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Physical Organic Chemistry of Transition Metal Carbene Complexes. 18.[1] Kinetics of Reversible Cyclization of the Fischer Carbene Complexes $(CO)_5M{=}C(SCH_2CH_2OH)Ph$ and $(CO)_5M{=}C(OCH_2CH_2OH)Ph$ (M = Cr, W) in Aqueous Acetonitrile

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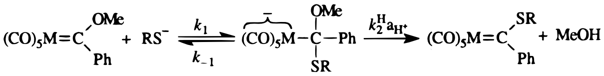
Abstract: Rate and equilibrium constants for the conversion of $(CO)_5Cr{=}C(OCH_2CH_2OH)Ph$ (**8-CrOOH**), $(CO)_5W{=}C(OCH_2CH_2OH)Ph$ (**8-WOOH**), $(CO)_5Cr{=}C(SCH_2CH_2OH)Ph$ (**8-CrSOH**), and $(CO)_5W{=}C(SCH_2CH_2OH)Ph$ (**8-WSOH**) into the corresponding cyclic adducts $(CO)_5\bar{M}{-}\overline{C(XCH_2CH_2O})Ph$ (**9-CrOO⁻** for M = Cr, X = O; **9-WOO⁻** for M = W, X = O; **9-CrSO⁻** for M = Cr, X = S; **9-WSO⁻** for M = W, X = S) are reported. Under basic conditions the reaction occurs via the respective oxyanions, $(CO)_5Cr{=}C(OCH_2CH_2O^-)Ph$ (**8-CrOO⁻**), etc.; under acidic conditions the reaction may either be concerted with water acting as a general base catalyst or stepwise via a zwitterionic intermediate. The absence of buffer catalysis suggests but does not prove the operation of the stepwise mechanism. The equilibrium constants for cyclization of **8-CrSO⁻** and **8-WSO⁻** are about 1 order of magnitude higher than for **8-CrOO⁻** and **8-WOO⁻**, respectively. For the *rate* constants the situation is reversed, with **8-CrOO⁻** and **8-WOO⁻** being substantially more reactive than **8-CrSO⁻** and **8-WSO⁻**, respectively. These results reflect transition state imbalances with respect to various factors such as steric effects, π-donor effects, resonance effects in the cyclic adduct, and possibly anomeric effects. Kinetic and equilibrium effective molarities of the cyclization reactions were also deduced and are discussed in the context of intramolecular reactions in general.

Introduction

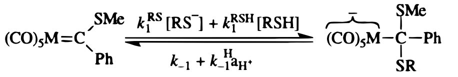
We have recently reported two kinetic studies of reactions of various thiolate ions with a number of Fischer carbene complexes. In the first, carbene complexes of the type **1-M**[2] were shown to undergo a stepwise process according to eq 1



$$(CO)_5M{=}C(OMe)Ph + RS^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (CO)_5\bar{M}{-}C(OMe)(SR){-}Ph \xrightarrow{k_2^{H}a_{H^+}} (CO)_5M{=}C(SR)Ph + MeOH \quad (1)$$

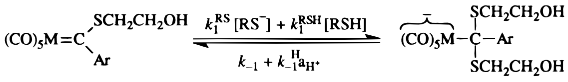
1-Cr (M = Cr) **2-Cr⁻** **3-Cr**
1-W (M = W) **2-W⁻** **3-W**

where the intermediate accumulates to detectable levels.[3] This allowed a dissection of the rate constants of each individual step. In the second study the rate constants of the reactions shown in eqs 2 ($RS^- = MeS^-$, n-PrS^-, $HOCH_2CH_2S^-$, $MeO_2CCH_2CH_2S^-$, and $MeO_2CCH_2S^-$) and 3 ($RS^- = HOCH_2CH_2S^-$) were determined.[1] These investigations have provided numerous insights into the structure−reactivity relationships of these reactions, including the effect nucleophile desolvation, steric crowding, π-donor effects (O vs S), transition state imbalances, polarizability effects of sulfur, and others.



$$(CO)_5M{=}C(SMe)Ph \underset{k_{-1}+k_{-1}^{H}a_{H^+}}{\overset{k_1^{RS}[RS^-]+k_1^{RSH}[RSH]}{\rightleftharpoons}} (CO)_5\bar{M}{-}C(SMe)(SR){-}Ph \quad (2)$$

4-Cr (M = Cr) **5-Cr⁻**
4-W (M = W) **5-W⁻**



$$(CO)_5M{=}C(SCH_2CH_2OH)Ar \underset{k_{-1}+k_{-1}^{H}a_{H^+}}{\overset{k_1^{RS}[RS^-]+k_1^{RSH}[RSH]}{\rightleftharpoons}} (CO)_5\bar{M}{-}C(SCH_2CH_2OH)_2{-}Ar \quad (3)$$

6-Cr (M = Cr) **7-Cr⁻**
6-W (M = W) **7-W⁻**

In this paper we report a kinetic study of the reversible formation of cyclic adducts by the intramolecular nucleophilic reactions shown in Scheme 1. The objective is to determine the various rate constants in the scheme in order to gain further insights into the structure−reactivity relationships of nucleophilic reactions at the carbene carbon of Fischer carbene complexes.

Results

Synthesis. The various **8-MOOH**[2] and **8-MSOH**[2] complexes have not been described before. They were synthesized by the reaction of the corresponding **1-M** with $NaOCH_2CH_2OH$ for **8-MOOH** and $NaSCH_2CH_2OH$ for **8-MSOH**.

General Features of the Cyclization Reactions. When **8-MOOH** or **8-MSOH** are added to a dilute KOH solution, there is a rapid conversion to the respective cyclic adducts **9-MOO⁻** or **9-MSO⁻** which manifests itself by the loss of the

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(1) Part 17: Bernasconi, C. F.; Ali, M. *J. Am. Chem. Soc.* **1999**, *121*, 11384.

(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.

(3) Bernasconi, C. F.; Kittredge, K. W.; Flores, F. X. *J. Am. Chem. Soc.* **1999**, *121*, 6630.

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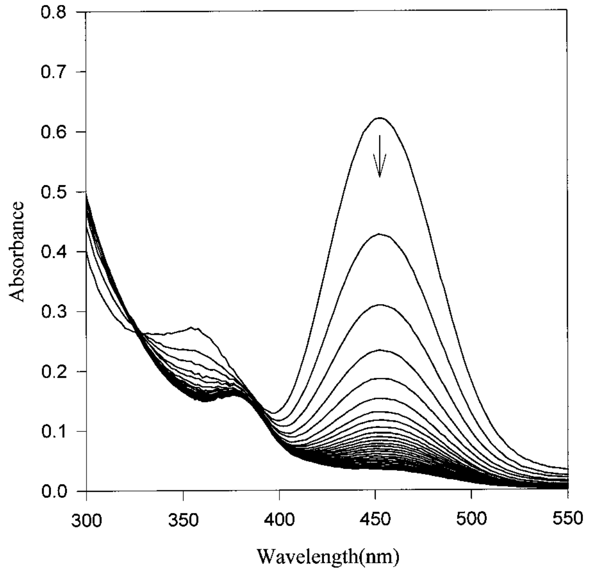
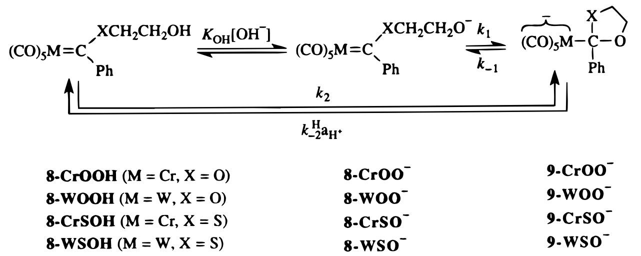


Figure 1. Conversion of **8-WSOH** ($\sim 10^{-5}$ M) to **9-WSO**$^-$ in the presence of 5.0×10^{-4} M KOH. First spectrum was taken in the absence of KOH; subsequent spectra were taken at 4 s intervals.

Scheme 1



carbene complex absorption and the appearance of a new spectrum in the UV region. This is shown in Figure 1 for the example of **9-WSO**$^-$. The spectrum of the new species, **9-WSO**$^-$, is very similar to that of the **2-W**$^-$ (R = n-Pr) generated in the reaction of **1-W** with n-PrS$^-$.[3]

Addition of HCl to the solutions shortly after the adducts have been formed leads to >95% recovery of the starting materials; if acidification is significantly delayed, there is less recovery due to gradual decomposition of the adducts in basic solution. Depending on the specific case, this decomposition is characterized by half-lives from several minutes to more than 1 h, with the tungsten derivatives being more stable. The nature of the decomposition reaction was not investigated.

For the longest-lived cyclic adducts (**9-WOO**$^-$ and **9-WSO**$^-$) it was also possible to obtain ^{1}H and ^{13}C NMR spectra which are consistent with the assigned structure (see Experimental Section).

Rate and Equilibrium Determinations. Spectrophotometric (stopped-flow and conventional) measurements were performed over an extended pH range by either measuring rates of cyclization in KOH and triethylamine buffer solutions or rates of ring opening in *N*-methylmorpholine and acetate buffers and, in some cases, HCl solutions. No significant buffer catalysis by any of the buffers could be detected at total buffer concentrations of up to 0.05 or 0.1 M. Figure 2 shows the pH–rate profiles for the reactions of **8-CrOOH**, **8-WOOH**, **8-CrSOH**, and **8-WSOH**.

All pH–rate profiles are consistent with Scheme 1 for which the observed pseudo-first-order rate constant is given by eq 4.

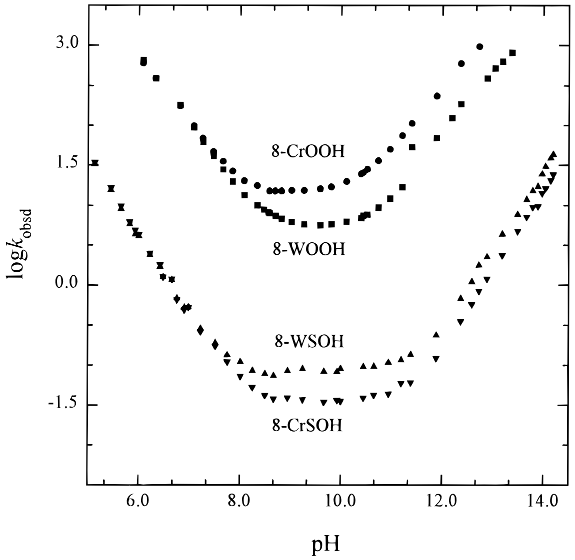


Figure 2. Dependence of log k_{obsd} on pH for the reversible cyclization of **8-MXOH** in 50% MeCN–H$_2$O at $I = 0.10$ M KCl and 25 °C.

For the reactions of **8-CrOOH**, **8-CrSOH**, and **8-WSOH**, $K_{OH}[OH^-] \ll 1$ under all conditions which simplifies eq 4 to eq 5.

$$k_{obsd} = \frac{K_{OH}k_1[OH^-] + k_2}{1 + K_{OH}[OH^-]} + k_{-1} + k^H_{-2}\, a_{H^+} \tag{4}$$

$$k_{obsd} = K_{OH}k_1[OH^-] + k_2 + k_{-1} + k^H_{-2}\, a_{H^+} \tag{5}$$

For the reaction of **8-WOOH** the onset of a leveling off at pH > 13 indicates that $K_{OH}[OH^-] \gtrsim 1$ at high pH; a similar leveling off would be expected for the reaction of **8-CrOOH**, but the rates at pH > 13 were too fast to be measured by the stopped-flow method.

The kinetic data allowed straightforward determination of $K_{OH}k_1$ and k^H_{-2} from the pH-dependent legs of the pH–rate profiles. For the reaction of **8-WOOH** an approximate K_{OH} value could also be obtained by curve fitting the data to eq 6 at high pH.[4]

$$k_{obsd} = \frac{K_{OH}k_1[OH^-]}{1 + K_{OH}[OH^-]} \tag{6}$$

The k_{-1} and k_2 values were evaluated by two different methods. The first one was based on the plateau values of the pH–rate profiles which are given by log($k_{-1} + k_2$). From the changes in absorption observed during the kinetic experiments it was deduced that the equilibrium position favors the cyclic adducts over the reactants in the pH range that defines the plateaus. This implies $k_2 > (\gg)\ k_{-1}$, and hence, the plateau values can be approximated by log k_2. In conjunction with k^H_{-2} one obtains $K_2 = k_2/k^H_{-2}$ for the pseudo acidity constants defined according to eq 7. This, in turn, allows calculation of $K_{OH}K_1 = K_2/K_w$ with K_w being the ionic product;[5] hence $k_{-1} = K_{OH}k_1/K_{OH}K_1$ is obtained.

$$\textbf{8-MXOH} \overset{K_2}{\rightleftharpoons} \textbf{9-MXO}^- + H^+ \tag{7}$$

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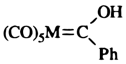
(4) At high pH, $k_2 + k_{-1} + k^H_{-2}a_{H^+} \ll K_{OH}k_1[OH^-]/(1 + K_{OH}[OH^-])$.

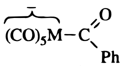
(5) pK_w = 15.19 in 50% MeCN–50% water at 25 °C, μ = 0.1 (KCl).[6]

The second method relied on a direct determination of K_2 by standard spectrophotometric procedure (see Experimental Section) from which k_2 was calculated as $K_2k_{-2}^{H}$ and k_{-1} obtained as before but using the spectrophotometric K_2 values to determine $K_{OH}K_1$. The agreement between the two methods was very good in most cases, except for **8-CrOOH** where the two values differ by 0.24 log units. This somewhat larger discrepancy may be attributed to difficulties in getting reproducible results by the spectrophotometric method, due to relatively rapid decomposition of the adduct (**9-CrOO$^-$**). For this case we shall therefore adopt the kinetic K_2 value in our further discussions. For the other three compounds the spectrophotometric K_2 values are considered more accurate than the kinetic ones because of some uncertainty in the plateau values of the pH rate profiles; hence they, as well as the k_2 and k_{-1} values derived therefrom, will be used in further discussions.

Discussion

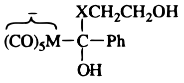
Mechanism. All our observations are consistent with Scheme 1 and inconsistent with alternative interpretations. Specifically, hydrolysis of **8-MXOH**, to form **10-M** or its conjugate base

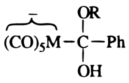

10-M

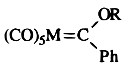

10-M$^-$

10-M$^-$, can be excluded based on several lines of reasoning. (1) The NMR spectra of the products match with the structure of **9-MXO$^-$** and not with **10-M** or **10-M$^-$**. (2) The fact that the original carbene complexes **8-MXOH** can be regenerated upon addition of acid to **9-MXO$^-$** is easily understood in terms of Scheme 1 but is not explainable if **10-M** or **10-M$^-$** are the observed products. (3) The measured rate constants for product formation ($K_{OH}k_1$ and k_2) are several orders of magnitude higher than what can be expected for the hydrolysis reactions.[7]

The hypothesis that the observed species are OH$^-$ adducts of **8-MXOH**, i.e., **11-M$^-$**, can also be discarded because

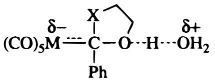

11-M$^-$


12-M$^-$


13-M

hydroxide adducts such as **12-M$^-$** that form as intermediates in the hydrolysis of Fischer carbene complexes of the general structure **13-M** do not accumulate to detectable levels because leaving group expulsion is much faster than nucleophilic addition.[8,9] And again, the NMR spectra and high rate constants are inconsistent with this hypothesis.

With respect to the $k_2 - k_{-2}^{H}$ pathway, there exist two mechanistic possibilities. The first is that the reaction is a concerted one-step process where water acts as a general base catalyst in the k_2 step and H_3O^+ as a general acid catalyst in the k_{-2}^{H} step, i.e., the transition state is as shown in **14**.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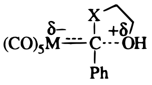
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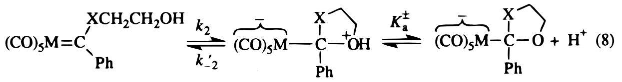
This is the mechanism that has been suggested for the addition of water to **1-M**[8] and the acid-catalyzed loss of MeO$^-$ from **2-M$^-$**.[3] Support for this mechanism came from the observation of general base/general acid catalysis by buffers, although in the reaction of **2-M$^-$** buffer catalysis was very weak and, under most conditions, barely detectable.

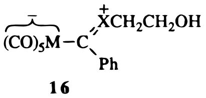
The second mechanistic possibility is that the reaction is stepwise, as indicated in eq 8, with transition state **15** and $k_{-2}^{H} = k'_{-2}/K_a^{\pm}$. The fact that no buffer catalysis was detectable is more easily rationalized with the stepwise process of eq 8, although this could be a case where buffer catalysis is too weak to lead to significant rate accelerations at buffer concentrations below 0.1 M. A potential problem with the mechanism of eq 8 is that the k'_{-2} step may be too fast for **9-MXOH$^{\pm}$** to exist as a real intermediate. For example, for **8-CrOOH** and **8-MOOH** $k_{-2}^{H} = 1.1 \times 10^9$ M^{-1} s^{-1} (Table 1) and hence $k'_{-2} = 1.1 \times 10^9 K_a^{\pm}$. It follows that if $K_a^{\pm} \geq 10^4$ one obtains $k'_{-2} \geq 10^{13}$ s^{-1} which corresponds to the rate of a molecular vibration.[10] This would imply that **9-MXOH$^{\pm}$** cannot exist as an intermediate and that the concerted mechanism via **14** would be enforced.[10]



8-MXOH **9-MXOH$^{\pm}$** **9-MXO$^-$**

Rate and Equilibrium Constants. The rate and equilibrium constants obtained in this study are summarized in Table 1. The good agreement between the spectrophotometrically and kinetically determined equilibrium constants (K_2) indicates good internal consistency of our results.

A. K_{OH}. In all but one case (**8-WOOH**), K_{OH} could not be measured directly and hence k_1 and K_1 are not known accurately except for the reaction of **8-WOOH**. The change of the metal from W to Cr is not expected to have a significant effect on K_{OH}, and hence, we assume K_{OH} for **8-CrOOH** to be the same as for **8-WOOH**. For **8-CrSOH** and **8-WSOH**, K_{OH} is expected to be lower than for **8-WOOH** because of the weaker electron-withdrawing inductive effect[11] of sulfur. This difference in the inductive effect of sulfur and oxygen in **8-MSOH** and **8-MOOH** is likely to be accentuated because of the stronger π-donor effect of oxygen (**16**) which leads to a larger partial positive charge on X when X = O.[13] On the basis of this reasoning, we shall assume that K_{OH} for **8-MSOH** is approximately 10-fold smaller than for **8-MOOH**. The k_1 and K_1 values reported in Table 2 were calculated using these estimates for K_{OH}.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B. Oxa vs Thia Complexes. The equilibrium constants for the thia complexes are higher than for the corresponding oxa complexes: $K_1(S)/K_1(O) \approx 5.0$ for the chromium derivatives

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

(7) For example, $k_{OH} = 26.7$ M^{-1} s^{-1} and $k_{H_2O} = 2.9 \times 10^{-3}$ s^{-1} for the reaction of **1-Cr** with OH$^-$ and H$_2$O, respectively, in 50% MeCN–50% water at 25 °C.[8] This compares with $K_{OH}k_1 = 5.55 \times 10^5$ M^{-1} s^{-1} and $k_2 = 11.5$ s^{-1} for **8-CrOOH** (Table 1).

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

(9) With a thiolate ion leaving group, leaving group expulsion can be expected to be even faster.[3]

(10) (a) Jencks, W. P. *Acc. Chem. Res.* **1976**, *9*, 425. (b) Jencks, W. P. *Acc. Chem. Res.* **1980**, *13*, 161. (c) Jencks, W. P. *Chem. Soc. Res.* **1981**, *10*, 345.

(11) Field effects are included in this term; $\sigma_F = 0.30$ and 0.20 for MeO and MeS, respectively.[12]

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

(13) The effect of the enhanced positive charge when X = O can be seen from the fact that the pK_a difference of 3 units between **8-WOOH** (13.41; see Table 1) and water (16.63)[14] in 50% MeCN–50% water is much greater than the pK_a difference of 0.94 units between 2-methoxyethanol (14.8)[14] and water (15.74) in water.

Table 1. Rate and Equilibrium Constants for the Reactions Defined in Scheme 1 in 50% MeCN−50% Water (v/v) at 25 °C, $\mu = 0.1$ (KCl)

carbene complex	$K_{OH}k_1$ ($M^{-1}\,s^{-1}$)	k^{H}_{-2}($M^{-1}\,s^{-1}$)	k_2(kin) (s^{-1})	k_2(spec) (s^{-1})	K_2(kin) (M)	K_2(spec) (M)	$K_{OH}K_1{}^{a}$ (M^{-1})	$K_{OH}{}^{b}$ (M^{-1})
$(CO)_5Cr{=}C(OCH_2CH_2OH)Ph$ (**8-CrOOH**)	$(5.55 \pm 0.04) \times 10^{5}$	$(1.10 \pm 0.01) \times 10^{9}$	15.0 ± 0.5	21.1 ± 1.0	$(1.36 \pm 0.05) \times 10^{-8}$	$(1.92 \pm 0.07) \times 10^{-8}$	1.63×10^{7}	ca. 77
$(CO)_5W{=}C(OCH_2CH_2OH)Ph$ (**8-WOOH**)	$(1.39 \pm 0.05) \times 10^{5}$	$(1.12 \pm 0.02) \times 10^{9}$	5.72 ± 0.20	5.0 ± 1.0	$(5.10 \pm 0.28) \times 10^{-9}$	$(4.49 \pm 0.81) \times 10^{-9}$	6.95×10^{6}	77.0 ± 6.0
$(CO)_5Cr{=}C(SCH_2CH_2OH)Ph$ (**8-CrSOH**)	$(2.35 \pm 0.05) \times 10^{2}$	$(5.04 \pm 0.19) \times 10^{6}$	$(3.70 \pm 0.05) \times 10^{-2}$	$(2.65 \pm 0.17) \times 10^{-2}$	$(7.34 \pm 0.37) \times 10^{-9}$	$(5.26 \pm 0.31) \times 10^{-9}$	8.14×10^{6}	ca. 7.7
$(CO)_5W{=}C(SCH_2CH_2OH)Ph$ (**8-WSOH**)	$(4.26 \pm 0.11) \times 10^{2}$	$(4.74 \pm 0.08) \times 10^{6}$	$(8.40 \pm 0.02) \times 10^{-2}$	$(7.11 \pm 0.40) \times 10^{2}$	$(1.77 \pm 0.05) \times 10^{-8}$	$(1.50 \pm 0.06) \times 10^{-8}$	2.32×10^{7}	ca. 7.7

[a] $K_{OH}K_1 = K_2/K_w$ with $K_w = 6.46 \times 10^{-16}$ M^2 and K_2(spec) except for **8-CrOOH** where K_2 (kin) was used (see text). [b] K_{OH} for **8-WOOH** which corresponds to a pK_a of 13.30 was determined experimentally; for the other compounds K_{OH} was estimated, see text.

and $K_1(S)/K_1(O) = 33$ for the tungsten derivatives (Table 4). There are at least four major factors that potentially may contribute to these ratios. They include steric effects, stabilization by geminal oxygen atoms in the case of **9-MOO**$^-$ (anomeric effect[15,16]), the relative π-donor effects of oxygen vs sulfur[17] (**16**), and the relative inductive effects of these two atoms. The greater electron withdrawing inductive effect[11] of oxygen and the anomeric effect should favor K_1 for **9-MOO**$^-$ over that of **9-MSO**$^-$. The same is true for the steric effect because steric hindrance in the cyclic adduct is greater for the thia derivatives. On the other hand, the stronger π-donor effect of oxygen leads to more effective stabilization of the corresponding reactant and hence reduces K_1 for **9-MOO**$^-$ more than for **9-MSO**$^-$. The fact that K_1 is larger for **9-MSO**$^-$ than for **9-MOO**$^-$ indicates that the first three factors are more than offset by the π-donor effect.

A similar conclusion was reached when comparing the equilibrium constants for thiolate ion addition to **4-M** with those for addition to **1-M**.[1]

In contrast to the equilibrium constants, the *rate* constants for nucleophilic attack (k_1 and k_2) as well as for its reverse (k_{-1} and k^{H}_{-2}) are lower for the thia than for the oxa complexes; the relevant ratios are summarized in Table 4. This reversal is again reminiscent of the reactions of thiolate ions with **4-M** vs **1-M**; it implies that the *intrinsic*[18] rate constants for the reactions of **8-MSO**$^-$ (or **8-MSOH**) are substantially lower than for the reactions of **8-MOO**$^-$ (or **8-MOOH**). One may estimate intrinsic rate constants based on eq 9 ($x = 1$ or 2), which

$$\log k_0 = \log k_x - 0.5 \log K_x \qquad (9)$$

corresponds to the simplest form of the Marcus equation.[19] The log k_0 values for the $k_1{-}k_{-1}$ pathway are included in Table 2, and those for the $k_2{-}k^{H}_{-2}$ pathway in Table 3.[20]

The reasons the intrinsic rate constants for oxa and thia complexes are so different have been discussed at length before,[1] and the earlier paper should be consulted for details. Briefly, these reasons are related to transition state imbalances[21,22] between bond formation and stabilizing/destabilizing factors such as resonance effects, steric effects, π-donor effects, and possibly others. Specifically, steric hindrance in the adducts probably develops ahead of bond formation[23] which, according to the principle of nonperfect synchronization (PNS),[24] lowers k_0 for the formation of the bulkier **9-MSO**$^-$ more than for **9-MOO**$^-$.

With respect to resonance effects, there is strong evidence that the negative charge in adducts such as **2-M**$^-$ (eq 1) is highly

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(14) Ballinger, P.; Long, F. A. *J. Am. Chem. Soc.* **1960**, *82*, 795.

(15) (a) Kirby, A. J. *The Anomeric Effect and Related Stereoelectronic Effects of Oxygen*; Springer-Verlag: Berlin, 1983. (b) Schleyer, P. v. R.; Jemmis, E. D.; Spitznagel, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 6393.

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(17) $\sigma_R = -0.43$ and -0.15 for MeO and MeS, respectively.[12]

(18) 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., $K_1 = 1$.

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(20) Note that even though the absolute intrinsic rate constants obtained from eq 9 should be regarded as rather uncertain, much of this uncertainty is likely to cancel when the log k_0 values are used for comparative purposes which is our focus.

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Table 2. Rate and Equilibrium Constants for the Cyclization Steps through the k_1-k_{-1} Pathway, Intrinsic Rate Constants, and Effective Molarities

no.	reaction	K_1[a]	k_1 (s^{-1})	k_{-1} (s^{-1})	log k_0[e]	EM(K_1) (M)	EM (k_1) (M)	EM(k_1)/EM(K_1)
1	$(CO)_5Cr{=}C(OCH_2CH_2O^-)Ph$ (**8-CrOO**$^-$)	$\approx 2.12 \times 10^5$	$\approx 7.21 \times 10^3$	3.40×10^{-2}	≈1.19	2.7×10^4	7.0×10^2	2.6×10^{-2}
2	$(CO)_5W{=}C(OCH_2CH_2O^-)Ph$ (**8-WOO**$^-$)	9.03×10^4	1.81×10^3	2.00×10^{-2}	≈0.78	1.1×10^4	9.9×10^1	9.0×10^{-3}
3	$(CO)_5Cr{=}C(SCH_2CH_2O^-)Ph$ (**8-CrSO**$^-$)	$\approx 1.06 \times 10^6$	≈30.5	2.88×10^{-5}	≈−1.53			
4	$(CO)_5W{=}C(SCH_2CH_2O^-)Ph$ (**8- WSO**$^-$)	$\approx 3.01 \times 10^6$	≈55.3	1.83×10^{-5}	≈−1.50			
5[b]	$(CO)_5Cr{=}C(OMe)Ph$ (**1-Cr**) + $HC{\equiv}CCH_2O^-$	167[c]	47.0[d]	0.281	0.56			
6[b]	$(CO)_5W{=}C(OMe)Ph$ (**1-W**) + $HC{\equiv}CCH_2O^-$	167[c]	84.0[d]	0.504	0.81			

[a] K_1 based on K_2(spec) for **8-WOO**$^-$, **8-CrSO**$^-$, and **8-WSO**$^-$ and based on K_2(kin) for **8-CrOO**$^-$, see text. [b] Reference 29. [c] In units of M^{-1}. [d] In units of M^{-1} s^{-1}. [e] Obtained from eq 7 with $n = 1$.

Table 3. Rate and Equilibrium Constants for the Cyclization Steps through the $k_2-k_{-2}^{H}$ Pathway: Intrinsic Rate Constants

reaction	K_2[a] (M)	k_2 (s^{-1})	k_{-2}^{H}(M^{-1} s^{-1})	log k_0[b]
$(CO)_5Cr{=}C(OCH_2CH_2OH)Ph$ (**8-CrOOH**)	1.36×10^{-8}	15.0	1.10×10^9	≈5.11
$(CO)_5W{=}C(OCH_2CH_2OH)Ph$ (**8-WOOH**)	4.49×10^{-9}	5.03	1.12×10^9	≈4.88
$(CO)_5Cr{=}C(SCH_2CH_2OH)Ph$ (**8-CrSOH**)	5.26×10^{-9}	2.65×10^{-2}	5.04×10^6	≈2.56
$(CO)_5W{=}C(SCH_2CH_2OH)Ph$ (**8-WSOH**)	1.50×10^{-8}	7.11×10^{-2}	4.74×10^6	≈2.76

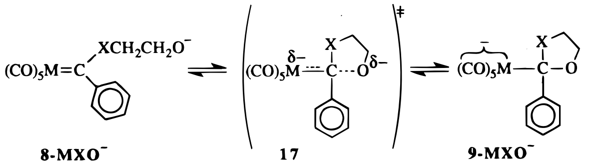
[a] K_2(spec) for **8-WOOH**, **8-CrSOH**, and **8-WSOH**, K_2(kin) for **8-CrOOH**; see text. [b] Obtained from eq 9 with $n = 2$.

Table 4. Oxa vs Thia Complexes as Reflected in the Equilibrium Constant Ratios and Rate Constant Ratios

	$(CO)_5Cr{=}C(XCH_2CH_2OH)Ph$ (**8-CrXOH**)	$(CO)_5W{=}C(XCH_2CH_2OH)Ph$ (**8-WXOH**)
$K_1(S)/K_1(O)$[a]	≈5.0	≈33
$k_1(S)/k_1(O)$	$\approx 4.2 \times 10^{-3}$	$\approx 3.1 \times 10^{-2}$
$k_{-1}(S)/k_{-1}(O)$	$\approx 8.5 \times 10^{-4}$	$\approx 9.2 \times 10^{-4}$
$k_2(S)/k_2(O)$	$\approx 1.8 \times 10^{-3}$	$\approx 1.4 \times 10^{-2}$
$k_{-2}^{H}(S)/k_{-2}^{H}(O)$	$\approx 4.6 \times 10^{-3}$	$\approx 4.2 \times 10^{-3}$

[a] $K_2(S)/K_2(O) = K_1(S)/K_1(O)$.

delocalized into the CO ligands,[25] a fact highlighted by showing the negative charge on top of the bracket symbol in all the adducts. On the other hand, in such situations, charge delocalization at the *transition state* has made little progress,[22] as highlighted in **17** by placing the partial negative charge on the *metal* rather than the CO ligands. As a consequence, the inductive effect of X leads to a disproportionately strong stabilization of the transition state relative to that of the adduct.[22] This enhances k_0, and more so for the reaction of **8-MOO**$^-$ than of **8-MSO**$^-$, because of the stronger inductive effect of the oxygen.



8-MXO$^-$ **17** **9-MXO**$^-$ (10)

The difference in the π-donor effect of oxygen and sulfur may also lead to differences in the intrinsic rate constants for the reactions of **8-MOO**$^-$ and **8-MSO**$^-$. However, there are two potential interaction mechanisms that oppose each other and hence a prediction as to which reaction benefits the most from this effect is difficult to make.[1]

One potential factor not discussed previously[1] is the anomeric effect. In principle, early development of this adduct stabilizing effect should lead to an increase in k_0 for **8-MOO**$^{-24}$ and contribute to enhancing the difference in the k_0 values for **8-MOO**$^-$ and **8-MSO**$^-$. However, in S_NV reactions no evidence for early development of the anomeric effect could be found[26] and hence it is not clear whether such early development occurs in the present case.

C. $k_2-k_{-2}^{H}$ vs k_1-k_{-1} Pathway. Even though the absolute values for k_2 (Table 3) are very much lower than for k_1 (Table 2), and those for k_{-2}^{H} much higher than for k_{-1}, as one would expect on the basis of $K_1 \gg K_2$, the $k_2(S)/k_2(O)$ ratios are quite similar to the $k_1(S)/k_1(O)$ ratios and the $k_{-2}^{H}(S)/k_{-2}^{H}(O)$ ratios are very comparable to the $k_{-1}(S)/k_{-1}(O)$ ratios (Table 4). This means that the differences in the log k_0 values between **8-MOOH** and **8-MSOH** for the $k_2-k_{-2}^{H}$ process are about the same as between **8-MOO**$^-$ and **8-MSO**$^-$ for the k_1-k_{-1} process. However, the absolute values of the log k_0 for the $k_2-k_{-2}^{H}$ process (Table 3, average log $k_0 \approx 4.99$ with X = O, average log $k_0 \approx 2.66$ with X = S) are much higher than for the $k_1 - k_{-1}$ process (Table 2, average log $k_0 \approx 0.98$ with X = O, average log $k_0 \approx 1.51$ with X = S).

There are at least two factors that are likely to contribute to this difference in the intrinsic rate constants for the two pathways. One is that in the k_1-k_{-1} pathway the nucleophile is a strongly basic alkoxide ion. The strong solvation of such oxyanions is known to reduce their kinetic reactivity.[27] This reduction is a classic PNS effect[24] and the result of a transition state where the loss of solvation is ahead of bond formation.[22,27]

The second factor is an electrostatic effect at the transition state. The transition state for the k_1-k_{-1} pathway is shown as **17**; the most likely transition state for the $k_2-k_{-2}^{H}$ pathway as **15**. In **17** there is a destabilizing effect resulting from the two partial negative charges, while in **15** there is a stabilizing interaction between the positive and negative charge.[28]

D. Chromium vs Tungsten Complexes. For the cyclization of the ethylene glycol derivatives, **8-MOO**$^-$ (**8-MOOH**), the

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(24) The PNS states that if the development of a product-stabilizing factor lags behind bond changes or charge transfer at the transition state, k_0 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_0 is enhanced.[22]

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

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

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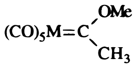
(28) The same argument still applies if the transition state for the $k_2-k_{-2}^{H}$ pathway is **14**.

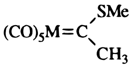
reaction of the chromium complex is thermodynamically as well as kinetically favored over that of the tungsten complex (K_1(Cr)/K_1(W) = 2.35, k_1(Cr)/k_1(W) = 3.98, k_2(Cr)/k_2(W) = 2.98). This contrasts with the β-mercaptoethanol derivatives, **8-MSO**$^-$ (**8-MSOH**), where cyclization of the tungsten complex is favored (K_1(Cr)/K_1(W) = 0.35, k_1(Cr)/k_1(W) = 0.55, k_2(Cr)/k_2(W) = 0.37).

The reasons for this reversal are not clear. On the basis of previous findings, it appears that the somewhat higher reactivity of the tungsten derivative found for **8-MSO**$^-$ (**8-MSOH**) is the norm. For example, for MeO$^-$ addition to **1-Cr** and **1-W** in methanol, K_1(W)/K_1(Cr) = 1.58 and k_1(W)/k_1(Cr) = 2.41[25] while for HC≡CCH$_2$O$^-$ addition to the same carbene complexes in 50% MeCN−50% water K_1(W)/K_1(Cr) = 1.0 and k_1(W)/k_1(Cr) = 1.79 (Table 1);[29] for the addition of various thiolate ions to **1-Cr** and **1-W** as well as their corresponding ethoxy derivatives in 50% MeCN−50% water, K_1(W)/K_1(Cr) varies between 1.27 and 1.53 while k_1(W)/k_1(Cr) varies between 2.56 and 3.16.[3]

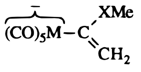
Another reaction that leads to similar anions as in nucleophilic additions is the deprotonation of acidic carbene complexes of the type **18-M** and **19-M** yielding **20-MX**$^-$ (X = O or S). Here the situation pertaining to the relative reactivities of the chromium and tungsten derivatives is more complex than in the nucleophilic reactions in that the relative thermodynamic and kinetic acidities often diverge. Thus, **18-W** (pK_a = 12.36) is somewhat more acidic than **18-Cr** (pK_a = 12.50) but the rate constants for deprotonation of **18-W** are lower than for **18-Cr** (k_1^{OH}(W)/k_1^{OH}(Cr) = 0.62 and k_1^{Pip}(W)/k_1^{Pip}(Cr) = 0.50).[6,30,31] In the case of the thiomethoxy analogues, **19-M**, the thermodynamic acidity is again higher for the tungsten (pK_a = 8.37) than for the chromium complex (pK_a = 9.03) while the kinetic acidity is slightly lower for the tungsten derivative with OH$^-$ as the base (k_1^{OH}(W)/k_1^{OH}(Cr) = 0.70) but higher for the tungsten than the chromium complex for other bases (e.g., k_1^{Pip}(W)/k_1^{Pip}(Cr) = 2.04).[31,32] Attempts to offer an all-encompassing interpretation of these conflicting findings will have to await further study.


$(CO)_5M{=}C(OMe)CH_3$

18-Cr (M = Cr)
18-W (M = W)


$(CO)_5M{=}C(SMe)CH_3$

19-Cr (M = Cr)
19-W (M = W)


$\overbrace{(CO)_5M}^{-}{-}C(XMe){=}CH_2$

20-MX$^-$

E. Intramolecular vs Intermolecular Reactions. Table 2 summarizes K_1, k_1 and k_{-1} values for the intramolecular reactions of **8-MOO**$^-$ and **8-MSO**$^-$ and for two *inter*molecular nucleophilic addition reactions reported elsewhere.[29] Reaction nos. 1 and 5[33] are of the same type; i.e., both refer to nucleophilic additions of an alkoxide ion to an alkoxycarbene complex and hence allow an approximate assessment of the equilibrium and kinetic effective molarities (EM);[34] the same is true for reactions nos. 2 and 6.[33] For the chromium derivatives K_1(intra)/K_1(inter) = 1.3 × 10^3 M, k_1(intra)/k_1(inter) = 150 M, and k_{-1}(intra)/k_{-1}(inter) = 0.12; for the tungsten derivatives K_1(intra)/K_1(inter) = 5.4 × 10^2 M, k_1(intra)/k_1(inter) = 22 M, and k_{-1}(intra)/k_{-1}(inter) = 4.0 × 10^{-2}. However, these ratios underestimate the effect of the intramolecularity because they do not take into account that HC≡CCH$_2$O$^-$ is more basic (pK_a = 14.73[29]) than the oxyanions in **8-MOO**$^-$ (pK_a = 13.41) and hence more nucleophilic. In adjusting the equilibrium effective molarities for the different basicities, it is reasonable to apply a correction factor of 21 which reflects the pK_a difference of the nucleophiles. In adjusting the *rate* constant ratios, we shall assume that the correction factor for the K_1(intra)/K_1(inter) ratios is equally distributed between the k_1(intra)/k_1(inter) and k_{-1}(intra)/k_{-1}(inter) ratios.[35] The corrected K_1(intra)/K_1(inter) and k_1(intra)/k_1(inter) ratios are included in Table 2 as EM(K_1) and EM(k_1), respectively.[36] Our EM(K_1) and EM(k_1) are at the low end of the range which is common for the formation of five-membered rings from conformationally flexible systems (10^4 to 10^8 M).[34]

A point of particular interest is the relationship between EM(k_1) and EM(K_1). This relationship can be expressed as EM(k_1)/EM(K_1) ratios or framed in terms of intrinsic rate constants[37] (Table 2). The results show that for the tungsten complex log k_0(intra) and log k_0(inter) are nearly the same while for the chromium complexes log k_0(intra) exceeds log k_0(inter) by about 0.6 units. There are only few intra/intermolecular reaction pairs with which to compare our results because in most cases studied only kinetic but not thermodynamic EM values are available.[34] For lactonization reactions of HXCH$_2$CH$_2$CH$_2$CO$_2$H (X = O or S) and derivatives where such data are available, the EM(k_1)/EM(K_1) ratios vary from 4.9 × 10^{-2} to 0.91 with EM(K_1) varying from 88 to 9.5 × 10^4 M.[34a] This translates into log k_0(intra) − log k_0(inter) values from 0.33 to 1.50.[37]

On the basis of this comparison, log k_0(intra) − log k_0(inter) for the cyclization of **8-MOO**$^-$ appears to be rather low. In analyzing possible reasons for these findings we focus on two major factors that distinguish intramolecular from intermolecular reactions and that have opposite effects on EM values. The first is entropy. To a good approximation the entropic disadvantage of the intermolecular reactions may be assumed to be about the same for the transition state as for the cyclic adduct.[34] Hence, in the absence of other factors, we would expect EM(k_1)/EM(K_1) ≈ 1 and log k_0(intra) $>(\gg)$ log k_0(inter).[37] This entropy effect on the difference between k_0(intra) and log k_0(inter) can also be understood in the context of the PNS,[24] i.e., the loss of the reactant stabilizing entropy in the intermolecular reaction is more advanced than bond formation at the transition state which reduces k_0(inter).

The second factor is ring strain which can reduce the difference between k_0(intra) and k_0(inter). This will occur if the development of the strain is more advanced at the transition state than bond formation because ring strain is a product destabilizing factor and, according to the PNS, should lower k_0(intra).[38] Hence, a possible explanation of the smaller log k_0(intra) − log k_0(inter) differences in the cyclizations of **8-MOO**$^-$ compared to the lactonization reactions is that in the reactions of **8-MOO**$^-$ there is either more strain or its development at

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(29) Bernasconi, C. F.; García-Río, L. To be published.

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

(31) Pip = piperidine.

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

(33) Numbering in Table 2.

(34) (a) Kirby, A. J. *Adv. Phys. Org. Chem.* **1980**, *17*, 183. (b) Mandolini, L. *Adv. Phys. Org. Chem.* **1986**, *22*, 1.

(35) Thus the corrected k_1(intra)/k_1(inter) ratio is obtained by multiplying the experimental ratio by $\sqrt{21}$ = 4.58 while the corrected k_{-1}(intra)/k_{-1}(inter) ratio is obtained by *dividing* the experimental ratio by 4.58.

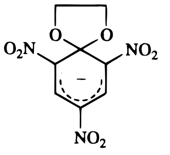
(36) Incidentally, the cyclic adducts are not only more stable than the noncyclic ones ({(CO)$_5$M}$^-$C(OMe$_2$)Ph and **2-M**) relative to their respective precursors but also more stable towards decomposition. However, since the nature of the decomposition is not known, not too much significance should be attached to these observations. The fact that there is little difference in the EM values between the Cr and W derivatives but a large difference in the stability toward decomposition, with the cyclic W adducts being more stable, indicates that there is no simple relationship between the two types of stabilities.

(37) Assuming eq 9 is valid, the relationship between relative intrinsic rate constants and EM(k_1)/EM(K_1) ratios is that log k_0(intra) − log k_0(inter) = log{EM(k_1)/EM(K_1)} + 0.5 log EM(K_1).

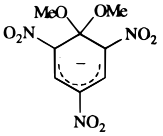
(38) Mandolini's[34b] treatment of this subject which uses a formalism based on thermodynamic relationships leads to the same conclusions.

the transition state is further ahead of bond formation than in the lactonization reactions.

Another reaction that provides an interesting comparison with the cyclization of **8-MOO**$^-$ is the formation of spiro Meisenheimer complexes such as **21**.[39] In fact formation of **21** bears a



21



22

closer similarity with the formation of **9-MOO**$^-$ than lactonizations. EM(K_1) = 1.6 × 10^4 M for the formation of **21** vs **22** is very nearly the same as for the cyclization of **8-MOO**$^-$, but EM(k_1) = 5.1 × 10^5 M and hence EM(k_1)/EM(K_1) = 32 is several orders of magnitude higher than for **8-MOO**$^-$; in terms of intrinsic rate constants, $\log k_0(\text{intra}) - \log k_0(\text{inter}) \approx 3.6$. In this case the large difference between log k_0(intra) and log k_0(inter) can be traced to some special stereoelectronic effects between the lone pair orbitals of the nonreacting oxygen and the benzene ring[39] which are not relevant to the reaction of **8-MOO**$^-$.

Conclusions

(1) All experimental observations are consistent with Scheme 1 and exclude other interpretations. With respect to the $k_2-k_{-2}^{\mathrm{H}}$ pathway, no firm conclusion as to whether it represents a single-step reaction (**14**) or a two-step process (**15**, eq 8) can be drawn.

(2) The equilibrium constants for cyclization of the thia complexes are somewhat larger than for the oxa complexes. This appears to be the result of the smaller π-donor effect of sulfur compared to oxygen; this factor apparently more than offsets the difference in the inductive, anomeric, and steric effects that all tend to favor cyclization of the oxa complexes.

(3) With respect to the *rate* constants for cyclization, it is the oxa complexes that are more reactive, indicating that the *intrinsic* rate constants for the oxa complexes are substantially higher than for the thia complexes. The higher intrinsic constants for the oxa complexes can be understood in terms of PNS effects that result from transition state imbalances. Specifically, early development of the steric effect reduces k_0(S) more than k_0(O), and a disproportionately strong transition state stabilization by the inductive effect of X that is the result of the lag in charge delocalization into the $(CO)_5M$ moiety increases k_0(O) more than k_0(S).

(4) The intrinsic rate constants for the $k_2-k_{-2}^{\mathrm{H}}$ pathway are substantially higher than for the k_1-k_{-1} pathway. This appears to be the combined result of three factors: a k_0 reducing PNS effect of the early desolvation of the oxyanion for the k_1-k_{-1} pathway, electrostatic destabilization of the transition state of the k_1-k_{-1} pathway, and electrostatic stabilization of the transition state of the $k_2-k_{-2}^{\mathrm{H}}$ pathway.

(5) There are some small differences in the equilibrium and rate constants between the chromium and tungsten complexes, but a lack of consistency renders a detailed interpretation difficult.

(6) The equilibrium and kinetic effective molarities of the cyclization reactions of **8-MOO**$^-$ and **8-MSO**$^-$ fall within the range commonly observed for the formation of rings from conformationally flexible precursors although especially the kinetic EM values are at the low end of this range. This translates into k_0(intra) values that are not as much enhanced over the corresponding k_0(inter) values as in comparable systems. This could possibly be the result of ring strain at the transition state whose development is further ahead of bond formation than in comparable systems.

Experimental Section

Instrumentation. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a 500 MHz Varian Unity instrument. UV−vis spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer. Kinetic experiments were performed on an Applied Photophysics DX.17MV stopped-flow apparatus (fast reactions) or a Hewlett-Packard 8452A spectrophotometer (slow reactions).

Reagents. Triethylamine and *N*-methylmorpholine were refluxed and distilled over Na/CaH_2 prior to use. Reagent grade acetic acid was used without further purification. Acetonitrile was purchased from Fischer Scientific and used as received. KOH and HCl solutions were prepared using “dilut it” from Baker Analytical. Water was taken from a Milli-Q purification system.

Synthesis of the ((2-Hydroxyethoxy)phenylcarbene)pentacarbonyl Complexes of Chromium(0) and Tungsten(0), 8-MOOH. These complexes were synthesized by the reaction of **1-M** with $NaOCH_2CH_2OH$ as follows. A $NaOCH_2CH_2OH$ solution was prepared by adding 0.27 g (11.7 nmol) of clean sodium metal to a mixture of 13 mL of ethylene glycol and 7 mL of THF under argon and stirring for 30 min until all the sodium had reacted. This solution was added to a solution of **1-M** (4 mmol) in 50 mL of dry THF over a period of 10 min during which time the solution turned light yellow. A 35 mL amount of an HCl solution in THF prepared from 6 mL of concentrated HCl in 100 mL of THF was then added dropwise with the resulting solution turning red/brown. Addition was complete after 15 min whereupon the reaction mixture was stirred for 1 h. All the above procedures were carried out under argon. The following operations were carried out in the open air. The volume of the reaction mixture was reduced to a minimum in a rotoevaporator, 80 mL of water followed by 100 mL of $CHCl_3$ was added, and the aqueous layer was discarded. The $CHCl_3$ layer was dried over anhydrous Na_2SO_4 and filtered, and the volume was reduced in a rotoevaporator to leave a dark red/brown oil residue. After passage of the residue through a silica gel (100−200 mesh) column (25 × 3 cm) using $CHCl_3$ and then 50% $CHCl_3$-50% ethyl acetate (v/v) as eluent, the solvent was removed under high vacuum at room temperature. **8-CrOOH** kept at −35 °C yielded a solid product which was recrystallized from pentane, mp 55−57 °C; for **8-WOOH**, mp = 79.5−80 °C.

Synthesis of ((2-Hydroxythioethoxy)phenylcarbene)pentacarbonyl Complexes of Chromium(0) and Tungsten(0), 8-MSOH. These complexes were synthesized by the reaction of **1-M** with $NaSCH_2CH_2OH$. A $NaSCH_2CH_2OH$ solution was prepared by adding 0.6 g of solid NaOH to 15 mmol of 2-mercaptoethanol in 20 mL of methanol saturated with argon. This solution was added to 8 mmol of **1-M** dissolved in 80 mL of benzene and then stirred for 10 min. A 35 mL amount of an HCl solution in methanol prepared from 6 mL of concentrated HCl in 100 mL of methanol was then added dropwise over a period of 25 min. The solution turned deep red and NaCl precipitated out. Stirring was continued for 2 h. All the above procedures were carried out under argon. The subsequent operations were carried out in the open air and were the same as for the synthesis of **8-MOOH** except that the chromatography was done with *n*-hexane as eluent. The eluted sample was reduced by means of a rotoevaporator and then placed under high vacuum over dry ice−acetone (−78 °C). No solids were obtained for these compounds.

NMR Spectra. The ^1H and ^{13}C NMR data for the synthesized compounds are summarized in Table 5.

Kinetic Measurements. All kinetic runs were conducted under pseudo-first-order conditions ensured by a large excess of KOH, HCl, or buffer over the substrate. The reactions were monitored at or near $\lambda_{\max}$ of the neutral carbene complex (**8-CrOOH**, 400 nm; **8-WOOH**, 396 nm; **8-CrSOH**, 468 nm; **8-WSOH**, 452 nm); at these wavelengths there is no absorption by the cyclic adducts (Figure 1).

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[39] Bernasconi, C. F.; Howard, K. *J. Am. Chem. Soc.* **1982**, *104*, 7248.

Table 5. ^1H and ^{13}C NMR Data in $CDCl_3$[a]

atom	**8-CrOOH**	**8-WOOH**	**8-CrSOH**	**8-WSOH**[b]	**9-WOO$^-$**	**9-WSO$^-$**[b]
			^1H NMR			
OH	1.93	1.89	1.54	1.94		
$\mathrm{XCH_2C}\mathit{H}_2\mathrm{OH}$	4.19	4.27	3.70	3.58		
$\mathrm{XC}\mathit{H}_2\mathrm{CH_2OH}$	4.92	5.06	2.97	2.81		
Ph	7.26, 7.42	7.44, 7.58	6.69, 7.44, 7.88	6.82, 7.29, 7.47		
			^{13}C NMR			
$\mathrm{XCH_2}\mathit{C}\mathrm{H_2OH}$	61.4	61.2	60.0	59.2	63.6[c]	67.8[e]
$\mathrm{X}\mathit{C}\mathrm{H_2CH_2OH}$	81.7	77.1	46.9	49.2		35.5[f]
Ph	122.9, 128.5	126.2, 128.2	123.1, 123.3	118.7, 128.4	117.7, 123.1	118.7, 122.9
	130.6, 154.0	131.8, 155.5	128.0, 159.8	129.2, 158.9	128.0, 159.8	127.5, 161.9
cis-CO	216.3	197.2	215.0	198.4	204.7	203.3
trans-CO	224.4	203.6	228.8	209.7	209.7	207.6
═C	351.3	321.2	363.4	331.8	118.4[d]	93.1[d]

[a] 500 MHz. [b] In CD_3CN. [c] $\mathrm{O}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2O}$. [d] Single-bonded carbon. [e] $\mathrm{SCH_2}\mathit{C}\mathrm{H_2O}$. [f] $\mathrm{S}\mathit{C}\mathrm{H_2CH_2O}$.

Equilibrium Measurements. The pseudo-acidity constants (K_2 in eq 7) were determined spectrophotometrically. The K_2 values were obtained by a nonlinear least-squares fit of A vs a_{H^+} according to eq 11 with A being the absorbance in *N*-methylmorpholine buffers, A_{max}

$$A = \frac{A_{max}a_{H^+} + A_{min}K_2}{K_2 + a_{H^+}} \qquad (11)$$

the absorbance in 0.1 M HCl (100% **8-MXOH**), and A_{min} the absorbance in 0.1 KOH (100% **9-MXO$^-$**). A was measured after equilibration between **8-MXOH** and **9-MXO$^-$** was complete but before significant decomposition of **9-MXO$^-$** could occur. Since some small degree of decomposition could not be avoided, A was determined by extrapolation to "zero time".

pH Measurements. The pH in 50% MeCN−50% water was determined according to eq 12[40] with pH_{meas} referring to the reading of

$$pH = pH_{meas} + 0.18 \qquad (12)$$

the pH meter calibrated with standard buffers. All pH measurements were done on an Orion 611 pH meter equipped with a glass electrode and a "Sure Flow" (Corning) reference electrode. The pH of reaction solutions for stopped-flow experiments was adjusted in mock-mixing experiments that mimicked the stopped-flow runs. The pK_a^{RSH} values of the thiols were determined potentiometrically.

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