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Fluoroolefin condensation catalyzed by aluminum chlorofluoride [1]

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Abstract

High-fluorine-content aluminum chlorofluoride, as prepared by Cl/F exchange of aluminum chloride with one of a number of organofluorine compounds, is a very active Lewis acid capable of condensing an allylic fluoride with another fluoroolefin at low temperature. In addition to a description of broader scope, details of the selective reaction of hexafluoropropene with tetrafluoroethylene to form *F*-pentene-2 are presented along with evidence supporting polyfluoroallyl cationic species as intermediates. *Ab initio* calculations confirm the feasibility of the proposed mechanism and further suggest that 1,3-fluorine shifts in fluorocarbocations are energetically accessible at modest temperatures. Revised heats of formation for C_3F_8 ($\Delta H_f^0 = -1750 \pm 12.4$ kJ mol^{-1}) and HFP ($\Delta H_f^0 = -1128 \pm 5$ kJ mol^{-1}) have been calculated. Fluoride affinities of some simple metallohalogens are reported.

Keywords: Fluoroolefins; Aluminum chlorofluoride; Condensation; Fluoroallyl cations; 1,3-Fluoride migration; NMR spectroscopy; Mass spectrometry

1. Introduction

Earlier work with aluminum chlorofluoride (ACF) has shown it to be effective in the condensation of chlorofluorocarbons such as dichlorofluoromethane with tetrafluoroethylene (TFE) [1]. It became clear during these studies that, although aluminum chloride itself can be used as catalyst in such reactions [2], ACF is formed as the actual catalyst and can be prepared either in situ or before hand. Whichever method is used, the ACF is so susceptible to deactivation by various impurities that strict control over reaction conditions is required to obtain optimum results.

Condensations of fluoroolefins such as hexafluoropropene require catalysts of very high Lewis acidity. Indeed, prior to the use of ACF reported here, antimony pentafluoride was the only catalyst known to cause formation of observable perfluoroallyl carbocation from hexafluoropropene [3] and to catalyze the reaction of hexafluoropropene with tetrafluoroethylene to form *F*-pentene-2 [4]. The antimony(V) halides do, however, suffer the disadvantages of expense and toxicity. Moreover, fluorocarbocations formed by the action of pentavalent antimony halides often give products accompanied by byproducts derived from oxidation reactions. The end-result in such instances is not only lowered yields of desired products, but also reduced catalyst efficiency. No such oxidative side-reactions occur with aluminum halides as catalyst, so that the reactions tend to be cleaner, require lower proportions of catalyst and proceed if necessary at relatively high temperature (up to at least 150 °C).

2. Results

2.1. Catalyst preparation

Trichlorofluoromethane has been used most often for reaction with aluminum chloride to give ACF and can be made to provide highly active catalyst [1]. The Cl/F exchange reaction is highly exothermic, but can be moderated by the presence of an inert liquid phase such as carbon tetrachloride. Characteristically, ACF prepared in this manner is a finely divided powder, even when aluminum chloride of larger particle size is used as the starting material. The color of ACF is pale yellow to yellow–green for very active samples and pale orange to orange for catalyst of lower activity. Deactivation occurs easily unless water and other proton sources such as alcohols and protic acids are strictly excluded. Many organic substrates, including hydrocarbon-based greases and oils as well as inhibitors such as D-limonene, also deactivate ACF. Accurate analytical values proved to be difficult to obtain, but compositions approximating $AlF_{2.8-2.9}Cl_{0.2-0.1}$ are the

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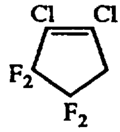
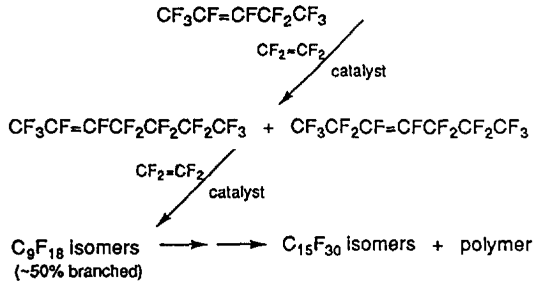
usual end-result. X-Ray analysis shows freshly prepared ACF to be amorphous, while samples exposed to some moisture contain crystalline domains of aluminum fluoride trihydrate. Determination of the surface area by N_2 BET adsorption in equipment in which sample preparation with exclusion of moisture is possible led to values as high as 140 $m^2\ g^{-1}$. These characteristics are in contrast to those of conventionally prepared aluminum trifluoride.

2.2. Condensations with tetrafluoroethylene (TFE)

Much of our work has involved condensations with TFE catalyzed by ACF. A summary of the reactions and conditions is given in Table 1. Addition of hexafluoropropene (HFP) as the reaction partner containing allylic fluorine proceeds rapidly and with high selectivity to form *F*-pentene-2 (Reaction 1). The *F*-pentene-2 can itself be added to TFE to form

Table 1
Summary of reactions and conditions

Example	Cat. (wt.%)	Reactants (molar ratio)	Temp. (time) (°C) ((h))	Pressure range (psig)	Products (% yield)
1	AlF_xCl_y (3)	$CF_3CF=CF_2+CF_2=CF_2$ (1:2)	25 (2), 80 (4)	266–68, 96–50	$F(CF_2)_2CF=CFCF_3$ (32%), $F(CF_2)_3CF=CF(CF_2)_2F$ (39%), $F(CF_2)_5CF=CF(CF_2)_2F$ $+F(CF_2)_4CF=CF(CF_2)_3F$ + others (2%)
2	AlF_xCl_y (5)	$CF_3CF=CF_2+CF_2=CF_2$ (1:4)	11–25 (0.5, 4) (2 TFE additions)	138–0, 173–0	C_7F_{14} (37%), C_9F_{18} (49%), $C_{11}F_{22}$ (15%), small amounts other olefins and solid polymer
3	AlF_xCl_y (3)	$CF_3CF=CFCF_2CF_3+CF_2=CF_2$ (1:1) carried out semibatch with TFE added continuously	35–40 (4)	40–60	C_7F_{14} (81%), C_9F_{18} (6%)
4	AlF_xCl_y (5)	$CF_3CH=CH_2+CF_2=CF_2$ (1:2)	25 (2), 60 (4)	230–400	$F(CF_2)_3CH=CH_2$ (low), mainly $CF_3CH=CH_2$ dimers
5	AlF_xCl_y (4)	 $F_2+CF_2=CF_2$(1:2)	80 (3)	334–19	1:1 adducts (36%), 1:2 adducts (32%)
6	$AlCl_3$ (2)	$CF_3CF=CF_2+CF_2=CF_2$ (1:1)	25 (0.5), 40 (2)	240–34	$F(CF_2)_2CF=CFCF_3$ (47), small amts. high boilers
7	AlF_xCl_y (4)	$CF_3CH=CF_2+CF_2=CF_2$ (1:1)	25 (3.5)	153–0	$CF_3CH=CFCF_2CF_3$ (80%), $F(CF_2)_2CF=CH(CF_2)_3F$ (low), plus others
8	AlF_xCl_y (4)	$CF_3CF=CF_2+CF_2=CFCl$ (1:1)	25 (4)	85–18	$CF_3CF_2CF=CClCF_3$ (36%), along with $CF_3CF_2CCl=CClCF_3$, $F(CF_2)_3CF=CClCF_2CF_3$, $F(CF_2)_4CCl=CClCF_3$ (18%) and others
9	AlF_xCl_y (4)	$CF_3CF=CF_2+CF_2=CF_2$ (1:10)	4–25 (3, 18) (2 TFE additions)	152–19, 240–1	C_7F_{14}, C_9F_{18}, $C_{11}F_{22}$ and $C_{13}F_{26}$ as major series, C_8F_{16}, $C_{10}F_{20}$, and solid polymer also formed
10	AlF_xCl_y (5)	$CF_3CF=CF_2+CF_2=CF_2$ (1:30)	25 (4), 50 (1) (2 TFE additions)	165–21, 179–44	C_6F_{12} to $C_{15}F_{30}$ liquids + 12% poly(TFE)
11	AlF_xCl_y (6)	C_7F_{14} isomers $+CF_2=CF_2$ (1:7)	25 (10), 50 (6)	198–0	C_6F_{12} (1%), C_7F_{14} (1%), C_8F_{16} (16%), C_9F_{18} (32%), $C_{10}F_{20}$ (16%), $C_{11}F_{22}$ (30%), $C_{12}F_{24}$ (3%), $C_{13}F_{26}$ (2%) plus polymer
12	AlF_xCl_y (5)	$(CF_3)_2CFCF=CFCF_3$ $CF_2=CF_2$ (1:3)	10–25 (6)	160–0	1:1 adducts (32%), 2:1 (54%), 3:1 (10%)
13	AlF_xCl_y (5)	$(CF_3)_2C=CFCF_2CF_3+CF_2=CF_2$ (1:3)	16–25 (8)	178–0	$CF_3CF_2CF_2C(CF_3)=CFCF_2CF_3$ (2%), considerable poly(TFE)
14	AlF_xCl_y (13)	*F*-cyclopentene $+CF_2=CF_2$ (1:2)	80 (21)	no readings	*F*-1-ethylcyclopentene (55%)



Scheme 1.

linear *F*-heptenes in 80% yield. Since SbF_5 does not catalyze *F*-heptene formation [4], ACF seems to be the stronger Lewis acid in practice. Further addition of the *F*-heptenes to TFE afford *F*-nonenes, albeit even more slowly, and subsequent additions have been observed to form $C_{15}F_{30}$ isomers and higher. Extensive branching is observed in the product *F*-nonenes and higher olefins. Scheme 1 is illustrative of the series of reactions.

$$CF_3CF{=}CF_2 + CF_2{=}CF_2 \xrightarrow[25\text{–}50\ °C]{ACF} CF_3CF{=}CFCF_2CF_3 \quad (1)$$

A spectrum of other olefins condense with TFE under the influence of ACF. The following selection indicates the range of products available.

$$CF_3CH{=}CF_2 + CF_2{=}CF_2 \longrightarrow CF_3CH{=}CFCF_2CF_3$$

$$CF_3CCl{=}CClCF_3 + CF_2{=}CF_2 \longrightarrow$$

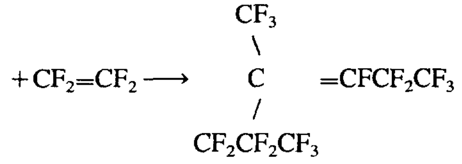
$$CF_3CF_2CF_2CCl{=}CClCF_3 \xrightarrow{CF_2=CF_2}$$

$$CF_3CF_2CF_2CCl{=}CClCF_2CF_2CF_3$$

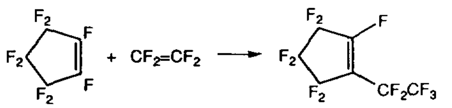
$$CF_3CCl{=}CCl_2 + CF_2{=}CF_2 \longrightarrow$$

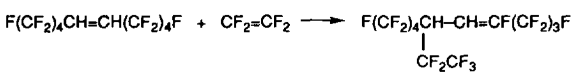
$$CF_3CF_2CF_2CCl{=}CCl_2 + CF_3CF_2CFClCCl{=}CCl_2 + CF_3CF_2CF{=}CClCCl_3$$

$$(CF_3)_2C{=}CFCF_2CF_3$$



$$+ CF_2{=}CF_2 \longrightarrow \overset{CF_3}{\underset{CF_2CF_2CF_3}{C}}{=}CFCF_2CF_3$$





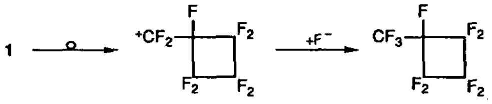
$$F(CF_2)_4CH{=}CH(CF_2)_4F + CF_2{=}CF_2 \longrightarrow F(CF_2)_4\underset{CF_2CF_3}{CH}{-}CH{=}CF(CF_2)_3F \quad (2)$$

3. Discussion

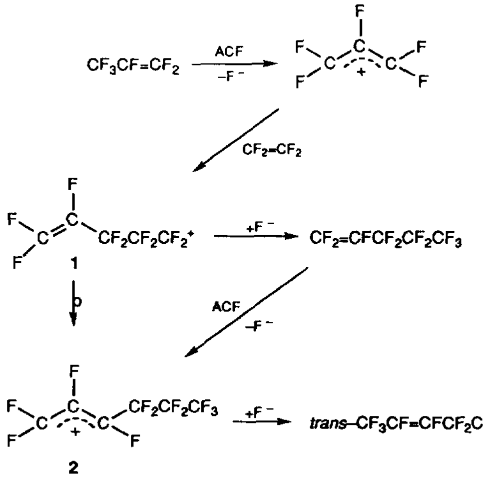
A few generalizations can be drawn from our results. As is usually observed in fluoroolefin chemistry, the favored structures are those in which the number of vinylic fluorine substituents is minimized. Thus, double bonds migrate to more stable internal positions, branched where possible, in perfluorinated products. The catalyst tolerates the presence of hydrogen and chlorine, and these substituents also tend to end up in vinylic positions. In several cases involving chlorine-containing substrates, as exemplified here with 1,1,2-trichlorotrifluoropropene as reactant, chlorine migration and disproportionation occur as well as straightforward addition. Finally, Reaction 2, which is viewed as proceeding via an allylic cation substituted by H at one end and F at the other, provides a clear example of the introduction of tetrafluoroethylene predominantly at the site remote from removal of F.

This last result lends credence to the mechanism we propose for these transformations, a mechanism that involves formation on the catalyst surface of incipient fluoroallyl cations as intermediates that are capable of addition to TFE. Two subsequent reaction paths are possible according to our calculations (vide infra), and we cannot target one or the other as the sole operational reaction path. Taking the HFP/TFE reactions as an example, we see that these two paths differ only in the direct or indirect conversion of the intermediate TFE adduct (**1**) into an *F*-pentane-2 isomer (see Scheme 2).

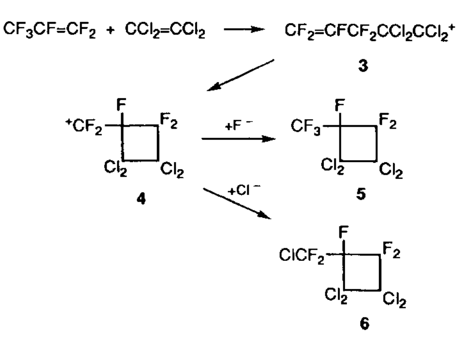
Good evidence for the formation of **1** is the observation that *F*-methylcyclobutane is obtained as a product in < 1% yield.



This acid-catalyzed 2 + 2 cycloaddition occurs more readily with tetrachloroethylene. When tetrachloroethylene was used as a solvent for *F*-pentene-2 synthesis, appreciable chlorine-containing byproducts formed. Reaction with hexafluoropropene only was catalyzed by ACF to form two cyclobutanes in 12% and 1% yield, respectively. The for-



Scheme 2.



Scheme 3.

mation of chlorodifluoromethylcyclobutane (**6**) as well as trifluoromethylcyclobutane (**5**) indicates that cation **4** may be a discrete intermediate to which either F^- or Cl^- can be transferred. Unlike the reaction involving **1**, where the transfer of F^- decisively beats cyclization to the *F*-cyclobutylmethyl cation, cyclization of **3** to **4** competes successfully (Scheme 3).

One unresolved problem is the source of the byproducts with even numbers of carbons. Such products become prominent, along with poly(TFE) formation, as the formation of fluoroallylcationic intermediates becomes increasingly difficult. Intriguing speculative scenarios such as the transfer of $C_2F_5^+$ from a highly hindered intermediate or the preferential adsorption of TFE on to the catalyst to give an activated TFE are as yet unsupported by hard evidence.

Catalyst ACF has been shown to be effective in the isomerization of Δ 1 *F*-olefins at 25 °C to the more stable internal olefins [5], so that *F*-pentene-1 formed via the indirect path is a real possibility as an intermediate to *F*-pentane-2. On the other hand, calculations of the energetics for 1,3-migration of fluorine in a model of cation **1** indicate that a low-lying transition state ($E_0^\ddagger = 6.5$ kcal mol^{-1}) is available to give **2**, the cationic precursor to *F*-pentane-2, directly. This favored 1,3-migration of fluorine stands in contrast to the well-established resistance of fluorine to undergo the 1,2-shifts common in other haloalkyl cations. As discussed below, the 1,2-shift of fluorine has a barrier height of 17.3 kcal mol^{-1}.

As the results cited above illustrate, the various fluoroalkylolefins fall in a scale of ease of fluoride removal with HFP near the top. Receptivity of the fluoroolefins to attack by the allyl cations so formed also varies greatly with structure, and accounts for the high selectivity often observed. For example, dimerization of HFP by attack of *F*-allyl cation on another molecule of HFP is essentially not observed in the presence of TFE, but occurs in high yield, although more slowly, with HFP as the sole reactant.

The energy of the condensation reaction (Reaction 1) was obtained from the calculated heats of HFP and *F*-pentene-2, and the experimental heat of formation of TFE. The heats of formation of HFP and *F*-pentene-2 were obtained as follows. Geometries were gradient optimized [6] with a double-zeta basis set augmented by polarization functions on C [7]. This basis set has been shown to give good results for the structures of a wide range of fluorocarbons [8]. Frequencies were calculated analytically [9] at this level and scaled by 0.9 for use in calculating the reaction energies. Final energies were obtained at the MP2/DZP/HF/DZ + D_C level [10]. All calculations were done with the program GRADSCF [3]. The heat of formation of HFP was calculated from the following reactions:

$$CF_2{=}CF_2 + CH_2{=}CHCF_3 \longrightarrow CH_2{=}CHF + CF_3CF{=}CF_2 \quad \Delta H = 2.6 \text{ kcal mol}^{-1} \qquad (3)$$

$$CF_3CF_2CF_3 + CF_2{=}CF_2 \longrightarrow CF_3CF{=}CF_2 + C_2F_6 \quad \Delta H = -16.3 \text{ kcal mol}^{-1} \qquad (4)$$

If the experimental value [11] for $\Delta H_f(C_3F_8) = -1783.2 \pm 7.3$ kJ mol^{-1} (-426.2 kcal mol^{-1}) is used, the heats of formation of HFP differ by 42.6 kJ mol^{-1} (10.2 kcal mol^{-1}). We thus calculated a value for the heat of formation of C_3F_8 of -1750 ± 12.4 kJ mol^{-1} (-418.3 kcal mol^{-1}) from the following reaction:

$$2C_2F_6 \rightarrow CF_4 + CF_3CF_2CF_3 \quad \Delta H = 1.0 \text{ kcal mol}^{-1} \qquad (5)$$

By using this new value, the heats of formation of HFP from Reactions (3) and (4) only differ by 10 kJ mol^{-1} and we average the two values to get $\Delta H_f(\text{HFP}) = -1128 \pm 5$ kJ mol^{-1} (-269.6 kcal mol^{-1}). This can be compared to previously estimated values near -267 kcal mol^{-1} [11]. The heat of formation of the pentene can be calculated from Reaction (6) for the *trans* isomer.

$$\text{n-}C_4F_{10} + CF_3CF{=}CF_2 \longrightarrow trans\text{-}CF_3CF{=}CFCF_2CF_3 + C_2F_6 \qquad (6)$$

$$\Delta H = -13.0 \text{ kcal mol}^{-1}$$

The value of $\Delta H_f(\text{n-}C_4F_{10}) = -2167.6$ kJ mol^{-1} (-518.1 kcal mol^{-1}) was calculated from Reaction (7). The value for ΔH_f of the *trans*-perfluoro-2-pentene is -2006.1 kJ mol^{-1} (-479.5 kcal mol^{-1}).

$$2C_3F_8 \rightarrow \text{n-}C_4F_{10} + C_2F_6 \quad \Delta H = -2.8 \text{ kcal mol}^{-1} \qquad (7)$$

These ΔH_f values can be used to calculate a value for the heat of reaction for Reaction (1) of -219 kJ mol^{-1} (-52.4 kcal mol^{-1}) at 298 K. For comparison, the heat of reaction can be calculated directly from the electronic energies, and, with zero point and temperature corrections included, the reaction energy is -250.2 kJ mol^{-1} (-59.8 kcal mol^{-1}). For comparison, we can calculate the energy of the most endothermic process for this type of coupling reaction as shown by Reaction (8). This reaction energy is -157.9 kJ mol^{-1} (-37.7 kcal mol^{-1}).

$$CF_4 + CF_2{=}CF_2 \rightarrow CF_3CF_2CF_3 \qquad (8)$$

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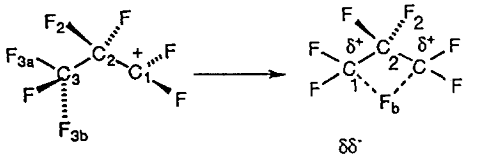
[3] GRADSCF is an *ab initio* program system designed and written by A. Komornicki at Polyatomics Research.

Table 2
Geometric parameters for carbocations [a]

Parameter	Value	Parameter	Value
$C_3F_7^+$ (*gs*)		$C_3F_7^+$ (*ts*)	
$r(C_1–C_2)$	1.578	$r(C_1–C_2)$	1.557
$r(C_2–C_3)$	1.560	$r(C_1–F_b)$	1.583
$r(C_1–F_1)$	1.218	$r(C_1–F_1)$	1.251
$r(C_2–F_2)$	1.300	$r(C_2–F_2)$	1.293
$r(C_3–F_{3a})$	1.286	$\theta(C_1C_2C_1)$	93.9
$r(C_3–F_{3b})$	1.306	$\theta(F_1C_1F_1)$	115.5
$\theta(F_1C_1F_1)$	117.5	$\theta(C_2C_1F_b)$	87.1
$\theta(C_1C_2C_3)$	109.2	$\theta(C_1F_bC_1)$	91.9
$C_2F_5^+$ (*gs*)		$C_2F_5^+$ (*ts*)	
$r(C_1–C_2)$	1.591	$r(C–C)$	1.474
$r(C_1–F_1)$	1.217	$r(C–F_1)$	1.243
$r(C_2–F_{2a})$	1.290	$r(C–F_b)$	1.573
$r(C_2–F_{2b})$	1.284	$\theta(CCF_b)$	62.1
$\theta(F_1C_1F_1)$	117.7	$\theta(CF_bC)$	55.9

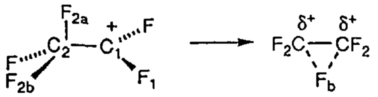
[a] Bond distances in Å. Bond angles in degrees.

The structures of the carbocations were also investigated for the model compound $CF_3CF_2CF_2^+$ [see Reaction (9)]. Geometries were first optimized at the DZ + D_C level and re-optimized at the DZ + P level. Important DZP geometry parameters are given in Table 2. The carbonium ion ground state has very short C–F bonds of 1.218 Å and is essentially planar. The C_1–C_2 bond (1.578 Å) is elongated as compared to the C_2–C_3 bond length of 1.560 Å. The C_2–F_2 bonds of 1.300 Å are longer than the C_3–F_{3a} bond length of 1.286 Å but shorter than the C_3–F_{3b} bond length of 1.306 Å. We also searched for a transition state for migration of a fluorine between C_1 and C_3. The CF_3 group must rotate about the C–C bond. The transition state for the transfer of fluorine is shown below. It is a true transition state with an imaginary frequency of 495*i* cm^{-1}. The transition state is 6.5 kcal mol^{-1} above the lowest energy structure. The geometry parameters for the transition state are also shown in Table 2. The C_1–C_2 bond lengths of 1.557 Å are slightly shorter than those in the open structure. The $C_1C_2C_1$ bond angle closes down to 93.9° from a value of 109.2° in the open structure. The $C_1F_bC_1$ angle is 91.9° and the C_1–F_b bond length is 1.583 Å. The C_1–F_1 bond length of 1.251 Å is longer than those in the free ion but shorter than those of the CF_3 group. The nature of the migrating fluorine in the transition state of Reaction (9) is of interest. The calculated electronic charge on F_b shows that it has a more negative character than the six remaining fluorines, so that there is some component of F^- in the transition state. Of course, the charge also show that the bridging fluorine does not have a full negative charge.



(9)

A similar set of calculations was done for $C_2F_5^+$ [see Reaction (10)] [4]. The resulting barrier for the 1,2-transfer of fluorine is much higher, 17.3 kcal mol^{-1}. Major differences in the ground state and transition state structures are the significant shortening of the C–C bond by 0.12 Å in the transition state and the small CF_bC bond angle of 55.9°. The C–F_b bond distance in the transition state for $C_2F_5^+$ is comparable to that in $C_3F_7^+$. It is likely that the increased barrier height for $C_2F_5^+$ is due in part to the strain of forming the three-membered ring. The CCF_b angle is reduced from 105.2° to 62.1° going from the open to bridged structure. The angle at the bridging fluorine in bridged $C_2F_5^+$ is also 36° smaller than the same angle in bridged $C_3F_7^+$. Furthermore, the angle at the bridging fluorine is 34° less than 90°, the angle between two 2p orbitals.



(10)

The first step in the reaction of $AlCl_xF_y$ for the condensation process is the transfer of F^- to $AlCl_xF_y$. The ability of a species to bind F^- is called its fluoride affinity (*FA*) as shown by Reaction (11).

$$A + F^- \rightarrow AF^- \qquad (11)$$

If this is an exothermic process, then the species A can bind F^-. Although one could calculate the *FA* of a species by directly calculating the energy of Reaction (11), it is difficult to do so because of the difficulty in calculating the electron affinity of F to give F^-. Thus it is much easier to calculate the *FA* by a relative process as shown below in Reaction (12).

$$AF^- + B \rightarrow A + BF^- \qquad (12)$$

If the *FA* of A is known, then the *FA* of B can be calculated. In previous calculations of *FA*s [12,13], we have used the *FA* of carbonyl fluoride (CF_2O) as a standard [14]. However, it has been shown recently [14b] that this value needs to be revised as it was based on the *FA* of hydrogen fluoride

Table 3
Fluoride affinities (*FA*) of metal halides in the gas phase (kcal mol^{-1} at 298 K)

Molecule	Relative *FA* [a]	Absolute *FA*
AlF_3	65.9	115.8
AlF_2Cl	69.6	119.5
$AlFCl_2$	72.0	121.9
$AlCl_3$	73.5	123.4
BF_3	34.8	84.7
GaF_3	58.4	108.3
SbF_5	69.4	119.3

[a] Fluoride affinity relative to *FA*(CF_2O). Positive value means *FA*(A) is greater than *FA*(CF_2O) = 49.9 kcal mol^{-1}.

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[4] The structure of the open form of $C_2F_5^+$ is difficult to optimize due to the essentially zero torsion frequency about the C–C bond near the minimum.

Table 4
Reaction energetics for Cl/F exchange on $AlCl_3$

Reaction	ΔH (kJ mol^{-1})	ΔH (kcal mol^{-1})
$CF_3Cl(g) + AlCl_3(g) \rightarrow CCl_4(g) + AlF_3(g)$	−12.8	−3.1
$CF_3Cl(g) + AlCl_3(s) \rightarrow CCl_4(g) + AlF_3(s)$	−192.9	−46.1
$3CFCl_3(g) + AlCl_3(g) \rightarrow 3CCl_4(g) + AlF_3(g)$	−46.6	−11.1
$3CFCl_3(g) + AlCl_3(s) \rightarrow 3CCl_4(g) + AlF_3(s)$	−226.7	−54.2

(HF) which was in error in the original work. The new value for $FA(CF_2O)$ is 49.9 kcal mol^{-1} based on a value [15] for $FA(HF) = 45.8 \pm 1.6$ kcal mol^{-1}.

The fluoride affinity calculations were all done at the MP2/DZ+P//HF/DZ+P level. The values for a number of halogenated metal species are shown in Table 3. These values can be compared to the only available experimental datum, $FA(AlF_3) = 119.0 + 1.6$ kcal mol^{-1} at 1100 K [16]. This can be transformed to a value of 115 kcal mol^{-1} at 298 K in excellent agreement with our calculated value of 115.8 kcal mol^{-1}.

It is also possible to provide information about the fluorination of the catalyst from halomethanes. From the known experimental thermochemical data for AlF_3 and $AlCl_3$ in the gas phase as well as in the crystal, together with the heats of formation of the halomethanes, it is possible to calculate the reaction energies shown in Table 4 [17]. In the gas phase, the exchange of Cl for F is slightly exothermic showing that the differences in the Al–Cl and Al–F bond strengths are comparable to the differences in the C–Cl and C–F bond strengths. In the solid phase, formation of the bridged Al–F–Al bond matrix is much more exothermic than in the gas phase, leading to significant heat release.

The inference we can draw from these calculations is that amorphous ACF retains surface sites having the very high fluoride affinities associated with the monomolecular aluminum halides of Table 3. Such high-energy dislocations are presumed to have fluoride-ion affinities approaching those of the aluminum halides and antimony pentafluoride, leading to catalysts highly active in fluoroolefin condensations.

4. Experimental details [5]

***CAUTION*: Both the Cl/F exchange reactions with $AlCl_3$ and the condensation of HFP and TFE to form *F*-pentene-2 are highly exothermic (see the Discussion), so that precautions to assure heat dissipation are necessary.**

4.1. Characterization of ACF

ACF prepared by treatment of aluminum chloride with excess trichlorofluoromethane under conditions known to replace nearly all the chlorine [1] is a light-colored, amorphous powder. Measurements of surface area (BET/N_2) led to a value of 70–140 m^2 g^{-1}, appreciably higher than that of the starting material. The catalyst is easily deactivated by protic materials and even by hydrocarbons, while the activity is greatly reduced in the presence of polychlorinated substrates such as carbon tetrachloride. Tests showed, for example, that ACF interacts exothermically with the inhibitor, D-limonene, after which the now dark brown ACF was inactive in *F*-pentene-2 formation.

A marked exothermic reaction also occurs when ACF is contacted with water. Use of a sufficient amount of water allowed for dissolution of nearly all the catalyst, giving clear 1–2 wt.% acidic solutions after filtration. This behavior is unlike that of conventionally prepared AlF_3, which is essentially insoluble in water.

4.2. Synthesis of F-pentene-2

Method A

A 400-ml metal tube, charged at −20 °C with 8.0 g of $AlF_{2.8}Cl_{0.2}$ (prepared from $AlCl_3 + CFCl_3$), 75 g (0.50 mol) of hexafluoropropene (HFP) and 50 g (0.50 mol) of tetrafluoroethylene (TFE), was shaken for 30 min while the temperature rose quickly to 20 °C and the pressure dropped to 8 psig. Distillation of the product afforded 88.0 g (70%) of *F*-pentene-2, b.p. 23–26 °C.

^{19}F NMR analysis indicated the product to be 89% *trans* and 11% *cis* isomer. IR (gas phase) (cm^{-1}): 1720 (*cis*–C=C, weak). ^{19}F NMR ϕ: *trans* isomer: −69.7 (d, $J_{FF} = 13$ Hz, 3F, CF_3C=); −85.3 (m, 3F, CF_3CF_2); −122.3 (d, $J_{FF} = 15.5$ Hz, 2F, CF_2); −158.0, −158.5 (AB d of m, $J_{FF} = 144.0$ Hz, 1F, CF=) (cf. Ref. [18]) ppm; *cis* isomer: −66.0 (m, 3F, CF_3C=); −84.6 (m, 3F, CF_3CF_2); −119.9 (p, $J_{FF} = 14.5$ Hz, 2F, CF_2); −137.0 (p, $J_{FF} = 8$ Hz, 1F, CF=); −141.6 (m, 1F, CF=) ppm. MS *m/e*: *trans* isomer: 249.984 9 (M^+); *cis* isomer: 249.980 6 (M^+); calc. for C_5F_{10}: 249.984 0. GC–MS showed a trace of HFP dimer to be present in the distilled product.

When runs were carried out on a larger scale in a 1-l stirred autoclave, conversions and yields of 90%–95% to *F*-pentene-2 were readily achieved in a highly selective reaction.

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[5] NMR spectra were generally measured for 20% solutions in $CDCl_3$ with $CFCl_3$ and, where appropriate, $(CH_3)_4Si$ as internal references. Exceptions were with the higher *F*-alkenes, in which cases lower concentrations and/or increased amounts of $CFCl_3$ as cosolvent were necessary. Mass spectra were EI at 70 eV unless otherwise specified.

Method B

The reaction can also be carried out with aluminum chloride as a catalyst which is activated in situ [1]. As indicated by the conditions for Table 1, entry 6, the activation step seems to require slightly elevated temperatures (35–55 °C) to proceed at a reasonable rate. These conditions for in situ activation stand in contrast to the ready Cl/F exchange between HFP and $AlCl_3$ [19]; we find the reaction between HFP and a slurry of $AlCl_3$ in CCl_4 to be markedly exothermic once started.

Method C

The need for effective heat management makes the presence of a solvent desirable for scale-up. Of the many solvents that allow good conversions to *F*-pentene-2, the most useful appears to be *F*-pentene-2 itself. Since *F*-pentene-2 is also condensed with TFE by ACF (vide infra), the reactivity ratio HFP/*F*-pentene-2 is shown to be very large indeed by the selectivity for adduct formation of HFP and TFE.

A 400-ml metal tube charged with 5.0 g of ACF, 49.5 g of *F*-pentane-2, 75 g (0.50 mol) of HFP and 50 g (0.50 mol) of TFE was agitated as it warmed from 0 °C. From a peak pressure (115 psig) at 16 °C, the pressure fell rapidly to 9 psig, while a slight exotherm carried the temperature to 28 °C before subsiding to 22 °C, all in 1 h. Heating at 60 °C produced no further sign of reaction. GC analysis of the crude product, 169 g, indicated that 110.1 g (88%) of C_5F_{10} had been formed. Only small amounts (<1%) of byproducts such as hexafluoropropene dimer were present.

4.3. Synthesis of *F*-n-heptene isomers

A 1-l stirred autoclave was charged with 30 g of ACF under a nitrogen atmosphere, closed, evacuated and 600 g (2.4 mol) of *F*-pentene-2 added from a metal cylinder (Table 1, entry 3). The suspension was stirred at 35 °C while TFE was added at the rate of 66 g h^{-1} until 270.6 g (2.71 mol) had been introduced. Some cooling was required to maintain the temperature at 35–40 °C. Stirring was continued for 2 h, after which the crude product of solid and 738 g of liquid was recovered. GC analysis of the liquid indicated 53 g (9%) of recovered C_5F_{10}, 621 g (75% conversion, 81% yield based on C_5F_{10}) of C_7F_{14} isomers and 61 g (6% conversion and yield based on C_5F_{10}) of C_9F_{18} isomers, along with smaller amounts of higher olefins. The C_7F_{14} mixture was identified by ^{19}F NMR analysis [20].

A similar tendency for the reaction to stop at the C_7F_{14} stage was observed in the 2:1 TFE/HFP condensation (Table 1, entry 1).

4.4. *F*-Nonene isomers

Higher ratios of TFE to HFP allow the production of higher olefins, albeit with lower selectivity. Conditions under which *F*-nonenes predominate in the product are given in Table 1, entry 2. The crude product from 40 g (0.27 mol) of HFP and 100 g of TFE was 122 g of liquid product with 3 g of solid polymer. Analysis of the liquid by GC–MS indicated the presence of 34.5 g (37% based on HFP) of C_7F_{14}, 59.0 g (49% based on HFP) of C_9F_{18} and 22.2 g (15% based on HFP) of $C_{11}F_{22}$ isomers. Small amounts of C_5F_{10}, $C_{13}F_{26}$, and (surprisingly) C_6F_{12}, C_8F_{16} and $C_{10}F_{20}$ were also present. Fractionation afforded C_7F_{14} isomers, b.p. 70–73.5 °C, followed by C_9F_{18}, b.p. 74–80 °C/200 mmHg and $C_{11}F_{22}$ isomers, b.p. 70–77 °C/50 mmHg.

^{19}F NMR spectroscopy showed the *F*-heptene fractions to be predominantly the *trans*-*F*-heptene-3 with lesser amounts of *trans*-*F*-heptene-2 and the corresponding *cis* isomers [20]. A sample of distilled C_7F_{14} contacted with ACF at 25 °C for 4 d was little changed; ^{19}F NMR analysis showed it to be 88.5% *trans*-3, 6.2% *cis*-3, 4.4% *trans*-2 and 0.9% *cis*-2. This result may be compared to that from isomerization of *F*-heptene-1 by ACF [5]. Apparently the composition of linear *F*-heptenes produced by equilibration with ACF at 25 °C is about 88.5% *trans*-3, 6% *cis*-3, 4.5% *trans*-2 and 1% *cis*-2. The presence of some *cis* isomer content was confirmed by weak IR absorption at 1710 cm^{-1}. MS *m*/*e*: 350 (M^+); 331 ($M^+ - F$); 281 ($M^+ - CF_3$); 231 ($M^+ - C_2F_5$); 181 ($M^+ - C_3F_7$). The peak intensities varied somewhat with isomer structure.

^{19}F NMR spectroscopy on the *F*-nonene fractions showed them to be over 50% linear molecules composed mainly of 3:1 *trans*-F-nonene-4/*trans*-F-nonene-3 isomers with minor amounts of *cis* isomers present (weak IR absorption 1708–1710 cm^{-1}). Considerable branched olefin was present, especially in the lower-boiling nonene fractions, as indicated by high CF_3/CF_2 ratios in the ^{19}F NMR spectra and the presence of medium to weak intensity IR absorption near 1665 cm^{-1} [$(R_F)_2C{=}CFR_F$]. MS *m*/*e*: 450 (M^+); 431 ($M^+ - F$); 381 ($M^+ - CF_3$); 331 ($M^+ - C_2F_5$); 281 ($M^+ - C_3F_7$). Some isomers showed no M^+ peak; these were assumed to have *F*-tris(alkyl)ethylene structures.

The *F*-undecene fractions were mainly branched structures of the type $(R_F)_2C{=}CFR_F$ (NMR, IR). MS *m*/*e*: 531 ($M^+ - F$); 481 ($M^+ - CF_3$); 431 ($M^+ - C_2F_5$); 381 ($M^+ - C_3F_7$).

GC–MS analyses also provided firm evidence for the presence of $C_{13}F_{26}$, C_6F_{12}, C_8F_{16} and $C_{10}F_{20}$ in small amounts in the crude product.

Product rich in *F*-nonenes can also be prepared by ACF-catalyzed addition of TFE to *F*-heptene isomers, and mixtures of higher *F*-alkenes are directly available from ACF-catalyzed additions of HFP to several equivalents of TFE (Table 1, entries 11, 9 and 10).

4.5. Addition of TFE to *F*-4-methylpentene-2

Table 1, entry 12 outlines results of a reaction of 45 g (0.15 mol) of *F*-4-methylpentene-2 (HFP dimer I), 50 g (0.50 mol) of TFE and 5.0 g of ACF. The complex liquid product, 69.7 g, isolated by vacuum transfer from 19.3 g of solid (mainly polymer of TFE) was fractionated. GC analysis indicated the total product was composed of 1.2 g of C_6F_{12} isomers, 19.4 g of 1:1 C_8F_{16} isomers, 40.5 g of 2:1 $C_{10}F_{20}$ isomers and 8.7 g of 3:1 $C_{12}F_{24}$ isomers. Examples of the fractions obtained follow.

^{19}F NMR spectroscopy showed the first cut, 0.1 g, b.p. 53–63 °C, contained essentially no HFP dimers, but was composed mainly of a 4:1 mixture of *trans-F*-n-hexene-3 and *trans-F*-n-hexene-2 [20]; MS *m/e*: 300 (M^+).

Analysis of the second cut, 7.3 g, b.p. 55.5–56 °C, indicated a 78:22 *E/Z* *F*-4-methylheptene-3 mixture, $CF_3CF_2CF{=}C(CF_3)CF_2CF_2CF_3$. MS *m/e*: 400 ($M^+$); 380.974 5 (mass measured; calc. 380.976 0 for C_8F_{15}). IR (neat) (cm^{-1}): 1675 [st, $(R_F)_2C{=}CFR_F$]. ^{19}F NMR ϕ: *E* isomer: -55.2 (m, 3F, $C\mathit{F}_3C{=}$); -81.3 (t, $J_{FF}=10$ Hz, 3F, $C\mathit{F}_3CF_2CF_2$); -83.0 (m, 3F, $C\mathit{F}_3CF_2$); -91.6 (br m, 1F, $={C\mathit{F}}$); -108.1 (m, 2F, $CF_2C\mathit{F}_2C{=}$); -116.2 (m, 2F, $CF_3C\mathit{F}_2C{=}$); -125.8 (m, 2F, $C\mathit{F}_2CF_2C{=}$) ppm (cf. Ref. [21]); *Z* isomer: -58.0 (t of t, $J_{FF}=25$, 12 Hz, 3F, $C\mathit{F}_3C{=}$); -81.2 (t, $J_{FF}=11$ Hz, 3F, $C\mathit{F}_3CF_2CF_2$); -82.8 (m, 3F, $C\mathit{F}_3CF_2C{=}$); -88.2 (br m, 1F, $={C\mathit{F}}$); -103.9 (m, 2F, $CF_2C\mathit{F}_2C{=}$); -115.7 (m, 2F, $CF_3C\mathit{F}_2C{=}$); -123.1 (m, 2F, $C\mathit{F}_2CF_2C{=}$) ppm.

For the third cut, 1.4 g, b.p. 83–85 °C/200 mmHg, IR (neat) (cm^{-1}): 1663 (st, *F*-trialkylethylene). GC: 9:1 mixture. For the major component, *F*-4-n-propylheptene-3, $CF_3CF_2CF{=}C(CF_2CF_2CF_3)_2$. MS *m/e*: 480.967 9 (mass measured; calc. 480.969 6 for $C_{10}F_{19}$). ^{19}F NMR ϕ: -81.0 (m, 6F, 2 $C\mathit{F}_3CF_2CF_2$); -82.5 (m, 3F, $C\mathit{F}_3CF_2C{=}$); -101.1 (m, 2F, $C\mathit{F}_2C{=}$); -105.3 (m, 2F, $C\mathit{F}_2C{=}$); -115.5 (m, 2F, $C\mathit{F}_2C{=}$); -121.5 (m, 2F, $C\mathit{F}_2$); -124.3 (m, 2F, $C\mathit{F}_2$) ppm.

A slightly higher boiling cut, 4.7 g, b.p. 88–91 °C/200 mmHg, contained isomeric C_{10} olefins such as *F*-4-methylnonene-4 in addition to the previous compound.

A fraction, 5.3 g, b.p. 98–99 °C/200 mmHg, showed IR (neat) (cm^{-1}): 1661 (st, *F*-trialkylethylene). MS *m/e*: 581 ($M^+ - F$) for the main components. The ^{19}F NMR spectrum was compatible with a mixture of structures such as $(CF_3CF_2CF_2)_2C{=}CF(CF_2)_3CF_3$ and $CF_3CF_2CF{=}C(CF_2CF_2CF_3)CF_2CF_2CF_2CF_2CF_3$.

A similar reaction of TFE with *F*-2-methyl-pentene-2 (HFP dimer II) also proceeded, but gave major amounts of polymer as well (Table 1, entry 13).

4.6. Preparation of 1,1,2-trichloroheptafluoropentene-1

A 400-ml metal tube charged with 100 g (0.50 mol) of 1,1,2-trichlorotrifluoropropene-1, 16 g of ACF and 50 g (0.50 mol) of TFE was shaken at 25 °C for 1.5 h while the pressure fell to 6 psig. The crude product, 155 g, was fractionated to give a foreshot, 25.4 g (25% recovery) of $CF_3CCl{=}CCl_2$, followed by 42.3 g (38% yield) of $CF_3CF_2CF_2CCl{=}CCl_2$, b.p. 63–68 °C/100 mmHg. IR (neat) (cm^{-1}): 1578 (C=C). ^{19}F NMR ϕ: -81.1 (t, $J_{FF}=9.7$ Hz, 3F, $C\mathit{F}_3$); -106.1 (q, $J_{FF}=9.7$ Hz, 2F, $C\mathit{F}_2C{=}$); -125.6 (s, 2F, $C\mathit{F}_2$) ppm (cf. Ref. [22]). MS *m/e*: 297.894 4 (mass measured M^+, calc. 297.895 3 for $C_5Cl_3F_7$) with expected Cl isotope peaks present at 300, 302 and 304.

Higher fractions, b.p. 86–114 °C/100 mmHg, were shown by GC–MS and ^{19}F NMR analyses to be mixtures containing both 1:1 and 2:1 adducts in which appreciable disproportionation of chlorine had occurred.

4.7. Addition of TFE to 2,3-dichlorohexafluorobutene-2

Reaction of 93.2 g (0.40 mol) of 2,3-dichlorohexafluorobutene-2, 5.0 g of ACF and 50 g (0.50 mol) of TFE was carried out at 80 °C for 2 h under pressure. Fractionation of the crude product gave 14.0 g (15% recovery) of the starting butene. This was followed by 54.1 g (48% yield) of a 58:42 mixture of *trans*- and *cis*-2,3-dichlorodecafluorohexene-2, b.p. 103–109 °C. IR (CCl_4) (cm^{-1}): 1595 (weak, *cis*-C=C). For the *trans* isomer: GC–MS *m/e*: 331.915 0 (mass measured M^+; calc. 331.921 7 for $C_6Cl_2F_{10}$) with Cl isotope peaks at 334 and 336. ^{19}F NMR ϕ: -63.4 (s, 3F, $C\mathit{F}_3C{=}$); -81.2 (t, $J_{FF}=9.6$ Hz, 3F, $C\mathit{F}_3CF_2$); -107.7 (q, $J_{FF}=9.6$ Hz, 2F, $C\mathit{F}_2C{=}$); -125.3 (s, 2F, $CF_3C\mathit{F}_2$) ppm. For the *cis* isomer: GC–MS *m/e*: 332, 334, 336 (M^+). ^{19}F NMR ϕ: -58.4 (t of t, $J_{FF}=21$, 9 Hz, 3F, $C\mathit{F}_3C{=}$); -81.2 (t, $J_{FF}=9.6$ Hz, 3F, $C\mathit{F}_3CF_2$); -104.6 (m, 2F, $C\mathit{F}_2C{=}$); -123.2 (m, 2F, $CF_3C\mathit{F}_2$) ppm.

Finally, there was obtained 21.4 g (20% yield) of a 77:23 mixture of *trans*- and *cis*-4,5-dichlorotetradecafluorooctene-4, b.p. 136–141 °C. IR (CCl_4) (cm^{-1}): 1583 (weak, *cis*-C=C). For the *trans* isomer: GC–MS *m/e*: 432, 434, 436 (M^+). ^{19}F NMR ϕ: -81.3 (t, $J_{FF}=9.5$ Hz, 3F, $C\mathit{F}_3$); -106.7 (q, $J_{FF}=9.5$ Hz, 2F, $C\mathit{F}_2C{=}$); -125.1 (s, 2F, $CF_3C\mathit{F}_2$) ppm. For the *cis* isomer: GC–MS *m/e*: 432, 434, 436 (M^+). ^{19}F NMR ϕ: -81.3 (t, $J_{FF}=9.5$ Hz, 3F, $C\mathit{F}_3$); -102.7 (m, 2F, $C\mathit{F}_2C{=}$); -122.7 (m, 2F, $CF_3C\mathit{F}_2$) ppm.

4.8. Addition of TFE to *F*-5*H*,6*H*-n-decene-5

A 400-ml metal tube charged with 5 g of ACF, 139 g (0.30 mol) of $F(CF_2)_4CH{=}CH(CF_2)_4F$ and 50 g (0.50 mol) of TFE was shaken at 25 °C for 17 h. Fractionation of the product afforded 97.2 g (57%) of 97% pure *trans-F*-6-ethyl-5*H*,6*H*-decene-4, b.p. 80–83 °C/50 mmHg. IR (neat) (cm^{-1}): 3118 (unsatd. CH); 2986 (satd. CH); 1717 (C=C). MS *m/e*: 563.981 3 (mass measured M^+; calc. 563.980 4 for $C_{12}H_2F_{22}$). ^{1}H NMR δ: 5.71 (d, $J_{HF}=27.9$ Hz, of d, $J_{HH}=11.3$ Hz, 1H, $={C\mathit{H}}$); 4.30 (t, $J_{HF}=18.8$ Hz, of d, $J_{HH}=11.3$ Hz, of t, $J_{HF}=6.2$ Hz, 1H, $C\mathit{H}$) ppm. ^{19}F NMR ϕ: -81.7 (t, $J_{FF}=9$ Hz, 3F, $C\mathit{F}_3$); -81.8 (t, $J_{FF}=10$ Hz, 3F, $C\mathit{F}_3$); -83.4 (s, 3F, $C\mathit{F}_3CF_2CH{=}$); -111.4, -113.9 (AB d, $J_{FF}=285.3$ Hz, 2F, $C\mathit{F}_2$); -113.3, -118.6 (A′B′ d, $J_{FF}=274.7$ Hz, 2F, $C\mathit{F}_2$); -118.0 (m, 1F, $={C\mathit{F}}$); -119.9 (m, 2F, $C\mathit{F}_2$); -121.3, -122.6 (A″B″ d, $J_{FF}=300.4$ Hz, 2F, $C\mathit{F}_2$); -125.6, -127.3 (A‴B‴ d, $J_{FF}=292.8$ Hz, 2F, $C\mathit{F}_2$); -129.9 (m, 2F, $C\mathit{F}_2$) ppm.

GC–MS and NMR analysis also indicated the presence of isomers such as $CF_3CF_2CF_2CF(CF_2CF_3)CH{=}CHCF_2CF_2CF_2CF_3$ in small amounts (3%).

4.9. 2 + 2 Cycloaddition catalyzed by ACF

Syntheses of *F*-pentene-2 in tetrachloroethylene as solvent gave moderate yields of pentene, but the reaction was accompanied by persistent byproduct formation. Reaction without TFE present was carried out using 5.0 g of ACF, 166 g (1.0 mol) of C_2Cl_4 and 125 g (0.83 mol) of HFP at 60 °C for 16 h under autogenous pressure to produce several of the byproducts noted previously. Distillation of the crude product gave 11.0 g of early fractions, b.p. 72–89 °C, containing varying amounts of three compounds. The first, ca. 0.8 g of 1-chloropentafluoropropene, was identified by GC–MS *m/e*: 166, 168 (M^+); 147, 149 ($M^+ - F$); 131 ($M^+ - Cl$); 116, 118 ($M^+ - CF_2$).

The next two products, 7.3 g, b.p. 84–89 °C, were in order of volatility, *trans*- and *cis*-2,3-dichlorooctafluoropentene-2. For the *trans* isomer: MS *m/e*: 281.920 0 (mass measured M^+; calc. 281.924 9 for $C_5Cl_2F_8$) with Cl isotope peaks. ^{19}F NMR ϕ: −63.5 (s, 3F, $C\mathit{F_3}C{=}$); −82.8 (s, 3F, $C\mathit{F_3}CF_2$); −111.0 (s, 2F, $C\mathit{F_2}$) ppm. For the *cis* isomer: IR (neat) (cm^{-1}): 1594 (C=C). MS *m/e*: 282 with Cl isotope peaks. ^{19}F NMR ϕ: −58.2 (t of q, $J_{FF} = 21$, 5.5 Hz, 3F, $C\mathit{F_3}C{=}$); −82.0 (q, $J_{FF} = 5.5$ Hz, 3F, $C\mathit{F_3}CF_2$); −108.2 (q, $J_{FF} = 21$ Hz, 2F, $C\mathit{F_2}$) ppm.

Isomerization and disproportionation of linear 1:1 HFP/C_2Cl_4 adducts can account for the formation of these two pentenes. They were also among the products obtained from TFE and chlorotrifluoroethylene (Table 1, entry 8), an indication that the disproportion occurs from lightly chlorinated adducts as well.

Further fractionation afforded 18.9 g (7%) of 1,1,2,2-tetrachloro-3-trifluoromethyltrifluorocyclobutane (**5**), b.p. 63 °C/50 mmHg. IR (neat) showed no C=C. MS (CI) *m/e*: 278.897 2 (mass measured $M^+ - Cl$; calc. 278.897 0 for $C_5Cl_3F_6$) with Cl isotope peaks. ^{19}F NMR ϕ: −72.4 (d of d of d, $J_{FF} = 9, 7, 4$ Hz, 3F, $C\mathit{F_3}$); −109.1 (A branch d of d of q, $J_{FF} = 205, 6, 4$ Hz, 1F, $C\mathit{F}F$); −109.9 (B branch d of q, $J_{FF} = 105, 9$ Hz, 1F, $CF\mathit{F}$); −161.4 (p, $J_{FF} = 7$ Hz, 1F, $C\mathit{F}$) ppm. Analysis: Calc. for $C_5Cl_4F_6$: C, 19.01; Cl, 44.90%. Found: C, 18.99; Cl, 45.05%.

A final fraction, 7.5 g, b.p. 55–59 °C/10 mmHg, contained (in addition to **5**) 2.7 g (1%) of 1,1,2,2-tetrachloro-3-chlorodifluoromethyltrifluorocyclobutane (**6**). GC–MS (CI) *m/e*: 259.895 1 (mass measured $M^+ - 2Cl$; calc. 259.898 6 for $C_5Cl_3F_5$) with Cl isotope peaks. ^{19}F NMR ϕ: −58.0 (A branch d of d of d, $J_{FF} = 182$, 13.1, 10.6 Hz, 1F, $ClC\mathit{F}F$); −61.6 (B branch d of d of t, $J_{HH} = 182$, 19, 3.3 Hz, 1F, $ClCF\mathit{F}$); −108.0 (A′ branch d of d of d, $J_{FF} = 203, 11, 3$ Hz, 1F, $C\mathit{F}F$); −110.8 (B′ branch d of d of d of d, $J_{FF} = 203$, 18, 13, 4 Hz, 1F, $CF\mathit{F}$); −151.3 (t of t, $J_{FF} = 11, 4$ Hz, 1F, $C\mathit{F}$) ppm.

The yields of products as judged by GC analysis were 12% of **5**, 1% of **6**, 4% of 1-chloropentafluoropropene and 4% *cis*- and *trans*-dichloropentenes, the latter representing acyclic addition products from HFP and tetrachloroethylene.

5. Conclusions

An aluminum-based catalyst, amorphous aluminum chlorofluoride, is shown to be an exceptionally active catalyst for the condensation of allyl fluorides with reactive fluoroolefins such as tetrafluoroethylene. The catalyst is also effective in the isomerization of fluoroolefins to more stable systems. These synthetic methods offer direct entrée to relatively large molecules from available building blocks. In particular, linear C_5–C_8 fluoroolefins are now readily available in one step. *Ab initio* electronic structure calculations show that 1,3-fluorine transfer will occur with much lower barrier heights than 1,2-fluorine transfer. The calculations also show that the condensation reaction is highly exothermic. Revised heats of formation for C_3F_8 and HFP are presented. High values of fluoride affinities for some simple metallohalogen species are predicted.

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