

Nucleophilicity of metal carbonyl anions in vinylic substitution reactions

Petr K. Sazonov^{a*}, Galina A. Artamkina^a and Irina P. Beletskaya^{a*}



Second order rate constants are reported for the reactions of metal carbonyl anions ($[M(CO)_nL]^-$) with several vinyl halides: $PhCCl=C(CN)_2$, *Z*- and *E*- $Ph(CN)C=CHHal$ ($Hal = Cl, Br$) which follow the addition–elimination (Ad_NE) substitution mechanism. The obtained data show that the nucleophilic reactivity of $[M(CO)_nL]^-$ anions towards vinyl halides increases in the same order as in aliphatic S_N2 reactions, but much more steeply, by 14 orders of magnitude in the row $\log\{k_{[M(CO)_nL]^-}/k_{[CpMo(CO)_3]^-}\}$: $[CpFe(CO)_2]^-$ (~14), $[Re(CO)_5]^-$ (7.8), $[Mn(CO)_5]^-$ 2.1, $[CpW(CO)_3]^-$ (0.7) > $[CpMo(CO)_3]^-$ (0). A good correlation exists between nucleophilicities of $[M(CO)_nL]^-$ anions towards vinyl (sp^2 -carbon) and alkyl halides (sp^3 -carbon) with slope 2.7. The reactivity of $[M(CO)_nL]^-$ in a halogen–metal exchange process (with *Z*- $PhC(CN)=CHI$) follows a similar 'large' scale as in the Ad_NE process. The nucleophilicity of $[M(CO)_nL]^-$ anions correlates better with their one-electron oxidation potentials (E_{ox}) than with their basicity (pK_a of $[M(CO)_nL]H$). Copyright © 2008 John Wiley & Sons, Ltd.

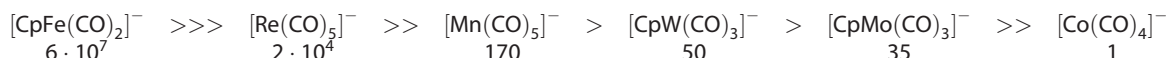
Supplementary electronic material for this paper is available in Wiley InterScience at <http://www.mrw.interscience.wiley.com/suppmat/0894-3230/suppmat/>

Keywords: nucleophilicity; metal carbonyl anions; S_NV ; nucleophilic vinylic substitution; reaction mechanisms

INTRODUCTION

The studies of aliphatic nucleophilic substitution reactions by C.K. Ingold laid the foundations of physical organic chemistry and the

characterized both by a remarkably high reactivity of $[CpFe(CO)_2]^-$ anion, often called a 'supernucleophile', and a very broad reactivity span between $[CpFe(CO)_2]^-$ and the least reactive $[Co(CO)_4]^-$ which exceeds seven orders of magnitude:



problem of nucleophilic reactivity has been an area of close interest ever since.^[1] An important landmark in this field was the constant selectivity relationship ($\log(k/k_0) = N^+$) discovered by Ritchie for the nucleophile addition reactions to stabilized carbocations.^[2] Later it was shown that the Ritchie relationship also describes the nucleophilicity in the reactions with other π -acceptors, such as carbonyl compounds, activated alkenes,^[3] transition metal π -complexes^[4] and even in nucleophilic aromatic substitution.^[5] Recent progress in the field is associated with the works of Mayr et al., who demonstrated that a nucleophile-specific selectivity factor has to be considered for an accurate description of all π -electrophile–nucleophile combinations. Using the proposed equation $\log k = s_N \cdot (N + E)$ ^[6] they have quantified the reactivity of a great number of nucleophiles (and π -electrophiles) of various classes and activity.^[7–10] Quite recently it has been shown that the nucleophilicity in aliphatic S_N2 reactions can also be described by the N parameters provided that the electrophile-specific selectivity factor ($s_E = 0.6$) is incorporated into the equation: $\log k = s_E \cdot s_N \cdot (N + E)$.^[7]

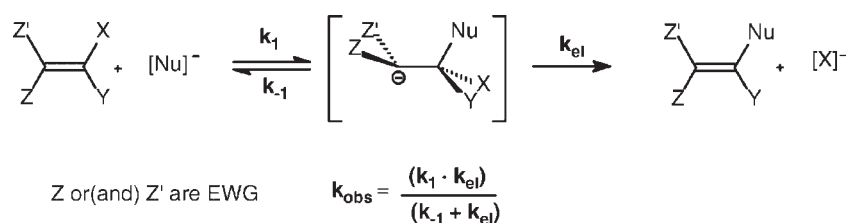
Metal carbonyl anions represent a family of useful and easily accessible model metal-centre nucleophiles.^[11] Their nucleophilicity was studied in aliphatic S_N2 reactions by Dessy et al.,^[12] Pearson and Figgore^[13] and later Atwood and co-workers.^[14] It is

(Averaged data from Reference^[12,13]. Data for $[CpFe(CO)_2]^-$ taken from Reference^[11]).

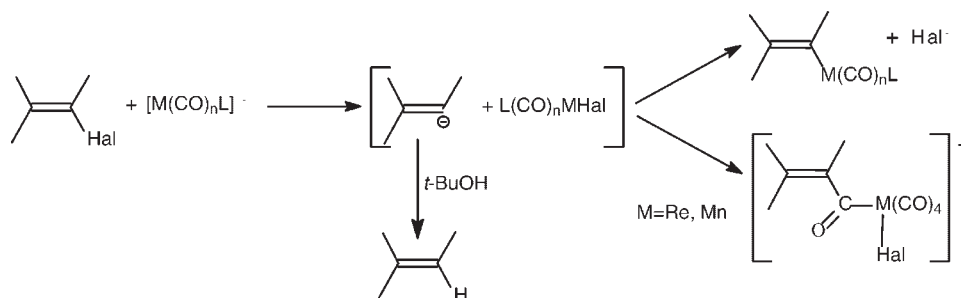
In our studies of nucleophilic vinylic substitution reactions^[15–18] we became increasingly aware that the differences in reactivity between metal carbonyl anions are much greater than found in aliphatic S_N2 reactions. The reactivity differences (vide infra) were so large that we could not compare all the metal carbonyl anions in the reactions with a single vinyl halide. Data for iron and rhenium carbonylates were obtained with α,β,β -trifluorostyrene, weakly nucleophilic carbonylates of manganese, tungsten and molybdenum had to be compared in the reactions with a highly electrophilic α -chlorobenzylidenemalononitrile. Bridging these two reactivity series turned out to be a most difficult task, and was finally achieved by comparing $[Re(CO)_5]^-$ and $[Mn(CO)_5]^-$ in the reactions with β -halo- α -phenylacrylonitriles ($Hal = Cl, Br, I$).

* Chemistry Department, M.V. Lomonosov Moscow State University, Leninskie Gory 1, Moscow 119992, Russian Federation.
E-mail: petr@elorg.chem.msu.ru

a P. K. Sazonov, G. A. Artamkina, I. P. Beletskaya
Chemistry Department, M.V. Lomonosov Moscow State University, Leninskie Gory 1, Moscow 119992, Russian Federation



Scheme 1. The addition–elimination (Ad_NE) mechanism of nucleophilic vinylic substitution



Scheme 2. The halogen–metal exchange (HME) mechanism of nucleophilic vinylic substitution

A comparison of reactivity makes sense only if the reactions under consideration follow the same mechanism. This is particularly true of the nucleophilic vinylic substitution reactions in view of a large diversity of possible mechanisms.^[19] However, in the reactions with metal carbonyl anions the choice is usually between two alternative pathways, addition–elimination (Ad_NE Scheme 1) and halogen–metal exchange (HME). The first one (Ad_NE) is the most common pathway of substitution in vinyl halides activated with β-EWG.^[20–22]

The HME pathway (Scheme 2) comes into play for the substrates with ‘heavier’ halogen leaving groups (Br, I and sometimes even Cl), with substituents stabilizing the vinyl carbanion (e.g. polyfluorinated) and steric hindrance to the attack of nucleophile at the double bond.^[18]

Reactions we used for the comparison of nucleophilicity do not follow the HME mechanism, which is evident from

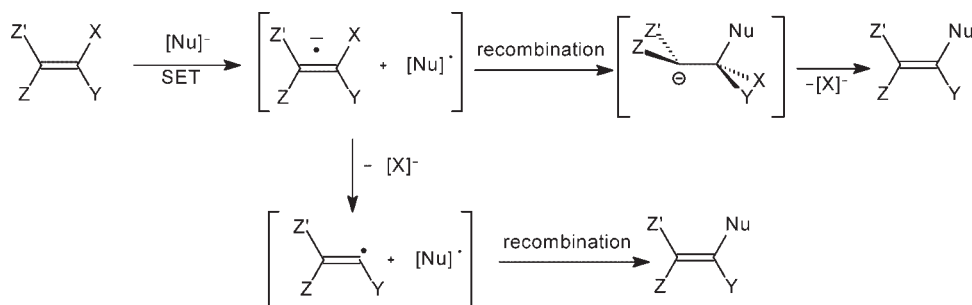
- high yield of σ-vinyl complexes as products, which does not become lower in the presence of ‘anion traps’. Anion traps protonate the vinyl carbanions, the formation of nucleophilic substitution products in case of HME mechanism (Scheme 2);

- formation of σ-vinyl complexes instead of halo(acyl)rhenate complexes in the reactions with [Re(CO)₅]Na, which is characteristic of HME mechanism (Scheme 2);

In our opinion, they can be interpreted in the framework of Ad_NE mechanism (Scheme 1). The observed retention of *Z/E*-configuration of the starting vinyl halide is consistent with this mechanism and indicates that the σ-adduct intermediate is very short lived, or even does not exist.^[20,23,24] (In this latter case, a one-step nucleophilic substitution with a transition state resembling a σ-adduct would occur.) The vinyl halides we have used are activated with β-EWG and have been shown previously to react via Ad_NE mechanism with other nucleophiles such as amines or thiolates.^[25–27]

The possibility of an alternative single-electron transfer (SET) pathway should not be overlooked (Scheme 3), especially since metal carbonyl anions are potent reducing agents.^[28] Similarly a SET-version may be drawn for HME pathway.

There is, however, no experimental evidence of a pathway involving free radicals. Reactions follow second order kinetics without inductive period, the yield of nucleophilic substitution products is high and no homocoupling or protodehalogenation



Scheme 3. The single-electron transfer (SET) mechanism of nucleophilic vinylic substitution

Table 1. The observed rate constants (k_{obs}) for the reaction of $[\text{CpFe}(\text{CO})_2]\text{K}$ and $\text{Re}(\text{CO})_5\text{Na}$ with α,β,β -trifluorostyrene (**1**), β -chloro- α,β -difluorostyrene (**1-Cl**)^[15,16] and perfluoro-3,3-dimethyl-1-butene (**2**)^[17]

$ \begin{array}{c} \text{R} \\ \diagup \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{F} \quad \text{F} \\ \text{Hal} \end{array} + [\text{M}(\text{CO})_n\text{L}] \text{M}' \xrightarrow{\text{THF}} \begin{array}{c} \text{R} \\ \diagup \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{F} \quad \text{F} \\ \text{M}(\text{CO})_n\text{L} \end{array} + \text{M}'\text{Hal} $ 1 R=Ph, Hal=F 1-Cl R=Ph, Hal=Cl 2 R=(CF ₃) ₃ C, Hal=F						
Vinyl halide						
Entry		R	Hal	$[\text{M}(\text{CO})_n\text{L}]\text{M}'$	T (°C)	k_{obs} (L · mol ⁻¹ · s ⁻¹) ¹
1	1	Ph	F	$[\text{CpFe}(\text{CO})_2]\text{K}$	-75	1.6
2	1	Ph	F	$[\text{CpFe}(\text{CO})_2]\text{K}$	-23	30
3	1-Cl	Ph	Cl	$[\text{CpFe}(\text{CO})_2]\text{K}$	-23	0.37
4	1	Ph	F	$[\text{Re}(\text{CO})_5]\text{Na}$	+21	0.00020
5	2	(CF ₃) ₃ C-	F	$[\text{Re}(\text{CO})_5]\text{Na}$	+21	0.0012
6	2	(CF ₃) ₃ C-	F	$[\text{Mn}(\text{CO})_5]\text{K}$	+21	≤10 ⁻⁷

products are formed (Supplementary material). When the reactions are monitored by ¹H NMR, no CIDNP effects are observed. Retention of vinyl halide *Z/E*-configuration is not consistent with a radical anion intermediate either. When the reactions of **1**, **1-Cl** or **2** with $[\text{CpFe}(\text{CO})_2]\text{K}$ were performed with the electrochemical one-electron reduction of the vinyl halide, mixtures of *Z*- and *E*-isomers of the substitution products were formed.^[29]

RESULTS AND DISCUSSION

The first set of reactivity data given in Table 1 were obtained for the reactions with trifluorovinyl derivatives (**1**) and (**2**). Reactions with $[\text{CpFe}(\text{CO})_2]\text{K}$ were very fast even at -75°C, and the reaction rate could be measured only for the less reactive trifluorostyrene (entries 1,2). Substitution of one β -fluorine in trifluorostyrene for chloride (in **1-Cl**) lowers the reactivity by two orders of magnitude (entry 3). This 'element effect' ($k_{\text{F}}/k_{\text{Cl}} \gg 1$) provides additional support for the Ad_NE mechanism.^[20]

In contrast, reactions of **1** and **2** with $[\text{Re}(\text{CO})_5]\text{Na}$ were slow at room temperature (entries 4, 5), and even the more reactive substrate **2** did not react with $[\text{Mn}(\text{CO})_5]\text{K}$ (entry 6). Only an estimate of $[\text{CpFe}(\text{CO})_2]\text{K}$: $[\text{Re}(\text{CO})_5]\text{Na}$ reactivity ratio could be obtained by the extrapolation to 21°C of the $[\text{CpFe}(\text{CO})_2]\text{K}$ data (k_{obs} at -75°C and -23°C) according to Arrhenius equation. This gives the $k_{[\text{CpFe}(\text{CO})_2]\text{K}} \sim 2 \times 10^2 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ at 21°C and $k_{[\text{CpFe}(\text{CO})_2]\text{K}}/k_{[\text{Re}(\text{CO})_5]\text{Na}} \sim 10^6$ which is nearly three magnitudes higher than observed in aliphatic S_N2 reactions.^[12]

α -Chlorobenzylidenemalononitrile (**3**) belongs to the highly electrophilic vinyl halides that can react with moderately weak nucleophiles, such as anilines.^[26,27] In the reactions of **3** with carbonylmetalates the nucleophilic substitution products are formed quantitatively. Their formation is not suppressed in the presence of *t*-BuOH – a negative test result for the HME mechanism (Scheme 2).

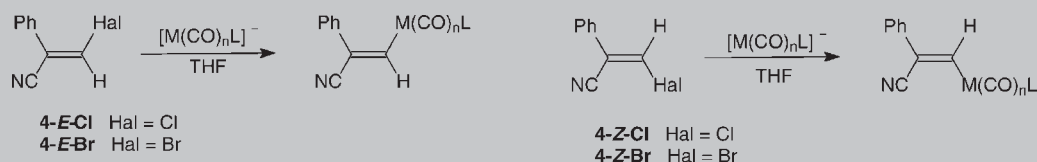
The reactivity difference between the metal carbonyl anions in the reaction with **3** (Table 2) is significantly larger than in aliphatic S_N2 reactions ($[\text{Mn}(\text{CO})_5]^-$ (**5**) > $[\text{CpW}(\text{CO})_3]^-$ (**1.4**) >

$[\text{CpMo}(\text{CO})_3]^-$ (**1**)^[12–14]), although the order of reactivity is retained. The four-fold difference between $[\text{CpW}(\text{CO})_3]^-$ and $[\text{CpMo}(\text{CO})_3]^-$ is particularly notable, since these anions have very similar steric requirements and almost the same reactivity in aliphatic S_N2 reactions.

β -Halo- α -phenylacrylonitriles (**4**, Hal = Cl, Br, I) proved to be especially useful models. Both *Z*- and *E*-isomers of **4-Cl** and **4-Br** (Hal = Cl, Br) gave the σ -vinyl complexes with quantitative yields. Reaction with *Z* or *E* isomers of **4** gave in each case only one isomer of substitution product. We assume that this result indicates retention of *Z/E* configuration of the starting vinyl halide. The assignment of *Z/E* configuration of the products is supported by the lower ν_{CN} in the IR spectra of *E*-isomers of the products in accordance with the literature data on β -substituted α -phenylacrylonitrile derivatives.^[25] It is also supported by the results of DFT calculations of the vibrational frequencies in the corresponding products. The geometry assignment is also confirmed by chemical shift of vinyl protons in the ¹H NMR spectra, which are observed in higher field for the *E*-isomers of the products, the same as in the starting vinyl halides. Anyway, it

Table 2. The observed rate constants (k_{obs}) for the reaction of α -chlorobenzylidenemalononitrile (**3**) with metal carbonyl anions ($[\text{M}(\text{CO})_n\text{L}]\text{M}'$), THF, 22°C

$ \begin{array}{c} \text{CN} \quad \text{Ph} \\ \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{CN} \quad \text{Cl} \end{array} + [\text{M}(\text{CO})_n\text{L}] \text{M}' \xrightarrow{\text{THF}} \begin{array}{c} \text{CN} \quad \text{Ph} \\ \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{CN} \quad \text{M}(\text{CO})_n\text{L} \end{array} + \text{M}'\text{Cl} $		
$[\text{M}(\text{CO})_n\text{L}]\text{M}'$	k_{obs} (L · mol ⁻¹ · s ⁻¹) ¹	Reactivity ratio
$[\text{Re}(\text{CO})_5]\text{Na}$	Too fast	—
$[\text{Mn}(\text{CO})_5]\text{K}$	30	170
$[\text{CpW}(\text{CO})_3]\text{K}$	0.7	4
$[\text{CpMo}(\text{CO})_3]\text{K}$	0.17	1

Table 3. The observed rate constants (k_{obs}) for the reaction of β -halo- α -phenylacrylonitriles (**4**, Hal = Cl, Br) with metal carbonyl anions ($[\text{M}(\text{CO})_n\text{L}]^-$), THF, 22°C

Vinyl halide

	Hal	$[\text{M}(\text{CO})_n\text{L}]^-$	k_{obs} ($\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$)	Reactivity ratios
4-Z-Cl	Cl	$\text{Re}(\text{CO})_5\text{Na}$	350	$5 \times 10^5:1$
4-Z-Cl	Cl	$\text{Mn}(\text{CO})_5\text{K}$	0.0007	
4-E-Cl	Cl	$\text{Mn}(\text{CO})_5\text{K}$	0.0028	
4-E-Cl	Cl	$[\text{CpW}(\text{CO})_3]\text{K}$	0.00010	28:1
4-Z-Br	Br	$\text{Mn}(\text{CO})_5\text{K}$	0.011	
4-Z-Br	Br	$[\text{CpW}(\text{CO})_3]\text{K}$	0.0013	
4-Z-Br	Br	$[\text{CpMo}(\text{CO})_3]\text{K}$	0.00016	170:5:1
4-E-Br	Br	$\text{Mn}(\text{CO})_5\text{K}$	0.04	
4-E-Br	Br	$[\text{CpW}(\text{CO})_3]\text{K}$	0.0011	
4-E-Br	Br	$[\text{CpMo}(\text{CO})_3]\text{K}$	0.00024	

is highly unlikely that reaction with activated vinyl halide such as **4** will proceed with complete inversion of configuration.

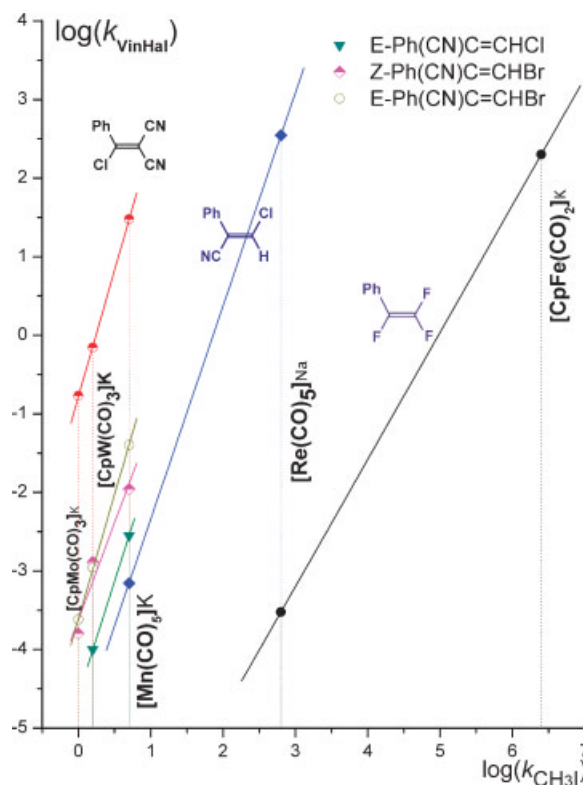
Anion trap (*t*-BuOH) had no effect on the course (and rate) of the reactions with **4**-Br (both *Z*- and *E*-isomers).

The observed rate constants summarized in Table 3 again show a very large difference in reactivity between manganese, tungsten and molybdenum carbonylmetallates, similar to those observed in the reactions with **3**. More importantly, the rate constant for the reaction of **4**-Z-Cl with $[\text{Re}(\text{CO})_5]\text{Na}$ allows to compare its reactivity with that of less reactive carbonylmetallates. The $[\text{Mn}(\text{CO})_5]\text{K}:[\text{Re}(\text{CO})_5]\text{Na}$ reactivity ratio is 1:500 000, which may be compared to 1:120 ratio typical for aliphatic $\text{S}_{\text{N}}2$ reactions.^[13,14]

Both *Z* and *E*-isomers of **4**-Br turned out to be more reactive than the corresponding chlorides **4**-Cl. The intermolecular element effect $k_{\text{Br}}/k_{\text{Cl}}$ reaches 15, the highest value observed so far in $\text{Ad}_{\text{N}}\text{E}$ nucleophilic vinylic substitution reactions. Typically $k_{\text{Br}}/k_{\text{Cl}}$ lie in the range 0.6–7,^[20] the maximum value of 11 having being reported by Rappoport, Shaiyana and co-workers.^[24]

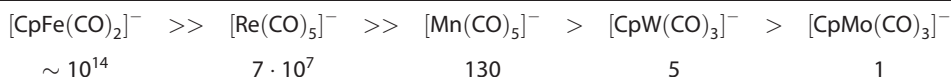
The great difference between the reactivity span of carbonylmetallates in aliphatic $\text{S}_{\text{N}}2$ and vinylic $\text{Ad}_{\text{N}}\text{E}$ substitution reactions is shown visually in Fig. 1, where the observed $\log(k_{\text{VinHal}})$ values are plotted against $\log(k_{\text{CH}_3\text{I}})$. It can be seen that the lines for all the vinyl halides except the trifluorostyrene have almost the same and rather steep slope varying from 2.5 to 3.2. The slope for trifluorostyrene (reactions with $[\text{CpFe}(\text{CO})_2]\text{K}$ and $[\text{Re}(\text{CO})_5]\text{Na}$) is lower (1.7) but still much higher than unity.

A similar selectivity observed for the reactions of **3**, **4**-Cl and **4**-Br with manganese, tungsten and molybdenum carbonylmetallates allows one to average the corresponding reactivity ratios. Taking into account the $[\text{Re}(\text{CO})_5]\text{Na}:[\text{Mn}(\text{CO})_5]\text{K}$ ratio (5×10^5) from the reaction with **4**-Z-Cl and $[\text{CpFe}(\text{CO})_2]\text{K}:[\text{Re}(\text{CO})_5]\text{Na}$ ($\sim 10^6$) ratio from the reaction with **1**, the following ranking of

**Figure 1.** The observed rate constants $\{\log(k_{\text{VinHal}})\}$ for the reaction of metal carbonyl anions with vinyl halides plotted against the rate constants with methyl iodide $\{\log(k_{\text{CH}_3\text{I}})\}$.^[13,14]

metal carbonyl anions reactivity in Ad_NE nucleophilic vinylic substitution reactions is obtained ($k_{[M(CO)_nL]M'}/k_{[CpMo(CO)_3]K}$):

reactivity of ordinary nucleophiles in Ad_NE vinylic substitution reactions usually increases in the same (or slightly larger)



It is shown graphically in Fig. 2. A good linear correlation with slope 2.16 is observed between $\log \{k_{[M(CO)_nL]M'}/k_{[CpMo(CO)_3]K}\}$ and $\log (k_{CH_3I})$ for all the data ($r = 0.992$), which improves ($r = 0.9996$, slope 2.75) if the data point for the $[CpFe(CO)_2]K$ (reaction with trifluorostyrene) is excluded. Such steep slopes are uncommon for the reactions of ordinary carbon, nitrogen or sulphur nucleophiles with the same (or similar) vinyl halides. The

proportion as in aliphatic S_N2 reactions, that is, the slopes are near or slightly above unity. The different slopes make the comparison of $[M(CO)_nL]^-$ anion nucleophilicity to that of ordinary nucleophiles ambiguous, the reactivity order being dependent on the reference substrate. However, the $[CpFe(CO)_2]^-$ anion still holds the lead, confirming its 'supernucleophile' status, as can be seen from the following rankings:

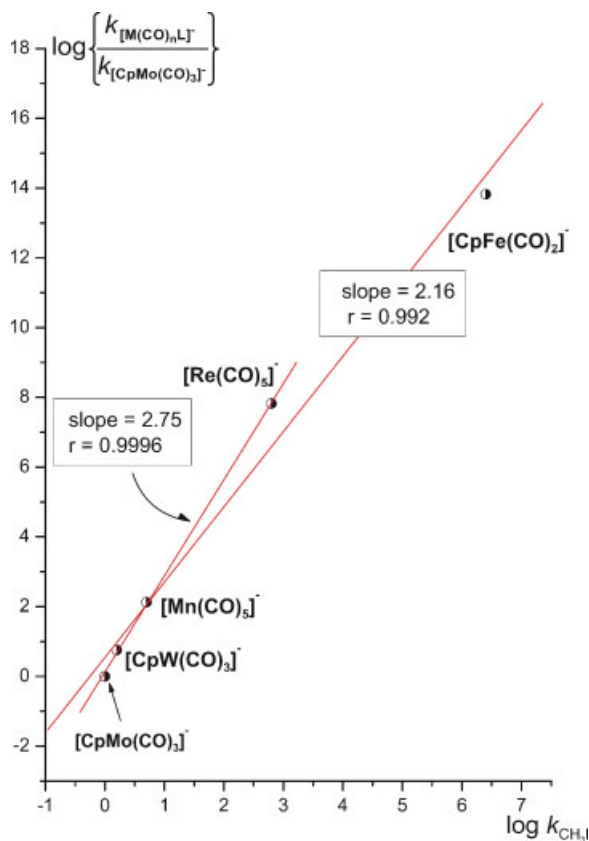
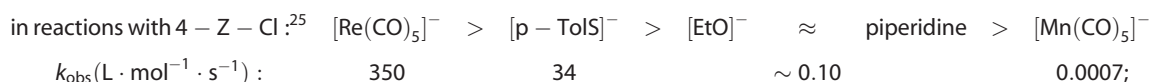
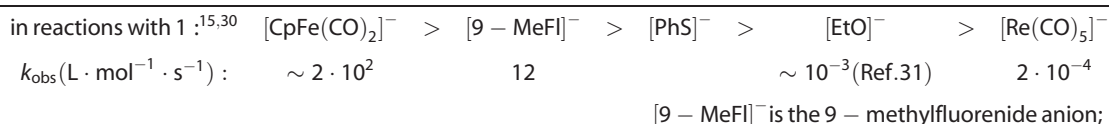


Figure 2. Correlation between the nucleophilicity of metal carbonyl anions in Ad_NE vinylic substitution reactions $\{\log(k_{[M(CO)_nL]M'}/k_{[CpMo(CO)_3]K})\}$ and S_N2 aliphatic nucleophilic substitution $\{\log(k_{CH_3I})\}$. This figure is available in colour online at www.interscience.wiley.com/journal/poc

The relative magnitude of nucleophilicity changes in different reactions can be compared through the corresponding Brønsted β_{Nuc} values. In the reaction of 9-substituted fluorenyl carbanions with trifluorostyrene (**1**) the slope of the Brønsted plot ($\beta_{Nuc} = 0.37$)^[32] is almost the same as in S_N2 reactions of these carbanions ($\beta_{Nuc} = 0.35$).^[32,33] The ratio of reactivity of morpholine and piperidine in reactions with **4-Cl**^[25] and the *p*-nitro analogue of **3**^[26] allows one to estimate $\beta_{Nuc} = 0.3-0.35$. These values fall in the range quite normal for aliphatic S_N2 reactions. Similar β_{Nuc} values are estimated for the *p*-MeC₆H₄S⁻ and *p*-ClC₆H₄S⁻ pair in reactions with **4-Cl**.^[25] While the nucleophilicity of metal carbonyl anions poorly correlates with their basicity (Fig. 3), the reactivity differences found in nucleophilic vinylic substitution with metal carbonyl anions (Fig. 2) correspond to β_{Nuc} values which are 2.16–2.75 times higher than in aliphatic S_N2 reactions, that is, β_{Nuc} about unity.

However, unusually high Brønsted β_{Nuc} values were observed in nucleophilic vinylic and aromatic substitution with weak soft nucleophiles in highly activated systems. Values of β_{Nuc} higher than unity (up to 1.4) have been recently reported for the reactions of 4-nitrobenzofurazan derivatives with 4-substituted anilines.^[34] Analysis of earlier published literature data^[27] on the reactions of anilines with α -halo(*p*-dimethylaminobenzylidene) malononitriles also gives high β_{Nuc} values that are about unity.

One should bear in mind the importance of rate-limiting stage of the Ad_NE substitution mechanism for the interpretation of the nucleophilicity data. The observed rate constants reflect the nucleophilicity of metal carbonyl anions ($k_{obs} = k_1$) as long as the first (addition) stage is rate limiting. But if it is not, the observed rate constant becomes composite (Scheme 1) and in the extreme case $k_{-1} \gg k_{el} \Rightarrow k_{obs} = \frac{k_{-1}}{k_{-1} + k_{el}} \cdot k_{el} = K \cdot k_{el}$ will reflect the thermodynamic affinity (equilibrium, *K*) of the nucleophiles. *A priori* metal carbonyl anions should be good

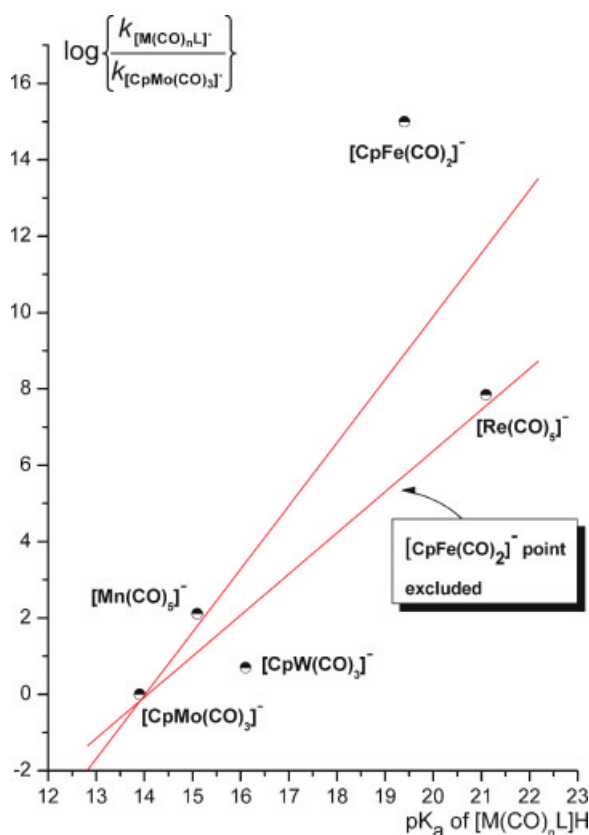


Figure 3. Correlation between the nucleophilicity of metal carbonyl anions in $\text{Ad}_\text{N}\text{E}$ vinylic substitution reactions $\{\log(k_{[\text{M}(\text{CO})_n\text{L}]^-}/k_{[\text{CpMo}(\text{CO})_3]^-})\}$ and their basicity $\{\text{p}K_\text{a} \text{ of } [\text{M}(\text{CO})_n\text{L}]\text{H}\}$.^[43] This figure is available in colour online at www.interscience.wiley.com/journal/poc

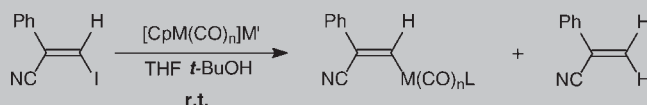
leaving groups (though their nucleofugality has never been quantified), however, it seems highly unlikely that they would be better leaving groups than chloride or bromide ions, and the condition of the rate-limiting addition $k_{-1} \ll k_\text{el}$ probably holds true for the studied systems. Yet, the alternative possibility, cannot be completely ruled out.

Vinyl halides with heavier halogens ($\text{Hal} = \text{Br}$ and I , but sometimes even Cl) can react with metal carbonyl anions via the HME mechanism (Scheme 2).^[18] While no indications of HME were found in the reactions with *Z*- and *E*-isomers of 4-Br, the corresponding iodide **4-Z-I** reacted with metal carbonyl anions by two competing pathways $\text{Ad}_\text{N}\text{E}$ and HME. In the presence of anion trap (*t*-BuOH) **4-Z-I** gave mixtures of substitution ($\text{Ad}_\text{N}\text{E}$) and protodehalogenation products (Table 4), the latter resulting from the protonation of the vinyl carbanion generated by HME. The carbanionic adduct intermediate in the $\text{Ad}_\text{N}\text{E}$ process is not protonated by *t*-BuOH most probably because of its low basicity. In the reaction with $[\text{Re}(\text{CO})_5]\text{Na}$ the HME is evident even without the anion trap by the formation of halo(acyl)rhenate complex instead of the 'normal' substitution product (Scheme 4). The vinyl carbanions generated by HME attack $\text{Re}(\text{CO})_5\text{Hal}$ at the coordinated CO instead of the metal centre.^[18]

Nucleophilic substitution products, $\text{Z-Ph}(\text{CN})\text{C}=\text{CHM}(\text{CO})_n\text{L}$, are formed primarily by the $\text{Ad}_\text{N}\text{E}$ pathway, since their yields do not change much in the presence of *t*-BuOH.

Surprisingly, the fraction of HME products grows up with the increase of metal carbonyl anion nucleophilicity from $[\text{CpMo}(\text{CO})_3]\text{K}$ to $[\text{Re}(\text{CO})_5]\text{Na}$ (Table 4). It means that the reactivity of $[\text{M}(\text{CO})_n\text{L}]^-$ in the HME process increases even more steeply than in $\text{Ad}_\text{N}\text{E}$ reactions (Fig. 4). However, the differences in HME/ $\text{Ad}_\text{N}\text{E}$ ratio are much smaller than the overall increase in reactivity from $[\text{CpMo}(\text{CO})_3]\text{K}$ to $[\text{Re}(\text{CO})_5]\text{Na}$. So, the overall result is that reactivity of metal carbonyl anions in HME and $\text{Ad}_\text{N}\text{E}$ reactions

Table 4. The observed rate constants (k_obs) and product ratios in the reactions of *Z*- β -iodo- α -phenylacrylonitrile (**4-Z-I**) with metal carbonyl anions ($[\text{M}(\text{CO})_n\text{L}]\text{M}'$), THF, 22 °C



$[\text{M}(\text{CO})_n\text{L}]\text{M}'$	Yields of (%)		% of HME ^a	k_obs ($\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$)	Reactivity ^b of $[\text{M}(\text{CO})_n\text{L}]\text{M}'$ in HME
$[\text{Re}(\text{CO})_5]\text{Na}$	60 ^c	≤ 2	97	Too fast	$\sim 1 \times 10^{10\text{d}}$
$[\text{Mn}(\text{CO})_5]\text{K}$	30	50	40	0.02	300
$[\text{CpW}(\text{CO})_3]\text{K}$	8	75	10	0.003	10
$[\text{CpMo}(\text{CO})_3]\text{K}$	12	65	15	0.0002	1

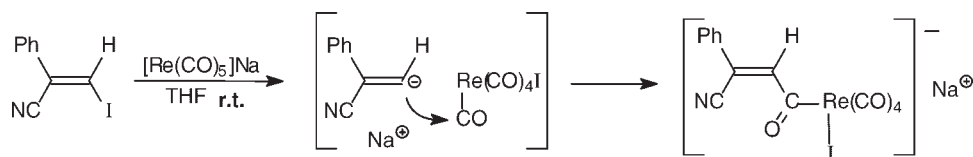
^a The percent of HME is calculated from the ratio of the yield of HME product ($\text{Ph}(\text{CN})\text{C}=\text{CH}_2$) to the total product yield.

^b Calculated as $k_\text{HME}^{[\text{M}(\text{CO})_n\text{L}]\text{M}'} / k_\text{HME}^{[\text{CpMo}(\text{CO})_3]\text{K}}$, where $k_\text{HME} = k_\text{obs} \cdot (\% \text{ of HME}) / 100$.

^c Without *t*-BuOH 65% of halo(acyl)rhenate $[\text{Z-Ph}(\text{CN})\text{C}=\text{CH}(\text{CO})\text{Re}(\text{CO})_4]\text{Na}$ is formed.

^d k_HME calculated from the reactivity ratio in the $\text{Ad}_\text{N}\text{E}$ reaction ($k_\text{AdNE}^{[\text{Re}(\text{CO})_5]\text{Na}} / k_\text{AdNE}^{[\text{Mn}(\text{CO})_5]\text{K}}$) with 4-Z-Cl:

$$k_\text{HME}^{[\text{Re}(\text{CO})_5]\text{Na}} = \frac{k_\text{AdNE}^{[\text{Re}(\text{CO})_5]\text{Na}}}{k_\text{AdNE}^{[\text{Mn}(\text{CO})_5]\text{K}}} \cdot \frac{(1 - \% \text{HME})^{[\text{Mn}(\text{CO})_5]\text{K}}}{(1 - \% \text{HME})^{[\text{Re}(\text{CO})_5]\text{Na}}} \cdot \frac{\% \text{HME}^{[\text{Re}(\text{CO})_5]\text{Na}}}{100} \cdot k_\text{obs}^{[\text{Mn}(\text{CO})_5]\text{K}}$$



Scheme 4. The HME mechanism of the halo(acyl)rhenate formation.

follows a similar scale in spite of the entirely different mechanisms and reaction centres involved (sp^2 -carbon *vis* halogen).

As can be seen from Fig. 5 nucleophilicity of metal carbonyl anions better correlates with their one-electron oxidation potentials (E_{ox})^[28] than with their basicity (Fig. 3). The slope of this correlation is again unusually steep. If both the rate data and the reduction potentials are converted into free energy terms, the slope of the correlation (for the Ad_NE substitution) will be near unity (0.97, Eqn (1)). It indicates that the changes in the free energies of activation $\Delta G^\ddagger$ of the Ad_NE nucleophilic vinylic substitution reaction are almost the same as the changes in the free energies of one-electron oxidation of metal carbonyl anions ΔG_{ET}° .

$$\log \left(\frac{k_{AdNE}^{[M(CO)_nL]M'}}{k_{AdNE}^{[CpMo(CO)_3]K}} \right) \cdot \frac{RT}{\log(2.718)} = 0.97 \cdot F \cdot E_{OX}^{[M(CO)_nL]M'} - 38500 \quad (1)$$

(F is the Faraday constant).

It is tempting to interpret these data in terms of a SET mechanism for both the Ad_NE (Scheme 3) and HME processes. Further still, steep nucleophilicity slopes (Figs 1 and 2) are equivalent to high Brønsted β_{Nuc} values (≥ 1), which previously have been interpreted as an indication of a complete SET prior to the coupling of nucleophilic and electrophilic partners.^[34–38] Similar nucleophilicity slopes for HME and Ad_NE (Fig. 4) also suggest a common or similar rate-limiting stage for these processes. However, the outer sphere SET pathway is not supported by any 'chemical' evidence and does not seem feasible, the difference between the E_{ox} of the donor ($[M(CO)_nL]^-$)^[14,28] and the E_{red} of the acceptor (**4**-Hal) being too large. E_{ox} of $[M(CO)_nL]^-$ decreases from -0.52 V for $[Re(CO)_5]^-$ to -0.33 V for $[CpW(CO)_3]^-$,^[28] E_{red} are -1.70 V for **4**-Z-Cl, -1.65 V for **4**-Z-Br and -1.60 V for **4**-Z-I (O.M. Nikitin and T.V. Magdesieva, personal communication, All E values are converted to SHE scale). The inner-sphere SET pathway, which in this context implies an electron-transfer more or less concerted with the bond formation between the electrophile and the nucleophile, is a viable alternative. In the framework of single

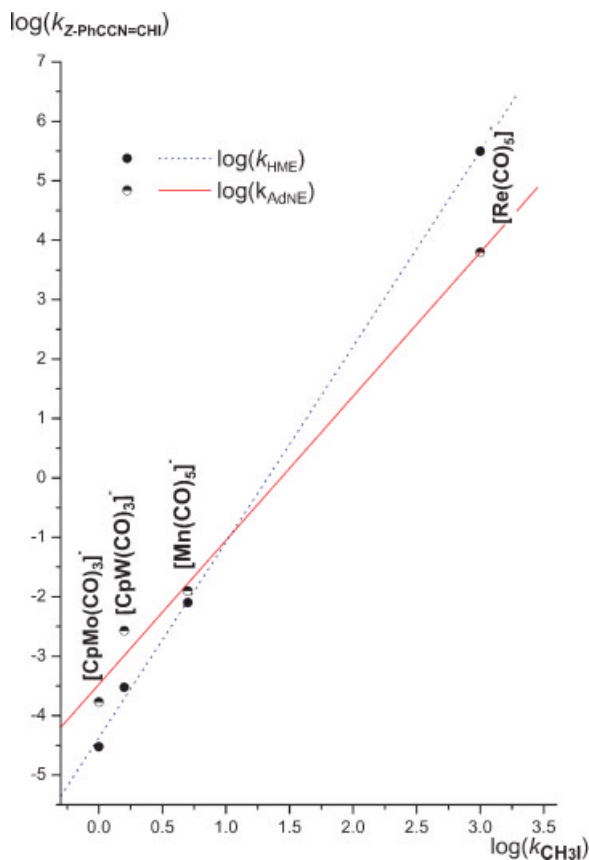


Figure 4. Nucleophilicity of metal carbonyl anions in Ad_NE vinylic substitution and halogen–metal exchange (HME) reactions with **Z**-PhCCN=CHI. The point for $[Re(CO)_5]^-$ is an estimate (footnote ^d to Table 4).

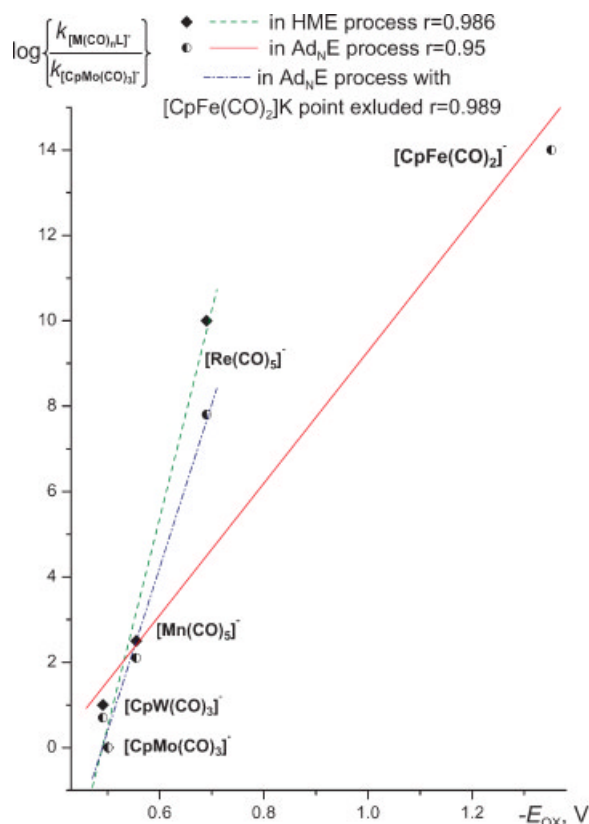


Figure 5. Correlation between the nucleophilicity of metal carbonyl anions $\{\log[k_{[M(CO)_nL]}/k_{[CpMo(CO)_3]K}]\}$ and their one-electron oxidation potentials E_{ox} (from Reference ^[28], versus ferrocene/ferrocenium).

electron shift concept^[39] it may be regarded as the initial stage in the transition form polar to SET pathway. However, the distinction between the inner-sphere SET and the polar Ad_NE pathway remains unclear at present.

EXPERIMENTAL

General

¹H NMR (400.13 MHz) and ¹³C NMR (100.61 MHz) spectra were obtained on a Bruker Avance spectrometer at 22°C and referenced to the signals of the solvent. UV-spectra and kinetic measurements were run on Hewlett-Packard-8452A diode array spectrophotometer. Preparation of metal carbonyl anion salts and their reactions with alkenyl halides were carried out in 'all-fused' glassware using vacuum-line techniques. Break-seal ampoules were used for the transfer of substances. Experiments with polyfluorinated vinyl halides **1**, **1**-Cl and **2** have been described previously.^[15–17]

Materials

THF was stored over sodium benzophenone ketyl and vacuum-transferred to the reaction vessels. Potassium salts of metal carbonyl anions were obtained quantitatively (95–98%) by reductive cleavage of the corresponding dimers [M(CO)_nL]₂ with excess of NaK_{2.8} alloy (0.10–0.15 mL per 0.5 mmol of dimer) in THF.^[40] [Re(CO)₅]Na was prepared by the reduction of Re₂(CO)₁₀ with 0.5% NaHg (30–50% excess) and purified by the low temperature crystallization from THF.^[16] Vinyl chlorides **3**,^[41] **4**-Z-Cl and **4**-E-Cl^[42] were obtained according to published procedures. Compounds **4**-Z-Br and **4**-E-Br were prepared similarly to **4**-Cl and vinyl iodide **4**-Z-I was obtained from **4**-Z-Br and NaI as described in the supporting material. Small portions of reagents required for a single experiment were sealed under vacuum into thin-walled glass vials.

Reaction products

The nucleophilic substitution products (metal carbonyl σ-vinyl complexes) were isolated by column chromatography on SiO₂ and characterized by NMR, IR, and MS or analytical data as described in the supporting material. The Product yields were determined by the integration of the ¹H NMR spectra of the crude reaction solutions using an internal standard (durene). The signals were referenced to the individual products by comparison to the spectra of the isolated compounds or with the literature data for the compounds previously described (such as metal carbonyl dimers).

Kinetic measurements

Relatively slow reactions ($k_{\text{obs}} < 5 \times 10^{-2} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) were monitored by ¹H NMR spectroscopy, with initial concentration of metal carbonyl anion 0.05–0.20 mol · L⁻¹ and a slight excess of vinyl halide. The reactions were carried out in undeuterated THF in vacuum-sealed glass tubes (~3.5 mm diameter) which were placed into standard NMR tubes containing acetone-*d*₆ for the lock signal. The concentrations of the starting [VinHal] and resulting [VinM] vinyl compounds were determined by the integration of the spectra using internal standard-durene. The concentration of metal carbonyl salt [M⁻] was determined similarly except for [M(CO)₅]K that was calculated as difference: [M⁻] = [M⁻]₀ – [VinM]. The second order rate constants (k_{obs})

were calculated by linear regression according to Eqn (2) giving good fit ($r > 0.99$) with experimental data.

$$\frac{1}{[\text{VinHal}]_0 - [\text{M}^-]_0} \cdot \ln \frac{[\text{M}^-]_0 \cdot [\text{VinHal}]}{[\text{VinHal}]_0 \cdot [\text{M}^-]} = k_{\text{obs}} \cdot t \quad (2)$$

The progress of reactions too fast for NMR method ($k_{\text{obs}} > 5 \times 10^{-2} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) was followed by UV spectroscopy by measuring the absorbance (*A*) changes in 280–360 nm range. The quartz cell was washed with a large excess of metal carbonyl salt solution that was then diluted to working concentration (about $5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$) and the cell was sealed under vacuum. The experiments were usually run with a slight excess of vinyl halide. Reaction coordinate *x* was calculated for several wavelengths as $x = (A - A_0)/(A_{\infty} - A_0)$ from which the concentrations of reagents were determined ($[\text{M}^-] = [\text{M}^-]_0 \cdot (1 - x)$; $[\text{VinHal}] = [\text{VinHal}]_0 - [\text{M}^-] \cdot x$) and fitted to the Eqn (2) to get second order rate constants.

Acknowledgements

The work was supported by the Grant of the President of the Russian Federation for the State Support of the Leading Research Schools (Grant No. HIII-6059.2006.3).

REFERENCES

- [1] M. Harris, S. P. McManus, (eds). In *Nucleophilicity*, Adv. Chem. Ser, Vol. 215, American Chemical Society: Washington, DC, **1987**.
- [2] C. D. Ritchie, *Acc. Chem. Res.* **1972**, 5, 348–354.
- [3] S. Hoz, D. Speizman, *J. Org. Chem.* **1983**, 48, 2904–2910.
- [4] L. A. P. Kane-Maguire, E. D. Honig, D. A. Sweigart, *Chem. Rev.* **1984**, 84, 525–543.
- [5] C. D. Ritchie, M. Sawada, *J. Am. Chem. Soc.* **1977**, 99, 3754–3761.
- [6] H. Mayr, M. Patz, *Angew. Chem. Int. Ed.* **1994**, 33, 938–957.
- [7] T. B. Phan, M. Breugst, H. Mayr, *Angew. Chem. Int. Ed.* **2006**, 45, 3869–3874.
- [8] H. Mayr, B. Kempf, A. R. Ofial, *Acc. Chem. Res.* **2003**, 36, 66–77.
- [9] S. Minegishi, H. Mayr, *J. Am. Chem. Soc.* **2003**, 125, 286–295.
- [10] A. R. Ofial, K. Ohkubo, S. Fukuzumi, R. Lucius, H. Mayr, *J. Am. Chem. Soc.* **2003**, 125, 10906–10912.
- [11] R. B. King, *Acc. Chem. Res.* **1970**, 3, 417–427.
- [12] R. E. Dessy, R. L. Pohl, R. B. King, *J. Am. Chem. Soc.* **1966**, 88, 5121–5124.
- [13] R. G. Pearson, P. E. Figdore, *J. Am. Chem. Soc.* **1980**, 102, 1541–1547.
- [14] C. K. Lai, W. G. Feighery, Y. Q. Zhen, J. D. Atwood, *Inorg. Chem.* **1989**, 28, 3929–3930.
- [15] G. A. Artamkina, M. M. Shtern, P. K. Sazonov, I. P. Beletskaya, *Zhurn. Org. Khimii.* **1996**, 32, 1319–1328.
- [16] P. K. Sazonov, M. M. Shtern, G. A. Artamkina, I. P. Beletskaya, *Zhurn. Org. Khimii.* **1998**, 34, 1807–1821.
- [17] P. K. Sazonov, G. A. Artamkina, I. P. Beletskaya, *Russ. J. Org. Chem.* **2000**, 36, 943–950.
- [18] P. K. Sazonov, V. A. Ivushkin, G. A. Artamkina, I. P. Beletskaya, *Arkivoc* **2003**, Part (X), 323–334.
- [19] Z. Rappoport, *Rec. Trav. Chim.* **1985**, 104, 309–349.
- [20] Z. Rappoport, *Acc. Chem. Res.* **1981**, 14, 7–15.
- [21] Z. Rappoport, *Acc. Chem. Res.* **1992**, 25, 474–479.
- [22] B. A. Shainyan, *Uspekhi. Khimii.* **1986**, 55, 942–973.
- [23] Y. Apeloig, Z. Rappoport, *J. Am. Chem. Soc.* **1979**, 101, 5095–5098.
- [24] M. Beit-Yannai, Z. Rappoport, B. A. Shainyan, Y. S. Danilevich, *J. Org. Chem.* **1997**, 62, 8049–8057.
- [25] Z. Rappoport, A. Topol, *J. Chem. Soc. Perkin Trans. 2*, **1975**, 982–988.
- [26] Z. Rappoport, A. Topol, *J. Chem. Soc. Perkin Trans. 2*, **1975**, 863–874.
- [27] Z. Rappoport, R. Ta-Shma, *J. Chem. Soc. B.* **1971**, 871–881.
- [28] M. Tilset, V. D. Parker, *J. Am. Chem. Soc.* **1989**, 111, 6711–6717.
- [29] I. I. Kukhareva, T. V. Magdesieva, G. A. Artamkina, I. P. Beletskaya, K. P. Butin, *Russ. Chem. Bull.* **1996**, 45, 1452–1457.

- [30] G. A. Artamkina, M. M. Shtern, P. K. Sazonov, I. P. Beletskaya, *Russ. J. Org. Chem.* **1996**, 32, 1281–1285.
- [31] H. F. Koch, A. J. Kielbania, *J. Am. Chem. Soc.* **1970**, 92, 729–730.
- [32] A. A. Solov'yanov, M. M. Shtern, I. P. Beletskaya, O. A. Reutov, *Zhurn. Org. Khimii.* **1983**, 19, 2233–2240.
- [33] A. A. Solov'yanov, P. I. Dem'yanov, I. P. Beletskaya, O. A. Reutov, *Zhurn. Org. Khimii.* **1976**, 12, 2489–2496.
- [34] F. Terrier, M. Mokhtari, R. Goumont, J.-C. Halle, E. Buncel, *Org. Biomol. Chem.* **2003**, 1, 1757–1763.
- [35] F. G. Bordwell, A. H. Clemens, *J. Org. Chem.* **1981**, 46, 1035–1037.
- [36] F. G. Bordwell, A. H. Clemens, D. E. Smith, J. Begemann, *J. Org. Chem.* **1985**, 50, 1151–1156.
- [37] V. M. Vlasov, I. A. Os'kina, D. Landini, A. Maia, *Russ. Chem. Bull.* **1995**, 44, 2211–2215.
- [38] V. M. Vlasov, I. A. Os'kina, *Russ. J. Gen. Chem.* **2004**, 74, 600–605.
- [39] A. Pross, *Acc. Chem. Res.* **1983**, 18, 212–219.
- [40] J. E. Ellis, E. A. Flom, *J. Organomet. Chem.* **1975**, 99, 263–268.
- [41] K. Friedrich, H. K. Thieme, *Synthesis* **1973**, 111–112.
- [42] M. Cariou, *Bull. Soc. Chim. Fr.* **1969**, 217–222.
- [43] E. J. Moore, J. M. Sullivan, J. R. Norton, *J. Am. Chem. Soc.* **1986**, 108, 2257–2263.