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A Pyridine-Stabilized Alumoxane Containing Two 1,3,2-Diazaalumina[3]ferrocenophane Units

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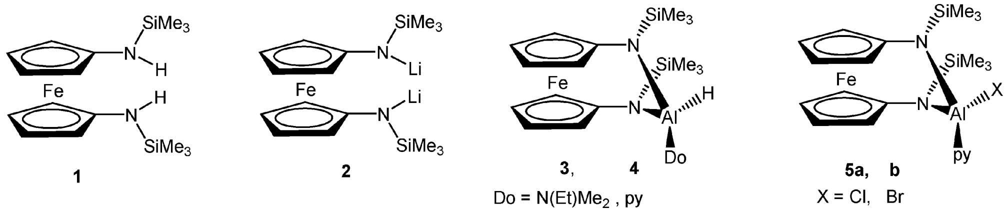
Dialuminoxane **6**, in which both aluminum atoms are coordinated by pyridine and each is part of a 1,3-bis(trimethylsilyl)-1,3,2-diazaalumina[3]ferrocenophane unit, was isolated as a side product accompanying the synthesis of the corresponding [3]ferrocenophane with Al–H or Al–Cl functionalities. Although attempted high-yield syntheses of **6** failed, its structure could be established by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy in solution and by X-ray structural analysis in the solid state. In various experiments to obtain **6**, crystalline material was isolated and identified as the desired dialuminoxane either with a linear Al–O–Al (**6A**) or bent Al–O–Al (**6B**) unit. This is the first example of a structurally characterized bis(amino)dialuminoxane.

Introduction

The use of methylaluminoxane (MAO) as a cocatalyst in olefin polymerization[1] has greatly stimulated research in the field of molecular compounds containing Al–O–Al units. Monomers of dialuminoxanes require bulky substituents at aluminum[2] and further stabilization by donor ligands in order to increase the coordination number of aluminum.[3] Bulky amino groups may also serve this purpose, as shown in principle for an alane containing a three-coordinate aluminum atom bearing two 2,2,6,6-tetramethylpiperidyl substituents and a 2,6-diisopropylphenoxy group at the aluminum atom.[4] With less bulky amino groups at the aluminum center and an Al–O functionality, the aluminum atom becomes four-coordinate either by dimerization or by adding a suitable donor ligand.[5] Various dialuminoxanes have been reported, in which the aluminum atom is four-coordinate and bears only one amino functional group.[6] Examples of dialuminoxanes with two amino functionalities at both aluminum atoms are rare.[7] Recently, we showed that 1,1′-bis(trimethylsilylamino)ferrocene (**1**)[8] and its *N*,*N*′-dilithium derivative **2**[9,10] can be readily converted into 1,3-diaza-2-alumina[3]ferrocenophanes with Al–H (**3**, **4**),[11] Al–halogen (**5**),[11] or Al–alkyl functionalities[12,13] (Scheme 1). In the course of these and related studies, we repeatedly observed a side product in the reaction mixtures, for which we had assumed a dialuminoxane structure stabilized as dipyridine adduct **6**. We have now succeeded in isolating and characterizing dialuminoxane **6**, and we have attempted to prepare **6** by various methods.

Results and Discussion

Attempts to prepare dialuminoxane **6** starting from aluminum hydrides **3** and **4** are summarized in Scheme 2. NMR spectra of solutions containing hydride **4** invariably show weak signals attributed to starting material **1** and another defined species. Repeated attempts to isolate the latter compound gave a small amount of orange air- and moisture-sensitive crystals identified as dialuminoxane **6**. Controlled hydrolysis by using solvents (CD_2Cl_2 or toluene) saturated with water did not give **6** in larger quantity. Instead,



Scheme 1. Starting materials for the synthesis of 1,3-diaza-2-alumina[3]ferrocenophanes and examples of such complexes.[11]

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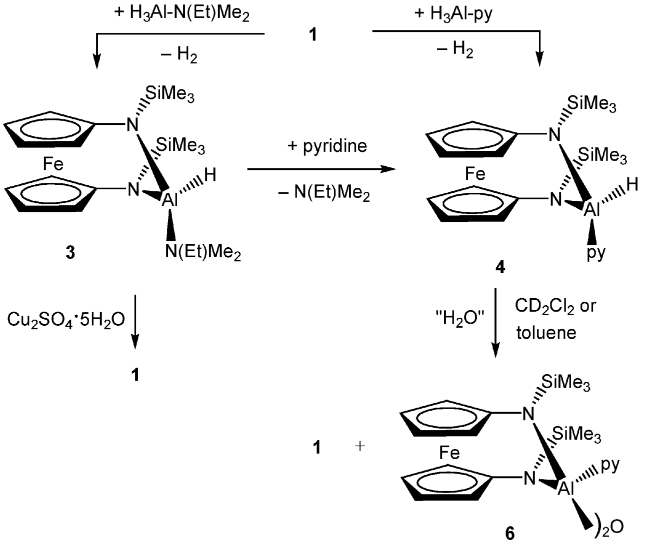
the amount of **1** in the reaction mixture increased. Similarly, treatment of **3** in toluene with copper(II) sulfate hydrate[14] gave only compound **1**.



Scheme 2. Attempted conversion of aluminum hydrides into dialuminoxanes.

NMR spectra of solutions of aluminum halides **5a** or **5b** sometimes revealed additional weak signals that could not be assigned with certainty. Attempts to convert the halides into dialuminoxane **6** are shown in Scheme 3. None of these attempts gave dialuminoxane **6** in appreciable yield. Apparently, a very specific source of hydrolysis is required to produce **6**. When we studied the reaction of *N,N'*-dilithium derivative **2** with Cp*$AlCl_2$,[15] we obtained chloride **5a**[11,12] instead of the expected 1,3-diaza-2-alumina[3]ferrocenophane with an Al-Cp* functionality. Together with chloride **5a**, the reaction solution contained **1** and **6**. The chloride was crystallized from toluene, then dissolved in CD_2Cl_2, and from this solution crystals of **6** slowly separated. At the same time, decomposition to give **1** and hexamethyldisiloxane was observed.

Dialuminoxane **6** in solution was characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy (Experimental Section). In contrast to the ^{1}H NMR spectrum, some of the ^{13}C(ferrocene) NMR signals overlap with those of **4**, which is always present in the mixtures. In the 2D ^{1}H–^{13}C NMR spectrum (Figure 1), this overlap is resolved, and the assignment is straightforward. The $\delta^{29}Si$ value (–0.8 ppm) is in the ex-

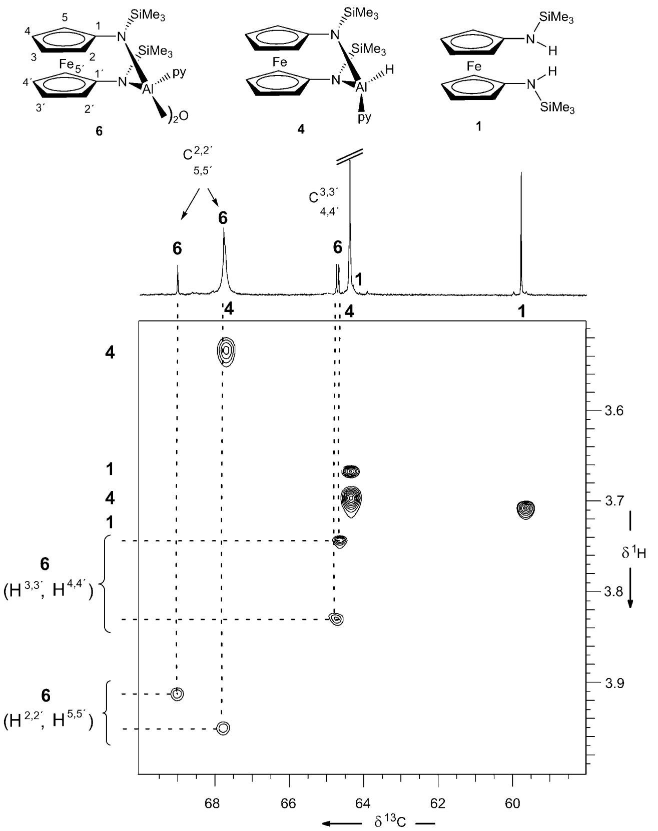
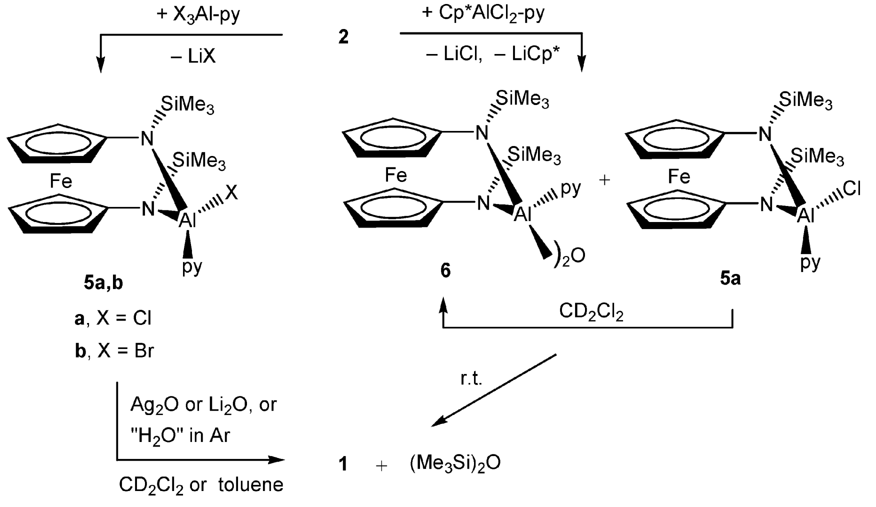


Figure 1. Contour plot of part of the 400 MHz 2D ^{1}H–^{13}C-correlated spectrum of a mixture containing **6**, **4**, and **1** (in CD_2Cl_2, at 23 °C), recorded by the gradient-selected (gs-)HSQC method.[16] The assignments for **6** are indicated by the dashed lines.



Scheme 3. Attempted conversion of aluminum halides into dialuminoxanes.

pected range and is comparable with the data for the pyridine adducts of corresponding aluminium hydride **4** (δ^{29}Si 2.9 ppm),[11] -chloride **5a** (δ^{29}Si 4.0 ppm)[11] or -alkyl [δ^{29}Si 2.5 ppm (Me),[13] 0.8 ppm (Et),[13] –1.1 ppm (*t*Bu)].[12]

X-ray Structural Studies of the Dialuminoxane 6

Two different modifications of **6** were isolated from the same solvent (CD_2Cl_2), **6A** from the sample containing hydride **4** and **6B** from the sample containing chloride **5a**. In the case of **6A**, a linear Al–O–Al unit and a center of symmetry are present (Figure 2), whereas the Al–O–Al unit is bent in **6B** and there is no center of symmetry (Figure 3). The crystal structure of **6A** was also determined at 173 K and there are only marginal differences in comparison to the data measured at ambient temperature (Table 1). The pyridine ligands are always located between the N–SiMe$_3$ groups, which is in contrast to the finding for **4**, **5**,[11] and the Al–Me and Al–Et derivatives.[13] However, the orientation of the Al–pyridine unit in **6** is analogous to that for the Al–*t*Bu compound,[12] which supports the suggestion that minimized steric repulsion controls this particular conformation.

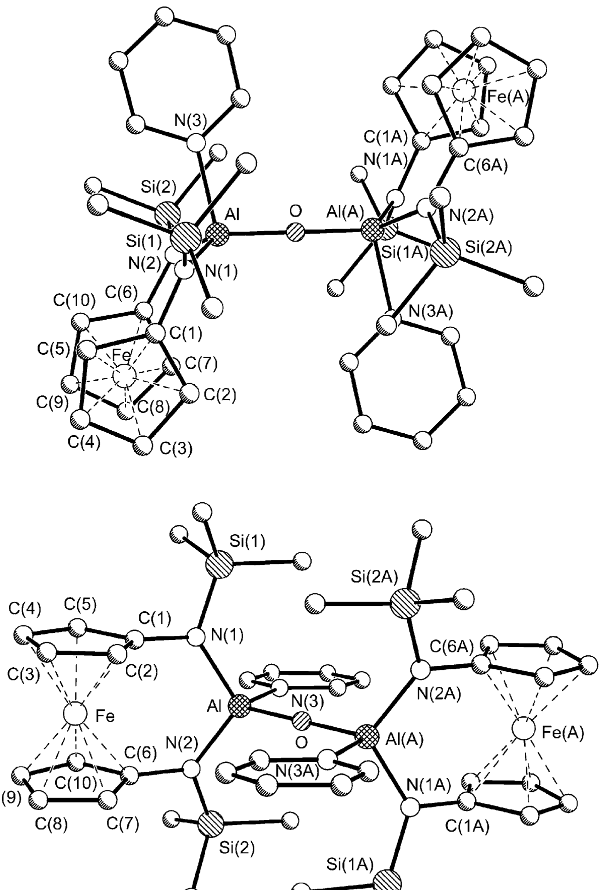


Figure 2. Different views of the molecular structure of **6A** at 293 K (top) and at 173 K (bottom); hydrogen atoms are omitted for clarity; see Table 1 for structural parameters.

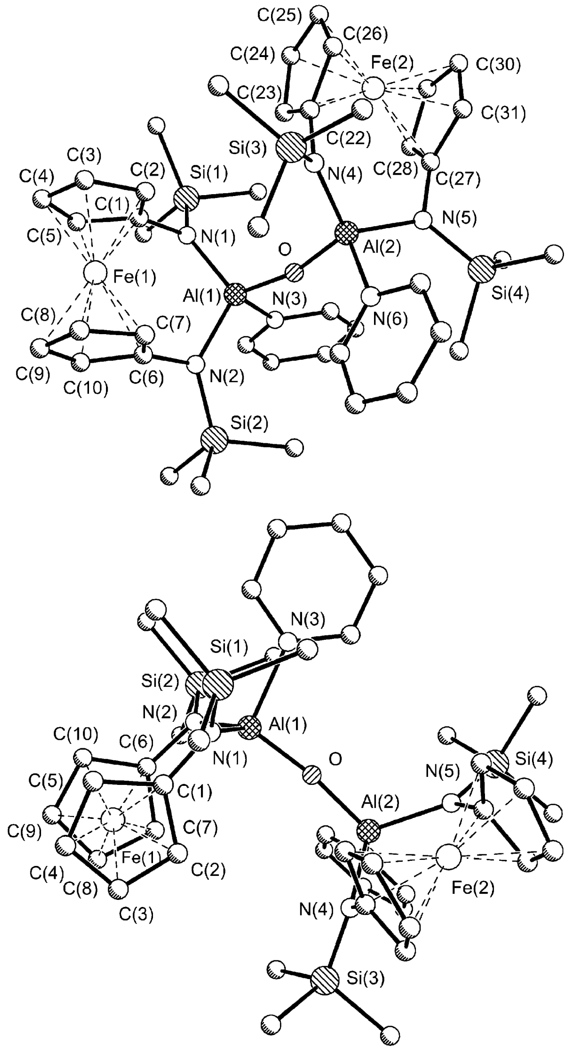


Figure 3. Two views of the molecular structure of **6B** at 293 K; hydrogen atoms are omitted for clarity; see Table 1 for structural parameters.

Except for the fairly large twist angle τ (17.7°) of the C^5 rings in one of the two ferrocenophane units in **6B**, the corresponding structural parameters (bond lengths and angles) of both **6A** and **6B** are similar to those for **4**,[11] **5a**,[11] and the Al–alkyl derivatives.[12,13] The Al–O bonds in **6A** and **6B** are only slightly longer than those in $\{[(Me_3Si)_2CH]_2Al\}_2O$ (d_{Al-O} = 168.7 pm), which contains three-coordinate Al atoms,[2a] and they are shorter than those in the Me$_3$NO adducts[2a] of this monomeric dialuminoxane (d_{Al-O} = 175.3 and 173.6 pm). The energy difference for dialuminoxanes with linear or bent Al–O–Al units appears to be small,[2a,18] and the different mutual arrangements of the pyridine and the ferrocenophane fragments in **6A** and **6B** indicate that there is no strong preference for a specific orientation of these groups with respect to the Al–O–Al unit.

Table 1. Selected bond lengths [pm] and angles [°][a] of dialuminoxanes **6A** and **6B**.

	6A[b] (293 K)		**6B** (293 K)
Al–N(1)	185.6(3)	Al(1)–N(1)	185.8(5)
Al–N(2)	185.4(3)	Al(1)–N(2)	185.2(5)
		Al(2)–N(4)	187.1(5)
		Al(2)–N(5)	186.3(5)
Al–N(3) (from py)	200.2(3)	Al(1)–N(3) (from py)	198.5(5)
		Al(2)–N(6) (from py)	200.6(5)
Al–O	169.4(1)	Al(1)–O	169.7(4)
		Al(2)–O	170.0(4)
N(1)–Si(1)	172.8(3)	N(1)–Si(1)	172.5(5)
N(2)–Si(2)	173.4(3)	N(2)–Si(2)	172.2(4)
		N(4)–Si(3)	172.2(5)
		N(5)–Si(4)	172.0(5)
N(1)···N(2)	311.3	N(1)···N(2)	312.9
		N(4)···N(5)	315.3
C(1)···C(6)	317.1	C(1)···C(6)	320.7
		C(22)···C(27)	321.2
Fe···Al	361.1	Fe(1)···Al(1)	346.2
		Fe(2)···Al(2)	348.7
N(1)–Al–N(2) (*endo*)	114.1(1)	N(1)–Al(1)–N(2) (*endo*)	115.0(2)
		N(4)–Al(2)–N(5) (*endo*)	115.2(2)
N(1)–Al–O	117.0(1)	N(1)–Al(1)–O	116.9(2)
N(2)–Al–O	116.8(1)	N(2)–Al(1)–O	114.9(2)
		N(4)–Al(2)–O	115.5(2)
		N(5)–Al(2)–O	116.3(2)
N(3)–Al–O	101.8(1)	N(3)–Al(1)–O	102.7(2)
		N(6)–Al(2)–O	103.1(2)
Al–O–Al(A)	180.0	Al(1)–O–Al(2)	166.1(2)
N(1)–Al–N(3) (from py)	102.0(1)	N(1)–Al(1)–N(3) (from py)	101.8(2)
N(2)–Al–N(3) (from py)	101.4(1)	N(2)–Al(1)–N(3) (from py)	102.2(2)
		N(4)–Al(2)–N(6) (from py)	102.5(2)
		N(5)–Al(2)–N(6) (from py)	100.9(2)
C(1)–N(1)–Si(1)	111.6(2)	C(1)–N(1)–Si(1)	113.3(3)
		C(22)–N(4)–Si(3)	115.5(3)
C(6)–N(2)–Si(2)	112.1(2)	C(6)–N(2)–Si(2)	112.8(3)
		C(27)–N(5)–Si(4)	112.5(4)
Al–N(1)–C(1)	119.3(2)	Al(1)–N(1)–C(1)	112.5(3)
		Al(2)–N(4)–C(22)	110.6(3)
Al–N(2)–C(6)	119.9(2)	Al(1)–N(2)–C(6)	113.4(3)
		Al(2)–N(5)–C(27)	115.7(4)
Al–N(1)–Si(1)	129.0(2)	Al(1)–N(1)–Si(1)	134.2(3)
		Al(2)–N(4)–Si(3)	133.8(3)
Al–N(2)–Si(2)	127.9(2)	Al(1)–N(2)–Si(2)	132.7(3)
		Al(2)–N(5)–Si(4)	131.5(3)
Fe–C(1)–N(1)–Al–N(2)–C(6) $\bar{\Delta}$ [pm][c]	12.3	Fe(1)–C(1)–N(1)–Al(1)–N(2)–C(6)	18.2
		Fe(2)–C(22)–N(4)–Al(2)–N(5)–C(27) $\bar{\Delta}$ [pm][c]	19.2
Distance of Al from the plane Fe–C(1)–N(1)–N(2)–C(4) [pm][c]	49.8	Distance of Al from the plane	
		Fe(1)–C(1)–N(1)–Al(1)–N(2)–C(6)	73.4
		Fe(2)–C(22)–N(4)–Al(2)–N(5)–C(27) [pm][c]	69.3
C^5/C^5 (α)	4.4	C^5/C^5 (α_1)	3.4
		C^5/C^5 (α_2)	4.5
C^5/N(1) (β_1)	0.0	C^5/N(1) (β_1)	0.8
C^5/N(2) (β_2)	1.0	C^5/N(2) (β_2)	0.7
	towards iron	C^5/N(4) (β_3)	1.9
		C^5/N(5) (β_4)	0.7
			towards iron
C^5–Fe–C^5 (γ)	175.7	C^5–Fe(1)–C_5 (γ_1)	175.9
		C^5–Fe(2)–C_5 (γ_2)	174.6
C^5/C^5 (twist) (τ)	5.2	C^5/C^5 (twist) (τ_1)	5.6
		C^5/C^5 (twist) (τ_2)	17.7
Fe–C^5 (centre)	163.7	Fe(1)–C^5 (centre)	163.7
	163.2		164.3
		Fe(2)–C^5 (centre)	164.3
			164.8

[a] The definition of the angles α, β, γ, and τ is given in ref.[17] [b] The crystal structure determination was repeated at 173 K,[20] and the structural parameters were the same except of marginal differences. [c] Mean deviation from plane.

Experimental Section

General: All preparative work as well as handling of the samples was carried out with precautions to exclude traces 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. The starting materials were prepared as described in the literature, that is, 1,1′-bis(trimethylsilylamino)ferrocene (**1**),[8] *N*,*N*′-dilithio-1,1′-bis(trimethylsilylamino)ferrocene (**2**) $[fc(NSiMe_3)_2Li_2]$,[9,10] Cp*$AlCl_2$.[15] NMR spectra were recorded with a Bruker ARX 250: ^{1}H, ^{13}C, ^{29}Si NMR [refocused INEPT[19] based on $^{2}J(^{29}Si,^{1}H) = 7$ Hz]; Varian INOVA 400: ^{1}H, ^{13}C NMR; chemical shifts are given with respect to $SiMe_4$ [$\delta^{1}H$ ($CHDCl_2$) 5.33, ($C_6D_5CD_2H$) = 2.08; $\delta^{13}C$ (CD_2Cl_2) = 53.8, ($C_6D_5\mathit{C}D_3$) = 20.4; $\delta^{29}Si$ = 0 for $\Xi(^{29}Si)$ = 19.867184 MHz]. The melting points (uncorrected) were determined with a Büchi 510 melting point apparatus.

1,3-Bis(trimethylsilyl)-2-hydro-2-pyridine-1,3,2-diazaalumina[3]ferrocenophane (4) and Isolation of Dialuminoxane 6A: A solution of 1,1′-bis(trimethylsilylamino)ferrocene (**1**; 240 mg, 0.67 mmol) in toluene (10 mL) was cooled to 0 °C, and a solution of freshly prepared AlH_3–py [from AlH_3–N(Et)Me_2 (0.5 M in toluene, 1.33 mL, 0.67 mmol) and pyridine (0.054 mL, 0.67 mmol) in toluene (10 mL)], was added dropwise. While stirring, gas evolution was observed. The mixture was stirred at 0 °C for 1 h and then allowed to reach ambient temperature and stirred for 20 h. Volatile materials were removed in vacuo to give 295 mg of a mixture either as a brown powder or a yellow-greenish oil. When these residues were redissolved in toluene or CD_2Cl_2 the presence of **4** (ca. 80%), **1** (ca. 10%), and **6** (ca. 10%) was evident from the ^{1}H, ^{13}C, and ^{29}Si NMR spectra (vide infra). In contrast, treatment with hexane (20 mL), centrifugation, and removal of the solvent in vacuo from the liquid phase left a mixture containing mainly **4** (70%), **1** (ca. 30%), and hardly any **6** as shown by the NMR spectra in CD_2Cl_2. After adding more pyridine (0.048 mL, 0.60 mmol), this CD_2Cl_2 solution was left at –20 °C for crystallization. Orange crystals of **6A** (m.p. >250 °C, decomp.) suitable for X-ray analysis were isolated after 4 d.

Reaction of *N*,*N*′-Dilithio-1,1′-bis(trimethylsilylamino)ferrocene (2) with Cp*$AlCl_2$ and Pyridine – Isolation of Dialuminoxane 6B: Freshly prepared $[fc(NSiMe_3)_2Li_2]$ (**2**; 310 mg, 0.83 mmol) was taken up in toluene (10 mL) and hexane (10 mL), and the solution was cooled to –78 °C. A solution of Cp*$AlCl_2$ (194 mg, 0.83 mmol) in toluene (10 mL) and pyridine (0.067 mL, 0.83 mmol) was added. The mixture was stirred for 1 h at –78 °C and then for 20 h at room temperature; insoluble materials were separated by centrifugation, and the clear liquid was collected. Volatile materials were removed in vacuo (0.01 Torr), and the resulting oil was washed with hexane (20 mL). The solid was dried in a vacuum to give 292 mg of a brown powder. NMR spectra in [D_8]toluene (^{1}H, ^{13}C, and ^{29}Si NMR) indicated that this material consisted mainly of **5a** (ca. 45%), **1** (ca. 45%), and **6** (ca. 5%). Crystals of **5a** were collected from the toluene solution and identified by X-ray analysis as the chloride.[11] All crystalline material was dissolved in CD_2Cl_2. This solution was left at room temperature for two weeks, after which orange crystals of **6B** (m.p. >250 °C, decomp.) suitable for X-ray analysis could be collected.

6: ^{1}H NMR (250.1 MHz, CD_2Cl_2, 25 °C): δ = –0.27 (s, 36 H, Me_3Si), 3.74, 3.83 (m, m, 4 H, 4 H, $H^{3,3'}$ and $H^{4,4'}$), 3.91, 3.95 (m, m, 4 H, 4 H, $H^{2,2'}$ and $H^{5,5'}$), 7.73 (m, 4 H, py-H_{β}), 8.15 (m, 2 H, py-H_{γ}), 9.32 (d, 4 H, py-H_{α}) ppm. ^{13}C NMR (62.9 MHz, CD_2Cl_2, 25 °C): δ = 2.2 (N-$SiMe_3$), 64.5, 64.6 (fc-$C^{3,4}$), 67.6, 68.9 (fc-$C^{2,5}$), 106.5 (fc-C^{1}), 125.5 (C_{β}), 142.1 (C_{γ}), 150.2 (C_{α}) ppm. ^{29}Si NMR (49.7 MHz, CD_2Cl_2, 25 °C): δ = –0.8 ppm.

Crystal Structure Determinations of the Dialuminoxanes 6A and 6B: Details pertinent to the crystal structure determinations are listed in Table 2.[20] Crystals of appropriate size were sealed under an atmosphere of argon in Lindemann capillaries. The data collections were carried out at 293 K for **6A** and **6B** and also at 173 K for **6A**.

Acknowledgments

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Table 2. Crystallographic data of dialuminoxanes **6A** and **6B**.

	6A (293 K)	**6B** (293 K)
Formula	$C_{42}H_{62}Al_2Fe_2N_6OSi_4$	$C_{42}H_{62}Al_2Fe_2N_6OSi_4$
Crystal	orange prism	orange prism
Dimensions (mm)	0.18 × 0.16 × 0.14	0.22 × 0.18 × 0.14
Crystal system	monoclinic	orthorhombic
Space group	*P*2$_1$/*n*	*Pbca*
Lattice parameters:		
a [pm]	1073.9(2)	2069.4(4)
b [pm]	1981.5(4)	1974.3(4)
c [pm]	1209.3(2)	2440.4(5)
β [°]	108.22(3)	
Z	2	8
Absorption coefficient μ [mm^{-1}]	0.765	0.750
Diffractometer	STOE IPDS I, Mo-K_{α}, λ = 71.073 pm, graphite monochromator	
Measuring Range () [°]	2.1–26.0	1.9–26.0
Reflections collected	16778	66238
Independent reflections [$I > 2\sigma(I)$]	4731	9769
Absorption correction [a]	none	none
Refined Parameters	259	514
wR_2/R_1 [$I > 2\sigma(I)$]	0.088/0.047	0.104/0.056
Max./min. Residual electron density [e pm^{-3} × 10^{-6}]	0.342/–0.239	0.443/–0.277

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

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[20] CCDC-656856 (for **6A** at 293 K), -656857 (for **6A** at 173 K), and -656855 (for **6B**) 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.

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