The Isolation of a Highly Arene-soluble Alkali Metal Tetrafluoroborate Complex, $LiBF_4 \cdot 4HMPA$ [HMPA = $O=P(NMe_2)_3$]: Evidence for Strong Li · · · F Interactions in Solution

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Reaction of $BF_3 \cdot OEt_2$ with 3 ($Bu^nLi \cdot HMPA$) [HMPA = $O=P(NMe_2)_3$] has been monitored by variable-temperature ^7Li and ^{11}B n.m.r. spectroscopy and shown to produce a highly arene-soluble, crystalline complex, $LiBF_4 \cdot 4HMPA$, (**1**); spectroscopic, cryoscopic, and conductimetric measurements indicate that this exists in solution as tight lithium and tetrafluoroborate components held by Li · · · F interactions.

We recently described[1] an oligomeric lithium chloride complex, $(LiCl)_4 \cdot 4HMPA$, [HMPA = $O=P(NMe_2)_3$], formed *in situ* by reaction of $Bu^t_2C=NLi \cdot HMPA$ with $AlCl_3$ in diethyl ether–hexane. Its most noteworthy property, as a form of *intact* lithium chloride (*cf.*, ion-separated crown ether complexes), is reasonable solubility in aromatic solvents. Accordingly, we have been seeking a soluble fluoride analogue, which may be a better fluoride source for fluorocarbon preparations than currently used suspensions (*e.g.*, of CsF in glymes),[2,3] and which could be weighed out to allow stoicheiometric control of such subsequent reactions. However, the initial reaction system chosen, boron trifluoride–diethyl ether with 3 equivalents of n-butyl-lithium and HMPA, affords not $(LiF \cdot HMPA)_n$ but an equally interesting lithium tetrafluoroborate complex, $(LiBF_4 \cdot 4HMPA)_n$, (**1**), of high solubility in aromatic solvents. Variable-concentration molecular mass, ^7Li and ^{11}B n.m.r. spectroscopic, and conductivity measurements all indicate that, unlike the recently reported liquid tetrafluoroborate solvate, $[Bu_4N]^+ \cdot [BF_4]^- \cdot 3$toluene,[4] (**1**) does not exist in solution as independent ions but that strong $Li^+ \cdots F^-$ interactions occur.

$$LiBF_4 \cdot 4[O=P(NMe_2)_3]$$
(**1**)

Addition of HMPA (15 mmol) followed by Bu^nLi in hexane (15 mmol) to a frozen (−196 °C) solution of $BF_3 \cdot OEt_2$ (5 mmol) in diethyl ether–toluene first produces a pink, cloudy mixture which nearer room temperature becomes a colourless solution, with no signs of LiF precipitation. Slight re-chilling gives colourless crystals (m.p. 122 °C) with high solubility in aromatic solvents, *e.g.*, over 2.5 g per cm^3 of toluene at 20 °C. The ^{1}H n.m.r. spectrum of this product in [^{2}H$_6$]benzene consists only of a doublet due to HMPA-protons, and elemental (C, H, Li, N, P) analysis shows it to be $LiBF_4 \cdot 4HMPA$, (**1**).

This reaction was monitored by ^{7}Li n.m.r. spectroscopy. [^{2}H$_8$]Toluene solutions of (i) Bu^{n}Li, (ii) Bu^{n}Li·HMPA, (iii) complex (**1**), and (iv) the $BF_3 \cdot OEt_2$–3(Bu^{n}Li·HMPA) reaction system initially mixed at −100 °C (all 1 mol dm^{-3} with respect to lithium) were examined at −100, −10, and 25 °C (Figure 1). At −100 °C, comparison of (iv) with (iii), and then with (i) and (ii), showed firstly that considerable amounts of (**1**) had formed even at this low temperature, and secondly that the broad resonance at δ −1.68 p.p.m.† represented other product(s) rather than unreacted Bu^{n}Li or its HMPA complex. When the reaction mixture was warmed to −10 °C [Figure 1(iv)], the broad resonance diminished relative to that of (**1**), and by 25 °C both signals merged. However, this does not represent decomposition of intermediate products to give more of (**1**) since this broad signal reappeared on cooling back to −10 °C. It was shown by line-narrowing to consist of a series of lines at δ −1.60 to −1.85 p.p.m. The ^{11}B n.m.r. spectrum (115.55 MHz) of the final mixture at 25 °C consists of (a) a singlet at δ 0.38 p.p.m.‡ due to (**1**), (b) a singlet at δ 28.7 p.p.m. which represents Bu^{n}BF$_2$, *i.e.*, despite the Li : B ratio of 3 : 1 employed, the reaction in the presence of HMPA does not proceed to Bu$_2$^{n}BF or Bu$_3$^{n}B, and (c) two close quartets (with central signals at δ 3.16/2.60 and δ 0.70/0.14 p.p.m.), one overlapping with the signal of (**1**) and so paralleling the pattern in the ^{7}Li spectra noted above; given this multiplicity, these signals can be assigned to LiBu^{n}BF$_3$ complexes, possibly with HMPA and Et_2O.

The implications of these studies are that the essential reagents BF_3 and Bu^{n}Li do indeed, at low temperature, give initially a monomeric LiF unit or a small oligomer, $(LiF)_n$. However, while the $AlCl_3$ and Bu$^t_2$C=NLi system produced an $(LiCl)_4$ cube whose further aggregation to the usual ionic lattice was prevented by HMPA alone, in this case the LiF formed not only adds this ligand but also behaves as a Lewis base towards BF_3, so giving (**1**), and towards the other primary reaction product, Bu^{n}BF$_2$, affording LiBu^{n}BF$_3$ complexes. Supporting this interpretation, direct reaction of anhydrous lithium fluoride with $BF_3 \cdot OEt_2$ in diethyl ether gives <10% yield of $LiBF_4$, while a 91% yield results from a 1 : 2 Bu^{n}Li : $BF_3 \cdot OEt_2$ system, implying efficient *in situ* production of a small $(LiF)_n$ unit. Addition of HMPA has a profound effect on the course of the former reaction as (**1**) then results in 95% yield. However, the inference that lithium fluoride is significantly soluble in HMPA at room temperature to give a low-association complex (and, as such, a potentially important fluoride source) which is then susceptible to 'ate formation with the BF_3 present is not supported by other experimental observations. Thus, any such dissolution only becomes apparent on heating LiF in HMPA to 180 °C, with complete solution occurring at 200 °C. The slightest cooling precipitates lithium fluoride alone, though a noisy ^{7}Li spectrum can just be recorded at 110 °C and shows a single resonance at the extremely low frequency of δ −6.88 p.p.m., presumably corresponding to the lithium of $[Li(HMPA)_x]^+ \cdot F^-$.

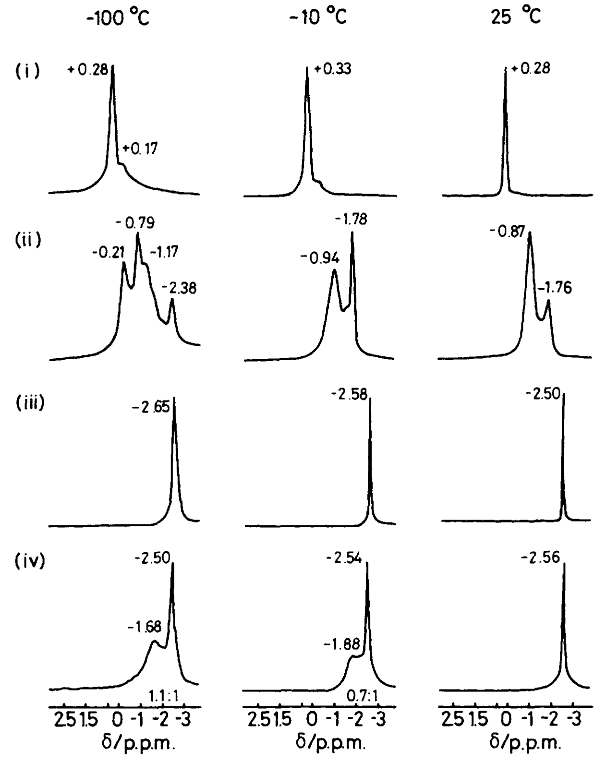

Figure 1. ^{7}Li n.m.r. spectra (139.96 MHz) of [^{2}H$_8$]toluene solutions of (i) Bu^{n}Li, (ii) Bu^{n}Li·HMPA, (iii) compound (**1**), and (iv) reaction mixture $BF_3 \cdot OEt_2$–3(Bu^{n}Li·HMPA), at −100, −10, and 25 °C.

Several sets of results shed light on the nature of (**1**) in aromatic solutions. Firstly, variable-concentration cryoscopic measurements in benzene give *n* values for $(LiBF_4 \cdot 4HMPA)_n$, (**1**), consistently increasing from 0.35 to 0.76 (0.5×10^{-2} to 1.4×10^{-1} mol dm^{-3} solutions). Such results are not compatible with an ionic formulation $[Li(HMPA)_4]^+ \cdot [BF_4]^-$ for which *n* *ca.* 0.5 would be expected in very dilute solution, increasing on concentration as more contact ion pairs form. Furthermore, the ^{7}Li n.m.r. spectrum of $[Li(HMPA)_4]^+ \cdot [Li_5(N{=}CPh_2)_6 \cdot HMPA]^-$ [5] in [^{2}H$_8$]toluene exhibits a sharp singlet due to the complexed cation at a very different shift (δ 0.34 p.p.m.) to that observed for (**1**) (*ca.* δ −2.5), while the ^{11}B n.m.r. signal of (**1**) is broader ($w_{\frac{1}{2}}$ *ca.* 8 Hz) than expected for free BF_4^-. Finally, the specific conductance of a toluene solution of (**1**) is extremely low (*ca.* $5 \times 10^{-8}\ \Omega^{-1}\ cm^{-1}$), and over four orders of magnitude less than that of the room-temperature molten solvate $[Bu_4N]^+ \cdot [BF_4]^- \cdot 3$toluene ($1.2 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$).[4] Such data is consistent with there being a considerable interaction between the lithium and tetrafluoroborate components of (**1**); perhaps significantly, dissociation of one and two HMPA molecules from monomeric $LiBF_4 \cdot 4HMPA$ on dissolution to give mono- and di-bridged species $(HMPA)_3Li \cdots F \cdot BF_3$ and $(HMPA)_2Li(\cdots F)_2 \cdot BF_2$ respectively, would give *n* values ranging down from 1 through 0.50 to 0.33. Analogous $K^+ \cdots F^-$ interactions have been proposed to occur in solutions of KF·18-crown-6,[6] for which ^{19}F n.m.r. spectra suggested very tight (crown)$K^+ \cdot F^-$ ion pairs or even a $(KF)_n$ aggregate with external crown ether molecules [*cf.* $(LiCl)_4 \cdot 4HMPA$]; in the case of (**1**), the 1 : 4 Li : HMPA ratio argues against the presence of $(LiBF_4)_n$ aggregates.

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† For ^{7}Li spectra all chemical shifts are relative to external phenyllithium in [^{2}H$_8$]toluene, Ξ value 38.863 883.

‡ For ^{11}B spectra all chemical shifts are relative to external $BF_3 \cdot Et_2O$.

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