

In memoriam Irmhild Steinke

METAL HYDRIDE-INDUCED HYDRODEFLUORINATION
OF FLUORINATED ALKENES AND ALLENES

Inaugural-Dissertation towards the academic degree
Doctor rerum naturalium (Dr. rer. nat.)

Submitted to the Department of Biology, Chemistry and Pharmacy,
Freie Universität Berlin

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June 2011

The present work was carried out under the supervision of Prof. Dr. Dieter Lentz from April 2007 to June 2011 at the Institute of Chemistry and Biochemistry, at the Freie Universität Berlin.

First Referee: Prof. Dr. Dieter Lentz

Second Referee: Prof. Dr. Konrad Seppelt

Date of Defense: 23. 09. 2011

Publications

Parts of this work have been published prior to submission of this manuscript:

Papers

M. F. Kühnel and D. Lentz, "Hydrometalation of fluoroallenes", *Dalton Transactions*, 2009, 4747-4755. <http://dx.doi.org/10.1039/B903300A>

M. F. Kühnel and D. Lentz, "Titanium-Catalyzed C-F Activation of Fluoroalkenes", *Angewandte Chemie International Edition*, 2010, **49**, 2933-2936. <http://dx.doi.org/10.1002/anie.200907162>

M. F. Kühnel and D. Lentz, "Titankatalysierte C-F-Aktivierung von Fluoralkenen", *Angewandte Chemie*, 2010, **122**, 2995-2998. <http://dx.doi.org/10.1002/ange.200907162>

M. F. Kühnel and D. Lentz, "Fluorinated dienes in transition-metal chemistry – the rich chemistry of electron-poor ligands", *Dalton Transactions*, 2010, **39**, 9745-9759. <http://dx.doi.org/10.1039/C0DT00097C>

M. F. Kuehnel, T. Schlöder, S. Riedel, B. Nieto-Ortega, F. J. Ramírez, J. T. López Navarrete, J. Casado and D. Lentz, "Synthesis of the Smallest Axially Chiral Molecule via Asymmetric Carbon-Fluorine Bond Activation", *Angewandte Chemie International Edition*, 2012. <http://dx.doi.org/10.1002/anie.201108105>

Lectures

M. F. Kühnel and D. Lentz, "Hydrometalation Reactions of Fluorinated Allenes", 15th European Symposium on Fluorine Chemistry, Prague, July 2007.

M. F. Kühnel and D. Lentz, "Hydrometallierung, Carbometallierung und Metallometallierung fluorierter Allene", 13ter Deutscher Fluortag, Schmitten, October 2008.

M. F. Kühnel and D. Lentz, "Hydrometalation of Fluoroallenes – From Isolated Compounds to Catalytic Hydrodefluorination", Graduate School GRK1582/1 Opening Symposium, Berlin, November 2009.

M. F. Kühnel and D. Lentz, "Hydrometalation of Fluoroallenes – From Isolated Compounds to Catalytic C-F Bond Activation", 16th European Symposium on Fluorine Chemistry, Ljubljana, July 2010.

M. F. Kühnel and D. Lentz, "Die Hydrometallierung fluorierter Allene - Von isolierten Verbindungen zur katalytischen C-F-Aktivierung", Karlsruher Institut für Technologie, Karlsruhe, September 2010.

M. F. Kühnel, D. Nitsch, M. Sparenberg, J. Schutt and D. Lentz, "Titanium-Catalyzed C-F Activation of Fluoroalkenes and -allenes - From Model Systems to the Catalytic Hydrodefluorination", 14ter Deutscher Fluortag, Schmitten, September 2010.

Posters

M. F. Kühnel and D. Lentz, "Hydrometalation, Carbometalation and Metallometalation of Fluoroallenes - New Approach to Fluorinated Organometallic Building Blocks", 23rd International Conference on Organometallic Chemistry, Rennes, 2008.

M. F. Kühnel, D. Nitsch, M. Sparenberg, J. Schutt and D. Lentz, "Titanium-Catalyzed C-F Activation of Fluoroalkenes and Allenes. From Model Systems to the Catalytic Hydrodefluorination", 17th International Symposium on Homogeneous Catalysis, Poznań, July 2010.

Acknowledgements

I wish to express my sincere gratitude to Prof. Dr. Dieter Lentz for giving me the opportunity to carry out the research work under his supervision, for sharing his theoretical and practical knowledge with me and for teaching me the essentials of scientific work.

I thank Prof. Dr. Konrad Seppelt for reviewing this thesis, for providing the gas chromatograph and for a gift of platinum dioxide.

I am indebted to all the former and present members of the Lentz research group, Floris Akkerman, Christian Ehm, Stefanie Fritz, Rainer Kickbusch, Juliane Krüger, Annika Meyer, Monika Mujkic, Denis Petri, Bernd Schmidt, Małgorzata Swak and Berit Topolinski for a supportive and enjoyable working atmosphere; special thanks go to my colleague and friend Thomas Hügler for inspiring discussions at room U103.

I am grateful to all the students who have contributed to my research project, especially Cindy Glor, Philipp Holstein, Meike Kliche, Luisa Losensky, Stefan Matthies, Dominik Nitsch, Veronika Rojek, Michael Sparenberg, Joseph Schutt, Christian Wende and Fritz Wernicke.

I thank the employees of the service departments of the FU for their support, especially Heinrich Gattner for his assistance with repairing the gas chromatograph, Dirk Busold for numerous urgent glassware repairs, Karl Bohl and Joachim Völter for their patience and Peter Scharmberg for technical support.

I wish to thank Prof. Dr. Thomas Braun for our encouraging discussions at the joint group seminar and graduate school meetings, Dr. Sebastian Riedel for theoretical calculations, Matthias Molski and Dr. Axel Rodenstein for help with EPR spectroscopy, Prof. Dr. Hans-Ulrich Reißig for a donation of platinum dioxide, Prof. Dr. Uwe Rosenthal for helpful discussions, Jakob J. Gutzmann for a gift of ethyl lactate and the librarian at Julius Kühn-Institut for after hours admission. The donation of chemicals by the Bundesanstalt für Materialprüfung und -forschung, DuPont, Hoechst and Solvay Fluor is gratefully acknowledged.

I thank the Deutsche Forschungsgemeinschaft for financial support withing the Graduate School program GRK 1582/1 "Fluor als Schlüsselement" and the AG Fluorchemie for a conference scholarship.

Finally and most importantly, I am grateful to my girlfriend Annett, my family, my godmother and my friends for their love, support, encouragement and patience.

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1. Introduction

1.1. General Aspects of Fluorine Chemistry

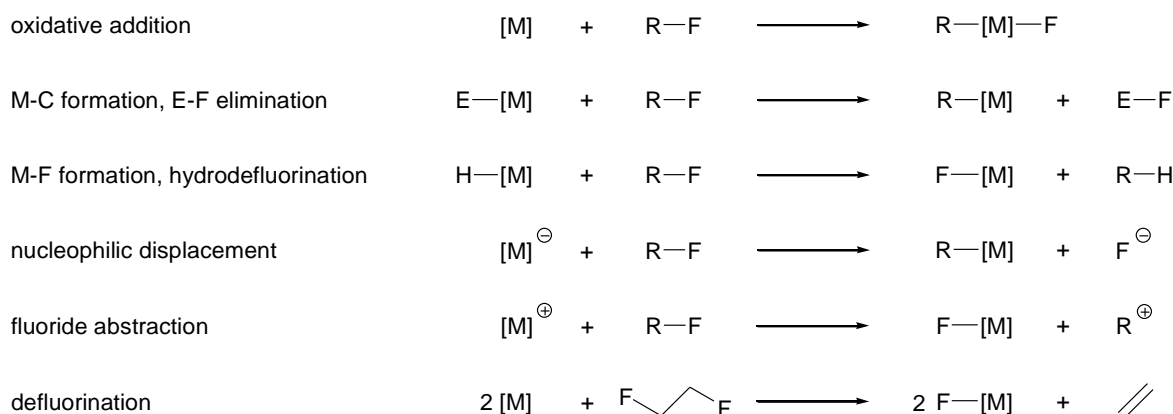
Metal-induced transformations of organic molecules are fundamental to synthetic chemistry. Organometallic reactions range from rather trivial Grignard-type alkylations to palladium-catalyzed cross-coupling reactions, and many of these have been honored with the Nobel Prize. Not only has metal catalysis facilitated known transformations under mild conditions such as the low-pressure alkene polymerization, but it has also generated completely new reactivity patterns, *e. g.* the olefin metathesis.^{1,2}

Among the numerous substrates subjected to such transformations, fluorinated alkenes and allenes are somewhat underrepresented. This has often been attributed to the different bonding polarities and energetics observed in carbon-fluorine bonds compared to their carbon-hydrogen analogs;³⁻⁵ their resulting altered reactivity has so far precluded most transformations based on metal coordination.⁶⁻⁹ The inherent kinetic and thermodynamic inertness of polyfluorocarbons accounts for important technical applications *e. g.* in chemically resistant polymers;^{10,11} the increase in hydrophobicity and metabolic stability induced by introduction of fluorine to organic molecules has allowed for a significant advance in medicinal chemistry.¹²⁻¹⁴ However, the prolonged persistence of halofluorocarbons in the upper atmosphere combined with their dipolar nature has had a deleterious impact on the ozone layer and contributes to global warming.¹⁵⁻¹⁷ This ambiguous role of fluorine substitution has created a need for means of both selective formation and cleavage of carbon-fluorine bonds under mild conditions.

The introduction of fluorine into complex organic molecules has been accomplished employing various electrophilic, nucleophilic and radical fluorination techniques.¹⁸⁻²² While perfluorination is rather easily achieved, the selective introduction of a defined substitution pattern remains challenging and in many cases costly. Typically, fluorination is performed at a relatively early stage of a multi-step synthesis in order to minimize functional group interference, thus limiting the synthetic flexibility. Alternatively, fluorine-containing building blocks can be introduced at a later stage to broaden the synthetic scope and to avoid the application of fluorinating agents to highly functionalized substrates. This strategy, however, is strongly dependent on the availability of a suitable synthon. A promising approach to such building blocks is the derivatization of readily available perfluorinated compounds by selective cleavage of carbon-fluorine bonds.²³⁻³²

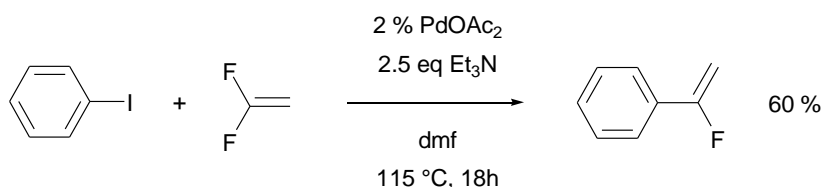
1.2. Metal-Induced Activation of Carbon-Fluorine Bonds

The intermolecular activation of carbon-fluorine bonds at a metal center proceeds *via* several distinct reactivity patterns (scheme 1.1).²⁸



Scheme 1.1. Different types of intermolecular metal-induced C-F bond activation (E = H, SiR₃, BR₂).

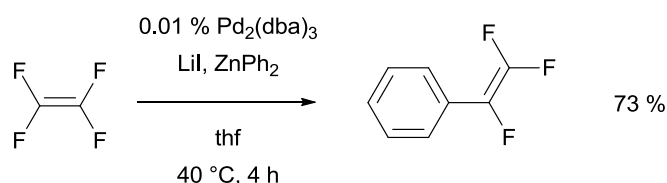
In all cases, the carbon-fluorine bond enthalpy of approximately $500 \pm 50 \text{ kJ mol}^{-1}$ is overcompensated by the formation of a stronger element-fluorine bond; examples include silicon, boron and hydrogen as well as main-group and transition metals. An increasing number of systems capable of catalytic aromatic C-F bond activation have been reported to date,³³⁻⁵³ whereas comparable processes involving fluoroalkenes have remained rare.⁵⁴⁻⁶⁴ The first example of a catalytic C-F bond functionalization was discovered by Heitz and Knebelkamp in 1991, albeit unintentionally.⁵⁴ Under Heck-type reaction conditions, iodoarenes undergo cross-coupling with difluoroethene to give α -fluorostyrenes (scheme 1.2); a preferred β -fluoride over β -hydride elimination from an intermediate fluoroalkyl species was postulated as the key step.



Scheme 1.2. Palladium-catalyzed cross-coupling of iodobenzene with difluoroethene.

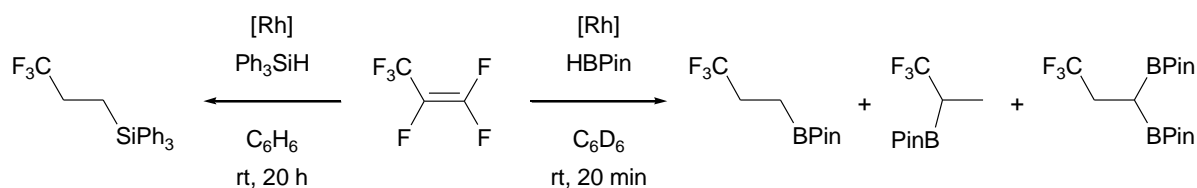
Negishi-type cross-coupling of fluoroalkenes with arylzinc halides was introduced by Saeki *et al.*⁵⁶ Very recently, Ohashi *et al.* reported on a related reaction employing tetrafluoroethene (scheme 1.3).⁶⁴ In this case, an oxidative addition of the alkene C-F bond to the palladium(0)

catalyst is promoted by lithium iodide; the resulting trifluorovinyl complex then follows the well-established Negishi-type cross-coupling mechanism to yield trifluorostyrene derivatives.



Scheme 1.3. Negishi-type cross-coupling of tetrafluoroethene with arylzinc reagents.

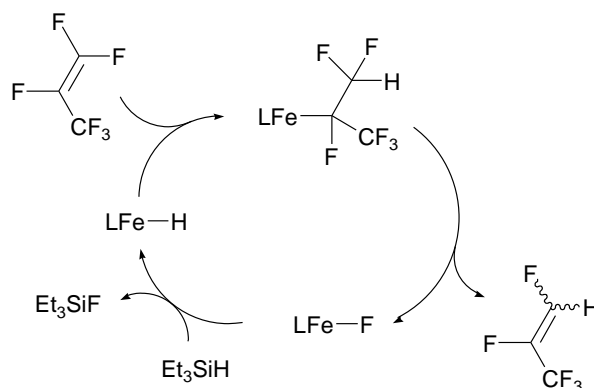
Carbon-fluorine bond cleavage at rhodium complexes has attracted increasing attention.³¹ Braun introduced a phosphine rhodium(I) perfluoropropenyl catalyst capable of a selective C-F bond silylation (scheme 1.4).⁶⁰ The key steps include hydrodefluorination and fluorosilane formation, oxidative addition of Si-H bonds and reductive elimination of C-H and C-Si bonds, the catalytically active species being a low-valent rhodium silyl or hydride species. Further studies on the phosphine rhodium(I) system led to the development of a catalytic C-F bond borylation reaction (scheme 1.4).⁶¹ C-F activation of hexafluoropropene and HF formation yield a rhodium(I) perfluoropropenyl complex, which oxidatively adds a borane molecule. Subsequent reductive elimination either leads to a rhodium hydride and a C-F borylation product or a rhodium boryl species and a hydrodefluorination product. Further C-F activation cycles eventually furnish trifluoropropyl borolanes with up to 250 turnovers; involvement of hydroboration and hydrogenation steps is likely.



Scheme 1.4. Rhodium-catalyzed functionalization of hexafluoropropene;
[Rh] = Rh(PEt₃)₃H or Rh(PEt₃)₃[(Z)-CF=CF(CF₃)].

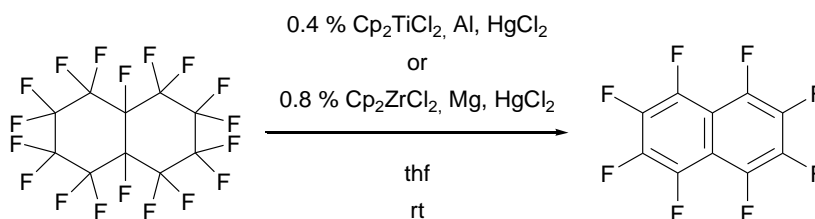
The simplest possible C-F bond activation of fluoroalkenes, namely the hydrodefluorination (HDF), has been reported by the group of Holland. Employing a diketiminate iron(II) fluoride catalyst, hexafluoropropene and trifluoropropene are converted to pentafluoropropene and difluoropropene, respectively (scheme 1.5).⁵⁷ Initially, the iron fluoride precatalyst reacts with triethyl silane to form triethyl fluorosilane and an iron hydride, which can insert a substrate molecule. The resulting fluoroalkyl species was detected by NMR spectroscopy; it undergoes a β -fluoride elimination to yield the HDF product and the iron fluoride. Turnover

numbers up to 9.8 were recorded for hexafluoropropene. A comparable turnover number was achieved in the HDF of fluoroethene in the presence of catalytic amounts of Wilkinson's catalyst as reported by McNeill.⁵⁸ A participation of rhodium fluoride and hydride species was suggested, but the stereochemical outcome ruled out a simple alkene insertion/ β -fluoride elimination mechanism.



Scheme 1.5. Iron-catalyzed hydrodefluorination of hexafluoropropene (L = Dipp₂Nacnac).

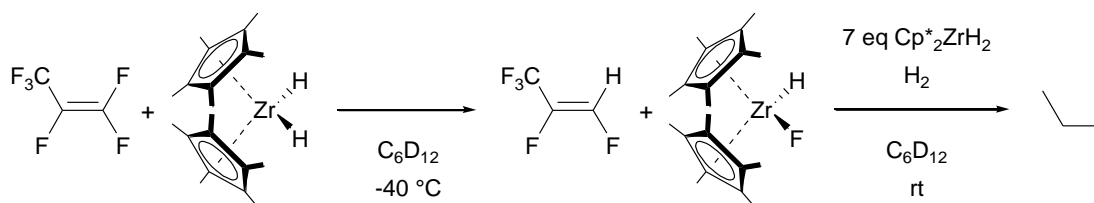
It is noteworthy that most examples of catalytic C-F activation are based on late transition metals. In addition to their high cost, these systems are often highly sensitive especially towards competing C-H bond activation processes.³² Despite their undoubted importance in catalysis,¹ comparable early transition-metal based transformations have remained sparse.^{36-38,42} Rosenthal has reported fluoroarene hydrodefluorination employing a zirconium catalyst, a zirconium hydride being the active species.⁴² Reductive defluorination of perfluorocarbons in the presence of catalytic amounts of group four metallocene dihalides was demonstrated by Richmond (scheme 1.6).^{36,37} Oxidative addition of a substrate C-F bond to an *in situ* generated low-valent metallocene was assumed to be the key step.



Scheme 1.6. Catalytic defluorination of fluorocarbons employing group four metallocenes.

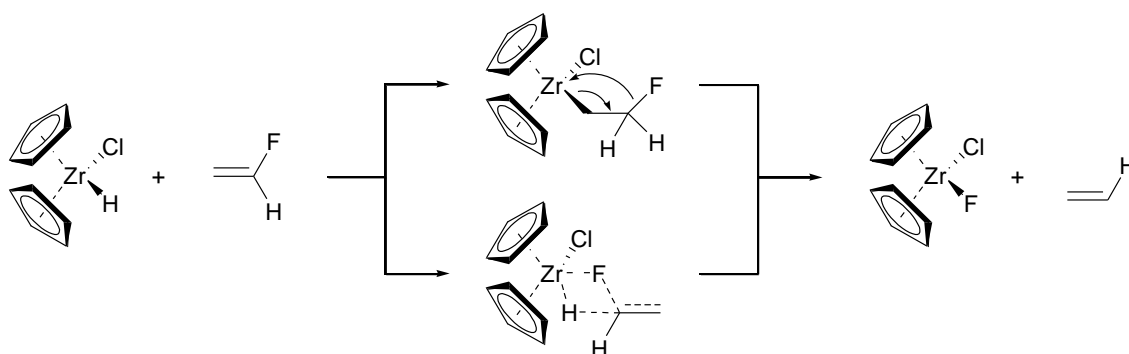
The activation of olefinic carbon-fluorine bonds by zirconium and hafnium hydrides has been thoroughly studied by Jones, albeit in stoichiometric reactions.⁶⁵⁻⁷⁰ Permethylzirconocene dihydride reacts with hexafluoropropene to form *E*-pentafluoropropene and a zirconium

fluoride hydride (scheme 1.7). Depending on the stoichiometry, complete HDF to propane was achieved in the presence of dihydrogen.



Scheme 1.7. Hydrodefluorination of hexafluoropropene by a zirconium hydride complex.

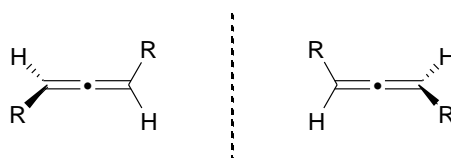
Mechanistic investigations support an alkene insertion/ β -fluoride elimination mechanism, however, a σ -bond metathesis pathway was observed for cyclic alkenes. Caulton studied the HDF of fluoroethene employing a related zirconocene chloride hydride.⁷¹ In agreement with Jones' findings, an insertion/elimination mechanism is favored over a metathesis by 54.4 kJ mol⁻¹ (scheme 1.8).



Scheme 1.8. Competing mechanisms in the zirconium hydride-induced hydrodefluorination: Alkene insertion followed by β -fluoride elimination (top) versus σ -metathesis (bottom).

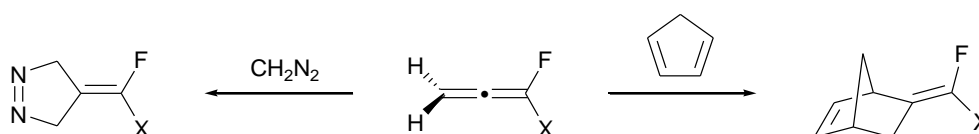
1.3. The Chemistry of Fluoroallenes

The synthetic chemistry of fluoroallenes is by far less developed than that of fluoroalkenes, but has recently received a growing interest.⁷² Allenes are recognized as valuable synthons in natural product synthesis, medicinal chemistry and material science due to their versatile reactivity towards both electrophilic and nucleophilic attack as well as inter- and intramolecular cycloadditions.⁷³⁻⁷⁶ The orthogonality of the two π -systems at the central carbon atom gives rise to the axial chirality of 1,3-disubstituted allenes rendering them the smallest possible C_2 -symmetric molecules (scheme 1.9).⁷⁷⁻⁸⁰ The theoretically predicted yet experimentally so far unobserved molecular parity violation (PV) of enantiomers has challenged chemists to find compact chiral molecules.⁸¹⁻⁸⁴ High-level theoretical calculations by Quack have shown 1,3-difluoroallene to be a promising candidate for experimental PV detection by high-resolution rovibrational spectroscopy.⁸⁵



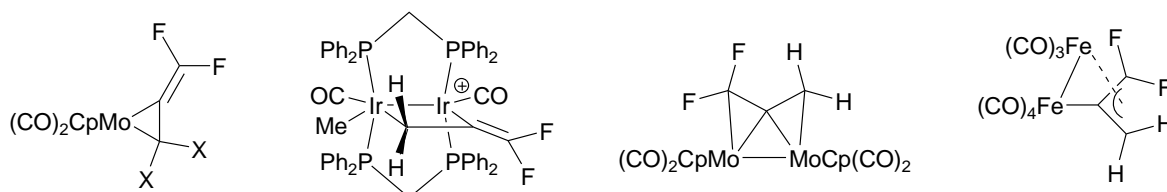
Scheme 1.9. Axial chirality in 1,3-disubstituted allenes.

While more than 150 naturally occurring allenic structures are known,⁸⁶ many of their fluorinated analogs are extremely reactive. Tetrafluoroallene is known to polymerize even at $-80\text{ }^\circ\text{C}$,⁸⁷ whereas allene (propadiene) can be pressurized and stored at room temperature. The organic chemistry of fluoroallene⁸⁸⁻⁹⁹ and 1,1-difluoroallene^{88,90,93,94,98-110} has been studied with emphasis on additions and cycloadditions (scheme 1.10), especially after efficient syntheses were developed by Dolbier.¹¹¹ Presumably due to its low stability, the parent tetrafluoroallene is considerably less explored,^{87,88,90,112-126} a straight-forward synthesis was reported by Burton.¹²³ The lack of a viable synthetic approach to 1,3-difluoroallene⁸⁸⁻⁹⁰ and trifluoroallene^{88,90,127} has so far precluded thorough investigations of their chemistry. In addition, a number of functionalized fluoroallenes are known and have been employed as versatile mono- and difluoromethylene synthons.¹²⁸⁻¹⁴⁷



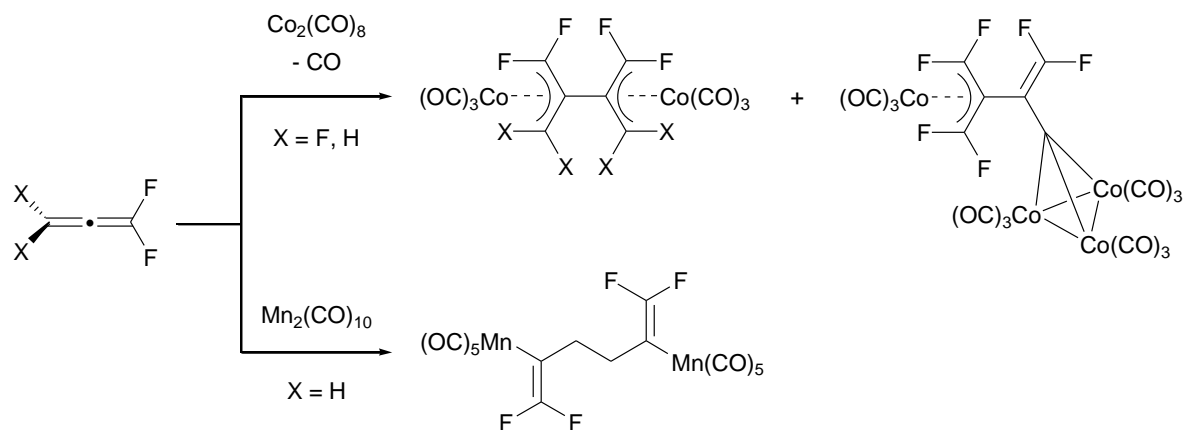
Scheme 1.10. Examples of cycloadditions to fluoroallenes (X = F, H).

Despite the importance of metal catalysis to the synthetic allene chemist,^{79,148} the organometallic chemistry of fluoroallenes has remained largely unexplored.¹⁴⁹⁻¹⁵⁷ Fluoroallenes were shown by Lentz to displace labile ligands from transition-metal complexes. While tetrafluoroallene coordinates exclusively in an η^2 fashion, 1,1-difluoroallene is also capable of adopting bridging μ_2 - $\eta^1:\eta^1$, μ_2 - $\eta^2:\eta^2$ and μ_2 - $\eta^1:\eta^3$ modes (scheme 1.11).^{149,151,155}

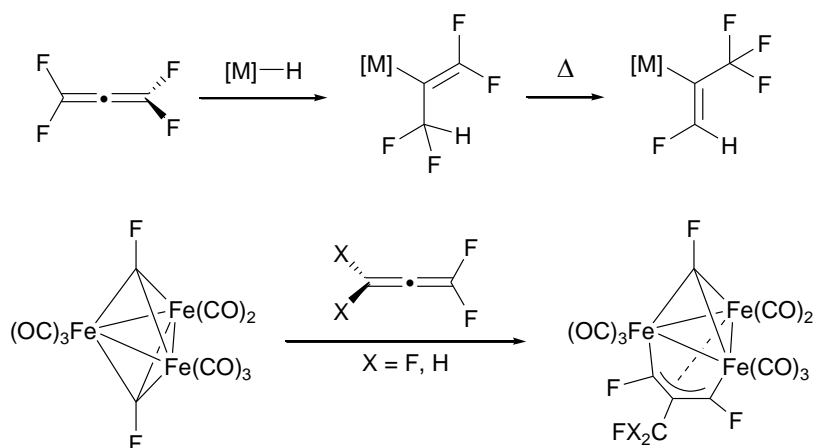


Scheme 1.11. Selected fluoroallene transition-metal complexes (X = F, H).

Examples of a metal-induced fluoroallene transformation are sparse. Dimerization of tetrafluoroallene and 1,1-difluoroallene in the coordination sphere of cobalt and manganese carbonyls yields bis(allyl) and hexadienyl ligands, respectively (scheme 1.12).¹⁵⁰ As a side-reaction, metal-induced defluorination leads to a μ_3 -alkylidyne cluster. Insertion of fluoroallenes into group five and six metal-hydride bonds was found to furnish vinyl complexes; upon heating, these undergo a stereoselective 1,3-fluorine shift to afford the presumed insertion products of tetrafluoropropyne, an even less stable tetrafluoroallene isomer (scheme 1.13).¹⁵⁸ A related rearrangement was observed during the photochemical insertion of fluoroallenes into carbon-metal bonds of the iron fluoromethylidyne cluster $\text{Fe}_3(\text{CO})_9(\mu_3\text{-CF})_2$. Coupling of a methylidyne carbon atom to the central allene carbon atom and a subsequent 1,3-fluorine shift generate a μ_3 - $\eta^1:\eta^1:\eta^3$ ligand.¹⁵²



Scheme 1.12. Metal-induced dimerization of fluoroallenes (X = F, H).



Scheme 1.13. Hydrometalation (top, $[\text{M}] = \text{Mn}(\text{CO})_5, \text{CpMo}(\text{CO})_3, \text{CpW}(\text{CO})_3$) and carbometalation (bottom) of fluoroallenes.

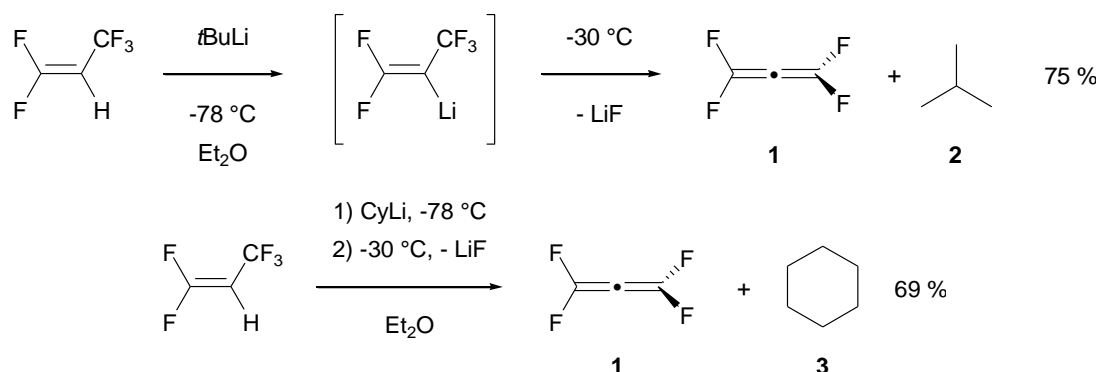
To date, other metal-induced derivatizations of fluoroallenes are unknown. The aim of this work is to study the stoichiometric and catalytic cleavage of olefinic and allenic carbon-fluorine bonds by metal-hydride complexes.

Results and Discussion

2. Hydrodefluorination of Fluoroallenes by Zirconium Hydrides

2.1. Synthesis of Tetrafluoroallene

The synthesis of tetrafluoroallene (**1**) by dehydrofluorination of commercially available 1,1,3,3,3-pentafluoropropene was first reported by Burton.¹²³ At low temperatures, deprotonation with *tert*-butyllithium generates an organolithium species, which upon warming eliminates lithium fluoride to give **1** in good yields after fractional condensation (scheme 2.1). On a larger scale, however, the purification step turns out to be very time-consuming and fails to remove the highly volatile by-product 2-methyl propane (**2**, bp -12 °C; **1**: -39 °C). In order to perform stoichiometrically precise reactions, an improved synthesis of pure **1** was developed, employing cyclohexyllithium as a base. Low-temperature distillation followed by fractional condensation allows for an efficient separation from cyclohexane (**3**, bp 81 °C) and affords **1** in comparable yield and high purity (>97 % by integration of ¹⁹F and ¹H NMR resonances versus an internal fluorobenzene standard).

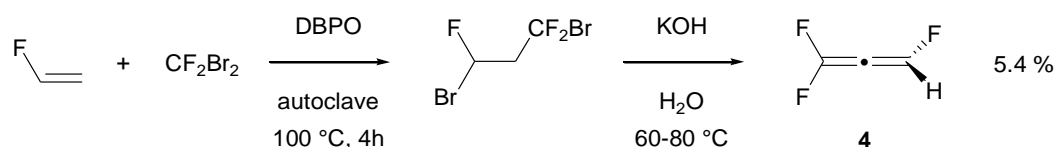


Scheme 2.1. Syntheses of tetrafluoroallene (**1**): Literature (top) and this work (bottom).

2.2. Hydrodefluorination of Tetrafluoroallene

2.2.1. Synthesis of Trifluoroallene

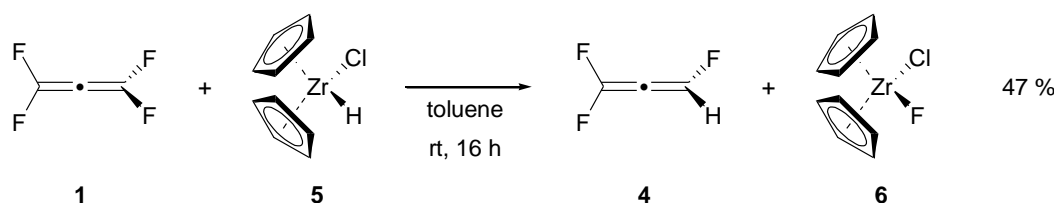
Trifluoroallene (**4**) has previously been synthesized by Zens *et al.* and was characterized by ¹³C NMR and IR spectroscopy.⁸⁸ The reported synthesis involves radical addition of dibromodifluoromethane to fluoroethene and subsequent dehydrobromination (scheme 2.2).



Scheme 2.2. Literature synthesis of trifluoroallene (**4**); DBPO = dibenzoyl peroxide.

The use of an autoclave and the required distillation after each step make this approach tedious and the overall yield is very low. The synthesis of **4** by hydrodefluorination of **1** is therefore an attractive alternative.

Based on preliminary results,¹⁵⁹ **1** was reacted with zirconocene chloride hydride (Schwartz' reagent, **5**) affording a mixture of hydrodefluorination products and zirconocene chloride fluoride (**6**). Preferential formation of **4** is achieved employing 1.2 equivalents of the hydride **5** in toluene suspension (scheme 2.3). However, an attempted purification by repeated fractional condensation did not succeed in separating **4** from **1** and other unidentified by-products. The isolation of pure **4** requires the application of preparative gas-liquid chromatography (pGLC). At room temperature, the reaction products' high volatility leads to an incomplete peak separation; a commercial chromatograph therefore had to be modified in order to allow for cooling of its column by means of an ice bath (figure 2.1). At 0 °C and using 15% Halocarbon oil on Chromosorb P-AW as the stationary phase, **4** was isolated in high purity (>95 %) and reasonable yield (47 %). **4** was characterized by ¹H and ¹⁹F NMR spectroscopy and its molecular structure was determined by single-crystal X-ray diffraction (see section 2.2.4).



Scheme 2.3. Synthesis of trifluoroallene (**4**) by zirconium hydride-induced hydrodefluorination.

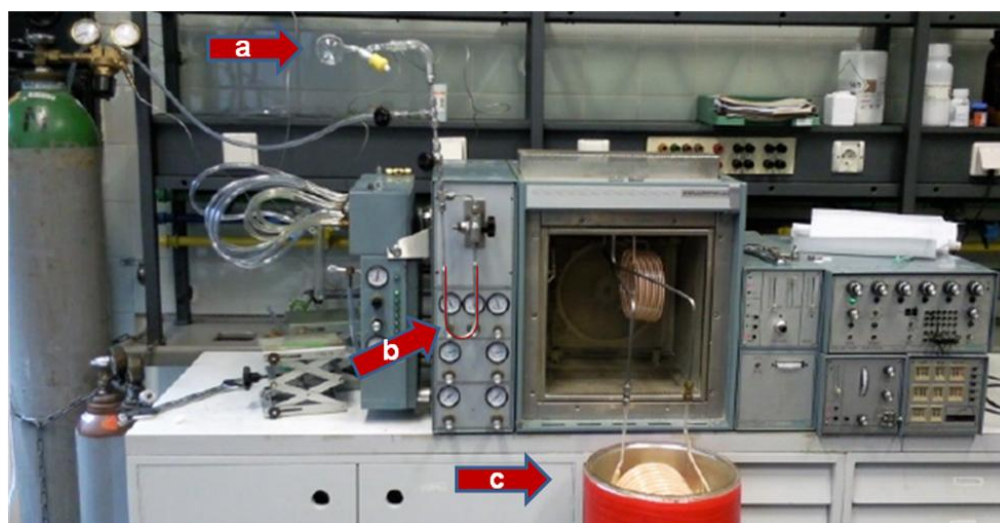
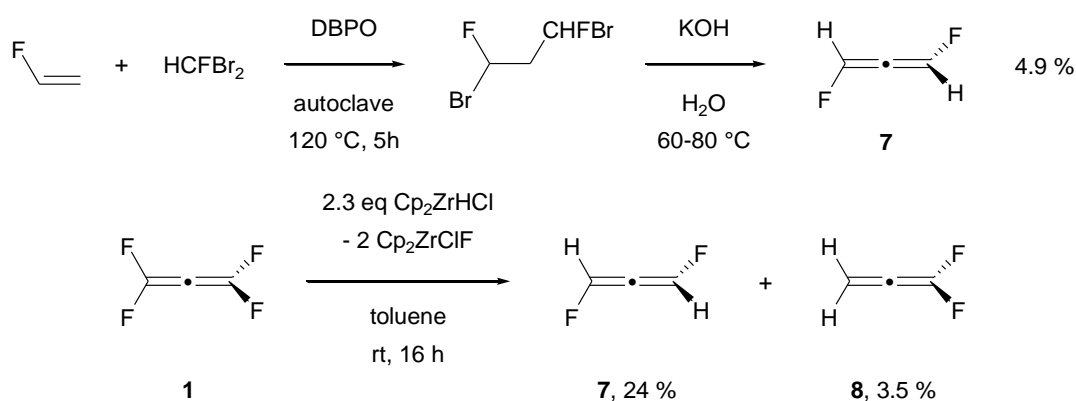


Figure 2.1. Modified pGLC for the isolation of **4**: a) Flask containing gaseous sample, b) U-shaped tube for condensing the sample, c) externally mounted column inside a cooling bath.

2.2.2. Synthesis of 1,3-Difluoroallene

The reported synthetic access to 1,3-difluoroallene (**7**) resembles that to **4** in both its tedious two-step procedure and the unsatisfying yield (scheme 2.4).⁸⁸ Consequently, a synthesis *via* C-F activation was attempted. Employing 2.3 equivalents of the hydride **5**, difluoroallenes **7** and **8** were synthesized by a two-fold hydrodefluorination of **1** (scheme 2.4). The thermodynamically less stable¹⁶⁰ **7** is formed as the main product in 87 % selectivity over its isomer **8**. Purification is again performed by pGLC at 0 °C and affords **7** in >95 % purity and 24 % yield, making a crystallographic characterization possible (see section 2.2.5).



Scheme 2.4. Synthesis of 1,3-difluoroallene (**7**): Literature (top) and this work (bottom).

Due to its C_2 symmetry, **7** exhibits interesting spectroscopic properties: The chemically equivalent yet magnetically inequivalent fluorine and hydrogen nuclei, respectively, give rise to an $AA'XX'$ spin system (figure 2.2). In order to determine the hydrogen-fluorine and fluorine-fluorine coupling constants, a least-squares refinement was performed using the

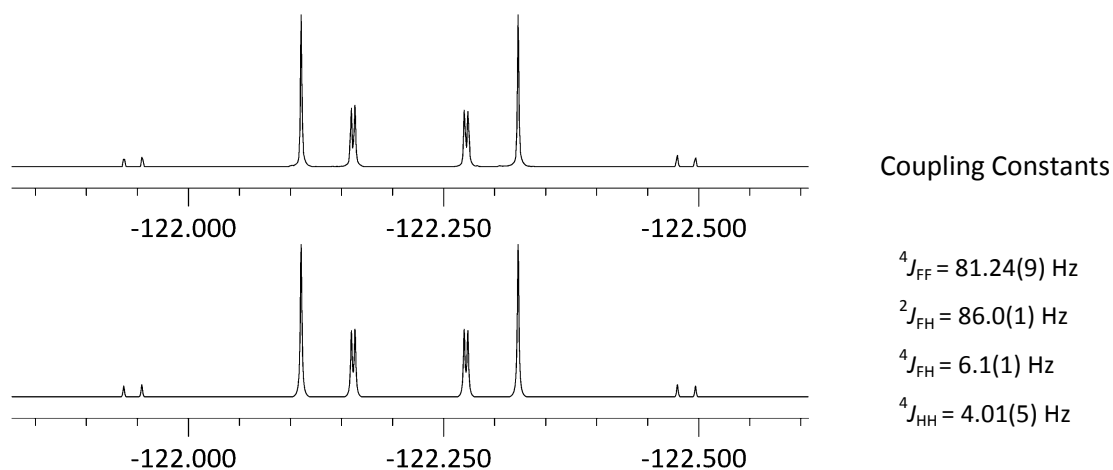
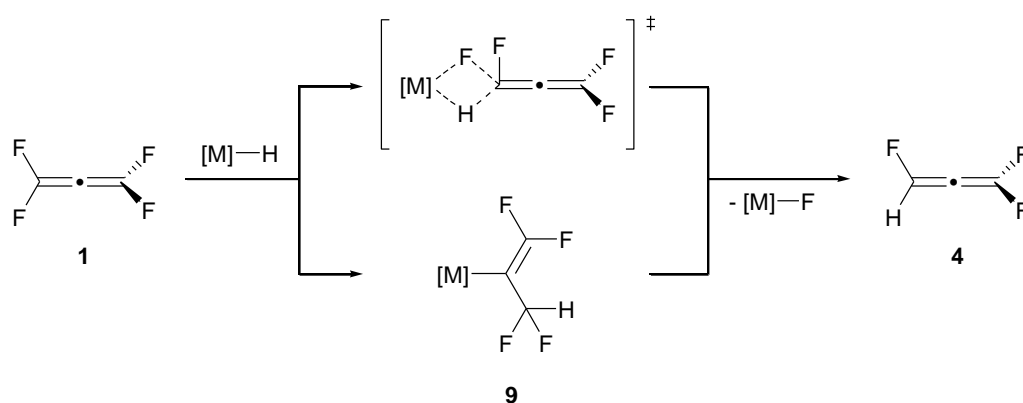


Figure 2.2. ^{19}F NMR spectrum of 1,3-difluoroallene (**7**): Observed (top) and calculated (bottom) spectrum; iterated coupling constants (right).

gNMR program package.¹⁶¹ Starting from typical J values of related compounds,¹⁶² the iteration converges to a residual of $R = 0.0134$ (figure 2.2); the resulting $^4J_{\text{FF}}$ of 81.24(9) Hz is in reasonable agreement with an *ab initio* value of 75.7 Hz computed on the coupled-cluster level of theory.¹⁶³

2.2.3. Mechanistic Considerations

As mentioned earlier, zirconocene hydride-induced hydrodefluorination of fluoroalkenes can proceed *via* two distinct pathways (*cf.* section 1.2): A β -hydride insertion/ β -fluoride elimination and a σ -bond metathesis mechanism, the preference being substrate-dependent.^{65-68,70,71} Looking at tetrafluoroallene (**1**), these two mechanisms differ from each other essentially in the existence of an intermediate fluorovinyl species **9** (scheme 2.5). Similar insertion products have been isolated employing group 6 and 7 hydrides, they are highly soluble in polar and apolar solvents.¹⁵⁶ In a low-temperature NMR study, no evidence of an insertion product **9** was found in the reaction mixture, only the resonances of **1**, **4** and **6** were detected. This finding suggests a metathesis pathway to be operative here. In either mechanism, the regioselectivity observed in the HDF of **4** is explained by a preferential hydride attack on the more electrophilic CF_2 group rather than the CFH group.



Scheme 2.5. Possible reaction mechanisms in the hydrodefluorination of tetrafluoroallene (**1**): σ -Metathesis (top) versus β -hydride insertion/ β -fluoride elimination (bottom); $[\text{M}] = \text{Cp}_2\text{ZrCl}$.

2.2.4. X-Ray Structure Determination of Trifluoroallene and 1,3-Difluoroallene

Single-crystalline samples of **4** and **7** suitable for X-ray structure determination were obtained *in situ* by maintaining sealed glass capillaries slightly below the melting points of 125 and 166 K, respectively. **4** crystallizes in the monoclinic space group $P2_1/c$ with a single molecule in the asymmetric unit. The allenic carbon skeleton $C_1-C_2-C_3$ deviates from the expected linearity by $4.4(3)$ degrees (figure 2.2, table 2.1). The carbon-fluorine bond distance in the CFH-group ($C_3-F_3 = 1.344(3)$ Å) is significantly longer than the observed mean distance in the CF_2 -group ($C_1-F_{1/2} = 1.315(4)$ Å); in addition, the CFH moiety is tilted towards a decreased angle ($C_2-C_3-F_3 = 121.6(2)^\circ$ vs. $C_2-C_1-F_1 = 125.8(5)^\circ$). These data differ significantly from structural parameters previously calculated from microwave spectra.¹²⁷ The discrepancies are most probably due to refinement constraints, such as an assumed linear geometry as well as identical C-F bond distances and C-C-F angles, respectively. Within the experimental errors, the reported solid-state structure of tetrafluoroallene (**1**)¹²⁴ perfectly matches the perfluorinated side of **4**. The structure of the CCFH-group is in agreement with the microwave spectra-derived structure of monofluoroallene (**10**),^{89,97} which was determined to exhibit a very similar distance $C_3-F_1 = 1.343$ Å and a slightly larger angle $C_2-C_3-F_1 = 122.78^\circ$ and distance $C_2-C_3 = 1.307$ Å in **10** compared to $C_2-C_3 = 1.287(4)$ Å in **4**. This sectional structure resemblance indicates a rather small geometrical influence of one side on the other, as is expected from their perpendicularity.

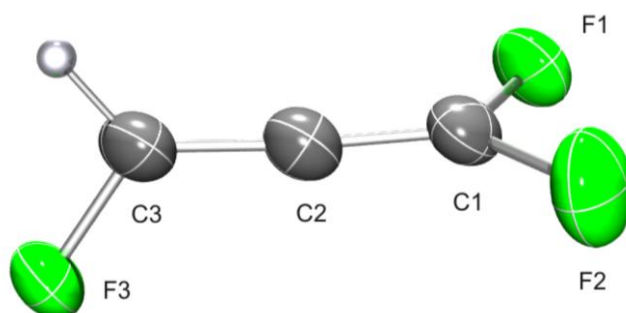


Figure 2.2. Molecular structure and numbering scheme for trifluoroallene (**4**).

7 crystallizes as a racemate in the monoclinic space group $P2_1/c$ with a single molecule in the asymmetric unit, the other enantiomer is generated by symmetry operations. Its structure shows strong resemblance to that of **4**. The allenic carbon chain $C_1-C_2-C_3$ deviates from linearity by $4.6(2)^\circ$ (figure 2.3, table 2.1) and the two CFH planes exhibit a torsion angle of

91.9(2) °. The distances $C_1-F_1 = 1.353(2)$ Å and $C_3-F_2 = 1.347(2)$ Å are almost identical within the experimental errors, the same holds true for $C_1-C_2 = 1.291(2)$ Å and $C_2-C_3 = 1.293(2)$ Å.

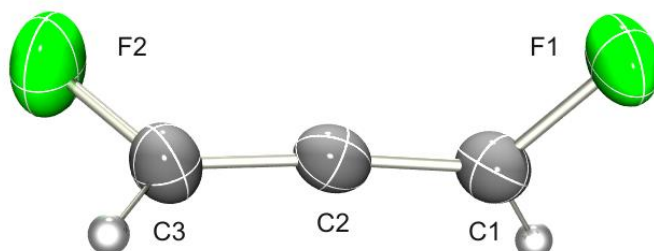
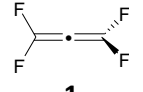
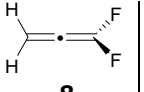
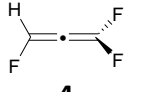
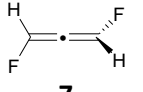
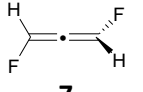
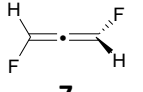
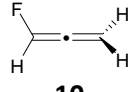


Figure 2.3. Molecular structure and numbering scheme for 1,3-difluoroallene (**7**).

Again, the observed geometry significantly deviates from data previously obtained from microwave spectroscopy (table 2.1). Although a similar twist of the two CFH planes was deduced, a linear carbon chain was assumed; as a result, the distance $C_1-F_1 = 1.330$ Å is underestimated while the angle $F_1-C_1-C_2 = 124.2$ ° is overestimated. A strong resemblance to the CFH groups of **4** and **7** is evident from almost identical bond angles and distances, again confirming the geometrical independence of the two terminal C_{sp^2} centers.

Table 2.1. Comparison of geometrical data for the known unsubstituted fluoroallenes (distances and angles in Å and °, respectively; MW = microwave).

| |  1 X-ray ¹²⁴ |  8 X-ray ¹²⁴ |  4 X-ray |  7 MW ¹²⁷ |  7 X-ray |  7 MW ^{89,127} |  10 MW ⁹⁷ |
|-----------|---|---|--|--|--|---|--|
| d(C-F) | 1.313(2) | 1.320(1) | 1.315(4) | 1.317 | 1.353(2) | 1.330 | 1.360(6) |
| d(C-F) | | 1.326(1) | 1.344(3) | | 1.347(2) | | |
| d(C=CF) | 1.277(2) | 1.289(1) | 1.281(4) | 1.299 | 1.292(4) | 1.306 | 1.301(4) |
| d(C=CH) | | 1.300(1) | 1.287(4) | 1.301 | | | 1.309(3) |
| ∠ F-C=C | 125.75(10) | 125.48(4) | 125.8(5) | 126.26 | 121.7(2) | 124.2 | 121.9(5) |
| ∠ F-C=C | | | 121.7(2) | 124.95 | | | |
| ∠ H-C=C | | 119.25(5) | 130(1) | 121.1 | 126(3) | 121.1 | 124.3(3) |
| ∠ H-C=C | | | | | | | 120.8(2) |
| ∠ C=C=C | 180.0 | 178.91(8) | 175.6(3) | 180 | 175.4(2) | 180 | 178.2(6) |
| ∠ F-C=C-F | 90.0 | | 90.6(6) | 90 | 91.9(2) | 92.0 | |

The observed distortions of the allenic backbones and the CFH-groups in **4** and **7** can be explained on the basis of negative hyperconjugation effects due to the unsymmetrical substitution pattern: A bent $C_3-C_2-C_1$ chain increases the antiperiplanar overlap of $\pi_{C_2C_1}$ with $\sigma_{C_3F_3}^*$ and results in an F_3-C_3 bond elongation (figure 2.4). The domination of antiperiplanar over synperiplanar hyperconjugation is held responsible for the stabilization of *Z*-1,2-difluoroethene relative to its *E*-isomer.¹⁶⁴ In addition, $n_{F_3} \rightarrow \pi_{C_2C_1}^*$ donation decreases the $F_3-C_3-C_2$ angle. In **4**, similar effects are to be expected from F_1 and F_2 , but the symmetrical substitution pattern levels these effects to zero. Due to the fluorine and hydrogen substituents' small size, steric effects can be excluded. A related distortion has been reported in the geminally donor-acceptor substituted allene **11** and explained on the basis of a synperiplanar $\pi_{CC} \rightarrow \sigma_{CP}^*$ donation (figure 2.4).¹⁶⁵ Consequently, the carbon skeleton of **11** is distorted in the opposite direction. Alternatively, electrostatic repulsion between the double-bond π electrons and a lone pair at the fluorine and nitrogen atom, respectively, may account for the observed distortions, as has been suggested for monofluoroallene.⁹⁷ The two-fold bend at either side of **7** results in twisting the two CFH planes away from each other.

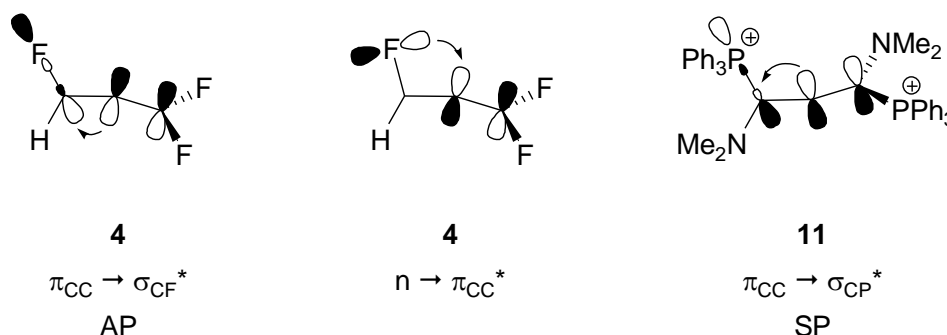


Figure 2.4. Hyperconjugation-induced distortions of trifluoroallene (**4**, left and middle) and 1,3-bis(dimethylamino)-1,3-bis(triphenylphosphonio)allene diiodide (**11**, right); AP = antiperiplanar, SP = synperiplanar.

Independent *ab initio* calculations on the gas-phase structures of **4**, **7** and **10** have confirmed these distortions and thus rule out the influence of packing effects.¹⁶⁶

2.3. Asymmetric Synthesis of 1,3-Difluoroallene

The axial chirality of **7** implies the existence of two enantiomers, which can be discriminated in a chiral environment. In the presence of excess cyclodextrin TRIMEB as a chiral host, two diastereomeric inclusion compounds are formed, so that the ^{19}F NMR spectrum of **7** splits into two sets of signals by approximately 11 ppb (figure 2.5).¹⁶⁷ Using the chiral solvent L-(–)-ethyl lactate, the difference in chemical shifts is only 2.2 ppb. As expected from an achiral synthesis, both enantiomers are equally abundant in **7** synthesized employing Schwartz' reagent; *i. e.* the product is a racemate. Because **7** represents one of the smallest possible chiral molecules, an enantioselective synthesis *via* hydrodefluorination of **4** was attempted.

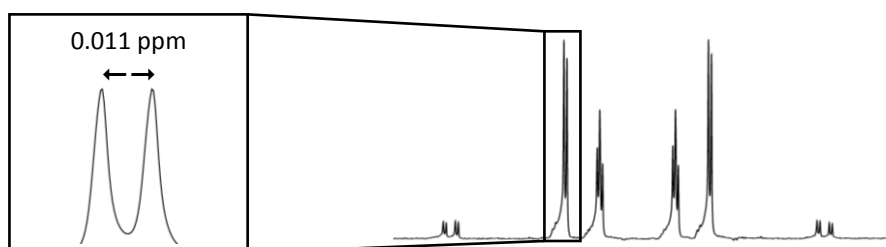
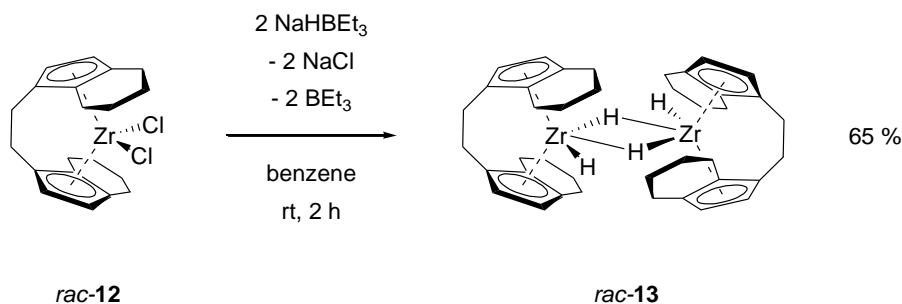


Figure 2.5. ^{19}F NMR spectrum of *rac*-1,3-difluoroallene (**7**) in the presence of the chiral host heptakis(2,3,6-tri-O-methyl)- β -cyclodextrin (TRIMEB).

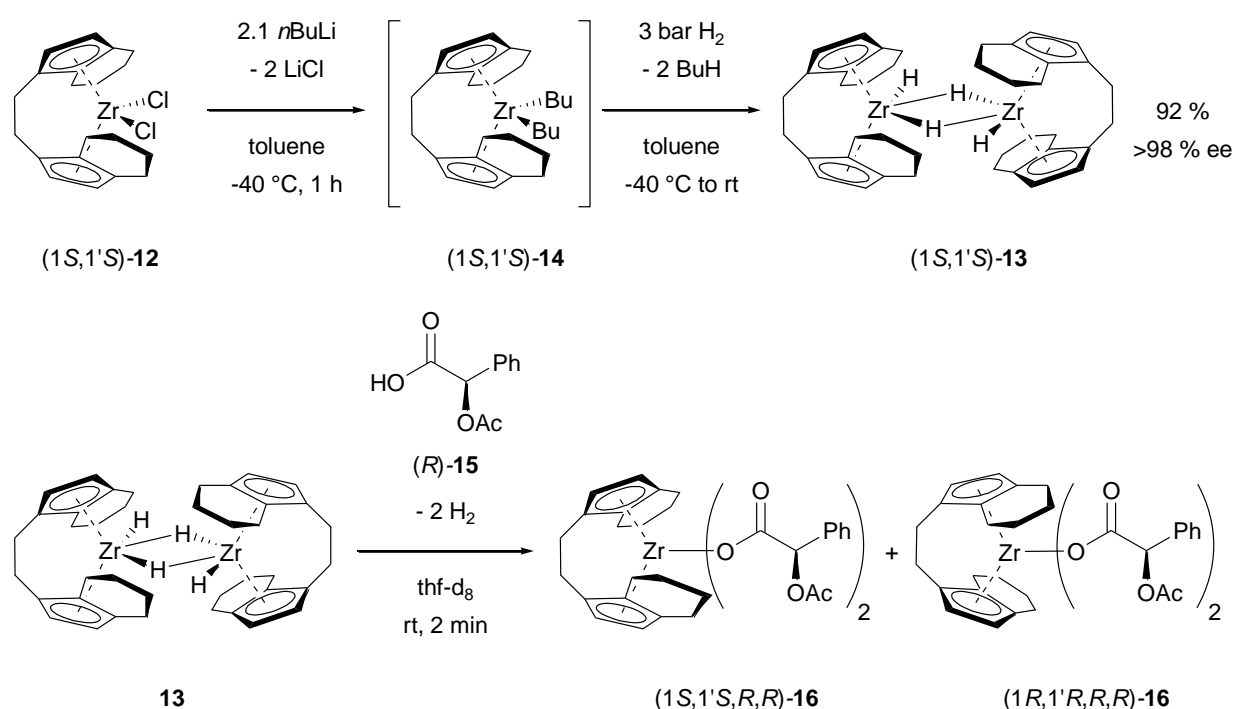
2.3.1. Synthesis of Enantiometrically Pure [(1*S*,1'*S*)-(ebthi)ZrH₂]₂ and [(*R,R*)-(ebthi)ZrH₂]₂

In order to perform an asymmetric hydrodefluorination reaction, a chiral zirconium hydride reagent available in its enantiopure form is needed. C₂-symmetrical 1,2-bis(tetrahydroindenyl)ethanediyl (ebthi) group 4 metal complexes were first prepared by Brintzinger;^{168,169} the rigidity and strong chiral induction of these so-called *ansa*-metallocenes have subsequently found numerous applications to synthesis and catalysis.¹⁷⁰ Buchwald has reported a straight-forward synthesis of the dimeric zirconium hydride [(ebthi)ZrH₂]₂ (**13**) from commercially available (ebthi)ZrCl₂ (**12**) by a salt metathesis route (scheme 2.6).¹⁷¹



Scheme 2.6. Literature synthesis of [*rac*-(ebthi)ZrH₂]₂ (*rac*-**13**).

This procedure, however, proves unsuitable for the synthesis of enantiopure (1*S*,1'*S*)- and (1*R*,1'*R*)-**13** from (1*S*,1'*S*)- and (1*R*,1'*R*)-**12**, respectively. Concomitantly formed triethylborane has to be removed from the crude reaction mixture by repeated washing with hexane. Similar to earlier reports on chiral *ansa*-zirconocenes, enantiomerically pure **13** was found to be much more soluble than the racemate,¹⁷² rendering a separation from the by-product impossible; attempted removal *in vacuo* and by recrystallization was not successful. Therefore, an alternative synthesis was developed, avoiding soluble side-products. The related unsubstituted zirconocene dichloride has been reported to form an unstable dibutyl derivative upon reaction with two equivalents of *n*-butyllithium.¹⁷³ Alkyl zirconium species are known to undergo hydrogenolysis to yield alkanes and zirconium hydrides.^{174,175} Based on this, two equivalents of *n*-butyllithium are added to a toluene solution of commercially available (1*S*,1'*S*)-**12** at -40 °C to yield the dibutyl derivative (1*S*,1'*S*)-**14**, which was not isolated. Subsequent hydrogenolysis at room temperature furnishes the desired hydride (1*S*,1'*S*)-**13** in high yield (scheme 2.7). The enantiomeric purity was determined by reacting (1*S*,1'*S*)-**13** with excess *R*-(-)-O-acetylmandelic acid ((*R*)-**15**) to form the known bis(O-acetylmandelate) derivative **16**.¹⁷² By integration of the ¹H NMR resonances of the bis(O-acetylmandelate) diastereomers (1*S*,1'*S*,*R,R*)-**16** and (1*R*,1'*R*,*R,R*)-**16**, the enantiomeric excess (ee) was found to be >98 %. Similarly, (1*R*,1'*R*)-**12** gives (1*R*,1'*R*)-**13** in >98 % ee.



Scheme 2.7. Synthesis of enantiopure [(1*S*,1'*S*)-(ebthi)ZrH₂]₂ (**13**) (top) and conversion to the bis(O-acetylmandelate) **16** for ee determination (bottom).

2.3.2. Asymmetric Hydrodefluorination of Trifluoroallene

Having a chiral zirconium hydride at hand, the synthesis of optically active 1,3-difluoroallene (**7**) was attempted. Trifluoroallene (**4**) was chosen as the starting material in order to minimize the required amount of costly hydride. Depending on the conditions, reaction of excess **4** with (1*S*,1'*S*)-**13** affords **7** in moderate yield (figure 2.6, table 6.1). pGLC purification was applied for the separation from excess **4** and concomitant 1,1-difluoroallene.

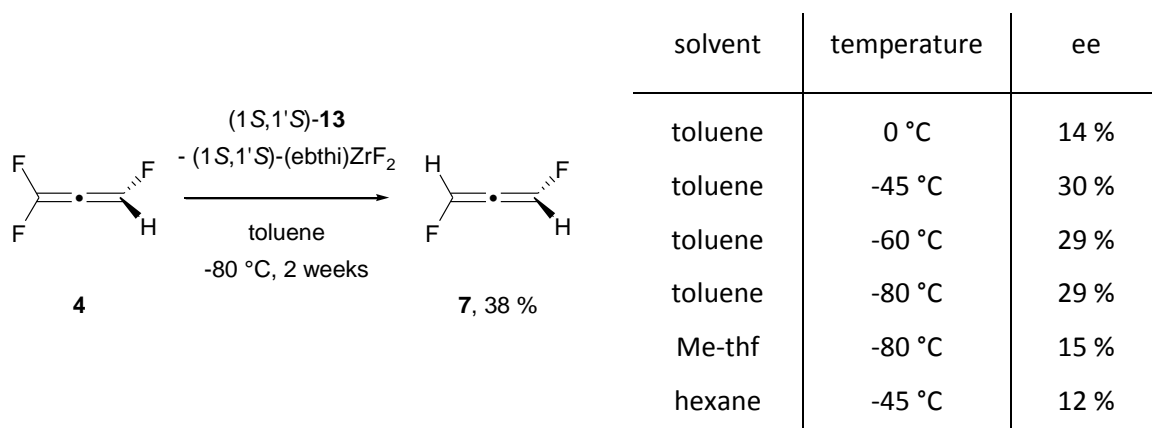


Figure 2.6. Asymmetric hydrodefluorination of trifluoroallene (**4**). Reaction scheme (left) and conditions (right).

The optical purity was determined by integration of the ^{19}F NMR resonances in the presence of excess TRIMEB (figure 2.7). The highest enantiomeric excess of 30 % is obtained at -45 °C or colder; further lowering of the temperature substantially slows down the reaction but does not result in an increased enantioselectivity. Employing the other enantiomer (1*R*,1'*R*)-**13** as a hydrodefluorinating agent reverses the enantioselectivity as expected (figure 2.7). These results represent the first example of an asymmetric carbon-fluorine bond activation reaction.

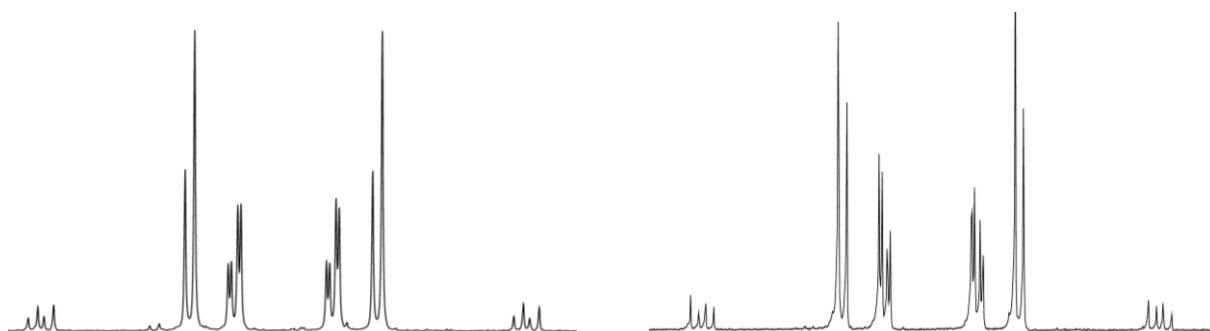
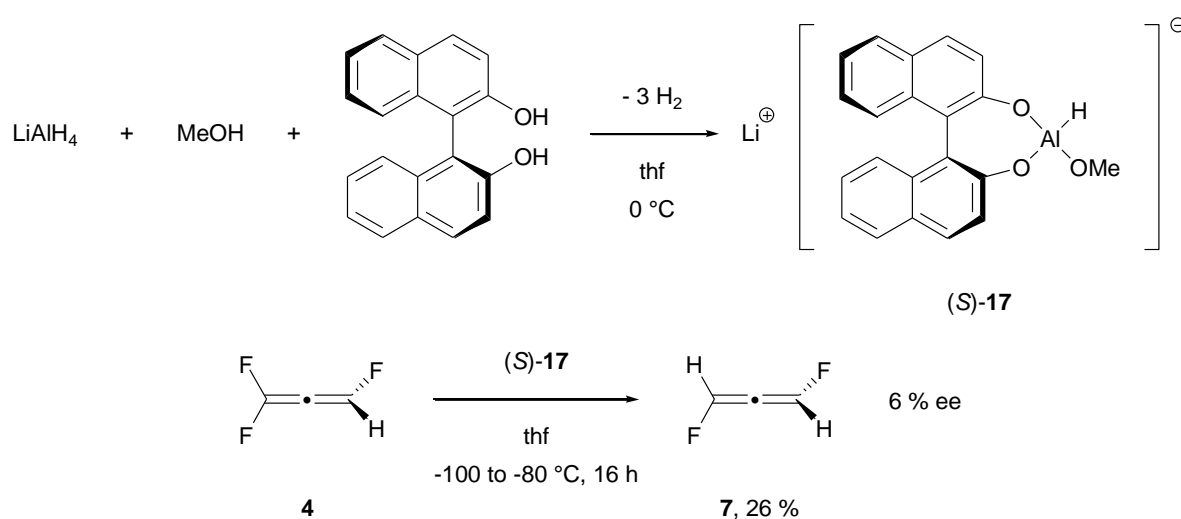


Figure 2.7. ^{19}F NMR spectra of optically active 1,3-difluoroallene (**7**) in the presence of excess TRIMEB synthesized using (1*S*,1'*S*)-**13** (left) and (1*R*,1'*R*)-**13** (right).

2.3.3. Excursus: Asymmetric Hydrodefluorination by an Aluminum Hydride

In addition to the successful zirconium-mediated reactions, related asymmetric reactions employing less costly chiral hydride reagents were investigated. Aluminum hydrides have been successfully applied to asymmetric reductions of prochiral ketones; BINAL-H (**17**), the most prominent chiral aluminum hydride has been developed by Noyori.¹⁷⁶⁻¹⁷⁸ The reactivity of aluminum hydrides towards fluorocarbons is well documented.²⁴ Consequently, an asymmetric synthesis of **7** *via* hydrodefluorination of **4** by **17** was attempted. (*S*)-**17** is generated *in situ* by treating a tetrahydrofuran solution of lithium aluminum hydride with methanol and (*S*)-1,1'-binaphthol; subsequent addition of **4** furnishes **7** after overnight reaction at low temperatures (scheme 2.8). Fractional condensation allows only for a partial separation from the solvent, a time-consuming purification by multi-run pGLC is required to obtain pure **7** in 26 % yield. Performing the reaction at -100 °C, an ee of 6 % was determined by NMR spectroscopy (-80 °C: 1.6 % ee). Compared to an ee of 30 % achieved in the zirconium-mediated synthesis, BINAL-H clearly is less enantioselective. This result demonstrates the strong chiral induction of Brintzinger-type metallocenes.



Scheme 2.8. Literature synthesis of (*S*)-BINAL-H (**17**, top) and its application to the asymmetric synthesis of 1,3-difluoroallene (**7**, bottom).

3. Catalytic Hydrodefluorination of Tetrafluoroallene

3.1. Envisioning a Catalytic Cycle

The good performance of zirconium hydride complexes in stoichiometric hydrodefluorination reactions prompted the development of a related catalytic system. The desired cyclic process comprises essentially two steps (figure 3.1):

- Conversion of substrate to product consuming the catalytically active species
- Reconversion of the spent catalyst to the active species by a stoichiometric reagent

While the former has already been studied in the preceding chapter, the regeneration of the metal hydride species from the metal fluoride is to be addressed here.

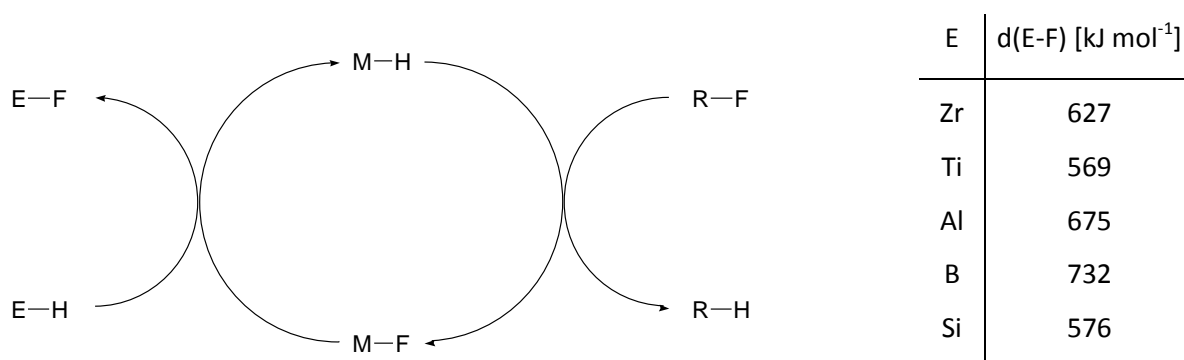
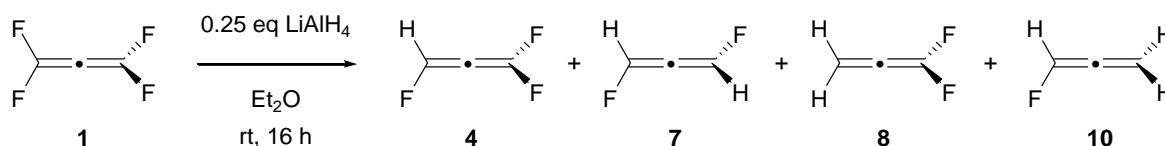


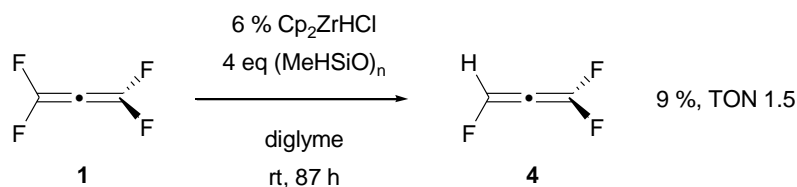
Figure 3.1. Schematic depiction of a catalytic hydrodefluorination process (left) and homolytic bond dissociation energies of diatomic molecules in the gas phase (right).¹⁷⁹

The hydrodefluorination reaction is thermodynamically driven by the exothermic formation of a zirconium-fluorine bond (figure 3.1). Cleavage of this bond is challenging as it requires the hydride donor to form a stronger bond to fluorine while being compatible with the substrate; in addition, the hydride reagent should be easily accessible. Aluminum hydrides have been reported to meet these criteria for the zirconium-catalyzed hydrodefluorination of pentafluoropyridine.⁴² In a substrate tolerance study, lithium aluminum hydride was added to a solution of **1**. Even in the absence of a zirconium fluoride, a complex mixture of fluoroallenes is obtained (scheme 3.1), again demonstrating the high reactivity of fluoroallenes compared to fluoroaromatics. Similarly, boron hydrides were found to be reactive towards **1**.



Scheme 3.1. Unselective reactivity of aluminum hydrides towards tetrafluoroallene (**1**).

Silanes have also frequently been used as hydride donors and fluoride acceptors (*cf.* section 1.2). However, addition of poly(methylhydrosiloxane) has nearly no effect on the hydrodefluorination of **1** employing substoichiometric amounts of Schwartz' reagent (scheme 3.2). Apparently, the silicon-fluorine bond enthalpy is not sufficient to regenerate the spent zirconium complex.

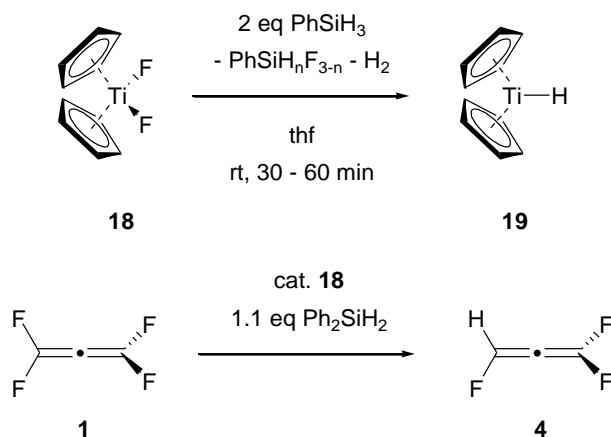


Scheme 3.2. Attempted zirconium-catalyzed hydrodefluorination of tetrafluoroallene (**1**); the yield was determined by ^{19}F NMR spectroscopy using an internal fluorobenzene standard.

These results suggest that it is not possible to find a hydride donor that is sufficiently reactive towards a zirconium fluoride while tolerating the presence of a highly reactive fluoroallene.

3.2. Titanium-Catalyzed Hydrodefluorination of Tetrafluoroallene

Looking at the dissociation energies, the titanium-fluorine bond is found to be significantly weaker than that of its heavier congener zirconium. Silanes are therefore capable of cleaving titanium-fluorine bonds.¹⁸⁰⁻¹⁸⁵ Buchwald has reported commercially available titanocene difluoride (**18**) to react with phenyl silane affording an intensely colored titanocene(III) hydride (**19**) which is highly sensitive to water and oxygen (scheme 3.3).¹⁸⁶



Scheme 3.3. Conversion of titanocene difluoride (**18**) to a titanium hydride species (**19**, top); titanium-catalyzed hydrodefluorination of tetrafluoroallene (**1**, bottom).

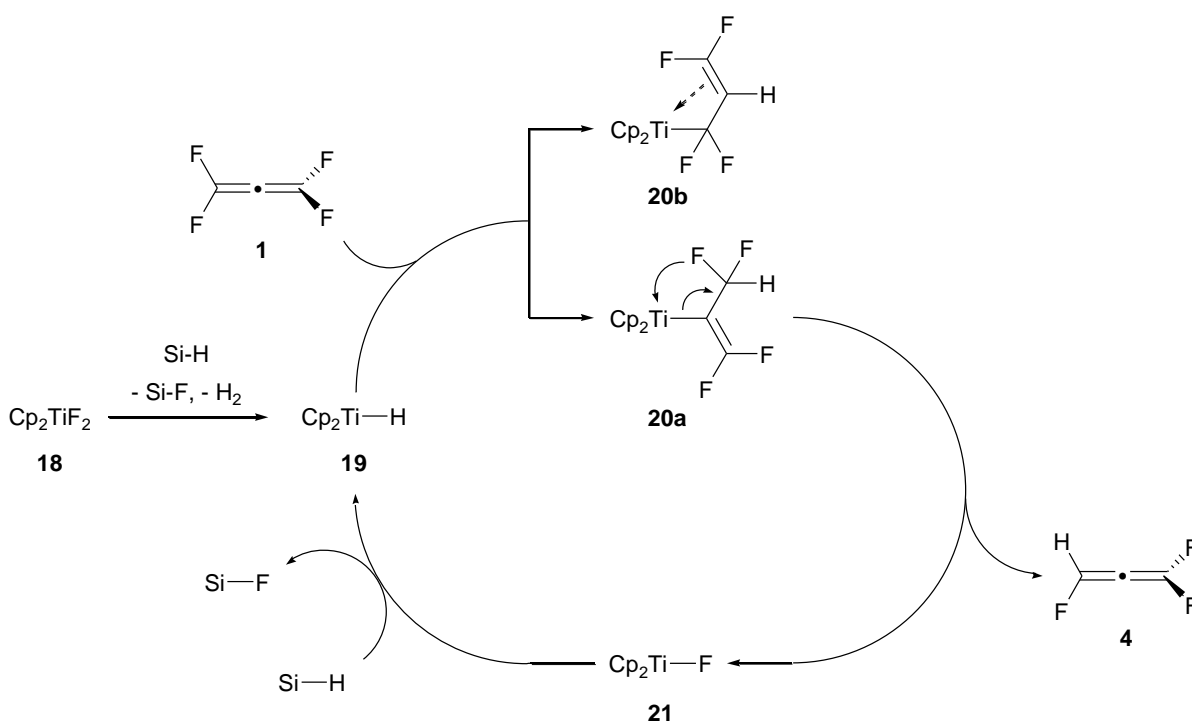
Table 3.1. Catalytic hydrodefluorination of tetrafluoroallene (dme = 1,2-dimethoxyethane, TMAF = tetramethyl ammonium fluoride; yields were determined from ^{19}F NMR spectra by integration versus internal fluorobenzene).

| solvent | Cp_2TiF_2 [mol %] | temperature | time [h] | TON | additive |
|---------|-----------------------------------|-------------|----------|-----|--|
| thf | 2.8 | 65 °C | 3 | 2.1 | |
| dme | 2.5 | 84 °C | 2 | 0.3 | |
| toluene | 2.9 | rt | 62 | 1.1 | 3 % TMAF |
| diglyme | 2.1 | rt | 19 | 0.1 | |
| diglyme | 0.9 | rt | 169 | 1.3 | |
| diglyme | 1.1 | rt | 16 | 2.7 | 2.2 % $\text{B}(\text{C}_6\text{F}_5)_3$ |
| diglyme | 0.8 | rt | 4 | 2.3 | 1 bar H_2 |
| diglyme | 3.9 | 65 °C | 3 | 2.2 | |
| diglyme | 4.2 | -25 °C | 48 | 0.0 | |

Inspired by this reactivity, **1** was reacted with catalytic amounts of the hydride **19**, *in situ* generated from air-stable **18** and less volatile diphenyl silane (scheme 3.3). Table 3.1 shows the performance of this catalytic system in the hydrodefluorination; the overall efficiency is very limited. Elevated temperatures appear to have a slightly beneficial effect, but lead to a rapid dimerization of the substrate.¹¹³ This can be circumvented by the addition of a Lewis-acid, allowing the reaction to proceed at room temperature; non-polar solvents like toluene require the addition of a Lewis-base for the reaction to take place at all. Performing the reaction under an atmosphere of dihydrogen has a positive effect, but the turnover numbers remain below three. Overall, this system is not suitable for the catalytic hydrodefluorination of tetrafluoroallene.

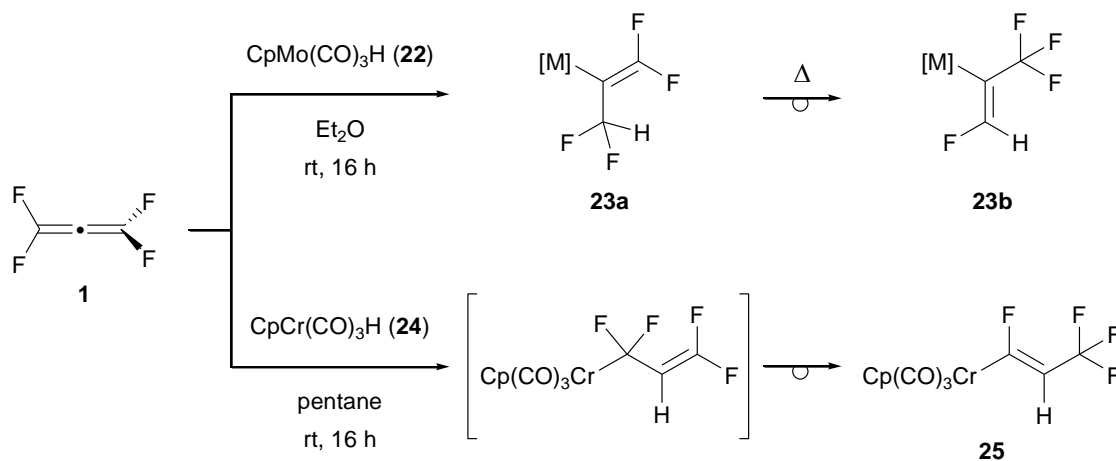
The poor efficiency may be explained by looking at the proposed reaction mechanism (scheme 3.4): In the activation step, **18** is supposed to react with the silane to form the catalytically active hydride **19**. Assuming a β -hydride insertion/ β -fluoride elimination route, two intermediates **20a** and **20b** are possible. **20a** can undergo a β -fluoride elimination to yield the product **4** and titanocene(III) fluoride (**21**); reconversion to the active hydride **19** by reaction with a silane molecule closes the catalytic cycle. **20b** does not have a β -fluorine substituent and cannot reenter the catalytic cycle. The regioselectivity in the insertion step is therefore crucial to the successful catalysis. In the stoichiometric HDF by Schwartz' reagent, **4** was obtained in 47 % yield (cf. section 2.2). Assuming 75 % selectivity here, the turnover

number (TON) converges to three which is close to the observed maximum of 2.7 turnovers. Attempts to isolate the side-product **20b** were not successful.



Scheme 3.4. Proposed mechanism of the titanium-catalyzed hydrodefluorination of tetrafluoroallene (**1**).

This assumption is further supported by a varying insertion selectivity observed in the hydrometalation of **1** with different group 6 hydrides: Tricarbonyl(cyclopentadienyl)-molybdenum hydride (**22**) forms an insertion product **23a**, in which the metal center is added to the central carbon atom; **23a** undergoes a 1,3-fluorine migration affording **23b**.¹⁵⁶ In contrast, its lighter congener **24** yields insertion product **25** by addition of the metal to a terminal carbon atom and a subsequent 1,3-fluorine shift (scheme 3.5).



Scheme 3.5. Hydrometalation of tetrafluoroallene (**1**) with group 6 hydride complexes.

25 was characterized by single-crystal X-ray diffraction, it crystallizes in the monoclinic space group $P2_1/c$ with a single molecule in the asymmetric unit (figure 3.2). The bond angles and distances are within the expected range;¹⁸⁷ the distances $\text{Cr-C}_1 = 2.105(2) \text{ \AA}$ and $\text{Cr-Cp} = 1.839(2) \text{ \AA}$ are significantly shorter than the distances $\text{Mo-C}_2 = 2.252(2) \text{ \AA}$ and $\text{Mo-Cp} = 2.000(4) \text{ \AA}$ in **23a**. The smaller radius of the chromium atom increases the steric bulk in its coordination sphere; in this confined space, addition of the metal fragment to the primary carbon atom should be strongly favored over an addition to the secondary carbon atom resulting in the observed selectivity. Regarding zirconium and titanium, a similar tendency is likely to account for the regioselectivity.

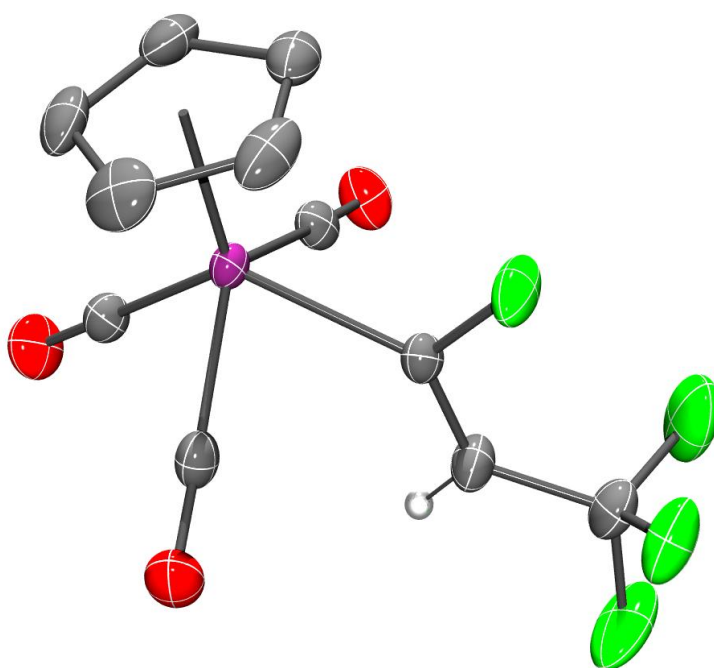


Figure 3.2. Molecular structure of insertion product **25** (carbon gray, fluorine green, oxygen red, chromium purple; hydrogen atoms on the Cp ring omitted for clarity).

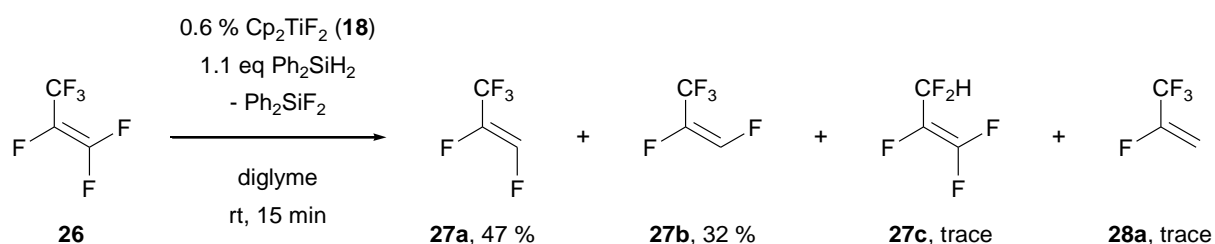
In conclusion, this system is capable of a catalytic hydrodefluorination, but due to regioselectivity problems, its efficiency is low. This assumption implies a better performance to be expected from the hydrodefluorination of a substrate that structurally avoids selectivity ambiguities.

4. Catalytic Hydrodefluorination of Fluoroalkenes

4.1. Titanium-Catalyzed Hydrodefluorination of Hexafluoropropene

4.1.1. Synthesis of Pentafluoropropene

Based on the results obtained in the hydrodefluorination of tetrafluoroallene (**1**), hexafluoropropene (**26**) was reacted with diphenyl silane in the presence of catalytic amounts of titanocene difluoride (**18**). In contrast to the reaction of **1**, the hydrodefluorination of **26** proceeds smoothly at room temperature to give the isomeric pentafluoropropenes **27a-c** in good yield (scheme 4.1).



Scheme 4.1. Titanium-catalyzed hydrodefluorination of hexafluoropropene (**26**).

The *E/Z* selectivity is slightly in favor of the *Z*-isomer **27a**, presumably the thermodynamically more stable one; traces of the regioisomer **27c** and the second HDF product **28a** were detected in the product mixture by NMR spectroscopy. Neither the regioisomer 1,1,3,3,3-pentafluoropropene (**29**) is detected nor does a prolonged reaction time lead to the formation of tetrafluoropropenes in more than trace amounts. The overall reaction is very fast: a turnover frequency (TOF) of 508 h⁻¹ was achieved in 0.5 M reactant solutions; at higher concentrations, the TOF reaches 1570 h⁻¹, and even at -25 °C, HDF proceeds at a TOF of 5 h⁻¹ (table 6.3); up to 125 turnovers are possible. This efficiency exceeds all literature known catalytic alkene hydrodefluorination reactions by far, *e. g.* the 9.8 turnovers that were observed after three hours at 100 °C when employing an iron catalyst.⁵⁷

4.1.2. Optimization of the Catalytic Process

In an attempt to improve the *E/Z* selectivity, a number of ring-substituted titanocene difluorides **30-35** were synthesized and tested for their catalytic activity (figure 4.1). As the steric bulk of the substituent is increased, the reaction rate is found to decrease dramatically. The stereoselectivity, however, is not significantly influenced. Electronic effects appear to play an important role as well, as can be seen comparing a trimethylsilyl to a *tert*-butyl substituent: Although approximately equal in size, the turnover frequencies of **31** and

32 differ by one order of magnitude, clearly favoring the electron-donating silyl substituent. The electron-withdrawing pentafluorophenyl groups in **35** decrease the TOF, a similar effect results from a distorted Cp-M-Cp angle due to the dimethylsilylene bridge in **33**. The diketiminate **36** is hardly active; the simple titanium fluorides **37** and **38** show no reactivity at all, confirming the importance of electron donation from a suitable ligand (*cf.* section 4.3).

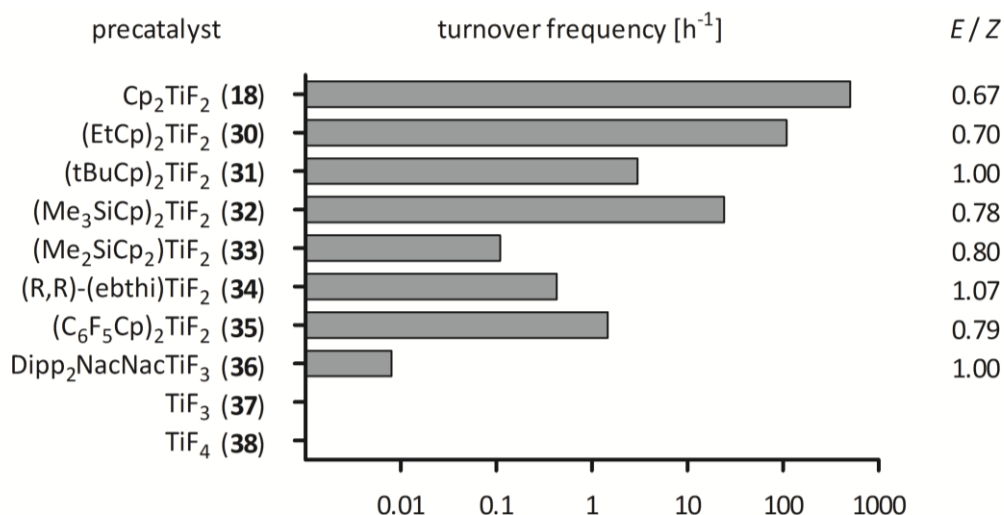


Figure 4.1. Turnover frequency and *E/Z* ratio of the hydrodefluorination of **26** depending on the precatalyst (data for **30** and **31** taken from other work).¹⁸⁸

In addition, the influence of the employed silane was investigated (figure 4.2). In order to facilitate separation from the gaseous hydrodefluorination products, high-boiling aryl and trialkyl silanes **39-42** as well as the polymeric siloxane **43** were studied. The primary silane **39** performs well, but is clearly behind the secondary silane **40**, while the tertiary silanes **41** and **42** fail to activate the catalyst at all. Surprisingly, the polymer **43** is as effective as **39**, this may be due to a rapid redistribution in the presence of the titanium catalyst.¹⁸⁹

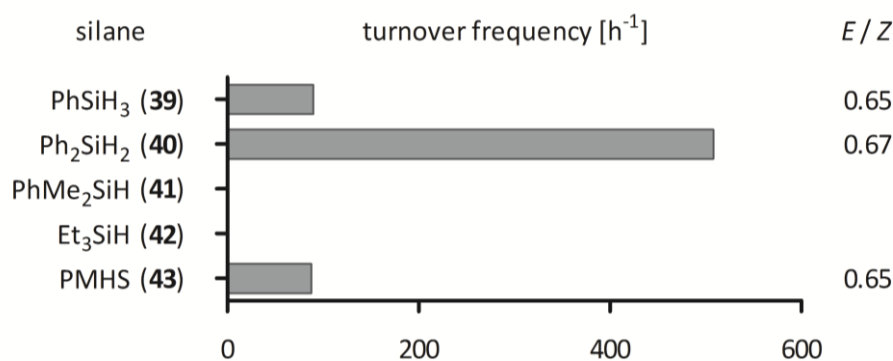


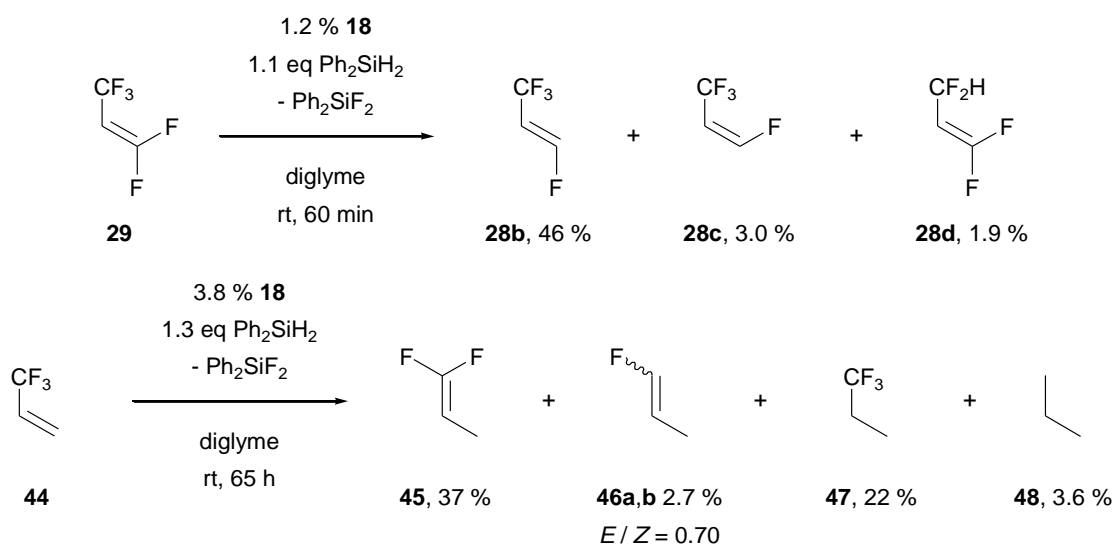
Figure 4.2. Turnover frequency and *E/Z* ratio of the hydrodefluorination of **26** catalyzed by **18** depending on the silane (PMHS = poly(methylhydrosiloxane)).

4.2. Scope and Limitations of the Titanium-Catalyzed Hydrodefluorination

Subsequent to the investigation on optimized reaction conditions, the catalytic system was applied to other substrates containing allylic and vinylic fluorine substituents.

4.2.1. Catalytic Hydrodefluorination of 1,1,3,3,3-Pentafluoropropene

Commercially available 1,1,3,3,3-pentafluoropropene (**29**) is treated with diphenyl silane in the presence of catalytic amounts of **18** to yield tetrafluoropropenes **28b**, **28c** and **28d** (scheme 4.2). The turnover frequency of 201 h^{-1} is clearly below the value of 508 h^{-1} observed for **26** under identical conditions but the selectivity is excellent; the *E*-isomer **28b** is formed in 90 % selectivity.



Scheme 4.2. Titanium-catalyzed hydrodefluorination of 1,1,3,3,3-pentafluoropropene (**29**, top) and 3,3,3-trifluoropropene (**44**, bottom).

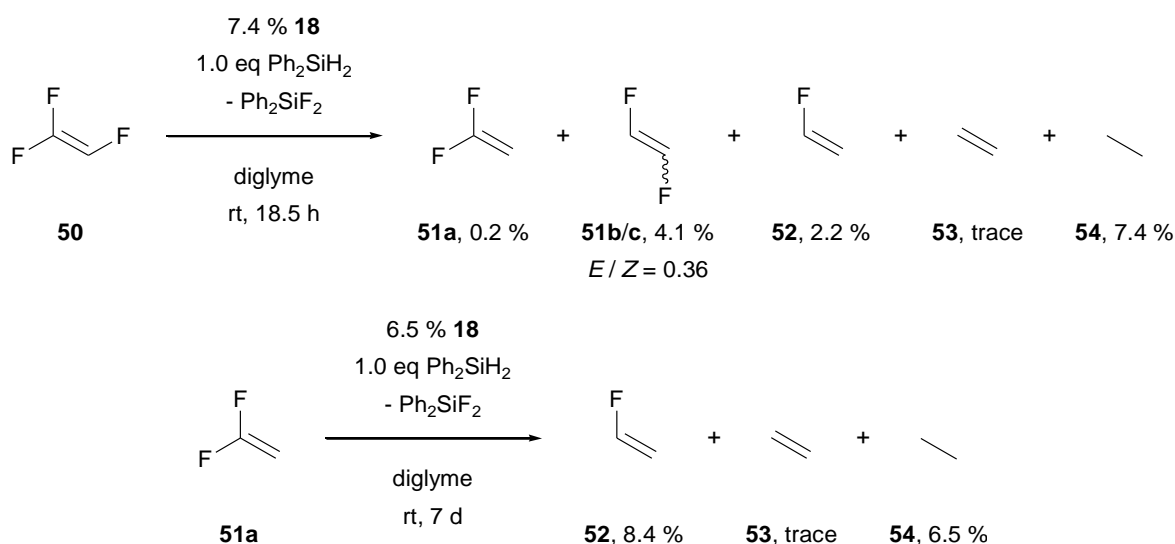
4.2.2. Catalytic Hydrodefluorination of 3,3,3-Trifluoropropene

Similarly, 3,3,3-trifluoropropene (**44**) reacts with diphenyl silane, but the reaction is much slower ($\text{TOF} = 7.2\text{ h}^{-1}$, scheme 4.2). Besides the expected HDF to give 1,1-difluoropropene (**45**) and monofluoropropenes **46a** and **46b**, a competing hydrogenation is found to yield 1,1,1-trifluoropropane (**47**) and propane (**48**). This side reaction may arise from the presence of dihydrogen formed by dehydrocoupling of the silane, which is also catalyzed by **18**;^{183,185} unlike the formation of **47**, the hydrogenation leading to **48** seems to poison the catalyst irreversibly, as indicated by the stoichiometric yield of **48** with respect to **18**. At low conversions, formation of **46a/b** is observed before the complete consumption of **44**.

Lowering the reaction temperature to 0 °C has no significant effect apart from slowing down the reaction. Mechanistic implications will be discussed below (*cf.* section 4.3).

4.2.3. Catalytic Hydrodefluorination of Fluoroethenes

A number of commercially relevant fluoroethenes **49-51a** were subjected to similar catalytic HDF conditions (scheme 4.3). While tetrafluoroethene (**49**) does not even react at elevated temperatures, trifluoroethene (**50**) affords a mixture of the difluoroethenes **51a-c**, monofluoroethene (**52**), ethene (**53**) and ethane (**54**), albeit it in low conversion (TON = 4.2). Similar to the stoichiometric reactions involving fluoroallenes (*cf.* section 2.2.2), the CF₂-group is apparently more readily attacked than the CFH-group; this can be seen from the relative yields of **51a** and **51b/c**, resulting from either a preferential formation of **51b** or a faster subsequent hydrodefluorination of **51a**. In either case, the second and third HDF steps are faster than the first, leading to **53** and **54** prior to a complete consumption of the starting material. As observed for the HDF of trifluoropropene, a HDF/hydrogenation product **54** is formed in an exactly stoichiometric amount. Similar results are observed starting from **51a** to give a mixture of **52**, **53** and **54** (TON = 3.4).

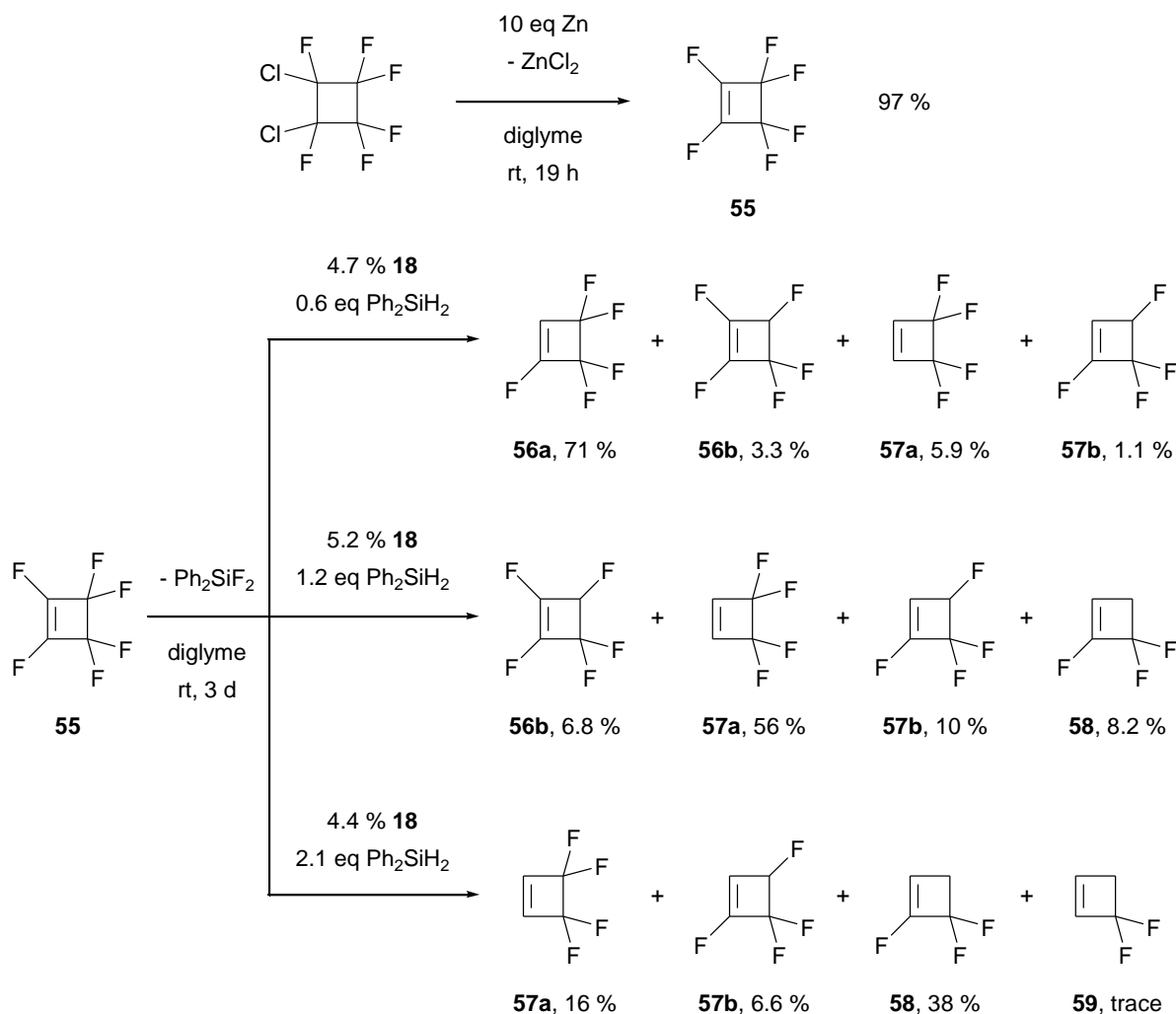


Scheme 4.3. Titanium-catalyzed hydrodefluorination of trifluoroethene (**50**, top) and 1,1-difluoroethene (**51a**, bottom).

4.2.4. Catalytic Hydrodefluorination of Hexafluorocyclobutene

To expand the scope of titanium-catalyzed hydrodefluorination to cyclic substrates, hexafluorocyclobutene (**55**) was synthesized and hydrodefluorinated in the presence of **18**.

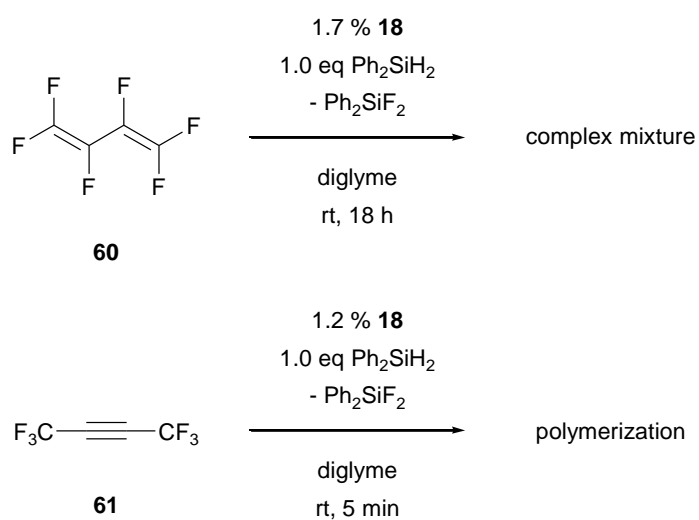
Reductive dechlorination of commercially available 1,2-dichloro-1,2,3,3,4,4-hexafluorocyclobutane using zinc dust furnishes **55** in almost quantitative yield (scheme 4.4). Unlike the examples above, the catalytic HDF of **55** is controlled by the relative amount of added silane to give penta-, tetra- or trifluorocyclobutenes. In order to ensure complete consumption of all silane-bound hydrogen, longer reaction times are necessary. Preferential formation of pentafluorocyclobutenes **56a** and **56b** over their HDF products **57a** and **57b** is achieved employing 0.6 equivalents of diphenyl silane (scheme 4.4). The less abundant isomer 1,2,3,3,4-pentafluorocyclobutene (**56b**) was enriched by pGLC and characterized by ^1H , ^{19}F and ^{19}F COSY NMR spectroscopy for the first time. 1.2 Equivalents of diphenyl silane furnish tetrafluorocyclobutenes **57a** and **57b** as the main products, whereas higher silane to substrate ratios result predominantly in the formation of trifluorocyclobutene **58** besides smaller amounts of **57a/b**, difluorocyclobutene **59** and a number of unidentified side products.



Scheme 4.4. Synthesis (top) and catalytic HDF (bottom) of hexafluorocyclobutene (**55**).

4.2.5. Other Substrates

In addition to the above mentioned alkenes, hexafluorobutadiene (**60**) was subjected to similar HDF conditions (scheme 4.5). A complex mixture of hydrodefluorination products was obtained in low conversion. In contrast, the isomeric hexafluorobut-2-yne (**61**) reacts rapidly to give a red polymer of unknown structure.



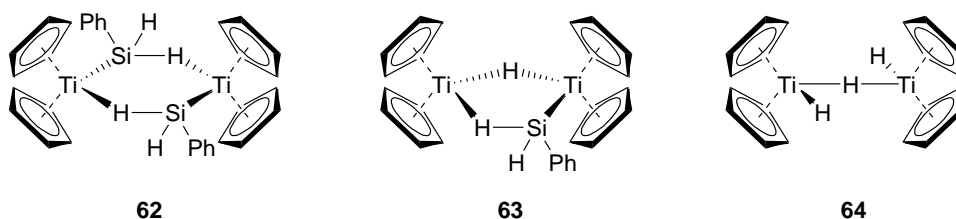
Scheme 4.5. Attempted catalytic HDF of hexafluorobutadiene (**60**, top) and hexafluorobut-2-yne (**61**, bottom).

4.3. Mechanistic Investigations

The initial assumption of titanocene(III) hydride (**19**) as the catalytically active species (*cf.* section 3.2) is in obvious contradiction to a previous report by Bercaw and Brintzinger.¹⁹⁰ While **19** is reported to be purple in color and prone to rapid decomposition in solution above -70 °C, the active catalyst forms a dark green solution and performs well at ambient temperature. This fact prompted a study on the nature of the active species in order to gain insight into the catalytic cycle.

4.3.1. Studies on the Active Species

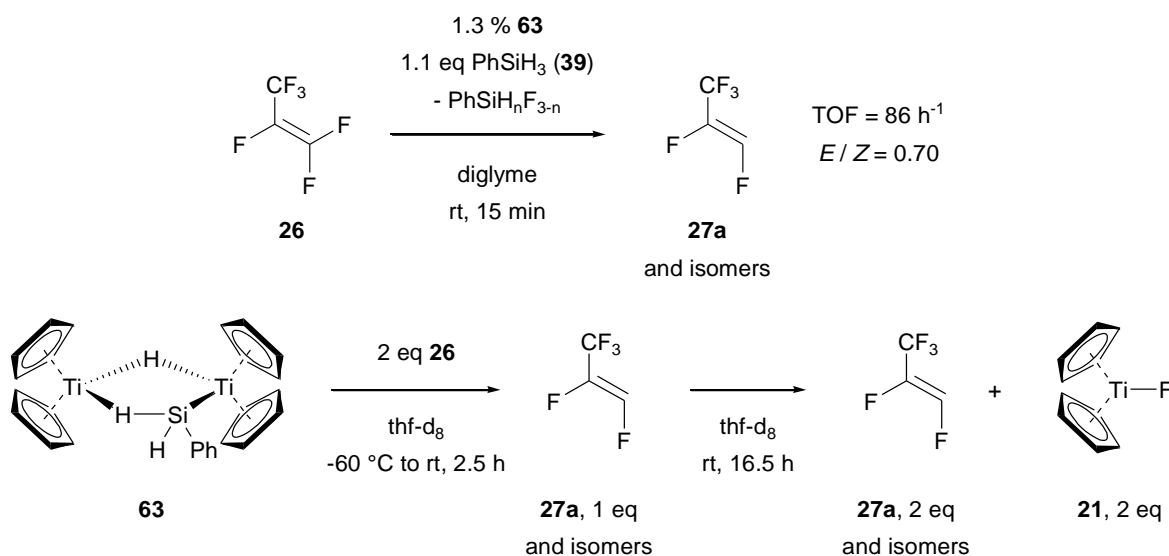
A solution of the activated catalyst was prepared from **18** and phenyl silane (**38**); upon cooling, crystals of $[\text{Cp}_2\text{Ti}(\mu\text{-SiH}_2\text{Ph})]_2$ (**62**) separated, which were isolated and identified by single-crystal X-ray diffraction. **62** has previously been observed as an intermediate in the titanium-catalyzed dehydrogenative coupling of primary and secondary silanes.^{183,191,192} In solutions containing excess silane, **62** is known to be in equilibrium with the dimeric silyl hydride complex $[\text{Cp}_2\text{Ti}(\mu\text{-SiH}_2\text{Ph})(\mu\text{-H})\text{TiCp}_2]$ (**63**) and the mixed-valence titanocene hydride **64** (scheme 4.6).^{185,193,194} Their relative abundances appear to be strongly dependent on the employed precatalyst, silane, solvent and reaction time; a shift of the equilibrium may account for the different turnover frequencies observed upon variation of the silane (*cf.* section 4.1.2). An additional equilibrium between dimeric and monomeric species was shown to exist in the presence of a suitable donor;¹⁹⁵ notably, catalytic HDF employing **18** only proceeds in donor solvents such as tetrahydrofuran or diglyme. Both **62** and **63** were detected in a toluene solution of the activated catalyst by ¹H NMR spectroscopy at low temperatures.



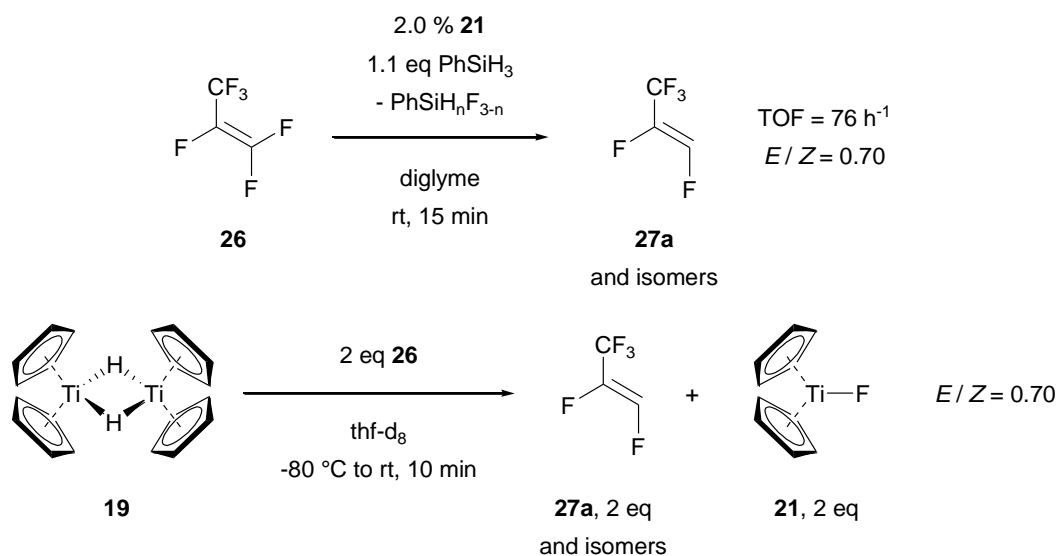
Scheme 4.6. Titanium species observed in solutions of the activated catalyst **18**.

Independently prepared **63** efficiently catalyzes the HDF of **26** in the presence of **39** (scheme 4.7) with a turnover frequency of 86 h⁻¹, almost identical to a value of 90 h⁻¹ achieved using **18** as the catalyst, thus confirming **63** to be part of or closely linked to the catalytic cycle. In

the absence of additional silane, **63** reacts at low temperature with **26** to give one equivalent of the HDF product **27**. Upon warming to room temperature, a second equivalent of **26** was slowly consumed accompanied by the formation of titanocene(III) fluoride **21**. This stepwise reaction process indicates that initially only one of the two titanium centers is capable of a HDF reaction, presumably because only one hydride ligand is present in the dimer **63**. Ligand scrambling at elevated temperatures is necessary to regenerate the hydride and allow for another HDF step.



Scheme 4.7. Catalytic (top) and stoichiometric (bottom) HDF by a dimeric titanium(III) silyl hydride **63**.



Scheme 4.8. Catalytic (top) and stoichiometric (bottom) HDF by the parent titanocene(III) hydride **19**.

The involvement of a titanium hydride was further confirmed by an independent preparation of the highly sensitive dimeric titanocene(III) hydride (**19**) from dimethyl titanocene and dihydrogen.¹⁹⁰ **19** reacts with two equivalents of **26** within minutes to give its HDF products and **21** (scheme 4.8). **21** can also be employed as a catalyst for the HDF of **26** achieving a slightly lower TOF of 76 h⁻¹ but an identical *E* / *Z* ratio.

21 was crystallized from the reaction mixture and identified by single-crystal X-ray diffraction (figure 4.3) and EPR spectroscopy.¹⁹⁶ **21** crystallizes in the orthorhombic space group P2₁2₁2₁ with one trimer of **21** and five molecules of thf in the asymmetric unit. The titanium and fluorine atoms are coplanar and exhibit slightly alternating distances (Ti-F_{short} = 2.053(5) Å, Ti-F_{long} = 2.063(6) Å, Ti-F-Ti = 158.5(4) °, F-Ti-F = 81.4(2) ° and Cp-Ti-Cp = 130.7(1) °). This geometry resembles that of the related dimeric 1,1'-dimethyltitanocene(III) fluoride (Ti-F = 2.091(3) Å, Ti-F-Ti = 109.57(8) °, F-Ti-F = 70.43(8) ° and Cp-Ti-Cp = 128.9(1) °).¹⁹⁷ The lower electron density in **21** shortens the titanium-fluorine bond and the decreased steric repulsion in the six-membered ring results in a larger angle Cp-Ti-Cp.

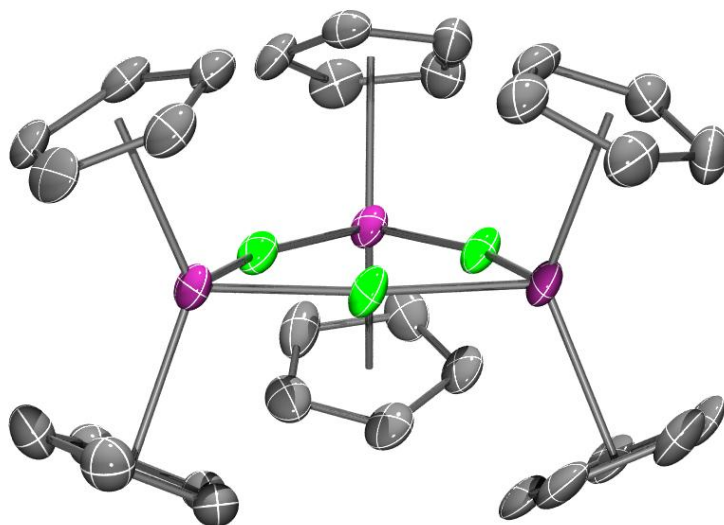
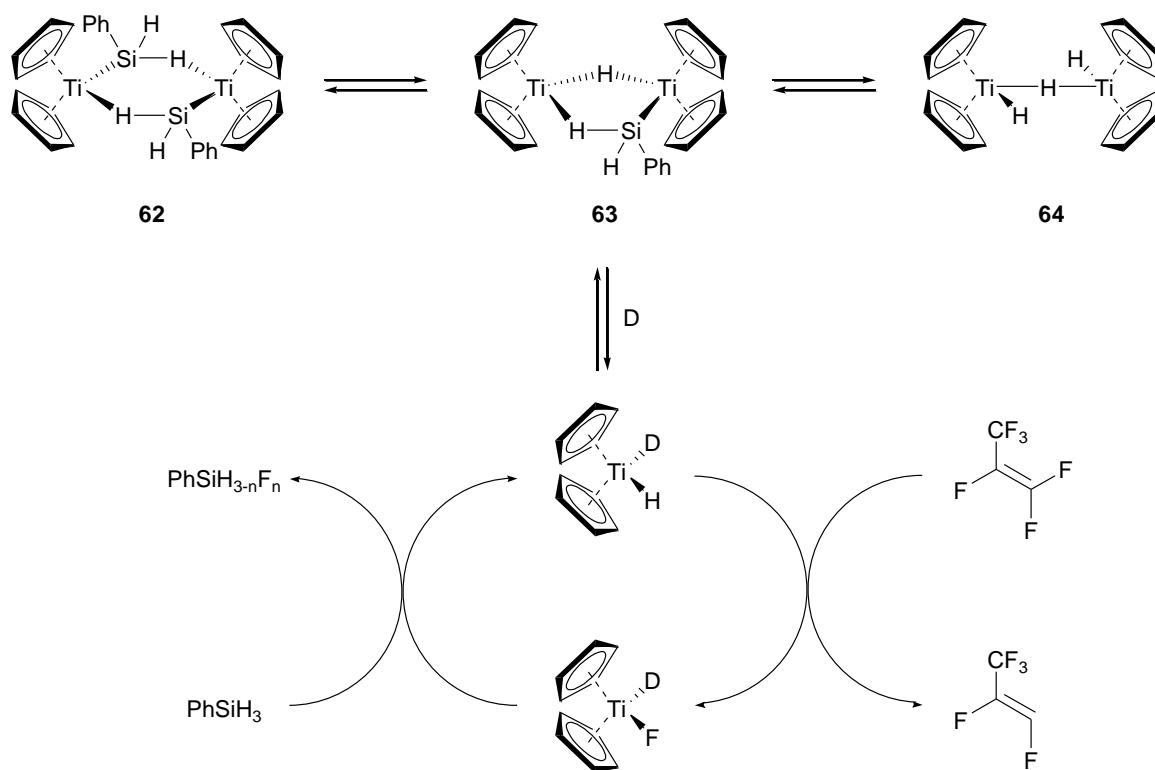


Figure 4.3. Molecular structure of trimeric titanocene(III) fluoride (**21**) (carbon gray, fluorine green, titanium purple; hydrogen atoms and solvent molecules omitted for clarity).

In conclusion, the aforementioned findings confirm a titanium hydride to act as the active species in the catalytic hydrodefluorination of hexafluoropropene. This hydride is likely to exist in an equilibrium with several dimeric titanium(III) silyl, silyl hydride and hydride species; their relative concentrations determine the turnover frequency. Transfer of the hydride to the substrate yields the HDF products and titanocene(III) fluoride, which is reconverted to the active species by reaction with excess silane (scheme 4.9).



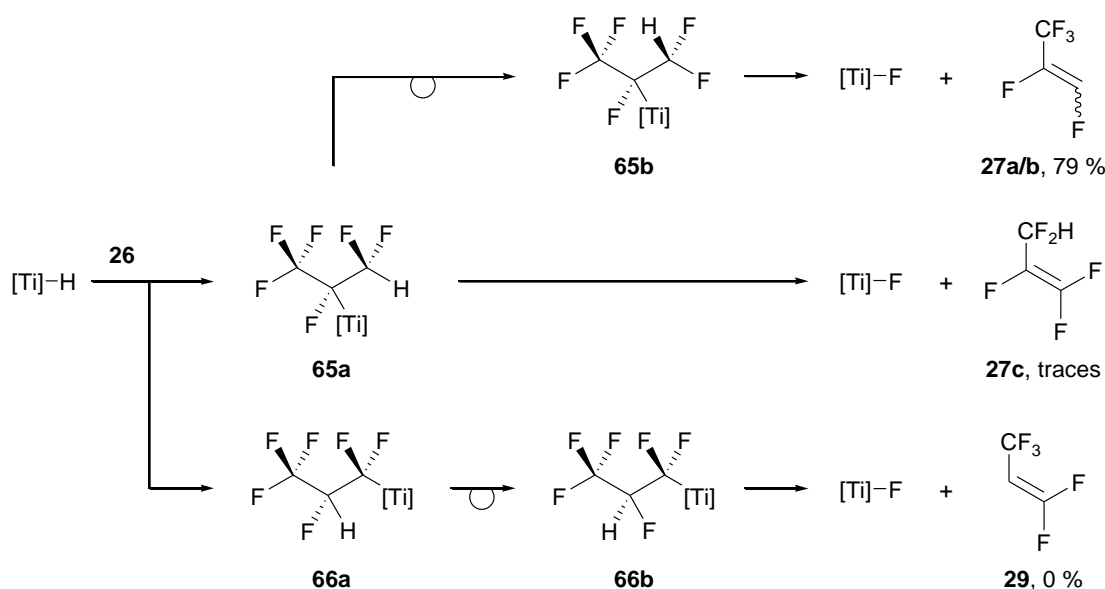
Scheme 4.9. Proposed catalytic cycle for the titanium-catalyzed HDF of hexafluoropropene (D = donor).

This conclusion is in good agreement with the observed influence of the catalyst structure on the turnover frequency (*cf.* section 4.1.2): Apart from the expectedly strong influence of sterically demanding substituents on a small 3d transition metal, a +I effect of a donating group at the cyclopentadienyl ligand increases the electron density at the metal and hence the hydridic character of the hydride ligand. In addition, a less electron deficient metal center should form a weaker bond to fluorine, facilitating the regeneration of the active hydride. The exact mechanism of the key hydrodefluorination step remains to be clarified.

4.3.2 Studies on the Hydrodefluorination Mechanism

Based on a metal hydride as the active species, two plausible mechanisms for the hydrodefluorination of **26** can be formulated. The addition/elimination pathway (A/E, scheme 4.10) comprises an insertion of the alkene double-bond into the titanium-hydrogen bond to yield an intermediate titanium fluoroalkyl species **65a**. Early transition-metal fluoroalkyl species are unstable¹⁹⁸ and prone to undergo β -fluoride elimination with formation of metal fluorides and alkenes.⁶⁷ Both β -addition and β -elimination reactions are well-known to proceed in a *syn* stereoselectivity;¹ formation of the main products **27a/b** must therefore include a rotation around the carbon-carbon single bond to enable β -fluoride

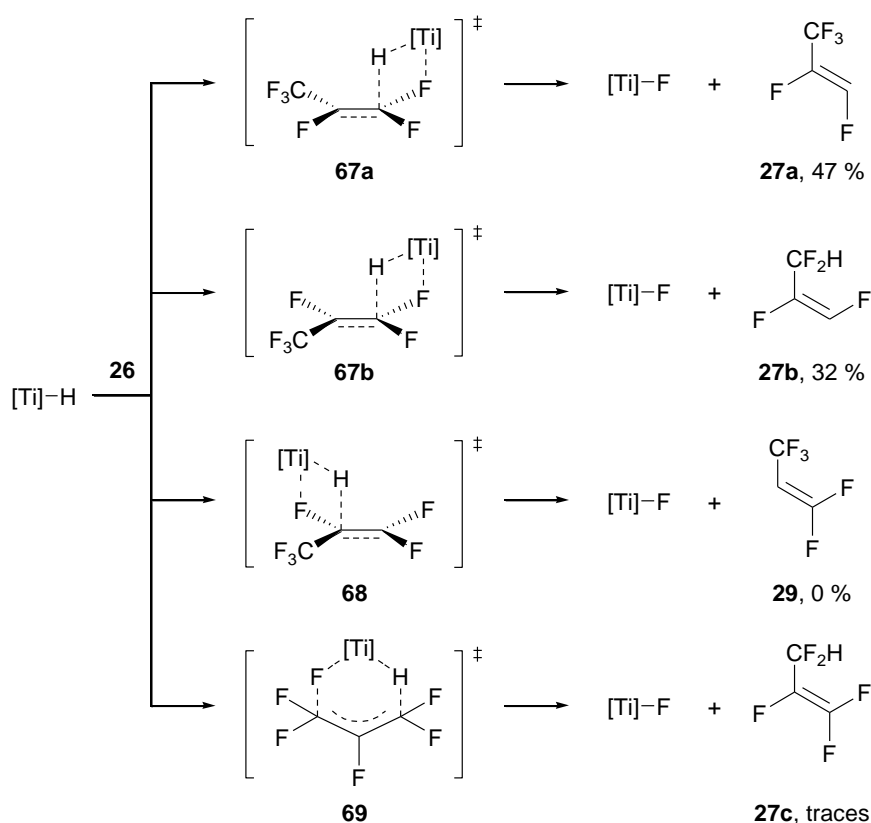
elimination from rotamer **65b**. Formation of **27c** does not require a rotation, but is found to occur only to a minor extent. This may be ascribed to the higher stability of CF₃ groups in comparison with CF₂H groups; however, this requires the elimination to be a rather slow process, otherwise, a higher yield of **27c** would be expected. Addition of the hydride to the central carbon atom would be necessary for the formation of **29** *via* intermediates **66a** and **66b**, but is not observed. Despite the higher steric hindrance expected from addition of the titanocene fragment to the secondary carbon atom, addition of the hydride to the CF₂-group is highly favored, because it is the most electrophilic site in the molecule.⁶⁶ Attempts to observe an intermediate **65a/b** by NMR spectroscopy at low temperature were not successful. Since monomeric Ti(III) species are paramagnetic and therefore likely to be unobservable by NMR, the existence of an intermediate is nevertheless possible.



Scheme 4.10. Possible HDF mechanism: Addition/elimination.

In contrast, the σ -bond metathesis mechanism (σ -m, scheme 4.11) does not include an intermediate. The HDF proceeds in one step *via* a four-membered transition state **67a**, **67b** or **68**; **67a** and **67b** should be quite similar in energy in agreement with the observed low *E/Z*-selectivity. For electronic and steric reasons, **68** is expected to be unfavorable. Formation of **27c** by σ -m requires a six-membered transition state **69**, resulting in a large F-Ti-H angle. Titanocene(III) halides typically prefer L-Ti-L angles well below 90°,^{197,199,200} **69** should therefore be highly strained and energetically not feasible. In summary, the

formation of **27a-b** is explained by either mechanism, while **27c** is more likely a product of A/E; thus A/E, σ -m or both mechanisms might be operative.

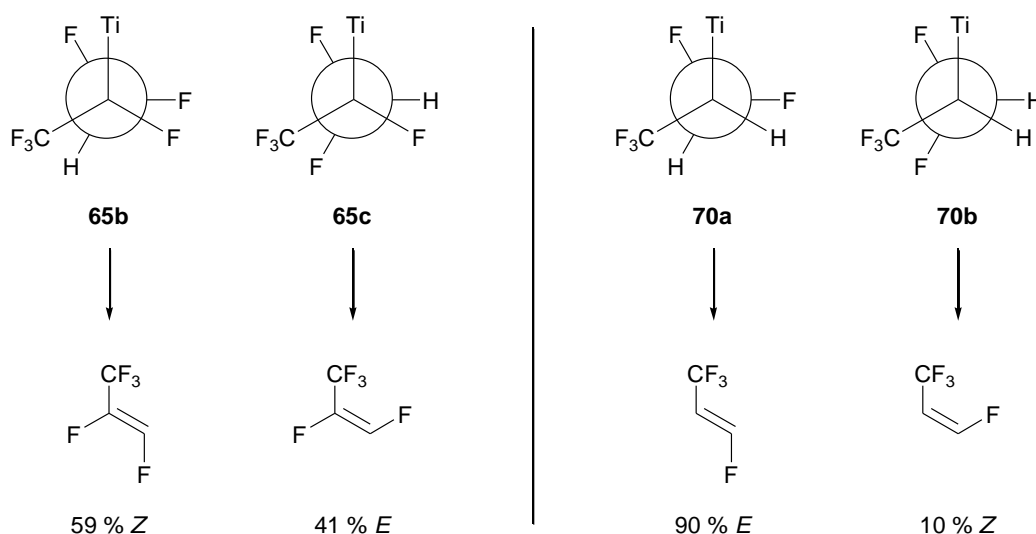


Scheme 4.11. Possible HDF mechanism: σ -Metathesis.

Looking at the HDF of **29**, the product distribution leads to a similar conclusion. The lower degree of fluorination decreases its electrophilicity resulting in a lower TOF. The pronounced *E*-selectivity demands a closer look at the possible intermediates expected from the A/E mechanism. Scheme 4.12 depicts rotamers of the proposed intermediates **65b/c** and **70a/b** leading to the different configurations in the HDF products of **26** and **29**, respectively. Both the preferred rotamers **65b** and **70a** avoid an eclipsed conformation of the CF_3 group and a vicinal fluorine atom for electrostatic reasons; **70a** is therefore energetically more favorable than **70b** and leads to 90% *E*-isomer. In **65b**, this energetic preference is attenuated by an unfavorable eclipsed conformation of the two vicinal fluorine atoms, resulting in only 59% *Z*-isomer. This selectivity cannot be explained on the basis of a σ -m mechanism.

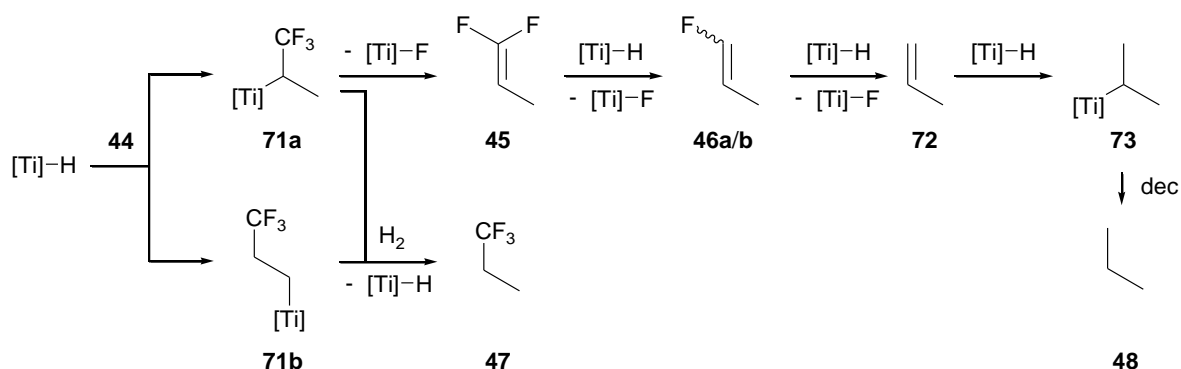
As **44** does not have any vinylic fluorine substituents, its HDF is likely to follow the A/E-mechanism. A decrease in the TOF by almost two orders of magnitude is unlikely to arise solely from a lowered electrophilicity compared to **26**. As pointed out before, the observed selectivities require the elimination step to be rather slow in order to allow for an

equilibration between the rotamers. Long-lived intermediates **71a-b** are subject to hydrogenolysis to furnish the observed hydrogenation product **47** (scheme 4.13).



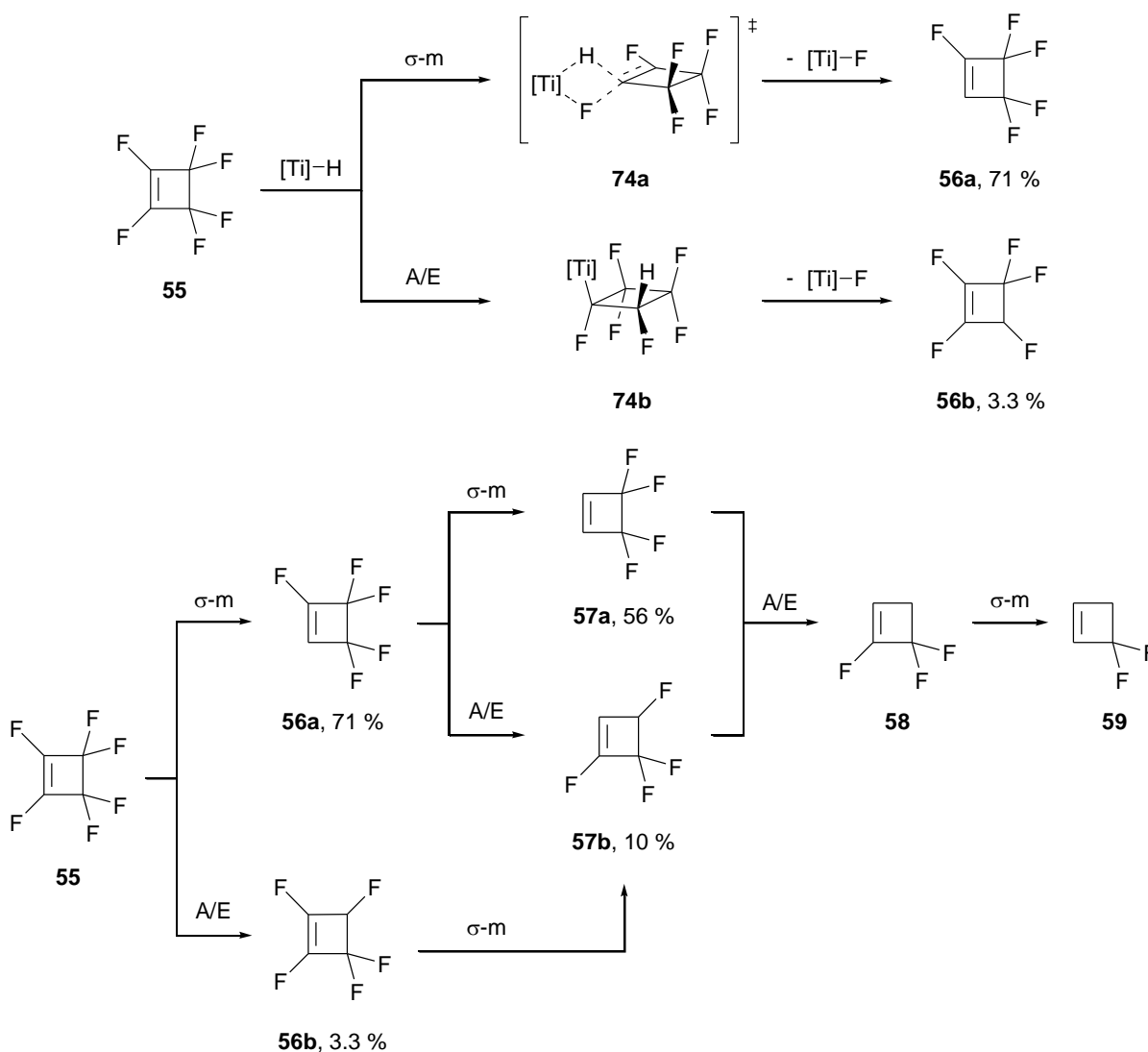
Scheme 4.12. Intermediates possibly responsible for the *E/Z*-selectivity.

In contrast, the σ -m-mechanism avoids an intermediate and may be faster but not always possible. The primary HDF product **45** features two vinylic fluorine substituents and should therefore be susceptible to σ -m; the observed formation of secondary HDF products before complete HDF of the starting material is in good agreement; no hydrogenation products of **45** and **46** were detected. Complete HDF yields propene (**72**) which upon insertion forms a titanocene(III) alkyl species **73**. This reaction removes titanium from the catalytic cycle, as **73** cannot undergo β -fluoride elimination. Instead, titanocene(III) alkyl species are unstable towards decomposition into alkanes and η^1 - η^5 -cyclopentadienyl or fulvalenyl titanium oligomers.^{201,202} The observed stoichiometric formation of **48** supports this assumption. Consistently, stoichiometric amounts of ethane (**53**) are observed in the HDF of fluoroalkenes **50** and **51**. It remains, however, unclear why tetrafluoroethene does not react at all.



Scheme 4.13. Proposed mechanism for the HDF of 3,3,3-trifluoropropene (**44**).

Unambiguous proof of the competition between both mechanisms is evident from the catalytic HDF of **55**. In a rigid cyclic substrate, stereochemical implications allow for a clear distinction between the mechanisms by which a HDF product is formed.⁷⁰ Addition of the titanium hydride to **55** yields intermediate **74b** (scheme 4.14). Subsequent β -fluoride elimination must proceed in a *syn*-geometry forming HDF product **56b**, which is detected in the product mixture in small amounts. The main HDF product **56a** can only be formed *via* the σ -metathesis mechanism. The second HDF step follows a similar pattern: The main product **57a** is formed by σ -m, whereas minor amounts of **57b** are formed by A/E; the side-product **56b** also yields **57b** by σ -m. **57a** does not comprise any vinylic fluorine atoms; further HDF must follow the A/E pathway while its HDF product **58** is again subject to σ -m.



Scheme 4.14. Competing mechanisms in the HDF of hexafluorocyclobutene (**55**).

In summary, mechanistic studies have clearly shown both the insertion/ β -fluoride elimination and the σ -bond metathesis mechanism to be operative in the catalytic HDF of fluoroalkenes. The former may account for the observed *E/Z* selectivities but is assumed to be rather slow and susceptible to hydrogenolysis; at least for cyclic alkenes, the latter proceeds at a faster rate, but is not always possible. Given the complex equilibrium of titanium species in a catalytically active solution, it is possible that one active species is able to react in both ways or two different species react in a single way each.

Alternatively, a radical mechanism is possible; however, the absence of dimers and oligomers of the substrate as well as hydrosilylation products render this type of pathway unlikely. Another mechanism comprising an α -fluoride elimination followed by a rearrangement has been discussed in the literature⁷⁰ but was not studied, as the highly reactive intermediate carbene species would be expected to yield numerous side-products.

5. Summary

This work has demonstrated the high reactivity of early transition-metal hydrides towards fluoroallenes and α -alkenes.

Zirconocene hydride chloride (Schwartz' reagent) reacts with tetrafluoroallene to give the hydrodefluorination products trifluoroallene and 1,3-difluoroallene, which were isolated and characterized by NMR spectroscopy and single-crystal X-ray diffraction. In both structures, the allenic carbon backbone is found to deviate from linearity; the distortions are attributed to negative hyperconjugation effects.

Employing the chiral zirconium hydrides [(1*S*,1'*S*)-(ebthi)ZrH₂]₂ and [(1*R*,1'*R*)-(ebthi)ZrH₂]₂, hydrodefluorination of trifluoroallene yields optically active 1,3-difluoroallene in 30 % enantiomeric excess, as determined by NMR spectroscopy of diastereomeric inclusion compounds formed with TRIMEB as a chiral host. An alternative synthesis using the chiral aluminum hydride (*S*)-BINAL-H resulted in only 6 % ee.

Attempts to develop a system capable of a catalytic fluoroallene hydrodefluorination were not successful (turnover number < 3); an insufficient regioselectivity is believed to account for the catalyst's inefficiency. Dependence of the regioselectivity on the metal center was demonstrated by the isolation of a tetrafluoroallene insertion product of a chromium hydride.

Titanocene difluoride was found to act as a precatalyst for the C-F activation of fluoroalkenes. Hexa-, penta- and trifluoropropene, tri- and difluoroethene and hexafluorocyclobutene undergo catalytic hydrodefluorination employing various silanes as a hydrogen source. Optimization on the *E/Z*-selectivity by introducing substituents to the titanocene cyclopentadienyl ligands was not successful. Mechanistic studies suggest that the catalytically active species is a titanocene(III) hydride; upon reaction with the substrate, titanocene(III) fluoride is formed, which was characterized by X-ray crystallography. The key hydrodefluorination step is likely to follow both an alkene insertion/ β -fluoride elimination and a σ -bond metathesis mechanism, as deduced from the stereochemical outcome of the hydrodefluorination of hexafluorocyclobutene.

In dieser Arbeit wurde die Reaktivität von Hydriden früher Übergangsmetalle gegenüber Fluorallen und –alkenen untersucht.

Zirkonocenhydridchlorid (Schwartz' Reagenz) reagiert mit Tetrafluorallen zu den Hydrodefluorierungsprodukten Trifluorallen und 1,3-Difluorallen, die isoliert und mittels NMR-Spektroskopie und Einkristall-Röntgenstrukturanalyse untersucht wurden. Die leicht gewinkelte Struktur ihrer Kohlenstoff-Gerüste kann mit negativer Hyperkonjugation erklärt werden.

Bei Verwendung der chiralen Zirkoniumhydride $[(1S,1'S)\text{-}(\text{ebthi})\text{ZrH}_2]_2$ und $[(1R,1'R)\text{-}(\text{ebthi})\text{ZrH}_2]_2$ liefert die Hydrodefluorierung von Trifluorallen optisch aktives 1,3-Difluorallen in 30 % Enantiomerenüberschuss, welcher durch NMR-Spektroskopie diastereomerer Einlagerungsverbindungen in den chiralen Wirt TRIMEB ermittelt wurde. Eine alternative asymmetrische Synthese unter Verwendung des chiralen Aluminiumhydrids (*S*)-BINAL-H lieferte lediglich 6 % ee.

Versuche, ein System zur katalytischen Hydrodefluorierung von Fluorallen zu entwickeln, waren nicht erfolgreich (Turnover-Number < 3); die mangelnde Effizienz des untersuchten Systems beruht vermutlich auf einer zu geringen Regioselektivität des Insertionsteilschrittes. Die Abhängigkeit der Regioselektivität vom verwendeten Metallhydrid wurde durch die Isolierung eines Insertionsproduktes von Tetrafluorallen in eine Chrom-Wasserstoff-Bindung belegt.

Es konnte gezeigt werden, dass Titanocendifluorid ausgezeichnet als Präkatalysator zur C-F-Aktivierung von Fluoralkenen geeignet ist. In Gegenwart verschiedener Silane als Hydridquelle lassen sich Hexa-, Penta- und Trifluorpropen, Tri- und Difluorethen sowie Hexafluorcyclobuten katalytisch hydrodefluorieren. Die Einführung von Substituenten an den Cyclopentadienyl-Liganden des Titanocendifluorids führte nicht zur erhofften Verbesserung der *E/Z*-Selektivität. Mechanistische Untersuchungen deuten auf ein Titanocen(III)hydrid als katalytisch aktive Spezies hin. Bei dessen Reaktion mit dem Substrat entsteht Titanocen(III)fluorid, welches durch Röntgenstrukturanalyse charakterisiert werden konnte. Aus dem stereochemischen Verlauf der Hydrodefluorierung von Hexafluorcyclobuten wurde geschlossen, dass die Hydrodefluorierung sowohl nach einem Additions/Eliminierungs-Mechanismus als auch in Form einer σ -Bindungs-Metathese ablaufen kann.

6. Experimental Section

6.1. General

6.1.1. Techniques

All reactions and manipulations were carried out in pre-dried glassware under an argon atmosphere by using standard Schlenk-type and vacuum-line techniques, or by working in an argon-filled MBraun glove box model LAB master SP. The amount of gaseous compounds was determined using pVT techniques or by condensing the gas into a weighed flask.

6.1.2. Chemicals

Diethyl ether, 1,2-dimethoxyethane, diglyme, 2-methyl-tetrahydrofuran, tetrahydrofuran, tetrahydrofuran- d_8 and toluene- d_8 were freshly distilled from sodium/benzophenone ketyl or stored over sodium/potassium alloy; diglyme for catalysis experiments was stored and manipulated inside a glovebox. Acetonitrile, hexane, toluene and pentane were dried over activated alumina using an MBraun solvent system model MB SPS-800. Methanol was distilled from magnesium turnings.

Cp_2TiF_2 (**18**),²⁰³ $(\text{Cp}_2\text{TiH})_2$ (**19**),¹⁹⁰ $\text{CpCr}(\text{CO})_3\text{H}$ (**24**),²⁰⁴ $(\text{Me}_3\text{SiCp})_2\text{TiCl}_2$,²⁰⁵ Me_3SnF ,⁵⁷ $(\text{Me}_3\text{SiCp})_2\text{TiCl}_2$,²⁰⁶ $\text{Dipp}_2\text{NacnacTiF}_3$ (**36**),²⁰⁷ hexafluorobutadiene (**60**)²⁰⁸ and $[\text{Cp}_2\text{Ti}(\mu\text{-SiH}_2\text{Ph})(\mu\text{-H})\text{TiCp}_2]$ (**63**)¹⁹¹ were synthesized by literature procedures. $[\text{Cp}_2\text{Ti}(\mu\text{-F})_2]$ (**21**) was synthesized by a modified literature procedure²⁰⁹ using zinc instead of aluminum powder. PhSiH_3 (**39**),²¹⁰ Ph_2SiH_2 (**40**),²¹⁰ PhMe_2SiH (**41**, Alfa Aesar), Et_3SiH (**42**, ABCR) and PMHS (**43**, Alfa Aesar) were purchased or synthesized, dried (calcium hydride **39-42**, molecular sieves **43**) and stored in a glovebox. Lithium powder (0.6 % Na, suspension in mineral oil, Sigma-Aldrich) was washed with dry pentane and dried *in vacuo*. CyCl (ACROS), Cp_2ZrHCl (**5**, 95 %, ABCR), L-(–)-ethyl lactate (Roth), heptakis(2,3,6-tri-O-methyl)- β -cyclodextrin (Wako), [(1*S*,1'*S*)-1,2-ethanediylbis(tetrahydroindenylidene)]dichlorozirconium ((1*S*,1'*S*)-**12**, MCAT), [(1*R*,1'*R*)-1,2-ethanediylbis(tetrahydroindenylidene)]dichlorozirconium ((1*R*,1'*R*)-**12**, MCAT), *n*BuLi (2.5 M in hexanes, ACROS), *R*-(–)-O-acetylmandelic acid (**15**, TCI Europe), LiAlH_4 (2.4 M in thf, ACROS), (*S*)-BINOL (Chem-Impex International), (*R,R*)-(ebthi) TiF_2 (**33**, Sigma-Aldrich), TiF_3 (**37**, ABCR), TiF_4 (**38**, ABCR), 1,1,3,3,3-pentafluoropropene (**29**, SynQuest Labs), trifluoroethene (**50**, SCM Specialty Chemicals), 1,1-difluoroethene (**51a**, SynQuest Labs), 1,2-dichloro-1,2,3,3,4,4-hexafluorocyclobutane (Ferak) and hexafluorobut-2-yne (**61**, ABCR) were obtained from commercial sources and used as received. Hexafluoropropene (**26**,

Solvay Fluor), 3,3,3-trifluoropropene (**44**, Hoechst) and tetrafluoroethene (**49**, Bundesanstalt für Materialprüfung und –forschung) were obtained free of charge and used as received.

6.1.3. Instrumentation

^1H , ^{13}C and ^{19}F NMR spectra were recorded on a JEOL LAMBDA 400 or ECS 400 spectrometer (399.65, 100.40, 376.00 MHz). Chemical shifts are reported in ppm (δ) relative to TMS and CFCl_3 , respectively, and were determined by reference to the residual solvent resonances (^1H and ^{13}C) or an external reference (^{19}F).

IR spectra were obtained from a Nicolet 5 SXC FTIR spectrometer equipped with a DTGS detector. Melting points are given without correction.

Single-crystal X-ray structure determination was performed on a Bruker-AXS SMART 1000 fitted with a CCD detector. Crystals suitable for X-ray structure determination were selected under a stream of cold nitrogen; gaseous samples were measured in a flame-sealed 0.3 mm glass capillary. Data collection, reduction and empirical absorption correction were performed using the SMART, SAINT and SADABS programs, respectively;²¹¹ the SHELX program package²¹² was used for structure solution and refinement. ORTEP²¹³ was employed for structure visualization.

Preparative gas-liquid chromatography was performed on a modified Carlo Erba FractoVap 4500 (model 1982) fitted with a 4 m x 1 cm glass column packed with 15 % Halocarbon oil on Chromosorb P-AW cooled to 0 °C, using helium as the carrier gas at 1 cm min⁻¹ flow rate.

EPR spectra were recorded on a Bruker ER 200D-SRIC spectrometer equipped with a B-E 25 magnet, external standard diphenylpicrylhydroxyl (DPPH) $g = 2.0037$.

Mass spectra were measured on a Varian MAT 711 spectrometer operating at 80 eV.

6.2. Preparations

6.2.1. Synthesis of Cyclohexyllithium

This compound was prepared by a modified literature procedure.^{214,215} In a two-necked Schlenk flask equipped with a reflux condenser and a dropping funnel, powdered lithium (0.6 % Na, 3.50 g, 504 mmol, 2.2 eq.) was suspended in toluene (500 mL). Cyclohexyl chloride (27.21 g, 229 mmol) was added dropwise over a period of 1 h while the reaction was initiated by heating until a temperature slightly above room temperature was maintained by itself. After 3 h, the now purple reaction mixture was filtered through a glass frit and the yellow filtrate was cooled to -80 °C to precipitate cyclohexyllithium as colorless crystals. The solvent was removed with a cannula, the crystals were washed with cold toluene and dried *in vacuo* overnight. Yield: 60 %. The purity was found to be >99 % by hydrolysis and subsequent titration with hydrochloric acid.

6.2.2. Synthesis of Tetrafluoroallene (**1**)

To a two-necked Schlenk flask, charged with cyclohexyllithium (4.52 g, 50.2 mmol, 1.1 eq.) was added cold diethyl ether (500 mL) at -80 °C. The mixture was cooled to -196 °C, degassed, and 1,1,3,3,3-pentafluoropropene (**29**, 6.06 g, 45.9 mmol) was condensed into the flask. After allowing the reaction mixture to warm to -100 °C, the flask was vented with argon and a low-temperature thermometer was inserted into the suspension. The mixture was stirred at -75 °C for 3 h and subsequently allowed to warm to -20 °C within 30 minutes. A 50 cm packed fractionation column was fitted onto the flask and the head was cooled to -80 °C. Distillation (bp -39 to +15 °C) gave a mixture of **1** and diethyl ether, fractional condensation of the distillate *via* two subsequent traps kept at -125 °C and -196 °C, respectively, gave **1** in >97 % purity in the second trap. Yield: 69 %. The purity was determined by ¹⁹F and ¹H NMR spectroscopy versus an internal fluorobenzene standard.¹²³ **1** was stored at -80 °C.

6.2.3. Synthesis of Trifluoroallene (**4**)

In a single-necked flask equipped with a J. Young PTFE valve, zirconocene chloride hydride (**5**, 95 %, 1.041 g, 3.847 mmol, 1.2 eq) was suspended in toluene (20 mL). After degassing, **1**

(371.5 mg, 3.316 mmol) was condensed onto the frozen mixture at $-196\text{ }^{\circ}\text{C}$. The mixture was allowed to warm to room temperature and stirred overnight. Fractional condensation of the reaction mixture *via* two subsequent traps kept at $-78\text{ }^{\circ}\text{C}$ and $-196\text{ }^{\circ}\text{C}$, respectively, gave 301 mg crude product in the second trap and a pale yellow residue (**6**) in the flask. pGLC of the crude product afforded **5** in $>95\%$ purity. Yield: 47 %. Mp $-148\text{ }^{\circ}\text{C}$. **4** was stored at $-80\text{ }^{\circ}\text{C}$.

4: δ_{H} (CDCl_3): 7.08 (1 H, dt, $^2J_{\text{HF}} = 88.4\text{ Hz}$, $^4J_{\text{HF}} = 0.92\text{ Hz}$, CFH); δ_{F} (CDCl_3): -78.0 (2 F, dd, $^4J_{\text{FF}} = 44.5\text{ Hz}$, $^4J_{\text{FH}} = 0.9\text{ Hz}$, CF₂), -98.0 (1 F, dt, $^2J_{\text{FH}} = 88.2\text{ Hz}$, $^4J_{\text{FF}} = 44.5\text{ Hz}$, CFH); δ_{C} (CDCl_3): 133.1 (dt, $^1J_{\text{CF}} = 275.6\text{ Hz}$, $^3J_{\text{CF}} = 5.8\text{ Hz}$, CFH), 144.8 (td, $^1J_{\text{CF}} = 275.0\text{ Hz}$, $^3J_{\text{CF}} = 6.2\text{ Hz}$, CF₂), 148.8 (td, $^2J_{\text{CF}} = 37.4\text{ Hz}$, $^2J_{\text{CF}} = 14.9\text{ Hz}$, =C=).

6: δ_{H} (toluene- d_8): 5.85 (10 H, s, Cp); δ_{F} (toluene- d_8): 59.9 (1 F, br s, ZrF). $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 3104 m (CH), 1438 m (CC), 1364 w, 1125 w, 1021 s, 1014 s, 847 w, 811 vs, 749 s, 612 w, 547 s, 530 m.

6.2.4. Synthesis of 1,3-Difluoroallene (**7**)

In a single-necked flask equipped with a J. Young PTFE valve, zirconocene chloride hydride (**5**, 95 %, 1.972 g, 7.266 mmol, 2.3 eq) was suspended in toluene (20 mL). After degassing, **1** (349.3 mg, 3.118 mmol) was condensed onto the frozen mixture at $-196\text{ }^{\circ}\text{C}$. The mixture was allowed to warm to room temperature and stirred overnight. Fractional condensation of the reaction mixture *via* two subsequent traps kept at $-78\text{ }^{\circ}\text{C}$ and $-196\text{ }^{\circ}\text{C}$, respectively, gave 128 mg crude product in the second trap and a pale yellow residue (**6**) in the flask. pGLC of the crude product afforded **7** in $>95\%$ purity. Yield: 24 %. Mp $-107\text{ }^{\circ}\text{C}$. **7** was stored at $-80\text{ }^{\circ}\text{C}$.

7: δ_{H} (CDCl_3): 7.09 (2 H, m, CFH); δ_{F} (CDCl_3): -123.9 (2 F, m, CFH); δ_{C} (CDCl_3): 133.1 (m, CFH), 175.9 (t, $^2J_{\text{CF}} = 13.2\text{ Hz}$, =C=).

Iterated coupling constants: $^2J_{\text{FH}} = 86.0(1)\text{ Hz}$, $^4J_{\text{FF}} = 81.24(9)\text{ Hz}$, $^4J_{\text{FH}} = 6.1(1)\text{ Hz}$, $^4J_{\text{HH}} = 4.01(5)\text{ Hz}$; R = 0.0134.

6.2.5. Synthesis of Bis[(1*S*,1'*S*)-1,2-ethanediylbis(tetrahydroindenylidene)]di- μ -hydrodihydro-dizirconium ((1*S*,1'*S*)-**13**) and (1*R*,1'*R*)-**13**

In a 500 mL single-necked flask equipped with a QVF PTFE valve, [(1*S*,1'*S*)-1,2-ethanediylbis(tetrahydroindenylidene)]dichlorozirconium ((1*S*,1'*S*)-**12**, 502.3 mg, 1.178 mmol) was dissolved in toluene (25 mL). After repeated degassing, *n*-butyllithium (2.5 M in hexanes, 1.0

mL, 2.5 mmol, 2.1 eq) was added dropwise at -78 °C over a period of 10 minutes. The now yellow solution was warmed to -40 °C (acetonitrile/dry ice slush) and stirred for 60 minutes. Subsequently, the mixture was degassed twice, vented with 1 bar dihydrogen at -196 °C and replaced into the acetonitrile/dry ice slush. Allowing the mixture to slowly come to room temperature overnight yielded an almost colorless suspension that was filtered over a fine glass frit (D4). The filtrate was evaporated *in vacuo* to give (1*S*,1'*S*)-**13** as a pale green powder. Yield: 92 %, ee >98 %. Mp 185 °C dec.

The ¹H NMR spectrum was identical to that reported for the racemate.¹⁷¹

The ee was determined by vacuum transfer of tetrahydrofuran-*d*₈ to a J. Young NMR tube containing (1*S*,1'*S*)-**13** (5.3 mg, 7.4 μmol) and *R*-(-)-*O*-acetylmandelic acid (**15**, 11.5 mg, 59 μmol, 8 eq) at -196 °C. Upon warming to room temperature, the solids dissolved with gas evolution to give a pale yellow solution of **16**. The ee was calculated from integration of the Cp resonances of (1*S*,1'*S*,*R,R*)-**16** at 5.70 and 5.18 ppm versus those of (1*R*,1'*R*,*R,R*)-**16** at 5.60 and 5.36 ppm in the ¹H NMR spectrum.¹⁷²

By the same procedure, (1*R*,1'*R*)-**13** was synthesized from (1*R*,1'*R*)-**12** in 65 % yield and > 98 % ee.

6.2.6. Synthesis of Optically Active 1,3-Difluoroallene (**7**) Employing (1*S*,1'*S*)-**13**

To a glass tube (8 mm o. d.) charged with (1*S*,1'*S*)-**13** (31.3 mg, 43.8 μmol) were added toluene (1 mL) and **4** (18.0 mg, 191 μmol, 4.4 eq) by vacuum transfer; the glass tube was flame sealed and subsequently immersed into a cooling bath at -78 °C. After two weeks, the tube was broken open inside a PVC hose connected to a cold trap and all volatiles were removed *in vacuo* leaving a pale yellow residue of (ebthi)ZrF₂.²¹⁶ Fractional condensation of the volatiles *via* two subsequent traps kept at -78 °C and -196 °C, respectively, gave 16.3 mg crude product in the second trap. pGLC of the crude product afforded **7** in >95 % purity. Yield: 38 % (relative to **13**). ee 29 %.

The ee was determined by condensing **7** (5.1 mg, 67 μmol) into a J. Young NMR tube containing a solution of heptakis(2,3,6-tri-*O*-methyl)-β-cyclodextrin (201.1 mg, 140.6 μmol,

2.1 eq) in methanol-d₄ (0.70 mL). The ee was calculated by integrating the resonance set centered at -125.7551 versus that centered at -125.7674 ppm in the ¹⁹F NMR spectrum.

Table 6.1. Different conditions for the asymmetric synthesis of 1,3-difluoroallene (**7**).

| solvent | temperature | ee | time | yield |
|---------|-------------|----|-------|-------|
| toluene | 0 °C | 14 | 1 h | 37 % |
| toluene | -45 °C | 30 | 89 h | n. d. |
| toluene | -60 °C | 29 | 60 h | n. d. |
| toluene | -80 °C | 29 | 14 d | 38 % |
| Me-thf | -80 °C | 15 | 18 h | 11 % |
| hexane | -45 °C | 12 | 115 h | < 5 % |

6.2.7. Synthesis of Optically Active 1,3-Difluoroallene (**7**) Employing (*S*)-**17**

In a Schlenk flask, methanol (1.0 M in thf, 1.0 mL, 0.25 mmol, 1.0 eq) and (*S*)-BINOL (0.2 M in thf, 1.25 mL, 0.25 mmol, 1.0 eq) were added to a solution of LiAlH₄ (2.4 M in thf, 0.10 mL, 0.24 mmol) in thf (5.0 mL) at 0 °C. The solution was stirred for 20 minutes at room temperature, then cooled to -196 °C and degassed. **4** (20.4 mg, 0.22 mmol, 0.9 eq) was added by vacuum transfer, the mixture was warmed to -100 °C and allowed to warm to -80 °C overnight and subsequently to room temperature within 45 minutes. Fractional condensation of the reaction mixture *via* two subsequent traps kept at -78 °C and -196 °C, respectively, gave 1.1 g crude product in the second trap. Multi-run pGLC of the crude product afforded **7** in >95 % purity. Yield: 26 % (relative to **4**). ee 6 %.

6.2.8. Attempted Zirconium-Catalyzed Hydrodefluorination of Tetrafluoroallene (**1**)

A single-necked flask equipped with a J. Young PTFE valve was charged with **5** (7.7 mg, 30 μmol, 6.2 mol %), **43** (122.7 mg, 2.04 mmol, 4.2 eq) and diglyme (2.0 mL). After degassing, **1** (54.5 mg, 0.486 mmol) was added by vacuum transfer and the mixture was stirred at room temperature for 87 hours. Fractional condensation of the reaction mixture *via* two subsequent traps kept at -78 °C and -196 °C, respectively, gave a mixture of **1** (0.230 mmol, 47 %) and **4** (45 μmol, 9.3 %) in the second trap. The yield was determined by integration of the product resonances in the ¹⁹F NMR spectrum versus an internal fluorobenzene standard.

6.2.9. Synthesis of (η^5 -Cyclopentadienyl)[η^1 -(Z-1,3,3,3-tetrafluoropropenyl)]tricarbonylchromium (25)

To a Schlenk flask charged with tricarbonyl(η^5 -cyclopentadienyl)hydridochromium (**24**, 475 mg, 2.35 mmol) were added pentane (20 mL) and **1** (5.0 mmol, 2.1 eq) by vacuum transfer. The reaction mixture was stirred at room temperature overnight, filtered over a glass frit and the frit was washed with additional pentane. The filtrate was cooled to -80 °C overnight to precipitate **25** as yellow crystals. Yield: 28 %. Mp 98 °C dec.

25: δ_{H} ($\text{C}_6\text{D}_5\text{CD}_3$): 3.99 (5 H, br s, Cp), 5.31 (1 H, d-qa, $^3J_{\text{HF}} = 46.0$ Hz, $^3J_{\text{HF}} = 7.7$ Hz, HCCF₃); δ_{F} ($\text{C}_6\text{D}_5\text{CD}_3$): -13.8 (1 F, d-qa, $^3J_{\text{FH}} = 46.0$ Hz, $^4J_{\text{FF}} = 14.2$ Hz, CrCF), -57.3 (3 F, dd, $^4J_{\text{FF}} = 14.2$ Hz, $^3J_{\text{FH}} = 7.9$ Hz, CF₃); δ_{C} ($\text{C}_6\text{D}_5\text{CD}_3$): 90.3 (s, Cp), 118.0 (qa-d, $^2J_{\text{CF}} = 32.6$ Hz, $^3J_{\text{CF}} = 3.35$ Hz, =CH), 121.4 (qa-d, $^1J_{\text{CF}} = 271.7$ Hz, $^3J_{\text{CF}} = 9.58$ Hz, CF₃), 204.9 (d-qa, $^1J_{\text{CF}} = 360.4$ Hz, $^3J_{\text{CF}} = 5.75$ Hz, CrCF), 237.2 (s, CO), 244.0 (s, CO).

ν_{max} / cm^{-1} (neat) 3135 w, 2963 vw, 2872 vw, 2112 vw, 2028 m, 1968 s, 1943 vs br, 1592 s, 1433 m, 1371 vw, 1283 s, 1244 m, 1124 m, 1097 s, 1064 m, 949 m, 873 w, 842 m, 768 m, 645 m, 632 m, 597 vs, 554 s.

m/z (EI, 40 °C) 313.9673 (M^+ , $\text{C}_{11}\text{H}_6\text{F}_4\text{CrO}_3$ requires 313.9658), 285.9 ($\text{M}^+ - \text{CO}$, 2 %), 258.1 ($\text{M}^+ - 2 \text{CO}$, 6 %), 229.9 ($\text{M}^+ - 3 \text{CO}$, 14 %), 211.0 ($\text{M}^+ - 3 \text{CO} - \text{F}$, 6 %), 136.0 (CpCrF^+ , 100 %), 117.2 (CpCr^+ , 5 %), 90.1 (CrF_2^+ , 3 %), 70.8 (CrF^+ , 18 %), 52.0 (Cr^+ , 13 %).

6.2.10. Synthesis of Bis[η^5 -(trimethylsilyl)cyclopentadienyl]difluorotitanium (32)

In a Schlenk flask equipped with a reflux condenser, dichlorobis[η^5 -(trimethylsilyl)cyclopentadienyl]titanium (500 mg, 1.27 mmol) and trimethyltin fluoride (500 mg, 2.74 mmol, 2.2 eq) were refluxed in acetonitrile (40 mL) for seven hours. After removal of the solvent *in vacuo*, the residue was sublimed at 85 °C and 10^{-3} mbar. Recrystallization of the sublimate from toluene gave **32** as a yellow powder. Yield: 89 %.

32: δ_{H} identical to the literature;²¹⁷ δ_{F} (CDCl_3): 74.4 (2 F, s, TiF₂).

6.2.11. Synthesis of Dimethylsilylene[bis(η^5 -cyclopentadienyldiene)]difluorotitanium (33)

In a Schlenk flask equipped with a reflux condenser, dichloro[dimethylsilylenebis(η^5 -cyclopentadienyldiene)]titanium (390 mg, 1.28 mmol) and trimethyltin fluoride (850 mg, 4.65 mmol, 3.6 eq) were refluxed in acetonitrile (40 mL) for seven hours. After removal of

the solvent *in vacuo*, the residue was sublimed at 110 °C and 10^{-3} mbar. Recrystallization of the sublimate from toluene gave **33** as yellow crystals. Yield: 52 %.

33: δ_{H} identical to the literature;²¹⁷ δ_{F} (CDCl_3): 68.8 (2 F, s, TiF_2).

6.2.12. Synthesis of Hexafluorocyclobutene (**55**)

A single-necked flask equipped with a J. Young PTFE valve was charged with diglyme (10 mL), 1,2-dichloro-1,2,3,3,4,4-hexafluorocyclobutane (477.4 mg, 2.05 mmol) and zinc dust (1.348 mg, 20.6 mmol, 10 eq), degassed and stirred overnight at room temperature. Fractional condensation of the reaction mixture *via* two subsequent traps kept at -78 °C and -196 °C, respectively, gave **55** in the second trap. Yield: 97 %.

55: δ_{F} identical to the literature.²¹⁸

6.2.13. Catalytic Hydrodefluorination of Fluoroalkenes and –allenes

Substrates, conditions and products are listed in table 6.2. A similar procedure was applied for all substrates: A single-necked flask equipped with a J. Young PTFE valve was charged with catalyst, silane and solvent (2.0 mL). After degassing, the solution was heated until the color changed from yellow to purple to green (no color change was observed when employing catalysts **36-38**). The substrate was then condensed onto the frozen solution, which was warmed to the desired temperature and stirred for a given period of time. Fractional condensation of the reaction mixture *via* two subsequent traps kept at -78 °C (-30 °C for the HDF of **55**) and -196 °C, respectively, gave the product mixture in the second trap, which was vacuum transferred to a J. Young NMR tube containing a standard solution of fluorobenzene (α,α,α -trifluorotoluene for the HDF of **49-51** and **55**) in chloroform- d_1 . The yields were determined from NMR spectra by integration of product resonances versus the internal standard.

Table 6.2. Titanium-catalyzed HDF of tetrafluoroallene (**1**); [a] 3 % tetramethylammonium fluoride added, [b] 2.2 % B(C₆F₅)₃ added; [c] under an H₂ atmosphere.

| substrate [mmol] | catalyst [mol %] | silane [mmol] | solvent [mL] | T [°C] | time [h] | TON | products |
|------------------|------------------|------------------|--------------|-----------------|----------|-----|-----------------------------------|
| 1 , 1.09 | 18 , 2.8 | 40 , 0.96 | thf, 3.0 | 65 | 3 | 2.1 | 5 : 5.8 %, 1 : 76 % |
| 1 , 1.05 | 18 , 2.5 | 40 , 1.10 | dme, 10.0 | 84 | 2 | 0.3 | 5 : 0.7 %, 1 : 60 % |
| 1 , 1.02 | 18 , 7.3 | 40 , 1.00 | toluene, 2.0 | rt | 14 | 0 | 1 : 84 % |
| 1 , 1.05 | 18 , 2.9 | 40 , 1.13 | toluene, 3.0 | rt ^a | 62 | 1.1 | 5 : 3.0 %, 1 : 73 % |
| 1 , 1.08 | 18 , 2.1 | 40 , 1.04 | diglyme, 2.0 | rt | 19 | 0.1 | 5 : 0.2 %, 1 : 81 % |
| 1 , 1.01 | 18 , 0.9 | 40 , 1.07 | diglyme, 2.0 | rt | 169 | 1.3 | 5 : 1.2 %, 1 : 56 % |
| 1 , 0.54 | 18 , 1.1 | 40 , 1.08 | diglyme, 2.0 | rt ^b | 16 | 2.7 | 5 : 3.1 %, 1 : 70 % |
| 1 , 1.32 | 18 , 0.8 | 40 , 1.07 | diglyme, 2.0 | rt ^c | 4 | 2.3 | 5 : 1.8 %, 1 : 50 % |
| 1 , 1.10 | 18 , 3.9 | 40 , 0.98 | diglyme, 2.0 | 65 | 3 | 2.2 | 5 : 8.5 %, 1 : 64 % |
| 1 , 0.50 | 18 , 4.2 | 40 , 1.02 | diglyme, 2.0 | -25 | 48 | 0.0 | 5 : 0.2 %, 1 : 70 % |

Table 6.3. Titanium-catalyzed HDF of fluoroalkenes; [a] formula units (HSiMeO), [b] reaction performed in an NMR tube, no workup done; [c] **28e**: E-1,2,3,3-tetrafluoropropene; [d] calculated per formula unit Cp₂Ti.

| substrate [mmol] | catalyst [mol %] | silane [mmol] | solvent [mL] | T [°C] | time [min] | TON | TOF [h ⁻¹] | E/Z | products |
|------------------|------------------|-------------------------------|---------------------------|--------|------------|-----|------------------------|-------|---|
| 26 , 1.06 | none | 40 , 1.07 | diglyme, 2.0 | rt | 3600 | 0.0 | 0.0 | | 26 : 91 % |
| 26 , 1.00 | 18 , 0.64 | 40 , 1.08 | diglyme, 2.0 | rt | 15 | 125 | 498 | 0.68 | 27a : 47 %, 27b : 32 %, 27c : 0.9 %, 28a : 1.1 %, 26 : 1.6 % |
| 26 , 0.98 | 18 , 0.61 | 39 , 1.11 | diglyme, 2.0 | rt | 15 | 23 | 90 | 0.68 | 27a : 8.2 %, 27b : 5.6 %, 26 : 61 % |
| 26 , 1.02 | 18 , 0.64 | 43 , 1.21 ^a | diglyme, 2.0 | rt | 15 | 22 | 88 | 0.68 | 27a : 8.3 %, 27b : 5.6 %, 27 : 60 % |
| 26 , 1.01 | 18 , 0.84 | 41 , 1.03 | diglyme, 2.0 | rt | 15 | 0.0 | 0.0 | | 26 : 87 % |
| 26 , 1.12 | 18 , 0.92 | 42 , 1.07 | diglyme, 2.0 | rt | 15 | 0.0 | 0.0 | | 26 : 89 % |
| 26 , 1.14 | 18 , 1.22 | 40 , 1.06 | diglyme, 2.0 | -25 | 75 | 6.3 | 5.0 | 0.68 | 27a : 4.5 %, 27b : 3.1 %, 26 : 51 % |
| 26 , 0.96 | 18 , 0.68 | 40 , 1.09 | toluene, 2.0 | rt | 15 | 0.3 | 1.2 | n. d. | 27a , 27b : traces, 26 : 76 % |
| 26 , 0.49 | 18 , 0.57 | 40 , 0.54 | diglyme, 0.5 ^b | rt | 3 | 79 | 1573 | 0.70 | 27a : 26 %, 27b : 18 %, 26 : 45 % |
| 26 , 1.06 | 18 , 1.66 | 40 , 2.11 | diglyme, 2.0 | rt | 1380 | 44 | 1.9 | 0.61 | 27a : 45 %, 27b : 28 %, 28a : 4.7 %, 28b : 1.7 %, 28e : 0.8 % ^c |
| 26 , 1.13 | 31 , 1.68 | 40 , 1.06 | diglyme, 2.0 | rt | 30 | 12 | 24 | 0.78 | 27a : 11 %, 27b : 9 %, 26 : 66 % |
| 26 , 1.03 | 32 , 1.40 | 40 , 0.53 | diglyme, 2.0 | rt | 300 | 0.6 | 0.11 | 0.80 | 27a : 0.43 %, 27b : 0.34 %, 26 : 87 % |
| 26 , 1.01 | 33 , 0.94 | 40 , 1.09 | diglyme, 2.0 | rt | 1170 | 8.4 | 0.43 | 1.07 | 27a : 4.1 %, 27b : 3.8 %, 26 : 85 % |
| 26 , 1.02 | 37 , 15.8 | 40 , 1.06 | diglyme, 2.0 | rt | 60 | 0.0 | 0.0 | | 26 : 87 % |
| 26 , 1.02 | 36 , 14.6 | 40 , 1.09 | diglyme, 2.0 | rt | 1020 | 0.0 | 0.0 | | 26 : 92 % |

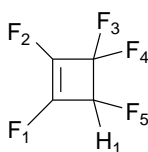
| | | | | | | | | | |
|----------|----------|----------|--------------|----|------|-----------------|-----------------|------|---|
| 26, 1.03 | 63, 1.31 | 39, 1.20 | diglyme, 2.0 | rt | 15 | 21 ^d | 86 ^d | 0.70 | 27a: 15 %, 27b: 11 %, 26: 57 % |
| 26, 1.21 | 21, 2.01 | 39, 1.10 | diglyme, 2.0 | rt | 15 | 19 ^d | 76 ^d | 0.70 | 27a: 22 %, 27b: 16 %, 26: 48 % |
| 26,1.16 | 34, 0.85 | 40, 1.36 | diglyme, 2.0 | rt | 1440 | 38 | 1.6 | 0.79 | 27a: 17 %, 27b: 13 %, 27c: 2.0 %, 26: 47 % |
| 26,0.90 | 29, 1.42 | 40, 1.09 | diglyme, 2.0 | rt | 15 | 27 | 498 | 0.68 | 27a: 23 %, 27b: 16 %, 27c: 2.8 %, 26: 32 % |
| 26,0.94 | 30, 0.64 | 40, 1.09 | diglyme, 2.0 | rt | 40 | 1.7 | 3.0 | 1.00 | 27a: 2 %, 27b: 2 %, 27c: trace, 26: 65 % |
| 26,1.13 | 38, 1.75 | 40, 1.20 | diglyme, 2.0 | rt | 1350 | 0.2 | 0.01 | 1.0 | 27a, 27b: traces, 26: 71 % |
| 29,1.05 | 18, 1.23 | 40, 1.11 | diglyme, 2.0 | rt | 60 | 42 | 0.69 | 0.07 | 28b: 46 %, 28c: 3.0 %, 28d: 1.9 %, 29: 46 % |
| 29,1.05 | 18, 0.62 | 40, 1.08 | diglyme, 2.0 | rt | 15 | 42 | 201 | 0.08 | 28b: 28 %, 28c: 2.1 %, 28d: 0.9 %, 29: 69 % |
| 44,1.05 | 18, 1.55 | 40, 1.07 | diglyme, 2.0 | rt | 1130 | 43 | 2.28 | 0.71 | 45: 39 %, 46a: 0.9 %, 46b: 0.6 %, 47: 25 %, 48: trace, 44: 7.1 % |
| 44,1.17 | 18, 3.85 | 40, 1.53 | diglyme, 2.0 | rt | 3820 | 17 | 0.26 | 0.70 | 45: 37 %, 46a: 1.6 %, 46b: 1.1 %, 47: 22 %, 48: 3.5 % |
| 44,1.12 | 18, 4.15 | 40, 2.12 | diglyme, 2.0 | 0 | 3128 | 14 | 0.27 | 0.38 | 45: 29 %, 46a: 1.7 %, 46b: 0.6 %, 47: 24 %, 48: trace |
| 49,0.98 | 18, 1.32 | 40, 1.18 | diglyme, 2.0 | rt | 180 | 0 | 0 | | 49: 86 % |
| 50,1.00 | 18, 7.35 | 40, 1.01 | diglyme, 2.0 | rt | 1103 | 4.2 | 0.23 | 0.36 | 51a: 0.2 %, 51b: 3.0 %, 51c: 1.1 %, 52: 2.2 %, 53: trace, 54: 7.4 %, 50: 55 % |
| 51a,1.00 | 18, 6.52 | 40, 1.03 | diglyme, 2.0 | rt | 7 d | 3.4 | 0.02 | | 52: 8.4 %, 53: trace, 54: 6.5 %, 51a: 51 % |
| 55,1.02 | 18, 4.66 | 40, 0.61 | diglyme, 2.0 | rt | 4147 | 19 | 0.28 | | 56a: 71 %, 56b: 3.3, 57a: 5.9 %, 57b: 1.1 %, 55: 9.0 % |
| 55,1.02 | 18, 5.19 | 40, 1.23 | diglyme, 2.0 | rt | 4303 | 32 | 0.44 | | 56b: 6.8 %, 57a: 56 %, 57b: 10 %, 58: 8.2 % |
| 55,1.02 | 18, 4.42 | 40, 2.14 | diglyme, 2.0 | rt | 4304 | 36 | 0.50 | | 57a: 16 %, 57b: 6.6, 58: 38 %, 59: trace |

HDF products were identified by NMR spectroscopy, using literature data for **27a**,²¹⁹ **27b**,²¹⁹ **28a**,²²⁰ **28b**,²²⁰ **28c**,²²⁰ **28e**,²²¹ **45**,²²² **46a**,²²² **46b**,²²² **47**,²²¹ **51b**,²²³ **51c**,²²³ **52**,²²³ **55**,²¹⁸ **56a**,²²⁴ **57a**,²²⁴ **58**,²²⁴ and **59**,²²⁵ or by comparison with authentic samples of **26**, **29**, **49**, **50**, **51a**, **53**, **60**.

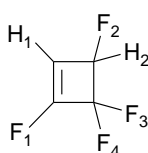
27c: δ_{H} (CDCl₃): 6.37 (1 H, dddt, ³J_{HF} = 14.9 Hz, ⁴J_{HF} = 2.7 Hz, ⁴J_{HF} = 1.3 Hz, ²J_{HF} = 51.1 Hz, =CF₂H); δ_{F} (CDCl₃): -93.7 (1 F, dddt, ²J_{FF} = 63.5 Hz, ³J_{FF} = 34.9 Hz, ⁴J_{FH} = 1.3 Hz, ⁴J_{FF} = 12.2 Hz, =CF₂), -113.8 (1 F, dddt, ³J_{FF} = 118.1 Hz, ²J_{FF} = 63.5 Hz, ⁴J_{FH} = 2.8 Hz, ⁴J_{FF} = 4.8 Hz, =CF₂), -123.0 (2 F,

dddd, $^2J_{FH} = 51.0$ Hz, $^3J_{FF} = 17.7$ Hz, $^4J_{FF} = 12.2$ Hz, $^4J_{FF} = 4.8$ Hz, CF₂H), -196.5 (1 F, dddd, $^3J_{FF} = 118.2$ Hz, $^3J_{FF} = 34.9$ Hz, $^3J_{FF} = 17.6$ Hz, $^4J_{FH} = 14.8$ Hz, -CF=).

28d: δ_H (CDCl₃): 4.69 (1 H, dq br, $^3J_{HF} = 23.1$ Hz, $^3J_{HF} = 7$ Hz, $^3J_{HH} = 7$ Hz, $^4J_{FH} = 0.9$ Hz, -CH=), 6.46 (1 H, dtt, $^2J_{FH} = 54.5$ Hz, $^3J_{HH} = 7.3$ Hz, CF₂H); δ_F (CDCl₃): -78.7 (1 F, ddt, $^2J_{FF} = 22.0$ Hz, $^4J_{FF} = 0.8$ Hz, $^4J_{FF} = 14.3$ Hz, $^2J_{FF} = 22$ Hz, =CF₂), -79.5 (1 F, dddd, $^2J_{FF} = 22.0$ Hz, $^3J_{FH} = 23.0$ Hz, $^4J_{FF} = 3.7$ Hz, $^4J_{FH} = 0.9$ Hz, =CF₂), -108.6 (2 F, dddd, $^2J_{FH} = 54.5$ Hz, $^4J_{FF} = 14.3$ Hz, $^3J_{FH} = 7.0$ Hz, $^4J_{FF} = 3.7$ Hz, CF₂H)

**56b**

56b: δ_F (CDCl₃): -113.1 (1 F, ddddd, $^2J_{F3F4} = 198.8$ Hz, $^4J_{F3F1} = 20.2$ Hz, $^3J_{F3F5} = 17.5$ Hz, $^3J_{F3F2} = 1.8$ Hz, $^3J_{F3H1} = 1.4$ Hz, F₃), -119.6 (1 F, dddd, $^2J_{F4F3} = 198.8$ Hz, $^4J_{F4F1} = 17.5$ Hz, $^3J_{F4F5} = 15.3$ Hz, $^3J_{F4F2} = 10.8$ Hz, F₄), -122.5 (1 F, ddddd, $^4J_{F1F3} = 20.2$ Hz, $^4J_{F1F4} = 17.5$ Hz, $^3J_{F1F2} = 10.8$ Hz, $^3J_{F1H1} = 4.1$ Hz, $^3J_{F1F5} = 2.3$ Hz, F₁), -127.4 (1 F, dtt, $^4J_{F2H1} = 17.5$ Hz, $^3J_{F2F1} = 10.8$ Hz, $^3J_{F2F3} = 1.8$ Hz, F₂), -187.1 (1 F, ddddd, $^2J_{F5H1} = 63.4$ Hz, $^3J_{F5F3} = 17.5$ Hz, $^3J_{F5F4} = 15.3$ Hz, $^3J_{F5F1} = 2.3$ Hz, $^4J_{F5F2} = 1.8$ Hz, F₅); δ_H (CDCl₃): 5.44 (1 H, dddd, $^2J_{H1F5} = 63.6$ Hz, $^4J_{H1F2} = 17.4$ Hz, $^3J_{H1F1} = 4.8$ Hz, $^3J_{H1F3} = 1.4$ Hz, H₁). Supported by ¹⁹F COSY.

**57b**

57b: δ_F (CDCl₃): -102.1 (1 F, dddd, $^4J_{F1H2} = 18.9$ Hz, $^3J_{F1F4} = 8.5$ Hz, $^3J_{F1H1} = 7.7$ Hz, $^4J_{F1F2} = 5.0$ Hz, F₁), -111.0 (1 F, dddd, $^2J_{F3F4} = 205.6$ Hz, $^3J_{F3F2} = 18.0$ Hz, $^4J_{F3H1} = 11.7$ Hz, $^3J_{F3H2} = 1.8$ Hz, F₃), -119.6 (1 F, dddd, $^2J_{F4F3} = 205.6$ Hz, $^3J_{F4F2} = 14.8$ Hz, $^4J_{F4H1} = 8.7$ Hz, $^3J_{F4F1} = 8.5$ Hz, F₄), -182.8 (1 F, ddddd, $^2J_{F2H2} = 62.5$ Hz, $^3J_{F2F3} = 18.0$ Hz, $^3J_{F2F4} = 14.8$ Hz, $^4J_{F2F1} = 5.0$ Hz, $^3J_{F2H1} = 0.9$ Hz, F₂); δ_H (CDCl₃): 5.38 (1 H, dddd, $^2J_{H2F2} = 62.3$ Hz, $^4J_{H2F1} = 19.2$ Hz, $^3J_{H2F3} = 1.8$ Hz, $^3J_{H2H1} = 0.9$ Hz, H₂), 5.85 (1 H, ddddd, $^4J_{H1F3} = 11.9$ Hz, $^4J_{H1F4} = 8.7$ Hz, $^3J_{H1F1} = 7.8$ Hz, $^3J_{H1F2} = 0.9$ Hz, $^3J_{H1H2} = 0.9$ Hz, H₁); δ_C (CDCl₃): 87.3 (dddd, $^1J_{CF} = 226$ Hz, $^1J_{CH} = 186$ Hz, $^2J_{CF} = 30$ Hz, $^2J_{CF} = 26$ Hz, $^3J_{CF} = 21$ Hz, CHF), 116.8 (dddd, $^1J_{CH} = 191$ Hz, $^2J_{CF} = 24$ Hz, $^3J_{CF} = 19$ Hz, $^3J_{CF} = 12$ Hz, $^2J_{CF} = 4.3$ Hz, CH), 118.1 (ddd, $^1J_{CF} = 282$ Hz, $^1J_{CF} = 278$ Hz, $^2J_{CF} = 19$ Hz, $^3J_{CH}$ unresolved due to overlap with **57a**, CF₂), 153.3 (dtdd, $^1J_{CF} = 352$ Hz, $^2J_{CF} = 26$ Hz, $^3J_{CF} = 21$ Hz, $^3J_{CH} = 9$ Hz, CF).

6.2.14. Stoichiometric Hydrodefluorination of Hexafluoropropene with $[\text{Cp}_2\text{Ti}(\mu\text{-SiH}_2\text{Ph})(\mu\text{-H})\text{TiCp}_2]$ (**63**)

To a J. Young NMR tube containing **63** (20.2 mg, 48.5 μmol) were condensed thf- d_8 (0.5 mL) and **26** (14.0 mg, 93.3 μmol , 1.9 eq) at $-196\text{ }^\circ\text{C}$. The tube was warmed to $-90\text{ }^\circ\text{C}$, shaken and introduced to the pre-cooled NMR spectrometer. Several spectra were recorded while the probe was gradually warmed to room temperature. The relative amounts of starting material and HDF products were determined by integration of their ^{19}F resonances.

Start ($-78\text{ }^\circ\text{C}$): **26**: 95 %, **27a**: 3.4 %, **27b**: 4.6 %.

1 h ($-30\text{ }^\circ\text{C}$): **26**: 87 %, **27a**: 5.8 %, **27b**: 7.5 %.

2 h ($-10\text{ }^\circ\text{C}$): **26**: 73 %, **27a**: 13 %, **27b**: 13 %.

2.5 h ($+20\text{ }^\circ\text{C}$): **26**: 63 %, **27a**: 19 %, **27b**: 18 %.

19 h ($+20\text{ }^\circ\text{C}$): **26**: 0 %, **27a**: 51 %, **27b**: 38 %, **28a**: 11 %.

6.2.15. Isolation of $(\text{Cp}_2\text{TiF})_3 \times 5\text{ thf}$ from the Reaction of Hexafluoropropene with **63**

To a Schlenk tube containing **63** (approx. 20 mg, 130 μmol) were condensed thf (2 mL) and **26** (1 mmol, approx. 10 eq) at $-196\text{ }^\circ\text{C}$. The tube was slowly warmed to room temperature and stirred overnight; the mixture changed its color from purple to blue green to forest green. After concentration of the solution *in vacuo* to approximately half its volume, light green prisms of **21** separated upon overnight cooling to $-80\text{ }^\circ\text{C}$. The yield was not determined.

6.2.16. Stoichiometric Hydrodefluorination of Hexafluoropropene with $[\text{Cp}_2\text{Ti}(\mu\text{-H})]_2$ (**19**)

To a J. Young NMR tube containing **19** (5.2 mg, 15 μmol) were condensed thf- d_8 (0.5 mL) and **26** (4.2 mg, 28 μmol , 1.9 eq) at $-196\text{ }^\circ\text{C}$. The tube was warmed to $-80\text{ }^\circ\text{C}$, shaken and allowed to warm to room temperature within 10 minutes. NMR and EPR spectra were recorded, the relative amounts of starting material and HDF products were determined by integration of ^{19}F resonances.

10 min (rt): **26**: 0 %, **27a**: 56 %, **27b**: 31 %, **28a**: 12 %.

EPR: broad singlet at $g = 1.979(3)$, identical to literature data.¹⁹⁶

6.3. Crystallography

6.3.1. Crystal Structure of Trifluoroallene (**4**)

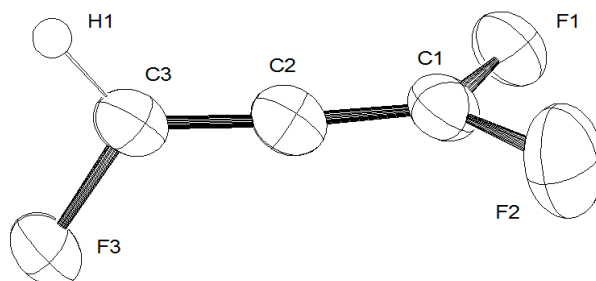


Figure 6.1. Molecular structure and numbering scheme for trifluoroallene (**4**), thermal ellipsoids drawn at a 50 % probability level.

Table 6.4. Experimental X-ray diffraction parameters and crystal data for **4**.

| | |
|---|--|
| Empirical formula | C ₃ HF ₃ |
| $M / \text{g mol}^{-1}$ | 94.04 |
| T / K | 123(2) |
| $\lambda / \text{\AA}$ | 0.71073 |
| Crystal system | Monoclinic |
| Space group | P2 ₁ /c |
| Lattice parameters | $a = 7.304(14) \text{\AA}$ $\alpha = 90^\circ$ $b = 8.271(16) \text{\AA}$ $\beta = 118.01(10)^\circ$ $c = 6.916(7) \text{\AA}$ $\gamma = 90^\circ$ |
| $V / \text{\AA}^3$ | 368.9(11) |
| Z | 4 |
| $D_{\text{calc}} / \text{g cm}^{-3}$ | 1.693 |
| μ / mm^{-1} | 0.206 |
| F(000) | 184 |
| No. reflns collected/independent | 1258 / 647 |
| R_{int} | 0.1018 |
| Absorption correction | Multi-scan |
| Data / restraints / parameters | 647 / 0 / 60 |
| Final R indices [$I > 2\sigma(I)$] | $R_1 = 0.0461$, $wR_2 = 0.127$ |
| R indices (all data) | $R_1 = 0.0541$, $wR_2 = 0.1346$ |
| Goodness-of-fit on F^2 | 1.056 |
| Largest diff. peak and hole / $e \text{\AA}^{-3}$ | 0.272 / -0.273 |

Table 6.5. Atomic coordinates and equivalent isotropic displacement factors for **4**.

| | x | y | z | $U_{\text{eq}} / \text{\AA}^2$ |
|----|-------------|-------------|-------------|--------------------------------|
| H1 | 0.826(3) | 0.827(3) | 0.834(3) | 0.042(6) |
| C1 | 0.3331(3) | 0.8736(3) | 0.6676(3) | 0.0366(6) |
| C2 | 0.5312(3) | 0.8755(3) | 0.7798(3) | 0.0388(6) |
| C3 | 0.7307(3) | 0.8713(3) | 0.8805(3) | 0.0409(7) |
| F1 | 0.21929(19) | 0.98544(18) | 0.5273(2) | 0.0501(6) |
| F2 | 0.2086(2) | 0.76271(18) | 0.6771(2) | 0.0635(6) |
| F3 | 0.84061(19) | 0.9353(2) | 1.08138(19) | 0.0536(6) |

Table 6.6. Anisotropic displacement factors in \AA^2 for **4**.

| | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} |
|----|------------|------------|------------|------------|------------|------------|
| C1 | 0.0383(12) | 0.0386(12) | 0.0296(11) | -0.0051(9) | 0.0133(9) | -0.0051(8) |
| C2 | 0.0406(13) | 0.0411(13) | 0.0310(11) | 0.0016(9) | 0.0136(10) | 0.0007(9) |
| C3 | 0.0383(13) | 0.0530(14) | 0.0278(11) | 0.0023(10) | 0.0126(9) | 0.0049(10) |
| F1 | 0.0410(8) | 0.0652(10) | 0.0321(8) | 0.0069(6) | 0.0072(6) | 0.0068(6) |
| F2 | 0.0482(9) | 0.0583(10) | 0.0719(11) | -0.0019(8) | 0.0181(8) | -0.0183(7) |
| F3 | 0.0362(8) | 0.0850(12) | 0.0296(8) | -0.0089(7) | 0.0070(6) | 0.0023(7) |

Table 6.7. Bond distances and angles for **4** in \AA and $^\circ$, respectively.

| | | | | | | |
|----|----|----------|----|----|----|-----------|
| C2 | C1 | 1.281(4) | C1 | C2 | C3 | 175.6(2) |
| C2 | C3 | 1.287(4) | C2 | C1 | F2 | 126.1(2) |
| C3 | H1 | 0.97(2) | C2 | C1 | F1 | 125.5(2) |
| F1 | C1 | 1.316(3) | F2 | C1 | F1 | 108.4(2) |
| F2 | C1 | 1.314(3) | C2 | C3 | F3 | 121.6(2) |
| F3 | C3 | 1.344(3) | C2 | C3 | H1 | 129.6(13) |
| | | | F3 | C3 | H1 | 108.8(13) |

6.3.2. Crystal Structure of 1,3-Difluoroallene (**7**)

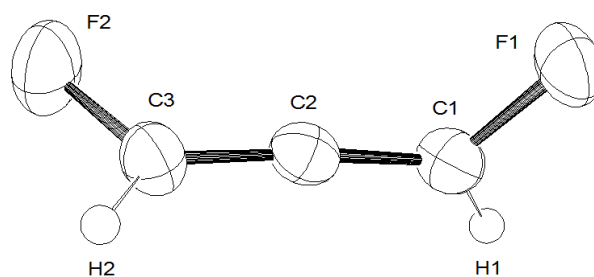
Figure 6.2. Molecular structure and numbering scheme for 1,3-difluoroallene (**7**), thermal ellipsoids drawn at a 50 % probability level.

Table 6.8. Experimental X-ray diffraction parameters and crystal data for **7**.

| | |
|---|--|
| Empirical formula | C ₃ H ₂ F ₂ |
| <i>M</i> / g mol ⁻¹ | 76.05 |
| <i>T</i> / K | 123(2) |
| λ / Å | 0.71073 |
| Crystal system | Monoclinic |
| Space group | P2 ₁ /c |
| Lattice parameters | <i>a</i> = 7.0297(14) Å α = 90 ° <i>b</i> = 6.7205(14) Å β = 114.399(4) ° <i>c</i> = 7.8245(16) Å γ = 90 ° |
| <i>V</i> / Å ³ | 336.64(12) |
| <i>Z</i> | 4 |
| <i>D</i> _{calc} / g cm ⁻³ | 1.50 |
| μ / mm ⁻¹ | 0.165 |
| F(000) | 152 |
| No. reflns collected/independent | 3861 / 684 |
| <i>R</i> _{int} | 0.0272 |
| Absorption correction | Multi-scan |
| Data / restraints / parameters | 684 / 0 / 55 |
| Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] | <i>R</i> ₁ = 0.0334, <i>wR</i> ₂ = 0.1028 |
| <i>R</i> indices (all data) | <i>R</i> ₁ = 0.0375, <i>wR</i> ₂ = 0.1056 |
| Goodness-of-fit on <i>F</i> ² | 1.271 |
| Largest diff. peak and hole / e Å ⁻³ | 0.181 / -0.190 |

Table 6.9. Atomic coordinates and equivalent isotropic displacement factors for **7**.

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> _{eq} / Å ² |
|----|--------------|-------------|-------------|---|
| F1 | -0.24237(13) | 0.16530(17) | 0.10712(14) | 0.0438(4) |
| F2 | 0.42588(16) | 0.06708(18) | 0.27485(17) | 0.0560(5) |
| C2 | 0.1061(2) | 0.2230(2) | 0.1803(2) | 0.0320(4) |
| C3 | 0.3022(2) | 0.2119(3) | 0.2916(2) | 0.0354(5) |
| C1 | -0.0883(3) | 0.2495(2) | 0.0707(2) | 0.0344(4) |
| H1 | -0.141(3) | 0.326(3) | -0.041(3) | 0.049(6) |
| H2 | 0.376(3) | 0.296(3) | 0.393(3) | 0.051(6) |

Table 6.10. Anisotropic displacement factors in \AA^2 for **7**.

| | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} |
|----|-----------|-----------|-----------|------------|-----------|------------|
| F1 | 0.0278(6) | 0.0571(8) | 0.0402(6) | 0.0045(5) | 0.0075(4) | -0.0058(4) |
| F2 | 0.0374(6) | 0.0595(8) | 0.0671(8) | -0.0140(6) | 0.0177(6) | 0.0100(5) |
| C2 | 0.0363(9) | 0.0297(8) | 0.0324(8) | -0.0039(6) | 0.0166(7) | -0.0045(6) |
| C3 | 0.0304(8) | 0.0380(9) | 0.0369(9) | -0.0062(7) | 0.0131(7) | -0.0030(7) |
| C1 | 0.0350(9) | 0.0352(9) | 0.0313(9) | 0.0008(7) | 0.0120(7) | -0.0033(7) |

Table 6.11. Bond distances and angles for **7** in \AA and $^\circ$, respectively.

| | | | | | | |
|----|----|------------|----|----|----|------------|
| F1 | C1 | 1.3524(19) | C1 | C2 | C3 | 175.40(17) |
| F2 | C3 | 1.347(2) | C2 | C3 | F2 | 121.85(15) |
| C2 | C1 | 1.291(2) | C2 | C3 | H2 | 126.7(13) |
| C2 | C3 | 1.293(2) | F2 | C3 | H2 | 111.4(13) |
| C3 | H2 | 0.94(2) | C2 | C1 | F1 | 121.50(16) |
| C1 | H1 | 0.95(2) | C2 | C1 | H1 | 126.3(12) |
| | | | F1 | C1 | H1 | 112.2(12) |

6.3.3. Crystal Structure of $(\eta^5\text{-Cyclopentadienyl})[\eta^1\text{-}(Z\text{-}1,3,3,3\text{-tetrafluoropropenyl})]\text{-tricarbonylchromium (25)}$

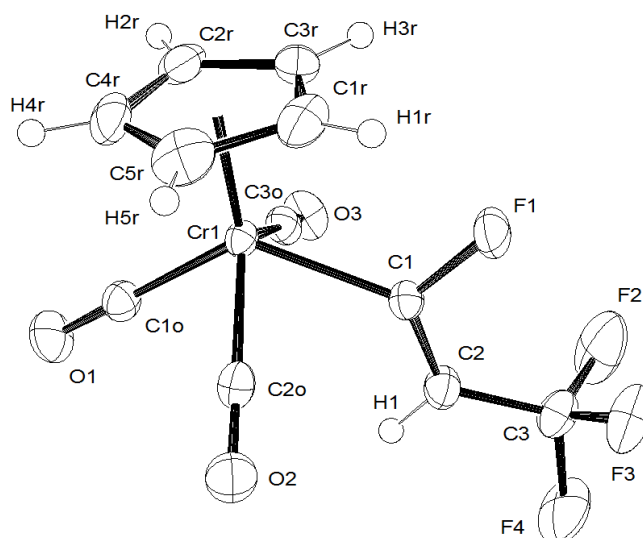


Figure 6.3. Molecular structure and numbering scheme for $(\eta^5\text{-cyclopentadienyl})[\eta^1\text{-}(Z\text{-}1,3,3,3\text{-tetrafluoropropenyl})]\text{-tricarbonylchromium (25)}$, thermal ellipsoids drawn at a 50 % probability level.

Table 6.12. Experimental X-ray diffraction parameters and crystal data for **25**.

| | |
|---|---|
| Empirical formula | $C_{11}H_6O_3F_4Cr_1$ |
| $M / g \text{ mol}^{-1}$ | 314.156 |
| T / K | 133(2) |
| $\lambda / \text{\AA}$ | 0.71073 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| Lattice parameters | $a = 7.8156(11) \text{\AA}$ $\alpha = 90^\circ$ $b = 14.074(2) \text{\AA}$ $\beta = 98.016(3)^\circ$ $c = 10.6116(15) \text{\AA}$ $\gamma = 90^\circ$ |
| $V / \text{\AA}^3$ | 1155.8(3) |
| Z | 4 |
| $D_{\text{calc}} / g \text{ cm}^{-3}$ | 1.805 |
| μ / mm^{-1} | 0.165 |
| F(000) | 624 |
| No. reflns collected/independent | 17965 / 3535 |
| R_{int} | 0.0254 |
| Absorption correction | Multi-scan |
| Data / restraints / parameters | 3535 / 0 / 172 |
| Final R indices [$I > 2\sigma(I)$] | $R_1 = 0.0285$, $wR_2 = 0.0706$ |
| R indices (all data) | $R_1 = 0.0359$, $wR_2 = 0.0706$ |
| Goodness-of-fit on F^2 | 1.046 |
| Largest diff. peak and hole / $e \text{\AA}^{-3}$ | 0.510 / -0.401 |

Table 6.13. Atomic coordinates and equivalent isotropic displacement factors in \AA^2 for **25**.

| | x | y | z | $U_{\text{eq}} / \text{\AA}^2$ |
|-----|--------------|--------------|-------------|--------------------------------|
| C1 | 0.45115(17) | 0.19019(10) | 0.39235(13) | 0.0214(2) |
| C1O | 0.46234(18) | 0.05260(10) | 0.25349(13) | 0.0250(3) |
| C1R | 0.2039(2) | 0.04239(14) | 0.45794(15) | 0.0369(4) |
| C2 | 0.58223(19) | 0.24025(11) | 0.35940(14) | 0.0279(3) |
| C2O | 0.21365(18) | 0.24005(11) | 0.24398(13) | 0.0240(3) |
| C2R | 0.1805(2) | -0.02607(12) | 0.35987(19) | 0.0397(4) |
| C3 | 0.7036(2) | 0.29850(12) | 0.44776(16) | 0.0314(3) |
| C3O | 0.22388(18) | 0.10642(10) | 0.10468(14) | 0.0250(3) |
| C3R | 0.0449(2) | 0.00544(13) | 0.26780(16) | 0.0357(4) |
| C4R | -0.01407(19) | 0.09271(13) | 0.30878(16) | 0.0335(3) |
| C5R | 0.0849(2) | 0.11609(13) | 0.42670(15) | 0.0333(3) |

| | | | | |
|-----|-------------|--------------|--------------|------------|
| Cr1 | 0.25551(3) | 0.111563(15) | 0.282052(19) | 0.01813(6) |
| F1 | 0.43770(14) | 0.19505(9) | 0.51970(9) | 0.0418(3) |
| F2 | 0.63413(18) | 0.37656(9) | 0.48834(16) | 0.0684(4) |
| F3 | 0.77542(14) | 0.25336(8) | 0.55268(11) | 0.0461(3) |
| F4 | 0.83743(17) | 0.32711(11) | 0.39082(13) | 0.0660(4) |
| H1R | 0.2864 | 0.0391 | 0.5326 | 0.044 |
| H2 | 0.5995 | 0.2386 | 0.2726 | 0.033 |
| H2R | 0.2447 | -0.0831 | 0.3565 | 0.048 |
| H3R | 0.0011 | -0.0268 | 0.1914 | 0.043 |
| H4R | -0.1050 | 0.1298 | 0.2649 | 0.040 |
| H5R | 0.0728 | 0.1716 | 0.4757 | 0.040 |
| O1 | 0.58547(15) | 0.01454(9) | 0.23691(12) | 0.0372(3) |
| O2 | 0.18290(17) | 0.31782(8) | 0.22139(11) | 0.0346(3) |
| O3 | 0.20354(17) | 0.10337(10) | -0.00396(11) | 0.0391(3) |

Table 6.14. Anisotropic displacement factors in \AA^2 for **25**.

| | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} |
|-----|-------------|-------------|-------------|------------|-------------|-------------|
| C1 | 0.0229(6) | 0.0225(6) | 0.0184(6) | 0.0000(5) | 0.0009(5) | -0.0005(5) |
| C1O | 0.0264(6) | 0.0235(6) | 0.0231(6) | -0.0007(5) | -0.0032(5) | -0.0007(5) |
| C1R | 0.0362(8) | 0.0478(10) | 0.0256(7) | 0.0145(7) | 0.0005(6) | -0.0173(7) |
| C2 | 0.0297(7) | 0.0307(7) | 0.0228(6) | -0.0017(5) | 0.0027(5) | -0.0090(6) |
| C2O | 0.0255(6) | 0.0278(7) | 0.0183(6) | -0.0001(5) | 0.0012(5) | 0.0027(5) |
| C2R | 0.0454(9) | 0.0265(8) | 0.0485(10) | 0.0122(7) | 0.0108(8) | -0.0085(7) |
| C3 | 0.0287(7) | 0.0281(7) | 0.0359(8) | -0.0004(6) | -0.0008(6) | -0.0076(6) |
| C3O | 0.0234(6) | 0.0271(7) | 0.0235(6) | 0.0005(5) | 0.0001(5) | 0.0007(5) |
| C3R | 0.0392(8) | 0.0377(9) | 0.0301(8) | -0.0027(6) | 0.0042(6) | -0.0214(7) |
| C4R | 0.0215(6) | 0.0468(9) | 0.0320(8) | 0.0024(7) | 0.0032(6) | -0.0087(6) |
| C5R | 0.0317(7) | 0.0438(9) | 0.0264(7) | -0.0031(6) | 0.0115(6) | -0.0125(7) |
| Cr1 | 0.01844(10) | 0.01914(11) | 0.01611(10) | 0.00130(7) | -0.00003(7) | -0.00170(7) |
| F1 | 0.0427(5) | 0.0635(7) | 0.0195(4) | -0.0071(4) | 0.0055(4) | -0.0251(5) |
| F2 | 0.0580(8) | 0.0387(6) | 0.0993(12) | -0.0328(7) | -0.0215(7) | 0.0067(5) |
| F3 | 0.0470(6) | 0.0423(6) | 0.0427(6) | 0.0058(5) | -0.0162(5) | -0.0135(5) |
| F4 | 0.0539(7) | 0.0909(11) | 0.0526(7) | 0.0040(7) | 0.0050(6) | -0.0485(7) |
| O1 | 0.0298(5) | 0.0379(6) | 0.0424(7) | -0.0058(5) | -0.0005(5) | 0.0100(5) |
| O2 | 0.0463(7) | 0.0261(6) | 0.0305(6) | 0.0030(4) | 0.0026(5) | 0.0099(5) |
| O3 | 0.0440(7) | 0.0508(8) | 0.0207(5) | -0.0011(5) | -0.0019(5) | 0.0013(6) |

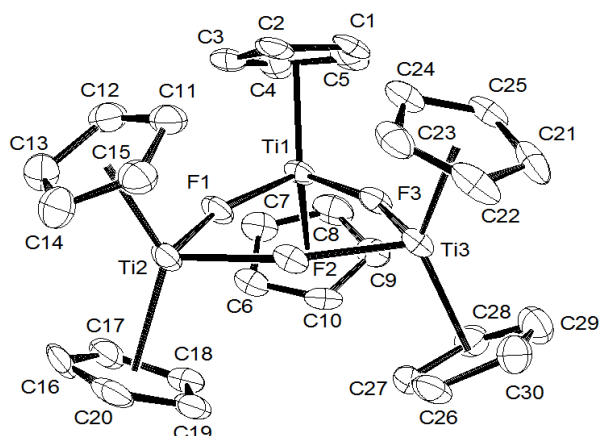
Table 6.15. Bond distances in \AA for **25**.

| | | | | | |
|-----|-----|------------|----|----|------------|
| Cr1 | C3O | 1.8653(15) | C3 | F2 | 1.324(2) |
| Cr1 | C2O | 1.8717(15) | C3 | F3 | 1.3356(19) |

| | | | | | |
|-----|-----|------------|-----|-----|------------|
| Cr1 | C1O | 1.8788(15) | C3 | F4 | 1.340(2) |
| Cr1 | C1 | 2.1055(13) | C1O | O1 | 1.1364(18) |
| Cr1 | C5R | 2.1702(15) | C2O | O2 | 1.1390(18) |
| Cr1 | C4R | 2.1810(15) | C3O | O3 | 1.1423(19) |
| Cr1 | C1R | 2.1919(15) | C1R | C5R | 1.402(3) |
| Cr1 | C3R | 2.2122(15) | C1R | C2R | 1.411(3) |
| Cr1 | C2R | 2.2164(16) | C2R | C3R | 1.409(3) |
| C1 | C2 | 1.330(2) | C3R | C4R | 1.402(3) |
| C1 | F1 | 1.3717(16) | C4R | C5R | 1.415(2) |
| C2 | C3 | 1.484(2) | | | |

Table 6.16. Bond angles in ° for **25**.

| | | | | | | | |
|-----|-----|-----|-----------|-----|-----|-----|------------|
| C3O | Cr1 | C2O | 79.93(6) | C5R | Cr1 | C2R | 62.72(7) |
| C3O | Cr1 | C1O | 79.40(6) | C4R | Cr1 | C2R | 62.27(7) |
| C2O | Cr1 | C1O | 121.35(6) | C1R | Cr1 | C2R | 37.34(7) |
| C3O | Cr1 | C1 | 124.41(6) | C3R | Cr1 | C2R | 37.11(7) |
| C2O | Cr1 | C1 | 72.77(6) | C2 | C1 | F1 | 113.60(12) |
| C1O | Cr1 | C1 | 75.37(6) | C2 | C1 | Cr1 | 131.20(11) |
| C3O | Cr1 | C5R | 134.98(6) | F1 | C1 | Cr1 | 115.12(9) |
| C2O | Cr1 | C5R | 91.04(7) | C1 | C2 | C3 | 125.07(14) |
| C1O | Cr1 | C5R | 138.98(7) | F2 | C3 | F3 | 105.50(15) |
| C1 | Cr1 | C5R | 93.54(6) | F2 | C3 | F4 | 106.18(15) |
| C3O | Cr1 | C4R | 97.59(6) | F3 | C3 | F4 | 104.79(14) |
| C2O | Cr1 | C4R | 90.15(7) | F2 | C3 | C2 | 114.11(14) |
| C1O | Cr1 | C4R | 146.69(7) | F3 | C3 | C2 | 114.90(13) |
| C1 | Cr1 | C4R | 129.16(6) | F4 | C3 | C2 | 110.57(14) |
| C5R | Cr1 | C4R | 37.95(6) | O1 | C1O | Cr1 | 178.07(14) |
| C3O | Cr1 | C1R | 145.87(7) | O2 | C2O | Cr1 | 177.85(14) |
| C2O | Cr1 | C1R | 124.44(7) | O3 | C3O | Cr1 | 179.61(14) |
| C1O | Cr1 | C1R | 101.88(7) | C5R | C1R | C2R | 108.51(15) |
| C1 | Cr1 | C1R | 88.04(6) | C5R | C1R | Cr1 | 70.42(9) |
| C5R | Cr1 | C1R | 37.49(7) | C2R | C1R | Cr1 | 72.28(9) |
| C4R | Cr1 | C1R | 62.57(6) | C3R | C2R | C1R | 107.69(16) |
| C3O | Cr1 | C3R | 84.96(6) | C3R | C2R | Cr1 | 71.28(9) |
| C2O | Cr1 | C3R | 122.11(7) | C1R | C2R | Cr1 | 70.39(9) |
| C1O | Cr1 | C3R | 109.85(7) | C4R | C3R | C2R | 107.97(15) |
| C1 | Cr1 | C3R | 150.30(6) | C4R | C3R | Cr1 | 70.18(9) |
| C5R | Cr1 | C3R | 62.83(6) | C2R | C3R | Cr1 | 71.61(9) |
| C4R | Cr1 | C3R | 37.22(7) | C3R | C4R | C5R | 108.38(16) |
| C1R | Cr1 | C3R | 62.27(6) | C3R | C4R | Cr1 | 72.60(9) |
| C3O | Cr1 | C2R | 109.71(7) | C5R | C4R | Cr1 | 70.61(9) |
| C2O | Cr1 | C2R | 151.33(7) | C1R | C5R | C4R | 107.45(16) |
| C1O | Cr1 | C2R | 87.26(7) | C1R | C5R | Cr1 | 72.10(9) |
| C1 | Cr1 | C2R | 117.48(6) | C4R | C5R | Cr1 | 71.44(9) |

6.3.4. Crystal Structure of Tris[bis(η^5 -cyclopentadienyl)- μ_2 -fluoro)titanium] (**21**)

Scheme 6.3. Molecular structure and numbering scheme for tris[bis(η^5 -cyclopentadienyl)- μ_2 -fluoro)titanium] (**21**); thermal ellipsoids are drawn at a 50 % probability level, hydrogen atoms and solvent molecules omitted for clarity.

Table 6.17. Experimental X-ray diffraction parameters and crystal data for **21**.

| | |
|---|---|
| Empirical formula | $C_{50}H_{70}F_3Ti_3O_5$ |
| $M / g mol^{-1}$ | 951.76 |
| T / K | 133(2) |
| $\lambda / \text{\AA}$ | 0.71073 |
| Crystal system | Orthorhombic |
| Space group | $P2_12_12_1$ |
| Lattice parameters | $a = 16.3896(78) \text{\AA}$ $\alpha = 90^\circ$ $b = 16.8366(74) \text{\AA}$ $\beta = 90^\circ$ $c = 17.2044(77) \text{\AA}$ $\gamma = 90^\circ$ |
| $V / \text{\AA}^3$ | 4747.47(37) |
| Z | 4 |
| $D_{\text{calc}} / g cm^{-3}$ | 1.332 |
| μ / mm^{-1} | 0.549 |
| F(000) | 2012 |
| No. reflns collected/independent | 49085 / 8618 |
| R_{int} | 0.1022 |
| Absorption correction | Multi-scan |
| Data / restraints / parameters | 8618 / 0 / 550 |
| Final R indices [$I > 2\sigma(I)$] | $R_1 = 0.0713$, $wR_2 = 0.1849$ |
| R indices (all data) | $R_1 = 0.0970$, $wR_2 = 0.2140$ |
| Goodness-of-fit on F^2 | 1.088 |
| Largest diff. peak and hole / $e \text{\AA}^{-3}$ | 1.279 / -0.750 |

Table 6.18. Atomic coordinates and equivalent isotropic displacement factors for **21**.

| | x | y | z | $U_{\text{eq}} / \text{\AA}^2$ |
|------|------------|------------|-----------|--------------------------------|
| C1 | 0.4929(4) | 0.2747(4) | 0.9038(4) | 0.0372(16) |
| C10 | 0.3514(4) | 0.4738(4) | 1.0295(4) | 0.0318(14) |
| C10L | 0.5791(4) | 0.4097(4) | 0.5899(4) | 0.0420(16) |
| C11 | 0.6553(4) | 0.4987(4) | 0.8243(4) | 0.0376(16) |
| C11L | 0.6616(4) | 0.3753(4) | 0.6146(5) | 0.0439(17) |
| C12 | 0.5934(4) | 0.5151(4) | 0.7704(4) | 0.0358(15) |
| C12L | 0.7070(5) | 0.3644(5) | 0.5380(5) | 0.051(2) |
| C13 | 0.5962(4) | 0.5972(4) | 0.7543(4) | 0.0382(15) |
| C13L | 0.3652(6) | 0.6598(6) | 0.2523(6) | 0.064(2) |
| C14 | 0.6625(4) | 0.6296(5) | 0.7956(4) | 0.0378(16) |
| C14L | 0.3076(6) | 0.6112(5) | 0.2064(6) | 0.060(2) |
| C15 | 0.6988(4) | 0.5707(4) | 0.8403(4) | 0.0356(15) |
| C15L | 0.2818(6) | 0.6591(6) | 0.1396(6) | 0.073(3) |
| C16 | 0.5225(5) | 0.7192(4) | 0.8686(4) | 0.0412(17) |
| C16L | 0.3423(9) | 0.7327(5) | 0.1458(6) | 0.085(4) |
| C17 | 0.4546(4) | 0.6762(4) | 0.8929(4) | 0.0354(15) |
| C17L | 0.1979(7) | 0.7093(6) | 0.8243(6) | 0.076(3) |
| C18 | 0.4683(4) | 0.6533(4) | 0.9708(4) | 0.0314(14) |
| C18L | 0.1371(10) | 0.6603(12) | 0.7832(9) | 0.145(8) |
| C19 | 0.5448(4) | 0.6830(4) | 0.9937(4) | 0.0325(14) |
| C19L | 0.1057(10) | 0.6068(11) | 0.8438(7) | 0.131(7) |
| C1L | 0.9900(8) | 0.4120(5) | 0.9279(9) | 0.106(5) |
| C2 | 0.5072(5) | 0.3304(4) | 0.8448(4) | 0.0380(16) |
| C20 | 0.5783(4) | 0.7229(3) | 0.9289(4) | 0.0388(15) |
| C20L | 0.1460(6) | 0.6243(6) | 0.9131(6) | 0.065(2) |
| C21 | 0.7124(4) | 0.3431(4) | 1.1144(5) | 0.0390(16) |
| C22 | 0.7579(4) | 0.4078(4) | 1.0832(5) | 0.0427(18) |
| C23 | 0.7387(4) | 0.4125(4) | 1.0040(4) | 0.0372(15) |
| C24 | 0.6819(4) | 0.3529(4) | 0.9855(4) | 0.0364(15) |
| C25 | 0.6652(4) | 0.3106(4) | 1.0554(4) | 0.0350(15) |
| C26 | 0.6151(4) | 0.5483(4) | 1.1626(4) | 0.0342(14) |
| C27 | 0.5331(4) | 0.5346(4) | 1.1428(4) | 0.0302(14) |
| C28 | 0.5110(4) | 0.4589(4) | 1.1722(4) | 0.0323(14) |
| C29 | 0.5775(4) | 0.4269(4) | 1.2092(4) | 0.0400(16) |
| C2L | 0.9266(6) | 0.4197(5) | 0.8749(8) | 0.086(4) |
| C3 | 0.4327(5) | 0.3460(4) | 0.8062(4) | 0.0375(15) |
| C30 | 0.6429(4) | 0.4817(4) | 1.2036(4) | 0.0390(16) |
| C3L | 0.8939(6) | 0.3360(5) | 0.8628(6) | 0.060(2) |
| C4 | 0.3724(5) | 0.2991(4) | 0.8418(4) | 0.0385(16) |
| C4L | 0.9673(5) | 0.2847(5) | 0.8788(5) | 0.052(2) |
| C5 | 0.4103(5) | 0.2563(4) | 0.9027(4) | 0.0410(17) |
| C5L | 0.6403(6) | 0.0492(5) | 0.7736(5) | 0.053(2) |

| | | | | |
|------|-----------|-------------|-----------|------------|
| C6 | 0.3175(4) | 0.4977(4) | 0.9577(4) | 0.0359(15) |
| C6L | 0.6353(5) | 0.1244(5) | 0.8241(5) | 0.053(2) |
| C7 | 0.2765(4) | 0.4320(4) | 0.9261(4) | 0.0388(15) |
| C7L | 0.5985(5) | 0.0940(5) | 0.8991(5) | 0.0511(19) |
| C8 | 0.2839(4) | 0.3680(4) | 0.9794(5) | 0.0422(17) |
| C8L | 0.6281(5) | 0.0074(5) | 0.8997(5) | 0.0495(19) |
| C9 | 0.3307(4) | 0.3941(4) | 1.0426(4) | 0.0350(15) |
| C9L | 0.5750(4) | 0.3875(4) | 0.5056(5) | 0.0452(17) |
| F1 | 0.4793(2) | 0.49621(19) | 0.8955(2) | 0.0307(8) |
| F2 | 0.6084(2) | 0.52525(19) | 0.9877(2) | 0.0285(7) |
| F3 | 0.5114(2) | 0.39995(19) | 1.0159(2) | 0.0285(7) |
| H1 | 0.5325 | 0.2534 | 0.9383 | 0.045 |
| H10 | 0.3829 | 0.5062 | 10.632 | 0.038 |
| H10A | 0.5338 | 0.3854 | 0.6196 | 0.05 |
| H10B | 0.5776 | 0.468 | 0.5968 | 0.05 |
| H11 | 0.6665 | 0.4483 | 0.8466 | 0.045 |
| H11A | 0.691 | 0.4124 | 0.6493 | 0.053 |
| H11B | 0.6546 | 0.3238 | 0.6417 | 0.053 |
| H12 | 0.5563 | 0.4778 | 0.7487 | 0.043 |
| H12A | 0.7598 | 0.3929 | 0.5396 | 0.061 |
| H12B | 0.7179 | 0.3074 | 0.5286 | 0.061 |
| H13 | 0.5599 | 0.6256 | 0.7214 | 0.046 |
| H13A | 0.3524 | 0.6558 | 0.3084 | 0.076 |
| H13B | 0.4219 | 0.6413 | 0.2439 | 0.076 |
| H14 | 0.6797 | 0.6835 | 0.7933 | 0.045 |
| H14A | 0.3346 | 0.5619 | 0.1885 | 0.072 |
| H14B | 0.2598 | 0.5966 | 0.2385 | 0.072 |
| H15 | 0.7436 | 0.5769 | 0.8748 | 0.043 |
| H15A | 0.2242 | 0.6759 | 0.1444 | 0.087 |
| H15B | 0.2893 | 0.63 | 0.0901 | 0.087 |
| H16 | 0.5294 | 0.7424 | 0.8187 | 0.049 |
| H16A | 0.3938 | 0.7224 | 0.1175 | 0.102 |
| H16B | 0.3169 | 0.7816 | 0.1248 | 0.102 |
| H17 | 0.4077 | 0.6643 | 0.8627 | 0.042 |
| H17A | 0.2471 | 0.7165 | 0.7917 | 0.091 |
| H17B | 0.1749 | 0.7622 | 0.8365 | 0.091 |
| H18 | 0.4321 | 0.6232 | 10.023 | 0.038 |
| H18A | 0.0928 | 0.6937 | 0.7615 | 0.174 |
| H18B | 0.1628 | 0.6299 | 0.7405 | 0.174 |
| H19 | 0.5694 | 0.6773 | 10.434 | 0.039 |
| H19A | 0.0462 | 0.6145 | 0.8502 | 0.158 |
| H19B | 0.1156 | 0.5508 | 0.829 | 0.158 |
| H111 | 0.9695 | 0.4216 | 0.9812 | 0.127 |
| H112 | 1.033 | 0.4516 | 0.9165 | 0.127 |
| H2 | 0.5584 | 0.3538 | 0.8328 | 0.046 |
| H20 | 0.6302 | 0.7479 | 0.9271 | 0.047 |
| H20A | 0.1611 | 0.5747 | 0.9405 | 0.078 |

| | | | | |
|------|------------|------------|------------|------------|
| H20B | 0.1103 | 0.6561 | 0.9476 | 0.078 |
| H21 | 0.7141 | 0.3253 | 11.668 | 0.047 |
| H22 | 0.7944 | 0.4414 | 11.108 | 0.051 |
| H23 | 0.7607 | 0.45 | 0.9684 | 0.045 |
| H24 | 0.6589 | 0.3427 | 0.9357 | 0.044 |
| H25 | 0.6281 | 0.2676 | 10.608 | 0.042 |
| H26 | 0.646 | 0.5943 | 11.503 | 0.041 |
| H27 | 0.4986 | 0.5698 | 11.148 | 0.036 |
| H28 | 0.459 | 0.4345 | 11.671 | 0.039 |
| H29 | 0.5794 | 0.3767 | 12.343 | 0.048 |
| H2L1 | 0.9468 | 0.4421 | 0.8253 | 0.104 |
| H2L2 | 0.8835 | 0.455 | 0.8957 | 0.104 |
| H3 | 0.4248 | 0.3816 | 0.764 | 0.045 |
| H30 | 0.6962 | 0.4745 | 12.241 | 0.047 |
| H3L1 | 0.849 | 0.3242 | 0.8996 | 0.073 |
| H3L2 | 0.874 | 0.3286 | 0.809 | 0.073 |
| H4 | 0.3164 | 0.2966 | 0.8276 | 0.046 |
| H4L1 | 0.9514 | 0.2372 | 0.9092 | 0.062 |
| H4L2 | 0.9925 | 0.267 | 0.8295 | 0.062 |
| H5 | 0.3836 | 0.2208 | 0.9373 | 0.049 |
| H5L1 | 0.6013 | 0.0529 | 0.7298 | 0.064 |
| H5L2 | 0.696 | 0.0431 | 0.7522 | 0.064 |
| H6 | 0.3217 | 0.5489 | 0.935 | 0.043 |
| H6L1 | 0.6901 | 0.1474 | 0.833 | 0.063 |
| H6L2 | 0.5998 | 0.165 | 0.7998 | 0.063 |
| H7 | 0.2487 | 0.4306 | 0.8777 | 0.047 |
| H7L1 | 0.5382 | 0.0972 | 0.8982 | 0.061 |
| H7L2 | 0.6194 | 0.1238 | 0.9446 | 0.061 |
| H8 | 0.2612 | 0.3165 | 0.9733 | 0.051 |
| H8L1 | 0.6855 | 0.0039 | 0.9174 | 0.059 |
| H8L2 | 0.5936 | -0.0257 | 0.9341 | 0.059 |
| H9 | 0.3457 | 0.3632 | 10.866 | 0.042 |
| H9L1 | 0.5555 | 0.3322 | 0.4993 | 0.054 |
| H9L2 | 0.5378 | 0.4235 | 0.4771 | 0.054 |
| O1 | 1.0232(4) | 0.3329(3) | 0.9223(4) | 0.0677(18) |
| O2 | 0.6207(4) | -0.0166(3) | 0.8215(3) | 0.0581(15) |
| O3 | 0.6571(3) | 0.3956(3) | 0.4780(3) | 0.0486(13) |
| O4 | 0.3563(6) | 0.7395(4) | 0.2265(4) | 0.085(2) |
| O5 | 0.2179(6) | 0.6686(6) | 0.8934(6) | 0.109(3) |
| Ti1 | 0.42009(6) | 0.39586(6) | 0.93445(7) | 0.0270(3) |
| Ti2 | 0.56528(6) | 0.58483(6) | 0.89134(6) | 0.0268(3) |
| Ti3 | 0.61383(6) | 0.44049(6) | 1.07338(7) | 0.0262(3) |

Table 6.19. Anisotropic displacement factors in Å² for **21**.

| | U ₁₁ | U ₂₂ | U ₃₃ | U ₂₃ | U ₁₃ | U ₁₂ |
|------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| C1 | 0.050(4) | 0.011(3) | 0.051(4) | -0.008(3) | 0.001(3) | 0.007(3) |
| C10 | 0.028(3) | 0.026(3) | 0.041(4) | -0.016(3) | 0.001(3) | 0.002(2) |
| C10L | 0.040(4) | 0.037(4) | 0.049(4) | 0.001(3) | 0.003(3) | -0.003(3) |
| C11 | 0.050(4) | 0.024(3) | 0.038(4) | -0.003(3) | 0.020(3) | 0.000(3) |
| C11L | 0.048(4) | 0.025(3) | 0.059(5) | 0.000(3) | -0.009(4) | -0.001(3) |
| C12 | 0.044(4) | 0.029(4) | 0.035(3) | -0.007(3) | 0.014(3) | -0.005(3) |
| C12L | 0.047(4) | 0.041(4) | 0.063(5) | -0.008(4) | -0.004(4) | 0.010(3) |
| C13 | 0.042(4) | 0.037(4) | 0.035(3) | 0.003(3) | 0.003(3) | 0.004(3) |
| C13L | 0.069(6) | 0.053(5) | 0.070(6) | -0.010(5) | 0.001(5) | 0.006(5) |
| C14 | 0.037(4) | 0.040(4) | 0.037(4) | 0.005(3) | 0.010(3) | -0.005(3) |
| C14L | 0.067(6) | 0.041(5) | 0.072(6) | -0.004(4) | 0.010(5) | 0.000(4) |
| C15 | 0.037(3) | 0.032(4) | 0.038(4) | -0.001(3) | 0.013(3) | 0.003(3) |
| C15L | 0.076(6) | 0.048(5) | 0.094(7) | -0.027(5) | -0.014(6) | 0.032(5) |
| C16 | 0.061(4) | 0.016(3) | 0.047(4) | 0.012(3) | 0.012(4) | 0.013(3) |
| C16L | 0.156(11) | 0.029(5) | 0.070(7) | 0.002(4) | 0.051(7) | 0.005(6) |
| C17 | 0.041(4) | 0.021(3) | 0.044(4) | -0.001(3) | -0.003(3) | 0.008(3) |
| C17L | 0.091(7) | 0.055(6) | 0.082(7) | 0.009(5) | -0.002(6) | -0.023(5) |
| C18 | 0.034(3) | 0.021(3) | 0.039(4) | -0.008(3) | 0.004(3) | 0.002(2) |
| C18L | 0.125(12) | 0.205(19) | 0.104(11) | 0.081(12) | -0.047(9) | -0.101(13) |
| C19 | 0.041(3) | 0.018(3) | 0.039(4) | -0.008(3) | -0.004(3) | 0.006(2) |
| C19L | 0.143(12) | 0.181(16) | 0.069(7) | 0.049(9) | -0.031(8) | -0.102(13) |
| C1L | 0.118(9) | 0.020(4) | 0.180(13) | -0.007(6) | -0.082(9) | 0.012(5) |
| C2 | 0.054(4) | 0.014(3) | 0.045(4) | -0.013(3) | 0.006(3) | 0.002(3) |
| C20 | 0.047(4) | 0.013(3) | 0.057(4) | -0.005(3) | 0.014(4) | -0.001(3) |
| C20L | 0.073(6) | 0.046(5) | 0.077(7) | 0.005(5) | 0.003(5) | -0.009(4) |
| C21 | 0.034(3) | 0.028(3) | 0.055(4) | 0.017(3) | 0.004(3) | 0.012(3) |
| C22 | 0.028(3) | 0.021(3) | 0.080(6) | 0.001(3) | -0.001(3) | 0.005(2) |
| C23 | 0.032(3) | 0.028(3) | 0.051(4) | 0.006(3) | 0.009(3) | 0.012(3) |
| C24 | 0.039(4) | 0.022(3) | 0.049(4) | -0.002(3) | 0.000(3) | 0.012(3) |
| C25 | 0.037(3) | 0.015(3) | 0.053(4) | 0.000(3) | 0.002(3) | 0.007(2) |
| C26 | 0.041(4) | 0.017(3) | 0.044(4) | -0.007(3) | -0.004(3) | 0.001(3) |
| C27 | 0.040(3) | 0.025(3) | 0.026(3) | 0.000(2) | 0.003(3) | 0.011(3) |
| C28 | 0.037(3) | 0.029(3) | 0.031(3) | -0.002(3) | 0.003(3) | -0.006(3) |
| C29 | 0.048(4) | 0.029(4) | 0.043(4) | 0.008(3) | 0.008(3) | 0.004(3) |
| C2L | 0.065(6) | 0.031(4) | 0.164(11) | -0.009(6) | -0.024(7) | 0.008(4) |
| C3 | 0.056(4) | 0.019(3) | 0.037(4) | -0.014(3) | -0.002(3) | 0.001(3) |
| C30 | 0.041(4) | 0.041(4) | 0.035(4) | -0.001(3) | -0.011(3) | 0.010(3) |
| C3L | 0.054(5) | 0.049(5) | 0.078(6) | -0.016(4) | -0.005(4) | 0.007(4) |
| C4 | 0.056(4) | 0.021(3) | 0.039(4) | -0.010(3) | -0.012(3) | -0.003(3) |
| C4L | 0.056(5) | 0.038(4) | 0.061(5) | -0.006(4) | -0.003(4) | -0.005(3) |
| C5 | 0.059(4) | 0.012(3) | 0.052(4) | -0.010(3) | 0.008(3) | -0.006(3) |
| C5L | 0.061(5) | 0.033(4) | 0.066(5) | -0.006(4) | 0.006(4) | 0.008(4) |
| C6 | 0.035(3) | 0.025(3) | 0.047(4) | -0.004(3) | 0.003(3) | 0.006(3) |
| C6L | 0.050(5) | 0.036(4) | 0.072(6) | -0.009(4) | -0.005(4) | 0.006(3) |

| | | | | | | |
|-----|------------|------------|------------|-------------|-------------|-------------|
| C7 | 0.034(3) | 0.036(4) | 0.046(4) | -0.008(3) | -0.003(3) | 0.002(3) |
| C7L | 0.049(4) | 0.037(4) | 0.067(5) | -0.013(4) | -0.010(4) | 0.013(3) |
| C8 | 0.036(4) | 0.027(4) | 0.064(5) | -0.007(3) | 0.009(3) | -0.010(3) |
| C8L | 0.048(4) | 0.041(4) | 0.059(5) | -0.003(4) | -0.017(4) | -0.003(3) |
| C9 | 0.034(3) | 0.027(3) | 0.043(4) | -0.002(3) | 0.007(3) | 0.000(3) |
| C9L | 0.040(4) | 0.032(4) | 0.064(5) | 0.001(3) | -0.001(3) | 0.001(3) |
| F1 | 0.0395(19) | 0.0134(16) | 0.0393(19) | -0.0006(14) | -0.0004(16) | -0.0013(14) |
| F2 | 0.0298(17) | 0.0189(17) | 0.0369(19) | -0.0027(14) | 0.0014(15) | 0.0031(14) |
| F3 | 0.0311(17) | 0.0154(17) | 0.0390(19) | -0.0043(14) | -0.0035(15) | 0.0016(14) |
| O1 | 0.078(4) | 0.026(3) | 0.099(5) | -0.006(3) | -0.033(4) | 0.012(3) |
| O2 | 0.079(4) | 0.036(3) | 0.059(4) | -0.011(3) | -0.010(3) | 0.003(3) |
| O3 | 0.048(3) | 0.046(3) | 0.051(3) | -0.003(3) | 0.000(2) | -0.005(2) |
| O4 | 0.139(7) | 0.046(4) | 0.069(5) | -0.013(3) | 0.026(4) | -0.016(4) |
| O5 | 0.094(6) | 0.094(6) | 0.140(8) | 0.033(6) | -0.033(6) | -0.034(5) |
| Ti1 | 0.0322(5) | 0.0128(5) | 0.0359(6) | -0.0032(4) | 0.0015(5) | -0.0024(4) |
| Ti2 | 0.0329(6) | 0.0145(5) | 0.0330(6) | 0.0015(4) | 0.0027(5) | 0.0008(4) |
| Ti3 | 0.0281(5) | 0.0154(5) | 0.0352(6) | 0.0003(4) | -0.0009(5) | 0.0033(4) |

Table 6.20. Bond distances in Å for **21**.

| | | | | | |
|-----|-----|----------|-----|-----|-----------|
| Ti1 | F3 | 2.052(4) | C11 | C12 | 1.402(11) |
| Ti1 | F1 | 2.060(4) | C11 | C15 | 1.433(10) |
| Ti1 | C9 | 2.369(7) | C12 | C13 | 1.411(10) |
| Ti1 | C3 | 2.370(6) | C13 | C14 | 1.408(10) |
| Ti1 | C2 | 2.373(7) | C14 | C15 | 1.389(10) |
| Ti1 | C10 | 2.379(6) | C16 | C20 | 1.385(11) |
| Ti1 | C8 | 2.408(7) | C16 | C17 | 1.393(10) |
| Ti1 | C4 | 2.409(6) | C17 | C18 | 1.412(10) |
| Ti1 | C5 | 2.417(6) | C18 | C19 | 1.407(9) |
| Ti1 | C1 | 2.422(6) | C19 | C20 | 1.411(10) |
| Ti1 | C6 | 2.434(7) | C21 | C25 | 1.389(11) |
| Ti1 | C7 | 2.435(7) | C21 | C22 | 1.425(10) |
| Ti2 | F1 | 2.054(4) | C22 | C23 | 1.400(11) |
| Ti2 | F2 | 2.063(4) | C23 | C24 | 1.406(10) |
| Ti2 | C11 | 2.368(7) | C24 | C25 | 1.425(10) |
| Ti2 | C15 | 2.369(7) | C26 | C30 | 1.402(10) |
| Ti2 | C17 | 2.378(6) | C26 | C27 | 1.405(10) |
| Ti2 | C18 | 2.393(6) | C27 | C28 | 1.418(9) |
| Ti2 | C16 | 2.401(6) | C28 | C29 | 1.373(10) |
| Ti2 | C14 | 2.413(7) | C29 | C30 | 1.416(11) |
| Ti2 | C13 | 2.421(7) | C1L | C2L | 1.388(14) |
| Ti2 | C20 | 2.422(6) | C1L | O1 | 1.442(11) |
| Ti2 | C12 | 2.433(7) | C2L | C3L | 1.522(13) |
| Ti2 | C19 | 2.438(6) | C3L | C4L | 1.507(12) |
| Ti3 | F2 | 2.053(4) | C4L | O1 | 1.435(10) |

| | | | | | |
|-----|-----|-----------|------|------|-----------|
| Ti3 | F3 | 2.064(3) | C5L | O2 | 1.418(10) |
| Ti3 | C25 | 2.363(6) | C5L | C6L | 1.537(11) |
| Ti3 | C26 | 2.377(6) | C6L | C7L | 1.513(12) |
| Ti3 | C27 | 2.386(6) | C7L | C8L | 1.536(11) |
| Ti3 | C24 | 2.389(7) | C8L | O2 | 1.411(10) |
| Ti3 | C30 | 2.393(7) | C9L | O3 | 1.434(9) |
| Ti3 | C21 | 2.407(6) | C9L | C10L | 1.499(11) |
| Ti3 | C28 | 2.414(7) | C10L | C11L | 1.532(10) |
| Ti3 | C23 | 2.416(6) | C11L | C12L | 1.524(12) |
| Ti3 | C29 | 2.422(7) | C12L | O3 | 1.418(10) |
| Ti3 | C22 | 2.431(6) | C13L | O4 | 1.421(12) |
| C1 | C5 | 1.388(10) | C13L | C14L | 1.477(13) |
| C1 | C2 | 1.401(10) | C14L | C15L | 1.467(14) |
| C2 | C3 | 1.416(11) | C15L | C16L | 1.591(15) |
| C3 | C4 | 1.405(11) | C16L | O4 | 1.413(14) |
| C4 | C5 | 1.416(10) | C17L | O5 | 1.411(13) |
| C6 | C7 | 1.404(10) | C17L | C18L | 1.474(17) |
| C6 | C10 | 1.411(10) | C18L | C19L | 1.471(16) |
| C7 | C8 | 1.420(11) | C19L | C20L | 1.395(15) |
| C8 | C9 | 1.400(10) | C20L | O5 | 1.434(12) |
| C9 | C10 | 1.403(10) | | | |

Table 6.21. Bond angles in ° for **21**.

| | | | | | | | |
|-----|-----|-----|-----------|-----|-----|-----|------------|
| F3 | Ti1 | F1 | 81.43(14) | C24 | Ti3 | C21 | 56.8(3) |
| F3 | Ti1 | C9 | 85.2(2) | C30 | Ti3 | C21 | 77.8(3) |
| F1 | Ti1 | C9 | 123.9(2) | F2 | Ti3 | C28 | 112.69(19) |
| F3 | Ti1 | C3 | 125.8(2) | F3 | Ti3 | C28 | 79.18(19) |
| F1 | Ti1 | C3 | 86.9(2) | C25 | Ti3 | C28 | 117.4(2) |
| C9 | Ti1 | C3 | 141.3(3) | C26 | Ti3 | C28 | 56.8(2) |
| F3 | Ti1 | C2 | 91.2(2) | C27 | Ti3 | C28 | 34.4(2) |
| F1 | Ti1 | C2 | 83.5(2) | C24 | Ti3 | C28 | 148.4(2) |
| C9 | Ti1 | C2 | 151.2(2) | C30 | Ti3 | C28 | 56.1(2) |
| C3 | Ti1 | C2 | 34.7(3) | C21 | Ti3 | C28 | 110.5(2) |
| F3 | Ti1 | C10 | 81.82(19) | F2 | Ti3 | C23 | 79.5(2) |
| F1 | Ti1 | C10 | 89.7(2) | F3 | Ti3 | C23 | 112.8(2) |
| C9 | Ti1 | C10 | 34.4(2) | C25 | Ti3 | C23 | 56.9(2) |
| C3 | Ti1 | C10 | 151.2(3) | C26 | Ti3 | C23 | 117.4(2) |
| C2 | Ti1 | C10 | 170.9(2) | C27 | Ti3 | C23 | 147.9(2) |
| F3 | Ti1 | C8 | 117.6(2) | C24 | Ti3 | C23 | 34.0(2) |
| F1 | Ti1 | C8 | 134.5(2) | C30 | Ti3 | C23 | 110.5(3) |
| C9 | Ti1 | C8 | 34.1(3) | C21 | Ti3 | C23 | 56.2(2) |
| C3 | Ti1 | C8 | 108.1(3) | C28 | Ti3 | C23 | 164.7(2) |
| C2 | Ti1 | C8 | 132.5(2) | F2 | Ti3 | C29 | 138.35(19) |
| C10 | Ti1 | C8 | 56.5(2) | F3 | Ti3 | C29 | 103.4(2) |

| | | | | | | | |
|-----|-----|-----|------------|-----|-----|-----|----------|
| F3 | Ti1 | C4 | 135.3(2) | C25 | Ti3 | C29 | 97.3(2) |
| F1 | Ti1 | C4 | 119.5(2) | C26 | Ti3 | C29 | 56.7(2) |
| C9 | Ti1 | C4 | 108.1(3) | C27 | Ti3 | C29 | 56.2(2) |
| C3 | Ti1 | C4 | 34.2(3) | C24 | Ti3 | C29 | 131.9(2) |
| C2 | Ti1 | C4 | 56.7(3) | C30 | Ti3 | C29 | 34.2(3) |
| C10 | Ti1 | C4 | 132.3(2) | C21 | Ti3 | C29 | 79.5(3) |
| C8 | Ti1 | C4 | 77.3(3) | C28 | Ti3 | C29 | 33.0(2) |
| F3 | Ti1 | C5 | 103.6(2) | C23 | Ti3 | C29 | 131.8(2) |
| F1 | Ti1 | C5 | 139.0(2) | F2 | Ti3 | C22 | 104.4(2) |
| C9 | Ti1 | C5 | 97.1(2) | F3 | Ti3 | C22 | 138.5(2) |
| C3 | Ti1 | C5 | 56.7(2) | C25 | Ti3 | C22 | 56.9(2) |
| C2 | Ti1 | C5 | 56.1(2) | C26 | Ti3 | C22 | 96.9(3) |
| C10 | Ti1 | C5 | 131.3(2) | C27 | Ti3 | C22 | 130.9(3) |
| C8 | Ti1 | C5 | 79.7(2) | C24 | Ti3 | C22 | 56.7(3) |
| C4 | Ti1 | C5 | 34.1(3) | C30 | Ti3 | C22 | 78.9(3) |
| F3 | Ti1 | C1 | 79.5(2) | C21 | Ti3 | C22 | 34.3(2) |
| F1 | Ti1 | C1 | 112.8(2) | C28 | Ti3 | C22 | 131.2(3) |
| C9 | Ti1 | C1 | 117.7(2) | C23 | Ti3 | C22 | 33.6(3) |
| C3 | Ti1 | C1 | 57.1(2) | C29 | Ti3 | C22 | 98.7(3) |
| C2 | Ti1 | C1 | 34.0(2) | C5 | C1 | C2 | 107.6(7) |
| C10 | Ti1 | C1 | 147.9(2) | C5 | C1 | Ti1 | 73.2(4) |
| C8 | Ti1 | C1 | 111.3(2) | C2 | C1 | Ti1 | 71.1(4) |
| C4 | Ti1 | C1 | 56.4(2) | C1 | C2 | C3 | 108.6(7) |
| C5 | Ti1 | C1 | 33.3(2) | C1 | C2 | Ti1 | 74.9(4) |
| F3 | Ti1 | C6 | 111.59(19) | C3 | C2 | Ti1 | 72.5(4) |
| F1 | Ti1 | C6 | 78.5(2) | C4 | C3 | C2 | 107.3(6) |
| C9 | Ti1 | C6 | 56.8(2) | C4 | C3 | Ti1 | 74.4(4) |
| C3 | Ti1 | C6 | 117.6(2) | C2 | C3 | Ti1 | 72.8(4) |
| C2 | Ti1 | C6 | 148.2(2) | C3 | C4 | C5 | 107.5(7) |
| C10 | Ti1 | C6 | 34.1(2) | C3 | C4 | Ti1 | 71.4(4) |
| C8 | Ti1 | C6 | 56.2(2) | C5 | C4 | Ti1 | 73.3(4) |
| C4 | Ti1 | C6 | 111.1(3) | C1 | C5 | C4 | 108.9(7) |
| C5 | Ti1 | C6 | 132.5(2) | C1 | C5 | Ti1 | 73.5(4) |
| C1 | Ti1 | C6 | 165.8(2) | C4 | C5 | Ti1 | 72.6(4) |
| F3 | Ti1 | C7 | 137.5(2) | C7 | C6 | C10 | 107.6(6) |
| F1 | Ti1 | C7 | 103.4(2) | C7 | C6 | Ti1 | 73.3(4) |
| C9 | Ti1 | C7 | 56.7(2) | C10 | C6 | Ti1 | 70.8(3) |
| C3 | Ti1 | C7 | 96.7(3) | C6 | C7 | C8 | 107.8(6) |
| C2 | Ti1 | C7 | 131.2(3) | C6 | C7 | Ti1 | 73.2(4) |
| C10 | Ti1 | C7 | 56.3(2) | C8 | C7 | Ti1 | 71.9(4) |
| C8 | Ti1 | C7 | 34.1(3) | C9 | C8 | C7 | 108.1(6) |
| C4 | Ti1 | C7 | 79.4(3) | C9 | C8 | Ti1 | 71.4(4) |
| C5 | Ti1 | C7 | 99.5(2) | C7 | C8 | Ti1 | 74.0(4) |
| C1 | Ti1 | C7 | 132.4(2) | C8 | C9 | C10 | 107.9(6) |
| C6 | Ti1 | C7 | 33.5(2) | C8 | C9 | Ti1 | 74.5(4) |
| F1 | Ti2 | F2 | 81.59(14) | C10 | C9 | Ti1 | 73.2(4) |
| F1 | Ti2 | C11 | 90.0(2) | C9 | C10 | C6 | 108.5(6) |

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|-----|-----|-----|-----------|-----|-----|-----|----------|
| F2 | Ti2 | C11 | 83.1(2) | C9 | C10 | Ti1 | 72.4(4) |
| F1 | Ti2 | C15 | 125.0(2) | C6 | C10 | Ti1 | 75.1(4) |
| F2 | Ti2 | C15 | 86.1(2) | C12 | C11 | C15 | 108.7(6) |
| C11 | Ti2 | C15 | 35.2(2) | C12 | C11 | Ti2 | 75.6(4) |
| F1 | Ti2 | C17 | 86.9(2) | C15 | C11 | Ti2 | 72.5(4) |
| F2 | Ti2 | C17 | 124.5(2) | C11 | C12 | C13 | 107.4(6) |
| C11 | Ti2 | C17 | 151.2(3) | C11 | C12 | Ti2 | 70.5(4) |
| C15 | Ti2 | C17 | 140.7(2) | C13 | C12 | Ti2 | 72.6(4) |
| F1 | Ti2 | C18 | 82.77(19) | C14 | C13 | C12 | 107.8(6) |
| F2 | Ti2 | C18 | 90.16(19) | C14 | C13 | Ti2 | 72.7(4) |
| C11 | Ti2 | C18 | 170.8(2) | C12 | C13 | Ti2 | 73.6(4) |
| C15 | Ti2 | C18 | 150.9(2) | C15 | C14 | C13 | 109.4(7) |
| C17 | Ti2 | C18 | 34.4(2) | C15 | C14 | Ti2 | 71.4(4) |
| F1 | Ti2 | C16 | 119.3(2) | C13 | C14 | Ti2 | 73.4(4) |
| F2 | Ti2 | C16 | 133.6(2) | C14 | C15 | C11 | 106.5(7) |
| C11 | Ti2 | C16 | 132.8(2) | C14 | C15 | Ti2 | 74.8(4) |
| C15 | Ti2 | C16 | 107.7(2) | C11 | C15 | Ti2 | 72.3(4) |
| C17 | Ti2 | C16 | 33.9(2) | C20 | C16 | C17 | 109.0(6) |
| C18 | Ti2 | C16 | 56.3(2) | C20 | C16 | Ti2 | 74.1(3) |
| F1 | Ti2 | C14 | 134.8(2) | C17 | C16 | Ti2 | 72.2(4) |
| F2 | Ti2 | C14 | 118.3(2) | C16 | C17 | C18 | 107.5(6) |
| C11 | Ti2 | C14 | 56.5(2) | C16 | C17 | Ti2 | 74.0(4) |
| C15 | Ti2 | C14 | 33.8(2) | C18 | C17 | Ti2 | 73.4(4) |
| C17 | Ti2 | C14 | 108.0(2) | C19 | C18 | C17 | 108.1(6) |
| C18 | Ti2 | C14 | 132.7(2) | C19 | C18 | Ti2 | 74.8(4) |
| C16 | Ti2 | C14 | 77.7(3) | C17 | C18 | Ti2 | 72.2(4) |
| F1 | Ti2 | C13 | 103.9(2) | C18 | C19 | C20 | 107.1(6) |
| F2 | Ti2 | C13 | 138.9(2) | C18 | C19 | Ti2 | 71.3(3) |
| C11 | Ti2 | C13 | 56.5(3) | C20 | C19 | Ti2 | 72.5(4) |
| C15 | Ti2 | C13 | 56.9(2) | C16 | C20 | C19 | 108.3(6) |
| C17 | Ti2 | C13 | 96.6(2) | C16 | C20 | Ti2 | 72.5(4) |
| C18 | Ti2 | C13 | 130.8(2) | C19 | C20 | Ti2 | 73.8(3) |
| C16 | Ti2 | C13 | 79.7(3) | C25 | C21 | C22 | 108.5(7) |
| C14 | Ti2 | C13 | 33.9(2) | C25 | C21 | Ti3 | 71.4(4) |
| F1 | Ti2 | C20 | 138.4(2) | C22 | C21 | Ti3 | 73.8(4) |
| F2 | Ti2 | C20 | 102.8(2) | C23 | C22 | C21 | 107.0(7) |
| C11 | Ti2 | C20 | 131.5(2) | C23 | C22 | Ti3 | 72.6(4) |
| C15 | Ti2 | C20 | 96.6(2) | C21 | C22 | Ti3 | 72.0(4) |
| C17 | Ti2 | C20 | 56.2(2) | C22 | C23 | C24 | 109.2(6) |
| C18 | Ti2 | C20 | 56.2(2) | C22 | C23 | Ti3 | 73.8(4) |
| C16 | Ti2 | C20 | 33.4(3) | C24 | C23 | Ti3 | 71.9(4) |
| C14 | Ti2 | C20 | 79.9(3) | C23 | C24 | C25 | 107.0(6) |
| C13 | Ti2 | C20 | 99.1(3) | C23 | C24 | Ti3 | 74.1(4) |
| F1 | Ti2 | C12 | 79.00(19) | C25 | C24 | Ti3 | 71.6(4) |
| F2 | Ti2 | C12 | 112.8(2) | C21 | C25 | C24 | 108.3(6) |
| C11 | Ti2 | C12 | 33.9(3) | C21 | C25 | Ti3 | 74.8(4) |
| C15 | Ti2 | C12 | 57.3(2) | C24 | C25 | Ti3 | 73.5(4) |

| | | | | | | | |
|-----|-----|-----|------------|------|------|------|------------|
| C17 | Ti2 | C12 | 117.8(2) | C30 | C26 | C27 | 107.6(6) |
| C18 | Ti2 | C12 | 147.9(2) | C30 | C26 | Ti3 | 73.6(4) |
| C16 | Ti2 | C12 | 111.8(2) | C27 | C26 | Ti3 | 73.2(4) |
| C14 | Ti2 | C12 | 56.1(2) | C26 | C27 | C28 | 107.8(6) |
| C13 | Ti2 | C12 | 33.8(2) | C26 | C27 | Ti3 | 72.5(3) |
| C20 | Ti2 | C12 | 132.4(2) | C28 | C27 | Ti3 | 73.9(4) |
| F1 | Ti2 | C19 | 111.9(2) | C29 | C28 | C27 | 108.4(6) |
| F2 | Ti2 | C19 | 78.25(19) | C29 | C28 | Ti3 | 73.8(4) |
| C11 | Ti2 | C19 | 148.5(3) | C27 | C28 | Ti3 | 71.7(4) |
| C15 | Ti2 | C19 | 117.5(2) | C28 | C29 | C30 | 108.3(6) |
| C17 | Ti2 | C19 | 56.5(2) | C28 | C29 | Ti3 | 73.2(4) |
| C18 | Ti2 | C19 | 33.9(2) | C30 | C29 | Ti3 | 71.8(4) |
| C16 | Ti2 | C19 | 55.8(2) | C26 | C30 | C29 | 108.0(6) |
| C14 | Ti2 | C19 | 111.8(2) | C26 | C30 | Ti3 | 72.3(4) |
| C13 | Ti2 | C19 | 132.3(2) | C29 | C30 | Ti3 | 74.0(4) |
| C20 | Ti2 | C19 | 33.8(2) | C2L | C1L | O1 | 109.0(8) |
| C12 | Ti2 | C19 | 166.1(2) | C1L | C2L | C3L | 105.5(8) |
| F2 | Ti3 | F3 | 81.42(14) | C4L | C3L | C2L | 103.0(7) |
| F2 | Ti3 | C25 | 124.4(2) | O1 | C4L | C3L | 106.3(7) |
| F3 | Ti3 | C25 | 85.47(19) | O2 | C5L | C6L | 107.6(7) |
| F2 | Ti3 | C26 | 86.2(2) | C7L | C6L | C5L | 103.0(7) |
| F3 | Ti3 | C26 | 124.67(19) | C6L | C7L | C8L | 101.6(7) |
| C25 | Ti3 | C26 | 142.0(2) | O2 | C8L | C7L | 103.8(6) |
| F2 | Ti3 | C27 | 82.74(18) | O3 | C9L | C10L | 104.7(6) |
| F3 | Ti3 | C27 | 90.49(19) | C9L | C10L | C11L | 102.4(6) |
| C25 | Ti3 | C27 | 151.4(2) | C12L | C11L | C10L | 103.7(6) |
| C26 | Ti3 | C27 | 34.3(2) | O3 | C12L | C11L | 107.7(6) |
| F2 | Ti3 | C24 | 89.7(2) | O4 | C13L | C14L | 107.0(8) |
| F3 | Ti3 | C24 | 82.7(2) | C15L | C14L | C13L | 107.4(8) |
| C25 | Ti3 | C24 | 34.9(2) | C14L | C15L | C16L | 101.3(8) |
| C26 | Ti3 | C24 | 151.2(2) | O4 | C16L | C15L | 103.4(8) |
| C27 | Ti3 | C24 | 170.5(2) | O5 | C17L | C18L | 106.9(9) |
| F2 | Ti3 | C30 | 118.6(2) | C19L | C18L | C17L | 103.8(11) |
| F3 | Ti3 | C30 | 134.9(2) | C20L | C19L | C18L | 108.1(11) |
| C25 | Ti3 | C30 | 108.6(2) | C19L | C20L | O5 | 107.3(9) |
| C26 | Ti3 | C30 | 34.2(2) | Ti2 | F1 | Ti1 | 158.5(2) |
| C27 | Ti3 | C30 | 56.6(2) | Ti3 | F2 | Ti2 | 158.39(19) |
| C24 | Ti3 | C30 | 132.7(2) | Ti1 | F3 | Ti3 | 158.68(19) |
| F2 | Ti3 | C21 | 135.5(2) | C4L | O1 | C1L | 108.4(7) |
| F3 | Ti3 | C21 | 117.5(2) | C8L | O2 | C5L | 108.1(6) |
| C25 | Ti3 | C21 | 33.8(3) | C12L | O3 | C9L | 105.4(6) |
| C26 | Ti3 | C21 | 109.0(3) | C16L | O4 | C13L | 104.3(7) |
| C27 | Ti3 | C21 | 132.7(2) | C17L | O5 | C20L | 105.1(8) |

7. Abbreviations

| | |
|--------------------------|--|
| A/E | addition / β -fluoride elimination (mechanism) |
| AP | antiperiplanar |
| BINAL-H | lithium [(1,1'-binaphthalene-2,2'-diolato- κ O, κ O')]hydromethoxyaluminate] |
| BINOL | 1,1'-binaphthalene-2,2'-diol |
| bp | boiling point |
| Bpin | 4,4,5,5-tetramethyl-1,3-dioxaborolanyl |
| br | broad |
| cat | catalytic amount |
| COSY | correlation spectroscopy |
| Cp | η^5 -cyclopentadienyl |
| Cp* | η^5 -pentamethylcyclopentadienyl |
| D | donor |
| d | doublet |
| dba | 1,5-diphenylpenta-1,4-diene-3-one |
| DBPO | dibenzoyl peroxide |
| dec | decomposition |
| diglyme | di(2-methoxyethyl) ether |
| Dipp ₂ NacNac | bis[2,6-bis(1-methylethyl)-N,N'-(1,3-dimethyl-1,3-propanediylidene)]benzenamine monoanion |
| dme | 1,2-dimethoxyethane |
| dmf | N,N-dimethylformamide |
| ebthi | 1,2-bis(η^5 -tetrahydroindenyl)ethanediyl |
| ee | enantiomeric excess |
| EPR | electron paramagnetic resonance (spectroscopy) |
| eq | equivalent(s) |
| HDF | hydrodefluorination |
| IR | infrared spectroscopy |
| m | medium (IR) multiplet (NMR) |
| Me-thf | 2-methyl-tetrahydrofuran |
| mp | melting point |
| MW | microwave spectroscopy |
| n. d. | not determined |
| NMR | nuclear magnetic resonance (spectroscopy) |
| o. d. | outside diameter |
| pGLC | preparative gas/liquid chromatography |
| PMHS | poly(methylhydrosiloxane) |
| ppb | parts per billion |
| ppm | parts per million |

| | |
|-------------|---|
| PTFE | poly(tetrafluoroethene) |
| PV | parity violation |
| qa | quartet |
| <i>rac</i> | racemic |
| rt | room temperature |
| s | strong (IR) singlet (NMR) |
| SP | synperiplanar |
| t | triplet |
| <i>tert</i> | tertiary |
| thf | tetrahydrofuran |
| TMAF | N,N,N,N-tetramethylammonium fluoride |
| TMS | tetramethylsilane |
| TOF | turnover frequency |
| TON | turnover number |
| TRIMEB | heptakis(2,3,6-tri-O-methyl)- β -cyclodextrin |
| vw | very weak |
| w | weak |
| σ -m | σ -bond metathesis (mechanism) |
| vs | very strong |

8. References

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