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Synthesis of Lithio-*F*-adamantanes: The First Documented ^{19}F NMR Spectrum of a Perfluoroalkyllithium and the Rearrangement of 2-Lithio-*F*-adamantane to 1-Lithio-*F*-adamantane

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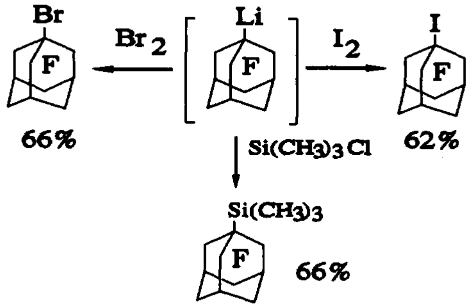
Summary: The synthesis, ^{19}F-NMR, and reactions of a very stable diamondoid perfluoroalkyllithium, 1-lithio-*F*-adamantane, and the observation of an unusual rearrangement of 2-lithio-*F*-adamantane to 1-lithio-*F*-adamantane are reported.

Recently, we reported the synthesis of 1- and 2-methyl-*F*-adamantanes from metalations of the corresponding chloro-*F*-adamantanes with methyllithium.[1] The mechanism of the reaction has not been investigated, but it is obvious that the reaction intermediates are 1- and 2-lithio-*F*-adamantanes, respectively. Like unfluorinated lithioadamantanes,[2,3] lithio-*F*-adamantanes were demonstrated to be very good synthons for making other perfluoroadamantane derivatives (see Scheme I). This prompted us to examine in more detail the possible mechanisms of these reactions. We report herein the synthesis, ^{19}F NMR, and reactions of a very stable diamondoid perfluoroalkyllithium, 1-lithio-*F*-adamantane, and the observation of an unusual rearrangement of 2-lithio-*F*-adamantane to 1-lithio-*F*-adamantane.

To synthesize 1-lithio-*F*-adamantane, 1-hydryl-*F*-adamantane (0.1 g, 0.246 mmol) was dissolved in 0.5 mL of diethyl ether in an NMR tube, and 0.2 mL of methyllithium ether solution (1.4 M, 0.28 mmol, halide 0.05 M) was injected dropwise at −78 °C under an N_2 atmosphere. The ^{19}F NMR spectrum was recorded immediately on a JEOL FX 90Q FTNMR spectrometer (omniprobe and NM-PVTS1 programmable VT system) at −60 °C operating at 84.74 MHz. The ^{19}F NMR spectra indicated that 1-hydryl-*F*-adamantane signals disappeared gradually and were no longer observed after 15 min, and a new set of signals which were assigned to 1-lithio-*F*-adamantane appeared. It appears that 1-lithio-*F*-adamantane obtained by this method is thermally stable at 0 °C as long as no other reactive species is present. The remarkable stability of 1-lithio-*F*-adamantane is understandable since "β elimination" of lithium fluoride to form an anti-Bredt's olefin is unfavorable and "α elimination" of lithium fluoride is not possible. The same ^{19}F NMR spectrum of 1-lithio-*F*-adamantane was observed from the reaction of 1-chloro-*F*-adamantane and *tert*-butyllithium or *n*-butyllithium. However, 1-lithio-*F*-adamantane could not be detected by ^{19}F NMR during the reaction of 1-chloro-*F*-adamantane and methyllithium. It is clear that the coupling reaction between 1-lithio-*F*-adamantane and methyl chloride formed in situ is very fast. 1-Lithio-*F*-adamantane generated from the reaction of 1-chloro-*F*-adamantane and *tert*-butyllithium or *n*-butyllithium is stable for 5 days at −78 °C and 3 days at 0 °C. After that time new peaks which may belong to 1-*tert*-butyl-*F*-adamantane (−110.55, −122.62, and −221.25 ppm) or 1-*n*-butyl-*F*-adamantane (−113.08, −121.05, and −219.00 ppm) appeared. These two major products isolated in small amounts have not been fully characterized. Clearly, steric hindrance makes the coupling reactions between the relatively more bulky *tert*-butyl and *n*-butyl groups and 1-lithio-*F*-adamantane somewhat less favorable. Steric hindrance was similarly involved in the synthesis of hexalithiobenzene.[4] 1-Lithio-*F*-adamantane is easily converted to 1-iodo-*F*-adamantane, 1-bromo-*F*-adamantane, and 1-(trimethylsilyl)-*F*-adamantane by the addition of iodine, bromine, and trimethylchlorosilane respectively (see Scheme I).

Scheme I



The ^{19}F NMR spectrum of 1-lithio-*F*-adamantane is interesting. It consists of a peak at −97.70 ppm, an AB pattern (ϕ_A = −118.11 ppm, ϕ_B = −122.50 ppm, J_{AB} = 282.08 Hz) in the CF_2 region, and a peak at −205.58 ppm in the CF region (see Figure 1). This appears to be the first documented ^{19}F NMR spectrum of a perfluoroalkyllithium compound. Interestingly, the chemical shifts are shifted to lower field relative to 1-hydryl-*F*-adamantane and the 1-halo-*F*-adamantanes.[5] This shift to lower field is opposite to that predicted by a simple inductive effect. The Li–C bond in 1-lithio-*F*-adamantane is partly anionic in nature. The large negative polarization at one bridgehead carbon atom of the *F*-adamantane skeleton may have large anisotropic or electronic effect on neighboring fluorine atoms shifting the chemical shifts to lower field and producing an AB pattern at the γ-position (CF_aF_b).[6,7]

The ^{19}F NMR spectra in Figure 2 show that the analogous reaction of 2-hydryl-*F*-adamantane and methyllithium initially gave 2-lithio-*F*-adamantane, which then rearranged to 1-lithio-*F*-adamantane within 2 h at −60 °C. The rearrangement is so facile that no pure 2-lithio-*F*-adamantane was observed by ^{19}F NMR even though the spectrum was taken immediately after methyllithium was added. When the rearrangement was complete, the reaction solution was quenched by water. The isolated

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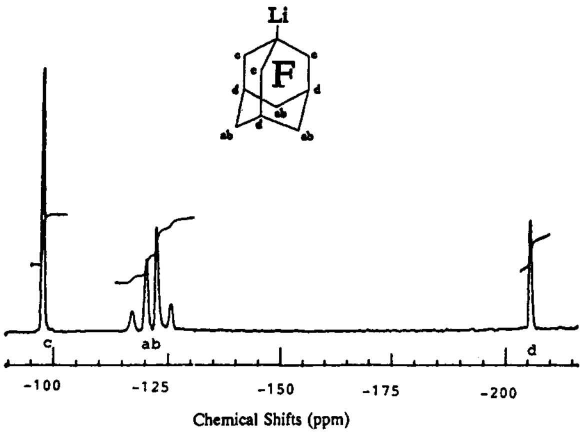


Figure 1. ^{19}F NMR spectrum of 1-lithio-*F*-adamantane.

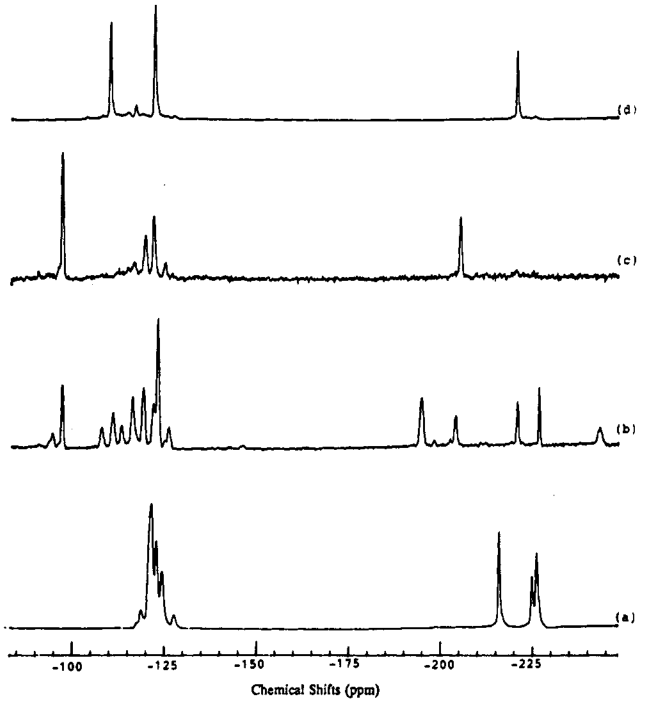
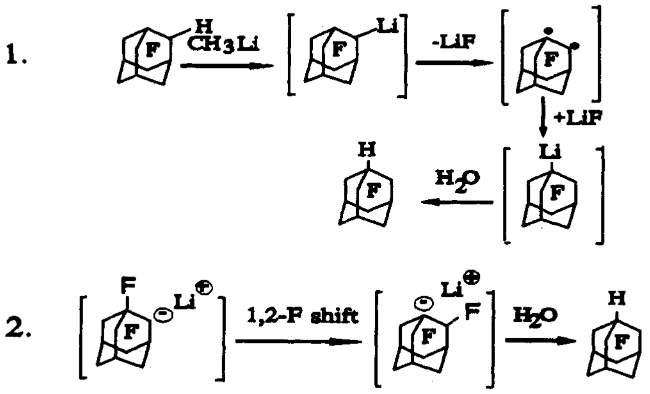


Figure 2. ^{19}F NMR spectra of 2-hydryl-*F*-adamantane (a), 10 min (b) and 120 min (c) after addition of methyllithium to 2-hydryl-*F*-adamantane, and after addition of water (d) to this reaction mixture.

products were identified as 1-hydryl-*F*-adamantane (95%) and 1-methyl-*F*-adamantane (5%); no 2-substituted *F*-adamantane derivativs were identified. This further substantiates that the rearrangement does take place. The thermodynamic driving force for this rearrangement arises from the greater stability of the tertiary bridgehead 1-*F*-adamantyl anion relative to the secondary 2-*F*-adamantyl anion. The rearrangement can be compared to that found in unfluorinated adamantanes where relative instability of the secondary 2-adamantyl cation causes rearrangement to the more stable tertiary bridgehead 1-adamantyl cation.[8] Similar rearrangement reactions, however, have not been found for any unfluorinated alkyllithium.[2] There are two possible rearrangement mechanisms leading to the formation of 1-lithio-*F*-adamantane (Scheme II). The first involves the formation of a biradical, while the second involves an intramolecular fluorine shift. A consequence of the latter mechanism, which violates orbital symmetry rules, is that the fluorine atom which shifts should carry a formal positive charge. These considerations cause us to favor the first mechanism. A similar biradical mechanism has been proposed by Tatlow et al. to explain the decomposition reactions of lithiated undecafluorobicyclo[2.2.1]heptane,[9] lithiated 1*H*,4*H*-decafluorobicyclo[2.2.1]heptane,[10] and lithiated 1*H*,4-(trifluoromethyl)decafluorobicyclo[2.2.1]heptane.[11]

Scheme II



Supplementary Material Available: Experimental procedures, characterization data, and ^{19}F NMR spectra of all compounds described in Scheme I (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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