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Halocarbon and arene coordination of lithium(I) in (1-anilino-3-phenyliminopropenyl)chloro(methyl)aluminium bis{[tetrakis(pentafluorophenyl)borato]lithium} benzene solvate

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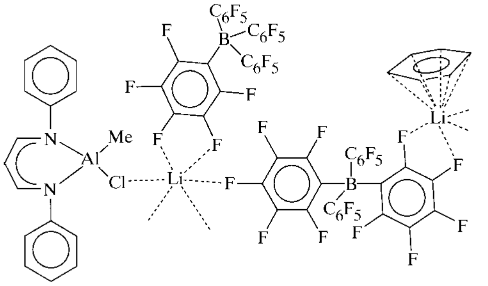
The crystal structure of the title compound, $[AlCl(CH_3)(C_{15}H_{13}N_2)][Li(C_{24}BF_{20})]_2\cdot C_6H_6$, is reported. The unusual coordination features of the lithium(I) cation, including Li-atom coordination to six organohalogen atoms and the shortest Li—F(C) distances so far observed, are discussed.

Comment

In recent reports, we have described the syntheses and structures of $[HC\{CMeN(2,6\text{-}^iPr_2Ph)\}_2]AlR_2$ and $[HC\{CMeN(2,6\text{-}^iPr_2Ph)\}_2]AlR^+$ complexes based on β-diketiminate ligands incorporating bulky *N*-aryl substituents (Radzewich *et al.*, 1998, 1999, 2000). The cationic species undergo unusual cycloaddition reactions with alkenes and alkynes. During efforts to extend this chemistry to the parent $[HC(CHNPh)_2]AlMe^+$ system, we isolated the novel compound $[HC(CHNPh)_2]AlMeCl\cdot 2[Li\{B(C_6F_5)_4\}]\cdot$benzene, (I), the structure of which is described here.



(I)

The asymmetric unit consists of one neutral $[HC(CHNPh)_2]AlMeCl$ complex, two $B(C_6F_5)_4^-$ anions, two Li^+ cations and a benzene solvate molecule. These moieties all participate in long-distance intermolecular interactions to form a three-dimensional framework of coordination bonds (Fig. 1). Important bond distances are listed in Table 1.

The Al atom possesses a distorted tetrahedral coordination sphere comprised of a methyl group, a Cl atom and the two N atoms of the chelating diketiminate ligand. The angles about the metal center range from 97.79 (10) (N1—Al—N2) to 115.94 (12)° (N2—Al—C1). Due to the coordination of the Cl atom to the Li1 cation (see below), the Al—Cl distance [2.2136 (11) Å] is somewhat longer than a typical Al—Cl bond distance [2.12 (2) Å]. The latter value was obtained by averaging the distances of 794 Al—Cl bonds found in compounds listed in the Cambridge Structural Database (CSD; Allen & Kennard, 1993). The Al—C distance [1.924 (3) Å] is shorter than a typical Al—Me bond distance [1.959 (19) Å; 1024 CSD entries], but is very similar to the Al—C distance in $[HC\{CMeN(p\text{-tolyl})\}_2]AlMe(OSO_2CF_3)$ [1.928 (6) Å; Qian *et al.*, 1998]. The Al—N bond distances [average 1.884 (2) Å] fall in the same range as observed for related aluminium diketiminate complexes, *e.g.* $[HC\{CMeN(p\text{-tolyl})\}_2]AlCl_2$ [1.850 (2) Å], $[HC\{CMeN(p\text{-tolyl})\}_2]AlMe(OSO_2CF_3)$ [1.875 (4) and 1.873 (4) Å], $[HC\{CMeN(p\text{-tolyl})\}_2]AlMe_2$ [1.905 (3) and 1.907 (3) Å] and $[HC(CHNPh)_2]AlMe_2$ [1.913 (4) Å; Radzewich *et al.*, 1998, 1999, 2000; Qian *et al.*, 1998]. Atoms N1, C2, C3, C4 and N2 of the diketiminate ligand are planar within 0.0316 (3) Å, and the Al atom is displaced by −0.32 Å out of this plane. The *ipso*-C atoms C5 and C11 of the phenyl rings are displaced by 0.324 (4) and 0.225 (4) Å, respectively, on the other side of this plane. The dihedral angles between the phenyl-ring planes and the N—C—C—C—N plane are 45.03 (11) and 43.67 (8)°.

This structure presents the first example of an Li^+ cation coordinated to six organohalogen atoms. Moreover, while six-coordinate Li^+ usually adopts an octahedral geometry (LiF and $LiSbF_6$), in (I), Li1 exhibits a distorted trigonal antiprismatic coordination sphere. Atom Li1 interacts with the Cl atom, atoms F36 and F37 of one of the $B(C_6F_5)_4^-$ anions, atoms F24 and F25 of another $B(C_6F_5)_4^-$ anion at ($-x$, $-y$, $1-z$), and atom F62 of a third $B(C_6F_5)_4^-$ anion at ($x-1$, y, z). Atoms F36 and F24 are *ortho*, F37 and F25 are *meta*, and F62 is a *para* substituent on the corresponding phenyl rings (Fig. 2). Although the Li1—Cl interaction results in an elongation of the Al—Cl bond, the Li1—Cl bond distance falls in the middle of the wide range of previously reported Li—Cl distances (2.169–2.792 Å, 162 CSD entries). The Li1—F bond distances vary in the range 2.100 (3)–2.246 (3) Å, with no apparent dependency on the F-atom position on the phenyl group. A CSD search showed that for 58 complexes, the Li—F distances vary in the range 1.771–2.355 Å. For comparison, the Li—F distance in crystalline LiF is 2.009 Å (Wells, 1984), the sum of the ionic radii for Li^+ (0.60 Å) and F^- (1.36 Å) according to Pauling (1960) is 1.96 Å, while the sum of the van der Waals radii for lithium (1.82 Å) and fluorine (1.47 Å) is 3.29 Å (Porterfield, 1998).

Atom Li2 is coordinated to atoms F21 and F22 of one $B(C_6F_5)_4^-$ anion, atoms F57 and F58 of the other $B(C_6F_5)_4^-$ anion and the solvate benzene molecule at ($x-1$, y, z) in an η^6 fashion (Fig. 3). The Li2—F distances differ considerably; the

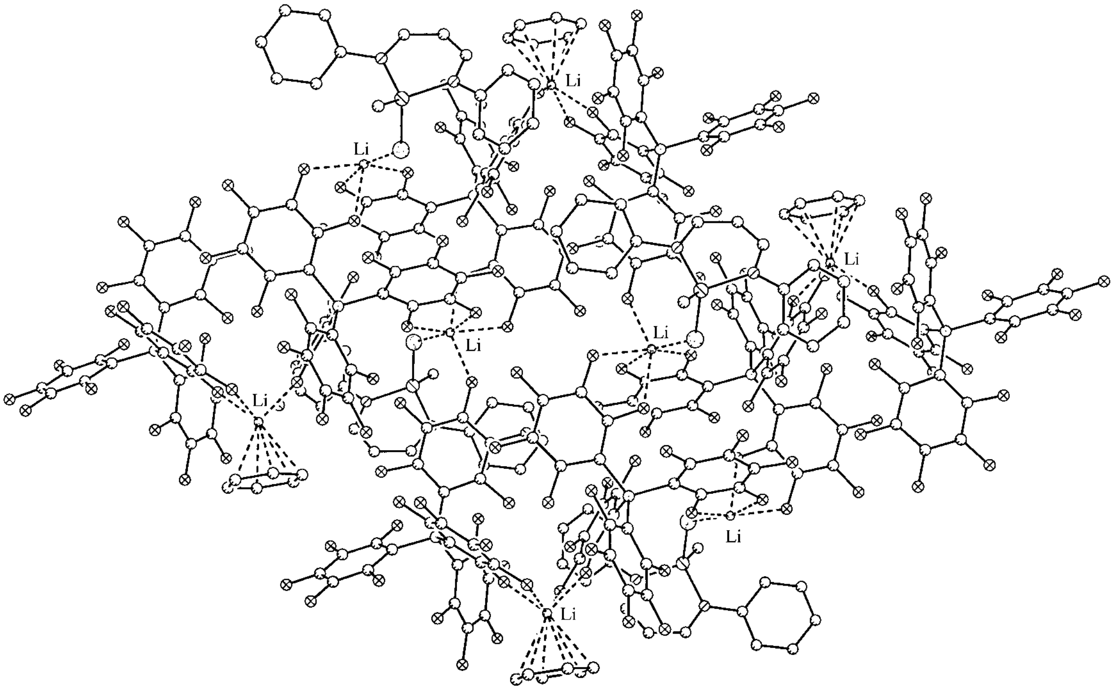


Figure 1
The three-dimensional framework formed by coordination bonds in (I).

ortho-F atom of each anion is coordinated more strongly [1.895 (3) Å for Li2—F22 and 1.956 (3) Å for Li2—F58] than the *meta*-F atoms [2.436 (3) Å each]. In fact, the Li2—F22 and Li2—F58 distances are the shortest Li—F(C) interactions reported to date. The shortest distance previously reported was 1.984 (9) Å in $LiAl[OC(Ph)(CF_3)_2]_4$ (Barbarich *et al.*, 1996). Conversely, the lengths of the Li2—F21 and Li2—F57 interactions exceed all other reported values for Li—F bond distances, regardless of whether fluorine is bound to another atom or not. Incidentally, the Li—F—C bond angles around F22 and F58 are 125.60 (16) and 128.14 (17)°, respectively, while the corresponding values for atoms F21 and F57 are 106.51 (15) and 106.91 (16)°, respectively. A review of the coordination chemistry of the F(C) unit with respect to lithium can be found in a paper by Plenio (1997). The Li2—C distances [average 2.53 (4) Å] are appreciably longer than the corresponding distances in other compounds with η^6-coordinated Li^+ cations, *e.g.* 2.38 (5) Å in $[Li\{Al(^iBu)_2(NMes)\}\{Al(N[C_6H_2(CH_3)_2CH_2])\}]_2$ (Mes = 2,4,6-$Me_3C_6H_2$; Horchler *et al.*, 1997), 2.32 (4) Å in $[Li(2,4,6\text{-}^iPr_3C_6H_2)]_4$ (Ruhklandt-Senge *et al.*, 1993), 2.34 (3) and 2.35 (7) Å in $[Li(^nBu)]_2$-

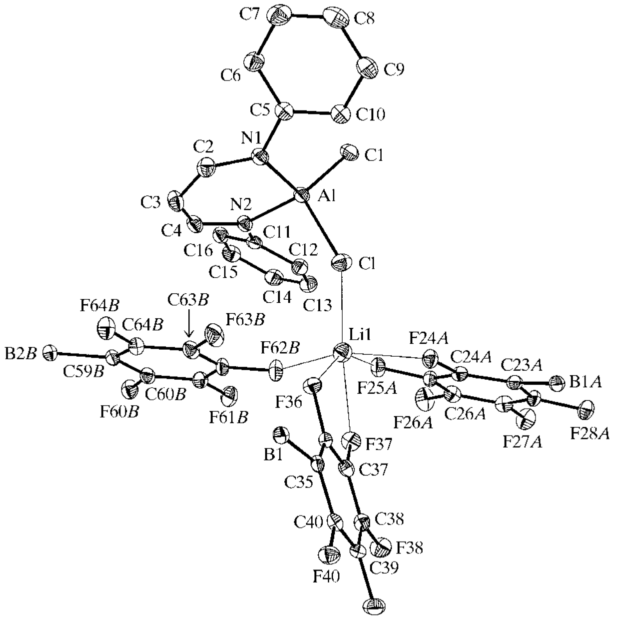


Figure 2
The coordination environment of the Li1 atom. The uncoordinated phenyl rings and the H atoms have been omitted for clarity. Displacement ellipsoids are plotted at the 30% probability level.

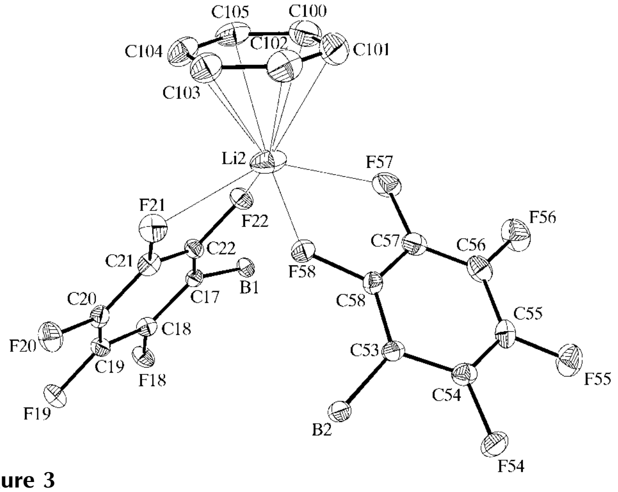


Figure 3
The coordination environment of the Li2 atom. The uncoordinated phenyl rings and the H atoms have been omitted for clarity. Displacement ellipsoids are plotted at the 30% probability level.

?tpbgc=^st_figpar_bgcolour]>(LiMes*)$_2$ (Mes* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$; Ruhklandt-Senge *et al.*, 1993), 2.37 (9) Å in [Li(^{n}Bu)]$_2$(LiMes*)$_2$·Mes*Br (Ruhklandt-Senge *et al.*, 1993), and 2.32 (1)–2.54 (1) Å in Li$_4$[P(Me)-{CH(C$_6$H$_4$)}$_2$]·2tmeda (tmeda is *N*,*N*,*N*′,*N*′-tetramethylethylenediamine; Winkler *et al.*, 1994). The elongation of the Li—C bonds in (I) is likely a consequence of the strong coordination of Li2 to F22 and F58.

The B1 B(C$_6$F$_5$)$_4^-$ anion coordinates to three Li atoms through two adjacent F atoms in each case. The coordinated atoms are Li1, Li1($-x$, $-y$, $1-z$) and Li2. The B2 B(C$_6$F$_5$)$_4^-$ anion interacts with two Li atoms, *i.e.* through a pair of vicinal F atoms to Li1 and with a *para*-F atom F62 to Li1($1 + x$, y, z). The different coordination environments of the anions do not result in variations of the geometries about the B atoms. The average C—F distance for the F atoms coordinated to Li$^+$ atoms is somewhat lengthened [1.372 (11) Å] compared with the other C—F bond distances in (I) [average 1.350 (8) Å], however, statistically, these average distances are not significantly different.

Experimental

A glass tube was charged with [HC(CHNPh)$_2$]AlMe$_2$ (50 mg, 0.18 mmol; Radzewich *et al.*, 1999, 2000), (Ph$_3$C)[B(C$_6$F$_5$)$_4$] (0.5 equivalents; 89 mg, 0.090 mmol) and C$_6$H$_6$ (10 ml). An orange oil was produced. Hexanes (20 ml) were added resulting in the formation of an orange solid. The tube was then flame sealed and heated to 323 K overnight to produce orange crystals of (I). The formation of (I) is believed to occur by reaction of a cationic aluminium methyl complex, [HC(CHNPh)$_2$]AlMe$^+$, with an LiCl impurity that is present in the neutral starting material.

Crystal data

[AlCl(CH$_3$)(C$_{15}$H$_{13}$N$_2$)]-[Li(C$_{24}$BF$_{20}$)]$_2$·C$_6$H$_6$
M_r = 1748.83
Triclinic, $P\overline{1}$
a = 12.2522 (9) Å
b = 13.8727 (10) Å
c = 22.2931 (16) Å
α = 79.743 (1)°
β = 80.829 (1)°
γ = 64.077 (1)°
V = 3339.2 (4) Å^3

Z = 2
D_x = 1.739 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4465 reflections
θ = 2–28°
μ = 0.230 mm^{-1}
T = 173 (2) K
Needle, pale yellow
0.50 × 0.34 × 0.25 mm

Data collection

Bruker CCD 1000 diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Blessing, 1995)
$T_{\min}$ = 0.894, $T_{\max}$ = 0.945
17 369 measured reflections
12 479 independent reflections

7428 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.024
$\theta_{\max}$ = 26.37°
h = −14 → 15
k = −16 → 17
l = −27 → 27

Refinement on F^2
$R[F^2 > 2\sigma(F)]$ = 0.043
$wR(F^2)$ = 0.094
S = 0.933

12479 reflections
1058 parameters
H-atom parameters constrained

Refinement

$w = 1/[\sigma^2(F_o^2) + (0.035P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max}$ = 0.34 e Å^{-3}
$\Delta\rho_{\min}$ = −0.29 e Å^{-3}

Table 1
Selected bondlengths (Å).

Al—N1	1.882 (2)	F37—Li1	2.246 (3)
Al—N2	1.885 (2)	F57—Li2	2.436 (3)
Al—C1	1.924 (3)	F58—Li2	1.895 (3)
Al—Cl	2.2136 (11)	F62—Li1$^{\rm i}$	2.113 (3)
Cl—Li1$^{\rm i}$	2.338 (3)	C100—Li2$^{\rm i}$	2.473 (4)
F21—Li2	2.436 (3)	C101—Li2$^{\rm i}$	2.494 (4)
F22—Li2	1.956 (3)	C102—Li2$^{\rm i}$	2.558 (4)
F24—Li1$^{\rm ii}$	2.165 (3)	C103—Li2$^{\rm i}$	2.569 (4)
F25—Li1$^{\rm ii}$	2.179 (3)	C104—Li2$^{\rm i}$	2.540 (4)
F36—Li1	2.100 (3)	C105—Li2$^{\rm i}$	2.5163

Symmetry codes: (i) $1 + x, y, z$; (ii) $-x, -y, 1 - z$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SHELXTL* (Sheldrick, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1092). Services for accessing these data are described at the back of the journal.

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