

Physical Organic Chemistry of Transition Metal Carbene Complexes. 10.¹ Opposing Effects of α -Alkyl Groups on the Thermodynamic and Kinetic Acidities of $(\text{CO})_5\text{Cr}=\text{C}(\text{OMe})\text{CHR}'\text{R}''$ -Type Fischer Carbene Complexes in Aqueous Acetonitrile. Analogy to the Nitroalkane Anomaly

Claude F. Bernasconi,* Weitao Sun, Luis Garcia-Río,² Kin Yan, and Kevin Kittredge

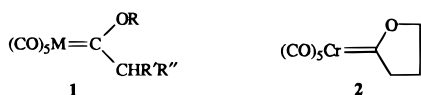
Contribution from the Department of Chemistry and Biochemistry of the University of California, Santa Cruz, California 95064

Received January 21, 1997[®]

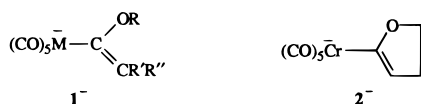
Abstract: The thermodynamic acidities of $(\text{CO})_5\text{Cr}=\text{C}(\text{OMe})\text{CH}_2\text{CH}_3$ (**3-Et**), $(\text{CO})_5\text{Cr}=\text{C}(\text{OMe})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (**3-Bu**), and $(\text{CO})_5\text{Cr}=\text{C}(\text{OMe})\text{CH}(\text{CH}_3)_2$ (**3-Pr**) have been determined in 50% acetonitrile–50% water (v/v) at 25 °C; after applying statistical corrections, the $\text{p}K_{\text{a}}$ values are 12.62 for **3-Et**, 12.84 for **3-Bu**, and 12.27 for **3-Pr**. These $\text{p}K_{\text{a}}$ values are all lower than $\text{p}K_{\text{a}} = 12.98$ for $(\text{CO})_5\text{Cr}=\text{C}(\text{OMe})\text{CH}_3$ (**3-Me**) determined previously and give an acidity order of **3-Me** < **3-Bu** < **3-Et** < **3-Pr**. If it is assumed that the main resonance structure of the conjugate anions of the carbene complexes has the negative charge delocalized onto the $(\text{CO})_5\text{Cr}$ moiety (e.g., **3-Et**[−]: $(\text{CO})_5\text{Cr}=\text{C}(\text{OMe})=\text{CHCH}_3$), the increased acidity with increasing alkyl substitution on the α -carbon can be understood as reflecting the well-known stabilization of alkenes by alkyl groups. Rate constants for the deprotonation of **3-Et**, **3-Bu**, and **3-Pr** by OH^- and by piperidine are also reported and compared with the corresponding rate constants for **3-Me** obtained previously. They follow the order **3-Me** > **3-Et** > **3-Bu** > **3-Pr**, essentially opposite to the order of the thermodynamic acidities. This leads to negative Brønsted α -values which are reminiscent of the nitroalkane anomaly. The observed kinetic order is the result of a lowering of the *intrinsic* rate constant by alkyl substitution. Four factors are identified that contribute to this lowering. (1) The disproportionately weak development of the C=C double bond at the transition state which prevents the latter from significantly benefiting from the alkene-stabilizing effect of the alkyl groups. (2) The disproportionately large negative charge on the α -carbon at the transition state that leads to a disproportionately strong destabilization of the transition state by the inductive/field effect of the alkyl groups relative to that of the product anion. (3) The destabilizing field effect of the alkyl groups on the partial negative charge on the hydroxide ion at the transition state. (4) Steric crowding at the transition state. Kinetic data on the hydrolysis of **3-Et**, **3-Bu**, and **3-Pr** over a wide pH range are also reported. They support a previously proposed mechanism that involves rate limiting protonation of the conjugate anion of the carbene complex that is concerted with cleavage of the bond between the carbene carbon and the metal. With **3-Pr** the hydrolysis is subject to catalysis by light.

Introduction

Fischer carbene complexes of the general type **1** are quite acidic and span a $\text{p}K_{\text{a}}$ range from



10.18 ($M = \text{W}$, $R = \text{Me}$, $R' = \text{H}$, $R'' = \text{Ph}$)³ to 14.47 (**2**)¹ in 50% acetonitrile–50% water (v/v). The relatively high acidity of these complexes can in large measure be attributed to strong stabilization of the conjugate bases (**1**[−] and **2**[−]) by delocalization of the charge onto the $(\text{CO})_5\text{M}$



moiety where it is further dispersed into the CO groups;^{4–6} this

stabilization is apparently much stronger than that in the conjugate base of carboxylic esters whose acidities are much lower (e.g., 26.5 for $\text{CH}_3\text{COOCH}_3$).⁷

In previous papers we have explored a number of structural factors that affect the thermodynamic and kinetic acidities of such complexes. They include the effect of changing the metal in **1** ($M = \text{Cr}$, W , Mo with $R = \text{Me}$, $R' = R'' = \text{H}$; $M = \text{Cr}$ and W with $R = \text{Me}$, $R' = \text{H}$, $R'' = \text{Ph}$),³ of changing the alkoxy group in **1** ($M = \text{Cr}$ or W , $R' = R'' = \text{H}$, $R = \text{Me}$ vs Et),³ of incorporating the oxygen into a cyclic structure (**2**),¹ and of changing the α -methyl to an α -benzyl group in **1** ($M = \text{Cr}$ or W , $R = \text{Me}$, $R' = \text{H}$, $R'' = \text{Ph}$ vs H).^{3,6} In the present paper we report on the effect of substituting one α -hydrogen in **3-Me** with a methyl (**3-Et**) or an *n*-propyl group (**3-Bu**) and also of substituting two α -hydrogens by two methyl groups (**3-**

(2) Current address: Departamento de Química Física, Universidade de Santiago de Compostela, 15706 Santiago de Compostela, Spain.

(3) Bernasconi, C. F.; Sun, W. *Organometallics* **1997**, *16*, 1926.

(4) Casey, C. P.; Anderson, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 1230.

(5) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1983.

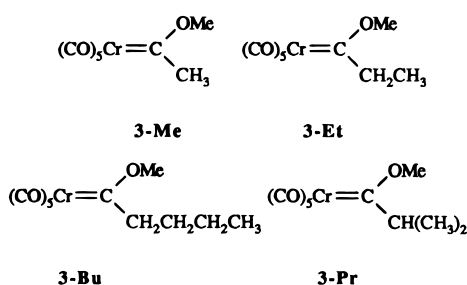
(6) Bernasconi, C. F.; Sun, W. *J. Am. Chem. Soc.* **1993**, *115*, 12526.

(7) Amyes, T. L.; Richard, J. P. *J. Am. Chem. Soc.* **1996**, *118*, 3129.

[®] Abstract published in *Advance ACS Abstracts*, May 15, 1997.

(1) Part 9: Bernasconi, C. F.; Leyes, A. E. *J. Am. Chem. Soc.* **1997**, *119*, 5169.

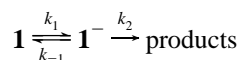
Pr).⁸ It will be shown



that the α -methyl groups and the n -propyl group enhance the thermodynamic acidities, i.e., **3-Pr** > **3-Et** > **3-Bu** > **3-Me** but lower the rate constants for deprotonation, i.e., **3-Pr** < **3-Bu** < **3-Et** < **3-Me**.

Our study includes kinetic measurements of the hydrolytic decomposition of **3-Et**, **3-Bu**, and **3-Pr**. For substrates of the general type **1**, this hydrolysis has been shown to involve the reaction of the conjugate anion of the carbene complex with a proton donor as illustrated in Scheme 1.^{9,10} The products are usually an aldehyde, $R'R''CHCH=O$, and $(CO)_5CrX$ with $X = OH^-$, B (buffer base) or the solvent, although with $R' = H$, $R'' = Ph$ the vinyl ether $PhCH=CHOMe$ was the main organic product.¹²

Scheme 1



$$k_1 = k_1^{H_2O} + k_1^{OH}[OH^-] + k_1^B[B] \quad (1)$$

$$k_{-1} = k_{-1}^{H^+}a_{H^+} + k_{-1}^{H_2O} + k_{-1}^{BH}[BH] \quad (2)$$

$$k_2 = k_2^{H^+}a_{H^+} + k_2^{H_2O} + k_2^{BH}[BH] \quad (3)$$

Results

General Features. When **3-Et**, **3-Bu** or **3-Pr** are placed into a KOH solution, the observed kinetic behavior is quite similar to that of **3-Me** and other carbene complexes of the general type **1**^{6,9} as well as complex **2**.^{1,11} There is a fast process in the stopped-flow time range (k_{obsd}^I) that represents deprotonation of the carbene complex, followed by a slower reaction (k_{obsd}^{II}) that corresponds to hydrolytic decomposition of the anion as indicated in Scheme 1. There are additional, still slower processes that remain unidentified; they are probably associated with further transformations of $(CO)_5CrOH^-$.

In contrast to the situation with most systems studied previously (e.g., **2** and **3-Me**), the deprotonation of **3-Et**, **3-Bu**, and **3-Pr** is only partially reversible. This state of affairs is indicated by the fact that the reaction of the respective anions (**3-Et**⁻, **3-Bu**⁻, and **3-Pr**⁻) with acid leads only to minimal recovery of the original carbene complex, as evidenced by the

(8) Note that **3-Me**, **3-Et**, **3-Bu**, and **3-Pr** are all of the general type **1**, but these specific designations are more convenient than, e.g., **1** ($M = Cr$, $R = Me$, $R' = R'' = H$ for **3-Me**, etc.). Henceforth the designation **1** will only be used when all the different **1**-type carbene complexes are meant; when we refer to a specific carbene complex, the specific designation (**3-Me**, **3-Et**, etc.) will be used.

(9) (a) Bernasconi, C. F.; Flores, F. X.; Sun, W. *J. Am. Chem. Soc.* **1995**, *117*, 4875. (b) Bernasconi, C. F.; Sun, W. *Organometallic* **1995**, *14*, 5615.

(10) In acidic solution a competing mechanism involving nucleophilic substitution of the alkoxy group by a hydroxyl group, followed by hydrolytic cleavage of $(CO)_5M=C(OH)CHR'R''$ cannot be excluded.¹¹

(11) Bernasconi, C. F.; Leyes, A. E. *J. Chem. Soc., Perkin Trans. 2* **1997**, in press.

(12) For the mechanistic details which explain the different types of products see ref 9.

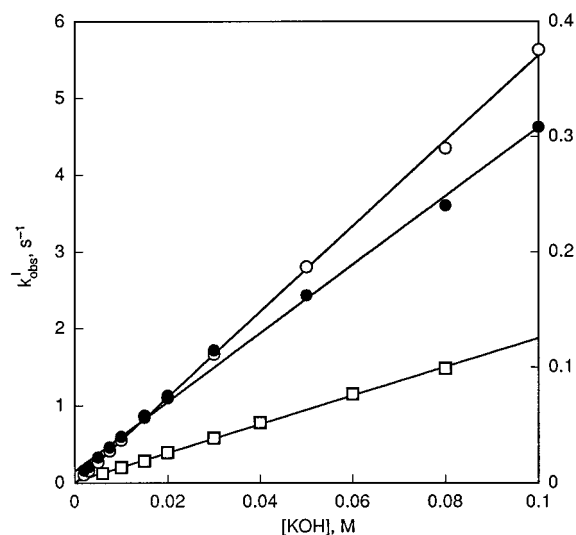


Figure 1. Plots of k_{obsd}^I vs $[KOH]$. \circ : **3-Et** at 370 nm (left y-axis); \square : **3-Bu** at 280 nm (left y-axis); \bullet : **3-Pr** at 370 nm (right y-axis).

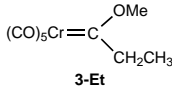
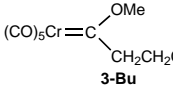
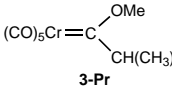
absorption spectra. This is the case even when the experiments are performed in a double mixing stopped-flow apparatus which allows addition of acid to the anion within a few milliseconds after it has been generated. As elaborated upon below, the reason for the incomplete reversibility is that, in contrast to the situation with **3-Me** and other **1**-type complexes where $k_{-1} \gg k_2$ (Scheme 1), k_2 is of comparable magnitude with k_{-1} . At lower pH k_{obsd}^I is no longer observed because the deprotonation is thermodynamically unfavorable and k_{obsd}^{II} becomes the dominant process.

All experiments were performed in 50% acetonitrile–50% water (v/v) at 25 °C, and an ionic strength of 0.1 M was maintained with KCl. Rates were measured in KOH, HCl, and various buffer solutions; all kinetic determinations were made spectrophotometrically under pseudo-first-order conditions with the carbene complex as the minor component.

Reactions in KOH Solutions. In the range of 0.01–0.1 M KOH k_{obsd}^I and k_{obsd}^{II} measured in the stopped-flow apparatus were well separated with $k_{\text{obsd}}^I/k_{\text{obsd}}^{II} \geq 10$; this allowed accurate determinations of both pseudo-first-order rate constants. In the range of 2×10^{-3} to 0.01 M KOH the separation was less satisfactory, and reliable values could only be obtained for k_{obsd}^I . The k_{obsd}^I values over the entire $[KOH]$ range are summarized in Tables S1–S3 of the Supporting Information.¹³ Plots of k_{obsd}^I vs $[KOH]$ are shown in Figure 1; they are based on data obtained at 370 nm for **3-Et** and **3-Pr** and at 280 nm for **3-Bu**. Similar plots (not shown) were constructed at 280 nm for **3-Et** and **3-Pr** and at 370 nm for **3-Bu**. The slopes which correspond to k_1^{OH} (eq 1) are summarized in Table 1; they are slightly different at the two wavelengths. The average from the two wavelengths was taken as the best value.

The data for k_{obsd}^{II} are summarized in Table 2. There were some problems that made it difficult to obtain highly accurate k_{obsd}^{II} values. The main one was that the changes in absorbance associated with the k_{obsd}^{II} process were relatively small compared to absorbance changes for the k_{obsd}^I process and those for the slower decomposition process alluded to earlier, especially at 370 nm. The situation was somewhat more favorable at 280 nm, especially for the case of **3-Et** and **3-Bu** where reproducible k_{obsd}^{II} values could only be obtained at 280 nm. In the case of **3-Pr** an additional complication was that the reaction is subject to catalysis by light. For example, when the hydrolysis of **3-Pr** was monitored at 370 nm in a stopped-flow apparatus equipped with a high intensity xenon lamp, the k_{obsd}^{II} values were

Table 1. Summary of Kinetic Parameters for the Reactions of **3-Et**, **3-Bu**, and **3-Pr** in 50% MeCN–50% Water at 25 °C^a

			
$k_1^{\text{OH}}, \text{M}^{-1} \text{s}^{-1}$	38.1 (280 nm) 55.7 (370 nm) ave 46.9	16.8 (280 nm) 26.5 (370 nm) ave 21.6	2.94 (280 nm) 2.99 (370 nm) ave 2.97
$k_2^{\text{H}_2\text{O}}, \text{s}^{-1}$	0.054 (280 nm) ^b	0.033 (280 nm)	3.35×10^{-3} (280 nm) 4.88×10^{-3} (370 nm) ave 4.11×10^{-3}
$k_1^{\text{OH}} k_2^{\text{H}_2\text{O}} / (k_{-1}^{\text{H}_2\text{O}} + k_2^{\text{H}_2\text{O}}), \text{M}^{-1} \text{s}^{-1}$	21.4 (370 nm)	8.87 (370 nm)	1.59 (370 nm)
$k_{-1}^{\text{H}_2\text{O}}, \text{s}^{-1}$	0.064	0.048	3.57×10^{-3}
$K_1^{\text{OH}} = k_1^{\text{OH}} / k_{-1}^{\text{H}_2\text{O}}, \text{M}^{-1}$	7.33×10^2	4.50×10^2	8.32×10^2
$\text{p}K_a^{\text{CH}}$	12.32	12.54	12.27
$k_1^{\text{H}_2\text{O}} k_2^{\text{H}} / (k_{-1}^{\text{H}} + k_2^{\text{H}}), \text{s}^{-1}$	3.15×10^{-5}		1.28×10^{-5}
$k_1^{\text{H}_2\text{O}}, \text{s}^{-1}$	$\geq 3.15 \times 10^{-5}$		$\geq 1.28 \times 10^{-5}$
$k_2^{\text{H}}, \text{M}^{-1} \text{s}^{-1}$	$\geq 6.58 \times 10^7$		$\geq 2.38 \times 10^7$
$k_1^{\text{Pip}}, \text{M}^{-1} \text{s}^{-1}$	48.4	32.1	0.194
$k_{-1}^{\text{PipH}}, \text{M}^{-1} \text{s}^{-1}$	9.88×10^2	1.09×10^3	3.55

^a Estimated error limits in experimental parameters: $\pm 10\%$ for k_1^{OH} , $\pm 15\%$ for $k_2^{\text{H}_2\text{O}}$, $\pm 7\%$ for $k_1^{\text{OH}} k_2^{\text{H}_2\text{O}} / (k_{-1}^{\text{H}_2\text{O}} + k_2^{\text{H}_2\text{O}})$, $\pm 10\%$ for $k_1^{\text{H}_2\text{O}} k_2^{\text{H}} / (k_{-1}^{\text{H}} + k_2^{\text{H}})$, $\pm 8\%$ for k_1^{Pip} . Estimated error limits in derived parameters: $\pm 20\%$ for $k_{-1}^{\text{H}_2\text{O}}$, $\pm 30\%$ for K_1^{OH} , ± 0.11 log units for $\text{p}K_a^{\text{CH}}$. ^b Average from stopped-flow (high intensity lamp) and conventional (low intensity lamp) spectrophotometer.

Table 2. $k_{\text{obsd}}^{\text{II}}$ for the Reaction of **3-Et**, **3-Bu**, and **3-Pr** with KOH in 50% MeCN–50% water at 25 °C

[KOH, M]	$k_{\text{obsd}}^{\text{II}}, \text{s}^{-1}$ 280 nm, SF ^a	$k_{\text{obsd}}^{\text{II}}, \text{s}^{-1}$ 280 nm, PE ^b	$k_{\text{obsd}}^{\text{II}}, \text{s}^{-1}$ 370 nm, SF ^a	$k_{\text{obsd}}^{\text{II}}, \text{s}^{-1}$ 370 nm, PE ^b
(CO) ₅ Cr=C(OMe)CH ₂ CH ₃ (3-Et)				
0.015	0.049			
0.020	0.056			
0.030	0.056			
0.040	0.059	0.054		
0.050		0.050		
0.060	0.058	0.043		
0.070		0.055		
0.080	0.059	0.055		
0.090		0.056		
0.10	0.57	0.056		
	ave 0.056	ave 0.052		
(CO) ₅ Cr=C(OMe)CH ₂ CH ₂ CH ₂ CH ₃ (3-Bu)				
0.05		0.033		
0.06		0.034		
0.07		0.034		
0.08		0.034		
0.09		0.030		
0.10		0.031		
		ave 0.033		
(CO) ₅ Cr=C(OMe)CH(CH ₃) ₂ (3-Pr)				
0.01	3.7×10^{-3}		0.019	4.9×10^{-3}
0.015			0.020	5.9×10^{-3}
0.02	3.3×10^{-3}		0.019	5.0×10^{-3}
0.03			0.017	
0.04	3.2×10^{-3}			
0.05			0.016	5.3×10^{-3}
0.08	3.2×10^{-3}		0.018	4.2×10^{-3}
0.10			0.019	4.0×10^{-3}
	ave 3.3×10^{-3}		ave 0.018	ave 4.9×10^{-3}

^a Measurements in Applied Photophysics stopped-flow apparatus with high intensity Xenon lamp. ^b Measurements in Perkin Elmer Lambda 2 spectrophotometer with low intensity deuterium lamp.

approximately 3.5–3.8-fold higher than in a conventional spectrophotometer equipped with a low intensity deuterium lamp. Reducing the slit width in the stopped-flow apparatus also brought down the rates to a level close to that observed in the conventional spectrophotometer. This photochemical acceleration is reminiscent of similar findings in the hydrolysis of (CO)₅Cr=C(OMe)CH₂Ph.^{9b}

In view of the above difficulties, we estimate that the error limits in the $k_{\text{obsd}}^{\text{II}}$ values could be as high as $\pm 15\%$. Despite

the rather large uncertainties, it is clear, though, that the $k_{\text{obsd}}^{\text{II}}$ values are independent of [KOH]. This implies that the equilibrium of the first step in Scheme 1 strongly favors **1**[−] and hence $k_{\text{obsd}}^{\text{II}}$ can be equated with $k_2^{\text{H}_2\text{O}}$.

Reactions with Piperidine. Rate constants for the deprotonation of **3-Et**, **3-Bu**, and **3-Pr** by piperidine were determined by reacting the carbene complexes with piperidine in the presence of 0.04 M KOH. Under these conditions the proton transfer equilibrium favors the anion and $k_{\text{obsd}}^{\text{I}}$ is given by eq 4. The raw data are reported in Table S4.¹³ From plots of $k_{\text{obsd}}^{\text{I}}$ vs

$$k_{\text{obsd}}^{\text{I}} = k_1^{\text{OH}}[\text{OH}^-] + k_1^{\text{Pip}}[\text{Pip}] \quad (4)$$

[piperidine] (not shown) the k_1^{Pip} values summarized in Table 1 were obtained.

Hydrolysis in Buffered Solutions and HCl. Rate constants for hydrolysis, $k_{\text{obsd}}^{\text{II}}$, were determined for **3-Et**, **3-Bu**, and **3-Pr** in triethylamine (pH 9.3–11.5) and for **3-Et** and **3-Pr** in *N*-methylmorpholine (pH 6.8–8.4), acetate (pH 5.93), and methoxyacetate buffers (pH 4.79) as well as in HCl solutions (pH 1.0–2.7). In this pH range the acid–base equilibrium disfavors the anion and hence the kinetic process for proton transfer is no longer observable.

The hydrolysis is subject to general base catalysis by the amines and carboxylate ions. Some representative plots of $k_{\text{obsd}}^{\text{II}}$ vs buffer base concentration are displayed in Figures S1 and S2 of the Supporting Information.¹³ The intercepts of these and similar plots, along with $k_{\text{obsd}}^{\text{II}}$ determined in HCl solutions, were used to construct the pH–rate profiles shown in Figure 2; there is some scatter in these plots that can be attributed to uncertainties in the intercepts of the buffer plots.

The pH–rate profiles in Figure 2 are similar in appearance to the pH–rate profiles in the hydrolysis of **3-Me**,^{9a} **1** (M = Cr, R = Me, R' = H, R'' = Ph),^{9b} and **2**.¹¹ However, their analysis is somewhat different in the present case. In the previous systems, the proton transfer was close to being entirely reversible, as indicated by the virtually complete recovery of the carbene complex upon reaction of the anion with an acidic buffer. This implied that in Scheme 1 $k_{-1} \gg k_2$ and that at pH $\ll \text{p}K_a^{\text{CH}}$ $k_{\text{obsd}}^{\text{II}}$ is given by eq 5.

(13) See paragraph concerning Supporting Information at the end of this paper.

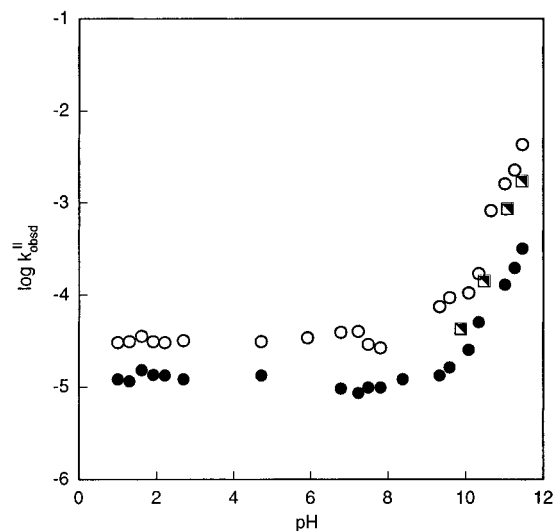


Figure 2. pH-rate profiles for the hydrolysis of **3-Et** (○), **3-Bu** (□), and **3-Pr** (●).

$$k_{\text{obsd}}^{\text{II}} = K_1^{\text{OH}} K_w k_2^{\text{H}} + K_1^{\text{OH}} k_2^{\text{H}_2\text{O}} [\text{OH}^-] + K_1^{\text{OH}} k_2^{\text{BH}} [\text{OH}^-] [\text{BH}]$$

$$= K_a^{\text{CH}} k_2^{\text{H}} + \frac{K_a^{\text{CH}}}{a_{\text{H}^+}} k_2^{\text{H}_2\text{O}} + \frac{K_a^{\text{CH}}}{K_a^{\text{BH}}} k_2^{\text{BH}} [\text{B}] \quad (5)$$

With **3-Et**, **3-Bu**, and **3-Pr** reaction of the respective anions with acid leads only to minimal recovery of the carbene complex, implying $k_{-1} < k_2$. Hence at $\text{pH} < \text{p}K_a^{\text{CH}}$ the anions (**3-Et**⁻, **3-Bu**⁻, and **3-Pr**⁻) need to be treated as steady state intermediates, and $k_{\text{obsd}}^{\text{II}}$ is given by eq 6. After extrapolation to zero buffer concentration, eq 6 for the pH-dependent leg of the pH-rate

$$k_{\text{obsd}}^{\text{II}} = \frac{(k_1^{\text{H}_2\text{O}} + k_1^{\text{OH}} [\text{OH}^-] + k_1^{\text{B}} [\text{B}]) (k_2^{\text{H}} a_{\text{H}^+} + k_2^{\text{H}_2\text{O}} + k_2^{\text{BH}} [\text{BH}])}{(k_{-1}^{\text{H}} + k_2^{\text{H}}) a_{\text{H}^+} + k_{-1}^{\text{H}_2\text{O}} + k_2^{\text{H}_2\text{O}} + (k_{-1}^{\text{BH}} + k_2^{\text{BH}}) [\text{BH}]} \quad (6)$$

profile ($k_1^{\text{OH}} [\text{OH}^-] \gg k_1^{\text{H}_2\text{O}}$; $k_{-1}^{\text{H}_2\text{O}} + k_2^{\text{H}_2\text{O}} \gg (k_{-1}^{\text{H}} + k_2^{\text{H}}) a_{\text{H}^+}$) simplifies to eq 7. In conjunction with k_1^{OH} and $k_2^{\text{H}_2\text{O}}$ obtained

$$k_{\text{obsd}}^{\text{II}} = \frac{k_1^{\text{OH}} k_2^{\text{H}_2\text{O}} [\text{OH}^-]}{k_{-1}^{\text{H}_2\text{O}} + k_2^{\text{H}_2\text{O}}} \quad (7)$$

above, eq 7 can be solved for $k_{-1}^{\text{H}_2\text{O}}$ which then allows calculation of $K_1^{\text{OH}} = k_1^{\text{OH}}/k_{-1}^{\text{H}_2\text{O}}$ to yield $\text{p}K_a^{\text{CH}}$. The various k_1^{OH} , $k_2^{\text{H}_2\text{O}}$, $k_1^{\text{OH}} k_2^{\text{H}_2\text{O}}/(k_{-1}^{\text{H}_2\text{O}} + k_2^{\text{H}_2\text{O}})$, $k_{-1}^{\text{H}_2\text{O}}$, and K_1^{OH} values are summarized in Table 1.

For the plateau region of the pH-rate profile ($k_1^{\text{H}_2\text{O}} \gg k_1^{\text{OH}} [\text{OH}^-]$; $(k_{-1}^{\text{H}} + k_2^{\text{H}}) a_{\text{H}^+} \gg k_{-1}^{\text{H}_2\text{O}} + k_2^{\text{H}_2\text{O}}$) eq 6 becomes eq 8. The average values of $k_1^{\text{H}_2\text{O}} k_2^{\text{H}}/(k_{-1}^{\text{H}} + k_2^{\text{H}})$ for **3-Et** and **3-Pr**

$$k_{\text{obsd}}^{\text{II}} = \frac{k_1^{\text{H}_2\text{O}} k_2^{\text{H}}}{k_{-1}^{\text{H}} + k_2^{\text{H}}} \quad (8)$$

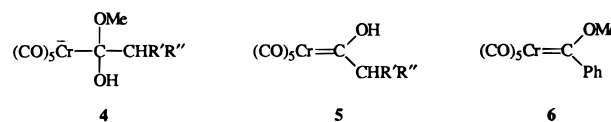
obtained from measurements at six HCl concentrations are reported in Table 1. In the absence of information about the $k_2^{\text{H}}/k_{-1}^{\text{H}}$ ratio, dissection of the individual rate constants $k_1^{\text{H}_2\text{O}}$, k_{-1}^{H} , and k_2^{H} is not possible.¹⁴ However, some upper and lower limits can be given as follows. If $k_{-1}^{\text{H}} \gg k_2^{\text{H}}$, $k_{\text{obsd}}^{\text{II}} = K_a^{\text{CH}} k_2^{\text{H}}$ and

(14) A further complication is that in acidic solution there may be a competing hydrolysis mechanism that involves nucleophilic attack by water on the carbene carbon.¹⁰

hence $k_{\text{obsd}}^{\text{II}}/K_a^{\text{CH}}$ represents a lower limit for k_2^{H} ; if $k_{-1}^{\text{H}} \ll k_2^{\text{H}}$, $k_{\text{obsd}}^{\text{II}} = k_1^{\text{H}_2\text{O}}$ and hence $k_{\text{obsd}}^{\text{II}}$ represents a lower limit for $k_1^{\text{H}_2\text{O}}$.¹⁵

Discussion

Mechanism. Even though our results are entirely consistent with Scheme 1, it is important to exclude potential alternatives. One such alternative, suggested by a referee, is that the k_1^{OH} process might represent nucleophilic attack by OH^- on the carbene carbon of **3-Et**, **3-Bu**, and **3-Pr** instead of deprotonation. This would imply that what we interpret to be the conjugate anion of the carbene complex (**1**⁻) is either the OH^- -adduct **4** or the substitution product **5**.¹⁶ There are several problems with



this alternative interpretation. (1) Adducts of the type **4** have been shown¹⁷ to rapidly convert to products of the type **5** by loss of methoxide ion,¹⁸ i.e., if **5** were formed by OH^- -attack, **4** would be a nonaccumulating steady state intermediate. (2) If **5** were the product of the OH^- -reaction, this process should have been visible over the entire pH range and not just at $[\text{KOH}] > 10^{-3}$ M, as observed in the hydrolysis of **6** and related carbene complexes.¹⁷ (3) Based on a comparison with the reaction of **6** it was recently concluded that the rate constant for nucleophilic attack on **3-Me** by OH^- should be $< 26.6 \text{ M}^{-1} \text{ s}^{-1}$.¹⁷ This compares with $k_1^{\text{OH}} = 456 \text{ M}^{-1} \text{ s}^{-1}$ for deprotonation of **3-Me**,⁶ for a proton transfer/nucleophilic attack ratio of > 17.1 . Nucleophilic additions to the carbene carbon of Fischer carbenes being *very* sensitive to steric effects,²⁰ it is likely that the proton transfer/nucleophilic attack ratio for **3-Et**, **3-Bu**, and **3-Pr** should become larger rather than smaller than for **3-Me**, i.e., competition by OH^- attack should be minimal.

Effect of the Alkyl Group on Thermodynamic and Kinetic Acidities. Before one can meaningfully assess the effect of replacing one or two hydrogens in **3-Me** by methyl or ethyl groups on the $\text{p}K_a^{\text{CH}}$ and on the proton transfer rate constants, statistical corrections for the different numbers of α -protons need to be applied. The statistically corrected $\text{p}K_a^{\text{CH}}$, k_1^{OH} , and k_1^{Pip} values are summarized in Table 3; for estimated error limit see footnote *a* in Table 1.

Thermodynamic Acidities. Our discussion will focus first on the effect of methyl groups, i.e., on a comparison of **3-Et** and **3-Pr** with **3-Me**; the *n*-butyl derivative (**3-Bu**) will be dealt with later. The order in the $\text{p}K_a^{\text{CH}}$ (corr) values is **3-Me** $>$ **3-Et** $>$ **3-Pr**, indicating that methyl groups on the α -carbon increase the acidity of carbene complexes.²¹ This acidity enhancement

(15) These lower limits are only valid if competition by the nucleophilic mechanism¹⁴ is insignificant.

(16) The referee further suggested that a distinction between proton transfer and nucleophilic addition/substitution could be based on UV spectra of the reaction products. In the reaction of **3-Me** with OH^- the lifetime of the conjugate base of **3-Me** (**3-Me**⁻) is long enough to allow measurements of a relatively clean UV spectrum in the stopped-flow apparatus;⁶ this is, however, not the case for **3-Et**, **3-Bu**, and **3-Pr** because decomposition of the anion sets in before reaction OH^- is complete.

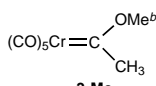
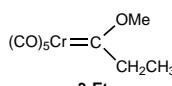
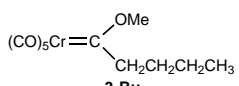
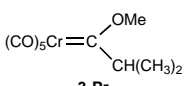
(17) Bernasconi, C. F.; Flores, F. X.; Kittredge, K. W. *J. Am. Chem. Soc.* **1997**, *119*, 2103.

(18) The rapid loss of methoxide ion is the result of intramolecular acid catalysis by the OH -group and/or rapid conversion of the type **4** adduct into its conjugate base which provides a strong electronic push for methoxide ion departure.¹⁷ In contrast, the MeO^- adduct of **6** ($(\text{CO})_5\text{Cr}-\text{C}(\text{OMe})_2\text{Ph}$) lacks the acidic OH group and accumulates to detectable levels at high methoxide ion concentrations.¹⁹

(19) Bernasconi, C. F.; Flores, F. X.; Gandler, J. R.; Leyes, A. E. *Organometallics* **1994**, *13*, 2186.

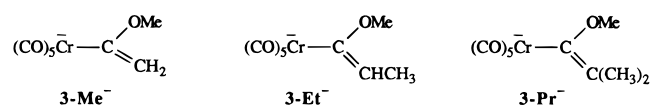
(20) Bernasconi, C. F.; Sun, W. Unpublished results.

Table 3. Summary of pK_a^{CH} Values and Rate Constants for Proton Transfer and Hydrolysis^a

				
	3-Me	3-Et	3-Bu	3-Pr
pK _a ^{CH}	12.50	12.32	12.54	12.27
pK _a ^{CH} (corr) ^c	12.98	12.62	12.84	12.27
k ₁ ^{OH} (corr), ^c M ⁻¹ s ⁻¹	152	23.4	10.8	2.97
k ₋₁ ^{H₂O} , s ⁻¹	0.91	0.064	0.048	3.57 × 10 ⁻³
k ₁ ^{Pip} (corr), ^c M ⁻¹ s ⁻¹	302	24.2	16.0	0.195
k ₁ ^{PipH⁺} , M ⁻¹ s ⁻¹	2.77 × 10 ⁴	9.86 × 10 ²	1.85 × 10 ³	3.55
k ₂ ^{H₂O} , s ⁻¹	0.16	0.054	0.033	4.11 × 10 ⁻³
k ₋₁ ^{H₂O} /k ₂ ^{H₂O}	5.69	1.18	1.45	0.87
log k ₀ ^{OH} ^c	1.07	0.09	-0.14	-0.99
log k ₀ ^{Pip} ^c	3.52	2.19	2.15	-0.11

^a Estimated error limits for log k₀^{OH} and log k₀^{Pip} are ±0.2 log units, see text; for error limits of the other parameters see footnote (a) in Table 2; the error limits for the various parameters for **3-Me** are lower than those for **3-Et**, **3-Bu**, and **3-Pr**: ±3% for k₁^{OH}(corr), ±10% for k₋₁^{H₂O}, ±0.05 log units for pK_a^{CH}(corr), ±5% for k₁^{Pip}, ±8% for k₂^{H₂O}, ±0.15 log units for log k₀^{OH} and log k₀^{Pip}. ^b References 7 and 10a. ^c Statistically corrected for the fact that **3-Me** has three equivalent protons, and **3-Et** and **3-Bu** have two equivalent protons.

may be attributed to an increase in the stability of the respective anions (**3-Pr**⁻ > **3-Et**⁻ > **3-Me**⁻) by the methyl groups. Assuming that the dominant resonance structure of the anions has the negative charge delocalized into the (CO)₅Cr moiety, the increased stability in the order **3-Pr**⁻ > **3-Et**⁻ > **3-Me**⁻



simply reflects the well-known stabilization of alkenes by methyl or alkyl groups.²² This stabilization is commonly attributed to hyperconjugation²² although other explanations have been offered.²³

The trend in the pK_a^{CH}(corr) values of the carbene complexes is reminiscent of similar findings for other carbon acids where the negative charge in the conjugate anion is delocalized away from the α-carbon. The best known and most dramatic examples are the nitroalkanes where the pK_a^{CH} values in water follow the order CH₃NO₂ (pK_a^{CH} = 10.22,²⁵ pK_a^{CH}(corr) = 10.70) > CH₃CH₂NO₂ (pK_a^{CH} = 8.60,²⁵ pK_a^{CH}(corr) = 8.90) > (CH₃)₂CHNO₂ (pK_a^{CH} = pK_a^{CH}(corr) = 7.84²⁶),²⁷ In this case the increased acidity has been attributed to a stabilization of the anion by the polar²⁸ and hyperconjugative effects^{28,29} of the

(21) Note that even though the measured pK_a^{CH} values of **3-Et** and **3-Pr** are indistinguishable within experimental error, the difference between the statistically corrected pK_a^{CH} values is significant and well outside the experimental uncertainties.

(22) (a) McMurry, J. *Organic Chemistry*, 3rd ed.; Brooks/Cole: Belmont, CA, 1992; p 190. (b) Fox, M. A.; Whitesell, J. K. *Organic Chemistry*; Jones and Bartlett: New York, 1994; p 40.

(23) For example, the higher stability of **3-Et**⁻ relative to **3-Me**⁻ may be explained on the basis of a bond strength argument. C_{sp}²-H bonds are stronger than C_{sp}³-H bonds and C_{sp}²-C_{sp}³ bonds are stronger than C_{sp}³-C_{sp}³ bonds, but the increase in bond strength is greater for the change from C_{sp}³-C_{sp}³ to C_{sp}²-C_{sp}³ than for the change from C_{sp}³-H to C_{sp}²-H.^{22a,24} Since conversion of **3-Et** to **3-Et**⁻ entails a change of one C_{sp}³-C_{sp}³ and one C_{sp}³-H bond into one C_{sp}²-C_{sp}³ and one C_{sp}²-H bond, respectively, but the conversion of **3-Me** to **3-Me**⁻ involves only changes of two C_{sp}³-H bonds to two C_{sp}²-H bonds, the conversion of **3-Et** to **3-Et**⁻ is more favorable.

(24) Streitwieser, A.; Heathcock, C. H.; Kosower, E. M. *Introduction to Organic Chemistry*, 4th ed.; Macmillan: New York, 1992; p 258.

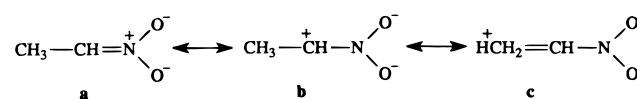
(25) Pearson, R. G.; Dillon, R. L. *J. Am. Chem. Soc.* **1953**, *75*, 2439.

(26) (a) Turnbull, D.; March, S. H. *J. Am. Chem. Soc.* **1943**, *65*, 212.

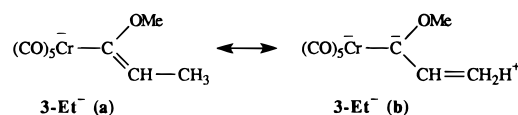
(b) Wheland, G. W.; Farr, J. *J. Am. Chem. Soc.* **1943**, *65*, 1433.

(27) In DMSO the pK_a^{CH} (pK_a^{CH}(corr)) values are 17.20 (17.68) for CH₃NO₂, 16.72 (17.02) for CH₃CH₂NO₂, and 16.88 (16.88) for (CH₃)₂CHNO₂.²⁸ A similar trend was found for ketones, e.g., the pK_a^{CH} (pK_a^{CH}(corr)) values in DMSO for PhCOCH₃ are 24.70 (25.18) while for PhCOCH₂CH₃ they are 24.4 (24.7).²⁸

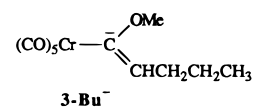
methyl groups. In valence-bond terminology this implies that the resonance structures **b** (polar effect) and **c** (hyperconjugation) are major contributors to the resonance hybrid.



The more dramatic effect of the α-methyl groups on the nitronate ion stabilities compared to the carbene complex anion stabilities may possibly be due to more effective hyperconjugation in the nitronate ions. This is because in **c** both negative charges are localized on the two oxygen atoms, whereas in the corresponding hyperconjugative structure for a carbene complex anion, e.g., **3-Et**⁻, the second negative charge is on a carbon which is less favorable.



Turning to **3-Bu**, it shows somewhat enhanced acidity compared to **3-Me**, but its pK_a^{CH}(corr) is significantly higher than that of **3-Et**. In view of the fairly large uncertainties in the pK_a^{CH}(corr) values, it is not clear how much significance one should attach to the fact that the pK_a^{CH}(corr) of **3-Bu** is closer to that of **3-Me** than that of **3-Et**. The reduced acidity of **3-Bu** compared to that of **3-Et** could be the result of less effective hyperconjugation when one of the β-hydrogens in **3-Et**⁻ (**b**) is replaced by an alkyl group and/or the consequence of more steric crowding in **3-Bu**⁻ which would reduce π-overlap/charge delocalization and lower the stability of **3-Bu**⁻.



It is noteworthy that 1-nitrobutane is also somewhat less acidic than nitroethane.²⁸

Kinetic Acidities. We again focus first on the comparison of **3-Et** and **3-Pr** with **3-Me** and discuss **3-Bu** later. The k₁^{OH}(corr) and k₁^{Pip}(corr) values are seen to decrease in the order **3-Me** >> **3-Et** >> **3-Pr**, i.e., substitution of α-hydrogen for

(28) Bordwell, F. G.; Bartmess, J. E.; Hautala, J. A. *J. Org. Chem.* **1978**, *43*, 3095.

(29) Kresge, A. J. *Can. J. Chem.* **1974**, *52*, 1897.

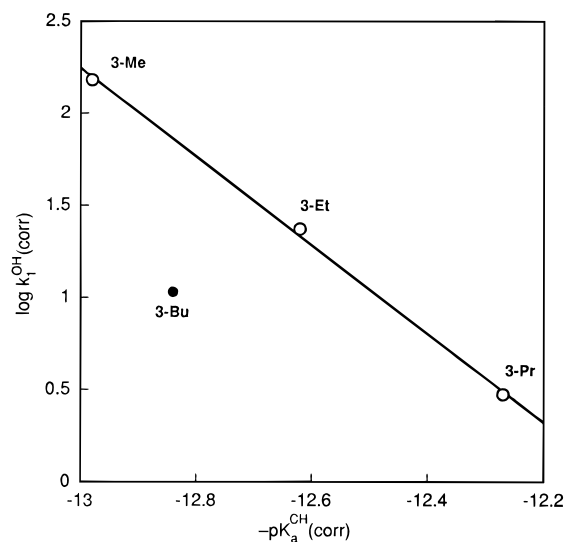
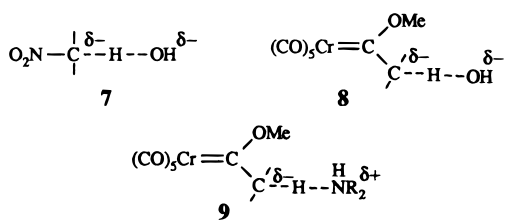


Figure 3. Brønsted plot for the deprotonation of carbene complexes by OH^- . The straight line defined by **3-Me**, **3-Et**, and **3-Pr** (open circles) yields $\alpha = -2.41 \pm 0.10$.

α -methyl reduces the rate substantially.³⁰ This leads to a situation where an increase in acidity is associated with a decrease in rate and the Brønsted α value ($d \log k_1(\text{corr})/d \log K_a^{\text{CH}}(\text{corr})$) is negative. The Brønsted plot for the reaction with OH^- is shown in Figure 3. The points for **3-Me**, **3-Et**, and **3-Pr** define a straight line that yields $\alpha = -2.41 \pm 0.10$. A similar plot (not shown) for the reaction with piperidine yields $\alpha = -4.49 \pm 0.85$.

Our findings that the rate constants decrease with increasing acidity of the carbon acid are unusual but not without precedent. A similar situation prevails in the deprotonation of the nitroalkanes whose $\text{p}K_a^{\text{CH}}$ values were discussed above: CH_3NO_2 ($k_1^{\text{OH}} = 27.6 \text{ M}^{-1} \text{ s}^{-1}$,³² $k_1^{\text{OH}}(\text{corr}) = 9.20 \text{ M}^{-1} \text{ s}^{-1}$) > $\text{CH}_3\text{CH}_2\text{NO}_2$ ($k_1^{\text{OH}} = 5.19 \text{ M}^{-1} \text{ s}^{-1}$,³² $k_1^{\text{OH}}(\text{corr}) = 2.60 \text{ M}^{-1} \text{ s}^{-1}$) > $(\text{CH}_3)_2\text{CHNO}_2$ ($k_1^{\text{OH}} = k_1^{\text{OH}}(\text{corr}) = 0.316 \text{ M}^{-1} \text{ s}^{-1}$).³² The Brønsted α value for this series was found to be -0.5 ± 0.1 ; because of its negative value it has been called the "nitroalkane anomaly".²⁹ The negative α value was attributed to the imbalanced nature of the transition state, **7**, in which charge delocalization into the nitro group lags strongly behind proton transfer.³³ As a result of this imbalance, the hyperconjugative



and polar effect of the methyl group that play a major role in the stabilization of the nitronate ion are only weakly developed at the transition state and hence contribute only minimally to its stabilization. In fact the methyl groups lead to a destabilization of the transition state which is mainly the result of a repulsive inductive/field effect between the methyl groups and

the disproportionately large negative charge on the α -carbon.²⁹ There is also a repulsive field effect between the methyl groups and the partial negative charge on the hydroxide ion which contributes to a destabilization of the transition state²⁹ and possibly a steric repulsion of the approaching base, at least in the case of $(\text{CH}_3)_2\text{CHNO}_2$.³⁴

Since the $(\text{CO})_5\text{Cr}$ moiety also acts as a strong π -acceptor, it is reasonable to expect that the transition states (**8**)³³ for the deprotonation of carbene complexes are imbalanced in a similar way as the transition states in the deprotonation of nitroalkanes and of carbon acids activated by π -acceptors in general.³⁵ Hence the same explanation for the negative α -values in the deprotonation of **3-Me**, **3-Et**, and **3-Pr** should be applicable, i.e., minimal development of the stabilizing effect of the methyl groups seen for the anions and repulsive field effects in the transition states.

In view of the large size of the $(\text{CO})_5\text{Cr}$ moiety, steric effects are potentially of greater importance in the carbene complex reactions which may explain the more dramatic reduction in the rate constants with increasing methyl substitution. This is certainly the case with the much bulkier piperidine as the base and reflected in the much larger negative α value compared to that for the hydroxide ion reaction. It should be noted that the larger steric effect with piperidine apparently more than offsets the change from a transition state destabilizing field effect between the methyl group and the partial negative charge on the catalyst (OH^- in **8**) to a transition state stabilizing field effect between the methyl groups and the partial positive charge on the catalyst (R_2NH in **9**).

The kinetic acidity of the *n*-butyl derivative (**3-Bu**) follows the same qualitative trend observed for **3-Me**, **3-Et**, and **3-Pr**, but there are some quantitative differences that require comment; these differences manifest themselves as a negative deviation from the Brønsted line defined by **3-Me**, **3-Et**, and **3-Pr**, as is apparent in Figure 3 and in the corresponding Brønsted plot for the piperidine reaction (not shown).

In trying to understand these deviations it is best to focus on a comparison of **3-Bu** to **3-Et**, because in both compounds one α -hydrogen of **3-Me** has been replaced by one alkyl group. In a first approximation one can assume that the destabilization of the transition state that results from the inductive and field effects of an *n*-propyl group on the negative charges at the α -carbon and hydroxide ion (**8**) should be about the same as the corresponding effects by a methyl group. Furthermore, it is reasonable to assume that the steric effects on the proton transfer rate constants are also approximately the same for both carbene complexes. If the steric effects were not comparable one would expect the $k_1^{\text{PIP}}(\text{corr})/k_1^{\text{OH}}(\text{corr})$ ratio for **3-Bu** to be significantly smaller than for **3-Et**, because a potentially larger steric effect on the reaction of **3-Bu** with OH^- should be magnified in the reaction of **3-Bu** with piperidine. However, the $k_1^{\text{PIP}}(\text{corr})/k_1^{\text{OH}}(\text{corr})$ ratios are quite similar, with the one for **3-Bu** (1.48) being even slightly larger than that for **3-Et** (1.03).

Based on the above considerations one concludes that if **3-Bu** and **3-Et** had the same $\text{p}K_a^{\text{CH}}(\text{corr})$, the rate constants for the two compounds would be approximately equal. However, since **3-Bu** is less acidic, its lower $k_1^{\text{OH}}(\text{corr})$ and $k_1^{\text{PIP}}(\text{corr})$ values simply reflect the normal trend of decreased deprotonation rates with decreasing thermodynamic acidity.

Intrinsic Rate Constants. Additional insights may be gained from a consideration of the *intrinsic* rate constants for proton transfer. The intrinsic rate constants, k_o , provide a measure of

(30) In the first qualitative study revealing that Fischer carbene complexes of the type **1** are quite acidic, Kreiter³¹ already noted that H/D exchange in a NaOMe/MeOD solution of **3-Et** was slower than a similar solution of **3-Me**.

(31) Kreiter, C. G. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 390.

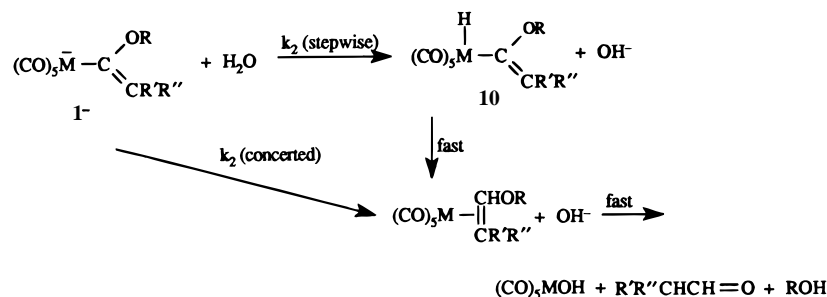
(32) Bell, R. P.; Goodall, D. M. *Proc. Roy. Soc. A* **1966**, *294*, 273.

(33) Structure **7** which shows all the transferred negative charge on the α -carbon is an exaggeration, i.e., there is probably a certain degree of charge delocalization into the nitro group even at the transition state. A similar comment applies to **8** and **9** discussed below.

(34) Bernasconi, C. F.; Panda, M.; Stronach, M. W. *J. Am. Chem. Soc.* **1995**, *117*, 9206.

(35) 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.

Scheme 2



the purely kinetic barrier (intrinsic reactivity) of the reaction that is independent of the thermodynamic acidity or $\text{p}K_{\text{a}}$ difference between the proton donor and proton acceptor.³⁵ They are defined as the statistically corrected rate constants for deprotonation of the carbene complex by a hypothetical base such that the statistically corrected equilibrium constant is equal to 1. In the reactions with hydroxide ion as the base, k_{o}^{OH} can be estimated based on the relationship $\log k_{\text{o}}^{\text{OH}} = \log k_1^{\text{OH}}(\text{corr}) - 0.5 \log K_1^{\text{OH}}(\text{corr})$ where $K_1^{\text{OH}} = K_{\text{a}}^{\text{CH}}/K_{\text{w}}$, with $K_{\text{w}} = 6.46 \times 10^{-16} \text{ M}^2$ ⁶ being the ionic product of the solvent; this relationship corresponds to the simplest version of the Marcus equation.³⁶ For the reactions with piperidine, $\log k_{\text{o}}$ was calculated as $\log k_{\text{o}}^{\text{Pip}} = \log(k_1^{\text{Pip}}(\text{corr})/q) - 0.62(\text{p}K_{\text{a}}^{\text{PipH}} - \text{p}K_{\text{a}}^{\text{CH}}(\text{corr}) + \log p/q)$ ³⁸ with 0.62 being the Brønsted β value for the deprotonation of **3-Me** by secondary alicyclic amines.⁶

The $\log k_{\text{o}}^{\text{OH}}$ and $\log k_{\text{o}}^{\text{Pip}}$ values are included in Table 3. It is difficult to give precise error limits for these parameters, because they depend not only on uncertainties in the rate constants and $\text{p}K_{\text{a}}^{\text{CH}}(\text{corr})$ values but also on the assumptions made to calculate the intrinsic rate constants. We estimate that the uncertainties in the intrinsic rate constants are ± 0.2 log units. Both $\log k_{\text{o}}^{\text{OH}}$ and $\log k_{\text{o}}^{\text{Pip}}$ are seen to decrease in the order **3-Me** \gg **3-Et** \approx **3-Bu** \gg **3-Pr**. It is this decrease in the intrinsic rate constants that may be regarded as the root cause for the divergence between the kinetic and thermodynamic acidities (negative α). There are four factors that contribute to the decrease in the $\log k_{\text{o}}^{\text{OH}}$ and $\log k_{\text{o}}^{\text{Pip}}$ values. (1) The disproportionately small stabilization of the transition state by the hyperconjugative effect: This factor is a textbook example of the manifestation of the Principle of Nonperfect Synchronization (PNS).³⁵ The PNS states that if the development of a product stabilizing factor (hyperconjugation in our case) lags behind the main bond changes (proton transfer in our case), there is a reduction in the intrinsic rate constant.

(2) The destabilization of the transition state by the repulsive inductive/field effect between the alkyl groups and the partial negative charge on the α -carbon: Because of the imbalance, the charge on the α -carbon is disproportionately large compared to that in the product anion. As a result the transition state suffers a disproportionately large destabilization relative to that of the product anion which leads to some reduction in the intrinsic rate constant.

(3) The destabilization of the transition state by the repulsive field effect between the alkyl groups and the partial negative charge on the hydroxide ion: The destabilization of the transition state by this effect is expected to be smaller than that by the

inductive/field effect of the alkyl groups on the negative charge on the α -carbon because of the greater distance between the alkyl groups and the hydroxide ion. However, because here there is no corresponding effect on the product ion, i.e., the entire transition state destabilization is reflected in the lowering of the intrinsic rate constant, the effect on the k_{o}^{OH} values may nevertheless be substantial.

(4) The steric effect: Just as with the third factor, this effect only operates on the transition state.

It should be noted that even though the first factor lowers k_{o} , it would not, in the absence of the other factors, lead to negative α -values; it would only attenuate the increase in k_1^{OH} and k_1^{Pip} with decreasing $\text{p}K_{\text{a}}^{\text{CH}}$ and result in reduced but still positive α -values. It is only the inductive and field effects and the steric factor that, if they lower k_{o} enough, can overcompensate for the slight increase in k_1^{OH} and k_1^{Pip} resulting from the hyperconjugative effect and lead to the net decrease in k_1^{OH} and k_1^{Pip} . As the data show, the lowering of k_{o} by factors (2)–(4) is indeed strong enough to result in large reductions in k_1^{OH} and k_1^{Pip} for **3-Et**, **3-Bu**, and **3-Pr** so that α becomes negative. In contrast, comparison of **3-Bu** with **3-Et** shows that the intrinsic rate constants for the deprotonation of these two carbene complexes are quite similar. This situation allows changes in $\text{p}K_{\text{a}}^{\text{CH}}$ to become the main factor affecting the actual rate constants and leads to the result that $k_1^{\text{OH}}(\text{corr})$ and $k_1^{\text{Pip}}(\text{corr})$ for **3-Bu** ($\text{p}K_{\text{a}}^{\text{CH}}(\text{corr}) = 12.84$) is lower than for **3-Et** ($\text{p}K_{\text{a}}^{\text{CH}}(\text{corr}) = 12.53$).

Hydrolysis Rates. A. Thermal Reaction. The mechanism of hydrolysis of several carbene complexes such as **3-Me** and **1** (e.g., $\text{M} = \text{Cr}$ or W , $\text{R} = \text{Me}$, $\text{R}' = \text{H}$, $\text{R}'' = \text{Ph}$) has been shown, at least in basic solution, to involve rate limiting reaction of the anion (**1**⁻) with a proton donor, to form the vinyl ether $\text{R}'\text{R}''\text{C}=\text{CHOMe}$ as the immediate product of this process.^{9,11} In most cases, this vinyl ether is rapidly converted to the corresponding aldehyde, $\text{R}'\text{R}''\text{CHCH}=\text{O}$. This conversion has been attributed to complexation with $(\text{CO})_5\text{M}$ which activates the vinyl ether toward hydrolysis even in basic solution.^{9a} Only with $\text{R}' = \text{H}$, $\text{R} = \text{phenyl}$ the vinyl ether is the final product, presumably because the steric bulk of $\text{PhCH}=\text{CHOMe}$ prevents efficient complexation with $(\text{CO})_5\text{M}$, and thus no hydrolysis of the vinyl ether occurs.^{9b}

Regarding the details of the rate limiting reaction of the anion with a proton donor, this may either be a stepwise or a concerted process, as shown in Scheme 2. The stepwise mechanism involves rate limiting protonation of the anion on the metal, followed by reductive elimination; in the concerted mechanism there is protonation on the carbene carbon which is simultaneous with cleavage of the bond between the metal and the carbene carbon. No firm distinction between the two mechanisms could be made on the basis of the experimental results although the concerted alternative was preferred on the grounds that the stepwise mechanism requires the $\text{p}K_{\text{a}}$ of **10** to be unrealistically high.^{9a}

(36) The Marcus³⁷ equation is given by $\Delta G^{\ddagger} = w_{\text{r}} + \Delta G_{\text{o}}^{\ddagger} + \Delta G_{\text{o}}/2 + (\Delta G_{\text{o}})^2/16\Delta G_{\text{o}}^{\ddagger}$ with ΔG^{\ddagger} being the free energy of activation, $\Delta G_{\text{o}}^{\ddagger}$ the Gibbs free energy, w_{r} a work term for assembling the reactants, and $\Delta G_{\text{o}}^{\ddagger}$ the intrinsic barrier of the reaction ($\Delta G_{\text{o}}^{\ddagger} = \Delta G^{\ddagger}$ when $\Delta G_{\text{o}} = 0$ and $w_{\text{r}} = 0$). If one neglects the w_{r} and $(\Delta G_{\text{o}})^2/16\Delta G_{\text{o}}^{\ddagger}$ terms which are likely to be very small in our case, this leaves $\Delta G^{\ddagger} \approx \Delta G_{\text{o}}^{\ddagger} + 0.5\Delta G_{\text{o}}$ which is equivalent to $\log k_1 = \log k_{\text{o}} + 0.5 \log K_1$.

The results of the present study support the concerted mechanism. This is because it is difficult to rationalize why the $k_2^{\text{H}_2\text{O}}$ values should depend so strongly on the α -alkyl groups if $k_2^{\text{H}_2\text{O}}$ referred to protonation of the anions **3-Me**⁻, **3-Et**⁻, **3-Bu**⁻, and **3-Pr**⁻ on the metal; the α -alkyl groups are simply too far away from the metal to have a substantial electronic or steric effect on its reactivity. In the concerted mechanism reaction occurs at the carbene carbon. Electronic effects may not be large either if the small dependence of the pK_a^{CH} (corr) values are taken as an approximate measure of relative stability of the anions. On the other hand, steric effects are likely to play an important role which would explain the reactivity order **3-Me** \gg **3-Et** \approx **3-Bu** \gg **3-Pr**. This reactivity order for $k_2^{\text{H}_2\text{O}}$ is qualitatively the same as that for $k_{-1}^{\text{H}_2\text{O}}$, but the dependence of $k_2^{\text{H}_2\text{O}}$ on alkyl substitution is quantitatively weaker than that of $k_{-1}^{\text{H}_2\text{O}}$. This means that the $k_{-1}^{\text{H}_2\text{O}}/k_2^{\text{H}_2\text{O}}$ ratios decrease in the order **3-Me** \gg **3-Bu** \approx **3-Et** $>$ **3-Pr** which explains why proton transfer is only close to fully reversible for **3-Me**.

B. Photochemical Pathway. The hydrolysis of **3-Pr** is catalyzed by light; a similar photochemical acceleration has been reported for the hydrolysis of $(\text{CO})_5\text{M}=\text{C}(\text{OMe})\text{CH}_2\text{Ph}$ (M = Cr and Mo).^{9b} A possible mechanism for the photochemical pathway which involves light induced exchange of a CO ligand for a CH_3CN ligand prior to reaction of the anion with water has been proposed.^{9b}

Experimental Section

Materials. Standard Schlenk techniques were employed in synthesizing and handling the Fischer carbene complexes, with argon as the protecting gas. More details about general synthetic procedures can be found in ref 39.

Following Fischer and Fischer,⁴⁰ (ethylmethoxycarbene)pentacarbonylchromium(0), **3-Et**, was prepared by adding 0.54 g (15 mmol) of EtLi in pentane to 3.30 g (15 mmol) of $\text{Cr}(\text{CO})_6$ dissolved in 120 mL of THF at ambient temperature. EtLi was made by treating Li with EtBr in pentane according to the method of Wakefield.⁴¹ The EtLi/ $\text{Cr}(\text{CO})_6$ mixture was stirred for 30 min before the solvent was removed under reduced pressure. The lithium salt dissolved in 40 mL of water was methylated by adding small portions of $\text{Me}_3\text{O}^+\text{BF}_4^-$ until a pH of about 7 was reached. The product was immediately extracted with pentane and dried with Na_2SO_4 , and the solvent was removed under reduced pressure. The orange oil was purified by flash chromatography. The product was obtained as an orange oil in 40% yield. ¹H NMR (250 MHz, CD_3CN) δ 1.00 (t, 3H, CH_3) (lit.⁴⁰ 0.75⁴²), δ 3.34 (q, 2H, CH_2) (lit.⁴⁰ 3.06⁴²), δ 4.74 (s, 3H, OCH_3) (lit.⁴⁰ 4.17⁴²); IR (CD_3CN) 2062/1939 cm^{-1} (CO) (lit.⁴⁰ 2065/1982/1961/1939 cm^{-1} in hexanes); UV/vis (50% CH_3CN –50% H_2O) λ_{max} = 370 nm, $\log \epsilon$ 3.78.

(*n*-Butylmethoxycarbene)pentacarbonylchromium(0), **3-Bu**, was prepared by the method of Hegedus;⁴³ 4.00 g (18.2 mmol) of $\text{Cr}(\text{CO})_6$ was added to 30 mL of diethyl ether. A 1.3 M solution of butyllithium in hexanes (15.4 mL, 20.0 mmol) was slowly added. The reaction was allowed to stir at room temperature overnight. Methanol was slowly added to quench any unreacted butyllithium in the reaction. The solvents were then removed by rotary evaporation. Water was added to the dark residue that remained in the flask. $\text{Me}_3\text{O}^+\text{BF}_4^-$ was slowly added until the pH was 2–3. The solution was now orange. The water

solution was then extracted several times with hexanes until no color was seen in the organic layer. The organics were combined, dried over magnesium sulfate, and filtered. The solvent was removed by rotary evaporation, and the crude carbene was purified by flash chromatography using hexanes as eluent. An orange oil was obtained in about 50% yield. ¹NMR (250 MHz, CD_3CN) δ 0.90 (t, 3H, CH_3) (lit.⁴³ 0.91⁴⁴), δ 1.32 (m, 2H, CH_2CH_3) (lit.⁴³ 1.32⁴⁴), δ 1.47 (m, 2H, CHCH_2CH_2) (lit.⁴³ 1.45⁴⁴), δ 3.32 (t, 2H, $=\text{CCH}_2$) (lit.⁴³ 3.30⁴⁴), δ 4.73 (s, 3H, OCH_3) (lit.⁴⁰ 4.70⁴⁴); IR (CD_3CN) 2061/1936 cm^{-1} (CO); UV/vis (50% CH_3CN –50% H_2O) λ_{max} = 370 nm, $\log \epsilon$ 3.81. A second batch of **3-Bu** was a gift from Professor Louis S. Hegedus.

The synthesis of (methoxyisopropylcarbene)pentacarbonylchromium(0), **3-Pr**, was based on the procedure of Fischer and Plabst.⁴⁵ Treating Li powder with *i*-PrCl in pentane provided *i*-PrLi.⁴⁶ *i*-PrLi (0.90 g, 18 mmol) in pentane was added to 3.9 g (18 mmol) of $\text{Cr}(\text{CO})_6$ dissolved in 200 mL of THF at ambient temperature within 20 min. The solution was stirred for 30 min before 5 mL of methanol was added to destroy the unreacted *i*-PrLi. After removing the solvent under reduced pressure a red-brown residue was obtained which was taken up into 50 mL of water and covered with 100 mL of pentane. Methylation was carried out by adding small portions of $\text{Me}_3\text{O}^+\text{BF}_4^-$ until the pH reached about 7. The carbene complex was extracted into pentane as soon as it formed. The pentane solution was dried over Na_2SO_4 , and the solvent was removed under reduced pressure. The crude product was run through a silica gel (100–200 mesh) column and recrystallized from pentane. Needle crystals were obtained in a 40% yield, mp 51–52.5 °C (lit.⁴⁵ 52°); ¹H NMR (250 MHz, CD_3CN) δ 0.97 (d, 6H, CH_3) (lit.⁴⁵ 1.00⁴⁷), δ 4.15 (m, 1H, CH) (lit.⁴⁵ 4.23⁴⁷), δ 4.76 (s, 3H, OCH_3) (lit.⁴⁵ 4.85⁴⁷); IR (KBr) 2061/1978/1943 cm^{-1} (CO) (lit.⁴⁵ 2065/1961/1945 cm^{-1} in hexane); UV/vis (50% CH_3CN –50% H_2O) λ_{max} = 368 nm, $\log \epsilon$ 3.94.

Acetonitrile was refluxed over CaH_2 and distilled under argon. Water was obtained from a Millipore water purification system. Both water and acetonitrile were degassed several times by the freeze–pump–thaw method. HCl and KOH solutions were prepared by diluting prepackaged stock solutions (Baker Analytical). Piperidine, triethylamine, and *N*-methylmorpholine were refluxed over sodium for 5 h in an argon atmosphere and then fractionally distilled. Acetic acid and methoxyacetic were used as received.

Reaction Solutions and Kinetics. All kinetic experiments were conducted in 50% CH_3CN –50% water (v/v) at 25 °C, μ = 0.1 M (KCl). All pH measurements were carried out with an Orion 611 pH-meter equipped with a glass electrode and a “SureFlow” (Corning) reference electrode and calibrated with standard aqueous buffers. Actual pH values were calculated by adding 0.18 to the measured pH, according to Allen et al.⁴⁸ Typical substrate concentrations were 5–10 \times 10⁻⁵ M. Rates were measured in an Applied Photophysics DX.17MV stopped-flow apparatus (fast reactions) or a Perkin-Elmer Lambda 2 spectrophotometer (slow reactions). Kinetics were followed by monitoring the reaction either at 370 or 280 nm.

Acknowledgment. This research has been supported by Grant No. CHE-9307659 from the National Science Foundation and by the donors of the Petroleum Research Fund administered by the American Chemical Society, Grant No. 30444-AC4. L.G.R. thanks the University of Santiago de Compostela for a postdoctoral fellowship. We also thank Professor Louis S. Hegedus for a sample of **3-Bu** when we ran out of our own.

Supporting Information Available: Tables S1–S4, kinetic data; Figure S1, representative buffer plots (6 pages). See any current masthead page for ordering and Internet access instructions.

JA970193Z

(43) Hegedus, L. S. Private communication.

(44) In CDCl_3 .

(45) Fischer, E. O.; Plabst, D. *Chem. Ber.* **1974**, *107*, 3326.

(46) Gilman, H.; Moore, F. W.; Baine, O. *J. Am. Chem. Soc.* **1941**, *63*, 2479.

(47) In CCl_4 .

(48) Allen, A. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1987**, *109*, 2774.

(37) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679.

(38) *q* is the number of equivalent basic sites on the amine (1 for piperidine), while *p* is the number of equivalent protons on the protonated amine (2 for piperidine).

(39) Sun, W. Ph.D. Thesis, University of California, Santa Cruz, 1994.

(40) Fischer, E. O.; Fischer, H. *Chem. Ber.* **1974**, *107*, 657.

(41) Wakefield, B. J. *Organolithium Methods*; Academic Press: New York, 1988; p 18.

(42) In benzene.