Physical Organic Chemistry of Transition Metal Carbene Complexes. 7.[1] Kinetics of Hydrolysis of $(CO)_5M=C(OR)Ph$ (M = Cr, W; R = Me, Et) and $(CO)_5Cr=(OMe)CH=CHPh$ in Aqueous Acetonitrile

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Abstract: A study of the hydrolysis of $(CO)_5Cr=C(OMe)Ph$ (**1a**), $(CO)_5Cr=C(OEt)Ph$ (**1b**), $(CO)_5Cr=C(OMe)CH=CHPh$ (**1c**), $(CO)_5W=C(OMe)Ph$ (**1d**), and $(CO)_5W=C(OEt)Ph$ (**1e**) in 50% MeCN−50% water (v/v) at 25 °C is reported. The reaction occurs in two stages; the first is the formation of $(CO)_5M=C(O^-)R$ or $(CO)_5M=C(OH)R$ (M = Cr or W, R = Ph or CH=CHPh) while the second, much slower stage is the formation of RCH=O and $(CO)_5MOH^-$. This paper reports a kinetic investigation of the first stage. It is shown that nucleophilic attack by OH^- at high pH and by water at low pH, presumably to form a tetrahedral intermediate, is rate limiting; in the presence of buffers general base catalysis of water addition is observed. Kinetic solvent isotope effects of ca. 1 for the OH^- and of 3 to 4.7 for the water pathways are also reported. The results lead to insights regarding the following points: (1) effect of changing the metal (Cr vs W), the alkoxy group (MeO vs EtO), and the R group (Ph vs CH=CHPh) on reactivity; (2) relative reactivity of Fischer carbene complexes vs carboxylic esters; (3) reasons why a tetrahedral intermediate is not detectable even though the equilibrium for its formation is probably favorable at high pH; and (4) reasons why the hydrolysis of Fischer carbene complexes containing an acidic proton such as $(CO)_5Cr=C(OMe)CH_3$ follow an entirely different mechanism.

The hydrolysis of Fischer type transition metal carbene complexes has, thus far, received very little attention. This is surprising in view of the growing importance of these metal carbene complexes in the laboratory of organic and organometallic chemists;[2] it probably derives from the fact that, until recently, the major interest in these compounds has been their potential utility in synthesis.

The first hydrolysis study we are aware of is that reported in 1993 by Aumann et al.,[3] who investigated the reaction of several Fischer carbene complexes of the type **1-R** (R = Ph, CH=CHPh,
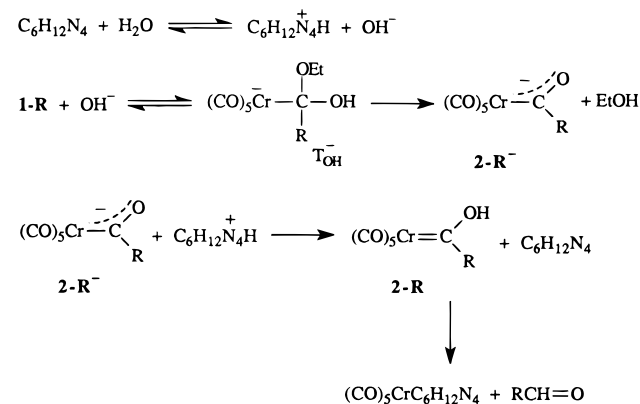

$$RCH=O + (CO)_5CrC_6H_{12}N_4 + EtOH \quad (1)$$
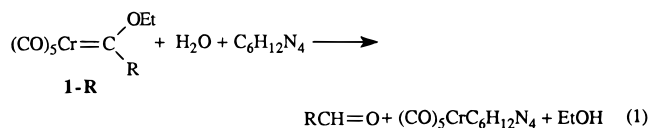
C_4H_3S, CH=CHC_4H_3S, and C≡CPh) in THF containing small quantities of water. In the presence of the tricyclic amine urotropine (hexamethylenetetramine, $C_6H_{12}N_4$) the aldehyde RCH=O is formed in ≥90% yield with all R groups except when R is C≡CPh; in this latter case the triple bond undergoes nucleophilic attack by the amine.

Scheme 1

Based on their product analysis, which also included the demonstration that in the presence of D_2O the aldehyde formed was RCD=O, Aumann et al.[3] proposed the mechanism shown in Scheme 1. It involves two principal stages. The first is a nucleophilic substitution of the ethoxy group of **1-R** by a hydroxy group which presumably proceeds through a tetrahedral intermediate (T_{OH}^-). The nucleophile, OH^-, is generated in the acid−base equilibrium between water and urotropine. The second stage is the conversion of **2-R** into the corresponding aldehyde, a known reaction reported by Fischer and Maasböl;[4] since under basic conditions the product of the first stage is undoubtedly present in its anionic form (**2-R$^-$**), fast protonation of **2-R$^-$** precedes the product forming step. Note that **2-R** and **2-R$^-$** with R = Ph or Me as well as the tungsten analogs are isolable compounds that have been fully characterized.[5]

[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1997.
(1) Part 6: Bernasconi, C. F.; Sun, W. *Organometallics* **1995**, *14*, 5615.
(2) For recent reviews see: (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1983. (b) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (c) Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, *25*, 121. (d) Wulff, W. D. *Adv. Met.-Org. Chem.* **1989**, *1*, 209. (e) Schubert, U., Ed. *Advances in Metal Carbene Chemistry*; Kluwer: Dordrecht, Holland, 1989. (f) Dötz, K. H. *New J. Chem.* **1990**, *14*, 433. (g) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1990; Vol. 5. (h) Schmidt, M. A.; Miller, J. R.; Hegedus, L. S. *J. Organomet. Chem.* **1991**, *413*, 143. (i) Veillard, A. *Chem. Rev.* **1991**, *91*, 743.
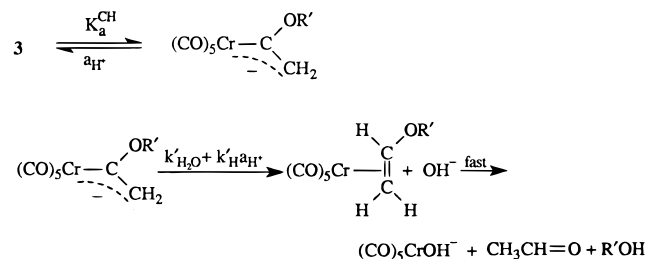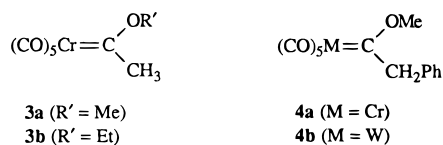
(3) Aumann, R.; Hinterding, P.; Krüger, C.; Goddard, R. *J. Organomet. Chem.* **1993**, *459*, 145.
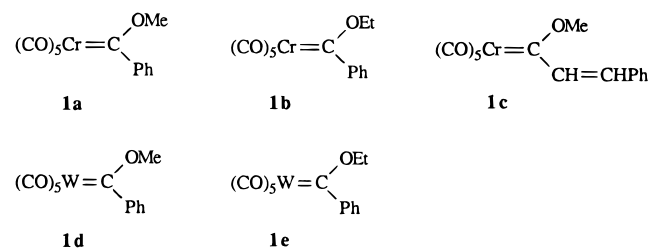(4) Fischer, E. O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2445.

Scheme 2

$$3 \quad \underset{a_{H^+}}{\overset{K_a^{CH}}{\rightleftharpoons}} \quad (CO)_5Cr \!-\! C\!\!\begin{array}{l} \diagup OR' \\ \diagdown CH_2 \end{array}$$

$$(CO)_5Cr \!-\! C\!\!\begin{array}{l} \diagup OR' \\ \diagdown CH_2 \end{array} \xrightarrow{k'_{H_2O} + k'_H a_{H^+}} (CO)_5Cr \!-\!\! \begin{array}{c} H \diagdown \; \diagup OR' \\ C \\ \| \\ C \\ H \diagup \; \diagdown H \end{array} \!+\! OH^- \xrightarrow{\text{fast}}$$

$$(CO)_5CrOH^- + CH_3CH\!\!=\!\!O + R'OH$$

Some other carbene complexes whose hydrolyses have recently been studied are of the type **3**[6] and **4**.[1] These reactions were investigated in 50% acetonitrile−50% water over a wide pH range. The carbene complex **3** yielded $CH_3CH\!\!=\!\!O$ and

$$(CO)_5Cr\!\!=\!\!C\!\!\begin{array}{l} \diagup OR' \\ \diagdown CH_3 \end{array} \qquad\qquad (CO)_5M\!\!=\!\!C\!\!\begin{array}{l} \diagup OMe \\ \diagdown CH_2Ph \end{array}$$

3a (R′ = Me)   **4a** (M = Cr)
3b (R′ = Et)   **4b** (M = W)

R′OH as the organic products while the main organic product in the reaction of **4** was $PhCH\!\!=\!\!CHOMe$. A detailed kinetic study revealed that these substrates hydrolyze by a mechanism that is quite different from that for **1-R** and involves the deprotonated forms of **3** and **4**, respectively, as the crucial intermediates (e.g., Scheme 2).[7]

The question why the mechanism of Scheme 2 is more favorable than the nucleophilic substitution pathway and hence is the mechanism that prevails in the hydrolysis of **3** and **4** is an interesting one. A kinetic study of the hydrolysis of non-ionizable carbene complexes such as **1-R**, under the same reaction conditions used in the hydrolysis of **3** and **4**, should provide some quantitative reactivity comparisons that bear directly on the question of competition between the two mechanisms. This paper reports such an investigation using **1a**−**1e** as substrates. Other objectives of the study include the

$$(CO)_5Cr\!\!=\!\!C\!\!\begin{array}{l} \diagup OMe \\ \diagdown Ph \end{array} \qquad (CO)_5Cr\!\!=\!\!C\!\!\begin{array}{l} \diagup OEt \\ \diagdown Ph \end{array} \qquad (CO)_5Cr\!\!=\!\!C\!\!\begin{array}{l} \diagup OMe \\ \diagdown CH\!\!=\!\!CHPh \end{array}$$

1a   **1b**   **1c**

$$(CO)_5W\!\!=\!\!C\!\!\begin{array}{l} \diagup OMe \\ \diagdown Ph \end{array} \qquad (CO)_5W\!\!=\!\!C\!\!\begin{array}{l} \diagup OEt \\ \diagdown Ph \end{array}$$

1d   **1e**

following. (1) Determine which step is rate limiting in Scheme 1 and whether any intermediate (T_{OH}^-, **2R**$^-$, **2R**) accumulates to detectable levels in the course of the reaction. (2) Assess how the reactivity of these carbene complexes depends on the metal (Cr vs W), the alkoxy group (MeO vs EtO), and the other substituent attached to the carbon (Ph vs Ch=CHPh). (3) Evaluate the potential competition between nucleophilic addition to the carbene carbon and to the PhCH carbon (Michael addition) of **1c**. (4) Generate data that are useful from a practical

(5) Fischer, E. O.; Kreis, G.; Kreissl, F. R. *J. Organomet. Chem.* **1973**, *56*, C37.

(6) Bernasconi, C. F.; Flores, F. X.; Sun, W. *J. Am. Chem. Soc.* **1995**, *117*, 4875.

(7) In the reaction of **4** the complex between $(CO)_5Cr$ and PhCH=CHOCH$_3$ is not hydrolyzed but dissociates into $(CO)_5CrOH^-$ and PhCH=CHOCH$_3$.[1]
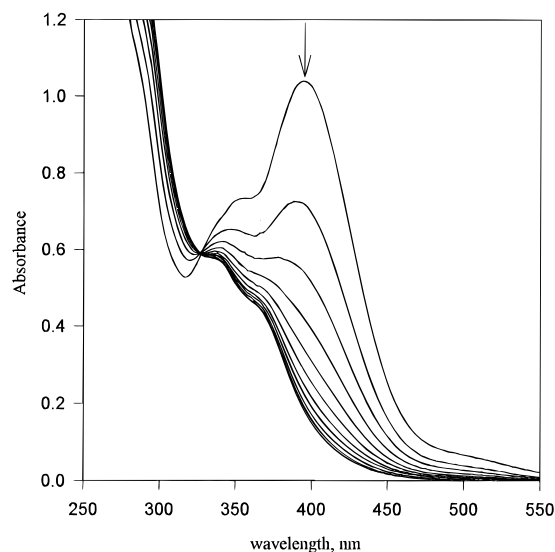
Figure 1. Time-dependent absorption spectra of **1d** in a triethylamine buffer at pH 10.63. Scans taken every 60 s. Arrow shows direction of change with time.
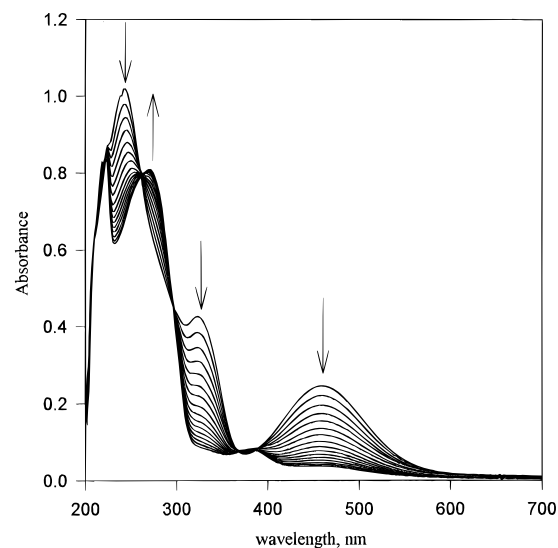
Figure 2. Time-dependent absorption spectra of **1c** in a 0.005 M KOH solution. Scans taken every 2 s. Arrows show direction of change with time.

point of view in that they allow an assessment of how strongly hydrolysis interferes with other reactions conducted in aqueous media.[8]

Results

General Features and Kinetics. All experiments were carried out in 50% acetonitrile−50% water (v/v) at 25 °C. When any of the carbene complexes **1a**−**1e** were placed into a KOH solution a rapid loss of the substrate was observed by monitoring the absorption spectrum of the sample. Two representative examples are shown in Figures 1 (**1d**) and 2 (**1c**). The presence of sharp isosbestic points is indicative of a clean reaction.

Rates were determined in KOH and HCl solutions as well as in triethylamine, *N*-methylmorpholine, and acetate buffers, covering a pH range from about 2 to 13 or 14. All rates were measured under pseudo-first-order conditions with either KOH,

(8) For example in the study of **1a** with amines[9a] and thiolate ions.[9b]

(9) (a) Bernasconi, C. F.; Stronach, M. W. *J. Am. Chem. Soc.* **1993**, *115*, 1341. (b) Bernasconi, C. F.; Flores, F. X.; Kittredge, K. W. To be submitted for publication.
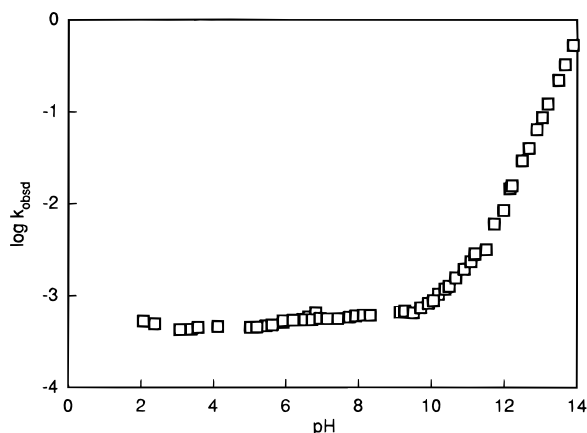
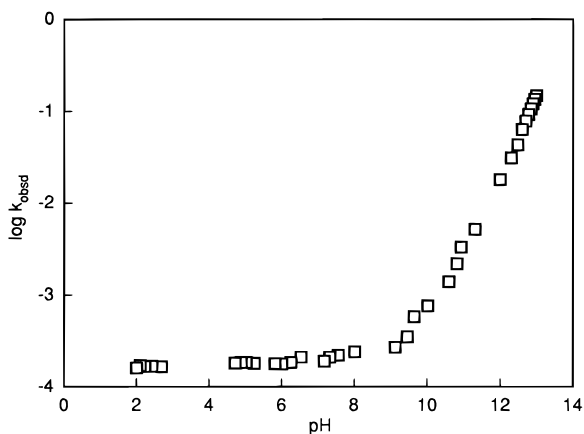**Figure 3.** pH−rate profile of the hydrolysis of **1b**.

Figure 4. pH−rate profile of the hydrolysis of **1c**.

HCl, or the buffer in large excess over the carbene complex. Two kinetic processes were observed. The first one is relatively fast and, at very high pH, is in the stopped-flow range. It corresponds to the decay of the carbene complex as shown in Figures 1 and 2. Above pH 3 or 4 this first process shows clean first-order kinetics without interference by the much slower second reaction. However, below pH 3 the slow process starts to become competitive with the first which manifests itself in biphasic kinetic traces.

In the present paper we focus on the first process; the second process will be the subject of a future report. The pH−rate profiles for the first process are very similar for all substrates studied. Figures 3 and 4 show two representative examples. For the reactions run in buffer solutions, general base catalysis by the buffer base was observed. In the typical buffer concentration range of 0.001 to 0.1 M increases in k_{obsd} due to catalysis of up to approximately 4-fold were observed. Some representative buffer plots are included under Supporting Information.[10] The points on the pH−rate profiles that refer to buffer solutions were obtained by extrapolation to zero buffer concentration. Some of the scatter in the intermediate region of the pH−rate profiles, especially Figure 3, may be attributed to uncertainties in the extrapolated intercepts of the buffer plots.

Our kinetic results imply that k_{obsd} is given by eq 2. The k_{H_2O} and k_{OH} values are

$$k_{obsd} = k_{H_2O} + k_{OH}a_{OH^-} + k_B[B] \qquad (2)$$

summarized in Table 1, the k_B values in Table 2.

(10) See paragraph concerning supporting information at the end of this paper.
(11) The spectrum of $(CO)_5CrX$ under the same reaction conditions has been published in ref 1.

Table 1. Summary of k_{H_2O} and k_{OH} Values Based on pH−Rate Profiles

	$k_{H_2O} = k_1^{H_2O},^a$ s^{-1}	$k_{OH} = k_1^{OH},$ $M^{-1} s^{-1}$
$(CO)_5Cr=C(OMe)Ph$ (**1a**)	2.9×10^{-3}	26.6 ± 0.3
$(CO)_5Cr=C(OEt)Ph$ (**1b**)	4.5×10^{-4}	10.5 ± 0.1
$(CO)_5Cr=C(OMe)CH=CHPh$ (**1c**)	1.8×10^{-4}	14.6 ± 0.2
$(CO)_5W=C(OMe)Ph$ (**1d**)	2.8×10^{-3}	26.3 ± 0.2
$(CO)_5W=C(OEt)Ph$ (**1e**)	4.7×10^{-4}	17.6 ± 0.3

a Estimated experimental error $\pm10\%$ or better.

With the objective of determining the kinetic solvent isotope effects on k_{OH} and k_{H_2O}, a number of experiments were conducted in KOD/MeCN/D₂O and DCl/MeCN/D₂O. In order to ensure complete comparability with the conditions in the deuterated solvent (see Experimental Section) a few corresponding experiments in KOH/MeCN/H₂O and HCl/MeCN/H₂O were rerun. The results are summarized in Tables 3 (k_{OH}, k_{OD}) and 4 (k_{H_2O}, k_{D_2O}); the k_{OH} and k_{H_2O} obtained in the reruns were virtually the same as the original values (Tables 1 and 2).

Product Study. Even though Aumann's[3] results suggested that the corresponding aldehyde should be the final product in our reactions as well, it seemed desirable to confirm this under our reaction conditions. Hence the hydrolysis of two representative substrates, **1a** and **1d**, was carried out at elevated concentrations but otherwise under the same conditions used in the kinetic experiments. Product analysis was performed by GC. A sample of **1a** subjected to hydrolysis in 0.1 M KOH for 1 h yielded 1.2% benzaldehyde. After an additional 23 h GC analysis yielded 67.9% benzaldehyde and 29.6% benzoic acid, for a total yield of 97.5%. From the kinetic measurements it is clear that the first stage of the reaction must have reached completion during the 1-h exposure to 0.1 M KOH, but the product analysis shows that the second stage has made little progress during that time. However, after another 23 h the second stage is complete. A similar experiment with **1d** yielded 80% benzaldehyde and 19% benzoic acid after completion of stage 2. The question as to how benzoic acid is being formed will be addressed in a future paper. As a control, a product analysis for the reaction of **1d** was also performed under the conditions used by Aumann et al.[3] It showed a 91% yield of benzaldehyde and a 4% yield of benzoic acid.

Discussion

Mechanism. The process described in the Results section can be attributed to the nucleophilic substitution of the OMe or OEt group in the carbene complex by OH which is essentially stage 1 in the Aumann mechanism (Scheme 1), while the second, much slower process must be the conversion of $(CO)_5M=C(OH)R$ to the aldehyde (stage 2 in Scheme 1). A possible alternative interpretation of our results would be that the observed fast kinetic process refers to the entire reaction, i.e., conversion of the carbene complex to the aldehyde. This would require that the second stage is faster than the first and that the observed slow kinetic process is the result of some decomposition reaction of the metal pentacarbonyl moiety. Two observations render this alternative interpretation untenable. (1) The absorption spectra at the end of the first process do not match those of a mixture of the aldehyde and $(CO)_5MX^{11}$ (X = OH⁻ and/or CH₃CN). (2) Only traces of benzaldehyde could be detected at the end of the first process in the reaction of **1a** and **1d**. The fact that **2a**, **2b**, **2d**, and **2e** (Scheme 3 below) have been shown to be stable enough to be isolated[5] also make the alternative interpretation unattractive.

Scheme 3 is a representation of the first stage of the reaction which takes into account all potential pathways under basic as

Table 2. Summary of k_B Values for General Base Catalysis[a]

	$k_{AcO^-} = k_1^{AcO}$,[b] $M^{-1} s^{-1}$	$k_{NMM} = k_1^{NMM}$,[c,d] $M^{-1} s^{-1}$	$k_{Et_3N} = k_1^{Et_3N}$,[e] $M^{-1} s^{-1}$
$(CO)_5Cr=C(OMe)Ph$ (**1a**)	3.30×10^{-2}	2.50×10^{-2}	1.58×10^{-1}
$(CO)_5Cr=C(OEt)Ph$ (**1b**)	9.67×10^{-3}	4.64×10^{-3}	3.00×10^{-2}
$(CO)_5Cr=C(OMe)CH=CHPh$ (**1c**)	1.56×10^{-4}		
$(CO)_5W=C(OMe)Ph$ (**1d**)	3.50×10^{-2}	3.60×10^{-2}	1.35×10^{-1}
$(CO)_5W=C(OEt)Ph$ (**1e**)	1.30×10^{-2}	8.18×10^{-3}	3.40×10^{-2}

[a] Estimated error in the k_B values ±15% or better. [b] $pK_a(AcOH) = 5.91$. [c] NMM = *N*-methylmorpholine. [d] $pK_a(NMMH^+) = 7.50$. [e] $pK_a(Et_3NH^+) = 10.20$.

Table 3. Summary of k_{OH} and k_{OD} Values[a]

	$k_{OH} = k_1^{OH}$, $M^{-1} s^{-1}$	$k_{OD} = k_1^{OD}$, $M^{-1} s^{-1}$	$k_{OH}/k_{OD} = k_1^{OH}/k_1^{OD}$
$(CO)_5Cr=C(OMe)Ph$ (**1a**)	26.7 ± 0.3	26.5 ± 0.6	1.01 ± 0.03
$(CO)_5Cr=C(OEt)Ph$ (**1b**)	10.7 ± 0.2	11.0 ± 0.2	0.97 ± 0.04
$(CO)_5W=C(OMe)Ph$ (**1d**)	28.2 ± 0.5	27.8 ± 0.5	1.01 ± 0.04
$(CO)_5W=C(OEt)Ph$ (**1e**)	16.9 ± 0.3	18.6 ± 0.7	0.91 ± 0.05

[a] k_{OH} based on the slope of k_{obsd} *vs* $[OH^-]$ at five concentrations in the range from 0.0048 to 0.048 M. [b] k_{OD} based on the slope of k_{obsd} *vs* $[OD^-]$ at five concentrations in the range from 0.004 to 0.04 M.

well as acidic conditions. Specifically, $k_1^{H_2O}$ and $k_1^{OH} a_{OH^-}$ represent nucleophilic addition of water and OH^-, respectively, while $k_{-1}^H a_{H^+}$ and $k_{-1}^{H_2O}$ refer to H^+-catalyzed and spontaneous loss of OH^- from T_{OH}^-, respectively. Regarding product formation, the scheme allows for the possibility of either direct conversion of T_{OH}^- to products by unimolecular ($k_2^{H_2O}$), H^+-catalyzed ($k_2^H a_{H^+}$) or intramolecularly acid catalyzed (k_2^i) expulsion of $R'O^-$, or of reaction via the dianionic form of the intermediate (T_{OH}^{2-}), again with either spontaneous ($k_3^{H_2O}$) or H^+-catalyzed (k_3^H) loss of $R'O^-$. Note that for simplicity the buffer-catalyzed pathways ($k_1^B[B]$, $k_{-1}^{BH}[BH]$, $k_2^{BH}[BH]$, $k_3^{BH}[BH]$) have been omitted from the scheme.

It is noteworthy that in view of reports of Michael addition products in the reaction of **1c** with organometallic reagents[12a] and enolate ions[12b] we find no evidence for OH^- or water attack on the PhCH carbons. It is conceivable that fast reversible Michael addition could precede nucleophilic substitution at the carbene carbon. However, if there were a substantial pre-equilibrium buildup of a Michael adduct, it would result in a downward curvature of the pH–rate profile at high pH which is not observed.

Reactions in Basic Solution. Does the Intermediate Accumulate? To facilitate the discussion we shall deal with the reactions in basic and acidic solution separately. We first consider the pH range where $k_{OH} a_{OH^-} \gg k_{H_2O}$ (eq 2), i.e., the sloping part of the pH–rate profiles, and ask the question whether T_{OH}^- or T_{OH}^{2-} accumulate to detectable levels during the reaction. In the hydrolysis of carboxylic esters, which are often regarded as models for Fischer carbene complexes,[2a,e,13] the corresponding tetrahedral intermediates (**5**) are very unstable,
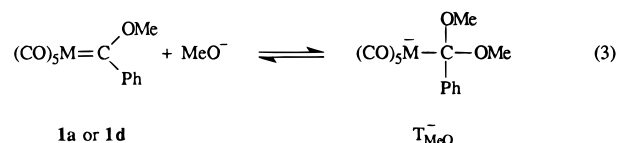
$$^-O-\underset{\underset{R}{|}}{\overset{\overset{OR'}{|}}{C}}-OH$$

5
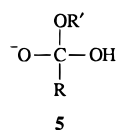
and to raise the possibility of their accumulation to detectable levels during hydrolysis would be far fetched.[14] However, T_{OH}^- in Scheme 2 is expected to be much more stable than **5**

(12) (a) Casey, C. P.; Brunsvold, W. R. *J. Organomet. Chem.* **1994**, *77*, 345. (b) Casey, C. P.; Brunsvold, W. R. *Inorg. Chem.* **1977**, *16*, 391.
(13) Werner, H.; Fischer, E. O.; Heckl, B.; Kreiter, C. G. *J. Organomet. Chem.* **1971**, *28*, 367.

and the notion that it could reach non-steady-state concentrations is not unrealistic. For example, equilibrium constants for MeO^- addition to **1a** and **1d** in methanol, eq 3, are 70.1 and 111 M^{-1},

$$(CO)_5M=C\overset{OMe}{\underset{Ph}{\diagup}} + MeO^- \rightleftharpoons (CO)_5\overset{-}{M}-\underset{\underset{Ph}{|}}{\overset{\overset{OMe}{|}}{C}}-OMe \quad (3)$$

1a or **1d** T_{MeO}^-

respectively.[16] This means that at $[MeO^-] = 0.01$ M about 50% of the carbene complex is present as adduct. Hydroxide ion in water is somewhat less basic and less nucleophilic than methoxide ion in methanol. For instance, the equilibrium constant for OH^- addition to 1,3,5-trinitrobenzene, to form a Meisenheimer complex in water, is about 6-fold smaller than the equilibrium constant for MeO^- addition in methanol;[17] a similar ratio can be estimated for MeO^- (MeOH) vs OH^- (H_2O) addition to methylbenzoate.[16] However, judging from $pK_w = 15.19$ in 50% acetonitrile–50% water,[18] the solvent used in this study, the basicity of OH^- in this medium is significantly higher than in pure water and one expects that this would be reflected in higher equilibrium constants for OH^- addition (K_1^{OH}) to electrophiles.[20] We conclude that the equilibrium constants for OH^- addition to **1a** and **1d** in 50% acetonitrile–50% water should not be substantially lower than the equilibrium constants for MeO^- addition in methanol and may be comparable to or even higher than the latter, especially if the statistical factor of 2[21] in favor of OH^- addition is taken into account.

Based on the above considerations, the equilibrium of the first step in Scheme 2 probably favors T_{OH}^- at the highest OH^- concentrations used (0.05 M), yet there is no evidence for the accumulation of an intermediate to significant concentrations. If such an accumulation were to occur, this should be reflected in a rate of product formation that is slower than the rate of decay of the substrate and would manifest itself in a wavelength dependence of k_{obsd}. The wavelength dependence at 0.05 M

(14) The equilibrium constant for formation of the tetrahedral intermediate in the reaction of methylbenzoate with OH^- has been estimated to be 8.3 $\times 10^{-8}$ M^{-1}.[15]
(15) Guthrie, J. P.; Cullimore, P. A. *Can. J. Chem.* **1980**, *58*, 1281.
(16) Bernasconi, C. F.; Flores, F. X.; Gandler, J. R.; Leyes, A. E. *Organometallics* **1994**, *13*, 2186.
(17) Bernasconi, C. F. *J. Am. Chem. Soc.* **1970**, *92*, 4682.
(18) At the ionic strength of 0.1 M used in the present work.[19]
(19) Bernasconi, C. F.; Sun, W. *J. Am. Chem. Soc.* **1993**, *115*, 12526.
(20) Based on the pK_a values of **3a**[19] one calculates equilibrium constants of 25.1 and 490 for the reaction $(CO)_5Cr=C(OMe)CH_3 + OH^- \rightleftharpoons (CO)_5Cr^- C(OMe)=CH_2 + H_2O$ in water and 50% acetonitrile–50% water, respectively. This shows that essentially the entire increase in pK_w is reflected in the enhanced equilibrium constant of this reaction, apparently because the strong charge dispersion in $(CO)_5Cr^-C(OMe)=CH_2 \leftrightarrow (CO)_5Cr=C(OMe)CH_2^-$ renders this anion insensitive to changes in solvation. In T_{OH}^- there is only charge dispersion into the CO groups so T_{OH}^- is expected to be somewhat more sensitive to the reduced solvation in 50% acetonitrile and the enhancement in K_1^{OH} should be less dramatic.
(21) The equilibrium constant for eq 3 is statistically disfavored because the loss of MeO^- from T_{MeO}^- is statistically favored over the loss of OH^- from T_{OH}^-.

Table 4. Summary of k_{H_2O} and k_{D_2O} Values

	$10^3(k_{H_2O} = k_1^{H_2O})$,[a] s^{-1}	$10^4(k_{D_2O} = k_1^{D_2O})$,[b] s^{-1}	$k_{H_2O}/k_{D_2O} = k_1^{H_2O}/k_1^{D_2O}$
(CO)$_5$Cr=C(OMe)Ph (**1a**)	3.36 ± 0.12	10.7 ± 0.8[c]	3.14 ± 0.37
(CO)$_5$Cr=C(OEt)Ph (**1b**)	0.423 ± 0.036	1.46 ± 0.03	2.90 ± 0.30
(CO)$_5$W=C(OMe)Ph (**1d**)	2.84 ± 0.12	7.54 ± 0.70	3.77 ± 0.52
(CO)$_5$W=C(OEt)Ph (**1e**)	0.495 ± 0.070	1.04 ± 0.03[c]	4.76 ± 0.81

[a] Average of five k_{obsd} values at [HCl] = 0.0001, 0.0003, 0.0005, 0.0007, and 0.001 M. [b] Average of five k_{obsd} values at [DCl] = 0.0002, 0.0004, 0.0006, 0.0008, and 0.001 M. [c] Average of four k_{obsd} values.

Scheme 3
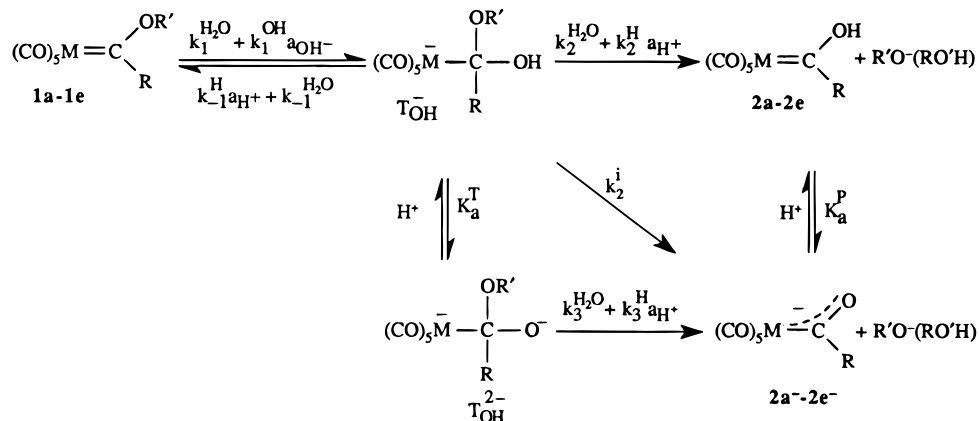
KOH was specifically tested in 10-nm intervals from 300 to 430 nm for **1b** and from 375 to 425 nm for **1d**. The observed variations in k_{obsd} were random and amounted to ±10% for **1b** and ±5% for **1d**, which is inconsistent with the accumulation of either T_{OH}^- or T_{OH}^{2-}, i.e., these species can be regarded as steady state intermediates.

The reason for the apparent contradiction between expectation and observation is that a favorable equilibrium in the first step is not the only condition that must be met for T_{OH}^- or T_{OH}^{2-} to accumulate to detectable levels. The second condition is that the *rate* of formation of T_{OH}^- be faster than, or at least comparable to, the rate of conversion of T_{OH}^- into products, i.e., $k_1^{OH} a_{OH^-} \geq k_2^{H_2O} + k_2^i + k_3^{H_2O} K_a^T/a_{H^+}$.[22] This second condition is apparently not met, i.e. we have $k_1^{OH} a_{OH^-} \ll k_2^{H_2O} + k_2^i + k_3^{H_2O} K_a^T/a_{H^+}$ instead, a situation reminiscent of that in the hydrolysis of β-methoxy-α-nitrostilbene.[23] The conclusion that formation of T_{OH}^- at high pH is slower than its conversion to products also means that the k_1^{OH} step is rate limiting, i.e., k_{OH} in eq 2 corresponds to k_1^{OH} in Scheme 3.

An interesting question is whether all pathways leading from T_{OH}^- to products, i.e., $k_2^{H_2O}$, k_2^i, and $k_3^{H_2O} K_a^T/a_{H^+}$, are faster than formation of T_{OH}^-. The rate constants for unimolecular MeO$^-$ expulsion from T_{OMe}^- (eq 3) are 1.10 s^{-1} for **1a** and 1.68 s^{-1} for **1d** in methanol, respectively.[16] It is unlikely that these rate constants would be significantly different in 50% aqueous acetonitrile.[24] Assuming that the electronic "push" provided by the OH group in T_{OH}^- is comparable to the push by the remaining MeO group in T_{MeO}^-, and taking into account the statistical factor of 2 that favors MeO$^-$ expulsion from T_{MeO}^-

over expulsion of MeO$^-$ from T_{OH}^-, one estimates $k_2^{H_2O}$ to be ≈0.5 s^{-1} for **1a** and ≈0.85 s^{-1} for **1d**, respectively. This compares with $k_1^{OH} a_{OH^-} = 1.3$ s^{-1} for **1a** and **1d** at 0.05 M KOH, i.e., in neither case does $k_2^{H_2O}$ exceed $k_1^{OH} a_{OH^-}$. For **1b** and **1e**, where the leaving group is ethoxy, $k_2^{H_2O}$ can be expected to be lower still,[26] probably rendering $k_1^{OH} a_{OH^-} > (\gg) k_2^{H_2O}$ at high pH. We conclude that it is only the k_2^i and/or $k_3^{H_2O} K_a^T/a_{H^+}$ terms which are larger than $k_1^{OH} a_{OH^-}$ and responsible for turning T_{OH}^- into a steady state intermediate. This conclusion is similar to one reached for the tetrahedral intermediate (**6**) in the hydrolysis of β-methoxy-α-nitrostyrene[23] and the Meisenheimer complex (**7**) in the hydrolysis of 1,3,5-trinitroanisole.[23]

6   **7**
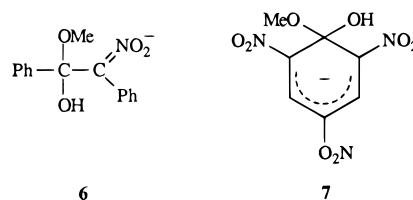
The driving force that makes the k_2^i step a potentially more favorable pathway than the $k_2^{H_2O}$ step is the intramolecular acid catalysis of leaving group departure by the OH group. The acidity of the OH group increases strongly along the reaction coordinate which renders proton transfer to the departing R′O group thermodynamically favorable at the transition state, a precondition for effective acid catalysis.[30] The proton transfer to the leaving group may either be direct (**8**) or via a bridging

(22) The rate terms for product formation via k_2^H and k_3^H are negligible at high pH.

(23) Bernasconi, C. F.; Fassberg, J.; Killion, R. B., Jr.; Schuck, D. F.; Rappoport, Z. *J. Am. Chem. Soc.* **1991**, *113*, 4937.

(24) The rate constant for the loss of MeO$^-$ from the Meisenheimer complex between 1,3,5-trinitrobenzene and MeO$^-$ is almost the same in methanol and in 22.5% methanol−77.5% water,[25] despite the presumably lower basicity of MeO$^-$ in the mixed solvent. The same lack of solvent dependence was observed for the loss of EtO$^-$ from the corresponding Meisenheimer complex in ethanol and in 19% ethanol−81% water.[25]

(25) Bernasconi, C. F.; Bergstrom, R. G. *J. Org. Chem.* **1971**, *36*, 1325.

(26) In the hydrolysis of PhCOOR′, the larger k_h/k_{ex} ratio (hydrolysis vs. [18]O exchange) for R′ = Me compared to R′ = Et suggests that loss of MeO$^-$ from **5** is at least 2-fold faster than loss of EtO$^-$;[27] departure of MeO$^-$ is 1.4-fold faster than EtO$^-$ departure from the respective RO$^-$ adducts of N,O-trimethylenephthalimidium cations;[28] the same rate ratio in the breakdown of 1,1-dialkoxy-2,4,6-trinitrocyclohexadianates is 1.5.[29]

(27) Shain, S. A.; Kirsch, J. *J. Am. Chem. Soc.* **1968**, *90*, 5848.

(28) Gravitz, N.; Jencks, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 507.

(29) Bernasconi, C. F.; Gandler, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 8117.

(30) Jencks, W. P. *J. Am. Chem. Soc.* **1972**, *94*, 4731.

water molecule (**9**); the latter would avoid ring strain at the transition state and is more likely.

In the pathway through T_{OH}^{2-}, the negative charge on the oxygen provides an extra electronic "push" in the form of transition state stabilization ($k_3^{H_2O}$-step) by the developing resonance in 2^-. It is for this reason that the collapse of T_{OH}^{2-} should be much faster than the collapse of T_{OH}^-.

The relatively rapid breakdown of T_{OH}^- to products has some other interesting consequences. According to Fischer et al.[31] the reactions of carbene complexes such as **1a** and **1d** with MeO$^-$ in methanol or EtO$^-$ in ethanol lead to products such as **10** and others of similar similar structure. These products are
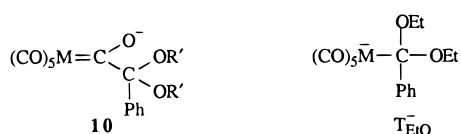
believed to be derived from the corresponding alkoxide ion adducts of **1a** and **1b** such as T_{MeO}^- or T_{EtO}^-. The availability of a more rapid reaction pathway in the case of T_{OH}^-, i.e. irreversible expulsion of MeO$^-$, must be the reason why there is no formation of products analogous to **10** in the basic hydrolysis of **1a** and **1d**.[32]

Reactions at Intermediate pH and in Acidic Solution. This is the range where $k_{H_2O} \gg k_{OH}a_{OH^-}$ (eq 2), i.e., the horizontal part of the pH−rate profiles. Except at the upper end of this pH range we can safely assume $k_1^{H_2O} \gg k_1^{OH}a_{OH^-}$, $k_{-1}^H a_{H^+} \gg k_{-1}^{H_2O}$, $k_2^H a_{H^+} \gg k_2^{H_2O}$ but not necessarily $k_2^H a_{H^+} \gg k_2^i + K_a^T k_3^H$. Treating T_{OH}^- and T_{OH}^{2-} as rapidly equilibrating steady state intermediates yields eq 4 for k_{H_2O}. At the low end of the pH range one can further assume $k_2^H a_{H^+} \gg k_2^i + K_a^T k_3^H$ so that eq 4 simplifies to eq 5. The fact that k_{H_2O} is pH independent

$$k_{H_2O} = \frac{k_1^{H_2O}(k_2^H a_{H^+} + k_2^i + K_a^T k_3^H)}{k_{-1}^H a_{H^+} + k_2^H a_{H^+} + k_2^i + K_a^T k_3^H} \tag{4}$$

$$k_{H_2O} = \frac{k_1^{H_2O} k_2^H}{k_{-1}^H + k_2^H} \tag{5}$$

over the entire pH range under consideration (e.g., pH 2−9) allows, in principle, two interpretations. One is that $k_2^H \gg k_{-1}^H$ and hence both eqs 4 and 5 simplify to eq 6. The other is

$$k_{H_2O} = k_1^{H_2O} \tag{6}$$

that $k_2^H a_{H^+} \gg k_2^i + K_a^T k_3^H$ over the entire range so that eq 5 applies to the entire range. This would leave open the possibility that k_2^H is not necessarily much larger than k_{-1}^H and that k_2^H may

be partially or completely rate limiting. However, the assumption that $k_2^H a_{H^+} \gg k_2^i + K_a^T k_3^H$ at pH values as high as 9 is not attractive; it is more likely that at the upper end of the pH range we have $k_2^H a_{H^+} \ll k_2^i + K_a^T k_3^H$ so that eq 4 simplifies to eq 6. This means it is only possible for k_{H_2O} to have the same value, i.e., $k_2^{H_2O}$ (eq 6) over the entire pH range under consideration if $k_2^H \gg k_{-1}^H$.[33]

Buffer Catalysis. In view of the above conclusion that the k_{H_2O} term in eq 2 represents rate limiting water attack, the k_B term for buffer catalysis must represent general base assisted water addition, a class *n* mechanism[34] with a transition state shown in **11**.
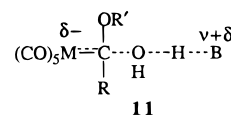
Rate Constants. The $k_1^{H_2O}$ and k_1^{OH} values are summarized in Table 1, the k_1^B values in Table 2, and the kinetic solvent isotope effects (KSIE) in Tables 3 and 4. The following points are noteworthy.

(1) The $k_1^{H_2O}$ and k_1^{OH} values depend very little on the metal as seen by comparing **1a** with **1d** and **1b** with **1e**. The same is true for the k_1^B values. This small dependence was already noted in the reactions of **1a** or **1d** with MeO$^-$ in methanol (eq 3) where not only the rate but also the equilibrium constants for nucleophilic addition were shown to be very similar for both **1a** and **1d**.[16] These results suggest that the stabilization of the negative charge in T_{OH}^- or T_{MeO}^- by the (CO)$_5$M moiety is about the same for M = Cr and W. Our findings contrast with the strong effect of the metal on the pK_a values of metal hydrido complexes of the type (η^5-C$_5$H$_5$)M(CO)$_3$H reported by Norton et al.,[35] e.g., in acetonitrile pK_a = 13.3 with M = Cr and pK_a = 16.1 with M = W. The apparent contradiction between our results for T_{OH}^- or T_{OMe}^- and those for the pK_a values of the hydrido complexes suggests that the strong metal dependence of the latter may reflect an effect on the neutral hydrido complexes rather than on the anion. In fact, before our results were known, Norton[35b] had argued that the higher acidity of the chromium hydrido complex is not the result of more effective charge stabilization in the anion but may be attributed to a smaller metal−H bond dissociation enthalpy of the Cr−H compared to the W−H bond. Our results add support to Norton's view.

(2) Substitution of a methoxy for an ethoxy group lowers the reactivity as seen when comparing **1a** with **1b** and **1d** with **1e**. The effect is most pronounced for $k_1^{H_2O}$ ($k_1^{H_2O}$(OMe)/ $k_1^{H_2O}$(OEt) $\approx$ 6), somewhat less for k_1^B (k_1^B(OMe)/k_1^B(OEt) $\approx$ 3 to 5), and smallest for k_1^{OH} (k_1^{OH}(OMe)/k_1^{OH}(OEt) $\approx$ 1.5 to 2). The lower reactivity for the ethoxy derivative can be attributed to a more effective reactant state stabilization by stronger π-donation (eq 7).[36] The decrease in the reactivity ratios from

(31) (a) Fischer, E. O.; Schubert, U.; Kalbfus, W.; Kreiter, C. G. *Z. Anorg. Allg. Chem.* **1975**, *416*, 135. (b) Schubert, U.; Fischer, E. O. *Liebigs. Ann. Chem.* **1975**, 393.

(32) The recently reported decomposition of T_{MeO}^- derived from **1a** and **1d** in MeO$^-$/methanol solution, which may be attributed to the formation of **10** (although this has not been proven), occurs on a time scale of several minutes[16] which is much too slow to compete with the loss of MeO$^-$ from T_{OH}^-.

(33) Unimolecular loss of MeO$^-$ or EtO$^-$ from tetrahedral intermediates is typically faster than loss of OH$^-$ although, in the case of EtO$^-$, the rate factor (EtO$^-$ vs OH$^-$) is not very large. For example, for **5** with R = Ph and R$'$O = EtO, EtO$^-$ loss is 6.3-fold faster than OH$^-$ loss.[27] However, H$^+$-catalyzed alkoxide ion departure becomes faster with increasing basicity of the leaving group,[28,29] which should favor EtO$^-$ and MeO$^-$ loss over OH$^-$ loss more than is the case in the spontaneous uncatalyzed reactions. Hence our conclusion that $k_2^H \gg k_{-1}^H$ is quite reasonable.

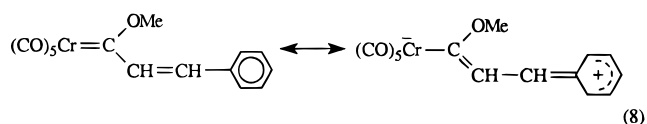(34) Jencks, W. P. *Acc. Chem. Res.* **1976**, *9*, 425.

(35) (a) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255. (b) Kristjánsdóttir, S. S.; Norton, J. R. In *Transition Metal Hydrides*; Dedieu, A., Ed.; Verlag Chemie: New York, 1992; p 309.

(36) There is extensive independent evidence that π-donation by R$'$O groups is unusually strong.[2a]

$$(CO)_5M=C\underset{R}{\overset{OR'}{|}} \quad \longleftrightarrow \quad (CO)_5\bar{M}-\overset{+}{C}\underset{R}{\overset{OR'}{|}} \qquad (7)$$
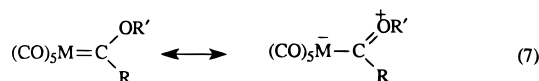
$k_1^{H_2O}$ to k_1^B to k_1^{OH} suggests that the transition state is relatively late for water addition and relatively early for OH$^-$ addition, consistent with the Hammond postulate[38] or the reactivity–selectivity principle.[39]

(3) The reactivity of OH$^-$ toward **1c** is just marginally lower than that toward **1a**, but attack by water on **1c** is 16-fold slower than on **1a**. A possible explanation of the lower reactivity of **1c** is in terms of extra resonance stabilization of the reactant state provided by the styryl group (eq 8); the red-shifted λ_{max}

$$(CO)_5Cr=C\underset{CH=CH-\bigcirc}{\overset{OMe}{|}} \quad \longleftrightarrow \quad (CO)_5\bar{Cr}-C\underset{CH-CH=\langle \stackrel{+}{\bigcirc} \rangle}{\overset{OMe}{|}} \qquad (8)$$

of the MLCT band of **1c** (Figure 2) compared to that for **1d** supports this interpretation. In **1a**, **1b**, **1d**, and **1e** the phenyl group may be turned out of the plane of the M=C double bond for steric reasons which would reduce or prevent π-donation in this case. X-ray crystal structures of **1a** and **1d** indicate that the phenyl group is perpendicular to the plane of the M=C bond; even though this does not prove that the same is the case in solution, it is suggestive evidence. Regarding the much larger effect on $k_1^{H_2O}$ than on k_1^{OH}, this may again be the result of a much later transition state for the water reaction compared to the OH$^-$ reaction.

(4) The k_1^{OH} values for OH$^-$ attack on **1a** and **1d** are $\approx$200-fold higher than for OH$^-$ attack on PhCOOMe ($k_1^{OH} = 0.72$ M^{-1} s^{-1}).[15] As discussed under "Mechanism", the *equilibrium* constants for OH$^-$ addition (K_1^{OH}) to **1a** and **1d** are expected to be quite similar to those for MeO$^-$ addition in methanol,[16] i.e., 70.1 M^{-1} for **1b** and 111 M^{-1} for **1d**, respectively. The corresponding equilibrium constant for PhCOOMe was estimated to be 8.3×10^{-8} M^{-1} in water,[15] implying K_1^{OH}(**1a** or **1d**)$/K_1^{OH}$(PhCOOMe) $\approx 10^9$. In view of this large equilibrium constant ratio the *rate* ratio appears to be disproportionately small. This indicates that the *intrinsic* rate constant, k_o,[41] for nucleophilic addition to the carbene complexes is lower, or the intrinsic barrier, $\Delta G_o^{\ddagger}$,[41] is higher than for addition to the ester. Based on the relationship of eq 9[44] one can estimate that log k_o

$$\log k_o = \log k_1^{OH} - 0.5 \log K_1^{OH} \qquad (9)$$

for the carbene complexes is about 2 log units lower than for the ester. A similar conclusion was reached when comparing **1a** or **1d** with PhCOOMe with respect to MeO$^-$ addition in methanol.[16] As discussed in more detail earlier,[16] the reduction of the intrinsic rate constants for the carbene complexes is probably mainly the result of delocalization of the negative charge into the CO groups of the (CO)$_5$M moiety of T$_{OH}^-$; such delocalization is not possible in **5**.

(5) The KSIE on the k_1^{OH} step is close to or slightly lower than unity for the four carbene complexes **1a**, **1b**, **1d**, and **1e** (Table 3). This is in line with KSIE values for the reaction of OH$^-$ (L = H or D) with esters or amides.[46] The KSIE on the $k_1^{H_2O}$ step is quite large, with $k_1^{H_2O}/k_1^{D_2O}$ values from about 3 to 4.7. These values are in the range observed for reaction of numerous electrophiles with L$_2$O;[46] they suggest a mechanism where *two* water molecules are involved, e.g., one acting as nucleophile and the other as base catalyst, as in **11** with B = H$_2$O.

Comparison with Alkoxymethyl Carbene Complexes. As mentioned in the Introduction, Fischer carbene complexes that have an acidic hydrogen on the carbon α to the carbene carbon (**3** and **4**) hydrolyze by the mechanism shown in Scheme 2.[6] This means that for these compounds the mechanism of Scheme 2 provides an energetically more favorable pathway than the mechanism of Scheme 3. Some insights into the relative effectiveness of the two mechanisms can be gained by the following reasoning. If the hydrolysis of **3** were interpreted in terms of Scheme 3 instead of Scheme 2 and, accordingly, k_{obsd} in the pH-dependent part of the pH–rate profile were equated with $k_1^{OH}a_{OH^-}$ instead of $K_a^{CH}k'_{H_2O}/a_{H^+}$, one would obtain $k_1^{OH} = 78.4$ M^{-1} s^{-1} for **3a** and $k_1^{OH} = 48.7$ M^{-1} s^{-1} for **3b**. This means that for the mechanism of Scheme 3 to be competitive with that of Scheme 2, k_1^{OH} would have to be of the order of 78.4 M^{-1} s^{-1} for **3a** and 48.7 M^{-1} s^{-1} for **3b**. These hypothetical k_1^{OH} values are considerably higher than the experimental k_1^{OH} values obtained for **1a** (26.6 M^{-1} s^{-1}) and **1b** (10.5 M^{-1} s^{-1}), respectively. Since we know that hydrolysis of **3a** and **3b** occurs via Scheme 2 rather than Scheme 3, this must mean that the actual k_1^{OH} values for nucleophilic attack on **3a** and **3b** are considerably lower than the hypothetical values and probably even lower than the k_1^{OH} values for **1a** and **1b**, respectively.

A lower electrophilic reactivity of **3a** and **3b** compared to **1a** and **1b**, respectively, requires that the phenyl group in **1a** and **1b** is electron withdrawing relative to the methyl group in **3a** and **3b**, respectively. Since phenyl groups are known to be inductively electron withdrawing but can also act as π-donors,[47,48] the inductive effect appears to be dominant in this case. This may be due to steric hindrance of coplanarity of the phenyl group with the M=C bond, a point alluded to earlier and consistent with X-ray data.[40] The notion that the phenyl group in **1a** is electron withdrawing relative to the methyl group in **3a** is also supported by chromium-53 NMR data; these data indicate more deshielding of the chromium atom of **1a** than of **3a**,[49] which suggests, although does not prove, that phenyl is more electron withdrawing.

(37) Schubert, U. *Coord. Chem. Rev.* **1984**, *55*, 261.

(38) (a) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334. (b) Leffler, J. E.; Grunwald, E. *Rates and Equilibria of Organic Reactions*; Wiley: New York, 1963. (c) Jencks, W. P. *Chem. Rev.* **1985**, *85*, 511.

(39) Pross, A. *Adv. Phys. Org. Chem.* **1977**, *14*, 69.

(40) (a) Mills, O. S.; Redhouse, A. D. *J. Chem. Soc. (A)* **1968**, 642. (b) Mills, O. S.; Redhouse, A. D. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 1082.

(41) The intrinsic rate constant, k_o, of a reaction with the forward rate constant k_1 and the reverse rate constant k_{-1} is defined as $k_o = k_1 = k_{-1}$ when the equilibrium constant $K_1 = 1$; the intrinsic barrier $\Delta G_o^{\ddagger}$ is defined as $\Delta G_o^{\ddagger} = \Delta G_1^{\ddagger} = \Delta G_{-1}^{\ddagger}$ when $\Delta G° = 0$. For an addition reaction where the molecularities in the two directions are different, these definitions are somewhat problematic because k_1 and k_{-1} have different units. Hine[42] has suggested a possible remedy but one that creates its own problems, as discussed elsewhere.[43] As long as the k_o or $\Delta G_o^{\ddagger}$ values defined above are only used for comparisons between systems of the same type, as is the case in the present study, the different molecularities are inconsequential.

(42) Hine, J. *J. Am. Chem. Soc.* **1971**, *93*, 3701.

(43) Bernasconi, C. F. *Adv. Phys. Org. Chem.* **1992**, *27*, 119.

(44) This is equivalent to applying the simplest version of the Marcus equation,[45] $\Delta G^{\ddagger} = \Delta G_o^{\ddagger} + 0.5\Delta G° + (\Delta G°)^{\ddagger}/16\Delta G_o^{\ddagger}$, and neglecting the third term, which can be assumed to be small in our case.

(45) (a) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679. (b) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891.

(46) Loughton, P. M.; Robertson, R. E. In *Solute–Solvent Interactions*; Coetzee, J. E., Ritchie, C. D., Eds.; Dekker: New York, 1969; p 399.

(47) This is reflected in various types of substituent constants.[48]

(48) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

(49) Hafner, A.; Hegedus, L. S.; de Weck, G.; Hawkins, B.; Dötz, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 8413.

It should be noted that the enhanced reactivity of the phenyl carbene complexes due to the electron withdrawing effect of the phenyl group is probably attenuated by the larger size of the phenyl compared to the methyl group which leads to greater steric hindrance in the transition state. In view of the small size of the nucleophile, this steric effect is likely to be small, though.[50]

Our conclusion, then, is that for the hydrolysis of **3a** and **3b** the mechanisms of Scheme 3 would only be competitive with the mechanisms of Scheme 2 if k_1^{OH} were at least 4- to 5-fold higher than what reasonably can be expected based on structure–reactivity considerations. On the other hand, the superiority of the mechanism of Scheme 2 is probably not dramatic which means that there may be a small degree of competition by Scheme 3. The fact that the kinetic solvent isotope effects, which constituted a major piece of evidence in favor of Scheme 2, are not quite as large as one might have expected[6] is consistent with the possibility of such competition.

The situation with the water reaction (plateau of pH–rate profile) is more ambiguous. Interpretation of the hydrolysis of **3a** in terms of Scheme 3 and equating the k_{obsd} values in the plateau region with $k_1^{H_2O}$ instead of $K_a^{CH}k'_H$[6] yields $k_1^{H_2O} = 6.01 \times 10^{-5}$ s^{-1}. This hypothetical $k_1^{H_2O}$ value is considerably *lower* than $k_1^{H_2O} = 2.9 \times 10^{-3}$ for **1a**. This means that the mechanism of Scheme 3 for the hydrolysis of **3a** in *acidic* solution could actually be a viable alternative to the mechanism of Scheme 2. Resolution of this ambiguity will require further study.

Experimental Section

General. ^{1}H NMR spectra were recorded on a Bruker 250-MHz instrument. Kinetic experiments were carried out on an Applied Photophysics DX.17MV stopped-flow spectrophotometer. UV–vis spectra were obtained on a Perkin-Elmer Lambda 2 or Hewlett-Packard 8562 diode array spectrophotometer. Gas chromatography was performed on a Hewlett-Packard 5890 series II *plus* equipped with a thermocoupled detector and a Hewlett-Packard 3396 series II integrator. The column used was an Alltech AT-1 30 m X 0.53 mm ID X 5 μm column.

Materials. (Methoxyphenylcarbene)pentacarbonylchromium(0), **1a**, and (methoxyphenylcarbene)pentacarbonyltungsten(0), **1d**, were available from a previous study.[16] (Ethoxyphenylcarbene)pentacarbonylchromium(0), **1b**, and (ethoxyphenylcarbene)pentacarbonyltungsten(0), **1e**, were synthesized by the procedure of Lam et al.:[52] **1b**, mp 26–27 °C (lit.[53] mp 29 °C), ^{1}H NMR (250 MHz, CDCl$_3$), δ 1.71 (t, 3H, CH$_3$), δ 4.99 (q, 2H, CH$_2$), δ 7.34–7.65 (m, 5H, Ph); **1e**, mp 54–55 °C (lit.[54] mp 54 °C), ^{1}H NMR (250 MHz, CDCl$_3$), δ 1.73 (t, 3H, CH$_3$), δ 5.05 (q, 2H, CH$_2$), δ 7.42–7.58 (m, 5H, Ph). (Methoxystyrylcarbene)pentacarbonylchromium(0), **1c**, was prepared as described by Casey

et al.:[55] mp 79–81 °C (lit.[55] mp 73–76 °C), ^{1}H NMR (250 MHz, CS$_2$), δ 4.80 (s, 3H, OCH$_3$), δ 6.80 (d, 1H, PhC*H*=CH), δ 7.81 (d, 1H, PhCH=C*H*), δ 7.87 (m, 5H, Ph).

The acetonitrile was reagent grade and used without further purification. Water was taken from a Milli-Q water purification system. All solvents and stock solutions were degassed by at least three cycles of the freeze–pump–thaw method. Amines were refluxed over NaOH and freshly distilled prior to use. Acetic acid was used as received. KOH and HCl solutions were prepared using "dilut-it" from Baker Analytical. DCl (Aldrich) was used as received. KOD was prepared by dissolving KOH pellets in D$_2$O. The concentrations of the DCl and KOD stock solutions were determined by titration against 0.1 M KOH or HCl using phenolphthalein as an indicator.

Product Studies. A. Hydrolysis of 1a. A 31.2-mg (0.10 mmol) amount of **1a** was hydrolyzed in 10 mL of 50% acetonitrile–50% water solution with 0.1 M KOH at ambient temperature under argon. After 1 h 100 μL of the reaction mixture was withdrawn and quenched in 900 μL of acetonitrile containing 0.15 M HCl and 0.10 mmol of toluene (Aldrich) as internal standard and analyzed by GC. Then after 24 h 0.10 mmol of toluene was added and the reaction mixture was again analyzed by GC. A solution containing known amounts of toluene, benzoic acid, and benzaldehyde was analyzed under the same conditions and served as reference.

B. Hydrolysis of 1d. A 44.4-mg (0.10 mmol) amount of **1d** was hydrolyzed in 10 mL of 50% acetonitrile–50% water solution with 0.1 M KOH at ambient temperature for 24 h under argon. Then 15.5 mg (0.0957 mmol) of hexamethylbenzene (Aldrich) was added as an internal standard and analyzed by GC. A solution containing known amounts of hexamethylbenzene, benzaldehyde (Aldrich), and benzoic acid (Aldrich) was analyzed under the same conditions and served as reference.

Kinetic Runs. In KOH (KOD) solutions the rates were measured by the stopped-flow method; all other rate determinations were performed by conventional spectrophotometry. All reactions were run under pseudo-first-order conditions, with the substrate as the minor component and, except where noted otherwise, monitored by following the decrease in absorbance at the λ_{max} of the substrate (398 nm for **1a**, **1b**; 396 nm for **1d**, **1e**; 458 nm for **1c**). Reaction solutions were always freshly prepared just prior to the experiment by injecting a small amount of stock solution of the carbene complex in pure acetonitrile (where it is relatively stable) into the 50% MeCN–50% water medium.

pH and pK_a Measurements. The pH in 50% acetonitrile–50% water was determined according to eq 10[56] with pH$_{meas}$ referring to the reading of the pH meter calibrated with standard buffers. The pK_a^{BH}

$$pH = pH_{meas} + 0.18 \qquad (10)$$

values of the amines and acetic acid were determined by measuring the pH of various buffer ratios and plotting log([B]/[BH]) vs pH according to the Henderson–Hasselbach equation pH = pK_a + log([B]/[BH]) where the intercept is the pK_a and the slope is unity. The pH of the reaction solutions for stopped-flow runs was measured in mock-mixing experiments that simulated the stopped-flow runs.

Supporting Information Available: Figure 1S, representative plots of k_{obsd} versus buffer concentration (1 page). See any current masthead page for ordering and Internet access instructions.

(50) Support for this contention comes from comparisons between rate constants for nucleophilic attack by primary aliphatic amines on **1a**[9a] and **3a**.[51]

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