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Mono- and binuclear σ-aryl iron–lithium hydrides; synthesis and molecular structure *

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Abstract

Phenyl- and *p*-tolyl-iron–lithium *trans*-dihydrides have been synthesised in the reaction of dihydrogen with the corresponding *at*-complexes of Fe^0 and Fe^{II}. The molecular structures and IR spectra of the complexes have been investigated as well as those of the binuclear iron(II)–lithium complexes produced from iron *trans*-dihydrides under the action of polar solvents (THF, diethyl ether). Unlike mononuclear dihydrides which are inert to dinitrogen, binuclear complexes react with N_2 producing new complexes containing reduced dinitrogen.

Introduction

Interaction of iron trichloride with excess phenyllithium has been reported [1] to produce the zero-valent-iron complex tetralithium-tetraphenylferrate $[FePh_4]Li_4 \cdot 4Et_2O$ **1**. This complex was found to react with dinitrogen, forming an N_2-containing compound which produces N_2 and N_2H_4 when decomposed by HCl. **1** was also found to react with other small molecules. In the case of H_2 it produces the dihydride. We report the structure of *trans*-dihydrides produced from **1** and from a similar *p*-tolyl complex as well as the structure of binuclear complexes formed from the dihydrides in reactions with solvents (THF and diethyl ether).

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* Dedicated to Professor Akio Yamamoto upon his retirement from Tokyo Institute of Technology and in honour of his contributions to organometallic chemistry.

Experimental

Complexes $[(H)_2FePh_4]Li_4\cdot 4Et_2O$ *(2) and* $[(H)_2Fe(p\text{-}Tol)_4]Li_4\cdot 4Et_2O$ *(3)*

Salt-free phenyllithium was prepared by exchange of n-BuLi with PhI in dry hexane. Iron trichloride was dissolved in dry ether in an argon atmosphere. The solution was added dropwise with intense stirring to an ether solution of salt-free phenyllithium at −30°C. The reaction mixture was slowly warmed to room temperature, the precipitate of LiCl filtered off, argon evacuated and the vessel filled with H_2 or D_2 (1 atm). Black crystalline dihydride **2** was formed immediately, the solution was decanted and the crystals dried by evacuation. Synthesis of *p*-tolyl dihydride **3** was performed similarly and crystalline **3** was obtained from concentrated ether solution at −20°C. Unlike **2**, complex **3** is readily soluble in ether. Complexes **2** and **3** are stable in the solid state at room temperature in the absence of oxygen and moisture.

IR spectra were measured on UR20 and Perkin–Elmer 325 spectrometers. The stated frequencies are accurate to $\pm(1\text{–}2)\ \mathrm{cm}^{-1}$ and $\pm(2\text{–}5)\ \mathrm{cm}^{-1}$ for narrow and broad bands, respectively. The samples were prepared under an inert atmosphere as tablets with KBr or Nujol mulls. Hermetically sealed cells with KBr windows were used. Electronic absorption spectra were recorded on a Specord UV–VIS spectrophotometer.

Single crystals of **2** and **3** were sealed in an inert atmosphere in thin-walled capillaries of diameter 0.5 mm; X-ray diffraction data were collected at −120°C using an automatic four-circle Syntex $P2_1$ diffractometer (Mo-K_α radiation, graphite monochromator, $\theta/2\theta$ scan mode, $2\theta < 86°$ (**2**) and 57° (**3**)). The crystals of **2** are tetragonal, at −120°C $a = b = 12.380(1)$, $c = 13.145(2)$ Å, $V = 2014.7(4)$ Å^3, $Z = 2$, space group $P\bar{4}2_1c$. The crystals of **3** are monoclinic, at −120°C $a = 16.249(3)$, $b = 16.508(3)$, $c = 17.739(3)$ Å, $\beta = 111.39(3)°$, $V = 4430(3)$ Å^3, $Z = 4$, space group $C2/c$. 1226 (**2**) and 3679 (**3**) unique reflections with $F \geqslant 8\sigma(F)$ from a total of 3414 (**2**) and 4413 (**3**) measured reflections were used in subsequent calculations. Both structures were solved by direct methods by means of the MULTAN program and refined by the full-matrix least-squares technique in the anisotropic–isotropic (H atoms) approximation. The refinement converged to $R = 0.032$, $R_w = 0.031$, GOF = 2.38 (**2**) and $R = 0.047$, $R_w = 0.047$, GOF = 2.89 (**3**). All the calculations were performed with the INEXTL [2] and SHELXTL PLUS (PC Version) program packages using Eclipse S/200 and IBM PC/AT computers for **2** and **3** respectively.

Complex $[Ph_3Fe(\mu_2\text{-}H)_3FePh_3]Li_5\cdot 5THF$ *(4)*

Crystals of **2** were dissolved in dry THF at −30°C, then the temperature was slowly raised to 20°C, the colour of the solution changing from bright violet ($\lambda_{max} = 515$ nm) to red-brown ($\lambda_{max} = 465$ nm). THF was then removed by evacuation, the residue dissolved in pentane–THF (volume ratio 20:1), the solution filtered and kept at −20°C. After several days large well-defined crystals of **4** precipitated.

X-ray diffraction data for **4** were collected using an automatic four-circle Syntex $P2_1$ diffractometer at −120°C (Mo-K_α radiation, graphite monochromator, $\theta/2\theta$ scan mode, $2\theta \leqslant 44°$). Crystals of **4** are triclinic, at −120°C $a = 12.889(10)$, $b = 19.994(15)$, $c = 21.351(20)$ Å, $\alpha = 78.11(8)$, $\beta = 75.88(6)$, $\gamma = 86.83(7)°$, $V = 5222(6)$

Å^3, $Z = 4$, space group $P\bar{1}$. 3425 reflections with $F \geqslant 4\sigma(F)$ from a total of 5272 measured reflections were used in subsequent calculations. The structure was solved by direct methods using the MULTAN program and refined by the block-diagonal least-squares technique in the anisotropic–isotropic (for C atoms) approximation. Positions of the hydride atoms were determined from difference Fourier synthesis, phenyl H atoms and H atoms of solvate THF molecules being placed in the geometrically calculated positions. All H atoms were included in the refinement as a fixed contribution with $B_{iso} = 4.0$ Å^2. The refinement converged to $R = 0.086$, $R_w = 0.084$ and GOF = 3.57. Rather high discrepancy factors are probably due to disorder of solvate molecules in the crystal.

*Complex [(*p-*Tol)$_3$Fe(μ_2-H)$_3$Fe(*p-*Tol)$_3$]Li$_5$ · 5(2,5-dimethyl-THF) (5)*

3 was dissolved in dry diethyl ether under an argon atmosphere at room temperature. In several days the solution changed from bright red ($\lambda_{max} = 505$ nm) to red-brown ($\lambda_{max} = 460$ nm). When this change was complete, ether was removed by evacuation and the dry residue was extracted with pentane–2,5-dimethyltetrahydrofuran mixture (volume ratio 20:1). On cooling (−5°C) crystals of **5** precipitated.

The X-ray diffraction data for complex **5** were collected at −90°C using a four-circle automatic Siemens P3/PC diffractometer (Mo-K_α-radiation, graphite monochromator, $\theta/2\theta$ scan mode, $2\theta \leqslant 46°$). Crystals of **5** are monoclinic, at −90°C $a = 17.062(3)°$, $V = 7010(4)$ Å^3, $Z = 4$, space group $P2_1/n$. 5542 unique reflections with $F \geqslant 4\sigma(F)$ from a total of 8326 measured reflections were used in subsequent calculations. The structure of **5** was solved by direct methods using the MULTAN program and refined by the least-squares technique in the anisotropic–isotropic (for the C atoms of five solvate 2,5-dimethyltetrahydrofuran molecules) approximation. The final refinement converged to $R = 0.089$, $R_w = 0.089$ and GOF = 6.57.

Results and discussion

Atomic coordinates and bond lengths are presented in Tables 1–8.

Interaction of iron trichloride with phenyllithium proceeds [3] according to the scheme:

$$\begin{tikzcd}
7\mathrm{PhLi} + \mathrm{FeCl_3} \arrow[r, "-30°\mathrm{C}", "\mathrm{Et_2O}"'] & {[\mathrm{Li_4Fe^{II}Ph_6}] + 3\mathrm{LiCl} + 0.5\mathrm{Ph_2}} \arrow[d, "20°\mathrm{C}"] \\
 & {[\mathrm{Fe^0Ph_4}]\mathrm{Li_4} \cdot 4\mathrm{Et_2O} + \mathrm{Ph_2}}
\end{tikzcd}$$

1

We have found that dihydrogen reacted with both the final complex **1** of Fe^0 and its precursor Li$_4$Fe^{II}Ph$_6$. In both cases within a few minutes of the introduction of H$_2$ dark well-defined crystals were formed. In the course of interaction with acid 2 mol of dihydrogen is produced for each mol of the complexes. In the case of D$_2$ the product of acid hydrolysis was found to be more than 90% HD. Analytical results correspond to four Li atoms per Fe atom. These results have led to the

Table 1

Atomic coordinates ($\times 10^4$, for Fe $\times 10^5$, for H $\times 10^3$) and their equivalent isotropic (isotropic for H atoms) temperature factors B_{eq} (Å^2) in **2**

Atom	x	y	z	B_{eq}
Fe	0	0	1/2	1.67(1)
O	−1247(2)	−2344(2)	2733(1)	3.68(5)
C(1)	442(2)	−1601(2)	4979(3)	2.20(5)
C(2)	233(2)	−2348(2)	5788(2)	2.67(7)
C(3)	491(2)	−3446(2)	5754(2)	3.53(8)
C(4)	984(2)	−3885(2)	4915(3)	3.88(8)
C(5)	1223(2)	−3218(2)	4117(2)	3.44(7)
C(6)	966(2)	−2115(2)	4149(2)	2.76(7)
C(7)	−727(3)	−2450(3)	1773(2)	5.4(1)
C(8)	−454(3)	−1371(3)	1378(3)	6.2(1)
C(9)	−1603(3)	−3399(3)	3085(3)	4.8(1)
C(10)	−2217(3)	−3282(3)	4016(3)	6.1(1)
Li	−761(4)	−1270(4)	3746(4)	2.96(9)
H(6)	122(2)	−167(2)	357(2)	1.5(5)
H(2)	−6(3)	−206(2)	641(2)	3.4(6)
H(3)	37(2)	−388(2)	638(2)	4.5(7)
H(4)	177(2)	−463(2)	487(2)	4.6(7)
H(5)	150(2)	−346(2)	359(2)	2.7(5)
H(7.1)	−2(3)	−299(3)	196(2)	8.3(9)
H(7.2)	−125(3)	−286(3)	121(3)	9(1)
H(8.1)	−0(6)	−88(3)	175(3)	11(1)
H(8.2)	−1(4)	−130(3)	77(3)	9(1)
H(9.1)	−90(3)	−385(3)	322(2)	7.2(9)
H(9.2)	−235(4)	−362(3)	269(4)	14(2)
H(10.1)	−260(3)	−407(3)	418(3)	9(1)
H(8.3)	−113(3)	−95(3)	150(3)	9(1)
H(10.2)	−279(3)	−265(4)	374(4)	12(1)
H(10.3)	−175(4)	−295(4)	456(4)	19(2)
H(1)	0	0	375(2)	2.9(6)

conclusion that the iron dihydride complex was formed as the product of oxidative addition of H_2 to **1**. X-ray structural study confirmed this conclusion (see below) and showed that the same complex was formed on interaction of the Fe^{II} precursor with H_2. In the latter case H_2 evidently replaces aryl groups, producing diphenyl.

To determine the influence of the nature of aryl groups on the arylating ability of organolithium compounds and also the reactivity of resulting aryl complexes with respect to H_2 we investigated the reaction of $FeCl_3$ with *o*-, *m*- and *p*-tolyllithium and mesityllithium. *o*-Tolyllithium and mesityllithium were found to be inert towards $FeCl_3$, presumably because of steric hindrances caused by methyl groups close to the carbon–lithium bond. *p*-Tolyllithium and *m*-tolyllithium arylate $FeCl_3$ in ether solution in reactions apparently similar to that of phenyllithium. The *m*- and *p*-tolyl-iron complexes react with dihydrogen at room temperature and atmospheric pressure. The reaction with the *m*-tolyl complex is complete within 24 h, that with *p*-tolyl complex within 3 h, whereas for the phenyl iron complex the reaction is complete within 5 min. These differences may be explained by steric hindrances on *cis–trans* isomerisation of the dihydride complexes: evi-

Table 2

Atomic coordinates ($\times 10^4$, for H $\times 10^3$) and their equivalent isotropic (isotropic for H atoms) temperature factors U_{eq} ($\times 10^3$ Å^2) in **3**

Atom	x	y	z	U
Fe	0	1194(1)	1/4	15(1)
C(1)	885(2)	1187(2)	1891(2)	21(1)
C(4)	2088(2)	1216(2)	1003(2)	33(1)
C(6)	1686(2)	1640(2)	2138(2)	26(1)
C(2)	746(2)	744(2)	1168(2)	26(1)
C(3)	1320(2)	762(2)	742(2)	32(1)
C(5)	2263(2)	1655(2)	1713(2)	32(1)
C(7)	2699(3)	1243(3)	534(3)	51(2)
C(8)	0	2441(3)	1/4	19(1)
C(13)	0	-53(3)	1/4	20(1)
C(11)	0	4213(3)	1/4	30(2)
C(16)	0	-1827(3)	1/4	27(2)
C(12)	0	5125(3)	1/4	48(3)
C(10)	-703(2)	3775(2)	1967(2)	27(1)
C(9)	-707(2)	2929(2)	1981(2)	22(1)
C(14)	-433(2)	-542(2)	1804(2)	22(1)
C(15)	-444(2)	-1388(2)	1799(2)	25(1)
C(17)	0	-2737(3)	1/4	43(2)
O(2)	-404(1)	2352(1)	147(1)	26(1)
O(1)	2627(1)	75(1)	3362(1)	27(1)
C(25)	2228(2)	-1117(2)	2549(2)	35(1)
C(24)	2827(2)	-397(2)	2765(2)	29(1)
C(18)	-853(3)	1824(2)	-518(2)	38(1)
C(19)	-1640(3)	1465(3)	-381(2)	43(1)
C(20)	380(2)	2778(2)	23(2)	33(1)
C(21)	683(3)	3386(2)	689(2)	39(1)
C(23)	3095(3)	1062(3)	4410(3)	48(2)
C(22)	3325(2)	636(2)	3767(2)	38(1)
Li(1)	-246(4)	1952(3)	1242(3)	25(2)
Li(2)	1395(3)	444(3)	2993(3)	26(2)
H(1)	-85	122	159	40

dently *cis*-dihydride must be formed initially and perhaps reversibly, and in the process of the more stable *trans*-isomer formation there should be some bending of the Fe–Ar bond hindered by methyl groups.

X-ray structural study has shown that the Fe^{II} dihydride complexes $[(H)_2FePh_4]Li_4 \cdot 4Et_2O$ (**2**) and $[(H)_2Fe(p\text{-}Tol)_4]Li_4 \cdot 4Et_2O$ (**3**) had similar structures with virtually identical geometry of the central octahedral moiety $[Ar_4FeH_2]$ and *trans*-positions of two hydride H atoms at the Fe atom. The structure of complex **2** is shown in Fig. 1. The central fragment of the structure of **3** (without diethyl ether solvate molecules) is shown in Fig. 2. Fe–H bond lengths are 1.64(3) and 1.69(2) Å, which is quite typical for known Fe–H distances in iron hydrides. In the IR spectrum of **2** a very intense broad band at 1200 cm^{-1} is found, corresponding to Fe–H vibration since it is shifted to 898 cm^{-1} on replacement of H_2 by D_2. For **3**, ν(Fe–H) and ν(Fe–D) are 1223 cm^{-1} and 910 cm^{-1} respectively.

The complexes may be considered formally as lithium salts of tetra-anions $[Ar_4FeH_2]^{4-}$ with lithium cations solvated by ether molecules. Four lithium ions

Table 3

Selected bond lengths d (Å) and bond angles ω (deg) in **2**

Bond	d	Angle	ω
Fe–C(1)	2.056(2)	C(1)–Fe–C(1′) [a]	90.0(1)
Fe–H(1)	1.64(3)	C(1)–Fe–C(1″) [b]	178.4(1)
Fe–Li	2.465(5)	C(1)–Fe–H(1)	89.2(6)
Li–H(1)	1.83(3)	Li–H(1)–Fe	90.2(8)
Li–O	1.976(5)	Li–H(1)–Li″ [b]	179.6(1.1)
Li–C(1)	2.238(6)	Fe–Li–O	175.1(3)
Li–C(1′) [a]	2.223(6)	Fe–C(1)–C(2)	124.3(2)
Li–C(2′) [a]	2.426(6)	Fe–C(1)–C(6)	124.3(2)
Li–C(6)	2.438(6)	C(2)–C(1)–C(6)	111.3(2)
C(1)–C(2)	1.434(4)	C(1)–C(2)–C(3)	124.2(2)
C(2)–C(3)	1.398(4)	C(2)–C(3)–C(4)	120.9(3)
C(3)–C(4)	1.372(4)	C(3)–C(4)–C(5)	118.4(3)
C(4)–C(5)	1.367(4)	C(4)–C(5)–C(6)	121.0(3)
C(5)–C(6)	1.403(4)	C(5)–C(6)–C(1)	124.3(3)
C(1)–C(6)	1.419(4)	C(7)–O–C(9)	109.6(2)
O–C(7)	1.423(4)	O–C(7)–C(8)	109.4(3)
O–C(9)	1.455(4)	O–C(9)–C(10)	109.7(3)
C(7)–C(8)	1.472(6)	Li–O–C(7)	121.5(2)
C(9)–C(10)	1.448(5)	Li–O–C(9)	118.8(2)

[a] The C(1′) and C(2′) are related to the reference C(1) and C(2) atoms by the symmetry operation (y, $-x$, $1-z$). [b] The C(1″) and Li″ are related to the reference C(1) and Li atoms by the symmetry operation ($-x$, $-y$, z).

are arranged tetrahedrally around the central iron atom (above each second face of the octahedron) at Fe–Li distances of 2.465(5) Å in **2** and 2.460(5) Å in **3**. The Li–Li distances are 3.37 and 4.11 Å (**3**). **2** has an ideal crystallographic symmetry $\bar{4}$, while for **3** the symmetry axis 2 passes through an iron atom and the C(8), C(11), C(12), C(13), C(16) and C(17) atoms of the two tolyl ligands. However, the non-crystallographic symmetry of complex **3** is also close to tetrahedral.

It is interesting to note that cell parameters and the structure of **2** are close to those found earlier [2] for the complex $Fe^0(PhLi)_4 \cdot (Et_2O)_4$ **1** in which the metal atom has a distorted square-planar coordination: the C–Fe–C bond angles are 61 and 119°. In **2** and **3** the C–Fe–C bond angles are, however, 90 and 180° and the equatorial ligands of the Fe atom in these complexes form ideally square-planar arrangement. The Fe–C bond lengths in **2** and **3** are almost equal, 2.056(2) Å and 2.058(4)–2.091(3) Å, and virtually coincide with those found for **1** (2.058(9) Å) though the Fe atoms in these complexes are in different valent states. It should be noted for comparison that in the tetrahedral naphthyl Fe^{II} complex the Fe–C bonds are 2.104(6) and 2.147(6) Å, *i.e.* considerably longer than in **1**, **2** and **3**.

In both structures **2** and **3** the Li atoms form ideal (**2**) and close to ideal (**3**) tetrahedral environments around the central Fe^{II} atom, and interact strongly with hydride ligands and carbon atoms of aryl rings. The Li–H(1) bond length in **2** is 1.83 Å, the angle Li–H(1)–Li′ 180(1)°. The bond lengths Li(1)–H(1) and Li(2)–H(1′) in **3** are 1.80(2) and 1.86(2) Å respectively, the corresponding angle at the H(1) atom being 177(1)°. Each Li atom in **2** forms four short Li–C contacts with the C(1), C(2), C(6) atoms of phenyl ligands (the Li ··· C distances are in the range

Table 4

Selected bond lengths *d* (Å) and bond angles *ω* (deg) in **3**

Bond	*d*	Angle	*ω*
Fe-C(1)	2.091(3)	C(1)-Fe-C(8)	90.3(1)
Fe-C(8)	2.059(4)	C(1)-Fe-C(13)	89.7(1)
Fe-C(13)	2.018(4)	C(8)-Fe-C(13)	180.0
Fe-Li(1)	2.460(5)	Fe-H(1)-Li(1)	87 (2)
Fe-Li(2)	2.448(5)	Fe-H(1')-Li(2)	90 (2)
Fe-H(1)	1.69(2)	Li-H(1)-Li(2')	177 (2)
Li(1)-H(1)	1.80(2)	Fe-Li(1)-O(2)	168.6(3)
Li(2)-H(1')	1.86(2)	Fe-Li(2)-O(1)	167.3(3)
Li(1)-C(1)	2.180(6)	Fe-C(1)-C(2)	123.8(2)
Li(1)-C(2)	2.598(7)	Fe-C(1)-C(6)	124.2(6)
Li(2)-C(1)	2.199(6)	Fe-C(8)-C(9)	124.3(2)
Li(2)-C(6)	2.635(7)	Fe-C(13)-C(14)	124.5(2)
Li(1)-C(8)	2.267(6)	C(2)-C(1)-C(6)	112.0(3)
Li(1)-C(9)	2.365(7)	C(1)-C(2)-C(3)	124.0(3)
Li(2)-C(13)	2.265(5)	C(2)-C(3)-C(4)	121.9(3)
Li(2)-C(14)	2.375(7)	C(3)-C(4)-C(5)	116.6(4)
Li(1)-O(2)	1.978(6)	C(4)-C(5)-C(6)	121.5(3)
Li(2)-O(1)	1.962(6)	C(5)-C(6)-C(1)	124.0(3)
C(1)-C(2)	1.421(4)	C(3)-C(4)-C(7)	121.8(3)
C(2)-C(3)	1.398(6)	C(5)-C(4)-C(7)	121.6(3)
C(3)-C(4)	1.383(5)	C(8)-C(9)-C(10)	129.5(3)
C(4)-C(5)	1.389(5)	C(9)-C(10)-C(11)	121.1(3)
C(5)-C(6)	1.403(6)	C(10)-C(9)-C(10')	117.3(4)
C(1)-C(6)	1.423(4)	C(10)-C(11)-C(12)	121.4(2)
C(4)-C(2)	1.510(7)	C(14)-C(13)-C(14')	111.1(4)
C(8)-C(9)	1.429(4)	C(13)-C(14)-C(15)	124.9(3)
C(9)-C(10)	1.397(4)	C(14)-C(15)-C(16)	120.9(3)
C(10)-C(11)	1.391(4)	C(15)-C(16)-C(15')	117.2(4)
C(11)-C(12)	1.505(7)	C(15)-C(16)-C(17)	121.4(2)
C(13)-C(14)	1.428(4)	Li(1)-O(2)-C(18)	116.8(3)
C(14)-C(15)	1.397(4)	Li(1)-O(2)-C(20)	119.3(2)
C(15)-C(16)	1.391(4)	C(18)-O(2)-C(20)	111.6(3)
C(16)-C(17)	1.503(7)	O(2)-C(18)-C(19)	108.2(3)
O(2)-C(18)	1.435(4)	O(2)-C(20)-C(21)	109.0(3)
O(2)-C(20)	1.438(5)	Li(2)-O(1)-C(22)	119.3(3)
O(1)-C(22)	1.438(4)	Li(2)-O(1)-C(24)	113.5(2)
O(1)-C(24)	1.443(5)	C(22)-O(1)-C(24)	111.5(3)
C(18)-C(19)	1.443(5)	O(1)-C(22)-C(23)	108.2(3)
C(20)-C(21)	1.499(5)	O(1)-C(24)-C(25)	108.6(3)
C(22)-C(23)	1.500(7)		

2.22–2.44 Å), the distance from two Li atoms to the C(1) atom σ-bonded to Fe being the shortest (2.223(6) and 2.238(6) Å).

Due to the strong Li–C interaction the C–C bonds in Ph ligands are somewhat elongated, *e.g.* the C(1)–C(2) and C(1)–C(6) bond lengths in **2** are 1..434(4) and 1.419(4) Å as compared with 1.39 Å in benzene. Similar elongation is observed for **3**, where the shortest distances are: Li(1) ··· C(1) 2.180(6), Li(1) ··· C(8) 2.267(6), Li(2) ··· C(1) 2.199(6) and Li(2) ··· C(13) 2.265(5) Å. In **2** the weak bands at 527,

Table 5

Atomic coordinates ($\times 10^4$, for Fe $\times 10^5$, for H $\times 10^3$) and their equivalent isotropic temperature factors B_{eq} (Å^2) in **4**

Atom	x	y	z	B_{eq}
Fe1	3600(3)	7314(2)	7088(2)	3.2(2)
Fe2	2425(3)	6521(2)	7909(2)	3.1(2)
Fe3	8679(3)	7841(2)	2958(2)	2.5(2)
Fe4	7218(3)	8133(2)	2027(2)	3.0(2)
O1	484(1)	694(1)	881(1)	5.4(5)
O2	379(1)	549(1)	631(1)	4.2(5)
O3	50(1)	821(1)	729(1)	5.1(5)
O4	601(1)	867(1)	565(1)	4.6(6)
O5	071(1)	484(1)	926(1)	5.3(6)
O6	748(1)	596(1)	243(1)	7.2(6)
O7	650(1)	900(1)	349(1)	6.4(7)
O8	992(1)	910(1)	146(1)	9.7(7)
O9	102(1)	711(1)	484(1)	8.6(7)
O10	424(1)	852(1)	50(1)	7.3(6)
C1	327(2)	833(1)	687(1)	4.7(7)
C2	305(2)	868(1)	741(1)	5.1(7)
C3	271(2)	940(1)	727(1)	7.5(9)
C4	255(2)	971(1)	669(1)	7.8(9)
C5	271(2)	941(1)	623(1)	6.3(8)
C6	302(2)	870(1)	629(1)	5.6(7)
C7	503(1)	745(1)	715(1)	3.3(6)
C8	552(2)	798(1)	729(1)	5.9(8)
C9	649(2)	802(1)	746(1)	8.2(9)
C10	716(2)	748(1)	743(1)	7.7(9)
C11	688(2)	691(1)	729(1)	4.7(7)
C12	587(2)	689(1)	714(1)	4.6(7)
C13	398(2)	724(1)	612(1)	5.3(7)
C14	310(2)	718(1)	582(1)	4.5(7)
C15	327(2)	703(1)	518(1)	6.4(8)
C16	428(2)	695(1)	487(1)	7.2(8)
C17	515(2)	695(1)	513(1)	8.6(10)
C18	497(2)	709(1)	576(1)	5.8(7)
C19	184(2)	573(1)	764(1)	4.4(7)
C20	113(2)	583(1)	722(1)	4.9(7)
C21	75(2)	532(1)	696(1)	6.6(8)
C22	111(2)	466(1)	713(1)	5.2(7)
C23	180(2)	454(1)	753(1)	4.4(7)
C24	214(2)	504(1)	779(1)	3.7(6)
C25	290(1)	595(1)	869(1)	2.6(6)
C26	252(1)	609(1)	935(1)	3.3(6)
C27	296(2)	576(1)	987(1)	4.3(7)
C28	372(2)	530(1)	978(1)	5.2(7)
C29	416(2)	515(1)	915(1)	5.1(7)
C30	374(2)	550(1)	864(1)	3.7(6)
C31	101(1)	684(1)	841(1)	2.8(6)
C32	003(2)	662(1)	844(1)	4.1(6)
C33	98(2)	692(1)	874(1)	5.2(7)
C34	92(2)	746(1)	905(1)	4.7(7)
C35	004(2)	767(1)	906(1)	4.2(6)
C36	100(2)	736(1)	877(1)	4.1(6)
C37	14(1)	781(1)	286(1)	1.9(5)
C38	46(1)	743(1)	243(1)	3.1(6)

Table 5 (continued)

Atom	*x*	*y*	*z*	B_{eq}
C39	147(2)	742(1)	232(1)	5.9(8)
C40	230(2)	780(1)	262(1)	7.0(8)
C41	210(2)	816(1)	308(1)	7.1(8)
C42	106(2)	815(1)	316(1)	5.4(7)
C43	874(1)	693(1)	353(1)	1.9(5)
C44	950(1)	640(1)	365(1)	3.1(6)
C45	946(2)	573(1)	402(1)	5.6(7)
C46	866(2)	559(1)	434(1)	4.7(7)
C47	783(2)	602(1)	424(1)	4.4(7)
C48	791(2)	668(1)	386(1)	4.5(7)
C49	896(1)	836(1)	369(1)	3.0(6)
C50	937(2)	905(1)	358(1)	3.6(6)
C51	947(1)	947(1)	408(1)	5.0(7)
C52	919(2)	925(1)	464(1)	4.6(7)
C53	884(2)	861(1)	478(1)	5.3(7)
C54	875(2)	818(1)	432(1)	3.7(6)
C55	601(1)	745(1)	184(1)	3.5(6)
C56	577(1)	710(1)	131(1)	3.0(6)
C57	497(2)	659(1)	123(1)	4.8(7)
C58	433(2)	645(1)	167(1)	7.1(8)
C59	455(2)	672(1)	222(1)	5.1(7)
C60	535(2)	723(1)	228(1)	4.2(7)
C61	631(1)	890(1)	191(1)	2.4(5)
C62	521(2)	894(1)	192(1)	4.4(7)
C63	458(2)	950(1)	186(1)	5.7(7)
C64	512(2)	11(1)	178(1)	7.5(9)
C65	616(2)	21(1)	176(1)	5.4(7)
C66	673(2)	961(1)	181(1)	4.3(7)
C67	738(1)	835(1)	110(1)	2.8(6)
C68	705(1)	892(1)	59(1)	3.1(6)
C69	717(1)	902(1)	996(1)	2.8(6)
C70	776(1)	855(1)	979(1)	2.8(6)
C71	820(1)	794(1)	27(1)	2.8(6)
C72	798(1)	788(1)	89(1)	2.7(6)
C73	429(2)	748(1)	916(1)	6.7(8)
C74	514(2)	782(1)	933(1)	8.8(10)
C75	729(1)	729(1)	934(1)	6.9(8)
C76	570(2)	668(1)	914(1)	7.0(8)
C77	331(2)	816(1)	67(1)	6.5(8)
C78	243(2)	865(1)	34(1)	7.9(9)
C79	272(2)	908(1)	978(1)	7.3(8)
C80	394(2)	917(1)	5(1)	4.6(7)
C81	10(2)	452(1)	904(1)	7.6(9)
C82	12(2)	372(1)	923(1)	6.9(8)
C83	122(2)	369(1)	933(1)	6.0(8)
C84	130(2)	431(1)	962(1)	7.1(8)
C85	680(2)	538(1)	263(1)	6.8(8)
C86	673(3)	506(1)	207(1)	10.9(11)
C87	778(2)	504(1)	194(1)	8.1(9)
C88	812(2)	578(1)	204(1)	6.7(8)
C89	466(2)	513(1)	654(1)	6.6(8)
C90	497(2)	461(1)	610(1)	6.6(8)
C91	392(2)	446(1)	593(1)	6.6(8)
C92	350(2)	520(1)	582(1)	5.8(8)

Table 5 (continued)

Atom	*x*	*y*	*z*	B_{eq}
C93	996(3)	976(1)	162(1)	11.7(12)
C94	31(2)	24(1)	110(1)	9.0(10)
C95	108(3)	985(1)	101(1)	13.7(14)
C96	38(3)	918(1)	93(1)	14.2(14)
C97	9(2)	801(1)	678(1)	4.9(7)
C98	58(2)	860(1)	656(1)	5.6(7)
C99	97(2)	885(1)	722(1)	7.1(8)
C100	6(2)	884(1)	748(1)	7.5(9)
C101	711(3)	852(2)	579(1)	14.4(14)
C102	786(3)	888(1)	512(1)	10.7(11)
C103	733(3)	865(2)	483(2)	17.2(16)
C104	612(2)	890(1)	508(1)	14.4(14)
C105	192(3)	666(1)	486(1)	11.0(11)
C106	219(2)	632(1)	558(1)	8.4(9)
C107	126(2)	632(1)	581(1)	9.9(10)
C108	46(2)	690(1)	539(1)	9.4(10)
C109	635(2)	974(1)	359(1)	10.1(10)
C110	534(5)	957(2)	380(2)	24.9(24)
C111	491(4)	898(2)	375(2)	19.6(19)
C112	585(3)	849(1)	381(1)	12.4(13)
Li1	433(4)	674(2)	815(2)	4.4(5)
Li2	307(4)	616(3)	674(2)	6.2(6)
Li3	163(4)	781(2)	760(2)	7.3(6)
Li4	489(4)	812(3)	630(3)	8.1(7)
Li5	131(4)	572(2)	873(2)	4.4(5)
Li6	−739(4)	681(2)	1264(2)	3.1(5)
Li7	−734(4)	877(3)	1298(2)	8.3(6)
Li8	−917(4)	837(2)	1185(2)	5.4(6)
Li9	−1015(4)	751(2)	1396(2)	5.7(6)
Li10	−561(4)	837(2)	1107(2)	5.7(7)
HM1	245	696	717	3.0
HM2	331	702	784	3.0
HM3	329	643	731	3.0
HM4	−822	769	1222	3.0
HM5	−840	840	1241	3.0
HM6	−730	770	1274	3.0
H2	317	842	789	4.0
H3	259	967	765	4.0
H4	227	22	664	4.0
H5	261	967	677	4.0
H6	310	845	589	4.0
H8	507	841	723	4.0
H9	666	847	761	4.0
H10	789	750	753	4.0
H11	739	650	726	4.0
H12	566	640	704	4.0
H14	228	722	610	4.0
H15	264	702	496	4.0
H16	441	682	439	4.0
H17	595	688	484	4.0
H18	561	707	599	4.0
H20	89	635	706	4.0
H21	19	544	668	4.0
H22	87	429	693	4.0
H23	207	404	764	4.0
H24	265	489	810	4.0
H26	196	647	945	4.0

473, 429 cm^{-1} correspond to lithium–carbon vibrations shifted to 547, 493, 438 cm^{-1} upon replacement of ^{7}Li by ^{6}Li. It should be noted that the Fe atom is somewhat displaced from the equatorial coordination plane formed by the phenyl carbon atoms. These atoms are pair-wise shifted by 0.028 Å from the mean plane. The planes of phenyl ligands form dihedral angles of 66.7° with the FeC_4 equatorial plane. In **3** the atoms of corresponding FeC_4 fragment are strictly coplanar, Ph rings forming dihedral angles of 128.7, 74.0 and 75.9° with the plane. Other geometric parameters of the structures investigated have the usual values.

The crystals of dihydrides **2** and **3** are readily soluble in 2,5-dimethyltetrahydrofuran and are stable in this solvent for a long time. In THF and diethyl ether the complexes are unstable. On standing in THF solution **2** is transformed into another complex which proved to be the dimeric iron–lithium hydride complex $(FePh_3(\mu_2\text{-}H)_3FePh_3)Li_5 \cdot 5THF$ (**4**). The complex **3** undergoes a similar but much slower transformation in diethyl ether, in which **3** as distinct from **2** is readily soluble, producing the dimeric complex **5**. The dimerisation of the complexes is accompanied by the loss of two LiPh and one LiH molecules without change in iron oxidation state. However, the process is apparently more complicated: phenyl groups form diphenyl which indicates that some redox process with the solvent takes place.

Molecular structures of both dimeric complexes **4** and **5** were determined using X-ray diffraction. A general view of one of the two independent molecules **4** is given in Fig. 3. Five solvate THF-molecule-coordinating lithium atoms are not shown here. Central fragments of structure **4** containing atoms of Fe, Li and bridging hydride H atoms are shown in Fig. 4.

Both complexes **4** and **5** have similar structures of the central fragments with two end-on and three bridging Li atom positions between the two Fe atoms, bound in the complex by the Fe–Fe bonds, 2.389(1) and 2.379(1) Å in **4** and 2.378 Å in **5**, indicating strong metal–metal interaction. End-on lithium atoms are positioned on the continuation of the Fe–Fe vector forming an almost linear Li–Fe–Fe–Li fragment. The symmetry of the bridging Li atom positions is close to third order (see Fig. 4).

In both independent molecules of **4** three μ_2 bridging hydride H atoms were objectively located. The similarities in synthetic procedure, and the similarity of the structures found by X-ray diffraction study and results of elemental analysis suggest that similar hydride bridges are present in compound **5**.

Complexes **4** and **5** are characterized by quite similar geometrical parameters. The bridging Li atoms are situated at the distances 2.61–2.73(1) Å from the Fe atoms, whereas the end-on Li atoms form significantly shorter bonds in the range 2.45–2.53(1) Å. The distances from the bridging hydride atoms to the Li atoms vary in the rather broad range 1.53–2.70 Å (see Fig. 4), all angles of the Li–H–Li type being close to 180°. Bridging H atoms are bonded to the Fe atoms symmetrically within the limits of accuracy of their localisation. The Fe–H bond lengths vary in the interval 1.43–1.78 Å, bond angles Fe–H–Fe are in the range 91–102°. All bridging Li and H atoms are coplanar within 0.05–0.07 Å (for two independent molecules of **4**), distances from their mean plane to Fe(1,2) and Fe(3,4) atoms being 1.16, 1.23 and 1.18, 1.19 Å respectively. The Fe–Fe bond vectors are almost normal to these planes. The H–H distances in the μ_2 bridges vary from 1.52 to 2.08 Å; however, the relatively low accuracy of localisation of H atoms does not

Table 6

Atomic coordinates ($\times 10^4$) and their equivalent isotopic ($\times 10^3$ Å^2) and isotopic (for C(43)–C(72) atoms) temperature factors U_{eq} ($\times 10^3$ Å^2) in **5**

Atom	*x*	*y*	*z*	U_{eq}
Fe(1)	142(1)	1933(1)	2236(1)	24(1)
Fe(2)	−279(1)	1918(1)	3467(1)	24(1)
Li(1)	572(12)	1966(10)	951(11)	46(8)
Li(2)	−716(11)	1900(9)	4772(11)	41(7)
Li(3)	−31(12)	2942(8)	2892(11)	38(7)
Li(4)	1053(12)	1363(8)	3332(11)	37(7)
Li(5)	−1189(11)	1382(8)	2349(11)	37(7)
O(1)	761(5)	2047(3)	−142(4)	49(3)
O(2)	−1044(4)	1902(3)	5755(4)	35(3)
O(3)	486(5)	3688(3)	3120(5)	52(3)
O(4)	1517(5)	609(3)	3503(5)	56(3)
O(5)	−2262(4)	1209(3)	1851(5)	46(3)
C(1)	147(6)	2662(5)	1655(6)	26(4)
C(2)	−547(6)	2992(5)	1450(6)	34(4)
C(3)	−565(7)	3512(5)	1096(7)	48(5)
C(4)	116(8)	3768(5)	894(7)	45(5)
C(5)	809(7)	3471(5)	1078(6)	41(5)
C(6)	826(6)	2937(5)	1435(6)	31(4)
C(7)	84(8)	4341(6)	510(8)	73(7)
C(8)	1259(6)	1704(5)	2120(6)	29(4)
C(9)	1893(6)	1960(5)	2600(6)	33(4)
C(10)	2686(6)	1800(5)	2631(7)	38(5)
C(11)	2920(7)	1385(5)	2152(7)	39(5)
C(12)	2318(7)	1125(5)	1670(7)	46(5)
C(13)	1534(7)	1278(5)	1650(7)	36(5)
C(14)	3776(7)	1208(6)	2197(8)	66(6)
C(15)	−383(6)	1461(5)	1359(6)	27(4)
C(16)	−301(6)	865(5)	1345(7)	39(4)
C(17)	−621(7)	517(6)	755(8)	50(5)
C(18)	−1076(8)	724(6)	104(8)	52(5)
C(19)	−1187(7)	1310(6)	84(7)	51(5)
C(20)	−858(6)	1662(5)	699(6)	37(4)
C(21)	−1417(8)	368(6)	−567(8)	85(7)
C(22)	−619(6)	2640(5)	3934(6)	28(4)
C(23)	−1277(6)	2959(4)	3578(6)	33(4)
C(24)	−1548(7)	3467(5)	3859(7)	41(5)
C(25)	−1180(7)	3694(5)	4538(7)	39(5)
C(26)	−536(7)	3412(5)	4906(7)	39(5)
C(27)	−265(6)	2911(5)	4619(6)	34(4)
C(28)	−1462(9)	4245(5)	4841(8)	72(6)
C(29)	459(6)	1662(4)	4390(6)	25(4)
C(30)	1204(6)	1938(5)	4603(6)	35(4)
C(31)	1754(7)	1786(5)	5233(7)	42(5)
C(32)	1601(7)	1351(5)	5717(7)	39(5)
C(33)	899(7)	1056(5)	5529(6)	39(5)
C(34)	368(6)	1200(5)	4898(6)	33(4)
C(35)	2186(7)	1202(6)	6430(7)	67(6)
C(36)	−1212(6)	1449(5)	3682(6)	28(4)
C(37)	−1197(7)	851(5)	3659(6)	38(4)
C(38)	−1848(8)	508(5)	3750(7)	51(5)
C(39)	−2565(7)	738(6)	3881(7)	44(5)
C(40)	−2596(7)	1312(6)	3925(6)	41(5)

Table 6 (continued)

Atom	x	y	z	U_{eq}
C(41)	−1961(6)	1658(5)	3834(6)	35(4)
C(42)	−3264(7)	363(6)	3939(8)	71(6)
C(43)	1177(12)	1624(9)	−538(11)	125(7)
C(44)	1283(13)	1971(10)	−1270(13)	155(9)
C(45)	837(11)	2418(8)	−1379(10)	113(7)
C(46)	619(9)	2566(6)	−597(8)	71(4)
C(47)	824(12)	1153(9)	−637(12)	161(9)
C(48)	−191(9)	2745(7)	−650(9)	90(5)
C(49)	−1885(7)	1940(6)	5852(7)	49(3)
C(50)	−1901(7)	1797(5)	6688(6)	47(3)
C(51)	−1104(7)	1946(6)	7081(7)	50(3)
C(52)	−543(7)	1846(6)	6490(7)	52(4)
C(53)	−2195(8)	2511(5)	5599(7)	59(4)
C(54)	161(7)	2210(5)	6527(7)	55(4)
C(55)	156(17)	4291(12)	3097(15)	171(10)
C(56)	984(21)	4539(16)	3208(20)	385(25)
C(57)	1044(20)	4372(13)	3898(18)	278(18)
C(58)	1307(15)	3646(12)	3707(16)	191(12)
C(59)	−482(12)	4436(10)	2706(13)	166(10)
C(60)	1781(14)	3591(11)	3278(14)	197(12)
C(61)	2177(13)	452(9)	4063(12)	124(7)
C(62)	2338(16)	−138(11)	3682(16)	231(13)
C(63)	1634(14)	−243(11)	4186(15)	175(10)
C(64)	911(16)	32(10)	3536(14)	173(10)
C(65)	2857(10)	733(8)	4107(10)	124(7)
C(66)	934(17)	−61(13)	2832(16)	287(19)
C(67)	−2646(12)	692(9)	1658(11)	116(7)
C(68)	−3419(11)	786(9)	1266(12)	127(7)
C(69)	−3520(13)	1369(10)	1287(14)	166(9)
C(70)	−2746(11)	1670(8)	1508(12)	119(7)
C(71)	−2240(9)	194(7)	1800(9)	84(5)
C(72)	−2741(9)	2165(7)	1898(9)	91(5)

allow the significance of these differences to be discussed. Coordination of Li atoms around iron in both structures is close to tetrahedral. The O atoms of solvent molecules coordinate the positively charged Li atoms as in all previous cases.

A characteristic feature of the structures is a large number of short contacts of the Li ··· C type with the aryl C atoms bonded to the Fe atom. Each end-on Li atom forms six Li ··· C contacts in the range 2.07–2.64 Å in **4** and 2.21–2.57 Å in **5**. Each bridging Li atom forms four Li ··· C contacts in the range 2.34–2.77 Å in **4** and 2.22–2.72 Å in **5**. An analogous Li ··· C interaction is typical for complexes **2**–**5** as also for lithium complexes with other transition metals [5,6]. Weak bands at 518, 457, 392, 385 cm^{-1} correspond to Li ··· C vibrations in IR spectra of the complexes, as they are shifted to 522, 474, 400 cm^{-1} on replacement of ^7Li by ^6Li.

Interaction with dinitrogen

Coordinatively saturated hydride Fe^{II} mononuclear complexes do not react with N_2, *e.g.* when dissolved in 2,5-dimethyltetrahydrofuran. In THF and ether they

Table 7

Selected bond lengths *d* (Å) in **4**

Molecule 1		Molecule 2	
Bond	*d*	Bond	*d*
Fe(1)–Fe(2)	2.389(1)	Fe(3)–Fe(4)	2.379(1)
Fe(1)–Li(1)	2.68(1)	Fe(3)–Li(6)	2.68(1)
Fe(1)–Li(2)	2.73(1)	Fe(3)–Li(7)	2.62(1)
Fe(1)–Li(3)	2.73(1)	Fe(3)–Li(8)	2.61(1)
Fe(1)–Li(4)	2.45(1)	Fe(3)–Li(9)	2.49(1)
Fe(2)–Li(1)	2.70(1)	Fe(4)–Li(6)	2.69(1)
Fe(2)–Li(2)	2.66(1)	Fe(4)–Li(7)	2.58(6)
Fe(2)–Li(3)	2.73(1)	Fe(4)–Li(8)	2.64(1)
Fe(2)–Li(5)	2.36(1)	Fe(4)–Li(10)	2.51(1)
Fe(1)–C(1)	2.04(1)	Fe(3)–C(37)	1.95(1)
Fe(1)–C(7)	1.94(1)	Fe(3)–C(43)	1.97(1)
Fe(1)–C(13)	2.02(1)	Fe(3)–C(49)	2.01(1)
Fe(2)–C(19)	2.02(1)	Fe(4)–C(55)	2.01(1)
Fe(2)–C(25)	2.04(1)	Fe(4)–C(61)	1.93(1)
Fe(2)–C(31)	2.03(1)	Fe(4)–C(67)	2.00(1)
Li(1)–O(1)	1.84(1)	Li(6)–O(6)	1.85(1)
Li(1)–C(7)	2.30(1)	Li(6)–C(43)	2.31(1)
Li(1)–C(12)	2.52(1)	Li(6)–C(48)	2.50(1)
Li(1)–C(25)	2.39(1)	Li(6)–C(55)	2.36(1)
Li(1)–C(30)	2.57(1)	Li(6)–C(60)	2.68(1)
Li(2)–O(2)	1.85(1)	Li(7)–O(7)	1.87(1)
Li(2)–C(13)	2.48(1)	Li(7)–C(49)	2.34(1)
Li(2)–C(14)	2.51(1)	Li(7)–C(50)	2.72(1)
Li(2)–C(19)	2.22(1)	Li(7)–C(61)	2.29(1)
Li(3)–O(3)	1.80(1)	Li(7)–C(66)	2.66(1)
Li(3)–C(1)	2.44(1)	Li(8)–O(6)	1.87(1)
Li(3)–C(2)	2.52(1)	Li(8)–C(37)	2.32(1)
Li(3)–C(36)	2.44(1)	Li(8)–C(67)	2.46(1)
Li(4)–O(4)	1.95(1)	Li(8)–C(72)	2.55(1)
Li(4)–C(1)	2.21(1)	Li(9)–O(9)	1.98(1)
Li(4)–C(6)	2.61(1)	Li(9)–C(37)	2.28(1)
Li(4)–C(13)	2.29(1)	Li(9)–C(42)	2.40(1)
Li(4)–C(18)	2.54(1)	Li(9)–C(43)	2.21(1)
Li(5)–O(5)	1.96(1)	Li(9)–C(44)	2.49(1)
Li(5)–C(19)	2.24(1)	Li(9)–C(49)	2.23(1)
Li(5)–C(24)	2.61(1)	Li(9)–C(54)	2.64(1)
Li(5)–C(25)	2.12(1)	Li(10)–O(10)	1.89(1)
Li(5)–C(26)	2.52(1)	Li(10)–C(55)	2.17(1)
Li(5)–C(31)	2.26(1)	Li(10)–C(56)	2.47(1)
Li(5)–C(32)	2.53(1)	Li(10)–C(61)	2.26(1)
C(1)–C(2)	1.43(1)	Li(10)–C(62)	2.50(1)
C(1)–C(6)	1.42(1)	Li(10)–C(67)	2.28(1)
C(7)–C(8)	1.36(2)	Li(10)–C(68)	2.45(1)
C(7)–C(12)	1.52(2)	C(37)–C(38)	1.46(1)
C(13)–C(14)	1.46(2)	C(37)–C(42)	1.41(1)
C(13)–C(18)	1.38(2)	C(43)–C(44)	1.42(1)
C(19)–C(20)	1.42(1)	C(43)–C(48)	1.43(1)
C(19)–C(24)	1.41(1)	C(49)–C(50)	1.46(1)
C(25)–C(26)	1.44(1)	C(49)–C(54)	1.41(1)
C(25)–C(30)	1.38(2)	C(55)–C(56)	1.41(1)
C(31)–C(32)	1.43(1)	C(55)–C(60)	1.42(1)
C(31)–C(36)	1.40(1)	C(61)–C(62)	1.42(1)
		C(61)–C(66)	1.48(1)
		C(67)–C(68)	1.40(1)
		C(67)–C(72)	1.43(1)

Table 8

Selected bond lengths *d* (Å) and bond angles *ω* (deg) in 5

Bond	*d*	Bond	*d*	Angle	*ω*
Fe(1)–Fe(2)	2.378(2)	Li(2)–C(41)	2.57(2)	Li(1)–Fe(1)–Fe(2)	179.1(5)
Fe(1)–Li(1)	2.48(2)	Li(3)–O(3)	1.98(2)	Li(2)–Fe(2)–Fe(1)	179.7(5)
Fe(1)–Li(3)	2.67(2)	Li(3)–C(1)	2.34(2)	C(1)–Fe(1)–Li(1)	79.7(5)
Fe(1)–Li(4)	2.67(2)	Li(3)–C(2)	2.58(2)	C(8)–Fe(1)–Li(1)	60.8(5)
Fe(1)–Li(5)	2.65(2)	Li(3)–C(22)	2.32(2)	C(15)–Fe(1)–Li(1)	58.0(6)
Fe(2)–Li(2)	2.52(2)	Li(3)–C(23)	2.59(2)	C(1)–Fe(1)–Fe(2)	120.3(3)
Fe(2)–Li(3)	2.67(2)	Li(4)–O(4)	1.95(2)	C(8)–Fe(1)–Fe(2)	119.8(3)
Fe(2)–Li(4)	2.66(2)	Li(4)–C(8)	2.35(2)	C(15)–Fe(1)–Fe(2)	122.3(3)
Fe(2)–Li(5)	2.65(2)	Li(4)–C(9)	2.49(2)	C(1)–Fe(1)–C(8)	96.1(4)
Fe(1)–C(1)	2.00(1)	Li(4)–C(29)	2.35(2)	C(1)–Fe(1)–C(15)	96.5(4)
Fe(1)–C(8)	2.02(1)	Li(4)–C(30)	2.60(2)	C(8)–Fe(1)–C(15)	95.7(4)
Fe(1)–C(15)	2.01(1)	Li(5)–O(5)	1.96(2)	Li(1)–Fe(1)–Li(3)	115.6(7)
Fe(2)–C(22)	2.01(1)	Li(5)–C(15)	2.37(2)	Li(1)–Fe(1)–Li(4)	117.4(6)
Fe(2)–C(29)	2.01(1)	Li(5)–C(16)	2.77(2)	Li(1)–Fe(1)–Li(5)	116.7(6)
Fe(2)–C(36)	2.01(1)	Li(5)–C(36)	2.36(2)	C(22)–Fe(2)–Li(2)	60.0(6)
Li(1)–O(1)	2.01(2)	Li(5)–C(37)	2.63(2)	C(29)–Fe(2)–Li(2)	59.1(5)
Li(1)–C(1)	2.24(2)	C(1)–C(2)	1.43(2)	C(36)–Fe(2)–Li(2)	58.5(5)
Li(1)–C(6)	2.46(3)	C(1)–C(6)	1.43(2)	C(22)–Fe(2)–Fe(1)	120.1(3)
Li(1)–C(8)	2.31(2)	C(8)–C(9)	1.41(1)	C(29)–Fe(2)–Fe(1)	120.6(3)
Li(1)–C(13)	2.50(2)	C(8)–C(13)	1.42(2)	C(36)–Fe(2)–Fe(1)	121.7(3)
Li(1)–C(15)	2.21(2)	C(15)–C(16)	1.41(2)	C(22)–Fe(2)–C(29)	96.1(4)
Li(1)–C(20)	2.52(2)	C(15)–C(20)	1.40(1)	C(22)–Fe(2)–C(36)	96.1(4)
Li(1)–C(20)	2.52(2)	C(15)–C(20)	1.40(1)	C(22)–Fe(2)–C(36)	96.1(4)
Li(2)–O(2)	1.89(2)	C(22)–C(23)	1.42(1)	C(29)–Fe(2)–C(36)	96.1(4)
Li(2)–C(22)	2.30(2)	C(22)–C(27)	1.42(1)	Li(2)–Fe(2)–Li(3)	116.4(6)
Li(2)–C(27)	2.53(2)	C(29)–C(30)	1.43(2)	Li(2)–Fe(2)–Li(4)	116.0(6)
Li(2)–C(29)	2.57(2)	C(29)–C(34)	1.43(2)	Li(2)–Fe(2)–Li(5)	116.0(6)
Li(2)–C(29)	2.27(2)	C(29)–C(34)	1.43(2)	Li(2)–Fe(2)–Li(5)	117.0(6)
Li(2)–C(34)	2.46(2)	C(36)–C(37)	1.41(2)	–	–
Li(2)–C(36)	2.26(2)	C(36)–C(41)	1.43(2)	–	–

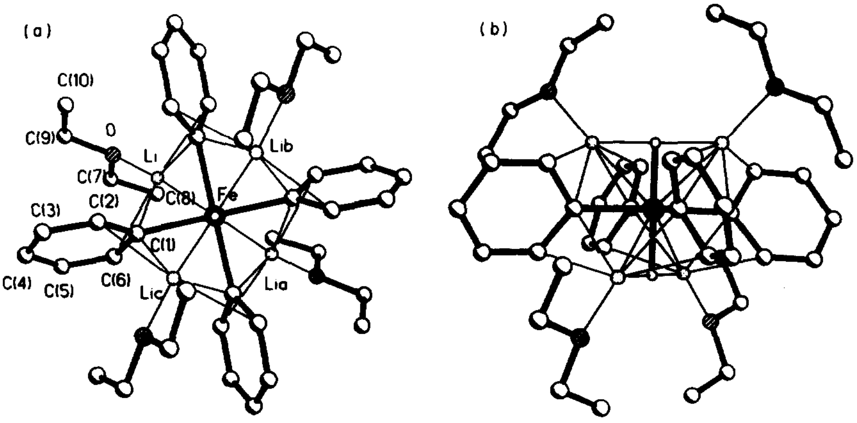

Fig. 1. Molecular structure of $[(H)_2FePh_4]Li_4 \cdot 4Et_2O$ (2). (a) and (b) show different views.

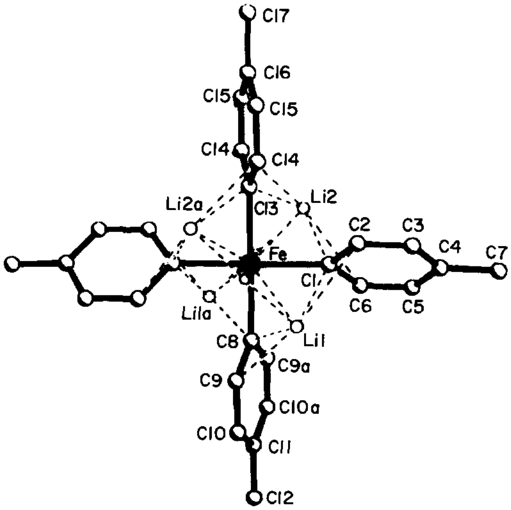

Fig. 2. Molecular structure of $[(H)_2Fe(p\text{-}Tol)_4]Li_4 \cdot 4Et_2O$ (3); the Et_2O molecules are omitted for clarity.

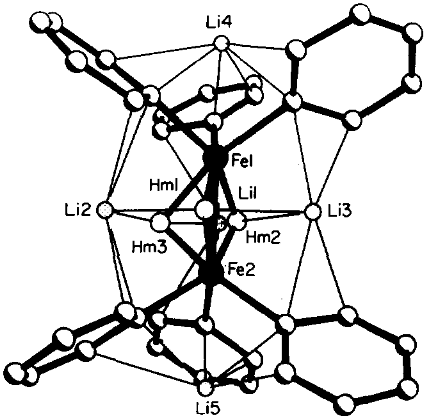

Fig. 3. Molecular structure of one of the two independent molecules $[Ph_3Fe(\mu_2\text{-}H)_3FePh_3]Li_5 \cdot 5THF$ (4); the THF molecules are omitted for clarity.

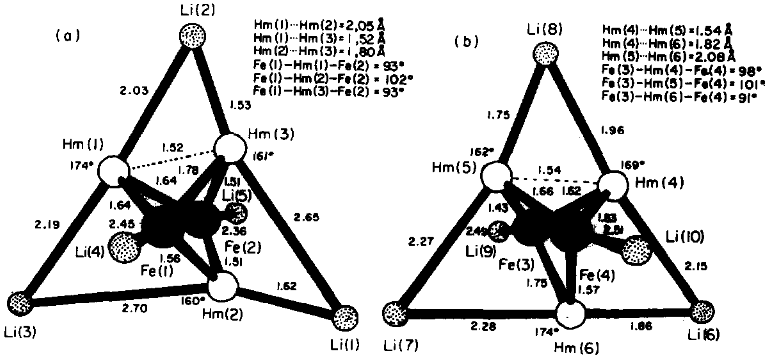

Fig. 4. Central fragment of the molecular structure of $[Ph_3Fe(\mu_2\text{-}H)_3FePh_3]Li_5 \cdot 5THF$ (4).

slowly acquire the ability to interact with dinitrogen. It has been found that it is the binuclear complexes **4** and **5**, produced from **2** and **3**, that are in fact active towards N_2. The isolated complexes **4** and **5** react with dinitrogen in THF or ether solutions forming N_2 complexes. These produce N_2H_4 (*ca.* 25% per Fe) and N_2 (*ca.* 75% per Fe) when decomposed by HCl. The structure of the complexes formed and the mechanism of N_2 coordination and reaction are presently under investigation.

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