

Halophilic reactions of pentafluorohalobenzenes with transition-metal carbonyl anions

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Abstract

In the present work we widen the scope of the halophilic mechanism of nucleophilic aromatic substitution, which we found earlier for the reaction of pentafluorochlorobenzene with $[\text{CpFe}(\text{CO})_2]^-$ anion, to reactions of pentafluorohalobenzenes ($\text{Hal} = \text{Cl}, \text{Br}, \text{I}$) with various metal carbonyl anions $[\text{Re}(\text{CO})_5]^-$, $[\text{Mn}(\text{CO})_5]^-$ and $[\text{CpFe}(\text{CO})_2]^-$. Nucleophilic aromatic substitution with the $[\text{CpFe}(\text{CO})_2]^-$ anion yields $\text{C}_6\text{F}_5\text{Fe}(\text{CO})_2\text{Cp}$, while with $[\text{Re}(\text{CO})_5]^-$ and $[\text{Mn}(\text{CO})_5]^-$ anions the halo(acyl)metallates $\text{cis}-[\text{C}_6\text{F}_5(\text{CO})\text{M}(\text{CO})_4\text{Hal}]\text{Na}$ ($\text{M} = \text{Mn}, \text{Re}$) are obtained. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Reaction mechanisms; Carbonylmetallates; Polyfluorinated aryl halides; Halogen–metal exchange; Nucleophilic aromatic substitution; Metal acyl anions

1. Introduction

Nucleophilic aromatic substitution in perfluoroarenes with transition-metal carbonyl anions is a convenient method for the syntheses of σ -aryl transition-metal complexes [1–3]. We [4] and other authors [1,5–7] have found that a heavy halogen ($\text{Hal} = \text{Cl}, \text{Br}, \text{I}$) is preferentially substituted in polyfluorinated aryl halides, which are also much more reactive with carbonylmetallates than perfluorinated analogues. In several cases this fact allowed one to obtain nucleophilic substitution (NS) products, which could not be prepared from the corresponding perfluoroarene [5,8], though the yield of NS products is often lowered by various redox side reactions [6,7,9]. In spite of all facts mentioned, these reactions were long considered in the framework of the classic addition–elimination mechanism. Recently we have shown that the reaction of pentafluorochlorobenzene with the cyclopentadienyldicarbonylferrate anion ($[\text{CpFe}(\text{CO})_2]^-$) actually involves halogen–metal exchange (HME) as the key step (Scheme 1) [10]. Evidence of a halophilic mechanism was obtained via trapping the intermediate $[\text{C}_6\text{F}_5]^-$ anion with certain

CH- or OH-acids. In the presence of these compounds the formation of the NS product was suppressed completely, and pentafluorobenzene and related products were formed.

The question now emerges as to how general the proposed mechanism is, and whether it is applicable to the whole range of metal carbonyl anions and halogen leaving groups ($\text{Cl}, \text{Br}, \text{I}$). In the present work we studied the reactions of pentafluorohalobenzenes $\text{C}_6\text{F}_5\text{Hal}$ ($\text{Hal} = \text{Cl}, \text{Br}, \text{I}$) with several carbonylmetallates, and proved the halophilic mechanism [10] (Scheme 1) for all of the reactions under study.

2. Results and discussion

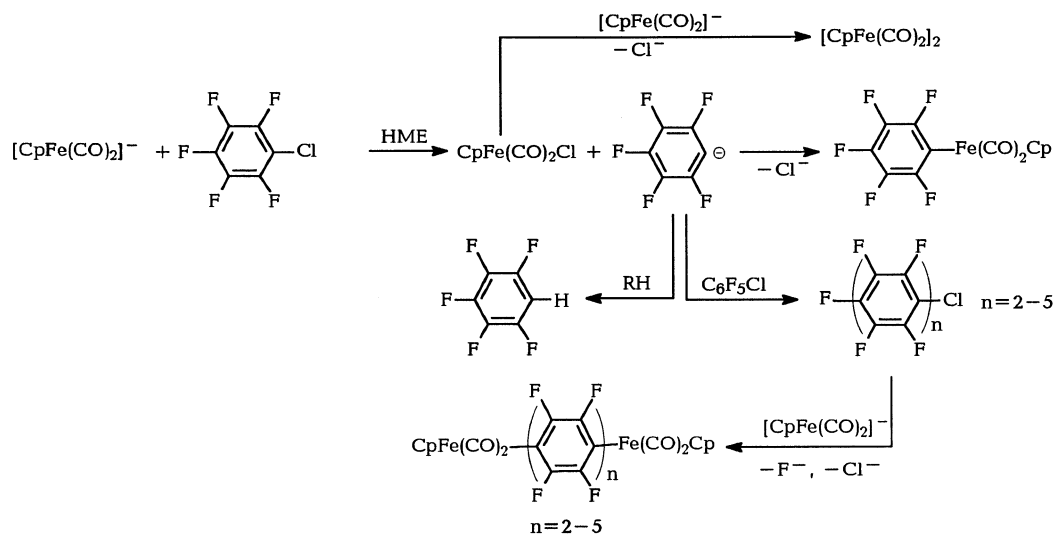
2.1. Reactions of $[\text{CpFe}(\text{CO})_2]^-$ anion with pentafluorohalobenzenes

When a slight excess of $\text{C}_6\text{F}_5\text{Hal}$ ($\text{Hal} = \text{Cl}, \text{Br}, \text{I}$) is added to $[\text{CpFe}(\text{CO})_2]\text{K}$ solution in THF at room temperature an instantaneous reaction takes place [11]¹. As illustrated in Eq. (1), quite a large number of

¹ The reported [11] rate constants for the reactions of $[\text{CpFe}(\text{CO})_2]\text{K}$ with $\text{C}_6\text{F}_5\text{Cl}$ and $\text{C}_6\text{F}_5\text{Br}$ in DMSO were $2.79 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ and $5.89 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$, respectively.

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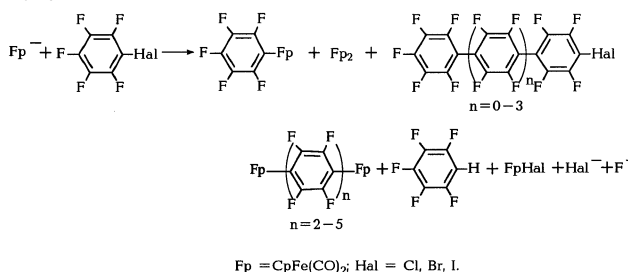
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Scheme 1. Halophilic mechanism for the reaction of C_6F_5Cl with $[CpFe(CO)_2]^-$ anion.Table 1
Product yields in the reaction of $[CpFe(CO)_2]K$ (FpK) with C_6F_5Hal , THF, r.t.

Entry	Reactants			Relative yield (%) ^a				
	Hal	C (FpK), (mol l ⁻¹)	C_6F_5Hal /FpK ratio	C_6F_5Fp	Fp_2	$C_6F_5(C_6F_4)_n C_6F_4Hal$ ($n = 0-3$)	$Fp(C_6F_4)_n Fp$ ($n = 2-5$)	C_6F_5H
1	Cl	0.087	1.25	58 (43)	39 (34)	6.5 (10)	3 (4.5)	2
2	Cl	0.043	1.47	(49)	(30)	(5.5)	2.5	—
3	Cl	0.053	1.19	50	43.5	4	6.5	4
4	Br	0.075	1.33	54 (49)	40 (19)	7 (15)	6 (3.5)	2
5	Br	0.077	1.48	61 (38)	37 (28)	8 (13)	2	4
6	I	0.070	1.14	77 (53)	23 (14)	(2.5)	0	10

^a The yields of the products are based on direct observation of the reaction mixtures by ^{19}F - and 1H -NMR spectroscopy, and are normalized to the 100% total yield of Fp-containing products. The isolated yields are given in brackets.

products are formed. The yields in Table 1 indicate that the principal compounds are $C_6F_5Fe(CO)_2Cp$, $[CpFe(CO)_2]_2$ and haloperfluoropolyphenyls. The yield of NS product is substantially improved over that which was previously obtained in this reaction by Bruce and Stone [6a], and is higher for C_6F_5I (77%) than for $C_6F_5Br(Cl)$ (50–60%).



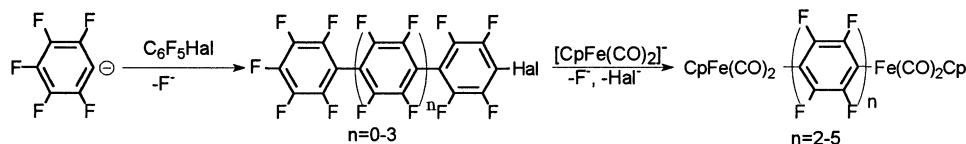
(1)

The interaction of $[CpFe(CO)_2]K$ with C_6F_5Br and C_6F_5I results in HME generating the $[C_6F_5]K$ intermediate, which can manifest itself in many different ways.

Such products as haloperfluoropolyphenyls $C_6F_5-(C_6F_4)_n C_6F_4Hal$ ($n = 0-3$) are particularly important, as they can be formed from C_6F_5Hal only by a series of NS reactions with $[C_6F_5]^-$ carbanion (Scheme 2) [12]. We have isolated three individual bromoperfluoropolyphenyls, their linear structure being evident from the ^{19}F -NMR spectrum. A small amount of pentafluorobenzene could result from trapping of the $[C_6F_5]^-$ anion by impurities in THF.

According to the halophilic mechanism outlined in Scheme 1, $C_6F_5Fe(CO)_2Cp$ results from the interaction of $[C_6F_5]^-$ and $CpFe(CO)_2Hal$ intermediates. The role of the $[C_6F_5]^-$ carbanion in the NS reaction is clearly demonstrated by trapping experiments summarized in Table 2 as was done earlier for the reaction of C_6F_5Cl with $[CpFe(CO)_2]K$ [10]. A sufficiently strong CH-acid², such as $PhCH(Et)CN$, added to the solution of

² The acidity of $PhCH(Et)CN$ (estimated $pK_a > 21$) lies between those of C_6F_5H ($pK_a = 25$) and $CpFe(CO)_2H$ ($pK_a = 19.2$) [13].



Scheme 2. Reaction sequence producing perfluoropolyphenyls.

Table 2

The effect of the anion and radical traps on the course of the reaction of C_6F_5Hal with $[CpFe(CO)_2]K$ (FpK), THF, r.t.

Entry	Reactants			Relative yields (%) ^a					Yield of other products (%)
	Hal	Trap	C (FpK) (mol l ⁻¹)	C_6F_5Hal/FpK ratio	C_6F_5Fp	Fp_2	$C_6F_5(C_6F_4)_n C_6F_4Hal$ ($n = 0-3$)	C_6F_5H	
1	Cl	Ph(Et)CHCN 3,5 equiv.	0.061	1.17	0	97	0	25	<i>p</i> -ClC ₆ F ₄ C(Et)(Ph)CN (10) <i>p</i> -HC ₆ F ₄ C(Et)(Ph)CN (8.5) <i>p</i> -HC ₆ F ₄ Fp (3)
2	Cl	Cy ₂ PH 7,6 equiv.	0.043	1.17	63	35	10	12	Fp(C ₆ F ₄) _n Fp, $n = 2-5$ (2)
3	Br	Ph(Et)CHCN 3,9 equiv.	0.049	1.29	0	97	0	33	<i>p</i> -HC ₆ F ₄ Fp (3)
4	Br	Cy ₂ PH 6,0 equiv.	0.042	1.31	54	41	5.5	12.5	Fp(C ₆ F ₄) _n Fp, $n = 2-5$ (2) C ₆ F ₅ Fe(CO) ₂ L _m ^b (3)
5	Br	C ₆ F ₅ Br ^c	0.073	13.1	40	48	23	5	CpFe(C ₅ H ₄ C ₆ F ₅) ^d (12)
6	I	Ph(Et)CHCN 6,6 equiv.	0.064	1.24	0	90	0	65	<i>p</i> -HC ₆ F ₄ Fp (10)
7	I	Cy ₂ PH 7,1 equiv.	0.041	1.23	65	35		58	

^a See footnote ^a to Table 1.^b Iron carbonyl σ -C₆F₅-derivative of unknown structure (signals in ¹⁹F-NMR (THF, δ_f): -103.6 (m, 2F), -162, 98 (t, 1F) and -164, 68 (m, 2F) relative to CCl₄).^c The solution of FpK was added dropwise to the solution of C₆F₅Br.^d Obtained only after separation of the reaction mixture on silica gel.

$[CpFe(CO)_2]K$ prior to the reaction, acts as an anionic trap, quantitatively intercepting the $[C_6F_5]K$ intermediate, completely precluding the formation of NS-substitution product $C_6F_5Fe(CO)_2Cp$ and haloperfluoropolyphenyls (Table 2). In anion trapping conditions only one half of the carbonylmetallate is consumed in the reaction with the starting aryl halide. The other half is supposed to react with $CpFe(CO)_2Hal$ to give the $[CpFe(CO)_2]_2$ dimer, which is formed almost quantitatively (Table 2). Consequently, the maximum possible yield of C_6F_5H (together with $Cp(CO)_2FeC_6F_4H$) resulting from protonation of the $[C_6F_5]^-$ carbanion is twice as low (50%) as the amount of $[CpFe(CO)_2]K$ entering the reaction. The amount of C_6F_5H formed from C_6F_5I in the presence PhCH(Et)CN (entry 6 Table 2) exceeds this stoichiometry. Presumably, the carbanion resulting from CH-acid, $[PhC(Et)CN]^-$, can also act as a halophilic agent towards C_6F_5I producing an additional amount of $[C_6F_5]^-$ ³. However, the same

³ We have shown that C_6F_5I is immediately and quantitatively converted to C_6F_5H when treated with $[Ph_2CCN]Na$ and an excess of Ph_2CHCN in THF. Halophilic reactions of activated aryl halides with good nucleophiles, such as carbanions or thiolates, are not usually regarded feasible. However, there are examples of such reactions with C_6F_5I and *o*-NO₂C₆H₄I [14], which are good positive halogen atom donors.

$[PhC(Et)CN]^-$ carbanion displaces the *p*-fluorine in C_6F_5Cl , as illustrated in Scheme 3.

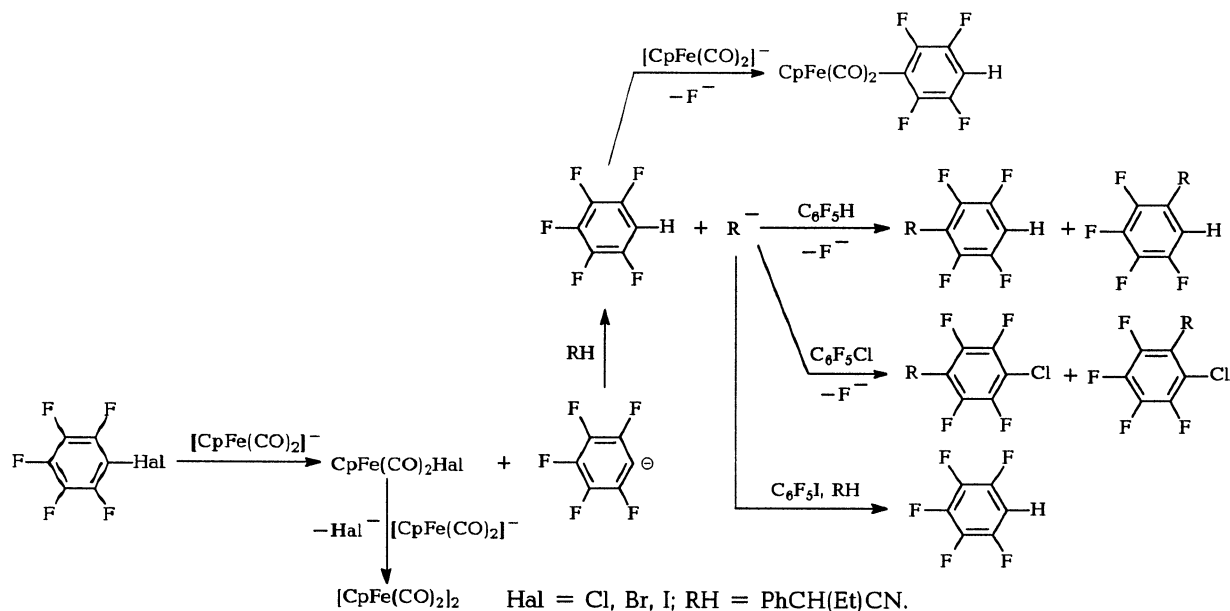
An aryl halide can itself act as a $[C_6F_5]^-$ carbanion trap: higher yields of bromoperfluoropolyphenyls and $[CpFe(CO)_2]_2$ are obtained when $[CpFe(CO)_2]K$ solution is slowly added to an excess of C_6F_5Br in THF (entry 5, Table 2).

The effect of a secondary phosphine Cy₂PH, which could act as a radical trap [15], is somewhat more ambiguous, though the yields of NS product and dimer do not change significantly, at least such is the case for C_6F_5Cl and C_6F_5Br (entries 2, 4, Table 2). In the case of C_6F_5I a large amount of C_6F_5H apparently results from a secondary reaction induced by Cy₂PH⁴.

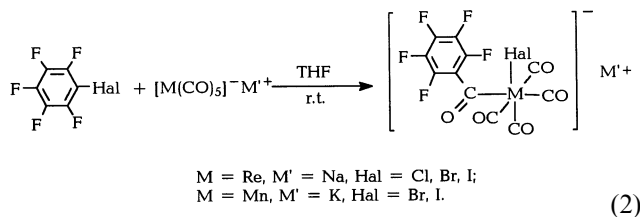
2.2. Reactions of $[Re(CO)_5]^-$ and $[Mn(CO)_5]^-$ anions with pentafluorohalobenzenes

The reaction of C_6F_5Hal with $[Re(CO)_5]Na$ (Hal = Cl, Br, I) and $[Mn(CO)_5]K$ (Hal = Br, I) in THF at room temperature takes place within the time of the reactant mixing, resulting in a clear light-yellow (Re) or

⁴ Even without carbonylate C_6F_5I is slowly reduced with Cy₂PH in THF producing C_6F_5H (24% after 24 h).

Scheme 3. Trapping of $[\text{C}_6\text{F}_5]^-$ carbanion by CH-acid.

dark-red (Mn) solution. In the case of $[\text{Re}(\text{CO})_5]\text{Na}$ reactions and the reaction of $[\text{Mn}(\text{CO})_5]\text{K}$ with $\text{C}_6\text{F}_5\text{I}$, the resulting solutions stay unchanged long enough to record the ^{19}F -NMR spectrum, which shows that the only product formed almost quantitatively is the haloacylmetallate complex $[\text{C}_6\text{F}_5(\text{CO})\text{M}(\text{CO})_4\text{Hal}]^- \text{M}'^+$ (Eq. (2), Table 3, entries 1–3, 7). The structure of haloacylmetallates was also confirmed by IR and ^{13}C -NMR spectroscopy.



Rhenium haloacylmetallates are relatively stable in solution, slowly decomposing to a complex mixture of σ -polyfluoroaryl rhenium complexes of unknown structure⁵. In the solid state all haloacylmetallates are unstable and decompose on evaporation of their solutions. Notably less stable than Re complexes are manganese haloacylmetallates, but their decomposition is a selective one, yielding $\text{C}_6\text{F}_5\text{Mn}(\text{CO})_5$ as the main product (Scheme 4). Although $[\text{C}_6\text{F}_5(\text{CO})\text{Mn}(\text{CO})_4\text{Br}]\text{K}$ is supposed to be formed with quantitative yield, it rearranges to a large extent before the NMR spectrum

can be recorded. Within a few minutes the precipitate begins to form, and after 15 min only 31% of the haloacylmetallate is left according to ^{19}F -NMR spectroscopy. The final yield (30 min) of $\text{C}_6\text{F}_5\text{Mn}(\text{CO})_5$ (80%, Table 3, entries 5, 6) is higher than obtained earlier in this reaction [5]. Much slower rearrangement of $[\text{C}_6\text{F}_5(\text{CO})\text{Mn}(\text{CO})_4\text{I}]\text{K}$ takes 35 h to complete and yields along with $\text{C}_6\text{F}_5\text{Mn}(\text{CO})_5$ (62%) two unidentified σ -Ar $_{\text{F}}$ complexes of Mn (Table 3, entry 7).

Several points should be kept in mind while discussing the mechanism of haloacylmetallate formation. (a) Migratory insertion of $\text{C}\equiv\text{O}$ in the $\text{Mn}-\text{C}_6\text{F}_5$ bond of $\text{C}_6\text{F}_5\text{Mn}(\text{CO})_5$ induced by KHal is hardly possible because C_6F_5 as a strongly electron-withdrawing group does not participate in the carbonylation reaction [16]. Moreover $[\text{C}_6\text{F}_5(\text{CO})\text{M}(\text{CO})_4\text{Hal}]^- \text{M}'^+$ are decomposed irreversibly with the elimination of KHal poorly soluble in THF. (b) The mechanism involving single-electron transfer is also scarcely possible in the reactions of $\text{C}_6\text{F}_5\text{Hal}$ (Hal = Cl, Br, I) with $[\text{Re}(\text{CO})_5]\text{Na}$ and $[\text{Mn}(\text{CO})_5]\text{K}$, because of the large difference between the redox potentials of these reactants [11,17]⁶.

There is little doubt that reactions of $\text{C}_6\text{F}_5\text{Hal}$ with $[\text{Re}(\text{CO})_5]\text{Na}$ and $[\text{Mn}(\text{CO})_5]\text{K}$ follow the same halophilic mechanism found for the reactions with $[\text{CpFe}(\text{CO})_2]\text{K}$, and it can easily be demonstrated by the same anion-trapping technique (Table 4). In the

⁵ Complex $[\text{C}_6\text{F}_5(\text{CO})\text{Re}(\text{CO})_4\text{Cl}]\text{Na}$ decomposes completely in 7 days; the Br-derivative *cis*- $[\text{C}_6\text{F}_5(\text{CO})\text{Re}(\text{CO})_4\text{Br}]\text{Na}$ is more stable and 80% of it decomposes after 45 days.

⁶ The same is true even for $[\text{CpFe}(\text{CO})_2]\text{K}$, the strongest reducing agent among carbonylmetallates.

Table 3

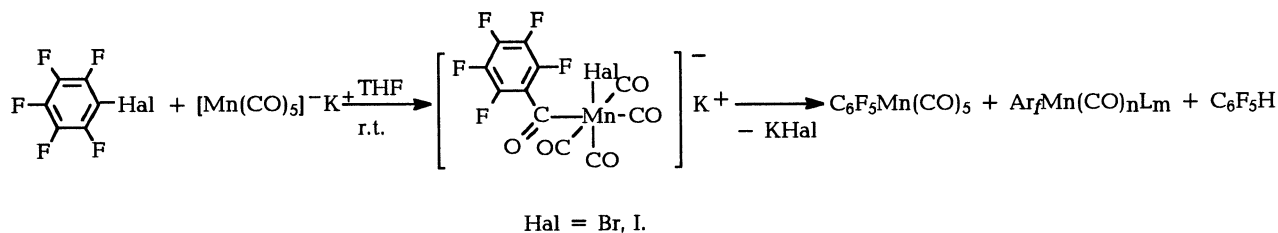
Product yields in the reaction of $[\text{Re}(\text{CO})_5]\text{Na}$ and $[\text{Mn}(\text{CO})_5]\text{K}$ with $\text{C}_6\text{F}_5\text{Hal}$, THF, r.t.

Entry	Reactants			Time	Yield (%)			
	Hal	$C [\text{M}(\text{CO})_5]\text{M}'$ (mol l ⁻¹)	$\text{C}_6\text{F}_5\text{Hal}/[\text{M}(\text{CO})_5]\text{M}'$ ratio		$[\text{C}_6\text{F}_5(\text{CO})\text{M}(\text{CO})_4\text{Hal}]\text{M}'$	$\text{C}_6\text{F}_5\text{Mn}(\text{CO})_5$	$\text{C}_6\text{F}_5\text{H}$	$\text{Ar}_f\text{M}(\text{CO})_n\text{L}_m^a$
1	Cl	$[\text{Re}(\text{CO})_5]\text{Na}$ (0.165)	1.53		95		0	Trace
2	Br	$[\text{Re}(\text{CO})_5]\text{Na}$ (0.312)	2.86		90		0	Trace
3	I	$[\text{Re}(\text{CO})_5]\text{Na}$ (1.38)	1.12		80 ^b		1.5	
4	Cl ^c	$[\text{Mn}(\text{CO})_5]\text{K}$ (0.360)	1.24	10 h	0	4.6	0.6	12
5	Br	$[\text{Mn}(\text{CO})_5]\text{K}$ (0.070)	1.09	30 min	0	51	5	3.6
6	Br	$[\text{Mn}(\text{CO})_5]\text{K}$ (0.420)	1.19	15 min	31	44	0	9
7	I	$[\text{Mn}(\text{CO})_5]\text{K}$ (0.083)	1.31	30 min	0	80	0	3
				18 min	91	2	9	1
				10 h	32.5	46	9	20
				35 h	0	62	9	23.5

^a In each of the experiments with $[\text{Mn}(\text{CO})_5]\text{K}$ several σ -polyfluoroaryl complexes of Mn of general formulae $\text{Ar}_f\text{Mn}(\text{CO})_n\text{L}_m$ are formed; L denotes an unknown ligand. The overall yield of these complexes is given in this column.

^b $\text{Re}(\text{CO})_5\text{I}$ was also formed (20%).

^c Main reaction products were $\text{Mn}_2(\text{CO})_{10}$ (80%) and $\text{C}_6\text{F}_5(\text{C}_6\text{F}_4)_n\text{C}_6\text{F}_4\text{Cl}$ ($n = 0-3$) (27%).



Scheme 4. Rearrangement of haloacylmanganates.

presence of anion traps, such as Ph_2CHCN or $^t\text{BuOH}$ ⁷, the formation of acyl complexes $[\text{C}_6\text{F}_5(\text{CO})\text{Mn}(\text{CO})_4\text{Hal}]\text{K}$ in the reaction of $\text{C}_6\text{F}_5\text{Hal}$ (Hal = Br, I) with $[\text{Mn}(\text{CO})_5]\text{K}$ is completely eliminated. Trapping of the $[\text{C}_6\text{F}_5]^-$ anion produces $\text{C}_6\text{F}_5\text{H}$, which under these conditions is the only product resulting from $\text{C}_6\text{F}_5\text{Hal}$. Proton transfer to the $[\text{C}_6\text{F}_5]^-$ anion should also generate the conjugated bases of CH- or OH-acid — $[\text{Ph}_2\text{CCN}]^-$ and $^t\text{BuO}^-$. Their fate is of certain interest in connection with the unexplainably large amount of $\text{C}_6\text{F}_5\text{H}$ observed in these reactions (Table 4, entries 2, 3). With $\text{C}_6\text{F}_5\text{I}$ it exceeds the maximum stoichiometric yield of 100%, possible if all the $[\text{Mn}(\text{CO})_5]\text{K}$ is spent in the reaction with the aryl halide, but not with the $\text{Mn}(\text{CO})_5\text{Hal}$ intermediate.

In the case of Ph_2CHCN the excessive yield of $\text{C}_6\text{F}_5\text{H}$ can be explained in the same way as it was for the reaction of $[\text{CpFe}(\text{CO})_2]\text{K}$ with $\text{C}_6\text{F}_5\text{I}$, that additional

$\text{C}_6\text{F}_5\text{H}$ originates from a halophilic reaction of $[\text{Ph}_2\text{CCN}]\text{K}$ with $\text{C}_6\text{F}_5\text{I}$. Yet we must propose a different explanation for the excessive yield of $\text{C}_6\text{F}_5\text{H}$ in the experiment with $^t\text{BuOH}$, considering that $^t\text{BuOK}$ as a 'hard' nucleophile replaces fluoride in $\text{C}_6\text{F}_5\text{I}$ to give $p\text{-(}^t\text{BuO)}\text{C}_6\text{F}_4\text{I}$ (70%)⁸. To our surprise, this product was not observed in the reaction of $\text{C}_6\text{F}_5\text{I}$ with $[\text{Mn}(\text{CO})_5]\text{K}$ in the presence of $^t\text{BuOH}$. Instead we found that $^t\text{BuOK}$ is trapped with $\text{Mn}(\text{CO})_5\text{I}$ to give another haloacylmanganate, $^t\text{BuO}(\text{CO})\text{Mn}(\text{CO})_4\text{I}]\text{K}$. This fact allows one to explain the absence of $\text{Mn}_2(\text{CO})_{10}$ among the reaction products. The complex $^t\text{BuO}(\text{CO})\text{Mn}(\text{CO})_4\text{I}]\text{K}$ was independently synthesized from $^t\text{BuOK}$ and $\text{Mn}(\text{CO})_5\text{I}$ in THF. Its dark-red solution decomposes in two days at room temperature giving $\text{Mn}(\text{CO})_5\text{I}$ as the only identified Mn product. We suppose that some reactive Mn anion (not necessarily $[\text{Mn}(\text{CO})_5]\text{K}$) is also generated in the decomposition process, and this anion abstracts halogen from the

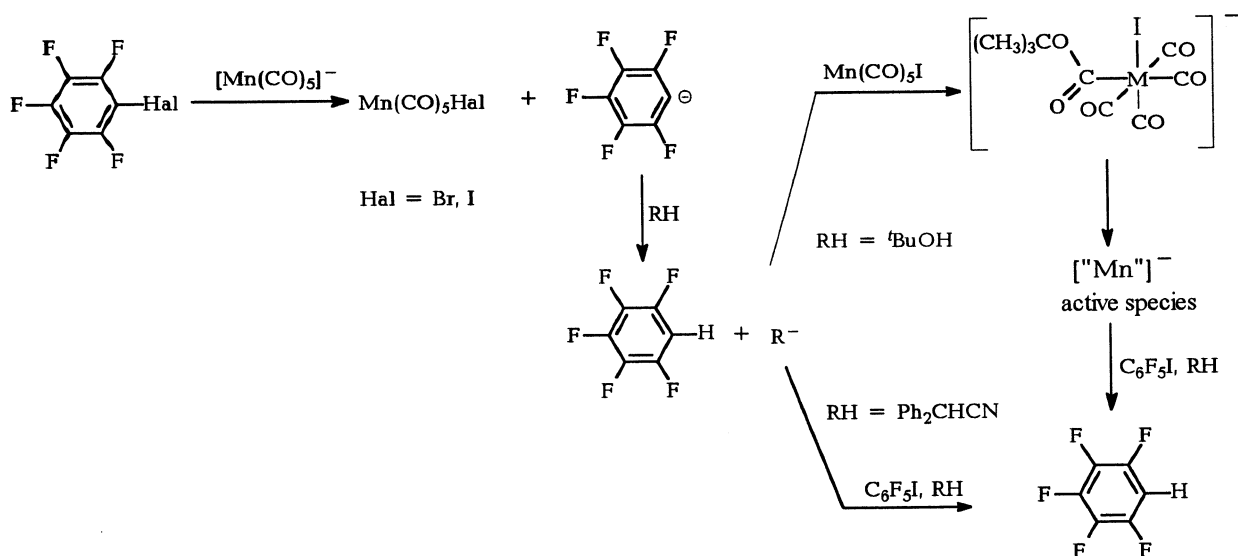
⁷ Both Ph_2CHCN ($\text{p}K_a = 18$) and $^t\text{BuOH}$ ($\text{p}K_a = 20$ for neat liquid) are weaker acids than $\text{Mn}(\text{CO})_5\text{H}$ ($\text{p}K_a = 15$) [13].

⁸ Shown in a separate blank experiment.

Table 4

The effect of the anion and radical traps on the course of the reaction of C_6F_5Hal with $[Mn(CO)_5]K$, THF, r.t.

Entry	Reactants				Yield (%)		Other products
	Hal	Trap, RH	C ([Mn(CO) ₅]K) (mol l ⁻¹)	C ₆ F ₅ Hal/[Mn(CO) ₅]K ratio	[C ₆ F ₅ (CO)- Mn(CO) ₄ Hal]K	C ₆ F ₅ H	
1	Br	Ph ₂ CHCN, 4.9 equiv.	0.054	1.20	0	100	Mn ₂ (CO) ₁₀
2	I	Ph ₂ CHCN, 4.1 equiv.	0.056	1.14	0	127	Mn ₂ (CO) ₁₀
3	I	^t BuOH, 5.2 equiv.	0.066	1.27	0	114	[^t BuO(CO)Mn(CO) ₄]K Mn(CO) ₅ I
4	I	Cy ₂ PH, 3.8 equiv.	0.053	1.26	51	68	

Scheme 5. Trapping of $[C_6F_5]^-$ anion in the reaction of $[Mn(CO)_5]K$ with C_6F_5Hal .

starting C_6F_5I , which actually accounts for the additional amount of C_6F_5H formed in the reaction of C_6F_5I with $[Mn(CO)_5]K$ in the presence of ^tBuOH (Scheme 5).

The effect of Cy₂PH as a radical trap in the reaction of C_6F_5I with $[Mn(CO)_5]K$ was also examined, but results were complicated because of the secondary reactions⁹ (entry 4, Table 4).

The experiments with anionic traps clearly demonstrate the intermediacy of the $[C_6F_5]^-$ anion in the reactions of Mn and Re carbonylmetallates with C_6F_5Hal . The $[C_6F_5]^-$ and $M(CO)_5Hal$ intermediates result from HME between the reactants, which is the first step in the general reaction mechanism (Scheme 6).

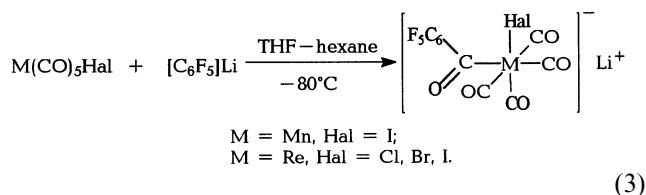
⁹ In the reaction with $[Mn(CO)_5]K$ in the presence of Cy₂PH an excess of C_6F_5I (relative to $[Mn(CO)_5]K$) is consumed completely to give $[C_6F_5(CO)Mn(CO)_4]K$ and C_6F_5H ; their total yield exceeds 100%.

Formation of such products as halo(acyl)metallates in the second step may be considered as 'autotrapping' of these intermediates, and as such is probably the most impressive evidence of the halophilic character of these reactions. In the reaction of C_6F_5I the first step may actually involve the formation of ate-complex [18], which transforms to haloacylmetallate via intramolecular rearrangement (Scheme 6)¹⁰. It is difficult to distinguish between these two pathways by anion-trapping experiments, because the C_6F_5 group in the ate-complex can be protonated just as the free $[C_6F_5]^-$ anion [20]. The choice between these alternatives is not really important for our study, because in both cases the key reaction involves the attack of carbonylmetallate on the halogen.

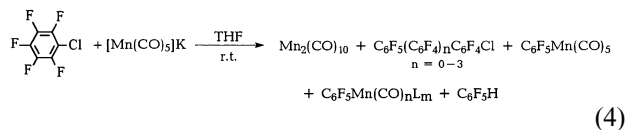
We have modelled the second stage in the proposed mechanism — the addition of the intermediate carban-

¹⁰ Stable iodine at complexes $[(C_6F_5)_2I]Li$ are known [19].

ion at C≡O group of $M(\text{CO})_5\text{Hal}$. The attack of different nucleophiles at the C≡O group is typical of various transition-metal carbonyls [16,21,22], but only a few cases of such reactions with metal carbonyl halides are known. The addition of MeLi to $\text{Re}(\text{CO})_5\text{Hal}$ (Hal = Cl, Br, I) and $\text{Mn}(\text{CO})_5\text{Br}$ was reported to give stable haloacylmetallates $[\text{Me}(\text{CO})\text{M}(\text{CO})_4\text{Hal}]\text{Li}$ [23], and in the reaction of $\text{Re}(\text{CO})_4(\text{PPh}_3)\text{Br}$ with the MeLi complex $[\text{CH}_3(\text{CO})\text{Re}(\text{CO})_3(\text{PPh}_3)\text{Br}]\text{Li}$ was observed as an intermediate, which turns thereafter into the σ -complex $\text{MeRe}(\text{CO})_4(\text{PPh}_3)$ [24]. We have found that reaction of $\text{C}_6\text{F}_5\text{Li}$ with $M(\text{CO})_5\text{Hal}$ allows one to obtain Li salts of the corresponding haloacylmetallates (Eq. (3)). The complexes are relatively stable at -60°C but decompose even faster than Na or K salts at room temperature. For example, $[\text{C}_6\text{F}_5(\text{CO})\text{Mn}(\text{CO})_4\text{I}]\text{Li}$ is completely decomposed in 30 min at room temperature giving $\text{Mn}(\text{CO})_5\text{I}$ and a set of σ -polyfluoroaryl complexes of Mn, including $\text{C}_6\text{F}_5\text{Mn}(\text{CO})_5$.



The reaction of $\text{C}_6\text{F}_5\text{Cl}$ with $[\text{Mn}(\text{CO})_5]\text{K}$ is rather sluggish. It takes 10 h to complete and leads to a complex mixture of products (Eq. (4), Table 3, entry 4), the major one being $\text{Mn}_2(\text{CO})_{10}$ (80%). Very weak signals observed in the ^{19}F -NMR spectrum correspond, with a high degree of probability, to a trace amount of haloacylmetallate $[\text{C}_6\text{F}_5(\text{CO})\text{Mn}(\text{CO})_4\text{Cl}]\text{K}$. A substantial amount of chloroperfluoropolyphenyls (27%) is formed, as it was the case in the reaction of $\text{C}_6\text{F}_5\text{Cl}$ with $[\text{CpFe}(\text{CO})_2]\text{K}$ (Reaction (4)). It is obvious that this reaction obeys the same HME mechanism, but because of the slow reaction between $[\text{C}_6\text{F}_5]^-$ and $\text{Mn}(\text{CO})_5\text{Cl}$, these intermediates are intercepted by $\text{C}_6\text{F}_5\text{Cl}$ and $[\text{Mn}(\text{CO})_5]\text{K}$, respectively.



In summary, we have shown that HME is a general mechanism for the reactions of pentafluorohalobenzenes with a series of carbonylmetallates $[\text{CpFe}(\text{CO})_2]^-$, $[\text{Re}(\text{CO})_5]^-$ and $[\text{Mn}(\text{CO})_5]^-$ covering a wide range of metal nucleophilicity.

3. Experimental

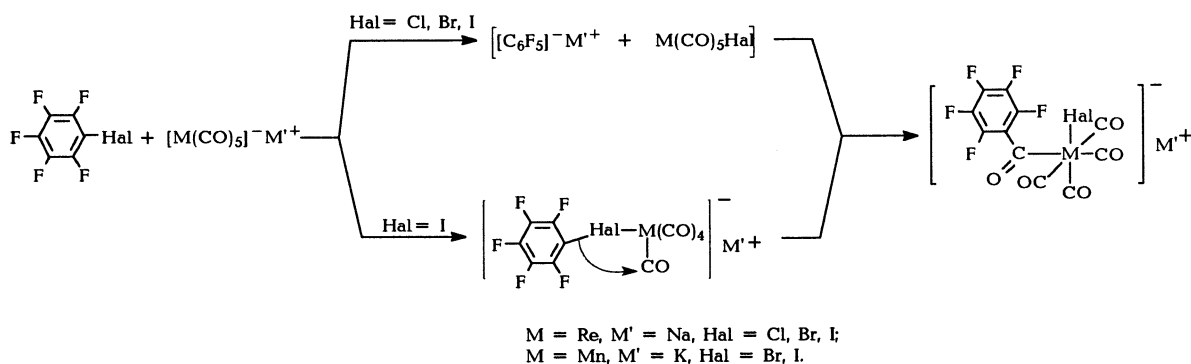
All air-sensitive reagents and reaction products were handled in vacuum or in a purified argon atmosphere using vacuum line and Schlenk techniques. Argon was further purified by passage through an oxygen scavenger and 4 Å molecular sieve columns.

3.1. Reagents and solvents

All solvents were refluxed over the appropriate drying agent and distilled prior to use. THF and THF- d_8 were vacuum transferred from sodium benzophenone ketyl. $(\text{Me}_3\text{Si})_2\text{O}$, $\text{C}_6\text{F}_5\text{Br}$ and PhCF_3 were fractionally distilled. $\text{C}_6\text{F}_5\text{I}$ was extracted with concentrated H_2SO_4 to remove any $\text{C}_6\text{F}_5\text{NH}_2$ impurity, washed with aqueous K_2CO_3 and water, dried with CaCl_2 and P_2O_5 and distilled under reduced pressure. The carbonylferate dimer $[\text{CpFe}(\text{CO})_2]_2$ was purified as described previously [25]. Ph_2CHCN was recrystallized from methyl alcohol.

Volatile reagents and standards were dried over the appropriate drying agent and vacuum transferred: $\text{C}_6\text{F}_5\text{Hal}$, $(\text{Me}_3\text{Si})_2\text{O}$ and PhCF_3 over the sodium mirror, Cy_2PH over P_2O_5 and $t\text{BuOH}$ over $t\text{BuOK}$.

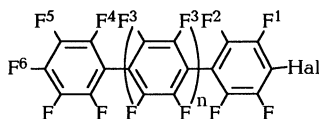
Metal carbonyl salts $[\text{CpFe}(\text{CO})_2]\text{K}$ and $[\text{Mn}(\text{CO})_5]\text{K}$ were obtained quantitatively (95–98%) [3,26] by reductive cleavage of the dimers $[\text{CpFe}(\text{CO})_2]_2$ and



Scheme 6. Alternative mechanisms of haloacylmetallate formation.

Table 5

The spectral data for haloperfluoropolyphenyls



Compound ^a	¹⁹ F-NMR Spectrum (THF, δ_f , ppm) ^b						Mass spectrum (m/z)
	F ¹	F ²	F ³	F ⁴	F ⁵	F ⁶	
C ₆ F ₅ C ₆ F ₄ Br	–132.02	–137.92		–137.16	–161.13	–150.74	394, 396 [M ⁺] (100%)
C ₆ F ₅ C ₆ F ₄ C ₆ F ₄ Br	–131.87	–137.65	–136.87	–136.87	–161.00	–150.36	542, 544 [M ⁺] (100%)
C ₆ F ₅ (C ₆ F ₄) ₂ C ₆ F ₄ Br	–131.83	–137.64	–136.65	–136.65	–160.97	–150.29	690, 692 [M ⁺] (100%)
C ₆ F ₅ (C ₆ F ₄) ₃ C ₆ F ₄ Br ^c							838, 840 [M ⁺]
C ₆ F ₅ C ₆ F ₄ I ^d	–120.04	–138.35		–137.31	–161.73	–151.12	442 [M ⁺] (100%)
C ₆ F ₅ C ₆ F ₄ C ₆ F ₄ I ^d	–119.90	–138.07	–137.49, –137.57	–136.93	–161.54	–150.63	590 [M ⁺] (68)

^a Spectra of chloroperfluoropolyphenyls and CpFe(CO)₂(C₆F₄)_nFe(CO)₂Cp ($n = 2-5$) were published earlier [10].^b C₆F₆ ($\delta_f = -162.9$ ppm) was used as an internal standard.^c In a mixture with C₆F₅(C₆F₄)₂C₆F₄Br.^d In a mixture with other iodoperfluoropolyphenyls C₆F₅(C₆F₄)_nC₆F₄I ($n = 0-3$).

Mn₂(CO)₁₀ with excess of NaK_{2.8} alloy (0.20–0.25 ml per 1 mmol of dimer) according to the procedure in the literature [26]. [Re(CO)₅]Na was prepared by the reduction of Re₂(CO)₁₀ with 0.5% NaHg [26] and purified by the low-temperature crystallization from THF [27]. In the preparation of Mn(CO)₅I we slightly modified the literature procedure [28], using potassium salt [Mn(CO)₅]K instead of sodium salt. The crude Mn(CO)₅I was recrystallized from hexane and further purified by column chromatography on silica gel (Merck, L 63/200). Re(CO)₅Cl was synthesized according to literature procedure [29].

3.2. Spectroscopic methods and reaction mixture analysis

The ¹H- (400 MHz), ¹⁹F- (376.3 MHz) and ¹³C-NMR (100, 56 MHz) spectra were recorded on a Varian VXR-4000 spectrometer at room temperature. The signals of the solvent were used as a chemical shift reference in ¹H- and ¹³C-NMR spectra. ¹⁹F-NMR chemical shifts are reported in ppm upfield from CFCl₃ relative to the signal of internal standard PhCF₃ (–61.96 ppm). Qualitative and quantitative analysis of the reaction mixtures was performed by ¹H- and ¹⁹F-NMR spectroscopy. The yields of the products were calculated from the ratio of the integral intensity of the respective signals and the signals of the internal standard, a weighted amount of which was added to the whole volume or an aliquot of the reaction mixture.

The IR spectra of the reaction mixtures and isolated products were recorded in THF solution on an UR-20 spectrophotometer in a 0.2 mm CaF₂ cell. Mass spectra were recorded on a MS-890 spectrometer operating

with electron impact ionization, 70 eV ionizing energy, using the direct inlet method, with a source temperature of 150°C. The spectra of the reaction products are presented in Tables 5 and 6.

3.3. The reaction of [CpFe(CO)₂]K with C₆F₅Hal (Hal = Br, I)

The general procedure for the reaction of [CpFe(CO)₂]K with C₆F₅Hal (Hal = Br, I) was almost identical to that previously described for the reaction of [CpFe(CO)₂]K with C₆F₅Cl [10]. In the preparative scale experiments 1.7–1.9 mmol of [CpFe(CO)₂]K was reacted with 1.9–2.8 mmol of C₆F₅Hal. The products were isolated by column chromatography on silica gel. When only NMR analysis was performed smaller amounts of reactants were used: 0.16–0.18 mmol of [CpFe(CO)₂]K and 0.20–0.24 mmol of C₆F₅Hal. In all of the experiments the aryl halide was in 15–50% excess, the concentration of [CpFe(CO)₂]K varied in the range 0.04–0.08 mol l^{–1}. In the experiment with the reverse order of mixing, a solution of [CpFe(CO)₂]K (0.52 mmol) in THF (6 ml) was added dropwise to the rapidly stirred solution of C₆F₅Br (1.68 g, 6.8 mmol) in THF (1.1 ml).

3.4. The reaction of C₆F₅Hal (Hal = Cl, Br, I) with [Re(CO)₅]Na and [Mn(CO)₅]K

The carbonylmetallate salt solution (0.25–0.56 mmol) in THF was transferred in vacuum from a break-seal ampoule into an NMR sample tube, and evaporated to a volume of 0.6–1.0 ml, to reach the concentration of 0.25–0.8 mol l^{–1}. The NMR tube was

Table 6

The spectral data for reaction products (THF, r.t.)

Compound	^{19}F -NMR spectrum (δ_{F})	^{13}C -NMR spectrum (δ_{C})		IR spectrum (ν , cm^{-1})			
		C=O	C=O	C=O	C=O	C=O	C=O
$\text{CpFe}(\text{C}_5\text{H}_4\text{C}_6\text{F}_5)^{\text{a}}$	–139.09, –159.32, –163.40						
$n\text{-(}^t\text{BuO)}\text{C}_6\text{F}_5\text{I}$	–122.17, –149.18						
$\text{cis-}[\text{C}_6\text{F}_5(\text{CO})\text{Re}(\text{CO})_4\text{Cl}]\text{Na}$	–150.21, –160.26, –162.09	185.45 (1C), 187.65 (2C), 188.18 (1C)	256.00	1928 s, 1998 vs, 2100 m	1607 w		
$\text{cis-}[\text{C}_6\text{F}_5(\text{CO})\text{Re}(\text{CO})_4\text{Br}]\text{Na}$	–149.66, –160.25, –161.95	187.69 (1C), 189.71 (3C)	256.60	1928 s, 1995 vs, 2099 m	1605 w		
$\text{cis-}[\text{C}_6\text{F}_5(\text{CO})\text{Re}(\text{CO})_4\text{I}]\text{Na}$	–148.05, –160.58, –162.49	187.06 (1C), 188.29 (1C), 188.63 (2C)	253.29	1928 s, 1992 vs, 2093 m	1605 w		
$\text{cis-}[\text{C}_6\text{F}_5(\text{CO})\text{Re}(\text{CO})_4\text{Cl}]\text{Li}^{\text{b}}$	–149.41, –158.55, –161.42			1936 s, 2005 vs, 2104 m	1581 w		
$\text{cis-}[\text{C}_6\text{F}_5(\text{CO})\text{Re}(\text{CO})_4\text{Br}]\text{Li}^{\text{b}}$	–148.90, –158.87, –161.50			1938 s, 1999 vs, 2099 m	1581 w		
$\text{cis-}[\text{C}_6\text{F}_5(\text{CO})\text{Re}(\text{CO})_4\text{I}]\text{Li}^{\text{b}}$	–146.43, –159.44, –161.99			1924 s, 1984 s, 2095 m	1575 w		
$\text{cis-}[\text{C}_6\text{F}_5(\text{CO})\text{Mn}(\text{CO})_4\text{Br}]\text{K}$	–148.24, –160.98, –162.59			1932 s, 1995 s, 2079 m	1612 w		
$\text{cis-}[\text{C}_6\text{F}_5(\text{CO})\text{Mn}(\text{CO})_4\text{I}]\text{K}$	–147.15, –161.42, –162.90	213.76 (2C), 214.61 (1C), 222.26 (1C)	270.55	1931 s, 1998 vs, 2073 s	1612 w		
$\text{cis-}[\text{C}_6\text{F}_5(\text{CO})\text{Mn}(\text{CO})_4\text{I}]\text{Li}^{\text{b}}$	–145.58, –160.06, –162.34			1940 s, 1990 s, 2074 m	1600 w		
$\text{cis-}[^t\text{BuO}(\text{CO})\text{Mn}(\text{CO})_4\text{I}]\text{K}$				1940 vs, 1987 vs, 2069 m	1619 w		

^a ^1H -NMR (δ) 4.12 (s, 5 H, Cp), 4.42 (t, 2H, $\text{C}_5\text{H}_4\text{C}_6\text{F}_5$), 4.75 (t, 2H, $\text{C}_5\text{H}_4\text{C}_6\text{F}_5$). MS (m/z): 352 [M^+] (100%), 121 [CpFe^+] (32%), 56 [Fe^+] (10%).

^b In 1:1 THF–hexane mixed solvent.

then frozen in liquid nitrogen, and thin glass spheres containing the substrate (0.29–0.97 mmol), THF- d_8 (ca. 0.2 ml) and PhCF_3 (NMR standard) were broken, their contents being vacuum transferred into the NMR sample tube, which was sealed off by flame. The tube was warmed to r.t., shaken to mix the reactants and immediately the recording of the NMR spectra was started.

We failed to isolate the rhenium haloacylmetallates in crystalline form. Their sodium salts immediately decompose when their THF solutions are evaporated to dryness. The stability of haloacylmetallates increased when the sodium cation was exchanged for the bulky $[(\text{Ph})_3\text{P}=\text{N}=\text{P}(\text{Ph})_3]^+$, but these salts precipitated as an oil from THF–ether mixed solvent, and decomposed slowly even at low temperature.

3.5. The reaction of $\text{C}_6\text{F}_5\text{Li}$ with $\text{Mn}(\text{CO})_5\text{I}$ and $\text{Re}(\text{CO})_5\text{Hal}$ ($\text{Hal} = \text{Cl}, \text{Br}, \text{I}$)

The solution of $\text{C}_6\text{F}_5\text{H}$ (0.134 g, 0.8 mmol) in THF (1 ml) was slowly added under Ar atmosphere to BuLi in hexane (0.25 mol l^{-1} , 2 ml) at -80°C [8]. The $\text{C}_6\text{F}_5\text{Li}$ solution obtained was quickly added to a solution of $\text{M}(\text{CO})_5\text{Hal}$ ($\text{M} = \text{Mn}, \text{Re}$) (0.5 mmol) in THF (2 ml) at -80°C . The resulting solutions were analysed by ^{19}F -NMR and IR spectroscopy.

3.6. The reaction of $\text{C}_6\text{F}_5\text{I}$ with $[\text{Ph}_2\text{CCN}]\text{Na}/\text{Ph}_2\text{CHCN}$

THF (3 ml) was vacuum distilled to a mixture of Ph_2CHCN (0.13 g, 0.66 mmol) and NaH (0.008 g, 0.33 mmol), upon which a vigorous reaction (with the evolu-

tion of hydrogen) followed. When the reaction was complete (< 5 min), $\text{C}_6\text{F}_5\text{I}$ (0.127 g, 0.43 mmol) was added to the obtained bright-yellow solution of $[\text{Ph}_2\text{CCN}]\text{Na}/\text{Ph}_2\text{CHCN}$. The reaction mixture immediately turned bright orange, but then the colour slowly disappeared. The reaction mixture was filtered into an NMR sample tube and analysed by ^{19}F -NMR spectroscopy.

3.7. The reaction of $\text{C}_6\text{F}_5\text{I}$ with $^t\text{BuOK}/^t\text{BuOH}$

Similarly, $^t\text{BuOK}$ (0.4 g, 3.6 mmol) and $^t\text{BuOH}$ (1.5 g, 20 mmol) were dissolved in THF (7.4 ml) to which $\text{C}_6\text{F}_5\text{I}$ (1.34 g, 4.6 mmol) dissolved in THF (10 ml) was then added. The obtained light-yellow reaction mixture was analysed by ^{19}F -NMR spectroscopy.

3.8. The reaction of $\text{C}_6\text{F}_5\text{I}$ with Cy_2PH

In a similar way the solutions of Cy_2PH (0.27 g, 1.4 mmol) in THF (4 ml) and $\text{C}_6\text{F}_5\text{I}$ (0.14 g, 0.46 mmol) in THF (10 ml) were mixed, without any visual change. The reaction mixture was analysed by ^{19}F -NMR spectroscopy.

3.9. The reaction of $\text{Mn}(\text{CO})_5\text{I}$ with $^t\text{BuOK}$

When a solution of $^t\text{BuOK}$ (0.028 g, 0.25 mmol) in THF (2.5 ml) was quickly added to the solution of $\text{Mn}(\text{CO})_5\text{I}$ (0.032 g, 0.1 mmol) in THF (2.5 ml) the reaction mixture immediately turned ruby. The reaction was monitored by IR spectroscopy.

Acknowledgements

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