

Synthesis and reactivity of Group 14 substituted amino-functionalised cyclopentadienyl compounds

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Abstract

Having isolated and characterised a series of sodium amino-functionalised cyclopentadienide salts, a number of Group 14 derivatives have been synthesised and characterised. These have potential as amino-functionalised cyclopentadienyl transfer reagents and a trimethylsilyl derivative has been used from a new type of 1,3-bisfunctionalised ferrocene compound. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cyclopentadienyl compounds; Group 14 derivatives; 1,3-Bisfunctionalised ferrocene

1. Introduction

We have been interested in transition metal amino-functionalised cyclopentadienyl compounds due to their catalytic applications [1] as well as their potential anti-tumour properties [2,3]. An excellent review of amino-functionalised cyclopentadienyl compounds has been written by Jutzi with many relevant references contained therein [4]. One area of interest is the synthesis of cyclopentadienyl functionalised Group 5 complexes in order to evaluate their catalytic potential. These can be difficult to make by metathesis with alkali metal cyclopentadienide salts due to reduction problems at the transition metal centre. Therefore, it was to this end that we wanted to synthesise Group 14 substituted amino-functionalised cyclopentadienyl compounds to act as cyclopentadienyl transfer reagents. Also, one of our aims was to try to modify the architecture of the transition metal bound amino-functionalised cyclopentadienyl ligand by addition of a second group to the cyclopentadienyl ring. We have previously reported a series of functionalised ferrocenes, [5,6] vanadocenes [6,7], titanocenes [2,3] and yttrium amino-functionalised cyclopentadienyl compounds [8].

This paper reports general and high yielding routes to the preparation and isolation of a series of amino-functionalised sodium cyclopentadienide salts. Part of this work has been previously communicated [6,9] and we present here a more detailed account with full experimental details and characterisation of the amino-functionalised sodium cyclopentadienide salts. We report new Group 14 amino-functionalised cyclopentadienyl compounds as well as a new bis-1,3-functionalised ferrocene derivative.

2. Results and discussion

The ligand precursors were used to synthesise the corresponding sodium salts $\text{NaC}_5\text{H}_4(\text{CH}_2)_2\text{NMe}_2$ (**1**), $\text{NaC}_5\text{H}_4(\text{CH}_2)_3\text{NMe}_2$ (**2**), $\text{NaC}_5\text{H}_4(\text{CH}_2)_3\text{NH}_2$ (**3**), $\text{NaC}_5\text{H}_4\text{CH}(\text{CH}_2)_4\text{NMe}$ (**4**), $\text{NaC}_5\text{H}_4(\text{CH}_2)_2\text{N}(\text{CH}_2)_5$ (**5**) and $\text{NaC}_5\text{H}_4(\text{CH}_2)_2\text{N}(\text{C}_5\text{H}_4\text{N})$ (**6**). These compounds are very water and air sensitive white/beige coloured powders, and after synthesis are stored in a glove box and used accordingly. They can be synthesised on a 20 g scale in up to 100% yield. Despite the air and moisture sensitive nature of these compounds they can be readily stored under inert atmospheres indefinitely. Preparation was achieved by addition of the substituted cyclopentadiene to a THF suspension of sodium hy-

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Table 1 (Continued)

6	
Chemical shift (δ)	Assignments
^1H	
8.26–8.24, 7.65–7.59, 7.29–7.25, 7.07–7.04 (4 x m, 1H)	$\text{NaC}_5\text{H}_4\text{CH}_2(\text{C}_5\text{H}_4\text{N})$
5.06, 5.43 (2 x s, 4H)	$\text{NaC}_5\text{H}_4\text{CH}_2(\text{C}_5\text{H}_4\text{N})$
4.05 (s, 2H)	$\text{NaC}_5\text{H}_4\text{CH}_2(\text{C}_5\text{H}_4\text{N})$
^{13}C	
167.3 (s)	quaternary $\text{NaC}_5\text{H}_4\text{CH}_2(\underline{\text{C}}_5\text{H}_4\text{N})$
149.9, 137.1, 123.7, 121.2 (4 x s)	$\text{NaC}_5\text{H}_4\text{CH}_2(\underline{\text{C}}_5\text{H}_4\text{N})$
115.1 (s)	quaternary $\text{Na}\underline{\text{C}}_5\text{H}_4\text{CH}_2(\text{C}_5\text{H}_4\text{N})$
104.3–103.1 (m)	$\text{Na}\underline{\text{C}}_5\text{H}_4\text{CH}_2(\text{C}_5\text{H}_4\text{N})$
39.6 (s)	$\text{Na}\underline{\text{C}}_5\text{H}_4\text{CH}_2(\text{C}_5\text{H}_4\text{N})$

dride. Effervescence was observed as hydrogen is released. The amino substituted cyclopentadiene was used in slight excess to minimise the chance of unreacted sodium hydride contaminating the final product.

Characterisation of these compounds was achieved by NMR spectroscopy since they are pyrophoric and also too air and moisture sensitive for microanalysis. The NMR data for the compounds **1–6** are shown in Table 1. Of particular interest is the NMR of **4** and **5**, which shows signals attributable to axial and equatorial protons of the piperidyl ring. ^1H – ^1H and $^1\text{H}\{^{13}\text{C}\}$ -NMR spectroscopy correlation experiments proved particularly useful in determining that the axial protons are furthest downfield in the ^1H -NMR spectrum. For **4**, there is a large difference in chemical shift of the axial, δ 3.81–2.78 ppm, and equatorial protons, δ 1.89–1.79 ppm, which are attached to the carbon atoms next to the nitrogen. The differences in the chemical shifts associated with the axial and equatorial protons are the result of the *trans* diaxial relationship between the C–H and the nitrogen lone-pair.

Synthesis of trialkyl Group 14 derivatives was achieved by the reaction of **4** with either trimethyl silyl chloride and triphenyl lead bromide to yield the 1,3 bis-substituted cyclopentadienyl derivatives $\text{Me}_3\text{Si}(\text{C}_5\text{H}_4)\text{CH}(\text{CH}_2)_4\text{NMe}$ **7**, $\text{Ph}_3\text{Pb}(\text{C}_5\text{H}_4)(\text{CH}_2)_5\text{NMe}$ **8**, and by the reaction of **5** with triphenyl lead bromide to yield $\text{Ph}_3\text{Pb}(\text{C}_5\text{H}_4)(\text{CH}_2)_2\text{N}(\text{CH}_2)_5$ **9** (Scheme 1). Compounds **8** and **9** have been characterised by ^1H and ^{13}C -NMR spectroscopy, microanalysis as well as X-ray crystallography in the case of **8**. The compound $\text{Me}_3\text{SiC}_5\text{H}_4(\text{CH}_2)_2\text{N}(\text{CH}_2)_5$ has previously been reported in the synthesis of $\text{Ti}\{\eta\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{N}(\text{CH}_2)_5\}_2\text{Cl}_3$ [10]. Reaction of **7** with BuLi yields the

bis-substituted lithium salt **10**. This air and water sensitive salt has been characterised by ^1H and ^{13}C -NMR spectroscopy. The synthesis and isolation of **10** is significant because it provides evidence of the possibility of adding increased steric properties to organometallic amino-functionalised cyclopentadienyl compounds.

The pertinent crystallographic details for **8** are given in Table 2. Crystals of **8** were obtained by recrystallisation from a petroleum ether (40–60 °C) solution and an X-ray structure analysis carried out. Selected bond lengths and angles are shown in Table 3. Compound **8**

Table 2
Crystallographic data for compounds **8** and **10**

Compound	8	11
Crystal description	Yellow prism	Orange plate
Crystal size (mm)	0.6 × 0.57 × 0.5 mm	0.14 × 0.08 × 0.08
Chemical formula	$\text{C}_{29}\text{H}_{31}\text{NPb}$	$\text{C}_{28}\text{H}_{50}\text{FeN}_2\text{Si}_2$
Temperature (K)	150(2)	150(2)
<i>a</i> (Å)	9.0220(3)	17.5063(3)
<i>b</i> (Å)	9.3607(6)	11.5794(3)
<i>c</i> (Å)	14.9421(6)	16.7952(4)
α (°)	94.473(2)	90
β (°)	98.369(2)	119.5310(10)
γ (°)	99.155(2)	90
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
<i>Z</i>	2	4
Reflections collected	14891	22456
Data measured	4784	2891
Unique data	4440 [$I > 2\sigma(I)$]	2511 [$I > 2\sigma(I)$]
R_{int}	0.1276	0.0577
Refinement method	Full	Full
Parameters refined	282	155
<i>R</i> (all data)	0.062	0.0454
R_w (all data)	0.1547	0.0943

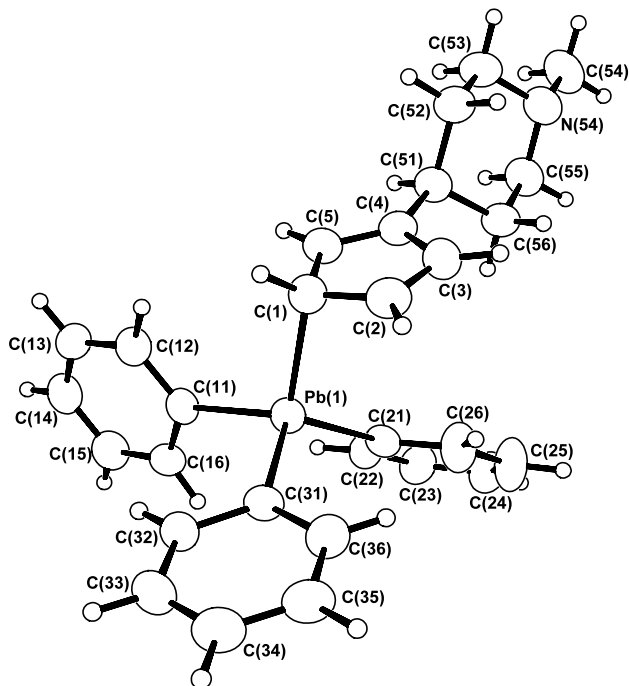
Table 3

Interatomic distances (Å) and angles between interatomic vectors (°) with s.u.s. in parentheses for compound **8**

Interatomic distances			
Pb(1)–C(31)	2.191(7)	Pb(1)–C(21)	2.191(7)
Pb(1)–C(11)	2.209(7)	Pb(1)–C(1)	2.280(9)
C(1)–C(5)	1.453(13)	C(1)–C(2)	1.460(14)
C(2)–C(3)	1.343(14)	C(3)–C(4)	1.472(13)
C(4)–C(5)	1.326(13)	C(4)–C(51)	1.523(13)
Interatomic angles			
C(31)–Pb(1)–C(21)	116.3(2)	C(31)–Pb(1)–C(11)	107.5(2)
C(21)–Pb(1)–C(11)	109.5(3)	C(31)–Pb(1)–C(1)	106.4(3)
C(21)–Pb(1)–C(1)	110.2(3)	C(11)–Pb(1)–C(1)	106.5(3)
C(16)–C(11)–Pb(1)	120.1(5)	C(12)–C(11)–Pb(1)	120.6(5)
C(22)–C(21)–Pb(1)	119.1(5)	C(26)–C(21)–Pb(1)	122.1(6)
C(32)–C(31)–Pb(1)	118.3(5)	C(36)–C(31)–Pb(1)	123.4(6)
C(5)–C(1)–C(2)	104.4(8)	C(5)–C(1)–Pb(1)	105.8(6)
C(2)–C(1)–Pb(1)	104.9(6)	C(3)–C(2)–C(1)	108.4(9)
C(2)–C(3)–C(4)	109.3(8)	C(5)–C(4)–C(3)	106.9(9)
C(5)–C(4)–C(51)	127.5(9)	C(3)–C(4)–C(51)	125.5(8)
C(4)–C(5)–C(1)	110.8(9)	C(56)–C(51)–C(4)	114.0(8)
C(52)–C(51)–C(4)	113.1(8)		

is the first structurally characterised example of a metal complex containing a functionalised cyclopentadienyl triphenylplumbyl substituted compound and the molecular structure shown in Fig. 1: the unsubstituted cyclopentadiene derivative PbPh_3Cp has been previously synthesised [11]. The structure of **8** shows the expected sp^3 hybridised triphenyl Pb(IV) centre bound in an η^1 fashion to the functionalised cyclopentadienyl ring. For the cyclopentadienyl unit bound to the Pb centre, the bond lengths and angles are similar to those found for PbPh_3Cp (Table 3) [11].

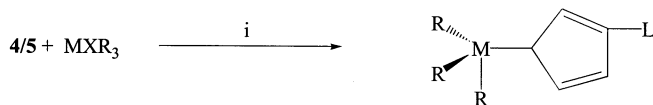
The NMR spectrum of **8** and **9** consists of an AA'BB' pattern, which is indicative of a molecular plane of symmetry. For **8** and **9** there are two sets of coupling constants for ($^{207}\text{Pb}-^1\text{H}$) of ~ 20 and ~ 60 Hz, which are indicative of the Pb(IV) centre being attached closer to one set of C–H cyclopentadiene peaks than the others. This is not in accordance with the structure found in the solid state, therefore, low temperature NMR experiments were carried out to try to elucidate if there was a fluxional process within the molecule. It could be envisaged that the ring can undergo a molecular flip as shown in Scheme 2. This could be a way of explaining the symmetrical nature of the molecule in solution. Collapse of the signals could not be achieved, even after cooling the sample to -90 °C.

Fig. 1. The molecular structure of compound **8**.

A similar phenomenon was observed for the unfunctionalised derivative PbPh_3Cp , where this sample was cooled to -40 °C [11].

There has been much interest in ferrocene and ferrocenium complexes for a variety of reasons, including their cytotoxic properties [12,13] and anti-malarial activities [14]. We have published in the area of synthesis and reactivity of mono-functionalised ferrocenes [5,6]. A 1,3 bis-substituted cyclopentadienyl ferrocene derivative has been synthesised by reaction of **10** and FeCl_2 to produce **11** as shown in Scheme 3. Compound **11** was characterised by ^1H and ^{13}C -NMR spectroscopy, micro-analysis as well as X-ray crystallography. The pertinent crystallographic details for **11** are given in Table 2.

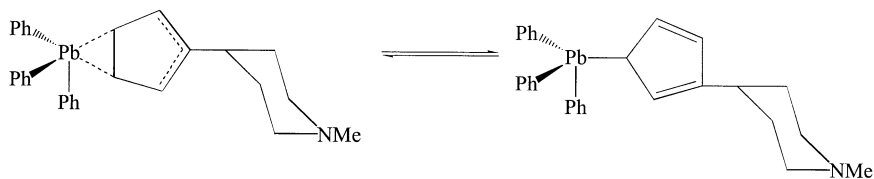
Crystals of **11** were obtained by slow evaporation from an ether solution and an X-ray structure analysis carried out. For **11**, there is half a molecule per symmetric unit and selected bond lengths and angles are shown in Table 4. Compound **11** is the first structurally characterised example of a metal complex containing a trimethylsilyl substituted amino-functionalised cyclopentadienyl ligand system and the molecular



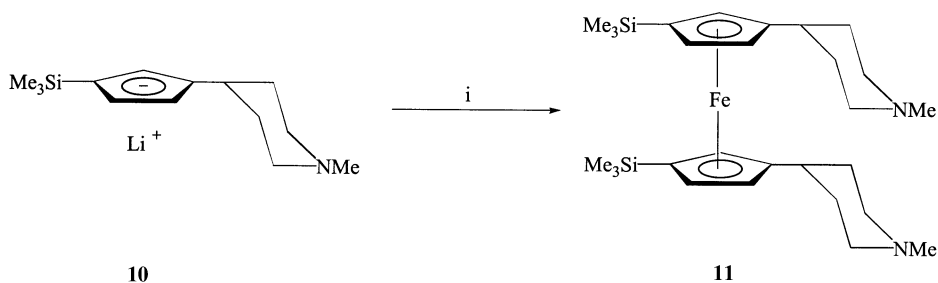
M = Si, R = Me, L = $\text{CH}(\text{CH}_2)_4\text{NMe}$; **7**

M = Pb, R = Ph, L = $\text{CH}(\text{CH}_2)_4\text{NMe}$; **8**

M = Pb, R = Ph, L = $(\text{CH}_2)_2\text{N}(\text{CH}_2)_5$; **9**



Scheme 2.

Scheme 3. (i) THF, FeCl₂.

structure shown in Fig. 2. The ligands contain *N*-methylpiperidiny ring substituents, which exist in a chair conformation. The cyclopentadienyl rings are virtually eclipsed with respect to each other and the *N*-methylpiperidiny side chains are in *cis*-conformation to each other. This is different to Fe[η-C₅H₄CH(CH₂)₄NMe]₂, [6] where the aminocyclopentadienyl groups lie virtually *trans* to each other. This is presumably due to the influence of the trimethylsilyl group. There are a number of possibilities of diastereoisomers which is indicated by NMR spectroscopy, which are similar to those reported for Fe[C₅H₃-1-PPh₂-3-^tBu](C₅H₅)₂ [15] and Fe[C₅H₃-1-PPh₂-3-SiMe₃](C₅H₅)₂ [16]. Crystallisation tends to favour the *meso* isomer. The iron ring-centroid distance for **11** is Fe(1)–Cp(cent) 1.66 Å, which is equal to that of the monofunctionalised ferrocene analogue, Fe[η-C₅H₄CH(CH₂)₄NMe]₂.

In conclusion, this paper reports the preparation and characterisation of a number of sodium cyclopentadienide salts, as well as some of their Group 14 analogues. Also presented is the synthesis, isolation and characterisation of a bis-1, 3 substituted ferrocene. The functionalised ferrocenes open up the possibilities of synthesising a range of ferrocenium compounds, which may have potential as anti-tumour reagents.

3. Experimental

3.1. General

Standard inert atmosphere techniques were used throughout. Petroleum ether (40–60°), diethyl ether, toluene and THF were distilled from Na–Ph₂CO. NMR

solvents were degassed by three freeze-pump-thaw cycles and stored over 3 Å molecular sieves in a dry box, except Acetonitrile-*d*₃, which was distilled from CaH₂. All reagents were purchased in reagent grade and used without further purification.

3.2. Instrumentation

¹H and ¹³C-NMR spectra were recorded on Bruker 250, 300 and 500 MHz spectrometers. *High resolution mass spectrometry was performed by the University of Leeds mass spectral service. Elemental analyses were performed by the University of Leeds microanalytical services.

3.3. Preparations

3.3.1. NaC₅H₄(CH₂)₂NMe₂ (**1**)

To a Schlenk tube charged with NaH (2.2 g, 0.092 mol) and THF (100 ml) was added C₅H₅(CH₂)₂NMe₂ (25.0 g) dropwise with stirring. Evolution of a gas and formation of a pale brown precipitate was observed. The reaction mixture was stirred for ca. 6 h. THF was then removed in vacuo and the product was washed with petroleum ether (b.p. 40–60 °C) (3 × 30 ml) to give a pale brown powdery solid.

3.3.2. NaC₅H₄(CH₂)₃NMe₂ (**2**)

To a Schlenk tube charged with NaH (3.0 g, 0.125 mol) and THF (100 ml) was added C₅H₅(CH₂)₃NMe₂ (37.9 g) dropwise with stirring. The reaction mixture was worked up in the same way as **1** to give a pale brown powdery solid, (16.5 g, 0.095 mol, 76%, based on NaH).

Table 4

Interatomic distances (Å) and angles between interatomic vectors (°) with s.u.s. in parentheses for compound **11**

Interatomic distances

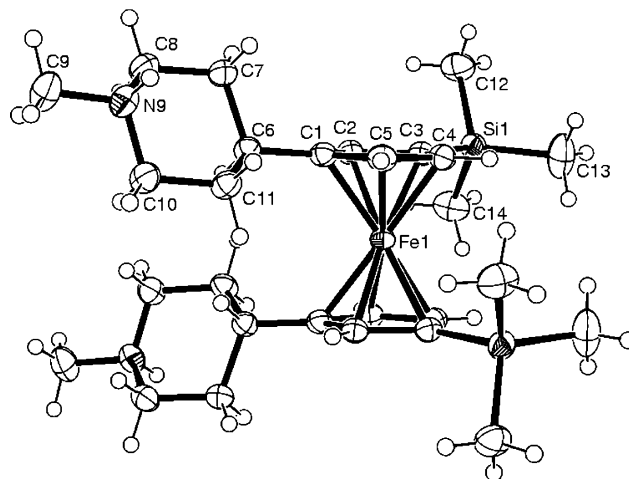
Fe(1)–C(1)	2.073(2)
Fe(1)–C(2)	2.0499(19)
Fe(1)–C(3)	2.0684(19)
Fe(1)–C(4)	2.045(2)
Fe(1)–C(5)	2.054(2)
Si(1)–C(3)	1.859(2)
C(1)–C(6)	1.508(3)

Interatomic angles

C(4)–Fe(1)–C(4)	115.32(12)	C(4)–Fe(1)–C(2)	133.49(8)
C(4)–Fe(1)–C(2)	67.87(8)	C(4)–Fe(1)–C(2)	67.87(8)
C(4)–Fe(1)–C(2)	133.49(8)	C(2)–Fe(1)–C(2)	146.14(11)
C(4)–Fe(1)–C(5)	40.51(8)	C(4)–Fe(1)–C(5)	146.33(8)
C(2)–Fe(1)–C(5)	109.80(8)	C(2)–Fe(1)–C(5)	67.80(8)
C(4)–Fe(1)–C(5)	146.33(8)	C(4)–Fe(1)–C(5)	40.51(8)
C(2)–Fe(1)–C(5)	67.80(8)	C(2)–Fe(1)–C(5)	109.80(8)
C(5)–Fe(1)–C(5)	172.29(12)	C(4)–Fe(1)–C(3)	41.06(8)
C(4)–Fe(1)–C(3)	108.76(8)	C(2)–Fe(1)–C(3)	172.59(8)
C(2)–Fe(1)–C(3)	40.86(8)	C(5)–Fe(1)–C(3)	69.04(8)
C(5)–Fe(1)–C(3)	114.33(8)	C(4)–Fe(1)–C(3)	108.76(8)
C(4)–Fe(1)–C(3)	41.06(8)	C(2)–Fe(1)–C(3)	40.86(8)
C(2)–Fe(1)–C(3)	172.59(8)	C(5)–Fe(1)–C(3)	114.33(8)
C(5)–Fe(1)–C(3)	69.04(8)	C(3)–Fe(1)–C(3)	132.33(11)
C(4)–Fe(1)–C(1)	172.59(8)	C(4)–Fe(1)–C(1)	68.25(8)
C(2)–Fe(1)–C(1)	40.57(7)	C(2)–Fe(1)–C(1)	114.93(8)
C(5)–Fe(1)–C(1)	133.10(8)	C(5)–Fe(1)–C(1)	40.42(8)
C(3)–Fe(1)–C(1)	145.39(8)	C(3)–Fe(1)–C(1)	69.27(8)
C(4)–Fe(1)–C(1)	68.25(8)	C(4)–Fe(1)–C(1)	172.59(8)
C(2)–Fe(1)–C(1)	114.93(8)	C(2)–Fe(1)–C(1)	40.57(7)
C(5)–Fe(1)–C(1)	40.42(8)	C(5)–Fe(1)–C(1)	133.10(8)
C(3)–Fe(1)–C(1)	69.27(8)	C(3)–Fe(1)–C(1)	145.39(8)
C(1)–Fe(1)–C(1)	109.04(11)	C(3)–Si(1)–C(13)	108.95(11)
C(3)–Si(1)–C(14)	111.78(10)	C(13)–Si(1)–C(14)	109.79(14)
C(3)–Si(1)–C(12)	107.21(10)	C(13)–Si(1)–C(12)	111.20(14)
C(14)–Si(1)–C(12)	107.89(12)	C(9)–N(9)–C(10)	111.72(18)
C(9)–N(9)–C(8)	110.87(18)	C(10)–N(9)–C(8)	110.80(17)
C(1)–C(2)–C(3)	110.35(18)	C(1)–C(2)–Fe(1)	70.58(11)
C(3)–C(2)–Fe(1)	70.26(11)	C(5)–C(4)–C(3)	109.42(18)
C(5)–C(4)–Fe(1)	70.07(11)	C(3)–C(4)–Fe(1)	70.32(11)
C(5)–C(1)–C(2)	106.57(17)	C(5)–C(1)–C(6)	127.59(18)
C(2)–C(1)–C(6)	125.72(18)	C(5)–C(1)–Fe(1)	69.08(11)
C(2)–C(1)–Fe(1)	68.85(11)	C(6)–C(1)–Fe(1)	129.91(14)
C(4)–C(5)–C(1)	108.61(17)	C(4)–C(5)–Fe(1)	69.42(11)
C(1)–C(5)–Fe(1)	70.50(11)	C(2)–C(3)–C(4)	105.05(17)
C(2)–C(3)–Si(1)	126.47(15)	C(4)–C(3)–Si(1)	128.33(16)
C(2)–C(3)–Fe(1)	68.88(11)	C(4)–C(3)–Fe(1)	68.61(11)
Si(1)–C(3)–Fe(1)	129.81(11)	N(9)–C(8)–C(7)	111.19(18)
C(8)–C(7)–C(6)	110.93(17)	C(1)–C(6)–C(11)	113.61(17)
C(1)–C(6)–C(7)	111.39(17)	C(11)–C(6)–C(7)	108.07(16)
N(9)–C(10)–C(11)	110.21(18)	C(10)–C(11)–C(6)	110.78(17)

3.3.3. $\text{NaC}_5\text{H}_4(\text{CH}_2)_3\text{NH}_2$ (**3**)

To a Schlenk tube charged with NaH (2.4 g, 0.100 mol) and THF (100 ml) was added $\text{C}_5\text{H}_5(\text{CH}_2)_3\text{NH}_2$ (35.0 g) dropwise with stirring. The reaction mixture was worked up in the same way as **1** to give a pale brown powdery solid, (8.7 g, 0.060 mol, 60%, based on NaH).

Fig. 2. The molecular structure of compound **11**.3.3.4. $\text{NaC}_5\text{H}_4\text{CH}(\text{CH}_2)_4\text{NMe}$ (**4**)

To a Schlenk tube charged with NaH (2.5 g 0.104 mol) and THF (100 ml) was added $\text{C}_5\text{H}_5\text{CH}(\text{CH}_2)_4\text{NMe}$ (50.0 g) dropwise with stirring. The reaction mixture was worked up in the same way as **1** to give a pale brown powdery solid, (17.7 g, 0.096 mol, 92%, based on NaH).

3.3.5. $\text{NaC}_5\text{H}_4(\text{CH}_2)_2\text{N}(\text{CH}_2)_5$ (**5**)

To a Schlenk tube charged with NaH (3.0 g, 0.125 mol) and THF (100 ml) was added $\text{C}_5\text{H}_5\text{CH}(\text{CH}_2)_2\text{N}(\text{CH}_2)_5$ (50.0 g) dropwise with stirring. The reaction mixture was worked up in the same way as **1** to give a pale brown powdery solid, (15.0 g, 0.075 mol, 60%, based on NaH).

3.3.6. $\text{NaC}_5\text{H}_4\text{CH}_2(\text{C}_5\text{H}_4\text{N})$ (**6**)

To a Schlenk tube charged with NaH (3.0 g, 0.125 mol) and THF (100 ml) was added a mixture of dicyclopentadiene and $\text{C}_5\text{H}_5\text{CH}(\text{CH}_2)_2\text{N}(\text{CH}_2)_5$ (24.7 g) dropwise with stirring. The reaction mixture was worked up in the same way as **1** to give a pale brown powdery solid, (22.4 g, 0.125 mol, 100%, based on NaH).

3.3.7. $\text{Me}_3\text{Si}(\text{C}_5\text{H}_4)\text{CH}(\text{CH}_2)_4\text{NMe}$ (**7**)

Under an atmosphere of nitrogen, **4** (2.28 g, 0.01 mol) was dissolved in dry THF (25 ml) with stirring. ClSiMe_3 (1.23g, 0.01 mol) was added producing a yellow solution with a white precipitate. The THF was removed under reduced pressure and the compound extracted in petroleum ether (b.p. 40–60 °C) (2×30 ml). The product was isolated as a clear oil. $^1\text{H-NMR}$ (CDCl_3 , 250 MHz, 300 K) δ 6.35 [m, 3H, $\text{C}_5\text{H}_3\text{H}(\text{SiMe}_3)\text{CH}(\text{CH}_2\text{CH}_2)_2\text{NMe}$], 3.1 [s, 1H, $\text{C}_5\text{H}_3\text{H}(\text{SiMe}_3)\text{CH}(\text{CH}_2\text{CH}_2)_2\text{NMe}$], 2.75 [m, 2H, $\text{C}_5\text{H}_4(\text{SiMe}_3)\text{CH}(\text{CH}_2\text{CH}_2)_2\text{NMe}$], 2.20 [m, 1H, $\text{C}_5\text{H}_4(\text{SiMe}_3)\text{CH}(\text{CH}_2\text{CH}_2)_2\text{NMe}$], 2.15 [m, 3H, $\text{C}_5\text{H}_4(\text{SiMe}_3)\text{CH}(\text{CH}_2\text{CH}_2)_2\text{NMe}$], 1.83 [m, 4H, $\text{C}_5\text{H}_4(\text{SiMe}_3)\text{CH}(\text{CH}_2\text{CH}_2)_2\text{NMe}$], 1.70 [m, 2H, $\text{C}_5\text{H}_4(\text{SiMe}_3)\text{CH}(\text{CH}_2\text{CH}_2)_2\text{NMe}$],

–0.2 [s, 9H, SiMe₃]. ¹³C{¹H}-NMR (CDCl₃, 250 MHz, 300 K) δ 138.0, 130.0, 138.1, [3 × s, C₅H₄(SiMe₃)CH(CH₂CH₂)₂NMe], 109.3 [s, CCH(CH₂CH₂)₂NMe], 57.0 [s, C₅H₄(SiMe₃)CH(CH₂CH₂)₂NMe], 51.0 [s, CHSiMe₃], 47.1 [s, C₅H₄(SiMe₃)CH(CH₂CH₂)₂NMe], 34.0 [s, C₅H₄(SiMe₃)CCH(CH₂CH₂)₂NMe], 32.0 [s, C₅H₄(SiMe₃)CH(CH₂CH₂)₂NMe], –2.0 [s, C₅H₄(SiMe₃)CH(CH₂CH₂)₂NMe].

3.3.8. Ph₃Pb(C₅H₄)CH(CH₂)₄NMe (8)

Ph₃PbBr (0.72 g, 0.0014 mol) was dissolved in toluene (30 ml) to give a clear solution to which **4** (0.25 g, 0.0014 mol) in toluene (30 ml), was added. The solution turned yellow immediately with a white precipitate and was left to stir for 24 h. The solution was filtered and the toluene removed under reduced pressure. The resulting yellow oily solid was extracted in petroleum ether (b.p. 40–60 °C) (50 ml) and recrystallised yielding large yellow crystals of Ph₃Pb((C₅H₄)(CH₂)₅NMe) (0.41 g, 0.000683 mol, 49% yield). Found: C, 57.8; H, 5.3; N, 2.3. Calc.: C, 58.0; H, 5.2; N, 2.3%. ¹H-NMR (C₆D₆, 500 MHz, 300 K) δ 7.22 [m 15H, (C₆H₅)₃Pb], 6.41 [m, 2H, C₅H₄, Pb(CH)₂(CH)₂C] ³J (²⁰⁷Pb–¹H) 19.0 Hz, 5.81 [m, 2H, C₅H₄, Pb(CH)₂(CH)₂C] ²J (²⁰⁷Pb–¹H) 60.0 Hz, 2.75 [m, 2H, PbC₅H₄CH(CH₂CH₂)₂NMe], 2.32 [m, 1H, PbC₅H₄CH(CH₂CH₂)₂NMe], 2.18 [m, 3H, PbC₅H₄CH(CH₂CH₂)₂NMe], 1.82 [m, 2H, PbC₅H₄CH(CH₂CH₂)₂NMe], 1.66 [m, 4H, PbC₅H₄CH(CH₂CH₂)₂NMe]. ¹³C{¹H}-NMR (C₆D₆, 500 MHz, 300 K) δ 153.3 [s, CPb], 148.6 [s, C₅H₄, Pb(CH)(CH)₂CCH(CH₂)₄NMe], 137.7 [s, CH (*meta*)] ²J (¹⁰⁷Pb–¹³C), 67.51 Hz, 130.0 [s, CH (*ortho*)] ¹J (¹⁰⁷Pb–¹³C) 79.91 Hz, 129.1 [s, CH (*para*)] ³J (¹⁰⁷Pb–¹³C) 18.53 Hz, 121.4 [s, C₅H₄, Pb(CH)₂(CH)₂C], 99.3 [s, C₅H₄, Pb(CH)₂(CH)₂C], 56.8 [s, PbC₅H₄CH(CH₂CH₂)₂NMe], 47.0 [s, PbC₅H₄CH(CH₂CH₂)₂NMe], 36.9 [s, PbC₅H₄CH(CH₂CH₂)₂NMe], 33.5 [s, PbC₅H₄CH(CH₂CH₂)₂NMe].

3.3.9. Ph₃Pb(C₅H₄)(CH₂)₂N(CH₂)₅ (9)

Ph₃PbBr (0.64 g, 0.0012 mol) was dissolved in toluene (30 ml) to give a clear solution to which **5** (0.25 g, 0.0012 mol) in toluene (30 ml), was added. The solution turned immediately yellow with a white precipitate and was left to stir for 24 h. The solution was filtered and the toluene removed under reduced pressure resulting in yellow oil Ph₃Pb(C₅H₄)(CH₂)₂N(CH₂)₅ (0.44 g, 0.000716 mol, 53% yield). Found: C, 58.5; H, 5.7; N, 2.1. Calc.: C, 58.6; H, 5.4; N, 2.3%. ¹H-NMR (C₆D₆, 500 MHz, 300 K) δ 7.27 [m 15H, (C₆H₅)₃Pb], 6.40 [m, 2H, C₅H₄, Pb(CH)₂(CH)₂C] ³J (²⁰⁷Pb–¹H) 22.8 Hz, 5.97 [m, 2H, C₅H₄, Pb(CH)₂(CH)₂C] ²J (²⁰⁷Pb–¹H) 51.5 Hz, 2.81 [m, 2H, PbC₅H₄(CH₂CH₂)N(CH₂)₅], 2.44 [m, 2H, PbC₅H₄(CH₂CH₂)N(CH₂)₅], 2.41 [m, 4H, PbC₅H₄(CH₂)₂N(CH₂CH₂)₂CH₂], 1.64 [m, 4H, PbC₅H₄(CH₂)₂N(CH₂CH₂)₂CH₂], 1.44 [m, 2H, PbC₅H₄(CH₂)₂N(CH₂)₄CH₂]. ¹³C{¹H}-NMR (C₆D₆, 500 MHz, 300

K) δ 155.0 [s, CPb], 142.8 [s, C₅H₄, Pb(CH)₂(CH)₂CCH₂], 137.0 [CH (*meta*)] ²J (¹⁰⁷Pb–¹³C) 67.74 Hz, 130.2 [CH (*ortho*)] ¹J (¹⁰⁷Pb–¹³C) 79.56 Hz, 129.3 [CH (*para*)] ³J (¹⁰⁷Pb–¹³C) 16.85 Hz, 128.2 [s, C₅H₄, Pb(CH)₂(CH)₂C], 102.6 [s, C₅H₄, (Pb(CH)₂(CH)₂C)], 60.7 [s, PbC₅H₄(CH₂CH₂)N(CH₂)₅], 55.2 [s, PbC₅H₄(CH₂)₂N(CH₂CH₂)₂CH₂], 28.7 [s, PbC₅H₄(CH₂CH₂)N(CH₂)₅], 27.0 [s, PbC₅H₄(CH₂)₂N(CH₂CH₂)₂CH₂], 25.5 [s, PbC₅H₄(CH₂)₂N(CH₂CH₂)₂CH₂].

3.3.10. Li{C₅H₃-1-SiMe₃-3-CH(CH₂)₄NMe} (10)

Under an atmosphere of nitrogen, C₅H₅CH(CH₂)₄NMe (3.54 g, 0.022 mol) was dissolved in dry THF (25 ml) with stirring. After addition of ⁿBuLi in hexanes (1.41 g, 0.022 mol), the solution turned from red to yellow. To this solution, ClSiMe₃ (2.4 g, 0.022 mol) was added producing a yellow solution with a white precipitate. The THF was removed under reduced pressure and the compound extracted in petroleum ether (b.p. 40–60 °C) (2 × 30 ml). ⁿBuLi in hexanes (1.16 g, 0.018 mol) was added to the resultant mixture yielding a white/yellow precipitate. The petroleum ether (b.p. 40–60 °C) was filtered off and the solid washed with the petroleum ether (b.p. 40–60 °C) (25 ml × 3). The resulting solid was dried under reduced pressure to yield Li(C₅H₃)(SiMe₃)(CH₂)₅NMe (3.7 g, 0.015 mol, 70%). ¹H-NMR (C₆D₆, 250 MHz, 300 K) δ 5.56 [m, 3H, C₅H₃(SiMe₃)CH(CH₂CH₂)₂NMe], 2.84 [m, 2H, C₅H₃(SiMe₃)CH(CH₂CH₂)₂NMe], 2.29 [m, 1H, C₅H₃(SiMe₃)CH(CH₂CH₂)₂NMe], 2.19 [m, 3H, C₅H₃(SiMe₃)CH(CH₂CH₂)₂NMe], 1.95 [m, 4H, C₅H₃(SiMe₃)CH(CH₂CH₂)₂NMe], 1.51 [m, 2H, C₅H₃(SiMe₃)CH(CH₂CH₂)₂NMe], 0.08 [s, 9H, SiMe₃]. ¹³C{¹H}-NMR (C₆D₆, 250 MHz, 300 K) δ 128.9 [s, CSiMe₃], 111.0, 108.7, 105.6, [3 × s, C₅H₃(SiMe₃)CH(CH₂CH₂)₂NMe], 109.3 [s, CCH(CH₂CH₂)₂NMe], 57.7 [s, C₅H₃(SiMe₃)CH(CH₂CH₂)₂NMe], 47.1 [s, C₅H₃(SiMe₃)CH(CH₂CH₂)₂NMe], 37.1 [s, C₅H₃(SiMe₃)CH(CH₂CH₂)₂NMe], 35.7 [s, C₅H₃(SiMe₃)CH(CH₂CH₂)₂NMe], 1.3 [s, C₅H₃(SiMe₃)CH(CH₂CH₂)₂NMe].

3.3.11. [Fe{C₅H₃-1-SiMe₃-3-CH(CH₂)₄NMe}₂] (11)

To a stirred solution of iron(II)chloride (0.095 g, 0.00075 mol) in THF at 0° was added a solution of the **10** (0.36, 0.0015 mol) in THF. The THF was removed under reduced pressure to leave a brown solid. The product was extracted with petroleum ether (b.p. 40–60 °C). Recrystallisation from petroleum ether (b.p. 40–60 °C) afforded an orange crystalline solid. Yield: 0.255 g, 65%. Found: C, 63.7; H, 9.9; N, 5.6. Calc.: C, 64.1; H, 9.2; N, 5.3%. ¹H-NMR (C₆D₆, 250 MHz, 300 K) δ 5.56 [m, 3H, C₅H₃(SiMe₃)CH(CH₂CH₂)₂NMe], 2.84 [m, 2H, C₅H₃(SiMe₃)CH(CH₂CH₂)₂NMe], 2.29 [m, 1H, C₅H₃(SiMe₃)CH(CH₂CH₂)₂NMe], 2.19 [m, 3H, C₅H₃(SiMe₃)CH(CH₂CH₂)₂NMe], 1.95 [m, 4H, C₅H₃(SiMe₃)CH(CH₂CH₂)₂NMe], 1.51 [m, 2H, C₅H₃(Si-

Me₃)CH(CH₂CH₂)₂NMe]. ¹³C{¹H}-NMR (C₆D₆, 250 MHz, 300 K) δ 97.0, 96.7 [s, CSiMe₃], 72.7, 72.0, 69.5, 69.0, 67.7, 66.6 [6 × s, C₅H₃(SiMe₃)CH(CH₂CH₂)₂NMe], 71.3, 71.2 [s, CCH(CH₂CH₂)₂NMe], 56.3 [2 × s, C₅H₃(SiMe₃)CH(CH₂CH₂)₂NMe], 46.4 [s, C₅H₃(SiMe₃)CH(CH₂CH₂)₂NMe], 35.6, 35.3 [2 × s, C₅H₃(SiMe₃)CH(CH₂CH₂)₂NMe], 35.2, 35.0, 32.9, 32.5 [4 × s, C₅H₃(SiMe₃)CH(CH₂CH₂)₂NMe], 1.3 [3 × s, C₅H₃(SiMe₃)CH(CH₂CH₂)₂NMe].

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