{THF})$ and FcH (^1H and ^{13}C NMR at 243 K). Pyridine (0.41 mL, 5 mmol) was added to a mixture of **1a/2a** in toluene (10 mL) at 0 °C. The solution was stirred for 20 h, insoluble materials were separated by centrifugation, and the clear liquid was collected and evaporated to leave an orange-yellow residue (673 mg), containing about 70% of **3a** along with **4a** and a small amount of ferrocene (^1H and ^{13}C NMR).

4a: ^1H NMR (399.8 MHz; toluene- $[\text{d}_8]$; 25 °C): $\delta = -0.12$ (s, 3H, CH_3Al), 4.23 (s, 5H, Cp), 4.24 (m, 2H, $\text{H}^{2,5}$), 4.42 (m, 2H, $\text{H}^{3,4}$), 6.68 (m, py- H_β), 7.03 (m, py- H_γ), 8.55 (m, py- H_α).

Alkyl = Et, **3b** and **4b**: The syntheses were carried out as described above for **3a/4a**, starting from 910 mg (4.74 mmol) of FcLi and Et_2AlCl (6.89 mL of a 1.0 M solution in hexane, 6.89 mmol), to give 1415 mg of a mixture containing **1b** and **2b** (ratio 1:6). Pyridine (0.60 mL; 7.42 mmol) was added to this mixture in toluene (10 mL) at 0 °C. The solution was stirred for 1 h and evaporated to leave a red-orange residue, containing about 60% of **4b**, 20% of **3b** along with FcH, $\text{Et}_2\text{AlCl}(\text{py})$, $\text{Et}_3\text{Al}(\text{py})$, and several unidentified side products (^1H and ^{13}C NMR).



Scheme 4. Attempted synthesis of the pyridine adduct of di(ferrocenyl)methylaluminum.

4b: ^1H NMR (399.8 MHz; CD_2Cl_2 ; 25 °C): δ = 0.10 (q, 2H, CH_2Al), 1.03 (t, 3H, CH_3), 4.12 (m, 2H, $\text{H}^{2,5}$), 4.18 (s, 5H, Cp), 4.41 (m, 2H, $\text{H}^{3,4}$), 7.76 (m, py- H_β), 8.08 (m, py- H_γ), 9.21 (m, py- H_α). ^1H NMR (399.8 MHz; toluene- $[\text{d}_8]$; 25 °C): δ = 0.50 (q, 2H, CH_2Al), 1.31 (t, 3H, CH_3), 4.25 (m, 2H, $\text{H}^{2,5}$), 4.255 (s, 5H, Cp), 4.40 (m, 2H, $\text{H}^{3,4}$), 6.81 (m, py- H_β), 7.15 (m, py- H_γ), 8.59 (m, py- H_α).

4.4. Reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{AlEt}_2(\text{py})]$ (**3b**) with AlCl_3 and pyridine

(a) A solution of **3b** (145 mg; 0.42 mmol) in toluene- $[\text{d}_8]$ (2 mL) was cooled to -40 °C and added to AlCl_3 (30 mg; 0.22 mmol). The mixture was stirred for 0.5 h at ambient temperature, and pyridine (0.10 mL; 1.24 mmol) was added

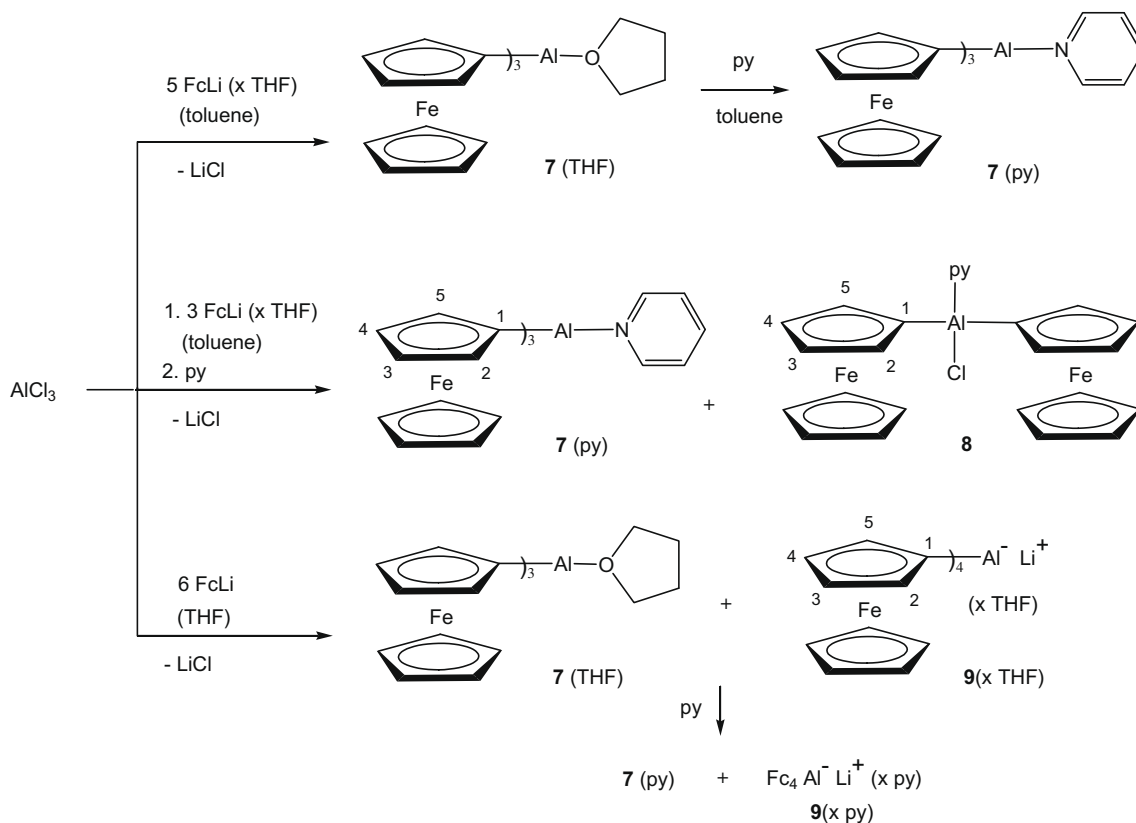
to the reaction mixture at 0 °C. The resulting mixture contained about 80% of **4b** together with FcH and $\text{Et}_2\text{AlCl}(\text{py})$ (^1H and ^{13}C NMR).

(b) A solution of **3b** (90 mg; 0.26 mmol) in toluene- $[\text{d}_8]$ (1 mL) was cooled to -40 °C and added to AlCl_3 (55 mg; 0.41 mmol). The mixture was stirred for 40 h at ambient temperature, and then pyridine (0.20 mL, 2.47 mmol) was added at 0 °C. The resulting mixture contained about 50% of **5**, 30% of **4b** along with small amounts of ferrocene, $\text{EtAlCl}_2(\text{py})$ and $\text{Et}_2\text{AlCl}(\text{py})$ (^1H and ^{13}C NMR).

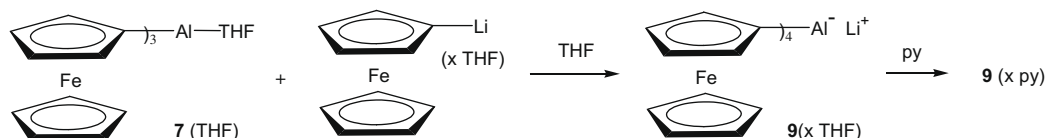
5: ^1H NMR (399.8 MHz; toluene- $[\text{d}_8]$; 25 °C): δ = 3.98 (m, 2H, $\text{H}^{2,5}$), 4.25 (s, 5H, Cp), 4.34 (m, 2H, $\text{H}^{3,4}$), 6.81 (m, py- H_β), 7.10 (m, py- H_γ), 8.55 (m, py- H_α). ^{13}C NMR (100.5 MHz; toluene- $[\text{d}_8]$; 25 °C): δ = 68.7 (Cp), 72.3 ($\text{C}^{3,4}$), 76.5 ($\text{C}^{2,5}$), 124.5 (py- C_β), 137.2 (py- C_γ), 149.0 (py- C_α).

$\text{Et}_2\text{AlCl}(\text{py})$: ^1H NMR (399.8 MHz; toluene- $[\text{d}_8]$; 25 °C): δ = 0.29 (q, 4H, CH_2Al), 1.22 (t, 6H, CH_3), 6.81 (m, py- H_β), 7.14 (m, py- H_γ), 8.45 (m, py- H_α).

$\text{EtAlCl}_2(\text{py})$: ^1H NMR (399.8 MHz; toluene- $[\text{d}_8]$; 25 °C): δ = 0.36 (q, 2H, CH_2Al), 1.11 (t, 3H, CH_3), 6.81 (m, py- H_β), 7.14 (m, py- H_γ), 8.55 (m, py- H_α).



Scheme 5. Attempts at the synthesis of tr(ferrocenyl)aluminum **7** as THF or pyridine adducts.



Scheme 6. Synthesis of lithium tetra(ferrocenyl)alunate with THF.

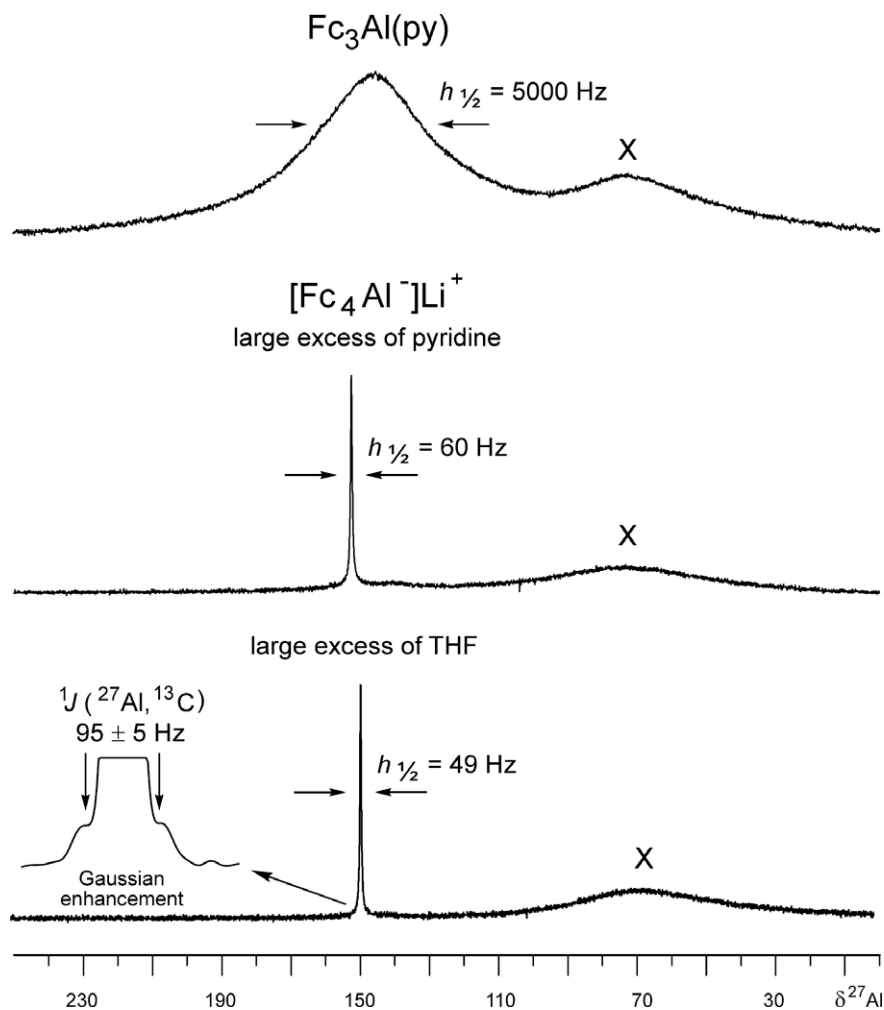


Fig. 2. 104.2 MHz $^{27}\text{Al}\{^1\text{H}\}$ NMR spectra of $\text{Fc}_3\text{Al}(\text{py})$ **7**(py) (upper trace), $[\text{Fc}_4\text{Al}^-]\text{Li}^+$ (excess of py) (**9**(x py)) in toluene- $[\text{d}_8]$ (middle trace), and diluted sample of **9**(x py) in THF showing ^{13}C satellites in the expansion (lower trace). The probehead background signal [20] is marked by X.

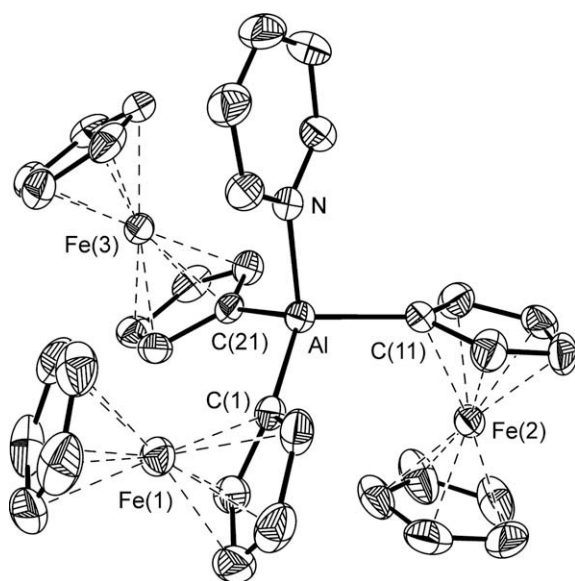


Fig. 3. Molecular structure of **7**(py) (ORTEP plot, 30% probability; hydrogen atoms are omitted for clarity (see Table 2 for structural parameters).

4.5. Di(ferrocenyl)(methyl)aluminum pyridine adduct $[\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\}_2\text{AlMe}(\text{py})]$ (**6a**)

The synthesis was carried out as described for **2a**, starting from 828 mg (4.31 mmol) of FcLi in toluene (30 mL), a solution of MeAlCl_2 (1.72 mL of a 1.0 M in hexane, 1.72 mmol) and 0.2 mL (2.5 mmol) of pyridine. The orange-yellow oil was washed with hexane (10 mL). The residue was dried in a vacuum to give 660 mg of a mixture containing about 80% of **6a**, together with ferrocene, **4a**, and several unidentified side products (^1H and ^{13}C NMR).

6a: ^1H NMR (399.8 MHz; toluene- $[\text{d}_8]$; 25 °C): $\delta = -0.03$ (s, 3H, MeAl), 4.12 (s, 10H, Cp), 4.23 (m, 4H, $\text{H}^{2,5}$), 4.43 (m, 4H, $\text{H}^{3,4}$), 6.42 (m, py- H_β), 6.79 (m, py- H_γ), 8.46 (m, py- H_α).

4.6. Tri(ferrocenyl)aluminum THF adduct $[\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\}_3\text{Al}(\text{THF})]$ (**7**(THF))

A suspension of freshly prepared FcLi (974 mg, 5.07 mmol) in toluene (30 mL) was cooled to -60 °C, and pure, degassed AlCl_3 (135 mg, 1.01 mmol) was added in one portion. After stirring the reaction mixture for 1 h at -60 °C and for 20 h at ambient temperature, insoluble materials were separated by centrifugation, the

Table 2

Selected bond lengths (pm) and angles ($^{\circ}$)^a of the ferrocenes **7(py)** (Fig. 3), and [Fc₃Si(py)]^b.

7(py)		[Fc ₃ Si(py)] ⁺	
Al–C(1)	197.1(5)	Si(1)–C(1)	183.2(6)
Al–C(11)	198.2(5)	Si(1)–C(11)	183.3(6)
Al–C(21)	197.7(5)	Si(1)–C(21)	184.3(6)
Al–N	200.0(4)	Si(1)–N(31)	185.8(5)
C(1)–Al–C(11)	111.3(2)	C(1)–Si(1)–C(11)	114.9(3)
C(1)–Al–C(21)	115.5(2)	C(1)–Si(1)–C(21)	115.0(3)
C(11)–Al–C(21)	113.0(2)	C(11)–Si(1)–C(21)	107.8(3)
C(1)–Al–N	107.21(19)	C(1)–Si(1)–N(31)	106.8(2)
C(11)–Al–N	101.73(18)	C(11)–Si(1)–N(31)	104.3(2)
C(21)–Al–N	106.78(18)	C(21)–Si(1)–N(31)	107.2(2)
C ₅ (Fe(1))/Al(β ₁)	13.9 (bent away from Fe)	C ₅ (Fe(2))/Si(1)(β ₂)	7.4 (towards Fe)
C ₅ (Fe(2))/Al(β ₂)	10.5 (towards Fe)		
C ₅ (Fe(3))/Al(β ₃)	6.7 (bent away from Fe)		
C ₅ /C ₅ (twist)(τ ₁) Fe(1)	5.8		
C ₅ /C ₅ (twist)(τ ₂) Fe(2)	9.0		
C ₅ /C ₅ (twist)(τ ₃) Fe(3)	6.3		

^a See Refs. [18,19] for the definition of the angles β, and τ.

^b Ref. [15].

clear liquid was evaporated to give 883 mg of **7(THF)** together with FcH.

7(THF): ¹H NMR (399.8 MHz; toluene-*[d*₈]; 25 °C): δ = 1.11 (m, THF-H_β), 3.68 (m, THF-H_α), 4.17 (s, 15H, Cp), 4.32 (m, 6H, H^{2,5}), 4.44 (m, 6H, H^{3,4}).

4.7. Tri(ferrocenyl)aluminum pyridine adduct [((η⁵-C₅H₅)Fe(η⁵-C₅H₄))₃Al(py)] (**7(py)**)

Pyridine (0.2 mL, 2.5 mmol) was added to a reaction mixture containing **7(THF)**/FcH (440 mg) in toluene, at –30 °C. The solution was stirred for 1 h, insoluble materials were separated by centrifugation, and the clear liquid was evaporated. The orange-brown oil thus obtained was washed with hexane (10 mL), the residue after removing of the hexane was dried in a vacuum to give 393 mg of a mixture containing **7(py)** (about 80%) together with FcH. Single orange crystals of **7(py)** for X-ray analysis were grown from a toluene-*[d*₈] solution after 2 weeks at –30 °C; m.p. 220–230 °C.

7(py): ¹H NMR (399.8 MHz; toluene-*[d*₈]; 25 °C): δ = 4.05 (s, 15H, Cp), 4.40 (m, 6H, H^{2,5}), 4.47 (m, 6H, H^{3,4}), 6.44 (m, 2H, py-H_β), 6.79 (m, 1H, py-H_γ), 8.78 (m, 2H, py-H_α).

4.8. Tri(ferrocenyl)aluminum pyridine adduct [((η⁵-C₅H₅)Fe(η⁵-C₅H₄))₃Al(py)] (**7(py)**) and chloro(di(ferrocenyl)aluminum pyridine adduct [((η⁵-C₅H₅)Fe(η⁵-C₅H₄))₂AlCl(py)] (**8**)

Freshly prepared FcLi (650 mg, 3.39 mmol) in toluene (40 mL) as a suspension was cooled to –20 °C, and pure, degassed AlCl₃ (151 mg, 1.13 mmol) was added in one portion. The mixture was kept stirring for 20 h at room temperature, cooled to 0 °C, and pyridine (0.18 mL, 2.22 mmol) was added. This solution was stirred for 1 h, insoluble materials were separated by centrifugation, and the clear liquid was evaporated. The orange-brown oil was washed with hexane (2 × 10 mL), dried in a vacuum to give 572 mg of a mixture containing **7(py)** (about 60%) and **8** (about 40%) together with a small amount of ferrocene (¹H and ¹³C NMR).

8: ¹H NMR (399.8 MHz; toluene-*[d*₈]; 25 °C): δ = 4.17 (s, 10H, Cp), 4.31 (m, 4H, H^{2,5}), 4.42 (m, 4H, H^{3,4}), 6.44 (m, py-H_β), 6.79 (m, py-H_γ), 8.78 (m, py-H_α).

4.9. Tri(ferrocenyl)aluminum THF adduct [((η⁵-C₅H₅)Fe(η⁵-C₅H₄))₃Al(py)] (**7(py)**) and lithium-tetra(ferrocenyl)alanate [((η⁵-C₅H₅)Fe(η⁵-C₅H₄))₄Al]Li (**9**)

A mixture of freshly prepared FcLi (624 mg, 3.25 mmol) and pure, degassed AlCl₃ (85 mg, 0.64 mmol) was prepared in a Schlenk-tube, cooled to –78 °C, and THF (20 mL) was added. After stirring for 1 h at –78 °C and for 20 h at ambient temperature, volatile materials were removed *in vacuo*, and toluene-*[d*₈] (4 mL) was added. Insoluble materials were separated by centrifugation, and the clear liquid was collected to give a mixture containing **7(THF)** and some **9**(× THF), along with a small amount of ferrocene. Pyridine (0.50 mL; 6.18 mmol) was added to this mixture at 0 °C. The solution was stirred for 1 h and analysed by NMR spectroscopy to contain **7(py)** (≈80%) and **9**(x py) (≈10%), a small amount of ferrocene and several unidentified side products (¹H and ¹³C NMR).

4.10. Lithium-tetra(ferrocenyl)alanate [((η⁵-C₅H₅)Fe(η⁵-C₅H₄))₄Al]Li (**9**)

A mixture of freshly prepared FcLi (147 mg, 0.77 mmol) and freshly prepared **7(THF)** (380 mg, 0.65 mmol) was placed into a Schlenk-tube, cooled to –78 °C, and THF (5.5 mL) was added. The mixture was warmed to RT, stirred for 30 min, and volatile materials were removed *in vacuo*. The remaining solid was dissolved in toluene-*[d*₈] (0.5 mL), a layer of brown-black oil was formed at the bottom. Then pyridine (finally 1 mL) was added in several portions. The reaction mixture contained **9**(x py) (about 80%), **7(py)** (about 5%) together with ferrocene and (Fc)₂.

9(x py) (x ≈ 100): ¹H NMR (399.8 MHz; toluene-*[d*₈]; 25 °C): δ = 4.24 (s, 20H, Cp), 4.41 (m, 8H, H^{2,5}), 4.72 (m, 8H, H^{3,4}), 6.97 (m, py-H_β), 7.34 (m, py-H_γ), 8.53 (m, py-H_α).

9(x py) (x ≈ 10) in THF: ¹H NMR (399.8 MHz; toluene-*[d*₈]; 25 °C): δ = 1.55 (m, THF-H_β), 3.45 (m, THF-H_α), 3.79 (s, 20H, Cp), 4.02 (m, 8H, H^{2,5}), 4.22 (m, 8H, H^{3,4}), 6.99 (m, py-H_β), 7.37 (m, py-H_γ), 8.37 (m, py-H_α).

Table 3

Crystallographic data of the ferrocene **7(py)**.

	7(py)
Formula	C ₃₅ H ₃₂ AlFe ₃ N
Crystal	red-orange prism
Dimensions (mm)	0.22 × 0.18 × 0.16
Crystal system	monoclinic
Space group	C2/c
Lattice parameters	
a (pm)	2085.4(4)
b (pm)	1354.1(3)
c (pm)	2136.8(4)
β (°)	105.29(3)
Z	8
Absorption coefficient μ (mm ⁻¹)	1.531
Diffraction	STOE IPDS I (Mo Kα, λ = 71.937 pm), graphite monochromator
Measuring range (θ, °)	1.8–25.9
Reflections collected	19 367
Independent reflections [I ≥ 2σ(I)]	5514
Absorption correction ^a	None
Refined parameters	361
wR2/R1 [I ≥ 2σ(I)]	0.0962/0.0472
Maximum/minimum residual electron density (e pm ⁻³ 10 ⁻⁶)	0.610/–0.295

^a Absorption corrections did not improve the parameter set.

4.11. Crystal structure determination of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)]_3\text{Al}(\text{py})$ (**7(py)**)

Details pertinent to the crystal structure determination are listed in Table 3. Crystals of appropriate size were sealed under argon in a Lindemann capillary, and the data collections were carried out at 20 °C (see Supplementary material).

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Appendix A. Supplementary material

CCDC 717954 contains the supplementary crystallographic data for **7(py)**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.ica.2009.05.019](https://doi.org/10.1016/j.ica.2009.05.019).

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