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Journal of Organometallic Chemistry 664 (2002) 245–257

Journal of Organo metallic Chemistry

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Lithiation of ferrocenylamines and vanadium dinitrogen chemistry

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Received 16 August 2002; accepted 24 September 2002

Abstract

The lithiation of ferrocenylamines [Fe(C_5H_5)($C_5H_4CH_2R$)] (R = NMe_2, NEt_2, CH_2NMe_2, NC_4H_8O or $NMeCH_2Ph$) with organolithium reagents does not proceed with clean reaction at position 2 of the ring. Generally a range of products is formed, these sometimes difficult to separate. The electronic condition of the iron in these complexes as tested by Mössbauer spectroscopy and electrochemistry, does not differ much between compounds. The crystal structures of several methylated derivatives of the ferrocenylamines are reported. All the ferrocenylamines seem to potentiate vanadium(II) to dinitrogen uptake, but the precise nature of the dinitrogen species formed could not be determined.

Keywords: Ferrocenylaminates; Lithiation; Quaternisation; Vanadium(II); Dinitrogen uptake; X-ray structures; Mössbauer spectra; Cyclic voltammetry

1. Introduction

Vanadium(II) has long been known to react with dinitrogen, both in chemical systems and (presumably) in the iron–vanadium nitrogenase [1]. Unlike the well known range of molybdenum(0) and tungsten(0) dinitrogen complexes, in which the supporting ligands are phosphines, for vanadium(II) the ligands that may support dinitrogen uptake are oxygen donors [2], sulfur donors (as in nitrogenase) [3] or nitrogen–carbon donors [4]. The complex *trans*-[$VCl_2(tmen)_2$] (which does not itself react with dinitrogen) reacts with LiC_6H_4–2-CH_2NMe_2 under dinitrogen to yield, after treatment with one equivalent of pyridine (py), a bridging dinitrogen complex [{V($C_6H_4CH_2NMe_2$)$_2$(py)}$_2$(μ-N_2)], whose structure was determined by X-ray crystallography [4]. This complex reacts with acids to yield ammonia [5].

Additional redox-active centres not involved in dinitrogen binding [6] might contribute electrons to any protonation reaction of dinitrogen and thus affect the mechanism and extent of protonation. Extrapolating from the work of Gambarotta and co-workers [4], it was postulated that incorporation of the ligand *N*,*N*-dimethylaminomethylferrocenyl into dinitrogen-binding compounds might provoke this kind of chemistry [6]. Derivatives of [Fe(C_5H_5)($C_5H_4CH_2NMe_2$)], which can be lithiated at a ring position adjacent to the dimethylaminomethyl group, can act as a ligand to titanium(IV) [6], vanadium(III) [6] and especially to vanadium(II) [7]. In the last case, dinitrogen is taken up in a stoichiometry approximating to that required to produce a bridging dinitrogen complex, analogous to the compound obtained first by Gambarotta and co-workers [4]. We wished to extend these observations by using a range of ferrocenyl derivatives to try to define the requirements of a ferrocenyl ligand to potentiate vanadium(II) to react with dinitrogen.

A monomeric lithiating agent seems to be essential for the metallation of ferrocenes to be carried out smoothly and in high yield [8]. The lithiation of *N*,*N*-dimethylaminomethylferrocene [9] is fast (ca. 1 h with $LiBu^n$ in anhydrous diethyl ether) and clean [10]. No X-ray structural analysis has so far been carried out, but the structure probably involves chelation of the carbon-bound 2-lithium with the amine nitrogen.

[Fe(C_5H_5)($C_5H_4CH_2CH_2NMe_2$)] is metallated with $LiBu^n$ in hexane–Et_2O at the 2-position of the ring in

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PII: S0022-328X(02)02018-1

good yield, but at half the rate of [Fe(C_5H_5)($C_5H_4CH_2NMe_2$)] [9,11,12]. The longer reaction times also appear to allow significant formation of dilithiated species. The dimethylaminoethyl derivative of benzene evidently cannot be metallated in this way [11,13].

2. Results and discussion

2.1. Lithiation of ferrocenylamines [Fe(C_5H_5)($C_5H_4CH_2R$)] (R = NMe_2, NEt_2, CH_2NMe_2, NC_4H_8O or $NMeCH_2Ph$)

The compound with R = NMe_2 gives a monolithiated 1,2-derivative (**I**) with LiBu^n that precipitates from a diethyl ether–hexane mixture [14]. However, the isolation of the lithium derivatives [Fe(C_5H_5)(LiC_5H_3–2-CH_2R)] (R = NEt_2 (**II**), CH_2NMe_2 (**III**), NC_4H_8O (**IV**) or $NMeCH_2Ph$ (**V**)) is difficult. They are highly soluble in hexane, even at low temperatures. In order to determine the yield and position of lithiation without isolating the individual products, the lithium salts were treated with D_2O and the ring-deuterated products examined by ^{1}H-, ^{2}H- and $^{13}C\{^1H\}$-NMR spectroscopies. The presence of several deuterated materials in each sample meant that the spectra were too complex to analyse.

The lithiated mixtures were then treated with PhBr, Pr^{i}Br, or MeI, which have the potential both to substitute the ring and to quaternise the amine nitrogen to produce salts. Only MeI often yielded easily tractable materials. The quaternised products were easier to separate from the reaction mixtures, and were often isolated in a crystalline form.

In order to determine the optimum conditions under which 2-lithiation of the ferrocenylamines occurs, compounds [Fe(C_5H_5)($C_5H_4CH_2R$)] were allowed to react with LiBu^n in 1:1, 1:1.5, 1:2 or 1:5 ratios with a range of reaction times (1–5, 16 and 24 h). The reaction mixtures were then treated in each case with a large excess of MeI. The yellow precipitate formed in each experiment was recrystallised from MeOH–Et_2O and the materials were characterised in solution by NMR spectroscopy and found that mixtures of the quaternised salts [Fe(C_5H_5){$C_5H_3Me(CH_2RMe)$}]I and [Fe(C_5H_5)($C_5H_4CH_2RMe$)]I. Typical ring-substituted quaternised products were [Fe(C_5H_5){$C_5H_3Me(CH_2RMe)$-1,2}]I (R = NMe_2 (**VI**), NEt_2 (**VII**), CH_2NMe_2 (**VIII**), NC_4H_8O (**IX**) or $NMeCH_2Ph$ (**X**)). Attempts to separate these products by recrystallisation and by various chromatographic techniques were unsuccessful. Consequently, we prepared [Fe(C_5H_5)($C_5H_4CH_2RMe$)]I (R = NMe_2 (**XI**), NEt_2 (**XII**), CH_2NMe_2 (**XIII**), NC_4H_8O (**XIV**) or $NMeCH_2Ph$ (**XV**)) individually by MeI quarternisation of the corresponding ferrocenylamines [Fe(C_5H_5)($C_5H_4CH_2R$)], and used their spectra to help analyse the products isolated from the reactions of the lithium reagent with iodomethane.

For R = NMe_2, the major product after 16 h reaction time in 1:1 [Fe(C_5H_5)($C_5H_4CH_2R$)]–LiBu^n ratio was the monolithiated product (**VI**, Fig. 1, Tables 1 and 2). For R = NEt_2, after 16 h reaction time in a 1:1 amine–LiBu^n ratio, lithiation did not occur to any significant degree. When a twofold excess of LiBu^n was used [Fe(C_5H_5)(LiC_5H_3–2-CH_2NEt_2)] (**II**) formed in reasonable yield. X-ray analysis carried out on a sample isolated from the reaction mixture after treatment with MeI, showed only 30% replacement of a hydrogen at the ring carbon atom C(7) by a methyl group, yielding [Fe(C_5H_5){$C_5H_3Me(CH_2NMeEt_2)$}]I (**VII**). The structure was not well enough refined to warrant detailed presentation, though the position of methylation was unequivocally determined. Monolithiation had occurred at the required ring position, but in rather low yield. The compounds (**VII**) and [Fe(C_5H_5)($C_5H_4CH_2NMeEt_2$)]I (**XII**) co-crystallise, and we were unable to separate them chromatographically, due to their high polarity. However, compound **XII** was prepared independently and characterised crystallographically (see below).

For R = CH_2NMe_2, after 2 h we obtained a mixture of monolithiated [Fe(C_5H_5)(LiC_5H_3–2-$CH_2CH_2NMe_2$)] (**III**) and unlithiated starting material [Fe(C_5H_5)-($C_5H_4CH_2CH_2NMe_2$)]. After 16 h, the presence of polylithiated products was evident.

In the ^{1}H- and $^{13}C\{^1H\}$-NMR spectra of compounds isolated after treating these metallation mixtures with MeI, several peaks corresponding to methyl groups attached to the Cp ring were present. For R = NC_4H_8O, the amount of monolithiated material was always exceeded by polylithiated product. For R =

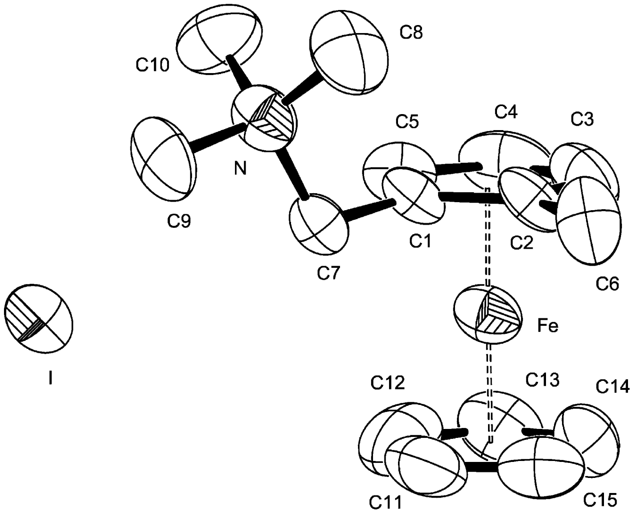


Fig. 1. Molecular structure of [Fe(C_5H_5){$C_5H_3Me(CH_2NMe_3)$}]I (**VI**), showing the atom numbering scheme; the picture was drawn with the use of the ORTEP program.

Table 1
Selected interatomic distances for [Fe(C_5H_5){$C_5H_3Me(CH_2NMe_3)$}]I (**VI**)

Atoms	Bond lengths (Å)
Fe–M(1) [a]	1.62(2)
Fe–M(2) [a]	1.65(2)
N–C(7)	1.535(19)
N–C(8)	1.50(2)
N–C(9)	1.512(17)
N–C(10)	1.53(2)

e.s.ds are in parentheses.

[a] M(1) and M(2) are the centroids of the C(1)-to-C(5) and C(11)-to-C(15) rings.

Table 2
Selected bond angles for complex [Fe(C_5H_5){$C_5H_3Me(CH_2NMe_3)$}]I (**VI**)

Atoms	Bond angles (°)
M(1)–Fe–M(2) [a]	178.7(9)
C(8)–N–C(9)	109.7(13)
C(8)–N–C(10)	109.0(15)
C(9)–N–C(10)	109.0(14)
C(8)–N–C(7)	111.4(12)
C(9)–N–C(7)	107.5(11)
C(10)–N–C(7)	110.2(12)

e.s.ds are in parentheses.

[a] M(1) and M(2) are the centroids of the C(1)-to-C(5) and C(11)-to-C(15) rings.

$NMeCH_2Ph$, lithiation was generally very slow and yields low. Preliminary X-ray crystal structure data for the compound isolated from the reactions of [Fe(C_5H_5)($C_5H_4CH_2NMeCH_2Ph$)] after 16 h showed the sample to be the ring methylated [Fe(C_5H_5){C_5H_3-Me($CH_2NMe_2CH_2Ph$)-1,2}]I (**X**). The residuals of the refinement are poor and the structure of this compound will not be discussed further.

Other lithium alkyls were also used as reagents in an attempt to improve both selectivity and/or reaction rate, but without appreciable success. Reaction with $LiBu^t$, seemed to proceed faster, but always gave products contaminated with polylithiated species.

^1H-NMR data for [Fe(C_5H_5){$C_5H_3Me(CH_2RMe)$}]I (R = NMe_2 (**VI**), NEt_2 (**VII**), CH_2NMe_2 (**VIII**) or $NMeCH_2Ph$ (**X**)) are displayed in Table 3. These assignments were supported by selective decoupling and $^1H\{^1H\}$-NOE experiments. We did not manage to isolate a pure-enough sample of [Fe(C_5H_5){C_5H_3-Me($CH_2NMeC_4H_8O$)}]I (**IX**) and ^1H-NMR data for this compound are not reported. In the ^1H-NMR spectra of **VI** and **X**, the $C_5H_3CH_2$ protons appear as the expected two AB doublets [15]. In **VII**, the diastereotopic $C_5H_3CH_2$ protons are accidentally equivalent and give rise to a singlet at $\delta = 4.49$ ppm. In **VIII**, the $C_5H_3CH_2$ protons are also chemically non-equivalent and appear as a multiplet in the region $\delta = 2.87–2.93$ ppm. Because the asymmetry of the ferrocenyl entity creates diastereotopic environments the NCH_3 groups of **X** are not equivalent. For the same reason, the NCH_2CH_3 and NCH_2CH_3 protons in **VII** appear as multiplets in the regions $\delta = 1.33–1.36$ and 3.25–3.36 ppm, respectively. The $PhCH_2N$ protons in X are isochronous and give rise to a singlet at $\delta = 4.52$ ppm. The apparent equivalence of these protons is coincidental.

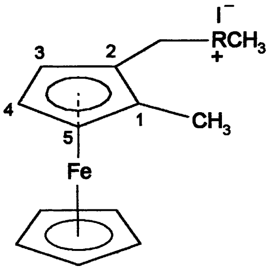
2.2. *Mössbauer and cyclic voltammetry studies*

The cyclic voltammetry and Mössbauer spectroscopy of the ferrocenylamines [Fe(C_5H_5)($C_5H_4CH_2R$)] were investigated, in order to determine whether they show significantly different electronic conditions.

The spectra obtained for the ferrocenylamines [Fe(C_5H_5)($C_5H_4CH_2R$)] (Table 4) are sharp, as indicated by the values of Γ (half-width at half maxima), and there is no sign in the spectra of iron-containing impurities. The isomer shifts (δ) lie within a narrow range, 0.56 ± 0.05 mm s^{-1}. Neither quaternisation with MeI nor ring-substitution with methyl at a position adjacent to the amine function induces major changes in the spread of values. Considering that the isomer shift (which measures the electron density on the Mössbauer atom) is determined mainly by the oxidation and spin state of the iron atoms in the sample, which have not been changed, this is disappointing but not surprising. Furthermore, these values do not differ significantly from those reported for [Fe(C_5H_5)(LiC_5H_3-2-CH_2NMe_2)], [V{Fe(C_5H_5)($C_5H_3CH_2NMe_2$)}$_2$Cl], several titanium derivatives of [Fe(C_5H_5)($C_5H_4CH_2NMe_2$)] ($\delta = 0.54(1)$ mm s^{-1} (mean value) at 77 K, referenced against iron foil) [6], for some stannylated derivatives of [Fe(C_5H_5)($C_5H_4CH_2NMe_2$)] [15], or ferrocene itself ($\delta = 0.51(5)$ mm s^{-1} at 80 K, referenced against iron foil) [16]. The lack of dependence of the isomer shifts on the nature of the substituents on the rings is a common feature of substituted ferrocenes [16].

Quadrupole splitting (q.s.) arises from the asymmetry of the electron cloud around the nucleus [16]. The quadrupole splittings for [Fe(C_5H_5)($C_5H_4CH_2R$)] lie within a narrow range, 2.38 ± 0.02 mm s^{-1} (Table 4). These values are very similar to that observed for ferrocene itself (q.s. = 2.40(3) mm s^{-1}) [16]. The small variation detected in the quadrupole splittings indicates that, in the double-sandwich electronic environments, the Fe^{II} orbitals are not very sensitive to the electron-withdrawal or donation effects generated by the substituents on the ferrocenyl moieties. The quaternised ferrocenylamines [Fe(C_5H_5){$C_5H_3R'(CH_2RMe)$}]I (except for R = CH_2NMe_2) show somewhat lower values of q.s. (average 2.34 mm s^{-1}, Table 4). Probably the positive charge on the nitrogen affects the electric field

Table 3
H^1-NMR data for $[Fe(C_5H_5)\{C_5H_3Me(CH_2RMe)\}]I$ (R = NMe_2 (**VI**), NEt_2 (**VII**), CH_2NMe_2 (**VIII**) or $NMeCH_2Ph$ (**X**)) in CD_3OD (in ppm, δ-scale, room temperature)



Proton	Chemical shifts			
	VI	**VII**	**VIII**	**X**
NCH_2CH_3	–	1.33–1.36 (m, 6H)	–	–
$C_5H_3CH_3$	2.12 (s, 3H)	2.11 (s, 3H)	2.03 (s, 3H)	2.13 (s, 3H)
$C_5H_3CH_2CH_2N$	–	–	2.87–2.93 (m, 2H)	–
NCH_3	3.03 (s, 9H)	2.81 (s, 3H)	3.23 (s, 9H)	2.80 (s, 3H) 2.85 (s, 3H)
NCH_2CH_3	–	3.25–3.36 (m, 4H)	–	–
$C_5H_3CH_2CH_2N$	–	–	3.36–3.47 (m, 2H)	–
C_5H_5	4.18 (s, 5H)	4.19 (s, 5H)	4.10 (s)	4.19 (s, 5H)
C_5H_3	4.30 (t, 1H)	4.29 (t, 1H)	3.99 (t, 1H)	4.34 (t, 1H)
$H5$	4.36 (m, 1H)	4.35 (m, 1H)	4.10 (m)	4.40 (m, 1H)
C_5H_3	4.48 (m, 1H)	4.46 (m, 1H)	4.13 (m, 1H)	4.51 (m, 1H)
$PhCH_2N$	–	–	–	4.52 (s, 2H)
$C_5H_3CH_2N$	4.52 (d, 1H, $J = 13.4$ Hz) 4.61 (d, 1H, $J = 13.4$ Hz)	4.49 (s, 2H)	–	4.62 (d, 1H, $J = 13.4$ Hz) 4.71 (d, 1H, $J = 13.4$ Hz)
Ph	–	–	–	7.52–7.57 (m, 5H)

gradient at the iron. We conclude that the Mössbauer technique is unlikely to give us the desired information on the relative electronic conditions, either of the ferrocenylamines or of their lithiated derivatives.

We reached a similar conclusion from our electrochemical studies. Cyclic voltammetric measurements on $[Fe(C_5H_5)(C_5H_4CH_2NMe_2)]$ and a series of other ferrocenylamines have been previously reported [17]. Under the same conditions, all the compounds $[Fe(C_5H_5)(C_5H_4CH_2R)]$ (R = NEt_2, CH_2NMe_2, $NMeCH_2Ph$ or NC_4H_8O) showed a single chemically and electrochemically reversible, one-electron couple **A** (see Table 5, values referenced against decamethylferrocene) in their cyclic voltammograms, due to the characteristic oxidation of the ferrocene iron redox centre. Consistent with other data [17], all non-protonated ferrocenylamines oxidise at approximately the same potential as ferrocene (0.48 V). The range of potentials is only 50 mV for five compounds, and the protonated materials $[Fe(C_5H_5)(C_5H_4CH_2RH)]BF_4$ display a similar small range, though at potentials about 200 mV more positive, a consequence of the higher Coulombic charge on the salts as compared to the non-protonated ferrocenylamines. Most of the electron density both in ferrocene and in the ferrocenium ion is apparently localised on the iron [18].

When the potential range was extended beyond 1.1 V an additional irreversible wave **E** was observed on the first anodic scan with at least a one-electron transfer ca. 800 mV positive of **A**. An additional cathodic wave $\mathbf{C_c}$ appears on the reverse sweep with the anodic component $\mathbf{C_a}$ on subsequent scans. This suggests an EECE mechanism where two successive electron transfers are followed by a chemical reaction, the product of which is also electroactive. Couple **C**, ca. 200 mV positive of **A**, is assigned to a reversible one-electron oxidation of a new ferrocenium species. A similar process was observed for a range of ferrocenylamines reported by Duffy et al. [17]. An irreversible wave **E** was attributed to the anodic oxidation of the amine. The cation radical generated in this manner abstracts a hydrogen from the solvent to form an ammonium salt. This is probably also true for the ferrocenylamines studied by us. The potential of **E** is the only one dependent on the *N*-substituent.

For the oxidation of the protonated ferrocenylamine to the ferrocenium species; only a single reversible one-electron couple was observed at the expected potential. This is additional evidence that the electrochemistry of

Table 4
Mössbauer parameters ([a]) for $[Fe(C_5H_5)(C_5H_4CH_2R)]$ and complexes **VI**–**XV** (77 K, referenced against iron foil)

Compound	δ [b] (mm s^{-1})	q.s. [c] (mm s^{-1})	Γ [d] (mm s^{-1})
$[FcCH_2NMe_2]$	0.53(1)	2.40(1)	0.15(1)
$[FcCH_2NEt_2]$	0.60(1)	2.39(1)	0.13(1)
$[FcCH_2CH_2NMe_2]$	0.54(1)	2.39(1)	0.11(1)
$[FcCH_2NC_4H_8O]$	0.52(1)	2.37(1)	0.14(1)
$[FcCH_2NMeCH_2Ph]$	0.61(1)	2.39(1)	0.17(1)
$[Fc'Me(CH_2NMe_3)]I$ (**VI**)	0.52(1)	2.35(1)	0.13(1)
$[Fc'Me(CH_2NMeEt_2)]I$ (**VII**)	0.53(1)	2.36(1)	0.15(1)
$[Fc'Me(CH_2CH_2NMe_3)]I$ (**VIII**)	0.53(2)	2.41(3)	0.17(1)
$[Fc'Me(CH_2NMeC_4H_8O)]I$ (**IX**)	0.52(1)	2.35(1)	0.12(1)
$[Fc'Me(CH_2NMe_2CH_2Ph)]I$ (**X**)	0.51(1)	2.32(1)	0.06(1)
$[FcCH_2NMe_3]I$ (**XI**)	0.53(2)	2.33(3)	0.11(1)
$[FcCH_2NMeEt_2]I$ (**XII**)	0.54(1)	2.35(1)	0.12(1)
$[FcCH_2CH_2NMe_3]I$ (**XIII**)	0.54(1)	2.41(1)	0.13(1)
$[FcCH_2NMeC_4H_8O]I$ (**XIV**)	0.53(1)	2.33(1)	0.13(1)
$[FcCH_2NMe_2CH_2Ph]I$ (**XV**)	0.53(1)	2.35(2)	0.13(1)

[a] Numbers in parentheses correspond to the experimental error in the last significant figure.
[b] Isomer shift.
[c] Quadrupole splitting.
[d] Half width at half height.

Table 5
Electrochemical data of ferrocenylamines $[Fe(C_5H_5)(C_5H_4CH_2R)]$ and their *N*-protonated derivatives

Substituent R	$E_{1/2}$ of $[FcCH_2R]$ [a,b]	$E_{1/2}$ of $[FcCH_2RH]BF_4$ [b,c]
NMe_2	0.48	0.69
NEt_2	0.49	0.69
CH_2NMe_2	0.46	0.56
NC_4H_8O	0.51	0.70
$NMeCH_2Ph$	0.50	0.69

[a] Half-wave potentials for the reaction $[Fc^+-CH_2R]+e^- \leftrightarrow [Fc-CH_2R]$ in volts; all potentials are referenced against decamethylferrocene; potential for ferrocene under the same conditions, 0.48 V.
[b] Determined by cyclic voltammetry in MeCN solution with 0.1 M $(Bu^t_4N)BF_4$ electrolyte with a scan rate of 100 mV s^{-1} at 20 °C.
[c] Half-wave potentials for the reaction $[Fc^+CH_2RH^+]+e^- \leftrightarrow [FcCH_2RH^+]$ in volts; all potentials are referenced against decamethylferrocene. The *N*-protonated derivatives of the ferrocenylamines were obtained by addition of $HBF_4 \cdot Et_2O$ to the corresponding ferrocenylamines.

$[Fe(C_5H_5)(C_5H_4CH_2R)]$ involves a protonation reaction.

In summary, the observed electrochemistry of $[Fe(C_5H_5)(C_5H_4CH_2R)]$ arises from an EECE mechanism involving two reversible couples $[Fc^+CH_2R]$/$[FcCH_2R]$, $[Fc^+CH_2RH^+]$/$[FcCH_2RH^+]$ similar to those of ferrocene and an irreversible oxidation/protonation of the amine function. It appears that the oxidation of the ferrocene redox centre for this set of compounds is not influenced by the substituent on the Cp ring.

$$[FcCH_2R] \overset{A}{\leftrightarrow} [Fc^+CH_2R] \overset{E}{\rightarrow} [Fc^+CH_2RH^+] \overset{C}{\leftrightarrow} [Fc^+CH_2RH^+]$$

2.3. *X-ray crystal structures*

As most of the dialkylaminomethyl and aminoethylferrocenes are liquids, available X-ray structural data on such compounds have been restricted mainly to their ammonium salts or other derivatives with further substitution on the cyclopentadienyl group [19,20]. We studied crystallographically the compounds $[Fe(C_5H_5)\{C_5H_3Me(CH_2RMe)\}]I$ derived by methylation of the products of the reaction of the corresponding $[Fe(C_5H_5)(LiC_5H_3CH_2R)]$ with $LiBu^n$. As discussed above, these compounds have the advantage that they can be isolated as solids and are easier to crystallise. $[Fe(C_5H_5)(LiC_5H_3CH_2NMe_2)]$ (**I**) certainly is methylated at a position adjacent to the ferrocenylamine side chain. As mentioned earlier, the X-ray crystal structure of $[Fe(C_5H_5)\{C_5H_3Me(CH_2NMe_3)\}]I$ (**VI**) is shown in Fig. 1, and selected bond lengths and angles are listed in Tables 1 and 2.

As stated above, X-ray crystallographic data obtained on a sample isolated from the reaction mixture of $[Fe(C_5H_5)(LiC_5H_3\text{-}2\text{-}CH_2NEt_2)]$ (**II**) with $LiBu^n$ after treatment with MeI, showed only 30% replacement of a hydrogen by a methyl group at the ring carbon atom adjacent to the amino substituent. Attempts to obtain the crystal structures of the ferrocenylamines $[Fe(C_5H_5)\{C_5H_3Me(CH_2CH_2NMe_3)\}]I$ (**VIII**) and $[Fe(C_5H_5)\{C_5H_3Me(CH_2NMeC_4H_8O)\}]I$ (**IX**) were fruitless, since we could only isolate crystals of the non-ring methylated derivatives $[Fe(C_5H_5)(C_5H_4CH_2CH_2NMe_3)]I$ (**XIII**) and $[Fe(C_5H_5)(C_5H_4CH_2NMeC_4H_8O)]I$ (**XIV**) from the reaction mixtures.

As a cross-section, the X-ray crystal structures of the compounds $[Fe(C_5H_5)(C_5H_4CH_2RMe)]I$ ($R = NEt_2$ (**XII**), CH_2NMe_2 (**XIII**), NC_4H_8O (**XIV**) or $NMeCH_2Ph$ (**XV**)) were determined (Figs. 2–5). Crystallographic data and selected bond dimensions are displayed in the Tables 6–13. Usually the compounds were crystallised from a methanolic solution layered with Et_2O as orange needles or plates.

The structures of the complexes **VI**, and **XII**–**XV** showed similarities to those of the compounds $[Fe(C_5H_5)(C_5H_4CH_2NMe_3)]I$ [21], $[Fe(C_5H_5)(C_5H_4CH_2NMe_3)]_2B_{10}H_{10}$, $[Fe(C_5H_5)(C_5H_4CH_2NMe_3)]_2[Mo_6O_{19}]$ [22], $[Fe(C_5H_5)\{C_5H_3PPh_2(CHMeNMe_2)\text{-}1,2\}]$ [20], $[Fe(C_5H_5)(C_5H_4CH_2NMe_2Et)]_2B_{20}H_{18}$ [23], $[Fe(C_5H_5)(C_5H_4CH_2NHMe_2)]_2[ZnCl_4] \cdot H_2O$ [24], $[Fe(C_5H_5)(C_5H_4CH_2NHCHO)]$ [25] and $[Fe(C_5H_5)$-

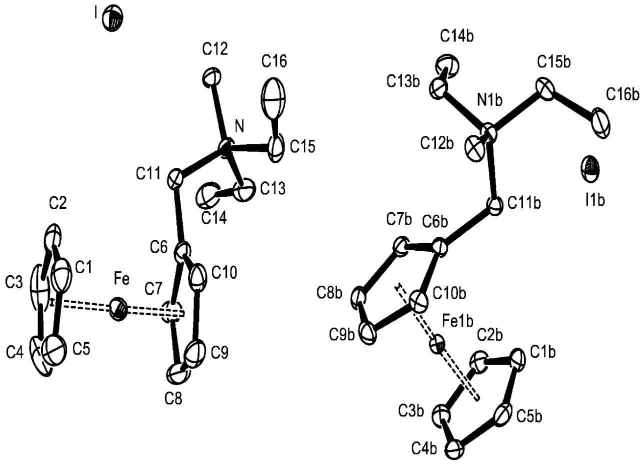


Fig. 2. Molecular structure of [Fe(C_5H_5)($C_5H_4CH_2NMeEt_2$)]I (**XII**), showing the atom numbering scheme; there are two independent molecules differing only in the conformation about the N–C(11) bond; the picture was drawn with the use of the ORTEP program.

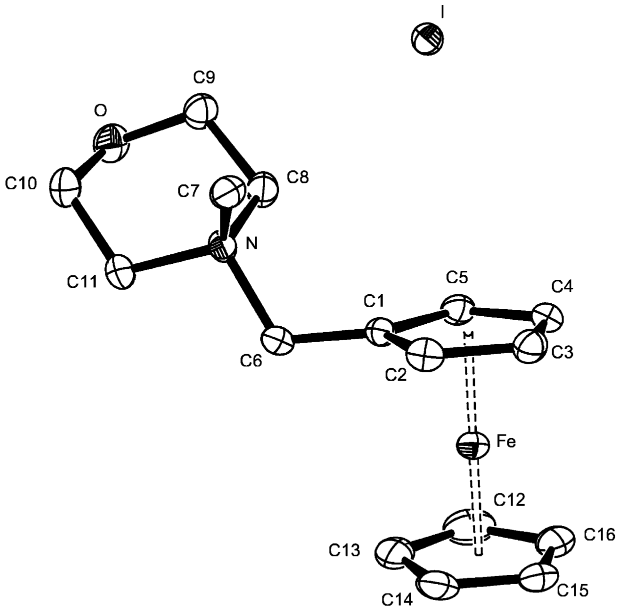


Fig. 4. Molecular structure of [Fe(C_5H_5)($C_5H_4CH_2NMeC_4H_8O$)]I (**XIV**), showing the atom numbering scheme; the picture was drawn with the use of the ORTEP program.

($C_5H_4CHMeNHMe_2$)]($C_4H_5O_6$)·$2H_2O$ [26]. Furthermore, the complex [{(μ-Cl)PdL}$_2$] (L = [Fe(C_5H_5)-{$C_5H_2Me(CH_2NMe_2)$-*C*,*N*}]) has been characterised crystallographically [27]. The ferrocenylaminate ligand in this compound contains a methyl substituent on the Cp ring at a position adjacent to the amine function (cf. compound **VI**). In compound **VI**, the C(2)–C(6) bond length is 1.44(2) Å, which is slightly shorter than the corresponding bond distance found in [{(μ-Cl)PdL}$_2$] (1.510 Å) [27].

In the unit cell of **XII** there are two independent molecules differing only in the conformation about the N–C(11) bond. The dimensions inside the ferrocenyl units of compounds **VI**, **XII**–**XV** are very similar to those in ferrocene itself [28]. The M(1)–Fe–M(2) angle is nearly linear, varying only from 178.2 to 179.4° for five compounds ('M' denotes the centroid of a Cp ring). The cyclopentadienyl rings are planar within experimental error, and approximately parallel and eclipsed. The ferrocenyl group in **VI** is removed by ca. 5.2° from the fully eclipsed position. In **XII**, one of the ferrocenyl groups differs by ca. 10.0° and the other by ca. 3.3° from the fully eclipsed position. In **XIII**, a larger deviation from the eclipsed arrangement is observed (ca. 16.4°). There is a perfectly eclipsed arrangement for the Cp rings in **XIV**.

2.4. N_2 uptake experiments

[VCl_2(tmen)$_2$] reacts with LiC_6H_4-2-CH_2NMe_2 under dinitrogen to yield, after treatment with one equivalent of pyridine (py) a bridging dinitrogen complex [{V($C_6H_4CH_2NMe_2$)$_2$(py)}$_2$(μ-N_2)] [4]. A series of experiments were carried out in order to determine whether there is N_2 uptake in the reaction of [VCl_2(tmen)$_2$] with two molar equivalents of [Fe(C_5H_5)(LiC_5H_3–2-CH_2R)] in THF (R = NMe_2, NEt_2, CH_2NMe_2, NC_4H_8O or $NMeCH_2Ph$). The dini-

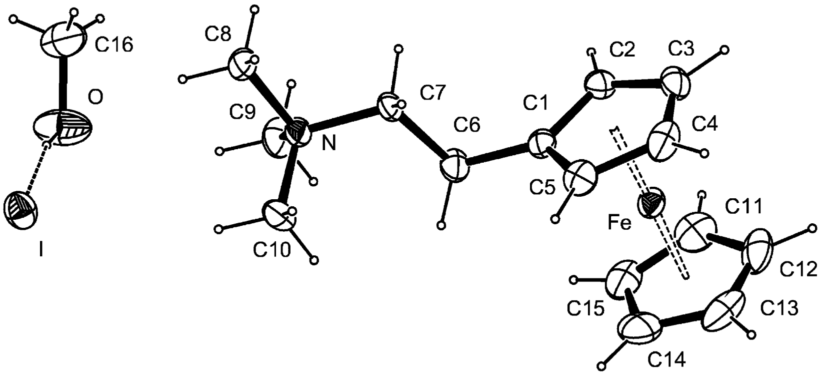


Fig. 3. Molecular structure of [Fe(C_5H_5)($C_5H_4CH_2CH_2NMe_3$)]I·MeOH (**XIII**), showing the atom numbering scheme; the picture was drawn with the use of the ORTEP program.

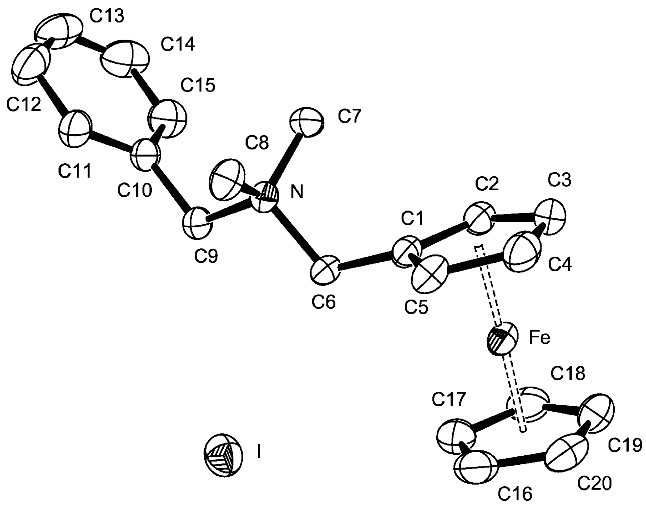


Fig. 5. Molecular structure of [Fe(C_5H_5)($C_5H_4CH_2NMe_2CH_2Ph$)]I (**XV**), showing the atom numbering scheme; the picture was drawn with the use of the ORTEP program.

Table 6
Selected interatomic distances for [Fe(C_5H_5)($C_5H_4CH_2NMeEt_2$)]I (**XII**)

Atoms	Bond lengths (Å)
Fe–M(1) [a]	1.654(4)
Fe–M(2) [a]	1.642(4)
N–C(11)	1.540(3)
N–C(12)	1.494(3)
N–C(13)	1.518(4)
N–C(15)	1.508(4)

e.s.ds are in parentheses.

[a] M(1) and M(2) are the centroids of the C(1)-to-C(5) and C(6)-to-C(10) rings.

Table 7
Selected bond angles for complex [Fe(C_5H_5)($C_5H_4CH_2NMeEt_2$)]I (**XII**)

Atoms	Bond angles (°)
M(1)–Fe–M(2) [a]	178.4(2)
C(12)–N–C(15)	111.0(2)
C(12)–N–C(13)	111.4(2)
C(15)–N–C(13)	103.4(3)
C(12)–N–C(11)	107.2(2)
C(15)–N–C(11)	112.2(2)
C(13)–N–C(11)	111.8(2)

e.s.ds are in parentheses.

[a] M(1) and M(2) are the centroids of the C(1)-to-C(5) and C(6)-to-C(10) rings.

trogen uptake was always less than one molecule for each two atoms of vanadium. No pure dinitrogen-containing products were isolated, and this is perhaps not surprising in view of the facts that the lithium reagents were usually not pure (for reasons, see above),

Table 8
Selected distances for [Fe(C_5H_5)($C_5H_4CH_2CH_2NMe_3$)]I · MeOH (**XIII**)

Atoms	Bond lengths (Å)
Fe–M(1) [a]	1.646(3)
Fe–M(2) [a]	1.655(3)
N–C(7)	1.517(3)
N–C(8)	1.506(3)
N–C(9)	1.491(3)
N–C(10)	1.498(3)
C(1)–C(6)	1.507(3)
C(6)–C(7)	1.518(3)
C(16)–O	1.400(4)

e.s.ds are in parentheses.

[a] M(1) and M(2) are the centroids of the C(1)-to-C(5) and C(11)-to-C(15) rings.

Table 9
Selected bond angles for [Fe(C_5H_5)($C_5H_4CH_2CH_2NMe_3$)]I · MeOH (**XIII**)

Atoms	Bond angles (°)
M(1)–Fe–M(2) [a]	178.5(2)
C(9)–N–C(10)	110.4(2)
C(9)–N–C(8)	109.0(2)
C(10)–N–C(8)	108.22(19)
C(9)–N–C(7)	110.95(19)
C(10)–N–C(7)	110.44(18)
C(8)–N–C(7)	107.73(17)

e.s.ds are in parentheses.

[a] M(1) and M(2) are the centroids of the C(1)-to-C(5) and C(11)-to-C(15) rings.

Table 10
Selected distances for compound [Fe(C_5H_5)($C_5H_4CH_2NMeC_4H_8O$)]I (**XIV**)

Atoms	Bond lengths (Å)
Fe–M(1) [a]	1.642(5)
Fe–M(2) [a]	1.641(6)
N–C(6)	1.524(6)
N–C(7)	1.504(7)
N–C(8)	1.517(7)
N–C(11)	1.523(6)

e.s.ds are in parentheses.

[a] M(1) and M(2) are the centroids of the C(1)-to-C(5) and C(12)-to-C(16) rings.

and that the dinitrogen complexes of this type are not very stable and are difficult to characterise.

The N_2 uptake was always very rapid, except for the mixture of [VCl_2(tmen)$_2$] with [Fe(C_5H_5)(LiC_5H_3–2-CH_2NEt_2)] for which zero uptake was observed. The data are summarised below as dinitrogen actually taken up as a percentage of that required to form a V–N_2–V system: [Fe(C_5H_5)(LiC_5H_3-2-CH_2R)] R = NMe_2 (55%), R = NEt_2 (0%), R = CH_2NMe_2 (35%), R = NC_4H_8O (30%) and R = $NMeCH_2Ph$ (40%). The fact that the uptake was always less than what would be consistent

Table 11
Selected bond angles for [Fe(C_5H_5)($C_5H_4CH_2NMeC_4H_8O$)]I (**XIV**)

Atoms	Bond angles (°)
M(1)–Fe–M(2) [a]	179.3(3)
C(7)–N–C(8) [a]	112.6(4)
C(7)–N–C(11)	111.9(4)
C(8)–N–C(11)	107.3(4)
C(7)–N–C(6)	109.1(4)
C(8)–N–C(6)	109.2(4)
C(11)–N–C(6)	106.4(4)

e.s.ds are in parentheses.

[a] M(1) and M(2) are the centroids of the C(1)-to-C(5) and C(12)-to-C(16) rings.

Table 12
Selected interatomic distances for [Fe(C_5H_5)($C_5H_4CH_2NMe_2CH_2Ph$)]I (**XV**)

Atoms	Bond lengths (Å)
Fe–M(1) [a]	1.641(2)
Fe–M(2) [a]	1.653(2)
N–C(6)	1.536(3)
N–C(7)	1.491(3)
N–C(8)	1.496(3)
N–C(9)	1.534(3)

e.s.ds are in parentheses.

[a] M(1) and M(2) are the centroids of the C(1)-to-C(5) and C(16)-to-C(20) rings.

Table 13
Selected bond angles for [Fe(C_5H_5)($C_5H_4CH_2NMe_2CH_2Ph$)]I (**XV**)

Atoms	Bond angles (°)
M(1)–Fe–M(2) [a]	178.2(1)
C(7)–N–C(8)	110.2(2)
C(7)–N–C(9)	110.28(18)
C(8)–N–C(9)	110.47(19)
C(7)–N–C(6)	109.88(19)
C(8)–N–C(6)	109.64(18)
C(9)–N–C(6)	106.30(18)

e.s.ds are in parentheses.

[a] M(1) and M(2) are the centroids of the C(1)-to-C(5) and C(16)-to-C(20) rings.

with the formation of a bridging dinitrogen complex, could be because the lithium-ferrocenylaminate starting materials were not sufficiently pure. The lithiation procedure needs to be improved, to ensure the 1:2 stoichiometric proportion for the reactants [$VCl_2(tmen)_2$] and [Fe(C_5H_5)(LiC_5H_3–2-CH_2R)].

2.5. Conclusions

The lithiation of the ferrocenylamines [Fe(C_5H_5)($C_5H_4CH_2R$)] (R = NMe_2, NEt_2, CH_2NMe_2, NC_4H_8O or $NMeCH_2Ph$) gives monolithiated 1,2-derivatives, but their isolation was difficult except for R = NMe_2. [$VCl_2(tmen)_2$] reacts with about two equivalents of the lithium derivatives in THF with the concomitant uptake of N_2 (except for R = NEt_2). No dinitrogen-containing complexes were isolated. If bridging N_2 complexes are formed, there are certainly other reactions occurring at the same time, which do not involve N_2 complexes. Neither Mössbauer spectroscopy nor cyclic voltammetry are suitable probes for the electronic condition of the ferrocenyl nucleus. The use of these techniques as indicators of the ability of the ferrocenylaminates to potentiate vanadium for dinitrogen binding is not promising.

3. Experimental

All operations were carried out under an inert atmosphere in an Ar-filled drybox or with use of standard Schlenk techniques. Solvents were dried by standard procedures [29] and distilled under N_2 prior to use. The commercial products 2-bromobenzyl bromide, *N*-bromosuccinimide, *n*-butyllithium (1.6 M solution in C_6H_{14}), *tert*-butyllithium (1.7 M solution in C_6H_{14}), 2-dimethylaminoethylchloride hydrochloride, 3-dimethylaminopropylchloride hydrochloride, *N*,*N*-dimethylbenzylamine, ferrocene, were used without further purification. Diallylamine, Et_2NH, morpholine, benzylmethylamine (Aldrich) and *N*,*N*-dimethylaminomethylferrocene (Lancaster) were dried and distilled prior to use.

Microanalyses were carried out at the University of Surrey using a Leenan CE 440 CHN elemental analyser, or at MEDAC, Brunel Science Centre, Surrey. IR spectra were recorded on a Perkin–Elmer Spectrum One FT-IR spectrometer, from Nujol mulls prepared under dinitrogen and spread on KBr plates. NMR spectra were obtained in the appropriate deuterated solvents using a Bruker 300 or 500 MHz instrument. (^{13}C, ^{1}H)-HETCOR NMR, $^{1}H\{^{1}H\}$-NOE and variable temperature ^{1}H-NMR experiments were carried out by Dr Tony Avent, University of Sussex. Mass spectra were taken by Dr Ali Abdul-Sada, at the University of Sussex, using a Kratos M580RF instrument for FAB spectra (and 3-nitrobenzyl alcohol as a matrix material), and a Fisons VG Autospec for EI spectra. Mössbauer data were recorded at 77 K by Professor Jack Silver, University of Greenwich. Spectra were referenced against iron foil at 298 K. Cyclic voltammetry measurements were performed under the supervision of Dr Christopher J. Pickett at the John Innes Centre, Norwich, using an EG&G PAR 362 scanning potentiostat. A three-electrode cell configuration was used, with a Pt wire secondary electrode and a silver wire pseudo reference electrode. The solvent used was MeCN with

0.1 M (Bu^t_4N)BF_4 as the supporting electrolyte. All potentials were referenced against decamethylferrocene. The measurements were carried out at room temperature (r.t.) under an atmosphere of purified dinitrogen.

X-ray crystal structure data were collected by the $2\theta-\omega$ scan method at 173(2) K using an Enraf–Nonius CAD4 diffractometer. During processing, the data were corrected for absorption by semi-empirical ψ-scan methods. The structures were solved by direct methods in SHELXS and refined by full-matrix least-square methods in SHELXN [30]. All non-hydrogen atoms were refined anisotropically. Diagrams of the molecular structure of complexes were drawn with the ORTEP package [31]. The crystallographic data are summarised in Table 14.

A series of methylenediamines were prepared according to literature methods [32]. These were subsequently allowed to react with ferrocene (see below) in order to prepare the corresponding ferrocenylamines [32,33]. $[Fe(C_5H_5)(LiC_5H_3{-}2{-}CH_2NMe_2)]$ (**I**) was prepared by literature methods [14,34].

3.1. Preparation of N,N-diethylaminomethylferrocene [33]

The reported procedure [32] for the synthesis of *N*,*N*-dimethylaminomethylferrocene was adopted for the synthesis of *N*,*N*-diethylaminomethylferrocene. *N*,*N*,*N*′,*N*′-tetraethylmethylenediamine (69.4 g, 440 mmol) was added dropwise to a well-stirred solution of phosphoric acid (45.0 g, 460 mmol) in 416 cm^3 of AcOH in a three-necked round-bottomed flask equipped with a condenser and a nitrogen inlet. Ferrocene (48.3 g, 260 mmol) was then added and the resulting suspension was heated on a steam bath for 16 h. The reaction mixture, a dark amber solution, was allowed to cool to r.t. and was diluted with 550 cm^3 of water. The unreacted ferrocene was removed by extracting the solution with three 325 cm^3 portions of Et_2O. The aqueous solution was then cooled in an ice bath and made alkaline by the addition of 245 g of NaOH pellets. The tertiary amine separated from the alkaline solution as an oil in the presence of some black tar. The mixture was extracted with three 500 cm^3 portions of Et_2O. The organic solution was washed with water and dried over Na_2SO_4. Crude diethylaminomethylferrocene was obtained as a dark red mobile liquid when the solvent was removed under vacuum. Distillation of the crude product under vacuum gave 30.5 g (110 mmol, 43%) of the ferrocenylamine.

^1H-NMR ($CDCl_3$, ppm): δ 1.02 (t, CH_3, 6H), 2.42 (q, NCH_2CH_3, 4H), 3.48 (s, $C_5H_4CH_2$, 2H), 4.08 (m, C_5H_4, 2H), 4.09 (s, C_5H_5, 5H), 4.14 (m, C_5H_4, 2H).

$^{13}C\{^1H\}$-NMR ($CDCl_3$, ppm): δ 11.87 (CH_3), 46.01 (NCH_2CH_3), 51.63 ($C_5H_4CH_2$), 67.65 (C_5H_4), 68.28 (C_5H_5), 70.00 (C_5H_4), 82.75 (C_{ipso} of C_5H_4).

3.2. Preparation of morpholinomethylferrocene [33]

As for the synthesis of *N*,*N*-diethylaminomethylferrocene with ferrocene (41.8 g, 220 mmol), bis(morpholino)methane (70.6 g, 380 mmol), phosphoric acid (39.0 g, 400 mmol) and AcOH (360 cm^3). The reaction mixture was heated on a steam bath for 20 h. Morpholinomethylferrocene was isolated as a reddish–brown solid (38.0 g, 133 mmol, 59%).

^1H-NMR ($CDCl_3$, ppm): δ 2.27 (t, NCH_2, 4H), 3.22 (s, $C_5H_4CH_2N$, 2H), 3.53 (t, OCH_2, 4H), 3.96–4.05 (m, C_5H_4, block of 9H), 4.00 (s, C_5H_5, block of 9H).

$^{13}C\{^1H\}$-NMR ($CDCl_3$, ppm): δ 52.63 (NCH_2), 58.24 ($C_5H_4CH_2N$), 66.29 (OCH_2), 67.59 (C_5H_4), 68.02 (C_5H_5), 69.73 (C_5H_4), 81.82 (C_{ipso} of C_5H_4).

3.3. Preparation of N-benzyl-N-methylaminomethylferrocene [33]

As for the synthesis of *N*,*N*-diethylaminomethylferrocene with ferrocene (98.1 g, 530 mmol), *N*,*N*′-dibenzyl-*N*,*N*′-dimethylmethylenediamine (229 g, 900 mmol), phosphoric acid (92.0 g, 940 mmol) and AcOH (850 cm^3). The reaction was performed at 100 °C for 24 h. The crude product was purified by high vacuum distillation to give the *N*-benzyl-*N*-methylaminomethylferrocene as a dark red liquid (30.9 g, 97.2 mmol, 18%).

^1H-NMR ($CDCl_3$, ppm): δ 2.10 (s, NCH_3, 3H), 3.40 (s, $PhCH_2N$ and $C_5H_4CH_2N$, 4H; coincidental overlap), 4.04 (s, C_5H_5, 5H), 4.08 (m, C_5H_4, 2H), 4.14 (m, C_5H_4, 2H), 7.28 (d, Ph, 5H).

$^{13}C\{^1H\}$-NMR ($CDCl_3$, ppm): δ 41.53 (NCH_3), 56.66 ($PhCH_2$), 60.79 ($C_5H_4CH_2$), 67.75 (C_5H_4), 68.31 (C_5H_5), 69.99 (C_5H_4), 82.99 (C_{ipso} of C_5H_4), 126.69 (Ph), 128.02 (Ph), 128.78 (Ph), 139.10 (C_{ipso} of Ph).

3.4. Preparation of N,N-dimethylaminoethylferrocene

N,*N*-Dimethylaminoethylferrocene was prepared by rearrangement of *N*,*N*-trimethylaminomethylferrocene iodide, using a method reported by Hauser et al. [35].

^1H-NMR ($CDCl_3$, ppm): δ 2.26 (s, NCH_3, 6H), 2.39–2.52 (m, CH_2, 4H), 4.03–4.08 (m, C_5H_4, 4H), 4.10 (s, C_5H_5, 5H).

$^{13}C\{^1H\}$-NMR ($CDCl_3$, ppm): δ 27.83 ($C_5H_4CH_2$), 45.47 (NCH_3), 60.85 (NCH_2), 67.10 (C_5H_4), 67.98 (C_5H_4), 68.40 (C_5H_5), 86.63 (C_{ipso} of C_5H_4).

3.5. Preparation of $[Fe(C_5H_5)(LiC_5H_3{-}2{-}CH_2NEt_2)]$ (II)

N,*N*-Diethylaminomethylferrocene (3.90 g, 14.4 mmol) was dissolved in 100 cm^3 of Et_2O and treated dropwise with a 1.6 M solution of butyllithium in C_6H_{14} (9.0 cm^3, 14.4 mmol) over 10 min. Stirring was continued for 16 h at r.t. The solvent was then removed

Table 14
Details of crystallographic structure determinations

Compound	$[Fe(C_5H_5)\{C_5H_3Me(CH_2NMe_3)\}]I$ (**VI**)	$[Fe(C_5H_5)(C_5H_4CH_2NMeEt_2)]I$ (**XII**)	$[Fe(C_5H_5)(C_5H_4CH_2CH_2NMe_3)]I \cdot MeOH$ (**XIII**)	$[Fe(C_5H_5)(C_5H_4CH_2NMeC_4H_8O)]I$ (**XIV**)	$[Fe(C_5H_5)(C_5H_4CH_2NMe_2CH_2Ph)]I$ (**XV**)
Formula	$C_{15}H_{22}FeIN$	$C_{16}H_{24}FeIN$	$C_{15}H_{22}FeIN \cdot (CH_4O)$	$C_{16}H_{22}FeINO$	$C_{20}H_{24}FeIN$
M (g mol^{-1})	399.09	413.11	431.13	427.10	461.15
Wavelength (Å)	Mo–K$_\alpha$ (mean) 0.71073	Mo–K$_\alpha$ (mean) 0.71073	Mo–K$_\alpha$ (mean) 0.71073	Mo–K$_\alpha$ (mean) 0.71073	Mo–K$_\alpha$ (mean) 0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	*Pbca* (No. 61)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	*Pbca* (No. 61)	$P2_1/n$ (No. 14)
Unit cell dimensions					
a (Å)	9.5787(8)	15.0030(3)	12.3565(3)	12.9152(5)	13.3985(3)
b (Å)	21.159(2)	10.8778(3)	10.9342(3)	18.4478(8)	10.9172(2)
c (Å)	16.154(2)	20.2922(5)	13.0520(5)	13.5502(5)	13.7018(4)
α (°)	90	90	90	90	90
β (°)	90	91.844(2)	93.438(2)	90	112.848(1)
γ (°)	90	90	90	90	90
V (Å^3)	3274.0(6)	3309.96(14)	1760.26(8)	3228.4(2)	1846.96(8)
Z	8	8	4	8	4
D_{calc} (g cm^{-3})	1.62	1.66	1.63	1.76	1.66
Absorption coefficient (mm^{-1})	2.79	2.77	2.61	2.84	2.49
Data collection range θ (°)	$3.82 \leq \theta \leq 21.99$	$3.76 \leq \theta \leq 30.04$	$3.73 \leq \theta \leq 27.91$	$3.73 \leq \theta \leq 25.04$	$3.73 \leq \theta \leq 27.85$
Index ranges	$-10 \leq h \leq 10$, $-22 \leq k \leq 22$, $-17 \leq l \leq 16$	$-17 \leq h \leq 21$, $-15 \leq k \leq 14$, $-28 \leq l \leq 28$	$-12 \leq h \leq 16$, $-9 \leq k \leq 14$, $-17 \leq l \leq 17$	$-13 \leq h \leq 15$, $-19 \leq k \leq 21$, $-16 \leq l \leq 12$	$-17 \leq h \leq 14$, $-11 \leq k \leq 14$, $-17 \leq l \leq 18$
Unique reflections	1957	9449	4172	2789	4306
Observed reflections [$I > 2\sigma(I)$]	1507	8128	3586	2426	3799
Refined parameters	167	344	195	181	208
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.076; 0.187	0.036; 0.078	0.028; 0.060	0.044; 0.120	0.031; 0.073
R_1, wR_2 (all data)	0.097; 0.199	0.045; 0.083	0.036; 0.064	0.051; 0.126	0.037; 0.077

under vacuum, leaving $[Fe(C_5H_5)(LiC_5H_3–2–CH_2NEt_2)]$ as a dark amber oil (2.91 g, 10.5 mmol). The product is very soluble even in non-polar solvents such as C_6H_{14}, which makes the isolation and purification of the lithium salt difficult. In subsequent reactions of metal complexes with the lithium ligand, the reactions were carried out directly, without Li-salt isolation.

3.6. Preparation of $[Fe(C_5H_5)(LiC_5H_3–2–CH_2CH_2NMe_2)]$ (*III*)

As for the synthesis of $[Fe(C_5H_5)(LiC_5H_3–2–CH_2NEt_2)]$ with *N*,*N*-dimethylaminoethylferrocene (4.69 g, 18.3 mmol) and butyllithium (1.6 M solution in C_6H_{14}, 12 cm^3, 19.2 mmol). The reaction mixture was stirred for ca. 5 h. The product $[Fe(C_5H_5)(LiC_5H_3–2–CH_2CH_2NMe_2)]$ was isolated as a dark amber oil (3.38 g, 12.9 mmol). The lithium salt is very soluble Et_2O, THF and in non-polar solvents such as C_6H_6 and C_6H_{14}. In subsequent reactions of metal complexes with the lithium reagent, the reactions were carried out directly, without Li-salt isolation.

3.7. Preparation of $[Fe(C_5H_5)(LiC_5H_3–2–CH_2NC_4H_8O)]$ (*IV*)

As for the synthesis of $[Fe(C_5H_5)(LiC_5H_3–2–CH_2NEt_2)]$ with $[Fe(C_5H_5)(C_5H_3CH_2NC_4H_8O)]$ (8.12 g, 28.6 mmol) and butyllithium (1.6 M solution in C_6H_{14}, 18 cm^3, 28.8 mmol). An orange/brown precipitate formed immediately after the addition of butyllithium. Stirring was continued for 16 h at r.t. and the resulting orange/brown solid was filtered off, washed with C_6H_{14} (20 cm^3) and dried under vacuum for 2 h (Yield: 2.02 g, 6.96 mmol, 24%).

^{1}H-NMR (C_6D_6, ppm): δ 2.25 (m, NCH_2, 4H), 3.16 (m, $C_5H_3CH_2N$, 2H), 3.58 (m, OCH_2, 4H), 3.96 (s, C_5H_5, block of 8H), 3.91–4.11 (m, C_5H_3 block of 8H).

3.8. Preparation of [Fe(C_5H_5)(LiC_5H_3–2-CH_2NMeCH_2Ph)] (V)

As for the synthesis of [Fe(C_5H_5)(LiC_5H_3–2-CH_2NEt_2)] with [Fe(C_5H_5)($C_5H_3CH_2NMeCH_2Ph$)] (11.5 g, 36.2 mmol) and butyllithium (1.6 M solution in C_6H_{14}, 23 cm^3, 36.5 mmol). The product [Fe(C_5H_5)(LiC_5H_3–2-CH_2NMeCH_2Ph)] was isolated as a dark amber oil (8.52 g, 26.3 mmol). The lithium salt is very soluble in Et_2O and C_6H_{14}.

3.9. Preparation of [Fe(C_5H_5){$C_5H_3Me(CH_2NMe_3)$}]I (**VI**)

This was prepared by direct reaction of MeI with (**I**) in about 75% yield.

3.10. Preparation of [Fe(C_5H_5){$C_5H_3Me(CH_2NMeEt_2)$}]I (**VII**)

To an amber solution of [Fe(C_5H_5)($C_5H_4CH_2NEt_2$)] (1.52 g, 5.63 mmol) in Et_2O (30 cm^3), 1.6 M solution of butyllithium in hexanes (3.5 cm^3, 5.60 mmol) was added carefully via a syringe. The reaction mixture was allowed to stir for 16 h at r.t., after which time, a solution of MeI (1.4 cm^3, 3.18 g, 22.4 mmol) in Et_2O was added slowly. The reaction mixture was continued to stir for a further 4 h, after which time, the yellow precipitate formed was filtered off, washed with Et_2O and dried under vacuum. Recrystallisation of this solid from a methanolic solution (5 cm^3) layered with Et_2O (10 cm^3) yielded yellow crystals (1.32 g, 3.10 mmol, 55%). The filtrate was evaporated to dryness yielding an amber oil.

EI-MS *m/z* (%) on amber oil: 285 (20) [Fe(C_5H_5)-{$C_5H_3Me(CH_2NEt_2)$}]$^+$, 213 (100) [Fe(C_5H_5)(C_5H_3Me-CH_2)]$^+$, 199 (27) [$C_{11}H_{11}Fe$]$^+$, 121 (64) [Fe(C_5H_5)]$^+$, 73 (26) [$HNEt_2$]$^+$.

In order to determine the optimum reaction conditions for the formation of [Fe(C_5H_5)(LiC_5H_3–2-CH_2NEt_2)], the same procedure was repeated with [Fe(C_5H_5)($C_5H_4CH_2NEt_2$)] and butyllithium in 1:1, 1:2 and 1:5 ratios, at a range of reaction times (1–5, 10, 24 and 48 h). The reaction mixture was treated in each case with a large excess of MeI. The yellow precipitate formed in each experiment was isolated and characterised by NMR spectroscopy.

3.11. Preparation of [Fe(C_5H_5){$C_5H_3Me(CH_2CH_2NMe_3)$}]I (**VIII**)

As for the synthesis of [Fe(C_5H_5){$C_5H_3Me(CH_2NMeEt_2)$}]I with [Fe(C_5H_5)($C_5H_4CH_2CH_2NMe_2$)] (1.21 g, 4.73 mmol), butyllithium (1.6 M, 3.0 cm^3, 4.80 mmol) and MeI (1.2 cm^3, 2.67 g, 18.8 mmol). In this manner, 1.54 g of yellow crystals were isolated (3.74 mmol, 79%).

EI-MS *m/z* (%): 286 (10) [Fe(C_5H_5){C_5H_3Me-($CH_2CH_2NMe_3$)}]$^+$, 271 (45) [Fe(C_5H_5){C_5H_3Me-($CH_2CH_2NMe_2$)}]$^+$, 257 (26) [Fe(C_5H_5)($C_5H_4CH_2$-CH_2NMe_2)]$^+$ (starting material), 213 (23) [Fe(C_5H_5)-($C_5H_3MeCH_2$)]$^+$, 121 (43) [Fe(C_5H_5)]$^+$, 58 (100) [CH_2NMe_2]$^+$.

3.12. Preparation of [Fe(C_5H_5){$C_5H_3Me(CH_2NMeC_4H_8O)$}]I (**IX**)

As for the synthesis of [Fe(C_5H_5){$C_5H_3Me(CH_2NMeEt_2)$}]I with [Fe(C_5H_5)($C_5H_4CH_2NC_4H_8O$)] (0.90 g, 3.17 mmol), butyllithium (1.6 M, 2.0 cm^3, 3.20 mmol) and MeI (0.8 cm^3, 1.82 g, 12.8 mmol). In this manner, 0.71 g of yellow crystals were isolated (1.61 mmol, 51%). The filtrate was evaporated to dryness yielding an amber oil.

EI-MS *m/z* (%) on amber oil: 299 (25) [Fe(C_5H_5)-{$C_5H_3Me(CH_2NC_4H_8O)$}]$^+$, 285 (95) [Fe(C_5H_5)(C_5H_4-$CH_2NC_4H_8O$)]$^+$ (starting material), 213 (36) [Fe(C_5H_5)-($C_5H_3MeCH_2$)]$^+$, 199 (100) [$C_{11}H_{11}Fe$]$^+$, 121 (86) [Fe(C_5H_5)]$^+$.

3.13. Preparation of [Fe(C_5H_5){$C_5H_3Me(CH_2NMe_2CH_2Ph)$}]I (**X**)

As for the synthesis of [Fe(C_5H_5){$C_5H_3Me(CH_2NMeEt_2)$}]I with [Fe(C_5H_5)($C_5H_4CH_2NMeCH_2Ph$)] (0.75 g, 2.36 mmol), butyllithium (1.6 M, 1.5 cm^3, 2.40 mmol) and MeI (0.6 cm^3, 1.33 g, 9.40 mmol). In this manner, 0.78 g of yellow crystals were isolated (1.65 mmol, 70%). The filtrate was evaporated to dryness yielding an amber oil.

EI-MS *m/z* (%) on amber oil: 333 (56) [Fe(C_5H_5)-{$C_5H_3Me(CH_2NMeCH_2Ph)$}]$^+$, 319 (100) [Fe(C_5H_5)-($C_5H_4CH_2NMeCH_2Ph$)]$^+$ (starting material), 213 (41) [Fe(C_5H_5)($C_5H_3MeCH_2$)]$^+$, 199 (83) [$C_{11}H_{11}Fe$]$^+$, 134 (9) [CH_2NMeCH_2Ph]$^+$, 121 (60) [Fe(C_5H_5)]$^+$, 91 (45) [CH_2Ph]$^+$.

3.14. Preparation of [Fe(C_5H_5)($C_5H_4CH_2NMe_3$)]I (**XI**)

This was prepared by the method described in Ref. [32].

^{1}H-NMR (CD_3OD, ppm): δ 3.02 (s, NCH_3, 9H), 4.28 (s, C_5H_5, 5H), 4.41 (m, C_5H_4, 2H), 4.52 (s, $C_5H_4CH_2N$, 2H), 4.53 (m, C_5H_4, 2H).

3.15. Preparation of [Fe(C5H5)(C5H4CH2NMeEt2)]I (XII)

As for the synthesis of [Fe(C_5H_5)($C_5H_4CH_2NMe_3$)]I, with methyl iodide (0.4 cm^3, 0.84 g, 5.55 mmol), [Fe(C_5H_5)($C_5H_4CH_2NEt_2$)] (1.01 g, 3.74 mmol) and MeOH (5 cm^3). Upon layering with 10 cm^3 of Et_2O orange crystals formed, which were filtered, washed with Et_2O and dried under vacuum. Yield: 1.42 g, 3.44 mmol, 92%. Anal. Found: C, 46.14; H, 5.94; N, 3.41. $C_{16}H_{24}FeIN$ requires: C, 46.52; H, 5.86; N, 3.39%.

^{1}H-NMR (CD_3OD, ppm): δ 1.37 (t, NCH_2CH_3, 6H), 2.89 (s, NCH_3, 3H), 3.24–3.40 (m, NCH_2CH_3, 4H), 4.33 (s, C_5H_5, 5H), 4.43 (m, C_5H_4, 2H), 4.52 (s, $C_5H_4CH_2N$, 2H), 4.57 (m, C_5H_4, 2H).

3.16. Preparation of [Fe(C5H5)(C5H4CH2CH2NMe3)]I (XIII)

As for the synthesis of [Fe(C_5H_5)($C_5H_4CH_2NMe_3$)]I, with methyl iodide (0.3 cm^3, 0.72 g, 4.78 mmol), [Fe(C_5H_5)($C_5H_4CH_2CH_2NMe_2$)] (0.82 g, 3.19 mmol) and MeOH (5 cm^3). Upon layering with 10 cm^3 of Et_2O orange crystals formed, which were filtered, washed with Et_2O and dried under vacuum. Yield: 1.22 g, 3.06 mmol, 96%. Anal. Found: C, 45.09; H, 5.52; N, 3.50. $C_{15}H_{22}FeIN$ requires: C, 45.14; H, 5.56; N, 3.51%.

^{1}H-NMR (CD_3OD, ppm): δ 2.85–2.91 (m, $C_5H_4CH_2$, 2H), 3.19 (s, NCH_3, 9H), 3.47–3.52 (m, NCH_2, 2H), 4.13 (t, C_5H_4, 2H), 4.19 (s, C_5H_5, 5H), 4.22 (m, C_5H_4, 2H).

3.17. Preparation of [Fe(C5H5)(C5H4CH2NMeC4H8O)]I (XIV)

As for the synthesis of [Fe(C_5H_5)($C_5H_4CH_2NMe_3$)]I, with methyl iodide (0.2 cm^3, 0.43 g, 2.85 mmol), [Fe(C_5H_5)($C_5H_4CH_2NC_4H_8O$)] (0.54 g, 1.90 mmol) and MeOH (5 cm^3). Upon layering with 10 cm^3 of Et_2O orange crystals formed, which were filtered, washed with Et_2O and dried under vacuum. Yield: 0.73 g, 1.71 mmol, 90%. Anal. Found: C, 44.62; H, 5.22; N, 3.21. $C_{16}H_{22}FeINO$ requires: C, 44.99; H, 5.19; N, 3.28%.

3.18. Preparation of [Fe(C5H5)(C5H4CH2NMe2CH2Ph)]I (XV)

As for the synthesis of [Fe(C_5H_5)($C_5H_4CH_2NMe_3$)]I, with methyl iodide (0.2 cm^3, 0.36 g, 2.40 mmol), [Fe(C_5H_5)($C_5H_4CH_2NMeCH_2Ph$)] (0.51 g, 1.60 mmol) and MeOH (5 cm^3). Upon layering with 10 cm^3 of Et_2O orange crystals formed, which were filtered, washed with Et_2O and dried under vacuum. Yield: 0.70 g, 1.52 mmol, 95%. Anal. Found: C, 51.25; H, 5.37; N, 3.07. $C_{20}H_{24}FeIN$ requires: C, 52.09; H, 5.25; N, 3.04%.

^{1}H-NMR (CD_3OD, ppm): δ 2.84 (s, NCH_3, 6H), 4.29 (s, C_5H_5, 5H), 4.44 (t, C_5H_4, 2H), 4.50 (s, $PhCH_2N$, 2H), 4.57 (m, C_5H_4, 2H), 4.62 (s, $C_5H_4CH_2N$, 2H), 7.55 (d, Ph, 5H).

3.19. Dinitrogen uptake experiments

The apparatus used consisted of a closable reaction vessel connected to a gas burette. About two molar equivalents of [Fe(C_5H_5)(LiC_5H_3-2-CH_2R)] (R = NMe_2, NEt_2, CH_2NMe_2, NC_4H_8O or $NMeCH_2Ph$) were then added. To a solution of [VCl_2(tmen)$_2$] in THF under N_2 at r.t. The reaction mixture changed immediately from blue to deep red–brown. The dinitrogen uptake was generally rapid, and complete within ca. 20 min.

Acknowledgements

We acknowledge the award of an EPSRC studentship to M.T.

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