Spectroscopic and Structural Characterization of 2,4,6-Tris(trifluoromethyl)phenyl-lithium·Et_2O: a Dimer Stabilized by Lithium ··· Fluorine Contacts

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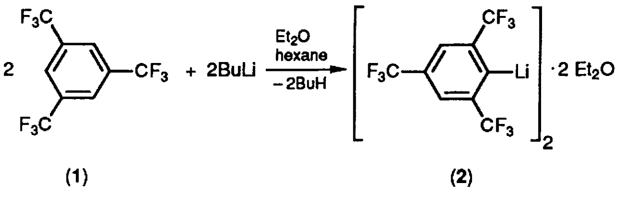
1,3,5-Tris(trifluoromethyl)benzene reacts with butyl-lithium in ether/hexane to form 2,4,6-tris(trifluoromethyl)-phenyl-lithium which has been characterized by low-temperature single-crystal *X*-ray analysis and NMR methods; the molecule exists as a dimer in which each lithium is stabilized by bonding to two carbon atoms, an oxygen of a diethyl ether molecule, and two fluorines from *ortho*-CF_3 groups.

Aryl groups with sterically demanding substituents have been used extensively to stabilize main group elements in low co-ordination numbers. Among the most well-known are 2,4,6-tri-t-butylphenyl, 2,4,6-trimethylphenyl, and 2,6-di-isopropylphenyl. Chambers *et al.* have extended this series to include 2,4,6-tris(trifluoromethyl)phenyl[1] which is sterically equivalent to 2,4,6-$Me_3C_6H_2$ but possesses quite different electronic properties giving rise to a remarkably stable diphosphene complex.[2] Of particular importance to the synthesis of 2,4,6-$(CF_3)_3C_6H_2$ derivatives is the intermediate lithium compound which, though known for some time, has not been structurally characterized.

Compound (**1**) reacts with a stoicheiometric amount of n-butyl-lithium at room temperature in diethyl ether/hexane to give the desired product (**2**); in contrast, the same reaction carried out in tetrahydrofuran can only be conducted at low temperatures. In the absence of excess of n-butyl-lithium, some of the ether/hexane solvent can be evaporated off, and upon cooling crystals of (**2**) form. Unlike 2,4,6-Bu^t_3-C_6H_2Li·*N,N,N′,N′*-tetramethylpropene-2,2-diamine,[3] (**2**) forms a dimer of formula [2,4,6-$(CF_3)_3C_6H_2Li·Et_2O]_2$.† The co-ordination geometry at lithium can be described as a distorted trigonal bipyramid (Figure 1). Two of the equatorial positions are occupied by the *ipso* carbon atoms of the phenyl groups, giving rise to a planar Li_2C_2 four-membered ring common to a number of $[Li(R)(donor)]_2$ molecules. The oxygen of a diethyl ether molecule lies in the third equatorial position producing a core structure similar to that found for $[Li\{N(SiMe_3)_2\}(Et_2O)]_2$.[4] At first sight the most striking feature of the molecule is that two fluorine atoms of *ortho*-CF_3 groups, one from each phenyl ring, are co-ordinated in the axial positions (Li–F_{av} 225.2 pm). This distance falls at the long end of the range observed for other compounds with Li ··· F contacts.[5,6] The hard Lewis acid lithium is co-ordinated by the hard Lewis base fluorine which is facilitated by the spatial arrangement of the planar C_2LiO and *ortho*-CF_3 groups. Though there do not appear to be any previous reports of structures involving trifluoromethyl fluorines acting as Lewis bases in this way, the effect is well established for other electron rich groups like $-OMe$ or $-NMe_2$.[7–9] In order to achieve the fluorine co-ordination, the two phenyl rings are canted with respect to each other forming a dihedral angle of 41°. The F–Li–F vector forms an angle of 164° with the C_2LiO plane. The average Li–C bond length is 226.4 pm which does not differ significantly from other related systems.[10–13] Even though no crystallographic symmetry exists, there are no substantial differences in the co-ordination geometries of the two lithium atoms. In contrast to 2,4,6-Bu^t_3-C_6H_2Li·*N,N,N′,N′*-tetramethylpropene-2,2-diamine, where the bulk of the substituents was believed to favour the



(**1**) (**2**)

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† *Crystal data* for (**2**) (−100 °C): $C_{26}H_{24}F_{18}Li_2O_2$, triclinic, space group $P\bar{1}$, a = 906.9(3), b = 1292.3(5), c = 1489.0(6) pm, α = 84.85(3), β = 76.78(3), γ = 69.68(2)°, U = 1.593 nm^3, Z = 2, D_c = 1.510 Mg m^{-3}, μ = 0.15 mm^{-1}, 4485 measured reflections, 4128 unique reflections, 2665 observed reflections $[|F_o| > 3.0\sigma(|F_o|)]$, $2\theta_{max.}$ = 45°, R = 0.068, R_W = 0.078. Data were collected on a Stoe-Siemens diffractometer system using graphite-monochromatized Mo-K_α radiation (λ = 0.71069 Å). The structure was solved by direct methods and refined by full-matrix least-squares techniques.[11] Only the fluorine atoms and the non-hydrogen atoms of the ether molecules were refined anisotropically. The *para*-CF_3 groups showed some rotational disorder which was modelled by the addition of a second minor component. The C–F and F–F distances where constrained to be equal for these groups. Hydrogen atoms were included in calculated positions. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

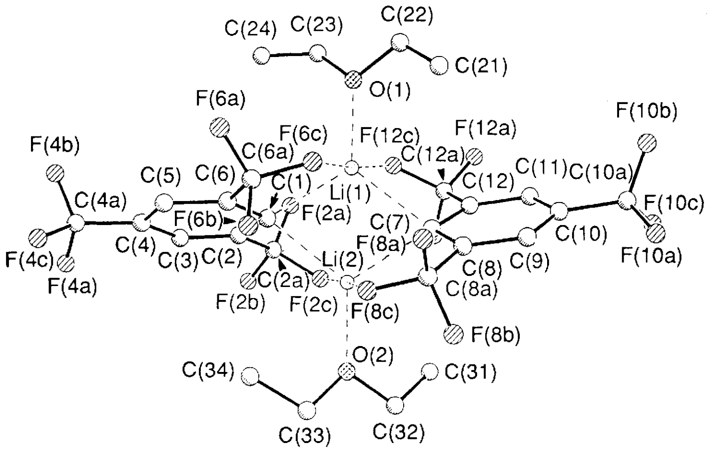

Figure 1. The *X*-ray structure of (**2**). Selected distances (pm) and angles (°): Li(1)–C(1) 222.3(9); Li(1)–C(7) 226.4(11); Li(1)–F(6c) 222.7(11); Li(1)–F(12c) 224.3(11); Li(1)–O(1) 196.4(10); Li(2)–C(1) 231.2(11); Li(2)–C(7) 225.8(9); Li(2)–F(2c) 224.3(12); Li(2)–F(8c) 229.3(12); Li(2)–O(2) 197.5(9); C(2)–Li(1)–C(7) 112.7(4); C(1)–Li(1)–O(1) 121.2(5); C(7)–Li(1)–O(1) 126.0(4); F(6c)–Li(1)–F(12c) 173.7(4); C(1)–Li(2)–C(7) 109.7(4); C(1)–Li(2)–O(2) 128.0(4); C(7)–Li(2)–O(2) 121.7(5); F(2c)–Li(2)–F(8c) 173.4(4).

monomeric form, in this compound the dimeric form is stabilized by the lithium–fluorine interactions. The absence of a chelating ligand here may also be a factor.

The ^{7}Li NMR spectrum in [^{2}H$_8$]toluene shows only a singlet at −1.24 ppm at temperatures down to −60 °C. The Li–F coupling which was observed in other systems[5] was not detected. The ^{19}F NMR spectrum in [^{2}H$_8$]toluene at −60 °C [δ −63.4 (p-CF$_3$); −63.2 ppm (o-CF$_3$); area ratio 1 : 2] showed that all *ortho*-fluorine atoms are equivalent on the NMR timescale‡ [^{1}H NMR: δ 7.9 (s, C_6H_2), 3.0 (q, CH_3CH_2), and 0.7 (t, CH_3CH_2), ratio 1 : 2 : 3].

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References

1 G. E. Carr, R. D. Chambers, and T. F. Holmes, *J. Organomet. Chem.*, 1987, **325**, 13.
2 M. Scholz, H. W. Roesky, D. Stalke, K. Keller, and F. T. Edelmann, *J. Organomet. Chem.*, 1989, **366**, 73.
3 T. Maetzke and D. Seebach, *Helv. Chim. Acta*, 1989, **72**, 624.
4 M. F. Lappert, M. J. Slade, A. Singh, J. L. Atwood, R. Rogers, and R. Shakin, *J. Am. Chem. Soc.*, 1983, **105**, 302.
5 D. Stalke, U. Klingebiel, and G. M. Sheldrick, *J. Organomet. Chem.*, 1988, **344**, 37.
6 D. Stalke, U. Klingebiel, and G. M. Sheldrick, *Chem. Ber.*, 1988, **121**, 1457.
7 D. Seebach, W. Bauer, J. Hansen, T. Laube, W. B. Schweizer, and J. D. Dunitz, *J. Chem. Soc., Chem. Commun.*, 1984, 853.
8 G. W. Klumpp, *Recl. Trav. Chim.*, 1986, **105**, 1.
9 D. R. Armstrong, D. Barr, R. Snaith, W. Clegg, R. E. Mulrey, K. Wade, D. Reed, *J. Chem. Soc., Dalton Trans.*, 1987, 1071.
10 D. Thoennes and E. Weiss, *Chem. Ber.*, 1978, **111**, 3157.
11 H. Hope and P. P. Power, *J. Am. Chem. Soc.*, 1983, **105**, 5320.
12 U. Schümann, J. Kopf, and E. Weiss, *Angew. Chem.*, 1985, **97**, 222; *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 215.
13 W. N. Setzer and P. v. R. Schleyer, *Adv. Organomet. Chem.*, 1985i, **24**, 353.
14 SHELXS-86, G. M. Sheldrick, Universität Göttingen.

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‡ Because of experimental limitations, the sample could not be cooled to lower temperatures.