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Persistent perfluoroalkyl radical investigations under reductive environment: reaction with electron-donating reagents

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This article is dedicated to Professor Emeritus Yoshiro Kobayashi on the occasion of his 75th birthday

Abstract

The reactivity of persistent perfluoroalkyl radical, perfluoro-3-ethyl-2,4-dimethyl-3-pentyl (**1**), with various electron-donating reagents was investigated. It is revealed that **1** which is robust under oxidative conditions is rather vulnerable under reductive conditions. Thus, Lewis bases such as triethylamine and triphenylpnictogens (Ph_3Pn, Pn=N, P, As, Sb, Bi) and some soft anions such as iodide or tetraphenyl borate reacted with **1** to give perfluoro-3-isopropyl-4-methylpent-2-ene (**2**) quantitatively. Even very weak Lewis bases such as diethyl ether and diethylsulfide also reacted with **1** to give **2** and additionally a hydrido product, perfluoro-3-ethyl-3-*H*-2,4-dimethylpentane (**4**). Hydrogen gas did not react with **1** at all without a catalyst, but in the presence of metal Pd adsorbed on charcoal, smoothly reacted to give **2** in quantitative yield. Metal hydrides such as $LiAlH_4$, $NaBH_4$, NaH, BH_3 (THF complex), Bu_3SnH, Me_2PhSiH reacted with **1** to give **2** and **4**. That an electron transfer mechanism is operating in the formation of **2** is obvious, but not conclusive in the formation of **4**. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Persistent perfluoroalkyl radical; Reduction; Electron transfer

1. Introduction

Persistent perfluoroalkyl radical **1**, perfluoro-3-ethyl-2,4-dimethyl-3-pentyl, is known to be amazingly stable. Radical **1** can be distilled and analyzed by gas chromatography without decomposition and shows no reactivity with conc. HCl, conc. H_2SO_4, and oxidizing agents such as oxygen, chlorine, bromine and iodine [1]. The stability of **1** arises not only from the inaccessibility of the radical center to the reagent due to sterical hindrance, but also from the electronic properties endowed by the perfluoro system. Radical **1** is prepared by reacting hexafluoropropene trimers, perfluoro-3-isopropyl-4-methylpent-2-ene (**2**) and perfluoro-3-ethyl-2,4-dimethylpent-2-ene (**3**), with elemental fluorine or in an electrochemical fluorination cell [2]. Other functionalized analogs of **1** have been prepared under similar conditions [3–7]. Although the chemistry of **1** in oxidative environments has been well characterized, little has been reported on the reaction of **1** with reducing agents and electron-donating reagents. The aim of this report is to reveal the nature of persistent perfluoroalkyl radical **1** under the reductive environments.

2. Results and discussion

2.1. Reaction of **1** with hydrogen gas

The experimental conditions investigated are summarized in Table 1. When a neat liquid containing radical **1** was stirred under H_2 atmosphere at ambient temperature, no reaction occurred even after seven days (Run 1). The same reaction at the forcing conditions leads to a formation of perfluoro-3-ethyl-3-*H*-2,4-dimethylpentane **4** in poor yields (Run 2). However, when a catalytic amount of 5% Pd on carbon is added to an ethereal solution of **1** (0.01 equivalents of Pd) a mildly exothermic reaction occurs to cause a gentle reflux of ether and **1** is quantitatively converted to **2** after

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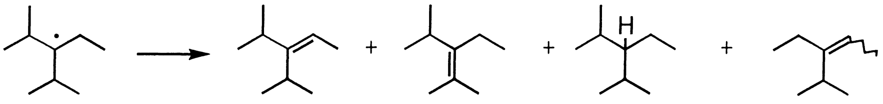
Table 1
Reaction of 1 with hydrogen (all unmarked bonds are to fluorines)



1 **2** **3** **4** **5**

Run	Conditions[a]	Time	Product distribution (%)[b]					Recovery (%)[b]
			2	3	4	5	1	
1	H_2	7 days	–	–	–	–	100	100
2	H_2, 80°C[c]	33 h	1.6	–	14.8	49.9	13.2	74.2
3	H_2/cat. 5%Pd/C	30 min	100	–	–	–	–	100
4	Ar/cat. 5%Pd/C	4.5 h	25.4	–	–	–	74.6	100
5	H_2/cat. 5%Pd/$BaSO_4$	30 min	100	–	–	–	–	100
6	Ar/cat. 5%Pd/$BaSO_4$	5 h	–	–	–	–	100	100

[a] Runs 3–6 were run in diethyl ether at room temperature and at atmospheric pressure of H_2 or Ar, while Runs 1 and 2 were carried out neat without solvent.

[b] Product distribution and % of recovery (defined as the sum of yields of all products including radical **1**) were calculated from GC data using perfluoro-2,4-dimethyl-3-ethylpentane as an internal standard.

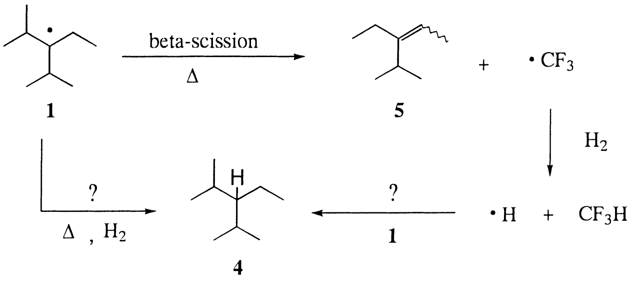
[c] The products other than **1**–**5** obtained are perfluoro-3-ethyl-2,3,4-trimethylpentane (9.9%) and an unknown with the retention time close to the former (9.6%).

30 min (Run 3). It should be emphasized here that ether which can dissolve radical **1** plays an important role in the smooth reaction. If ether is not included, the Pd catalyst floats on the surface of a perfluoro phase and thus is not well dispersed into it and easily expelled out on the vessel wall, resulting in no reaction. The wettability of the Pd catalyst and solubility of **1** in ether seem to be important factors for the successful reaction.

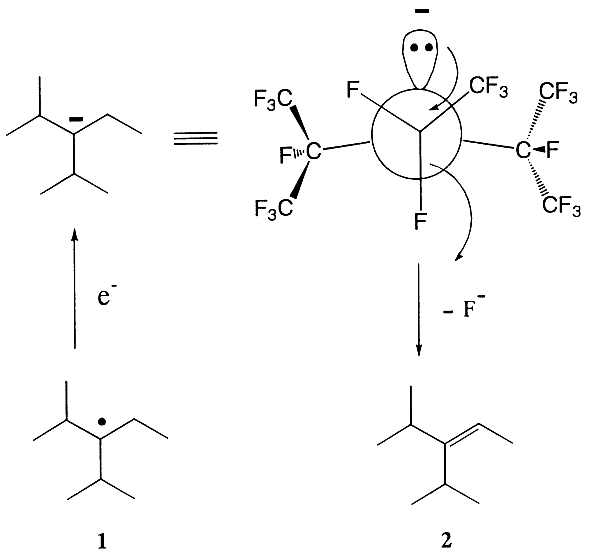
Surprisingly, even under Ar atmosphere, the conversion of **1** to **2** still occurred when the same 5% Pd on carbon was added to an ethereal solution of **1**, although at a much slower rate than when hydrogen was present (Run 4). Substituting $BaSO_4$ for carbon as the catalyst support resulted in no reaction over argon (Run 6), but the same rapid reaction was observed again in the presence of hydrogen to quantitatively prepare **2** (Run 5). These results suggest that the Pd catalyst can transfer an electron to **1** forming the anion which eliminates a fluoride ion to form **2**. The Pd catalyst is then rapidly reduced by H_2 or slowly reduced by the carbon support. When the inert $BaSO_4$ is used as the support, the electrons lost from the Pd are not replenished and no significant reaction is observed.

Alkane **4** is formed in ca. 11% yield (calcd; recovery ×product distribution/100 in Table 1) when **1** is heated to 80°C in the presence of H_2 for 33 h. Competing with the addition of hydrogen are (1) the first order decomposition of **1** by beta-scission to form a CF_3 radical and *E*- and *Z*-perfluoro-3-ethyl-4-methylpent-2-ene (**5**) [1] and (2) radical combination reaction between CF_3 and **1** which gives perfluro-3-ethyl-2,3,4-trimethylpentane (**6**) in the yield of 9.9% comparable to the one of **4**. It is not known if **4** is formed from **1** by direct reaction with H_2 or by reaction with hydrogen atoms formed from the reaction between CF_3 and H_2 (Scheme 1). Regardless of the reaction mechanism, it is rather amazing to know that such a sterically demanding trifluoromethyl radical [8] can combine with a sterically shielded radical center of **1** under hydrogen gas atmosphere to give such a yield comparable with the one of the hydrido product **4**. This result suggests the access of much smaller hydrogen molecule to the radical center of **1** is highly probable. In this regard, the inertness of radical **1** could be interpreted as being not only from the sterical hindrance but also from the nature of the perfluoro system.

Exclusive formation of kinetically favored **2** over thermodynamically favored **3** in the electron transfer reaction is understood by the availability of fluorine atoms on β-carbons to be anti-periplanar to the lone pair electrons of the intermediate anion. A space-filling model of the anion can be constructed only when the two perfluoroisopropyl groups are conformationally arranged in the manner depicted in Scheme 2. Both 3°-fluorines on the perfluoroisopropyl groups are orthogonal to the orbital of the lone pair electrons, while one of the two 2°-fluorine atoms on the perfluoroethyl group is in the preferred anti-periplanar position to leave as a fluoride ion to form **2**. Alkene **2** is subject to reversible nucleophilic attack by fluoride, and when pure **2** is stirred with a catalytic amount of fluoride for several hours at room temperature, it is isomerized to the



Scheme 1. All unmarked bonds are to fluorines.



Scheme 2. Schematic drawing of the intermediate anion.

thermodynamic equilibrium mixture of approximately 33% of **2** and 67% of **3** [9].

2.2. *Reaction of* **1** *with electron-donating reagents*

We next examined a series of electron-donating reagents (Table 2). Alkyl radical **1** in acetonitrile is reported to have a non-reversible reduction potential between 0.55 and 0.575 V by cyclic voltammetry [10]. Thus, iodide with a redox half reaction potential of 0.535 V should reduce **1** while bromide with a potential of 1.06 V should not [11]. Mixing an aqueous KI/acetone solution (1 mmol KI in 0.2 ml of H_2O and 1 ml of acetone) with **1** (0.5 mmol) gave **2** almost quantitatively in 10 minutes (97.6% yield, Run 1), but no reaction occurred with aqueous KBr/acetone (Run 2).

Radical **1** is reduced by organic bases to form **2** with loss of a fluoride ion. Reaction rates tend to increase with increasing base strength. An immediate exothermic reaction occurred when **1** was mixed with triethylamine at room temperature, giving **2** quantitatively (Run 3). A much more vigorous reaction was observed between **1** and the electron-rich tetrakis(dimethylamino)ethene [12] which resulted in the formation of tars and a low yield of **2** and **3** in a 1:2 ratio (Run 4). Although **2** may have been formed initially in Run 4, the fluoride ion and great amount of heat produced from the reduction of **1** isomerized **2** to **3**. The soft anion tetraphenyl borate also reacted with **1** to give **2** exclusively, but at a slower rate than the amines (Run 5). Triphenylamine reacted smoothly with **1** over 10 min to give **2** quantitatively (Run 6). Formation of the intermediate cation radical of triphenylaminium by an electron transfer process is obvious from the sudden appearance of a deep blue color by the addition of **1** into the ethereal solution of triphenylamine at room temperature [13]. The deep color is soon followed by a reddish brown color, suggesting a dimerized cation radical species [14]. It is noteworthy to point out that pyridine did not react with **1** after 24 h stirring at room temperature even though it is more basic and nucleophilic than triphenylamine.

In contrast with triphenylamine, only a faint yellow coloration occurred with triphenylphosphine probably due to a CT band (vide infra), but no deep coloration occurred. Another peculiar difference is the formation of white precipitation which suddenly appeared after a few minutes of

Table 2
Reaction of **1** with various electron-donating reagents

$$\mathbf{1} + \xrightarrow[\text{Reagents RT}]{\text{Ether}} \mathbf{2} + \mathbf{3} + \mathbf{4}$$

Run	Reagents[a]	Time	Product distribution (%)				Recovery (%)[b]
			2	**3**	**4**	**1**	
1	Aq. KI/acetone	10 min	97.6	2.4	–	–	100
2	Aq. KBr/acetone	20 h	–	–	–	100	100
3	Et_3N	<1 min	100	–	–	–	100
4	$[(Me_2N)_2C{=}]_2$	<1 min	21.9	46.8	–	–	44.7
5	$Ph_4B^-Na^+$	3 h	91.8	–	–	8.2	93.3
6	Ph_3N	10 min	100	–	–	–	100
7	Ph_3P	30 min	100	–	–	–	100
8	Ph_3As	3 h	24.5	–	–	75.5	100
9	Ph_3Sb	3 h	43.8	–	–	56.2	99.9
10	Ph_3Bi	3 h	19.6	–	–	80.3	99.8
11	Et_2O	41 h	37.1	–	28.9	34.0	95.1
12	THF	45 h	46.2	–	45.7	8.1	97.2
13	Et_2S	44 h	87.1	–	3.9	9.0	85.9
14	DMF	48 h	–	–	–	100	100

[a] The molar ratio of the reagent to **1** is one except aq. KI/acetone and aq. KBr/acetone where the ratio is two. A large excess is used for Runs 11–14.

[b] Recoveries (defined as the sum of yields of all products including radical **1**) are calculated from GC data using perfluoro-3-ethyl-2,4-dimethylpentane as an internal standard.

stirring. Although the rate of the reaction is slower, **2** is also formed quantitatively from **1** and triphenylphosphine over 30 min (Run 7). Other triphenylpnictogens Ph_3Pn (Pn=As, Sb, Bi) also reacted with **1** in a manner similar to Ph_3P, but with much slower rates (Runs 8–10).

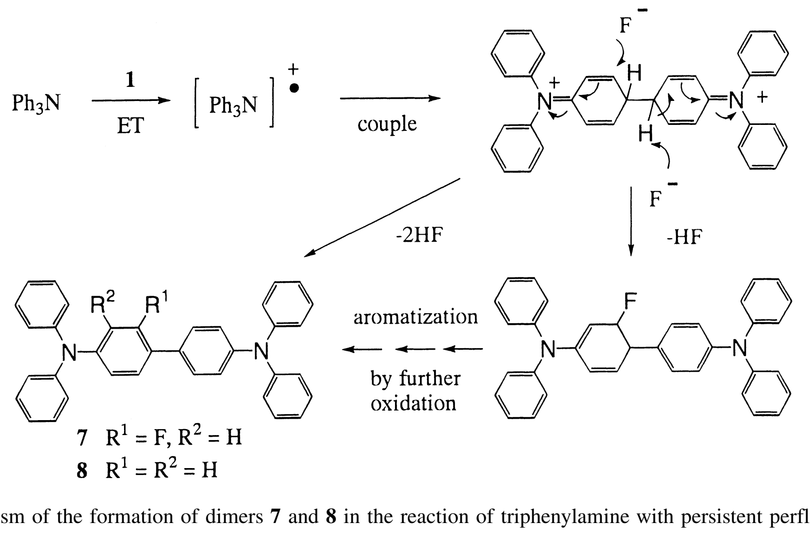
The oxidation products of triphenylpnictogens were not intensively studied, but it is worth commenting on these to some extent. The main product isolated from the reaction mixture of triphenylamine with **1** is *N,N,N′,N′*-tetraphenylbenzidine (ca. 20% yield), of which formation is well known in both processes of electrochemical [15] and chemical [16] oxidation of triphenylamine. Accompanied with the main product is a mono-fluoro derivative of *N,N,N′,N′*-tetraphenylbenzidine, the structure of which was estimated as **7** based on the spectroscopic data (MS, ^{19}F-NMR, ^{1}H-NMR, ^{13}C{1H}- and ^{13}C{^{1}H, ^{19}F}-NMR, IR). We tentatively assigned the structure **7** by considering the reaction mechanism depicted in Scheme 3. MS of **7** isolated by HPLC (see Section 3) shows a molecular ion *m/z* 506 as a parent ion with right intensities of ^{13}C-isotopic peaks M+1 and M+2 [*m/z* 507 (40.9) and *m/z* 508 (7.8), respectively]. The peak found at *m/z* 253 (74.9) was M^{2+} molecular ion similar to M^{2+} at *m/z* 244 (ca. 50) reported for *N,N,N′,N′*-tetraphenylbenzidine [17]. The fragment ions of both half of the molecule with the compositions of $C_{18}H_{13}FN$ ($Ph_2NC_6H_3F$) and $C_{18}H_{14}N$ ($Ph_2NC_6H_4$) were found at *m/z* 262 (1.4) and 244 (4.2), respectively.

A large recovery of triphenylamine (ca. 50%) is consistent with the observation of the formation of more easily oxidizable *N,N,N′,N′*-tetraphenylbenzidine [18]. Half of the initial triphenylphosphine was recovered unchanged also in the reaction of **1** with triphenylphosphine and the remaining half was recovered as triphenylphosphine oxide after work up, which is probably formed with reaction of moisture. No signals corresponding to the dimerized products and M–F fragment ion of Ph_3PF_2 [19] were observed in MS of the crude reaction product measured by a direct inlet (DI) mode. The reason why only a half consumption of the triphenylphosphine was observed is yet not known. In contrast with the triphenylphosphine, Ph_3AsF_2 and Ph_3BiF_2 were obtained as sole products in the reaction of **1** with Ph_3As and Ph_3Bi. Why most of the initial Ph_3As and Ph_3Bi (60–70%) remained intact in both reactions is again not known. The reaction of **1** with Ph_3Sb gave, on the other hand, a very complex reaction mixture.

We noticed that a pale yellow color appeared when **1** was added to diethyl ether or THF. If the ethereal solution (**1** is soluble in ether) is kept at room temperature for a prolonged time (41 h), 68% of **1** is converted to **2** and **4** (Run 11). When the heterogeneous mixture of **1** and THF was vigorously stirred at room temperature over 45 h, it followed almost the same as the above, but with a little faster reaction rate than in diethyl ether. The end of the reaction was easily monitored with discoloration. Diethylsulfide did not dissolve **1**, but a purple color developed in the upper sulfide layer when mixed. After the heterogeneous mixture was vigorously stirred for 44 h at room temperature, the color of the upper layer became faint. GC analysis of the lower layer showed that ca. 90% of **1** was consumed and **2** (87.1%) was formed as a main product in addition to a small amount of by-product **4** (Run 13). Interestingly, dimethyformamide (DMF) did not react with **1** at all after 48 h stirring of its heterogeneous mixture (Run 14).

Burdeniuc et al. recently reported that a hexane solution of triethylamine and a cyclic perfluoroalkane such as perfluorodecalin shows a CT band at 270 nm with no observable changes in both reagents under the conditions for the UV measurement [20]. The coloration by the dissolution of **1** in ether or by mixing of **1** with sulfide is very likely to be caused by a CT complex formation between **1** and these ethers because the color disappeared after **1** was consumed.

The relative reaction rates (N>P>Sb>As,Bi) observed for the triphenylpnictogens series is rather surprising in the light of literature reports of the relative basicity (As>N>Bi,Sb>P) [21] and rates of single electron oxidation (P>As,Sb>N>Bi) [22]. Neither order is consistent with the observed relative



Scheme 3. Mechanism of the formation of dimers **7** and **8** in the reaction of triphenylamine with persistent perfluoroalkyl radical **1**.

rates. However, considering the difference of the reaction products in the pnictogen series used, it is realized that it is difficult to make a simple comparison among all pnictogen series. The unexpectedly fast relative reaction rate observed for the Ph_3N could be explained by taking into account the formation of the dimer which has an electrochemical oxidation rate known to be faster than the starting triphenylamine [23]. It would be desirable to use the tri-*p*-tolylpnictogen series for the kinetic study because tri-*p*-tolylamine is known to be resistant toward dimerization [24,25]. This will be the subject of a future investigation.

2.3. Reaction of **1** *with various metal hydrides*

Tin and silicon hydride reducing agents which readily undergo hydrogen abstraction [26–28] (Runs 1–3) gave a mixture of **4** and **2** from **1**. With tributyltin hydride at room temperature **4** was obtained as a main product in addition to **2** in a combined yield of 78%. Dimethylphenylsilane reacted similarly to tributyltin hydride, while diphenylsilane gave **2** and **4** in a 1: 1 ratio. There is no doubt that an electron transfer (ET) mechanism worked for the formation of **2**, but it is beyond the scope of this paper to refer to the mechanism for the formation of **4**. Both tetrabutyltin and tetramethyltin did not react with **1** at all (Runs 4 and 5), suggesting the Sn–H bond is responsible for the ET process of the reaction.

Since vigorous reaction was expected, the reaction of **1** with $LiAlH_4$ was first conducted in dry-ice acetone bath by using a molar ratio of $LiAlH_4$:**1**=0.25:1. However, GC analysis of the lower perfluoro phase of the 20 min sample showed no reaction at all. Therefore, the temperature was raised to room temperature and the sample was stirred continually for 2 h, then quenched by H_2O and 15% aq. NaOH. GC analysis showed that most of **1** ($93\times0.715=66.5\%$) remained unchanged (Run 6). The same reaction was conducted at room temperature throughout the reaction, but the same result was obtained (Run 7). The reaction was conducted in a concentration (0.1 M in THF) much less than the solubility of $LiAlH_4$ in THF (1.0 M solution is commercially available); thus the reaction system is almost homogeneous. However, a vigorous effervescent reaction occurred in the quenching process in both cases, suggesting that only a part of hydrogen among the four hydrogens of $LiAlH_4$ is active for this reaction and the rest are in a dormant state until being quenched. When the molar ratio of $LiAlH_4$ was increased to 1, ca. 26% of **1** still remained unchanged. While doing this reaction, we noticed that THF is a rather poor solvent for **1** and thus a perfluoro phase existed not only at low temperature but also at room temperature. We roughly estimated the solubility of the stock radical solution by adding it into THF or diethyl ether with vigorous stirring at room temperature until the first tiny perfluoro drop appeared. Solubilities thus obtained were only 17 mg in 1 ml of THF and 262 mg in 1 ml of diethyl ether. This surprising solubility difference prompted us to repeat the same reduction by using diethyl ether as solvent. Again, about the same amount of **1** (ca 20%) remained unreactive (Run 9). It is rather surprising to know such a radical system even susceptible to the solvent like ether can survive through contact with a very strong reducing agent like $LiAlH_4$. The unexpected high recovery of **1** in the reaction of **1** with powerful reducing agents such as $LiAlH_4$, $NaBH_4$ (Run 10) and NaH (Run 11), even at room tem-

Table 3
Reaction of **1** with various metal hydrides

$$\mathbf{1} + \xrightarrow[\text{Reagents RT}]{\text{Solvent}} \mathbf{2} + \mathbf{3} + \mathbf{4}$$

Run	Reagents	Molar ratio[a]	Solvent	Time (h)	Product distribution (%)					Recovery (%)[c]
					2	**3**	**4**	**1**	Others[b]	
1	Bu_3SnH	1	Neat	2.0	37.0	–	63.0	–	–	78.2
2	Me_2PhSiH	1	Et_2O	4.0	40.4	–	59.6	–	–	81.5
3	Ph_2SiH_2	1	Et_2O	3.5	47.3	2.3	44.9	5.5	–	84.7
4	Bu_4Sn	1	Neat	7 days	–	–	–	100	–	100
5	Me_4Sn	1	Neat	5 days	–	–	–	100	–	100
6	$LiAlH_4$[d]	0.25	THF	2.0	18.6	–	9.9	71.5	–	93.0
7	$LiAlH_4$	0.25	THF	1.0	16.3	–	5.5	76.3	1.9	98.0
8	$LiAlH_4$	1	THF	1.0	54.0	1.3	7.2	26.9	10.6	96.0
9	$LiAlH_4$	1	Et_2O	1.0	21.2	1.1	50.9	20.4	6.4	94.5
10	$NaBH_4$	1	Et_2O	1.0	9.4	–	6.3	83.8	0.5	98.7
11	NaH[d]	1	Et_2O	4.0	13.4	–	–	86.6	–	100
12	BH_3/THF	1	THF	4.0	57.0	–	43.0	–	–	100

[a] The molar ratio to the reagent of **1**.

[b] Not investigated further.

[c] Recoveries (defined as the sum of yields of all products including radical **1**) are calculated from GC data using perfluoro-3-ethyl-2,4-dimethylpentane as an internal standard.

[d] The reaction was conducted at −78°C at first, then warmed to room temperature and continued for the time described in the table.

perature, was probably caused by passivation due to the formation of a passive coat on the surface of the suspended reagents. Both, that vigorous effervescence occurred in the quenching process of the alkali metal hydrides and that a BH_3/THF adduct soluble in THF completely reacted with **1** in the homogeneous system to give a mixture of the products **2** and **4** (Run 9), are consistent with this explanation of passivation.

There are two things which should be mentioned on the product distribution. One is a remarkable solvent effect found in reduction with $LiAlH_4$. Thus, the olefin **2** is the main product (54.0%) in the case of THF (Run 8); in contrast, the hydrido product **4** is main (50.9%) in the case of diethyl ether (Run 9). The other is the selective formation of **2** in the reduction of **1** with NaH.

In summary, it was found that the persistent perfluoroalkyl radical **1**, which is very stable under oxidative conditions, reacts with various kinds of electron-donating reagents to form **2** exclusively through an ET process, or additionally a hydrido product **4** depending upon the reagents used. Thus, alkyl amines reacted rapidly with **1**; however, for the series of triphenylpnictogens the reaction rates did not correlate with the reported basicities or rates of single electron oxidations due to the divergence of the reaction paths observed among the pnictogens used. Diethyl ether, the weakest electron-donating reagent among the reagents surveyed was found to give a coloration when mixed with **1** probably due to the formation of the charge transfer complex and was found to be reactive with **1**. Monohydrido alkane **4** can be formed from **1** in modest yields with tin and silicon hydrides; however, direct reaction between **1** and H_2 to form **4** is observed in poor yields under forcing conditions and when the reaction between **1** and H_2 is conducted in the presence of Pd catalyst, quantitative formation of **2** through an ET process is observed.

3. Experimental details

3.1. Measurements and materials

Infrared spectra were measured in a KBr disk method with a Shimadzu FTIR-8000. Mass spectra (EI, 70 eV) were measured on a Shimadzu QP-5000 quadrupole mass spectrometer using a capillary column (60 m×0.25 mm i.d., 1.5 μm thick NEUTRA BOND-1, GL Sciences) for volatile compounds and using a DI mode for non-volatile compounds. Negative chemical ionization (NCI) mass spectra (70 eV) were recorded on a Perkin-Elmer 281 spectrometer with HP accessory 18962A (NCI packages). Argon gas was used as the reagent gas. ^{19}F-, ^{13}C-, ^{1}H- and ^{31}P-NMR spectra were measured with a Varian FT-NMR spectrometer (UNITY INOVA-300) operated at 282.01, 75.423, 299.95 and 121.42 MHz, respectively. Deuterated chloroform was used as an NMR solvent. Chemical shifts of ^{19}F-NMR are reported on the δ scale with $CFCl_3$ as an internal standard and negative values for upfield shifts. Chemical shifts of ^{1}H- and ^{13}C-NMR are reported on the δ scale, with TMS as an internal standard. Triphenyl phosphate was used as an internal standard for ^{31}P-NMR. A glass column (3 mm i.d.×5 m) packed with 12.1% Fomblin (YH/VAC 40/11) on Chromosorb P (AW-DMCS, 100–120 mesh) was used for GC analysis. Perfluoro-3-ethyl-2,4-dimethylpentane was used as an internal standard for GC calculation. Preparative HPLC (Shimadzu LC-6A) was performed with a Chromatorex B-5 column (Fuji Silysia Chemical, 5 μm SiO_2, 10 mm i.d.×250 mm) eluted with 2.5% CH_2Cl_2 in hexane at 2.0 ml/min, using a Shimadzu UV detector (SPD-6A) operating at 254 nm. TLC (0.25 mm thick Silica gel 60 F_{254}, Merck) was used.

A mixture of hexafluoropropene trimers **2** and **3** was prepared by the reported method [29]. All chemicals were reagent grade and used as received. Pd on charcoal (5%) was purchased from Kawaken Fine Chemicals. Diethyl ether and THF were distilled over sodium/benzophenone ketyl just before use. DMF was dried over CaH_2. The liquid phase used for GC analyses, Fomblin (YH/VAC 40/11), was a gift from Ausimont K.K.

3.2. Preparation of the stock solution of **1**

A hexafluoropropene trimer mixture (186.7 g) consisting of **2** (82.0%) and **3** (18.0%) and a Teflon-coated magnetic stirring bar were placed in a glass tube (24 mm i.d.×400 mm). Undiluted fluorine gas was introduced into the bottom of the tube at a rate of 4.2 ml/min at room temperature (ca. 27°C) with vigorous stirring. After 34.5 h fluorination, all of **2** and **3** were consumed to give a radical solution (185.5 g), of which GC analysis showed it contains 86% of **1** as a main product and 14% of F_2 adduct, perfluoro-3-ethyl-2,4-dimethylpentane, as a "by-product" (82% yield!). The content of **1** in this stock solution did not change for three years when stored in a refrigerator. At room temperature, content of **1** gradually decreased to 85% of the initial level after six months.

3.3. Reaction of **1** with hydrogen gas

3.3.1. Reaction in the presence of Pd catalyst

Catalytic amount of 5% Pd on charcoal or on $BaSO_4$ (35 mg) was placed in a 20 ml two-necked flask and dried by a heat gun under reduced pressure. After filling the reaction vessel with hydrogen gas, dried ether (2 ml) and the stock radical solution obtained above (1.09 g, 2 mmol **1**) were introduced by a syringe with vigorous stirring. A pale yellow color developed and an exothermic reaction occurred to reflux. The reflux almost subsided after 15 min, and the GC analysis of the reaction mixture showed all the radical was quantitatively converted to **2** after 30 min stirring. When the same reaction using 5% Pd on charcoal was conducted without ether solvent, no reaction occurred after 24 h stirring at room temperature.

3.3.2. Thermal reaction in the absence of Pd catalyst

1 g of the radical solution (86% content) and a Teflon-coated magnetic stirring bar were placed in a two-necked flask fitted with a Dimroth condenser and a rubber septum. The air was replaced with H_2 by three cycles of freeze-and-thaw. Hydrogen gas was supplied by a hydrogen balloon connected at the end of the condenser. The flask was immersed into an oil bath maintained at 83°C and the contents were vigorously stirred. The reaction mixture was periodically sampled by a syringe through a septum and was monitored by GC. Product distributions were calculated by perfluoro-3-ethyl-2,4-dimethylpentane included in the stock radical solution as an internal standard. Relative sensitivity of the products and the internal standard toward TCD are known to be approximately the same [2], and calculated accordingly. After 33 h (about 3 half-lives of **1**), the reaction mixture consisting of compounds **1–5** [30], one new compound perfluoro-3-ethyl-2,3,4-trimethylpentane (**6**) and one unknown was obtained. Spectroscopic data for **6** were the following. δ_F: −54.32 (3F, brs), −65.96 (12F, brs), −75.09 (3F, brs), −93.29 (2F, m), −157.58 (2F, m); MS: *m/z* (%), 331 (2.6), 281 (8.6), 262 (1.6), 243 (4.4), 231 (8.2), 193 (3.5), 181 (8.9), 169 (2.7), 151 (3.9), 143 (3.2), 124 (1.6), 119 (6.2), 100 (3.4), 93 (5.8), 82 (5.4), 74 (1.6), 73 (3.5), 69 (100); NCI–MS: *m/z* (%), 419 (6.4), 370 (7.8), 369 (100), 350 (6.1). Compound **4** is known, but its spectroscopic data is not available in literature and thus included here [2]. δ_F: −71.1 (6F, bs), −75.7 (6F, bs), −84.7 (3F, t, J=18.6 Hz), −107.8 (2F, bs), −167.4 (2F, bs); δ_H: 4.63 (1H, t, J=11.9 Hz); MS: *m/z* 451 (M^+, 0.2), 313 ($(CF_3)_2C{=}CH{-}C(CF_3)_2$, 3.4), 263 ($CF_3CF{=}CH{-}C(CF_3)_2$, 5.5), 213 ($CF_2{=}CH{-}C(CF_3)_2$, 7.0), 169 (9.6), 163 ($CF_2{=}CH{-}CFCF_3$, 5.4), 119 (43.9), 113 ($CF_2{=}CH{-}CF_2$, 4.7), 100 (4.5), 69 (100).

3.4. Reaction of **1** *with electron-donating reagents*

Unless otherwise stated all reactions of Sections 3.4 and 3.5 were carried out at room temperature under Ar atmosphere.

3.4.1. Reaction with aqueous KI and KBr

An aqueous KI acetone solution was prepared by dissolving KI (166 mg, 1 mmol) in 200 µl of water, then adding 1 ml of acetone. Into this aqueous KI acetone solution was added the stock radical solution (273 mg, 0.5 mmol **1**) with vigorous stirring at room temperature. Brown color developed immediately after the addition of the radical due to I_2 formation. After 10 min stirring the bottom layer of the perfluoro phase was analyzed by GC. An aqueous KBr acetone solution was prepared by dissolving KBr (119 mg, 1 mmol) in 400 µl of water, then adding 1 ml of acetone. Into this aqueous KBr acetone solution was added the same amount of the stock radical solution as the above. GC analysis of the perfluoro phase after 20 h showed no reaction. Results of both analyses are summarized in Table 2.

3.4.2. Reaction with triethylamine and tetrakis(dimethylamino)ethene

Into an ethereal radical **1** solution (1.09 g, 2 mmol **1** in 5 ml of dry ether) was added triethylamine with vigorous stirring. An exothermic reaction occurred immediately after addition to give a brown colored solution. The accompanying viscous brown material was not characterizable. The ethereal phase was analyzed by GC. The same kind of reaction was conducted by using tetrakis(dimethylamino)ethene (400 mg, 2 mmol). A vigorous exothermic reaction occurred with fuming. A blackish dense color appeared immediately after the addition, but the color soon disappeared with the formation of orange-colored tarry material on the vessel of which characterization was not tried. The ethereal phase was analyzed by GC. Results of the GC analyses are summarized in Table 2.

3.4.3. Reaction with sodium tetraphenylborate

Into a suspension of sodium tetraphenylborate (684 mg, 2 mmol) in 5 ml of dry ether was added the stock radical solution (1.09 g, 2 mmol **1**) with vigorous stirring. No visible change except the usual pale yellow coloration occurred. GC analysis showed most of **1** was consumed after 3 h. Data are summarized in Table 2.

3.4.4. Reaction with triphenylamine

Into an ethereal solution of triphenylamine (490.6 mg, 2 mmol in 5 ml ether) was added the stock radical solution (1.09 g, 2 mmol **1**) with vigorous stirring over 1 min. Only a drop of **1** gave a blue color to the solution, and soon turned to reddish purple by further addition, then green for a short period of time, and finally a very dense persistent blue color. GC analysis of the 10 min sample showed that **1** was quantitatively converted to **2**. Ether was removed by evaporation and the remaining brown viscous material (420 mg) was subjected to column chromatography (SiO_2, CH_2Cl_2:Hex=1:3). Triphenylamine was recovered (Rf=0.54, 244 mg, 50%) and a mixture of *N,N,N′,N′*-tetraphenyl-2-fluorobenzidine **7** and *N,N,N′,N′*-tetraphenylbenzidine **8** were obtained (133 mg, Rf=0.37). Each component was isolated by preparative HPLC using a Chromatorex B-5 column in the yields of 7.1% and 19.9%, respectively. Spectroscopic data for **7** were the following. δ_F: −117.07 (dd, J=16.5, 10.4 Hz); δ_H: 7.40 (2H, dd, J=8.4, 1.5 Hz), 7.24∼7.32 (9H, overlapped), 7.12∼7.16 (8H, overlapped), 7.0∼7.1 (6H, overlapped), 6.78∼6.90 (2H, overlapped); $^{13}C\{^1H\}$ δ_C: 160.22 (d, J_{CF}=247 Hz), 148.30 (d, J_{CF}=10.1 Hz), 147.72, 147.20, 146.94, 130.40 (d, J_{CF}=5.5 Hz), 129.68 (d, J_{CF}=11.2 Hz), 129.44, 129.39 (d, J_{CF}=3.2 Hz), 129.28, 125.03, 124.54, 124.35 (d, J_{CF}=72.5 Hz), 123.66, 123.43, 122.97, 118.39 (d, J_{CF}=2.9 Hz), 110.00 (d, J_{CF}=26.2); MS: *m/z* (%), 508 (7.8), 507 (40.9), 506 (M, 100), 338 (M-NPh_2, 2.3), 262 (M-$C_6H_4NPh_2$, 1.4), 253 (M_2, 74.9), 244 (M-$C_6H_3FNPh_2$, 4.2), 214 (9.2), 168 (Ph_2N, 7.3), 77 (Ph, 8.5); IR (KBr, ν_{max} cm^{-1}) 1587, 1489, 1275, 818, 752.

3.4.5. *Reaction with triphenylphosphine*

Into an ethereal solution of triphenylphosphine (524 mg, 2 mmol in 5 ml ether) was added the stock radical solution (1.09 g, 2 mmol **1**) with vigorous stirring over 1 min. A pale yellow colored solution was obtained. A white precipitate suddenly appeared 1.5 min after the completion of the addition. When the color disappeared after 30 min stirring at room temperature, the reaction mixture was analyzed by GC using a FOMBLIN column. The GC showed that **1** was completely converted to **2**. The white precipitate (240 mg) was collected by filtration, dried, and analyzed by DI-MS. The MS was consistent with the one of the authentic sample of triphenylphosphine oxide. ^{31}P-NMR showed the signals of triphenyl phosphine oxide and one unknown at 33.8 and 49.1 ppm with the integrations of 13:1. The unknown signal was quartet with a coupling constant of 7.0 Hz. The filtrate was condensed by evaporation and dried in vacuo. The white powder (284 mg) obtained was analyzed by ^{31}P-NMR and found to comprise 84% of the initial triphenyl phosphine and 16% of triphenyl phosphine oxide. Thus, the mass balance roughly calculated on the basis of ^{31}P-NMR are triphenyl phosphine (46%), triphenyl phosphine oxide (48%) and an unknown (6%).

3.4.6. *Reaction with other triphenylpnictogens*

The reaction was done in the same manner as the above. After 3 h stirring at room temperature the volatile products were analyzed by GC. The results are summarized in Table 2.

3.4.6.1. Reaction with triphenylarsine. Colorless crystals appeared from the tea-colored reaction mixture after 21 h vigorous stirring. GC analysis showed that **1** was completely converted to **2** (96.9%) and **4** (3.1%). Colorless crystals (162 mg) were found to be difluorotriphenylarsine (23.5% yield). A large amount of triphenylarsine was recovered intact (467 mg, 76.3%). Spectroscopic data of the colorless crystal were the following. δ_F: −87.8 ppm (s) (reported data −86.5) [31]; δ_H: 7.40–7.64 (9H, m), 8.08–8.22 (6H, m); MS (DI) of a colorless crystal *m*/*z*: 344 (Ph_3AsF_2, 0.6), 325 (M–F, 3.1), 306 (M–2F, 2.4), 249 (5.9), 248 (M–PhF, 42.4), 227 (7.3), 171 (11.5), 155 (13.6), 154 (Ph–Ph, 100), 153 (9.1), 152 (PhAs, 14.8), 151 (8.8), 77 (30.0), 51 (34.2), 50 (9.6).

3.4.6.2. Reaction with triphenylantimony. A brownish yellow color developed in this reaction. After 18 h stirring at room temperature, **1** was completely converted to **2** (97.3%) and **4** (2.7%). Volatile compounds and the solvent were removed by evaporation, and the remaining white powder was examined by ^{19}F-NMR ($CDCl_3$). Many signals were found at −65.05 (s), −74.99 (d, *J*=6.2 Hz), −76.61 (s), −83.51 (s), −87.80 (s), −154.33 (s) with the integration of 3:6:12:26:37:15. No further characterization was carried out.

3.4.6.3. Reaction with triphenylbismuth. A pale brownish color developed in this reaction. After 35 h stirring at room temperature, **1** was completely converted to **2** (87.2%) and **4** (12.8%). ^{19}F-NMR ($CDCl_3$) of the white powder obtained in the same manner as the above showed only one broad signal at −161.0 ppm, consistent with the reported data (−158 ppm) of Ph_3BiF_2. ^{1}H-NMR showed that this white powder comprised the starting Ph_3Bi and the fluorinated product Ph_3BiF_2 with a ratio of 66:34. No further effort to isolate the product was done.

3.4.7. *Reaction of* **1** *with solvents*

This reaction was conducted as a blank test. Into 5 ml of dry diethyl ether was added the stock radical solution (1.09 g, 2 mmol **1**) with vigorous stirring. The pale yellowish solution obtained was continually stirred. Reactions with other solvents (THF, diethyl sulfide and DMF) were carried out in a heterogeneous state due to the mutual immiscibility. In the case of diethyl sulfide, purple color developed in the upper diethyl sulfide layer while a tea-like brown color appeared in the lower layer. No coloration occurred in the DMF case. The reactions were followed by GC for 3 days with ca. 24 h intervals. The results on the 2-day samples are summarized in Table 2.

3.5. *Reaction of* **1** *with metal hydrides*

3.5.1. *Reaction with some organotin derivatives and some organosilane derivatives*

3.5.1.1. Reaction with tributyltin hydride and tetraalkyltins. Into the stock radical solution of **1** (1.09 g, 2 mmol **1**) was added tributyltin hydride (600 mg, 554 µl, 2 mmol, purity 97%) by syringe with vigorous stirring. An exothermic reaction occurred immediately after addition of the hydride to give a white precipitate. Into the slurry obtained after 2 h stirring at room temperature was added 5 ml of ether and filtered through a glass wool. The obtained colorless solution was analyzed by GC. Both reactions of **1** (1.09 g, 2 mmol **1**) with tetrabutyltin (694 mg, 2 mmol) and with tetramethyltin (357.7 mg, 2 mmol) were conducted in the same manner. Both tetraalkyltins are immiscible with **1**, thus the reactions were conducted in a heterogeneous state with vigorous stirring at room temperature. The upper tetraalkytin layers were very slightly colored from the beginning (brownish in the case of tetrabutyltin and yellowish in the case of tetramethyltin). Lower perfluoro phases were analyzed by GC over 5–7 days. The GC results are summarized in Table 3.

3.5.1.2. Reaction with dimethylphenylsilane and diphenylsilane. Into an ethereal solution of radical **1** (1.09 g, 2 mmol **1** in 5 ml of dry ether) was added dimethylphenylsilane (272.5 mg, 2 mmol) with vigorous stirring. The yellow color became faint with time and disappeared after 1 h. The reaction with diphenylsilane

(380.0 mg, 2 mmol, purity 97%) was conducted in the same manner. The ether layer was analyzed by GC. GC results are summarized in Table 3.

3.5.2. Reaction with alkali metal hydrides

3.5.2.1. Reaction with lithium aluminum hydride. Reaction of **1** with lithium aluminum hydride was conducted in four reaction conditions (a)–(d) depending on temperature, molar ratio of reagents, and solvent: (a) −78°C at first, then at room temperature, 0.25, THF; (b) room temperature, 0.25, THF; (c) room temperature, 1, THF; (d) room temperature, 1, diethyl ether, respectively.

(a) Into a suspended solution of $LiAlH_4$ (57 mg, 1.5 mmol) in 5 ml of dry THF cooled in dry-ice acetone bath was added the stock radical solution (3.27 g, 6 mmol **1**) over 5 min with vigorous stirring. Perfluoro phase iced out and the stirring was very erratic. The bath was removed after 10 min and continually stirred for 2 h until quenched with H_2O (60 μl), 15% aq. NaOH (60 μl), and H_2O (100 μl). GC analysis of the lower perfluoro phase showed that volatile compounds are only **1**, **2**, **4** with recovery of 93.0% calculated by using internal standard (perfluoro-3-ethyl-2,4-dimethylpentane). The distribution among **1**, **2**, and **4** is shown in Table 3.

(b) Into a solution of $LiAlH_4$ (19 mg, 0.5 mmol) in 5 ml of dry THF was added the radical stock solution (1.09 g, 2 mmol **1**) with vigorous stirring at room temperature. Slightly exothermic reaction occurred to give a gray colored suspension. After 60 min stirring at room temperature, 20 μl of H_2O, 20 μl of 15% aq. NaOH, and 40 μl of H_2O were added in that order. Perfluoro phase separated at the bottom of the vessel was analyzed by GC (see Run 7 in Table 3).

(c) Into a suspension of $LiAlH_4$ (75.9 mg, 2 mmol) in 5 ml of dry THF was added the stock radical solution (1.09 g, 2 mmol **1**) with vigorous stirring at room temperature. After 1 h stirring, 80 μl of H_2O, 80 μl of 15% aq. NaOH, and 160 μl of H_2O were added in that order. Perfluoro phase separated at the bottom of the vessel was analyzed by GC (see Run 8 in Table 3).

(d) The same reaction as (c) was carried out by using 5 ml of dry diethyl ether instead of THF. The ether layer was analyzed by GC (see Run 9 in Table 3).

3.5.2.2. Reaction with sodium borohydride. Into a suspension of $NaBH_4$ (76 mg, 2.0 mmol) in 5 ml dry diethyl ether was added the stock solution of **1** (1.09 g, 2.0 mmol) with vigorous stirring at room temperature over 3 min. No exothermic reaction occurred, and the ether layer was colored pale yellow. After 1 h stirring, the ether layer, the color of which was still sustained, was analyzed by GC (see Run 10 in Table 3).

3.5.2.3. Reaction with sodium hydride. Into a suspension of NaH (48 mg, 2 mmol) in 5 ml of dry diethyl ether cooled in dry-ice acetone bath was added the radical stock solution (1.09 g, 2 mmol) with vigorous stirring over 2 min. After completion of the addition, the bath was removed. After 30 min and 4 h stirring at room temperature, the ethereal layer was sampled by a syringe and analyzed by GC. Both 30 min and 4 h GC data were totally the same and are quoted as 4 h data in Table 3. When methanol was added into the 4 h reaction mixture, a vigorous effervescent reaction occurred.

3.5.2.4. Reaction with borane–THF complex. Into the radical stock solution (2.73 g, 5 mmol **1**) was added 5 ml of 1 M borane–THF solution with vigorous stirring at room temperature. A slightly exothermic reaction occurred to give a heterogeneous two-layer mixture. The upper THF layer was slightly yellow. GC analysis of the lower perfluoro phase was conducted. After 2 h stirring 77% of **1** was converted to **2** (42%) and **4** (58%). After 4 h stirring **1** was completely consumed (see Run 12 in Table 3).

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