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Five- and Four-Coordinate 1,3-Diaza-2-yttria- and 1,3-Diaza-2-scandia-[3]ferrocenophanes

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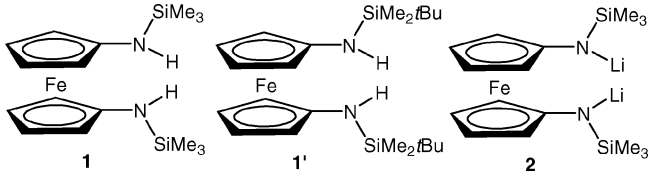
2-Chloro-1,3-bis(trimethylsilyl)-1,3-diaza-2-metalla-[3]ferrocenophanes with M = Y (**3**) and Sc (**4**) have been prepared as the dipyridine adducts, starting from YCl_3 and $ScCl_3$, respectively, and *N*,*N*′-dilithio-*N*,*N*′-bis(trimethylsilyl)-1,1′-diaminoferrocene (**2**). The reaction of **3** with sodium pentamethylcyclopentadienide (NaCp*) gave the complex **5**, in which the yttrium atom is four-coordinate, bearing the diamido ligand, Cp* and one pyridine ligand. An ate complex of four-coordinate yttrium (**6**) was obtained, when YCl_3 was treated with 2 equiv. of **2**. In **6a**, the lithium atom is threefold coordinated by two of the four amido nitrogen atoms and by pyridine, and addition of an excess of pyridine gave the separated ion pairs (**6b**) in solution. The molecular structures of **3**, **5** and **6a** were determined by X-ray structural analysis, and the solution-state structures were deduced from consistent NMR spectroscopic data sets (^1H, ^{13}C, ^{29}Si, ^{89}Y NMR). The ^{89}Y nuclear magnetic shielding of amido complexes appears to increase with the coordination number (3, 4, 5) of yttrium.

Introduction

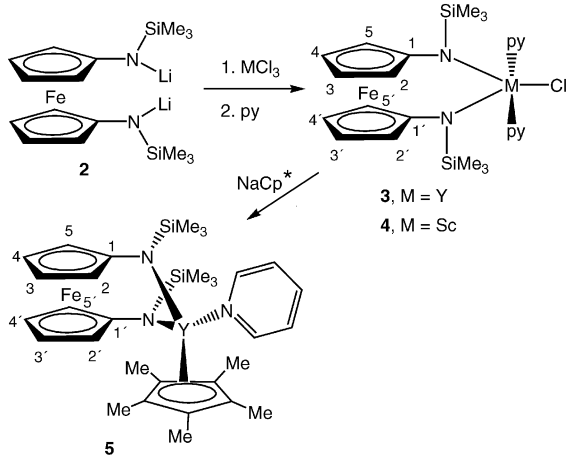
In transition metal amide chemistry, chelating amides are of particular interest considering structure and reactivity.[1,2] In this context, the 1,1′-diaminoferrocene derivatives **1**[3] and **1**′[4] (Scheme 1) have already been used to prepare 1,3-diaza-2-metalla-[3]ferrocenophanes with titanium,[3,5] zirconium,[3,5,6] vanadium,[7] uranium[4,8] and scandium,[9] respectively, in the 2-position of the bridge. 1,3-Diaza-2-metalla-[3]ferrocenophanes bearing other substituents than silyl groups at the nitrogen atoms have also been synthesized,[10a,10b] including complexes of polyazaferrocene macrocyclic ligands.[10c] Mainly, these substituents are aryl groups.[11] Recently, we have reported on various aspects of boron[12] and aluminum chemistry[13] using **1** and **2**. Moreover, structural studies of 1,*n*-diaza-[*n*]ferrocenophanes with different other main group elements in the bridge have been carried out.[14] In the present work, we report on one example of a scandium amide and several examples of yttrium amides with different coordination numbers of yttrium.



Scheme 1. 1,1′-Bis(silylamino)ferrocene derivatives as starting materials for the synthesis of 1,3-diaza-2-metalla-[3]ferrocenophanes.

Results and Discussion

The reactions of the dilithiated chelating amido ligand **2** with anhydrous yttrium or scandium trichloride followed by addition of pyridine affords the desired 1,3-diaza-2-metalla-[3]ferrocenophanes as the dipyridine adducts **3** and **4**, respectively. In the case of **3**, treatment with (pentamethylcyclopentadienyl)sodium (NaCp*) gives the [3]ferrocenophane **5**, in which only one pyridine ligand is coordinated to the yttrium atom (Scheme 2). Attempts to use the reac-



Scheme 2. Reactions of yttrium and scandium trichloride with the dilithium amide **2** and pyridine. Conversion of the yttrium chloride **3** into the yttrium–Cp* complex.

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Table 1. ^{13}C, ^{29}Si, and ^{89}Y NMR spectroscopic data[a] of the [3]ferrocenophanes **3**–**6**.

Compound	**3**	**4**	**5**[b]	**6a**[c]	**6b**[c]
$\delta^{13}C(SiMe_3)$	1.2 (55.2)	1.1 (55.5)	1.4 (br.) (55.3)	2.2 (54.0) (Me_3SiNLi) 3.2 (55.3) (Me_3SiN)	3.1 (53.9)
$\delta^{13}C(fc\text{-}C^1)$	101.8	98.2	109.2 [1.0]	104.4, 104.8	107.1
$\delta^{13}C(fc\text{-}C^{2,5})$	67.0	67.7	64.7 ($fc\text{-}C^2$), 67.9 ($fc\text{-}C^5$)	64.7, 66.3, 68.6, 69.0	66.5
$\delta^{13}C(fc\text{-}C^{3,4})$	66.9	67.6	63.2 ($fc\text{-}C^3$), 68.2 ($fc\text{-}C^4$)	65.8, 66.5, 67.5, 68.3	65.2
Pyridine	124.7 (C^β) (br.) 138.3 (C^γ) (br.) 150.2 (C^α) (br.)	124.5 (C^β) (br.) 138.3 (C^γ) (br.) 150.4 (C^α) (br.)	124.6 (C^β) 139.5 (C^γ) 150.4 (C^α)	124.7 (C^β) 137.9 (C^γ) 149.4 (C^α)	123.9 (C^β) 136.0 (C^γ) 150.0 (C^α)
$\delta^{89}Y$	134.0	–	387.3	331.3	301.7
$\delta^{29}Si$	–6.0 {1.6}	–4.3	–7.4 {2.4}	–5.4 {1.6} (55.3) (SiN), –0.8 (SiNLi)	–6.7

[a] In CD_2Cl_2 (**3**, **4**, **5**), [D_8]toluene (**6a**, **6b**); at 298 K; coupling constants (±0.5 Hz) $^1J(^{29}Si,^{13}C)$ are given in parentheses; $^nJ(^{89}Y,^{13}C)$ in brackets; $^3J(^{89}Y,^{29}Si)$ in braces; (br.) denotes broad ^{13}C resonances due to dynamic effects. [b] $\delta^{13}C$ (for Cp*) = 12.3 (CH_3), 117.6 [1.3] (CCH_3) ppm. [c] All signals are slightly broadened.

tion of **1** with $Y[N(SiMe_3)_2]_3$ in order to prepare a three-coordinate yttrium complex with the $Y–N(SiMe_3)_2$ fragment in 2-position of the [3]ferrocenophane failed. There was no reaction at room temperature, and prolonged periods of heating at 60 °C in [D_8]toluene led to the formation of $HN(SiMe_3)_2$, accompanied by decomposition.

The extremely moisture-sensitive yttrium complexes **3** and **5** could be isolated in pure form as orange crystalline solids (vide infra), whereas the scandium complex **4** was contaminated with varying amounts of **1** and could not be completely purified so far. The coordination geometry of **3** and **5** in the solid state was established by X-ray structural analysis and in solution by multinuclear magnetic resonance (see Table 1). The NMR spectroscopic data set for the scandium complex **4** is very similar to that of **3** indicating an analogous geometry. The presence of an excess of pyridine causes fast exchange of the coordinated and non-coordinated pyridine molecules. However, at low temperature, this exchange becomes slow as compared to the NMR time scale, and the fivefold coordination of yttrium and scandium is retained in solution. The NMR spectra recorded at low and ambient temperatures support the trigonal-bipyramidal surroundings of the yttrium and scandium atoms with the pyridine ligands in the axial positions.

In the case of the yttrium complex **5**, the solution-state NMR spectroscopic data are in agreement with the proposed structure, since four different signals are observed for $^1H^{2,3,4,5}$ as well as for $^{13}C^{2,3,4,5}$. Thus, the pyridine ligand is tightly linked to the yttrium atom, and any exchange of the pyridine ligand does not proceed by a primarily dissociative mechanism. The 1D $^1H/^1H$ NOE difference spectra[15] (Figure 1) serve to establish the solution-state structure and for the assignment of the $^1H^{2,3,4,5}$ NMR signals. In addition, intensities of exchange signals owing to magnetization transfer[16] can be observed (Figure 1, trace D). This results from slow inversion of the non-planar ring containing Fe,C,C,N,N and Y, by which the magnetizations of the $^1H^2$ and $^1H^5$ nuclei are exchanged.

In the amide chemistry of yttrium and the lanthanides, the formation of ate complexes instead of the neutral amide

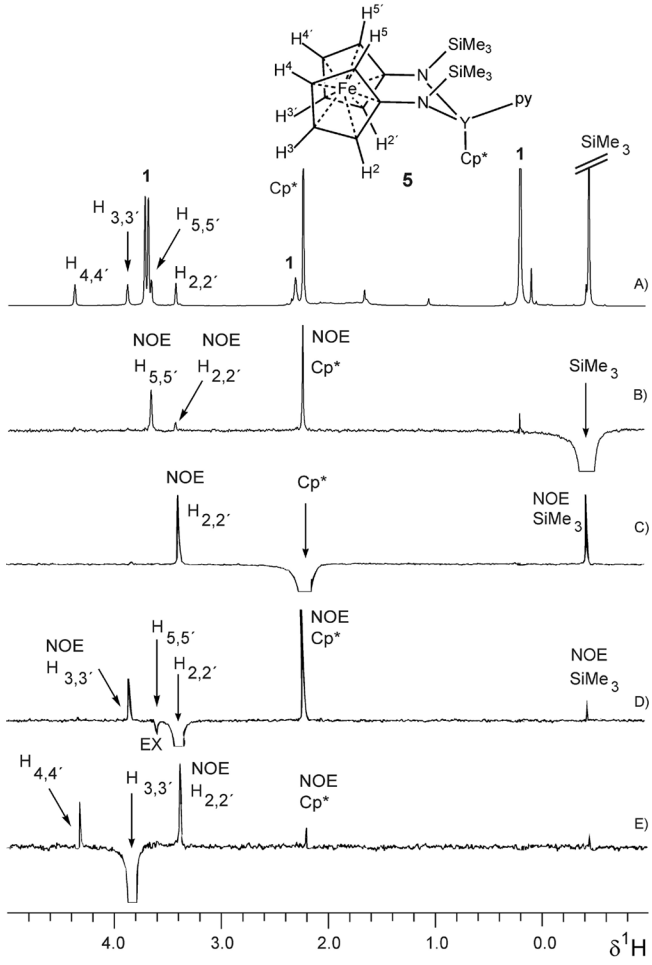


Figure 1. 400 MHz $^1H/^1H$ NOE difference spectra (gradient-enhanced[15]) of a mixture containing **5** and **1** (in CD_2Cl_2, at 23 °C; relaxation delay 1.5 s; mixing time 0.8 s). The irradiated transitions are marked by arrows; the resulting intensities arising from NOE or exchange are indicated. (A) Normal ^1H NMR spectrum. (B) Irradiation: $^1H(NSiMe_3)$; response: $^1H^{5,5'}$ and $^1H^{2,2'}$, ^1H(Me) of the Cp* group. (C) Irradiation: ^1H(Me) of the Cp* group; response: $^1H^{2,2'}$ and $^1H(SiMe_3)$. (D) Irradiation: $^1H^{2,2'}$; response: magnetization transfer[16] to $H^{5,5'}$, NOE for $^1H^{3,3'}$, ^1H(Me) of the Cp* group, and $^1H(SiMe_3)$. (E) Irradiation: $^1H^{3,3'}$; response: $^1H^{2,2'}$, $^1H^{4,4'}$, ^1H(Me) of Cp* group.

complexes is frequently observed.[17] Therefore, we have studied the reaction of anhydrous yttrium trichloride with 2 equiv. of the dilithiated amido ligand **2** in the presence of pyridine. The NMR spectra of the reaction solutions were puzzling at a first glance, since they appeared to be inconsistent and irreproducible in the beginning. When it turned out that the amount of pyridine was crucial, a product was identified with a ratio Li/pyridine/Y = 1:1:1, for which defined ^{1}H, ^{13}C and ^{29}Si NMR spectra could be measured (Table 1; Figures 2 and 3). The number of NMR signals is in support of the structure **6a**, and this compound was subsequently isolated as crystalline material suitable for X-ray structural analysis. Other reproducible ^{1}H, ^{13}C and ^{29}Si NMR spectra were obtained, when an excess of pyridine was added to solutions containing **6a**, and we assign this compound as **6b**, in which the lithium cation is separated by multiple coordination with pyridine from the anion (Scheme 3).

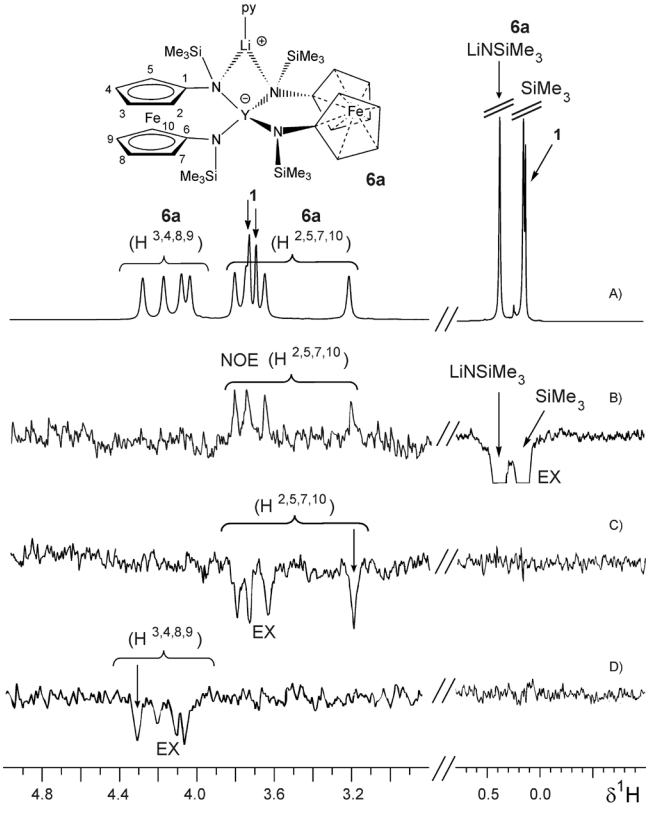


Figure 2. 400 MHz $^{1}H\{^{1}H\}$ NOE difference spectra (gradient-enhanced[15]) of a mixture containing **6a** and **1** (in [D_8]toluene, at 23 °C; relaxation delay 3.0 s; mixing time 0.4 s). The irradiated resonance signals are marked by arrows; the resulting intensities arising from NOE or exchange are indicated. (A) Normal ^{1}H NMR spectrum. (B) Irradiation: $^{1}H(LiNSiMe_3)$; response: magnetization transfer to $^{1}H(SiMe_3)$,[16] NOE for $^{1}H^{2,5,7,10}$. (C) Irradiation: low-frequency signal of $^{1}H^{2,5,7,10}$; response: magnetization transfer to three signals out of $H^{2,5,7,10}$. (D) Irradiation: high-frequency signal of $^{1}H^{3,4,8,9}$; response: magnetization transfer to three of $^{1}H^{3,4,8,9}$.

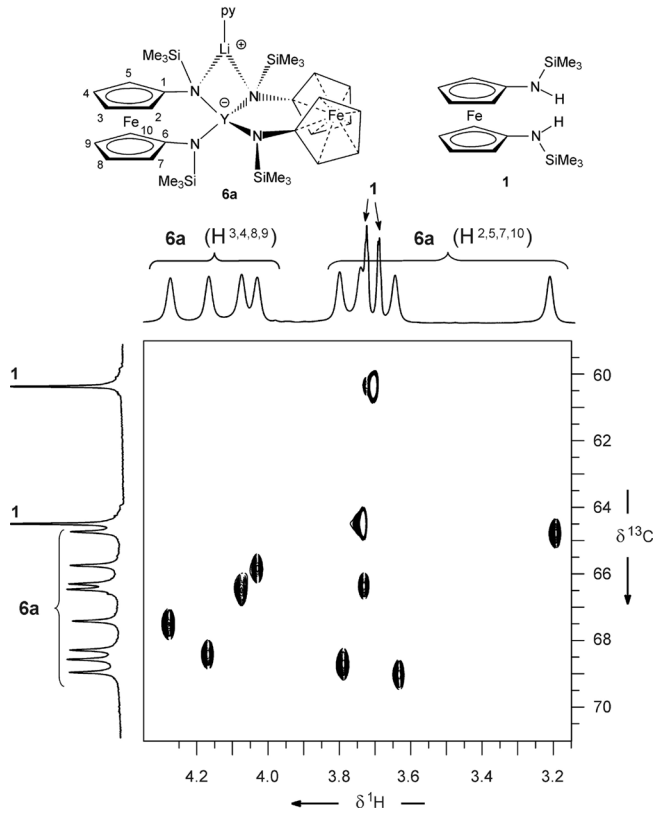
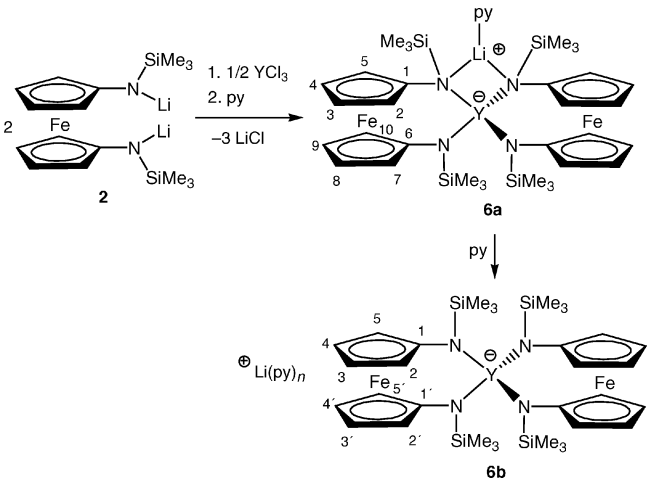


Figure 3. Contour plot of a part of the 400 MHz 2D $^{1}H/^{13}C$ correlated spectrum of a mixture containing **6a** and **1** (in [D_8]toluene, at 23 °C), recorded by the gradient-selected (gs-)HSQC method.[18]



Scheme 3. Reaction of yttrium trichloride with 2 equiv. of the dilithium amide **2**; in the presence of a small amount of pyridine, **6a** can be characterised in solution and in the solid state, whereas an excess of pyridine causes ion pair separation.

^{89}Y NMR Studies

Since ^{89}Y is a spin $I = 1/2$ nucleus with 100% natural abundance, ^{89}Y NMR studies are attractive,[19] although the magnetic moment of ^{89}Y is low and relaxation times $T_1(^{89}Y)$ might be long.[20] It turned out that the ^{89}Y NMR

spectra could be readily acquired by using single-pulse experiments (30° pulses) without relaxation delays, in contrast to recommendations (60 s delay, 48 h;[19a] 20 s delay, 10 mm tubes, 17 h[19d]). Additive ligand contributions to δ^{89}Y data have been proposed,[19a] and relationships between coordination number and δ^{89}Y appear to be less straightforward. However, the nature of many yttrium complexes in solution is not well defined, and reliable temperature-dependent ^{89}Y NMR measurements for studying varying degrees of association have not been performed. The δ^{89}Y data measured here indicate greater nuclear magnetic shielding for five-coordinate yttrium in **3** (δ = +134.0 ppm) as compared with four-coordinate yttrium in **6** (δ = +331.3, +301.7 ppm). Including δ^{89}Y for three-coordinate yttrium in the case of $Y[N(SiMe_3)_2]_3$ (δ = +570 ppm), one finds a dependence of δ^{89}Y on the coordination number at least for amido ligands. There is a difference of 30 ppm in the δ^{89}Y values for **6a** (δ = +331.3 ppm) and **6b** (δ = +301.7 ppm), with ^{89}Y in **6a** being slightly deshielded. This is the expected trend, because in **6a** two of the four amido nitrogen atoms are coordinated to the yttrium and lithium atoms. The deshielding influence of a cyclopentadienyl ligand on ^{89}Y has been noted.[19] In the case of **5** (δ = +387.3 ppm), the coordination of the yttrium atom can be described as pseudooctahedral (if Cp* is considered to occupy three positions at Y) or as four-coordinate. The latter description would fit better to the observed δ^{89}Y value.

X-ray Structural Studies of the Yttrium Complexes 3, 5 and 6a

The molecular structures of the yttrium complexes **3**, **5** and **6a** are shown in Figures 4, 5 and 6, respectively. Selected structural parameters are given in Table 2. The trigonal-bipyramidal surroundings of the yttrium atom in **3** have two noticeable consequences for the structure of the ferrocene moiety. The accommodation of the yttrium atom between the two amide nitrogen atoms exactly opposite to the iron atom enforces the observed non-parallel orientation of the cyclopentadienyl groups, tilted at C(1) and C(6) away from the iron atom [Figure 4 (A)], and at the same time the cyclopentadienyl groups are twisted against eclipsed positions [Figure 4 (B); τ = 13° (mean value)]. Otherwise, bond lengths and angles are in the expected ranges, by comparison with other distantly related yttrium complexes.[17a,22] Typically, the Y–N(amide) distances are considerable shorter than those for Y–N(py).

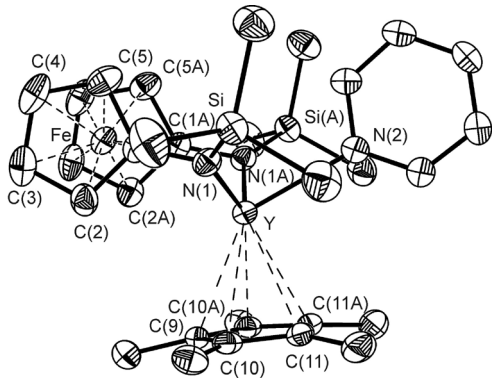


Figure 5. Molecular structure of **5** (ORTEP plot, 40% probabilities; hydrogen atoms are omitted for clarity); see Table 2 for structural parameters.

This also holds[23] for complex **5**. The symmetry of **5** requires eclipsed cyclopentadienyl rings, which, however, are also forced out of the parallel orientation, and, in addition, the C–N vectors are shifted out of the C_5 planes (see angles[21] α and β in Table 2). All Y–N bonds in **5** are slightly longer when compared with those of **3**. This can be traced to greater steric repulsion in **5** rather than to the change in the yttrium coordination number.

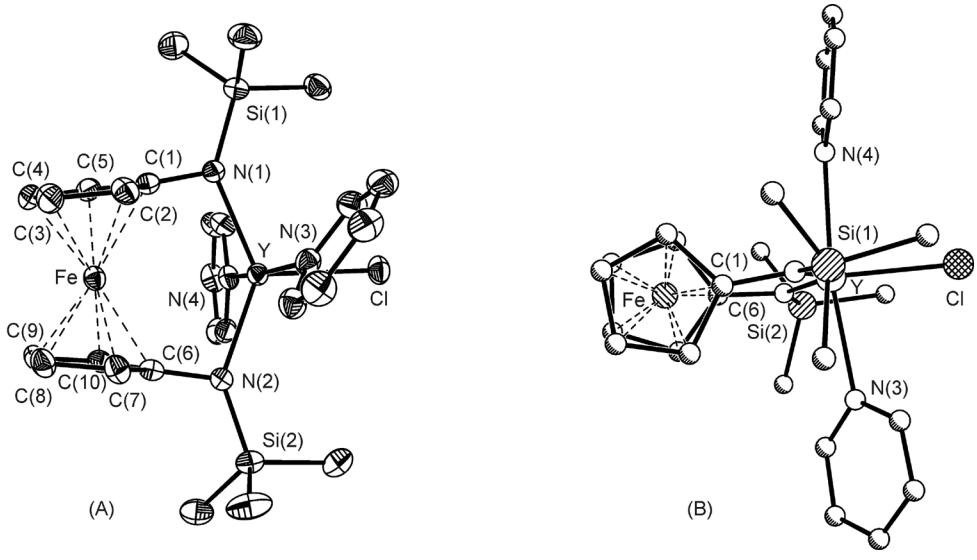


Figure 4. Molecular structure of **3** (A) (ORTEP plot, 40% probabilities) and (B) (ball-and-stick model); hydrogen atoms are omitted for clarity; see Table 2 for structural parameters.

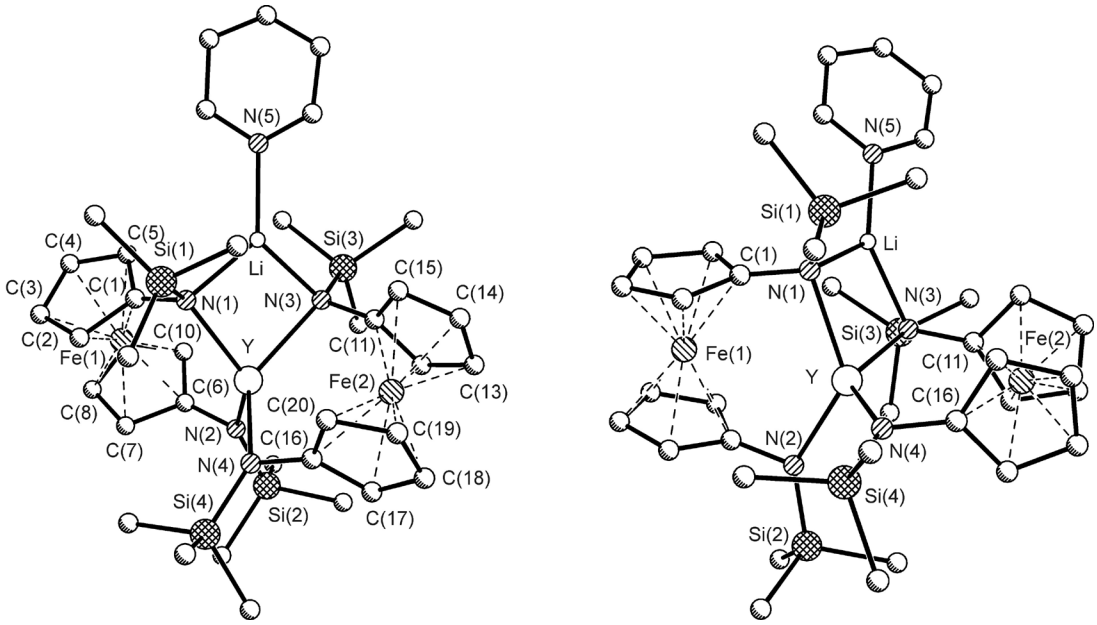


Figure 6. Two views of the molecular structure of **6a**; [D_8]toluene and hydrogen atoms are omitted for clarity; see Table 2 for structural parameters.

In the case of **6a**, the surroundings of the iron atom correspond to that in **3** (similar angles[21] τ and α) and also to that in **5** (similar angles β). The Y–N bonds are markedly elongated for both nitrogen atoms coordinated to Li, whereas the other two Y–N bond lengths correspond closely to the analogous ones in **5**. The coordination of the lithium atom in **6a** is trigonal-planar within the experimental error. Although the Li–Y distance is only 300 pm, there is no other structural or spectroscopic evidence for a bonding interaction. By comparison of bond lengths and angles, the bonding situation of the lithium atom in the N–Li(py)–N moiety of **6a** appears to be similar to the analogous surroundings in fc[N($SiMe_3$)Li–py]$_2$.[14a]

Conclusions

The first yttrium complexes containing 1,3-bis(trimethylsilyl)-1,3-diaza-2-yttria-[3]ferrocenophane units were prepared, and their structures were characterized both in solution and in the solid state. The size of the Y^{3+} ion is very similar to those of the late lanthanide Ln^{3+} ions, and it can therefore be expected that the chemistry observed here mirrors that of these lanthanide ions. The chelating ferrocenediamido group appears to be a versatile ligand for both main group elements and transition metals, and this ligand readily accommodates heavy transition metal atoms by slight distortions of the ideal ferrocene-like geometry. The measurement of ^{89}Y NMR spectra is encouraged by observing less prohibitive conditions for acquiring meaningful spectra.

Experimental Section

General: All preparative work as well as handling of the samples was carried out observing 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 argon. All other solvents were distilled from Na metal under argon. The starting materials were prepared as described in the literature: 1,1′-bis(trimethylsilylamino)ferrocene (**1**),[3] *N*,*N*′-dilithio-1,1′-bis(trimethylsilylamino)ferrocene (**2**) [fc($NSiMe_3$)$_2$$Li_2$].[3] Other starting materials were purchased from Aldrich [butyllithium (1.6 M in hexane), YCl_3], Acros (Cp*Na), ABCR ($ScCl_3$) and used without further purification. NMR measurements: Bruker ARX 250: ^{1}H, ^{13}C, ^{29}Si NMR [refocused INEPT[24] based on $^2J(^{29}Si,^1H)$ = 7 Hz]; Varian INOVA 400: ^{1}H, ^{13}C NMR; Bruker DRX 500: ^{1}H, ^{13}C, ^{89}Y NMR; chemical shifts are given with respect to $SiMe_4$ [δ^{29}Si = 0 ppm for $\Xi(^{29}Si)$ = 19.867184 MHz] [$\delta^1H(CHDCl_2)$ = 5.33 ppm, $\delta^1H(C_6D_5CD_2H)$ = 2.08 ppm; $\delta^{13}C(CD_2Cl_2)$ = 53.8 ppm, $\delta^{13}C(C_6D_5CD_3)$ = 20.4 ppm]; YCl_3 in D_2O [δ^{89}Y = 0 ppm for $\Xi(^{89}Y)$ = 4.900200 MHz]. The assignments of ^{1}H and ^{13}C NMR signals are based on ^{1}H/^{1}H NOE difference, and 2D ^{1}H/^{13}C HETCOR experiments. The melting points (uncorrected) were determined with a Büchi 510 melting point apparatus. Owing to the fairly unstable nature of the complexes and the difficulty in their handling, elemental analyses were not reliable.

2-Chloro-1,3-bis(trimethylsilyl)-1,3-diaza-2-yttria-[3]ferrocenophane–Dipyridine(*Y*–*N*) (3): A solution of freshly prepared fc($NSiMe_3$)$_2$$Li_2$ (**2**) (288 mg, 0.77 mmol) in toluene (20 mL) was cooled to –78 °C, and added to pure, degassed YCl_3 (151 mg; 0.77 mmol) at –30 °C through a syringe. The reaction mixture was stirred at –78 °C for 40 min, after which pyridine (0.249 mL, 3.10 mmol) was added dropwise. After stirring of the reaction mixture at –70 °C for 1 h and then at ambient temperature for 18 h, insoluble materials were separated by centrifugation, and the clear liquid was collected. Volatile materials were evaporated, and the remaining oil was washed with hexane (10 mL), and a solid was

Table 2. Selected bond lengths [pm] and angles [°][a] of the [3]ferrocenophanes **3** (Figure 4), **5** (Figure 5), and **6a** (Figure 6).

3		**5**		**6a**[c]	
Y–N(1)	221.8(2)	Y–N(1)	224.4(3)	Y–N(2)	225.6(6)
Y–N(2)	221.3(2)			Y–N(4)	225.0(6)
Y–N(3) (from py)	249.0(2)	Y–N(2) (from py)	252.0(5)	Y–N(1)	234.2(6)
Y–N(4) (from py)	250.1(2)			Y–N(3)	237.0(6)
Y–Cl	257.01(11)	Y···Cp*(centre)	240.7	Y···Li	300.6(15)
				N(5)–Li	201.4(17)
				N(1)–Li	202.2(16)
				N(3)–Li	208.0(14)
N(1)–Si(1)	170.9(2)	N(1)–Si(1)	172.0(4)	N(2)–Si(2)	171.1(7)
N(2)–Si(2)	171.4(2)			N(4)–Si(4)	171.9(7)
				N(1)–Si(1)	174.7(6)
				N(3)–Si(3)	174.0(6)
N(1)···N(2)	409.7	N(1)···N(1A)	390.8	N(1)···N(2)	418.0
				N(2)···N(3)	419.2
C(1)···C(6)	362.8	C(1)···C(1A)	358.0	C(1)···C(6)	362.0
				C(11)···C(16)	362.6
Fe···Y	332.1	Fe···Y	321.2	Fe(1)···Y	343.4
				Fe(2)···Y	345.0
N(1)–Y–N(2) (*endo*)	135.27(8)	N(1)–Y–N(1A) (*endo*)	121.10(19)	N(1)–Y–N(2) (*endo*)	130.8(2)
N(1)–Y–N(3) (from py)	89.26(7)	N(1)–Y–N(2) (from py)	85.03(11)	N(3)–Y–N(4) (*endo*)	130.3(2)
N(2)–Y–N(3) (from py)	92.35(8)			N(1)–Y–N(3) (*endo*)	85.7(2)
N(1)–Y–N(4) (from py)	90.47(7)			N(1)–Y–N(4) (*endo*)	104.7(2)
N(2)–Y–N(4) (from py)	94.04(8)			N(2)–Y–N(4) (*endo*)	102.7(2)
N(3)–Y–N(4) (from py)	171.17(7)			N(2)–Y–N(3) (*endo*)	106.1(2)
				N(1)–Li–N(5) (from py)	128.1(7)
				N(3)–Li–N(5) (from py)	128.7(8)
				N(1)–Li–N(3)	102.8(7)
N(1)–Y–Cl	111.71(6)	N(1)–Y–Cp*(centre)	118.5	N(1)–Y–Li	42.2(3)
N(2)–Y–Cl	112.95(6)	N(2)–Y–Cp*(centre)	114.3	N(3)–Y–Li	43.6(3)
N(3)–Y–Cl	84.96(6)			N(2)–Y–Li	129.4(3)
N(4)–Y–Cl	86.94(5)			N(4)–Y–Li	127.8(3)
C(1)–N(1)–Si(1)	116.69(16)	C(1)–N(1)–Si(1)	116.5(3)	C(11)–N(3)–Si(3)	112.0(5)
C(6)–N(2)–Si(2)	115.54(16)			C(16)–N(4)–Si(4)	116.8(5)
				C(1)–N(1)–Si(1)	113.0(5)
				C(6)–N(2)–Si(2)	116.1(5)
Y–N(1)–C(1)	102.36(15)	Y–N(1)–C(1)	98.5(2)	Y–N(3)–C(11)	100.5(4)
Y–N(2)–C(6)	102.86(15)			Y–N(4)–C(16)	105.6(4)
				Y–N(1)–C(1)	101.1(4)
				Y–N(2)–C(6)	104.9(5)
Y–N(1)–Si(1)	140.50(12)	Y–N(1)–Si(1)	144.8(2)	Y–N(3)–Si(3)	132.3(3)
Y–N(2)–Si(2)	141.52(12)			Y–N(4)–Si(4)	136.8(3)
				Y–N(1)–Si(1)	132.6(3)
				Y–N(2)–Si(2)	138.7(3)
$\bar{\Delta}$ [pm]:[b]		$\bar{\Delta}$ [pm]:[b]		$\bar{\Delta}$ [pm]:[b]	
Fe–C(1)–N(1)–Y–N(2)–C(6)	3.7	Fe–C(1)–N(1)–Y–N(1A)–C(1A)	25.2	Fe(1)–C(1)–N(1)–Y–N(2)–C(6)	3.5
				Fe(2)–C(11)–N(3)–Y–N(4)–C(16)	3.9
Distance of Y from the plane [pm]:[b]		Distance of Y from the plane [pm]:[b]		Distance of Y from the plane [pm]:[b]	
Fe–C(1)–N(1)–N(2)–C(6)	4.3	Fe–C(1)–N(1)–N(1A)–C(1A)	98.0	Fe(1)–C(1)–N(1)–N(2)–C(6)	2.8
				Fe(2)–C(11)–N(3)–N(4)–C(16)	8.4
C_5/C_5 (α)	12.7	C_5/C_5 (α)	11.6	C_5/C_5 (α_1) [for Fe(1)]	12.1
				C_5/C_5 (α_2) [for Fe(2)]	12.1
C_5/N(1) (β_1)	4.2	C_5/N(1) (β_1)	1.8	C_5/N(1) (β_1)	8.2
C_5/N(2) (β_2)	3.9		bent away from Fe	C_5/N(2) (β_2)	5.4
	bent away from Fe			C_5/N(3) (β_3)	8.9
				C_5/N(4) (β_4)	4.8 bent away from Fe
C_5–Fe–C_5 (γ)	171.9	C_5–Fe–C_5 (γ)	173.0	C_5–Fe(1)–C_5 (γ_1)	172.1
				C_5–Fe(2)–C_5 (γ_2)	172.2
C_5/C_5 (twist) (τ)	13	C_5/C_5 (twist) (τ)	0 (symmetry)	C_5/C_5 (twist) (τ_1) [for Fe(1)]	13
				C_5/C_5 (twist) (τ_2) [for Fe(2)]	13
Fe–C_5 (centre)	166.9	Fe–C_5 (centre)	167.3	Fe(1)–C_5 (centre)	167.2
	166.5				167.2
				Fe(2)–C_5 (centre)	167.3
					167.4

[a] The definition of the angles α, β, γ and τ is given in ref.[21] [b] Mean deviation from plane. [c] **6a** contains ordered [D_8]toluene in the crystal.

obtained. This solid was dried in vacuo to give **3** as a brown-green powder (231 mg; 47%). Single orange crystals of **3** for X-ray analysis were grown from [D_8]toluene solution at –30 °C after 5 d; m.p. 170–180 °C (dec.). ^{1}H NMR (250.1 MHz, CD_2Cl_2, 25 °C): δ = –0.04 (s, 18 H, Me_3Si), 2.92 (m, 4 H, $H^{2,2',5,5'}$), 4.13 (m, 4 H, $H^{3,3',4,4'}$), 7.44 (br. m, 4 H, py-H^{β}), 7.83 (br. m, 2 H, py-H^{γ}), 8.87 (br. m, 4 H, py-H^{α}) ppm.

2-Chloro-1,3-bis(trimethylsilyl)-1,3-diaza-2-scandia-[3]ferrocenophane–Dipyridine(*Sc–N*) (4): A solution of freshly prepared $fc(NSiMe_3)_2Li_2$ (**2**) (320 mg, 0.86 mmol) in toluene (20 mL) was cooled to –78 °C, and $ScCl_3$ (130 mg, 0.86 mmol) was added. The reaction mixture was stirred at –78 °C for 2 h, and then at –40 °C for 30 min. Pyridine (0.277 mL, 3.44 mmol) was added dropwise. After stirring of the reaction mixture at –40 °C for 3 h and then at ambient temperature for 1 h, thf (15 mL) was added, and the mixture was stirred for 18 h. Insoluble materials were separated by centrifugation, and the clear liquid was collected. The solvent was removed in vacuo to give 482 mg of a mixture containing **4** (ca. 50%) and **1** (ca. 50%) as a yellow-brown oil. ^{1}H NMR (250.1 MHz, CD_2Cl_2, 25 °C): δ = –0.03 (s, 18 H, Me_3Si), 2.98 (m, 4 H, $H^{2,2',5,5'}$), 4.18 (m, 4 H, $H^{3,3',4,4'}$), 7.50 (br., py-H^{β}), 7.77 (br., py-H^{γ}), 9.02 (br., py-H^{α}) ppm.

2-(Pentamethylcyclopentadienyl)-1,3-bis(trimethylsilyl)-1,3-diaza-2-yttria-[3]ferrocenophane–Pyridine(*Y–N*) (5): A solution of freshly prepared $fc(NSiMe_3)_2Li_2$ (**2**) (232 mg, 0.62 mmol) in toluene (20 mL) was cooled to –78 °C and added to pure, degassed YCl_3 (151 mg; 0.77 mmol) at –30 °C through a syringe. After stirring of the reaction mixture at –78 °C for 3 h, pyridine (0.150 mL, 1.87 mmol) was added. The reaction mixture was stirred at –78 °C for 1 h and then at ambient temperature for 18 h. This solution was cooled to 0 °C and added to pure, degassed NaCp* (99 mg; 0.62 mmol) at 0 °C through a syringe. The mixture was stirred for 6 h, centrifuged, and the clear liquid was collected. Volatile materials were evaporated in vacuo to give 290 mg of a mixture containing **5** (about 40%) together with **1**. Single yellow-orange crystals (131 mg, 35%) of **5** for X-ray analysis were grown from [D_8]toluene solution at –30 °C after 2 weeks; m.p. >350 °C (dec.). ^{1}H NMR (399.8 MHz, CD_2Cl_2, 25 °C): δ = –0.46 (s, 18 H, Me_3Si), 2.23 (s, 15 H, Cp*), 3.43 (m, 2 H, $H^{2,2'}$), 3.66 (m, 2 H, $H^{5,5'}$), 3.89 (m, 2 H, $H^{3,3'}$), 4.38 (m, 2 H, $H^{4,4'}$), 7.51 (m, 2 H, py-H^{β}), 7.92 (m, 1 H, py-H^{γ}), 8.72 (m, 2 H, py-H^{α}) ppm.

Synthesis of the Ate Complexes [Li(py)][Y{fc(NSiMe$_3$)$_2$}$_2$] (6a) and [Li(py)$_n$][Y{fc(NSiMe$_3$)$_2$}$_2$] (6b): The synthesis was carried out as described for **3**, starting from 280 mg (0.75 mmol) of $fc(NSiMe_3)_2Li_2$ (**2**), YCl_3 (73 mg, 0.38 mmol) and pyridine (0.181 mL, 2.26 mmol). Insoluble materials were separated by centrifugation, and the clear liquid was collected. Volatile materials were evaporated in vacuo to give 332 mg of a mixture containing **6a** (about 50%) together with **1**. Crystallisation from [D_8]toluene at –20 °C gave after 10 d red-orange crystals of **6a** (240 mg; 45%); m.p. 260–270 °C (dec.). ^{1}H NMR (399.8 MHz, [D_8]toluene, 25 °C): δ = 0.16 (s, 18 H, Me_3SiN), 0.39 (s, 18 H, Me_3SiNLi), 3.22, 3.66, 3.76, 3.82 (m, m, m, m, 2 H, 2 H, 2 H, 2 H, $H^{2,2',5,5',7,7',10,10'}$), 4.06, 4.10, 4.19, 4.30 (m, m, m, m, 2 H, 2 H, 2 H, 2 H, $H^{3,3',4,4',8,8',9,9'}$), 6.52 (m, 2 H, py-H^{β}), 6.74 (m, 1 H, py-H^{γ}), 8.45 (m, 2 H, py-H^{α}) ppm. Then pyridine (0.200 mL, 2.49 mmol) was added to this reaction mixture in [D_8]toluene at 0 °C. The solution was stirred for 20 min. The resulting mixture contained the ate complex **6b** together with a small amount of **1** (ca. 10%, according to ^{1}H NMR). ^{1}H NMR (399.8 MHz, [D_8]toluene, 25 °C): δ = 0.41 (s, 36 H, Me_3Si), 3.99 (m, 8 H, $H^{2,2',5,5'}$), 4.04 (m, 8 H, $H^{3,3',4,4'}$), 6.77 (br., 8 H, py-H^{β}), 7.11 (br., 8 H, py-H^{γ}), 8.42 (br., 4 H, py-H^{α}) ppm.

Crystal Structure Determinations of the Yttrium Complexes 3, 5 and 6a: Details pertinent to the crystal structure determinations are listed in Table 3.[25] Crystals of appropriate size were sealed under argon in Lindemann capillaries. The data collections were carried out with Mo-K_α radiation (λ = 71.073 pm, graphite monochromator) at 133 K for **3**, at 293 K for **5** and at 173 K for **6a**.

Table 3. Crystallographic data of the [3]ferrocenophanes **3**, **5** and **6a**.

	3	**5**	**6a**
Temperature [K]	133	293	173
Empirical formula	$C_{26}H_{36}ClFeN_4Si_2Y$	$C_{31}H_{46}FeN_3Si_2Y$	$C_{37}H_{57}Fe_2LiN_5Si_4Y\cdot(C_7D_8)$
Crystal	yellow orange prism	yellow orange needle	dark orange rhomb
Dimensions [mm]	0.22 × 0.18 × 0.15	0.28 × 0.15 × 0.12	0.28 × 0.22 × 0.18
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/m$	$P2_1/m$	Cc
Lattice parameters:			
a [pm]	991.3(2)	978.6(2)	1786.9(4)
b [pm]	1420.3(3)	1513.4(3)	1445.7(3)
c [pm]	2169.3(4)	1094.0(2)	2085.0(4)
α [°]	90	90	90
β [°]	102.62(3)	95.54(3)	112.61(3)
γ [°]	90	90	90
Z	4	2	4
Absorption coefficient μ [mm^{-1}]	2.615	2.338	1.864
Diffractometer	STOE IPDS II	STOE IPDS I	STOE IPDS I
Measuring range (θ) [°]	1.7–25.7	1.9–26.0	1.9–26.1
Reflections collected	11020	11544	17032
Independent reflections [$I > 2\sigma(I)$]	5648	3080	9122
Absorption correction	numerical	none[a]	none[a]
Refined parameters	316	187	454
wR_2/R_1 [$I > 2\sigma(I)$]	0.062/0.029	0.109/0.048	0.129/0.059
Max./min. residual electron density [e pm^{-3} 10^{-6}]	0.421/–0.241	0.768/–0.335	0.709/–0.374

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

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[25] CCDC-681432 (**3** at 133 K), -681431 (**5** at 293 K) and -681433 (**6a** at 173 K) contain the supplementary crystallographic data. 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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