Lithium fluoride formed *in situ* is trapped by [$TiF_3(C_5Me_5)]_2$: an equilibrium with cleavage of a Ti–F–Ti bond and a model compound for molecular lithium fluoride

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Synthesis and structure of [{(C_5Me_5)TiF_3}$_4$(LiF)] and its solution equilibrium involving cleavage of a titanium–fluorine–titanium bond is reported.

Fluorine bridging accounts for structural diversity of fluorides of main group elements and transition metals and for formation of reaction intermediates.[1] The reactivity of a Ti–F–Ti unit in fluorotitanium compounds is of particular interest since the cleavage of this unit would leave the titanium centre with high electrophilicity due to polar Ti–F bonds.[2] The catalytic activity of the fluorotitanium binaphthol complex used in the enantioselective addition of allylsilanes to aldehydes[3] was explained by cleavage of two Ti–F–Ti bonds during the catalytic cycle.[2] Here, we report on the equilibrium of cleavage and reformation of two Ti–F–Ti bonds in a solution of [{(C_5Me_5)TiF_3}$_4$(LiF)] **1** observed by ^{19}F NMR spectroscopy.

The high lattice energy of lithium fluoride explains the absence of its solid complexes.[4] Lithium fluoride, prepared *in situ* from lithium chloride and trimethyltin fluoride, has now been successfully trapped by [$TiF_3(C_5Me_5)]_2$ to yield **1**. The reaction of [$TiF_3(C_5Me_5)]_2$, Me_3SnF and LiCl in a molar ratio of 2 : 1 : 1 in THF followed by evaporation of Me_3SnCl and solvent and recrystallization from pentane afforded red crystals of **1**.‡ The molecule of **1** in the solid state§ consists of two [$Ti_2F_6(C_5Me_5)_2$] units connected by a lithium atom and a bridging fluorine atom (Fig. 1). Each titanium atom is coordinated by five fluorines and a C_5Me_5 ligand. The lithium atom is coordinated by four fluorines arranged in a distorted tetrahedron. The Li–F distances are similar to those in Li[{$(Me_3Si)_3C$}AlF_3]·THF[5] with fourfold coordinated lithium, however shorter than those in lithium fluoride (2.009 Å).[6] Bonding to lithium as well as *trans*-positioned C_5Me_5 ligand causes elongation of the Ti–F bonds. The Ti–F–Ti bonds not affected by the *trans*-C_5Me_5 ligand are on average 10% longer than the terminal Ti–F bonds.

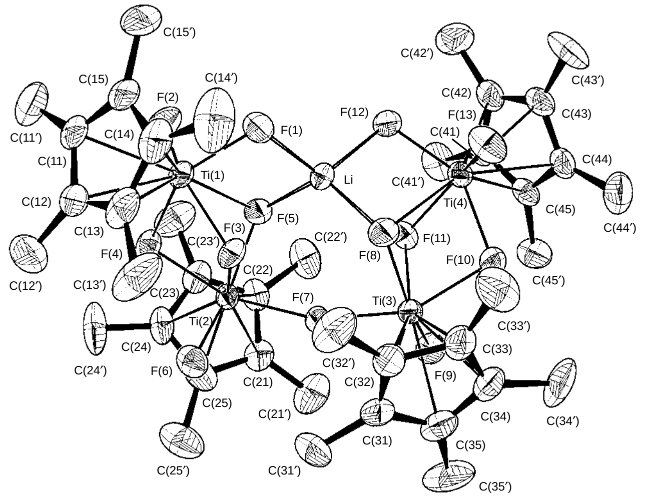


Fig. 1 Crystal structure of **1**. Hydrogen atoms are not shown. Selected bond lengths (Å) and angles (°): Ti(1)–F(1) 1.873(4), Ti(1)–F(2) 1.822(6), Ti(1)–F(3) 1.978(4), Ti(1)–F(4) 1.999(4), Ti(1)–F(5) 2.421(5), Ti(2)–F(6) 1.826(5), Ti(2)–F(5) 1.966(4), Ti(2)–F(7) 2.007(3), Ti(2)–F(4) 2.024(4), Ti(2)–F(3) 2.136(5), Li–F(1) 1.864(13), Li–F(5) 1.926(13), Li–F(8) 1.932(12), Li–F(12) 1.866(12); F(1)–Ti(1)–F(2) 93.0(2), F(1)–Ti(1)–F(5) 75.3(2), F(1)–Ti(1)–F(3) 85.0(2), F(1)–Ti(1)–F(4) 142.9(2), Ti(2)–F(8)–Ti(3) 161.1(2), F(1)–Li–F(12) 110.1(7), F(1)–Li–F(5) 89.1(4), F(5)–Li–F(8) 121.0(7).

A color change from orange to red is observed when cooling toluene or chloroform solutions of **1** from 322 to 272 K. Two temperature dependent sets of resonances are found in variable temperature (VT) ^{19}F NMR spectra of $CDCl_3$ or [$^2H_8$]toluene solutions of **1**. The high temperature set of five resonances reversibly converts to a low temperature set of seven resonances on cooling as shown in Fig. 2 in [$^2H_8$]toluene solution. The changes in spectra are in agreement with the equilibrium shown in Scheme 1. Four sharp resonances in the high temperature set (intensity ratio of 2 : 2 : 1 : 2) are assigned to [{$(C_5Me_5)_2Ti_2F_7$}Li] **1a** by comparison with the ^{19}F NMR spectrum of [{$(C_5Me_5)_2Ti_2F_7$}$_2$Ca].[7] The assignment is consistent with

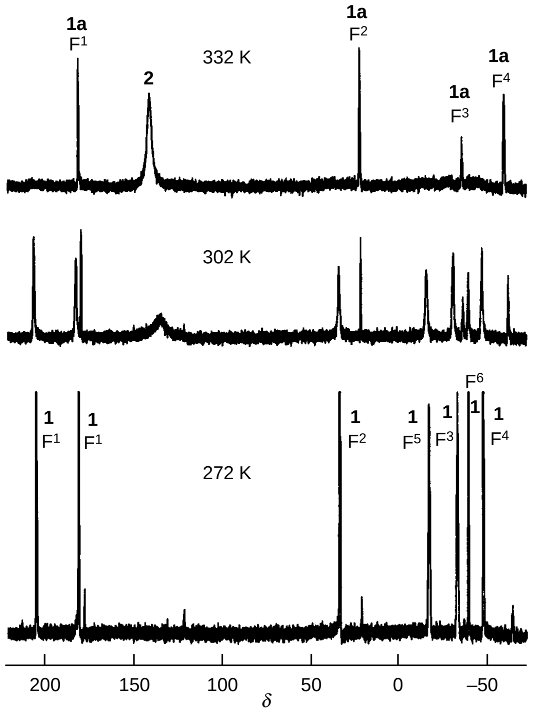
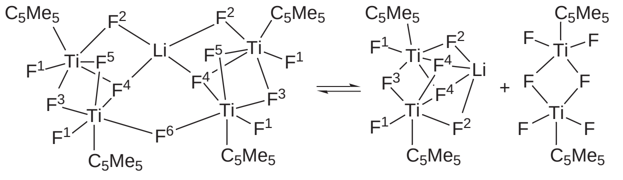


Fig. 2 ^{19}F NMR spectra of **1** ([$^2H_8$]toluene solution) at 332, 302 and 272 K. See Scheme 1 for labels. The area of the signal at δ −38.8 (F^6) in 272 K trace is one half of the respective areas of the other signals.



Scheme 1 Equilibrium in solution of **1**

lithium symmetrically bonded to two terminal and to two bridging fluorines from the $[Ti_2F_7(C_5Me_5)_2]^-$ moiety. The bonding of fluorines to quadrupolar lithium causes decoupling of fluorine resonances and a high field shift as already observed in the calcium compound.[7] The resonance of terminal fluorines appears as a quintet due to coupling to four fluorine atoms. The remaining, fifth, broad line of the high temperature set is attributed to the resonance of $[(C_5Me_5)TiF_3]_2$.¶ The low temperature set has six resonances of equal intensities and one with half of the intensity that could be assigned to **1** having six pairs of equivalent fluorine atoms and a single fluorine atom bridging two $[Ti_2F_6(C_5Me_5)_2]$ units. The ^7Li NMR signal of **1** appears as a singlet at 302 K, and as a quintet at 272 K, showing coupling to four fluorine atoms.

The equilibrium shown in Scheme 1 was studied by VT ^{19}F NMR of a $[^2H_8]$toluene solution of **1** in the temperature range 272–312 K, and resulted in $\Delta H = 75 \pm 3$ kJ mol^{-1} and $\Delta S = 197 \pm 2$ J mol^{-1} K^{-1}.‖ The large positive ΔS value supports an entropy driven dissociation equilibrium. Moreover, a shift of the equilibrium to dissociation was observed in ^{19}F NMR spectra after diluting the solution of **1**. The dissociation involves cleavage of two titanium–fluorine–titanium bonds and changes in the lithium coordination sphere. The determined enthalpy could be therefore only a crude estimate of the binding energy of the titanium–fluorine bond.

In conclusion, *in situ* prepared lithium fluoride was trapped with $[TiF_3(C_5Me_5)]_2$ giving **1**. Dissociation of **1** to **1a** and $[TiF_3(C_5Me_5)]_2$ is accompanied by a cleavage of Ti–F–Ti bonds. In solution observed **1a** could serve as a model compound for studying the reactivity of 'lithium fluoride' since the lithium atom is in a rather distorted coordination sphere. Its reactivity is already demonstrated by reforming **1** at low temperatures.

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Notes and References

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‡ Lithium fluoride in bulk is unreactive towards $[TiF_3(C_5Me_5)]_2$.[8] *Data for* **1**. Decomposition 100–110 °C. Anal. Calc. for $C_{40}H_{60}F_{13}LiTi_4$: C, 48.71; H, 6.13. Found: C, 47.86; H, 6.22%. ^1H NMR (300 MHz, $CDCl_3$, 302 K) δ 2.10 (s) and 2.14 (s). ^{19}F NMR (282 MHz, $CDCl_3$, 302 K), resonances of **1a**: δ 148.4 (qnt, 2 F, $^2J_{FF}$ 40 Hz), 25.0 (s, 2 F), −32.4 (m, 1 F), −62.1 (s, 2 F); resonances of **1**: δ 183.6 (s, 2 F), 149.5 (s, 2 F), 32.0 (s, 2 F), −10.4 (s, 2 F), −30.8 (s, 2 F), −36.8 (s, 1 F), −43.2 (s, 2 F); resonance of **2**: δ 121 (br s). ^7Li NMR (116 MHz, $CDCl_3$, 302 K): δ −1.64 (s); 272 K: δ −1.63 (qnt, $^1J_{LiF}$ 49 Hz). IR (Nujol) (cm^{-1}): 630s, 615vs, 522m, 494s.

§ *X-Ray crystallography. Crystal data for* **1**: $C_{40}H_{60}F_{13}LiTi_4$, $M = 986.36$, red parallelepiped crystal of dimensions $0.4 \times 0.4 \times 0.2$ mm, triclinic, space group $P1$, $a = 11.144(2)$, $b = 11.660(1)$, $c = 20.730(3)$ Å, $\alpha = 96.609(9)$, $\beta = 99.970(9)$, $\gamma = 112.746(8)°$, $U = 2397.0(6)$ Å^3, $Z = 2$, $D_c = 1.367$ g cm^{-3}, $T = 293$ K, Enraf-Nonius CAD-4 diffractometer using Mo-Kα radiation ($\lambda = 0.710\,73$ Å) in the 2θ range 2–56°, 12 080 reflections total, 11 483 unique. The structure was solved by direct methods and refined using Xtal 3.2.[9] Full matrix, least squares refinement on F of 523 parameters converged at $R = 0.065$ and $wR = 0.059$ using 3867 reflections with $I > 2.5\sigma(I)$. CCDC 182/814.

¶ Dimeric $[TiF_3(C_5Me_5)]_2$ exists in the solid state.[10] The ^{19}F NMR spectrum of $[TiF_3(C_5Me_5)]_2$ at 248 K in $CDCl_3$ has resonances of terminal (δ 158.7, s, 4 F) and bridging (δ −40.6, s, 2 F) fluorine atoms that coalesce at 273 K to a broad singlet (δ 114).

‖ By integrating the ^{19}F NMR resonances of terminal fluorines bound to lithium (F^2) in **1** and **1a**, respectively, (0.02 M $[^2H_8]$toluene solution) the following $C_{\mathbf{1}}/C_{\mathbf{1a}}$ concentration ratios were found: 1.54 (312 K), 2.18 (302 K), 3.38 (297 K), 4.62 (292 K), 6.26 (287 K), 7.87 (282 K), 15.04 (272 K).). The equilibrium constants were calculated using equation: $K = C_{\mathbf{1a}}C_{\mathbf{2}}/C_{\mathbf{1}} = C^2_{\mathbf{1a}}/C_{\mathbf{1}}$.

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