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Titanium-Catalyzed Vinylic and Allylic C–F Bond Activation—Scope, Limitations and Mechanistic Insight

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Dedicated to Prof. Dr. François Diederich on the occasion of his 60th birthday

Abstract: The hydrodefluorination (HDF) of fluoroalkenes in the presence of a variety of titanium catalysts was studied with respect to scope, selectivity, and mechanism. Optimization revealed that the catalyst requires low steric bulk and high electron density; secondary silanes serve as the preferred hydride source. A broad range of substrates yield partially fluorinated alkenes, such as previously unknown (*Z*)-1,2-(difluorovinyl)ferrocene. Mechanistic studies indicate a titanium(III) hydride as the active species, which forms a titanium(III) fluoride by H/F exchange with the substrate. The HDF step can follow both an insertion/elimination and a σ-bond metathesis mechanism; the *E*/*Z* selectivity is controlled by the substrate. The catalysts' ineffieciency towards fluoroallenes was rationalized by studying their reactivity towards Group 6 hydride complexes.

Keywords: catalysis · C–F activation · fluoroalkenes · hydrodefluorination · titanium

Introduction

Metal-catalyzed transformations of organic molecules are fundamental to the synthetic chemist and cover a broad range of substrates and functionalities.[1] Among the numerous reactants, fluoroalkenes are somewhat underrepresented; this has often been attributed to their altered bond polarities and energies in comparison with their hydrocarbon analogues.[2] Fluorine forms the strongest σ bond to carbon with a homolytic dissociation energy of (500 ± 50) kJ mol^{-1}.[3] This thermodynamic stability combined with an inherent kinetic inertness has allowed for technical applications of fluorocarbons, for example, as refrigerants or chemically resistant polymers,[4] but has also led to an accumulation of halofluorocarbons in the upper atmosphere, where they have had a deleterious impact on the ozone layer and contribute to global warming.[5] On the other hand, the increase in hydrophobicity and metabolic stability induced by introduction of fluorine into organic molecules has allowed for significant advances in medicinal chemistry.[6] This ambiguous role of fluorine chemistry has created a need for means of both selective construction and deconstruction of carbon–fluorine bonds.

The introduction of fluorine into complex organic molecules has been accomplished by employing various fluorination techniques.[7,8] While perfluorination is rather easily achieved, the introduction of a defined substitution pattern remains challenging; the use of fluorine-containing building blocks circumvents this problem, but relies on the availability of a suitable synthon. A promising approach to such building blocks is based on derivatization of readily available perfluorinated compounds by selective cleavage of carbon–fluorine bonds.[9]

A number of systems capable of catalytic aromatic,[10,11] and aliphatic[12,13] C–F bond activation have been reported to date, whereas comparable processes involving fluoroalkenes have remained rare (Scheme 1).[10r,11z,14,15] Negishi-type cross-coupling of fluoroalkenes with arylzinc reagents was introduced by Saeki et al.;[11z] very recently, and Ohashi et al. extended this approach and developed an efficient protocol for the synthesis of trifluorostyrenes via C–F activation of tetrafluoroethene.[15a,b] Rhodium-catalyzed silylation and borylation of vinylic carbon–fluorine bonds has been achieved by the group of Braun.[14d,15c]

Despite the increasing importance of hydrofluoroolefins (HFOs) as low-GWP (GWP = global warming potential) replacements for hydrofluorocarbons (HFCs), the simplest possible C–F activation of fluoroalkenes, namely the hydrodefluorination (HDF) is still underdeveloped. Low-coordinate iron fluorides were shown by Holland to act as precatalysts for the HDF of hexafluoropropene and trifluoropropene (Scheme 1).[10r] Turnover numbers (TONs) up to 5 were achieved at 100 °C. A slightly higher efficiency was reported in the HDF of fluoroethene in the presence of Wilkinsons's catalyst.[14e]

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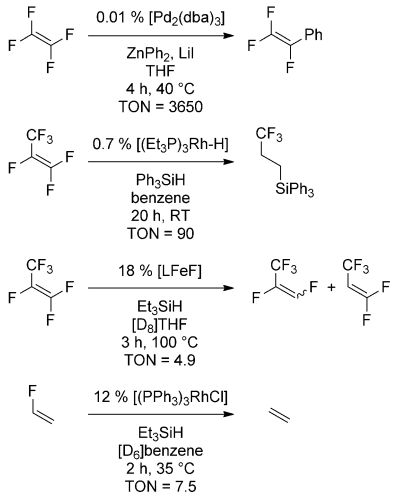


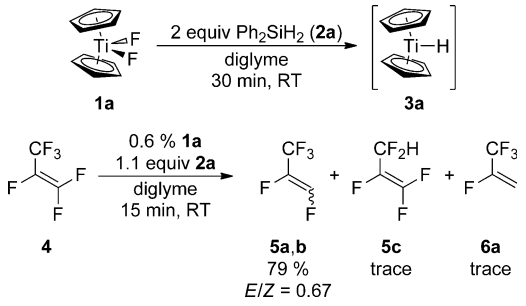
Scheme 1. Literature examples of catalytic fluoroalkene C–F bond activation (L = (2,6-diisopropylphenyl){(2*E*,4*E*)-4-[(2,6-diisopropylphenyl)imino]pent-2-en-2-yl}amide).

However, these limited efficiencies, the narrow substrate scope and the high cost of most late-transition-metal-based catalysts have rendered C–F activation a rather academic research area and prompted us to focus on early transition metals. A few examples of Group 4 catalyzed C–F activation have appeared in the literature.[9a,10o,y,ad,ae,13g] The cleavage of olefinic carbon–fluorine bonds by zirconocene and hafnocene hydrides has been thoroughly studied by Jones, albeit in stoichiometric reactions.[9p,16] The concomitant formation of stable zirconium and hafnium fluoro complexes is considered the driving force in these reactions, but also the main obstacle in developing a catalytic process. In contrast, the titanium congener is more reactive towards various hydride reagents.

Based on this difference in reactivity, we recently reported our preliminary results on the titanium-catalyzed HDF of fluoroalkenes.[17] In this paper, we present our detailed study on the scope and mechanism of this catalyst system.

Results and Discussion

Owing to the limited number and high sensitivity of isolable titanium hydride complexes, we followed Buchwald's in situ preparation of a purported titanocene(III) hydride **3a** by reacting air-stable titanocene difluoride (**1a**) with excess diphenyl silane (**2a**, Scheme 2) in ether-based solvents;[18] due to its low vapor pressure, we chose diglyme in order to facilitate its separation from the gaseous substrates and products, THF or dioxane give similar results. Stirring at ambient temperature for 30 min or at elevated temperatures for a few minutes results in a sudden color change from bright yellow through purple to dark green. The resulting solution is active for the catalytic hydrodefluorination of fluoroalkenes (Scheme 2). Addition of hexafluoropropene (**4**) yields pentafluoropropenes **5a** and **5b** as the main products besides



Scheme 2. Titanium-catalyzed HDF of hexafluoropropene (**4**).

trace amounts of the allylic HDF product **5c** and the twofold HDF product **6a**; no HDF at the secondary carbon atom is observed. The stereoselectivity is rather low (*E*/*Z* = 0.67) and is not influenced by the reaction temperature.

Optimization: A variety of high-boiling silanes **2a**–**2e** were evaluated as hydride source for the HDF of **4** in terms of turnover frequency (TOF) and *E*/*Z* selectivity (Figure 1). While the secondary silane **2a** performs best with a TOF of 500 h^{-1}, the primary silane **2b** as well as the polymer **2e** slow down the reaction by almost one order of magnitude with no influence on the stereoselectivity. Tertiary silanes **2c** and **2d** fail to activate the catalyst.

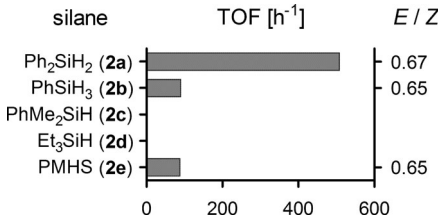


Figure 1. Influence of the employed silane **2a**–**2e** on the HDF of **4** in the presence of **1a**. TOF determined by ^{19}F NMR spectroscopy after 15 min at room temperature.

The influence of the catalyst structure was studied by introducing various substituents to the cyclopentadienyl ligands. As the substituent's steric bulk increases, the reactivity is found to decrease substantially, while the selectivity is only slightly affected (Figure 2). Interestingly, the trimethylsilyl derivative **1d** is more active than its *tert*-butyl analogue **1c**, although both moieties are similar in size. Apparently, electron donation by the silyl group has a beneficial effect on the HDF reaction; this conclusion is further supported by the low TOFs achieved by acceptor-substituted titanocene **1h** and diketiminate **1i**; consistently, the simple titanium fluorides **1j** and **1k** exhibit no catalytic activity in the absence of suitable donating ligands. Further optimization of the *E*/*Z* selectivity was attempted by the synthesis of an unsymmetrically substituted titanocene difluoride **1f**. However, apart from a higher activity than the symmetrically substituted precatalyst **1d**, no gain in selectivity was ob-

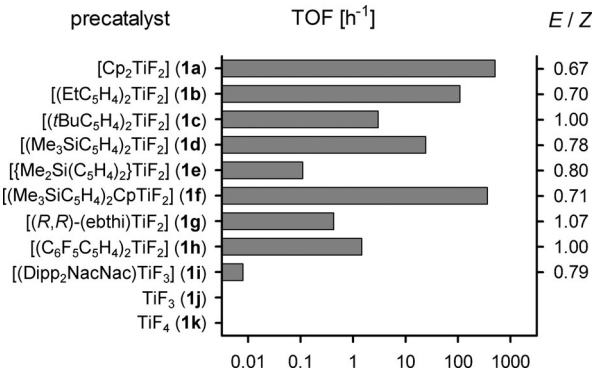


Figure 2. Influence of the employed titanium precatalyst **1a**–**1e** on the catalytic HDF of **4** using **2a** as the hydride source ($Dipp_2$NacNac = (2,6-diisopropylphenyl){(2*E*,4*E*)-4-[(2,6-diisopropylphenyl)imino]pent-2-en-2-yl}amide, ebthi = 1,2-bis(4,5,6,7-tetrahydro-1*H*-inden-1-yl)ethane-1,2-diyl). TOF determined by ^{19}F NMR spectroscopy after 15 min at room temperature (**1a**,**b**,**d**,**f**) or at low conversion (**1c**,**e**,**h**,**i**,**j**); **1a**,**f** reached complete conversion within this time.

served. The solid-state structures of complexes **1e**, **1f**, and **1h** were determined by single-crystal X-ray diffraction (Figure 3). Their structural parameters are very similar and within the expected range. **1f** was found to crystallize in two polymorphs ($P2_1/c$) and ($P\bar{1}$), which differ essentially in the orientation of the silyl moiety.

Substrate scope: A number of fluorinated alkenes were subjected to similar HDF conditions (Table 1). 1,1,3,3,3-Pentafluoropropene (**5d**) reacts with **2a** to yield tetrafluoropropenes **6b**–**6d** (Table 1, entry 2). The TOF of 200 h^{-1} is clearly below the value of 500 h^{-1} observed for **4** under identical conditions, but the selectivity is excellent; the *E* isomer of **6b** is formed in 90% overall selectivity (entry 1). 3,3,3-Trifluoropropene (**7**) reacts much slower (TOF = 7.2 h^{-1}) to give difluoropropene (**8**) and monofluoropropenes **9a** and **9b** (entry 3); a competing hydrogenation is found to yield 1,1,1-trifluoropropane (**10**) and propane (**11**). This side reaction may arise from the presence of dihydrogen formed by dehydrocoupling of the silane, which is also catalyzed by **1a**;[19] unlike the formation of **10**, the hydrogenation leading to **11** seems to poison the catalyst irreversibly, as indicated by the stoichiometric yield of **11** with respect to **1a**. At low conversions, formation of **9a**,**b** is observed before the complete consumption of **7**. Lowering the reaction temperature to 0 °C has no significant effect apart from slowing down the reaction.

The catalytic HDF of fluoroethenes **12**, **13**, and **14c** proceeds significantly less smoothly. Even at elevated temperatures, no HDF products of tetrafluoroethene (**12**; Table 1, entry 4) were obtained; trifluoroethene (**13**) affords a mixture of difluoroethenes **14a**–**14c**, monofluoroethene (**15**), and ethane (**16**), albeit with low efficiency (TON = 4.2, entry 5). The CF_2 group is apparently more readily attacked than the CFH group; this can be seen from the relative yields of **14a** and **14b** with respect to **14c**, resulting from either a preferential formation of **14a** and **14b** or a faster

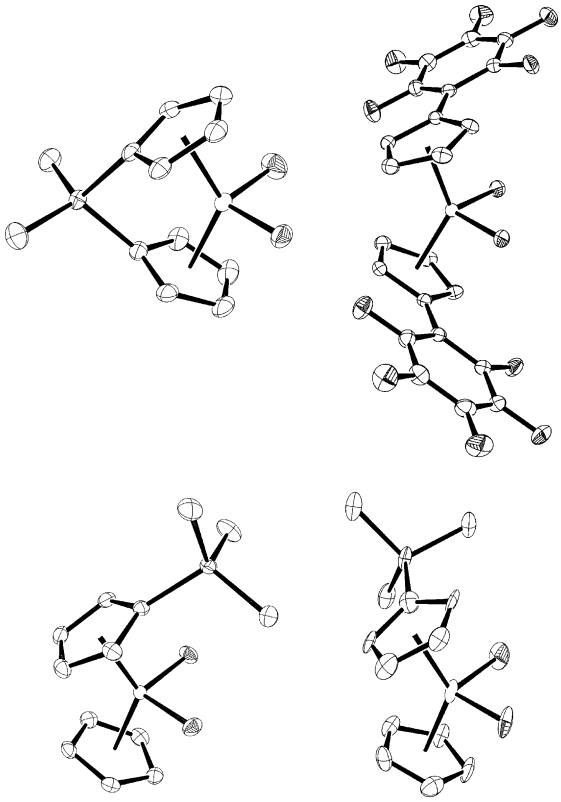


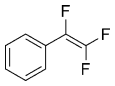
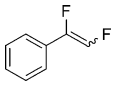
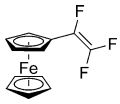
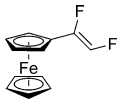
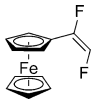
Figure 3. Molecular structures of **1e** (top left), **1h** (top right). and **1f** ($P2_1/c$ and $P\bar{1}$, bottom left and right, respectively) determined by single-crystal X-ray diffraction (C principal ellipse, F shaded octant, Si cutout ellipse, Ti plain ellipse; hydrogen atoms omitted for clarity, thermal ellipsoids drawn at 50% probability).

subsequent hydrodefluorination of **14c**. In either case, the second and third HDF steps are faster than the first, resulting in the formation of **15** prior to the complete consumption of the starting material. As observed in the HDF of **7**, a HDF/hydrogenation product **16** is formed in an exactly stoichiometric amount. Similar results are observed starting from **14c** to give a mixture of **15** and **16** (TON = 3.4; entry 6).

Depending on the stoichiometry, **17** undergoes H/F exchange to give penta-, tetra-, tri- and difluorocyclobutenes **18**–**21** (Table ; entry 7). In order to ensure complete consumption of all silane-bound hydrogen, longer reaction times were employed. Preferential formation of pentafluorocyclobutenes **18a** and **18b** over their HDF products **19a** and **19b** is achieved using 0.6 equivalents of **2a**. The use of 1.2 equivalents of **2a** furnishes tetrafluorocyclobutenes **19a** and **19b** as the main products (entry 8), whereas higher silane to substrate ratios result predominantly in the formation of trifluorocyclobutene **20** in addition to smaller amounts of **19a** and **19b**, difluorocyclobutene **21**, and a number of unidentified side products (entry 9).

The catalytic HDF of aryl-substituted fluoroalkenes requires elevated temperatures in order to reach completion within reasonable time. Trifluorostyrene (**22**) yields (1,2-difluoroethenyl)benzenes **23a** and **23b** in good yields and

Table 1. Substrate scope—reactions performed in diglyme solution at room temperature. Isolated yields of gaseous products were determined by integration of product resonances in the ^{19}F NMR spectra relative to an internal standard.

	Substrate	**1a** [mol %]	**2a** [equiv]	*t* [h]	Products				TON
1	 **4**	0.64	1.0	0.25	 **5a**,**b** 79 % *E*/*Z* = 0.67	 **5c** 0.9 %	 **6a** 1.1 %		125
2	 **5d**	1.23	1.1	1	 **6b**,**c** 49 % *E*/*Z* = 0.07	 **6d** 1.9 %			42
3	 **7**	3.85	1.5	64	 **8** 37 %	 **9a**,**b** 2.7 % *E*/*Z* = 0.71	 **10** 22 %	 **11** 3.5 %	17
4	 **12**	1.32	1.2	3	none				0
5	 **13**	7.35	1.0	18	 **14a**,**b** 4.1 % *E*/*Z* = 0.36	 **14c** 0.2 %	 **15** 2.2 %	**16** 7.4 %	4.2
6	**14c**	6.52	1.0	168	**15** 8.4 %	**16** 6.5 %			3.4
7	 **17**	4.66	0.6	70	 **18a** 71 %	 **18b** 3.3 %	 **19a** 5.9 %	 **19b** 1.1 %	19
8	**17**	5.19	1.2	72	**18b** 6.8 %	**19a** 56 %	**19b** 10 %	 **20** 8.2 %	32
9	**17**	4.42	2.1	72	**19a** 16 %	**19b** 6.6 %	**20** 38 %	 **21** trace	36
10	 **22**	5.00	1.1	10[a]	 **23a**,**b** 79 % *E*/*Z* = 0.50	 **24a**,**b** traces	 **24c** trace		16
11	 **25**	4.97	1.2	66.5[b]	 **26a** 16 %	 **26b** trace	 **27** trace	 **28** trace	4
12	 **29**	0.86	1.1	169	 **30** 1.1 %				1.3

trace amounts of the (monofluoroethenyl)benzenes **24a**–**24c** after 10 h at 65 °C (Table ; entry 10). Previously unknown *Z*-(1,2-difluoroethenyl)ferrocene (**26a**) was isolated in 16 % yield from the HDF of (trifluoroethenyl)ferrocene (**25**) at 90 °C; traces of the *E* isomer **26b**, *Z*-(monofluoroethenyl)-ferrocene (**27**) and ethenylferrocene (**28**) were detected in the crude reaction mixture (entry 11). The overall low yield is due to the competing thermal dimerization of **25**.[20] Compound **26a** was characterized by single-crystal X-ray diffraction. It crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit. As observed in **25**, the cyclopentadienyl rings exhibit an eclipsed conformation and the difluoroethenyl moiety is twisted out of the C_5H_4 plane by 25.8° due to intermolecular hydrogen bonding (Figure 4).

Finally, we probed the catalyst system's applicability to the HDF of tetrafluoroallene (**29**). Although small amounts of trifluoroallene (**30**) are formed, the turnover number hardly exceeds one, even after prolonged reaction times; forcing conditions led to a slight increase, but mainly resulted in thermal dimerization of the starting material (Table ; entry 12).[21]

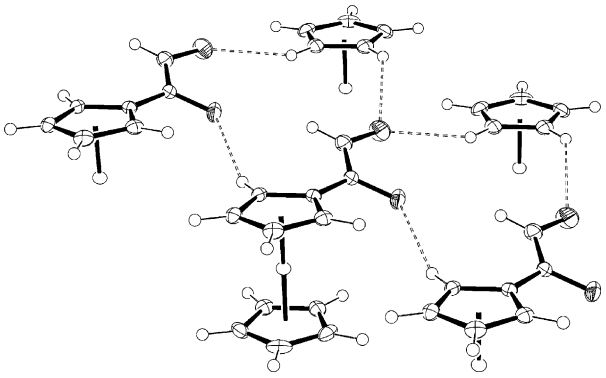
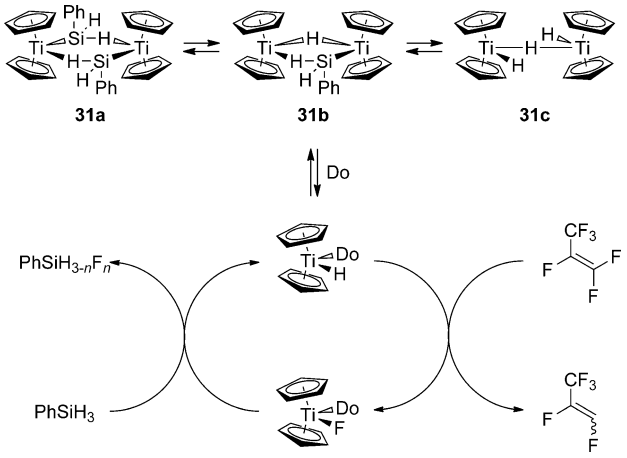


Figure 4. Molecular structure and packing diagram of *Z*-(1,2-difluoroethenyl)ferrocene (**26a**) determined by single-crystal X-ray diffraction (C principal ellipse, F shaded octant, Fe plain ellipse, H circles; thermal ellipsoids drawn at 50% probability).

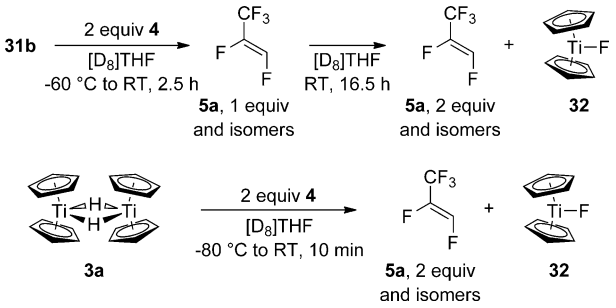
Active species: The initial assumption of titanocene(III) hydride (**3a**) as the catalytically active species is in evident contradiction to a report by Bercaw and Brintzinger.[22] While **3a** is purple and prone to rapid decomposition in solution above −70°C, the active catalyst forms a dark green solution and performs well at ambient temperature. This fact prompted us to study the nature of the active species in order to gain insight into the catalytic cycle.

A solution of the activated catalyst in THF was prepared from **1a** and **2b**; upon cooling, crystals of [{$Cp_2Ti(\mu\text{-}SiH_2Ph)$}$_2$] (**31a**) separated, which were isolated and identified by single-crystal X-ray diffraction. Compound **32a** has previously been characterized as an intermediate in the titanium-catalyzed dehydrogenative coupling of primary and secondary silanes.[19b,23] In solutions containing excess silane, **31a** is known to be in equilibrium with the dimeric silyl hydride complex [$Cp_2Ti(\mu\text{-}SiH_2Ph)(\mu\text{-}H)TiCp_2$] (**31b**) and the mixed-valence titanocene hydride [$(Cp_2TiH)_2(\mu\text{-}H)$] (**31c**, Scheme 3).[19a,24] Their relative abundances depend on the employed precatalyst, silane, solvent, and reaction time; a shift of this equilibrium is likely to account for the different turnover frequencies observed in the catalytic HDF upon variation of the silane. An additional equilibrium between dimeric and monomeric species was shown to exist in the presence of a suitable donor;[25] notably, catalytic HDF employing **1a** only proceeds in donor solvents such as THF or diglyme. Both **31a** and **31b** were detected in a solution of the activated catalyst in toluene by ^{1}H NMR spectroscopy at low temperatures.



Scheme 3. Proposed catalytic cycle for the titanium-catalyzed HDF of **4** (Do = donor solvent).

Independently prepared **31b** reacts with excess **4** to give one equivalent of its HDF products **5a**–**5c**; upon standing, a second equivalent of **4** is slowly consumed accompanied by the formation of titanocene(III) fluoride (**32**, Scheme 4).



Scheme 4. Stoichiometric HDF of **4** by different titanium hydride species.

This stepwise reaction process indicates that initially only one of the two titanium centers is capable of a HDF reaction, consistent with the presence of only one hydride ligand. Ligand scrambling at elevated temperatures is necessary to regenerate the hydride and allow for another HDF step. The involvement of a titanium hydride was further confirmed by an independent preparation of the highly sensitive parent dimeric titanocene(III) hydride (**3a**).[22] Compound **3a** reacts with excess **4** within minutes to give two equivalents of its HDF products and **32** (Scheme 4). Compounds **31a**, **31b**, and **32** can also be employed as precatalysts for the HDF of **4** with performances similar to **1a**, thus confirming them to be part of or closely linked to the catalytic cycle.

These findings suggest a catalytic cycle, in which titanocene(III) hydride reacts with the substrate to give titanocene(III) fluoride (**32**) and the HDF product (Scheme 3). Compound **32** subsequently reacts with a silane molecule to regenerate the active hydride under fluorosilane formation. This cycle is consistent with the observed benefits of electron-donating ligands on the precatalyst. Higher electron densitiy at the metal increases the hydridicity of the active species and weakens the titanium–fluorine bond.

Compound **32** was crystallized from the reaction mixture and identified by single-crystal X-ray diffraction (Figure 5) and EPR spectroscopy.[26] Compound **32** crystallizes as a trimer in the orthorhombic space group $P2_12_12_1$ with 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-

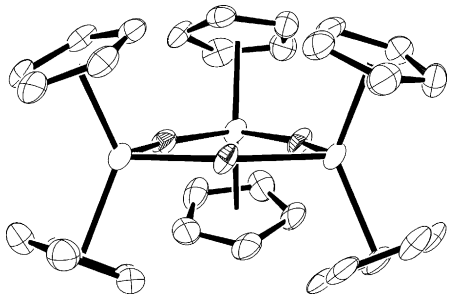
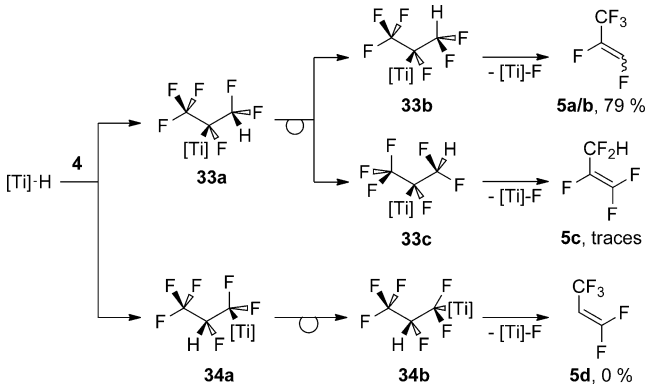


Figure 5. Molecular structure of trimeric [Cp_2TiF] (**32**) determined by single-crystal X-ray diffraction (C principal ellipse, F shaded octant, Ti plain ellipse; hydrogen atoms and solvent molecules omitted for clarity, thermal ellipsoids drawn at 50% probability).

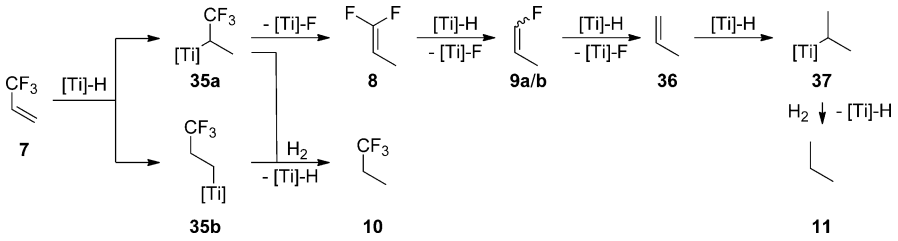


Scheme 5. The β-hydride addition/β-fluoride elimination mechanism (IE) for the HDF of **4**.

Ti = 158.5(4)°, F-Ti-F = 81.4(2)° and Cp-Ti-Cp = 130.7(1)°). This geometry resembles that of the related 1,1′-dimethyltitanocene(III) fluoride, which is dimeric in the solid state (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)°).[27] The shorter titanium–fluorine bonds in **32** are due to lower electron density at the metal; the six-membered Ti_3F_3 ring is less sterically crowded than the four-membered Ti_2F_2 ring, resulting in a less acute Cp-Ti-Cp angle. Interestingly, a similar Ti_3F_3 ring is also observed in solid TiF_4 ($Ti–F_{short}$ = 1.964(4) Å, $Ti–F_{long}$ = 1.976(3) Å, Ti-F-Ti = 159.3(3)° and F-Ti-F = 80.7(2)°).[28]

Mechanistic studies: Two distinct mechanisms for the hydrodefluorination of alkenes by metal hydride complexes have been discussed in the literature: The β-hydride addition/β-fluoride elimination mechanism (IE) and the σ-bond metathesis mechanism (SBM).[16b,c,e,29] The former comprises an insertion of the alkene double-bond into the titanium-hydrogen bond to yield an intermediate titanium fluoroalkyl species **33a** (Scheme 5). Early-transition-metal fluoroalkyl species are unstable[30] and prone to undergo β-fluoride elimination with formation of metal fluorides and alkenes.[9p] Both β-addition and β-elimination reactions are known to proceed in a *syn* stereoselectivity;[1a] product formation must therefore include a rotation around the carbon–carbon single bond to enable β-fluoride elimination from rotamer **33b** to give **5a** and **5b** or **33c** to give **5c**. Formation of **5c** through elimination from **33c** is found to occur only to a minor extent; this may be ascribed to the higher stability of CF_3 groups in comparison with CF_2H groups.[2c,31] Addition of the hydride to the central carbon atom would be necessary for the formation of **5d** via intermediates **34a** and **34b**, but is not observed. Despite the higher steric hindrance expected from addition of the titanocene fragment to the secondary carbon atom, hydride addition to the CF_2 group is highly favored, because it is the most electrophilic site in the molecule.[16b] The lower TOFs observed in the HDF of **5d** and **7** agree well with this assumption, because the substrates' lower degrees of fluorination reduce their electrophilicity. Attempts to observe an intermediate **33a**–**33c** at low temperature were not successful.

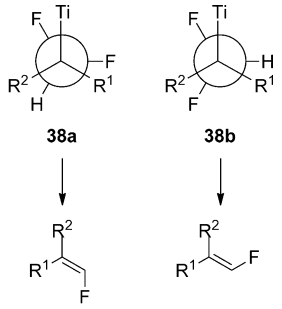
As **7** does not have vinylic fluorine substituents, its HDF by means of the IE mechanism must involve β-fluoride elimination from a stable CF_3 group. Consistently, the TOF is almost two orders of magnitude lower than for **4**. In addition, long-lived intermediates **35a** and **35b** are expected to be subject to hydrogenolysis (or silanolysis) to furnish the observed hydrogenation product **10** (Scheme 6). The primary HDF product **8** features vinylic fluorine substituents and therefore undergoes rapid HDF to yield **9a** and **9b** prior to the complete consumption of **7**. The final product propene removes titanium from the catalytic cycle by insertion to yield a titanium propyl complex **37**, which is incapable of β-fluoride elimination. Moreover, titanocene(III) alkyl species are unstable towards decomposition into alkanes and η^1-η^5-cyclopentadienyl or fulvalenyl titanium oligomers.[32] The observed stoichiometric formation of **11** supports this assumption. Similarly, the poor results employing **13** or **14c** as substrates may be due to catalyst deactivation by formation of the HDF/hydrogenation product **16** in stoichiometric amount. It remains, however, unclear why tetrafluoroethene (**12**) does not react at all.



Scheme 6. Proposed mechanism for the HDF of 3,3,3-trifluoropropene (**7**).

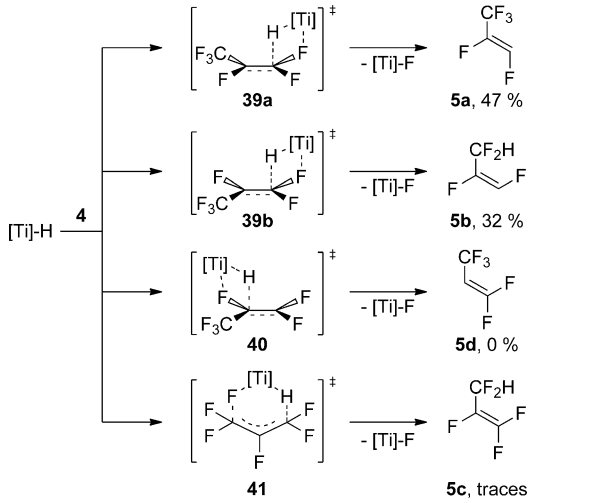
The observed low reactivity of the catalyst system towards aryl alkenes **22** and **25** at room temperature is most probably due to steric repulsion between the titanocene moiety and the geminal aryl substituent in the intermediate insertion product.

The substrate-dependent variations in *E*/*Z* selectivity demand a closer look at the conformation of the presumed intermediate. β-Fluoride elimination requires a *syn* geometry of the metal fragment and the β-fluorine substituent, resulting in an eclipsed conformation of either R^1 (**38a**) or R^2 (**38b**) with a vicinal fluorine substituent (Scheme 7). The relative sizes of R^1 and R^2 are therefore expected to determine the preferred orientation and hence the selectivity. Consistently, for $R^1 \ll R^2$ and $R^1 \gg R^2$ selectivity reaches up to 94 and 73%, respectively, while for $R^1 \approx R^2$, almost no selectivity is observed.



Substrate	R^1	R^2		
5d	H	CF_3	94 %	6 %
25	F	Fc	86 %	14 %
22	F	Ph	66 %	33 %
4	F	CF_3	60 %	40 %
8	H	CH_3	40 %	60 %
13	F	H	27 %	73 %

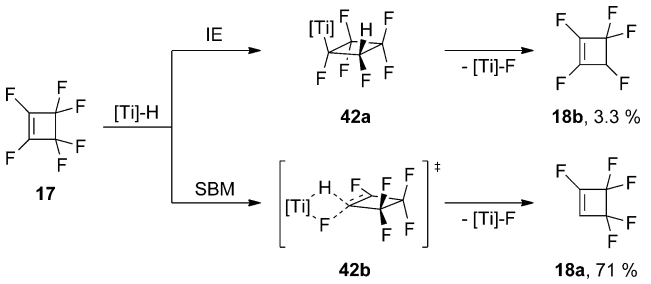
Scheme 7. The origin of *E*/*Z*-selectivity explained by the IE mechanism (percentages represent relative yields, Fc = ferrocenyl).



Scheme 8. The σ-bond metathesis mechanism (SBM) for the HDF of **4**.

In contrast, the SBM mechanism (Scheme 8) does not include an intermediate. The HDF of **4** proceeds in one step via a four-membered transition state **39a**, **39b**, or **40**; transition states **39a** and **39b** should be similar in energy consistent with the observed low *E*/*Z*-selectivity. For electronic and steric reasons, **40** is expected to be unfavorable. Formation of **5c** by SBM requires a six-membered transition state **41**, resulting in a large F-Ti-H angle. Titanocene(III) halides typically prefer L-Ti-L angles well below 90°,[27,33] rendering **41** highly strained and energetically not feasible. Neither the increased selectivity nor the lowered reactivity in the formation of **6a**, **6b**, **23a**, **23b**, **26a**, and **26b** are explained on the basis of this mechanism, because steric bulk at the β-carbon atom is unlikely to affect SBM.[16b] The HDF of **7** by SBM involves an unfavorable six-membered transition state, consistent with the low TOF; however, no explanation for the competing hydrogenation is possible.

Nevertheless, unambiguous proof of the competition between both mechanisms is evident from the catalytic HDF of **17**. In this rigid cyclic substrate, stereochemical implications allow for a clear distinction between the mechanisms by which a HDF product is formed.[16e] Addition of the titanium hydride to **17** yields intermediate **42a** (Scheme 9).

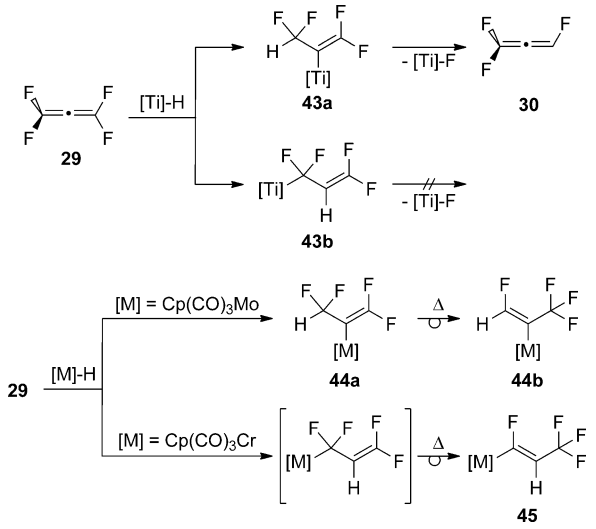


Scheme 9. Competing mechanisms in the HDF of hexafluorocyclobutene (**17**).

Subsequent β-fluoride elimination must proceed in a *syn* geometry forming allylic HDF product **18b**, which is detected in the product mixture in small amounts. The main vinylic HDF product **18a** can only be formed by σ-metathesis via **42b**. The second HDF step follows a similar pattern: The main product **19a** is formed by SBM, whereas minor amounts of **19b** are formed by β-hydride addition/β-fluoride elimination mechanism (IE); the side-product **18b** also yields **19b** by SBM. Compound **19a** does not contain any vinylic fluorine atoms; further HDF must follow the IE pathway, while its HDF product **20** is again subject to SBM to yield **21**.

Alternative mechanisms such as a radical mechanism or an α-fluoride elimination followed by a rearrangement have been discussed in the literature,[16e] but the absence of dimers, oligomers, and hydrosilylation products render these pathways unlikely.

The poor performance of the catalyst system in the HDF of **29** starkly contrasts the high reactivity attributed to fluorinated cumulenes. This is especially surprising, since **29** is the only substrate for which the titanium-catalyzed reaction differs significantly from a related stoichiometric reaction involving zirconium hydride complexes.[34] This indicates a substrate-specific deactivation pathway. Assuming an IE mechanism, two hydrometalation products **43a** and **43b** are possible (Scheme 10). While **43a** can undergo β-fluoride elimination to yield **30** and **32**, **43b** does not have a β-fluorine substituent and cannot continue the catalytic cycle. The



Scheme 10. Top: Proposed intermediates in the titanium-catalyzed hydrodefluorination of tetrafluoroallene (**29**). Bottom: Hydrometalation of **29** with Group 6 hydride complexes.

regioselectivity in this insertion step is therefore crucial to the successful catalysis. In the stoichiometric HDF using the Schwartz reagent, **30** was obtained in 47% yield.[34] Assuming 60% selectivity here, the turnover number would converge to 1.5, close to the experimental value of 1.2. As attempts to isolate a catalyst deactivation product **43b** failed, we studied the reactivity of **29** towards Group 6 hydride complexes (Scheme 10). As reported previously,[35] $[Cp(CO)_3MoH]$ and **29** form a hydrometalation product **44a** by addition of the metal center to the central carbon atom; compound **44a** undergoes a 1,3-fluorine migration affording **44b**. In contrast, the chromium congener forms insertion product **45** by addition of the metal to a terminal carbon atom and a subsequent 1,3-fluorine shift. Compound **45** 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 6). The bond angles and distances are within the expected range; the distances Cr–C1 = 2.105(2) Å and Cr–Cp = 1.839(2) Å are significantly shorter than the distances Mo–C2 = 2.252(2) Å and Mo–Cp = 2.000(4) Å in **44a**. Apparently, the chromium atom's smaller radius increases the steric bulk in its coordination sphere so that an addition of the metal fragment to the less

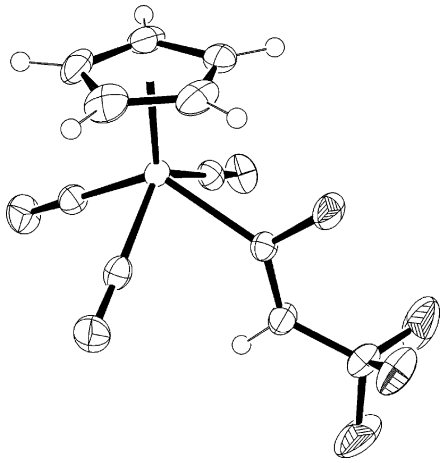


Figure 6. Molecular structure of **45** determined by single-crystal X-ray diffraction (C principal ellipse, F shaded octant, Cr plain ellipse, H circles, O cutout ellipse; thermal ellipsoids drawn at 50% probability).

sterically crowded primary carbon atom is strongly favored over an addition to the secondary carbon atom. As the steric trends in Groups 4 and 6 are very similar, the same selectivity issues are likely to be responsible for the titanium catalyst's poor performance.

Conclusion

In summary, we have developed a simple and inexpensive system for the catalytic C–F activation of fluoroalkenes, which exceeds all previously known systems in both activity and scope. Titanocene difluoride (**1a**) as a precatalyst was shown to effect the hydrodefluorination of a number of vinylic and allylic fluorides with varying efficiencies and selectivities. Optimization on the *E*/*Z* selectivity by introducing substituents to the titanocene cyclopentadienyl ligands was not successful, but demonstrated the importance of electron donation to the metal. This is consistent with mechanistic studies indicating a titanium(III) hydride as the active species; upon reaction with the substrate, titanocene(III) fluoride (**32**) 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 HDF of hexafluorocyclobutene (**17**). Conformational aspects of the insertion/elimination mechanism explain the observed substrate-dependent *E*/*Z* selectivity.

Experimental Section

Techniques: All reactions and manipulations were carried out in predried 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 com-

Table 2. Selected X-ray crystallographic data.

	1c	**1h**	**1f**	**1f**	**26a**	**32**	**45**
formula	$C_{12}H_{14}F_2SiTi$	$C_{22}H_8F_{12}Ti$	$C_{13}H_{18}F_2SiTi$	$C_{13}H_{18}F_2SiTi$	$C_{12}H_{10}F_2Fe$	$C_{50}H_{70}F_3O_5Ti_3$	$C_{11}H_6CrF_4O_3$
M_r	272.22	548.18	288.26	288.26	248.05	951.76	314.16
crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$	$C2/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$	$P2_1/c$
a [Å]	7.906(3)	20.957(5)	10.1318(17)	6.058(3)	5.7200(10)	16.390(8)	7.8156(11)
b [Å]	14.771(6)	5.7686(14)	11.1388(19)	11.799(6)	7.3943(13)	16.837(7)	14.074(2)
c [Å]	10.165(4)	16.298(4)	11.969(2)	19.594(10)	23.140(4)	17.204(8)	10.6116(15)
α [°]	90.00	90.00	90.00	75.534(10)	90.00	90.00	90.00
β [°]	98.626(9)	109.988(5)	99.710(4)	81.612(11)	90.919(4)	90.00	98.016(3)
γ [°]	90.00	90.00	90.00	86.056(12)	90.00	90.00	90.00
V [Å^3]	1173.7(9)	1851.6(8)	1331.4(4)	1341.0(11)	978.6(3)	4747(4)	1155.8(3)
T [K]	133(2)	133(2)	133(2)	133(2)	133(2)	133(2)	133(2)
Z	4	4	4	4	4	4	4
μ [mm^{-1}]	0.825	0.591	0.731	0.726	1.528	0.549	1.043
total reflns	18606	14381	14632	8571	15494	49085	17965
unique reflns	3593	2842	3931	3760	2994	8618	3535
R_{int}	0.0354	0.0173	0.0132	0.0815	0.0178	0.1022	0.0254
R_1 [$I>2\sigma(I)$]	0.0402	0.0303	0.0211	0.0748	0.0228	0.0713	0.0285
$wR(F^2)$ [$I>2\sigma(I)$]	0.1066	0.0838	0.0622	0.1847	0.0609	0.1849	0.0706
R_1 (all data)	0.0536	0.0340	0.0223	0.1252	0.0242	0.0970	0.0359
$wR(F^2)$ (all data)	0.1133	0.0865	0.0629	0.2167	0.0617	0.2140	0.0754
GOF on F^2	1.090	1.053	1.080	1.026	1.059	1.088	1.046

pounds was determined using pVT techniques or by condensing the gas into a weighed flask.

Chemicals: Diglyme, 1,4-dioxane, THF, [D$_8$]THF, and [D$_8$]toluene 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, toluene, and pentane were dried over activated alumina using an MBraun solvent system model MB SPS-800. [Cp_2TiF_2] (**1a**),[36] [Cp_2TiH] (**3a**),[22] [$(Me_3SiC_5H_4)_2TiCl_2$],[37] Me_3SnF,[10r] [$(Me_2SiC_5H_4)_2TiCl_2$],[38] [$(C_6F_5C_5H_4)_2TiCl_2$],[39] [$(Me_3SiC_5H_4)CpTiCl_2$],[40] [$(Dipp_2Nacnac)TiF_3$] (**1i**),[41] hexafluorocyclobutene (**17**),[42] (Trifluoroethenyl)benzene (**22**),[43] (trifluoroethenyl)ferrocene (**25**),[20] [$Cp_2Ti(\mu\text{-}SiH_2Ph)(\mu\text{-}H)TiCp_2$] (**31b**)[23a] tetrafluoroallene (**29**),[35] and [$Cp(CO)_3CrH$][44] were synthesized by literature procedures. [Cp_2TiF] (**32**) was synthesized by a modified literature procedure[45] using zinc instead of aluminum powder. Ph_2SiH_2 (**2a**),[46] $PhSiH_3$ (**2b**),[46] $PhMe_2SiH$ (**2c**, Alfa Aesar), Et_3SiH (**2d**, ABCR) and PMHS (**2e**, Alfa Aesar) were purchased or synthesized, dried (calcium hydride **2a**–**2d**, molecular sieves **2e**) and stored in a glovebox. [$(EtC_5H_4)_2TiCl_2$] (MCAT), [$(tBuC_5H_4)_2TiCl_2$] (MCAT), [(*R*,*R*)-(ebthi)TiF_2] (**1g**, Sigma–Aldrich), TiF_3 (**1j**, ABCR), TiF_4 (**1k**, ABCR), 1,1,3,3,3-pentafluoropropene (**5d**, SynQuest Labs), trifluoroethene (**13**, SCM Specialty Chemicals), and 1,1-difluoroethene (**14c**, SynQuest Labs) were obtained from commercial sources and used as received. Hexafluoropropene (**4**, Solvay Fluor), 3,3,3-trifluoropropene (**7**, Hoechst) and tetrafluoroethene (**12**, Bundesanstalt für Materialprüfung und -forschung) were obtained free of charge and used as received.

CCDC-874358 (**1c**), 874361 (**1h**), 874360 (**1f**; space group $P2_1/c$), 874359 (**1f**; space group $P\bar{1}$), 874362 (**26a**), 874363 (**32**) and 874364 (**45**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Instrumentation: ^{1}H, ^{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, respectively). Chemical shifts are reported in ppm (δ) relative to TMS (^{1}H and ^{13}C) and $CFCl_3$ (^{19}F), and were determined by reference to the residual solvent resonances (^{1}H and ^{13}C) or an external reference (^{19}F). IR spectra were obtained from a Nicolet iS10 FTIR spectrometer equipped with a Smart DuraSamplIR 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. Data collection, reduction and empirical absorption correction were performed using the SMART, SAINT and SADABS programs, respectively;[47] the SHELX program package[48] was used for structure solution and refinement (see Table 2 for structural details). ORTEP[49] and POV-RAY[50] were employed for structure visualization. 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* (EI) or an Agilent 6210 ESI-TOF, solvent flow rate 4 μL min^{-1}, spray voltage 4 kV, drying gas flow rate 10^5 Pa, all other parameters were adjusted for a maximum abundance of the relative $[M+H]^+$ (ESI).

Synthesis of bis(η^5-ethylcyclopentadienyl)difluorotitanium (1b): In a Schlenk flask equipped with a reflux condenser, dichlorobis(η^5-ethylcyclopentadienyl)titanium (310 mg, 1.02 mmol) and trimethyltin fluoride (384 mg, 2.10 mmol, 2.1 equiv) were refluxed in acetonitrile (20 mL) for 4 h.[27] After removal of the solvent in vacuo, the residue was sublimed at 130 °C and 10^{-3} mbar to give **1b** as a yellow powder. Yield: 85 %; m.p. 130 °C; ^{1}H NMR ($CDCl_3$): $\delta=6.36$ (m, 4H; C_5H_4), 6.01 (m, 4H; C_5H_4), 2.53 (q, $^3J(H,H)=7.8$ Hz, 4H; CH_2), 1.14 ppm (t, $^3J(H,H)=7.8$ Hz, 6H; CH_3); ^{13}C NMR ($CDCl_3$): $\delta=143.6$ (s, C_5H_4), 116.3 (s, C_5H_4), 115.1 (s, C_5H_4), 22.3 (s, CH_2), 13.1 ppm (s, CH_3); ^{19}F NMR ($CDCl_3$): $\delta=61.2$ ppm (s, 2F; TiF_2); IR (ATR): $\tilde{\nu}=3114$ (w), 2966 (m), 2933 (w), 2869 (w), 1499 (m), 1456 (m), 1427 (w), 1402 (w), 1369 (m), 1312 (w), 1236 (w), 1092 (w), 1058 (m), 1031 (m), 954 (w), 917 (m), 842 (s), 821 (s), 686 (w), 608 (w), 562 (vs), 543 cm^{-1} (vs); MS (EI, 40 °C): *m*/*z* (%): 272.0849 (30) $[M]^+$ ($C_{14}H_{18}F_2Ti$ requires 272.0856), 253 (19) $[M-F]^+$, 252 (31) $[M-HF]^+$, 232 (85) $[M-2HF]^+$, 229 (23) $[M-C_2H_4-CH_3]^+$, 179 (100) $[M-EtC_5H_4)]^+$, 159 (16) $[M-EtC_5H_4-HF)]^+$, 158 (21) $[M-EtC_5H_5-HF)]^+$, 151 (51) $[CpTiF_2]^+$, 145 (11 %), 132 (10) $[CpTiF]^+$, 106 (5) $[Et_2Ti]^+$, 93 (29) $[EtC_5H_4]^+$, 91 (45) $[Et_2Ti-CH_3]^+$, 86 (11) $[TiF_2]^+$, 78 (13) $[EtTiH]^+$, 77 (29) $[EtTi]^+$, 67 (6) $[TiF]^+$, 65 (8) $[C_5H_5]^+$; elemental analysis calcd (%) for $C_{14}H_{18}F_2Ti$: C 61.78, H 6.67; found: 61.48, H 6.61.

Synthesis of bis(η^5-*tert*-butylcyclopentadienyl)difluorotitanium (1c): In a Schlenk flask equipped with a reflux condenser, dichlorobis(η^5-*tert*-butylcyclopentadienyl)titanium (375 mg, 1.04 mmol) and trimethyltin fluoride (475 mg, 2.60 mmol, 2.6 equiv) were refluxed in acetonitrile (20 mL) for 6 h. After removal of the solvent in vacuo, the residue was sublimed at 130 °C and 10^{-3} mbar to give **1c** as a yellow powder. Yield: 85 %; m.p. 187 °C; ^{1}H NMR ($CDCl_3$): $\delta=6.37$ (m, 4H; C_5H_4), 6.17 (m, 4H; C_5H_4),

1.22 ppm (s, 18H; CH_3); ^{13}C NMR ($CDCl_3$): $\delta = 150.1$ (s, C_5H_4), 115.6 (s, C_5H_4), 114.8 (s, C_5H_4), 33.4 (s, $C(CH_3)_3$), 30.4 ppm (s, CH_3); ^{19}F NMR ($CDCl_3$): $\delta = 62.2$ ppm (s, 2F; TiF_2); IR (ATR): $\tilde{\nu} = 3109$ (w), 3097 (w), 2954 (m br), 2905 (w), 2874 (w), 1491 (m), 1460 (m), 1417 (w), 1397 (w), 1383 (w), 1358 (m), 1276 (m), 1202 (w), 1158 (m), 1058 (w), 1045 (m), 1022 (w), 928 (w), 915 (w), 894 (m), 844 (m), 813 (s), 688 (m), 610 (m), 566 (s), 542 cm^{-1} (vs); MS (EI, 70 °C): *m/z* (%): 328.1490 (41) $[M]^+$ ($C_{18}H_{26}F_2Ti$ requires 328.1482), 309 (7) $[M-F]^+$, 293 (29) $[M-HF-CH_3]^+$, 274 (4) $[M-HF_2-CH_3]^+$, 207 (100) $[M-t\mathrm{Bu}C_5H_4]^+$, 185 (25) $[M-t\mathrm{Bu}TiF_2]^+$, 172 (25) $[M-t\mathrm{Bu}C_5H_4-HF-CH_3]^+$, 121 (62) $[t\mathrm{Bu}C_5H_4]^+$, 105 (32) $[t\mathrm{Bu}Ti]^+$, 91 (14) $[t\mathrm{Bu}Ti-CH_3]^+$, and smaller fragment ions; elemental analysis calcd (%) for $C_{18}H_{26}F_2Ti$: C 65.86, H 7.98; found: 85.87, H 7.95.

Synthesis of bis[η⁵-(trimethylsilyl)cyclopentadienyl]difluorotitanium (1d): In a Schlenk flask equipped with a reflux condenser, dichlorobis[η⁵-(trimethylsilyl)cyclopentadienyl]-titanium (500 mg, 1.27 mmol) and trimethyltin fluoride (500 mg, 2.74 mmol, 2.2 equiv) were refluxed in acetonitrile (40 mL) for 7 h. 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 **1d** as a yellow powder. Yield: 89%. ^1H NMR identical to the literature;[51] ^{19}F NMR ($CDCl_3$): $\delta = 74.4$ ppm (s, 2F; TiF_2).

Synthesis of dimethylsilylene[bis(η⁵-cyclopentadienylidene)]difluorotitanium (1e): In a Schlenk flask equipped with a reflux condenser, dichloro[dimethylsilylenebis(η⁵-cyclopentadienylidene)]titanium (390 mg, 1.28 mmol) and trimethyltin fluoride (850 mg, 4.65 mmol, 3.6 equiv) were refluxed in acetonitrile (40 mL) for 7 h. 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 **1e** as yellow crystals. Yield: 52%. ^1H NMR identical to the literature;[51] ^{19}F NMR ($CDCl_3$): $\delta =$ 68.8 ppm (s, 2F; TiF_2).

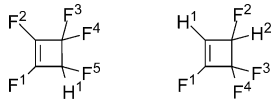
Synthesis of (η⁵-cyclopentadienyl)[η⁵-(trimethylsilyl)cyclopentadienyl]difluorotitanium (1f): In a Schlenk flask equipped with a reflux condenser, dichloro(η⁵-cyclopentadienyl)[η⁵-(trimethylsilyl)cyclopentadienyl]titanium (1.57 g, 4.89 mmol) and trimethyltin fluoride (1.78 g, 9.78 mmol, 2.0 equiv) were stirred in toluene (30 mL) at 80 °C for 4 h. After removal of the solvent in vacuo, the residue was sublimed at 130 °C and 10^{-3} mbar. Recrystallization of the sublimate from toluene/pentane (1:3) gave **1f** as yellow crystals. Yield: 90%; m.p. 142 °C (polymorph $P2_1/c$), 144 °C (polymorph $P\bar{1}$); ^1H NMR ([D₈]toluene): $\delta = 6.86$ (m, 2H; $C_5H_4SiMe_3$), 6.60 (m, 2H; $C_5H_4SiMe_3$), 6.54 (s, 5H; C_5H_5), 0.27 ppm (s, 9H; CH_3); ^{13}C NMR ([D₈]toluene): $\delta = 132.9$ (s, $CSiMe_3$), 126.1 (s, C_5H_5), 117.7 (s, $C_5H_4SiMe_3$), 116.5 (s, $C_5H_4SiMe_3$), −1.1 ppm (s, $SiMe_3$); ^{19}F NMR ([D₈]toluene): $\delta = 93.0$ ppm (s, 2F; TiF_2); IR (ATR): $\tilde{\nu} = 3125$ (w), 3090 (w), 3083 (w), 2956 (m), 1450 (m), 1400 (m), 1369 (m), 1244 (s), 1186 (m), 1034 (s), 1011 (m), 906 (m), 837 (vs), 821 (vs), 752 (s), 697 (m), 630 (s), 608 (vs), 577 cm^{-1} (vs); MS (ESI-TOF): *m/z* calcd for $C_{13}H_{18}F_2TiSiNa$: 311.0523; found: 311.0604 $[M+Na]^+$; *m/z* calcd for $C_{26}H_{36}F_4Ti_2Si_2Na$: 599.1148; found: 599.1303 $[M_2+Na]^+$.

Synthesis of bis[η⁵-(pentafluorophenyl)cyclopentadienyl]difluorotitanium (1i): In a Schlenk flask equipped with a reflux condenser, dichlorobis[η⁵-(pentafluorophenyl)cyclopentadienyl] titanium (279 mg, 0.48 mmol) and trimethyltin fluoride (252 mg, 1.38 mmol, 2.9 equiv) were refluxed in acetonitrile (5 mL) for 12 h. Upon cooling to room temperature, yellow crystals of **1i** separated, which were filtered off, washed with acetonitrile (10 mL) and sublimed (190 °C, 10^{-3} mbar). Yield: 19%; m.p. 219 °C; ^1H NMR ([D₈]THF): $\delta = 6.76$ ppm (m, 4H; C_5H_4); $^{13}C\{^1H\}$ NMR ([D₈]THF): $\delta = 117.4$ (s, C_5H_4), 116.3 ppm (s, C_5H_4); $^{13}C\{^{19}F\}$ NMR ([D₈]THF): $\delta = 145.1$ (s, C_6F_5), 140.2 (s, C_6F_5), 137.9 ppm (s, C_6F_5); ^{19}F NMR ([D₈]THF): $\delta = 110.4$ (br s, 2F; TiF_2), −149.0 (br d, $J = 18.2$ Hz, 4F; C_6F_5), −157.6 (tt, $J = 20.9$ Hz, $J = 1.8$ Hz, 2F; C_6F_5), −165.2 ppm (m, 4F; C_6F_5); IR (ATR): $\tilde{\nu} = 3152$ (w), 3118 (vw), 1660 (w), 1622 (w), 1534 (m), 1491 (s), 1415 (m), 1385 (w), 1342 (w), 1321 (vw), 1263 (vw), 1235 (w), 1136 (vw), 1106 (w), 1086 (w), 1056 (s), 979 (s), 931 (w), 911 (m), 879 (w), 860 (m), 824 (s), 782 (s), 676 (vw), 618 (w), 607 (w), 574 (s), 560 cm^{-1} (s); MS (EI, 150 °C): *m/z* (%): 547.9893 (7) $[M]^+$ ($C_{22}H_8F_{12}Ti$ requires 547.9914), 529 (1) $[M-F]^+$, 336 (3) $[M-C_6F_4C_5H_4]^+$, 317 (53) $[M-C_6F_5C_5H_4]^+$, 300 (3) $[M-C_6F_5C_5H_4-F]^+$, 231 (82) $[M-C_6F_5C_5H_4TiF_2]^+$, 212 (36) $[M-C_6F_5C_5H_4TiF_2-F]^+$, 211 (52) $[M-C_6F_5C_5H_4TiF_2-HF]^+$, 205 (42) $[M-C_6F_5C_5H_4TiC_5H_4]^+$, 193 (100) $[M-C_6F_5C_5H_4TiF_2]^+$, and smaller fragment ions.

Catalytic hydrodefluorination: Substrates, conditions and products are listed in Table 1 in the Supporting Information. A similar procedure was applied for all substrates except **22** and **25**: A single-necked flask equipped with a J. Young PTFE valve was charged with catalyst, silane, and solvent. After degassing, the mixture was heated until the color changed from yellow to purple to green (no color change was observed when employing catalysts **1i–1k**). The substrate was then condensed onto the frozen solution, which was warmed to the desired temperature and stirred for a given period of time under autogenous pressure. Fractional condensation of the reaction mixture through two subsequent traps kept at −78 °C (−30 °C for the HDF of **17**) and −196 °C, respectively, gave the product mixture in the colder 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 **12–14** and **17**) in $CDCl_3$. The yields were determined from NMR spectra by integration of product resonances versus the internal standard.

HDF products were identified by NMR spectroscopy, using literature data for **5a**,[52] **5b**,[52] **5c**,[17a] **6a**,[53] **6b**,[53] **6c**,[53] **6d**,[17a] **6e**,[54] **8**,[55] **9a**,[55] **9b**,[55] **10**,[54] **14a**,[56] **14b**,[56] **15**,[56] **17**,[57] **18a**,[58] **19a**,[58] **20**,[58] **21**,[59] **23a,b**,[60] **24a,b**,[61] **25**[62] and **30**[34] or by comparison with authentic samples of **4**, **5d**, **12**, **13**, **14c**, **28** and **29**.

Data for 18b (Scheme 11): ^1H NMR ($CDCl_3$): $\delta = 5.44$ ppm (dddd, $^2J(H^1,F^5) = 63.6$ Hz, $^4J(H^1,F^2) = 17.4$ Hz, $^3J(H^1,F^1) = 4.8$ Hz, $^3J(H^1,F^3) = 1.4$ Hz, 1H; H^1); ^{19}F NMR ($CDCl_3$): $\delta = -113.1$ (ddddd, $^2J(F^3,F^4) = 198.8$ Hz, $^4J(F^3,F^1) = 20.2$ Hz, $^3J(F^3,F^5) = 17.5$ Hz, $^3J(F^3,F^2) = 1.8$ Hz, $^3J(F^3,H^1) = 1.4$ Hz, 1F; F^3), −119.6 (dddd, $^2J(F^4,F^3) = 198.8$ Hz, $^4J(F^4,F^1) = 17.5$ Hz, $^3J(F^4,F^5) = 15.3$ Hz, $^3J(F^4,F^2) = 10.8$ Hz, 1F; F^4), −122.5 (ddddd, $^4J(F^1,F^5) = 20.2$ Hz, $^4J(F^1,F^4) = 17.5$ Hz, $^3J(F^1,F^2) = 10.8$ Hz, $^3J(F^1,H^1) = 4.1$ Hz, $^3J(F^1,F^5) = 2.3$ Hz, 1F; F^1), −127.4 (dtt, $^4J(F^2,H^1) = 17.5$ Hz, $^3J(F^2,F^1) = 10.8$ Hz, $^3J(F^2,F^3) = 1.8$ Hz, 1F; F^2), −187.1 ppm (ddddd, $^2J(F^5,H^1) = 63.4$ Hz, $^3J(F^5,F^3) = 17.5$ Hz, $^3J(F^5,F^4) = 15.3$ Hz, $^3J(F^5,F^1) = 2.3$ Hz, $^4J(F^5,F^2) = 1.8$ Hz, 1F; F^5); supported by ^{19}F COSY.



18b 19b

Scheme 11. Numbering schemes for 1,2,3,3,4-pentafluorocyclobutene (**18b**) and 1,3,4,4-tetrafluorocyclobutene (**19b**).

Data for 19b (Scheme 11): ^1H NMR ($CDCl_3$): $\delta = 5.85$ (ddddd, $^4J(H^1,F^3) = 11.9$ Hz, $^4J(H^1,F^4) = 8.7$ Hz, $^3J(H^1,F^1) = 7.8$ Hz, $^3J(H^1,F^2) = 0.9$ Hz, $^3J(H^1,H^2) = 0.9$ Hz, 1H; H^1), 5.38 ppm (dddd, $^2J(H^2,F^2) = 62.3$ Hz, $^4J(H^2,F^1) = 19.2$ Hz, $^3J(H^2,F^3) = 1.8$ Hz, $^3J(H^2,H^1) = 0.9$ Hz, 1H; H^2); ^{19}F NMR ($CDCl_3$): $\delta = -102.1$ (dddd, $^4J(F^1,H^2) = 18.9$ Hz, $^3J(F^1,F^4) = 8.5$ Hz, $^3J(F^1,H^1) = 7.7$ Hz, $^4J(F^1,F^2) = 5.0$ Hz, 1F; F^1), −111.0 (dddd, $^2J(F^3,F^4) = 205.6$ Hz, $^3J(F^3,F^2) = 18.0$ Hz, $^4J(F^3,H^1) = 11.7$ Hz, $^3J(F^3,H^2) = 1.8$ Hz, 1F; F^3), −119.6 (dddd, $^2J(F^4,F^3) = 205.6$ Hz, $^3J(F^4,F^2) = 14.8$ Hz, $^4J(F^4,H^1) = 8.7$ Hz, $^3J(F^4,F^1) = 8.5$ Hz, 1F; F^4), −182.8 ppm (ddddd, $^2J(F^2,H^2) = 62.5$ Hz, $^3J(F^2,F^3) = 18.0$ Hz, $^3J(F^2,F^4) = 14.8$ Hz, $^4J(F^2,F^1) = 5.0$ Hz, $^3J(F^2,H^1) = 0.9$ Hz, 1F; F^2); ^{13}C NMR ($CDCl_3$): $\delta = 153.3$ (dtdd, $^1J(C,F) = 352$ Hz, $^2J(C,F) = 26$ Hz, $^3J(C,F) = 21$ Hz, $^3J(C,H) = 9$ Hz, =CF), 118.1 (ddd, $^1J(C,F) = 282$ Hz, $^1J(C,F) = 278$ Hz, $^2J(C,F) = 19$ Hz, $^3J(C,H)$ unresolved due to overlap with a signal of **19a**, CF_2), 116.8 (ddddd, $^1J(C,H) = 191$ Hz, $^2J(C,F) = 24$ Hz, $^3J(C,F) = 19$ Hz, $^3J(C,F) = 12$ Hz, $^2J(C,F) = 4.3$ Hz, =CH), 87.3 ppm (ddddd, $^1J(C,F) = 226$ Hz, $^1J(C,H) = 186$ Hz, $^2J(C,F) = 30$ Hz, $^2J(C,F) = 26$ Hz, $^3J(C,F) = 21$ Hz, CHF).

Catalytic hydrodefluorination of trifluoroethenylbenzene (22): A single-necked flask equipped with a J. Young PTFE valve was charged with **1a** (10.8 mg, 0.05 mmol, 5 mol%), **2a** (203 mg, 1.10 mmol, 1.1 equiv), and THF (5.0 mL). After degassing, the mixture was heated until the color changed to blue-green and **22** (158 mg, 1.00 mmol) was added by syringe. The reaction mixture was degassed again and stirred at 65 °C for 10 h. Subsequently, water (5 mL) was added and the mixture was extracted with pentane (3×5 mL). The combined extracts were washed with water, dried over sodium sulfate and filtered through a pad of silica. Fractional condensation through two subsequent traps kept at −78 °C and −196 °C,

respectively, afforded a mixture of **23a**, **23b**, **24a**, **24b** and **24c** (2:1:0.0072:0.0050:0.0094) in the colder trap. Yield: 79%.

Catalytic hydrodefluorination of trifluoroethenylferrocene (25): A single-necked flask equipped with a J. Young PTFE valve was charged with **1a** (48.1 mg, 0.22 mmol, 5 mol%), **2a** (946 mg, 5.13 mmol, 1.2 equiv) and dioxane (2.0 mL). After degassing, the mixture was heated until the color changed to blue-green. A solution of **25** (1.18 g, 4.43 mmol) in dioxane (35 mL) was added. The reaction mixture was degassed again and stirred at 90 °C for 66.5 h. Subsequently, the solvent was removed in vacuo and the crude product was purified by column chromatography on silica gel with pentane as eluent to give **26a**. Yield: 16%; m.p. 63 °C; ^{1}H NMR ($CDCl_3$): $\delta = 6.54$ (dd, $^2J(H,F) = 74.0$ Hz, $^3J(H,F) = 17$ Hz, 1H; CF=CFH), 4.35 (brs, 2H; C_5H_4), 4.28 (brs, 2H; C_5H_4), 4.23 ppm (s, 5H; C_5H_5); ^{13}C NMR ($CDCl_3$): $\delta = 148.0$ (dd, $^1J(C,F) = 245.4$ Hz, $^2J(C,F) = 10.5$ Hz, C_2F_2H), 130.8 (dd, $^1J(C,F) = 253.0$ Hz, $^2J(C,F) = 15.8$ Hz, C_2F_2H), 74.0 (dd, $^2J(F,F) = 25.4$ Hz, $^3J(F,F) = 2.9$ Hz, ipso), 69.6 (s, C_5H_5), 69.3 (s, C_5H_4), 65.3 ppm (t, $J(C,F) = 2.4$ Hz, C_5H_4); ^{19}F NMR ($CDCl_3$): $\delta = -134.6$ (t, $^3J(F,F) = 16.2$ Hz, $^3J(F,H) = 16.2$ Hz, 1F; C_5H_4CF=CFH), −164.2 ppm (ddd, $^2J(F,H) = 73.8$ Hz, $^3J(F,F) = 16.2$ Hz, $^3J(F,H) = 3.6$ Hz, 1F; C_5H_4CF=C*F*H); IR (ATR): $\tilde{\nu} = 3117$ (w), 3083 (vw), 2955 (w), 2924 (m), 2850 (w), 1747 (vw), 1702 (m), 1537 (w), 1476 (m), 1381 (m), 1308 (m), 1277 (m), 1225 (w), 1130 (s), 1103 (m), 1072 (s), 1029 (m), 999 (m), 901 (s), 867 (w), 818 (s). 788 (s). 766 (s), 659 (m), 571 cm^{-1} (m); MS (EI, 30 °C): *m/z* (%): 248.0094 (100) $[M]^+$ ($C_{12}H_{10}F_2Fe$ requires 248.0100), 153 (24) $[M-FeF-HF]^+$, 152 (13) $[M-Fe-2\,HF]^+$, 140 (124) $[C_5H_5FeF]^+$, 124 (6) $[M]^{2+}$, 108 (6) $[M-C_5H_5FeF]^+$, 89 (51) $[M-C_5H_5FeF_2]^+$, 63 (10) $[C_2F_2H]^+$, and smaller fragment ions; elemental analysis calcd (%) for $C_{12}H_{10}F_2Fe$: C 58.10, H 4.06; found: 59.01, H 4.21.

*Data for **26b**, identified from the crude product*: ^{1}H NMR ($CDCl_3$): $\delta =$ 7.26 (dd, $^2J(H,F) = 75.8$ Hz, $J = 3.2$ Hz, 1H; CF=CFH), 4.57 (brs, 2H; C_5H_4), 4.34 (brs, 5H; C_5H_5), 4.31 ppm (brs, 2H; C_5H_4); ^{19}F NMR ($CDCl_3$): $\delta = -161.4$ (d, $^3J(F,F) = 126.4$ Hz, 1F; C_5H_4CF=CFH), −179.5 (dd, $^3J(F,F) = 126.4$ Hz, $^2J(F,H) = 75.6$ Hz, 1F; C_5H_4CF=C*F*H).

*Data for **27**, identified from the crude product*: ^{1}H NMR ($CDCl_3$): $\delta =$ 6.55 (dd, $^2J(H,F) = 83$ Hz, $^3J(H,H) = 5$ Hz, 1H; ArCH=CF*H*), 5.33 (dd, $^3J(H,F) = 45$ Hz, $^3J(H,H) = 5$ Hz, 1H; ArC*H*=CFH), 4.44 (brs, 2H; C_5H_4), 4.35 (brs, 2H; C_5H_4), 4.21 ppm (brs, 5H; C_5H_5); ^{19}F NMR ($CDCl_3$): $\delta =$ −125.7 (dd, $^2J(H,F) = 83$ Hz, $^3J(F,H) = 44$ Hz, 1F; ArCH=CFH).

Stoichiometric hydrodefluorination of 4 using 31b: [D$_8$]THF (0.5 mL) and **4** (14.0 mg, 93.3 μmol, 1.9 equiv) at −196 °C were condensed into a J. Young NMR tube containing **31b** (20.2 mg, 48.5 μmol). The tube was warmed to −90 °C, shaken, and introduced into 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 NMR resonances: Start (−78 °C): **4**: 95%, **5a**: 3.4%, **5b**: 4.6%; 1 h (−30 °C): **4**: 87%, **5a**: 5.8%, **5b**: 7.5%; 2 h (−10 °C): **4**: 73%, **5a**: 13%, **5b**: 13%; 2.5 h (+20 °C): **4**: 63%, **5a**: 19%, **5b**: 18%; 19 h (+20 °C): **4**: 0%, **5a**: 51%, **5b**: 38%, **28a**: 11%.

Isolation of [Cp$_2$TiF (32)] from the reaction of 4 with 31b: THF (2 mL) and **4** (1 mmol, approx. 10 equiv) were condensed into a Schlenk tube containing **31b** (ca. 20 mg, 130 μmol) held at −196 °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 **32** separated upon overnight cooling to −80 °C. The yield was not determined.

Stoichiometric hydrodefluorination of 4 using 3a: [D$_8$]THF (0.5 mL) and **4** (4.2 mg, 28 μmol, 1.9 equiv) were condensed ino a J. Young NMR tube containing **3a** (5.2 mg, 15 μmol) held at −196 °C. The tube was warmed to −80 °C, shaken and allowed to warm to room temperature within 10 min. NMR and EPR spectra were recorded, the relative amounts of starting material and HDF products were determined by integration of ^{19}F NMR resonances: 10 min (RT): **4**: 0%, **5a**: 56%, **5b**: 31%, **6a**: 12%; EPR: broad singlet at $g = 1.979(3)$, identical to literature data for **32**.[26]

(η^5-Cyclopentadienyl)[η^1-{(*Z*)-1,3,3,3-tetrafluoropropenyl}]tricarbonylchromium (45): pentane (20 mL) and **29** (5.0 mmol, 2.1 equiv) were added to a Schlenk flask charged with tricarbonyl(η^5-cyclopentadienyl)-hydridochromium (475 mg, 2.35 mmol) 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 **45** as yellow crystals. Yield: 28%; m.p. 98 °C (decomp); ^{1}H NMR ([D$_8$]toluene): $\delta = 5.31$ (dq, $^3J(H,F) = 46.0$ Hz, $^3J(H,F) = 7.7$ Hz, 1H; HC=CF_3), 3.99 ppm (brs, 5H; C_5H_5); ^{13}C NMR ([D$_8$]toluene): $\delta = 244.0$ (s, CO), 237.2 (s, CO), 204.9 (qd, $^1J(C,F) = 360.4$ Hz, $^3J(C,F) = 5.75$ Hz, CrCF), 121.4 (qd, $^1J(C,F) = 271.7$ Hz, $^3J(C,F) = 9.58$ Hz, CF_3), 118.0 (qd, $^2J(C,F) = 32.6$ Hz, $^3J(C,F) = 3.35$ Hz, =CH), 90.3 ppm (s, C_5H_5); ^{19}F NMR ([D$_8$]toluene): $\delta = -13.8$ (qd, $^3J(F,H) = 46.0$ Hz, $^4J(F,F) = 14.2$ Hz, 1F; CrCF), −57.3 ppm (dd, $^4J(F,F) = 14.2$ Hz, $^3J(F,H) = 7.9$ Hz, 3F; CF_3); IR (ATR): $\tilde{\nu} = 3135$ (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 cm^{-1} (s); MS (EI, 40 °C): *m/z* (%): 313.9673 (4) $[M]^+$ ($C_{11}H_6F_4CrO_3$ requires 313.9658), 286 (2) $[M-CO]^+$, 258 (6) $[M^+-2\,CO]^+$, 230 (14) $[M^+-3\,CO]^+$, 211 (6) $[M^+-3\,CO-F]^+$, 136 (100) $[CpCrF]^+$, 117 (5) $[CpCr]^+$, 90 (3) $[CrF_2]^+$, 71 (18) $[CrF]^+$, 52 (13) $[Cr]^+$.

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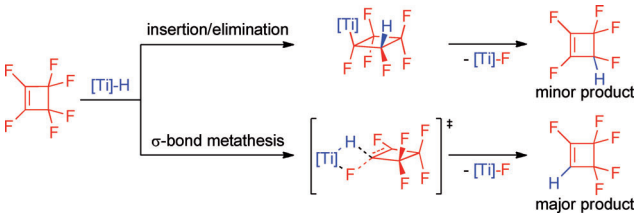

The broad application of the catalytic hydrofluorination of fluoroalkenes by the system $[Cp_2TiF_2]$/silane is demonstrated. Isolated yields up to 79% could be obtained for various substrates. Mechanistic studies indicate two competing reaction mechanisms.

C–F Bond Activation

*M. F. Kuehnel, P. Holstein, M. Kliche, J. Krüger, S. Matthies, D. Nitsch, J. Schutt, M. Sparenberg, D. Lentz** ..... ▮▮▮▮–▮▮▮▮

Titanium-Catalyzed Vinylic and Allylic C–F Bond Activation—Scope, Limitations and Mechanistic Insight