

REVIEW COMMENTARY

CARBONYLMETALLATES AND CARBANIONS IN AROMATIC AND VINYLIC NUCLEOPHILIC SUBSTITUTION

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The kinetic data on the reactions of carbonylmethylates $M'M(CO)_nL_m$, with polyfluorinated arenes and alkenes are reported. The behaviour of these transition metal anionic nucleophiles is compared with the reactivity of both carbanions, and non-transition metal centred anions.

1. INTRODUCTION

This paper considers the reactions of aromatic and vinyl nucleophilic substitution with anionic transition metal carbonyl complexes of the series $M'M(CO)_nL_m$ where $M(CO)_nL_m = Fe(CO)_2Cp$, $Re(CO)_5$, $W(CO)_3Cp$, $Mo(CO)_3Cp$, $Mn(CO)_5$ and $M' = K, Na, Li$. Although these nucleophiles have received adequate attention in aliphatic nucleophilic substitution, the data on their nucleophilic reactivity with unsaturated compounds is scarce or even lacking. The demand to bridge this gap is becoming vital, as such reactions may serve as key models for the study of a broad range of homogeneous catalytic processes of great importance both in industry and in laboratory-scale fine organic synthesis. Moreover, recent studies have shown that the products of such substitution, σ -aryl and σ -vinyl complexes of transition metals, possess very interesting properties which may allow their use as, e.g., valuable additives to motor fuels and lubricants and as flame retardants and antioxidants.

In our studies we have mainly used polyfluorinated arenes and alkenes, sometimes containing atoms of heavier halogens which allowed us to investigate the differences in the regiochemistry of substitution between various types of nucleophiles. In order to obtain evidence on mechanistic aspects of substitution, the kinetics were measured with special attention paid to the influence of the nature of the nucleophile, counterion and leaving group, and media effects.

We discovered that general trends in the nucleophilic reactivity of carbonylmethylates in the reactions under

study are altogether different from those observed in the otherwise identical reactions with more traditional nucleophiles, e.g. carbanions.

RESULTS AND DISCUSSION

Reactions of carbonylmethylates and other nucleophiles with electron-deficient aryl halides

Reactivity of carbonylmethylates in the reactions with perfluoroarenes

Although the reactions of several carbonylmethylates with reactive aryl halides such as hexafluorobenzene and perfluoropyridine have been reported, the yields observed in these reactions were poor (11–60%).¹ In order to perform a meaningful kinetic study, we first had to optimize the conditions of these reactions to achieve near to quantitative yields.

The reactivity of carbonylmethylates varies in a very broad range. Some of these anionic complexes resemble common carbanions in reactivity, whereas others are so highly reactive that they are often referred to as super-nucleophiles. Consequently, it is often impossible to measure experimentally the reaction rates for the whole range of both carbonylmethylates and substrates. For the most reactive pentafluoropyridine, kinetic measurements were done only for the least reactive $KW(CO)_3Cp$ and $KMn(CO)_5$ in THF at room temperature. For more reactive $NaRe(CO)_5$, the rate of reaction with less reactive hexafluorobenzene can be measured at 25 °C, whereas with supernucleophilic $KFe(CO)_2Cp$ even the rate of reaction with hexafluorobenzene was measured only at –52 °C (Table 1).²

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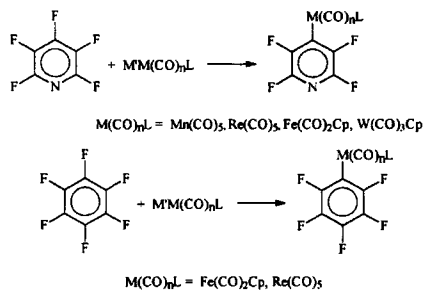
Table 1. Rate constants for reactions of carbonylmetallates with pentafluoropyridine and hexafluorobenzene^a

Reaction	Solvent	Additive, mol per mole of $M(\text{CO})_n\text{L}^-$	Counterion, M'	k_2 ($1 \text{ mol}^{-1} \text{ s}^{-1}$)
$M'\text{Mn}(\text{CO})_5 + \text{C}_5\text{F}_5\text{N}^b$	THF	—	K	8.8×10^{-3}
	THF	18-crown-6, 2	K	4.0×10^{-3}
	THF	HMPA, 20	K	1.23×10^{-3}
	THF	—	Ph_4As	0.65×10^{-3}
	Ether	—	K	130×10^{-3}
	THF	—	Li	0.62×10^{-3}
$M'\text{W}(\text{CO})_3\text{Cp} + \text{C}_5\text{F}_5\text{N}^b$	THF	—	Li	6.4×10^{-3}
	THF	HMPA, 20	K	8.45×10^{-2}
	THF	HMPA, 55	K	3.4×10^{-2}
	Ether	—	K	46.8×10^{-2}
$M'\text{Re}(\text{CO})_5 + \text{C}_6\text{F}_6^b$	THF	—	Na	2.15×10^{-1}
	THF	HMPA, 20	Na	1.25×10^{-1}
	THF	$\text{Ph}_4\text{AsClO}_4$, 1	Na	1.03×10^{-1}
	THF	Ph_4AsCl , 1	Na	1.12×10^{-1}
	Ether	—	Na	10.5×10^{-1}
	THF	NaBPh ₄ , 10	Na	3.05×10^{-1}
$M'\text{Fe}(\text{CO})_2\text{Cp} + \text{C}_6\text{F}_6^c$	THF	—	K	8.05×10^{-2}
	THF	HMPA, 20	K	1.75×10^{-2}
	THF	18-crown-6, 1	K	2.47×10^{-2}
	THF	18-crown-6, 2	K	2.16×10^{-2}
	THF	$\text{Ph}_4\text{AsClO}_4$, 1	K	1.53×10^{-2}
	Ether	—	K	480×10^{-2}
	THF	—	Li	23×10^{-2}
	THF	HMPA, 20	Li	1.70×10^{-2}

^a $[M(\text{CO})_n\text{L}^-]_0 = 1 \times 10^{-3} - 6 \times 10^{-2} \text{ M}$, $[\text{ArF}]_0 = 4.2 \times 10^{-3} - 6 \times 10^{-1} \text{ M}$.

^b At 25 °C.

^c At -52 °C.



All carbonylmetallates invariably showed a decrease in rate in the presence of solvating additives (HMPA or 18-crown-6 ether). The addition of salts such as Ph_4AsCl or $\text{Ph}_4\text{AsClO}_4$, which as a result of the counterion exchange help to form looser ion pairs and free ions, also retarded the reactions. On the other hand, unexpectedly, the addition of common ion salt or the use of a less polar ether in place of THF resulted in an increase in rates.

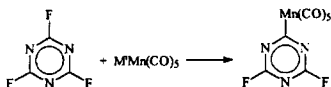
The influence of the counterion is more complex and is additionally affected by the nature of the carbonylmetallate. Thus, in the case of $M'\text{Mn}(\text{CO})_5$, the rate is lower for the lithium derivative than the potassium derivative, in perfect agreement with theoretical considerations, as lithium salts indeed usually prefer to form

looser solvent-separated ion pairs or even free ions owing to better solvation of the smaller lithium cation by basic solvents, whereas the salts of the large potassium cation usually form contact ion pairs in solution. However, in the case of carbonylferrate derivatives, the effect of the counterion is the opposite, as lithium salts were observed to react faster than potassium salts, which may be explained by the different behaviour of carbonylferrate salts in solution.* For both $\text{LiMn}(\text{CO})_5$

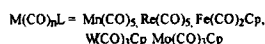
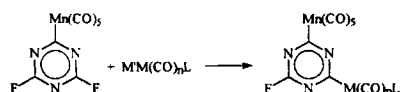
* The salts of carbonylmetallates exist as a mixture of solvent-separated and contact ion pairs in diethyl ether and similar solvents.³⁻⁸ For the range of concentrations typically used for kinetic measurements (*ca.* 10^{-2} M), $\text{NaMn}(\text{CO})_5$ predominantly forms contact ion pairs and $\text{NaW}(\text{CO})_3\text{Cp}$ or $\text{NaMo}(\text{CO})_3\text{Cp}$ almost exclusively form contact ion pairs. Data on pentacarbonylrhenates are lacking. $\text{LiMn}(\text{CO})_5$ occurs mostly as solvent-separated ion-pairs and free ions with less than 10% contact ion pairs present.⁵ In contact ion pairs of the aforementioned carbonylmetallates the counterion is bound to the oxygen atom of a carbonyl ligand.⁶⁻⁸ The carbonylferrates, however, reveal a different behaviour. Thus, for instance, $\text{LiFe}(\text{CO})_2\text{Cp}$ in THF solution forms contact ion pairs of two distinct sorts in which the cation is bound to either carbonyl oxygen or iron.⁷ In all cases the addition of solvating agents causes the transformation of contact ion pairs into solvent-separated ion pairs and further to free ions.

and Li Fe(CO)₂Cp salts the addition of HMPA leads to a rate decrease.

The same trends were observed in the reactions with 2-(4,6-difluoro-1,3,5-triazinyl)pentacarbonylmanganese which is readily formed by an extremely fast reaction of cyanuric fluoride with pentacarbonylmanganate salt.⁹

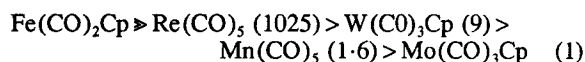


As a single pentacarbonylmanganese substituent makes this molecule less reactive, it turned out to be perfectly suited for kinetic measurements with the whole range of carbonylmetallates. All of the bimetallic substitution products were isolated in high yields (88–91%).



The third fluorine atom was unreactive under the conditions studied. Hence the measurement of reaction rates with this substrate (Table 2) allowed the determi-

nation of the relative reactivities for all carbonylmetallates. The observed reactivity order was shown to be identical with that reported earlier for S_N2 reactions of these nucleophiles with alkyl halides:^{10–12*}



Reactivity trends for the reactions of carbonylmetallates with this substrate were found to be the same as with other aryl fluorides, since the addition of solvating agents such as HMPA or 18-crown-6 ether retarded the reactions, whereas the use of less polar solvent diethyl ether resulted in a rate increase.

Thus, in the reactions of carbonylmetallates with perfluoroarenes, contact ion pairs turned out to be more reactive than solvent-separated ion pairs and free ions.

Reactivity of carbanions in nucleophilic aromatic substitution

Unusual reactivity trends observed in the reactions of carbonylmetallate nucleophiles obviously required a comparative study of more conventional nucleophiles, such as carbanions, in the same processes.

Nitroaryl halides are the most extensively studied models for kinetic studies of nucleophilic aromatic substitution. Some kinetic data on the reactions of these

Table 2. Rate constants for reactions of carbonylmetallates with 2-(4,6-difluoro-1,3,5-triazinyl)pentacarbonylmanganese^a

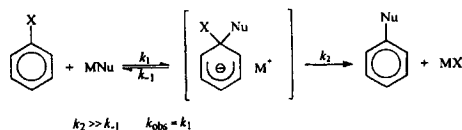
M'M(CO) _n L	Solvent	Additive, mol per mole of M(CO) _n L ⁻	Temperature (°C)	k ₂ × 10 ² (l mol ⁻¹ s ⁻¹)
KFe(CO) ₂ Cp	THF	—	-52	397
	THF	18-crown-6, 2		107
	THF	HMPA, 20		88
	Ether	—		Too high
LiFe(CO) ₂ Cp	THF	—	-18	580
	THF	HMPA, 20		89
NaRe(CO) ₅	THF	—	-18	820
	THF	HMPA, 20		298
	THF	Ph ₄ AsClO ₄ , 1		266
	THF	—		7.2
KW(CO) ₃ Cp	THF	—	-18	11.8
	THF	—	-12	1.27
KMn(CO) ₅	THF	—	-18	2.37
	THF	—	0	7.23
	THF	18-crown-6, 2	0	5.14
	THF	HMPA, 20	0	2.41
	THF	Ph ₄ AsClO ₄ , 1	0	2.12
	Ether	—	0	53.5
	THF	—	0	1.9
	THF	—	-18	0.78
LiMn(CO) ₅	THF	—	0	2.95
KMo(CO) ₃ Cp	THF	—	-18	0.78
	THF	—	0	2.95

^a [M(CO)_nL⁻]₀ = 2.3 × 10⁻³–20.5 × 10⁻³ M, [ArF]₀ = 2.6 × 10⁻³–26.4 × 10⁻³ M.

* Ph₃Sn (1.1 × 10⁸) > Fe(CO)₂Cp (7.0 × 10⁷) > PhS (2.6 × 10⁶) > Re(CO)₅ (2.5 × 10⁴) > W(CO)₃Cp (500) > Mn(CO)₅ (77) > Mo(CO)₃Cp (67) > Co(CO)₄ (1).¹⁰

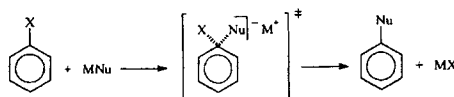
substrates with carbanions such as alkali metal salts of alkyl malonate, cyanoacetate and acetoacetate are available from the literature.¹³⁻¹⁸

These reactions are believed to proceed via the classical two-stage Bunnett-Miller mechanism, according to which rate-determining addition of nucleophile is followed by fast elimination of the leaving group.¹⁹⁻²²



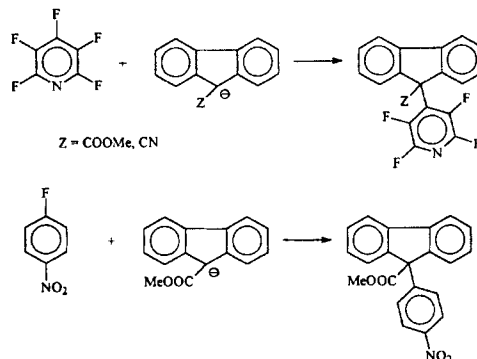
Although this mechanism is well supported by many kinetic and other data, in the case when halogen is the leaving group the corresponding 1,1- σ -anionic complexes have never been detected experimentally.

As the first stage of this mechanism is slow, the influence of the nature of the leaving group on the net rate of a given substitution reaction would reflect not the strength of the ruptured bond, but rather such factors as electronegativity. Indeed, for the reactions with a majority of common nucleophiles, which usually have an element of the second period of the Periodic Table (C, N, O) as the nucleophilic centre, the ease of substitution follows the order $\text{F} > \text{Cl} > \text{Br} > \text{I}$. However, a certain, although much smaller, number of substitution reactions are known to obey just the opposite trend, $\text{I} > \text{Br} > \text{Cl} > \text{F}$. Such a deviation is usually ascribed to either a change of the rate-determining step or the realization of a concerted $\text{S}_{\text{N}}2$ -like mechanism.^{23,24}



For the only example of the reaction with fluorenyl carbanions studied earlier, the order of the influence of the nature of leaving group closely resembled the normal trend $\text{F} > \text{Cl} \approx \text{Br} \approx \text{I}$.²⁵

We have undertaken a kinetic study of the reaction of potassium salts of 9-methoxycarbonylfluorene and 9-cyanofluorene with pentafluoropyridine, and of 9-methoxycarbonylfluorene with *p*-fluoronitrobenzene in THF solutions.^{26,27} These carbanion salts at the concentrations typically used for kinetic measurements predominantly form contact ion pairs (Table 3).²⁸



As 9-methoxycarbonylfluorenyl anion is more reactive than 9-cyanofluorenyl anion [in fair agreement with their relative acidity: $\text{p}K_{\text{a}}(9\text{-MeOCOFIH}) \approx 10$ and $\text{p}K_{\text{a}}(9\text{-NCFIH}) \approx 8^{29}$], it permits one to measure the kinetics of reaction of the former carbanion not only with pentafluoropyridine, but also with less reactive *p*-fluoronitrobenzene. Table 3 shows the second-order rate constants measured for these reactions, including the values obtained in the presence of 18-crown-6 ether, HMPA and an excess of NaBPh_4 as a common

Table 3. Rate constants for reactions of potassium salts of 9-fluorenyl anions with pentafluoropyridine and *p*-fluoronitrobenzene (THF, 20 °C)^a

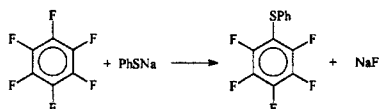
Reaction	Additive, mol per mole of carbanion	$k_2 \times 10^2$ ($\text{l mol}^{-1} \text{s}^{-1}$)
9-MeOCOFIK + $\text{C}_5\text{F}_5\text{N}$	—	1.37
	18-crown-6, 2	9.37
	18-crown-6, 1	8.8
	HMPA, 20	9.55
	NaBPh_4 , 10	1.00
	—	1.04
9-NCFIK + $\text{C}_5\text{F}_5\text{N}$	—	1.04
	18-crown-6, 1	6.75
	HMPA, 20	6.74
	NaBPh_4 , 10	0.57
9-MeOCOFIK + <i>p</i> - $\text{FC}_6\text{H}_4\text{NO}_2$	—	0.088
	18-crown-6, 2	0.467
	HMPA, 20	0.483
	NaBPh_4 , 10	0.049
	—	0.049

^a $[\text{R}^-]_0 = 2.3 \times 10^{-3} - 1.7 \times 10^{-2} \text{ M}$, $[\text{ArF}]_0 = 7.0 \times 10^{-3} - 2.3 \times 10^{-2} \text{ M}$.

ion salt. The reaction of pentafluoropyridine with 9-methoxycarbonylfluorene is 1.5 times faster than the reaction with 9-cyanofluorene. The rate constant for the reaction of 9-methoxycarbonylfluorene with *p*-fluoronitrobenzene is an order of magnitude smaller than that for the reaction of the same carbanion with pentafluoropyridine. The data in Table 3 also show that these reactions follow the reactivity pattern, i.e. free anions and solvent separated ion pairs react faster than contact ion pairs, which is common for nucleophilic reactions of carbanions. Thus, the addition of 18-crown-6 ether or HMPA leads to an increase in rate, whereas the addition of NaBPh₄ retards the reaction. However, in this case the differences in reactivity are less pronounced than in the alkylation of carbanions.³⁰

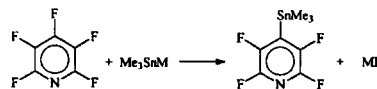
Reactivity of other heteroatom nucleophiles

In order to be able to establish whether the abnormal reactivity of carbonylmetallates is unique, the reaction of two highly reactive heteroatom nucleophiles, PhSNa and Me₃SnM (M = K or Li), with both pentafluoropyridine and hexafluorobenzene were studied.^{26,27} The reactivity of thiophenolate was shown to resemble that of carbanions and other normal nucleophiles, with free ions being more reactive than ion pairs (Table 4).



On the other hand, the behaviour of Me₃SnM, a species in which the nucleophilic centre is at a non-

transition metal, is similar to that of carbonylmetallates. As the reactivity of this nucleophile is extremely high, the kinetics of the reaction with pentafluoropyridine were studied in THF at a temperature as low as -52 °C.



For example, the lithium salt, which is dissociated to a greater extent than the potassium salt owing to better solvation of lithium cation by basic solvents, reacts more slowly than the latter.^{31,32} Again, the addition of solvating agents resulted in retardation whereas the addition of the respective common ion salt accelerated the substitution (Table 5).

Influence of the leaving group

Leaving group effects are commonly used in mechanistic considerations to distinguish between several possible mechanisms. We have studied the reactions of all kinds of nucleophiles used (9-XFIM, M'M(CO)_nL, PhSNa, Me₃SnM) with chloropentafluorobenzene. The regioselectivity of the reactions with this substrate turned out to be entirely different for normal and abnormal nucleophiles. The carbanions and thiolate anion substitute the fluorine atom at the *para* position to chlorine whereas all metal-centred nucleophiles, including carbonylmetallates and Me₃SnM, substitute exclusively the chlorine atom. These results agree with scarce literature data, as it was earlier shown that Mn(CO)₅⁻ is unreactive towards hexafluorobenzene,³³ but displaces bromide ion in the reaction with C₆F₅Br.

Table 4. Rate constants for reactions of PhSNa with hexafluorobenzene^a

Temperature (°C)	Additive, mol per mole of PhSNa	k_2 (1 mol ⁻¹ s ⁻¹)
-40	—	0.03
	NaBPh ₄ , 4	0.003
-78	—	0.001
	18-crown-6, 10	0.6

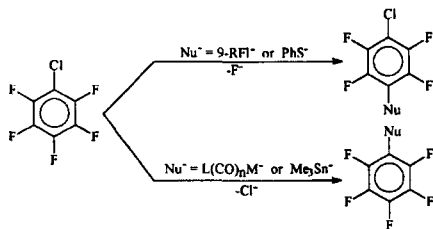
^a [PhSNa]₀ = 1.26 × 10⁻³–11.4 × 10⁻³ M, [C₆F₆]₀ = 4.02 × 10⁻³–35.8 × 10⁻³ M.

Table 5. Rate constants for reactions of Me₃SnM' with pentafluoropyridine^a

Counterion, M'	Additive, mol per mole of Me ₃ SnM'	$k_2 \times 10^2$ (1 mol ⁻¹ s ⁻¹)
K	—	93.0
	HMPA, 20	12.4
Li	—	12.4
	LiBPh ₄ , 10	98.3

^a [Me₃SnM']₀ = 1.7 × 10⁻³–4.6 × 10⁻³ M, [C₅F₅N]₀ = 8.2 × 10⁻³–12.2 × 10⁻³ M, -52 °C.

Methylate ion was shown to substitute only fluoride ion from *para* sites of C_6F_5Cl and C_6F_5Br .^{34,35}

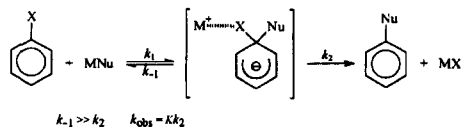


Thus the first group of nucleophiles behave exactly as required by classical aromatic nucleophilic substitution mechanism in which the nucleophile attacks preferentially the most electrophilic site at the rate-determining step, and therefore it is indeed fluoride ion which must be substituted. The second group of nucleophiles attacks the site with a better leaving group, which is chloride. Thus the leaving group effect observed for metal-centred nucleophiles can be regarded as extra evidence in favour of the realization of a non-classical substitution mechanism, in which the coordination of the counterion and the leaving group plays a major role.

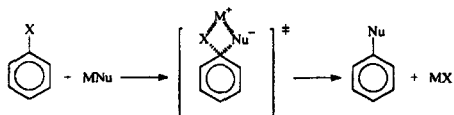
Possible mechanisms of substitution

As the classical mechanism of aromatic nucleophilic substitution fails to explain the anomalies in the reactions of organometallic nucleophiles, some other scheme must be applied. At least three mechanisms which involve interaction between the leaving group and the counterion in the rate-limiting step may be considered.

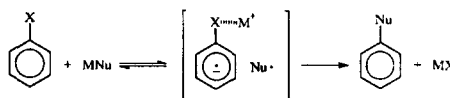
First we may assume only the changeover of the rate-limiting step in the frame of the classical mechanism. Possibly in this case, rupture of the C—Nu bond, i.e. the reverse elimination of an organometallic nucleophile from a σ -complex, is much faster than the rupture of the C—X bond. Hence, the counterion may lend electrophilic assistance for cleavage of the leaving group.



Another alternative is a concerted S_N2 -like process occurring with the frontal attack of nucleophile, in such a manner that carbon atom, leaving group, nucleophile and its counterion form a four-membered transition state. The interaction between the counterion and leaving group facilitates the substitution by lowering the energy of the transition state.



Finally, there is a possibility of a mechanism involving the one-electron reduction of arene by electron-rich organometallic anions leading to the formation of a transient anion radical. The coordination of the counterion and leaving group facilitates the cleavage of the anion radical intermediate and prevents the reverse electron transfer.



Certainly, correct discrimination between these possibilities is a far more involved task and is hardly achievable.

Electrochemical study of the reactivity of η^5 -cyclopentadienylcarbonylferrate in reactions with perfluoroarenes

The rates of very fast substitution reactions of $Fe(CO)_2Cp^-$ with C_6F_6 , C_6F_5Cl , C_6F_5Br and C_5F_5N were measured at room temperature in DMSO by applying the electrochemical method with a rotating ring-disk electrode.³⁶ The reaction rates decrease in the order $C_5F_5N > C_6F_5Br > C_6F_5Cl > C_6F_6 > C_6F_5H$ (cf. Table 6).

As was shown earlier, for C_6F_5Cl and C_6F_5Br the atoms being substituted are chlorine and bromine. The substitution in C_6F_5H is directed at the fluorine atom *para* to the hydrogen atom. It should be noted that the order of reactivity is different from the order of reduction potentials, which may be regarded as an argument against the single electron transfer mechanism. However, in this case the difference between the rates of reactions with different arenes is not high (by 5–10 times), probably because $Fe(CO)_2Cp^-$ is the most reactive anion of the series.

Reactions of carbonylmetalates with reactive olefins

Perfluorinated olefins readily react with carbonylmetalates giving the substitution products in high yields. We

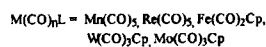
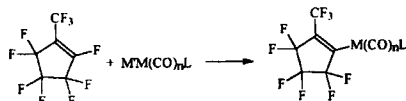
Table 6. Rate constants for reactions of $Fe(CO)_2Cp^-$ with fluorinated substrates estimated by electrochemical titration at diffuse layer, and the reduction half-wave potentials of the substrates^a

Substrate	$-E_{1/2}(ArX)$ (V)	k_2 ($l\ mol^{-1}\ s^{-1}$)
C_5F_5N	2.12	6.8×10^4
C_6F_5Br	1.89	5.98×10^4
C_6F_5Cl	1.98	2.79×10^4
C_6F_6	2.03	1.14×10^4
C_6F_5H	2.11	0.58×10^4

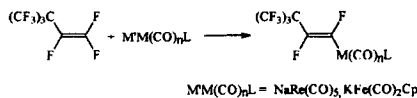
^a 20 °C, DMSO, Pt, 0.05 M Bu_4NBF_4 , Ag/AgCl. $[Fe(CO)_2Cp^-]_0 = 2 \times 10^{-3}$ M, $[ArF]_0 = 4 \times 10^{-4}$ M.

have studied the reaction of perfluoro-1-methylcyclopentene with several carbonylmethylates at low temperatures. In all cases only the vinylic atom of fluorine is selectively substituted.³⁷

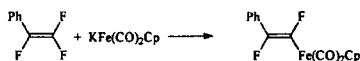
At room temperature, all carbonylmethylates under study, independently of their relative nucleophilicity, are oxidized by both perfluoro-1-methylcyclopentene and perfluoro-2-methylpent-2-ene, giving only the corresponding binuclear metal carbonyl complexes. For example, in the reaction with $\text{KFe}(\text{CO})_2\text{Cp}$, the complex $[\text{Fe}(\text{CO})_2\text{Cp}]_2$ was isolated in 73% yield. The lower the temperature, the smaller is the contribution of redox-process, giving way to nucleophilic substitution. All substituted products were obtained and isolated in high yields (77–90%).³⁷



Perfluoro-*tert*-butylethylene reacts with carbonylmethylates at -90°C in a highly selective manner. Only the fluorine atom at the *trans* site relative to the perfluoro-*tert*-butyl group is substituted.³⁸

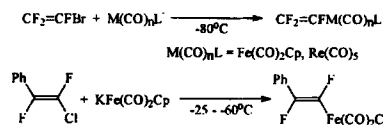


The reaction of $\text{KFe}(\text{CO})_2\text{Cp}$ with α,β,β -trifluorostyrene at -75°C is also selective, as the product of *trans* substitution was isolated in 80% yield. However, in this case up to 1.5% of the *cis* isomer is also formed, in addition to the dimeric carbonyl complex $[\text{Fe}(\text{CO})_2\text{Cp}]_2$.^{39*}

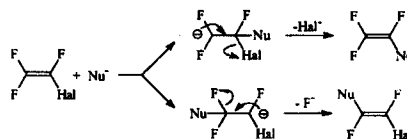


As in the case of aromatic substrates containing both fluorine and heavy halogens (Cl, Br), the problem of chemoselectivity also arises for fluorinated olefins with vinylic chlorine or bromine atoms. These atoms are preferentially substituted by carbonylmethylate

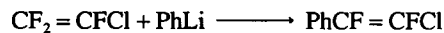
nucleophiles.^{40†}



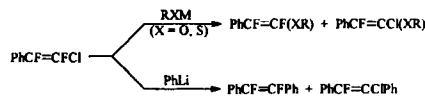
For the classical addition–elimination mechanism of vinylic nucleophilic substitution in unsymmetrical olefins, the nucleophile can attack either of the two vinylic carbons.



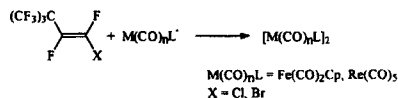
According to the literature data, fluoride ion is substituted in the reaction of phenyllithium with trifluorochloroethylene.



However, both chlorine and fluorine atoms are substituted in the reactions of β -chloro- α,β -difluorostyrene with phenyllithium, alkali metal alcoholates or thiolates.^{41,42}



For 1-chloroundecafluoro-2-*tert*-butylethylene and the corresponding bromide, no substitution products were obtained in the reaction with carbonylmethylates, even at low temperatures, while the binuclear carbonyl complexes were the only products isolated.³⁸

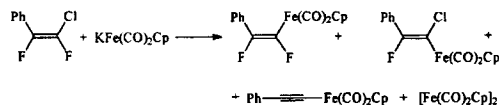


Unlike the *Z*-isomer, the *E*-isomer of β -chloro- α,β -difluorostyrene gave a complex mixture of products in the reaction with $\text{KFe}(\text{CO})_2\text{Cp}$. The relative amounts of different products were dependent on temperature,

* Two possible explanations for the formation of the binuclear complex may be given. The first and most evident is the redox process leading to the formation of radicals, which may undergo a recombination. The second explanation, applicable only to the substrates bearing heavy halogens besides fluorine, involves the nucleophilic (often referred to as halophilic) attack of the electron-rich iron nucleophile not at carbon, but at the halogen atom, leading to the formation of $\text{Fe}(\text{CO})_2\text{CpHal}$, which in turn may react with $\text{Fe}(\text{CO})_2\text{Cp}^-$ to give the binuclear complex.

† At higher temperatures, the formation of the binuclear complex $[\text{Fe}(\text{CO})_2\text{Cp}]_2$ is also observed. For example, at room temperature the ratio of substitution product to $[\text{Fe}(\text{CO})_2\text{Cp}]_2$ is 77:23. The addition of solvating agents which facilitate the dissociation of salts results in an increase in the yield of substitution product at the expense of $[\text{Fe}(\text{CO})_2\text{Cp}]_2$, as even at room temperature in the presence of 18-crown-6 ether the yield of the substitution product becomes almost quantitative. On the other hand, the factors decreasing the dissociation, e.g. the use of the less polar ether in place of THF, result in a dramatic increase in unwanted dimerization.

which is indicative of the situation when several concurrent pathways are realized.³⁹



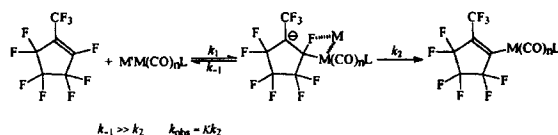
Reactivity of carbonylmetallates in vinylic nucleophilic substitution

Kinetic measurements were performed on three fluoroolefins: perfluoromethylcyclopentene, β,β,α -trifluorostyrene and (*Z*)- β -chloro- α,β -difluorostyrene.

The first substrate is highly reactive towards carbonylmetallates even at low temperatures. The complexes of tungsten and manganese were the most convenient for this purpose, as the rates of reactions with iron and rhenium complexes were too high to allow for measurement. The kinetic data are gathered in Table 7. The observed kinetic trends were in general very close to those observed for aromatic substitution. Thus, the addition of 18-crown-6 ether or HMPA resulted in a rate decrease, whereas the use of diethyl ether in place of THF gave a significant acceleration of substitution.³⁷

By analogy, it can be suggested that these reactions

proceed by an addition-elimination mechanism with slow second step at which the leaving group is eliminated. The assistance of a counterion facilitates the cleavage of the carbon-halogen bond in the intermediate. The possibility of a concerted S_N2 -like process with frontal attack of nucleophile seems much less probable. As in most cases the formation of binuclear complexes arising as a result of one-electron oxidation of nucleophile is not observed, the single electron transfer mechanism is also unlikely in these reactions.



However, α,β,β -trifluorostyrene and (*Z*)- β -chloro- α,β -difluorostyrene showed an entirely different behaviour. The addition of 18-crown-6 ether accelerated the reactions, whereas both common ion salt and less polar solvent resulted in a retardation, although the effect was not large. Thus, in these cases, the reactions with free ions are apparently faster than the reactions with ion pairs (Table 8). These trends are in fair agreement with the classical addition-elimination mechanism with the

Table 7. Rate constants for reactions of carbonylmetallates with perfluoro-1-methylcyclopentene^a

M'M(CO) _n L	Solvent	Additive, mol per mole of M(CO) _n L ⁻	Counterion, M'	k ₂ (l mol ⁻¹ s ⁻¹)
M'W(CO) ₃ Cp ^b	THF	—	K	2.86
	THF	18-crown-6, 2	K	1.08
	THF	HMPA, 20	K	0.80
	Ether	—	K	Too high
M'Mn(CO) ₅ ^c	THF	—	K	4.90
	THF	18-crown-6, 2	K	2.70
	THF	HMPA, 20	K	2.15
	THF	—	Li	0.42
	Ether	—	K	>50

^a [M(CO)_nL⁻]₀ = 2 × 10⁻³–8.4 × 10⁻³ M, [olefin]₀ = 2.1 × 10⁻³–7.5 × 10⁻³ M.

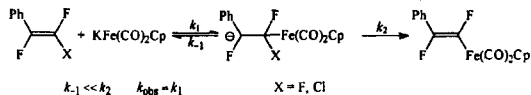
^b At -84 °C.

^c At -70 °C.

Table 8. Rate constants for reactions of KFe(CO)₂Cp with α,β,β -trifluorostyrene (1) and β -chloro- α,β -difluorostyrene (2)

Substrate	Solvent	Additive, mole per mole of KFe(CO) ₂ Cp	Temperature (°C)	k ₂ (l mol ⁻¹ s ⁻¹)
1	THF	—	-75	1.6
	THF	18-crown-6, 2		9.0
	THF	KBPh ₄ , 3		1.2
	THF-ether (1:2)	—		0.15
2	THF	—	-25	0.37
	THF	18-crown-6, 2		3.2
	THF	KBPh ₄ , 3		0.19
	THF-ether (1:2)	—		0.065

first slow step, in which the nucleophile adds to a double bond to form the intermediate carbanion.³⁹



The higher reactivity of α,β -trifluorostyrene ($k_2 = 1.6 \text{ l mol}^{-1} \text{ s}^{-1}$ at -75°C) as compared to Z- β -chloro- α,β -difluorostyrene ($k_2 = 0.37 \text{ l mol}^{-1} \text{ s}^{-1}$ at -25°C) provides extra evidence in favor of the classical mechanism. The preferential elimination of chloride here has a simpler explanation than in the case of pentafluorochlorobenzene, as in the intermediate carbanion of vinylic substitution mechanism both halogens are available for elimination from the same carbon atom, while chloride is a far better leaving group than fluoride.

It remains unclear why a change of olefin causes a change in mechanism in the reaction with carbonylmetallates. The mechanism of substitution turned out to be very sensitive to the nature of the nucleophile and substrate, and also to the conditions. Possibly the different behaviour of these olefins is associated either with their different electrophilicity or with the different stability of the carbanion intermediate. Further investigations targeted at gaining more data on these complex phenomena are under-way.

EXPERIMENTAL

The salts or carbanions and carbonylmetallates were obtained using a standard vacuum line technique from the corresponding CH-acids and binuclear complexes. The kinetic runs were performed in a purified argon atmosphere. The samples of reaction mixtures were withdrawn and analysed after work-up on the content of halide ions using the respective ion-selective electrodes. For the reactions with carbanion salts, kinetic measurements were also performed by measuring the optical absorbance of the carbanion with a UV-visible spectrophotometer. In all cases the kinetics were treated using the second-order rate equation. The second-order rate plots were linear up to nearly quantitative conversions. All reaction products were preparatively isolated and characterized by microanalyses, IR and NMR spectroscopy.

Electrochemical measurements were performed using an SVA-1B-M voltammetric system at stationary and rotating platinum and mercury film electrodes with an exposed surface area of 11.8 mm^2 in anhydrous DMSO and acetonitrile at 20°C with $0.05 \text{ M } n\text{-Bu}_4\text{NBF}_4$ as a supporting electrolyte in an argon atmosphere. The geometric parameters of the rotating ring-disk electrode were: disc radius $r_1 = 2.57 \text{ mm}^2$, ring inner radius $r_2 = 2.65 \text{ mm}^2$ and ring outer radius $r_3 = 3.68 \text{ mm}^2$. The counter-electrode in all experiments was platinum the

reference electrode was aqueous $\text{Ag}/\text{AgCl}/\text{KCl}$. Cyclic voltammograms were recorded with scan rates of 50, 100, 200 and 500 mV s^{-1} and at a rotating electrode at a scan rate of 20 mV s^{-1} . The electrode rotation speed varied from 480 to 3450 min^{-1} .

ACKNOWLEDGEMENT

Financial support from the Russian Fund of Fundamental Research is gratefully acknowledged.

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