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FERROCENYLLITHIUM DERIVATIVES: LITHIATION OF α-*N*,*N*-DIMETHYLAMINOETHYLFERROCENE AND THE SINGLE CRYSTAL X-RAY STRUCTURE OF $[(\eta^5\text{-}C_5H_4Li)Fe(\eta^5\text{-}C_5H_3LiCH(Me)NMe_2)]_4[LiOEt]_2(TMED)_2$ *

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Summary

The documented lithiation reactions of ferrocene and α-*N*,*N*-dimethylaminoethylferrocene (I) have been reinvestigated. The ^{7}Li NMR spectra of the dilithio-TMED (TMED = tetramethylethylenediamine) adducts of ferrocene and I have been recorded.

The single crystal X-ray crystallographic study of $[(\eta^5\text{-}C_5H_4Li)Fe(\eta^5\text{-}C_5H_3LiCH(Me)NMe_2)]_4[LiOEt]_2[TMED]_2$ (V) is described. Crystals of V are monoclinic, a 36.998(4), b 9.6224(13), c 23.611(2) Å, β 113.983(5)°, $Z = 4$, space group $C2/c$. The structure was solved by conventional heavy-atom methods and was refined by full-matrix least-squares procedures to R 0.070 and $R_w = 0.079$ for 3058 observed reflections. The structure consists of discrete molecules possessing exact C_2 symmetry; each containing four ferrocene moieties, ten Li atoms, two TMED units, and two ethoxy groups. Each of the five independent Li atoms achieves a distorted tetrahedral coordination in a different way. An extremely short Li–C bond (2.04(3) Å) has been observed.

Introduction

The synthetic utility of the metallation of ferrocene with n-butyllithium and TMED (tetramethylethylenediamine) has been widely demonstrated [1–3]. The 1,1′-dilithioferrocene-TMED adduct precipitates from hexane solution as a pale orange pyrophoric powder when ferrocene is lithiated with two molar equivalents of n-butyllithium and one equivalent of TMED [4–6]. Attempts to prepare a crystalline sample of this adduct have been unsuccessful although Rausch and coworkers were able to obtain a crystalline sample of the 1,1′-dilithioferrocene-PMDT (PMDT = pentamethyldiethylenetriamine), which was subjected to a single crystal X-ray diffraction analysis [7].

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* Dedicated to Professor H.J. Emeléus on the occasion of his 80th birthday on 22nd June, 1983. W.R. Cullen was a Ph.D. student of Professor Emeléus during the period 1956–1958.

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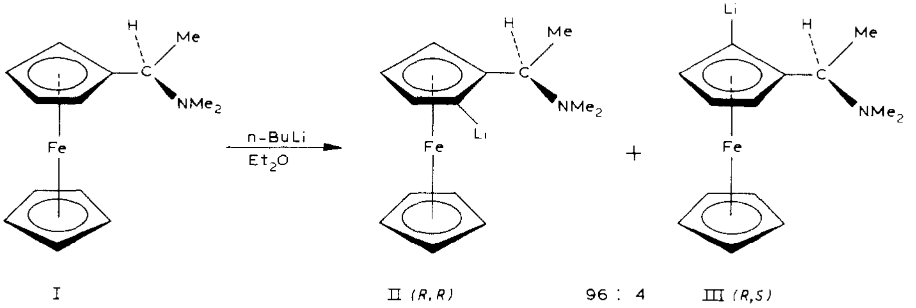
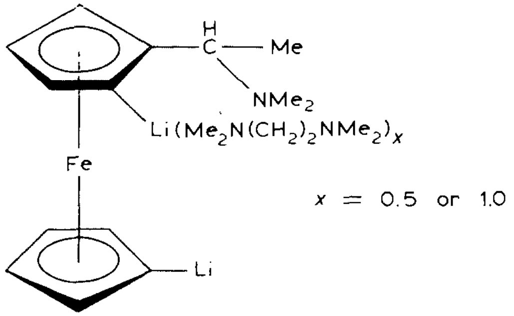
The monolithiation of α-*N*,*N*-dimethylaminoethylferrocene (FA) (I), proceeds stereoselectively at the 2 or 4 positions [5], for example the lithiation of the resolved amine (*R*)-FA, under ambient conditions gives the lithiated products (*R*,*R*)-lithio-FA and (*R*,*S*)-lithio-FA in a ratio of 96 to 4 (eq. 1).



(1)

The derivative II is thought to be stabilized by coordination to lithium of the adjacent nitrogen atom in the side chain. Subsequent addition of a further molar equivalent of n-butyllithium and a molar equivalent of TMED to the ethereal solution of II and III, results in the formation of the heteroannularly dilithiated products IV which may be precipitated from solution by addition of hexane [8].

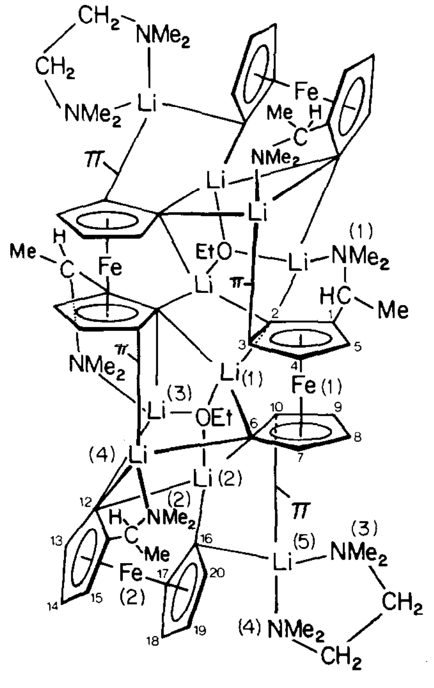


$\left.\begin{matrix}(R,R)\\(R,S)\end{matrix}\right\}$ IV

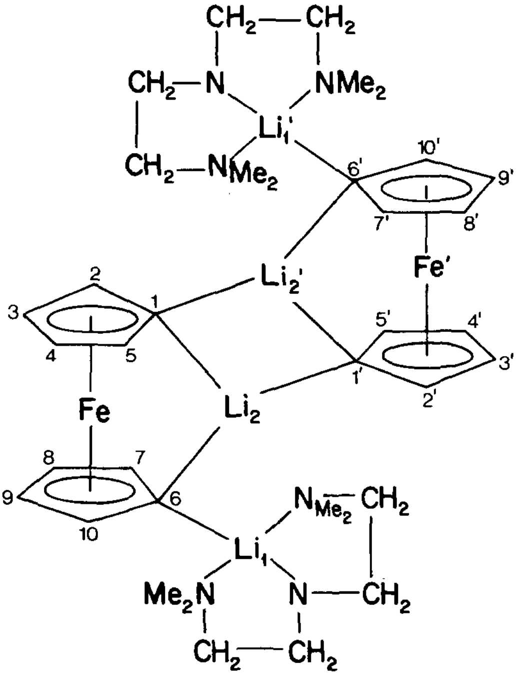
During the course of our synthetic studies [9] we have attempted to obtain information concerning the nature of the interaction of the lithium with the dimethylamino functionalities of TMED and FA. With this in mind we have obtained ^{7}Li NMR spectra of 1,1′-dilithioferrocene-TMED and the dilithio-α-*N*,*N*-dimethylaminoethylferrocene-TMED (IV) derivatives. We have also obtained a crystalline sample of a dilithiated FA derivative, $[(\eta^5\text{-}C_5H_4Li)Fe(\eta^5\text{-}C_5H_3LiCH(Me)NMe_2)]_4[LiOEt]_2][TMED]_2$ (V) formed by slow crystallisation from an ethereal solution of IV. This compound has been the subject of a single crystal X-ray diffraction analysis.

Results and discussion

Adducts of dilithioferrocene-TMED and dilithio-FA-TMED (IV) were prepared according to the literature procedures essentially by precipitation of the adducts from hexane or hexane/diethyl ether solutions [1–6]. During the preparation of IV it was observed that a red crystalline deposit slowly formed on the reaction vessel walls near the surface of the solution when it was kept under a N_2 atmosphere. These crystals were subjected to a single crystal X-ray diffraction analysis and were found to have the formula $[(\eta^5\text{-}C_5H_4Li)Fe(\eta^5\text{-}C_5H_3LiCH(Me)NMe_2)]_4[LiOEt]_2[TMED]_2$, (V). The crystals were initially thought to be a crystalline sample of IV however the structure was found to be more complex. The ethoxy groups present in the structure presumably arise by reaction of a lithium species with the ethereal solvent. Attempts at the preparation of a crystalline sample of the dilithioferrocene-TMED adduct were unsuccessful, however, further attempts to prepare a crystalline sample of IV were successful but the crystals thus formed were small aggregates and were inadequate for a structural analysis.



V π = Li–πC bonds



VI

Crystal structure of V

The structure consists of discrete molecules (Fig. 1 and structure V) possessing exact C_2 symmetry; each containing four ferrocene moieties, ten Li atoms, two TMED units, and two ethoxy groups. The ethoxy and TMED carbon atoms as well as the N(2) α-(*N*,*N*-dimethylamino)ethyl side chain display a high degree of thermal motion. Minor disordering is suspected for these segments of the molecule and is believed to be responsible for the apparent shortening of some bond lengths (e.g. N(2)–C(28) 1.29(1) Å).

There are several similarities between the present structure and that of dilithioferrocene-pentamethyldiethylenetriamine (VI) [7], but the α-(*N*,*N*-dimethylamino)ethyl substituents on one cyclopentadienyl ring of each ferrocene group in addition to the incorporation of the extra $LiOCH_2CH_3$ moieties result in a more complex overall structure. Common features between the two structures include bridging by a single Li atom between the two cyclopentadienyl rings associated with each ferrocene unit, and the fact that each of the crystallographically independent Li atoms is in a different environment. This structure represents the only crystallographic example of five independent Li atoms in five distinct environments.

The central portion of the asymmetric unit features a distorted tetrahedron of Li atoms [Li(1–4)], with Li · · · Li distances ranging from 2.50(3) to 2.78(2) Å. The mean Li · · · Li separation of 2.64 Å is close to the corresponding value of 2.68 Å observed for $(CH_3Li)_4$ [10] which consists of a regular Li_4 tetrahedron, each face being symmetrically bridged by carbon (unique Li–C 2.31(5) and 2.36(5) Å). In V, three of the four faces of the tetrahedron are capped by single atoms: the Li(1,2,3) face by the ethoxy O atom, Li(1,2,4) by C(6), and Li(2,3,4) by C(12). The remaining face, Li(1,3,4), is spanned by atoms C(2′) and C(3′), the latter involved in a π-interaction with Li(4) and the former bridging the Li(1) · · · Li(3) edge while also coordinating Li(1′) thus connecting the two symmetry-related Li_4 tetrahedron. Each Li atom achieves distorted tetrahedral coordination via coordination to one additional atom: Li(1)–C(2), Li(2)–C(16), Li(3)–N(1′), and Li(4)–N(2). It should be noted that C(2), C(6), C(12), and C(16) are the deprotonated cyclopentadienyl carbon atoms. The result is the formation of two cubane-like Li_4OC_3 moieties, each having one edge [Li(4) · · · C(2′) or Li(4′) · · · C(2)] bridged by an extra carbon atom [C(3) or C(3′)], edge linked to one another [Li(1)–C(2′) to C(2)–Li(1′)]. The central Li_2C_2 ring in V (C_2 symmetry) is similar to that in VI (C_i symmetry) in that the Li atoms bridge between the two cyclopentadienyl rings of each ferrocene as well as forming one-atom bridges between the two symmetry-related ferrocenes. The bridging Li atom in VI is three-coordinate and is believed to interact directly with the iron atom via the ferrocene e_g molecular orbital (Li–Fe 2.667(8) Å). In the present case each of the two ferrocene-bridging Li atoms are tetrahedrally coordinated and any direct Li–Fe interaction is less likely than in VI, Fe · · · Li distances being longer than those in VI (Fe(1) · · · Li(1) 2.72(2), Fe(2) · · · Li(2) 2.75(2) Å for V).

Each of the five symmetry-independent Li atoms in V achieves distorted tetrahedral coordination in a different way, the coordination spheres being comprised as follows: Li(1); μ_3-O, 3μ_3-C; Li(2); μ_3-O, 2μ_3-C, μ-C; Li(3); μ_3-O, amino-N, 2μ_3-C; Li(4); amino-N, 2μ_3-C, π-C; Li(5); 2 TMED-N, μ-C, π-C. The solvated Li(5) atom is joined to Li(2) by a single atom bridge through C(16) and by a two atom bridge via a π-interaction with C(10) which is adjacent to the triply-bridging atom C(6). The two-atom μ_3-C–π-C bridge between Li(2) and Li(5) is analogous to that between Li(3) and Li(4). Bond angles about Li range from 85.6(12) to 142.1(9)°, the smallest angle [N(3)–Li(5)–N(4)] is in good agreement with values observed in other Li-TMED complexes [11]. The three Li–O distances are equal within experimental error, mean Li–O 1.91(2) Å, and the Li–N distances range from 2.10(2) to 2.25(3) Å, mean Li–N 2.19(6) Å. Both Li–O and Li–N distances assume normal values [11]. There are three distinct types of Li–C bonds present in the structure of V: those involving doubly-bridging or triply-bridging deprotonated cyclopentadienyl ring carbon atoms and those involving Li–C(π) interactions. The Li–C(μ_3) distances range from 2.18(2) to 2.36(2) Å with a mean of 2.27 Å, comparable with the Li–C(μ_3) distances of 2.31(5)–2.36(5) Å in $(MeLi)_4$ [10] and 2.184(3)–2.300(4) Å in

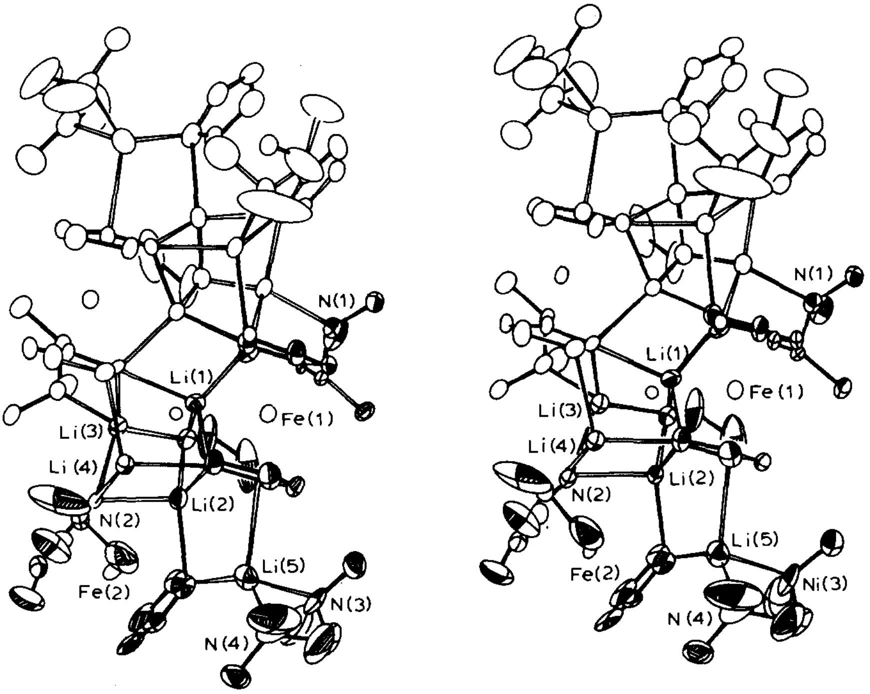


Fig. 1. Stereoview of V.

$(C_6H_{11}Li)_6$ [12]. The Li–C(μ) distances are the only Li–C interactions of the same type as those in VI, the mean Li–C distances being 2.144 in VI and 2.16 Å in V. The Li–C bond to the solvated Li(5) atom, at 2.04(3) Å, is remarkably short. The Li–C(π) distances, mean 2.54(3) Å, are similar to those observed in other structures (e.g. 2.51(1) Å in [$\overline{CHSiMe_2C(SiMe_3)C}_{10}H_8$][Li(TMED)]$_2$ [13]).

The geometry of the ferrocene groups is as expected. Each ferrocene moiety exhibits eclipsed cyclopentadienyl rings which are nearly parallel, the dihedral angles between normals to mean planes being 4.3 and 4.8° for the Fe(1) and Fe(2) ferrocene groups respectively. The corresponding parameter for VI is 2.0°. The mean Fe–C distance is 2.045 Å (2.040 Å for VI) and, as noted for VI, the lithiated carbons are involved in longer Fe–C bonds (mean 2.118(6) Å in V, 2.114(5) Å in VI) than the remaining cyclopentadienyl carbon atom (mean Fe–C 2.026 Å for V, 2.021 Å for VI). Both the Fe–C distances and the mean C–C (cyclopentadienyl) distances of 1.425 Å are as expected [14]. The longest cyclopentadienyl ring C–C distances are generally associated with the lithiated carbons (range 1.41(2)–1.486(11) Å, mean 1.438 Å), the overall bond length trends in the cyclopentadienyl rings are analogous to that in VI.

^{7}Li NMR

Pure TMED adducts of dilithioferrocene and dilithio-FA were prepared essentially using the procedure of Rausch and Clappenelli [4]. The ^{7}Li NMR spectra of these compounds were recorded at 31.14 MHz and the chemical shifts referenced to

0.1 *M* LiCl in D_2O. The spectrum of LiCl-TMED was recorded initially; this gave an observed chemical shift of 0.24 ppm. The organometallic lithium compounds tended to give broad line-widths, ~ 5 Hz, which may be attributed to the non-spherical nature of the lithium nuclei in these compounds and our inability to tune the magnetic field on the samples. The chemical shifts of the TMED adducts of dilithioferrocene and dilithio-FA in dimethoxyethane were found to be 2.76 and 0.85 ppm, respectively, but an interpretation of these numbers in terms of shielding is impossible without more knowledge of the species in solution. The spectrum of dilithio-FA shows no obvious splitting pattern at room temperature (the same sample gave no signal at −50°C). The spectrum suggests that the lithium atoms are all equivalent and the complex is fluxional at room temperature. This is in agreement with Rausch [4] who has observed coalescence phenomena in the proton NMR spectrum of the dilithioferrocene compound.

The ^7Li NMR spectrum of the ethereal mixture of n-butyllithium, FA, and TMED used to prepare dilithio-FA was also recorded. This showed a series of broad overlapping singlets with chemical shifts 1.85; 0.86; −0.80; and −1.19 ppm respectively. The assignment of this spectrum is difficult because of the marked solvent shifts in the lithium signal [15].

Experimental

All manipulations were carried out using conventional Schlenk tube techniques or under an inert glove box atmosphere.

Preparation of dilithioferrocene-TMED and IV. The TMED adducts of dilithioferrocene and dilithio-FA were prepared according to the literature procedures [1–6]. A crystalline sample of the latter compound was obtained from a dilute solution of diethyl ether.

Preparation of V. Compound V was prepared from the mother liquor obtained following the preparation of dilithio-FA [8]. The ethereal solution was allowed to stand for 4 weeks (20°C) under a nitrogen atmosphere. Red crystals of V appeared on the vessel walls and were allowed to grow to crystallographic size. The crystals were isolated in a glove box atmosphere and several suitable crystals were sealed in glass capillaries.

X-ray crystallographic analysis of V

A crystal bounded by the 8 faces: ±(100) [0.16], ±(−110) [0.20], ±(21−3) [0.26], and ±(001) [0.25] (the figures in square brackets being the appropriate distances in mm from a common origin) was mounted under nitrogen in a Lindemann glass capillary. Unit-cell parameters were refined by least-squares on $2\sin\theta/\lambda$ values for 25 reflections ($2\theta = 35$–$43°$) measured on a diffractometer with Mo-K_{α_1} radiation (λ 0.70930 Å). Crystal data at 22°C are: $C_{72}H_{110}Fe_4Li_{10}N_8O_2$, FW = 1412.5. Monoclinic, *a* 36.998(4), *b* 9.6224(13), *c* 23.611(2) Å, β 113.983(5)°, *V* 7680(2) Å^3, $Z = 4$, d_c 1.222 g cm^{-3}, $F(000) = 2992$, μ(Mo-K_α) 7.9 cm^{-1}. Absent reflections: *hkl*, $h + k$ odd, and *h*0*l*, *l* odd. Space group $C2/c$ (C^6_{2h}, No. 15) from structure analysis.

Intensities were measured with graphite-monochromatized Mo-K_α radiation (λ 0.71073 Å) on an Enraf-Nonius CAD4-F diffractometer. An ω-2θ scan at 1.55–10.06° min^{-1} over a range of $(0.80 + 0.35 \tan\theta)°$ in ω (extended by 25% on both sides for background measurement) was employed. Data ($\pm h,k,l$) were measured to $2\theta = 50°$.

TABLE 1

FINAL POSITIONAL (FRACTIONAL $\times 10^4$, Fe$\times 10^5$) AND ISOTROPIC THERMAL PARAMETERS ($U \times 10^3$ Å^2) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	U_{eq}^a/U_{iso}
Fe(1)	47831(4)	52152(16)	34948(6)	48
Fe(2)	31739(5)	25371(27)	11820(7)	91
O	4355(2)	1808(8)	2271(3)	62
N(1)	5573(3)	1664(10)	4311(4)	58
N(2)	3626(4)	6382(15)	1173(5)	91
N(3)	3456(5)	2542(29)	3691(7)	180
N(4)	3201(6)	5434(33)	3212(8)	191
C(1)	5223(3)	3853(11)	3934(4)	42
C(2)	5240(3)	4207(11)	3333(4)	44
C(3)	5286(3)	5694(11)	3376(5)	59
C(4)	5290(4)	6210(12)	3952(5)	67
C(5)	5273(3)	5064(12)	4295(4)	54
C(6)	4256(3)	4882(13)	2692(4)	57
C(7)	4330(4)	6290(13)	2870(5)	71
C(8)	4355(4)	6575(15)	3468(6)	86
C(9)	4316(3)	5292(17)	3721(5)	78
C(10)	4248(3)	4258(13)	3236(5)	66
C(11)	3348(4)	4079(19)	732(6)	83
C(12)	3695(3)	3283(14)	1126(5)	63
C(13)	3577(4)	1906(15)	877(5)	80
C(14)	3194(4)	1884(21)	389(6)	100
C(15)	3055(4)	3254(22)	308(6)	105
C(16)	3277(5)	2702(24)	2133(6)	114
C(17)	3229(5)	1270(25)	1913(7)	128
C(18)	2844(7)	1116(30)	1393(11)	159
C(19)	2657(5)	2373(35)	1294(10)	162
C(20)	2916(5)	3333(23)	1719(7)	128
C(21)	5185(3)	2395(11)	4111(4)	50
C(22)	5003(3)	2275(13)	4600(5)	74
C(23)	5534(4)	169(15)	4324(6)	100
C(24)	5870(3)	2170(15)	4894(5)	81
C(25)	3330(6)	5611(27)	715(11)	186
C(26)	2907(5)	6195(24)	412(10)	180
C(27)	3442(6)	6611(34)	1629(10)	250
C(28)	3729(6)	7584(30)	1049(18)	365
C(29)	3181(9)	3450(57)	3825(15)	255
C(30)	3237(16)	4971(66)	3801(23)	332
C(31)	3815(5)	2353(34)	4241(8)	219
C(32)	3248(10)	1251(47)	3421(13)	316
C(33)	2806(6)	5657(37)	2741(8)	272
C(34)	3366(10)	6800(45)	3336(23)	308
C(35)	4432(7)	484(19)	2498(7)	152
C(36)	4278(9)	208(24)	2964(9)	247
Li(1)	4675(5)	3418(19)	2551(7)	50
Li(2)	3897(6)	2918(26)	2156(8)	78
Li(3)	4296(5)	2404(21)	1469(7)	60
Li(4)	4075(5)	4955(21)	1665(7)	68
Li(5)	3510(7)	3826(41)	2934(11)	132

[a] $U_{eq} = 1/3 \text{ trace}(U_{\text{diagonal}})$.

TABLE 2

BOND LENGTHS (Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES [a]

Bond	Length (Å)	Bond	Length (Å)
Fe(1)–C(1)	2.018(10)	C(1)–C(2)	1.486(11)
Fe(1)–C(2)	2.114(9)	C(1)–C(5)	1.410(13)
Fe(1)–C(3)	2.043(10)	C(1)–C(21)	1.487(14)
Fe(1)–C(4)	1.988(13)	C(2)–C(3)	1.440(14)
Fe(1)–C(5)	2.023(9)	C(2)–Li(1)	2.28(2)
Fe(1)–C(6)	2.119(10)	C(2)–Li(1′)	2.36(2)
Fe(1)–C(7)	2.012(11)	C(2)–Li(3′)	2.35(2)
Fe(1)–C(8)	2.036(11)	C(3)–C(4)	1.442(14)
Fe(1)–C(9)	2.006(10)	C(3)–Li(4′)	2.51(2)
Fe(1)–C(10)	2.038(11)	C(4)–C(5)	1.383(15)
Fe(2)–C(11)	2.074(15)	C(6)–C(7)	1.41(2)
Fe(2)–C(12)	2.112(10)	C(6)–C(10)	1.428(13)
Fe(2)–C(13)	1.997(11)	C(6)–Li(1)	2.22(2)
Fe(2)–C(14)	2.006(13)	C(6)–Li(2)	2.36(3)
Fe(2)–C(15)	2.048(14)	C(6)–Li(4)	2.24(2)
Fe(2)–C(16)	2.125(12)	C(7)–C(8)	1.403(15)
Fe(2)–C(17)	2.05(2)	C(8)–C(9)	1.40(2)
Fe(2)–C(18)	2.02(2)	C(9)–C(10)	1.46(2)
Fe(2)–C(19)	2.038(15)	C(10)–Li(5)	2.56(3)
Fe(2)–C(20)	2.023(13)	C(11)–C(12)	1.46(2)
O–C(35)	1.37(2)	C(11)–C(15)	1.39(2)
O–Li(1)	1.90(2)	C(11)–C(25)	1.48(2)
O–Li(2)	1.93(2)	C(12)–C(13)	1.44(2)
O–Li(3)	1.90(2)	C(12)–Li(2)	2.26(2)
N(1)–C(21)	1.492(12)	C(12)–Li(3)	2.20(2)
N(1)–C(23)	1.45(2)	C(12)–Li(4)	2.18(2)
N(1)–C(24)	1.453(14)	C(13)–C(14)	1.42(2)
N(1)–Li(3′)	2.21(2)	C(14)–C(15)	1.40(2)
N(2)–C(25)	1.40(2)	C(16)–C(17)	1.46(3)
N(2)–C(27)	1.50(2)	C(16)–C(20)	1.43(2)
N(2)–C(28)	1.29(2)	C(16)–Li(2)	2.28(2)
N(2)–Li(4)	2.10(2)	C(16)–Li(5)	2.04(3)
N(3)–C(29)	1.47(4)	C(17)–C(18)	1.46(3)
N(3)–C(31)	1.44(2)	C(18)–C(19)	1.37(3)
N(3)–C(32)	1.46(4)	C(19)–C(20)	1.41(3)
N(3)–Li(5)	2.25(3)	C(21)–C(22)	1.561(12)
N(4)–C(30)	1.41(5)	C(25)–C(26)	1.54(2)
N(4)–C(33)	1.45(2)	C(29)–C(30)	1.48(8)
N(4)–C(34)	1.43(4)	C(35)–C(36)	1.45(3)
N(4)–Li(5)	2.18(4)		

[a] Here and elsewhere in this report primed atoms have coordinates related to those in Table 1 by the symmetry operation $(1-x, y, 1/2-z)$.

The intensities of three check reflections, measured each hour of X-ray exposure time, gave no evidence of crystal decay during the data collection. After data reduction [16] an absorption correction was applied using the Gaussian integration method [17,18]. Transmission factors ranged from 0.732 to 0.802 for 164 integration points. Of the 6774 independent reflections measured, 3058 (45%) had intensities greater than $3\sigma(I)$ above background where $\sigma^2(I) = S + 2B + (0.04(S-B))$ [17] with S = scan count and B = normalized background count.

(Continued on p. 193)

TABLE 3

BOND ANGLES (deg) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Bonds	Angle (deg)	Bonds	Angle (deg)
C(35)–O–Li(1)	128.6(11)	C(12)–C(11)–C(25)	124.1(14)
C(35)–O–Li(2)	127.0(12)	C(15)–C(11)–C(25)	123(2)
C(35)–O–Li(3)	126.3(10)	C(11)–C(12)–C(13)	100.3(11)
Li(1)–O–Li(2)	89.1(9)	C(11)–C(12)–Li(2)	126.0(9)
Li(1)–O–Li(3)	84.5(8)	C(11)–C(12)–Li(3)	158.6(9)
Li(2)–O–Li(3)	87.4(8)	C(11)–C(12)–Li(4)	100.2(11)
C(21)–N(1)–C(23)	112.6(10)	C(13)–C(12)–Li(2)	102.1(10)
C(21)–N(1)–C(24)	113.7(8)	C(13)–C(12)–Li(3)	83.7(9)
C(21)–N(1)–Li(3′)	95.4(7)	C(13)–C(12)–Li(4)	159.1(11)
C(23)–N(1)–C(24)	110.8(10)	Li(2)–C(12)–Li(3)	72.6(7)
C(23)–N(1)–Li(3′)	113.3(9)	Li(2)–C(12)–Li(4)	68.5(8)
C(24)–N(1)–Li(3′)	110.2(8)	Li(3)–C(12)–Li(4)	75.7(8)
C(25)–N(2)–C(27)	101(2)	C(12)–C(13)–C(14)	112.5(14)
C(25)–N(2)–C(28)	121(2)	C(13)–C(14)–C(15)	106.7(14)
C(25)–N(2)–Li(4)	106.0(13)	C(11)–C(15)–C(14)	107.7(15)
C(27)–N(2)–C(28)	107(2)	C(17)–C(16)–C(20)	102.3(15)
C(27)–N(2)–Li(4)	100.7(11)	C(17)–C(16)–Li(2)	94.0(13)
C(28)–N(2)–Li(4)	118.1(13)	C(17)–C(16)–Li(5)	141(2)
C(29)–N(3)–C(31)	110(2)	C(20)–C(16)–Li(5)	128.9(12)
C(29)–N(3)–C(32)	108(3)	C(20)–C(16)–Li(5)	109(2)
C(29)–N(3)–Li(5)	98(2)	Li(2)–C(16)–Li(5)	83.5(10)
C(31)–N(3)–C(32)	114(3)	C(16)–C(17)–C(18)	109(2)
C(31)–N(3)–Li(5)	115.9(14)	C(17)–C(18)–C(19)	108(2)
C(32)–N(3)–Li(5)	109(2)	C(18)–C(19)–C(20)	108(2)
C(30)–N(4)–C(33)	118(3)	C(16)–C(20)–C(19)	112(2)
C(30)–N(4)–C(34)	103(3)	N(1)–C(21)–C(1)	110.1(8)
C(30)–N(4)–Li(5)	103(3)	N(1)–C(21)–C(22)	112.4(8)
C(33)–N(4)–C(34)	104(3)	C(1)–C(21)–C(22)	113.3(9)
C(33)–N(4)–Li(5)	111(2)	N(2)–C(25)–C(11)	120(2)
C(34)–N(4)–Li(5)	119(2)	N(2)–C(25)–C(26)	120(2)
C(2)–C(1)–C(5)	109.9(9)	C(11)–C(25)–C(26)	114(2)
C(2)–C(1)–C(21)	122.0(8)	N(3)–C(29)–C(30)	117(3)
C(5)–C(1)–C(21)	128.0(8)	N(4)–C(30)–C(29)	113(5)
C(1)–C(2)–C(3)	102.1(9)	O–C(35)–C(36)	113(2)
C(1)–C(2)–Li(1)	108.5(7)	O–Li(1)–C(2)	142.1(9)
C(1)–C(2)–Li(1′)	147.6(9)	O–Li(1)–C(6)	101.3(8)
C(1)–C(2)–Li(3′)	87.3(7)	O–Li(1)–C(2′)	104.0(7)
C(3)–C(2)–Li(1)	115.5(9)	C(2)–Li(1)–C(6)	97.6(7)
C(3)–C(2)–Li(1′)	109.1(8)	C(2)–Li(1)–C(2′)	101.6(7)
C(3)–C(2)–Li(3′)	131.6(9)	C(6)–Li(1)–C(2′)	106.4(8)
Li(1)–C(2)–Li(1′)	65.5(7)	O–Li(2)–C(6)	95.6(8)
Li(1)–C(2)–Li(3′)	105.6(7)	O–Li(2)–C(12)	97.2(9)
Li(1′)–C(2)–Li(3′)	65.7(6)	O–Li(2)–C(16)	140.5(13)
C(2)–C(3)–C(4)	111.3(9)	C(6)–Li(2)–C(12)	108.7(9)
C(2)–C(3)–Li(4′)	78.5(8)	C(6)–Li(2)–C(16)	115.2(11)
C(4)–C(3)–Li(4′)	119.0(9)	C(12)–Li(2)–C(16)	95.7(8)
C(3)–C(4)–C(5)	106.9(9)	O–Li(3)–C(12)	100.0(8)
C(1)–C(5)–C(4)	109.5(8)	O–Li(3)–N(1′)	139.3(11)
C(7)–C(6)–C(10)	102.0(9)	O–Li(3)–C(2′)	104.2(8)
C(7)–C(6)–Li(1)	126.3(9)	C(12)–Li(3)–N(1′)	110.4(8)
C(7)–C(6)–Li(2)	157.9(10)	C(12)–Li(3)–C(2′)	109.6(9)
C(7)–C(6)–Li(4)	103.2(9)	N(1′)–Li(3)–C(2′)	90.7(6)

TABLE 3 (continued)

Bonds	Angle (deg)	Bonds	Angle (deg)
C(10)–C(6)–Li(1)	98.0(9)	N(2)–Li(4)–C(6)	116.0(9)
C(10)–C(6)–Li(2)	86.2(9)	N(2)–Li(4)–C(12)	89.0(8)
C(10)–C(6)–Li(4)	151.7(11)	N(2)–Li(4)–C(3′)	109.8(10)
Li(1)–C(6)–Li(2)	71.7(8)	C(6)–Li(4)–C(12)	116.6(10)
Li(1)–C(6)–Li(4)	77.1(7)	C(6)–Li(4)–C(3′)	100.4(8)
Li(2)–C(6)–Li(4)	65.7(8)	C(12)–Li(4)–C(3′)	125.6(8)
C(6)–C(7)–C(8)	114.4(11)	N(3)–Li(5)–N(4)	85.6(12)
C(7)–C(8)–C(9)	106.2(11)	N(3)–Li(5)–C(10)	107.3(11)
C(8)–C(9)–C(10)	106.3(10)	N(3)–Li(5)–C(16)	108(2)
C(6)–C(10)–C(9)	111.0(11)	N(4)–Li(5)–C(10)	116(2)
C(6)–C(10)–Li(5)	103.1(9)	N(4)–Li(5)–C(16)	125.4(14)
C(9)–C(10)–Li(5)	98.9(10)	C(10)–Li(5)–C(16)	110.3(11)
C(12)–C(11)–C(15)	113(2)		

TABLE 4

INTRA-ANNULAR TORSION ANGLES (deg); STANDARD DEVIATIONS IN PARENTHESES

Atoms	Value (deg)
Li(3′)–N(1)–C(21)–C(1)	−46.0(9)
C(2)–C(1)–C(21)–N(1)	76.9(11)
C(21)–C(1)–C(2)–Li(3′)	−46.6(10)
C(1)–C(2)–Li(3′)–N(1)	10.9(8)
C(21)–N(1)–Li(3′)–C(2)	18.7(8)
Li(4)–N(2)–C(25)–C(11)	11(3)
C(12)–C(11)–C(25)–N(2)	−12(3)
C(25)–C(11)–C(12)–Li(4)	6(2)
C(11)–C(12)–Li(4)–N(2)	0.1(8)
C(25)–N(2)–Li(4)–C(12)	−5.7(15)
Li(5)–N(3)–C(29)–C(30)	−38(5)
N(3)–C(29)–C(30)–N(4)	60(6)
Li(5)–N(4)–C(30)–C(29)	−41(5)
C(30)–N(4)–Li(5)–N(3)	16(4)
C(29)–N(3)–Li(5)–N(4)	10(2)

TABLE 5

NON-BONDED DISTANCES WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atoms	Distance (Å)	Atoms	Distance (Å)
Fe(1)···Li(1)	2.72(2)	Li(3)···Li(4)	2.69(3)
Fe(2)···Li(2)	2.75(2)	Li(1)···Li(1′)	2.51(3)
Li(1)···Li(2)	2.68(2)	Li(2)···Li(5)	2.89(3)
Li(1)···Li(3)	2.56(2)	Li(2)···C(10)	2.68(2)
Li(1)···Li(4)	2.78(2)	Li(3)···C(13)	2.50(2)
Li(2)···Li(3)	2.64(2)	Li(4)···C(2′)	2.63(2)
Li(2)···Li(4)	2.50(3)		

The centrosymmetric space group $C2/c$ was indicated both by the E-statistics and the Patterson function, from which the coordinates of the iron atoms were determined. The coordinates of the remaining non-hydrogen atoms were determined from subsequent difference syntheses. Full-matrix least-squares refinement of all non-hydrogen atoms with anisotropic thermal parameters resulted in $R = 0.084$. Hydrogen atoms were placed in idealized positions [C(sp^3)–H 0.98, C(sp^2)–H 0.97 Å, $B_H = B_C + 1.0$, for (staggered) methyl groups $B_H = 1.25B_C$] and included as fixed atoms in subsequent cycles of refinement. Neutral atom scattering factors and anomalous scattering factors for Fe were taken from Ref. 19. The structure was refined with unit weights to $R = 0.070$ and $R_w = 0.079$ for 3058 observed reflections. The function minimized was $\Sigma(|F_o| - |F_c|)^2$, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = (\Sigma(|F_o| - |F_c|)^2/\Sigma|F_o|^2)^{1/2}$.

On the final cycle of refinement the mean and maximum parameter shifts corresponded to 0.06 and 0.71σ respectively (the latter being associated with U_{22} of C(28)). The mean error in an observation of unit weight was 1.921. No unusual features were noted on the final difference map, the largest peak being 0.85e Å^3 near Fe(1). The final positional parameters and equivalent isotropic thermal parameters for the non-hydrogen atoms appear in Table 1. Bond lengths, bond angles, intra-anular torsion angles, and selected non-bonded distances are given in Tables 2–5, respectively. Tables of calculated positional and thermal parameters for hydrogen atoms, anisotropic thermal parameters, torsion angles, and structure factors are available from the authors.

^{7}Li NMR

The ^{7}Li NMR of various lithiated species were recorded (Table 6) using a double tube technique on a Bruker WP 80 operating at 31.14 MHz. The lithioferrocene adducts were dissolved in freshly distilled dimethoxyethane predried over calcium hydride. The dimethoxyethane solution was placed in a 5 mm NMR tube which was subsequently sealed in vacuo. The 5 mm tube was placed in a 10 mm NMR tube, centred with Teflon discs. The 10 mm tube contained a deuterated solvent (either D_2O or $CDCl_3$) which provided the lock for the spectrometer. All the spectra are referenced to 0.1 *M* LiCl in D_2O. The spectrometer was pre-tuned on the reference

TABLE 6

SELECTED ^{7}Li NMR SPECTRAL DATA [a]

Sample [b]	Solvent	Lock	Chemical shift (ppm)	Shape
LiCl	D_2O	D_2O	0.00	sharp singlet
LiCl(TMED)	DME	D_2O	0.25	sharp singlet
PhLi	C_6H_{12}	$CDCl_3$	1.40	broad singlet
Li_2Fc(TMED)	DME	D_2O	2.76	broad singlet
Li_2FA(TMED)	DME	D_2O	0.85	broad singlet
Reaction solution	Et_2O	$CDCl_3$	1.85; 0.86 −0.80; −1.19	broad multiplet

[a] All spectra references to 0.1 *M* LiCl in D_2O. Positive shifts to higher frequencies. [b] FcLi$_2$ = dilithioferrocene; FA-Li$_2$ = dilithio-α-*N*,*N*-dimethylaminoethylferrocene; DME = dimethoxyethane; Reaction solution was an ethereal mixture of n-butyllithium, FA, and TMED.

sample and could not be tuned to any further advantage, since the organolithium solutions contain no deuterium.

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