Supporting Information

An Amorphous Lewis-acidic Zirconium Chlorofluoride as HF Shuttle: C-F Bond Activation and Formation

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General techniques and materials

The samples were prepared in a MBraun glovebox and all reactions were performed in JYoung NMR tubes using conventional Schlenk techniques, if not indicated elsewise. C_6D_{12} was purchased from Eurisotop and stored over molecular sieves. CD_3CN was purchased from Eurisotop and used as received. CCl_3F, 1-fluoropentane, 4-trifluoromethylphenylacetylene, (4-nitrophenyl)acetylene were obtained from Sigma-Aldrich and stored under an argon atmosphere in Schlenk flasks. $ZrCl_4$ (sublimed grade), 5-phenyl-1-pentyne, fluorocyclohexane 4-fluorophenylacetylen and pentafluorophenylacetylen were obtained from ABCR and used as received. 1-hexyne, 3-hexyne were obtained from Tokyo Chemical Industry (TCI). Phenylacetylene was obtained from Lancaster Synthesis.

Synthesis of zirconium chlorofluoride

$ZrCl_4$ (1 eq, 12.8 mmol, 3 g) was placed in a 3-neck flask and dispersed in 5 mL dry CCl_4. The flask was equipped with a dry ice cooler. Over the period of 2 h $CFCl_3$ (6 eq, 77 mmol) was added slowly over a syringe. Due to the exothermic behavior of the reaction the reaction flask was cooled with an ice bath. The dry ice cooler was charged with an isopropanol/dry ice mixture to obtain a cooling mixture at 76 °C. After the complete addition of $CFCl_3$ the reaction mixture was stirred for 1 h at 0 °C. The temperature was raised slowly to room temperature. After further stirring for 2 h the solvent was removed under vacuum. ZCF was obtained after further drying for 16 hours and was analyzed using STEM/EDX spectroscopy to determine the stoichiometry $ZrCl_{0.2}F_{3.8}$.

NMR spectroscopy

Liquid NMR spectra were recorded at a Bruker DPX 300, Bruker AVANCE II 300 or a Bruker AVANCE II 500 spectrometer at room temperature. ^1H NMR chemical shifts δ were referenced to residual $C_6D_{11}H$ (δ = 1.38 ppm).^{19}F NMR spectra were calibrated externally to $CFCl_3$ (δ = 0 ppm).

X-ray powder diffraction

X-ray powder diffraction measurements were performed on an STOE Stadi MP diffractometer equipped with a Dectris Mythen 1 K linear silicon strip detector and Ge(111) double-crystal monochromator (Mo-K radiation) in a transmission geometry.

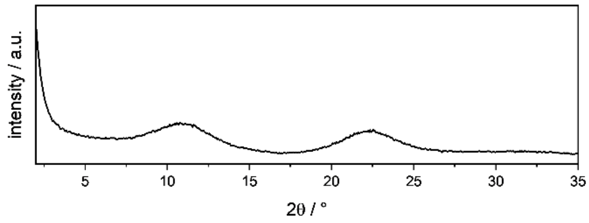

Figure S1: Diffractogram of ZCF.

Infrared spectroscopy

The IR-spectra were recorded in a glovebox at a Bruker Alpha II spectrometer with a diamond ATR (attenuated total reflectance) or DRIFTS (Diffuse reflectance Infrared Fourier transform spectroscopy) measuring unit (Pyroelectric DTGS detector).

Surface area determination and pore size analysis

Low temperature adsorption isotherms of nitrogen at 77 K were determined with an Autosorb iQ from Anton Paar. Approximately 150 mg of the samples were tempered at 200 °C for 7 h immediately before the measurement at the device. The evaluation was carried out according to the BET theory.[1] The BJH method was used to determine the pore size. The pore volume was determined at $P/P_0 = 0.95$.[2]

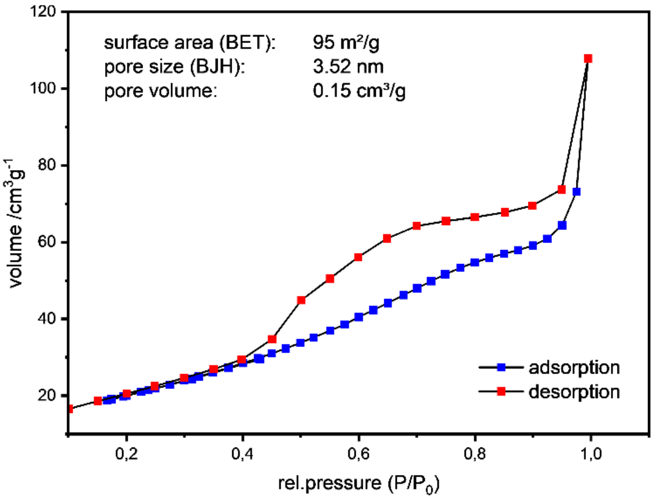

Figure S2: N_2 adsorption and desorption isotherm for ZCF at 77 K.

Transmission electron microscopy

High-resolution transmission electron microscopy (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy dispersive X-ray analysis (EDX) elemental mapping were carried out on a FEI Talos F200S scanning/transmission electron microscope (S/TEM) at an acceleration voltage of 200 kV. A dry TEM grid preparation was carried out. Therefore, TEM grids were carefully swiped across the powder samples. The excess of powder on the grids were removed by tapping lightly.

Thermogravimetric analysis (TGA) / Differential scanning calorimetry (DSC)

The TGA and DSC measurements were performed on a TGA/DSC 3+ from Mettler Toledo, Switzerland. Samples were weighed in in a glovebox and sealed with the A2 closing stamp. The closed crucible was pinned in a N_2 stream by the sample robot. The samples were heated from 25 to 600 °C at a rate of 10 K/min. Afterwards the samples were cooled down to 25 °C at the same rate.

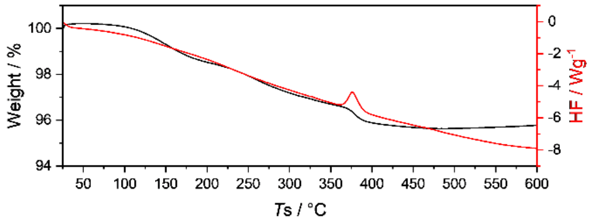

Figure S3: TGA trace (black) and DSC trace (red) of ZCF.

Temperature programmed desorption (TPD)

NH_3-TPD measurements were performed on an Autosorb iQ equipped with a TCD detector from Anton Paar. Approximately 200 mg of the sample were placed between two layers of quartz wool in a quartz cell. The cell was evacuated for 5 min and then tempered to 200 °C with a heating rate of 5 K/min while in a helium flow. Then, the cell was cooled down to 120 °C and NH_3 gas was added for 15 min. After that, the gas flow was changed again to helium and the detector was turned on. Helium was then flowed for 30 min to get rid of the non-adsorbed NH_3 on the sample surface. The TPD measurement was then performed starting at 80 °C until 510 °C with a heating rate of 10 K/min.

Extended X-ray Absorption Fine Structure spectroscopy (EXAFS)

EXAFS measurements were performed at the BAM*line* at BESSY-II,[3] according to the experimental arrangement displayed in figure 1. The beam was monochromatized using a double-crystal monochromator (DCM) installed at the beamline, with a resolution ($\Delta E/E$) of about $2x10^{-4}$. The slits were adjusted to provide a 4mm (H) x 1mm (V) spot size.

The measurements were performed @ Zr K-edge (17.889 keV) in transmission, as the sample preparation allowed choosing the adequate thickness for optimal absorption, establishing an edge jump factor of about 2. This was achieved by diluting the powder samples with Boron Nitride (BN).

The excitation energy was varied from -200 eV to -20 eV below the edge in 10 eV steps, from -20 eV below the edge and 200 eV above the edge in 1 eV steps, and in the EXAFS region with a constant step in the *k*-space of 0.04 Å^{-1} until k = 16 Å.

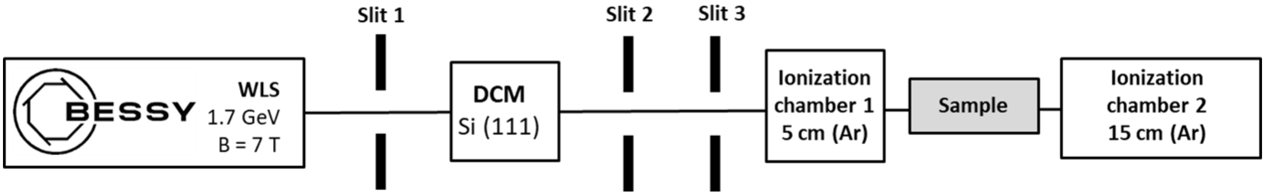

Figure S4: Layout of EXAFS experiments in transmission @ the BAMline, BESSY-II.

EXAFS data were processed by ATHENA and ARTEMIS[4] . This GUIs programs belongs to the main package IFEFFIT (v. 1.2.12). The AutoBK background subtraction procedure was used with the Rbkg parameter set to 1.0 Å and kw=1. Afterwards all spectra were normalized to the far post-edge region, free from absorption features. Regarding the EXFAS region, with ATHENA one can plot $\chi(k)$ against R (Å) and the oscillations represent different frequencies, which correspond to the different distances for each coordination shell. Hence, Fourier transforms (FT) are necessary for the analysis process. The FT from the k-space to R-space were performed with a Hanning-type window with a range of 1.5 Å to 14 Å. By analyzing the signal in the frequency domain in ATHENA the window range was selected to exclude the noisy part of the signal.

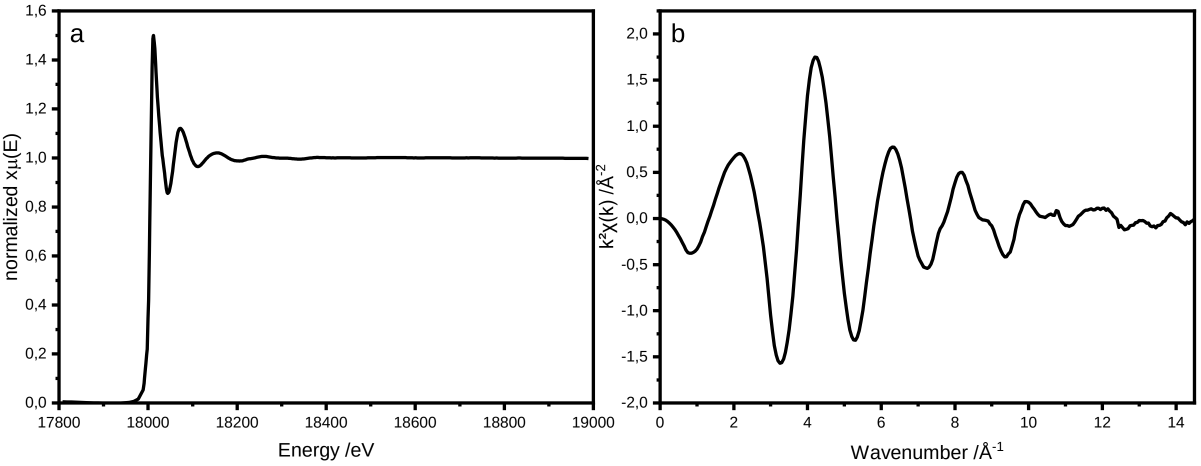

Figure S5: (a) Normalized Zr K-edge spectrum of ZCF (b) EXAFS data of ZCF shown in k² space.

Table S1: Interatomic distances fitted on EXAFS Zr-K-edge spectra.

		scattering path	N	σ²	R_{eff} [Å]	R_{fit}[Å]	R_{diff}[Å]	R_{diff}^2 [Å²]
				Shown in Figure S6				
S_0^2	1.03(6)	Zr1-F3.1	2	0.00576	2.03730	2.05593	0.01863	$3.47\text{x}10^{-4}$
Amplitude reduction factor		Zr1-F2.1	2	0.00576	2.08840	2.10703	0.01863	$3.47\text{x}10^{-4}$
ΔE	-3.88	Zr1-F1.1	2	0.00576	2.14520	2.16383	0.01863	$3.47\text{x}10^{-4}$
R-factor	0.027	Zr1-F3.2	2	0.00576	2.19150	2.21013	0.01863	$3.47\text{x}10^{-4}$
				Shown in Figure 4				
S_0^2	0.98(0)	Zr1-F3.1	2	0.00458	2.03730	2.05511	0.01863	$3.47\text{x}10^{-4}$
Amplitude reduction factor		Zr1-F2.1	2	0.00458	2.08840	2.10621	0.01863	$3.47\text{x}10^{-4}$
ΔE	-3.89	Zr1-F1.1	2	0.00458	2.14520	2.16301	0.01863	$3.47\text{x}10^{-4}$
		Zr1-F3.2	1.5	0.00458	2.19150	2.20931	0.01863	$3.47\text{x}10^{-4}$
R-factor	0.014	Zr1-Cl2.1	0.5	0.00356	2.30740	2.49598	0.18858	0.0355

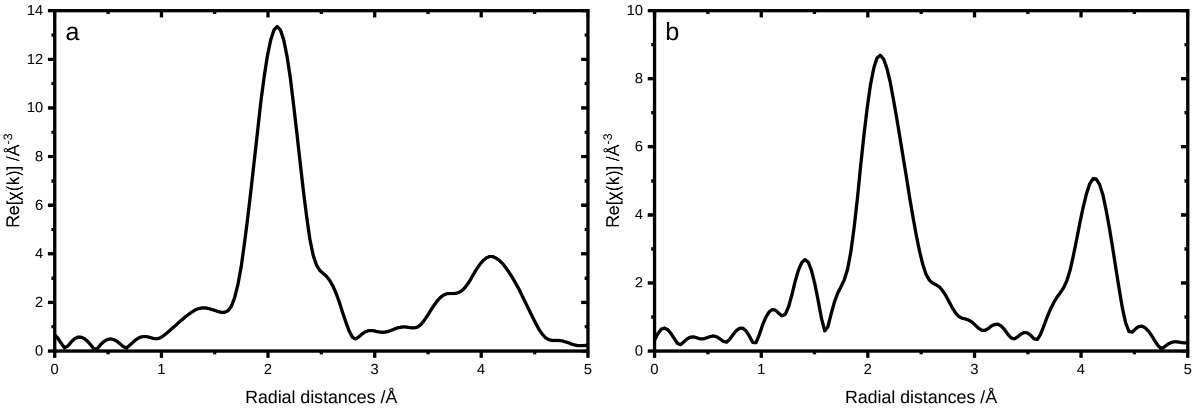

Figure S6:Fourier transform of the Zr-K-edge EXAFS data. Magnitude of χ in real space from (a) ZrF_4 (b) $ZrCl_4$.

Formation of ZCF·CD_3CN

The powder ZCF (200 mg) was suspended in an excess of CD_3CN in a Schlenk flask and stirred at 25 °C for two hours. The excess of CD_3CN was removed under vacuum to obtain a brown powder.

ZCF mediated hydrofluorination of alkynes

HF (gift from Solvay Fluor GmbH) was dried using potassium hexafluoronickelate prior to the loading onto the surface of ZCF. In a flow of an argon stream, HF was condensed onto the drying agent, forming a deep red mixture. The dry HF was condensed onto 1 g of ZCF for 30minutes, and the excess of HF was then removed under vacuum.
A PFA inliner was loaded with 25mg of HF-loaded ACF inside a Glove-box and put in a closed JYoung NMR tube. The Phenylacetylene (0.3mmol) was added together with C_6D_{12} as a solvent (0.4mL) under Schlenk conditions in the PFA inliner. The difluorination product was identified by ^{19}F NMR spectroscopy.

CAUTION! Appropriate safety precautions must be taken when using HF,which is a highly toxic and irritant compound. Severe burns can be caused when HF comes in contact with the skin.

Reactivity studies using fluoroalkanes (1-fluoropentane, fluorocyclohexane)

15 mg of ZCF were placed in a JYoung NMR tube and alkyne (0.2 mmol) was added resulting in a dark suspension. Then, the fluoroalkane (0.4 mmol) was added. Subsequently, C_6D_{12} was added to the reaction mixture. The products were analyzed by NMR spectroscopy. If an alkene was used as fluorination target 15 mg of ZCF were placed in a JYoung NMR tube and alkene (styrene or *trans*- stilbene) (0.2 mmol) was added resulting in a dark suspension. Then, the fluoroalkane (0.2 mmol) was added. After that C_6D_{12} was added to the reaction mixture. The products were analyzed by NMR spectroscopy.
Reactions displayed in Scheme 2 were performed similarly. 15 mg of ZCF was placed in a JYoung NMR tube and fluoropentane (0.2 mmol) was added resulting in a dark suspension. Subsequently, C_6D_{12} and C_6D_6 was added to the reaction mixture, respectively. The products were analyzed by NMR spectroscopy.

Table S1: ZCF catalysed hydrofluorinations of alkynes .[a]

Entry	R'	R''	*T*[°C]	*t* [h]	Conversion [%][b]
1	Et	Et	r.t	24	39 (60:1)
2[d]	Et	Et	r.t	24	21 (13:1)
3[e]	Et	Et	r.t	24	53 (11:1)
4	C_4H_9	H	r.t	24	12 (10:1)
5	$C_6H_5(CF_3)$	H	r.t	168	67 (31:1)
6	$C_6H_2(CH_3)_3$	H	r.t	96	7 (0:1)
7	C_6H_4F	H	r.t	168	8 (1:2)
1	Ph	H	r.t	96	traces
2	$C_6H_4(NO_2)$	H	r.t	384	traces
3	C_6F_5	H	50	168	2

[a] 15 mg of catalyst in a JYoung NMR tube using C_6D_{12} as solvent [b] determined from ^{19}F NMR data based on the fluoroalkane starting compound [c] ratio of difluoroalkane: monofluoroalkene in parentheses

Note that a stochiometric reaction by taking all deployed Zr atoms into account (including bulk atoms) would lead to a maximum conversion of 22%. As only a fraction of the Zr atoms will be Lewis-acidic and catalytically active, a catalytical conversion can be assumed.

Table S2: Selected ^{1}H and ^{19}F NMR resonances of the reactants and products of the catalytic reactions in C_6D_{12}.

Entry	Product/reagent	δ(^{1}H NMR) in ppm	δ(^{19}F NMR) in ppm	Entry	Product/reagent	δ(^{19}F NMR) in ppm
1	$F(CH_2)_4CH_3$	4.32 (dt, ^{2}J(H,F) = 47.6 Hz, ^{3}J(H,H) = 6.2 Hz, 2H, CH_2F)	–218.4 (hept, ^{2}J(F,H) = 23.5 Hz)	14	SiF_4[c]	-163.5 (s)
2	$CH_{11}F$	4.45 (dm, ^{2}J(H,F) = 48.6 Hz, 1H)	-174 (s)	15	2-fluorohex-1-ene	-94 (dq ^{3}J(H,F) = 51 Hz, ^{3}J(H,F) = 18 Hz)
3	1-hexyne	[b]	-	16	2,2-difluorohexane	-91.5 (sextett, ^{3}J(H,F) = 17.2 Hz)
4	3-hexyne	[a]	-	17	3-fluorohex-3-ene	-108 (dt, ^{3}J(H,F) = 38 Hz, ^{3}J(H,F) = 15 Hz
5	PhC_2H	2.8 (s, 1H)	-	18	3,3-difluorohexane	-101 (q, ^{3}J(H,F) = 15 Hz
6	$C_6H_4(F)C_2H$	2.8 (s, 1H)	-110 (m)	19	$C_6H_2(CH_3)_3CFCH_2$	-82.4 (dd ^{3}J(H,F) = 47.7 Hz, ^{3}J(H,F) = 13.5 Hz)
7	$C_6F_5C_2H$	3.4 (s, 1H)	-136.6 (m, 2F), -153 (t, ^{3}J(F,F) = 20.5 Hz, 1F),-163 (m, 2F)	20	$C_6F_5CF_2CH_3$	-94.9 (dq, ^{3}J(H,F) = 48 Hz, ^{3}J(F,F) = 16 Hz
8	$C_6H_4(CF_3)C_2H$	3 (s, 1H)	-64.3 (s)	21	$C_6H_4FCFCH_2$	-106,8 (dd, ^{3}J(H,F) = 46 Hz, ^{3}J(H,F)= 17.9 Hz
9	$C_6H_2(CH_3)_3C_2H$	2.8 (s, 1H)	-	22	$C_6H_4FCF_2CH_3$	-88.5 (q, J = 17.8 Hz)
10	$C_6H_4(NO_2)C_2H$	7.54 (d, ^{3}J(H,H) = 8.5 Hz), 8.14 (d, ^{3}J(H,H) = 8.5 Hz)	-	23	$C_6H_4(CF_3)CFCH$	-108.7 (dd, ^{3}J(H,F) = 50 Hz, ^{3}J(H,F) = 17 Hz)
11	(E/Z)-pent-2-ene	5.41 (m, 2H, $CH_3CH{=}CHCH_2CH_3$)	-	24	$C_6H_4(CF_3)CF_2CH_3$	-90.5 (q, J = 17.8 Hz)
12	C_6H_{10}	5.6 (s, 2H)	-			
13	$(PhC_3H_6)C_2H$	[b]	-			

[a] not determined [b] terminal alkyne signal is overlapping with other signals [c] can be detected due to performing the reactions in glassware

References

1 S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, 1938, **60**, 309–319.

2 E. P. Barrett, L. G. Joyner and P. P. Halenda, *J. Am. Chem. Soc.*, 1951, **73**, 373–380.

3 A. Guilherme Buzanich, M. Radtke, K. V. Yusenko, T. M. Stawski, A. Kulow, C. T. Cakir, B. Röder, C. Naese, R. Britzke, M. Sintschuk and F. Emmerling, *J. Chem. Phys.*, 2023, **158**, 244202.

4 B. Ravel and M. Newville, *J Synchrotron Radiat*, 2005, **12**, 537–41.

Author Contributions

Christian Heinekamp performed the synthesis, analysis (TEM, NMR IR, TGA XRD), model fitting and drafted the first version of the manuscript. Ana Guilherme Buzanich performed the XAS measurements. The EXAFS data were jointly analyzed by Christian Heinekamp and Ana Guilherme Buzanich. Thomas Braun and Franziska Emmerling supervised the work and contributed to manuscript writing. Mike Ahrens was involved in scientific discussions. All authors contributed to the manuscript.