SYNTHESIS OF LITHIUM (PERFLUOROALKYL)TRIHYDROALUMINATES Li[RFAlH3]

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Abstract: (Perfluoroalkyl)trimethylsilanes were shown to react with $LiAlH_4$ in ethereal solvents to give lithium (perfluoroalkyl)trihydroaluminates $Li[R_FAlH_3]$, which, when $R_F = C_2F_5$ and $n\text{-}C_3F_7$, can be isolated as stable complexes solvated with ethereal solvents, for example $Li[C_2F_5AlH_3]\cdot 2DME$, $Li[^nC_3F_7AlH_3]\cdot 2DME$.

Key words: lithium aluminum hydride, (perfluoroalkyl)trimethyl silanes, lithium (perfluoroalkyl)trihydroaluminates

We have previously shown that the reaction of $NaBH_4$ with CF_3SiMe_3 in diglyme does not produce $Na[CF_3BH_3]$, and instead, gives HCF_2SiMe_3 as a major product [1]. We also failed to prepare (trifluoromethyl)borohydrides by the action of $NaBH_4$ or BH_3 (obtained *in situ* by the reaction of $NaBH_4$ with $ClSiMe_3$) in a diglyme solution on $CF_3B(OMe)_2$ or $K[CF_3B(OMe)_3]$. The resulting products proved to be unstable and decomposed during isolation, in some cases with strong explosions. The recent report on the synthesis of (perfluoroalkyl)borohydrides indirectly supports our results, and it shows that more stable potassium and cesium (pentafluoroethyl)borohydrides, obtained in pure forms, explode upon friction [2].

A natural question that arose when studying the reaction of R_FSiMe_3 with $NaBH_4$, is how a similar reaction will proceed with $LiAlH_4$? We have shown that R_FSiMe_3 reacts with $LiAlH_4$ in ethereal solvents to furnish $Li[R_FAlH_3]$ and $HSiMe_3$ [3]. In the present paper, we present the results of these studies.

It turned out, that following the addition of CF_3SiMe_3 (1.1 equiv.) to a solution of $LiAlH_4$ (1 equiv.) in diglyme at room temperature, a highly exothermic reaction is observed after a few

minutes. When carrying out this reaction while controlling the temperature of the reaction mixture at ~20°C for 5.5 hours, analysis of the reaction mixture by ^{1}H NMR confirmed the formation of HSiMe$_3$ (^{1}H NMR, d: 0.56 (d, 9H, $^3J_{HH}$ = 5 Hz, SiMe$_3$), 4.44 (dec, 1H, HSi); ^{29}Si {^{1}H} NMR, d: -16 (s)), the conversion of CF$_3$SiMe$_3$ is 58% (in 24 h, the conversion of CF$_3$SiMe$_3$ is 79%). The ^{19}F NMR spectrum of the reaction mixture contains a broad peak with a maximum at -175 ppm, indicating the formation of aluminum fluoride complexes [4] (*e.g.*, in [^{n}Bu$_4$N][Me$_2$AlF$_2$] and Li[(Me$_3$Si)$_3$CAlF$_3$]´THF, the fluorine atoms resonate at -154 [5] and -169 ppm [6], respectively), and also a residual signal of unreacted CF$_3$SiMe$_3$ at -67 ppm. This is consistent with the data of the ^{29}Si{^{1}H} NMR spectrum, which shows the peak corresponding to CF$_3$SiMe$_3$ at d =5 (q, $^2J_{SiF}$ = 37 Hz, CF$_3$Si). Taking into account that the ^{1}H NMR spectrum of the reaction mixture contains several broad upfield signals (d: -0.7 and -0.75 ppm), it can be assumed that in this reaction, in addition to HSiMe$_3$, lithium aluminum hydrofluoride complexes are formed. No characteristic peaks appear in the ^{7}Li and ^{27}Al NMR spectra. The reaction in THF provides a similar result. The degree of conversion of CF$_3$SiMe$_3$ to HSiMe$_3$ is 36% (8 h), 55% (32 h), and 63% (56 h); also, lithium aluminum hydrofluoride complexes are formed having similar spectral characteristics. The removal of THF *in vacuo*, together with the volatile components of the mixture (HSiMe$_3$ and unreacted CF$_3$SiMe$_3$), provides a white solid, which actively reacts with water and methanol. The mass of the residue, as well as the low fluorine content (5%), established by elemental analysis, suggests that this product is Li[AlFH$_3$], which contains unreacted LiAlH$_4$ and solvating THF, probably resulting from the decomposition of the initially formed Li[CF$_3$AlH$_3$]. Purification and identification of lithium aluminum hydrofluoride complexes formed in this reaction was not performed.

In contrast, C$_2$F$_5$SiMe$_3$ reacts with LiAlH$_4$ in diglyme virtually without heat evolution. According to ^{1}H and ^{29}Si{^{1}H} NMR data, the reaction provides HSiMe$_3$, and in the ^{19}F NMR spectrum, in addition to peaks for the starting C$_2$F$_5$SiMe$_3$ (d: -132 (s, 2F, CF$_2$), -82 (s, 3F, CF$_3$); ^{29}Si {^{1}H} NMR d: 7.8 (t, $^2J_{SiF}$ = 27 Hz, CF$_2$Si)), signals for the product bearing C$_2$F$_5$ moiety (d: -126 (br. s, 2F, CF$_2$Al), -84 (s, 3F, CF$_3$)) are observed, where this product is, as we hypothesize, an *ate* complex of Li[C$_2$F$_5$AlH$_3$], which is consistent with the data of the ^{27}Al NMR spectra, showing the peak at 116 ppm (br.d, CF$_2$Al). However, based on the data of ^{1}H, ^{19}F, ^{27}Al, and ^{29}Si NMR spectra, it turned out that C$_2$F$_5$SiMe$_3$ (1.1 equiv.) reacts with c LiAlH$_4$ (1 equiv.) in diglyme at ~20°C within several days with incomplete conversion of ~70%. This circumstance significantly complicates the isolation of the Li[C$_2$F$_5$AlH$_3$] complex in pure form, due to the presence of unreacted LiAlH$_4$ in the solution. This is confirmed by the ^{27}Al NMR spectrum containing a peak at 102 ppm, br.s (the signal, which should represent a quintet, was not resolved, probably due to the

solvent effect [7-8]). Therefore, we investigated the effect of the nature of the solvent, the reagent ratio, and the reaction time on the degree of conversion of the starting compounds (see Table).

$$LiAlH_4 \; + \; C_2F_5SiMe_3 \; \xrightarrow[\text{rt, Time}]{\text{Solv.}} \; Li[C_2F_5AlH_3] \; + \; HSiMe_3$$
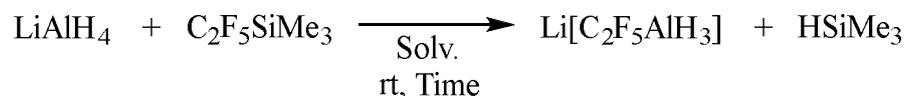
№ Ex.	Solvent	Conversion of $C_2F_5SiMe_3$[*], % (time, h)		
1	Diglyme	34 (6)	69 (28)	74 (72)
2	DME	36 (8)	56 (32)	61 (72)
3	DME $C_2F_5SiMe_3$ (3 eq.)	65 (7)	81 (31)	91 (100)
4	DME $C_2F_5SiMe_3$ (5 eq.)	-	-	94 (90)
5	THF	47 (7.5)	-	66 (79)
6	Et_2O	17 (7)	-	24 (79)
7	1,4-Dioxane	0 (6)	0 (30)	-
8	HMDSO	-	0 (24)	-
9	NEt_3	-	0 (24)	-
10	TMEDA	-	0 (24)	-

[*]The conversion degree for $C_2F_5SiMe_3$ was determined based on a data set of the ^{1}H NMR spectra (ratio of signals at d = 0.80 ($C_2F_5SiMe_3$) and 0.57 ($HSiMe_3$)) and ^{19}F NMR spectra (ratio of signals at d = -126 ($LiC_2F_5AlH_3$) and -132 ($C_2F_5SiMe_3$)). Also, the amount of unreacted $LiAlH_4$ (ratio of signals at d = 116 ($LiC_2F_5AlH_3$) and 102 ($LiAlH_4$)) was recorded from the ^{27}Al NMR spectra.

The above data show that the reaction proceeds equally well in strongly solvating donor ethereal solvents such as diglyme, monoglyme, and THF (runs 1-5). At the same time, the conversion of (pentafluoroethyl)trimethyl silane in diethyl ether for a similar time is significantly lower (run 6). In turn, $C_2F_5SiMe_3$ does not react with $LiAlH_4$ in 1,4-dioxane, most likely, due to the very low solubility of $LiAlH_4$ (solubility of $LiAlH_4$ in 1,4-dioxane at 25°C is 0.1 g in 100 g [9]). No reaction was also observed using hexamethyldisiloxane, triethylamine, and TMEDA as a solvent, probably, for similar reasons (runs 8-10). In terms of the convenience of isolating complex $Li[C_2F_5AlH_3]$, relatively low boiling solvents such as THF and monoglyme are the most suitable. Thus, we have shown that when carrying out the reaction in monoglyme, to achieve almost complete conversion of $LiAlH_4$, a large (3-5 equiv.) excess of $C_2F_5SiMe_3$ and an increase in the reaction time to 5 days are required (runs 3-4). A further increase in the reaction time to 9 days leads to the accumulation of side-formed fluorine-containing impurities, the content of which in the isolated product increases from ~ 2% (if the reaction is carried out for 5 days) to 12% (during the

reaction time of 9 days). Being carried out under optimal conditions, with the subsequent removal of volatiles *in vacuo* and toluene purification of the product, the reaction gives a solvated Li[$C_2F_5AlH_3$]´ 2DME complex. Similarly, Li[$C_2F_5AlH_3$]´ 2THF complex was obtained.

It should be noted that we failed to carry out this reaction using a slight excess of (pentafluoroethyl)trimethyl silane up to complete conversion of LiAlH$_4$ by shifting the equilibrium towards the formation of products through distilling off low-boiling HSiMe$_3$ (bp 7°C). The process almost terminates at 70-80% conversion, and only using a large excess of $C_2F_5SiMe_3$ (>3 equiv.) is it possible to achieve a high degree of LiAlH$_4$ conversion.

Ethereal solvents (Et$_2$O, THF) can be completely removed from their complexes with LiAlH$_4$ by heating in a dynamic vacuum (~0.5 Torr) at a temperature of 60-70°C [9-10]. However, an attempt to remove a solvent from Li[$C_2F_5AlH_3$]´ 2DME by performing such a procedure at 55-60°C leads to decomposition of this complex hydride accompanied by a strong explosion (decomposition point of LiAlH$_4$ >100-150°C [9-10]).

Thus synthesized Li[$C_2F_5AlH_3$]´ 2DME is a colorless liquid with the following spectral characteristics. Hydride protons appear in the ^{1}H NMR spectra as a broad singlet at 3.5 ppm (for the THF complex, the signal is sharper, with d =3.2 ppm), which is quite close to the value of a chemical shift of protons in LiAlH$_4$ (d = 2.9 ppm (in DME)) [11]. The ^{19}F NMR spectrum contains two pairs of signals corresponding to the C_2F_5 moiety (d: -126 (br.s, 2F, CF$_2$Al), -83.8 (s, 3F, CF$_3$) and d: -128 (br.s, 2F, CF$_2$Al), -84 (s, 3F, CF$_3$), in a ratio of 2.5:1. Accordingly, there are two signals for CF$_3$ moeties in the ^{13}C{^{1}H} NMR spectrum appearing as a quartet of triplets at ~123 ppm ($^1J_{CF}$ = 283 Hz, $^2J_{CF}$ = 30 Hz) and a highly broadened triplet at 132 ppm corresponding to the aluminum-bonded CF$_2$ moiety. The ^{7}Li and ^{27}Al NMR spectra show a singlet of -0.7 ppm and a highly broadened singlet at 117 ppm respectively. When recording the ^{19}F and ^{27}Al NMR spectra in a dilute solution in monoglyme, the form of the spectra becomes similar to that of the reaction mixture. Namely, in the fluorine NMR spectrum, signals for nearly one C_2F_5 moiety are observed (d: -126 (br.s, 2F, CF$_2$Al), -84.3 (s, 3F, CF$_3$)) (the content of the second pairs of signals for the C_2F_5 moiety decreases from 25% to 6%), while the ^{27}Al NMR spectrum contains a highly broadened quartet at 117 ppm ($^1J_{AlH}$ = ~170 Hz) (for comparison, the ^{27}Al-^{1}H coupling constant in the AlH$_4$$^-$ anion is 170-175 Hz [10]).

When stored in a sealed ampoule for several weeks, the liquid Li[$C_2F_5AlH_3$]´ 2DME complex transforms into a crystalline-like but in fact a gel-like product. Raman spectra of the liquid complex and the gel-like compound formed 2 weeks later are identical, which suggests that the change in the state of aggregation does not occur through the decomposition of the complex. When

refrigerated (~ -25°C), the liquid complex transforms into a white crystalline substance that can be stored for a long time without visible decomposition.

In the presence of chelating agents such as TMEDA or DABCO in ethereal solvents, Li[$C_2F_5AlH_3$] decomposes, so we failed to obtain complexes of the type $LiAlH_4$-TMEN [11] (TMEN = TMEDA), although triethylamine does not react with Li[$C_2F_5AlH_3$] under these conditions.

(*n*-Heptafluoropropyl)trimethyl silane reacts with $LiAlH_4$ similarly. At the same time, when carrying out the reaction of $^nC_3F_7SiMe_3$ with $LiAlH_4$, under optimal conditions (DME, 5 equiv. of the silane, 5 days), a noticeable decrease (to 77%) in the yield of Li[$^nC_3F_7AlH_3$]·2DME along with an increase in the yield of fluorine-containing by-products up to 7-12% is observed. The resulting *n*-heptafluoropropyl complex Li[$^nC_3F_7AlH_3$]´ 2DME is also a liquid and its spectral characteristics are identical to those for the complex bearing C_2F_5 moiety.

With a further elongation of the perfluoroalkyl substituent, reactions begin to dominate affording fluorine-containing by-products. Thus, $^nC_6F_{13}SiMe_3$ reacts with $LiAlH_4$ in THF for 2 days to give, according to ^1H, ^{19}F, and ^{27}Al NMR spectra, the corresponding (*n*-perfluorohexyl)trihydroaluminate complex in ~30% yield. However, as the reaction proceeds further, significant amounts of by-products begin to appear in the reaction mixture, which makes it impossible to isolate the Li[$^nC_6F_{13}AlH_3$]´ 2THF complex in pure form.

Similar changes in the reactivity of (perfluoroalkyl)trimethyl silanes associated with the length of the perfluoroalkyl radical were also observed earlier. For example, it is known that CF_3SiMe_3 and $C_2F_5SiMe_3$ perfluoroalkylate $B(OMe)_3$ almost quantitatively in the presence of KF in THF or diglyme solution to afford corresponding borate salts. At the same time, $^nC_3F_7SiMe_3$ reacts with $B(OMe)_3$ under similar conditions to give K[$^nC_3F_7B(OMe)_3$] in a very low yield [12].

It is known from the literature, that Na[$EtAlH_3$] is unstable in solution and exists as an equilibrium mixture with the products of its disproportionation, namely, $NaAlH_4$ and Na[Et_2AlH_2], which was established from the ^{27}Al NMR spectrum containing three signals corresponding to these compounds [13]. Unlike its ethyl analog, Na[$^iBuAlH_3$] is stable and can be obtained *via* the reaction between $NaAlH_4$ and $NaAl^iBu_4$ or Al^iBu_3 [13]. Other examples of lithium alkyl- and aryltrihydroaluminates have also been reported, the stability of which is determined by the steric volume of an aliphatic or aromatic substituent on the aluminum atom, *e.g.*, Li[$(Me_3Si)_3CAlH_3$] and Li[$(Me_2PhSi)_3CAlH_3$] [14], and also Li[$(2,4,6-^iPr_3C_6H_2)AlH_3$] and Li[$(2,4,6-^tBuC_6H_2)AlH_3$] [15].

We found that Li[$C_2F_5AlH_3$] and Li[$^nC_3F_7AlH_3$] solvated with DME or THF are fairly stable compounds and can be obtained in pure form from the corresponding (perfluoroalkyl)trimethyl silanes and $LiAlH_4$ in good yields. In this reaction, R_FSiMe_3 react with $LiAlH_4$ like aliphatic

derivatives of alkali, alkaline-earth metals, Zn, Cd, B, and Al [9]. However, we failed to obtain pure forms of lithium (perfluoroalkyl)trihydroaluminates bearing CF_3 and $^nC_6F_{13}$ moieties, probably due to their instability under reaction conditions. It is interesting to note that recently, two papers have been simultaneously published on the synthesis of the tetrakis(pentafluoroethyl)aluminate anion, $[Al(C_2F_5)_4]^-$ [16, 17], which, according to the authors, is the first characterized perfluoroalkyl aluminum derivative containing an R_F-Al bond. In this case, one of the synthetic procedures to obtain $Li[(C_2F_5)_4Al]$, a salt which is unstable in ether solution or solid state and solvated with Et_2O, comprised the reaction of $(C_2F_5)_3SiMe$ or $(C_2F_5)_3SiH$ with $LiAlH_4$ to produce exclusively a tetrakis-substituted product and corresponding hydrosilanes [16]. In the reaction of $C_2F_5SiMe_3$ with $LiAlH_4$ discovered by us, the formation of poly-C_2F_5-substituted aluminates was not observed.

To conclude, a general possibility of synthesizing stable perfluoroalkyl aluminum derivatives by replacing the substituent in the coordination sphere of the tetrahedral aluminum anion with a perfluoroalkyl group has been demonstrated for the first time, which opens up prospects for further study of the properties of this, as yet exotic, class of compounds. Even though the first, the most natural idea of using $Li[C_2F_5AlH_3]$´2DME for the synthesis of lithium (pentafluoroethyl) alkoxyaluminates has not been fully realized by us, since reactions with alcohols lead to partial substitution of the C_2F_5 group furnishing the difficultly separable mixture of products, one can expect that the replacement the Li cation with bulky organic cations such as PNP or EtP_4H (as in [16]) can be a possible approach to obtain $[C_2F_5Al(OR)_3]^-$ anions.

Experimental

^1H, ^{13}C, ^{19}F, ^{27}Al, ^{29}Si, and ^7Li NMR spectra were recorded on a Bruker AM-300, Bruker AVANCE-400, Bruker AVANCE-500, or Bruker AVANCE-600 spectrometers with 300.13, 400.13, 500.13, and 600.22 MHz working frequencies for ^1H, respectively. The frequencies of other nuclei, depending on the instrument used, are given in the Experimental Section below when referring to the NMR spectra of the corresponding compounds. Chemical shifts were referenced to the residual proton chloroform peak (7.26 ppm in $CDCl_3$) and reported in ppm units relative to TMS. Chemical shifts in ^{13}C NMR spectra were referenced to the ^{13}C nucleus peak (77.0 ppm in $CDCl_3$) and reported in ppm units relative to TMS. Chemical shifts in ^{19}F NMR spectra were reported in ppm units relative to an external $CFCl_3$ reference. Chemical shifts in ^{27}Al NMR spectra were reported in ppm units relative to an external $Al(NO_3)_3$ reference. Chemical shifts in ^{29}Si NMR spectra were reported in ppm units relative to an external TMS reference. Chemical shifts in ^7Li NMR spectra were reported in ppm units relative to an external LiCl reference. Positive values of chemical shift correspond to the downfield shift of the indicator nucleus signal. Raman spectra

were recorded on a Jobin Yvon LabRam spectrometer. Elemental analysis was performed in the Laboratory of Microanalysis of INEOS RAS.

All experiments were carried out in an inert atmosphere using anhydrous solvents and standard working procedures. Before use, commercially available $LiAlH_4$ was purified by the standard method [9]: it was dissolved in Et_2O, the insoluble grey residue was allowed to settle down, the clear solution was separated, evaporated *in vacuo* to dryness or to a concentrated solution from which the hydride was precipitated by adding toluene and separated by filtration. The resulting white powdered $LiAlH_4$ was dried at 60-65°C (<0.5 Torr). (Perfluoroalkyl)trimethylsilanes: CF_3SiMe_3, $C_2F_5SiMe_3$, $^nC_3F_7SiMe_3$, and $^nC_6F_{13}SiMe_3$ are prepared by the procedure developed by us earlier [18-19].

To analyze the reaction mixtures, ~0.3 mL of the reaction solution was sealed in a glass ampoule (~3 mm diameter and 110-130 mm length). This ampoule was then placed in a standard 5 mm NMR ampoule, $CDCl_3$ was added as an external standard, and the reaction mixture was analyzed by NMR.

Synthesis of Li[C₂F₅AlH₃]´2DME.

To a stirred suspension of $LiAlH_4$ (1 g, 0.026 mol) in DME (50 mL), $C_2F_5SiMe_3$ (25 g, 0.13 mol) is added. The resulting mixture is stirred for several hours until homogeneous, and then kept for 5 days, periodically stirring the solution. Volatiles are then removed *in vacuo* (<0.5 Torr) and collected in a trap to provide a white solid, which turns into a liquid upon prolonged drying *in vacuo* (<0.5 Torr).

To the residue, toluene (20 mL) is added and the resulting mixture is stirred until dissolution and the formation of a liquid two-phase mixture, from which the solvent is distilled off *in vacuo* (<0.5 Torr). The liquid residue is dried for several hours *in vacuo* (<0.5 Torr) to give a colorless liquid (7.8 g, yield 90%).

Found, %: C, 35.52; H, 6.73. $C_{10}H_{23}AlF_5LiO_4$. **Calculated, %:** C, 35.73; H, 6.90.

¹H NMR (500.13 MHz) δ: 3.45-3.65 (br.s, 3H, AlH_3), 3.95 (s, 12H, OCH_3), 4.14 (s, 8H, CH_2CH_2);

¹⁹F NMR (470.59 MHz) δ: two sets of signals at -128 (s, 2F, CF_2), -84 (s, 3F, CF_3), and -126 (br.s, 2F, CF_2), -83.8 (s, 3F, CF_3) in a ratio of 1:2.5;

¹³C{¹H} NMR (125.75 MHz) δ: 59 (s, CH_3O), 70 (s, CH_2O), 123 (qt, $^1J_{CF}$ = 283 Hz, $^2J_{CF}$ = 30 Hz, CF_3), 132 (br.t, CF_2Al);

²⁷Al NMR (104.26 MHz) δ: 117 (br.s);

⁷Li NMR (155.5 MHz) δ: -0.66 (s).

Raman spectrum of Li[ⁿC₃F₇AlH₃]´2DME
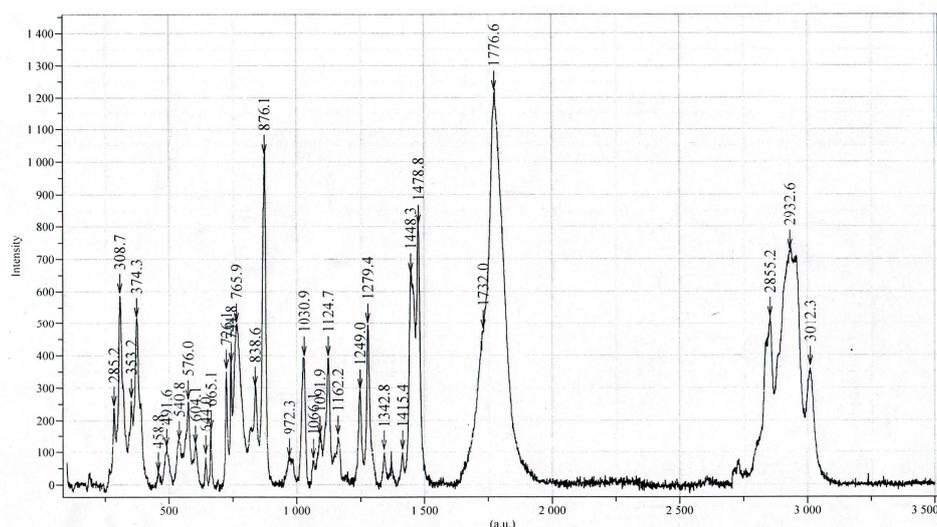
Synthesis of Li[^{n}C$_3$F$_7$AlH$_3$]´2DME.

Synthesized similarly to Li[^{n}C$_3$F$_7$AlH$_3$]´ 2DME. Colorless viscous liquid, which is partially solidified at -25°C.

Found, %: C, 34.21; H, 6.26. C$_{11}$H$_{23}$AlF$_7$LiO$_4$. **Calculated, %:** C, 34.21; H, 6.00.

^{1}H NMR (500.13 MHz) δ: 3.45-3.65 (br.s, 3H, AlH$_3$), 3.9 (s, 12H, OCH$_3$), 4.1 (s, 8H, CH$_2$CH$_2$);

^{19}F NMR (282.4 MHz) δ: two pairs of signals in the CF$_2$ region -128 (s, 2F, $\underline{CF_2}$CF$_2$Al), -126.3 (s, 2F, CF$_2\underline{CF_2}$Al), and -126.6 (s, 2F, $\underline{CF_2}$CF$_2$Al), -126.1 (s, 2F, CF$_2\underline{CF_2}$Al) in a ratio of 1:4, -81.3 (s, 3F, CF$_3$);

^{13}C{^{1}H} NMR (125.75 MHz) δ: 59 (s, CH$_3$O), 70 (s, CH$_2$O), 112 (tq, $^1J_{CF}$ = 251 Hz, $^2J_{CF}$ = 28 Hz, CF$_2$), 119 (qt, $^1J_{CF}$ = 288 Hz, $^2J_{CF}$ = 38 Hz, CF$_3$), 135 (br.t, CF$_2$Al);

^{27}Al NMR (104.26 MHz) δ: -117 (br.s);

^{7}Li NMR (155.5 MHz) δ: -0.64 (s).

Raman spectrum of Li[^{n}C$_3$F$_7$AlH$_3$]´ 2DME
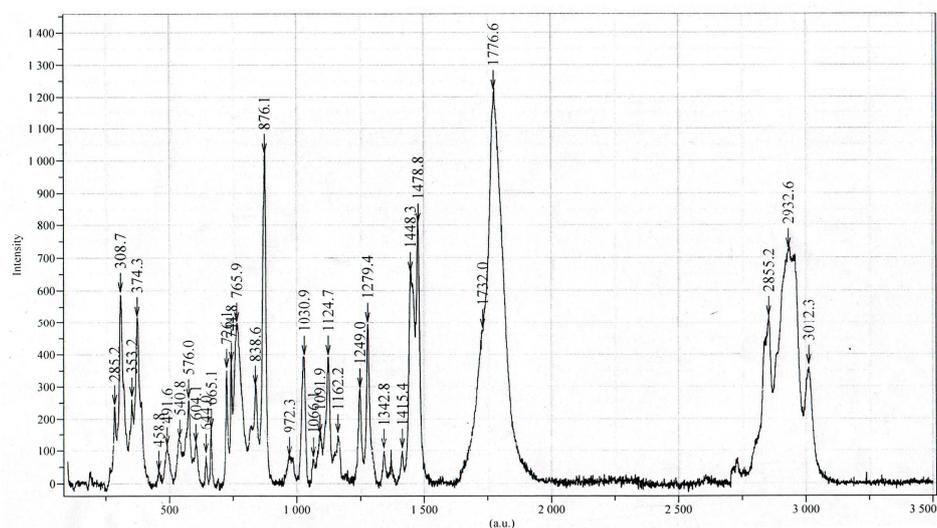
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