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Physical Organic Chemistry of Transition Metal Carbene Complexes. 19.[1] Kinetics of Reversible Alkoxide Ion Addition to Substituted (Methoxyphenylcarbene)pentacarbonylchromium(0) and (Methoxyphenylcarbene)pentacarbonyltungsten(0) in Methanol and Aqueous Acetonitrile

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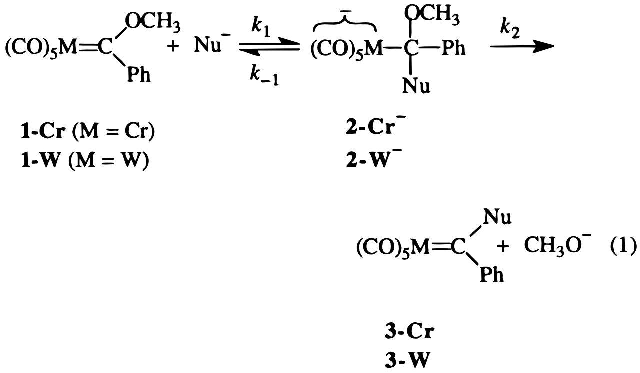
Abstract: Rate and equilibrium constants for the nucleophilic addition of MeO^- in methanol and in 90% MeCN−10% MeOH, of $HC{\equiv}CCH_2O^-$ and $CF_3CH_2O^-$ in 50% MeCN−50% water, and of OH^- in 50% MeCN−50% water (rate constants only) to Fischer carbene complexes of the type $(CO)_5M{=}C(OMe)C_6H_4$-4-Z (M = Cr and W) are reported. The reactions lead to the formation of tetrahedral adducts of the type $(CO)_5\bar{M}{-}C(OMe)(OR)C_6H_4$-4-Z. The kinetics of general acid catalyzed loss of MeO^- from the MeO^- adducts by phenol, 4-bromophenol, and 3,5-dichlorophenol, to regenerate the carbene complex, were also investigated. Hammett ρ and ρ_n values as well as approximate β_{nuc} (β^n_{nuc}) values were determined. They suggest that the transition state for alkoxide ion addition to the carbene complexes is imbalanced in the sense that charge delocalization into the CO ligands lags somewhat behind C−O bond formation. This finding is consistent with the fact that the intrinsic rate constants for these reactions are substantially lower than those for alkoxide ion addition to carboxylic esters. Another type of imbalance is seen for the transition state of the general acid catalyzed MeO^- departure from the MeO^- adducts. Here proton transfer to the leaving group is ahead of C−O bond cleavage.

Introduction

The substitution of an alkoxy group in Fischer type carbene complexes such as **1-M**[2] by nucleophiles[3−8] has generally been assumed to occur by the stepwise mechanism of eq 1. This mechanism is analogous to the one established for the reactions of carboxylic esters with nucleophiles. However, there is a major difference between the two classes of electrophiles in that **2-Cr**$^-$ or **2-W**$^-$ are much more stable than the respective tetrahedral intermediates in the ester reactions. As a result, **2-Cr**$^-$ or **2-W**$^-$ are directly detectable in the reactions of **1-Cr** and **1-W** with thiolate ions in 50% aqueous acetonitrile.[4e] In another investigation, the symmetrical dimethoxy adducts **4-M**$^-$ were generated in measurable concentrations in the reactions of **1-Cr** and **1-W** with MeO^- in methanol.[9]



1-Cr (M = Cr)
1-W (M = W)

2-Cr$^-$
2-W$^-$

3-Cr
3-W

(1)

Besides providing the most compelling evidence for the stepwise mechanism, these studies allowed the determination of the rate constants of the various steps (k_1, k_{-1}, k_2) and their

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[1] For part 18, see: Bernasconi, C. F.; Ali, M.; Lu, F. *J. Am. Chem. Soc.* **2000**, *122*, 1352.

[2] When using the symbols **1-M**, **2-M**, etc., both the Cr and W derivative will be meant. If only one derivative is referred to, the symbols **1-Cr**, **1-W**, **2-Cr**$^-$, **2-W**$^-$, etc. will be used.

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[8] Other nucleophiles: (a) Fischer, E. O.; Kreis, G.; Kreissl, F. R.; Kreiter, C. G.; Müller, J. *J. Chem. Ber.* **1973**, *106*, 3910. (b) Casey, C. P.; Brunsvold, W. P. *Inorg. Chem.* **1977**, *16*, 391. (c) Bell, R. A.; Chisholm, M. H.; Couch, D. A.; Rankel, L. A. *Inorg. Chem.* **1977**, *16*, 677.

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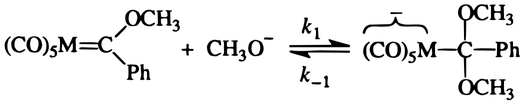


(2)

1-Cr (M = Cr) **4-Cr$^-$** (M = Cr)

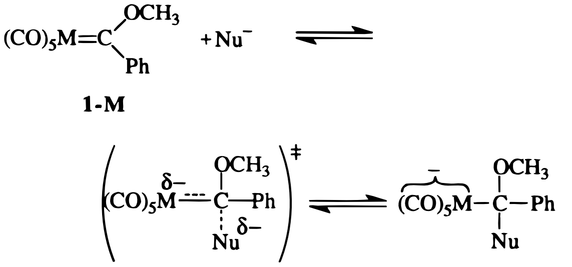
1-W (M = W) **4-W$^-$** (M = W)

dependence on a variety of structural parameters. Two important conclusions that have emerged from this work can be summarized as follows.

(1) The equilibrium constants, $K_1 = k_1/k_{-1}$, for nucleophilic addition to **1-M** are many orders of magnitude higher than those for addition to esters or carboxylic acids. For example, K_1 for MeO$^-$ addition to **1-Cr** (70.1 M^{-1})[9] is 2×10^8 to 10^9 fold higher than that for MeO$^-$ addition to methyl benzoate[10] and K_1 for n-PrS$^-$ addition to **1-Cr** (1.06×10^4 M^{-1})[4e] is $\approx 10^{17}$ fold higher than that for EtS$^-$ addition to acetic acid ($\approx 7.9 \times 10^{-14}$ M^{-1}).[11] These comparisons show that the (CO)$_5$M moieties are much more electron withdrawing than the carbonyl oxygen of an ester or carboxylic acid. This is, in large measure, due to the π-acceptor properties of the (CO)$_5$M moieties which, in the adducts, lead to delocalization of the negative charge into the CO ligands.[12]

(2) As one would expect, the rate constants, k_1, for nucleophilic attack on **1-Cr** and **1-W** are also higher than those for nucleophilic attack on the corresponding acyl compounds. However, the extent to which the k_1 values for **1-Cr** and **1-W** exceed those for the acyl compounds is less dramatic than what one might expect on the basis of the high ratios of the K_1 values. This indicates that the *intrinsic* rate constants[14] for nucleophilic addition to the carbene complexes are substantially lower than those for addition to the acyl compounds. The lowering of the intrinsic rate constant is a manifestation of the well-documented inverse relationship between intrinsic rate constants of anion-forming reactions and the degree of resonance stabilization of the anion.[15] The underlying reason for this inverse relationship is that the development of the resonance effect lags behind bond formation or charge transfer at the transition state (“transition state imbalance”). As a result, the stabilization of the transition state by the resonance effect is disproportionately small compared to the stabilization of the anion and hence the intrinsic rate constant is depressed.[16]

For the addition of a nucleophile to a Fischer carbene complex, the situation may be described by eq 3, which shows the charge at the transition state mostly localized on the metal while in the adduct the charge is mostly delocalized into the CO ligands, a point highlighted by the brace symbol on **2-M$^-$**.

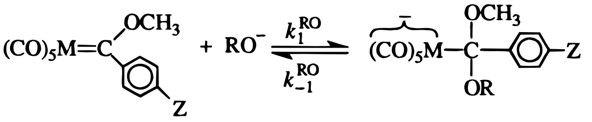


(3)

1-M

5 **2-M$^-$**

In reactions leading to carbanions stabilized by more conventional π-acceptors such as nitro groups, carbonyl groups, and others, there is independent evidence for the imbalanced nature of the transition state. This evidence is based on structure−reactivity coefficients such as Brønsted α and β values.[15] So far, no such evidence has been presented for reactions of Fischer carbene complexes. A major objective of the present work is to look for such evidence by studying the reaction of phenyl-substituted Fischer carbene complexes, **6-M**, with alkoxide ions.



(4)

6-Cr-Z (M = Cr) **7-Cr-Z$^-$** (M = Cr)

6-W-Z (M = W) **7-W-Z$^-$** (M = W)

Results

Reactions in Methanol. A. Chromium Carbene Complexes. The reaction of the substituted chromium carbene complexes **6-Cr-Z** (Z = 4-OMe, 4-Me, H, 4-F, 4-Cl, 3-Cl, and 4-CF$_3$) with NaOMe in methanol follows the general pattern described for the reaction with the parent compound (**6-Cr-H** ≡ **1-Cr**[9]). There is a rapid process that leads to the reversible formation of the corresponding adducts (**7-Cr-Z$^-$**) followed by a slower reaction that leads to unidentified decomposition products. Reversibility was demonstrated by recovering the carbene complex upon acidification of the adduct immediately after its formation; when acidification was delayed there was only partial or no recovery as judged from the absorption spectra.

Two types of kinetic experiments were performed. In the first, reaction was initiated by mixing a methanolic solution of the carbene complex with a methanolic solution of NaOMe in a stopped-flow spectrophotometer. NaOMe was always in large excess over the substrate, ensuring pseudo-first-order conditions. The pseudo-first-order rate constants showed a linear dependence on [MeO$^-$] according to eq 5. Representative plots of

$$k_{\mathrm{obsd}} = k_1^{\mathrm{MeO}}[\mathrm{MeO}^-] + k_{-1}^{\mathrm{MeO}} \tag{5}$$

k_{obsd} vs [MeO$^-$] are shown in Figure 1. The k_1^{MeO} and k_{-1}^{MeO} values are reported in Table 1; for the most reactive carbene complexes (Z = 4-Cl and 4-CF$_3$), the intercepts were too small to yield a reliable k_{-1}^{MeO} value.

In the second type of experiment, equilibrium was approached from the adduct side by reacting **7-Cr-Z$^-$** with phenol, 4-bromophenol, and 3,5-dichlorophenol buffers. Because the adducts are quite unstable, the reaction was initiated within 0.5−2 s after the adduct had been generated with 0.1 M NaOMe in a sequential stopped-flow apparatus. In these experiments, k_{obsd} is given by eq 6, with B$^-$ and BH representing the buffer base and buffer acid, respectively.[17] Plots of k_{obsd} vs [BH] at

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[10] K_1 for MeO$^-$ addition to methylbenzoate has been estimated to be between $>1.1 \times 10^{-7}$ and 5.0×10^{-7} M^{-1}.[9]

[11] Guthrie, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 5892.

[12] The strong electron-withdrawing effect of M(CO)$_n$ moieties has also been expressed in terms of a high electronegativity.[13]

[13] Labinger, J. A.; Bercaw, J. E. *Organometallics* **1988**, *7*, 926.

[14] For a reaction with the forward rate constants k_1 and the reverse rate constant k_{-1}, the intrinsic rate constant is defined as $k_o = k_1 = k_{-1}$ when the equilibrium constant, $K_1 = 1$ ($\Delta G^\circ = 0$).

[15] (a) Bernasconi, C. F. *Acc. Chem. Res.* **1987**, *20*, 301. (b) Bernasconi, C. F. *Acc. Chem. Res.* **1992**, *25*, 9. (c) Bernasconi, C. F. *Adv. Phys. Org. Chem.* **1992**, *27*, 119.

[16] This relationship between intrinsic rate constants and transition state imbalances is the manifestation of a more general principle which is not restricted to resonance effects and has been called the principle of nonperfect synchronization (PNS).[15]

[17] In principle, eq 6 should include terms for spontaneous MeOH addition (k_1^{MeOH}) and its reverse, H$^+$-catalyzed MeO$^-$ departure ($k_{-1}^{\mathrm{H}}a_{\mathrm{H}^+}$), but under the reaction conditions these terms are negligible.

Table 1. Rate and Equilibrium Constants for Reversible MeO⁻ Addition to **6-Cr-Z** and **6-W-Z** in Methanol at 25 °C

Z	k_1^{MeO},[a] $M^{-1}\,s^{-1}$	k_{-1}^{MeO},[a] s^{-1}	k_{-1}^{MeO},[b] s^{-1}	k_{-1}^{MeO},[c] s^{-1}	$K_1^{MeO} = k_1^{MeO}/k_{-1}^{MeO}$, M^{-1}	$k_1^{MeO^-}$(90% MeCN), $M^{-1}\,s^{-1}$
6-Cr-Z						
4-Me_2N						45.7 ± 0.6
4-MeO	14.4 ± 1.3	3.80 ± 0.20	3.80 ± 0.21	3.80 ± 0.20	3.68 ± 0.45	(1.06 ± 0.02) × 10^3
4-Me	31.2 ± 1.3	3.03 ± 0.06	2.07 ± 0.06	2.55 ± 0.48	12.2 ± 2.6	(2.65 ± 0.03) × 10^3
H	77.1 ± 3.4	0.98 ± 0.28	0.67 ± 0.08	0.82 ± 0.16	94 ± 22	(4.04 ± 0.05) × 10^3
4-F	188 ± 5	0.74 ± 0.02	0.61 ± 0.10	0.68 ± 0.07	276 ± 36	(7.47 ± 0.25) × 10^3
4-Cl	330 ± 6	0.27 ± 0.02	0.36 ± 0.03	0.31 ± 0.04	(1.06 ± 0.15) × 10^3	(1.44 ± 0.08) × 10^4
3-Cl	554 ± 4					(2.51 ± 0.03) × 10^4
4-CF_3	817 ± 14			0.090 ± 0.012[d]	(9.07 ± 1.4) × 10^3 [e]	(3.36 ± 0.12) × 10^4
6-W-Z						
4-MeO	46.3 ± 0.6	4.42 ± 0.65			10.5 ± 1.7	(2.96 ± 0.06) × 10^3
4-Me	105 ± 1	3.95 ± 0.14			26.6 ± 4.7	(4.86 ± 0.06) × 10^3
H	186 ± 3	1.60 ± 0.21			116 ± 17	(9.03 ± 0.09) × 10^3
4-F	683 ± 40	1.80 ± 0.08			379 ± 41	(1.63 ± 0.03) × 10^4
4-Cl	806 ± 15	0.72 ± 0.09			(1.12 ± 0.19) × 10^3	(3.32 ± 0.06) × 10^4

[a] From experiments with NaOMe (eq 5). [b] From experiments in phenol or 4-bromophenol buffers (eq 7), see text. [c] Adopted value for the reactions of **6-Cr-Z**, see text. [d] k_{-1}^{MeO} calculated as k_1^{MeO}/K_1^{MeO}, with K_1^{MeO} obtained from eq 7, see text. [e] K_1^{MeO} obtained from eq 7, see text.

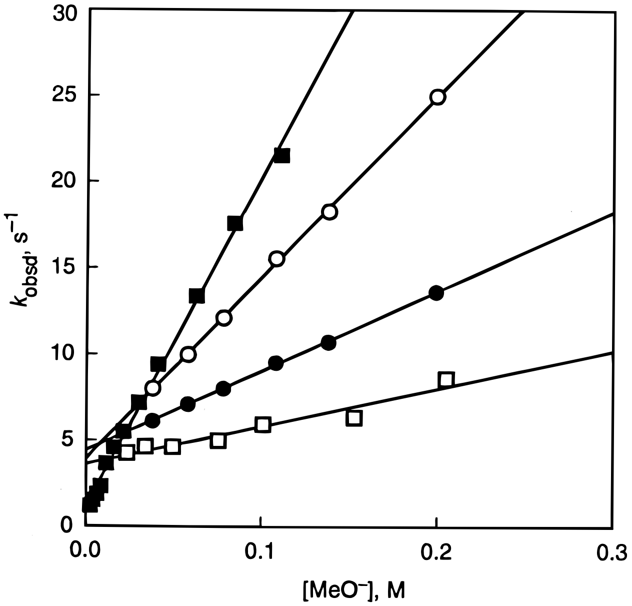

Figure 1. Representative plots of k_{obsd} vs [MeO⁻] (eq 5) for the reactions of MeO⁻ with **6-Cr-F** (■), **6-W-Me** (○), **6-W-MeO** (●), and **6-Cr-MeO** (□).

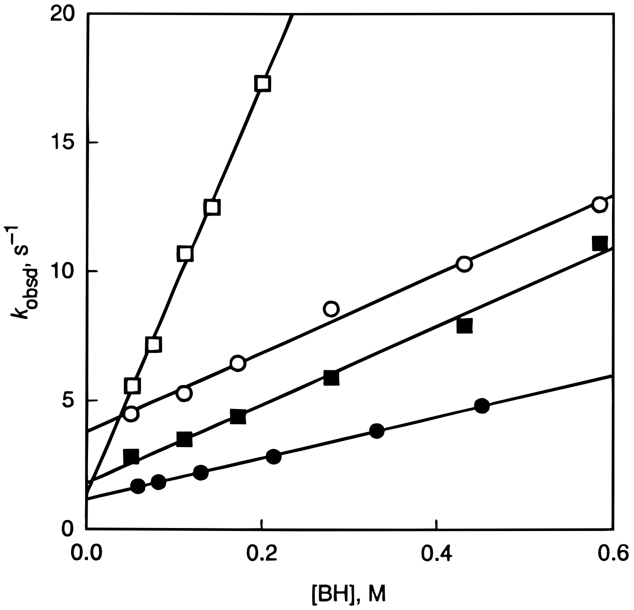

Figure 2. Representative plots of k_{obsd} vs buffer acid concentration for the reactions of phenol buffers with **6-Cr-MeO** (○), **6-Cr-Me** (■), and **6-Cr-H** (●) and of 4-bromophenol buffers with **6-Cr-Me** (□).

$$k_{obsd} = k_1^{MeO}[MeO^-] + k_{-1}^{MeO} + k_1^{B}[B^-] + k_{-1}^{BH}[BH] \quad (6)$$

constant buffer ratio provide slopes given by eq 7, with K_a^{BH}

$$\text{slope} = \frac{k_1^{B}K_a^{BH}}{a_{H^+}} + k_{-1}^{BH} = k_{-1}^{BH}\left(\frac{K_1^{MeO}K_S}{a_{H^+}} + 1\right) \quad (7)$$

being the acidity constant of the buffer, K_S the ionic product of the solvent,[18] and $K_1^{MeO} = k_1^{MeO}/k_{-1}^{MeO}$ the equilibrium constant for MeO⁻ addition. The intercepts of these plots are given by $k_1^{MeO}[MeO^-] + k_{-1}^{MeO}$. Some representative plots are shown in Figure 2.

The amount of information obtained from these plots varied depending on Z because of the large variation in the K_1^{MeO} values (Table 1). The salient features can be summarized as follows.

Z = 4-MeO. Due to the small K_1^{MeO} values, the $k_1^{MeO}[MeO^-]$ and $k_1^{B}[B^-]$ terms in eq 6 are negligible and the plots of k_{obsd} vs [BH] yield k_{-1}^{BH} and k_{-1}^{MeO} directly from slope and intercept, respectively. The k_{-1}^{MeO} values (3.80 ± 0.21 s^{-1} for the phenol and 3.74 ± 0.36 s^{-1} for the 4-bromophenol buffers) are in perfect agreement with k_{-1}^{MeO} = 3.80 ± 0.20 s^{-1} obtained from the experiments in NaOMe solutions (Table 1). The intercept from the plot of k_{obsd} vs [3,5-dichlorophenol] are too small to give a reliable k_{-1}^{MeO} value. The slopes of the buffer plots yield k_{-1}^{BH} from which k_1^{B} is calculated as $k_{-1}K_1^{MeO}K_S/K_a^{BH}$.

Z = 4-Me. The $k_1^{MeO}[MeO^-]$ and $k_1^{B}[B^-]$ terms are again negligible. The k_{-1}^{MeO} value (2.07 ± 0.06 s^{-1}) obtained in phenol buffers is in reasonably good agreement with that obtained in NaOMe solutions (3.03 ± 0.6 s^{-1}); the average value (2.55 s^{-1}) will be adopted. No reliable k_{-1}^{MeO} values could be obtained in the other buffers because the intercepts of the buffer plots were too small. The k_{-1}^{BH} and k_1^{B} values were obtained as for Z = MeO.

Z = H. The $k_1^{MeO}[MeO^-]$ and $k_1^{B}[B^-]$ terms are negligible in the 4-bromophenol and 3,5-dichlorophenol buffers but not in the phenol buffers. From the pH dependence of the intercepts of the plots of k_{obsd} vs [BH] in the phenol buffers, k_1^{MeO} =

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[18] pK_S = 16.92, Rochester, C. H.; Rossall, B. *Trans. Faraday Soc.* **1969**, *65*, 1004.

Table 2. Rate and Equilibrium Constants for Buffer-Catalyzed Addition of Methanol to **6-Cr-Z** at 25 °C

Z	BH	pK_a^{BH}	k_1^B, M^{-1} s^{-1}	k_{-1}^{BH}, M^{-1} s^{-1}	$K_1^{B\ a}$
4-MeO	PhOH	14.46	$(1.94 \pm 0.30) \times 10^{-1}$	15.3 ± 0.6	$(1.27 \pm 0.15) \times 10^{-2}$
	4-BrC_6H_4OH	13.5	$(1.19 \pm 0.20) \times 10^{-1}$	84.9 ± 4.4	$(1.40 \pm 0.17) \times 10^{-3}$
	$3,5\text{-Cl}_2C_6H_3OH$	12.1	$(7.56 \pm 0.85) \times 10^{-2}$	$(1.36 \pm 0.10) \times 10^3$	$(5.56 \pm 0.68) \times 10^{-5}$
4-Me	PhOH	14.46	$(5.74 \pm 1.32) \times 10^{-1}$	13.6 ± 0.2	$(4.22 \pm 0.90) \times 10^{-2}$
	4-BrC_6H_4OH	13.5	$(3.69 \pm 0.88) \times 10^{-1}$	79.6 ± 2.5	$(4.64 \pm 0.99) \times 10^{-3}$
	$3,5\text{-Cl}_2C_6H_3OH$	12.1	$(2.35 \pm 0.61) \times 10^{-1}$	$(1.28 \pm 0.07) \times 10^3$	$(1.84 \pm 0.39) \times 10^{-4}$
H	PhOH	14.46	2.70 ± 0.82	8.32 ± 0.61	$(3.25 \pm 0.76) \times 10^{-1}$
	4-BrC_6H_4OH	13.5	1.51 ± 0.41	42.3 ± 1.7	$(3.57 \pm 0.82) \times 10^{-2}$
	$3,5\text{-Cl}_2C_6H_3OH$	12.1	1.04 ± 0.27	$(7.34 \pm 0.22) \times 10^2$	$(1.42 \pm 0.33) \times 10^{-3}$
4-F	PhOH	14.46	4.40 ± 1.67	4.27 ± 1.14	1.03 ± 0.12
	4-BrC_6H_4OH	13.5	3.53 ± 0.56	31.2 ± 0.6	$(1.13 \pm 0.13) \times 10^{-1}$
	$3,5\text{-Cl}_2C_6H_3OH$	12.1	2.32 ± 0.38	$(5.18 \pm 0.24) \times 10^2$	$(4.48 \pm 0.53) \times 10^{-3}$
4-Cl	PhOH	14.46	5.91 ± 2.65	1.61 ± 0.50	3.67 ± 0.52
	4-BrC_6H_4OH	13.5	5.88 ± 1.11	14.6 ± 0.7	$(4.03 \pm 0.57) \times 10^{-1}$
	$3,5\text{-Cl}_2C_6H_3OH$	12.1	3.50 ± 0.66	$(2.19 \pm 0.12) \times 10^2$	$(1.60 \pm 0.22) \times 10^{-2}$
4-CF_3	4-BrC_6H_4OH	13.5	9.66 ± 2.90	2.80 ± 0.41	3.45 ± 0.53
	$3,5\text{-Cl}_2C_6H_3OH$	12.1	7.63 ± 1.26	55.7 ± 1.1	$(1.37 \pm 0.20) \times 10^{-1}$

[a] $K_1^B = K_1^{MeO}K_S/K_a^{BH}$ with $K_S = 1.20 \times 10^{-17}$ ($pK_S = 16.92$). [b] $k_1^B = k_{-1}^{BH}K_1^B$.

84.2 ± 12.6 M^{-1} s^{-1} and $k_{-1}^{MeO} = 0.67 \pm 0.08$ s^{-1} are obtained, in fair to good agreement with $k_1^{MeO} = 77.1 \pm 3.4$ M^{-1} s^{-1} and $k_{-1}^{MeO} = 0.98 \pm 0.28$ s^{-1} determined in NaOMe solutions.[9] The average values with will be adopted. The intercepts of the buffer plots with 4-bromophenol and 3,5-dichlorophenol were too small to yield k_{-1}^{MeO} values. The k_{-1}^{BH} value for phenol was obtained according to eq 7 while k_1^B was calculated in the usual way. For k_{-1}^{BH} and k_1^B for 4-bromophenol and 3,5-dichlorophenol, the procedures described for Z = MeO were used.

Z = 4-F. The situation is quite similar to that for Z = H. In phenol buffers $k_1^{MeO} = 138 \pm 18$ M^{-1} s^{-1} and $k_{-1}^{MeO} = 0.61 \pm 0.10$ s^{-1} are obtained, in reasonably good agreement with the values determined in NaOMe solutions ($k_1^{MeO} = 199 \pm 3$ M^{-1} s^{-1} and $k_{-1}^{MeO} = 0.74 \pm 0.02$ s^{-1}). The latter rate constants appear to be more accurate and will be adopted. The k_{-1}^{BH} and k_1^B values were obtained as described for Z = H.

Z = 4-Cl. The $k_1^{MeO}[MeO^-]$ and $k_1^B[B^-]$ terms are important in phenol as well as in 4-bromophenol buffers. For the phenol buffers, one obtains $k_1^{MeO} = 239 \pm 24$ M^{-1} s^{-1} and $k_{-1}^{MeO} = 0.20 \pm 0.13$ s^{-1}, and for the 4-bromphenol buffers, $k_1^{MeO} = 419 \pm 32$ M^{-1} s^{-1} and $k_{-1}^{MeO} = 0.36 \pm 0.03$ s^{-1}, respectively. This compares with $k_1^{MeO} = 330 \pm 6$ M^{-1} s^{-1} and $k_{-1}^{MeO} = 0.27 \pm 0.02$ s^{-1} obtained in NaOMe solutions; for k_{-1}^{MeO} the average of 0.27 and 0.36 will be adopted. The k_{-1}^{BH} and k_1^B values for phenol and 4-bromophenol were evaluated as described for Z = F with the phenol buffers; k_{-1}^{BH} and k_1^B for 3,5-dichlorophenol were obtained as described for Z = MeO.

Z = CF₃. In phenol buffers, the $k_1^{MeO}[MeO^-]$ terms is much larger than k_{-1}^{MeO} and only $k_1^{MeO} = (1.01 \pm 0.09) \times 10^3$ M^{-1} s^{-1} could be obtained which is in good agreement with $k_1^{MeO} = 820 \pm 14$ M^{-1} s^{-1} determined in NaOMe solutions. In 4-bromophenol buffers, $k_1^{MeO} = 810 \pm 110$ M^{-1} s^{-1} is obtained but no reliable value for k_{-1}^{MeO} could be determined. A different source of k_{-1}^{MeO} comes from treating K_1^{MeO} in eq 7 as an unknown. From the plot of slope vs $a_{H^+}^{-1}$ (4-bromophenol) shown in Figure 3, one obtains $K_1^{MeO} = (9.07 \pm 0.14) \times 10^3$ M^{-1} from which $k_{-1}^{MeO} = 0.090 \pm 0.012$ s^{-1} is calculated. All k_{-1}^{BH} and k_1^B values are summarized in Table 2.

B. Tungsten Carbene Complexes. Rate constants (k_1^{MeO} and k_{-1}^{MeO}) for the reaction of MeO^- with the tungsten carbene complexes **6-W-Z** (Z = MeO, Me, H, 4-F, and 4-Cl) were determined as described for the Cr analogues. The results are included in Table 1.

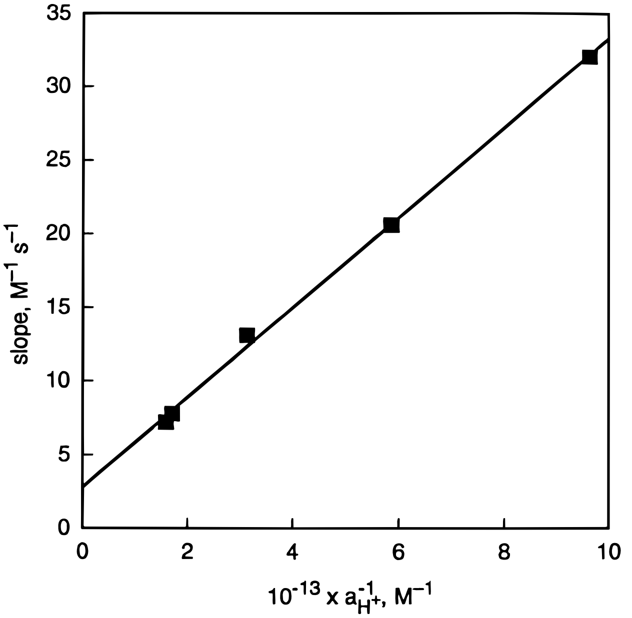


Figure 3. Plot of slope vs $a_{H^+}^{-1}$ according to eq 7 for the reaction of **6-Cr-CF₃** with 4-bromophenol buffers.

Reactions with MeO⁻ in 90% MeCN−10% MeOH. Rate constants for MeO^- addition to **6-Cr-Z** and **6-W-Z** (k_1^{MeO}) were determined in 90% MeCN−10% MeOH with NaOMe as the base. In this solvent the equilibrium for nucleophilic addition is more favorable than in pure methanol. This allowed inclusion of the rather unreactive **6-Cr-NMe₂** in our series. The plots of k_{obsd} vs $[MeO^-]$ were all linear with intercepts ≈0 or too small to yield a reliable k_{-1}^{MeO} value. The results are included in Table 1.

Reactions with OH⁻, HC≡CCH₂O⁻, and CF₃CH₂O⁻ in 50% MeCN−50% Water (v/v). A. OH⁻. Rates were measured in the range of 0.01 to 0.1 M KOH. The slopes of the linear plots of k_{obsd} vs [KOH] yielded the k_1^{OH} values reported in Table 3. Because **6-Cr-CF₃** is quite unstable in 50% MeCN−50% water, the experiments with this compound had to be performed using stock solutions in pure MeCN which may have introduced some experimental errors as described in the Experimental Section.

B. HC≡CCH₂O⁻ and CF₃CH₂O⁻. Alkoxide ion solutions were made by adding the respective alcohol to a KOH solution. $[RO^-]$ and $[OH^-]$ were calculated on the basis of the pK_a^{ROH} of

Table 3. Rate and Equilibrium Constants for the Reactions of **6-Cr-Z** and **6-W-Z** with OH^-, $HC{\equiv}CCH_2O^-$, and $CF_3CH_2O^-$ in 50% MeCN−50% Water (v/v) at 25 °C

Z	k_1^{OH}, M^{-1} s^{-1}	k_1^{OPGYL}, [a] M^{-1} s^{-1}	k_{-1}^{OPGYL},[a] s^{-1}	K_1^{OPGYL},[a] M^{-1}	k_1^{OTFE},[b] M^{-1} s^{-1}	k_{-1}^{OTFE},[b] s^{-1}	K_1^{OTFE},[b] M^{-1}
				6-Cr-Z			
4-Me_2N	0.131 ± 0.004						
4-MeO	3.35 ± 0.18						
4-Me	13.2 ± 0.2	25.3 ± 0.6	0.496 ± 0.003	51.0 ± 1.5			
H	26.6 ± 0.3[c]	47 ± 1	0.281 ± 0.001	167 ±4			
4-F	37.1 ± 0.9	87 ± 1	0.250 ± 0.002	348 ± 7			
4-Cl	76.8 ± 1.9	121 ± 4	0.150 ± 0.008	807 ± 69	43.6 ± 0.2	0.493 ± 0.003	88.4 ± 1.3
3-Cl	80.1 ± 1.3	162 ± 4					
4-CF_3	105 ± 1	240 ± 3	0.087 ± 0.003	2759 ± 136	61 ± 2	0.199 ± 0.005	307 ± 18
				6-W-Z			
4-MeO	6.85 ± 0.20						
4-Me	17.2 ± 0.9	50.0 ± 3.9	0.988 ± 0.006	50.6 ± 4.2			
H	26.3 ± 0.2[c]	84.0 ± 1.8	0.504 ± 0.007	167 ± 6			
4-F	48.0 ± 1.0	158 ± 3	0.465 ± 0.003	340 ± 9			
4-Cl	55.7 ± 1.4	232 ± 6	0.272 ± 0.006	853 ± 41	62.9 ± 1.9	1.08 ± 0.01	58.2 ± 2.3

[a] PGYL = $HC{\equiv}CCH_2$; pK_a^{PGYLOH} = 14.73. [b] TFE = CF_3CH_2; pK_a^{TFEOH} = 13.68. [c] Reference 4e.

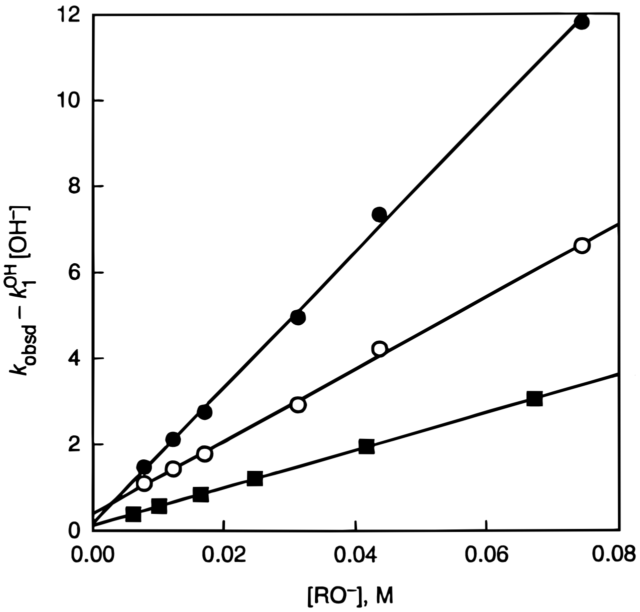


Figure 4. Representative plots of $k_{obsd} - k_1^{OH}[OH^-]$ vs $[RO^-]$ according to eq 8 for the reactions of **6-W-F** with $HC{\equiv}CCH_2O^-$ (●), of **6-W-H** with $HC{\equiv}CCH_2O^-$ (○), and of **6-Cr-Cl** with $CF_2CH_2O^-$ (■).

the alcohol, the total concentration of ROH, and the measured pH. In the experiments that were initiated by mixing the carbene complex with the RO^-/OH^- solutions, k_{obsd} can be approximated by eq 8; it is an approximation because only the OH^- reaction

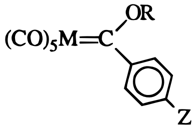
$$k_{obsd} = k_1^{OH}[OH^-] + k_1^{RO}[RO^-] \qquad (8)$$

is irreversible (see Discussion) while the RO^- reaction leads to reversible adduct formation. k_1^{RO} (Table 3) was obtained as the slope of plots of $\{k_{obsd} - k_1^{OH}[OH^-]\}$ vs $[RO^-]$. Representative examples are shown in Figure 4. For the reactions with $CF_3CH_2O^-$, the equilibrium for adduct formation was only favorable enough to allow measurements with the most strongly activated carbene complexes (**6-Cr-Cl**, **6-Cr-CF$_3$**, **6-W-Cl**), while with $HC{\equiv}CCH_2O^-$ these measurements were feasible with all but the least activated carbenes (**6-M-OMe**). For the reactions with **6-Cr-CF$_3$**, the experiments again had to be performed using stock solutions in pure MeCN.

Rate constants for the loss of RO^- from the respective alkoxide ion adducts, k_{-1}^{RO} (Table 3), were obtained after generating the adducts in pure acetonitrile in the presence of 5×10^{-4} M NaOR and then adding these adducts to a triethylamine buffer at pH 10.5. At this pH the concentration of the alkoxide ion is quite small. Hence the equilibrium for adduct formation becomes very unfavorable and the adduct decomposes by competing loss of RO^- to revert back to reactants (k_{-1}^{RO}) and loss of MeO^- to form the RO-substituted carbene complex **8-M-Z** (k_2^{MeO}, special case of k_2 in eq 1). Thus, k_{obsd} is given by eq 9. In principle, determination of the ratio of recovered substrate to the substitution product by HPLC could provide the k_{-1}^{RO}/k_2^{MeO} ratio[19] which, in conjunction with eq 9, would allow dissection of k_{-1}^{RO} and k_2^{MeO}. However, both **6-M-Z** and

$$k_{obsd} = k_{-1}^{RO} + k_2^{MeO} \qquad (9)$$

8-M-Z are too unstable under the reaction conditions to allow such analysis. But $HC{\equiv}CCH_2O^-$ and $CF_3CH_2O^-$ are better leaving groups than MeO^- and the push provided by the methoxy group left behind for the k_{-1}^{RO} process is stronger than the push by the alkoxy groups left behind in the k_2^{MeO} process. Both factors contribute to render $k_{-1}^{RO} > (\gg)\ k_2^{MeO}$, especially for $RO^- = CF_3CH_2O^-$.[21] It is therefore reasonable to approximate k_{obsd} by k_{-1}^{RO} in eq 9 (more on this in the Discussion section).



8-Cr-Z (M = Cr)
8-W-Z (M = W)

Discussion

Mechanism. The reactions of **6-M-Z** with MeO^-, $HC{\equiv}CCH_2O^-$, and $CF_3CH_2O^-$ all lead to nucleophilic addition to form the corresponding **7-M-Z**$^-$ type adducts. Upon standing for extended periods of time (several minutes or longer), the adducts decompose into unidentified byproducts as discussed in more

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(19) This type of analysis was successfully applied to the competing loss of MeO^- and $CF_3CH_2O^-$ from $PhC(OMe)(OCH_2CF_3)C(Ph){=}NO_2^-$.[20]

(20) Bernasconi, C. F.; Schuck, D. F.; Ketner, R. J.; Eventova, I.; Rappoport, Z. *J. Am. Chem. Soc.* **1995**, *117*, 2719.

(21) For an example where $CF_3CH_2O^-$ and $HC{\equiv}CCH_2O^-$ are shown to be much better leaving groups than MeO^-, see ref 22.

Table 4. Hammett ρ and Normalized ρ (ρ_n) Values[a] for Alkoxide and Hydroxide Ion Addition to **6-M-Z**

reaction	$\rho(k_1^{OR})$	$\rho(k_{-1}^{OR})$	$\rho(K_1^{OR})$	$\rho_n(k_1^{OR})^b$	$\rho_n(k_{-1}^{OR})^b$
6-Cr-Z + MeO^- in MeOH	2.20 ± 0.23 (2.67 ± 0.10)	−2.04 ± 0.10 (−2.24 ± 0.15)	4.22 ± 0.35 (4.92 ± 0.12)	0.52 ± 0.02 (0.54 ± 0.02)	−0.48 ± 0.02 (−0.46 ± 0.02)
6-Cr-Z + MeO^- in 90% MeCN−10% MeOH	2.15 ± 0.14 (2.36 ± 0.13)				
6-Cr-Z + $HC{\equiv}CCH_2O-$ in 50% MeCN−50% H_2O	1.34 ± 0.16 (1.39 ± 0.14)	−0.90 ± 0.20 (−1.06 ± 0.11)	2.25 ± 0.29 (2.45 ± 0.24)	0.59 ± 0.05 (0.57 ± 0.01)	−0.41 ± 0.05 (−0.43 ± 0.01)
6-Cr-Z + HO^- in 50% MeCN−50% H_2O	2.20 ± 0.20 (2.23 ± 0.29)				
6-W-Z + MeO^- in MeOH	2.58 ± 0.48 (2.37 ± 0.22)	−1.60 ± 0.20 (−1.67 ± 0.17)	4.18 ± 0.31 (4.04 ± 0.08)	0.63 ± 0.07 (0.59 ± 0.05)	−0.37 ± 0.07 (−0.41 ± 0.05)
6-W-Z + MeO^- in 90% MeCN−10% MeOH	2.11 ± 0.14 (2.07 ± 0.13)				
6-W-Z + $HC{\equiv}CCH_2O^-$ in 50% MeCN−50% H_2O	1.73 ± 0.31 (1.68 ± 0.17)	−1.38 ± 0.11 (−1.39 ± 0.16)	3.11 ± 0.26 (3.07 ± 0.01)	0.56 ± 0.06 (0.55 ± 0.05)	−0.44 ± 0.06 (−0.45 ± 0.05)
6-W-Z + HO^- in 50% MeCN−50% H_2O	1.78 ± 0.34 (1.68 ± 0.32)				

[a] First number, ρ based on all substrates; second number (in parentheses), ρ based on excluding 4-F and 4-CF_3, see text. [b] Normalized values obtained from plots of log k_1^{OR} vs log K_1^{OR} and log k_{-1}^{OR} vs log K_1^{OR}, respectively.

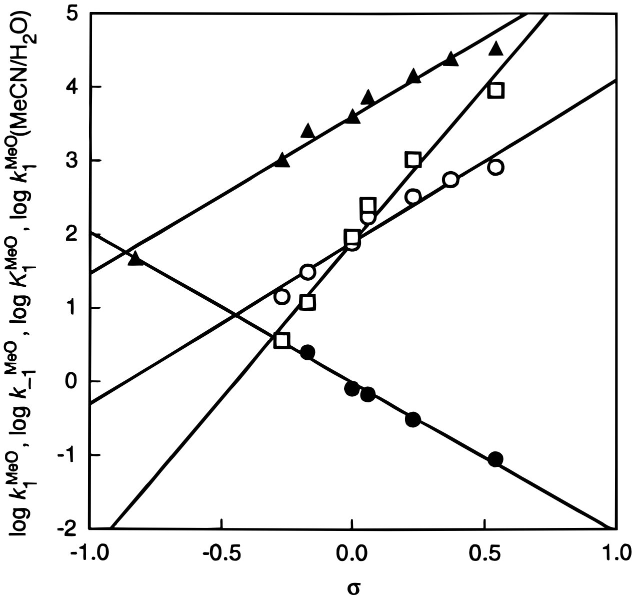


Figure 5. Representative Hammett plots for the reaction of **6-Cr-Z** with MeO^- in methanol (○, k_1^{MeO}; ●, k_{-1}^{MeO}; □, K_1^{MeO}) and in 90% MeCN−10% MeOH (▲, k_1^{MeO}).

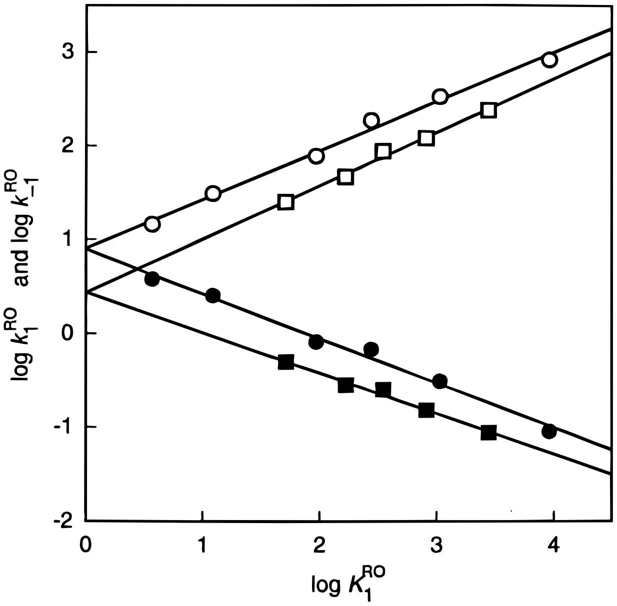


Figure 6. Representative Brønsted plots for the reactions of **6-Cr-Z** with MeO^- in MeOH (○, ●) and of **6-Cr-Z** with $HC{\equiv}CCH_2O^-$ in 50% MeCN−50% water (□, ■).

detail elsewhere.[9] However, on a much shorter time scale, the adducts revert back to reactants upon removal of the alkoxide ion from equilibrium by rapid acidification of the solution. This is the case for the symmetrical MeO^- adducts and at least to a good approximation for the $HC{\equiv}CCH_2O^-$ and $CF_3CH_2O^-$ adducts as well; as mentioned in the Results section, the competing loss of MeO^- from these latter adducts is expected to be substantially slower than the loss of $HC{\equiv}CCH_2O^-$ and $CF_3CH_2O^-$, respectively.

The reactions of **6-M-Z** with OH^- presumably also lead to adducts of the type **7-M-Z**$^-$ with R = H. However, loss of MeO^- to form **8-M-Z** (R = H) with subsequent further decomposition is much faster than loss of OH^- to regenerate **6-M-Z**[5b] and hence no adducts can be detected.

Structure−Reactivity Relationships. The major objective of this study was to determine substituent effects on the reactions of **6-Cr-Z** and **6-W-Z** with MeO^-, $HC{\equiv}CCH_2O^-$, $CF_3CH_2O^-$, and OH^- in various solvents. The results were treated in terms of Hammett correlations and, for the reactions that allowed determination of both rate and equilibrium constants, also in terms of Brønsted correlations (log k_1 vs log K_1 and log k_{-1} vs log K_1). Representative Hammett and Brønsted plots are shown in Figures 5 and 6, respectively. On most plots, there is a tendency for the 4-F derivatives to deviate positively and for the 4-CF_3 derivative to deviate negatively from the lines defined by the other substituents. Whether this represents a systematic error or indicates true curvature is difficult to decide; experimental problems in obtaining highly accurate results with **6-Cr-CF$_3$** (see Results section) suggest that, at least for this compound, there may be some systematic error involved. For the 4-F derivatives, the positive deviations are more pronounced in the Hammett plots than in the Brønsted plots, especially in methanol, suggesting that the standard σ value for the 4-F substituent may not be appropriate in methanol.

Table 4 summarizes all ρ (Hammett plots) and normalized ρ values (ρ_n, Brønsted plots) for the reactions with OH^- and alkoxide ions, while Table 5 gives a summary of the normalized ρ values for the reversible buffer-catalyzed MeOH addition to **6-Cr-Z** in methanol.[23] Because of the problems with the 4-F and 4-CF_3 derivatives mentioned above, the ρ and ρ_n values were calculated with and without including these derivatives; inclusion or exclusion of these points has only a small influence

Table 5. Normalized ρ Values (ρ_n) for Buffer-Catalyzed Methanol Addition to **6-Cr-Z**[a]

B^-	$\rho_n(k_1^B)$	$\rho_n(k_{-1}^{BH})$
PhO^-	0.62 ± 0.07 (0.60 ± 0.09)	−0.38 ± 0.07 (−0.40 ± 0.09)
$4\text{-}BrC_6H_4O^-$	0.58 ± 0.07 (0.46 ± 0.09)	−0.42 ± 0.07 (−0.54 ± 0.09)
$3,5\text{-}Cl_2C_6H_3O^-$	0.59 ± 0.06 (0.67 ± 0.06)	−0.41 ± 0.06 (−0.33 ± 0.06)

[a] First number, ρ_n based on all substituents; second number (in parentheses), ρ_n based on excluding 4-F and 4-CF$_3$, see text.

on the actual ρ and ρ_n values except for the buffer-catalyzed reactions with $4\text{-}BrC_6H_4O^-$ and $3,5\text{-}Cl_2C_6H_3O^-$ (Table 5), but in most cases the standard deviations for the ρ_n values are smaller than for the ρ values.

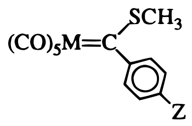
Hammett ρ Values. A. Reactions with MeO$^-$ and OH$^-$. On the basis of the Hammett plots including *all* substituents, the ρ values for k_1^{MeO}, k_{-1}^{MeO}, and K_1^{MeO} are, within the rather large experimental uncertainties, about the same for the chromium and tungsten carbene complexes, i.e., in MeOH on the order of 2.2−2.6 for k_1^{MeO}, −1.6 to −1.0 for k_{-1}^{MeO}, 4.2 for K_1^{MeO}, and 2.1 for k_1^{MeO} in 90% MeCN−10% MeOH. On the other hand, based on the plots from which the 4-F and 4-CF$_3$ derivatives are excluded, the standard deviations of most ρ values are significantly smaller which allows some distinctions between the two types of carbene complexes to be made. In particular, $\rho(k_{-1}^{MeO})$ for **6-Cr-Z** (−2.24) appears to be significantly more negative than that for **6-W-Z** (−1.67) while $\rho(K_1^{MeO})$ is significantly larger for **6-Cr-Z** (4.92) than for **6-W-Z** (4.04); $\rho(k_1^{MeO})$ is probably also larger for the chromium carbene complexes, as suggested by the results in methanol as well as in 90% MeCN−10% MeOH, although the standard deviations are still too large for a definite conclusion. The stronger substituent effect on the rate constant for oxyanion addition to the chromium carbene complexes is also seen in the larger $\rho(k_1^{OH})$ values for **6-Cr-Z** (2.23) compared to **6-W-Z** (1.68).

The smaller $\rho(K_1^{MeO})$ and $\rho(k_1^{MeO})$ values for **6-W-Z** compared to **6-Cr-Z** are consistent with the somewhat higher K_1^{MeO} and k_1^{MeO} values for the tungsten derivatives, especially those with electron-donating substituents (Table 1). The enhanced reactivity of the tungsten carbene complexes which has been noted before[4e] probably reflects a somewhat stronger stabilization of the negative charge by the (CO)$_5$W moiety in **7-W-Z$^-$** than by the (CO)$_5$Cr moiety in **7-Cr-Z$^-$**. This reduces the demand for further stabilization by the Z-substituent and lowers the ρ values.

B. Reactions with HC≡CCH$_2$O$^-$ in 50% MeCN−50% Water. The most notable feature of the reactions with $HC{\equiv}CCH_2O^-$ is that the $\rho(k_1^{RO})$ and $\rho(K_1^{RO})$ values are significantly smaller than those for the reactions with MeO$^-$, especially for the chromium carbene complexes (Table 4). For example, $\rho(K_1^{OR}) = 2.25$ (2.45)[24] for $HC{\equiv}CCH_2O^-$ vs 4.22 (4.92)[24] for MeO$^-$, or $\rho(k_1^{OR}) = 1.73$ (1.68)[24] for $HC{\equiv}CCH_2O^-$ vs 2.20 (2.67)[24] for MeO$^-$. For the tungsten carbene complexes, the differences in the ρ values for the two reactions are smaller; whether this is an artifact caused by systematic errors or a real difference between the two kinds of complexes cannot be decided. Because eq 8 is only an approximation, the k_1^{RO} values, and with them the K_1^{RO} values, may indeed be subject to significant systematic errors that are not reflected in their standard deviations.

A major factor that is likely to contribute to the smaller $\rho(K_1^{OR})$ and $\rho(k_1^{OR})$ values for the $HC{\equiv}CCH_2O^-$ reactions is the higher polarity of 50% MeCN−50% water ($\epsilon = 58.8$)[25] compared to that of methanol ($\epsilon = 32.6$). The change in nucleophile may constitute an additional factor. Since the $HC{\equiv}CCH_2O$ group in **7-M-Z$^-$** is more electron withdrawing than the MeO group, it contributes more to the stabilization of the negative charge in **7-M-Z$^-$** and the transition state leading to it than the methoxy group. This, just as is the case with a more polar solvent, reduces the requirement for stabilization of the charge by the Z-substituent.

ρ_n and β_{nuc}^n. Is There a Transition State Imbalance? The normalized ρ values for all reactions are all very close, especially the ones obtained by excluding the 4-F and 4-CF$_3$ substrates which are virtually indistinguishable, with an average value of 0.56 for $\rho_n(k_1^{OR})$ and −0.44 for $\rho_n(k_{-1}^{RO})$. Interestingly, this is also very close to $\rho_n(k_1^{RS}) = 0.54$ for the reaction of $HOCH_2CH_2S^-$ with **9-W-Z**[26] even though the Hammett ρ values for this latter reaction are quite different. It appears that the fraction of negative charge seen by the Z-substituent at the transition state relative to the charge seen on the adduct is about the same for all reactions, i.e., independent of the metal, the leaving group or the nucleophile. What is less clear is whether $\rho_n(k_1^{RO})$ can be considered a measure of C−O bond formation at the transition state. If the transitions state is imbalanced (see eq 3), $\rho_n(k_1^{RO})$ would not be such a measure. This is because the closer proximity of the negative charge to the phenyl group at the transition state compared to the situation in the adduct tends to enhance $\rho_n(k_1^{RO})$, i.e., bond formation will be less than suggested by $\rho_n(k_1^{RO})$.



9-Cr-Z (M = Cr)
9-W-Z (M = W)

The normalized β_{nuc} values (β_{nuc}^n) summarized in Table 6 can shed some light on this question. Following traditional views,[27] β_{nuc}^n may be considered an approximate measure of bond formation or charge transfer at the transition state.[28] For the reactions of **6-Cr-Cl** and **6-W-Cl** with $HC{\equiv}CCH_2O^-$ and $CF_3CH_2O^-$, the β_{nuc}^n values are 0.46 (**6-Cr-Cl**) and 0.49 (**6-W-Cl**), respectively, i.e., somewhat lower than $\rho_n(k_1^{RO})$ for the reactions of $HC{\equiv}CCH_2O^-$ with **6-Cr-Z** (0.59 (0.57)) and **6-W-Z** (0.56 (0.55)). β_{nuc}^n might actually be still lower than the values reported in Table 6, i.e., the latter should be considered upper limits because the K_1^{RO} values (Table 3) were obtained under the assumption that in eq 9 k_2^{MeO} is negligible compared to k_{-1}^{RO} (see Results section). If k_2^{MeO} were not negligible

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(22) Bernasconi, C. F.; Ketner, R. J.; Chen, X.; Rappoport, Z. *J. Am. Chem. Soc.* **1998**, *120*, 7461.

(23) ρ_n values can also be obtained as $\rho(k_1^{RO})/\rho(K_1^{RO})$ and $\rho(k_{-1}^{RO})/\rho(K_1^{RO})$ ratios, etc., but the direct determination from Brønsted plots reduces the experimental uncertainty substantially.

(24) The numbers in parentheses are based on excluding the 4-F and 4-CF$_3$ derivatives from the Hammett plots.

(25) Moreau, C.; Douhéret, G. *J. Chem. Thermodyn.* **1976**, *8*, 403.

(26) Bernasconi, C. F.; Ali, M. *J. Am. Chem. Soc.* **1999**, *121*, 11384.

(27) (a) Leffler, J. E.; Grunwald, E. *Rates and Equilibria of Organic Reactions*; Wiley: New York, 1963; p 128. (b) Kresge, A. J. In *Proton-Transfer Reactions*; Caldin, E. F., Gold, V., Eds.; Wiley: New York, 1975; p 179. (c) Jencks, W. P. *Chem. Rev.* **1985**, *85*, 511.

(28) The traditional view is not universally accepted.[29]

Table 6. Brønsted Coefficients and Intrinsic Rate Constants for the Reactions of $HC{\equiv}CCH_2O^-$ and $CF_3CH_2O^-$ with **6-Cr-Cl**, **6-Cr-CF$_3$** and **6-W-Cl** in 50% MeCN-50% Water

	6-Cr-Cl	6-W-Cl	6-Cr-CF$_3$
$\beta_{nuc} = \dfrac{d \log k_1^{OR}}{d\, pK_a^{ROH}}$	0.42	0.54	0.57
$\beta_{lg} = \dfrac{d \log k_{-1}^{RO}}{d\, pK_a^{ROH}}$	≤ -0.49	≤ -0.57	≤ -0.34
$\beta_{eq} = \dfrac{d \log K_1^{RO}}{d\, pK_a^{ROH}}$	≥ 0.91	≥ 1.11	≥ 0.91
$\beta_{nuc}^{n} = \dfrac{d \log k_1^{RO}}{d \log K_1^{RO}}$	≤ 0.46	≤ 0.42	≤ 0.62
$\beta_{lg}^{n} = \dfrac{d \log k_{-1}^{RO}}{d \log K_1^{RO}}$	≤ -0.54	≤ -0.51	≤ -0.38
$\log k_o$	≥ 0.74	≥ 0.94	≥ 0.23

compared to k_{-1}^{RO}, the true k_{-1}^{RO} values would be somewhat lower and the true K_1^{RO} somewhat higher than the reported ones, especially for $RO = HC{\equiv}CCH_2O$. This would mean that the actual β_{nuc}^{n} values would be somewhat lower than those listed in Table 6.

The fact that β_{nuc}^{n} is lower than $\rho_n(k_1^{RO})$ is suggestive of a small imbalance, but more definite conclusions will have to await further study for two reasons. (1) The β_{nuc}^{n} value for **6-Cr-CF$_3$** does not fit the pattern seen for **6-Cr-Cl** and **6-W-Cl**. This may or may not be related to the problems with systematic errors in the kinetic data for **6-Cr-CF$_3$** mentioned earlier. (2) The fact that β_{nuc}^{n} is based on only two nucleophiles leaves too much room for uncertainty in these values. Nevertheless, the notion that the transition state of these reactions is imbalanced in the sense shown in eq 3 is consistent with observations for the reaction of thiolate ions with **9-W-H** and **9-Cr-H**[26] where the β_{nuc} values are very much lower than $\rho_n(k_1^{RS})$.[30] It is also consistent with the intrinsic rate constants discussed in the next section.[31]

Intrinsic Rate Constants. The logarithmic values of the intrinsic rate constants for the addition of MeO^- to **6-Cr-H** and **6-W-H** in methanol were estimated previously to be around 0.96 and 1.25, respectively.[9] From the two-point Brønsted plots for $HC{\equiv}CCH_2O^-$ and $CF_3CH_2O^-$ addition to **6-Cr-Cl** and **6-W-Cl** in 50% MeCN−50% water, one obtains $\log k_o = 0.74$ and 0.94, respectively (Table 6); these values are virtually the same as those for the above reactions of MeO^-. For the reaction of **6-Cr-CF$_3$**, $\log k_o = 0.23$ is somewhat lower, part of which may again be an artifact.

Table 7. Brønsted Coefficients for Buffer Catalysis of MeOH Addition to **6-Cr-Z**

Z	β (k_1^{B})	α (k_{-1}^{BH})
4-MeO	0.17 ± 0.02	0.83 ± 0.02
4-Me	0.16 ± 0.02	0.84 ± 0.02
H	0.17 ± 0.04	0.83 ± 0.04
4-F	0.12 ± 0.02	0.88 ± 0.02
4-Cl	0.10 ± 0.04	0.90 ± 0.04

Table 8. ^1H NMR Data for the Carbene Complexes in $CDCl_3$

	4-Me$_2$N	4-MeO	4-Me	4-F	4-Cl	3-Cl	4-CF$_3$
			6-Cr-Z				
CH_3O	4.81	4.87	4.84	4.80	4.77	4.75	4.75
Ar	6.63	6.85	7.24	7.08	7.35	7.18, 7.25	7.30
	7.99	7.77	7.36	7.48		7.36	7.65
Z	3.11	3.89	2.40				
			6-W-Z				
CH_3O		4.76	4.77	4.78	4.77		
Ar		6.92	7.23	7.10	7.43		
		7.89	7.63	7.71	7.54		
Z		3.79	2.40				

As elaborated upon previously,[9] the $\log k_o$ values are about 2 log units lower than those for MeO^- addition to carboxylate esters. This is consistent with the notion that the transition state in the carbene complex reactions is imbalanced while no such imbalance occurs in the ester reactions because there is no charge delocalization in the tetrahedral adducts.

On the other hand, the intrinsic rate constants for alkoxide ion addition to the carbene complexes are not as low as for MeO^- addition to some other electrophiles such as 2,6-dinitro-4-methylsulfonylanisole ($\log k_o \approx -0.76$)[34] or β-methoxy-α-nitrostilbene ($\log k_o \approx -3.9$).[35] A similar finding was reported for thiolate ion addition to **6-Cr-H** and **6-W-H** where the intrinsic rate constants were estimated to be about 2 orders of magnitude higher than for thiolate ion addition to β-methoxy-α-nitrostilbene.[4e] These results imply that resonance stabilization of **7-M-Z$^-$** resulting from charge delocalization is not as strong as in the adducts derived from these other electrophiles. This, in turn, suggests that the transition state imbalance for the carbene complex reactions should not be very large, consistent with the relatively small differences between $\rho_n(k_1^{RO})$ and β_{nuc}^{n} discussed in the previous section.

Buffer-Catalyzed MeOH Addition to 6-Cr-Z. $\rho_n(k_1^{B})$ values for reversible methanol addition to **6-Cr-Z** catalyzed by PhO^-, $4\text{-}BrC_6H_4O^-$, and $3,4\text{-}Cl_2C_6H_3O^-$ buffers are summarized in Table 5. Although the experimental uncertainties are larger than for the $\rho_n(k_1^{RO})$ values for MeO^- addition (Table 4), thus precluding firm conclusions, it nevertheless appears that the $\rho_n(k_1^{B})$ values are somewhat larger than the $\rho_n(k_1^{OR})$ values and the $\rho_n(k_{-1}^{BH})$ values somewhat smaller than the $\rho_n(k_{-1}^{RO})$ values. This suggests transition states with more advanced charge development on the $(CO)_5Cr$ moiety and more bond formation than in the MeO^- reactions. Since methanol is a weaker nucleophile than MeO^-, even when assisted by a general base, these results are consistent with the Hammond−Leffler principle.[27a,36]

Additional information about the transition state is obtained from the dependence of k_1^{B} and k_{-1}^{BH} on the pK_a^{BH} of the buffer, which yields the Brønsted β and α values summarized in Table 7. The β values are quite small (0.10−0.17) and the α values

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[29] (a) Johnson, C. D. *Tetrahedron* **1980**, *36*, 3461. (b) Pross, A. *J. Org. Chem.* **1984**, *49*, 1811. (c) Bordwell, F. G.; Hughes, D. L. *J. Am. Chem. Soc.* **1985**, *107*, 4737.

[30] In these reactions, desolvation of the nucleophile complicates the picture but still allows the conclusion that bond formation has made very little progress at the transition state.[26]

[31] A reviewer has raised the question as to whether the observed transition state imbalance might "be an effect imposed by the specific solvent chosen rather than an inherent feature of the reaction system." On the basis of numerous studies that show the characteristics of imbalanced transition states for a variety of reactions in a variety of solvents[15,32] as well as in the absence of any solvent,[33] we conclude that imbalances *are* inherent features of the reaction. On the other hand, the *magnitude* of the imbalance often depends on the solvent.[15,32,33]

[32] Bernasconi, C. F.; Wenzel, P. J. *J. Am. Chem. Soc.* **1996**, *118*, 11446.

[33] (a) Bernasconi, C. F.; Wenzel, P. *J. Am. Chem. Soc.* **1994**, *116*, 5405. (b) Bernasconi, C. F.; Wenzel, P. J.; Keeffe, J. R.; Gronert, S. *J. Am. Chem. Soc.* **1997**, *119*, 4008.

[34] Terrier, F.; Millot, F.; Morel, J. *J. Org. Chem.* **1976**, *41*, 3892.

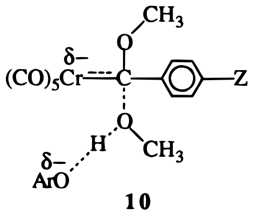
[35] Bernasconi, C. F.; Fassberg, J.; Killion, R. B.; Schuck, D. F.; Rappoport, Z. *J. Am. Chem. Soc.* **1991**, *113*, 4937.

[36] Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

Table 9. ^{13}C NMR Data for the Carbene Complexes in $CDCl_3$

	4-Me_2N	4-MeO	4-Me	4-F	4-Cl	3-Cl	4-CF_3
			6-Cr-Z				
C=	326.0	351.2	348.3	346.8	348.0	348.8	350.0
$(CO)_5$ trans	223.6	224.8	224.0	223.7	223.8	223.8	223.7
cis	217.7	215.7	216.5	216.2	216.1	215.8	215.6
CH_3O	66.1	65.7	67.2	67.4	67.4	67.4	67.4
Ar	153.8	154.0	151.0	162.3	151.7	154.8	156.2
	139.9	132.1	141.9	149.9	137.0	134.0	130 or 128
	132.3	129.6	128.8	127.3	128.4	129.9	125.4
		123.8	124.8	115.0	125.4	122.0	122.4
Z	39.9	55.7	21.4				130 or 128
			6-W-Z				
C=		313.4	319.4	318.1	319.1		
$(CO)_5$ trans		203.0	203.3	203.1	203.2		
cis		197.8	197.6	197.2	197.1		
CH_3O		69.8	70.0	70.1	70.1		
Ar		164.0	152.2	167.1	153.1		
		146.9	143.6	163.1	131.3		
		132.1	128.9	130.1	128.8		
		124.3	128.0	130.0	128.1		
Z		55.6	21.6				

quite large (0.83−0.90), suggesting that the proton is close to the methanol oxygen at the transition state (**10**). This, then, is another type of transition state imbalance where proton transfer to the buffer base apparently lags behind C−O bond formation.



10

Experimental Section

Materials. The various carbene complexes, **6-Cr-Z** (Z = 4-Me_2N, 4-MeO, 4-Me, 4-F, 4-Cl, 3-Cl, and 4-CF_3) and **6-W-Z** (Z = 4-MeO, 4-Me, and 4-Cl), were synthesized as described by Fischer et al.[37] Tables 8 and 9 summarize their ^1H and ^{13}C NMR data which were recorded in $CDCl_3$ on a Bruker 250 MHz spectrometer. **6-Cr-H** and **6-W-H** were available from a previous study.[9] Phenol was recrystallized from toluene; 4-bromophenol and 3,5-dichlorophenol (Aldrich) were used without further purification. Triethylamine was refluxed over Na/CaH_2 and freshly distilled prior to use. Methanol and reagent grade acetonitrile were purified by fractional distillation and stored over 4-Å molecular sieves. Water was taken from a Milli Q purification system.

Solutions of NaOMe in methanol were prepared by adding freshly cut Na metal to methanol at 0 °C and allowing the reaction to go to completion under nitrogen or argon. The concentrations of NaOMe stock solutions were determined by titration against 0.08 M HCl using phenolphthalein as indicator.

Stopped-Flow Kinetics. In the conventional mode, rates were measured by monitoring the disappearance of the carbene complexes around 400 nm (450 nm for **6-M-NMe$_2$**) in an Applied Photophysics DX.17MV stopped-flow apparatus. For UV spectra of **1-M** and adducts of the general structure **2-M**$^-$, see refs 4d, 4e, and 9. Stock solutions of the substrate were initially prepared in acetonitrile where the carbene complexes are more stable than in methanol or aqueous acetonitrile. Reaction solutions in methanol or aqueous acetonitrile were only prepared immediately prior to an experiment; the stability of these solutions could be enhanced by adding 2.5×10^{-3} M CH_3SO_3H in methanol or 2.5×10^{-3} M HCl in 50% MeCN−50% water. For **6-Cr-CF$_3$**, the decomposition in aqueous acetonitrile even in the presence of HCl was too rapid to allow the preparation of reaction solutions outside the stopped-flow apparatus. Hence the experiments were conducted by mixing a solution of **6-Cr-CF$_3$** in pure MeCN with that of the appropriate nucleophile in water, yielding a 50% MeCN−50% water solution in the course of the stopped-flow experiment. Because the mixing of water with MeCN leads to a decrease in temperature, the initial temperature of the separate solutions was set at 29.5 °C in order to achieve a temperature of 25 °C after mixing. The assumed 4.5° temperature drop was based on an Arrhenius plot of the reaction of **6-Cr-Cl** with 0.1 M KOH. This attempt at correcting for the cooling of the reaction solution is somewhat crude and may have contributed to the rate constants for the reactions of **6-Cr-CF$_3$** to be deviating negatively from the Hammett plots.

For the experiments in the sequential mixing mode, the methoxide ion adducts were generated in the presence of 0.1 M NaOMe. After a delay time of 0.5−5 s, the solution containing the adduct was mixed with the buffer solution; the buffer solution was such as to both fully neutralize the NaOMe and leave enough free buffer acid to give a convenient [B]/[BH] ratio.

The reactions of the $HC{\equiv}CCH_2O^-$ and $CF_3CH_2O^-$ adducts with triethylamine buffers were conducted in a different manner. Because of competition with the OH^- reaction, the adducts could not easily be generated at sufficient concentrations in 50% MeCN−50% water. Hence they were generated in pure acetonitrile instead by adding small amounts of $HC{\equiv}CCH_2O^-/HC{\equiv}CCH_2OH$ and $CF_3CH_2O^-/CF_3CH_2OH$ (5×10^{-4} M) to the carbene complex. The adducts generated in this manner were stable for approximately 20 min, thus obviating the need for sequential mixing stopped-flow experiments. The kinetics of their reversal to reactants were conducted by mixing the acetonitrile solution of the adduct with an aqueous solution of the triethylamine buffer in the stopped-flow apparatus. As described above for the reactions of **6-Cr-CF$_3$**, the initial temperature was set at 29.5 °C in order to compensate for the cooling during the mixing process.

p*K*$_a$ of HC≡CCH$_2$OH and CF$_3$CH$_2$OH in 50% MeCN−50% Water. These pK_a values were obtained as $pK_a = pK_w - \log K_{OH}$, with pK_w being the ionic product of the solvent[38] and K_{OH} being defined by eqs 10 and 11. K_{OH} was determined by measuring the pH of solutions

$$ROH + OH^- \overset{K_{OH}}{\rightleftharpoons} RO^- + H_2O \tag{10}$$

$$K_{OH} = [RO^-]/[ROH][OH^-] \tag{11}$$

prepared by adding 1.60×10^{-2} M KOH and various concentrations of the respective alcohol to the solvent, and making use of the relationships $[RO^-] + [OH^-] = [KOH]_0$ and $[RO^-] + [ROH] = [ROH]_0$. In evaluating the actual pH, 0.18 unit was added to the measured pH according to Allen and Tidwell.[40] These measurements were made with an Orion 611 pH meter equipped with a glass electrode and a Sure Flow (Corning) reference electrode.

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