

Nucleophilic vinylic substitution with transition metal carbonyl anions—a rare case of a halophilic reaction mechanism

Formation of halo(acyl)rhenate complexes and X-ray structure of *cis*-[CF₂=CF(CO)Re(CO)₄Br]Na

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Abstract

Reactions of polyfluorinated alkenyl halides *Z*-(CF₃)₃CCF=CFHal (Hal = Cl, **I-Cl**, Hal = Br, **I-Br**) and CF₂=CFBr (**II-Br**) with [CpFe(CO)₂]K (FpK) and [Re(CO)₅]Na proceed through the initial attack of metal carbonyl anion on halogen. Reaction with FpK gives minor amounts of σ -alkenyl complexes *Z*-R_fCF=CFFe(CO)₂Cp (**I-Fe**, **II-Fe**) (3–30%), but primarily leads to dimer [CpFe(CO)₂]₂. Reaction with [Re(CO)₅]Na produces anionic halo(acyl)rhenates *cis*-[*Z*-R_fCF=CF(CO)Re(CO)₄Hal]Na (**V-Cl**, **V-Br**, **VI**) (70–90%) which were isolated, and halo(acyl)rhenate **VI** (R_f = F) was characterized by X-ray structure analysis. Halo(acyl)rhenates result from the attack of the intermediate carbanion [R_fCF=CF][−] on the carbonyl ligand of Re(CO)₅Hal. The involvement of [R_fCF=CF][−] is demonstrated by their trapping with *t*-BuOH or CH-acid, which gives the protodehalogenated alkenes **I-H** and **II-H**, and suppresses the nucleophilic substitution reaction leading to **I-Fe**, **II-Fe** or **V-Cl**. Arguments against a radical/SET mechanism for the substitution reaction are also advanced.

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1. Introduction

Nucleophilic substitution with metal carbonyl anions is the most straightforward method of forming transition metal–carbon σ -bond(s). Only aliphatic nucleophilic substitution with metal carbonyl anions was studied in some detail, the operation of both S_N2 [1] and SET reaction mechanisms being demonstrated [2]. The substitution mechanisms at sp²-carbon atom in aromatic and vinylic systems were not studied with these anions prior to our publications [3,4]. Having embarked upon such an investigation, we have recently shown that an

unusual halophilic mechanism (Scheme 1) operates in nucleophilic aromatic substitution reaction of metal carbonyl anions with halopentafluorobenzenes [5,6]. The evidence of halogen–metal exchange (HME) on the first reaction step was obtained via trapping of [C₆F₅][−] carbanion intermediate with certain CH- or OH-acids: in the presence of *t*-BuOH or PhCH(Et)CN formation of nucleophilic substitution (NS) products was suppressed completely, and pentafluorobenzene and related products were formed (Scheme 2).

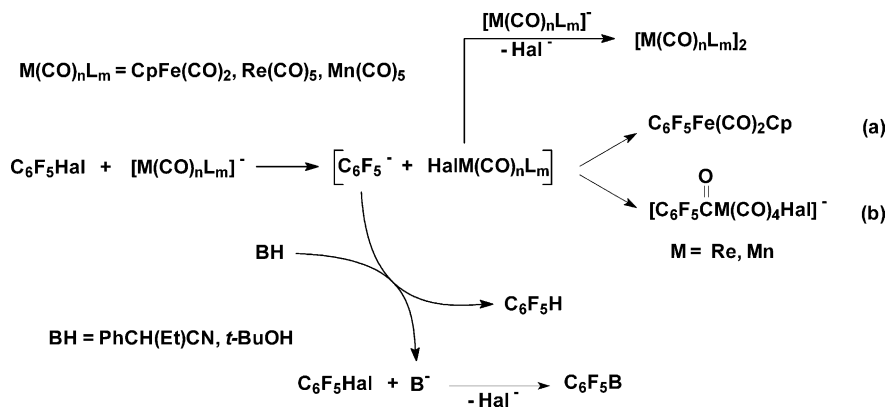
And though the reactions of [CpFe(CO)₂][−] anion and [M(CO)₅][−] (M = Re, Mn) anions with halopentafluor-



Scheme 1.

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obenzenes give absolutely different types of products, the σ -aryl iron complexes (a) and the manganese and rhenium halo(acyl)metallate adducts (b) respectively (Scheme 2), they all follow the same two-step halophilic mechanism. The intermediate metal carbonyl halide behaves as an ambident electrophile and can be attacked by the aryl carbanion not only at the metal center but also at the carbonyl ligand. In the latter case, the intermediates simply “collapse” preserving their identity in the halo(acyl)metallate products, this being probably the best proof of the halophilic mechanism.

Despite the notorious mechanistic diversity of nucleophilic vinylic substitution [7], the halophilic mechanism (Scheme 1) still lacks experimental confirmation. Substitution pathway via attack on halogen is accepted for acetylenic systems [8,9]. By contrast, in vinylic systems halophilic processes are usually associated with unwanted halophilic reduction of the alkenyl halides [10]. The only, yet notable exceptions are the substitution reactions with $[R_3Sn]^-$ [11] and $[R_2P]^-$ [12] anions in alkenyl bromides, for which the halophilic mechanism was suggested. However, no attempt was made to prove it experimentally. In this paper, we are going to show that the reactions of metal carbonyl anions with certain vinylic substrates follow this halophilic pathway.

The alkenyl halides suitable for our task should be good positive halogen atom donors (their hydrogen analogs should be strong CH-acids). At the same time the double bond in these substrates should be as little activated towards nucleophilic attack as possible, to avoid competition from the addition–elimination route. Polyfluorinated alkenyl halides without strong EWG groups in β -position to halogen, such as (*Z*)-1-chloro-(bromo)-1,2,4,4,4-pentafluoro-3,3-bis(trifluoromethyl)-1-butenes (I-Cl and I-Br) and bromotrifluoroethylene (II-Br), appeared to be the suitable models. Furthermore, our own preliminary results, when $[CpFe(CO)_2]^-$ anion substituted bromine in bromotrifluoroethylene [4], already suggested the halophilic substitution mechanism.

2. Results and discussion

2.1. Reaction of polyfluoroalkenyl halides with $[CpFe(CO)_2]K$ (FpK)

The reactions were carried out at -50°C in THF with a slight excess of alkenyl halide and even at that low temperature were almost instantaneous¹ as can be judged by the rapid color change from orange-red of the starting anion to deep cherry of metal carbonyl dimer, Fp_2 . Indeed, the Fp_2 dimer was the principal product in these reactions, its yield varying from 60 to 100% (Table 1). Surprisingly, no products corresponding to the alkenyl halide reduction (dehalogenation) were detected, which at present has no satisfactory explanation.

The σ -alkenyl iron complexes (I-Fe and II-Fe), which are the products of NS of halogen (Cl, Br), were formed in minor quantities. Their yields varied from trace with I-Cl to modest with alkenyl bromides (entries 1–3, Table 1, Scheme 3). Traces of iron carbonyl bromide $FpBr$ (entries 2 and 3) were also found among the reaction products.

Next we carried out the same reactions in the presence of proton donors, $PhCH(Et)CN$ (estimated $pK_a > 21$) and *t*-butyl alcohol ($pK_a \geq 20$), that had proved their efficiency previously in our study of halophilic reactions with halopentafluorobenzenes.² With the added proton donor no NS products with Fp^- anion were formed (entries 4,5 and 7), or, in case of II-Br and CH-acid, the yield of II-Fe decreased from 30 to 5% (entry 6). Instead the hydrodehalogenated alkenes (I-H and II-H) (in 28–

¹ At -90°C the reaction with $Z-(CF_3)_3CCF=CFCl$ still takes no more than several minutes.

² The choice of proton donors for anion trapping is of particular importance, as their pK_a should fit into relatively narrow pK_a interval between that of FpH ($pK_a = 19.2$ [13]) and parent alkenyl hydride (pK_a values of 20 ± 4 and 27 cited for $CF_2=CFH$ [14] may be considered as lower and upper limits for polyfluorinated alkenes without α -EWG substituents).

Table 1
The effect of proton donors on the product composition in the reaction of FpK with alkenylhalides Z-R_fCF=CFHal (**I-Cl**, **I-Br**, **II-Br**) (THF, -50 °C)

Entry	R _f	Hal	Initial concentration (mol l ⁻¹)		Proton donor (equivalents per mol of FpK)	Yield (%) ^a		Other products, yield (%) ^a	
			Alkenyl halide	FpK		R _f CF=CFFp	Fp ₂	R _f CF=CFH	FpBr, trace
1	(CF ₃) ₃ C	Cl	0.105	0.070	No additive	3	90	3	
2	(CF ₃) ₃ C	Br	0.065	0.060	No additive	22	60	4	FpBr, trace
3	F	Br	0.25	0.042	No additive	30	60	- ^b	FpBr, trace
4	(CF ₃) ₃ C	Cl	0.072	0.063	α-PhCH(Et)CN (1.5)	< 1 ^c	100	28	E-(CF ₃) ₃ CCF=CFC(Et)(Ph)CN (24)
5	(CF ₃) ₃ C	Br	0.059	0.068	α-PhCH(Et)CN (5)	< 1 ^c	82	50	FpBr (12)
6	F	Br	0.055	0.056	α-PhCH(Et)CN (6)	5	77	> 30 ^d	CFH=CFC(Et)(Ph)CN (9); CFHBrCF ₂ C(Et)(Ph)CN (6) ^e
7	F	Br	0.21	0.077	<i>t</i> -BuOH (15)	< 1 ^c	95	> 30 ^d	<i>t</i> -BuOCF ₂ CFHBr (140) ^f

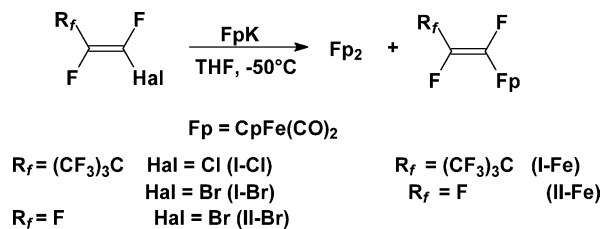
^a The product composition of the reaction mixtures was directly quantified by ¹⁹F- and ¹H-NMR spectroscopies, the resonances in the spectra of the reaction solutions being referenced to the individual products by comparison to the spectra of the isolated compounds. The yields were calculated from the relative integral intensity using internal standard (also see Section 4).
^b Not determined.

^c The corresponding signals were not observed in NMR spectrum (noise level).

^d Not determined quantitatively, as part of CF₂=CFH could be in the gas phase.

^e Pair of diastereoisomers.

^f *t*-BuONa catalyzed the addition of *t*-BuOH to CF₂=CFBr, present in excess, so the yield calculated relative to the amount of FpK may be more than 100%.



Scheme 3.

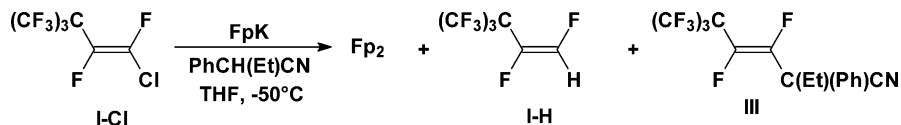
50% yield) were produced, together with such compounds as **III** and **IV** (Schemes 4 and 5). All these compounds were identified by their characteristic patterns in ¹H- and ¹⁹F-NMR spectra of reaction solutions (Table 2), and (**I-H**) also by chromat-mass spectrum.

2.2. Reaction of polyfluoroalkenyl halides with [Re(CO)₅]Na

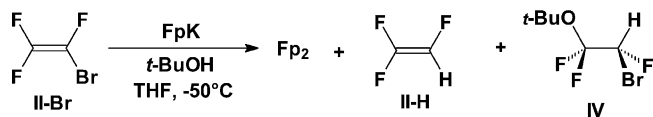
The reactions were carried out at room temperature with a slight excess of alkenyl halide. In marked contrast to the reactions with FpK, no σ-alkenyl rhenium complexes were detected in these reactions. Nucleophilic substitution of halogen with [Re(CO)₅]Na (Cl or Br, but not F) gave anionic halo(acyl)rhenates (Scheme 6), as was clearly demonstrated by IR, ¹³C- (Table 3) and ¹⁹F-NMR spectra (Table 2) of the reaction mixtures. Minor amounts of Re(CO)₅Br (5–10%) were also detected in the case of alkenyl bromides. Reactions with [Re(CO)₅]Na, which is much less nucleophilic than FpK [1], allowed us to compare the reactivity of alkenyl halides. The reaction of **I-Cl** took about 1 h to complete, while the reactions of both alkenyl bromides **I-Br** and **II-Br** were completed in less than 4 min (first NMR spectrum recorded) at room temperature.

Halo(acyl)rhenates **V-Cl**, **V-Br** and **VI** were isolated in the form of crystalline complexes with 18-crown-6 and dioxane. Addition of dioxane (5%, v/v) to the diethyl ether solution of halo(acyl)rhenate containing 18-crown-6 caused immediate crystallization of the complex. The complexes gave satisfactory element analysis and were characterized by solution IR spectra. All bands in metal C≡O frequencies region, and especially the lowest frequency band, corresponding to the ν_{as} of two equatorial CO groups (B₂ mode), were shifted to lower frequencies, compared to spectra of the same halo(acyl)rhenates without 18-crown-6 (Table 3). Surprisingly, ν_(C=O) of acyl group, which is usually supposed to be the coordination site of the cation in metal acyl anions, exhibited small or no shift in the presence of 18-crown-6. This raises the question about the site and mode of coordination of sodium in halo(acyl)rhenates; however, it lies beyond the scope of the present work.

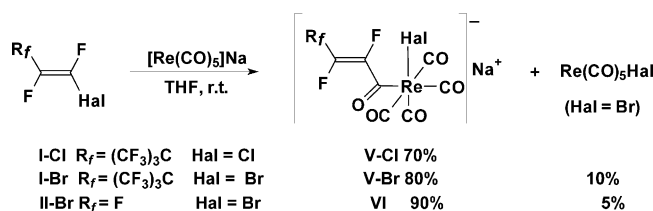
The structure of halo(acyl)rhenate salt **VI** was confirmed by single crystal X-ray diffraction analysis of its



Scheme 4.



Scheme 5.



Scheme 6.

complex with 18-crown-6 containing one molecule of dioxane. The structure of the complex is shown in Fig. 1. The acyl anion VI has an expected geometry of a distorted octahedron, with acyl group occupying a *cis*-

position to bromine. The *cis*-geometry has always been assumed for the previously described halo(acyl)rhenate anions $[\text{R}(\text{CO})\text{Re}(\text{CO})_4\text{Hal}]^-$ [15,16], though they were obtained only as intermediates in solutions and were never isolated. The same geometry with *cis*-arrangement of non-carbonyl ligands is found in various $\text{Re}(\text{CO})_4\text{X}_2$ complexes, a large number of them structurally characterized by now, including several acyl anions [17]. The bond lengths and angles in VI are in the range expected from the previous data. No direct contacts between the cationic and anionic parts of the complex (VI-18-crown-6-dioxane) are observed, which may be described as a complex of a “naked” acyl anion. The sodium cations are bound in a polymeric chain with bridging dioxane molecules, which together with six donor oxygen atoms of the crown ether form around sodium a completely saturated coordination sphere of eight donor centers (Fig. 2).

The effect of proton donors on the formation halo(acyl)rhenate salts (V-Cl, V-Br, VI) was examined

Table 2

^{19}F -NMR spectral data (THF, 23 °C)

Compound X	δ_{F} , ppm ($^n J_{\text{F-H}}$, Hz)			$^n J_{\text{F-F}}$, Hz			
	F ¹	F ²	CF ₃	³ J _{F¹-F²}	⁴ J _{CF₃-F¹}	⁵ J _{CF₃-F²}	
Formula A							
I-Cl	Cl	-149.23 d m	-99.80 d m	-62.44 dd	136	12.0	16.2
I-Br	Br	-143.02 d m	-97.87 d m	-62.44 dd	144	12.2	15.5
I-Fe	Fe(CO) ₂ Cp	-149.5 d m	-75.6 d m	-62.51 dd	131	13.6	18.0
I-H	H	-170.06 dd m (³ J _{H-F} = 9)	-154.51 dd m (² J _{H-F} = 72)	-62.63 dd	133	11.9	15.5
III	C(Et)(Ph)CN	-150.4 d m	-131.5 d m	-62.04 dd	136	12.2	18.0
V-Cl	[CORe(CO) ₄ Cl]Na	-166.22 d m	-129.41 d m	-62.07 dd	134	12.6	17.6
V-Br	[CORe(CO) ₄ Br]Na	-166.09 d m	-128.62 d m	-62.00 dd	135	12.5	17.0
		F ¹	F ²	F ³	³ J _{F¹-F²}	² J _{F¹-F³}	³ J _{F²-F³}
Formula B							
II-Br	Br	-116.21 dd	-144.15 dd	-96.08 dd	123	73	53
II-Fe	Fe(CO) ₂ Cp	-130.5 dd	-136.8 dd	-84.4 dd	115	102	41
II-H	H	-126.2 ddd (³ J _{H-F} = 4.5)	-204.2 ddd (² J _{H-F} = 71)	-100.5 ddd (³ J _{H-F} = 13)	118	86	33
VI	[CORe(CO) ₄ Br]Na	-106.5 dd	-161.0 dd	-101.5 dd	108.6	24.1	33.5
VIII	CHPh ₂	-107.72 d	-130.93 d	– (Y = Br)	141	–	–
Formula C							
IV	<i>t</i> -BuO	-76.66 ddd (³ J _{H-F} = 3)	-155.30 d t (² J _{H-F} = 48)	-77.82 ddd (³ J _{H-F} = 6)	14	141	15
IX	CHPh ₂	-102.68 dd	-150.13 d t (² J _{H-F} = 46)	-107.43 dt	~ 18	263	~ 18

Table 3
IR and ^{13}C -NMR spectra of rhenium carbonyl complexes (THF, r.t.)

Compound	IR spectrum ^a , ν , cm^{-1} (ϵ , $\times 10^{-3}$)		^{13}C -NMR spectrum, δ_{C} , ppm ($J_{\text{C-F}}$, Hz)	
	$\nu_{\text{C-O}}$	$\nu_{\text{C=O}}$	C=O	C=O
$[\text{Re}(\text{CO})_5]\text{Na}$		1840s, 1875vs, 1918s		219.43 br
$\text{Re}_2(\text{CO})_{10}$		1977 (3.6), 2017 (18), 2076 (5.0)		192.5 br (4C), 183.2 br (1C)
$\text{Re}(\text{CO})_5\text{Cl}$		1988 (1.8), 2047 (6.7), 2160 (0.08)		–
$\text{Re}(\text{CO})_5\text{Br}$		1991 (2.2), 2047 (8), 2158 (0.2)		–
$[\text{Z}-(\text{CF}_3)_3\text{CCF}=\text{CF}(\text{CO})\text{Re}(\text{CO})_4\text{Cl}]\text{Na}$ (V-Cl)	1592 m	1936 s, 1996 vs, 2101 m	258.47 d ($J=42$)	190.66 s (1C), 190.13 t (2C, $J \approx 3$), 187.48 d (1C, $J \approx 5$)
V-Cl ·18-crown-6	1592 m	1920 s, 1991 vs, 2095 m	–	–
$[\text{Z}-(\text{CF}_3)_3\text{CCF}=\text{CF}(\text{CO})\text{Re}(\text{CO})_4\text{Br}]\text{Na}$ (V-Br)	1593 m	1936 s, 1997 vs, 2100 m	^b	189.52 s, 189.45 d ($J \approx 3.5$) (3C), 187.09 d (1C, $J \approx 6$)
V-Br ·18-crown-6	1590 m	1921 s, 1992 vs, 2095 m	–	–
$[\text{CF}_2=\text{CF}(\text{CO})\text{Re}(\text{CO})_4\text{Cl}]\text{Na}^{\text{c}}$ (VI)	1556 m	1933 s, 1993 vs, 2097 m	258.77 d ($J=47$)	190.03 s (1C), 189.96 d (2C, $J=4.5$), 187.98 d (1C, $J=8.5$)
VI ·18-crown-6 ^d	1560 m	1918 s, 1977 sh, 1992 vs, 2093 m	–	–
$[t\text{-BuO}(\text{CO})\text{Re}(\text{CO})_4\text{Cl}]\text{Na}$ (VII)	1605 br, m (0.5)	1930 (3), 1986 (4), 2094 (0.4)	207.90 s	191.77 s, 191.68 s (3C), 188.20 s (1C)

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

^b Out of the recorded spectral range.

^c $\nu_{\text{C-C}} = 1722$ cm^{-1} (s).

^d $\nu_{\text{C-C}} = 1727$ cm^{-1} (s).

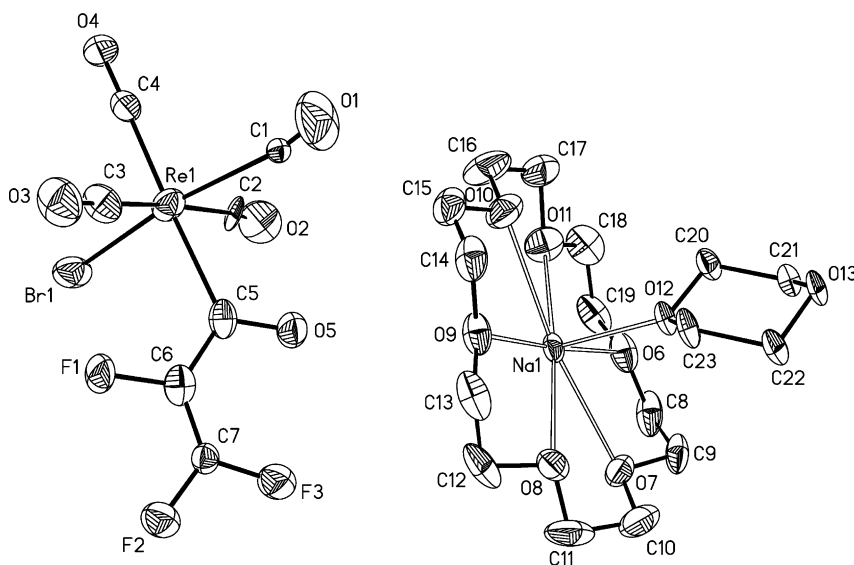


Fig. 1. The general view of the compound **VI**·18-crown-6-dioxane (40% probability ellipsoids); the positions of disordered carbonyl group and Br atom with occupancies 0.4 are not shown. Selected bond distances (\AA) and angles ($^\circ$): $\text{Re}(1)\text{--C}(5)$, 2.231(9); $\text{Re}(1)\text{--C}(4)$, 1.984(9); $\text{Re}(1)\text{--C}(3)$, 1.968(9); $\text{Re}(1)\text{--Br}(1)$, 2.500(2); $\text{C}(5)\text{--Re}(1)\text{--C}(3)$, 92.3(3); $\text{C}(5)\text{--Re}(1)\text{--C}(4)$, 175.1(3); $\text{C}(5)\text{--Re}(1)\text{--Br}(1)$, 89.0(2).

in the reaction of $[\text{Re}(\text{CO})_5]\text{Na}$ with **I-Cl**. In the presence of *t*-butyl alcohol (10 equivalents), only 6% **V-Cl** was formed and **I-H** (30%) was the only other fluoroalkene-derived product (Scheme 7). Characteristic bands of a different halo(acyl)rhenate anion (corresponding to $\approx 30\%$ yield) were also observed in the IR spectrum of the reaction mixture. We suppose that these bands belong to *cis*- $[t\text{-BuO}(\text{CO})\text{Re}(\text{CO})_4\text{Cl}]\text{Na}$ (**VII**). And indeed they coincided with the IR spectrum of halo(acyl)rhenate **VII** obtained independently from *t*-BuONa and $\text{Re}(\text{CO})_5\text{Cl}$ (Table 3).

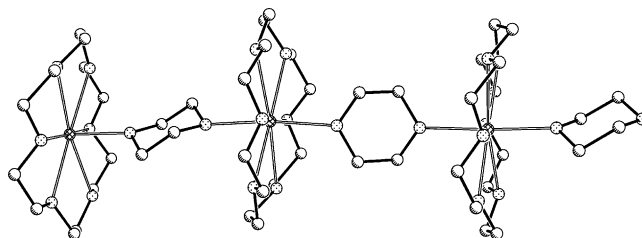
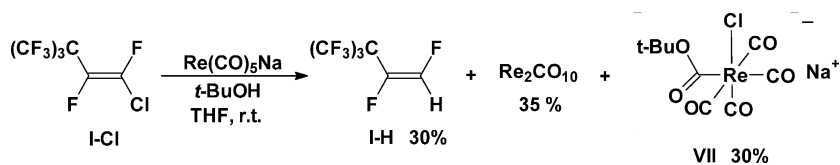
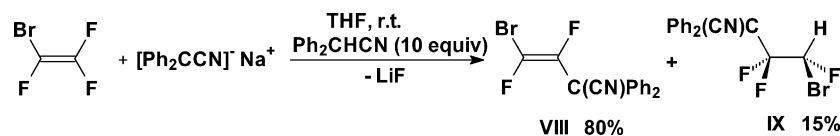


Fig. 2. View of the polymeric chain formed by Na cations and dioxane molecules in the crystal structure of **VI**·18-crown-6-dioxane.



Scheme 7.



Scheme 8.

In the reaction of **I-Cl** with $[\text{Re}(\text{CO})_5]\text{Na}$, besides halo(acyl)rhenate **V-Cl** up to 25% $\text{Re}_2(\text{CO})_{10}$ is formed. Interestingly, carrying out this reaction in the presence of tertiary phosphine PET_3 (2.5 equivalents) allows one to avoid the formation of $\text{Re}_2(\text{CO})_{10}$, leading to almost quantitative yield of **V-Cl** (90%).

2.3. Reaction of bromotrifluoroethylene (**II-Br**) with $[\text{Ph}_2\text{CCN}]^-$ carbanion

To demonstrate that the choice between the halophilic and “normal” (addition–elimination) substitution mechanisms also depends on the nucleophile, we have carried out the reaction of $\text{CF}_2=\text{CFBr}$ with a soft carbanion nucleophile (Scheme 8). In marked contrast to its reactions with metal carbonyl anions (Schemes 3 and 6), vinylic fluorine (*trans* to bromine) was substituted in a highly selective manner with the sodium salt of α,α' -diphenylacetonitrile. The reaction was carried out in the presence of a large excess (10 equivalents) of anion trap, Ph_2CHCN ($\text{p}K_a = 18$), to protonate the trifluorovinyl carbanion should it be formed as intermediate. Yet $\text{CF}_2=\text{CFH}$ was not detected in the reaction mixture by ^{19}F -NMR. In addition to the signals of nucleophilic substitution product **VIII** (80% yield, isolated in 70% yield), a characteristic pattern corresponding to RCF_2CFHX adduct (15% yield according to the integral intensity) was also observed in ^{19}F -NMR spectrum. It seems reasonable to suppose that it is **IX**—the product of nucleophilic addition of Ph_2CHCN to $\text{CF}_2=\text{CFBr}$.

2.4. The halophilic mechanism: supporting arguments

All of the NS reactions discussed in this paper, both with iron and rhenium carbonylates, have one very important feature in common: NS is suppressed by proton donors. Thus, the intermediacy of alkenyl carbanion species is clearly indicated. Their protonation, or we may call it “trapping”, by *t*-BuOH or CH-acid gives the protodehalogenated alkenes **I-H** or **II-H**, while the reaction of the conjugated base of the proton

donor, $[\text{t-BuO}]^-$ or $[\text{PhC}(\text{Et})\text{CN}]^-$, with the starting alkenyl halide produces such compounds as **III** and **IV** (Scheme 9). Interestingly, the fate of $[\text{t-BuO}]^-$ is different in the case of $[\text{Re}(\text{CO})_5]\text{Na}$. The alkoxide $[\text{t-BuO}]^-$ is trapped by $\text{Re}(\text{CO})_5\text{Cl}$ to give halo(acyl)rhenate **VII**, indicating that $\text{Re}(\text{CO})_5\text{Cl}$ is much more electrophilic than FpHal , or the starting alkenyl halide.³

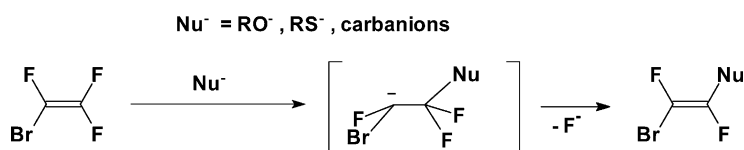
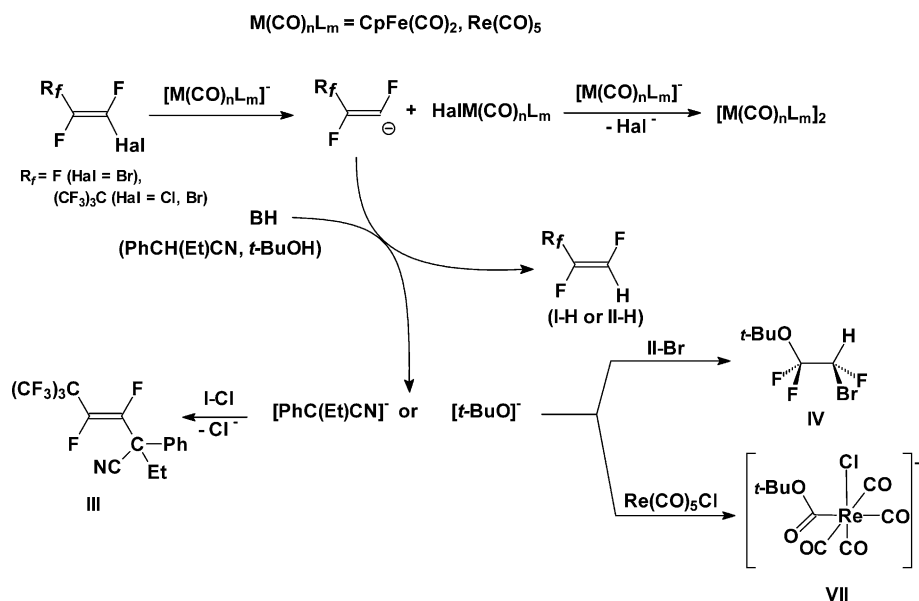
It is worth noting that halo(acyl)rhenates **V-Cl**, **V-Br**, **VI** and σ -alkenyl iron complexes **I-Fe** and **II-Fe** are not protodemetalated with alcohols and could not be the source of **I-H** or **II-H** under our reaction conditions.

Reaction with $\text{CF}_2=\text{CFBr}$ provides us with another argument in favor of the halophilic (but also SET) reaction mechanism, the so-called intramolecular vicinal “element effect”. Only bromine is substituted by both carbonylates (Schemes 3 and 6). If the reaction followed the addition–elimination mechanism⁴ normal for vinylic NS (Scheme 10) the fluorine from CF_2 group would be substituted, as it happens in the reaction with $[\text{Ph}_2\text{CCN}]^-$ carbanion (Scheme 8) or other common nucleophiles (RS^- , RO^- , amines) [20]. The intermolecular “element effect” observed in the reaction of $[\text{Re}(\text{CO})_5]\text{Na}$ with alkenyl halides (**I-Br** more active than **I-Cl**, see Section 2.2) also shows that C–Hal bond breaking takes place on the rate-limiting stage of reaction and is not consistent with the addition–elimination mechanism [7,10,20], but agrees well with the proposed HME pathway (Scheme 1).

Arguments against the SET pathway will be discussed in detail later, in connection with the halo(acyl)rhenate complexes. Here, we will only point to the complete retention of *Z/E* configuration of the starting alkenyl halide (**I-Cl**, **I-Br**) both in NS and reduction (**I-H**)

³ We are not going to discuss it here, but as it was mentioned previously [6] the halophilic mechanism does not necessarily involve free carbanion and metal carbonyl halide intermediates. They may be bound together in an at-complex $[\text{R-Hal-M}(\text{CO})_n]^-$ [18,9], which transforms to NS products via intramolecular rearrangement. In the protonation reaction, such at-complexes may give the same products, **I-H** and **II-H**, as the free carbanions [19].

⁴ With the rate-limiting addition step.



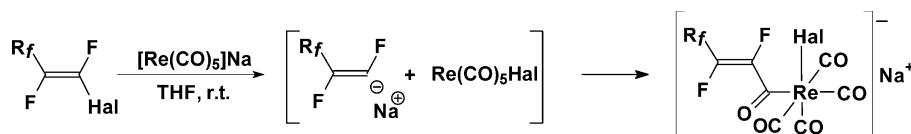
products. When the reaction of the same substrates **I-Cl** and **I-Br** with FpK was carried out under “electrochemical activation” conditions, and the cathode reduction of the alkenyl halide produced the corresponding radicals, both *Z* and *E* isomers of the product **I-Fe** were formed [21].

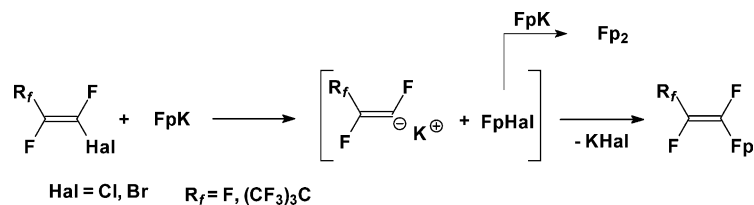
However, the halophilic mechanism reveals itself most vividly in the reactions with $[\text{Re}(\text{CO})_5]\text{Na}$, when halo(acyl)rhenates **V-Cl**, **V-Br** and **VI** are formed. In contrast to σ -vinyl complexes, or other possible products of reactions that may follow the HME step, halo(acyl)rhenates are formed by a simple recombination reaction (Scheme 11) and contain structurally intact fragments of alkenyl carbanion and $\text{Re}(\text{CO})_5\text{Hal}$. This fact allows one to regard formation of halo(acyl)rhenate as an “auto-trapping” of both HME intermediates and the most impressive proof of the halophilic character of these reactions.

Obviously, halo(acyl)rhenates cannot be formed by addition–elimination reaction (Scheme 10), which

would have given “normal” nucleophilic substitution products, the σ -alkenyl metal complexes in case of carbonylates. One may argue that the initially formed σ -alkenyl $\text{Re}(\text{CO})_5$ complex could undergo migratory insertion of $\text{C}\equiv\text{O}$ ligand induced by NaHal giving halo(acyl)rhenate products. This alternative can be easily rejected, since σ -alkenyl $\text{M}(\text{CO})_5$ complexes ($\text{M} = \text{Re}, \text{Mn}$) are known to be stable under our reaction conditions [22,23] and, more importantly, NaCl or NaBr are not soluble in THF. Moreover, lithium bromide (LiBr) failed to induce Me group migration in $\text{Re}(\text{CO})_5\text{Me}$ [15], and this migration would be much more facile than the migration of polyfluoroalkenyl EWG group.

On the other hand, the nucleophilic addition to CO ligand is very well documented for various classes of metal carbonyls, including metal carbonyl halides, in which the sight of nucleophilic attack is often not the metal atom but the CO ligand. The addition of MeLi to rhenium carbonyl halides $\text{Re}(\text{CO})_5\text{Hal}$ and





Scheme 12.

Re(CO)₄PPh₃Br giving halo(acyl)rhenate complexes has been reported [15,16]. If halo(acyl)rhenates **V-Cl**, **V-Br** and **VI** are formed through the same carbanion addition pathway, and we see no alternative, the alkenyl carbanion and Re(CO)₅Hal intermediates have to be generated on the preceding reaction stage, and this first stage has to be HME (Scheme 11).

An alternative of a radical or a radical chain mechanism for halo(acyl)rhenates formation does not seem feasible at all. While the addition to CO group of a metal carbonyl is typical for nucleophilic agents, it would be quite an unusual reaction for the free radicals. A much more likely reaction pathway for alkenyl radicals would be the hydrogen atom abstraction from the solvent, THF, giving **I-H** or **II-H**. Yet only small amounts of **I-H** or **II-H** are formed in the absence of proton donors. Furthermore, almost quantitative formation of halo(acyl)rhenate **V-Cl** in the presence of PET₃ shows that there are no rhenium-centered radical intermediates in this reaction. The CO ligand substitution in metal carbonyl radicals with phosphines is an extremely fast reaction ($k_2 \sim 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$) [24], which makes it a sort of mechanistic probe for such radical intermediates [25].

2.5. Comments on the reactions with FpK

One cannot but admit that in the case of FpK the evidence available in support of the halophilic mechanism is not as conclusive as in the reactions with [Re(CO)₅]Na. While the trapping of alkenyl carbanions leaves little doubt as to their involvement in the NS reaction, we have no direct proof for the other HME intermediate—the FpHal. The presence of FpBr in the reaction mixtures (entries 2,3 and 5, Table 1) certainly is a point in favor of the proposed scheme, but cannot serve as its final proof. Besides, it is not clear why FpCl is not found among the reaction products, neither with alkenyl chloride **I-Cl** nor with the aryl chlorides studied earlier [5,6]. Nevertheless, the halophilic mechanism remains the best possible interpretation for the observed FpK chemistry (Scheme 12).

The relatively low yield of σ -alkenyl Fp complexes **I-Fe** and **II-Fe** in these reactions poses another problem, especially in comparison to much higher yields of halo(acyl)rhenates **V-Cl**, **V-Br** and **VI**. Reasonably, the presence of a donor Cp ligand makes FpHal less reactive

towards carbanions than Re(CO)₅Hal.⁵ On the other hand, the rate constants for the reactions of Re(CO)₅Hal with [Re(CO)₅][−] and FpHal with [Fp][−] have been measured and are of the same order of magnitude [26]. As a result, a large part of FpHal will be consumed in a very fast [26,27] competing reaction with FpK giving Fp₂ (Scheme 12).

Alkenyl bromides **I-Br** and **II-Br** give higher yields of NS products in the reaction with FpK than the alkenyl chloride **I-Cl** (entries 1–3, Table 1). The simplest though not necessarily the only explanation is that a higher steady-state concentration of the HME intermediates is generated in the reaction with the more reactive substrates (**I-Br** and **II-Br**), which increases the production rate of NS product quadratically ($\sim k_{\text{NS}}[\text{Vin}^-][\text{FpHal}]$), while the increase in Fp₂ production rate is only first order in FpHal ($\sim k_{\text{Fp}_2}[\text{FpK}][\text{FpHal}]$).

3. Conclusions

Attack on halogen has turned out to be the most favorable pathway for the reactions of metal carbonyl anions, FpK and [Re(CO)₅]Na, with polyfluorinated alkenyl halides **I-Cl**, **I-Br** and **II-Br**. The interaction between metal carbonyl halide and alkenyl carbanion intermediates on the second reaction stage gives two types of substitution products, different for iron and rhenium. “Ordinary” σ -alkenyl complexes are formed with the iron carbonylate (Scheme 12); the rhenium carbonyl halides reveal their ambident character and are attacked by the alkenyl carbanion at the CO ligand leading to halo(σ -acyl)rhenate anions (Scheme 11). This halophilic pathway of vinylic substitution may indeed be of rare occurrence and require a super-halophilic reagent such as metal carbonyl anion. Even soft carbanions ([Ph₂CN][−]), which are considered especially reactive halophiles [28], react with **II-Br** via “common” addition–elimination mechanism (Scheme 10).

⁵ The same may be presupposed from the higher $\nu_{\text{C=O}}$ frequencies observed for Re(CO)₅Hal (Table 3) than for FpHal ($\sim 2005, 2045 \text{ cm}^{-1}$).

4. Experimental

Preparation of metal carbonyl anion salts and their reactions with alkenyl halides were carried out in “all-fused” glassware using vacuum-line techniques. Less air-sensitive materials, such as the reaction products, were handled under argon atmosphere, when necessary. THF, diethyl ether and dioxane were vacuum-transferred from sodium benzophenone ketyl.

Bromotrifluoroethylene was a gift from Dr. U.V. Zeifman (INEOS, RAS, Moscow). The syntheses of **I-Cl** and **I-Br** are described elsewhere [29]. Volatile reagents and NMR standards were dried over the appropriate drying agent (**I-Cl**, **I-Br**, **II-Br**, PEt_3 , $\text{C}_6\text{H}_5\text{CF}_3$, $\text{C}_6\text{H}_5\text{F}$ —over sodium mirror, *t*-BuOH—over *t*-BuOK) and deoxygenated by several freeze-pump-thaw cycles. Small portions required for a single experiment were vacuum-transferred into thin-walled glass spheres, which were sealed off. Portions of alkene **II-Br**, a gas at room temperature (r.t.) (b.p.: 3 °C), were prepared in a similar manner, except that they were measured out by vapor pressure (20–300 Torr), diluted with THF and kept frozen in liquid nitrogen. FpK was obtained quantitatively (95–98%) by reductive cleavage of the dimer Fp_2 with excess of $\text{NaK}_{2.8}$ alloy (0.10–0.15 ml per 1 mmol of dimer) [30]. $[\text{Re}(\text{CO})_5]\text{Na}$ was prepared by the reduction of $\text{Re}_2(\text{CO})_{10}$ with 0.5% NaHg (30–50% excess) and purified by the low-temperature crystallization from THF [31].

NMR spectroscopy (^1H and ^{19}F) was used as a primary tool for the analysis of reaction solutions, allowing us to determine the yields of all the reaction products, including volatile or unstable compounds. ^1H -NMR (400 MHz), ^{19}F -NMR (376.3 MHz) and ^{13}C -NMR (100.57 MHz) spectra were obtained on a Varian VXR-400 spectrometer at r.t. $\text{C}_6\text{H}_5\text{F}$ (δ_{F} –112.75 ppm) and PhCF_3 (δ_{F} –61.96 ppm) were used as internal standards both for fluorine chemical shift reference and determination of the product yields, which were calculated from the relative integral intensity of the signals of the products and the signal of internal standard. The signals in the spectra of reaction solutions were referenced to the individual components by comparison to the spectra of the isolated compounds or with the literature data. Compounds **I-Fe**, **I-Re** [32], **II-Fe** [23] and **II-H** have been described previously and were identified spectroscopically without isolation.

IR spectra of reaction mixtures and isolated products were recorded using UR-20 spectrophotometer. Mass spectra were recorded on an MS-890 spectrometer, with electron impact ionization, 70 eV ionizing energy, the direct inlet method, with a source temperature of 150 °C.

4.1. Reaction of alkenyl halides with FpK

In a typical experiment, ~0.15 mmol of alkenyl halide was mixed (breaking the thin-walled glass sphere) with ~2 ml of FpK solution (0.06 mol l^{-1}) pre-cooled in a cold bath (–50 °C). Immediately the solution became darker, turning from orange-red of FpK to dark cherry of Fp_2 . After 10–15 min the reaction mixture was allowed to reach r.t. and part of it was filtered through Celite into NMR sample tube.

To isolate the volatile product **I-H** the preparative experiment was carried out in diglyme instead of THF. FpK was obtained from 197 mg Fp_2 and 0.15 ml $\text{NaK}_{2.8}$ in 10 ml THF, which was replaced with 1.5 ml diglyme, and the $\text{PhCH}(\text{Et})\text{CN}$ “anion trap” (295 mg) was added. The reaction mixture was cooled to –50 °C and 290 mg of alkene **I-Cl** was added. After 15 min at –50 °C the reaction mixture was allowed to reach r.t. The volatile fraction (135 mg) was evaporated at r.t. and collected in a cold trap. According to NMR and chromatography spectra, it contained 35% of the starting **I-Cl**, 55% **I-H**, small amounts of diglyme and THF. *E*-($^?F_3$)₃CCF=CFH (**I-H**): ^1H -NMR (acetone- d_6 , δ , ppm): 8.188 dd ($J_{\text{H-F}} = 71.6, 9.1 \text{ Hz}$). MS, m/z : 283 $[\text{M}+\text{H}]^+$ (22%), 282 M^+ (87%), 263 $[\text{M}-\text{F}]^+$ (60%), 243 $[\text{M}-\text{HF}, -\text{F}]^+$ (19%), 213 (67%), 194 (86%), 181 (36%), 175 (94%). The rest of the reaction mixture was evaporated in vacuo at 80 °C, removing diglyme and the major part of $\text{PhCH}(\text{Et})\text{CN}$ (part of **III** could have been lost at this stage), and separated by column chromatography on silica gel (60/200). The first fraction eluted with hexane– Et_2O (30:1) contained **III** (26 mg), which was purified by plate chromatography on Silufol UV-254. *E*-($^?F_3$)₃CCF=CFC(C_6H_5)(C_2H_5)CN (**III**): ^1H -NMR (acetone- d_6 , δ , ppm): 7.45–7.60 m (C_6H_5 , 5H), 2.53 m (CH_2 , 1H), 2.35 m (CH_2 , 1H), 1.091 t (CH_3 , $^3J_{\text{H-H}} = 7.2 \text{ Hz}$, 3H). MS, m/z : 425 M^+ (65%), 397 $[\text{M}-\text{C}_2\text{H}_4]^+$ (92%), 356 (39%), 328 (100%), 177 (52%).

4.2. Reaction of alkenyl halides with $[\text{Re}(\text{CO})_5]\text{Na}$

Typically ~0.7 ml of $[\text{Re}(\text{CO})_5]\text{Na}$ solution (~0.3 mol l^{-1}) was mixed with all additives (if necessary) and then with ~0.25 mmol of alkenyl halide at r.t. The reaction solution was immediately decanted into NMR sample, which was sealed off, and the reaction progress was monitored by ^{19}F -NMR spectroscopy at r.t. Hallo(acyl)rhenate *cis*-[Z-(CF_3)₃CCF=CF(CO)Re(CO)₄Cl] Na (**V-Cl**) was isolated from the reaction mixture obtained from 100 mg **I-Cl** and $[\text{Re}(\text{CO})_5]\text{Na}$ (1.25 ml of 0.34 mol l^{-1} solution). The yellow solution was filtered through Celite, THF was removed in vacuo, and the residue was dissolved in 3 ml Et_2O . The addition of an excess of 18-crown-6 (~150 mg) and 0.2 ml dioxane resulted in an immediate precipitation of yellow crystals of the complex **V-Cl**·18-crown-6·2 dioxane (220

mg). Calc. for $C_{31}H_{40}ClF_{11}NaO_{15}Re$: C, 33.66; H, 3.64. Found: C, 33.52; H, 3.54%. The complex itself is highly soluble in diethyl ether, but its solubility drops down sharply in the presence of dioxane. The crystalline complex of *cis*-[*Z*-(CF_3)₃CCF=CF(CO)Re(CO)₄Br]Na (**V-Br**) with 18-crown-6 and two molecules of dioxane (185 mg) was prepared similarly from **I-Br** (126 mg) and [Re(CO)₅]Na (1 ml of 0.34 mol l⁻¹ solution). Calc. for $C_{31}H_{40}BrF_{11}NaO_{15}Re$: C, 32.36; H, 3.50; F, 18.16. Found: C, 32.10; H, 3.66; F, 17.99%. Similarly, from **II-Br** (200 mg) and 0.85 mmol [Re(CO)₅]Na (not crystallized; prepared from 326 mg Re₂(CO)₁₀ and 0.8 ml 0.5% NaHg in 8 ml THF; estimated yield ≈ 85% [30,31]) was obtained the orange-yellow complex (**VI**) *cis*-[CF₂=CF(CO)Re(CO)₄Br]Na·18-crown-6·dioxane (450 mg). Calc. for $C_{23}H_{32}BrF_3NaO_{13}Re$: C, 32.03; H, 3.74; Br, 9.26; F, 6.61. Found: C, 32.40; H, 3.82; Br, 10.08; F, 5.93%. Crystalline complexes of halo(acyl)rhenates with dioxane and 18-crown-6 are thermally stable at r.t. and can be handled in the open air for short periods of time (hours), but are oxidized being exposed to air for several weeks. Crystals of **VI**·18-crown-6·dioxane suitable for X-ray diffraction were grown by solvent diffusion in Et₂O–dioxane system.

cis-[*t*-BuO(CO)Re(CO)₄Cl]Na (**VII**) was obtained with the purpose of identifying its bands in the IR spectra of reaction solutions. The solution of *t*-BuONa (25 mg) in 2 ml THF was added to Re(CO)₅Cl (95 mg) dissolved in 5 ml THF. The product was characterized in solution by IR and ¹³C-NMR spectra.

Similarly for the purpose of identification *t*-BuOCF₂CFHBr (**IV**) was obtained by the reaction of **II-Br** (0.74 mmol in 0.15 ml THF) with an excess of *t*-BuOH in the presence of *t*-BuOK (12.7 mg) in THF (2 ml) at r.t. and characterized by ¹⁹F-NMR.

4.3. Reaction of CF₂=CFBr with [Ph₂CCN]⁻ carbanion

4.3.1. Reaction of **II-Br** with [Ph₂CCN]Na: the isolation of Ph₂C(CN)CF=CFBr (**VIII**)

Ph₂CHCN (112 mg) dissolved in 2 ml THF was treated with excess of NaH. When vigorous liberation of gas ceased the bright yellow solution was filtered and **II-Br** (0.8 mmol) was added by vacuum transfer. After 30 min at r.t. the solution became colorless and a crimson colored gel formed. Reaction mixture was placed on a column with silica gel and eluted with petroleum ether–CH₂Cl₂ mixture, gradually increasing the solvent ratio from 5:1 to 1:2. The fraction corresponding to the first colorless band was collected yielding 135 mg Ph₂C(CN)CF=CFBr (**VIII**). Calc. for $C_{16}H_{10}BrF_2N$: C, 57.51; H, 3.02; N, 4.19. Found: C, 57.54; H, 3.08; N, 4.47%. MS, *m/z* (relative to 79Br): 333 [M]⁺ (1%), 254 [M–Br]⁺ (55%), 234 [M–Br, –F]⁺ (40%), 177 [M–Br, –C₆H₅]⁺ (40%), 176 [M–Br, –C₆H₆]⁺

(100%), 165 [C₁₃H₉]⁺ (20%), 151 (20%), 77 [C₆H₅]⁺ (25%).

4.4. X-ray crystallographic data

The crystal of complex **VI** with 18-crown-6 and dioxane (C₂₃H₃₂BrF₃NaO₁₃Re, *M* = 862.59) is monoclinic, space group *P*2₁/*n*, at *T* = 110 K; *a* = 12.5403(18) Å, *b* = 21.308(3) Å, *c* = 13.938(2) Å, β = 112.661(4)°, *V* = 3436.8(9) Å³, *Z* = 4, *D*_{calc} = 1.667 Mg m⁻³, *F*(0 0 0) = 1688, μ = 4.781 mm⁻¹.

Total of 26 167 reflections were measured on a Bruker SMART CCD 1000 diffractometer (λ(Mo–K_α), graphite monochromator, ω-scans, θ_{max} = 27°) and corrected for Lorentz and polarization effects and for absorption [33]. The structure was determined by direct methods and refined by full-matrix least-squares technique with anisotropic thermal parameters for non-hydrogen atoms. The positions of one carbonyl group and Br atom are statistically disordered with occupancies 0.6:0.4. The position of carbonyl group with occupancy 0.4 was refined isotropically. The hydrogen atoms were placed in calculated positions and refined in riding model with fixed thermal parameters. The final divergence factors were *R*₁ = 0.0675 for 4515 independent reflections with *I* > 2σ(*I*) and *wR*₂ = 0.1863 for all 7421 independent reflections. All calculations were carried out by use of the SHELXTL PLUS (PC Version 5.0) program [34].

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 194840 for **VI**·18-crown-6·dioxane. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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