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TRANSITION METAL CATALYSED C-C-COUPLING REACTIONS OF 3,3,3-TRIFLUOROPROPENE

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SUMMARY

Attempts to dimerize 3,3,3-trifluoropropene catalytically with homogeneous nickel catalysts were unsuccessful In a stoichiometric reaction a new dimer was formed.

Reactions to telomerize 3,3,3-trifluoropropene with tetrachloromethane in the presence of copper salts yielded new telomers

INTRODUCTION

Fluoroolefins are of substantial industrial interest and there are many synthetic routes available for their preparation One special group of fluoroolefins embraces oligomers and polymers derived by C-C-linkage Within the framework of our investigations to dimerize or oligomerize propene [1], we became interested in including hexafluoropropene and 3,3,3-trifluoropropene in our investigations Our major aim was the synthesis of new products of industrial interest as well as enlarging our understanding of homogeneous transition metal catalyzed C-C-linkages There are only scattered reports in the open literature dealing with the latter approach [2,3] Considering the many organometallic complexes, which possess fluorine-containing olefins as ligands, it is quite surprising, that transition metal catalyzed C-C-linkages of F-containing olefins are rare

RESULTS AND DISCUSSION

Dimerization of 3,3,3,-trifluoropropene (TFP)

The two complexes (I) and (II) oligomerize ethene and propene [1]

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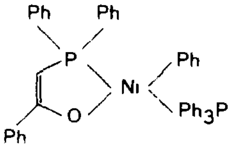
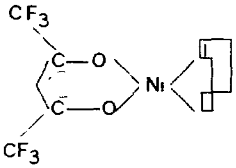
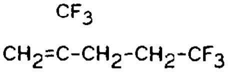


(I)



(II)

However, attempts to dimerize or oligomerize hexafluoropropene or 3,3,3-trifluoropropene (TFP) with (I) and (II) were disappointing. Only a stoichiometric reaction was observed with complex (I) providing the new dimer (III) in yields of 19 6%



$$CH_2{=}\overset{CF_3}{C}{-}CH_2{-}CH_2{-}CF_3$$

(III)

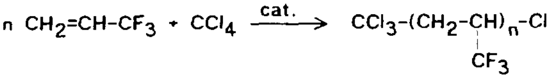
The dimer (III) was separated by preparative gas chromatography and fully characterized by ^{19}F- and ^{1}H-NMR spectroscopy Also the MS data are in agreement with structure (III) Isomers of (III) have been reported previously by R N Haszeldine [4]

The failure to catalytically oligomerize fluorine-containing olefine by transition metals may be due to the ease of HF abstraction in the presence of transition metals, which we have observed in many instances [5] Presumably, due to their stability, transition metal fluorides are formed which are catalytically inactive

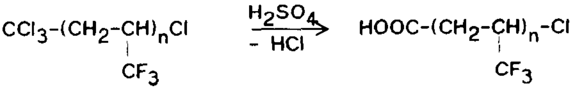
Telomerization of 3,3,3-trifluoropropene

There are many telomerization reactions of fluoroolefins known, but few deal with 3,3,3-trifluoropropene Telogens applied are alcohols/tetrahydrofuran [6], CF_3I [7-9] and CBr_4 [10]

In the past, we have explored the telomerization of 1,3-dienes with organometallic complexes quite extensively [11], and we became interested to extend this telomerization to fluorine-containing olefins using CCl_4 Reactions according to eqn. (1) were chosen, because these could provide a useful route to carboxylic acids as in eqn (2).



$$n\ CH_2{=}CH{-}CF_3 + CCl_4 \xrightarrow{cat.} CCl_3{-}(CH_2{-}\underset{CF_3}{CH})_n{-}Cl \qquad (1)$$



$$CCl_3{-}(CH_2{-}\underset{CF_3}{CH})_nCl \xrightarrow[-\ HCl]{H_2SO_4} HOOC{-}(CH_2{-}\underset{CF_3}{CH})_n{-}Cl \qquad (2)$$

Copper complexes turned out to be excellent catalysts yielding the telomers (IVa-e) in yields up to 97% Table I summarizes our results Yields and selectivities depend on various reaction parameters such as temperature, pressure and type of copper compound used

TABLE I

Telomerization of 3,3,3-trifluoropropene with CCl_4[a]

Exp No.	catalyst	CCl_4 [ml]	TFP [g]	yield %	selectivity (mole ratio) (IVa)	(IVb)	(IVc)	(IVd)	(IVe)
1	$CuCl_2$	25	4 6	83	1 0	0 06	-	-	-
2	$CuCl_2$	25	5.4	63	1 0	0 95	0.62	0 33	0 10
3	$CuCl_2/LiCl$[b]	25	5 6	71	1 0	0 09	-	-	-
4	$CuCl_2/LiCl$[b]	20	4 8	97	1.0	0 14	0 02	-	-
5	$Cu(CN)_2$	20	4 9	96	1.0	0.11	0.04	-	-
6	$CuSO_4$	5	6 3	92	1 0	0 96	0 77	0 58	0 23
7	$CuSO_4$[c]	6	15 2	32	1 0	8 0	10 00	10 00	3 00
8	Cuacac	20	5.5	72	1.0	1 60	0.60	0.15	0 25

[a] 170°C, 10 5 h, 5 ml acetonitrile.

[b] ratio 1:4.

[c] 50 ml acetonitrile.

Generally no reaction occurs up to 140°C, above 170°C polymeric material is formed Addition of water proved beneficial if the copper salts are poorly soluble in acetonitrile, the solvent of choice In comparison with other solvents such as toluene and alcohols nitriles turned out to be the best Besides acetonitrile also benzonitrile turned out to be a good solvent.

With copper (II) chlorides (exp 1) the 1 1-addition product prevailed Decreasing the amount of CCl_4 and adding more acetonitrile the product distribution is shifted towards higher telomers (exp 6 or 7) Enhancing the pressure by addition of N_2 or CO increases the yield and shifts the selectivity towards higher telomers

Mechanism

Regarding the reaction mechanism we propose a free radical pathway. Acetonitrile will form a free radical with copper (II) according to eqn (3) [12], giving copper (I), which reacts with CCl_4 as shown in eqn (4)

$$Cu^{2+} + CH_3CN \longrightarrow Cu^{+} + H^{+} + CH_2CN \quad (3)$$

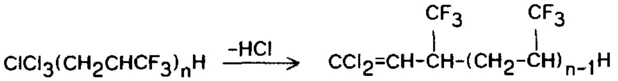
$$Cu^{+} + CCl_4 \longrightarrow Cu^{2+} + Cl^{-} + CCl_3 \quad (4)$$

The trichloromethyl radical reacts with trifluoropropene as in eqn (5) Chain termination occurs with a chlorine radical.

$$n\ H_2C{=}CH{-}CF_3 + \cdot\ CCl_3 \longrightarrow CCl_3(CH_2CHCF_3)_n \quad (n = 1\text{-}5) \quad (5)$$

As side products we observed small amounts of compounds (Va-c), which can be formed via termination with a hydrogen atom as in eqn (6) and (7)

$$CCl_3(CH_2CHCF_3)_n + HCH_2CN \longrightarrow [CCl_3(CH_2CHCF_3)_nH] + CH_2CN \quad (6)$$



$$ClCl_3(CH_2CHCF_3)_nH \xrightarrow{-HCl} CCl_2{=}CH{-}\overset{CF_3}{\overset{|}{C}}H{-}(CH_2{-}\overset{CF_3}{\overset{|}{C}}H)_{n-1}H \quad (7)$$

(Va-c) (n = 1-3)

In Fig 1 the proposed reaction cycle is shown

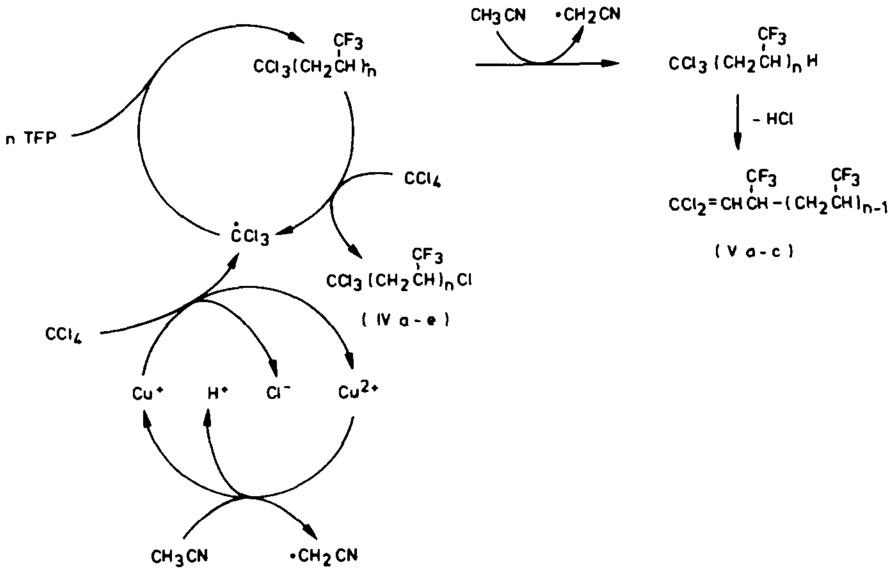


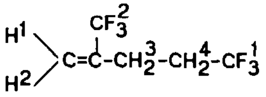
Fig 1 Mechanism for telomerization.

ANALYTICAL DATA

Compound (III)

TABLE II

NMR data of compound (III)



	δ/ppm	Coupling	J/H_2	Integration
F^{1a}	- 67.29	tr	10.0	3
F^2	- 65.31	d,d,tr	2/6.1/2	3
H^{1b}	6.38	qa,d,tr	2/16	1
H^2	5.78	qa,d.tr	6.2/15.7/1.5	1
H^3	2.3-2.5	m		2
H^4	2.1-2.3	tr,qa		2

[a] Ext. standard $CFCl_3$.

[b] Ext. standard TMS, $CDCl_3$.

Compound (IVa-e)

The products have been separated through preparative GC and fractionated distillation respectively and were characterized by ^{19}F-NMR, ^1H-NMR, ^{13}C-NMR and chemical analyses.

In the mass spectra the molecular peak ($M^\oplus$) was not detected but a mass corresponding to the molecular peak minus 35 was observed (related to the lowest peak in the typical isotope pattern). The highest masses of the spectra form a series separated by 96 which is the molecular weight of TFP.

Generally the following masses appear: 177 ($Cl_2C_3H_2CF_3^\oplus$), 143 ($Cl_3C_3H_2^\oplus$), 117 ($CCl_3^\oplus$), 96 ($Cl_2C{=}CH_2^\oplus$), 83 ($CHCl_2^\oplus$), 77 ($CF_2{=}CHCH_2^\oplus$), 69 ($CF_3^\oplus$) und 49 ($CH_2Cl^\oplus$).

TABLE III

Chemical analyses of the telomers (IVa-c)

Telomer	Purity (GC)	Total molecular formula		%C	%H	%Cl	%F
(IVa)	99%	$C_4H_3Cl_4F_3$	calc.	19.23	1.21	56.75	22.81
			found	19 30	1 16	56 50	22.70
(IVb)	97%	$C_7H_6Cl_4F_6$	calc	24.30	1.75	40.99	32 50
			found	24.49	1 78	41.00	32.50
(IVc)	93%	$C_{10}H_9Cl_4F_9$	calc.	27.19	2 05	32 09	38.69
			found	27 44	2.03	32 10	38.50

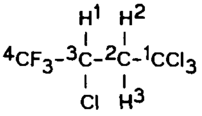
Characteristic peaks for the individual telomers are the following·

(IVa)	213 ($M^{\oplus}$Cl)
(IVb)	309 ($M^{\oplus}$Cl), 273 ($M^{\oplus}$-Cl-HCl), 289 ($M^{\oplus}$-Cl-HF), 237 ($M^{\oplus}$-HCl-2Cl)
(IVc)	405 ($M^{\oplus}$-Cl), 369 ($M^{\oplus}$-Cl-HCl), 349 ($M^{\oplus}$-2HCl-F), 265 ($M^{\oplus}$-HCl-HF-F).
(IVd)	501 ($M^{\oplus}$-Cl).
(IVe)	597 ($M^{\oplus}$-Cl).

NMR data of the telomers (IVa), (IVb), (IVc)

TABLE IV

NMR data of telomer (IVa)



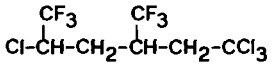
$$^{4}CF_3-{}^{3}\underset{Cl}{\overset{H^1}{C}}-{}^{2}\underset{H^3}{\overset{H^2}{C}}-{}^{1}CCl_3$$

	δ/ppm	Coupling	J/Hz	Integration
F	- 71 8	d	7	3 F
H^1	5.0	d,d,qa	7/7 9/2	1 H
H^2	3.6	d,d	2/16.3	1 H
H^3	3 4	d,d	7.9/16.3	1 H
C^1	96.2	d	5	1 C
C^2	56.2	tr	137.7	1 C
C^3	54.5	d,d,qa	7/33/148	1 C
C^4	124.6	qa	278	1 C

The molecule (IVa) has C_1-symmetry, therefore the protons H^2 and H^3 are diastereotopic and show separate signals. The protons form an ABX-system. The appearance of only one signal in the ^{19}F-NMR and of only one peak in the GC shows that only one isomer has been produced.

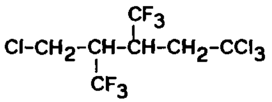
The NMR spectra of the higher telomers are more complex. Thus an unambiguous assignment of the signals to the individual molecules cannot be made. Nevertheless a plausible proposal for the structures of the higher telomers can be made by the following arguments:

The compound (IVb) is found in the GC as a 1:1 mixture of two isomers as can be also confirmed from the mass spectra. In the F-H-decoupled ^{19}F-NMR spectrum four signals of about equal intensity are found in the region typical for CF_3 groups (-65.7, -66.2, -70.5 and -71.5 ppm). As only one isomer of (IVa) is found it can be assumed that the path of reaction in terms of regioselectivity does not split before the addition of the second molecule of TFP to the growing chain. Because of the two possibilities of addition only the following structures are probable:



$Cl\text{-}\overset{CF_3}{\overset{|}{C}}H\text{-}CH_2\text{-}\overset{CF_3}{\overset{|}{C}}H\text{-}CH_2\text{-}CCl_3$

and



$Cl\text{-}CH_2\text{-}\underset{CF_3}{\underset{|}{C}}H\text{-}\overset{CF_3}{\overset{|}{C}}H\text{-}CH_2\text{-}CCl_3$

(IVa) (IVb)

Upon the attack of the $\bullet CCl_3$ free radical the stability of the existing secondary radical as well as steric factors determine the regioselectivity of the addition rather than the polarity of the double bond in the TFP molecule or electrophilicity of the CCl_3 free radical [13].

Because of the close presence of the CF_3 group the electrophilicity of the 1:1-addition product radical is even greater than the electrophilicity of the $\cdot CCl_3$ free radical. Therefore the double bond is attacked on the negatively polarized site.

The ^1H-NMR of the product (IVb) shows various multiplets at 2.3, 2.6, 3.0, 3.2, 4.8 and 4.9 ppm and a doublet at 3.3 ppm. Identification of the appropriate protons is not possible.

The telomer (IVc) appears in the GC as a mixture of six isomers (ratio 8:7:7:6:4:3). The complexity of the NMR spectra makes a detailed analysis impossible. Because of the chemical shift fluorine containing groups other than CF_3 can be excluded.

The telomers (IVd) and (IVe) are identified only through their mass spectra.

EXPERIMENTAL

GC-Analysis

Carlo Erba 2900, Column 50 m PB-1 WGA, temperature program 50-280°C 10 min isothermal, heating rate 12°C/min, evaporation temperature 175°C, carrier gas 1 0 10^5 Pa helium, injection volume 0.5 μl, detector FID.

Quantitative analysis with toluene as external standard, correction factors 5.6 (IIIa), 5 096 (IIIb), 5.081 (IIIc), 5 0 (IIId) and (IIIe).

Mass spectroscopy

Varian 3700 with open coupling to MS, spectrometer Varian MAT 112 S, temperature (ion source) 200°C, pressure (ion source) 2.6 10^{-4} Pa, ion current 0 7 mA, ion energy 70 eV, data system Varian SS MAT 188

NMR spectroscopy

^{1}H-NMR: Bruker 200 MHz FT, standard TMS.
^{19}F-NMR: Bruker WP 80 SY and Jeol VXR 300, ext standard $CFCl_3$, solvent acetone-d_6

Autoclaves

Volume 80 to 100 ml, bottom part: material zirconium or Hastelloy B2, top part: material Hastelloy C4 or Hastelloy B2.

Preparation of (III)

The complex (I) (4 25 g, 6.07 mmol) was dissolved in 12 ml benzene and filled into the autoclave TFP (12.13 g, 126 mmol) was added. After 20.5 h stirring at 90°C, the products are distilled and separated by preparative GC (yield 2.37 g, 19.6% related to TFP).

Telomerization

Table I lists the experimental details for the described telomerizations. A typical run was conducted as follows·

The catalyst, the solvent and CCl_4 were filled into the autoclave. TFP was added and the reaction mixture was stirred for 10.5 h at 170°C After distillation the mixture was analyzed by GC.

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