STRUCTURE OF THE INTERMEDIATE IRON(0) COMPLEX ISOLATED FROM THE DINITROGEN FIXING SYSTEM LiPh + FeCl$_3$

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Summary

The structure of the complex Fe^0(LiPh)$_4$(Et$_2$O)$_4$, active towards dinitrogen, reveals a flat rectangular structure formed by carbon atoms of four phenyl rings linked by σ-bonds with Fe^0 atom. The comparatively short interatomic distance between two carbon atoms of phenyl rings indicates some interaction between them. The possible mechanism of the reaction with N$_2$ is considered.

Introduction

At present, a number of systems are known which contain transition metal compounds and strong reducing agents in aprotic media and reduce dinitrogen finally to nitride complexes of the transition metal [1,2]. The structure of intermediate low valent transition metal complexes active towards dinitrogen is usually unknown and this naturally hinders the mechanistic conclusions about the reaction with dinitrogen.

The kinetic study of dinitrogen reduction in homogeneous ether solutions containing a mixture of interacting FeCl$_3$ and PhLi has led to the mechanism, where an iron(0) complex (complex A) was suggested to be active towards N$_2$ [3]. The complex may be accumulated in considerable concentrations under an argon atmosphere. In the present paper the results of an X-ray study of single crystals of the complex isolated from the solution are described, which have helped to reveal its structure. Some conclusions about its reaction with N$_2$ are also made from the structure. A preliminary communication concerning the subject has been published elsewhere [4].

Experimental

The synthesis and isolation of the Fe^0 complex were performed as follows: an ether solution of iron trichloride was added dropwise to an ether solution of

TABLE 1

FRACTIONAL ATOMIC COORDINATES AND THEIR ANISOTROPIC PARAMETERS^a ($\times 10^4$)

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	5000(0)	5000(0)	5000(0)	76	76	60	63	0	0
C(1)	4590(8)	3422(8)	5015(14)	117	75	90	61	52	62
C(2)	4778(10)	2674(10)	5792(9)	76	85	94	40	30	−15
C(3)	4589(12)	1623(16)	5817(12)	107	120	127	−56	64	−2
C(4)	4114(13)	1227(14)	5029(15)	190	196	158	−18	−234	41
C(5)	3890(14)	1880(12)	4127(10)	181	80	131	−34	43	−42
C(6)	4063(10)	2941(12)	4243(11)	67	123	106	65	−77	22
O	6215(10)	2751(11)	2711(8)	194	298	105	26	35	56
C(7)	5761(18)	2668(17)	1834(17)	506	214	120	130	24	−38
C(8)	6467(22)	1728(19)	2994(16)	616	292	160	633	−309	−112
C(9)	5403(20)	3723(24)	1435(18)	188	695	173	−181	22	180
C(10)	7215(21)	1527(21)	3787(24)	223	384	529	353	330	397
Li	5596(18)	3659(29)	3734(16)	85	284	69	−122	5	18

^{a} $T = \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

phenyllithium at $-20°C$ under vigorous stirring up to a $LiC_6H_5 : FeCl_3$ ratio = 10 : 1. The final Fe complex concentration was ca. 1×10^{-2} M. The solution was subsequently warmed up to $0°C$, lithium chloride precipitated from the solution was removed by filtration and the solution was kept at room temperature for about 24 hours. The raspberry-red solution then was evaporated to dryness, the excess of C_6H_5Li and of diphenyl formed was washed on the filter with pentane and the dry powder of the product dissolved in ether (conc. $3-4 \times 10^{-2}$ M). After standing for several days at $-15°C$, dark-red (almost black) crystals of complex A precipitated and were used for crystallographic analysis.

The precipitation of the crystals from the solution is possibly the result of the removal of some ether molecules from the coordination sphere of the complex (e.g., cf. [5]). The spectrum of the solutions formed on dissolving the crystals in tetrahydrofuran (at low temperature) is similar to that in ether before precipitation. However, THF solutions of complex A change colour to red-brown at room temperature; presumably THF molecules replace those of ether in the coordination sphere. The complex A solution in THF (as well as initial solutions in ether) is active towards N_2. Thus when standing in N_2 atmosphere for ca. 24 h the complex in THF reduces N_2 to a product forming N_2H_4 on decomposition with dry HCl, the amount of hydrazine per iron complex being close to that in initial ether solution of the whole system, $FeCl_3 + LiC_6H_5$ [3].

For X-ray investigations a single crystal of complex A (size $0.2 \times 0.3 \times 0.7$ mm) was sealed in a glass capillary (diameter 0.05 cm) under argon. Cell dimensions of the crystals of A and intensities ($I \geqslant 2\sigma$) of 502 independent reflections in the range $(\sin \theta / \lambda)_{max} = 0.589$ were measured (Syntex P$\bar{1}$ diffractometer, $\lambda / Mo\text{-}K_\alpha$), graphite monochromator, $\theta / 2\theta$ scan, no absorption correction). The structure was solved by the direct method and refined by a least-squares procedure using full matrix

TABLE 2

COORDINATES AND ISOTROPIC THERMAL PARAMETERS FOR H ATOMS AND C–H BOND LENGTHS

Atom	x	y	z	B_j (Å^2)	C–H (Å)
H(2) [a]	0.481(9)	0.326(7)	0.634(7)	5.6	1.0(1)
H(3)	0.504(14)	0.106(9)	0.639(8)	8.4	1.2(1)
H(4)	0.400(8)	0.031(9)	0.502(7)	8.1	1.2(1)
H(5)	0.321(10)	0.181(11)	0.367(10)	9.5	1.1(2)
H(6)	0.362(9)	0.360(10)	0.382(7)	7.8	1.1(1)
H(7)	0.603(12)	0.222(13)	0.110(10)	10.1	1.2(2)
H(7′)	0.540(9)	0.205(11)	0.205(9)	10.1	1.0(1)
H(8)	0.674(12)	0.139(11)	0.234(13)	10.3	1.0(2)
H(8′)	0.591(12)	0.107(11)	0.315(11)	10.3	1.1(2)
H(9)	0.472(12)	0.381(11)	0.127(10)	11.2	0.9(2)
H(9′)	0.591(12)	0.375(11)	0.080(10)	11.2	1.1(2)
H(9″)	0.563(11)	0.408(12)	0.210(9)	11.2	1.0(2)
H(10)	0.768(14)	0.084(14)	0.384(10)	11.4	1.0(2)
H(10′)	0.785(14)	0.185(14)	0.395(10)	11.4	0.9(2)
H(10″)	0.667(12)	0.150(13)	0.447(10)	11.4	1.1(2)

[a] Numbering of the hydrogen atoms corresponds to that of the carbon atoms which they are bonded to.

refinement with anisotropic temperature factors for all non-hydrogen atoms. Hydrogen atoms were localized by a difference synthesis. Isotropic temperature parameters of the respective carbon atoms were assigned to the H atoms and positional parameters were refined. The final R index was equal to 0.078. All the calculations were performed using the Roentgen-75 program [6].

Coordinates of non-hydrogen atoms and their anisotropic temperature factors are listed in Table 1. H atom coordinates with isotropic temperature parameters are presented in Table 2, corresponding C–H bond lengths being listed in the last column of the Table.

Results and discussion

The crystals of complex A were found to be tetragonal, $a = b = 12.624(4)$ Å, $c = 13.250(8)$ Å, $V = 2110.6$ Å^3, $M = 688.519$, $d_{calc.} = 1.08$ g/cm^3, $Z = 2$, space group $P4_22_12$. The projection of the structure of A along the c direction is shown in Fig. 1.
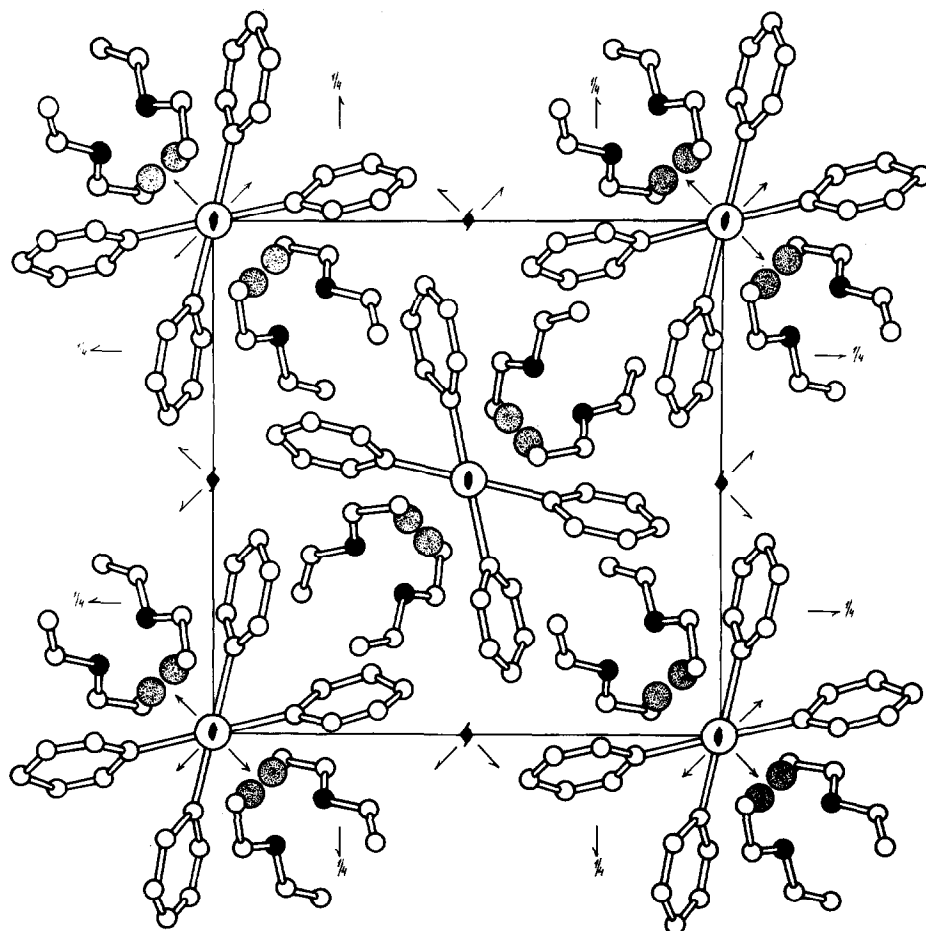

Fig. 1. The crystal structure of the complex $[(C_6H_5)_4Fe][LiO(C_2H_5)_2]_4$, projected along the c axis.
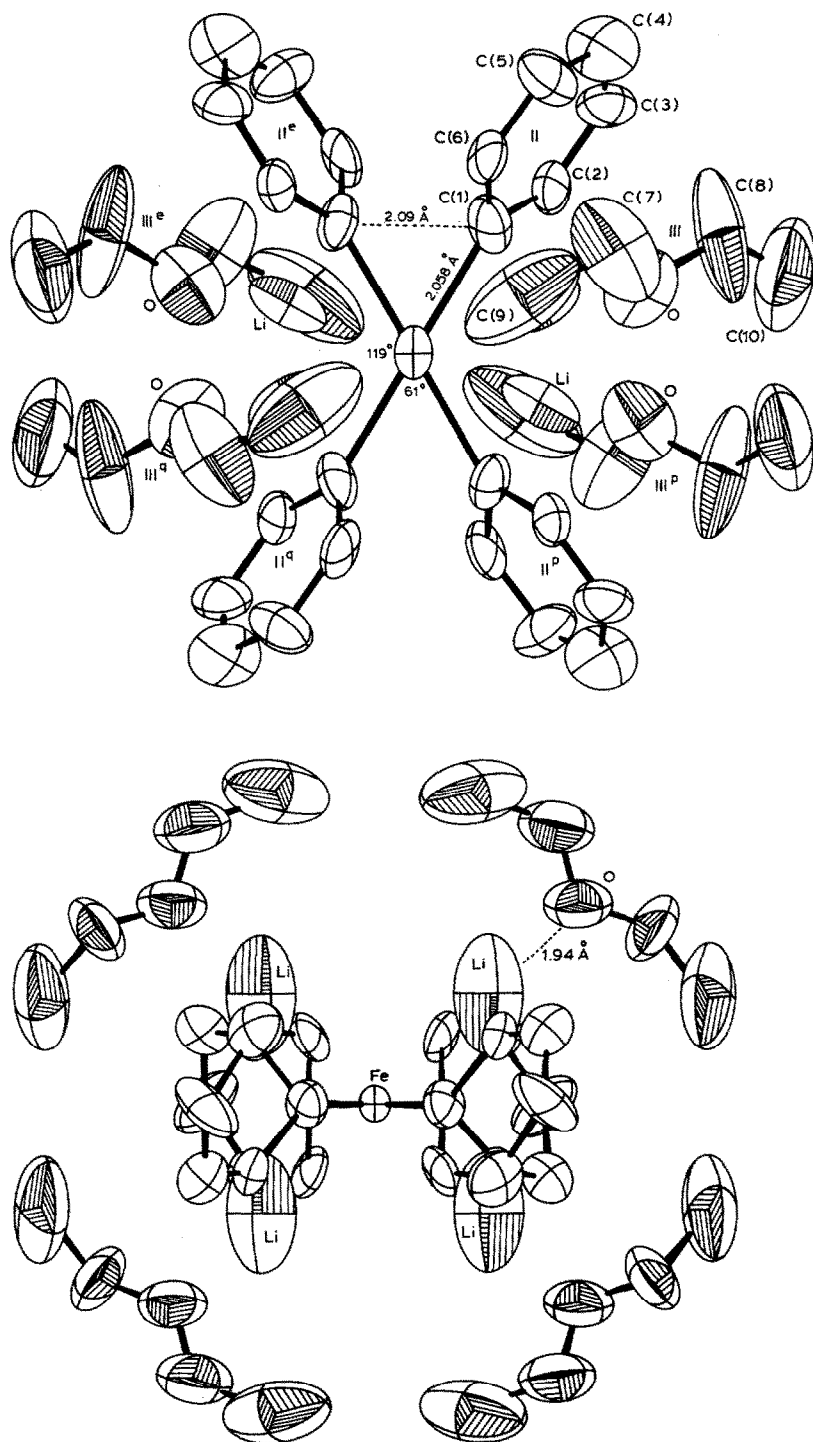
Fig. 2. (a) Some important interatomic distances (Å) and bond angles (deg.) in the complex; (b) molecular structure of the complex, projected onto average plane of four Li atoms and the Fe atom.

The complex (of composition $Fe(LiPh)_4(Et_2O)_4$) may be considered as the lithium salt of the anion $[FePh_4]^{4-}$, each lithium cation being solvated by an diethyl ether molecule. Thus the zero oxidation state of iron in complex A, which was suggested in the mechanistic study of the interaction of iron trichloride with phenyllithium [3], was confirmed.

Some interatomic distances and angles in complex A are given in Fig. 2a. Figure 2b shows the structure of the complex projected onto the averaged plane of the four Li and the Fe atoms. The iron atom occupies a special 222 position in the crystal and has a flat-rectangular configuration with four σ-bonded carbon atoms of phenyl rings, C–Fe–C angles being 61 and 119°. A full list of bond lengths and angles of the complex is presented in Table 3. As can be seen from the Table, the value of the σ-bond length of Fe–C in complex A is equal to 2.058(9) Å, whereas the values of the two corresponding bond lengths in tetrahedral naphthyl complex of Fe^{II} are somewhat longer (2.104(6) and 2.147(6) Å [7]).

The comparatively short distance (2.09 Å) between two carbon atoms of the neighbouring phenyl groups (Fig. 2a) deserves special attention, since it demonstrates the existence of interaction between the phenyl groups in the complex.

The lithium cations are located approximately on the straight lines connecting Fe and O atoms (Fe–Li–O angle is 172°) and Li^+ ions are rather close not only to ether oxygen atoms $r(Li \cdots O) = 1.94$ Å, but also to two carbon atoms $r[Li \cdots C(1)] = 2.14$ Å and $r[Li \cdots C(6)] = 2.24$ Å. The interatomic $Li \cdots Fe$ distance equals to 2.50 Å and is shorter than that for a naphthyliron complex (2.797 Å).

TABLE 3

INTERATOMIC DISTANCES d (Å) AND BOND ANGLES ω (deg)

Distance	d	Angle	ω
Fe–C(1)	2.058(9)	C(1)–Fe–C(1 ^{e})	61(1)
C(1)–C(2)	1.42(2)	C(1)–Fe–C(1 ^{p})	119(1)
C(2)–C(3)	1.35(2)	C(1)–Fe–Li	55(1)
C(3)–C(4)	1.30(3)	Li–Fe–Li ^{e}	92(1)
C(4)–C(5)	1.48(3)	Li–Fe–Li ^{p}	149(1)
C(5)–C(6)	1.37(2)	Li–Fe–Li ^{q}	96(1)
C(6)–C(1)	1.36(2)	Fe–Li–O	172(1)
O–C(7)	1.30(3)	Fe–Li–C(1)	52(1)
O–C(8)	1.38(3)	O–Li–C(1)	135(2)
C(7)–C(9)	1.50(4)	O–Li–C(2)	109(2)
C(8)–C(10)	1.44(5)	Fe–C(1)–C(2)	128(1)
C(1) $\cdots$ C(1 ^{e}) ^{a}	2.09(2)	Fe–C(1)–C(6)	123(1)
C(1) $\cdots$ C(1 ^{p})	3.55(2)	C(2)–C(1)–C(6)	109(1)
Li–Fe	2.50(1)	C(1)–C(2)–C(3)	130(1)
Li–O	1.94(3)	C(2)–C(3)–C(4)	116(2)
Li–C(1)	2.14(3)	C(3)–C(4)–C(5)	121(2)
Li–C(6)	2.24(3)	C(4)–C(5)–C(6)	115(1)
Li $\cdots$ Li ^{e}	3.61(4)	C(5)–C(6)–C(1)	127(1)
Li $\cdots$ Li ^{q}	3.70(4)	C(7)–O–C(8)	106(2)
Li $\cdots$ C(7)	2.82(4)	O–C(7)–C(9)	112(2)
Li $\cdots$ C(8)	2.85(4)	O–C(8)–C(10)	121(2)

^{a} Symmetry matrices (in Tables 3 and 4): e: $y, x, 1-z$, p: $1-y, 1-x, 1-z$, q: $1-x, 1-y, z$.

TABLE 4

COEFFICIENTS OF $Ax + By + Cz = D$ EQUATIONS FOR SOME PLANE FRAGMENTS AND DEVIATIONS OF ATOMS FROM THESE PLANES (Å)

Atom	I	II	III	IV	V	Dihedral angles (deg)			
Fe	0.000			−0.013	0.000	I : II	55	I : III	123.5
C(1)	0.020	−0.027		−0.003		I : IV	54	I : V	90
C(1 ^{e})	−0.020					II : III	16	II : IV	59
C(1 ^{p})	−0.020					II : V	59	II : II ^{e}	61
C(1 ^{q})	0.020					II : II ^{p}	99	II : II ^{q}	47
C(2)		0.003				III : IV	71	III : V	52
C(3)		−0.006				III : III ^{e}	76	III : III ^{p}	68
C(4)		0.027				III : III ^{q}	113	IV : V	65
C(5)		−0.050				IV : IV ^{e}	50	IV : IV ^{p}	88
C(6)		0.053		0.998 ^{a}		IV : IV ^{q}	109		
O			0.099	−0.019					
C(7)			−0.061						
C(8)			0.095						
C(9)			−0.033						
C(10)			−0.100						
Li	1.677 ^{a}	−1.794 ^{a}	1.449 ^{a}	0.035	0.665				
Li ^{e}					0.665				
Li ^{p}					−0.665				
Li ^{q}					−0.665				
A	0.000	11.346	10.511	9.985	8.925				
B	−0.001	−2.250	0.532	−2.454	8.924				
C	13.250	−5.300	−7.313	7.684	−0.001				
D	6.625	1.753	4.795	7.594	8.924				

^{a} Distances corresponding to atoms not defining the plane.

Additional information about the geometry of complex A is given in Table 4, where equations of average planes of some fragments of complex A are presented, as well as deviations of atoms from the planes and dihedral angles between them. The identification of these planes is also given in Fig. 2. The average plane V through the four Li and the Fe atoms is approximately perpendicular to the plane of the four σ Fe–C bonds. This is seen in Fig. 2b, where the complex structure is projected onto plane V, where ether molecules in the complex form a bind of solvate shell.

The structure of complex A allows one to make some conclusions about the mechanism of its reaction with dinitrogen. The flat structure of the fragment $\begin{smallmatrix} C \\ C \end{smallmatrix} Fe \begin{smallmatrix} C \\ C \end{smallmatrix}$ makes it plausible to suggest approach of an N_2 molecule along the line perpendicular to the plane to form a linear $Fe \cdots N \equiv N$ fragment. The lithium cation, which must be situated close to N_2 in the complex thus formed, may take part in the subsequent reaction of the coordinated dinitrogen molecule. The addition of Li^+ to a dinitrogen molecule will facilitate the electron transfer from an iron atom:

$$Fe^0 \cdots N \equiv N \xrightarrow{Li^+} Fe^{II} - N = N - Li$$
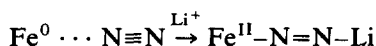
The electrophilic action of Li^+ would be similar to that of the protonating action of an acid in dinitrogen complexes of Mo^0 and W^0 [8] and also in an unspecified

iron complex [9] observed earlier. The strong reducing properties of Fe^0 suggest a two-electron reduction of N_2, the double $N \equiv N$ bond being stabilized by additional interaction with filled iron d orbitals. The short interatomic distance between carbon atoms of two phenyl rings will naturally help in further formation of biphenyl in the presence of an agent capable of reducing the complex (after its oxidation by dinitrogen). Stabilization of the transition state in the recombination of aryl rings in the coordination sphere of transition metal compounds is an obvious reason for the prevalence of such a reaction in the reduction of arylmetal complexes.

It is of interest to note that the coordination and reduction of dinitrogen with the participation of Fe^0 may be considered as a homogeneous model of N_2 reaction at the surface of metallic iron in catalytic ammonia synthesis from N_2 and H_2. Further investigation will show to what extent this suggestion is valid.

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