localized in the p orbital perpendicular to the ring plane, while in **1** the highest spin density is in the ring plane.

Photolysis of 4-iodo-2,3,5,6-tetrafluoroazidobenzene (**7**) offers an access to the until now unknown C_6F_4N potential energy surface and to the unusual high-spin nitrene radical **1**. The influence of different topologies and substituents on the spin state of nitrene radicals will be investigated in future studies.

Experimental Section

Matrix experiments were carried out according to standard techniques[22] using a Sumitomo Heavy Industries RDK-408D closed-cycle cryostat. The lowest temperature available with this system is 2.7 K. Matrices were produced by codeposition of a large excess of neon or argon (Messer-Griesheim, 99.9999 %) and the substance to be isolated on top of a cold CsI window. During deposition of argon matrices the temperature of the window was maintained at 30 K. Argon matrices for ESR spectroscopy were deposited at 13 K on a 2 mm OFHC-copper rod, cooled by an APD-HC2 closed-cycle cryostat. IR spectra were recorded with a Bruker Equinox 55 FTIR spectrometer with a resolution of 0.5 cm^{-1} in the range of 400 – 4000 cm^{-1}. ESR spectra were recorded with a Bruker Elexsys E500 spectrometer. Irradiations were carried out with a Gräntzel low-pressure mercury lamp (254 nm) and an Osram HBO-500-W/2 high-pressure mercury arc lamp in an Oriel housing with quartz optics, a dichroic mirror, and a Schott cutoff filter (320 nm). DFT calculations were performed with the Gaussian 98 suite of programs.[23]

4-Iodo-2,3,5,6-tetrafluoroaniline: Yellow HgO (12.8 g, 59.1 mmol) was added to a solution of 2,3,5,6-tetrafluoroaniline (12.8 g, 77.6 mmol) in ethanol (200 mL). The solution was vigorously stirred and iodine (19.8 g, 78.0 mmol) added. The mixture was stirred overnight and filtered over celite. After addition of Na_2SO_3 (1 g) the solution was concentrated to a residual volume of 50 mL using a rotary evaporator. Water (200 mL) was added and the precipitate was filtered off. Recrystallization from 25 % ethanol in water and subsequent drying in vacuo yielded 4-iodo-2,3,5,6-tetrafluoroaniline (16.2 g, 55.7 mmol, 72 %) as dark crystals. MS: m/z(%): 291 (M^+, 100), 164 (50), 144 (25), 137 (60), 127 (30), 117 (25), 69 (20).

4-Iodo-2,3,5,6-tetrafluoroazidobenzene (**7**): 4-Iodo-2,3,5,6-tetrafluoroaniline (3.0 g, 10.3 mmol) was dissolved in trifluoroacetic acid (30 mL) and cooled to 0 °C. A solution of sodium nitrite (0.81 g, 11.7 mmol) in water (15 mL) was slowly added while stirring and cooling with an ice bath. The solution was stirred for further 15 min at 0 °C. A solution of sodium azide (0.75 g, 11.5 mmol) in water (15 mL) was added to the stirred solution, which was subsequently stirred for 1 h at room temperature. After addition of ether (100 mL) the organic phase was washed with water and dilute aqueous NaOH, dried (Na_2SO_4), and evaporated. Chromatography (silica/pentane) yielded **7** (2.18 g, 67 %) as a colorless oil. MS: m/z (%): 317 (M^+, 10), 289 (30), 162 (100), 127 (30), 117 (20), 112 (10), 98 (25), 69 (25). ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 66.3$ (t, $J = 28.0$ Hz), 120.5 (tt, $J = 2.9$ Hz, 12.3 Hz), 140.0 (dm, 256.4 Hz), 147.2 ppm (dm, 248.1 Hz). IR (Ar, 3 K): $\tilde{\nu}$ (%): 2229.9 (5), 2196.8 (5), 2130.9 (100), 2112.4 (18), 1634.5 (10), 1492.2 (95), 1478.4 (49), 1307.6 (15), 1223.2 (31), 1012.1 (31), 1001.9 (13), 974.3 (39), 955.3 (6), 807.8 (11), 768.3 (22), 664.5 cm^{-1}(5).

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Conversion of Hexafluoropropene into 1,1,1-Trifluoropropane by Rhodium-Mediated C−F Activation**

Thomas Braun,* Daniel Noveski, Beate Neumann,
and Hans-Georg Stammler

Interest in the activation of carbon – fluorine bonds by transition metal centers has been increasing dramatically over the last decade.[1] Recent discoveries include the stochiometric[2] and catalytic[3, 4] derivatization of aromatic compounds

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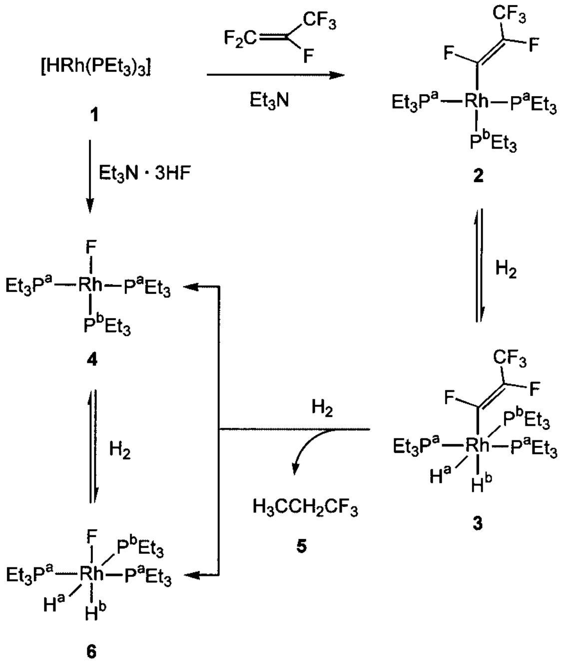
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

by C–F activation.[1] One of the major achievements was the catalytic conversion of hexafluorobenzene into pentafluorobenzene with $[HRh(PMe_3)_4]$ as catalyst.[4] However, there are only a few examples of the activation of a C–F bond in fluorinated olefins reported.[1c, 5–8] The reactions include the activation of hexafluoropropene with $[H_2Ir(PPh_3)_2]_3PW_{12}O_{40}$, which led to the generation of a propenyl complex.[5b] The formation of organofluorine compounds by C–F activation of olefins, followed by derivatization and cleavage reactions within the coordination sphere of the metal is even less developed.[1c, 6–8] With regard to the defluorination of perfluorinated olefins, Jones et al. reported that hexafluoropropene can be converted into propane by using seven equivalents of $[(\eta^5\text{-}C_5Me_5)_2ZrH_2]$. The reaction initially forms the complex $[(\eta^5\text{-}C_5Me_5)_2ZrHC_3H_7)]$, which is then allowed to react with hydrogen to yield propane.[6] In a recent report Whittlesey et al. described the reaction of hexafluoropropene with a ruthenium dihydride, which led to a mixture of lower fluorinated olefins.[7]

Herein we describe the selective conversion of a perfluorinated olefin into a partially fluorinated alkane by metal-induced hydrodefluorination exclusively at the double bond.[2e] We show that hexafluoropropene can selectively and under very mild conditions be activated at a rhodium center to give the propenyl complex **2** (Scheme 1). On treatment of **2** with hydrogen, the fluorinated vinyl unit is converted into a nonfluorinated alkyl group, and 1,1,1-trifluoropropane (**5**) together with the rhodium fluoride complex **4** is obtained.



Scheme 1. The synthesis and reactivity of **2**.

Table 1. Selected spectroscopic data for **2–6**; ^1H NMR: 500 MHz, ^{19}F NMR: 470.4 MHz, ^{31}P NMR 202.4 MHz; labeling of atoms as in Scheme 1.

2: ^{19}F NMR (C_6D_6): $\delta = -64.5$ (m, 3F; CF_3), -95.4 (dm, $^3J(F,F) = 117.7$ Hz, 1F; CF), -174.4 ppm (dm, $^3J(F,F) = 117.1$ Hz, 1F; CF); ^{31}P NMR (C_6D_6): $\delta = 18.5$ (m, P^b), 15.5 ppm (m, P^a).

3: ^1H NMR (C_6D_6): $\delta = -11.3$ (dm, $^2J(P^b,H) \approx 150$ Hz, 1H; H^a), -12.0 ppm (dm, $^1J(Rh,H) \approx 20$ Hz, 1H; H^b); ^{19}F NMR (C_6D_6): $\delta = -63.6$ (m, 3F; CF_3), -87.2 (dm, $^3J(F,F) = 118.9$ Hz, 1F; CF), -166.2 ppm (dm, $^3J(F,F) = 118.2$ Hz, 1F; CF); ^{31}P NMR (C_6D_6): $\delta = 28.5$ (dm, $^1J(Rh,P) \approx 98$ Hz; P^a), 11.8 ppm (m; P^b).

4: ^{19}F NMR ($[D_8]$toluene, 213 K): $\delta = -277$ ppm (dm, br, $^1J(P^b,F) \approx 188$ Hz); ^{31}P NMR ($[D_8]$toluene, 213 K): $\delta = 45.2$ (ddt, $^2J(P,F) = 187.0$, $^1J(Rh,P) = 180.2$, $^2J(P,P) = 42.2$ Hz; P^b), 25.1 ppm (ddd, $^1J(Rh,P) = 138.3$, $^2J(P,F) = 22.0$, $^2J(P,P) = 42.2$ Hz; P^a).

5: ^1H NMR (C_6D_6): $\delta = 0.58$ (t, $^3J(H,H) = 7.5$ Hz, 3H; CH_3), 1.45 ppm (m, 2H; CH_2); ^{19}F NMR (C_6D_6): $\delta = -69.1$ ppm (t, $^3J(F,H) = 10.4$ Hz).

6: ^1H NMR (C_6D_6): $\delta = -9.6$ (dm, $^2J(P^b,H) = 154.7$ Hz, 1H; H^a), -24.9 ppm (ddm, $^2J(F,H) \approx 94$, $^1J(Rh,H) = 20$ Hz, 1H; H^b); ^{19}F NMR (C_6D_6): $\delta = -274$ ppm (m, br); ^{31}P NMR (C_6D_6): $\delta = 28.9$ (ddm, $^1J(Rh,P) = 107.7$, $^2J(P,P) = 18.4$ Hz; P^a), 12.2 ppm (m; P^b).

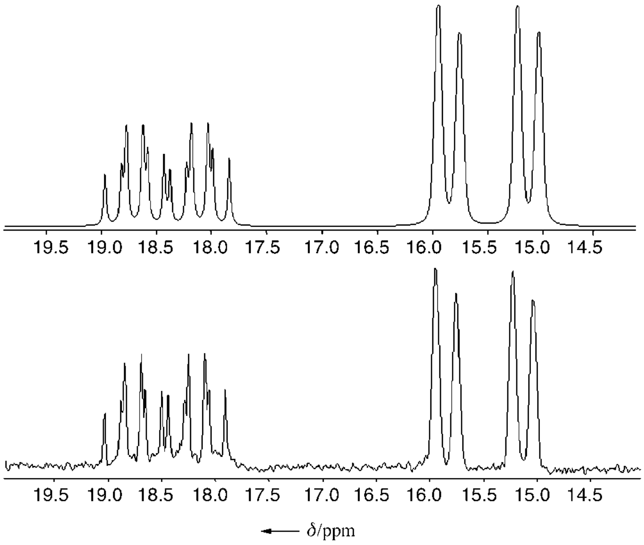


Figure 1. ^{31}P NMR spectrum of complex **2**; observed (bottom) and simulated (top) using the following coupling constants (Hz): $^1J(Rh,P^a) = 145.7$, $^3J(P^a,F) = 6.0$, $^4J(P^a,F) = 4.6$, $^5J(P^a,F) = 4.0$, $^2J(P^a,P^b) = 39.1$, $^1J(Rh,P^b) = 119.3$, $^3J(P^b,F) = 27.2$, $^4J(P^b,F) = 0.2$, $^5J(P^b,F) = 0.1$ Hz; labeling of atoms as in Scheme 1.

Treatment of the rhodium hydrido complex **1** with hexafluoropropene in benzene in the presence of triethylamine results in the fast and regioselective formation of the C–F activation product **2** (Scheme 1). Note that treatment of $[HRh(CO)(PPh_3)_3]$ with tetrafluoroethene leads to the insertion of the olefin into the rhodium–hydrogen bond.[9] The proposed structure for **2** is supported by the ^{31}P and ^{19}F NMR spectroscopic data (Table 1). The spectra are of higher order, and coupling constants have been determined by simulation of the ^{31}P NMR spectrum by using the program g-NMR (Figure 1).[10] The ^{19}F NMR spectrum shows three resonance signals at $\delta = -64.5$, -95.4, and -174.4 ppm with a ratio 3:1:1, and thus reveals the presence of the propenyl ligand. The chemical shifts and the coupling constants of the olefinic fluorine atoms ($J = 117.1$ Hz) indicate their *trans* orientation.[5b, 11] The configuration at the double bond in **2** was confirmed by an X-ray diffraction analysis at low temperature (Figure 2).[12] The rhodium–carbon bond in **2** (2.029(4) Å) is

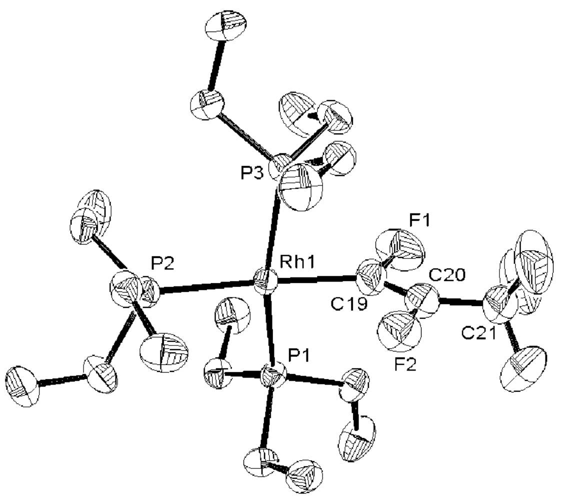


Figure 2. Molecular structure of **2** (ORTEP plot) in the crystal. Selected bond lengths [Å] and angles [°]: Rh1-C19 2.029(4), C19-C20 1.303(7), C19-F1 1.429(5), C20-F2 1.423(6); Rh1-C19-F1 120.8(3), Rh1-C19-C20 130.5(4), C20-C19-F1 108.7(4), C19-C20-F2 114.0(4), C19-C20-C21 136.8(6), C21-C20-F2 109.2(5).

shorter than the corresponding bond in the rhodium(I) complex *trans*-[Rh{C(CN)=C(C_6H_4OMe)$_2$}(CO)(P*i*Pr$_3$)$_2$] (**7**; (2.106(4) Å), which bears a nonfluorinated vinyl ligand.[13] The C–C double bond in **2** (1.303(7) Å) is likewise shorter than the C–C double bond **7** (1.367(3) Å), but is comparable to the C–C double bond length in hexafluoropropene (1.31 Å), which was determined by electron diffraction in the vapor phase.[13, 14]

Upon addition of hydrogen to a solution of **2** in C_6D_6 at 300 K a new set of signals emerges in the NMR spectra, which corresponds to the dihydrido complex **3**. Compound **3** could not be isolated in the solid state, and a solution of **3** is only stable for about 30 min at room temperature. Under vacuum, **3** loses hydrogen, and the re-formation of **2** is observed. The ^{1}H NMR spectrum of **3** exhibits resonance signals for the hydrido ligands at $\delta = -11.3$ ($^2J(\mathrm{P,H}_{trans}) \approx 150$ Hz) and -12.0 ppm. This finding confirms the *cis-mer* configuration and indicates the presence of an anionic bound carbon ligand *trans* to one of the hydrido ligands.[4, 15, 16] The ^{31}P NMR spectrum is of higher order and shows two multiplets at $\delta = 28.5$ and $\delta = 11.8$ ppm with a phosphorus–phosphorus coupling constant ^2J(P,P) of about 25 Hz, which is consistent with the presence of a Rh^{III} compound (Table 1).[15–17]

In the presence of hydrogen, the formation of the compounds **4**–**6** is observed after a reaction time of 30 min. The presence of a base (Et_3N or Cs_2CO_3) has almost no influence on the product distribution. Assignments in the NMR spectra are partially based on ^{31}P–^{1}H and ^{1}H–^{1}H COSY NMR spectra. The ^{19}F NMR spectrum of **4** at 213 K displays a broad doublet at $\delta = -277$ ppm with a coupling constant of $^2J(\mathrm{P,F}_{trans}) \approx 188$ Hz, which is consistent with a nonbridging fluoro ligand *trans* to a phosphane ligand.[18] The ^{31}P NMR spectrum shows two signals at $\delta = 45.2$ and $\delta = 25.1$ ppm for the phosphorus nuclei with the expected coupling pattern (Table 1).[15, 16, 18a] The ^{1}H and ^{31}P NMR spectroscopic data for **6** resemble those for *cis-mer*-[RhCl(H)$_2$(PEt$_3$)$_3$].[15] The fluorine bound to the rhodium center displays an additional coupling $^2J(\mathrm{H,F}_{trans}) \approx 94$ Hz in the ^{1}H NMR spectrum and a broad signal at $\delta = -274$ ppm in the ^{19}F NMR spectrum.[18] The formation of 1,1,1-trifluoropropane (**5**) was confirmed by ^{1}H and ^{19}F NMR spectroscopy by comparison with an authentic sample. The yield is 80% according to the ^{19}F NMR spectrum.

The fluoro complex **4** can also be synthesized by reaction of **1** with $Et_3N \cdot 3HF$, which is a mild source of HF.[2c, 21] Treatment of a solution of **4** with hydrogen affords compound **6**, which under vacuum converts back to **4**.

One possible mechanism for the C–F activation of the perfluorinated olefin is by loss of HF from an alkyl compound, which was initially formed by insertion.[1c, 5b] Other possibilities include an electron transfer mechanism or a base-induced, nucleophilic reaction pathway.[19] The formation of **5** might involve α-fluoro- and β-fluoro-elimination reactions with concomitant formation of HF and subsequent hydrogenation of the generated propynyl ligand or of trifluoropropyne.[2e, 6, 20] However, a direct cleavage of the Rh–C bond by hydrogen followed by repeated C–F activation and analogous Rh–C cleavage steps by hydrogen is also conceivable.[4] Mechanistic investigations concerning both the activation of the C–F bond in perfluoropropene and the formation of **5** are in progress.

In conclusion, we have demonstrated the direct conversion of a fluorinated alkenyl unit into a nonfluorinated alkyl group by selective rhodium-mediated C–F activation starting from hexafluoropropene. There is no indication for a defluorination of the trifluoromethyl group. To the best of our knowledge, it is the first example for a selective and complete hydrodefluorination of a perfluorinated olefin, for which only the fluorine atoms at the double bond have been removed.[6, 22] Moreover, dihydrogen has been used for the reduction of the perfluorovinyl ligand after the activation of the olefin with a rhodium hydrido complex. Note that in the zirconium-mediated conversion of hexafluoropropene into propane a zirconium hydride is the main hydrogen source.[6] We believe that the reaction described offers a new and general method for preparing hydrofluorocarbons, some of which are of current interest as compounds with less or no ozone depletion potential.[23]

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[12] Data for the X-ray structure analysis of **2**: $C_{21}H_{45}F_5P_3Rh$ (M_r = 588.39): crystal dimensions 0.40 × 0.10 × 0.08 mm, monoclinic, $P2_1/n$, $a = 10.1568(6)$), $b = 14.5420(9)$, $c = 19.5829(12)$ Å, $\beta = 104.311(10)^\circ$, $Z = 4$, $V = 2802.6(3)$ Å^3, $\rho_{calcd} = 1.394$ g cm^{-3}, $T = 183(2)$ K, $\theta_{max.} = 24.99^\circ$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), 12648 reflections collected, 4808 were unique ($R_{int} = 0.0403$), Siemens Smart CCD diffractometer, semiempirical absorption corrections (from equivalents, min./max. transmission 0.9373/0.7350), $\mu = 0.820$ mm^{-1}. The structure was solved by direct methods (SHELXTL PLUS) and refined with the full-matrix least-squares methods on F^2 (SHELX-97). Final R_1, wR_2 values on all data: 0.0508, 0.1019. R_1, wR_2 values for 3852 reflections with $I_o > 2\sigma(I_o)$: 0.0388, 0.0953, goodness-of-fit on F^2 1.067, data-to-parameter ratio 13.1, residual electron density $+0.755/-0.722$ e Å^{-3}. CCDC-179384 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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Barrier Height Titration by Tunable Photoionization Combined with Chemical Monitoring: Unimolecular Keto/Enol Tautomerization of the Acetamide Cation Radical[**]

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Dedicated to Professor Petr Čársky
on the occasion of his 60th birthday

The keto/enol tautomerization is generally assumed to proceed easily. The rapid equilibration of keto and enol tautomers in solution is due to solvent-mediated proton-transfer catalysis. In aprotic solvents, the isomerization is slowed down and simple enols can exhibit significant lifetimes.[1] In the gas phase, keto and enol isomers hardly interconvert at all at ambient internal energies because the barriers associated with intramolecular 1,3-hydrogen migration are rather large, generally exceeding 2 eV.[2] Furthermore, for simple, nonconjugated carbonyl compounds, the keto forms are thermochemically more stable (Table 1).[3, 4]

Three features are associated with the ionization of carbonyl compounds to the corresponding cation radicals.[5]

Table 1. Relative stabilities (in eV)[a] of neutral and ionized keto and enol tautomers.[b]

	Neutral	Cation radical
acetaldehyde (CH_3CHO)	0.42	−0.66
acetone (CH_3COCH_3)	0.43	−0.60
acetic acid (CH_3COOH)	1.20[c]	−0.89
acetamide (CH_3CONH_2)	1.07	−0.82[d]
methyl acetate (CH_3COOCH_3)	1.18[c]	−1.08

[a] $\Delta_f H^\circ$(enol) − $\Delta_f H^\circ$(keto). [b] Taken from ref. [6] unless noted otherwise. [c] Calculated G2 value taken from ref. [4]; also see ref. [3]. [d] Calculated G2 value taken from ref. [10].

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