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π-BIS(BENZENE)CHROMIUM(0)-CATALYZED OLIGOMERIZATION OF PERFLUOROPROPYLENE

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Summary

In the presence of zerovalent π-bis(benzene)chromium(0) (I), perfluoropropylene (II) was found to undergo oligomerization under very mild conditions to dimers (b.p. 46°, M^+, 300) and trimers (b.p. 100—102°C, $M^+ - 19$, 431) in the ratio of 2.5—3.0 to 1. One mol of metal complex could catalyze the conversion of 50 mol of perfluoropropylene. On the basis of ^{19}F NMR, the structures of the dimers are III and IV in a ratio of ca. 80/20 and the trimers V and VI; VII and VIII also seemed to be present. V/VI/(VII + VIII) is 80/10/4. In benzene solution, perfluoropropylene was shown not to be catalytically oligomerized by fluoride ion (KF, CrF_2 or $(CH_3)_4NF$) nor by monovalent π-dibenzenechromium(I). A possible mechanism of the reaction was proposed.

Since Zeiss and Tsutsui [1] reported their finding of σ—π rearrangement and elucidated the structure of π-dibenzenechromium(0) (I), Huang et al. [2] found that perfluoropropylene (II) could be oligomerized catalytically to dimers and trimers by I under very mild conditions, while Tsutsui et al. [3] found that an alkene could be polymerized catalytically by I, but only at its decomposition temperature. However, Stone et al. [4] reported that fluoro-alkanes and -alkynes reacted with a variety of metal complexes to give a number of stable compounds. So far as we know, no report was given in the literature concerning the catalytic oligomerization and polymerization of fluoro-alkenes and -alkynes by metal complexes. On the other hand, pure π-dibenzenechromium(0) (I) does not catalyze the polymerization of a variety of alkenes, with the exception of acrylonitrile [5].

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* Formerly spelled as Yao-Tseng Huang. Xiuying Gong and Huaqing Bao participated in part of the work. Chiwen Wang participated in the discussion of ^{19}F NMR.

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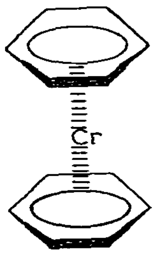
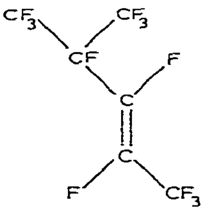


(I)

$CF_3CF{=}CF_2$

(II)

In this paper, we deal with, in detail, the catalytic oligomerization of perfluoropropylene (II) by π-dibenzenechromium(0) (I). In the presence of I, perfluoropropylene was oligomerized to dimers (b.p. 46°C, M^+, 300) and trimers (b.p. 100—102°C, $M^+ - 19$, 431), in the ratio of 2.5—3.0 to 1. One mol of I could catalyze the conversion of 50 mol of perfluoropropylene. Although preparative gas chromatography of the dimers under our conditions showed a single peak, on the basis of ^{19}F NMR, as compared with the known structures of the dimers of II, they were a mixture of III and IV (III/IV 80/20). Preparative gas chromatography of the trimers gave three components among which two were identified as V and VI. The third one, a minor portion, was shown by ^{19}F NMR to be a mixture, which contained VII and VIII; V/VI/(VII + VIII) 80/10/4.



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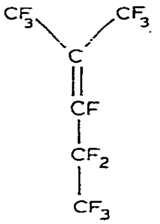
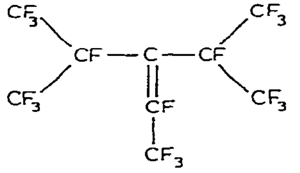
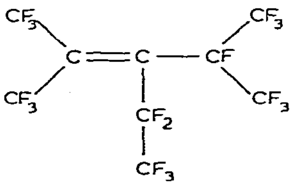


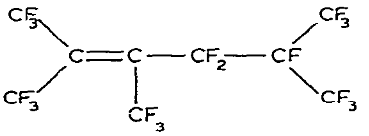
(IV)



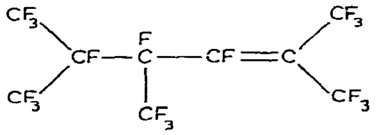
(V)



(VI)



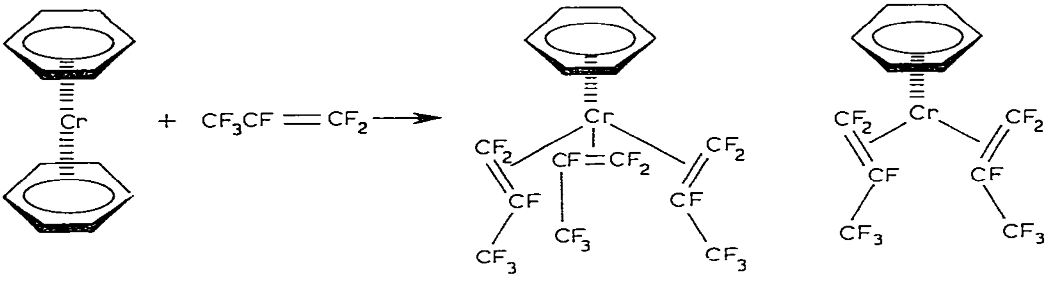
(VII)



(VIII)

In order to confirm that in our reaction in benzene solution II was not catalyzed by fluoride ion, KF, CrF_2 or $(CH_3)_4NF$ was used instead of π-dibenzenechromium(0). No reaction occurred at all in each case.

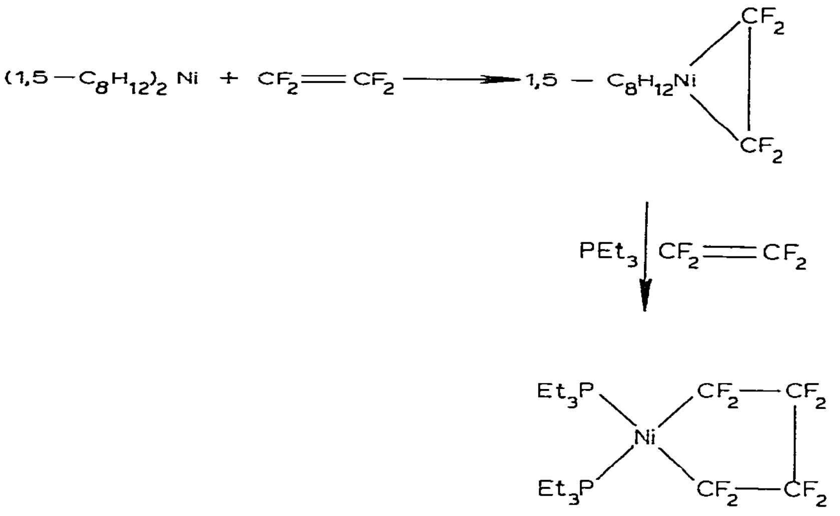
The mechanism of our reaction is suggested to be as follows: at first two or three molecules of perfluoropropylene are complexed to chromium at the expense of one molecule of benzene, forming an intermediate IX, as in the case of polymerization of an alkene catalyzed by dicyclopentadienylchromium on a silicon support [6] (eqn. 1).



(IX)

(1)

Whether intermediate IX undergoes oligomerization directly or in a stepwise fashion through the formation of a three-membered ring by oxidative addition, ring enlargement by insertion of a second molecule of perfluoropropylene to give a five-membered ring, as in the case of the reaction of di-1,5-cyclooctadienenickel with tetrafluoroethylene [7] (eq. 2) and finally to the formation of dimer III by reductive elimination, remains obscure.



(2)

Nevertheless, the first step of our postulated mechanism was confirmed by a reaction carried out in toluene solution, in which almost the requisite amount of benzene displaced by perfluoropropylene was obtained. Obviously, IV was formed from III, and VI from V, by isomerization. In contrast to zerovalent π-dibenzenechromium(0), monovalent π-dibenzenechromium(I) did not catalyze the oligomerization of perfluoropropylene in benzene solution. Further study of the mechanism is being pursued.

π-Dibenzenechromium(0) could also catalyze the polymerization of perfluorobut-2-yne under very mild conditions. The results will be published elsewhere.

TABLE 1

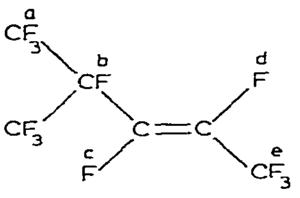
^{19}F NMR DATA OF COMPOUND III

	Found: δ(CF_3COOH(ext.)) (ppm)	Data reported in literature		
		δ(CF_3COOH) (ppm) [8]	δ($CFCl_3$(int.)) (ppm) [9]	δ(CF_3COOH(ext.) (ppm) [10]
F(a)	3(6)	—6.3 (6)	75.5	—0.2 (6)
F(b)	115 (1)	111 (1)	190	111 (1)
F(c)	84 (1)	80 (1)	158	80.1 (1)
F(d)	86 (1)	82 (1)	161	81.4 (1)
F(e)	—3 (3)	0 (3)	69.5	—6.4 (3)
	J_{cd}, 134 Hz		J_{cd}, 135 Hz	
	J_{db}, 21.6 Hz		J_{db}, 20.5 Hz	

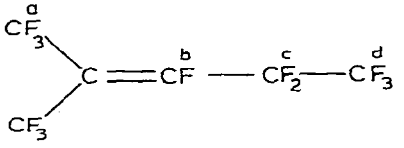
Experimental *

Oligomerization of perfluoropropylene by π-dibenzenechromium(0)

A 100 ml sealed tube, flushed with O_2-free N_2, was charged with 40 ml of a benzene solution of π-dibenzenechromium(0) (3.9 mmol). After cooling in a solid CO_2/acetone bath, the sealed tube was evacuated, filled with N_2 and the process repeated several times. Into the tube then was charged 28 g (190 mmol) of perfluoropropylene. After sealing, the sealed tube was taken from the cooling bath. As soon as benzene melted, an exothermic reaction ocurred. The sealed tube was allowed to stand for 24 h and the product isolated by filtration and removal of volatiles. Yield of oligomer, 24 g. Fractional distillation gave two fractions: one boiled at 46—46.5°C, M^+, 300, and the other boiled at 100—102°C $M^+ - 19$, 431. Although a preparative gas chromatogram (stationary phase: 20% squalane on silanized 102 diatomaqueous support (60—80 mesh). Column length 7 m. Detector: thermoconductivity. Flow rate of N_2, 20 ml/min. Temperature of column, 20°C) of the former showed a single peak, it contained two isomers III and IV as shown by ^{19}F NMR (Tables 1 and 2).



(III)



(IV)

From Tables 1 and 2, it was shown that our data were completely in coincidence with those found in the literature. On the basis of integral areas of CF_3 the ratio of III to IV was estimated to be 4/1. IR: ν_{max}^{neat} (cm^{-1}) 1690s (C=C); 1710m (C=C). Anal. Found, F, 76.31. C_6F_{12} calcd., F, 76.00%.

Preparative gas chromatography of the trimer gave three components,

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* ^{19}F NMR was determined with an R-32F (84.6 MHz) apparatus.

TABLE 2

^{19}F NMR DATA OF COMPOUND IV

	Found: δ(CF$_3$COOH(ext.)) (ppm)	Data reported in literature	
		δ(CF$_3$COOH) (ppm) [8]	δ(CF$_3$COOH(ext.)) (ppm) [10]
F(a)	−16, −13 (3,3)	−20.9, −17.5 (3,3)	−18.6, −16.6 (3,3)
F(b)	25 (1)	22.4 (1)	21.3 (1)
F(c)	44 (2)	44.7 (2)	40.4 (2)
F(d)	10.3 (3)	7.3 (3)	7.0 (3)

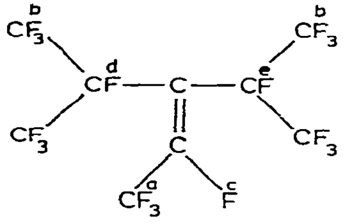
TABLE 3

^{19}F NMR DATA OF COMPOUND V

	Found: δ(CF$_3$COOH(ext.)) (ppm)	Data reported in literature	
		δ(CFCl$_3$(int.)) (ppm) [9]	δ(CF$_3$COOH(ext.) (ppm) [11]
F(a)	−9.5 (3)	63.5 (3)	−12.7 (3)
F(b)	0 (12)	73 (12)	−3.3 (12)
F(c)	5.8 (1)	79 (1)	2 (1)
F(d)	95.5 (1)	169 (1)	90.8 (1)
F(e)	98.5 (1)	172 (1)	94.0 (1)
	J_{ad}, 52.6 Hz	J_{ad}, 50 Hz	J_{ad}, 45.1 Hz

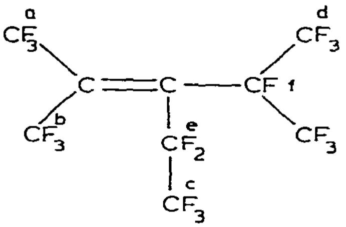
(IR of compound V: ν_{max}^{neat} (cm^{-1}): 1650s (C=C). Anal.: Found: F, 75.98. C$_9$F$_{18}$ calcd.: F, 76.00%.)

among which one was identified by ^{19}F NMR as V (Table 3).

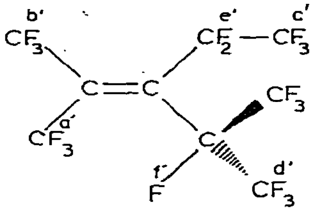


(V)

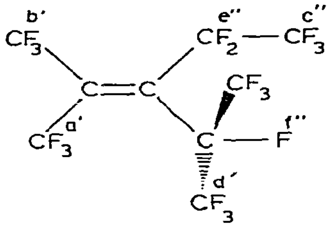
The second component of the trimer fraction was identified as compound VI [12] which contained two conformers VI′ and VI″ (VI′/VI″ = 3/1) by ^{19}F NMR determination at room temperature as shown in Table 4.



(VI)



(VI′)



(VI″)

TABLE 4

^{19}F NMR DATA OF COMPOUND VI

^{19}F	Found δCF_3COOH(ext.) (ppm)	Data reported in literature		
		$\delta CFCl_3$(int.) (ppm) [12]	δCF_3COOH(ext.) (ppm) [11]	$\delta CFCl_3$(int.) (ppm) [9]
a′	−16.5	56.1	−19.5	57
b′	−14.2	59.1	−17.3	59
c′	−2.0	71.2	−5.2	70.5
d′	−3.0	70.3	−6.1	71.5
e′	14.5	87.7	11.4	88
f′	86.5	159.8	82.5	160
c″	1.0	74.1		
e″	19.5	91.5		
f″	83	156.1		
	Ja′f′, 51 Hz	Ja′f′, 52 Hz	Ja′f′, 44.2 Hz	Ja′f′, 50 Hz

(IR of compound VI: ν_{max}^{neat} (cm^{-1}) 1620m (C=C). Anal.: Found: F, 75.97. C_9F_{18} calcd.: F, 76.00%.)

The third component of the trimer, a mixture, had IR absorptions at 1650, 1670, 1690 and 1740 cm^{-1}, and ^{19}F NMR at −14.5, −13, −4, −3, 1, 3, 7.5, 22.5, 34.5, 53, 100 ppm. The trimers with the structures VII and VIII seemed to be present.

Attempt of oligomerization of perfluoropropylene by monovalent π-dibenzenechromium(I)

To a 60 ml sealed tube was added 20 ml of a benzene solution of π-dibenzenechromium(0) (20 mg of π-dibenzenechromium(0) per ml). Air was allowed to pass in through the solution so as to obtain a suspension of π-dibenzenechromium(I) in benzene. To it was charged 17.0 g of perfluoropropylene in the usual manner and the mixture was allowed to stand for 48 h. Perfluoropropylene was recovered quantitatively.

Oligomerization of perfluoropropylene by π-dibenzenechromium(0) in toluene solution

To 1.2 g of π-dibenzenechromium(0) was added, under an N_2 stream, 50 ml of benzene-free toluene to form a toluene solution. Toluene was distilled off (ca. 40 ml) under reduced pressure and to the mixture fresh benzene-free toluene was added. The process was repeated until no benzene was detected in the distillate by gas chromatography. Fresh benzene-free toluene was added to make the solution containing 10 mg of catalyst per ml.

To a sealed tube containing 20 ml of toluene solution of catalyst was charged 14 g of perfluoropropylene in the usual way, and the mixture allowed to stand for 24 h. There was obtained a mixture of oligomers, 8.5 g, yield 60%. The toluene layer was distilled under a stream of O_2-free N_2. The distillate was examined by GLC. As compared with a standard of the mixture of toluene and benzene, it contained 0.4% of benzene. Theoretical amount of benzene to be displaced from π-dibenzenechromium(0) by perfluoropropylene is 0.43%.

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