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STRUCTURE OF THE NAPHTHYL IRON(II) COMPLEX FORMED IN THE REACTION OF $FeCl_3$ AND $C_{10}H_7Li$

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Summary

The structure of $[(C_{10}H_7)_4Fe][LiO(C_2H_5)_2]_2$, formed by interaction of $FeCl_3$ and $C_{10}H_7Li$, has been determined. Unlike the phenyl complex, $[(C_6H_5)_4Fe]$-$[LiO(C_2H_5)_2]_4$, the naphthyl complex is not able to reduce N_2.

Molecular nitrogen has been found [1,2] to be reduced in an ether solution of the iron complex formed by the interaction of $FeCl_3$ and LiC_6H_5. The kinetics and mechanism of the interaction of the components of the nitrogen-fixing system have been studied to indicate that Fe^0 derivatives are active towards nitrogen [3]; this has been proved by isolation from the solution of the complex $[(C_6H_5)_4Fe][LiO(C_2H_5)_2]_4$ active towards nitrogen [4a].

To better understand the mechanism of this complex formation and the reason for its activity towards N_2, it is of interest to compare the earlier results with those obtained in the study of the systems formed in the interaction of iron chloride with some other organolithium compounds, particularly naphthyllithium, where the reaction with nitrogen does not take place.

Experimental

The synthesis of $[(C_{10}H_7)_4Fe][LiO(C_2H_5)_2]_2$ (complex A) [4b] was carried out under nitrogen or argon. An ether solution of $FeCl_3$ (5×10^{-4} M, 14 ml) was added dropwise to 33 ml ether solution of $C_{10}H_7Li$ (5×10^{-3} M) while vigorously stirring at -20°C. An intense crimson-purple colour of an naphthyl iron derivative was observed already at low temperature ($\lambda_{max} = 517$ nm) followed by formation of an abundant white precipitate of LiCl. The reaction mixture was gradually (during

TABLE 1

POSITIONAL PARAMETERS OF ATOMS AND THEIR ANISOTROPIC THERMAL FACTORS ($\times 10^4$) OF THE FORM $T = \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	5000(0)	2500(0)	1216(1)	30	16	78	6	0	0
C(1)	3800(4)	2350(2)	276(5)	55	17	85	−1	10	11
C(2)	3052(4)	2530(2)	801(5)	46	22	152	11	−23	−5
C(3)	2171(4)	2363(3)	336(8)	39	36	193	14	6	33
C(4)	2002(5)	1984(3)	−574(7)	60	27	175	5	−52	3
C(5)	2681(4)	1795(3)	−1131(7)	42	24	126	3	−66	5
C(6)	2520(5)	1411(3)	−2060(7)	63	33	117	6	−57	6
C(7)	3178(6)	1211(3)	−2612(6)	81	33	126	−8	−46	−12
C(8)	4067(5)	1418(3)	−2228(6)	83	30	106	11	−8	−3
C(9)	4255(4)	1787(2)	−1289(6)	61	21	85	9	−14	15
C(10)	3587(4)	1980(2)	−694(5)	57	19	82	14	2	6
C(11)	4830(4)	1771(3)	2381(6)	38	28	118	2	−10	8
C(12)	4446(4)	1818(3)	3480(6)	59	32	123	4	41	15
C(13)	4323(5)	1403(4)	4347(7)	85	37	132	1	64	−1
C(14)	4598(5)	888(4)	4159(7)	78	47	112	−19	11	41
C(15)	4963(4)	791(3)	3088(7)	45	21	122	−1	6	35
C(16)	5237(5)	276(3)	2796(9)	79	27	179	−5	−38	23
C(17)	5570(5)	174(3)	1770(10)	78	26	200	13	−5	3
C(18)	5643(4)	598(3)	922(6)	70	21	153	13	−16	−11
C(19)	5409(3)	1116(2)	1113(6)	54	25	97	10	20	−20
C(20)	5056(3)	1230(3)	2212(6)	31	21	125	−2	−36	−3
O	2473(3)	1001(2)	1751(4)	75	33	162	−2	39	−18
C(21)	2198(7)	499(4)	993(9)	120	39	278	13	33	−11
C(22)	1686(6)	1067(4)	2364(10)	98	52	256	−2	105	−32
C(23)	2983(6)	403(4)	398(8)	141	38	212	38	71	−41
C(24)	1948(7)	1526(5)	3233(8)	157	75	185	65	20	−29
Li	3489(6)	1604(4)	1564(9)	51	29	132	−4	−19	38

several hours) warmed up to room temperature, the LiCl precipitate was filtered off, and the iron complex solution was placed in a refrigerator ($T = -4$°C). Approximately a day later, dark-crimson crystals precipitated from the solution. They were then separated, washed with ether and dried under vacuum. The crystals were stable at room temperature in the absence of oxygen and moisture. For further X-ray investigations a single crystal of complex A (size: 0.5 × 0.3 × 0.3 mm) was sealed up in a glass capillary (0.07 cm) under argon.

Cell dimensions of the $[(C_{10}H_7)_4Fe][LiO(C_2H_5)_2]_2$ crystals and intensities of 1312 unique reflections with $I \geqslant 2\sigma$ were measured with a Syntex P $\bar{1}$ four-circle automatic diffractometer (λ(Mo-K_α)), graphite monochromator, $\theta/2\theta$ scan $(\sin \theta/\lambda)_{max} = 0.56$. No absorption correction was applied. The structure was solved by direct methods and refined by a least squares procedure using a full-matrix anisotropic approximation. Twenty hydrogen atoms were localized by a difference synthesis and the four hydrogen atoms of methyl groups from the ether molecule were calculated geometrically. Isotropic temperature parameters of the respective carbon atoms were assigned to the hydrogen atoms and positional parameters were refined. The final R index was equal to 0.056. All the calculations were performed using the Roentgen-75 programm [5]. Coordinates of non-hydrogen atoms and their

TABLE 2

COORDINATES ($\times 10^3$) OF HYDROGEN ATOMS

Atom [a]	x	y	z
H(2)	322(3)	280(2)	149(5)
H(3)	166(3)	245(2)	102(5)
H(4)	133(3)	182(2)	−72(5)
H(6)	189(3)	131(2)	−232(5)
H(7)	311(3)	89(2)	−332(5)
H(8)	457(3)	123(2)	−266(5)
H(9)	493(3)	194(2)	−100(5)
H(12)	426(3)	217(2)	351(5)
H(13)	400(3)	148(2)	507(5)
H(14)	453(3)	61(2)	478(5)
H(16)	510(3)	4(2)	344(5)
H(17)	581(3)	−22(2)	158(5)
H(18)	593(3)	48(2)	7(5)
H(19)	542(3)	137(2)	48(5)
H(21)	197(3)	71(2)	31(5)
H(21_1)	173(3)	17(2)	147(5)
H(22)	126(3)	133(2)	180(5)
H(22_1)	130(3)	79(2)	285(5)
H(23)	334(3)	18(2)	82(5)
H(23_1)	264(3)	2(2)	−4(5)
H(23_2)	325(3)	65(2)	−36(5)
H(24)	169(3)	165(2)	391(5)
H(24_1)	223(3)	133(2)	375(5)
H(24_2)	214(3)	180(2)	264(5)

[a] Numbering of the hydrogen atoms is in accordance with that of the corresponding carbon atoms.

anisotropic temperature factors are listed in Table 1. Hydrogen atom coordinates are presented in Table 2.

Results and discussion

The crystals of complex A are found to be monoclinic, $a = 15.38(2)$, $b = 23.47(5)$, $c = 11.56(2)$ Å, $\gamma = 102.8(1)°$, $V = 4070(2)$ Å, $M = 726.635$, $d_m = 1.19$ g/cm^3, $d_c = 1.19$ g/cm^3, $Z = 4$, space group $B2/b$. It is shown by the structure investigation that the complex is a Li salt of the dianion $[Fe(C_{10}H_7)_4]^{2-}$, where each Li^+ cation is solvated by an ether molecule, $(C_2H_5)_2O$. Figure 1 illustrates the projection of the crystal structure A along the c direction. The dianion of Fe^{II} is located on the two-fold axis and the Fe atom is coordinated in a distorted tetrahedron by σ bonds with four α-carbon atoms of naphthyl cycles. Figure 2 gives a general configuration of the complex: (a) is the view with minimum overlapping of atoms and (b) is the view along the C(1)–Fe bond; the atoms numbering scheme is also given here.

Bond lengths and angles in complex A are listed in Tables 3 and 4. The values of σ-bonds lengths of Fe–C(1) and Fe–C(11) are equal to 2.104(6) and 2.147(7) Å, respectively, and are comparable with the value of the Fe–$C(C_6H_5)$ bond (2.11 Å) in the complex $(\pi\text{-}C_5H_5)Fe(CO)(\pi\text{-}C_6H_5)Ph_3$ [6], as well as with the values of the three Fe–C σ-bonds (2.006, 2.097, and 2.088 Å) in the complex $Fe_2(CO)_6(C_6H_5C_2H)_3$ [7].

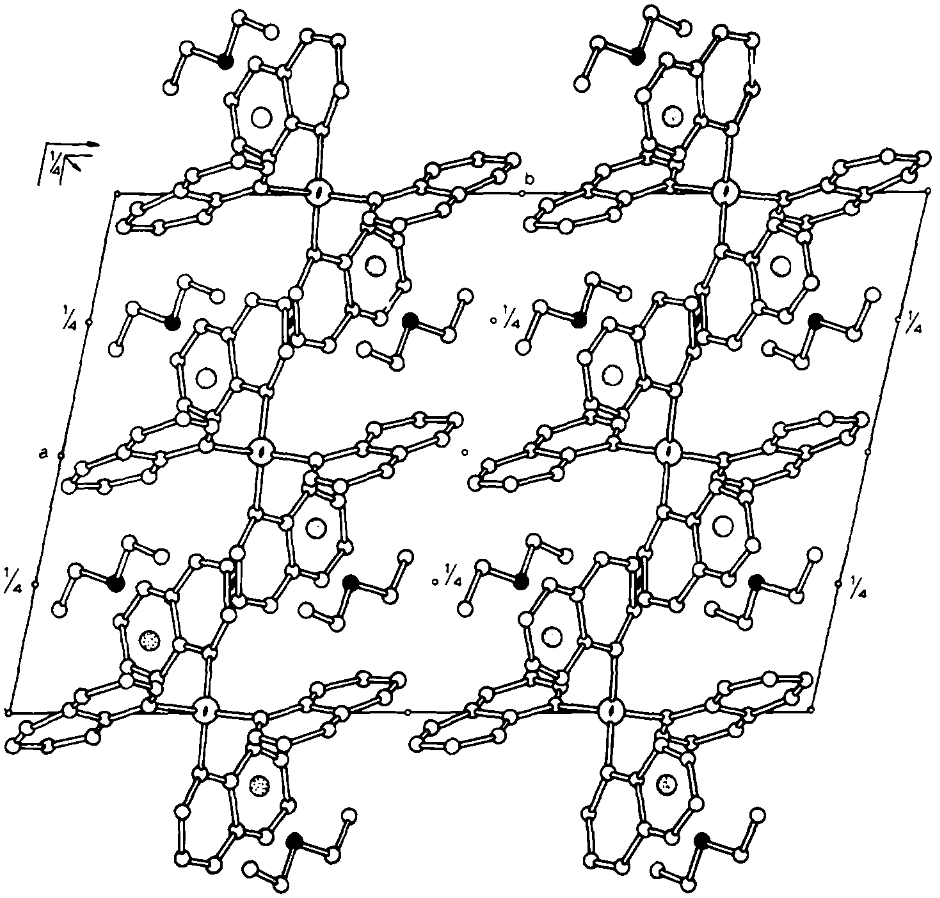

Fig. 1. Projection of the crystal structure along the *c* direction.

The other iron–carbon interatomic distances in complex A, e.g. Fe–C(2) = 3.051 Å and Fe–C(12) = 3.089 Å are much larger than the latter.

Table 5 gives the equations of the average planes of some fragments in complex A and the deviations of atoms from these planes. As can be seen from Table 5, the two naphthyl cycles, I and II (the notations of the planes are given also in Fig. 2), are non-equivalent towards the metal atom: the Fe atom is located at 0.482 Å from the plane of cycle I, whereas it is at only 0.158 Å from the plane of cycle II. The angle between the Fe–C(1) bond and plane I is 12.5°, and that between the Fe–C(11) bond and plane II is 3°. The deviations of carbon atoms from the average plane of the cycle are greater for naphthyl cycle I than for naphthyl cycle II. The low accuracy in the determination of carbon–carbon bond lengths (0.01 Å) does not allow a detailed analysis. Nevertheless, even a qualitative comparison of the geometry of naphthyl cycles in complex A with the geometry of naphthalene itself [8,9] shows the C(1)–C(2) and C(11)–C(12) bonds to be somewhat elongated.

The Li^+ cations in the crystal lie between the two naphthyl cycles, which can be seen in the left side of Fig. 2b, and they have short contacts with oxygen atoms of diethyl ether, Li–O (1.874(9) Å), and two α-carbon and two β-carbon atoms of the

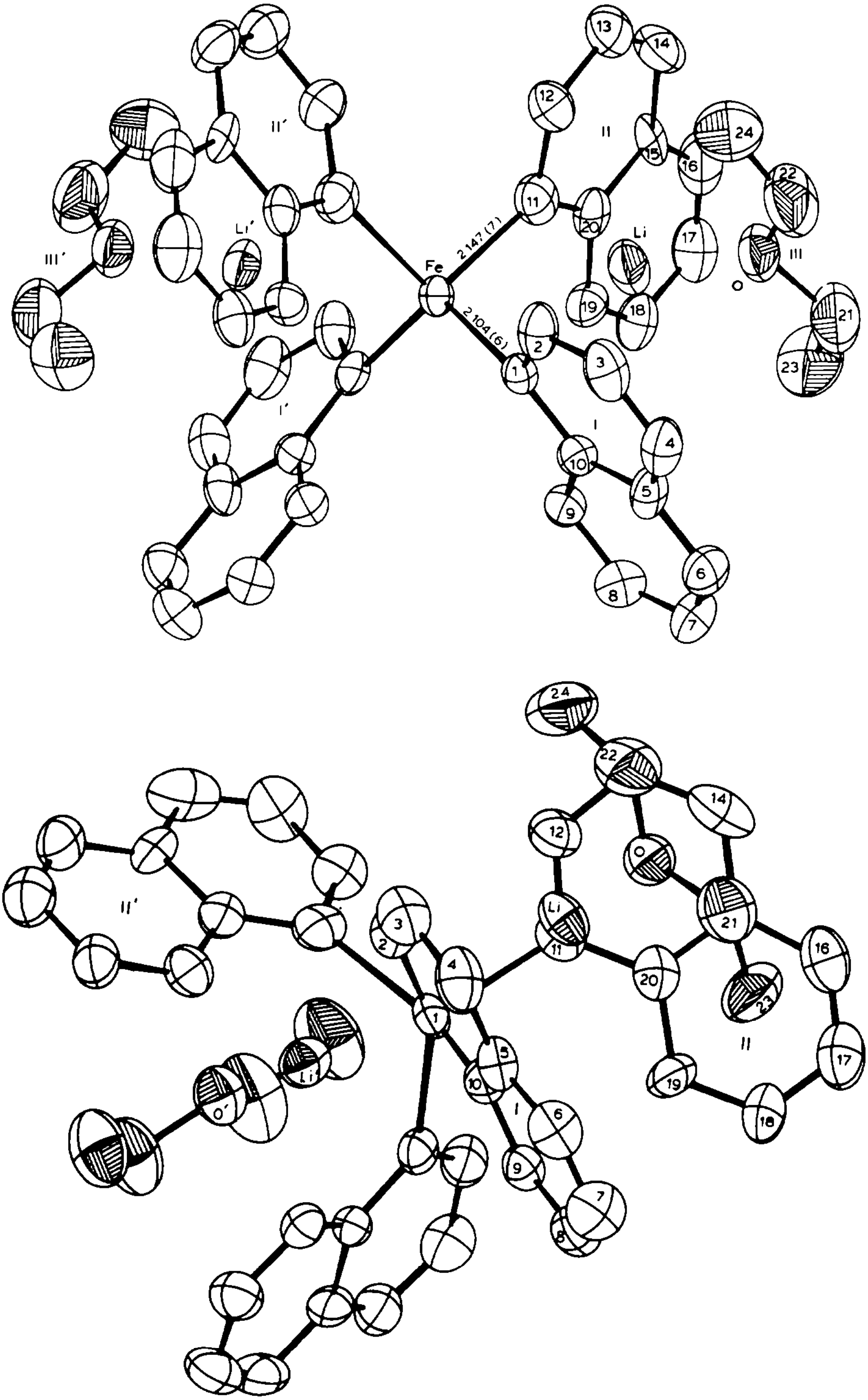

Fig. 2. The complex structure: a) projection along the direction of minimum atom overlapping; b) projection along the C(1)-Fe bond.

TABLE 3

BOND LENGTHS d(Å)

Bond	d	Bond	d
Fe–C(1)	2.104(6)	Li–O	1.874(9)
C(1)–C(2)	1.444(8)	Li–C(1)	2.267(11)
C(2)–C(3)	1.430(8)	Li–C(2)	2.569(12)
C(3)–C(4)	1.365(11)	Li–C(11)	2.223(11)
C(4)–C(5)	1.381(11)	Li–C(12)	2.646(12)
C(5)–C(6)	1.389(10)	C(2)–H(2)	1.02(5)
C(5)–C(10)	1.455(8)	C(3)–H(3)	1.16(5)
C(6)–C(7)	1.365(12)	C(4)–H(4)	1.03(4)
C(7)–C(8)	1.417(11)	C(6)–H(6)	0.99(5)
C(8)–C(9)	1.379(9)	C(7)–H(7)	1.10(5)
C(9)–C(10)	1.393(9)	C(8)–H(8)	1.09(5)
C(10)–C(1)	1.412(7)	C(9)–H(9)	1.07(5)
Fe–C(11)	2.147(7)	C(12)–H(12)	0.93(5)
C(11)–C(12)	1.416(9)	C(13)–H(13)	1.01(6)
C(12)–C(13)	1.381(11)	C(14)–H(14)	0.96(5)
C(13)–C(14)	1.383(13)	C(16)–H(16)	0.92(5)
C(14)–C(15)	1.399(11)	C(17)–H(17)	1.09(5)
C(15)–C(16)	1.406(11)	C(18)–H(18)	1.14(6)
C(15)–C(20)	1.429(10)	C(19)–H(19)	0.94(5)
C(16)–C(17)	1.335(14)	C(21)–H(21)	1.03(6)
C(17)–C(18)	1.384(12)	C(21)–H(21_1)	1.08(5)
C(18)–C(19)	1.360(9)	C(22)–H(22)	1.19(5)
C(19)–C(20)	1.430(9)	C(22)–H(22_1)	0.96(5)
C(20)–C(11)	1.402(10)	C(23)–H(23)	0.97(5)
O–C(21)	1.454(10)	C(23)–H(23_1)	1.06(5)
O–C(22)	1.440(11)	C(23)–H(23_2)	1.08(5)
C(21)–C(23)	1.450(14)	C(24)–H(24)	0.94(5)
C(22)–C(24)	1.463(14)	C(24)–H(24_1)	0.92(6)
Li–Fe	2.797(9)	C(24)–H(24_2)	0.95(6)

naphthyls (2.267, 2.223 and 2.569, 2.646 Å, respectively) (Table 3). It should be noted that the latter distances are shorter than Li–O and Li–C(phenyl) found in the structure of the complex $\{C_6H_5[NaO(C_2H_5)_2]_2[(C_6H_5)_2Ni]_2N_2Na \cdot Li_6(OC_2H_5)_4\text{-}O(C_2H_5)_2\}_2$ [10]. The interatomic distance Li–Fe is 2.797(9) Å; the Li–Fe–Li′ and Fe–Li–O angles are 163.5° and 178.4°, respectively. An average plane drawn through atoms C(1), C(11), O and Li, makes dihedral angles of approximately 90° to the planes of naphthyl cycles I and II and the plane of ether molecule III (Table 5).

Thus, the interaction of $LiC_{10}H_7$ with $FeCl_3$ results in the formation of an iron(II) complex resistant to further reduction by naphthyllithium. Evidently, the steric hindrance arising in the case of four iron-bonded naphthyl groups prevents the subsequent reaction of complex A with naphthyllithium. But in the case of phenyllithium, further reduction to Fe^0 is possible (probably via coordination of additional phenyl groups to the iron with the subsequent formation of biphenyl).

Complex A is apparently not able to reduce nitrogen, since, for example, in the reduction of N_2 with Li^+ transfer to the Fe atom coordinating the N_2 molecule, iron should increase its oxidation state from Fe^{II} to Fe^{IV} (the same mechanism is

TABLE 4

BOND ANGLES (°)

Angle		Angle	
C(1)FeC(11)	104.1(2)	C(11)C(12)C(13)	126.2(7)
C(1)FeC(1′)	117.8(2)	C(12)C(13)C(14)	118.8(8)
C(1)FeC(11′)	113.9(3)	C(13)C(14)C(15)	119.5(8)
C(11)FeC(11′)	102.3(3)	C(14)C(15)C(16)	124.0(8)
LiFeLi′	163.5(3)	C(14)C(15)C(20)	119.3(7)
FeC(1)C(2)	117.4(4)	C(16)C(15)C(20)	116.6(7)
FeC(1)C(10)	126.1(5)	C(15)C(16)C(17)	124.6(8)
C(2)C(1)C(10)	115.0(5)	C(16)C(17)C(18)	118.3(7)
C(1)C(2)C(3)	122.0(6)	C(17)C(18)C(19)	122.2(7)
C(2)C(3)C(4)	120.0(7)	C(18)C(19)C(20)	119.9(6)
C(3)C(4)C(5)	121.3(7)	C(11)C(20)C(15)	123.3(6)
C(4)C(5)C(6)	122.0(6)	C(11)C(20)C(19)	118.3(6)
C(4)C(5)C(10)	119.0(7)	C(15)C(20)C(19)	118.4(6)
C(6)C(5)C(10)	118.9(6)	C(21)OC(24)	106.4(6)
C(5)C(6)C(7)	123.1(7)	OC(21)C(23)	108.0(7)
C(6)C(7)C(8)	117.9(7)	OC(22)C(24)	108.4(7)
C(7)C(8)C(9)	120.9(7)	FeLiO	178.4(6)
C(8)C(9)C(10)	121.7(6)	OLiC(1)	131.1(6)
C(1)C(10)C(5)	122.4(6)	OLiC(11)	132.1(6)
C(1)C(10)C(9)	120.3(6)	C(1)LiC(11)	96.5(4)
C(5)C(10)C(9)	117.3(6)	OLiC(2)	110.4(5)
FeC(11)C(12)	118.7(5)	OLiC(12)	112.5(5)
FeC(11)C(20)	128.5(5)	C(2)LiC(12)	111.5(4)
C(12)C(11)C(20)	112.8(6)		

TABLE 5

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

	I	II	III	IV	Angles between planes (°)	
Fe[a]	0.482	−0.158			I:II	85.3
C(1)	0.027			0.013	I:I′	75.4
C(2)	0.029				I:II′	60.3
C(3)	−0.042				II:II′	39.4
C(4)	−0.002				III:I	163.1
C(5)	−0.015				III:II	77.8
C(6)	0.021				IV:I	86.6
C(7)	0.031				IV:II	86.4
C(8)	−0.028				IV:III	91.8
C(9)	−0.027					
C(10)	0.005					
C(11)		−0.039		0.014		
C(12)		0.013				
C(13)		0.035				
C(14)		−0.005				

TABLE 5 (continued)

	I	II	III	IV	Angles between planes (°)
C(15)		−0.018			
C(16)		−0.016			
C(17)		−0.002			
C(18)		0.029			
C(19)		0.012			
C(20)		−0.009			
O			0.072	0.021	
C(21)			−0.017		
C(22)			0.020		
C(23)			−0.028		
C(24)			−0.046		
Li				−0.048	
A	−0.537	13.088	4.293	−7.141	
B	18.266	4.802	−16.411	15.592	
C	−7.074	3.900	8.132	7.780	
D	3.920	8.061	0.915	1.178	

[a] Atom not included in the calculation of the planes.

assumed as for the reaction of the $[(C_6H_5)_4Fe][LiO(C_2H_5)_2]_4$ complex with nitrogen), which here is undoubtedly thermodynamically unfavourable.

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