DOI: 10.1002/anie.200907162

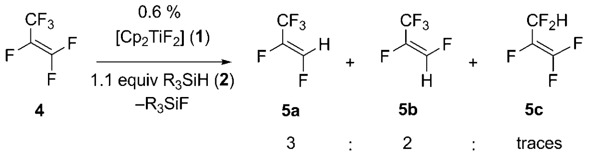
# Titanium-Catalyzed C–F Activation of Fluoroalkenes**

*Moritz F. Kühnel and Dieter Lentz**

The thermodynamic and kinetic inertness of carbon–fluorine bonds has proven to be a mixed blessing to mankind. Ideally suited for practical applications, organofluorine compounds have found their way into everyday life in chemically stable polymers like polytetrafluoroethene (PTFE) and in modern pharmaceutical chemistry, where fluorine substitution has beneficial effects on the physicochemical and physiological properties of organic molecules.[1] However, halofluorocarbons have also found their way into the upper atmosphere, where their long-time persistence has had a deleterious effect on the ozone layer and has contributed to global warming.[2] Consequently, there is a long-standing interest in selectively activating the inert carbon–fluorine bond, although the number of catalytically active systems for such applications is still very sparse.[3,4] Most of these catalysts are based on late transition metals, but recently they have been competing with first-row transition metals as well as with Lewis acidic main-group species.[5,6]

The few examples of catalytic activation of fluoroalkenes have a common drawback, as they are either costly or slow and inefficient in terms of turnover frequencies (TOFs) and turnover numbers (TONs), not to mention that the high sensitivity of most catalysts limits possible practical applications.[7] Complexes of the less expensive Group 4 metals are reactive towards fluoroalkenes, as shown by Jones et al. in stoichiometric hydrodefluorination (HDF) employing zirconium and hafnium hydrides.[8] However, C–F activation catalyzed by Group 4 metals is known only for fluoroarenes.[9] We were surprised to find that titanium, despite its broad application in homogeneous catalysis, has rarely been used in C–F activation.[10] In fact only two examples of titanium-catalyzed C–F activation can be found in the literature.[11] Richmond et al. have shown that titanocene dihalides under reducing conditions can catalytically defluorinate perfluorinated cycloalkanes to give perfluoroarenes and their HDF products. Herein, we report the first titanium-catalyzed HDF of fluoroalkenes to give hydrofluoroalkenes at room temperature as part of our studies on the hydrometalation of fluorinated substrates.[12]

As reported previously,[13] treatment of a solution of air-stable titanocene difluoride (**1**) with silanes **2a**–**c** results in the formation of the titanium(III) hydride species **3**. Upon addition of hexafluoropropene (**4**), the green color of the metal complex changes to red within minutes and 1,2,3,3,3-pentafluoropropene (**5a**, **b**) is obtained in high yields (Scheme 1).



***Scheme 1.*** Hydrodefluorination of hexafluoropropene (**4**) to give (*Z*)-pentafluoropropene (**5a**) and (*E*)-pentafluoropropene (**5b**); $R_3SiH = Ph_2SiH_2$ (**2a**), $PhSiH_3$ (**2b**), poly(methylhydrosiloxane) (PMHS, **2c**).

The reaction is very fast: TOFs of up to 26 $min^{-1}$ have been observed at 20 °C; it even proceeds at −25 °C with a TOF of 0.1 $min^{-1}$, and more than 125 turnovers are possible (Table 1). These values dramatically exceed the scarce published data on comparable reactions: A TOF of 0.05 $min^{-1}$ at 100 °C and a TON of less than 10 have been reported for the HDF of **4** employing a β-diketiminate iron(II) fluoride catalyst;[7g] a TOF of 0.2 $min^{-1}$ at 35 °C and a TON of 8 were observed for the related HDF of fluoroethylene using Wilkinsons's catalyst.[7e] However, the recently published rhodium-catalyzed functionalization of **4** to give fluoroalkyl boronates achieves a TOF of 12.5 $min^{-1}$ at room temperature with a TON of up to 250.[7a] The high chemoselectivity of the titanium catalyst is demonstrated by the absence of any 1,1,3,3,3-pentafluoropropene (**6**) in the reaction mixture.

To expand the scope of titanium-catalyzed C–F activation, we subjected the commercially relevant 1,1,3,3,3-pentafluoropropene (**6**) and 3,3,3-trifluoropropene (**8**) to similar reaction conditions (Scheme 2). Hydrodefluorination of **6** proceeded smoothly at room temperature, leading to 1,3,3,3-tetrafluoropropene (**7a**,**b**) and 1,1,3,3-tetrafluoropropene (**7c**). The reaction was significantly slower with a TOF of 0.69 $min^{-1}$, but highly selective leading to predominantly the *E*-isomer **7a** (90 %) along with small amounts of the *Z*-isomer **7b** (6 %) and **7c** (4 %; Scheme 2).

Although **8** does not contain any olefinic fluorine substituents, HDF is possible, but the reaction proceeds less smoothly. A drastically lowered TOF of 0.04 $min^{-1}$, formation of large amounts of the hydrogenation product **9b**, and the generation of the secondary HDF products **9c**,**d** prior to complete consumption of the starting material make this

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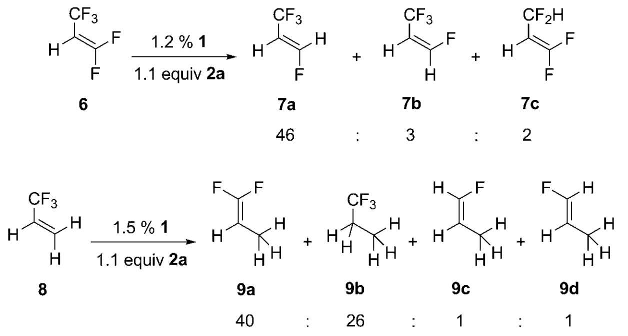
[*] M. F. Kühnel, Prof. Dr. D. Lentz
Freie Universität Berlin
Institut für Chemie und Biochemie, Anorganische Chemie
Fabeckstrasse 34–36, 14195 Berlin (Germany)
Fax: (+49) 30-838-52440
E-mail: lentz@chemie.fu-berlin.de

[**] We thank Solvay Germany for donating hexafluoropropene and Hoechst for donating trifluoropropene. This work was supported financially by the Deutsche Forschungsgemeinschaft as part of the graduate school program GRK 1582/1 “Fluor als Schlüsselelement”. We thank S. Matthies, D. Nitsch, and. M. Sparenberg for their contributions.

*Table 1:* Catalytic hydrodefluorination of fluoroalkenes with titanocene difluoride (**1**).[a]

| [**1**] [μmol] | Substrate (mmol) | Solvent (mL) | *t* [min] | Silane (mmol) | Yield after workup[b] | Recovered substrate[b] [%] | TON[c] |
|---|---|---|---|---|---|---|---|
| 6.9 | **4** (1.09) | diglyme (2.0) | 15 | **2a** (1.08) | **5a**: 47%, **5b**: 32% | **4** (0) | 125 |
| 6.0 | **4** (0.98) | diglyme (2.0) | 15 | **2b** (1.11) | **5a**: 8%, **5b**: 6% | **4** (61) | 22 |
| 6.5 | **4** (1.02) | diglyme (2.0) | 15 | **2c** (1.21) | **5a**: 8%, **5b**: 6% | **4** (60) | 22 |
| 0.0 | **4** (1.05) | diglyme (2.0) | 3600 | **2a** (1.07) | 0% | **4** (91) | |
| 13.9[d] | **4** (1.14) | diglyme (2.0) | 75 | **2a** (1.06) | **5a**: 5%, **5b**: 3% | **4** (60) | 6 |
| 2.8 | **4** (0.49) | diglyme (0.5) | 3 | **2a** (0.54) | **5a**: 26%, **5b**: 18% | **4** (0) | 79 |
| 6.5 | **4** (0.96) | toluene (2.0) | 15 | **2a** (1.09) | **5a**, **5b**: traces | **4** (76) | <1 |
| 13.0 | **6** (1.05) | diglyme (2.0) | 60 | **2a** (1.11) | **7a**: 46%, **7b**: 3%, **7c**: 2% | **6** (46) | 42 |
| 16.2 | **8** (1.05) | diglyme (2.0) | 1130 | **2a** (1.07) | **9a**: 39%, **9b**: 25%, **9c**: 1%, **9d**: 1% | **8** (7) | 43 |

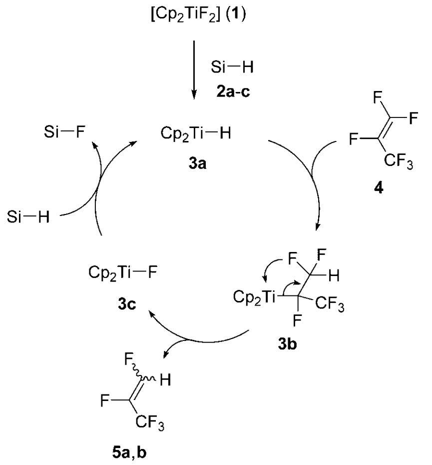
[a] Reactions conducted at room temperature. [b] Yields were determined by integration of $^{19}$F NMR resonances in the product mixture (versus internal fluorobenzene) after workup. [c] TON is defined as the total moles of product divided by the moles of precatalyst. [d] Reaction conducted at −25 °C.



*Scheme 2.* Catalytic hydrodefluorination of **6** and **8**.

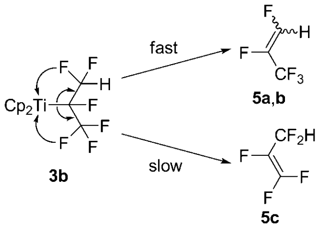
reaction suitable for further optimization. The hydrogenation can be explained by the presence of hydrogen resulting from the competing silane dehydrocoupling also catalyzed by **1**.[13c–e]

We assume the reaction mechanism to follow the well-established sequence of olefin insertion followed by β-fluoride elimination (Scheme 3), which was previously described for the stoichiometric reaction of zirconium hydrides with **4** to give **5b**.[8b–e] In the activation step, the precatalyst **1** reacts with silane **2** forming catalytically active titanium (III) hydride (or silyl hydride) **3a**, an intermediate previously postulated in the context of imine hydrosilylation and silane dehydrocoupling.[13] Insertion of **4** into the metal–hydride bond yields a titanium fluoroalkyl species **3b**, which is prone to undergo β-fluoride elimination[14] to form the strong titanium–fluorine bond in **3c** and the hydrodefluorination products **5a**,**b**. The fluoride **3c** can then be reconverted into the active species **3a** by reaction with silane **2**, since fluorosilane formation provides a thermodynamic sink.[13f]



*Scheme 3.* Proposed mechanism of the hydrodefluorination of **4** catalyzed by **1**.

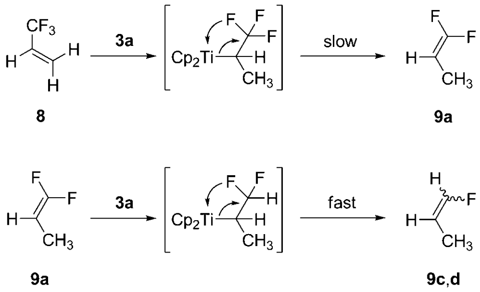
These assumptions are supported by the fact that besides the main hydrodefluorination products **5a**,**b**, trace amounts of the isomeric 1,1,2,3,3-pentafluoropropene (**5c**) were identified in the reaction mixture by their $^{19}$F NMR spectra. This compound is formed by fluoride elimination from the less reactive $CF_3$ group rather than the more reactive $CF_2H$ group in **3b** (Scheme 4).



*Scheme 4.* Formation of **5c** during HDF of **4** to give **5a**,**b**.

The formation of 1,1-difluoropropene (**9a**) from **8** must involve an addition step to explain the formation of a methyl group (Scheme 5). Subsequent β-fluoride elimination from the $CF_3$ group in the intermediate, again, is expected to be slow. In contrast, HDF of the primary product **9a** should be significantly faster as it involves an elimination step from a more reactive $CF_2H$ group. This is in good agreement with the observed formation of monofluoropropenes **9c**,**d** prior to the complete consumption of **8**.

In summary, we have shown that air-stable titanocene difluoride can act as a highly efficient catalyst for the hydrodefluorination of fluoroalkenes. The HDF of hexafluoropropene proceeds at room temperature in high yields and outstanding turnover frequencies of up to 26 min$^{-1}$ and turnover numbers of up to 125. 1,1,3,3,3-Pentafluoropro-



***Scheme 5.*** Formation of **9a** and **9c,d** from **8**.

pene and 3,3,3-trifluoropropene can also be converted effectively to tetrafluoropropene and difluoropropene, respectively. These results represent a rare example of the catalytic activation of fluoroalkenes leading to less fluorinated compounds, which have a negligible global-warming potential.[15] This type of reaction may also provide a promising means of detoxifying highly toxic perfluoroalkenes like perfluoroisobutene and perfluorocyclobutene.[16] Further studies to elucidate the underlying mechanism as well as to expand the scope of the titanium-catalyzed C–F activation are currently in progress.

## *Experimental Section*

All preparations were performed using standard vacuum-line techniques or by working in an argon-filled glove box. Diglyme and toluene were distilled from sodium/benzophenone; diphenylsilane (**2a**) and phenylsilane (**2b**) were distilled from calcium hydride; PMHS (**2c**) was dried over molecular sieves. Titanocene difluoride (**1**) was prepared following Roesky's method;[17] hexafluoropropene (**4**) (Solvay), 1,1,3,3,3-pentafluoropropene (**6**) (SynQuest Labs), and 3,3,3-trifluoropropene (**8**) (Hoechst) were used as received.

Reaction conditions are listed in Table 1. In a 50 mL single-necked flask equipped with a PTFE valve, a solution of silane **2a–c** and titanocene difluoride (**1**) was heated until its color changed to green (1–5 min). After repeated degassing, fluoropropene **4**, **6**, or **8** was condensed into the reaction vessel, which was subsequently stirred at room temperature for the designated period of time. The crude reaction mixture was purified by fractional condensation under vacuum through two subsequent traps kept at −80 °C and −196 °C, respectively. The contents of the second trap were condensed into an NMR tube containing a standard $CDCl_3$ solution of fluorobenzene. Hydrodefluorination products were identified by their characteristic NMR spectra.[18,19]

Received: December 18, 2009

**Keywords:** C–F activation · alkenes · homogeneous catalysis · hydrodefluorination · titanium

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[1] a) B. E. Smart in *Molecular Structure and Energetics*, *Vol. 3* (Eds.: J. F. Liebman, A. Greenberg), VCH, Weinheim, **1986**, p. 141; b) M. Hudlicky, A. Pavlath, *Chemistry of Organic Fluorine Compounds II, a Critical Review*, American Chemical Society, Washington, DC, **1995**; c) B. E. Smart, *J. Fluorine Chem.* **2001**, *109*, 3–11.

[2] a) D. G. Victor, G. J. MacDonald, *Clim. Change* **1999**, *42*, 633–662; b) C. M. Roehl, D. Boglu, C. Brühl, G. K. Moortgat, *Geophys. Res. Lett.* **1995**, *22*, 815–818; c) M. J. Molina, F. S. Rowland, *Nature* **1974**, *249*, 810–812.

[3] For reviews on C–F bond activation see: a) H. Amii, K. Uneyama, *Chem. Rev.* **2009**, *109*, 2119–2183; b) R. N. Perutz, T. Braun in *Comprehensive Organometallic Chemistry III*, *Vol. 1* (Eds.: R. T. Crabtree, M. P. Mingos), Elsevier, Oxford, **2007**, pp. 725–758; c) H. Torrens, *Coord. Chem. Rev.* **2005**, *249*, 1957; d) U. Mazurek, H. Schwarz, *Chem. Commun.* **2003**, 1321–1326; e) T. Braun, R. N. Perutz, *Chem. Commun.* **2002**, *48*, 1818–1822; f) J. Burdeniuc, B. Jedlicka, R. H. Crabtree, *Chem. Ber.* **1997**, *130*, 145–154; g) J. L. Kiplinger, T. G. Richmond, C. E. Osterbert, *Chem. Rev.* **1994**, *94*, 373.

[4] For recent work on C–F bond activation see: a) A. Nova, R. Mas-Balleste, G. Ujaque, P. Gonzalez-Duarte, A. Lledos, *Dalton Trans.* **2009**, 5980–5988; b) W. Gu, M. R. Haneline, C. Douvris, O. V. Ozerov, *J. Am. Chem. Soc.* **2009**, *131*, 11203–11212; c) S. P. Reade, A. L. Acton, M. F. Mahon, T. A. Whittlesey, *Eur. J. Inorg. Chem.* **2009**, 1774–1785; d) G. B. Deacon, C. M. Forsyth, P. C. Junk, J. Wang, *Chem. Eur. J.* **2009**, *15*, 3082–3092; e) S. P. Reade, M. F. Mahon, M. K. Whittlesey, *J. Am. Chem. Soc.* **2009**, *131*, 1847–1861; f) A. Nova, S. Erhardt, N. A. Jasim, R. N. Perutz, S. A. Macgregor, J. E. McGrady, A. C. Whitwood, *J. Am. Chem. Soc.* **2008**, *130*, 15499–15511; g) S. Erhardt, S. A. Macgregor, *J. Am. Chem. Soc.* **2008**, *130*, 15490–15498; h) A. Nova, R. Mas-Belleste, G. Ijaque, P. Gonzalez-Duarte, A. Lledos, *Chem. Commun.* **2008**, 3130–3132; i) T. Wang, J. A. Love, *Organometallics* **2008**, *27*, 3290–3296; j) L. Schwartsburd, R. Cohen, L. Konstantinovski, D. Milstein, *Angew. Chem.* **2008**, *120*, 3659–3662; *Angew. Chem. Int. Ed.* **2008**, *47*, 3603–3606; k) R. J. Lindup, T. B. Marder, R. N. Perutz, A. C. Whitwood, *Chem. Commun.* **2007**, 3664–3666; l) T. Braun, D. Noveski, M. Ahijado, F. Wehmeier, *Dalton Trans.* **2007**, 3820–3825; m) W. Liu, K. Welch, C. O. Trindle, M. Sabat, W. H. Myers, W. D. Harman, *Organometallics* **2007**, *26*, 2589.

[5] Recent examples: a) S. A. Johnson, E. T. Taylor, S. J. Cruise, *Organometallics* **2009**, *28*, 3842–3855; b) T. Zheng, H. Sun, Y. Chen, X. Li, S. Durr, U. Radius, K. Harms, *Organometallics* **2009**, *28*, 5771–5776; c) N. Y. Adonin, S. A. Prikhod'ko, V. V. Bardin, V. N. Parmon, *Mendeleev Commun.* **2009**, *19*, 260–262; d) S. A. Prikhod'ko, N. Y. Adonin, D. E. Babushkin, V. N. Parmon, *Mendeleev Commun.* **2008**, *18*, 211–212; e) S. Camadanli, R. Beck, U. Floerke, H.-F. Klein, *Dalton Trans.* **2008**, 5701–5704; f) T. Schaub, P. Fischer, A. Steffen, T. Braun, U. Radius, A. Mix, *J. Am. Chem. Soc.* **2008**, *130*, 9304–9317; g) T. Schaub, M. Backes, U. Radius, *Eur. J. Inorg. Chem.* **2008**, 2680–2690.

[6] Recent examples: a) W. Gu, M. R. Haneline, C. Douvris, O. V. Ozerov, *J. Am. Chem. Soc.* **2009**, *131*, 11203–11212; b) G. Meier, T. Braun, *Angew. Chem.* **2009**, *121*, 1575–1577; *Angew. Chem. Int. Ed.* **2009**, *48*, 1546–1548; c) M. Ali, L.-P. Liu, G. B. Hammond, B. Xu, *Tetrahedron Lett.* **2009**, *50*, 4078–4080; d) C. Douvris, O. V. Ozerov, *Nature* **2008**, *321*, 1188–1190; e) J. Terao, S. A. Begum, Y. Shinohara, M. Tomita, Y. Naitoh, N. Kambe, *Chem. Commun.* **2007**, 855–857; f) M. Klahn, C. Fischer, A. Spannenberg, U. Rosenthal, I. Krossing, *Tetrahedron Lett.* **2007**, *48*, 8900–8903; g) R. Panisch, M. Bolte, T. Müller, *J. Am. Chem. Soc.* **2006**, *128*, 9676–9682.

[7] a) T. Braun, M. A. Salomon, K. Altenhöner, M. Teltewskoi, S. Hinze, *Angew. Chem.* **2009**, *121*, 1850–1854; *Angew. Chem. Int. Ed.* **2009**, *48*, 1818–1822; b) T. Braun, F. Wehmeier, K. Altenhöner, *Angew. Chem.* **2007**, *119*, 5415–5418; *Angew. Chem. Int. Ed.* **2007**, *46*, 5321–5324; c) S. Yamada, T. Takahashi, T. Konno, T. Ishihara, *Chem. Commun.* **2007**, 3679–3681; d) S. Yamada, M. Noma, T. Konno, T. Ishikara, H. Yamanka, *Org. Lett.* **2006**, *8*, 843–845; e) A. A. Peterson, K. McNeill, *Organometallics* **2006**, *25*, 4938–4940; f) T. Saeki, Y. Takashima, K. Tamao, *Synlett* **2005**, 1771–1774; g) J. Vela, J. M. Smith, Y. Yu,

N. A. Ketterer, Ch. J. Flaschenriem, R. J. Lachicotte, P. L. Holland, *J. Am. Chem. Soc.* **2005**, *127*, 7857 – 7870.

[8] a) R. D. Rieth, W. W. Brennessel, W. D. Jones, *Eur. J. Inorg. Chem.* **2007**, 2839 – 2847; b) E. Clot, C. Mégret, B. M. Kraft, O. Eisenstein, W. D. Jones, *J. Am. Chem. Soc.* **2004**, *126*, 5647 – 5653; c) W. D. Jones, *Dalton Trans.* **2003**, 3991 – 3995; d) B. M. Kraft, W. D. Jones, *J. Am. Chem. Soc.* **2002**, *124*, 8681 – 8689; e) L. A. Watson, D. V. Yandulov, K. G. Caulton, *J. Am. Chem. Soc.* **2001**, *123*, 603 – 611; f) B. M. Kraft, R. J. Lachicotte, W. D. Jones, *J. Am. Chem. Soc.* **2000**, *122*, 8559 – 8560.

[9] a) U. Jäger-Fiedler, M. Klahn, P. Arndt, W. Baumann, A. Spannenberg, V. V. Burlakov, U. Rosenthal, *J. Mol. Catal. A* **2007**, *261*, 184 – 189; b) J. L. Kiplinger, T. G. Richmond, *Chem. Commun.* **1996**, 1115 – 1116.

[10] a) B. C. Bailey, J. C. Huffman, D. J. Mindiola, *J. Am. Chem. Soc.* **2007**, *129*, 5302 – 5303; b) P. A. Deck, M. M. Konaté, B. V. Kelly, C. Slebodnick, *Organometallics* **2004**, *23*, 1089 – 1097; c) M. W. Bouwkamp, J. de Wolf, I. D. H. Morales, J. Gercama, A. Meetsma, S. I. Troyanov, B. Hessen, J. H. Teuben, *J. Am. Chem. Soc.* **2002**, *124*, 12956 – 12957; d) C. Santamaría, R. Beckhaus, D. Haase, W. Saak, R. Koch, *Chem. Eur. J.* **2001**, *7*, 622 – 626; e) M. J. Burk, D. L. Staley, W. Tumas, *J. Chem. Soc. Chem. Commun.*. **1990**, 809 – 810; f) P. M. Treichel, M. A. Chaudhari, F. G. A. Stone, *J. Organomet. Chem.* **1963**, *1*, 98 – 100.

[11] a) B.-H. Kim, H.-G. Woo, W.-G. Kim, S.-S. Yun, T.-S. Hwang, *Bull. Korean Chem. Soc.* **2000**, *21*, 211 – 214; b) J. L. Kiplinger, T. G. Richmond, *J. Am. Chem. Soc.* **1996**, *118*, 1805 – 1806.

[12] a) M. F. Kühnel, D. Lentz, *Dalton Trans.* **2009**, 4747 – 4755.

[13] a) J. F. Harrod, *Coord. Chem. Rev.* **2000**, *206–207*, 493 – 531; b) L. Bareille, S. Becht, J. L. Cui, P. Le Gendre, C. Moïse, *Organometallics* **2005**, *24*, 5802 – 5806; c) K. Selvakumar, K. Rangareddy, J. F. Harrod, *Can. J. Chem.* **2004**, *82*, 1244 – 1248; d) Q. Wang, J. Y. Corey, *Can. J. Chem.* **2000**, *78*, 1434 – 1440; e) F. Lunzer, Ch. Marschner, S. Landgraf, *J. Organomet. Chem.* **1998**, *568*, 253 – 255; f) X. Verdaguer, U. E. W. Lange, M. T. Reding, S. L. Buchwald, *J. Am. Chem. Soc.* **1996**, *118*, 6784 – 6785, and references therein.

[14] For titanium fluoroalkyl and fluoroalkenyl complexes see: a) N. A. Barnes, A. K. Brisdon, I. R. Crossley, R. G. Pritchard, J. E. Warren, *Organometallics* **2004**, *23*, 2680 – 2685; b) F. L. Taw, B. L. Scott, J. L. Kiplinger, *J. Am. Chem. Soc.* **2003**, *125*, 14712 – 14713; c) K. K. Banger, A. K. Brisdon, *J. Organomet. Chem.* **1999**, *582*, 301 – 309; d) M. D. Rausch, D. J. Sikora, D. C. Hrncir, W. E. Hunter, J. L. Atwood, *Inorg. Chem.* **1980**, *19*, 3817 – 3821.

[15] a) V. C. Papadimitriou, R. K. Talukdar, R. W. Portmann, A. R. Ravishankara, J. B. Burkholder, *Phys. Chem. Chem. Phys.* **2008**, *10*, 808 – 820; b) M. D. Hurley, J. C. Ball, T. J. Wallington, *J. Phys. Chem. A* **2007**, *111*, 9789 – 9795.

[16] a) Ch. M. Timperley, *J. Fluorine Chem.* **2004**, *125*, 685 – 693.

[17] a) A. Herzog, F.-Q. Liu, H. W. Roesky, A. Demsar, K. Keller, M. Noltemeyer, F. Pauer, *Organometallics* **1994**, *13*, 1251 – 1256.

[18] a) H. Koroniak, K. W. Palmer, W. R. Dolbier, Jr., H. Q. Zhang, *Magn. Reson. Chem.* **1993**, *31*, 748 – 751; b) R. N. Haszeldine, D. W. Keen, A. E. Tripping, *J. Chem. Soc. C* **1970**, 414 – 421; c) V. W. Weiss, P. Beak, W. H. Flygare, *J. Chem. Phys.* **1967**, *46*, 981 – 988; d) M. Y. DeWolf, J. D. Baldeschwieler, *J. Mol. Spectrosc.* **1964**, *13*, 344 – 359; e) D. D. Elleman, L. C. Brown, D. Williams, *J. Mol. Spectrosc.* **1961**, *7*, 322 – 340.

[19] **5c**: $^{1}H$ (400 MHz, $CDCl_3$): $\delta = 6.37$ ppm (dddt, 1H, $^{3}J_{HF} = 14.9$ Hz, $^{4}J_{HF} = 2.7$ Hz, $^{4}J_{HF} = 1.3$ Hz, $^{2}J_{HF} = 51.1$ Hz, $CF_2H$); $^{19}F$ (376 MHz, $CDCl_3$): $\delta = -93.7$ (dddt, 1F, $^{2}J_{FF} = 63.5$ Hz, $^{3}J_{FF} = 34.9$ Hz, $^{4}J_{FH} = 1.3$ Hz, $^{4}J_{FF} = 12.2$ Hz, $=CF_2$), $-113.8$ (dddt, 1F, $^{3}J_{FF} = 118.1$ Hz, $^{2}J_{FF} = 63.5$ Hz, $^{4}J_{FH} = 2.8$ Hz, $^{4}J_{FF} = 4.8$ Hz, $=CF_2$), $-123.0$ (dddd, 2F, $^{2}J_{FH} = 51.0$ Hz, $^{3}J_{FF} = 17.7$ Hz, $^{4}J_{FF} = 12.2$ Hz, $^{4}J_{FF} = 4.8$ Hz, $CF_2H$), $-196.5$ ppm (dddt, 1F, $^{3}J_{FF} = 118.2$ Hz, $^{3}J_{FF} = 34.9$ Hz, $^{3}J_{FF} = 17.6$ Hz, $^{4}J_{FH} = 14.8$ Hz, $-CF=$). **7c** $^{1}H$ (400 MHz, $CDCl_3$): $\delta = 4.69$ (dq br, 1H, $^{3}J_{HF} = 23.1$ Hz, $^{3}J_{HF} = 7$ Hz, $^{3}J_{HH} = 7$ Hz, $^{4}J_{FH} = 0.9$ Hz, $-CH=$), 6.46 ppm (dtt, 1H, $^{2}J_{FH} = 54.5$ Hz, $^{3}J_{HH} = 7.3$ Hz, $CF_2H$); $^{19}F$ (376 MHz, $CDCl_3$): $-78.7$ (ddt, 1F, $^{2}J_{FF} = 22.0$ Hz, $^{4}J_{FF} = 0.8$ Hz, $^{4}J_{FF} = 14.3$ Hz, $^{2}J_{FF} = 22$ Hz, $=CF_2$), $-79.5$ (ddtt, 1F, $^{2}J_{FF} = 22.0$ Hz, $^{3}J_{FH} = 23.0$ Hz, $^{4}J_{FF} = 3.7$ Hz, $^{4}J_{FH} = 0.9$ Hz, $=CF_2$), $-108.6$ ppm (dddd, 2F, $^{2}J_{FH} = 54.5$ Hz, $^{4}J_{FF} = 14.3$ Hz, $^{3}J_{FH} = 7.0$ Hz, $^{4}J_{FF} = 3.7$ Hz, $CF_2H$).