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The Structure of the 3:2 Adduct of 1,1′-Dilithioferrocene with Tetramethylethylenediamine

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The red solid obtained by treating ferrocene with *n*-BuLi in the presence of tetramethylethylenediamine (TMED) has the unexpected and novel stoichiometry $[(\eta^5\text{-}C_5H_4Li)_2Fe]_3[TMED]_2$ as determined by an X-ray diffraction study. Crystal data: monoclinic, space group $C2/c$; $a = 21.565$ (2) Å, $b = 10.8023$ (7) Å, $c = 17.9956$ (13) Å, $\beta = 99.840$ (1)°, $V = 4130.3$ (5) Å, $R = 0.041$ for 3084 reflections. There are three distinct lithium environments, one essentially four-coordinate and two approximately three-coordinate. The four-coordinate lithium atoms Li(3) are bonded to the TMED nitrogen atoms and to two deprotonated carbon atoms C(1) and C(11) of different ferrocene groups. One three-coordinate lithium Li(1) bridges two carbon atoms C(1) and C(6) of one ferrocene group and is bonded to C(6)′ of a second. The second three-coordinate lithium Li(2) bridges C(11) and C(11)′ of one group and is bonded to C(6) of another. Li(2) and Li(2)′ are unique in that both bridge one ferrocene group. This unit sits like a "seesaw" on top of the rest of the molecule such that the four lithium atoms (1), (1)′, (2), and (2)′ form an approximate tetrahedron; a C_5H_4 group is situated asymmetrically over each face. Other interesting features such as short Li–C and Li–N bonds and short Li⋯Fe and Li⋯CH interactions are discussed.

There is a fascinating variety in the known structures of organolithium derivatives, and there is much interest in this field from both a practical and theoretical point of view.[2,3]

The lithiation of ferrocene derivatives is a facile process and results in many synthetically useful derivatives.[3,4] In particular 1,1′-dilithioferrocene is commonly prepared by reacting ferrocene with 2 equiv of *n*-butyllithium in the presence of TMED (tetramethylethylenediamine). The TMED adduct precipitates from solution. The adduct was originally formulated as the 1:1 derivative 1,1′-dilithioferrocene–TMED, on the basis of some microanalytical results.[5] Rausch and co-workers[6] reformulated this as a 1:2 adduct on the basis of more complete analytical results. Attempts to obtain a crystal of the adduct for X-ray structure determination were unsuccessful so the structure of the 1:1 adduct formed with pentamethyldiethylenetriamine (PMDT) **1**, a dimer in the solid state (Figure 1), was determined instead.[7] This result was generally taken to indicate that the adduct with TMED also had the 1:1 stoichiometry first formulated.[5]

We have recently described[8] the novel structure of a dilithio derivative of [α-(dimethylamino)ethyl]ferrocene which was found to be $[(\eta^5\text{-}C_5H_4Li)Fe(\eta^5\text{-}C_5H_3Li(CH(Me)NMe_2)\text{-}1,2)]_4[LiOEt]_2[TMED]_2$, **2** (Figure 2). The structure is similar to **1** although considerably more complicated because of the presence of the extra donor moieties $-NMe_2$ and $-OEt$. In **1** the two "terminal" lithium atoms are four-coordinate with three sites occupied by the added PMDT. There are two lithium atoms in similar positions in **2**; however, the preference for four-coordination is met by binding to one carbon and *two* nitrogen atoms from TMED as in **1**. The fourth unprecedented interaction is with a single carbon atom of another hydrocarbon ring, the carbon atom being adjacent to the deprotonated one.

This result suggests that the structure of the TMED adduct of dilithioferrocene should show some interesting features and be worth reinvestigation. Our expectations have proven to be well founded, and we now report our results for the novel 3:2 compound $[(\eta^5\text{-}C_5H_4Li)_2Fe]_3[TMED]_2$, **3** (Figure 3).

Experimental Section

Lithiation of Ferrocene. The reaction was carried out in conventional Schlenk type apparatus under argon. Diethyl ether and tetramethylethylenediamine (TMED) were distilled under argon from calcium hydride prior to use.

A stirred solution of ferrocene (5.0 g, 26.9 mmol) in diethyl ether (60 mL) maintained at 20 °C was treated sequentially with a solution of *n*-butyllithium (36 mL of a 1.55 M solution in hexanes, Aldrich Chemical Co.) and TMED (3.2 g, 27.6 mmol). A clear orange solution resulted. The stirrer was stopped and the reaction mixture allowed to stand for 48 h. Large red crystals of the product were deposited mainly on the vessel walls. These were dislodged with a spatula. The crystals were isolated by filtration through a sintered filter and were washed with diethyl ether (20 mL). The sample was then dried in vacuo.[9]

Crystals for X-ray diffraction studies were removed prior to vacuum drying and mounted individually in 0.5-mm capillary tubes under an argon atmosphere in a drybox.

Crystallographic Analysis of $[(C_5H_4Li)_2Fe]_3(Me_2NCH_2CH_2NMe_3)_2$, 3. Crystallographic data are presented in Table I. The unit-cell parameters were determined by least squares on $2(\sin\theta)/\lambda$ values for 25 reflections (with $35 < 2\theta < 45°$) measured with Mo $K\alpha_1$ radiation. The intensities of three standard reflections, measured each hour of X-ray exposure time throughout the data collection, showed only small random fluctuations. The data were corrected for absorption[10,11] (Gaussian integration over 82 sampling points), transmission factor range being given in Table I.

The structure was originally solved by conventional heavy-atom methods in the noncentrosymmetric space group Cc, the Fe atoms being positioned from the Patterson map and the remaining non-hydrogen atoms from subsequent different maps. It was

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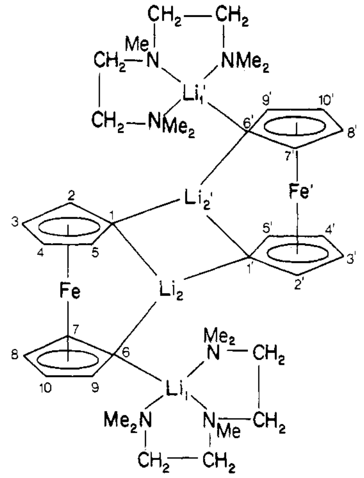

Figure 1. Structure of 1 taken from ref 7.

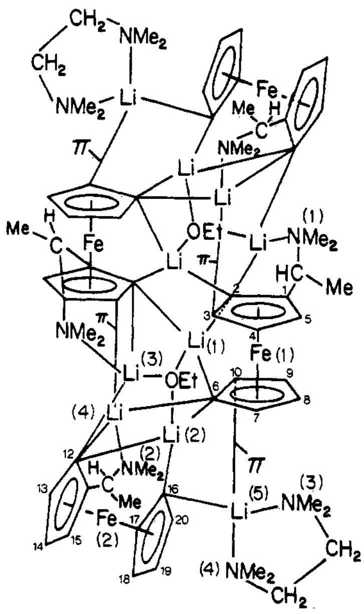

Figure 2. Structure of 2 taken from ref 4.

Table I. Crystallographic Data[a]

compd	$[(C_5H_4Li)_2Fe]_3(Me_2NCH_2CH_2NMe_2)_2$
formula	$C_{42}H_{56}Fe_3Li_6N_4$
fw_1	826.11
cryst system	monoclinic
space group	$C2/c$
a, Å	21.565 (2)
b, Å	10.8023 (7)
c, Å	17.9956 (13)
α, deg	90
β, deg	99.840 (4)
γ, deg	90
V, Å^3	4130.3 (5)
Z.	4
D_{calcd}, g/cm^3	1.328
$F(000)$	1728
μ(Mo Kα), cm^{-1}	10.72
cryst dimens, mm	0.25 × 0.45 × 0.55
transmissn factors	0.553–0.789
scan type	ω–2θ
scan range, deg in ω	0.70 + 0.35 tan θ
scan speed, deg/min	1.12–10.06
data collected	$\pm h,+k,+1$
$2\theta_{max}$, deg	55
unique reflctns	4710
reflctns with $2 \geq 3\sigma(I)$	3084
number of variables	249
R	0.041
R_w	0.046
S	1.844
mean Δ/σ (final cycle)	0.03
max Δ/σ (final cycle)	0.19
residual density, e/Å^3	−1.32 to +0.57

[a] Temperature 22 °C; Enraf-Nonius CAD4-F diffractometer; Mo Kα radiation ($\lambda_{K\alpha_1}$ = 0.709 30, $\lambda_{K\alpha_2}$ = 0.713 59 Å); graphite monochromator; takeoff angle 2.7°; aperture (2.0 + tan θ) × 1.0 mm at a distance of 173 mm from the crystal; scan range extended by 25% on both sides for background measurement; $\sigma^2(I) = S + 2B + [0.04(S - B)]^2$ (S = scan count, B = normalized background count); function minimized $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, and $S = (\sum w(|F_o| - |F_c|)^2/(m - n))^{1/2}$. Values given for R, R_w, and S are based on those reflections with $I \geq 3\sigma(I)$.

apparent at this point that the molecule displayed twofold symmetry and the refinement of the structure was completed in the centrosymmetric space group $C2/c$. All non-hydrogen atoms were

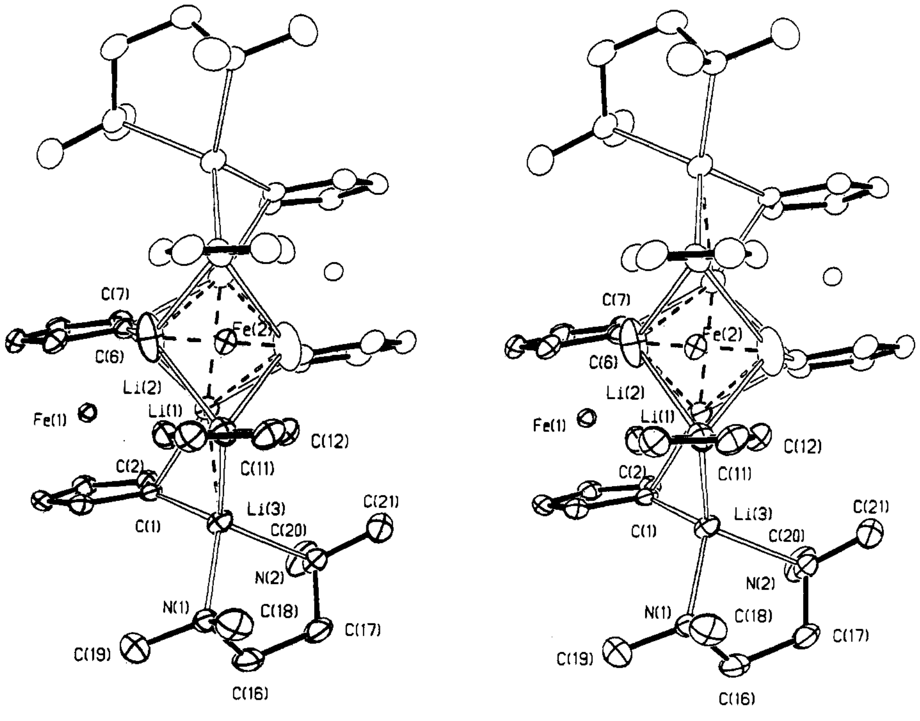

Figure 3. Stereoview of 3; 25% probability thermal elipsoids are shown, and hydrogen atoms are omitted.

Table II. Final Positional (Fractional × 10^4, Fe × 10^5) and Isotropic Thermal Parameters ($U \times 10^3$ Å^2) with Estimated Standard Deviations in Parentheses

atom	x	y	z	U
Fe(1)	−701 (2)	21752 (4)	8751 (2)	31
Fe(2)	0	69462 (5)	25000	34
N(1)	−2188 (1)	5160 (2)	605 (1)	47
N(2)	−2235 (1)	3692 (2)	1962 (1)	48
C(1)	−996 (1)	2777 (3)	936 (2)	39
C(2)	−927 (1)	1437 (3)	970 (2)	41
C(3)	−706 (1)	948 (3)	331 (2)	47
C(4)	−633 (1)	1955 (3)	−142 (2)	51
C(5)	−803 (1)	3048 (3)	222 (2)	47
C(6)	481 (1)	3071 (3)	1782 (2)	41
C(7)	564 (1)	1746 (3)	1815 (2)	47
C(8)	775 (1)	1280 (3)	1171 (2)	50
C(9)	839 (1)	2297 (3)	694 (2)	53
C(10)	667 (1)	3368 (3)	1062 (2)	49
C(11)	−707 (2)	5744 (3)	1960 (2)	55
C(12)	−929 (1)	6584 (4)	2476 (2)	59
C(13)	−837 (2)	7845 (3)	2284 (2)	65
C(14)	−559 (2)	7841 (3)	1637 (2)	60
C(15)	−485 (2)	6587 (3)	1442 (2)	52
C(16)	−2736 (2)	4431 (4)	709 (2)	73
C(17)	−2793 (2)	4261 (4)	1520 (2)	70
C(18)	−2251 (2)	6440 (4)	844 (2)	79
C(19)	−2128 (2)	5137 (4)	−187 (2)	79
C(20)	−2245 (2)	2350 (4)	1877 (3)	82
C(21)	−2212 (2)	3972 (4)	2760 (2)	73
Li(1)	−517 (3)	3317 (9)	2002 (3)	88
Li(2)	313 (4)	4917 (6)	1929 (4)	93
Li(3)	−1481 (2)	4306 (5)	1368 (3)	47

Table III. Bond Lengths (Å) with Estimated Standard Deviations in Parentheses[a]

Fe(1)–C(1)	2.120 (3)	C(1)–C(5)	1.445 (4)
Fe(1)–C(2)	2.046 (3)	C(1)–Li(1)	2.100 (6)
Fe(1)–C(3)	2.034 (3)	C(1)–Li(3)	2.169 (5)
Fe(1)–C(4)	2.030 (3)	C(2)–C(3)	1.420 (4)
Fe(1)–C(5)	2.033 (3)	C(3)–C(4)	1.407 (5)
Fe(1)–C(6)	2.085 (3)	C(4)–C(5)	1.429 (4)
Fe(1)–C(7)	2.038 (3)	C(6)–C(7)	1.443 (4)
Fe(1)–C(8)	2.051 (3)	C(6)–C(10)	1.456 (4)
Fe(1)–C(9)	2.046 (3)	C(6)–Li(1)	2.269 (6)
Fe(1)–C(10)	2.029 (3)	C(6)–Li(2)	2.051 (6)
Fe(2)–C(11)	2.109 (3)	C(6)–Li(1)′	2.193 (7)
Fe(2)–C(12)	2.034 (3)	C(7)–C(8)	1.408 (4)
Fe(2)–C(13)	2.028 (3)	C(8)–C(9)	1.416 (5)
Fe(2)–C(14)	2.039 (3)	C(9)–C(10)	1.414 (5)
Fe(2)–C(15)	2.047 (3)	C(11)–C(12)	1.436 (5)
N(1)–C(16)	1.458 (4)	C(11)–C(15)	1.443 (4)
N(1)–C(18)	1.461 (4)	C(11)···Li(1)	2.653 (10)
N(1)–C(19)	1.453 (4)	C(11)–Li(2)	2.384 (9)
N(1)–Li(3)	2.086 (5)	C(11)–Li(3)	2.393 (6)
N(2)–C(17)	1.461 (4)	C(11)–Li(2)′	2.222 (8)
N(2)–C(20)	1.458 (5)	C(12)–C(13)	1.427 (5)
N(2)–C(21)	1.459 (4)	C(13)–C(14)	1.399 (5)
N(2)–Li(3)	2.196 (5)	C(14)–C(15)	1.414 (5)
C(1)–C(2)	1.456 (4)	C(16)–C(17)	1.496 (5)
Fe(1)···Li(1)	2.689 (6)	Li(1)···Li(2)′	2.567 (10)
Fe(2)···Li(2)	2.560 (6)	Li(1)···Li(3)	2.440 (8)
Li(1)···Li(1)′	2.611 (11)	Li(2)···Li(2)′	2.642 (14)
Li(1)···Li(2)	2.506 (11)		

[a] Here and elsewhere in this report primed atoms are related by the twofold axis to unprimed atoms, symmetry operation $-x$, y, $^1/_2 - z$.

refined with anisotropic thermal parameters, and hydrogen atom parameters were calculated [C(sp^2)–H = 0.97 Å and C(sp^3)–H = 0.98 Å, methyl hydrogen positions idealized from observed positions] and included as fixed contributors to the structure.

Neutral atom scattering factors from ref 12 were used for all atoms except hydrogen, which were taken from ref 13 . Anomalous scattering factors from ref 14 were employed for Fe atoms. Final positional and equivalent isotropic thermal parameters [$U_{\mathrm{eq}} = {}^1/_3\,\mathrm{trace}\,(U_{\mathrm{diagonalized}})$] for the non-hydrogen atoms are given in Table II. Selected interatomic distances, bond angles, and intra-annular torsion angles appear in Tables III–V, respectively. Calculated coordinates and temperature factors for H atoms, anisotropic thermal parameters, and observed and calculated structure factor amplitudes (Tables VI–VIII) are included as supplementary material.[15]

Table IV. Bond Angles (deg) with Estimated Standard Deviations in Parentheses

C(16)–N(1)–C(18)	110.8 (3)	C(6)–C(7)–C(8)	112.1 (3)
C(16)–N(1)–C(19)	109.1 (3)	C(7)–C(8)–C(9)	107.6 (3)
C(16)–N(1)–Li(3)	101.2 (2)	C(8)–C(9)–C(10)	106.8 (3)
C(18)–N(1)–C(19)	109.5 (3)	C(6)–C(10)–C(9)	111.8 (3)
C(18)–N(1)–Li(3)	108.6 (2)	C(12)–C(11)–C(15)	101.7 (3)
C(19)–N(1)–Li(3)	117.4 (3)	C(12)–C(11)–Li(2)	131.4 (3)
C(17)–N(2)–C(20)	111.4 (3)	C(12)–C(11)–Li(3)	114.5 (3)
C(17)–N(2)–C(21)	109.6 (3)	C(12)–C(11)–Li(2)′	78.0 (3)
C(17)–N(2)–Li(3)	102.6 (2)	C(15)–C(11)–Li(2)	79.2 (3)
C(20)–N(2)–C(21)	107.9 (3)	C(15)–C(11)–Li(3)	113.9 (2)
C(20)–N(2)–Li(3)	104.3 (2)	C(15)–C(11)–Li(2)′	135.8 (3)
C(21)–N(2)–Li(3)	120.9 (2)	Li(2)–C(11)–Li(3)	108.8 (2)
C(2)–C(1)–C(5)	101.3 (2)	Li(2)–C(11)–Li(2)′	69.9 (3)
C(2)–C(1)–Li(1)	102.0 (3)	Li(3)–C(11)–Li(2)′	105.7 (3)
C(2)–C(1)–Li(3)	142.6 (3)	C(11)–C(12)–C(13)	111.8 (3)
C(5)–C(1)–Li(1)	125.7 (3)	C(12)–C(13)–C(14)	107.1 (3)
C(5)–C(1)–Li(3)	113.2 (2)	C(13)–C(14)–C(15)	107.0 (3)
Li(1)–C(1)–Li(3)	69.7 (3)	C(11)–C(15)–C(14)	112.3 (3)
C(1)–C(2)–C(3)	112.5 (3)	N(1)–C(16)–C(17)	113.3 (3)
C(2)–C(3)–C(4)	106.9 (3)	N(2)–C(17)–C(16)	112.7 (3)
C(3)–C(4)–C(5)	107.3 (3)	C(1)–Li(1)–C(6)	98.1 (3)
C(1)–C(5)–C(4)	112.1 (3)	C(1)–Li(1)–C(6)′	143.7 (4)
C(7)–C(6)–C(10)	101.8 (3)	C(6)–Li(1)–C(6)′	106.7 (3)
C(7)–C(6)–Li(1)	102.9 (3)	C(6)–Li(2)–C(11)	123.5 (4)
C(7)–C(6)–Li(2)	169.2 (3)	C(6)–Li(2)–C(11)′	117.3 (4)
C(7)–C(6)–Li(1)′	95.5 (3)	C(11)–Li(2)–C(11)′	92.4 (3)
C(10)–C(6)–Li(1)	122.9 (3)	N(1)–Li(3)–N(2)	86.3 (2)
C(10)–C(6)–Li(2)	89.1 (3)	N(1)–Li(3)–C(1)	116.4 (3)
C(10)–C(6)–Li(1)′	153.3 (3)	N(1)–Li(3)–C(11)	112.4 (2)
Li(1)–C(6)–Li(2)	70.7 (4)	N(2)–Li(3)–C(1)	112.8 (2)
Li(1)–C(6)–Li(1)′	71.6 (3)	N(2)–Li(3)–C(11)	119.8 (2)
Li(2)–C(6)–Li(1)′	74.3 (3)	C(1)–Li(3)–C(11)	108.2 (2)

Table V. Intra-annular Torsion Angles (deg)[a]

Li(3)–N(1)–C(16)–C(17)	48.2 (4)
N(1)–C(16)–C(17)–N(2)	−56.7 (5)
Li(3)–N(2)–C(17)–C(16)	29.0 (4)
C(17)–N(2)–Li(3)–N(1)	−2.4 (3)
C(16)–N(1)–Li(3)–N(2)	−23.6 (3)

[a] Standard deviations in parentheses.

Results and Discussion

The dilithioferrocene–TMED adduct was prepared essentially by the literature method[5] using *n*-butyllithium to lithiate ferrocene in the presence of TMED except that the reaction was carried out in diethyl ether rather than hexane. (Use of ether is reported[6] to lead to lower yields of "product"). A crystalline solid is readily obtained if the reaction mixture is unstirred after the initial mixing. Red crystals of the product were found to have the 3:2 stoichiometry $[(\eta^5\text{-}C_5H_4Li)_2Fe]_3[TMED]_2$ during the course of the structural analysis. The microanalytical data for the same sample appears to indicate the same result al-

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(15) The computer programs used include locally written programs for data processing and locally modified versions of the following: ORFLS, full-matrix least squares, and ORFFE, function and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; FORDAP, Patterson and Fourier syntheses, by A. Zalkin; ORTEP II, illustrations, by C. K. Johnson.

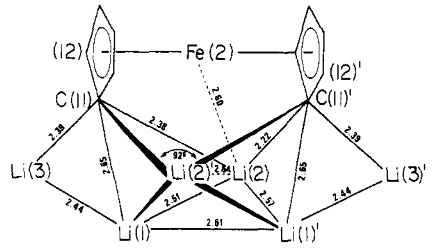


Figure 4. Fragment of the structure of 3 showning the dilithio-bridged ferrocene group and the tetrahedron of lithium atoms Li(1), Li(1)′, Li(2), and Li(2)′.

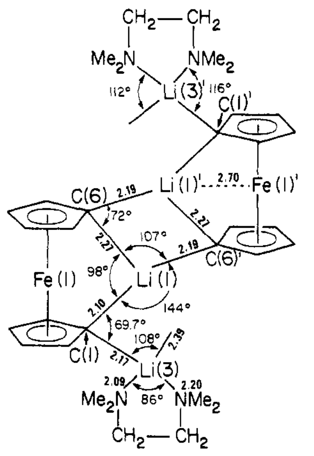


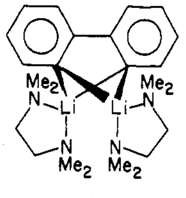
Figure 5. Fragment of the structure of 3 showing the portion which is essentially equivalent to that found in 1 (Figure 1).

though difficulty was found in reproducing the values from other samples.[16] It is possible that other stoichiometries may be present; however, it seems more likely that the variation simply reflects handling difficulties. The analytical results of Rausch and co-workers[16] nevertheless do suggest that a 1:2 compound may be isolated from hexane solution.

The Structure of 3. The essential structure of 3 (Figure 3) can be built from that of 1 simply by placing the dilithioferrocene fragment defined by Fe(2)C(11)C(11)′Li(2)Li(2)′ of Figure 4 on top of the fragment of 3 equivalent to 1 shown in Figure 5. In this way Li(3) and Li(3)′ achieve four-coordination by bonding to C(11) and C(11)′, respectively, compensating for the loss of a nitrogen donor on changing from PMDT to TMED.[17]

The sum of the angles around Li(2) in 1 is 360° (Figure 1), the atom being three-coordinate with the possibility of additional bonding to Fe through the e_g orbitals (Fe⋯Li(2) distance = 2.677 (8) Å) and to Li(2)′(Li(2)⋯Li(2)′ = 2.367 (17) Å). In 3 the sum of the angles around the equivalent atom Li(1) (Figure 5) is 349° and the Li(1)–Fe(1) distance (2.689 (6) Å) allows the possibility of bonding. The Li(1)⋯Li(1)′ distance is long (2.610 (11) Å) as are all the other Li⋯Li distances involving Li(1); the shortest at 2.440 (8) Å involves Li(1) and Li(3). The Li(1)⋯C(11) distance is too long for any bonding to be considered (2.653 (10) Å) (Figure 4).

The dilithio fragment based on Fe(2), Li(2), and Li(2)′ has some unique features. The positioning of the two lithium atoms between the two C_5H_4 rings is quite different from the arrangement found in 1 and in the equivalent portion of 2. The arrangement seen in Figure 4 is roughly similar to that recently found in the dilithio derivative of biphenyl 1,1′-$C_{12}H_8Li_2$·2TMED, 4[18], where each Li atom is coordinated to the two 1,1′-carbon atoms and to a molecule of TMED.



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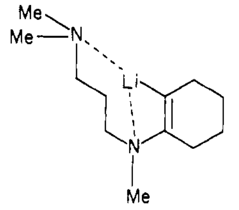

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The distance between Li(2) and Li(2)′ is probably too long (2.64 (1) Å) for bonding as is discussed below, but both Li atoms are close to Fe(2) (2.600 (6) Å) and seem to be well situated to interact with the e_g orbital. The Li(2)–Fe(2)–Li(2)′ angle is 61.1 (2)°. In addition to C(11) and C(11)′, Li(2) is bonded to C(6) at a distance of 2.051 (6) Å. This is one of the shortest Li–C lengths to be reported.[19,20] The angles around Li(2) involving the three carbon atoms sum to 333° so that the geometry is only slightly different from that seen around Li(1). The stronger interaction with Fe(2) probably accounts for the increased doming.

The Li_4 Tetrahedron. Tetrahedra of Li atoms are found in a number of structures such as $(MeLi)_4$,[21] $(EtLi)_4$,[22] $(MeLi)_4(TMED)_2$,[23] $(PhC{\equiv}CLi)_4(TMED)_2$,[24] $(C_6H_4(CH_2NMe_2)Li\text{-}1,2)_4$,[25] and 2. The Li–Li distances vary from 2.42 Å in $(EtLi)_4$ to 2.78 Å in 2. There seems to be little if any direct Li–Li bonding in these molecules which are held together by closed four-center bonds involving three Li atoms and one carbon.[2] The central tetrahedron of Li atoms in 3, Li(1), Li(1)′, Li(2), and Li(2)′, has similar Li⋯Li distances (Figure 4).

The structural fragment in Figure 4 shows that C(11) is situated above one face of the tetrahedron and is bound unsymmetrically to the two Li atoms Li(2) and Li(2)′. There is little if any interaction with Li(1). The other two faces of this tetrahedron also have C_5H_4 rings containing C(6) and C(6)′, respectively, situated in an asymmetric "face centered" position. In these cases the bonding appears to be stronger as evidenced by the bond lengths which range from the very short Li(2)–C(6) distance of 2.051 (6) Å, mentioned above, to 2.193 (1) and 2.264 (6)

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[16] Some microanalytical data are as follows [found (calcd)]:

	C	H	N
this study, 3:2 compound	60.0 (61.1)	7.20 (6.83)	6.72 (6.78)
this study, random sample	58.7	7.48	6.62
1:1 compound[4]	61.1 (61.2)	7.38 (7.71)	
1:2 compound[5]	61.5 (61.4)	9.40 (9.37)	13.0 (13.0)

Fe, 13.0 (13.0); Li, 3.65 (3.23)

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Å for the distances to Li(1)′ and Li(1), respectively.

It should be noted that the aryl ring in $(C_6H_4(CH_2NMe_2)Li\text{-}1,2)_4$ is one of the few examples[25] where an aryl group is involved in this type of "face-centered" bonding to three Li atoms. Here the carbon is closest to one Li atom (2.254 (8) Å) and the nitrogen is bound to another on the same face.[25a] In **2** (Figure 2) the cyclopentadienyl ring bearing the $-NMe_2$ moiety is situated in a "face-centered" manner although it is not possible to decide if the carbon and the nitrogen have closest contacts with the same lithium atom, e.g., Li(4) or different lithium atoms Li(4) and Li(3). However, it is probably the same since Li(3) is also bound to another NMe_2 moiety.

In **2** unsubstituted cyclopentadienyl rings are also "face centered" over the faces of Li_4 tetrahedra. A unique feature of **3**, however, is the presence of two cyclopentadienyl rings which are "face centered" with respect to a Li_3 fragment which is not part of a tetrahedron. This is best seen in Figure 4 where C(11) is sitting over the face of Li(3), Li(2), and Li(2)′, the bond lengths ranging from 2.222 (8) to 2.393 (6) Å.

The Tetrahedral Li Atoms Li(3) and Li(3)′. The angle C(1)Li(3)C(11) is 108.2 (2)° with the TMED ligand subtending an angle of 86.3 (2)°. The small angle is due to the small bite of the ligand and is characteristic of many TMED–lithium compounds[26]. Generally the coordination at Li(3) can be described as distorted tetrahedral. The Li(3)–N bond lengths are different, one at 2.196 (5) (2) Å being in the usual range and the other at 2.086 (5) Å being considerably shorter. Another short Li–TMED interaction of 2.04 (2) Å has been reported recently.[27] A distance of 2.05 Å has been found for the *internal* N–Li bond in the dimer of **5**.[28,29] The Li–N distance in $(C_6H_4(CH_2NMe_2)\text{-}Li\text{-}1,2)_4$[25] is very short at 2.011 (9) Å.

The Li(3)–C(1) bond length in **3** is 2.169 (5) Å. The equivalent bond in **2** is considerably shorter at 2.04 (3) Å.[3,20]

The Li(3)–C(11) distance is longer at 2.393 (6) Å possibly because C(11) is bound to three Li atoms.

η^1-Bonding and Li$\cdots$CH Interaction. Recent theoretical studies[30] have indicated that the Li atom in LiC_5H_5 should be bound in an η^5-mode. Direct evidence for this is provided by the crystal structure of $[C_5H_4(SiMe_3)]LiTMED$ where the Li atom is situated above the centroid of the planar cyclopentadienyl ring.[31] A similar situation pertains for $[C_5H_2(SiMe_3)_3]LiTMED$.[32] Indenyl- and fluorenyl analogues in particular appear to have η^3-bonding to Li.[2,26,33,34] This mode and possibly η^4-bonding is probably present in some other structures.[2,26,27,35]

In Figure 2 the long bond between Li(5) and C(10) (2.56 (3) Å) completes the coordination at the tetrahedral Li(5) atom. As mentioned above the carbon atom, C(10), also bears a hydrogen atom so that Li(5) can be regarded as being bonded either in a η^1-mode to this substituted cyclopentadienyl ring or as interacting with the C–H bond. There is one recent precedent for the η^1-possibility;[36] the ipso C atom of a phenyl ring is 2.40 (3) Å from an otherwise two-coordinate Li atom in $Li[C(SiMe_2Ph)_3][THF]$. Interactions between Li and C–H units have been invoked to account for the stereochemistry and bonding of alkyllithiums,[37] "ate" species,[38] and more recently trimeric (dibenzylamido)lithium.[39] In the last example the C–Li distances of interest are about 2.80 Å.

There seems little doubt that the interaction exists in the case of **2**; the problem is that the data are not good enough to distinguish between the possibilities, or to indicate alternatives.

As described above, in **3** Li(2) is bonded to C(11)′ and C(11), both deprotonated carbon atoms, at distances of 2.222 (8) and 2.384 (9) Å, respectively. The closest distances from Li(2) to other C atoms are as follows: C(12)′, 2.381 (9) Å; C(10), 2.496 (7) Å. Thus Li(2) is certainly within the bonding distance of C(12)′ on the same ring as C(11)′, and the Li(2)–H(12)′ distance of 2.29 Å is the shortest interaction of this type. Again the data are not good enough to establish if these possible interactions are important.[40]

The Li(2)–C(10) distance is longer at 2.496 (7) Å; however, the hydrogen attached to this carbon atom H(10) is close to Li(2) (2.33 Å) and appears to occupy a fourth coordination site, assuming that the other three are occupied by C(11), C(11)′, and C(6) as described above. Again the possibility of a Li$\cdots$C–H interaction cannot be ignored.[40]

The Cyclopentadienyl Rings. The two different ferrocene fragments in **3** have essentially eclipsed rings as is found in **1** and **2**, and the rings in each fragment are nearly parallel again as in **1** and **2**. Three of the rings are planar but those which include C(1), C(6), and C(16) show small but statistically significant deviations from planarity.

The C(1)–Fe(1), C(6)–Fe(1), and C(11)–Fe(2) distances of 2.120 (3), 2.085 (3), and 2.109 (3) Å are longer than the other ring C–Fe distances. The difference in the two lengths involving Fe(1) is probably significant. The other ring C–Fe distances average 2.038 Å. Similar C–Fe distances have been found in **1** and **2** including the lengthening observed when the carbon atom is deprotonated.

It is difficult to say much about the C–C distances in the rings because of uncertainties. The values range from 1.456 (4) Å for C(6)–C(10) and C(1)–C(2) to 1.400 (5) Å for C(13)–C(14), and in general the longer bonds in a given ring involve the deprotonated carbon atom. As in **1** two of the short bonds are opposite each other, C(13)–C(14) and C(13)′–C(14)′, and across the ring from the deprotonated C atom. This same trend appear to hold in the other C_5H_4 rings.

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Supplementary Material Available: Tables of calculated hydrogen atom parameters (Table VI), anisotropic thermal parameters (Table VII), and observed and calculated structure factors (Table VIII) (23 pages). Ordering information is given on any current masthead page.

Bimetallic Complexes Containing Copper. The Crystal Structures of (tmed)CuMo$(CO)_3(\eta^5\text{-}C_5H_5)$ and $[(C_6H_5)_3P]_3$CuV$(CO)_6$

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The reaction of phosphine- or diamine-substituted copper(I) halides with various metal carbonyl anions leads to the formation of heteronuclear bimetallic complexes where one of the metals is copper. These complexes exhibit a wide range of Cu-M and Cu-CO interactions. $(Ph_3P)_3CuV(CO)_6$, prepared from $(Ph_3P)_2CuCl$ and Na(diglyme)$_2$V$(CO)_6$, exists as discrete trigonal planar $(Ph_3P)_3Cu^+$ cations and octahedral $V(CO)_6^-$ anions. The compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.669$ (1) Å, $b = 12.691$ (2) Å, $c = 19.432$ (2) Å, $\alpha = 102.17$ (2)°, $\beta = 92.03$ (1)°, $\gamma = 108.25$ (1)°, and $Z = 2$. The structure was solved by heavy-atom techniques and refined by full-matrix least squares to $R = 0.050$ and $R_w = 0.054$. The $L_nCuM(CO)_3(\eta^5\text{-}C_5H_5)$ complexes ($L_n = (Ph_3P)_2$ or $(CH_3)_2NCH_2CH_2N(CH_3)_2$; M = Cr, Mo, W) all appear to have a Cu-M bond with a single terminal and two semibridging carbonyl groups. (tmed)CuMo$(CO)_3(\eta^5\text{-}C_5H_5)$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 8.134$ (1) Å, $b = 14.632$ (2) Å, $c = 13.993$ (2) Å, $\beta = 94.76$ (1)°, and $Z = 4$. The final residuals are $R = 0.027$ and $R_w = 0.032$.

Introduction

A number of heteronuclear bimetallic complexes containing copper with well-defined compositions have been prepared in the past two decades.[1-9] Our recent work with Cu-Co complexes[10] and the work by Carlton and coworkers[8] with some Cu-W complexes have shown some interesting metal carbonyl interactions which were not fully appreciated in the earlier literature. For example, in the case of the Cu-Co complexes a fairly strong interaction between the copper and one of the carbonyl groups was observed in the solid state for (tmed)CuCo$(CO)_4$, but this interaction was apparently not present for similar complexes containing phosphine ligands. These relationships prompted us to expand the scope of our work to include a number of other Cu-metal complexes and metal-ligand combinations.

Results and Discussion

Although the reaction of many metal carbonyl anions with substituted copper halides is often quite straightforward leading to bimetallic species in good yields, there are a number of complications that arise in certain cases. Two of the factors which influence the success of these reactions are the lability of the ligands bound to copper and the reducing properties of the metal carbonyl anions. Di- and triamine-substituted copper(I) halides such as (tmed)CuCl (tmed = *N,N,N′,N′*-tetramethylethylenediamine) are quite easily reduced to copper metal by strong reducing agents. At room temperature in the presence of $V(CO)_6^-$, (tmed)CuCl is quantitatively converted to the metal along with the concurrent formation of $V(CO)_6$. Phosphine-substituted copper(I) halides tend to be much less susceptible to reduction than the amine complexes, and it is often possible to prepare the bimetallic complexes from the phosphine derivative even with relatively strongly reducing anions. The use of phosphine ligands, particularly monodentate phosphines, often introduces another complication in the preparation of the bimetallic complexes. Due to the lability of these ligands, one often finds mixtures of products in which the ligand/copper ratio differs from that of the starting phosphine-substituted copper halide.[10] In the case of the reaction of $[(C_6H_5)_3P]_2CuCl$ with Na(diglyme)$_2$V$(CO)_6$, the tris(phosphine) derivative is the only Cu-V product which can be isolated

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