

Anions of Transition Metals Carbonyls in Nucleophilic Vinyl Substitution: VII.* Carbonylates Reaction with 1-Chloro-2-(trifluoromethyl)- and 1-Chloro-2-(perfluoro-*tert*-butyl)hexafluorocyclopent-1-enes, and with *Z* and *E* Isomers of β -Chloro- α,β -difluorostyrenes. Halophilic and/or Nucleophilic Reaction mechanism**

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Abstract—Reactions were studied between 1-chloro-2-(trifluoromethyl)-hexafluorocyclopent-1-ene with anions $[\text{CpFe}(\text{CO})_2]^-$, $[\text{Re}(\text{CO})_5]^-$, $[\text{Mn}(\text{CO})_5]^-$, $[\text{CpMo}(\text{CO})_3]^-$, and $[\text{CpW}(\text{CO})_3]^-$. The effect of proton donors on the composition of reaction products was established. The reactions with $[\text{Re}(\text{CO})_5]^-$ and $[\text{Mn}(\text{CO})_5]^-$ were shown to proceed quantitatively along nucleophilic route ($\text{S}_{\text{N}}2\text{Vin}$) resulting in σ -vinyl complexes of rhenium and manganese. The $[\text{CpMo}(\text{CO})_3]^-$ and $[\text{CpW}(\text{CO})_3]^-$ anions turned out to be 10^4 times less nucleophilic than $[\text{Mn}(\text{CO})_5]^-$. In this case the main course of the reaction is the metal-halogen exchange with concurrent nucleophilic substitution. In reaction of $[\text{CpMo}(\text{CO})_3]^-$ and $[\text{CpW}(\text{CO})_3]^-$ with 1-chloro-2-(trifluoromethyl)-hexafluorocyclopent-1-ene the σ -vinyl complexes arise along an unusual autocatalytic mechanism: the reaction of carbonyl occurs not with the initial substrate but with pentafluoromethylcyclopent-1-ene that forms from the substrate under the action of a fluoride ion. In an extremely fast reaction of the same substrate with $[\text{CpFe}(\text{CO})_2]\text{K}$ the main process is carbonylate oxidation along unestablished mechanism. The reaction between carbonylates and 1-chloro-2-(perfluoro-*tert*-butyl)hexafluorocyclopent-1-ene proceeds exclusively as metal-halogen exchange that with $[\text{Re}(\text{CO})_5]^-$ furnishes anionic acyl complex $\text{cis}[\text{C}_9\text{F}_{15}\text{C}(\text{O})\text{Re}(\text{CO})_4\text{Cl}]^-$. The reaction of *Z* and *E* isomers of β -chloro- α,β -difluorostyrenes with $[\text{CpFe}(\text{CO})_2]^-$ in the presence of proton donors confirmed the previously assumed ($\text{S}_{\text{N}}2\text{Vin}$) mechanism of nucleophilic substitution and also the intermediate formation of alkenyl carbanions in the parallel redox process.

Nucleophilic vinyl substitution effected by metal carbonyls anions*** is known since a fairly long time, and one of the procedures for preparation of σ -alkenyl metal complexes is based thereon [2].

At the same time the real nature of alkenyl halides reactions with carbonylates and their mechanism are still poorly understood. In the most cases the nucleophilic vinyl substitution is only one among many competing directions of the reaction. In our investigations on reactions between carbonylates and perfluoro-

methylcyclopent-1-ene [3], trifluorostyrene [4, 5], *Z*- and *E*- β -chloro- α,β -difluorostyrenes [5] we frequently observed certain side processes resulting in carbonylate oxidation and olefin dehalogenation, but we did not study the redox processes.

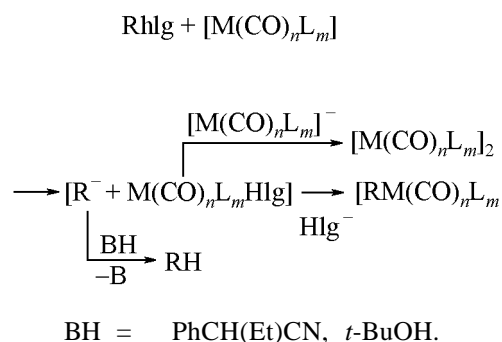
We recently showed that nucleophilic aromatic substitution in pentafluorohalobenzenes effected by carbonylates was actually a halophilic reaction [6, 7]. Two main reaction paths, halogen replacement yielding $\text{C}_6\text{F}_5\text{M}(\text{CO})_n\text{L}_m$, and reductive dehalogenation of $\text{C}_6\text{F}_5\text{Hlg}$ have actually the same initial stage, namely metal-halogen exchange. The carbonylate attack on halogen is here more feasible than the attack on the π -system of the aromatic ring. The possibility of practically quantitative protonation of the intermediate carbanion $[\text{C}_6\text{F}_5]^-$ formed by exchange occurring in the presence of specially selected CH-acid or

* For communication VI, see [1].

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*** The anions of transition metals carbonyls are also called "carbonylates."

Scheme 1.



tert-butanol, the so-called “anion traps,” was the main proof of the reaction mechanism (Scheme 1).

Taking into account certain common features of the nucleophilic aromatic and vinyl substitution it is presumable that the halophilic pathway may occur also in reactions of carbonylates with polyfluoroalkenyl halides containing “heavy” halogens (Cl, Br). Examples of such reactions were recently found: Just this route took the reaction of carbonylates with trifluorobromoethylene and *Z*-2-(perfluoro-*tert*-butyl)-1,2-difluoro-1-chloro(bromo)ethylenes [8, 9]. Here we extend the study on the possible routes of carbonylates reactions with polyfluoroalkenyl halides by an example of reaction of a carbonylate series ($[\text{CpFe}(\text{CO})_2]^-$, $[\text{Re}(\text{CO})_5]^-$, $[\text{Mn}(\text{CO})_5]^-$, $[\text{CpW}(\text{CO})_3]^-$, $[\text{CpMo}(\text{CO})_3]^-$) with an extremely active alkenyl chloride, 1-chloro-2-(trifluoromethyl)-

hexafluorocyclopent-1-ene. We believe that not only nucleophilic vinyl substitution proper is interesting, but also the concurrent process of alkenyl halide reduction with the carbonylate. Note that all alkenyl halides previously studied in reactions with carbonylates may be regarded as low active. We also repeated the investigation of reactions between *Z*- and *E*- β -chloro- α,β -difluorostyrenes with $[\text{CpFe}(\text{CO})_2]\text{K}$ [5] and studied the effect of the “anion traps” to test also in this case the hypothesis of the halophilic mechanism and to elucidate the nature of the redox-processes.

1-Chloro-2-(trifluoromethyl)-hexafluorocyclopent-1-ene (**I-Cl**) is an agent of high electrophilicity and reacts with the most carbonylates, including also weakly nucleophilic $[\text{Mn}(\text{CO})_5]^-$, $[\text{CpW}(\text{CO})_3]^-$, and $[\text{CpMo}(\text{CO})_3]^-$.

Nucleophilic vinyl substitution by anions of rhenium and manganese pentacarbonyl in alkene (**I-Cl**) results in quantitative formation of σ -vinyl derivatives (**I-Mn**, **Re**, Scheme 2) with no side reactions. The direct monitoring of the reaction by ^{19}F NMR spectroscopy demonstrated total absence even of traces of the other intermediate or final products beside σ -vinyl complexes (**I-Mn**, **Re**). It virtually excludes halophilic reaction mechanism that would have afforded halo(acyl)metalates of rhenium and manganese $[\text{R}_\nu(\text{CO})\text{M}(\text{CO})_4\text{Cl}]^-$ ($\text{M}=\text{Mn}$, **Re**) as a result of reaction between alkenyl carbanion with $\text{M}(\text{CO})_5\text{Cl}$ [7-9].

Scheme 2.

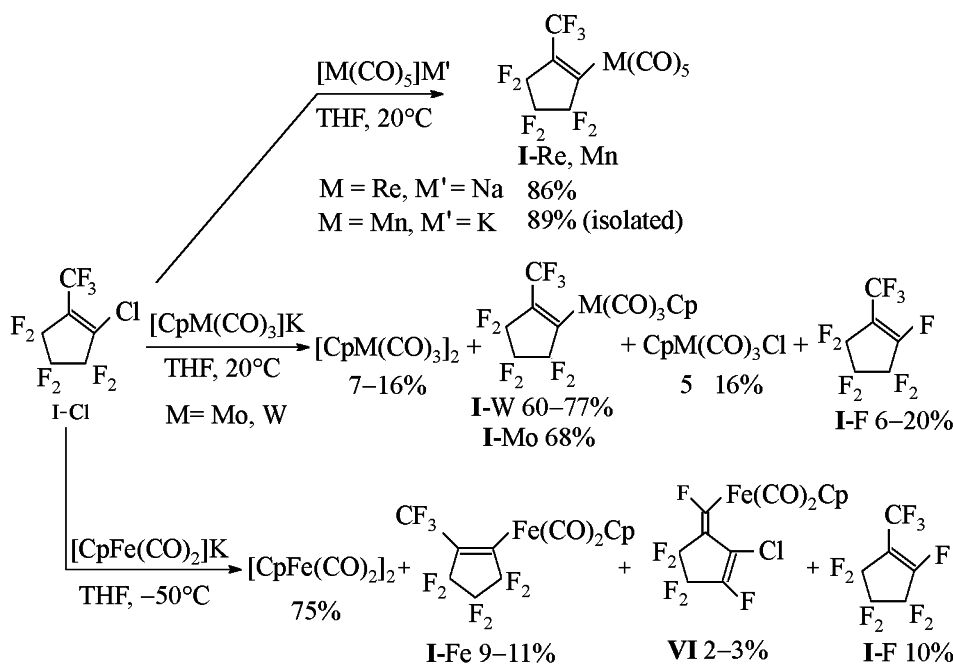


Table 1. Composition of reaction products of $[\text{CpM}(\text{CO})_3]\text{M}'$ ($\text{M} = \text{Mo}, \text{W}$; $\text{M}' = \text{Li}, \text{K}$) and 1-chloro-2-(trifluoromethyl)hexafluorocyclopent-1-ene (**I-Cl**), THF, 20°C. Influence of “anion traps”

Run no.	M'	M	Initial concentration $[\text{CpM}(\text{CO})_3]\text{K}$, mol l^{-1}	Ratio I-Cl / $[\text{CpM}(\text{CO})_3]\text{K}$	“Anion trap,” equiv. per 1 mole $[\text{CpM}(\text{CO})_3]\text{K}$	Yield of reaction product, % ^a				
						I-W , Mo	$[\text{M}(\text{CO})_3\text{Cp}]_2$	$\text{CpM}(\text{CO})_3\text{Cl}$	I-H	I-F
1 ^b	K	Mo	0.18	1.4	No additives	68	9	7	<1	7
2	K	W	0.21	1.2–1.5	No additives	77	7	5	<1	6
3	K	W	0.25	2.5	Ph_2CHCN , 3.5	75	– ^c	6	4	12
4	K	W	0.11	5	<i>t</i> -BuOH, 5	70	7	13	11	15
5	K	W	0.05	12	No additives	60	16	16	<2	20
6 ^{d,e}	Li	Mo	0.11	0.9	No additives	11	40	17	<1	<1
7 ^d	Li	Mo	0.16	0.9	<i>t</i> -BuOH, 6	16	45	11	16	<1

^a Yields of reaction products were determined from ¹H and ¹⁹F NMR spectra of reaction mixtures by internal standard method.

^b Also forms 3% (*E*-**II**-Mo).

^c Signals of Cp and Ph_2CHCN overlap.

^d Yield **F*** 25%.

^e In overall yield 16% form (*Z*- and *E*-**II**-Mo).

At room temperature and reagents concentrations $\geq 0.1 \text{ mol l}^{-1}$ both reaction occur instantly. With the less nucleophilic of the two carbonylates, $[\text{Mn}(\text{CO})_5]\text{K}$, we succeeded by reducing the reagents concentrations 100-fold to measure by spectrophotometric method the second order rate constant ($k_2 \approx 10 \text{ l mol}^{-1} \text{ s}^{-1}$). The quantitative formation of σ -vinyl complex (**I-Mn**) (yield 85–90%) was also obtained in the presence of Ph_2CHCN ($\text{p}K_a$ 18 [10]) that can protonate the alkenyl carbanion, an intermediate in the halophilic reaction. The strength of the conjugate CH-acid of the alkenyl carbanion may be estimated regarding it as analog of the secondary polyfluoro-

alkanes ($\text{p}K_a > 20$) for at the acid center of (**I-H**) are formally present two perfluorinated organic radicals [10]. Quantum-mechanical calculation by AM1 method shows that in the gas phase compound (**I-H**) has acidity ($\approx 5 \text{ kcal mol}^{-1}$) similar to that of $(\text{CF}_3)_3\text{CCF}=\text{CFH}$. Carbanion of the latter is trapped even by $\text{PhCH}(\text{Et})\text{CN}$ ($\text{p}K_a \geq 22$) [9]. Therefore the experiment with the “anion trap” is justified and can additionally prove the nucleophilic ($S_N2\text{Vin}$) mechanism, i.e., involving carbonylate attack on the carbon atom of the π -bond, in the reaction of carbonylates $[\text{M}(\text{CO})_5]^-$ ($\text{M} = \text{Mn}, \text{Re}$) with alkene (**I-Cl**) that is presented in Scheme 3.

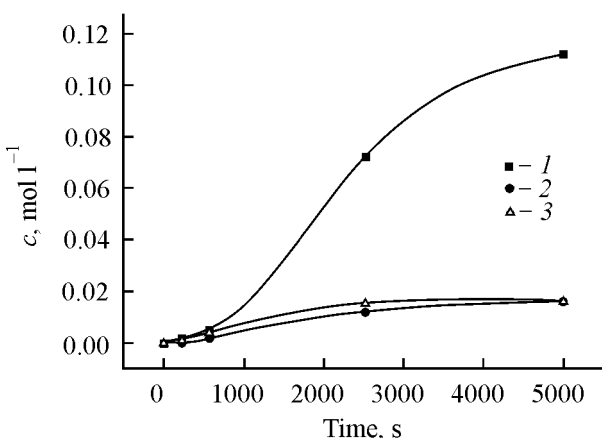
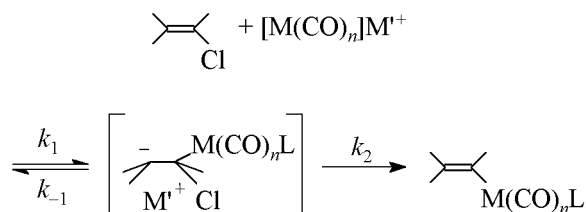


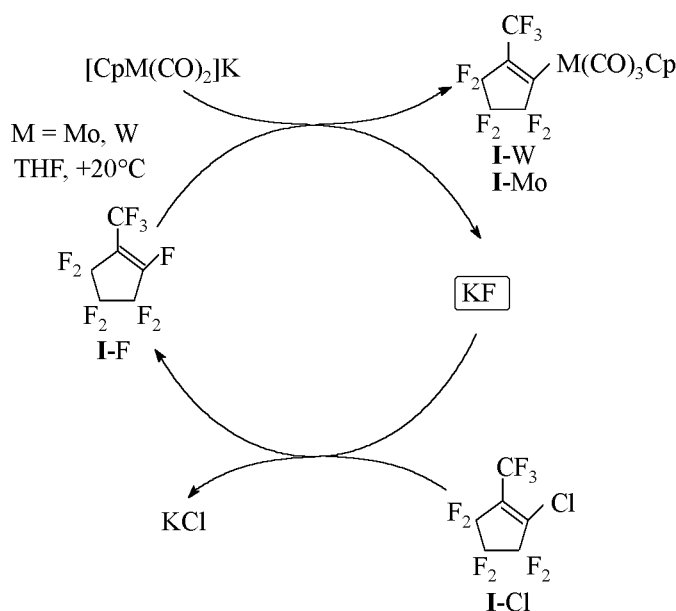
Fig. 1. Kinetic curves of reaction between $[\text{CpMo}(\text{CO})_3]\text{K}$ and chloroalkene (**I-Cl**), THF, 20°C. Initial concentration: (**I-Cl**) 0.25 mol l^{-1} ; $[\text{CpMo}(\text{CO})_3]\text{K}$ 0.18 mol l^{-1} . (1) Product of nucleophilic substitution, (2) $[\text{CpMo}(\text{CO})_3]_2$, (3) $\text{CpMo}(\text{CO})_3\text{Cl}$.

Note that in the framework of this mechanism is also assumed carbanion intermediate formation. The latter however is not fixed with the “anion traps.” The reason of it is the extremely short life time of the intermediate given the presence of so good leaving group as chloride ion. This mechanism can degenerate into one-step reaction where the cleavage of the leaving group occurs without activation barrier within a single elementary act with the addition of the nucleophile across the π -bond [11].

Scheme 3.



Scheme 4.



The reaction of tungsten and molybdenum carbonylates $[\text{CpM}(\text{CO})_3]\text{K}$ ($\text{M} = \text{Mo, W}$) with chloroalkene (**I-Cl**) provided in a fair yield the σ -vinyl complexes (**I-Mo, W**) alongside some dimers and metal carbonyl chlorides (Scheme 2, Table 1). However the reaction monitoring with ^{19}F NMR showed that at low conversion all the three products were present in comparable amounts. The kinetic curve of accumulation of the nucleophilic substitution product (**I-Mo**) contained an obvious induction period (Fig. 1). No less curious was appearance in the reaction mixture of perfluoro-2-methylcyclopent-1-ene (**I-F**) (Scheme 2, Table 1). A control run demonstrated that chlorine is slowly replaced by fluorine in chloroolefin (**I-Cl**) already in the presence of KF in THF , and at addition of 10 mol% of 18-crown-6 fluoroalkene (**I-F**) forms quantitatively within several minutes. Note that fluoride ion was detected in the reaction products of chloroalkene (**I-Cl**) and $[\text{CpM}(\text{CO})_3]^-$ (run nos. 6, 7, Table 1). It forms *in situ*, and probably can replace chlorine in chloroalkene (**I-Cl**) without additional activation.

All the above reasoning allows an assumption that in formation of the nucleophilic substitution product (**I-Mo, W**), at least of its main quantity, operates quite unusual "catalysis" (Scheme 4): In the nucleophilic substitution by carbonylate takes part not the initial compound **I-Cl** but a lot more active fluoroalkene **I-F** arising under the action of the fluoride ion. To our knowledge it is the first example of such catalysis with fluoride ion in reaction of nucleophilic

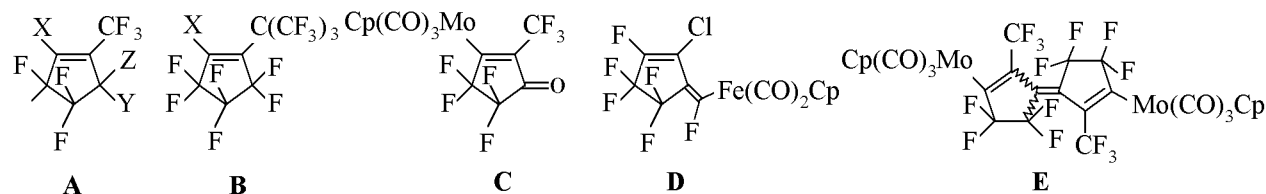
vinyl and aromatic substitution. In the framework of this scheme became clear why the "anion traps" did not affect the yield of nucleophilic substitution product **I-W** (run nos. 3, 4, Table 1) whereas the greater excess of alkene **I-Cl** somewhat reduced the fraction of complex **I-W** in the reaction mixture (run nos. 2-5, Table 1). The initial source of the fluoride ion necessary to initiate the catalytic circle also was revealed; that will be discussed later.

To test the assumed "catalytic" mechanism of the nucleophilic substitution we studied the reaction between the lithium carbonylate $[\text{CpMo}(\text{CO})_3]\text{Li}$ with chloroalkene **I-Cl**. The "catalytic" route in this case should be excluded since the fluoride ion should be bound as LiF . Our forecast was supported by experiments (run nos. 6, 7, Table 1): The yield of **I-Mo** complex was reduced to 11%, the kinetic curve of its accumulation had a common exponential character, and no fluoroolefin **I-F** was found in the reaction mixture. Under these conditions the main final product was a dimer $[\text{CpMo}(\text{CO})_3]_2$; note however that at the start of the reaction no dimer was present, and appeared in 1:2 ratio complex **I-Mo** and $\text{CpMo}(\text{CO})_3\text{Cl}$. During the further course of the reaction in the ^1H and ^{19}F NMR spectra appeared signals of two additional isomeric σ -vinyl complexes with $\text{Mo}(\text{CO})_3\text{Cp}$. Apparently the complexes have triene structure (*Z*- and *E*-**II-Mo**) (Scheme 5), or the features of their ^{19}F NMR spectra cannot be understood.

In the spectrum of an isomer (*E*-**II-Mo**) the signal of CF_3 group appears as a triplet apparently due to coupling with the CF_2 group (Table 2). In the spectrum of the other isomer as in all monomer polyfluoromethylcyclopentenes the coupling of CF_3 and CF_2 groups is not manifested; however the signal of one CF_2 group appears as *AA'**BB'* system. This evidences the coupling of fluorine nuclei [$J(\text{AB}') \approx 20$ Hz, $J(\text{AA}') \approx 30$ Hz] of equivalent CF_2 groups from different rings. Quantum-mechanical calculations* show that in both isomers (*Z*- and *E*-**II-Mo**) the distance between the fluorine atoms of CF_3 and CF_2 groups from the neighboring rings is less than the sum of their van der Waals radii.

As a result the lone electron pairs of the adjacent fluorine atoms overlap providing a possibility of a through-space coupling [12] that is observed in the spectra of the complexes (*Z*- and *E*-**II-Mo**). The repulsion of the fluorine atoms drawn close together

* Calculation by AM1 method on a mode of the corresponding fully fluorinated triene with $\text{CpMo}(\text{CO})_3$ groups excluded.

Table 2. ^{19}F NMR of polyfluoric cyclopentenes, THF, $22\times\text{C}$ 

Compd.	X	Y	Z	CF ₂		CF ₂	C=CF	CF ₃ ^a		
				δ_{F} , ppm	δ_{F} , ppm			$J_{\text{F-F}}$, Hz	δ_{F} , ppm	δ_{F} , ppm
Formula A				δ_{F} , ppm	δ_{F} , ppm	$J_{\text{F-F}}$, Hz	δ_{F} , ppm	δ_{F} , ppm	$J_{\text{F-F}}$, Hz	
I-Cl	Cl	F	F	-109.00	-114.61	-	-129.55	-	-60.77	-
I-F	F	F	F	-108.33	-119.40	15 d	-129.47	-111.92	-59.98	15.2 d
I-H [14]	H	F	F	-110.60	-111.18	-	-130.72	-63.68	-	-
I-Mn	Mn(CO) ₅	F	F	-98.35	-110.07	-	-132.55	-	-56.78	-
I-Re	Re(CO) ₅	F	F	-98.21	-109.41	-	-131.78	-	-57.07	-
I-Mo	CpMo(CO) ₃	F	F	-99.28	-109.30	-	-130.99	-	-57.30	-
I-W	CpW(CO) ₃	F	F	-99.19	-109.12	-	-131.20	-	-56.58	-
I-Fe	CpFe(CO) ₂	F	F	-100.33	-109.26	-	-131.55	-	-57.33	-
Formula B										
V-F	F	-	-	-103.82	-120.45	18 d	-130.69	-99.84	-62.61	16 d, 9.5 t
V-Cl	Cl	-	-	-104.17	-113.95	-	-131.52	-	-60.12	10.5 t
Formula C										
IV				-101.24	-126.73	4.2 t			-59.53	2.4 t
Formula D				CF ₂	C1C=OF		CF ₂		=CFFe(CO) ₂ Cp	
VI				-109.82	-149.54	36 d, 15 t	-119.20		2.28	36 d, 15 t

Table 2. (Contd.)

Compd.	X	Y	Z	CF ₂			CF ₂			CF ₃		C=CF	
				δ _F (F ¹)	δ _F (F ²)	² J _{F-F} , Hz	δ _F (F ¹)	δ _F (F ²)	² J _{F-F} , Hz	δ _F	J _{F-F} , Hz		
Formula A				δ _F (F ¹)	δ _F (F ²)	² J _{F-F} , Hz	δ _F (F ¹)	δ _F (F ²)	² J _{F-F} , Hz	δ _F	J _{F-F} , Hz	δ ^F	
III	F	OBu- <i>t</i>	H	-113.73 d	-122.69 d.d	262	-117.62 d	-124.46 d	241	-60.42 d	16 d	-126.05	
VII	F	CpFe(CO) ₂	H	-97.86 d	-103.83 d ^b	234	-114.05 d	-124.96 d	260	-60.27 d	15 d	-137.68	
Formula E													
Z-II-Mo		-		-103.73 d	-104.21 d.d	≈253	-104.08	-121.07 ^c	≈235	-55.16	-	-	
E-II-Mo		-		-104.16 d	-105.08 d	≈250	-115.42 d	-126.61 d	≈233	-56.15 t.t	16 t, 3 t	-	
Formula B													
	X	CF ₂			CF ₂			CF ₂			CF ₃		
		δ _F (F ¹)	δ _F (F ²)	² J _{F-F} , Hz	δ _F (F ¹)	δ _F (F ²)	² J _{F-F} , Hz	δ _F (F ¹)	δ _F (F ²)	² J _{F-F} , Hz	δ _F	J _{F-F} , Hz	J _{F-F} , Hz
V-Re^d	[C(ORe)(CO) ₄ Cl]Na	-99.50 d	-117.52 d	270	-99.88 d	-112.42 d	265	132.09 d	138.66 d	235	-60.95 d.d	14	7.5

^a All signals are of complicated multiplet structure not always fully resolved (for compounds of formula A J 2–6 Hz, for compound **IV** J < 1 Hz) additional to splittings indicated in the table.

^b J 26 Hz.

^c AA'BB' System: ${}^2J_{F-F}(AB) \approx 235$ Hz, $J(AB') \approx 20$ Hz, $J(AA') \approx 30$ Hz, $J(BB') \approx 0$ Hz.

^d T 64°C, reference C₆H₅F (-112.75 ppm).

also results in noncoplanarity of the five-membered rings [13] in the (*Z*- and *E*-**II**-Mo) complexes, the geminal fluorines in the CF₂ groups become diastereotopic and thus chemically nonequivalent in the ¹⁹F NMR spectra. Moreover, according to the calculations in the *cis*-isomer (*Z*-**II**-Mo) the short contact of equivalent fluorines from the neighboring CF₂ groups occurs only in one among two possible pairs (AA'). Actually in the ¹⁹F NMR spectrum of (*Z*-**II**-Mo) in the AA'BB' system the constant $J(BB') \approx 0$ Hz.

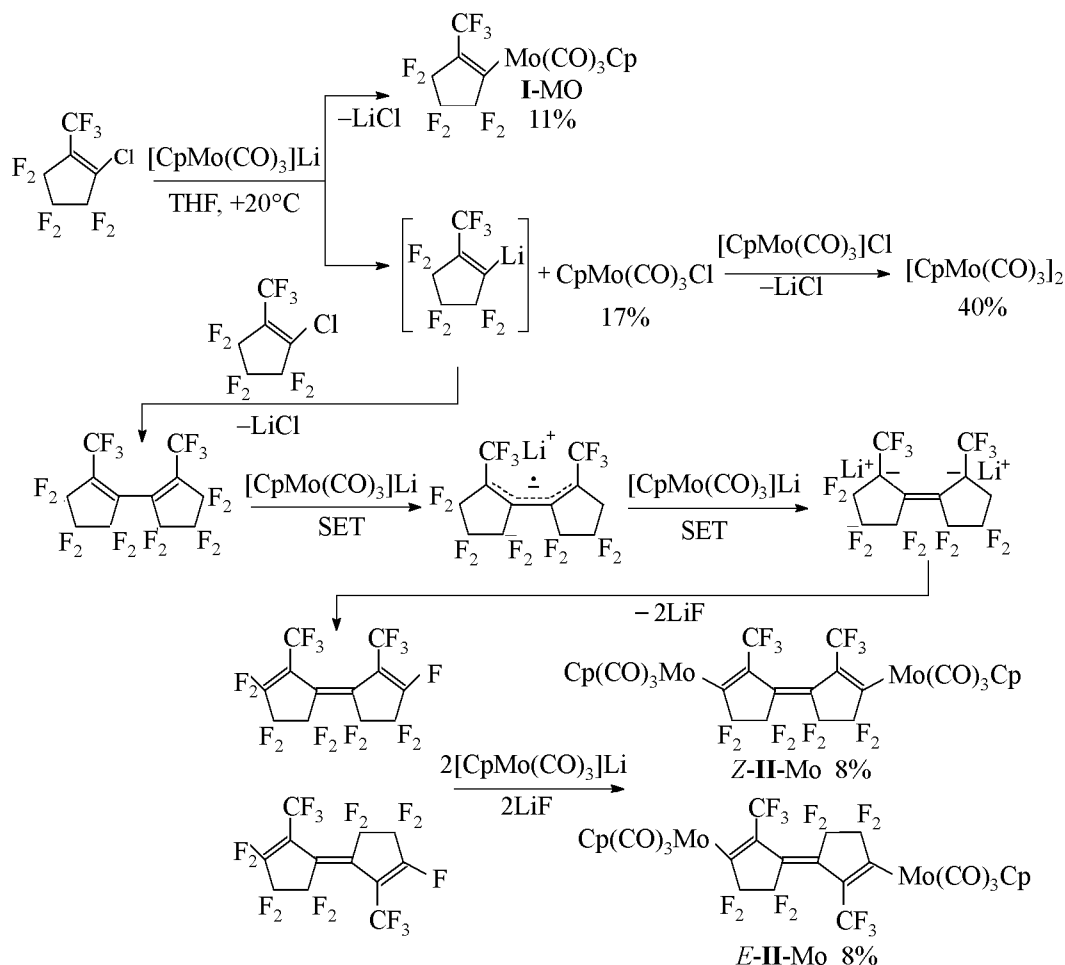
The results obtained allow to presume that the main path in the reaction between carbonylates [CpM(CO)₃]⁻ (M = Mo, W) and chloroalkene (**I**-Cl) is the metal-halogen exchange, and the carbonyl dimer and complexes (*Z*- and *E*-**II**-Mo) arise in the later stages of the reaction (Scheme 5).

The intermediate formation of an alkenyl carbanion (A) is evidenced by formation of its protonation products in the presence of *tert*-butanol,

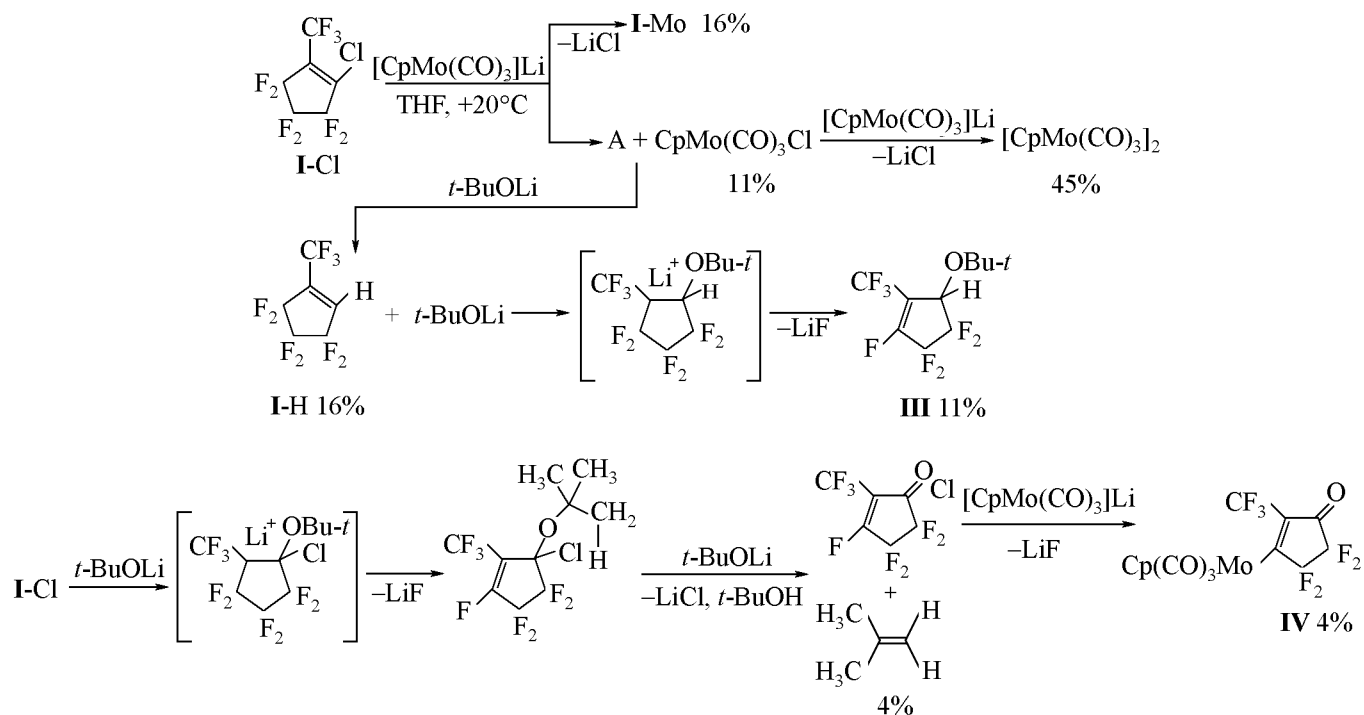
hexafluoro-2-hydro-1-(trifluoromethyl)cyclopent-1-ene (**I**-H) and 5-(*tert*-butoxy)octafluoro-5-hydro-1-methyl-1-cyclopentene (**III**) (run no. 7, Table 1). The latter compound is apparently the product of *tert*-C₄H₉OLi addition across the π-bond in the (**I**-H) followed by fluoride ion elimination from the allyl position. Allyl substitution with lithium *tert*-butylate in the initial (**I**-Cl) results in an unstable α-chloro-(polyfluoroalkyl) *tert*-butyl ether that in the presence of bases readily cleaves isobutylene to afford enone (Scheme 6). The isobutylene and tetrafluoro-2-(trifluoromethyl)-3-(η⁵-cyclopentadienylnitricarbonylmolybdeno)-2-cyclopenten-1-one (**IV**) in low amount (yield 4%) were also found in the reaction mixture.

A significant distinction from the previously studied halophilic reaction [6–8] consists in no negative effect of *t*-BuOH on the formation of σ-vinyl complex (**I**-Mo). In this case this compound is a true product of the nucleophilic substitution. The nucleophilic substitution proceeds concurrent with the

Scheme 5.



Scheme 6.



M-Hlg exchange, and it may be represented as addition-elimination type of a mechanism (Scheme 3). No reaction between alkenyl carbanion (**A**) and CpMo(CO)₃Cl is apparently due to the low electrophilicity of the latter [15] as compared, e.g., with Re(CO)₅Hlg or CpFe(CO)₂Hlg and to the great, on the contrary, electrophilicity of 1-chloro-2-(trifluoromethyl)hexafluorocyclopent-1-ene (**I-Cl**) that just reacts with the intermediate carbanion (**A**) yielding diene [13]. The successive stages of diene reduction and nucleophilic substitution with carbonylate (Scheme 5) result in complexes (*Z*- and *E*-**II**-Mo) and in notable release of fluoride ion (run no. 6, Table 1). A similar process in reaction with potassium salts of [CpM(CO)₃]⁻ (M = Mo, W) can serve as a source of fluoride ion required for initiation of the catalytic mechanism of nucleophilic substitution (Scheme 4).

The formation of anion-radical of diene (**B**) (Scheme 5) is confirmed by ESR data. In the course of reaction is observed an intense ESR signal. Its intensity was the greatest after 10 min since the start of the process, and then the signal diminished and totally disappeared to the end of reaction (in 60 min). The spectrum (Fig. 2) belongs to a stable anion-radical where the unpaired electron is delocalized in a system of conjugated bonds, interacts with 14 approximately equivalent fluorine nuclei $a_F(14F) \approx 13.5$ Gs, g 2.0028. The observed value of the hyperfine coupling constant is characteristic of the

interaction with β -fluorine atoms in the anion-radicals of perfluorinated alkenes [16], and consequently the spectrum is in good agreement with the structure of anion-radical (**B**). Thus 1-chloro-2-(trifluoromethyl)hexafluorocyclopent-1-ene (**I-Cl**) can react with carbonylates along both nucleophilic (S_N2V in, Scheme 3) and halophilic routes (S_N2Hal , Schemes 5 and 6) depending on the character of the carbonylate. The carbonylates of tungsten and molybdenum turned out to be significantly less reactive toward (**I-Cl**) than [Mn(CO)₅]K: The nucleophilicity of [CpM(CO)₃]K (M = Mo, W) revealed in this reaction is at least by four orders of magnitude lower than that expected

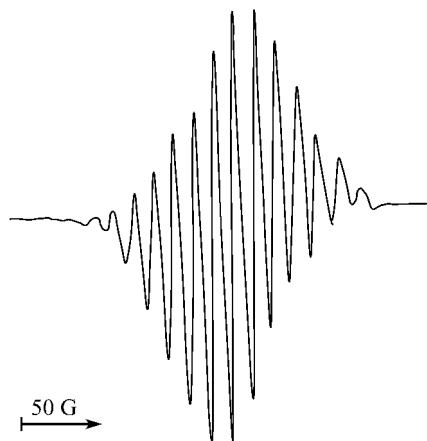


Fig. 2. ESR spectrum of diene anion-radical (**B**), THF, 20°C.

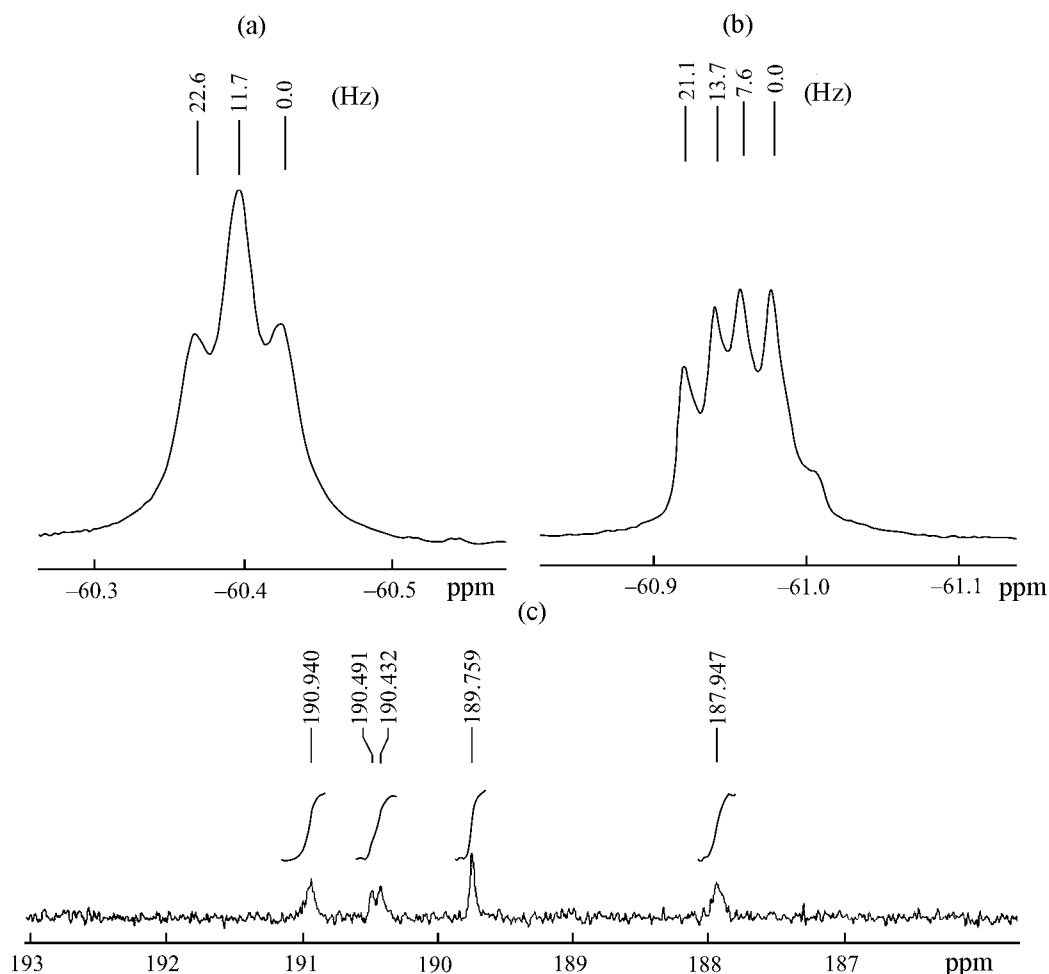


Fig. 3. NMR spectra of acyl complex (**V-Re**). (a) ^{19}F NMR spectrum, signal of the group $(\text{CF}_3)_3\text{C}$, 20°C ; (b) ^{19}F NMR spectrum, signal of the group $(\text{CF}_3)_3\text{C}$, -64°C ; and (c) ^{13}C NMR spectrum, signals of the groups $\text{Re}(\text{CO})_4\text{Cl}$, -64°C .

from the known series of carbonylates nucleophilicity* [17, 18]. The prevailing halophilic route of reaction with tungsten and molybdenum carbonylates may be due just to their unexpectedly low nucleophilicity.

The direction of carbonylate attack in alkenyl halides either on the halogen atom or on the π -system is also strongly affected by steric factors. It is well illustrated by the reaction of $[\text{Re}(\text{CO})_5]\text{Na}$ and $[\text{CpMo}(\text{CO})_3]\text{Li}$ with 1-chloro-2-(perfluoro-*tert*-butyl)hexafluorocyclopent-1-ene (**V-Cl**) (Scheme 7).

* The carbonylates activity in the reactions of S_N2 type by the data of Dessy *et al.* [17] changes in the series $\{\log(k/k_0)\}$: $[\text{CpW}(\text{CO})_3]^-$ (2.7) > $[\text{Mn}(\text{CO})_5]^-$ (1.9) > $[\text{CpMo}(\text{CO})_3]^-$ (1.8) > $[\text{Co}(\text{CO})_4]^-$ (0); Atwood *et al.* observed somewhat different series for carbonylate salts with $[(\text{Ph}_3\text{P})_2\text{N}]^+$ in THF [18]: $[\text{Mn}(\text{CO})_5]^-$ (2.25) > $[\text{CpW}(\text{CO})_3]^-$ (1.75) > $[\text{CpMo}(\text{CO})_3]^-$ (1.55) > $[\text{Co}(\text{CO})_4]^-$ (0).

The double bonds in (**I-Cl**) and (**V-Cl**) are approximately equally activated to the nucleophilic attack, but the perfluoro-*tert*-butyl group hinders the carbonylate attack at the double bond in compound (**V-Cl**). Its reaction with $[\text{CpMo}(\text{CO})_3]\text{Li}$ yielded only dimer $[\text{CpMo}(\text{CO})_3]_2$ and $\text{CpMo}(\text{CO})_3\text{Cl}$. The steric effect of the perfluoro-*tert*-butyl group crucially affects the direction of reaction also with rhenium carbonylate. Instead of the quantitative nucleophilic substitution observed with alkene (**I-Cl**) with alkene (**V-Cl**) selectively proceeds M-Hlg exchange to afford in high yield anion complex *cis*- $[\text{C}_9\text{F}_{15}\text{C}(\text{O})\text{Re}(\text{CO})_4\text{Cl}]\text{Na}$ (**V-Re**) (Scheme 7).

Unlike the previously studied anionic acyl complexes [7-9] in the ^{19}F and ^{13}C NMR spectra of (**V-Re**) complex is observed the effect of hindered rotation of $\text{C}(\text{O})\text{Re}(\text{CO})_4\text{Cl}$ group. The signals in the spectra at room temperature are strongly broadened;

Table 3. Composition of products from reaction of [CpFe(CO)₂]K with 1-chloro-2-(trifluoromethyl)hexafluorocyclopent-1-ene (I-Cl) in THF. The effect of anion and radical “traps”

Run no.	Temperature, °C	Additive, equiv per 1 mole [CpFe(CO) ₂]K	Consumption of (I-Cl) calculated [CpFe(CO) ₂]K, %	Yield of reaction product, % ^a				
				I-Fe	[CpFe(CO) ₂] ₂	VI	VII	I-F
1	-50	No additives	-	9	75	2	<0.5	10
2	0	Ph(Et)CHCN, 5	50	5	70	5	4	<2
3	-115	Ph(Et)CHCN, 5	75	11	75	<1	2	3.5
4	-60	<i>t</i> -BuOH, 6	100	5	70	2.5	5	35 ^b
5	-50	(<i>cyclo</i> -C ₆ H ₁₁) ₂ PH, 5	- ^c	6	70	3	4.5	- ^d
6	-50	PEt ₃ , 1	- ^c	10	75	2.5	<1	- ^d
7	-90	MeOH, 100 CH ₂ (CN) ₂ , 10 ^e	55	9	75	<3	<2	<2 ^f

^a Yields of products were determined from ¹H and ¹⁹F NMR spectra of the reaction mixtures relative to internal standard.

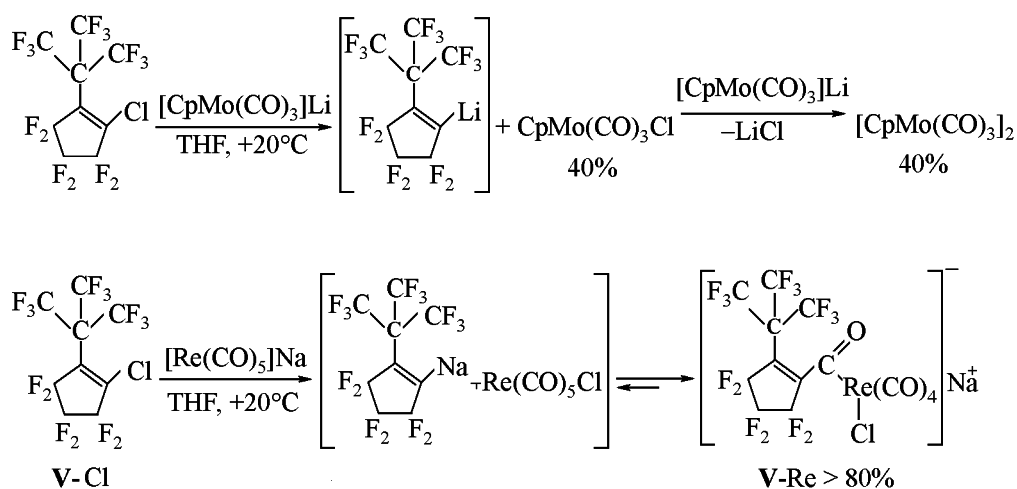
^b Yield of F⁻ 10%.

^c Chloroalkene (I-Cl) reacted with phosphines giving a complex products mixture.

^d Not determined.

^e MeOH and CH₂(CN)₂ were added 2 min after charging chloroalkene (I-Cl), i.e. after completion of the reaction.

^f Yield of F⁻ 35%.

Scheme 7.

nonetheless, the chemical nonequivalence of fluorines in CF₂ groups due to the hindered rotation of the *cis*-C(O)Re(CO)₄Cl group is quite obvious (Table 2).

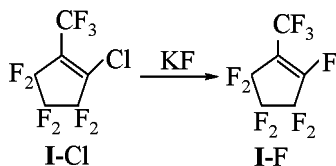
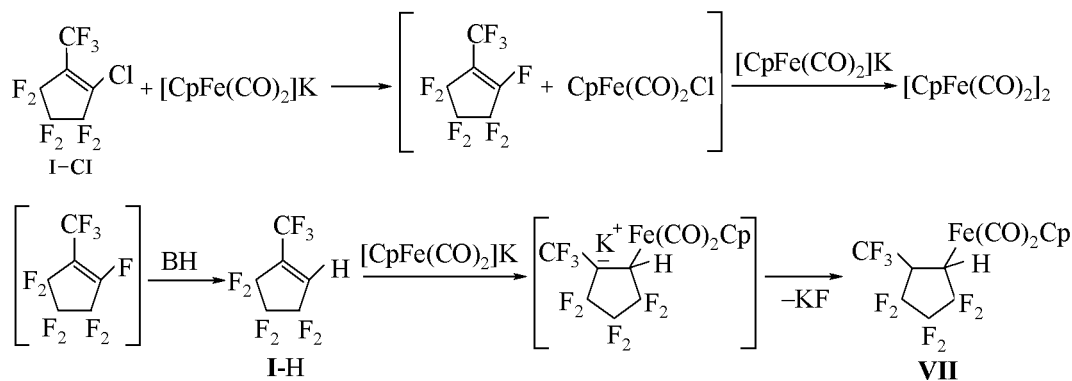
At cooling to -64°C the peaks get narrower, and the triplet from (CF₃)₃C group in the ¹⁹F NMR spectrum becomes a doublet of doublets (Fig. 3), i.e., the coupling with each proton of the CF₂ group occurs with a separate constant. Such acyl complexes at fast rotation of the organic ligand possess a plane of symmetry, and thus two C=O groups get equivalent [7-9]. On the contrary, at low temperature in the ¹³C NMR spectrum of (V-Re) complex to each C=O group belongs a separate signal (Fig. 3).

Complex (V-Re) is of low stability and apparently exists in the equilibrium with Re(CO)₅Cl and the corresponding alkenyl carbanion.*

In the presence of the air oxygen the solution of (V-Re) complex suffer relatively fast decomposition quantitatively affording Re(CO)₅Cl and a mixture of

* IR spectrum of diluted solutions of (V-Re) complex in THF is a combination of Re(CO)₅Cl spectrum and that of acyl rhenium complex (ν, cm⁻¹ 1604 m, ≈ 2000 v.s., 1938 s, 2104 m); yet in a concentrated solution of the reaction mixture in the ¹³C NMR spectrum no signals from Re(CO)₅ are registered.

Scheme 8.



polyfluorohydrocarbons that separated from the THF solution as heavy oil.

The main pathway in the extremely fast reaction of $[\text{CpFe}(\text{CO})_2]\text{K}$ with chloroalkene (I-Cl) is not the nucleophilic substitution but carbonylate oxidation into a dimer $[\text{CpFe}(\text{CO})_2]_2$. The expected σ -vinyl derivative (I-Fe) was registered only as one of the minor products. A significant amount of perfluoro-2-methylcyclopent-1-ene (I-F) was found (Scheme 2, Table 3) evidencing formation of a fluoride ion in the course of the reaction. The ^{19}F NMR spectrum indicates also presence in the reaction mixture of small amounts of the other products. Among the latter we succeeded in isolation and identification of complex (VI) (Scheme 2). The structure of complex (VI) is revealed by the ^{19}F NMR spectrum (Table 2). Thus the presence in the molecule of a fragment $(\text{R}_p)_2\text{C}=\text{CFFe}(\text{CO})_2\text{Cp}$ is confirmed by a signal in a very weak field (2.28 ppm) [1], and the splitting of the signal into a doublet with a constant $J_{\text{F-F}}$ 36 Hz corresponds just to trans-1,4-position of the fluorine atoms in the 1,3-diene system.

A number of experiments with the use of "traps" (run nos. 2–7, Table 3) did not elucidate the nature of the redox processes in the reaction between $[\text{CpFe}(\text{CO})_2]\text{K}$ and alkene (I-Cl). The surprising thing is that the composition of the reaction products is equally weakly affected by such proton donors as

PhCH(Et)CN and $t\text{-BuOH}$ (run nos. 2–4, Table 2) and by $(\text{cyclo-C}_6\text{H}_{11})_2\text{PH}$ commonly used as hydrogen donor in radical processes* [19] (run no. 5, Table 3).

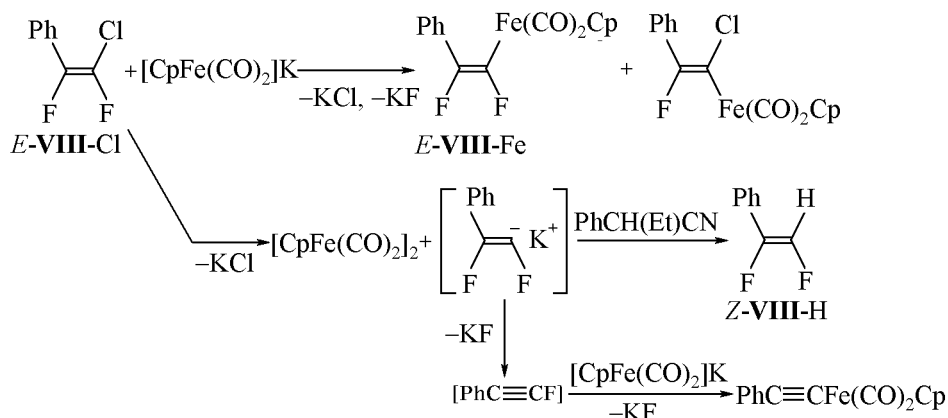
The yield of the product of the nucleophilic substitution is reduced by 5%, and at the same time in 5% yield arises a new σ -allyl complex VII (Scheme 8). The latter apparently is the addition product of $[\text{CpFe}(\text{CO})_2]\text{K}$ across the π -bond in hexafluoro-2-hydro-1-trifluoromethyl)cyclopent-1-ene (I-H) with subsequent elimination of a fluoride-ion from the allyl position (Scheme 8). The change in the reaction products composition effected by the "traps" is so insignificant that their efficiency is dubious.

In this connection we performed an additional experiment by adding into the reaction mixture stronger "acids," MeOH and $\text{CH}_2(\text{CN})_2$, 1–2 min after the mixing of the reagents (run no. 7, Table 3). We failed to detect in this run the protonation products of vinyl carbanion (I-H) and (VII); thus after completion of the reaction between (I-Cl) and $[\text{CpFe}(\text{CO})_2]\text{K}$ no vinyl carbanions were present in the solution.

The reaction carried out in the presence of a tertiary phosphine may be used for revealing the participation of metal carbonyl radicals [4]. This test is based on an extremely fast ligand substitution ($k_2 > 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$) in such radicals as $[\text{CpFe}(\text{CO})_2]$ [20, 21]. In the reaction under study the phosphine test gave negative result: no phosphine iron complexes were found in the reaction mixture (run no. 6, Table 3).

* Presumably the $(\text{cyclo-C}_6\text{H}_{11})_2\text{PH}$ in this case behaves as an acid.

Scheme 9.



As a result we should state that the fraction of intermediates trapped with radical or carbanion “traps” is too small for definite conclusion on halophilic or SET mechanism of the redox process. Chloroolefin (**I-Cl**) is weaker oxidant in the SET processes in the outer sphere ($E^{\text{Red}} = -1.62 \text{ B}^*$) than $(\text{CF}_3)_3\text{CCF}=\text{CFCl}$ ($E^{\text{Red}} = -1.04 \text{ B}$) [22]; however the reaction of the latter takes the halophilic route [9].

By analogy with the reaction with molybdenum and tungsten carbonylates we may assume (Scheme 5) that the oxidation of $[\text{CpFe}(\text{CO})_2]\text{K}$ effected by chloroolefin (**I-Cl**) occurs via M-Hlg exchange (Scheme 8). At the same time it should be taken into consideration that perfluoro-2-methylcyclopent-1-ene (**I-F**) where the halophilic attack is totally impossible also is capable to oxidize the $[\text{CpFe}(\text{CO})_2]\text{K}$ [3].

The reactions of *Z*- and *E*- β -chloro- α,β -difluorostyrenes (**Z-VIII-Cl** and **E-VIII-Cl**) with $[\text{CpFe}(\text{CO})_2]\text{K}$ we previously [5] interpreted as addition-elimination process including the direct attack of the nucleophile on the π -bond (Scheme 3); together with the possibility of the halophilic reaction path (Scheme 1) was not considered, and no experiments with “anion traps” were performed.

There are no published data on CH-acidity of the α,β -difluorostyrene (**VIII-H**), conjugate acid of the probable reaction intermediate, but the acidity of $\text{PhCH}(\text{Et})\text{CN}$ and *tert*-butanol is obviously higher [10], and thus they are suitable for trapping $[\text{PhCF}=\text{CF}]^-$ carbanion. It turned out that the presence of proton donors in the reaction mixture

* Potential of the reduction peak on a Pt electrode measured by the cyclic voltammetric method in CH_3CN , 0.05 M Bu_4NBF_4 , $\text{Ag}/\text{AgCl}/\text{KCl}$, 20°C.

virtually did not affect the yield of the products of the nucleophilic substitution (cf. run nos. 1 and 2, 3 or 4 and 5, Table 4). Consequently, in formation of these products do not take part alkenyl carbanions. Thus there is no reason for changing the previously assumed mechanism of nucleophilic substitution in the chlorodifluorostyrenes effected by $[\text{CpFe}(\text{CO})_2]\text{K}$ [5] (Scheme 3).

In the preceding paper [5] we already stated that concurrent with the nucleophilic vinyl substitution prevailing in the *Z*-isomer of styrene (**Z-VIII-Cl**) (run no. 1, Table 4) occurred also oxidation of $[\text{CpFe}(\text{CO})_2]\text{K}$, the main pathway for reaction with *E*-isomer (**E-VIII-Cl**) (run no. 4, Table 4). The presence in the reaction mixture of $\text{PhCH}(\text{Et})\text{CN}$ as a proton donor crucially changed the composition of the reduction products originating from *E*-chlorodifluorostyrene (**E-VIII-Cl**) (Scheme 9, run no. 5, Table 4). The formation of $\text{PhC}\equiv\text{CFe}(\text{CO})_2\text{Cp}$ is completely suppressed, and the only reduction product of styrene (**E-VIII-Cl**) is then *Z*-difluorostyrene (**Z-VIII-H**, yield 23%).

Similarly in reaction of $[\text{CpFe}(\text{CO})_2]\text{K}$ with the other isomer (**Z-VIII-Cl**) in the presence of *tert*-butanol grows the yield of *E*-difluorostyrene (run no. 3, Table 4). These facts support the earlier assumption [5] that in this process operate alkenyl carbanions (Scheme 9); however the halophilic mechanism of styrenes (**VIII-Cl**) reduction is not unambiguously confirmed by these data.

The formation of alkenyl carbanions may be described as succession of two acts of one-electron transfer (SET) on condition that reduction of the alkenyl radical occurs faster than its other transformations. On the other hand the conservation of the

Table 4. Effect of “anion traps” on the products of reaction between $[\text{CpFe}(\text{CO})_2]\text{K}$ and *Z*- and *E*-isomers of β -chloro- α,β -difluorostyrene (*Z*- and *E*-VIII-Cl) in THF^a

Run no.	Temperature, °C	Geometrical configuration of styrene	Anion trap, equiv. per 1 mole $[\text{CpFe}(\text{CO})_2]\text{K}$	Geometrical configuration and yield of reaction product, % ^b			Other products, yield, % ^b
				$\text{PhCF}=\text{CFFe}(\text{CO})_2\text{Cp}$	$[\text{Fe}(\text{CO})_2\text{Cp}]_2$	$\text{PhCF}=\text{CFH}$	
1	20	<i>Z</i>	No additives	<i>Z</i> , 64	19	<i>E</i> , 4	–
2	20	<i>Z</i>	α -PhCH(Et)CN, 5	<i>Z</i> , 76	19	No data	–
3	20	<i>Z</i>	<i>t</i> -BuOH, 15	<i>Z</i> , 65	18	<i>E</i> , 6	–
4	–30	<i>E</i>	No additives	<i>E</i> , 17 ^c	41	<i>Z</i> , 2	$\text{PhC}\equiv\text{CFe}(\text{CO})_2\text{Cp}$, 9
5	–30	<i>E</i>	α -PhCH(Et)CN, 5	<i>E</i> , 20 ^c	50	<i>Z</i> , 23	

^a Initial concentrations: $[\text{CpFe}(\text{CO})_2\text{K}]_0 \approx 0.05\text{--}0.07 \text{ mol l}^{-1}$, $[\text{PhCF}=\text{CFCl}]_0 \approx 0.08\text{--}0.012 \text{ mol l}^{-1}$. Data on the run nos. 1 and 4 from [5].

^b Yields of products were determined from ¹H and ¹⁹F NMR spectra of the reaction mixtures relative to internal standard.

^c In the reaction also formed 6–8% of *Z*-PhCF=CClFe(CO)₂Cp.

Table 5. ¹H NMR and IR spectra, THF, 22°C

Compound	¹ H NMR spectrum, δ , ppm		IR spectrum, ^a ν , cm^{-1}
	Cp		
$[\text{CpMo}(\text{CO})_3]\text{K}$	4.988 s	–	–
$[\text{CpMo}(\text{CO})_3]\text{Li}$	5.011 s	–	–
$[\text{CpMo}(\text{CO})_3]\text{Cl}$	5.778 s	–	1965 sh, 1979 vs, 2056 s
$[\text{CpMo}(\text{CO})_3]_2$	5.37 br.s	–	1895 sh, 1919 vs, 1963 vs, 2018 s
$[\text{CpW}(\text{CO})_3]\text{K}$	5.038	–	–
$[\text{CpW}(\text{CO})_3]\text{Cl}$	5.896 s	–	1961 vs.br, 2049 s
$[\text{CpW}(\text{CO})_3]_2$	5.470 s	–	1900 sh, 1910 vs, 1961 vs, 2013 s
$[\text{CpMo}(\text{CO})_3]_2\text{Hg}$	5.544 s	–	–
I-Mn	–	–	2035 sh, 2051 vs, 2088 vs, 2042 s
I-Re	–	–	2030 sh, 2047 vs, 2091 m, 2157 s
I-Mo	5.908 s	–	1975 sh, 1988 vs, 2058 s
I-W	6.022 s	–	1955 sh, 1974 vs, 2052 s
I-Fe	5.205	–	2004 vs, 2051 vs
I-H	–	7.895 m	–
<i>Z</i> -II-Mo	5.875 s	–	1953 s, 1993 vs, 2058 s
<i>E</i> -II-Mo	5.855 s	–	1953 s, 1993 vs, 2058 s
IV	5.994 s	–	1760 s, 1970 sh, 1987 vs, 2058 s
VI	5.236 s	–	2000 vs, 2048 vs
VII	5.005 s	2.979 d.t. ^b	1987 vs, 2035 vs

^a $l_{\text{cell}} 0.02 \text{ cm}$, region 1600–2300 cm^{-1} .

^b In acetone-*d*₆ [^d $J_{\text{H-F}}$ 26.0, ¹ $J_{\text{H-F}}$ 7.5 Hz, $\text{CHFe}(\text{CO})_2\text{Cp}$].

double bond configuration in hydrodehalogenation both of *E*- and *Z*-isomers of styrenes (VIII-Cl) is hardly consistent with the radical reaction mechanism. The alkenyl radicals and anion-radicals are known to be prone to rapid *Z/E* isomerization, and e.g. reaction of $[\text{CpFe}(\text{CO})_2]\text{K}$ with olefins (*Z*-VIII-Cl, *E*-VIII-Cl)

under conditions of one-electron reduction, the so-called electrochemical activation, results in a mixture of *Z*- and *E*-isomers of the products of nucleophilic substitution [23]. In conclusion, we believe that for the redox process under consideration the mechanism via exchange stage M-Hlg is more probable.

EXPERIMENTAL

All operations with reagents sensitive to the air oxygen were carried out in a vacuum or under purified argon in sealed glassware or systems of Schlenk type as described in the previous articles [1, 4–6].

1-Chloro-2-(trifluoromethyl)hexafluorocyclopent-1-ene (I-Cl) was purchased in the Stock Company P&M (Moscow), 1-chloro-2-(perfluoro-*tert*-butyl)hexafluorocyclopent-1-ene (**V-Cl**) was synthesized from the corresponding perfluoroalkene kindly supplied to us by Yu. V. Zeifman (Institute of Organoelemental Compounds of the Russian Academy of Sciences, Moscow). The isolation of individual isomers of β -chloro- α,β -difluorostyrenes (**VIII-Cl**) [5], the preparation and purification procedures for the dimers of metal carbonyls, the methods of preparation and dosage of reagents and solvents were repeatedly described in the previous communications [1, 4–6].

The carbonylate salts was obtained in quantitative yield by reduction of the corresponding dimers: $[\text{CpFe}(\text{CO})_2]\text{K}$, $[\text{Mn}(\text{CO})_5]\text{K}$, $[\text{CpW}(\text{CO})_3]\text{K}$ and $[\text{CpMo}(\text{CO})_3]\text{K}$ with $\text{NaK}_{2.8}$ alloy in THF [24], $[\text{CpMo}(\text{CO})_3]\text{Li}$ with 0.1% LiHg; $[\text{Re}(\text{CO})_5]\text{Na}$ prepared by reduction of the dimer with 0.5% NaHg was additionally purified by low-temperature crystallization from THF [4].

^1H (400 MHz), ^{19}F (376.3 MHz), and ^{13}C (100.58 MHz) NMR spectra were registered on spectrometer Varian VXR-400. Chemical shifts in the ^{19}F NMR spectra are given in δ_{F} scale and are measured with respect to one among the following internal references: C_6F_6 ($\delta_{\text{F}} = -162.9$ ppm), PhCF_3 ($\delta_{\text{F}} = -61.96$ ppm), and $\text{C}_6\text{H}_5\text{F}$ ($\delta_{\text{F}} = -112.75$ ppm), chemical shifts of standards in the special experiment were referred to C_6F_6 in THF. The ESR spectra were registered on Varian E-12A spectrometer. IR spectra were recorded on UR-20 spectrophotometer. Mass spectra were measured on MS-890 instrument, electron impact, 70 eV, source temperature 150°C. Kinetic measurements on reaction of $[\text{Mn}(\text{CO})_5]\text{K}$ with alkenyl halide (**I-Cl**) were carried out on spectrophotometer Hewlett-Packard-8452A by measuring the optical density in the carbonylate absorption region (λ 306 nm). The conditions of the electrochemical experiments were as described before [22].

The ^1H and ^{19}F NMR spectra were used to determine qualitative and quantitative composition of the reaction mixtures, for monitoring the reactions of molybdenum and tungsten carbonylates with alkenyl

halide (**I-Cl**) [1, 4–6]. The yield of fluoride and chloride ions was determined with ion-selective electrodes. Main products of reactions between carbonylates and alkenyl halides (**I-Cl**) and (**VIII-Cl**) were previously described and characterized in sufficient measure, and thus they were identified by spectral data without isolation (Tables 2, 5).

Authentic samples of $\text{CpMo}(\text{CO})_3\text{Cl}$ and $\text{CpW}(\text{CO})_3\text{Cl}$ were prepared in order to identify them in the reaction mixture. To this end excess $\text{ClCF}_2\text{CFCl}_2$ reacted with $[\text{CpW}(\text{CO})_3]\text{K}$ and $[\text{CpMo}(\text{CO})_3]\text{K}$ at room temperature. Alkene (**I-H**) was synthesized similarly to 1-hydroheptafluorocyclopent-1-ene [25] by protodemetalation of σ -vinyl complex (**I-Mn**) in 80% H_2SO_4 (110°C, 18 h) and was characterized by GC-MS method, m/z (I_{rel} , %): 244 (60) M^+ , 225 (80) $[M-F]^+$, 194 (100) $[M-CF_2]^+$, 175 (80) $[M-CF_3]^+$, 125 (20) $[\text{C}_4\text{HF}_4]^+$, 75 (15) $[\text{C}_3\text{HF}_2]^+$, 69 (10) $[\text{CF}_3]^+$.

1-(Pentacarbonylmanganese)-2-(trifluoromethyl)hexafluorocyclopent-1-ene (I-Mn) was prepared by treating with $[\text{Mn}(\text{CO})_5]\text{K}$ obtained from $[\text{Mn}(\text{CO})_5]_2$ (159 mg, 0.82 mmol) and 80 μl of $\text{NaK}_{2.8}$ in THF (4 ml), chloroolefin (**I-Cl**, 244 mg, 0.88 mmol) at 20°C. The isolation of the product was performed by column chromatography on silica gel (Merck, L 63/200), eluent hexane–dichloromethane, 4:1, yield of (**I-Mn**) 320 mg (89%).

Anionic complex (V-Re) was obtained by treating alkene (**V-Cl**, 110 mg, 0.25 mmol) with recrystallized $[\text{Re}(\text{CO})_5]\text{Na}$ (0.190 mmol in 0.56 ml of THF) at 20°C directly in an NMR tube. ^{13}C NMR spectrum (THF, -64°C, δ_{C} , ppm): 256.91 m (C=O), 190.95 m (C \equiv O), 190.47 d ($J_{\text{C-F}}$ 6.2 Hz, C \equiv O), 189.76 s (C \equiv O), 187.95 m (C \equiv O), 121.39 q.m ($^1J_{\text{C-F}}$ 292.5 Hz, CF_3).

Z- and E-Isomers of bis(tetrafluoro-2-(trifluoromethyl)-3-(η^5 -cyclopentadienyl)tricarbonylmolybdeno)cyclopent-2-enylidene) (Z- and E-II-Mo) were isolated from the mixture of reaction products obtained from chloroolefin (**I-Cl**, 188 mg, 0.68 mmol) and $[\text{CpMo}(\text{CO})_3]\text{Li}$ prepared from $[\text{CpMo}_3]_2$ (170 mg, 0.69 mmol) and 0.05–0.1% LiHg (0.5 ml) in THF (10 ml) at 20°C. The residue after evaporation of THF was dissolved in 3 ml of CHCl_3 , and the separated precipitate of $[\text{CpMo}(\text{CO})_3]_2$ was filtered off. About a half of the filtrate was subjected to chromatography on a column packed with silica gel (Merck, L 63/200), eluent hexane–ether, gradient elution from a mixture 3:1 till 1:1. The zones eluted in succession were as follows: cranberry-red, $[\text{CpMo}(\text{CO})_3]_2$; light yellow, $[\text{CpMo}(\text{CO})_3]_2\text{Hg}$

(<5 mg); yellow (**I-Mo**); brick-red, $\text{CpMo}(\text{CO})_3\text{Cl}$; bright yellow wide zone containing 20 mg of a mixture of (*Z*- and *E*-**II-Mo**, $\approx 15\%$). At the beginning of the last zone was collected a fraction of (*Z*-**II-Mo**). Found, %: C 36.77; H 1.05. $\text{C}_{28}\text{H}_{10}\text{F}_{14}\text{Mo}_2\text{O}_6$. Calculated, %: C 37.36; H 1.12. From trienes (*Z*- and *E*-**II-Mo**) were not obtained plausible mass spectra both at ionization with the electron impact or under conditions of the chemical ionization at atmospheric pressure (APCI). However their characteristic ^{19}F NMR spectra are reported in Table 2.

Tetrafluoro-2-(trifluoromethyl-3-(η^5 -cyclopentadienyltricarbonylmolybdeno)cyclopent-2-en-1-one (IV) was isolated from the products of the reaction between $[\text{CpMo}(\text{CO})_3]\text{Li}$ and chloroalkene (**I-Cl**) in THF/*t*-BuOH by means of TLC on Silufol UV-254 plate, eluent hexane-dichloromethane, 2:1 (R_f 0.2). Mass spectrum (IV), m/z (I_{rel} , %): cluster 434–442 (10) $[\text{M}-\text{CO}]^+$, cluster 378–386 (30) $[\text{M}-3\text{CO}]^+$, cluster 195–203 (80) $[\text{CpMoF}_2]^+$, cluster 176–184 (100) $[\text{CpMoF}]^+$, 106 (50) $[\text{C}_4\text{HF}_3]^+$, 75 (60) $[\text{C}_3\text{HF}_2]^+$, 65 (60) $[\text{Cp}]^+$. GC-MS spectrum of a volatile fraction from the same reaction mixture in combination with ^{19}F NMR data permitted identification therein of 5-(*tert*-butoxy)octafluoro-5-hydro-methylcyclopent-1-ene (**III**), m/z (I_{rel} , %): 283 (80) $[\text{M}-\text{CH}_3]^+$, 225 (100) $[\text{M}-\text{C}_4\text{H}_9\text{O}]^+$, 175 (15) $[\text{C}_5\text{HF}_6]^+$, 113 (10) $[\text{C}_3\text{HF}_4]^+$, 69 (10) $[\text{CF}_3]^+$, 57 (30) $[\text{C}_4\text{H}_9]^+$.

5-(*E*)-(3-(η^5 -Cyclopentadienyl)dicarbonyliron)fluoromethylene]-1-chloropentafluorocyclopent-1-ene (VI) and pentafluoro-5-(3-(η^5 -cyclopentadienyl)dicarbonyliron)-5-hydro-1-(trifluoromethyl)cyclopent-1-ene (**VII**) were separated from the mixture of products obtained in reaction of $[\text{CpFe}(\text{CO})_2]\text{K}$ prepared from $[\text{CpFe}(\text{CO})_2]_2$ (74 mg, 0.215 mmol) and $\text{NaK}_{2.8}$ (40 μl) with chloroalkene (**I-Cl**, 178 mg, 0.64 mmol) in a mixture of THF and *t*-BuOH at -60°C . The reaction products were eluted from a column packed with silica gel (Merck, L 63/200) with a mixture hexane-dichloromethane, from 9:1 to 3:2. The fractions collected in succession were as follows: bright yellow, 8 mg (**VII**, 4.5%); light yellow, 12 mg (**I-Fe**, 6%); and dark yellow, 5 mg (**VI**, 3%). Mass spectrum of compound **VI**, m/z (I_{rel} , %): 398 (30) M^+ , 379 (20) $[\text{M}-\text{F}]^+$, 370 (20) $[\text{M}-\text{CO}]^+$, 342 (50) $[\text{M}-2\text{CO}]^+$, 248 (80) $[\text{M}-2\text{CO}, -\text{Fe}, -2\text{F}]^+$, 213 (100) $[\text{C}_{11}\text{H}_5\text{F}_4]^+$, 193 (50) $[\text{C}_{11}\text{H}_4\text{F}_3]^+$, 187 (60) $[\text{Cp}_2\text{FeH}]^+$, 186 (60) $[\text{Cp}_2\text{Fe}]^+$, 140 (70) $[\text{CpFeF}]^+$, 75 (50) $[\text{C}_3\text{HF}_2]^+$, 65 (50) $[\text{Cp}]^+$. Mass spectrum of compound **VII**, m/z (I_{rel} , %): 402 (2) M^+ , 374 (1) $[\text{M}-\text{CO}]^+$, 364 (1) $[\text{M}-2\text{F}]^+$, 308 (3) $[\text{M}-2\text{CO}$,

$-2\text{F}]^+$, 206 (40) $[\text{C}_6\text{HF}_7]^+$, 187 (60) $[\text{Cp}_2\text{FeH}]^+$, 186 (60) $[\text{Cp}_2\text{Fe}]^+$, 140 (100) $[\text{CpFeF}]^+$, 137 (90) $[\text{C}_5\text{HF}_4]^+$, 121 (90) $[\text{CpFe}]^+$, 75 (20) $[\text{C}_3\text{HF}_2]^+$, 69 (20) $[\text{CF}_3]^+$, 65 (15) $[\text{Cp}]^+$.

Reaction of chloroalkene (**I-Cl**, 205 mg, 0.74 mmol) with KF (58 mg, 1 mmol, dried in a vacuum at 180°C for 2 h) was carried out in 1.5 ml of THF at stirring. After 45 min the yield of chloride ion according to potentiometric titration was $\approx 1\%$; then into the reaction mixture was added 18-crown-6 (20 mg, 0.076 mmol), and already 10 min later the yield of the chloride ion was quantitative. In the ^{19}F NMR spectrum were observed broad (up to 100 Hz) signals of perfluoromethylcyclopentene (**I-F**), the original alkene was absent.

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