The Reaction of the $[CpFe(CO)_2]^-$ Anion with Pentafluorochlorobenzene: Nucleophilic Aromatic Substitution by Halogen–Metal Exchange

G. A. Artamkina, P. K. Sazonov, V. A. Ivushkin, I. P. Beletskaya*

Abstract: In the reaction of the $[CpFe(CO)_2]^-$ anion with pentafluorochlorobenzene, $[CpFe(CO)_2]_2$ and *p*-chloroperfluoropolyphenyls $C_6F_5(C_6F_4)_n$-C_6F_4Cl ($n = 0-3$) are formed alongside the expected chlorine substitution product $[C_6F_5Fe(CO)_2Cp]$. The relative yield of these products depends on the ratio of initial reactants, solvent (THF, ether, DMSO, MeCN), counterion (K^+, K^+18-crown-6, $[(C_6H_5)_3P{=}N{=}P(C_6H_5)_3]^+$ [PPN^+]) and temperature. The highest yield of $[C_6F_5Fe(CO)_2Cp]$ ($\approx 50\%$) was obtained in THF, with a slight excess of pentafluorochlorobenzene added to $[CpFe(CO)_2]K$ at room temperature. In the presence of proton donors *t*BuOH or PhCH(Et)CN the reaction does not yield $[C_6F_5Fe(CO)_2Cp]$ and *p*-chloroperfluoropolyphenyls at all; instead C_6F_5H and $[CpFe(CO)_2]_2$ are formed. This fact and other data point to the $[C_6F_5]^-$ anion as the key intermediate in all of the observed transformations, among them the formation of $[C_6F_5Fe(CO)_2Cp]$. The evidence from the use of radical traps (R_2PH and PEt_3) indicates that free radicals are not involved in the major reaction pathway. Halogen–metal exchange is proposed as the first step of the reaction mechanism. The subsequent competition between the possible reactions of the exchange intermediates, $[CpFe(CO)_2Cl]$ and $[C_6F_5]^-$, is discussed to account for the highly variable ratio of the final products.

Keywords: carbonyl complexes · halogen–metal exchange · iron · nucleophilic aromatic substitutions · reaction mechanisms

Introduction

Nucleophilic substitution with metal carbonyl anions, carbonylmetallates, may be considered as a model of oxidative addition of organic halide to transition metal, which is a key step of various processes catalysed by transition metal complexes, such as carbonylation or cross-coupling. Only aliphatic nucleophilic substitution with carbonylmetallates was studied in detail, the operation of both S_N2 and radical reaction mechanisms being demonstrated.[1] The interaction of carbonylmetallates with polyfluoroarylhalides, which represents a well-established synthetic approach to σ-polyfluoroaryl metal complexes,[2, 3] has not yet received appropriate mechanistic consideration. However, recent studies have shown that σ-aryl metal carbonyl complexes, especially di- or poly-metal-substituted aromatics, are of considerable interest. They can serve as models of intermediates in catalytic processes, for the study of intramolecular charge transfer and as a base of new materials possessing unique electronic and optical properties.[4]

The reactions of carbonylmetallates as well as other metal-centred anions with aryl halides possess a number of features that distinguish them from nucleophilic aromatic substitution reactions with conventional nucleophiles.[5–7] These reactions do not obey one of the basic mechanistic criteria of the addition–elimination mechanism, the element effect (i.e. higher reactivity of aryl fluorides as compared to other haloarenes).[8] Reverse leaving group ability order[2, 5–7] ($I > Br \gg Cl > F$) resembles the reactivity observed in the oxidative addition to unsaturated metal complexes.[9] Reduction of the organic substrate and oxidation of the nucleophile frequently observed as a side process[2, 5a] is another point not consistent with the classical S_N2Ar mechanism. Up to now no reaction scheme to account for these differences has been generally accepted.

We have previously studied the kinetics of fluorine substitution in perfluorinated arenes by carbonylmetallates, when reduction does not interfere with nucleophilic substitution.[5] An unusual ion-pairing effect has been observed: close-contact ion pairs were more reactive than free ions and solvent-separated ion pairs.[5] With the primary aim of rationalising the nature of the reactivity pattern distinguishing carbonylmetallates we have now extended our research to the substrate having both fluorine and chlorine moieties in one molecule, where competition between several reaction pathways is possible. The reaction of pentafluorochlorobenzene with the dicarbonylcyclopentadienylferrate anion $[CpFe(CO)_2]^-$ chosen as a model in the current study has already been reported by Bruce and Stone;[2a] however, the necessary study of the entire product composition is lacking and certain

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points, such as the formation of proton-containing complex p-HC_6F_4Fp ($Fp = [CpFe(CO)_2]$) in *pure* THF, were not confirmed in our work.[6] Moreover, we observed additional products that were not reported earlier, such as p-chloroperfluoropolyphenyls, which led us to carry out a comprehensive examination of the reaction mechanism, including the effects of radical and carbanionic traps. Considerable attention is given to various factors controlling the course of the reaction, such as the reactant ratio, the solvent, counterion and temperature. Important as it is for the optimisation of reaction conditions of carbonylmetallates with haloarenes, to the best of our knowledge no similar investigation has ever been attempted previously.

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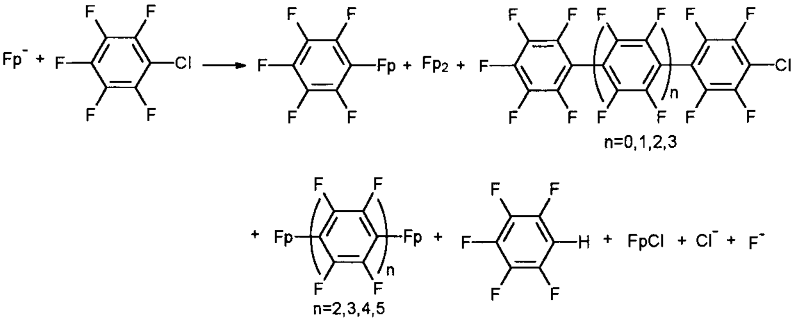
Abstract in Russian:

В реакции аниона $CpFe(CO)_2{}^-$ с пентафторхлорбензолом наряду с ожидаемым продуктом нуклеофильного замещения хлора образуются также димер $[CpFe(CO)_2]_2$ и n-хлорперфторполифенилы, $n-C_6F_5(C_6F_4)_nC_6F_4Cl$ (n = 0 – 3). Относительные выходы указанных продуктов зависят от соотношения реагентов, растворителя (ТГФ, эфир, ДМСО, MeCN), противоиона (K^+, $K^+\cdot 18$-краун-6, PPN^+) и температуры. Наиболее высокий выход $C_6F_5Fe(CO)_2Cp$ (≈50%) получен в тетрагидрофуране при добавлении небольшого избытка C_6F_5Cl к $CpFe(CO)_2K$ при комнатной температуре. В присутствии доноров протона, *t*BuOH и PhCH(Et)CN, n-хлорперфторполифенилы и $C_6F_5Fe(CO)_2Cp$ вообще не обнаружены среди продуктов реакции, вместо них образуются димер $[CpFe(CO)_2]_2$ и C_6F_5H. Этот факт, наряду с другими полученными данными, показывает, что пентафторфенильный анион является ключевым интермедиатом во всех наблюдаемых превращениях, в том числе в процессе образования $C_6F_5Fe(CO)_2Cp$. Ловушки свободных радикалов не оказывают существенного влияния на ход реакции. Обмен металл–галоген предложен в качестве первой стадии механизма реакции. Рассмотрение конкуренции, возможной между различными путями последующих превращений промежуточных продуктов обмена, $[C_6F_5]^-$ и $CpFe(CO)_2Cl$, позволяет объяснить сильную зависимость соотношения конечных продуктов реакции от условий ее проведения.

Results and Discussion

The course of the reaction: The starting carbonylferrate is obtained quantitatively in the form of FpK[10] by reduction of the dimer Fp_2 with sodium/potassium alloy; thus, we were able to determine not only the relative distribution but also the absolute yields of the products. Reaction occurred instantaneously on the addition of C_6F_5Cl (15 – 50 % excess) to the solution of carbonylferrate salt,[a] making direct kinetic measurements impossible. The basic set of the products [Eq. (1)] was the same in all of the experiments, while the product distribution changed considerably depending on the reaction conditions.



(1)

In the reactions of carbonylmetallates with activated aryl halides the higher yields of transition metal σ-aryl complexes are usually obtained at lower temperatures (– 78 °C).[3d, 5, 11, 12] In contrast, the yield of the nucleophilic substitution product, C_6F_5Fp, in the reaction of FpK with C_6F_5Cl is higher at room temperature (50 – 60 %) than at – 50 °C (13 – 20 %), when the dimer Fp_2 and other products of the redox process[b] are primarily formed (entries 1 – 3 Table 1). These include chloroperfluoropolyphenyls C_6F_5H and FpCl, though only traces of the latter were observed. Its presence in the reaction mixtures was not confirmed by ^1H NMR spectra, probably owing to the overlapping of the Cp-group signals with C_6F_5Fp. Pentafluorobenzene could arise both from proton and hydrogen-atom abstraction from the solvent or Cp group by the intermediate pentafluorophenyl anion or radical respectively.

The principal products of the reduction of C_6F_5Cl were chloroperfluoropolyphenyls, $C_6F_5(C_6F_4)_nC_6F_4Cl$, never previ-

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[*] Members of the Editorial Board will be introduced to readers with their first manuscript.

[a] The rate constant $k = 2.79 \cdot 10^4$ L mol^{-1} s^{-1} in DMSO has been reported in the literature.[7]

[b] In the context of this work the term redox process corresponds only to the net result of the transformation, oxidation of Fp^- and reduction of C_6F_5Cl, but not to its mechanism.

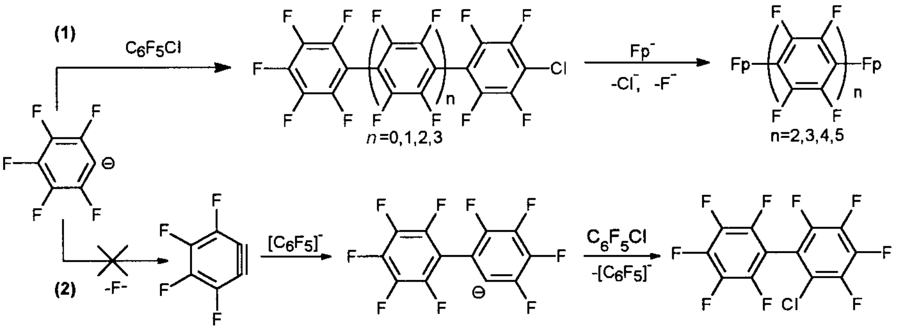
Table 1. Temperature, solvent polarity and cation effects on the course of the reaction of FpM with C_6F_5Cl.

Entry	Reactants and reaction conditions[a]				Relative yields [%][b]			
	M^+	Solvent	T [°C]	Ratio $\nu(C_6F_5Cl)/\nu(Fp^-)$	C_6F_5Fp	Fp_2	$C_6F_5(C_6F_4)_nC_6F_4Cl$ ($n = 1-3$)	C_6F_5H
1	K	THF	−50	1.44	22	78	15	7.5
2	K	THF	RT	1.47	(49)	(30)	(8)	
3	K	THF	RT	1.25	57 (43)	43 (32)	11	2.5
4	Li[c]	THF/Et_2O[d]	RT	1.36	2	98	50	15.5
5	K	THF/DMSO[e]	RT	1.23	29 (22)	71 (48)	27 (17)	3
6	K/18-crown-6[f]	THF	RT	1.17	17	83	11	3
7	PPN^+	THF	RT	1.39	19	81	16	
8	K	THF[g]	−50	1.26	19	81	13	4

[a] The initial concentrations of reactants were 0.03–0.09 M. RT = room temperature. [b] Isolated yields are shown in brackets. Product ratio was determined by means of ^1H and ^{19}F NMR spectroscopy with internal standard ($(Me_3Si)_2O$ or C_6H_6 in ^1H, $PhCF_3$ or C_6F_6 in ^{19}F NMR). The yields are normalised to 100% total yield of Fp-containing products, while the corresponding experimental value varied in the range 75–120%. The yield of chloroperfluoropolyphenyls was calculated per aromatic ring. [c] The Li salt was used since the K salt is insoluble in ether. [d] The mixture contained ≈30% THF. [e] The mixture contained ≈30% $[D_6]$DMSO. [f] ν(18-crown-6)/ν(FpK) = 2. [g] CH_3OH (4 equiv) was introduced immediately after the mixing of the reactants.

ously detected in reactions of that type. Mass spectra of the isolated individual homologues of chloroperfluoropolyphenyls ($n = 0-3$) exhibit high-intensity molecular ion peaks, while the fragmentation is negligible. Small amounts of Fp-substituted perfluoropolyphenyls, $Fp(C_6F_4)_nFp$ ($n = 2-5$), were also detected in the reaction, but the individual components could not be separated because of their close R_f values. Nevertheless the ^1H NMR spectrum of the mixture displayed a characteristic set of signals in the Cp region ($\delta = 5.1-5.2$) with consecutively decreasing intensity.

Taking into consideration the linear structure of the phenylene chain in chloroperfluoropolyphenyls, evident from ^{19}F NMR spectra, the most obvious route to their formation from C_6F_5Cl appears to consist of a series of nucleophilic substitution reactions with the $[C_6F_5]^-$ anion (Scheme 1, route 1). It should be mentioned that the reactions of perfluoroarenes with nucleophiles belong with the classic examples of nucleophilic aromatic substitution, and could hardly be regarded as specific C–F bond activation as was suggested in several recent publications.[13] The substitution of the fluorine *para* to chlorine on the aromatic ring with a carbon-centred nucleophile agrees well with the predictions derived from previous studies.[5a, 6, 14] The possibility of tetrafluorodehydrobenzene participation in these reactions may be excluded, as in that case the aromatic rings could not be concatenated *para*[15] (Scheme 1, route 2).



Scheme 1. Possible pathways for *p*-chloroperfluoropolyphenyl formation.

To evaluate the rate of the reaction of the $[C_6F_5]^-$ anion with C_6F_5Cl, methanol was added immediately after the reactants (C_6F_5Cl and FpK) were mixed at −50 °C (entry 8, Table 1). The yields of the products, including C_6F_5H, remained the same as in the blank experiment (entry 1, Table 1). Thus the intermediate $[C_6F_5]^-$ anion must be rapidly consumed before it could be protonated by methanol.

The stoichiometry of the reaction is also highly suggestive. Less than one mole of C_6F_5Cl is consumed for one mole of Fp^-. When Fp_2 is primarily formed, the reaction balance approximates to Equation (a), that is, roughly two moles of FpK per mole of C_6F_5Cl.

$$(2n+2)\,FpK + (n+2)\,C_6F_5Cl \longrightarrow$$
$$(n+1)\,Fp_2 + \underset{n=0-3}{C_6F_5(C_6F_4)_nC_6F_4Cl} + (n+1)\,KCl + (n+1)\,KF \qquad (a)$$

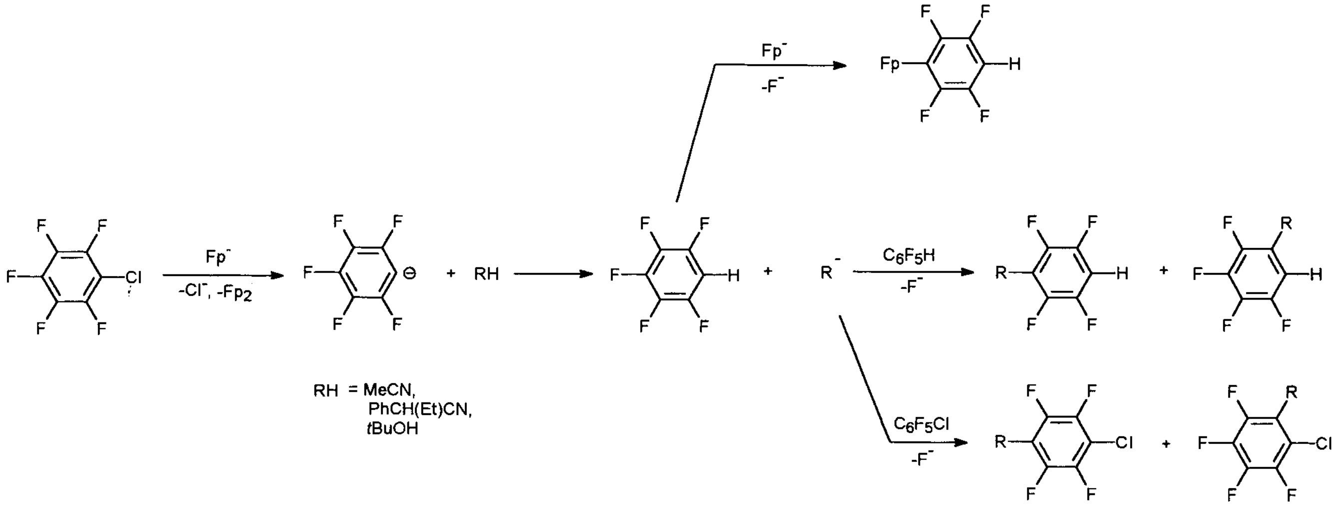
Solvent and counterion effects: The ion pairing in the carbonylmetallate strongly influences the course of the reaction, revealing an unusual bell-shaped dependence, the highest yield of C_6F_5Fp being observed in the reaction with potassium salt in THF at room temperature (entries 2–3, Table 1). Factors increasing the dissociation of the carbonylmetallate salt, for example the addition of more polar solvent (DMSO), crown ether or the exchange of the K^+ counterion for the bulky PPN^+ cation, reduced the ratio of C_6F_5Fp to the products of the redox process (entries 5–7, Table 1). But a similar yet much greater effect is caused by the use of Li salts with partial exchange of THF for the less polar diethyl ether, when stronger ion pairing and aggregation of carbonylmetallate is expected to take place (entry 4, Table 1).

Data is scarce concerning cation and solvent effects on the product distribution pattern (redox vs. substitution) in the reactions of carbonylmetallates with haloarenes bearing heavier halogens (Cl, Br, I). Certain studies were conducted only for the reactions of carbonylferrate salts with tricarbonylchromium haloarene complexes, when the use of bulky cations and low temperatures resulted in higher yields of the substitution product.[12, 16] We observed similar behaviour

Table 2. The effect of anion traps on the course of the reaction of C_6F_5Cl with Fp^- at room temperature.

Entry	Reactants and reaction conditions[a]			Relative yields [%][b]					
	Cation M^+	Solvent/Trap	Ratio $\nu(C_6F_5Cl)/\nu(Fp^-)$	C_6F_5Fp	Fp_2	$C_6F_5(C_6F_4)_nC_6F_4Cl$ ($n = 0-3$)	C_6F_5H	Other products	Yields [%]
1	K	THF (no trap)	1.25	57	43	11	2.5		
2	K	MeCN/MeCN	1.24	26	67	0	25.5	p-$ClC_6F_4CH_2CN$	4.5
								p-HC_6F_4Fp	7.5
3	PPN	MeCN/MeCN	1.31	27	64	0	28	p-$ClC_6F_4CH_2CN$	9.3
								p-HC_6F_4Fp	9
4	K	THF/*t*BuOH (16 equiv)	1.24	0	91	0	44	p-ClC_6F_4O*t*Bu	39
								o-ClC_6F_4O*t*Bu	5
								p-HC_6H_4O*t*Bu	3
								p-HC_6F_4Fp	9
5	K	PhCH(Et)CN (3.5 equiv)	1.17	0	97	0	25	p-ClC_6F_4C(Et)(Ph)CN	10
								p-HC_6F_4C(Et)(Ph)CN	8.5
								p-HC_6F_4Fp	3
6	K	THF/C_6F_5Cl (10 equiv[c])	9.72	31	69	34	7		

[a] The initial concentrations of reactants were 0.03–0.09 M. [b] Concerning the determination and calculation of the product yields see footnote [b] to Table 1. [c] The solution of FpK was added dropwise to the solution of C_6F_5Cl.



Scheme 2. Products originating from protonation of the $[C_6F_5]^-$ carbanion by alcohol or CH acid.

recently in nucleophilic vinylic substitution reaction between Fp^- and chlorodifluorostyrene.[17] Also worth mentioning is one more work reporting that the use of FpLi in ether/hexane solution in the reaction with $C_6F_4Hal_2$ (all isomers, Hal = Cl, Br) furnishes the monosubstitution products FpC_6F_4Hal in moderate yield,[11] yet nothing is known about the course of the same reactions in THF. This data is hardly compatible with our current results, and does not help us in answering the question why ether and large cations caused similar effects.

The effect of anion scavengers: The results obtained indicate that aryl carbanions play an important role in the reaction of FpK with C_6F_5Cl, at least in the reduction of aryl halide. Carrying out the reaction in the presence of anion scavengers (proton donors) is likely to provide further evidence of the $[C_6F_5]^-$ anion participating in the process. The solvent MeCN turned out to be sufficiently acidic[c] to protonate the $[C_6F_5]^-$ carbanions that are involved in the formation of chloroperfluoropolyphenyls, since the latter were not observed in the reaction carried out in MeCN. The dehalogenation process in that case yields only proton-containing products, C_6F_5H and p-HC_6F_4Fp. It is noteworthy that the reduction of the C_6F_5Cl becomes the major reaction pathway in MeCN, the ratio C_6F_5Fp/Fp_2 decreasing more than threefold compared with that in THF (entries 1–3, Table 2), but this effect could be also caused by the change of medium polarity.

Anion scavengers added to the FpK solution prior to the addition of C_6F_5Cl prevent the nucleophilic substitution pathway of the reaction entirely; not even traces of the product C_6F_5Fp are detected (Scheme 2; entries 4,5, Table 2). We investigated the effect of both O–H and C–H acids, choosing for that purpose *t*BuOH and PhCH(Et)CN, which are stronger acids than C_6F_5H ($pK_a \approx 25$[19]), but less acidic than FpH ($pK_a = 19.2$[21]). (In fact, because of hydrogen bonding, the acidity of *t*BuOH is heavily concentration-dependent, varying from $pK_a = 20$ for the neat liquid to $pK_a = 30$ for the dilute solution in DMSO.[20] The pK_a value of PhCH(Et)CN is possibly slightly higher than of $PhCH_2CN$ ($pK_a = 21.3$ in DMSO[20]). It was shown that Fp^- is protonated

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[c] The acidity of MeCN media may be even higher than reported for MeCN ($pK_a = 29$) in dilute solution in DMSO.[18]

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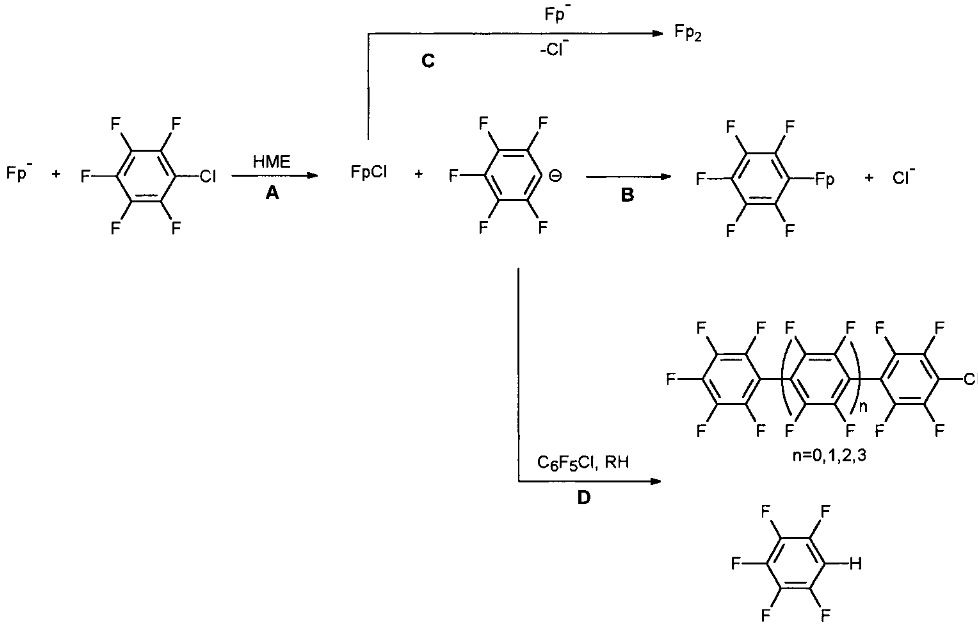
only to a small extent even in THF/*t*BuOH (1:1) mixed solvent.[22]) The reaction pattern observed was the same with both traps, the yield of the dimer Fp_2 being near to quantitative and only proton-containing products (mainly C_6F_5H) being formed from the reduction of C_6F_5Cl (entries 4,5, Table 2).



Scheme 3. General mechanism of the reaction.

The protonation of pentafluorophenyl carbanion by *t*BuOH or CH acid gave rise to another anion derived from the proton donor. These anions enter into nucleophilic substitution reactions with C_6F_5Cl and C_6F_5H, displacing fluorine chiefly in the *para* position, though minor amounts of *ortho* isomers were also detected (Scheme 2). This reaction consumes [*t*BuO]⁻ anion quantitatively, since the total yields of the products containing the *t*BuO group and of the products derived from the protonation of pentafluorophenyl carbanion are approximately the same (about 50 %).[d] The total yield of substitution products with $[CH_2CN]^-$ and $[PhC(Et)CN]^-$ carbanions is considerably smaller and does not exceed 20 %, indicating the operation of yet another reaction pathway where carbanions are consumed. The same is true for the transformations of the $[C_6F_5]^-$ carbanion, the observed yield of chloroperfluoropolyphenyls being usually three to seven times lower than of Fp_2 (Table 1), while according to the reaction balance [Eq. (a)] it should not be less than half[d, e] of the yield of Fp_2.

Several conclusions may be drawn from the results of anion scavenging experiments. a) The substitution of chlorine for the Fp group does not involve direct attack of the carbonylmetallate nucleophile on carbon; this rules out the S_N2Ar mechanism. Strictly speaking it should not be referred to as a nucleophilic substitution reaction. b) Pentafluorophenyl carbanion is proved to be the essential intermediate in the formation of the chlorine substitution product, C_6F_5Fp. c) The overall reaction scheme must consist of at least two steps, the first one, producing $[C_6F_5]^-$ carbanions, the same for all products formed in the following step(s). Halogen–metal exchange (HME) as the first step of the reaction (reaction A, Scheme 3) appears to be the only plausible choice, provided the alternative of a radical reaction pathway is positively excluded. It should be pointed out that double electron transfer could also produce $[C_6F_5]^-$ carbanions.

On the electron-transfer mechanism: Outer-sphere electron transfer (ET) from FpK to C_6F_5Cl does not seem feasible considering the large difference between the redox potentials of the reactants ($E^{Red}_{C_6F_5Cl/C_6F_5Cl^{\bullet-}} = -2.02$ V,[7] $E^{\circ}_{Fp^-/Fp^\bullet} = -1.16$ V[23]). The ET rate constant ($k < 10^{-4}\,L\,mol^{-1}\,s^{-1}$) calculated from Eberson formulae based on Marcus–Hush theory[24] is strongly underestimated, as the reaction happens within the time of mixing even at −100 °C.

The effect of radical scavengers on the product composition was carefully examined. Secondary phosphines are good hydrogen-atom donors and their use is well established in the detection of the radical steps in various nucleophilic substitution reactions;[25] we utilised *i*Pr_2PH and *t*Bu_2PH to intercept $C_6F_5^\bullet$ radicals. The product distribution data for these experiments summarised in Table 3, and the high yield of C_6F_5Fp in particular, imply that $C_6F_5^\bullet$ is not involved in the reaction (entries 2,3, Table 3). It seems somewhat puzzling that even a slight increase in the yield of C_6F_5Fp was observed in comparison with the standard experiment. An increased amount of C_6F_5H is also formed while the proportion of chloroperfluoropolyphenyls is reduced in the presence of the secondary phosphine (entries 2,3, Table 3); however, it is not clear whether this results from radical or anion trapping.

The ability of tertiary phosphines to intercept metal carbonyl radicals, even when they are formed as short-lived intermediates, arises from facile ligand substitution typical of these species.[26] When the reaction was performed in the presence of PEt_3 (entry 4, Table 3) the primary organometallic products remained the same, yet the yield of C_6F_5Fp was distinctly lower and a variety of additional, presumably phosphine-substituted products were formed, though each in trace amount. Judging from ^1H, ^{19}F and ^{31}P NMR spectra of the reaction mixture the majority of the new products are not dimeric iron carbonyls but belong to the $[Ar_FFe(L_x)Cp]$ type. Taking into account that the starting carbonylmetallate [26a, c] and the reaction products are inert towards phosphine substitution, we have to admit that $Fp^\bullet$ radicals are formed as intermediates in a certain step of at least one of the reaction

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[d] Relative to the amount of FpK entering in the reaction.

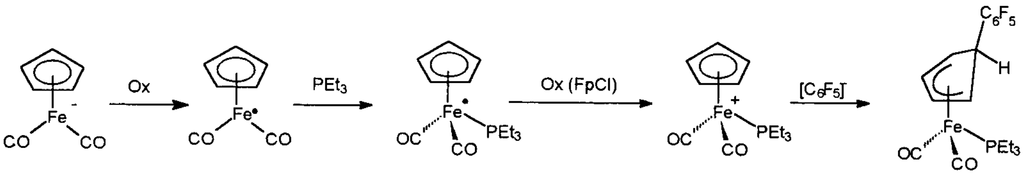
[e] For example, if only $C_6F_5C_6F_4Cl$ is formed its stoichiometric yield should be 100 %.

Table 3. The effect of radical traps on the course of the reaction of C_6F_5Cl with FpK in THF at room temperature.

Entry	Reactants and reaction conditions[a]		Relative yields [%][b]			
	Trap	Ratio $\nu(C_6F_5Cl)/\nu(Fp^-)$	C_6F_5Fp	Fp_2	$C_6F_5(C_6F_4)_nC_6F_4Cl$ $(n = 0-3)$	C_6F_5H
1	–	1.25	57	43	11	2.5
2	iPr$_2$PH (9 equiv)	1.11	71	29	–	11
3	tBu$_2$PH (13 equiv)	1.40	65	35	3	9
4	Et_3P[c] (4 equiv)	1.11	35	48	3	4

[a] The initial concentrations of reactants were 0.03–0.09 M. [b] Concerning the determination and calculation of the product yields see footnote [b] to Table 1. [c] The yield of $[\{\eta^4\text{-}C_6F_5C_5H_5\}Fe(CO)_2PEt_3] \approx 5\,\%$ and the yields of other Cp-containing products $\approx 12\,\%$.

pathways. The only isolated and identified product containing phosphine was $[\{\eta^4\text{-}(C_6F_5)C_5H_5\}Fe(CO)_2PEt_3]$ (yield 5%). Complexes of this type have recently been obtained with high yield in the three-component reaction of FpHal, RLi and R_3P,[27] and adopting the mechanism proposed[28] the formation of the complex in our case is described in Scheme 4. The detection of such a complex provides extra evidence for HME in the reaction.



Scheme 4. Mechanism of the formation of $[\eta^4\text{-}(C_6F_5C_5H_5)Fe(CO)_2PEt_3]$, based on ref. [28]. The oxidant Ox is other than C_6F_5Cl.

Thus, experiment not having confirmed the hypothesis of a radical reaction pathway producing $[C_6F_5]^-$ carbanions, the following discussion will be based on the framework of the HME mechanism (Scheme 3).

The halogen–metal exchange mechanism: Nucleophilic aromatic substitution by an HME mechanism is rather uncommon; the few examples known are limited to the reactions of metal-centred nucleophiles with nonactivated halobenzenes, where the S_N2Ar substitution mechanism is unfeasible. Thus, for the reactions of the Me_3Sn^- anion with halobenzenes the mechanism with halogen transfer in the solvent cage as a key step was established by Kuivila et al.[29]

The effect of MeCN, similar to that observed in our study, has been reported in the reaction of another metal-centred nucleophile, $[Re(O)(R-C{\equiv}C-R)_2]^-$ (R = Et, Ph) with halobenzenes.[30] Instead of the σ-aryl rhenium complex observed in benzene solution, when the reaction was carried out in MeCN cyanomethyl complex $NCCH_2-[Re(O)(RC{\equiv}CR)_2]$ was formed with the equivalent amount of benzene.[30] The authors ascribed the effect to the interception of phenyl radicals by MeCN.[30] Probably these results may be reinterpreted in favour of phenyl anions being trapped by the solvent, taking into account the clear evidence obtained on this point in the current study of a similar reaction.

In reactions of both Me_3Sn^- and $[Re(O)(R-C{\equiv}C-R)_2]^-$ nucleophiles[29, 30] the leaving group effect is the opposite of that usually observed in nucleophilic aromatic substitution ($F \gg Cl,Br,I$), the reactivity of halobenzenes increasing in parallel with the ease of halogen transfer ($I > Br \gg Cl > F$).[31] The HME mechanism now proposed for the reaction of Fp^- with C_6F_5Cl, can apparently be extended to other reactions of carbonylmetallates with halopolyfluoroaromatics, giving an insight into the reverse leaving-group effect that hitherto lacked adequate explanation.[2, 5–7] It is particularly remarkable that halopolyfluoroarenes are sufficiently activated to react according to an S_N2Ar mechanism,[6, 8, 14] though they can be metalated with certain halophilic reagents, such as alkyllithiums.[15, 31b]

The question concerning the origin of specific halophilic reactivity of metal-centred anions is certainly intriguing, but lies beyond the scope of our current study. At present one could refer to the HSAB principle[32] predicting the interaction of the soft base with the soft acid center, in our case the metal-centered anion with the halogen atom[31a] of the aryl halide. The higher energy of metal–halogen as compared to carbon–metal bonds may be also taken into consideration.[33] It was shown recently that even in *o*-nitroiodobenzene, representative of a typical S_N2Ar-reactive substrate, soft nucleophiles such as thiol anions attack not carbon but iodine atoms, the substitution product being possibly formed through this pathway.[34]

Scheme 3 summarises the reactions that can follow the initial HME step. It is important to note that in the halogen transfer process along with pentafluorophenyl carbanions an equivalent amount of FpCl should be generated. However, no FpCl was detected in the experiments when pentafluorophenyl carbanion was trapped with anion scavengers. Instead Fp_2 was formed almost quantitatively. We suppose that FpCl is formed only as an intermediate, and converted to Fp_2 in the rapid reaction with FpK (the reported value of the rate constant for the reaction of Fp^-PPN^+ with FpCl in MeCN is $10^3\,L\,mol^{-1}\,s^{-1}$[35]) which is assumed to follow the electron transfer (step **C** in Scheme 3).[26a, 35] The reported value of the rate constant for the reaction of Fp^-PPN^+ with FpCl in MeCN is $10^3\,l\,mol^{-1}\,s^{-1}$.[35] In our case $Fp^{\bullet}$ radicals should recombine predominantly in the solvent cage, since they are not trapped by triethylphosphine (entry 4, Table 3).

$$Fp^- + FpCl \xrightarrow[-\,Cl^-]{} [\,Fp^{\bullet}\ Fp^{\bullet}\,] \longrightarrow Fp_2 \qquad (2)$$

When the pentafluorophenyl carbanion is not captured by anion scavengers, reaction **C** competes with its coupling with FpCl [step **B** and Eq. (2)], thus decreasing the yield of C_6F_5Fp.

We expected to obtain FpCl as the final product in the experiment when FpK was added dropwise to the tenfold excess of C_6F_5Cl (entry 6, Table 2). The rates of the reactions of the anions Fp^- and $[C_6F_5]^-$ with C_6F_5Cl (**A** and **D** in Scheme 3) are increased, but the reactions consuming FpCl (**B** and **C**) are not affected. The fact that not even traces of FpCl could be detected in this experiment forces us to assume that the increase in the production rate of FpCl is not sufficient to counterbalance its disappearance. However, the product composition did change, the ratio of products C_6F_5Fp to Fp_2 decreasing almost threefold and the yield of chloroperfluoropolyphenyls, especially *p*-$ClC_6F_4C_6F_5$, considerably increasing (entry 6, Table 2). These results point to the role of C_6F_5Cl as an anion scavenger. The interception of the pentafluorophenyl anion by C_6F_5Cl (reaction **D**, Scheme 3) competes with the reaction of the anion with FpCl (**B**). This conclusion is confirmed by the detection of Fp-substituted perfluoropolyphenyls in standard runs because it obviously indicates that chloroperfluoropolyphenyls are formed in the reaction when Fp^- is still present, that is, concurrently with C_6F_5Fp.

Thus, the first halogen transfer step of the reaction, common to all products formed (**A** in Scheme 3), appears to be rate-limiting, given the absence of FpCl among the products. The actual product distribution is determined in the subsequent rapid steps of the reaction (**B**, **C** and **D**). Each of the two exchange products, FpCl and $[C_6F_5]^-$, participates in a side reaction, **C** or **D** respectively, giving rise to Fp_2 and the reduction products of C_6F_5Cl. The fact that there are *two* reactions in competition with the reaction yielding C_6F_5Fp (reaction **B**) suggests a possible explanation of the solvent and counterion effects on the product ratio. We believe that the temperature effect has its origin in ion pairing and is related to the increase of the dielectric constant at lower temperatures (for THF $\varepsilon = 7.4$ at 25 °C and 11.6 at −70 °C[37]). Let us consider the following arguments: Ion pairing is known to decrease the reactivity of carbanions in nucleophilic aromatic substitution.[5a, 6, 36] On the other hand the reactions of carbonylmetallates with metal carbonyl halides or corresponding cationic complexes exhibit the reverse reactivity pattern: tight ion pairs react faster than free ions.[26a] No data is available concerning the effect of ion pairing in the reactions of carbanions with metal carbonyl halides (**B**, Scheme 3); however, let us speculate that it is less dramatic than in the competitive reactions **C** and **D**. As a result of strong ion pairing in the low-polarity solvent (Et_2O/THF) the reaction of FpCl with Fp^- (**C**) becomes the fastest in the competition, consuming almost all the FpCl initially formed. The fastest process in polar solvent or with bulky cations will be the interception of $[C_6F_5]^-$ anion by C_6F_5Cl (**D**), where it prevails over the production of C_6F_5Fp. On the other hand it may be that in these conditions the reaction of FpCl with $[C_6F_5]^-$ anion may itself produce a substantial amount of Fp_2 instead of C_6F_5Fp. That the highest yield of C_6F_5Fp was obtained in THF indicates that all competitive pathways are relatively slow in the solvent of medium polarity.

Conclusion

In the reaction of pentafluorochlorobenzene with the carbonylferrate anion, nucleophilic substitution of chlorine and aryl halide reduction are not competing pathways. All of the observed transformations take place in the framework of a single mechanism. Halogen transfer between aryl halide and metal-centred anion, generating pentafluorophenyl carbanion, is proposed as the key step of the entire process. Investigation of the reactions of other carbonylmetallates ($[Re(CO)_5]^-$, $[Mn(CO)_5]^-$, etc.) with halopolyfluorobenzenes is currently in progress in an attempt to obtain further evidence to confirm the halogen–metal exchange mechanism, and to estimate the scope of this unusual reactivity. The question concerning the mechanism of the reactions of carbonylmetallates with perfluoroarenes is of particular interest in the context of the characteristic ion-pairing effect in these reactions.

Experimental Section

A vacuum-line technique was used for handling carbonylferrate and carbanion salts. All other air-sensitive compounds, such as neutral metal carbonyl derivatives, were handled in a vacuum or under argon with Schlenk techniques. Argon was purified by passage through oxygen scavenger and 4 Å molecular sieve columns.

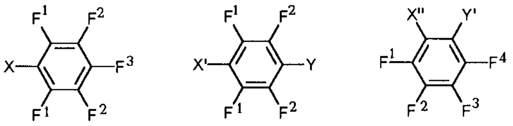
Solvents and reagents: All solvents were distilled from an appropriate drying agent. MeCN, [D$_3$]MeCN and [D$_6$]DMSO were vacuum-transferred from the sodium salt of 9-benzylfluorene; THF, [D$_8$]THF and Et_2O from sodium benzophenone ketyl. $(Me_3Si)_2O$, C_6F_5Cl, $C_6H_5CF_3$, 18-crown-6-ether were fractionally distilled prior to use. Carbonylferrate dimer (Fp_2) was purified according to the previously described method.[17] Bis(diphenylphosphinoiminium) chloride (PPN^+Cl^-) and LiCl were dried in vacuum (10^{-2} Torr) at 120–140 °C for 1.5 h.

Break-seal ampoules were used for the transfer of substances. Volatile reagents and standards were degassed and vacuum-transferred from the appropriate drying agent: C_6F_5Cl, C_6F_6, $(Me_3Si)_2O$, C_6H_6, PEt_3 and $C_6H_5CF_3$ from sodium mirror, *i*Pr_2PH and *t*Bu_2PH from P_2O_5, *t*BuOH from *t*BuOK, Ph(Et)CHCN from NaH. The ^{19}F NMR spectrum of C_6F_5Cl agrees with that reported in the literature.[38] Small volumes (< 0.5 mL) of the reagents were placed in thin-walled glass phials that were evacuated and flame-sealed. For the low-temperature experiments C_6F_5Cl was dosed as THF solution.

Spectroscopic methods and reaction mixture analysis: ^1H (400 MHz) and ^{19}F (376.3 MHz) NMR spectra were obtained on a Varian VXR-400 spectrometer at room temperature. The chemical shifts δ for ^1H NMR spectra were reported relative to TMS and referred to the signals of the internal reference standards, either $(Me_3Si)_2O$ ($\delta = 0.05$) or C_6H_6 ($\delta = 7.27$). ^{19}F NMR chemical shifts δ were reported in ppm downfield from $CFCl_3$ relative to signals of the internal reference standards C_6F_6 ($\delta = -162.9$) or $C_6H_5CF_3$ ($\delta = -61.5$). The routine analysis of the reaction mixtures was performed by NMR spectroscopy in undeuterated solvents, in which case ^1H NMR spectra were recorded using long pulse delay (PD $\leq$ 7 s) and short impulses (PW = 1 μs). We observed that pulse delay variation (1–30 s) has no impact on the relative integral intensity of the signals in ^{19}F NMR spectra. The yields of the products were calculated separately from ^1H and ^{19}F NMR spectra by comparison of the integral intensity of corresponding signals, Cp groups in particular, to that of the internal standard (one of the above listed). If no fluorine standard was added, then the signal of C_6F_6 impurity in C_6F_5Cl was used for the chemical shift reference in ^{19}F NMR spectra and the product yields were calculated relative to that of C_6F_5Fp, determined from the ^1H NMR spectrum.

IR spectra were recorded on a UR-20 spectrophotometer in 0.2 mm CaF_2 cell. Mass spectra were recorded on a MS-890 spectrometer operating with

Table 4. Spectral data for the reaction products.



		Solvent	^1H NMR δ	^{19}F NMR δ[a]	IR $\tilde{\nu}_{C\equiv O}$ [cm^{-1}]	MS m/z
Fp_2		THF	4.82(s)		1791(s), 1960(s), 1999(s)	
Fp_2		MeCN	4.80(s)			
FpCl		THF	5.12(s)			
FpCl		MeCN	5.05(s)			
X						
Fp		THF	5.11(s)	–105.38(F^1), –163.59(F^2), –161.18(t,F^3)	1999(s), 2042(s)	344 $[M]^+$, 316 ($[M-CO]^+$, 288 $[M-2CO]^+$, 268 $[M-2CO-HF]^+$, 232 $[C_6F_5Cp]^+$, 213 $[C_6F_5Cp-F]^+$, 194 $[C_6F_3Cp]^+$, 193 $[C_6F_3Cp-H]^+$, 168 $[C_6F_5H]^+$, 175 $[C_6F_2Cp]^+$, 174 $[C_6F_2Cp-H]^+$, 140 $[CpFe]^+$
Fp		MeCN	5.01(s)	–105.73(F^1), –163.90(F^2), –161.34(t, F^3)		
C_6F_4Cl		THF		–137.52, –137.91, –139.87, –161.11(F^2), –150.69(t, F^3)		350 $[M]^+$ (100%)
$(C_6F_4)_2Cl$		THF		–136.85, –136.93, –137.68, –139.67, –137.16, –160.98(F^2), –150.34(t, F^3)		498 $[M]^+$ (100%)
$(C_6F_4)_3Cl$		THF		–136.85, –136.93, –137.16, –137.68, –139.69, –160.98(F^2), –150.34(t, F^3)		646 $[M]^+$ (100%)
$(C_6F_4)_4Cl$		THF		–136.58, –136.77, –137.09, –137.64, –139.69, –160.96(F^2), –150.26(t, F^3)		794 $[M]^+$ (100%)
H		THF		–138.61(F^1), –162.57(F^2), –154.71(t, F^3)		
$[\{\eta^4\text{-}C_5H_5\}Fe(CO)_2PEt_3]$[b]		THF		–145.214 (F^1), –164.13(F^2), –159.84(t, F^3)	1918(s), 1976(s)	462 $[M]^+$, 434 ($[M-CO]^+$, 406 $[M-2CO]^+$, 344 $[M-PEt_3]^+$, 288 $[M-2CO-PEt_3]^+$, 268 $[M-2CO-PEt_3-HF]^+$, 232 $[C_6F_5Cp]^+$, 213 $[C_6F_5Cp-F]^+$, 194 $[C_6F_3Cp]^+$, 193 $[C_6F_3Cp-H]^+$, 168 $[C_6F_5H]^+$, 175 $[C_6F_2Cp]^+$, 174 $[C_6F_2Cp-H]^+$, 140 $[CpFe]^+$, 118 $[PEt_3]^+$
X′	**Y**					
Fp	H	THF	5.10	–107.30 (F^1), –140.78 (F^2)		
Fp	C_6F_4Fp	THF	5.17(s)	–106.55 (F^1), –141.39 (F^2)	1993(s), 2042(s)	650 $[M]^+$, 594 $[M-2CO]^+$, 538 $[M-4CO]^+$, 362 $[HC_6F_4C_6F_4Cp]^+$, 298 $[HC_6F_4C_6F_4H]^+$, 186 $[FeCp_2]^+$, 121 $[FeCp]^+$
Fp	$(C_6F_4)_2Fp$	THF	5.20(s)	–105.41 (F^1), –141.33 (F^2)		
Fp	$(C_6F_4)_3Fp$	THF	5.21(s)	–105.22 (F^1), –141.15 (F^2)		
Cl	CH_2CN	MeCN		–144.06, –147.50		
H	C(Ph)(Et)CN	THF		–137.00 (F^1), –137.70 (F^2)		
Cl	C(Ph)(Et)CN	THF		–135.89, –140.49		
H	*t*BuO	THF		–140.37 (F^1), –151.43 (F^2)		
Cl	*t*BuO	THF		–141.08 (F^1), –150.18 (F^2)		
X″	Y′					
Cl	*t*BuO	THF		–140.03 (dd, F^1), –158.62, –162.14 (t, F^2, F^3), –148.05 (F^4)		

[a] All signals are second-order multiplets except where noted otherwise. [b] ^{31}P NMR chemical shift for $[\{\eta^4\text{-}C_6F_5C_5H_5\}Fe(CO)_2PEt_3]$ is $\delta = 63$ relative to H_3PO_4 (external standard).

electron impact ionisation, 70 eV ionising energy, direct inlet method, with a source temperature of 150 °C.

General procedure for the reaction of Fp^- with C_6F_5Cl: FpK was obtained by reducing Fp_2 with $NaK_{2.8}$ alloy in THF according to the literature procedure;[10] the resulting anion solution was then filtered through a fine-pore glass filter. PPN^+Fp^- was prepared beforehand and FpLi was obtained in situ by the exchange reactions of FpK with PPN^+Cl^-[39] and LiCl accordingly. If necessary THF was replaced with another solvent. In the experiments from which the reaction products were isolated, 0.8–1.3 mmol of Fp^- was allowed to react with 0.9–2.0 mmol of C_6F_5Cl. When only NMR analysis was performed smaller amounts of Fp^- (0.11–0.17 mmol) and C_6F_5Cl (0.15–0.22 mmol) were used. In all of the experiments the substrate was in excess (15–50%); the concentration of Fp^- varied in the range of 0.03–0.13 mol L^{-1}. Various additives (18-crown-6, radical or anion trap), C_6F_5Cl, NMR standard(s) were introduced by breaking thin-walled glass phials containing these substances (usually in the sequence above). The solution was rapidly stirred by magnetic stir bar or by manual shaking of the apparatus at the moment when the substrate was added. The reaction proceeded instantly; the mixture immediately turned red/black in colour and turbid. After 10–20 min about 0.6–1 mL of the reaction mixture was filtered through Celite into the NMR sample tube fused to the apparatus, and deuterated solvent was added to the filtrate (≈ 0.2 mL of $[D_8]$THF or CD_3CN). The NMR sample tube was then frozen in liquid nitrogen and sealed off with flame. The apparatus was filled with argon and in some cases a sample was withdrawn for analysis by IR spectroscopy. In the preparative-scale experiments the remaining solution was transferred under argon pressure through a teflon hose to the column with a Celite filter. The solution was filtered into a round-bottomed flask and evaporated with silica gel at reduced pressure.

Isolation of the reaction products: The dry residue from the reaction of FpK (prepared from 236 mg, 0.667 mmol Fp_2) with C_6F_5Cl (396 mg, 1.96 mmol) in THF (31.2 mL) at RT was subjected to column chromatography on silica gel (40/100, $L = 15$ cm, $d = 1.5$ cm). Elution with petroleum ether produced a colourless band from which a mixture of chloroperfluoropolyphenyls (17.9 mg, ≈8%, approximate yield calculated for one aromatic ring) was obtained. Elution with CH_2Cl_2/petroleum ether (1:4) afforded two bright yellow bands. The first band after removal of the solvent afforded crude C_6F_5Fp (225 mg, 0.654 mmol, 49%). The second band consisted primarily of $Fp(C_6F_4)_nFp$ ($n = 2-5$, 10.0 mg, ≈2.5%, approximate yield calculated for one aromatic ring) contaminated with C_6F_5Fp. Elution with CH_2Cl_2/petroleum ether (1:1) gave a purple band from which Fp_2 (70.0 mg, 0.396 mmol, 30%) was obtained. Elution with Et_2O gave a brick-red band from which a red-brown solid (10.4 mg) was obtained, in which FpCl was found by TLC comparison with an authentic sample. Isolated substances were dried under vacuum. Individual homologues of chloroperfluoropolyphenyls were isolated and $Fp(C_6F_4)_nFp$ was purified by preparative-plate chromatography on Silpearl. Pure C_6F_5Fp was obtained by crystallisation from C_6H_6/hexane (1:1) at −30 °C.

Addition of reagents in reverse order: Solution of FpK (0.216 mmol) in THF (1.2 mL) was added dropwise (over 5 min) through a capillary to the rapidly stirred solution of C_6F_5Cl (2.10 mmol) in THF (3.2 mL). After complete mixing and addition of the NMR standard, part of the reaction mixture was transferred to an NMR sample tube. The apparatus was then filled with argon and a sample for IR spectroscopy was taken.

Product structure assignment: Spectra are presented in Table 4. All isolated compounds were characterised by ^1H and ^{19}F NMR spectroscopy and mass spectrometry. Metal carbonyl derivatives were also characterised by IR spectroscopy. The spectral properties of C_6F_5Fp,[40, 41] p-$FpC_6F_4C_6F_4Fp$,[40, 41] $[\{\eta^4\text{-}C_6F_5C_5H_5\}Fe(CO)_2PEt_3]$[27, 42] are in good agreement with the literature data for these or similar compounds.

A number of reaction products were not isolated, but identified as follows. Signals in ^{19}F NMR spectra of the reaction mixture corresponding to C_6F_5H and p-HC_6F_4Fp were identified by comparison with the spectrum of an authentic sample of C_6F_5H and the reported[40] spectrum of p-HC_6F_4Fp. The products resulting from the interaction of carbanions ($[CH_2CN]^-$, $[PhC(Et)CN]^-$) and $[t\text{BuO}]^-$ with C_6F_5Cl or C_6F_5H were identified similarly. To recognise their signals in the spectrum of the complex product mixture obtained in the reaction of FpK with C_6F_5Cl, separate test experiments were conducted. Carbanion salts were prepared by transmetalation of PhCH(Et)CN and MeCN with Ph_3CK. An excess of substrate was added to the carbanion or $[t\text{BuO}]^-$ solution in the appropriate solvent (THF or MeCN) and the ^{19}F NMR spectrum of the resulting solution was recorded. The signals of the major substitution products observed in the test experiments coincided with the signals in question to within 0.1 ppm. These products were assigned structures in accordance with general regularities of fluorine chemical shifts and coupling constants.[38, 40]

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