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Reductive defluorination of perfluoropropylene trimer and perfluoro-$\Delta^{9(10)}$-octalin by "Cr–H"

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Abstract

Defluorotrimers of perfluoropropene ($((CF_3)CF_2{=})CC(CF_2CF_3){=}C(CF_3)_2$ (**5**) and $(CF_3)CF_2{=}CC({=}CFCF_3)CF(CF_3)_2$) (**6**)) were formed by reduction of trimer $(CF_3)_3C{=}C(CF_2CF_3)CF(CF_3)_2$) (**4**) with "Cr–H" species derived from p-$CH_3C_6H_4$-$CrCl_2(THF)_3/NaH$, $C_6H_5CrCl_2(THF)_3$, n-Bu_3Cr, i-Bu_3Cr and $CrCl_3/LiAlH_4$. The hydrogen source for the formation of **5** and **6** in the oligomerization of perfluoropropene catalyzed by bis(η^6-benzene)chromium(0) was from the ligand benzene through η^6-η^1 rearrangement. Perfluoro-$\Delta^{9(10)}$-octalin (**7**) was reduced by "Cr–H" species to form the corresponding dienes.

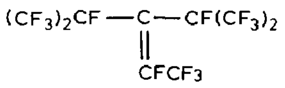
In previous papers [1,2], we have reported that bis(η^6-arene)chromium(0) could oligomerize perfluoropropene catalytically at room temperature to give two dimers **1**, **2**, two trimers **3**, **4** and two defluorotrimers **5**, **6**.

$(CF_3)_2CF{-}CF{=}CF{-}CF_3$

(**1**)

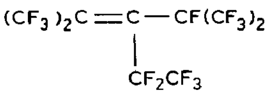
$(CF_3)_2C{=}CF{-}CF_2{-}CF_3$

(**2**)



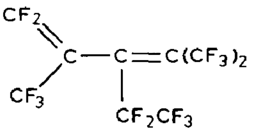
$(CF_3)_2CF{-}C({=}CFCF_3){-}CF(CF_3)_2$

(**3**)

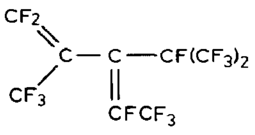


$(CF_3)_2C{=}C(CF_2CF_3){-}CF(CF_3)_2$

(**4**)



(**5**)



(**6**)

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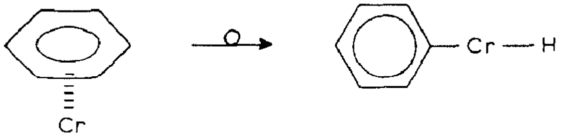
We have suggested that the formation of **5** and **6** was attributable to the hydrogenation of **4** followed by spontaneous elimination of two molecules of HF which then added to perfluoropropene to form 2-hydroheptafluoropropane [2]. Here we find that the hydrogen source of this reduction was the ligand of the catalyst instead of the solvent. When bis(η^6-benzene)chromium(0) catalyzed oligomerization of perfluoropropene was carried out in benzene-d_6 solution, GC-MS of the low-boiling point product showed the formation of only 2-hydroheptafluoropropane (m/e 151 ($M^+ - 19$), 101, 82, 69, 51) and no 2-deuteroheptafluoropropane was present. By contrast, when the oligomerization of perfluoropropene was catalyzed by bis(η^6-deuterobenzene)chromium(0) in benzene solution, GC-MS of the low-boiling point product showed markedly the presence of 2-deuteroheptafluoropropane (m/e 152 ($M^+ - 19$), 102, 83, 69, 52). These results strongly suggest that the hydrogen source for reductive defluorination of **4** is to be sought in the ligand of catalyst, presumably through η^6-η^1 rearrangement (eq. 1).



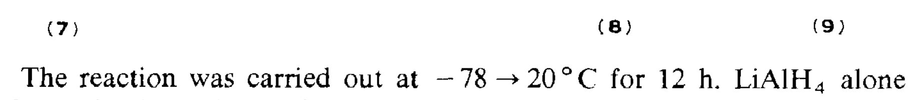
(1)

Sneeden and Zeise have reported that alkylchromium compounds react in the absence of added hydrogen with olefins to give hydrogenation products [3]. The results implied a direct transfer of hydrogen from a metal-bonded alkyl group to olefin, while Ashby and Lin reported that alkenes were reduced with $LiAlH_4$ in admixture with $CrCl_3$ to corresponding alkanes and they proposed that the active species was "Cr–H" [4].

In order to confirm our speculation that the reductive defluorination of **4** may be due to a "Cr–H" species, we carried out a number of reactions. The substrate used was a mixture of **3** and **4** in a proportion of 52/48 and the hydrogenation reagents were $p\text{-}CH_3C_6H_4CrCl_2(THF)_3/NaH$, $C_6H_5CrCl_2(THF)_3/NaH$, n-Bu_3Cr, i-Bu_3Cr and $CrCl_3/LiAlH_4$. All the reactions were carried out between −78 and 20 °C for 12 h (eq. 2). Compound **3** remained intact in these reactions. As a blank test, $LiAlH_4$ or NaH alone did not convert **4** into **5** and **6**. The results of these reactions are shown in Table 1 .

$$\text{"Cr–H"} + \mathbf{4} \xrightarrow[-78 \to 20\,°\text{C}/12\text{ h}]{\text{THF}} \mathbf{5} + \mathbf{6} \qquad (2)$$

Perfluoro-$\Delta^{9(10)}$-octalin (**7**) was also reduced with "Cr–H" species derived from n-Bu_3Cr, i-Bu_3Cr, or $CrCl_3/LiAlH_4$ to form a sole product perfluoro-$\Delta^{1(9)}$-$\Delta^{4(10)}$-hexalin (**8**) or perfluoro-$\Delta^{1(9)}$-$\Delta^{5(10)}$-hexalin (**9**). The physical properties of our products were consistent with those reported in the literature [5] (eq. 3).



(3)

(7) (8) (9)

The reaction was carried out at −78 → 20 °C for 12 h. $LiAlH_4$ alone did not effect reduction. The results are shown in Table 2.

Table 1

Reaction of "Cr–H" with **4**

"Cr–H"	Product [b] **5**/**6**	Yield [a] (%)
p-$CH_3C_6H_4CrCl_2(THF)_3/NaH$	95/5	30
$C_6H_4CrCl_2(THF)_3/NaH$		25
n-Bu_3Cr	98/2	86
i-Bu_3Cr	94/6	56
$CrCl_3/LiAlH_4$	91/9	55
$(C_6H_6)_2Cr$	75/25	

[a] Checked both by gas chromatography and by ^{19}F NMR spectroscopy. [b] Determined by ^{19}F NMR spectroscopy.

Table 2

Reaction of "Cr–H" with **7**

"Cr–H"	Yield [a] (%)
n-Bu_3Cr	83
i-Bu_3Cr	45
$CrCl_3/LiAlH_4$	41

[a] Checked both by gas chromatography and by ^{19}F NMR spectroscopy.

In view of the fact that octafluoro-1,3-hexadiene readily reacts with maleic anhydride [6], we attempted the Diels–Alder reaction of **8** or **9** with maleic anhydride in order to determine the structure of the product, but no reaction occurred.

When the co-oligomerization of perfluoropropene and perfluorobut-2-yne was carried out with bis(η^6-benzene)chromium(0) catalyst, the HF that was evolved in this reaction was added to the oligomer [7].

It is noteworthy that to the best of our knowledge, the rearrangement of bis(η^6-benzene)chromium to ["C_6H_5Cr–H"] has not been reported in the literature. Our studies thus provides the first example of η^6-η^1 rearrangement of a carbon-bonded chromium, although a similar rearrangement of a carbon-bonded osmium has been reported [8].

Experimental

^{19}F NMR spectra were obtained with an EM-360, XL-200 apparatus, using TFA as external standard (high field positive). GC-MS was taken with a Finnigan-4021 spectrometer. Gas chromatography was carried out with a G-102 instrument. Stationary phase: 16% perfluorotriazine on a 102 white support. For convenience the trimers were prepared from perfluoropropene using KF in DMF as catalyst by a published procedure [9]. The proportion of **3**/**4** in perfluoropropene trimers was 52/48. $CrCl_3(THF)_3$ was prepared by a literature method [10]. All experiments were performed under nitrogen. Reagents and solvents were dried before use.

The yields were estimated by both gas chromatography and ^{19}F NMR: A mixture of **5** and **6** (unseparable) and compound **8** (or **9**) were obtained at first by preparative gas chromatography. The GLC peak area was plotted against the amount of sample. The yields of products (Table 1 and Table 2) were found from the curve. The yields could also be estimated on the basis of the integrated ^{19}F NMR spectra. The two methods gave similar results.

I. Oligomerization of perfluoropropene by bis(η^6-benzene)chromium(0) in benzene-d_6

To a solution of benzene-d_6 (15 ml) and bis(η^6-benzene)chromium(0) (0.5 g) was added perfluoropropene (17 g) and the mixture was allowed to stand at room temperature for 24 h. The oligomer (6.3 g) was obtained. The distillate that boiled below 60 ° C was subjected to GC-MS, which revealed perfluoropropene dimers and 2-hydroheptafluoropropane were the only products. No 2-deuteroheptafluoropropane was detected.

II. Oligomerization of perfluoropropene by bis(η^6-benzene-d_6)chromium(0) in benzene

Bis(η^6-benzene-d_6)chromium(0) was prepared by a published procedure [11] for the preparation of bis(η^6-benzene)chromium(0), but using benzene-d_6 instead of benzene.

To a solution of bis(η^6-benzene-d_6)chromium(0) (0.5 g) in benzene (15 ml), was added perfluoropropene (14.4 g). The reaction yielded the oligomers perfluoropropene (2.7 g). The low-boiling point distillate (< -20 ° C) was determined by GC-MS to be mainly 2-deuteroheptafluoropropane.

*III. Reaction of p-$CH_3C_6H_4CrCl_2(THF)_3$/NaH and $C_6H_5CrCl_2(THF)$/NaH with **4***

(a) A THF solution of $CrCl_3(THF)_3$ (10 ml, containing ca. 6 mmol of $CrCl_3$) was transferred into a vessel with an outlet. *p*-Tolylmagnesium bromide (8 ml, ca. 8 mmol) was slowly added dropwise at -78 ° C the mixture was stirred for 30 min, and then NaH (0.5 g) was added. After a few minutes the perfluoropropene trimer (6 g) was introduced, the mixture was stirred at room temperature for a further 12 h, and then hydrolyzed with 0.5 *N* HCl. The mixture was washed with water three times and dried over $CaCl_2$. The products were separated by preparative chromatography.

5: $M^+ = 412$; m/e 393, 343, 293, 205, 93, 69. ^{19}F NMR: -7.5, -5.8(2F), -18.0, -17.6(6F), -16.3(3F), 33.3(2F), 5.2(3F) ppm.

6: $M^+ = 412$; m/e 393. 343, 293, 205, 93, 69. ^{19}F NMR: 16.7(3F), -9.1, -7.1(2F), -7.5(3F), -1.9(3F), 0.6(3F), 22.0(1F), 100.3(1F) ppm.

(b) The reaction of $C_6H_5CrCl_2(THF)_3$/NaH with **4** was carried out similarly but phenylmagnesium bromide was used instead of *p*-tolylmagnesium bromide.

*IV. Reaction of n-Bu_3Cr with **4** and **7***

(a) A suspension of $CrCl_3$ (0.5 g, 3 mmol) and a trace of Zn dust in THF (15 ml) was refluxed for 4 h and then cooled to -78 ° C, and n-butylmagnesium bromide (10 ml, 0.012 mol) was added dropwise. After stirring for 1 h, the perfluoropropene trimer (2.8 g) was added. The reaction mixture was then agitated at room temperature for another 12 h. The product was worked up in a manner similar to that of III.

(b) Compound **7** (1.3 g) was treated with n-Bu_3Cr in the same manner as described in (a).

8 or **9**: $M^+ = 386$; m/e 367, 317, 267, 248, 217, 198, 179, 167, 148, 117, 93, 69. ^{19}F NMR: 39.5(4F), 38.0(2F), 45.3(4F), 59.2(4F).

*V. Reaction of n-Bu$_3$Cr with **4** and 7*

All operations were similar to those in IV except i-butylmagnesium bromide was used instead of n-butylmagnesium bromide.

*VI. Reaction of CrCl$_3$/LiAlH$_4$ with **4** and 7*

(a) A mixture of $CrCl_3$, (3 mmol), a trace of Zn dust and THF (15 ml) was refluxed for 4 h, and cooled to −78 °C. $LiAlH_4$ (0.15 g) was added and the mixture was stirred for 1 h. Then the perfluoropropene trimer (2.8 g) was added. The reaction was carried out at room temperature for further 12 h and worked up in the usual way.

(b) Reaction of $CrCl_3/LiAlH_4$ with 7 was carried out in the same manner as described in (a).

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