

Physical Organic Chemistry of Transition Metal Carbene Complexes.
17.¹ Kinetics of the Reactions of
(Arylthioalkoxycarbene)pentacarbonyl Complexes of Chromium(0)
and Tungsten(0) with Thiolate Ions in Aqueous Acetonitrile: pK_a
Values of the Metal-Protonated Tetrahedral Adducts Formed between
Carbene Complexes and Thiolate Ion

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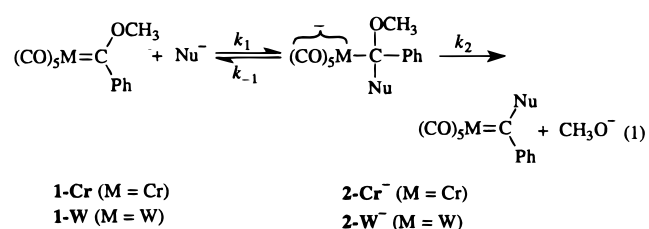
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Abstract: Rate and equilibrium constants for the nucleophilic attachment of various thiolate ions to (CO)₅M=C(SMe)Ph (M = Cr and W) and for the attachment of HOCH₂CH₂S⁻ to (CO)₅W=C(SCH₂CH₂OH)C₆H₄Z (Z = CF₃, Cl, F, H, Me, MeO, and Me₂N) have been determined in 50% MeCN–50% water (v/v) at 25 °C. For some of the adducts, those of the general structure (CO)₅M(C(SR,SR')C₆H₄Z), a kinetic determination of the pK_a of their metal-protonated conjugate acid, (CO)₅M(H)C(SR,SR')C₆H₄Z, is also reported. On the basis of Brønsted coefficients, Hammett ρ values and comparisons with the reactions of the same thiolate ions with methoxy carbene complexes such as (CO)₅M=C(OMe)Ph, insights into the role played by desolvation of the nucleophile prior to C–S bond formation, by the smaller π-donor and inductive but larger steric effects of the MeS compared to the MeO group, by transition state imbalances, etc. are discussed. The pK_a values obtained for (CO)₅M(H)C(SR,SR')C₆H₄Z were used to resolve a mechanistic ambiguity in the hydrolysis of Fischer carbenes that have acidic protons on the α-carbon, e.g., (CO)₅Cr=C(OMe)Me.

Introduction

Fischer carbene complexes of the type **1-M**² undergo facile nucleophilic substitution of the methoxy group by a variety of nucleophiles.^{1,3–8} Qualitatively, these reactions are quite similar to nucleophilic substitutions of carboxylic esters and have been

assumed to proceed by a stepwise mechanism (eq 1)³ involving



the tetrahedral intermediates **2-M**⁻.² However, with respect to reactivity there are large differences between the carbene complexes and esters in that the former are much more reactive than the latter.^{1,9,10} This is because the stabilization of the negative charge of **2-M**⁻ by delocalization into the CO ligands of the (CO)₅M moieties is much more effective than the charge stabilization by the oxygen in the corresponding intermediates in ester reactions. As a result, **2-M**⁻ type intermediates may accumulate to detectable levels in reactions with strong nucleophiles.

Early examples where such intermediates were detectable are the reactions of **1-M** with MeO⁻ in MeOH which yield the

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(2) When using the symbols **1-M**, **2-M**, etc., both the Cr and W derivative will be meant. If only one of the derivatives is referred to, we will use the symbols **1-Cr**, **1-W**, **2-Cr⁻**, **2-W⁻**, etc.

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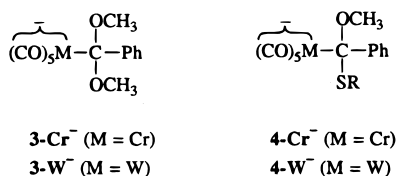
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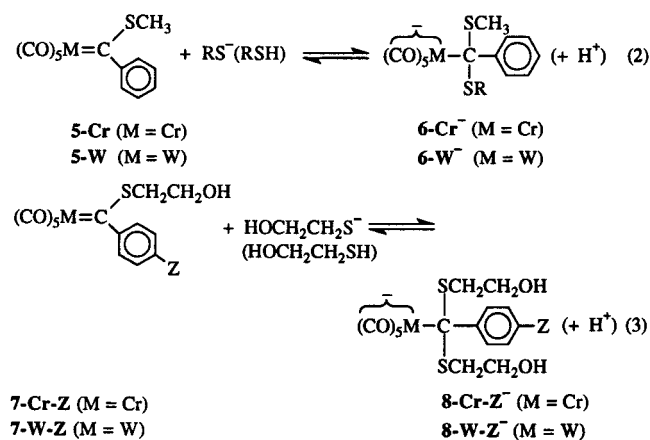
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symmetrical adducts 3-M^- .^{2,10} More recently, the intermediates



4-M^- in the reactions of 1-M and the corresponding ethoxy complexes with alkanethiolate ions in 50% MeCN–50% water were observed by UV and NMR spectroscopy.^{1,4d} Not only do these findings constitute the strongest evidence for the step-wise mechanisms, but the accumulation of the intermediates also allows a detailed kinetic study of the various elementary steps (k_1 , k_{-1} , k_2) in eq 1. Determination of these rate constants in turn leads to a better understanding of how various structural factors affect reactivity. Some of the factors that were found to be important in the reactions of 1-M with MeO^- and thiolate ions include soft–soft, soft–hard, and hard–hard interactions between nucleophile and carbene complex, partial desolvation of the nucleophile as integral component of the activation process, the reactant stabilizing π -donor effect of the MeO group, and acid catalysis of MeO^- departure from the intermediate.^{1,4d,10} It was also observed that the effect of changing the metal from Cr to W on the equilibrium constant for nucleophilic addition is almost negligible but significant on the rate constants k_1 and k_{-1} ($W > \text{Cr}$), indicating that the intrinsic¹¹ rate constant for the tungsten complexes is higher than for the chromium complexes.

In this paper we report kinetic data on eq 2 ($\text{RS}^- = n\text{-PrS}^-$, CH_3S^- , $\text{HOCH}_2\text{CH}_2\text{S}^-$, $\text{Me}_2\text{OCCH}_2\text{CH}_2\text{S}^-$, and $\text{MeO}_2\text{CCH}_2\text{S}^-$) and on eq 3 ($Z = \text{CF}_3$, Cl, F, H, Me, MeO, and Me_2N) in



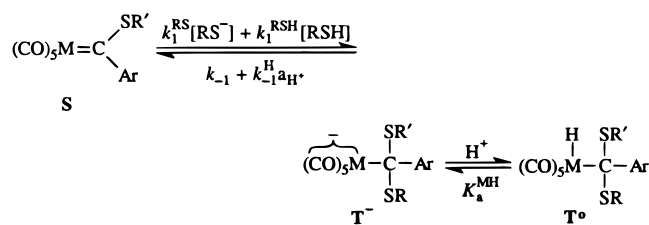
aqueous acetonitrile at 25 °C. Our main focus is on the following questions.

(1) How does substitution of the methoxy group (1-M) by the thiomethoxy group (5-M) or other RS groups (7-M-Z) affect the rate and equilibrium constants of thiolate ion addition? These effects are not easily predictable because differences between the MeO and RS groups with respect to their inductive, π -donor, and steric effects are all expected to affect the kinetic and thermodynamic parameters in different ways.

(2) Is the progress of the C–S bond formation at the transition state as small as in the reactions of thiolate ions with 1-M^1 so

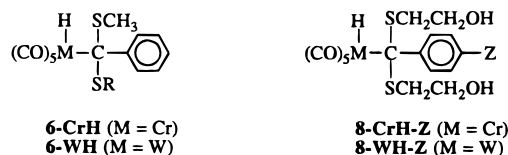
(11) For a reaction with a forward rate constant k_1 and a reverse rate constant k_{-1} , the intrinsic rate constant, k_0 , is defined as $k_0 = k_1 = k_{-1}$ when the equilibrium constant is unity, i.e., $K_1 = 1$.

Scheme 1



that the partial desolvation of the nucleophile becomes a major component of the activation process, as manifested by negative β_{nuc} values?

(3) Is it possible to determine the $\text{p}K_a$ of metal protonated adducts such as 6-MH or 8-MH-Z ? Such $\text{p}K_a$ values of Fischer



carbene complex adducts have, thus far, been elusive. A kinetic $\text{p}K_a$ determination might be possible by reacting, say, 6-M^- with acid which leads to regeneration of 5-M , preceded by rapid reversible protonation of 6-M^- on the metal, a situation akin to the reaction of nitronate ions where rapid reversible nitronic acid formation precedes slow carbon protonation¹² or leaving-group departure.¹³

Results

General Features. The reactions reported in this paper can be described by the general Scheme 1 where \mathbf{S} stands for 5-M or 7-M-Z , \mathbf{T}^- for 6-M^- or 8-M-Z^- and \mathbf{T}^0 is the protonated form of \mathbf{T}^- , i.e., 6-MH or 8-MH-Z . It is assumed that in \mathbf{T}^0 the proton is attached to the metal, in analogy to hydrido transition metal complexes such as $\text{HCrCp}(\text{CO})_3$ or $\text{HWcP}(\text{CO})_3$.¹⁴

All experiments were performed at 25 °C in buffered solutions under pseudo-first-order conditions with \mathbf{S} as the minor component. Most of the results were obtained in 50% MeCN–50% water (v/v), but a number of experiments were carried out in 70%, 80%, and 90% MeCN. The ionic strength was maintained at 0.1 M with KCl unless otherwise stated. The equilibrium constants were determined under the same conditions as the rate constants.

Reaction of \mathbf{S} with Thiolate Ions at High pH. The carbene complexes were reacted with thiolate ions in triethylamine buffers at pH 10.40; for the reactions of 5-M with CH_3S^- and $n\text{-PrS}^-$ the thiolate ion/thiol mixtures were used as their own buffers at pH values between 11.3 and 12.6. Formation of the adducts (\mathbf{T}^-) was quite fast and easily monitored by the change in the UV/vis spectrum. Representative spectra are shown in Figure 1 (spectrum 1, \mathbf{S} ; spectrum 2, \mathbf{T}^-). The pseudo-first-order rate constants, k_{obsd} , showed a linear dependence on thiolate ion concentration according to eq 4

$$k_{\text{obsd}} = k_1^{\text{RS}}[\text{RS}^-] \quad (4)$$

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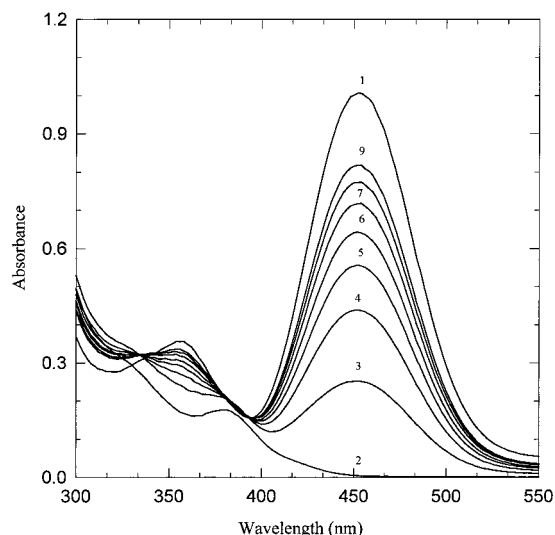


Figure 1. Absorption spectra of $S = 7\text{-W-H}$ under different conditions in 50% MeCN-50% water. Spectrum 1: 7-W-H in $\text{Cl}_2\text{-CHCO}_2\text{H}$ buffer at pH 3.50. Spectrum 2: $\text{T}^- = 8\text{-W-H}$ generated from 7-W-H in the presence of 0.004 M $\text{HOCH}_2\text{CH}_2\text{S}^-$. Spectra 3-9: Gradual conversion of 8-W-H back into 7-W-H in a $\text{Cl}_2\text{-CHCO}_2\text{H}$ buffer at pH 3.50 (spectra 3 to 9 taken at 4 s intervals).

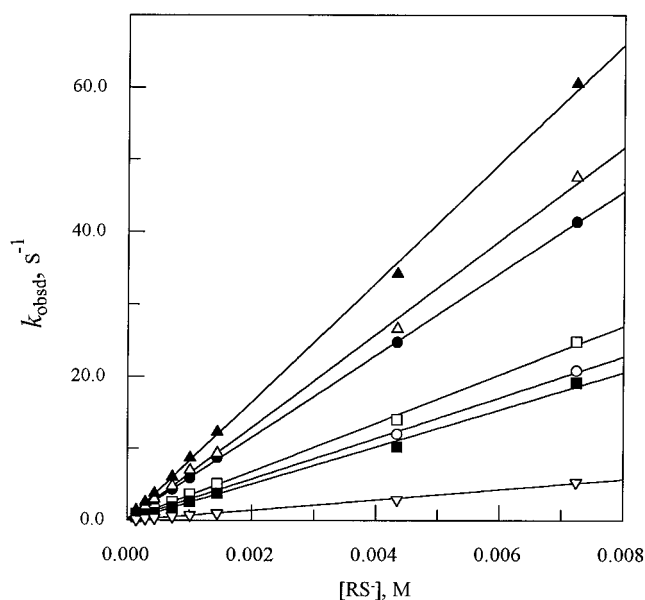


Figure 2. Representative plots of k_{obsd} vs $[\text{RS}^-]$ (eq 4) in basic solution for the reaction of $\text{HOCH}_2\text{CH}_2\text{S}^-$ with 7-W-Z in 50% MeCN-50% water. $Z = \text{CF}_3$ (▲), Cl (△), F (●), Me (□), H (○), MeO (■), Me_2N (▽).

(Figure 2) from which k_1^{RS} was obtained as the slope; the intercepts of these plots were negligible.

Reaction of T^- with Carboxylate and *N*-Methylmorpholine Buffers. In these experiments T^- derived from a number of selected carbene complexes was first generated by reaction of the carbene complex with a 0.004 M solution of the respective thiolate ion. The T^- solution was then mixed with a series of dilute acetate (pH 5.14–6.64), methoxyacetate (pH 4.08–5.97) or cyanoacetate buffers (pH 2.78–3.85) which led to H^+ -catalyzed conversion of T^- back to S , with virtually quantitative recovery of the carbene complex (Figure 1, spectra 2, 3, 4, 5, etc.). Representative plots of k_{obsd} vs a_{H^+} are shown in Figure 3; they yield k_{-1}^{H} from the slope and k_{-1} from the intercept according to eq 5.

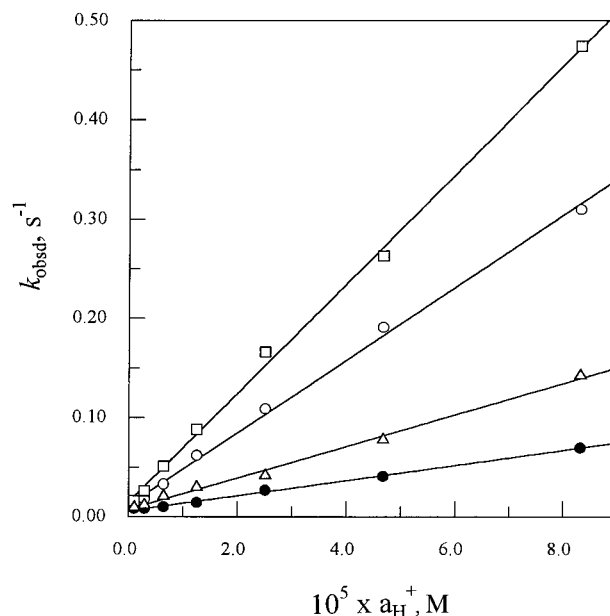


Figure 3. Plots of k_{obsd} vs a_{H^+} (eq 5) for the reaction of 8-W-Z in methoxyacetate buffers, 50% MeCN-50% water. $Z = \text{MeO}$ (□), Me (○), H (△), F (●).

$$k_{\text{obsd}} = k_{-1}^{\text{H}} a_{\text{H}^+} + k_{-1} \quad (5)$$

In the majority of cases the intercept was rather small, and hence the k_{-1} values are typically subject to a significant uncertainty. In some cases a more accurate method to obtain k_{-1} was available which is based on equilibrium measurements as described below.

Buffer Catalysis. Buffer catalysis in the carboxylate buffers was weak and contributed negligibly at the buffer concentrations (0.005–0.05 M total buffer) used in the above-described experiments. However, experiments conducted by reacting S with thiols in *N*-methylmorpholine buffers showed a modest catalytic effect. For example, in the reaction of 7-W-H with $\text{HOCH}_2\text{CH}_2\text{SH}$ a 25% rate enhancement was observed in a 0.2 M *N*-methylmorpholine buffer at pH 8.16.

Reaction of T^- with HCl. A. 50% MeCN-50% Water. These experiments were conducted in a way similar to the ones in the carboxylate buffers, except that T^- was reacted with HCl solutions at concentrations from 0.005 to 0.25 or 0.35 M. Most plots of k_{obsd} vs $[\text{HCl}]$ showed some downward curvature (Figure 4) except for the reactions of 7-W-CF_3 and $7\text{-W-Me}_2\text{N}$ (eq 3), where the plots were linear with even a slight tendency toward an upward curvature (Figure 5).

The most plausible reason for the downward curvature is the onset of rapid reversible protonation of T^- on the $(\text{CO})_5\text{M}$ moiety (Scheme 1). This leads to eq 6 for k_{obsd} .^{15,16}

$$k_{\text{obsd}} = \frac{K_a^{\text{MH}} k_{-1}^{\text{H}} [\text{H}^+]}{K_a^{\text{MH}} + [\text{H}^+]} \quad (6)$$

A nonlinear least-squares fit yields k_{-1}^{H} and K_a^{MH} . The agreement between k_{-1}^{H} obtained in carboxylate buffers (eq 5) and in HCl (eq 6) is seen to be quite satisfactory (Tables 1 and 2), although in most cases k_{-1}^{H} from eq 5 is slightly higher than from eq 6. For further discussion the values obtained from eq 5 will be adopted.

(15) Note that in eq 6 we use $[\text{H}^+]$ as equivalent to $[\text{HCl}]$, while in eq 5 a_{H^+} refers to what is being measured by the pH meter.

(16) In these experiments k_{-1} is negligible.

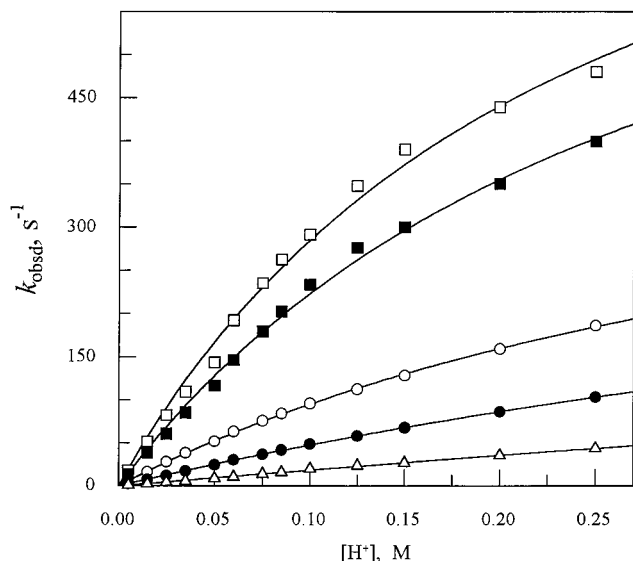


Figure 4. Plots of k_{obsd} vs $[\text{H}^+]$ (eq 6) for reaction of **8-W-Z⁻** with HCl in 50% MeCN–50% water. Electron-donating and moderately electron-withdrawing substituents: Z = MeO (□), Me (■), H (○), F (●), Cl (△).

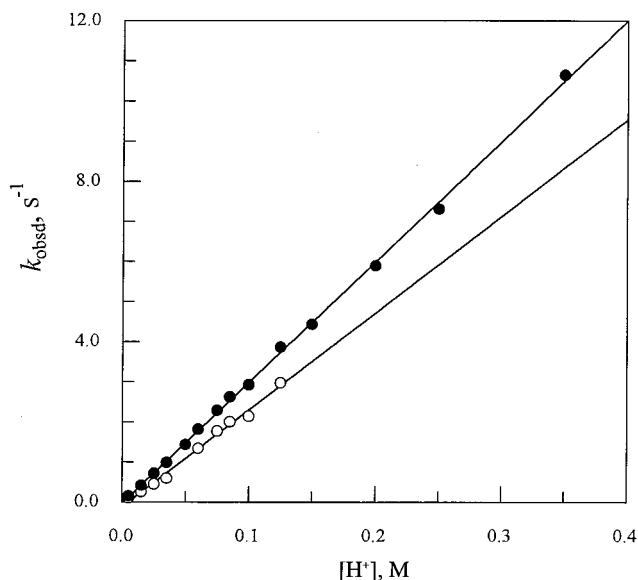


Figure 5. Plots of k_{obsd} vs $[\text{H}^+]$ (eq 6) in 50% MeCN–50% water for the reaction of **8-W-Z⁻** with strongly electron-withdrawing Z⁻ substituents: Z = CF₃ (●), Me₂NH⁺ (○).

The question whether there may be a different interpretation of the downward curvature needs to be raised. This is because for the runs at $[\text{HCl}] > 0.1$ M the ionic strength was no longer held constant at 0.1 M, and this could possibly be a reason for the curvature. Due to the limited solubility of KCl in 50% MeCN–50% water, experiments at higher ionic strength maintained by KCl were not feasible. However, NaClO₄ is much more soluble, and hence experiments with **8-Cr-H⁻** and **8-W-H⁻** in HClO₄/NaClO₄ solutions were performed at an ionic strength of 0.3 M (plots not shown). Applying eq 6 to these data yielded the following results: $\text{p}K_{\text{a}}^{\text{MH}} = 0.71 \pm 0.05$ and $k_{-1}^{\text{H}} = (2.98 \pm 0.20) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for **8-Cr-H⁻** and $\text{p}K_{\text{a}}^{\text{MH}} = 0.24 \pm 0.04$ and $k_{-1}^{\text{H}} = (1.98 \pm 0.08) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for **8-W-H⁻**, i.e., the $\text{p}K_{\text{a}}^{\text{MH}}$ values are very close to those obtained in HCl/KCl solutions (Table 2), while the k_{-1}^{H} values are somewhat higher in HClO₄/NaClO₄. That high $[\text{NaClO}_4]$ enhances k_{-1}^{H} was independently confirmed by measuring k_{obsd} for

Table 1. Rate and equilibrium constants for the reactions of **5-M** with various thiolate ions (eq 2) in 50% MeCN–50% water (v/v) at 25°C, $\mu = 0.1$ M (KCl)

parameter	(CO) ₅ Cr=C-(SMe)Ph 5-Cr	(CO) ₅ W=C-(SMe)Ph 5-W	5-W/5-Cr
MeS ⁻ ($\text{p}K_{\text{a}}^{\text{RSH}} = 11.86$)			
$k_1^{\text{RS}}, \text{M}^{-1} \text{ s}^{-1}$	$(1.87 \pm 0.08) \times 10^3$	$(6.84 \pm 0.29) \times 10^3$	3.65
k_{-1}, s^{-1}	$(4.19 \pm 0.40) \times 10^{-3}$	$(6.02 \pm 0.10) \times 10^{-3}$	1.44
$K_1^{\text{RS}}, \text{M}^{-1}$	$(4.46 \pm 0.62) \times 10^5$	$(1.14 \pm 0.07) \times 10^6$	2.55
$k_{-1}^{\text{H}}, \text{M}^{-1} \text{ s}^{-1}$	$(5.09 \pm 0.19) \times 10^3$	$(3.86 \pm 0.13) \times 10^3$	0.76
$k_{-1}^{\text{H}}, \text{M}^{-1} \text{ s}^{-1}$	$(4.64 \pm 0.12) \times 10^3$	$(3.42 \pm 0.26) \times 10^3$	0.74
$k_1^{\text{RSH}}, \text{M}^{-1} \text{ s}^{-1}$	$(2.86 \pm 0.60) \times 10^{-3}$	$(5.37 \pm 0.86) \times 10^{-3}$	1.88
$K_1^{\text{RSH}}, \text{M}^{-1}$	$(6.16 \pm 1.17) \times 10^{-7}$	$(1.57 \pm 0.17) \times 10^{-6}$	2.55
$K_{\text{a}}^{\text{MH}}, \text{M}^{-1}$	0.287 ± 0.039	0.310 ± 0.033	1.08
$\text{p}K_{\text{a}}^{\text{MH}}$	0.54 ± 0.06	0.51 ± 0.04	
<i>n</i> -PrS ⁻ ($\text{p}K_{\text{a}}^{\text{RSH}} = 11.94$)			
$k_1^{\text{RS}}, \text{M}^{-1} \text{ s}^{-1}$	$(5.33 \pm 0.11) \times 10^2$	$(1.58 \pm 0.05) \times 10^3$	2.96
k_{-1}, s^{-1}	$(4.85 \pm 0.29) \times 10^{-4}$	$(3.33 \pm 0.30) \times 10^{-4}$	0.69
$K_1^{\text{RS}}, \text{M}^{-1}$	$(1.10 \pm 0.04) \times 10^6$	$(4.75 \pm 0.28) \times 10^6$	4.32
HOCH ₂ CH ₂ S ⁻ ($\text{p}K_{\text{a}}^{\text{RSH}} = 10.79$)			
$k_1^{\text{RS}}, \text{M}^{-1} \text{ s}^{-1}$	$(6.60 \pm 0.30) \times 10^2$	$(2.95 \pm 0.07) \times 10^3$	4.47
k_{-1}, s^{-1}	$(1.78 \pm 0.11) \times 10^{-3}$	$(5.82 \pm 0.26) \times 10^{-4}$	0.33
$K_1^{\text{RS}}, \text{M}^{-1}$	$(3.07 \pm 0.05) \times 10^5$	$(3.76 \pm 0.07) \times 10^6$	12.2
MeO ₂ CCH ₂ CH ₂ S ⁻ ($\text{p}K_{\text{a}}^{\text{RSH}} = 10.69$)			
$k_1^{\text{RS}}, \text{M}^{-1} \text{ s}^{-1}$	$(6.80 \pm 0.20) \times 10^2$	$(4.78 \pm 0.22) \times 10^3$	7.03
k_{-1}, s^{-1}	$(2.28 \pm 0.14) \times 10^{-3}$	$(7.92 \pm 0.78) \times 10^{-4}$	0.35
$K_1^{\text{RS}}, \text{M}^{-1}$	$(2.90 \pm 0.10) \times 10^5$	$(3.22 \pm 0.17) \times 10^6$	11.1
MeO ₂ CCH ₂ S ⁻ ($\text{p}K_{\text{a}}^{\text{RSH}} = 9.45$)			
$k_1^{\text{RS}}, \text{M}^{-1} \text{ s}^{-1}$	$(2.02 \pm 0.13) \times 10^3$	$(8.67 \pm 0.36) \times 10^3$	4.29
k_{-1}, s^{-1}	$(8.72 \pm 1.05) \times 10^{-3}$	$(6.57 \pm 0.44) \times 10^{-3}$	0.75
$K_1^{\text{RS}}, \text{M}^{-1}$	$(1.80 \pm 0.10) \times 10^5$	$(9.15 \pm 0.20) \times 10^5$	5.08

^a From eq 4 in Et₃N buffers. ^b From eq 5 in acetate buffers. ^c From k_1^{RS}/k_{-1} . ^d From eq 6 in HCl. ^e $k_1^{\text{RSH}} = k_{-1}^{\text{H}} K_1^{\text{RSH}}$ with k_{-1}^{H} (AcOH). ^f $K_1^{\text{RSH}} = K_1^{\text{RS}} K_{\text{a}}^{\text{RSH}}$. ^g From eq 5 in *N*-methylmorpholine buffers. ^h $k_{-1} = k_1^{\text{RS}}/K_1^{\text{RS}}$. ⁱ Spectrophotometric value, from eq 7.

8-W-CF₃⁻ as a function of $[\text{NaClO}_4]$ at pH 1.82, a pH where protonation of **T⁻** is negligible and $k_{\text{obsd}} = k_{-1}^{\text{H}} a_{\text{H}^+} k_{\text{obsd}} = 0.67, 0.76, 0.82,$ and 1.04 s^{-1} at $[\text{NaClO}_4] = 0.05, 0.15, 0.25,$ and 0.35 M, respectively.

B. 70%, 80%, and 90% MeCN. Additional experiments in HCl solutions were performed in 70, 80, and 90% MeCN with **6-W⁻** (eq 2, R = Me) and **8-W-H⁻** (eq 3). The plots of k_{obsd} vs $[\text{HCl}]$ again showed downward curvature which, however, was more pronounced than in 50% MeCN, consistent with a higher $\text{p}K_{\text{a}}^{\text{MH}}$ in the solvent richer in MeCN (Figure 6). The results of these experiments (k_{-1}^{H} and $\text{p}K_{\text{a}}^{\text{MH}}$) are summarized in Table 3.

Equilibrium Measurements. The equilibrium constants, K_1^{RS} , for thiolate ion addition to **5-M** were determined spectrophotometrically by exploiting the large difference in the absorbance between the carbene complex and the adduct at 466 nm for the Cr and 454 nm for the W complexes. Since the K_1^{RS} values are quite large ($> 10^6 \text{ M}^{-1}$), the measurements had to be made in *N*-methylmorpholine or acetate buffers in order to achieve low enough thiolate ion concentration ($\sim 10^{-7}$ to 3×10^{-5} M) while maintaining $[\text{RSH}]_{\text{tot}} \gg [\text{S}]_0$. The absorbance measurements were fitted to eq 7

$$\frac{A_0 - A_{\infty}}{A - A_{\infty}} = 1 + K_1[\text{RS}^-] \quad (7)$$

with A_0 being the absorbance in the absence of RS^- , A_{∞} the absorbance at high $[\text{RS}^-]$ so that conversion of **S** to **T⁻** is

Table 2. Rate and equilibrium constants for the reactions of **7-M-Z** with HOCH₂CH₂S⁻ (eq 3) in 50% MeCN–50% water (v/v) at 25 °C, $\mu = 0.1$ M (KCl)

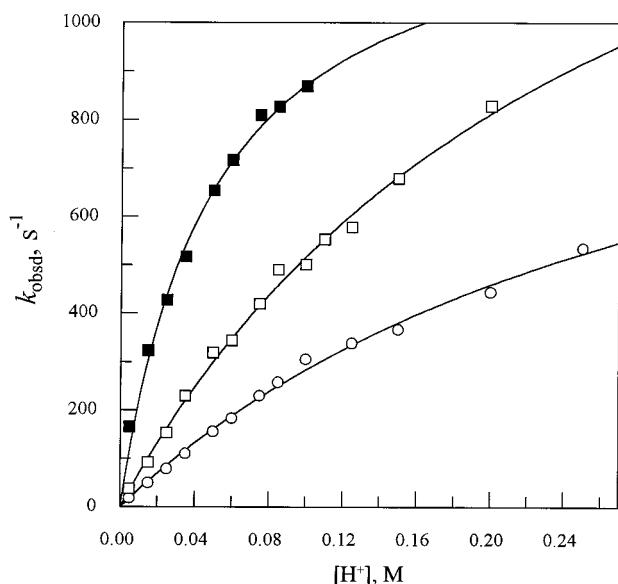
complex	$10^{-3} \times k_1^{\text{RS}^a}$ M ⁻¹ s ⁻¹	$10^3 \times k_{-1}^b$ s ⁻¹	$10^{-5} \times K_1^{\text{RS}^c}$ M ⁻¹	$10^{-2} \times k_{-1}^{\text{H}^+}(\text{HCl})^d$ M ⁻¹ s ⁻¹	$10^{-2} \times k_{-1}^{\text{H}^+}(\text{BH})^b$ M ⁻¹ s ⁻¹	$10^3 \times k_1^{\text{RSH}^e}$ M ⁻¹ s ⁻¹	$10^6 \times K_1^{\text{RSH}^f}$	$K_3^{\text{MH}}/(\text{p}K_a^{\text{MH}})^d$ M
7-W-NHMe₂⁺				0.24 ± 0.01	0.28 ± 0.02			
7-W-CF₃	8.23 ± 0.11	2.60 ± 0.07	31.6 ± 1.3	0.30 ± 0.01	0.45 ± 0.01	2.31 ± 0.23	51.2 ± 4.1	>>1 (<<0)
7-W-Cl	6.45 ± 0.10	4.96 ± 0.39	13.0 ± 1.2	1.91 ± 0.10	2.78 ± 0.03	5.87 ± 0.79	21.1 ± 2.7	2.54 ± 0.99 (-0.47 ± 0.15)
7-W-F	5.67 ± 0.06	6.17 ± 0.63	9.19 ± 1.01	5.31 ± 0.20	7.64 ± 0.17	11.4 ± 2.4	14.9 ± 2.2	0.865 ± 0.050 (0.06 ± 0.03)
7-W-H	2.88 ± 0.10	7.44 ± 1.94	3.87 ± 1.12	11.7 ± 0.12	15.9 ± 0.4	9.99 ± 3.10	6.28 ± 1.82	0.428 ± 0.020 (0.37 ± 0.03)
7-W-Me	3.36 ± 0.05	11.6 ± 0.3	2.90 ± 0.12	30.0 ± 1.0	36.6 ± 0.9	17.2 ± 1.7	4.70 ± 0.37	0.291 ± 0.033 (0.54 ± 0.05)
7-W-OMe	2.58 ± 0.06	14.6 ± 4.1	1.77 ± 0.53	40.4 ± 1.8	55.1 ± 1.1	15.8 ± 5.1	2.87 ± 0.86	0.240 ± 0.030 (0.62 ± 0.05)
7-W-NMe₂	0.80 ± 0.02	19.7 ± 1.4	0.406 ± 0.039				0.658 ± 0.085	
7-Cr-H	0.67 ± 0.02			15.2 ± 0.8				0.184 ± 0.022 (0.74 ± 0.05)

^a From eq 4 in Et₃N buffers. ^b From eq 5 in methoxyacetate buffers (Z = F, H, Me and MeO) or cyanoacetate buffers (Z = Me₂NH⁺, CF₃, Cl). ^c $K_1^{\text{RS}} = k_1^{\text{RS}}/k_{-1}$. ^d From eq 6 in HCl. ^e $k_1^{\text{RSH}} = k_{-1}^{\text{H}^+} K_1^{\text{RSH}}$ with $k_{-1}^{\text{H}^+}(\text{BH})$. ^f $K_1^{\text{RSH}} = K_1^{\text{RS}} K_a^{\text{RSH}}$ with $\text{p}K_a^{\text{RSH}} = 10.79$.

Table 3. Rate constants for H⁺-catalyzed expulsion of MeS⁻ from **6-W⁻** (eq 2) and of HOCH₂CH₂S⁻ from **8-W-H⁻** (eq 3), and $\text{p}K_a^{\text{MH}}$ values of the respective adducts in various MeCN–water mixtures at 25 °C, $\mu = 0.1$ M (KCl)

Adduct	% MeCN	$10^{-3} \times k_{-1}^{\text{H}^+}$ ^a	$\text{p}K_a^{\text{MH}}$
$(\text{CO}_2)\text{WC}(\text{SMe})_2\text{Ph}$ (6-W⁻)	50	3.86 ± 0.13	0.51
	70	4.00 ± 0.08	0.55
	80	7.13 ± 0.26	0.58
	90	26.8 ± 1.7	1.32
$(\text{CO}_2)\text{WC}(\text{SCH}_2\text{CH}_2\text{OH})_2\text{Ph}$ (8-W-H⁻)	50	1.17 ± 0.12	0.37
	80	3.06 ± 0.06	0.57
	90	13.0 ± 0.1	1.11

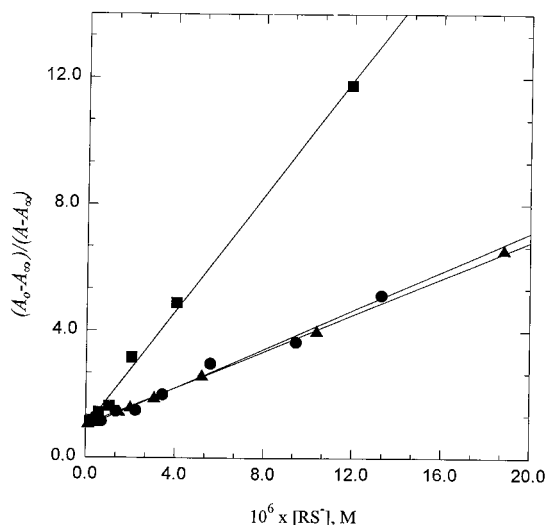
^a From eq 6 in HCl.

**Figure 6.** Plots of k_{obsd} vs $[\text{H}^+]$ (eq 6) for the reaction of **6-W⁻** with HCl in different solvents: 90% MeCN–10% water (■), 80% MeCN–20% water (□), 50% MeCN–50% water (○).

quantitative, and A the absorbance at intermediate $[\text{RS}^-]$, respectively. Representative plots according to eq 7 are shown in Figure 7; they provide K_1^{RS} from the slopes.

Discussion

The rate and equilibrium constants determined in this study are summarized in Tables 1–3; all error limits given are standard

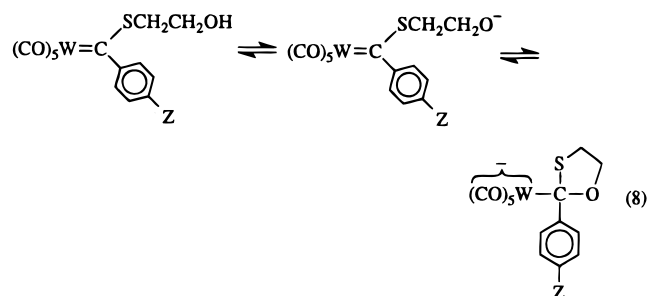
**Figure 7.** Representative plots of $(A_0 - A_\infty)/(A - A_\infty)$ vs $[\text{RS}^-]$ according to eq 7. **5-W** + MeO₂CCH₂S⁻ (■); **5-Cr** + MeO₂CCH₂S⁻ (▲); **5-Cr** + HOCH₂CH₂S⁻ (●).

deviations. Some comments regarding the source of the various parameters are in order. For the reactions of **5-M** with *n*-PrS⁻, HOCH₂CH₂S⁻, MeO₂CCH₂S⁻, and MeO₂CCH₂S⁻ (Table 1) the k_{-1} values were obtained as $k_{-1} = k_1^{\text{RS}}/K_1^{\text{RS}}$ with K_1^{RS} being spectrophotometrically determined (eq 7). A direct determination of k_{-1} from the intercepts of plots of k_{obsd} vs a_{H^+} in carboxylate buffers (the method used for the reactions of **5-M** with MeS⁻ and of **7-M-Z** with HOCH₂CH₂S⁻) would not have given accurate k_{-1} values. This is because the respective adducts can lose either RS⁻ or MeS⁻, i.e., the intercepts of plots of k_{obsd} vs a_{H^+} represent the sum of the rate constants of RS⁻ and MeS⁻ loss.

For the reaction of **5-M** with MeS⁻ (Table 1) the spectrophotometric method did not yield reproducible K_1^{RS} values, presumably because of the high volatility of MeSH. Hence, the reported K_1^{RS} values were obtained as k_1^{RS}/k_{-1} , with k_{-1} being determined from the intercepts of plots according to eq 5. It should be noted, however, that in this case the experimental uncertainty of k_{-1} and K_1^{RS} is probably substantially larger than that of the standard deviations given in Table 1. This is because the intercepts were quite small and also may contain some contribution from a $k_1^{\text{RS}}[\text{RSH}]$ term.

For the reactions of **7-W-X** with HOCH₂CH₂S⁻ (Table 2) the K_1^{RS} values were also obtained as k_1^{RS}/k_{-1} ; a spectrophotometric determination was precluded due to competing cyclization

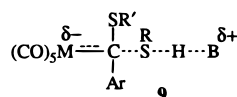
according to eq 9.



With respect to k_{-1}^H and pK_a^{MH} , these parameters could only be determined for the reactions that lead to symmetrical adducts, i.e., **5-M** with MeS^- (Table 1) and **7-W-Z** with $\text{HOCH}_2\text{CH}_2\text{S}^-$ (Table 2). No such parameters are reported for the reactions of **5-M** with $n\text{-PrS}^-$, $\text{HOCH}_2\text{CH}_2\text{S}^-$, $\text{MeO}_2\text{CCH}_2\text{CH}_2\text{S}^-$, and $\text{MeO}_2\text{CCH}_2\text{S}^-$ (Table 1) because the acid-catalyzed collapse of the respective adducts would lead to competitive loss of both the MeS and the RS group and hence would not provide k_{-1}^H values.

Mechanism. All kinetic data are consistent with the mechanism of Scheme 1. The reactions are clean, and no significant side reactions occur on the time scale of the experiments. Specifically, when **T**⁻ is acidified within <1 min after it has been formed, recovery of **S** is virtually quantitative. However, solutions of **T**⁻ slowly decompose to unidentified byproducts, as seen by spectral changes and by the fact that recovery of **S** upon addition of acid to **T**⁻ is incomplete if acidification is delayed.

The mechanism of the $k_1^{\text{RSH}} - k_{-1}^H$ pathway probably involves general base catalysis by the solvent in the forward and general acid catalysis by H_3O^+ in the reverse direction, implying a transition state as shown in **9** ($\text{B} = \text{H}_2\text{O}$). Support



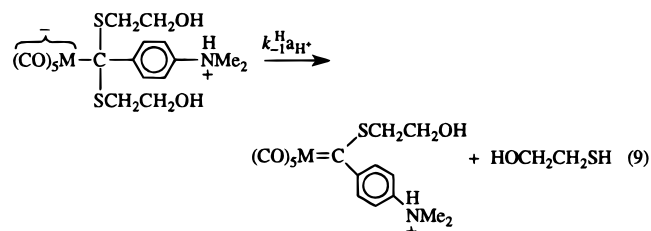
for this notion comes from observation of catalysis by *N*-methylmorpholine (NMM) buffers which presumably involves a transition state as shown in **9** ($\text{B} = \text{NMM}$).¹⁷ It is notable, though, that this catalysis is quite weak ($k_1^{\text{RSH}}(\text{NMM})/k_1^{\text{RSH}} = 4.3$) and that with methoxyacetate and cyanoacetate buffers the catalysis is too weak to allow an accurate determination of the catalytic rate constants.

(17) A reviewer has suggested that the $k_1^{\text{RSH}} - k_{-1}^H$ pathway may alternatively involve a stepwise mechanism, with rate-limiting RSH addition followed by rapid deprotonation in the k_1^{RSH} direction and rapid protonation of the leaving group followed by rate-limiting RSH departure in the k_{-1}^H direction. As an argument in favor of this mechanism he points out that the ratio for the rate constants of acid-catalyzed alkoxide ion departure from **4-M**⁻ ($\sim 5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$)¹ and of thiolate ion departure from **6-M**⁻ ($\sim 5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, this work) is around 10^5 , a difference "close to that expected for the pK_a 's of the oxygen and sulfur atoms." According to this reviewer, the catalysis by *N*-methylmorpholinium ion "could result from a preassociation type trapping of thiolate ion, thus retarding/eliminating any back capture of the newly formed metal carbene complex." There are two major problems with this suggestion. (1) If the ratio of 10^5 were to correspond to the difference in the pK_a 's of the oxygen and sulfur atoms, this would imply that the protonated oxygen and sulfur leaving groups depart with the same rates. This is highly unlikely. (2) The reviewer's explanation of the *N*-methylmorpholinium catalysis violates the principle of microscopic reversibility because the trapping of the thiolate ion would lead to a rate reduction in the nucleophilic addition direction, whereas the observed buffer catalysis means that the reaction is accelerated in *both* directions.

Table 4. Brønsted coefficients for the reactions of thiolate ions with **5-M** (eq 2)

	$(\text{CO})_5\text{Cr}=\text{C}(\text{SMe})\text{Ph}$ 5-Cr	$(\text{CO})_5\text{W}=\text{C}(\text{SMe})\text{Ph}$ 5-W
$\beta_{\text{nuc}}(k_1^{\text{RS}})$	-0.24 ± 0.07	-0.30 ± 0.04
$\beta_{\text{lg}}(k_{-1})$	-0.53 ± 0.02	-0.57 ± 0.07
$\beta_{\text{eq}}(K_1^{\text{RS}})$	0.30 ± 0.07	0.27 ± 0.07

The reaction of the Me_2N -substituted carbene complexes (**7-NMe₂**) requires some comment. In the experiments where **T**⁻ is reacted with acid the Me_2N group is rapidly protonated which means that k_{-1}^H in eq 6 refers to the reaction of eq 9 (first entry in Table 2). On the other hand, k_{-1} in eq 5 refers to the



spontaneous loss of RS^- from **T**⁻ where the M_2N group is *not* protonated.

A particularly interesting finding is that rapid reversible protonation of the $(\text{CO})_5\text{M}$ moiety of **T**⁻ could be inferred from the curved plots of k_{obsd} vs $[\text{H}^+]$ (Figures 4 and 6). As shown in the Results, this curvature in HCl solutions is not an artifact stemming from a higher ionic strength at high HCl concentration since the same curvature is observed in HClO_4 solution where a constant ionic strength is maintained with NaClO_4 . Additional support for this interpretation comes from the fact that the curvature of the plots of k_{obsd} vs $[\text{HCl}]$ diminishes as the phenyl substituent becomes more electron-withdrawing; for the two adducts with the strongest electron-withdrawing groups, CF_3 and Me_2NH^+ no curvature could be detected. These findings would be difficult to explain if the higher ionic strength were the cause of the curvature but they are consistent with the expected decrease in pK_a^{MH} with increasing electron-withdrawing strength of Z (Table 2; more on substituent effects below).

It should be noted that the Fischer carbene adducts reported in this work, **6-M**⁻ and **8-M-Z**⁻ are the first ones for which a pK_a^{MH} determination has been feasible. For **3-M**⁻ and **4-M**⁻, H^+ -catalyzed alkoxide ion departure was too fast (see k_2^H in Table 6) to allow kinetic measurements at a pH low enough to lead to protonation of the $(\text{CO})_5\text{M}$ moiety.^{10,18} With **6-M**⁻ and **8-M-Z**⁻ the leaving groups are thiolate ions and the reduced sensitivity to acid catalysis of thiolate ion departure translates into lower k_{-1}^H values (Tables 1–3), allowing kinetic measurements at much lower pH than with methoxy carbene complexes.

Dependence of k_1^{RS} , k_{-1} , and K_1^{RS} on pK_a^{RSH} . Figure 8 shows Brønsted plots for k_1^{RS} , k_{-1} , and K_1^{RS} for the reactions of **5-W** with various thiolate ions (eq 2). Similar plots (not shown) pertain to the reaction of **5-Cr**. The corresponding Brønsted coefficients are summarized in Table 4. Just as was observed in the reactions of **1-M** with thiolate ions,¹ the β_{nuc} values are negative and the β_{eq} values are much smaller than unity. Apparently, the negative β_{nuc} and low β_{eq} values are characteristic of the thiolate ion nucleophiles and not very much

(18) Bernasconi, C. F.; García-Río, L., to be published.

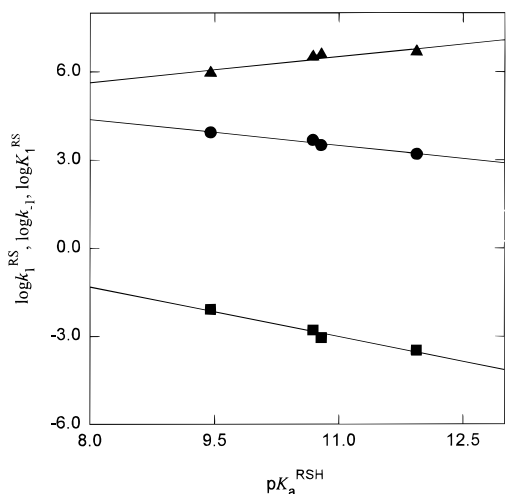


Figure 8. Brønsted plots of k_1^{RS} (●), k_{-1} (■), and K_1^{RS} (▲) for the reaction of **5-W** with $n\text{-PrS}^-$, MeS^- , $\text{HOCH}_2\text{CH}_2\text{S}^-$, $\text{MeO}_2\text{CCH}_2\text{CH}_2\text{S}^-$, and $\text{MeO}_2\text{CCH}_2\text{S}^-$.

dependent on whether the carbene complex is a methoxy or a thiomethoxy derivative.

The negative β_{nuc} values are unusual¹⁹ and probably the combined result of minimal progress of C–S bond formation at the transition state and the requirement for partial desolvation of the nucleophile before it enters the transition state.²⁰ In a first approximation, β_{nuc} may be expressed by eq 10

$$\beta_{\text{nuc}} = \beta_{\text{d}} + \beta'_{\text{nu}} \quad (10)$$

where $\beta_{\text{d}} = \text{d} \log K_{\text{d}} / \text{d} \text{p}K_{\text{a}}^{\text{RSH}}$ ²⁰ and $\beta'_{\text{nu}} = \text{d} \log k_1' / \text{d} K_{\text{a}}^{\text{RSH}}$, with K_{d} referring to the equilibrium constant for partial desolvation of the nucleophile and k_1' to the rate constant of the partially desolvated nucleophile. Since desolvation becomes more difficult with increasing basicity of the nucleophile, $\beta_{\text{d}} < 0$, which along with a small β'_{nuc} can lead to $\beta_{\text{nuc}} < 0$. A more refined treatment of the problem has been presented elsewhere.¹

The low β_{eq} values fit a pattern observed in reactions of thiolate ions with a variety of electrophiles.²³ This may be the combined result of the high polarizability of sulfur bases and the requirement for partial desolvation discussed above and elaborated upon earlier.¹

Substituent Effects. Figure 9 shows Hammett plots for k_1^{RS} , k_{-1} , K_1^{RS} , k_{-1}^{H} , and K_{a}^{MH} for the reactions of $\text{HOCH}_2\text{CH}_2\text{S}^-$ with **7-W-Z** (eq 3). The respective ρ values are reported in Table 5. The positive ρ values for k_1^{RS} and K_1^{RS} and the negative ρ value for k_{-1} are consistent with a nucleophilic addition reaction. However, the ρ values for k_1^{RS} and K_1^{RS} are rather small and considerably smaller than for MeO^- addition to **1-M** in methanol ($\rho(k_1) = 2.19$ and 2.60 for **1-Cr** and **1-W**, respectively).¹⁸

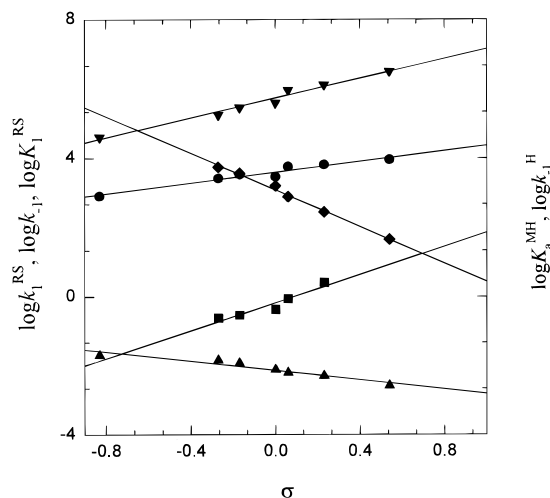
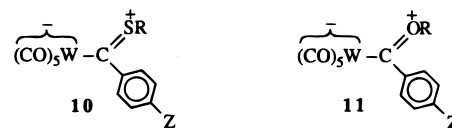


Figure 9. Hammett plots for k_1^{RS} (●), k_{-1} (▲), K_1^{RS} (▼), k_{-1}^{H} (◆), and K_{a}^{MH} (■) for the reaction of **7-W-Z** with $\text{HOCH}_2\text{CH}_2\text{S}^-$.

Table 5. Hammett ρ values for the reactions of $\text{HOCH}_2\text{CH}_2\text{S}^-$ with **7-W-Z** (eq 3)

parameter	ρ	parameter	ρ
k_1^{RS}	0.78 ± 0.09	k_1^{RSH}	-1.04 ± 0.12
k_{-1}	-0.67 ± 0.09	k_{-1}^{H}	-2.65 ± 0.11
K_1^{RS}	1.45 ± 0.10	K_{a}^{MH}	2.08 ± 0.25

A number of factors may contribute to the differences in ρ values. One is the smaller π -donor effect of sulfur (**10**) compared to oxygen (**11**).²⁴ As has been discussed elsewhere²⁶ the positive



ρ values in the nucleophilic additions to **1-M** are the result not only of the build-up of negative charge on the $(\text{CO})_5\text{M}$ moiety of the adduct but also of the π -donor effect of the methoxy groups. The reasoning is as follows. Since, due to the delocalization into the CO ligands, the negative charge on **11** is quite remote from the phenyl substituent, while the positive charge is concentrated on the oxygen atom and thus closer to Z, the destabilizing substituent effect on the positive charge must be greater than the stabilizing effect on the negative charge. The net result is an increase in reactivity with electron-withdrawing substituents. Inasmuch as with **7-W-Z** the π -donor effect of sulfur (**10**) is smaller than with **1-M** (**11**), the contribution of this factor to the $\rho(K_1)$ and $\rho(k_1)$ values should be correspondingly reduced.

Another factor may be related to the greater polarizability of sulfur compared to oxygen. The polarizability of sulfur is known to stabilize anions;^{27,28} the effect is very strong when the sulfur substituent is directly attached to the atom bearing the negative

(19) Negative β_{nuc} values have been reported for some phosphoryl transfer reactions to amines²⁰ and for reactions of highly reactive carbocations with amines;²¹ β_{nuc} values close to zero have also been found in the reaction of diphenylketene with amines.²²

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(24) $\sigma_{\text{R}} = -0.43$ and -0.15 for MeO and MeS, respectively.²⁵

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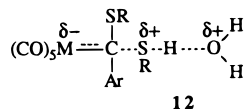
Table 6. Rate and equilibrium constants for the reactions of *n*-PrS⁻ with **5-M** and **1-M**

	(CO) ₅ Cr=C(SMe)Ph 5-Cr	(CO) ₅ Cr=C(OMe)Ph 1-Cr	(CO) ₅ W=C(SMe)Ph 5-W	(CO) ₅ W=C(OMe)Ph 1-W
$k_1^{RS}, M^{-1} s^{-1}$	$(5.33 \pm 0.11) \times 10^2$	1.34×10^4	$(1.58 \pm 0.05) \times 10^3$	4.21×10^4
k_{-1}, s^{-1}	$(4.85 \pm 0.29) \times 10^{-4}$	1.26^a	$(3.33 \pm 0.30) \times 10^{-4}$	3.11^a
K_1^{RS}, M^{-1}	$(1.10 \pm 0.04) \times 10^6$	1.06×10^4	$(4.75 \pm 0.28) \times 10^6$	1.35×10^4
$k_{-1}^H, M^{-1} s^{-1}$	$(5.09 \pm 0.09) \times 10^3$		$(3.86 \pm 0.13) \times 10^3$	
$k_2^H, M^{-1} s^{-1}$		5.39×10^8		5.69×10^8

^a Refers to loss of *n*-PrS⁻ from tetrahedral adduct between **1-M** and *n*-PrS⁻. ^b Refers to H⁺-catalyzed loss of MeS⁻ from tetrahedral adduct **6-M** with R = Me; k_{-1}^H is not statistically corrected. ^c Refers to H⁺-catalyzed loss of MeO⁻ from **4-M** with R = Me and R' = *n*-Pr.

charge but can still be significant one atom removed from the site of negative charge.²⁹ If the polarizability effect of the two HOCH₂CH₂S groups leads to increased stabilization of the negative charge in **8-W-Z**⁻, this could reduce the demand for further stabilization by the phenyl substituent and hence reduce the ρ values.

The ρ values for both k_1^{RSH} (the Hammett plot for k_1^{RSH} is not shown in Figure 9 due to strong overlap with the points for k_{-1}) and k_{-1}^H are negative, indicating that electron-withdrawing substituents destabilize the transition state relative to reactants and adducts. This result suggests a transition state **12** that is



imbalanced in the sense that deprotonation of the thiol by water has made less progress than C–S bond formation. This places a partial positive charge on the sulfur atom of the nucleophile. Apparently the destabilization of this positive charge by an electron-withdrawing phenyl substituent is greater than the stabilization of the partial negative charge on the (CO)₅M moiety, perhaps because this latter is partially³⁰ delocalized; the net result is a negative ρ value for k_1^{RSH} .

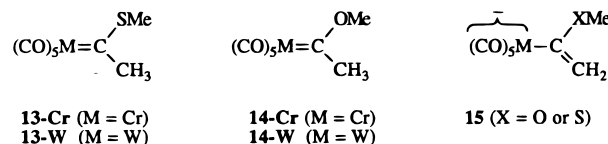
With respect to ρ for K_1^{MH} , even though its value is slightly higher than ρ for K_1^{RS} , the difference is probably not significant, suggesting that the stabilization of the negative charge of the anion is the main factor determining these ρ values. This further supports the above reasoning that the reduced π -donor effect of the RS group in **7-M-Z** is a major reason $\rho(K_1^{RS})$ is so much smaller than the $\rho(K_1)$ values for MeO⁻ addition to **1-M**.

Solvent Effects. Table 3 reports k_{-1}^H and pK_a^{MH} values for **6-W**⁻ and **8-W-H**⁻ in various MeCN–water mixtures. The trend toward increasing k_{-1}^H and increasing pK_a^{MH} values with increasing MeCN content of the solvent is qualitatively reasonable because the stability of **6-W**⁻ and **8-W-H**⁻ is expected to decrease with decreasing solvent polarity. The solvent effects are not dramatic, though, presumably because the negative charge in the anions is highly dispersed.

Effect of Changing the MeO Group to a MeS Group. A. K_1^{RS} . Table 6 provides a comparison of rate and equilibrium constants between the reactions of *n*-PrS⁻ with **5-M** and **1-M**. The equilibrium constants for the MeS carbene complexes are significantly larger than for the MeO complexes: $K_1^{RS}(\mathbf{5-Cr})/K_1^{RS}(\mathbf{1-Cr}) \approx 106$ and $K_1^{RS}(\mathbf{5-W})/K_1^{RS}(\mathbf{1-W}) \approx 352$. There are at least three major factors that may affect these ratios. (1) The

stronger electron-withdrawing inductive effect of the MeO³² group should enhance the stability of **T**⁻ derived from the MeO complexes relative to **T**⁻ derived from the MeS complexes and hence lower these ratios. (2) The larger size of sulfur compared to oxygen³³ should lead to more extensive steric hindrance in **T**⁻ derived from the MeS derivatives; this should also lower the equilibrium constant ratios. (3) The stronger π -donor effect of the MeO group which results in a more effective stabilization of the MeO carbene complexes should enhance the equilibrium constant ratios. The experimental results show that the π -donor effect is dominant and more than offsets the steric and inductive effects.

The enhanced equilibrium constants for nucleophilic attachment to the MeS carbene complexes is reminiscent of the higher acidity of **13-M** compared to **14-M**: $pK_a(\mathbf{13-Cr}) = 9.05^{36}$ vs $pK_a(\mathbf{14-Cr}) = 12.50^{37}$ and $pK_a(\mathbf{13-W}) = 8.37^{36}$ vs $pK_a(\mathbf{14-W}) = 12.36^{38}$. In the acidity comparisons the steric effect, which



in the nucleophilic reactions partially offsets the reduced π -donor effect of the MeS group, does not play a significant role since no crowding occurs in the respective anions (**15**). This must be the main reason the differences in the K_1^{RS} values are smaller compared to the differences in the pK_a values.

B. k_1^{RS} and k_{-1} . Kinetically, it is the MeO derivatives that are more reactive toward thiolate ion attack, with $k_1^{RS}(\mathbf{5-Cr})/k_1^{RS}(\mathbf{1-Cr}) = 3.98 \times 10^{-2}$ and $k_1^{RS}(\mathbf{5-W})/k_1^{RS}(\mathbf{1-W}) = 4.65 \times 10^{-2}$, respectively. This reversal indicates that the *intrinsic* rate constants, k_o ,¹¹ for the MeS complexes are substantially larger than for the MeO complexes. The fact that the $k_{-1}(\mathbf{5-M})/k_{-1}(\mathbf{1-M})$ ratios, 3.84×10^{-4} and 1.33×10^{-4} for the chromium and tungsten derivatives, respectively, are even smaller than the corresponding $k_1^{RS}(\mathbf{5-M})/k_1^{RS}(\mathbf{1-M})$ ratios is a manifestation of the same phenomenon. One may estimate a ratio for the intrinsic rate constants based on eq 11.³⁹

(31) 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.

(32) $\sigma_F = 0.30$ and 0.20 for MeO and MeS, respectively.²⁵

(33) Taft's³⁴ steric substituent constants, E_s , are -0.55 for MeO and -1.07 for MeS, respectively, while Charton's ν_{er} ³⁵ values are 0.36 for MeO and 0.64 for MeS, respectively.

(34) Unger, S. H.; Hansch, C. *Prog. Phys. Org. Chem.* **1976**, *12*, 9.

(35) Charton, M. *Stud. Org. Chem.* **1991**, *42*, 629.

(36) Bernasconi, C. F.; Ali, M. *J. Am. Chem. Soc.* **1999**, *121*, 3039.

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

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

(39) Equation 11 is based on the simplest version of the Marcus equation,⁴⁰ $\Delta G^\ddagger = \Delta G_o^\ddagger + 0.5\Delta G^\circ + (\Delta G^\circ)^2/16\Delta G_o^\ddagger$, where ΔG_o^\ddagger is the intrinsic barrier, and neglecting the third term which should be quite small.

(29) Bernasconi, C. F.; Ketner, R. J.; Brown, S. D.; Chen, X.; Rappoport, Z. *J. Org. Chem.* **1999**, *64*, 8829.

(30) In reactions that lead to resonance delocalized products, the charge delocalization at the transition state generally lags behind bond formation.³¹

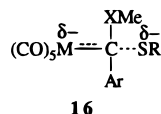
$$\log \frac{k_o(\mathbf{5-M})}{k_o(\mathbf{1-M})} = \log \frac{k_1^{\text{RS}}(\mathbf{5-M})}{k_1^{\text{RS}}(\mathbf{1-M})} - 0.5 \log \frac{K_1^{\text{RS}}(\mathbf{5-M})}{K_1^{\text{RS}}(\mathbf{1-M})} \quad (11)$$

It yields $\log\{k_o(\mathbf{5-Cr})/k_o(\mathbf{1-Cr})\} = -2.41$ and $\log\{k_o(\mathbf{5-W})/k_o(\mathbf{1-W})\} = -2.60$, respectively.

These differences in the intrinsic rate constants are indicative of transition state imbalances^{31,41} where one or several of the factors—inductive, steric, and π -donor—either lag behind or are ahead of bond formation. As a result of the imbalances the relative importance of these factors in how they affect the rate constants is different from how they affect the equilibrium constants, and this is the reason the intrinsic rate constants differ. The principle of nonperfect synchronization (PNS)⁴² provides guidance as to what factors play a central role.

1. Steric Effect. One factor that appears to contribute strongly toward making $\log k_o$ for $\mathbf{5-M}$ lower than for $\mathbf{1-M}$ is steric hindrance. According to the PNS, if development of steric hindrance at the transition state is ahead of bond formation, $\log k_o$ is lowered. Since steric hindrance is stronger for the reaction with $\mathbf{5-M}$, $\log k_o$ for $\mathbf{5-M}$ will be reduced more than $\log k_o$ for $\mathbf{1-M}$. Recent evidence from S_NV reactions suggests that early development of steric hindrance indeed appears to be the rule.⁴³

2. Inductive Effect. Even though inductive effects are thought to develop synchronously with bond formation and, therefore, should not affect intrinsic rate constants per se, they can contribute to differences in intrinsic rate constants because of imbalances arising from other factors, especially resonance/delocalization effects.³¹ There is strong evidence that in adducts such as $\mathbf{2-M}^-$, $\mathbf{3-M}^-$, $\mathbf{4-M}^-$, etc. the negative charge is dispersed into the CO ligands¹⁰ which provides substantial resonance stabilization to these adducts, a point highlighted by the bracket symbol on the adduct structures. The same must be true for \mathbf{T}^- in Scheme 1. There is also abundant evidence that in reactions that lead to resonance delocalized products charge delocalization lags behind transfer or bond formation.³¹ This is symbolized in **16** (and **9**) by placing the partial negative charge in the transition



state on the *metal* rather than the CO ligands. Inasmuch as the negative charge is closer to X at the transition state than in the adduct, the transition state derives a disproportionately strong stabilization (relative to the degree of bond formation) from the inductive effect of X compared to the adduct. This enhances k_o and contributes to the difference in $\log k_o$ between $\mathbf{5-M}$ and $\mathbf{1-M}$ because of the stronger inductive effect of oxygen.

3. π -Donor Effect. The influence of the π -donor effect of X on the intrinsic rate constants is difficult to predict because of two opposing interaction mechanisms. One is the loss of resonance stabilization of the reactant (**10** or **11**) that that is expected to run ahead of bond formation and, according to the

PNS,⁴² lower $\log k_o$. The π -donor ability of oxygen being stronger than that of sulfur, there will be a stronger reduction in $\log k_o$ for $\mathbf{1-M}$ than for $\mathbf{5-M}$ and hence a decrease in the difference in $\log k_o$ for the two systems. The other interaction mechanism is the preorganization of the structure of the $(\text{CO})_5\text{M}$ moiety in $\mathbf{5-M}$ or $\mathbf{1-M}$ toward its electronic configuration in the adducts that results from the π -donor effect. As a consequence, the lag in the charge delocalization into the CO ligands at the transition state is reduced, and the intrinsic rate constant is not as strongly depressed by the PNS effect associated with this lag. Since the reaction of $\mathbf{1-M}$ will benefit more from this effect, this will enhance the difference between $\log k_o(\mathbf{5-M})$ and $\log k_o(\mathbf{1-M})$.

On the basis of our results it cannot be decided which of these interaction mechanisms is the dominant one; there are precedents for either situation in similar systems as discussed elsewhere.³⁶ The fact that $\log k_o$ for $\mathbf{1-M}$ exceeds $\log k_o$ for $\mathbf{5-M}$ by such a large amount (more than two log units) suggests that the steric and inductive/field effects may not be sufficient to account for the entire difference in the $\log k_o$ values, i.e., there may have to be a contribution by the π -donor effect. This would imply that the preorganization factor is dominant.⁴⁴ Note, though, that this is not a firm conclusion; in other reactions the k_o -reducing resonance loss has been found to be dominant.⁴⁵

C. k_{-1}^{H} . H^+ -catalyzed MeO^- expulsion from $\mathbf{4-M}^-$ ($\text{R} = n\text{-Pr}$), k_2^{H} , is much faster than H^+ -catalyzed RS^- expulsion, k_{-1}^{H} , and hence no k_{-1}^{H} value is available for this latter process that could provide a comparison with k_{-1}^{H} for acid-catalyzed MeS^- loss from the MeS^- adducts, $\mathbf{6-M}^-$. But even without a precise value for k_{-1}^{H} for $\mathbf{4-M}^-$, it is clear that thiolate ion departure from Fischer carbene adducts is much less sensitive to acid catalysis than alkoxide departure. It is this low sensitivity to acid catalysis which makes the k_{-1}^{H} values relatively low and has allowed the determination of $\text{p}K_a^{\text{MH}}$ values based on eq 6.

Effect of Changing the Metal. As seen in Table 1, the rate and equilibrium constants for thiolate addition to the tungsten carbene complexes ($\mathbf{5-W}$) are larger than for addition to the chromium analogues ($\mathbf{5-Cr}$). The $k_1^{\text{RS}}(\mathbf{5-W})/k_1^{\text{RS}}(\mathbf{5-Cr})$ ratios vary between 3 and 7, with an average of about 4.5, while the $K_1^{\text{RS}}(\mathbf{5-W})/K_1^{\text{RS}}(\mathbf{5-Cr})$ ratios vary from about 4.3 to 12, with an average of about 8, except for a low ratio of 2.55 for the reaction with MeS^- . The low ratio for this latter reaction may be an artifact of the “abnormal” $k_{-1}(\mathbf{5-W})/k_{-1}(\mathbf{5-Cr})$ ratio (>1)⁴⁶ which may just reflect an unusually large experimental error, as mentioned at the beginning of the Discussion.

It is noteworthy that the effect of changing the metal on the electrophilic reactivity of $\mathbf{5-W}$ vs $\mathbf{5-Cr}$ is much larger than for the corresponding methoxy carbenes ($\mathbf{1-M}$). For example, the average $k_1^{\text{RS}}(\mathbf{1-W})/k_1^{\text{RS}}(\mathbf{1-Cr})$ ratio for thiolate ion addition to $\mathbf{1-M}$ is about 1.3, the average $K_1^{\text{RS}}(\mathbf{1-W})/K_1^{\text{RS}}(\mathbf{1-Cr})$ ratio is less than 3.¹ The larger influence of the metal on the electrophilic reactivity of the MeS compared to the MeO carbene complexes parallels the larger effect of the metal on the $\text{p}K_a$ of $\mathbf{13-M}$ compared to that of $\mathbf{14-M}$: $\text{p}K_a = 8.37$ ³⁶ for $\mathbf{13-W}$ vs $\text{p}K_a =$

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

(41) (a) Jencks, D. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 7948. (b) Jencks, W. P. *Chem. Rev.* **1985**, *85*, 511.

(42) The PNS states that if the development of a product-stabilizing factor lags behind bond changes or charge transfer at the transition state, k_o is reduced. The same is true if the loss of a reactant-stabilizing factor runs ahead of bond changes or charge transfer. For product-stabilizing factors that develop early or reactant-stabilizing factors that are lost late, k_o is enhanced.³¹

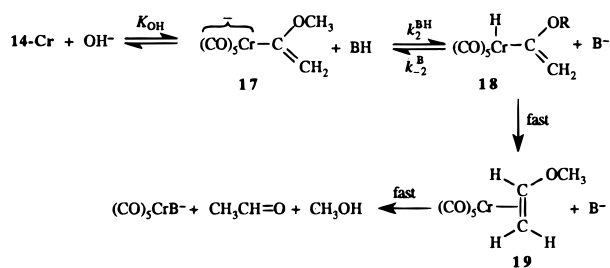
(43) Bernasconi, C. F.; Ketner, R. J.; Chen, X.; Rappoport, Z. *Can. J. Chem.* **1999**, *77*, 584.

(44) For examples where the preorganization effect is dominant, see: (a) Bernasconi, C. F.; Renfrow, R. A.; Tia, P. R. *J. Am. Chem. Soc.* **1986**, *108*, 4541. (b) Bernasconi, C. F.; Zitomer, J. L.; Schuck, D. F. *J. Org. Chem.* **1992**, *57*, 1132.

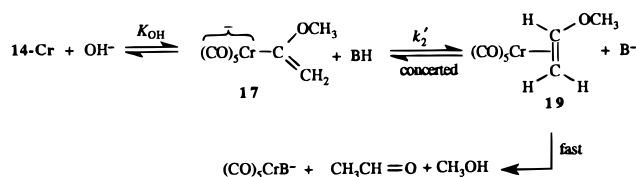
(45) For examples where the k_o -reducing resonance effect is dominant, see: (a) Bernasconi, C. F.; Panda, M. *J. Org. Chem.* **1987**, *52*, 3042. (b) Bernasconi, C. F.; Killion, R. B., Jr. *J. Org. Chem.* **1989**, *54*, 2878. (c) Bernasconi, C. F.; Flores, F. X.; Claus, J. J.; Dvořák, D. *J. Org. Chem.* **1994**, *59*, 4917.

(46) K_1^{RS} was calculated as k_1^{RS}/k_{-1} . Note that the $k_{-1}^{\text{H}}(\mathbf{5-W})/k_{-1}^{\text{H}}(\mathbf{5-Cr}) = 0.76$ is “normal,” i.e., <1 .

Scheme 2



Scheme 3



9.05³⁶ for **13-Cr**,³⁶ and $pK_a = 12.36$ ³⁸ for **14-W** vs $pK_a = 12.50$ for **14-Cr**.³⁷ As discussed elsewhere,³⁶ a possible reason for the larger sensitivity to the metal for the MeS complexes is the weaker π -donor effect of the MeS compared to that of the MeO group.

Acidity of the Metal Proton. The pK_a^{MH} values of **6-MH** (R = Me) are of the order of 0.5 (Table 1), those of **8-MH-Z** (Z = H) around 0.4 for **8-CrH-H** and 0.7 for **8-WH-H** (Table 2).

6-MH and **8-MH-Z** bear some resemblance to hydrido transition metal complexes such as $HMCp(CO)_3$ whose pK_a^{MH} values have been determined in water, methanol, and acetonitrile: in water $pK_a^{MH} = 5.4$ (Cr) and 8.0 (W), respectively; in methanol $pK_a^{MH} = 6.4$ (Cr) and 9.0 (W), respectively.¹⁴ In 50% MeCN–50% water, the pK_a^{MH} values are expected to be somewhat higher than in pure water, perhaps similar to the values in methanol.

The fact that the pK_a^{MH} values for **6-MH** and **8-MH-Z** are several units lower than for $HMCp(CO)_3$ is consistent with the effect of replacing the electron-donating Cp group with two electron-withdrawing CO ligands and the $C(SR)_2C_6H_4Z$ moiety. What is more difficult to understand is why there is such a small metal dependence of the pK_a^{MH} values of **6-MH** and **8-MH-Z** but a strong dependence for $HMCp(CO)_3$. Attempts to explain this contrasting behavior will have to await further study.

The pK_a^{MH} values of **6-MH** and **8-MH-Z** may be used to resolve an ambiguity regarding the mechanism of OH^- -catalyzed hydrolysis of **14-Cr** and similar carbene complexes with acidic protons on the α -carbon.⁴⁷ The two proposed mechanisms are shown in Schemes 2 and 3. The difference between Schemes 2 and 3 is that in Scheme 2 conversion of **17** to **19** occurs stepwise with rate-limiting metal protonation of **17** followed by rapid reductive elimination of **18**, while in Scheme 3 conversion of **17** to **19** is a one-step reaction in which protonation of the carbene carbon and cleavage of the C–Cr bond is concerted.

If we assume that the pK_a^{MH} of **18** is similar to that of **6-MH**, i.e., ~ 0.5 , one can estimate an upper limit for the k_2^{BH} step in Scheme 2 based on eq 12

$$k_2^{BH} = k_{-2}^B K_a^{BH} / K_a^{MH} \quad (12)$$

and assuming that the k_{-2}^B step is diffusion-controlled ($k_{-2}^B \approx$

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

Table 7. Summary of 1H NMR chemical shifts in $CDCl_3$

carbene complex	OH	SCH ₂	OCH ₂	phenyl	Z
7-Cr-H	1.54	2.97(t)	3.70(t)	6.69 and 7.44	
7-W-H	1.71	2.97(t)	3.74(t)	6.85 and 6.90	
7-W-F	1.61	2.86(t)	3.77(t)	6.78 and 7.14	
7-W-Cl	1.58	2.84(t)	3.77(t)	6.72 and 7.43	
7-W-CF₃	1.64	2.79(t)	3.79(t)	6.86 and 7.71	
7-W-OMe	1.70	2.96(t)	3.75(t)	6.85 and 6.89	3.79 ^a
7-W-Me	1.64	2.88(t)	3.75(t)	6.69 and 7.25	2.37 ^b
7-W-NMe₂	1.74	3.27(t)	3.86(t)	6.70 and 7.18	3.11 ^c
5-Cr		2.29(s) ^d		6.64, 7.25, 7.46	
5-W		2.14(s) ^d		6.72, 7.23, 7.74	

^a CH₃O. ^b CH₃. ^c (CH₃)₂N. ^d CH₃S.

$10^{10} M^{-1} s^{-1}$).⁴⁸ For example, for BH = AcOH ($pK_a^{BH} = 5.93$) one obtains $k_2^{AcOH} \approx 3.7 \times 10^4 M^{-1} s^{-1}$, while for BH = H₂O ($pK_w = 15.19$)³⁷ $k_2^{H_2O} \approx 2.0 \times 10^{-5} s^{-1}$.⁴⁹ On the basis of the work of Norton et al.^{14,50} on metal hydrido complexes such as $HMCp(CO)_3$ it is unlikely that the k_{-2}^B step would be even close to diffusion-controlled; hence, we conclude that $k_2^{AcOH} \ll 3.7 \times 10^4 M^{-1} s^{-1}$ and $k_2^{H_2O} \ll 2.0 \times 10^{-5} s^{-1}$. This is inconsistent with the experimental rate constant of $3.4 \times 10^4 M^{-1} s^{-1}$ for AcOH-catalyzed and $0.16 s^{-1}$ for water-catalyzed conversion of **17** to **19**,⁴⁷ and hence, Scheme 2 cannot be the correct mechanism. This conclusion contradicts the widely held view⁵¹ that the pyridine-catalyzed decomposition of alkoxy carbene complexes such as **14-Cr** into enol ethers proceeds by the mechanism of Scheme 2 although the difference in the experimental conditions may possibly allow for differences in the mechanism.

Conclusions

(1) The reactions of eqs 2 and 3 can be described by Scheme 1. In basic solution they follow the pathway $k_1^{RS} - k_{-1}$ ($S \rightleftharpoons T^-$), in acidic solution the pathway $k_1^{RSH} - k_{-1}^H$, which includes the fast proton-transfer equilibrium, i.e., $S \rightleftharpoons T^- \rightleftharpoons T^0$. The transition state for the $k_1^{RSH} - k_{-1}^H$ pathway includes a water molecule (**9**).

(2) The thiolate ion adducts of **5-M** and **7-W-Z** are the first examples of tetrahedral intermediates derived from Fischer carbene complexes for which protonation on the metal has been observed and pK_a^{MH} values could be determined. These pK_a^{MH} values provide compelling evidence for an earlier mechanistic proposal relating to the hydrolysis of methyl carbene complexes such as **14-M**.

(3) The β_{nuc} values for thiolate ion attachment to **5-M** are negative. This implies that desolvation of the nucleophile is an important part of the activation process and that C–S bond formation has made very little progress at the transition state. This is similar to earlier observations for thiolate ion attachment to methoxy carbene complexes (**1-M**) and appears to be characteristic for the reactions of thiolate ions with Fischer carbene complexes.

(4) The substituent dependence of k_1^{RS} and K_1^{RS} as expressed by Hammett ρ values is relatively small, considerably smaller than for MeO⁻ addition to **1-M**. Possible reasons include the smaller π -donor effect of the RS group in **7-M-Z** and the stabilization of the adducts (**8-M-Z**) by the polarizability

(48) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1.

(49) In the case that BH = H₂O eq 12 becomes $k_2^{H_2O} = k_{-2}^B K_w / K_a^{MH}$.

(50) Eididin, R. T.; Sullivan, J. M.; Norton, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 3945.

(51) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*, 2nd ed.; University Science Books: Sausalito, California, 1999; p 148.

Table 8. Summary of ^{13}C NMR chemical shifts in CDCl_3

carbene complex	CO	SCH ₂	OCH ₂	phenyl	=C	Z
7-Cr-H	215.5 (cis) 228.8 (trans)	46.9	60.0	117, 127, 129, 132.5	363.4	
7-W-H	198.4 (cis) 209.7 (trans)	49.2	59.2	128.7, 129.3, 134.7, 158.9	332	
7-W-F	197.0 (cis) 208.7 (trans)	47.3	59.5	115.6, 119.7, 130.7, 154.3	327.5	
7-W-Cl	196.8 (cis) 208.5 (trans)	47.3	59.4	118.9, 128.6, 133.2, 156.5	325.8	
7-W-CF₃	196.6 (cis) 208.6 (trans)	47.3	59.2	117.4, 125.5, 128.2, 161.0	324	
7-W-OMe	197.3 (cis) 208.5 (trans)	55.3	59.7	113.5, 120.9, 128.7, 159.7	328.6	47.7 ^a
7-W-Me	197.2 (cis) 209.0 (trans)	47.2	59.7	117.9, 128.6, 137.7, 155.6	330.1	21.2 ^b
7-W-NMe₂	197.8 (cis) 207.8 (trans)	48.8	60.2	110.4, 128.2, 146.4, 152.3	318.2	40.3 ^c
5-Cr	215.0 (cis) 228.1 (trans)	27.9 ^d	—	116.5, 126.6, 128.1, 156.6	362.2	
5-W	197.2 (cis) 208.8 (trans)	28.7 ^d	—	117.2, 127.2, 128.4, 157.9	329.2	

^a CH₃O. ^b CH₃. ^c (CH₃)₂N. ^d CH₃S.

effect of the sulfur groups. The ρ values for k_1^{RSH} and k_{-1}^{H} are both negative, indicating an imbalanced transition state in which deprotonation of the thiol nucleophile has made less progress than C–S bond formation.

(5) The equilibrium constants for thiolate ion addition to **5-M** are considerably higher than for addition to **1-M**; this can be attributed to the stabilization of **1-M** by the strong π -donor effect of the MeO group which more than offsets the weaker inductive and larger steric effect of the MeS group. In contrast, the rate constants for thiolate ion addition to **5-M** are lower than for addition to **1-M**, indicating that the intrinsic rate constants for the reactions of **5-M** are substantially smaller than for the reaction of **1-M**. This can be attributed to the combined result of several transition state imbalances. One is the development of the steric effect that runs ahead of C–S bond formation, another the lag in the charge delocalization into the (CO)₅M moiety behind C–S bond formation which leads to enhanced transition state stabilization by the inductive effect of the MeO group in **1-M**; a potential third contribution is an imbalance involving the π -donor effects of the MeO and MeS groups.

(6) The tungsten carbene complexes are somewhat more reactive than the chromium analogues, just as **13-W** is more acidic than **13-Cr**.

Experimental Section

Materials. A. Synthesis of Carbene Complexes. 5-Cr, 5-W, 7-Cr-H and 7-W-H were synthesized following a procedure by Lam et al.⁵² developed for (CO)₅M=C(SPh)CH₃. The method is illustrated for the synthesis of **7-Cr-H**. In a 250 mL three-necked round-bottom flask 80 mL of benzene was saturated with Ar. **1-Cr** (2.0 g, 8 mmol), available from previous studies,¹ was added followed by 1.05 g (15.0 mmol) of NaSCH₂CH₂OH (Aldrich, AR) prepared by dissolving HOCH₂CH₂SH in 20 mL of methanol saturated with Ar and adding 0.6 g of NaOH pellets. The resulting solution was stirred for 10 min, and 35 mL of a methanolic solution of HCl, prepared by mixing 6 mL of concentrated HCl in 100 mL of methanol, was added dropwise over a period of 25 min. The solution turned deep red, and NaCl precipitated out. Stirring was continued for 2 h.

The following operations were carried out in open air. The volume of the reaction mixture was reduced to a minimum by means of a rotoevaporator, 80 mL of H₂O followed by 100 mL of *n*-hexane was added, and the aqueous layer was discarded immediately by means of

a separating funnel. The hexane layer was dried over anhydrous Na₂SO₄ for a few minutes. Na₂SO₄ was removed by filtration, and the volume of the filtrate was reduced by means of a rotoevaporator to leave a dark red/brown oily residue. The residue was purified on a silica gel (100–200 mesh) column (25 × 3 cm) with *n*-hexane as the eluent. After evaporating most of the solvent in a rotoevaporator, the remaining solvent was removed under high vacuum at –78 °C (dry ice–acetone). ¹H NMR and ¹³C NMR (500 MHz, CDCl₃) data are summarized in Tables 7 and 8.

The synthesis of **7-W-Z** (Z = CF₃, Cl, F, Me, MeO, and Me₂N) was the same as for **7-W-H**; the precursors, (CO)₅W=C(OMe)C₆H₄Z, were prepared as described by Fischer et al.⁵³ The **7-W-Z** residue obtained after drying in high vacuum at room temperature was dissolved in a minimum volume of CHCl₃ and passed through a silica gel column. Elution involved CHCl₃ followed by 50% CHCl₃–50% ethyl acetate (v/v). The solvent was removed under high vacuum at room temperature which yielded an oily residue. The spectral data are included in Table 7.

B. Other Reagents. *N*-methylmorpholine and triethylamine (Aldrich) were of reagent grade and further purified by refluxing over Na/CaH₂ and freshly distilled prior to use. Reagent grade dichloroacetic, methoxyacetic, acetic acid, and KOH were used to prepare the buffers of the desired pH. Acetonitrile (Fischer Scientific), HClO₄, and NaClO₄ were used as received. KOH and HCl solutions were prepared using “Dilut It” from Baker Analytical. Water was taken from a Milli-Q purification system.

Kinetic Runs and Spectra. Stock solutions of the carbene complexes were relatively stable in pure acetonitrile and were used to make appropriate reaction solutions prior to use. Typical concentrations of **5-M** and **7-M-Z** for kinetic runs were (5.0–9.0) × 10^{–5} M. UV–vis spectra were taken in a Hewlett-Packard 8452A diode array spectrophotometer. Kinetic measurements were carried out in an Applied Photophysics DX.17MV stopped-flow apparatus or, for some of the slower reactions, in the Hewlett-Packard instrument.

The pH was measured in mock mixing experiments with an Orion 611 pH meter equipped with a glass electrode and a Sure Flow (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 and Tidwell.⁵⁴

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