Spectroscopic and Structural Characterization of 2,4,6-Tris(trifluoromethyl)phenyl-lithium·Et₂O: 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*-CF₃ 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-Me₃C₆H₂ 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-(CF₃)₃C₆H₂ 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-But₃-C₆H₂Li·N,N,N',N'-tetramethylpropene-2,2-diamine,[3]   (2) forms a dimer of formula [2,4,6-(CF₃)₃C₆H₂Li·Et₂O]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 Li₂C₂ 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(SiMe₃)₂}(Et₂O)]₂.[4] At first sight the most striking feature of the molecule is that two fluorine atoms of *ortho*-CF₃ 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 C₂LiO and *ortho*-CF₃ 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 −NMe₂.[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 C₂LiO 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-But₃-C₆H₂Li·N,N,N',N'-tetramethylpropene-2,2-diamine, where the bulk of the substituents was believed to favour the
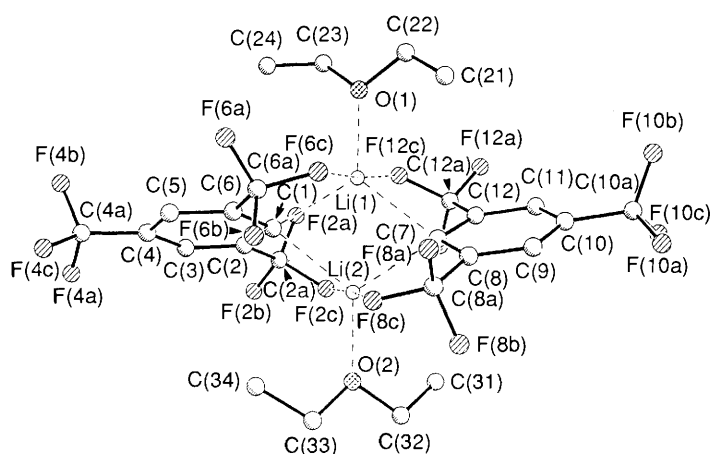
(1)   (2)
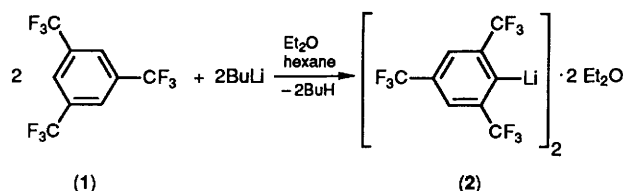
Figure 1. The X-ray structure of (**2**). Selected distances (pm) and angles (°): Li(1)–C(1) 222.3(9); Li(1)–C(7) 226.4(11); Li(1)–F(6c) 222.7(11); Li(1)–F(12c) 224.3(11); Li(1)–O(1) 196.4(10); Li(2)–C(1) 231.2(11); Li(2)–C(7) 225.8(9); Li(2)–F(2c) 224.3(12); Li(2)–F(8c) 229.3(12); Li(2)–O(2) 197.5(9); 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$_6$H$_2$), 3.0 (q, CH$_3$CH$_2$), and 0.7 (t, CH$_3$CH$_2$), ratio 1 : 2 : 3].

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