# Physical Organic Chemistry of Transition Metal Complexes. 31.[†] Nucleophilic Attachment of the Malononitrile Anion to Fischer Carbene Complexes

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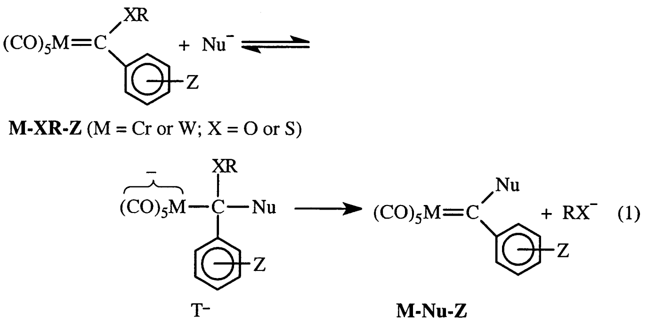
Rate constants for the attachment of $CH(CN)_2^-$ to Fischer carbene complexes of the type $(CO)_5M{=}C(XR)C_6H_4Z$ with M = Cr, W and XR = OMe, OEt, SMe in 50% MeCN−50% water (v/v) at 25 °C are reported. The malononitrile anion shows a much higher reactivity toward these carbene complexes than $OH^-$, primary aliphatic amines (e.g. *n*-butylamine), or secondary alicyclic amines (e.g. piperidine) but is slightly less reactive than thiolate ions (e.g. $HOCH_2CH_2S^-$). The alkoxycarbene complexes react more quickly than the thiomethyl derivatives, consistent with previous findings for alkoxide ion, $OH^-$, amine, and thiolate ion nucleophiles. Hammett $\rho$ values are 0.69 for the reaction with $(CO)_5Cr{=}C(SMe)C_6H_4Z$ and 2.88 for the reaction with $(CO)_5Cr{=}C(OMe)C_6H_4Z$. The much larger $\rho$ value for the methoxycarbene complexes fits a pattern observed previously with other nucleophiles and can be explained by the $\pi$-donor effect of the methoxy group, which is much stronger than that of the thiomethyl group.

## Introduction

Most transition-metal carbene complexes of the Fischer type are highly electrophilic at the carbene carbon.[1−3] In fact, nucleophilic substitution of an alkoxy or alkylthio group of carbene complexes such as **M-XR-Z** is one of the prototypical reactions of Fischer carbene complexes. There is strong evidence that these reactions proceed via tetrahedral intermediates, $T^-$, in analogy to the reactions of carboxylic esters with nucleophiles. Equation 1 shows the reaction scheme involving an anionic nucleophile, while reactions with neutral nucleophiles such as amines include a proton transfer as additional step (eq 2).



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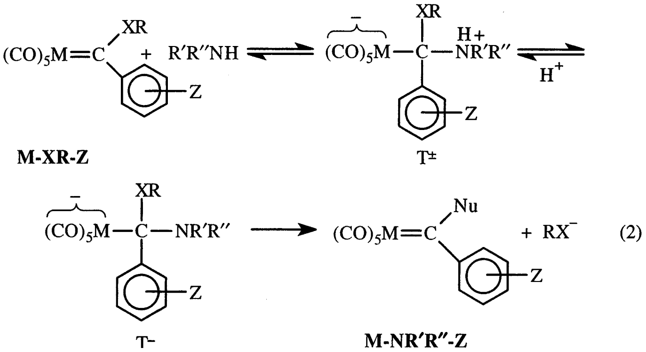

(2)

Most synthetic applications have involved common nucleophiles such as amines,[1,3,4−7] hydrazine,[1,8] oximes,[1,9] alkoxide ions,[1,3,10] thiolate ions,[1,3,11−13] and carbanions[13,14−18] (mainly aryl- and alkyllithium), as well as others.[1,19−21] There have been relatively few *kinetic*

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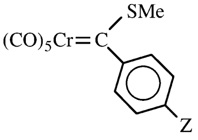
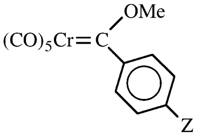
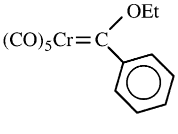
studies in the early literature; these investigations focused mainly on reactions with amines[3,22−24] and phosphines[3,25,26] in weakly polar organic solvents. More recently, a number of rate studies with alcohol,[27,28] alkoxide ions,[27,28] water,[29−33] $OH^-$,[29−33] thiol,[34−36] thiolate ions,[34−36] and amines[33,37−40] in polar (mainly water−acetonitrile mixtures) solvent were reported. However, notably absent from this list are carbanion nucleophiles. We now report a kinetic investigation of the reaction of malononitrile anion $CH(CN)_2^-$ with **Cr-SMe-Z** (Z = $Me_2N$, MeO, Me, H, F, Cl, $CF_3$), **Cr-OMe-Z** (Z = $Me_2N$, MeO, H, F), **Cr-OEt-H**, **W-OMe-H**, and **W-OEt-H** in 50% MeCN−50% water (v/v). $CH(CN)_2^-$ is a strong carbanionic nucleophile that can be used in aqueous acetonitrile; this allows us to make comparisons with other nucleophiles studied in the same solvent.



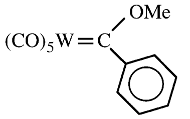
**Cr-SMe-Z**



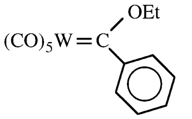
**Cr-OMe-Z**



**Cr-OEt-H**



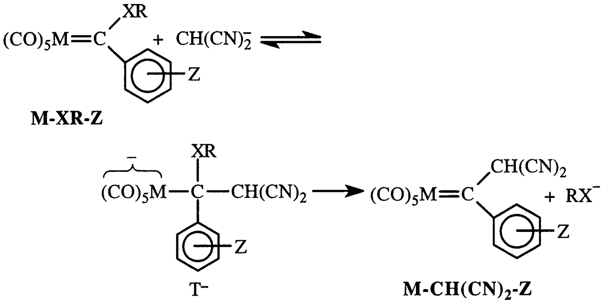
**W-OMe-H**



**W-OEt-H**

## Results

The reaction of $CH(CN)_2^-$ with **M-XR-Z** leads to the respective substitution products as shown in eq 3.



(3)

Figure 1, which is representative, shows time-resolved spectra of the reaction with **Cr-SMe-NMe₂**. The presence of isosbestic points indicates the reaction is quite clean. Formation of the substitution product was confirmed for the case of **Cr-CH(CN)₂-OMe** by isolating the synthesized product and comparing its UV/vis spectra with an infinity solution of a kinetic run.

Kinetic experiments were carried out in basic solution ([KOH] = 0.003 M), where malononitrile is present mainly in the form of its anion ($pK_a = 11.56$). Under these conditions the malononitrile solutions were relatively stable. Attempts to run the reactions at a lower pH were unsuccessful, because the increased concentration of the neutral malononitrile leads to faster decomposition resulting from the reaction of $CH(CN)_2^-$ with malononitrile.

Pseudo-first-order conditions, with the carbene complexes as the minor component, were used throughout. All measurements were performed in a stopped-flow spectrophotometer, and rates were monitored at the wavelength of the substrate.

For the reactions of $CH(CN)_2^-$ with **Cr-SMe-Z** one kinetic process was observed, while for the reactions with the alkoxycarbene complexes two processes were observed. Plots of $k_{obsd}$, the pseudo-first-order rate constant, versus $[CH(CN)_2^-]$ for the reactions with **Cr-SMe-Z** were all linear with intercepts that were indistinguishable from zero. Second-order rate constants, interpreted as $k_1$ for nucleophilic attack (see Discussion) and calculated as the slopes of plots of $k_{obsd}$ versus $[CH(CN)_2^-]$, are summarized in Table 1. For comparison purposes, rate constants for the reaction of **Cr-SMe-Z** with $OH^-$ were also determined in a similar way and reported in Table 1.

For the reactions of $CH(CN)_2^-$ with the alkoxycarbene complexes the plots of pseudo-first-order rate constants for the first kinetic process ($k_{obsd}^{I}$) versus $[CH(CN)_2^-]$ were also linear but, in some cases, had a measurable intercept, as shown in Figure 2 for a representative example. Just as for the thiomethyl carbene complexes, the slopes of the linear plots can be identified as $k_1$. The plots of $k_{obsd}^{II}$ (second process) were curved, as shown in Figure 3 for a representative case. A possible interpretation of this second process will be offered in the Discussion.

## Discussion

**Mechanism.** As mentioned in the Introduction, kinetic studies of the reaction of carbene complexes such as **Cr-SMe-Z** and **Cr-OMe-Z** with a variety of nucleophiles have been reported in recent years. In terms of its nucleophilic reactivity, $CH(CN)_2^-$, which has an $N_+$ value of 9.54,[41,42] appears to be more closely related to

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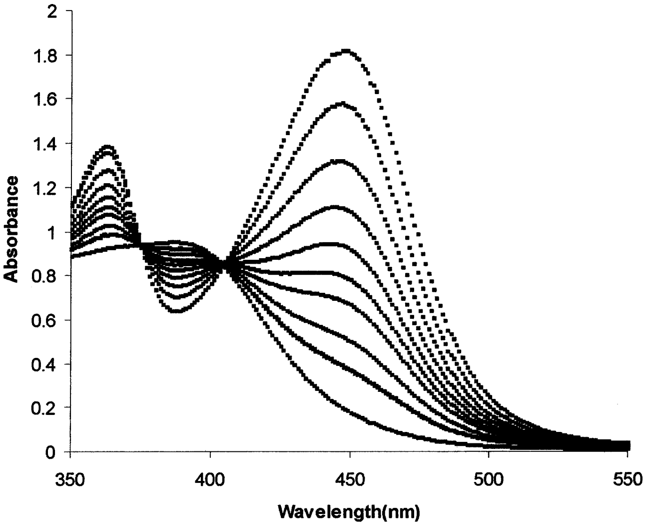

**Figure 1.** Time-resolved spectra for the reaction of **Cr-OMe-Me$_2$N** ($\lambda_{max}$ = 447 nm) with 0.005 M $CH(CN)_2^-$. Time intervals were 0.4 s for the first six spectra. The last spectrum was taken after 80 s.

**Table 1. Rate Constants for the Reactions of $CH(CN)_2^-$ and $OH^-$ with $(CO)_5Cr{=}C(SMe)C_6H_4Z$ (Cr-SMe-Z) in 50% MeCN−50% Water (v/v) at 25 °C[a,b]**

| Z | $\sigma$ | $k_1(CH(CN)^-)$, $M^{-1}\ s^{-1}$ | $k_1(OH^-)$, $M^{-1}\ s^{-1}$ |
|---|---|---|---|
| 4-Me$_2$N | −0.83 | 28.2 | 0.015 |
| 4-MeO | −0.27 | 88.0 | 0.072 |
| 4-Me | −0.17 | 105 | 0.091 |
| 4-H | 0 | 146 | 0.137 |
| 4-F | 0.06 | 146 | 0.277 |
| 4-Cl | 0.23 | 195 | 0.261 |
| 3-Cl | 0.37 | 198 | 0.388 |
| 4-CF$_3$ | 0.54 | 258 | 0.537 |

[a] $\mu$ = 0.1 M (KCl). [b] Error limits for all rate constants better than ±4%.

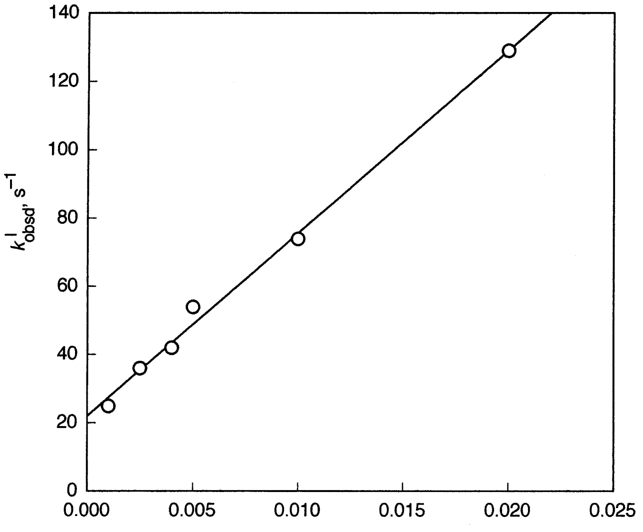

**Figure 2.** Reaction of **Cr-OMe-H** with $CH(CN)_2^-$. Plot of $k^{I}_{obsd}$ versus [$CH(CN)_2^-$].

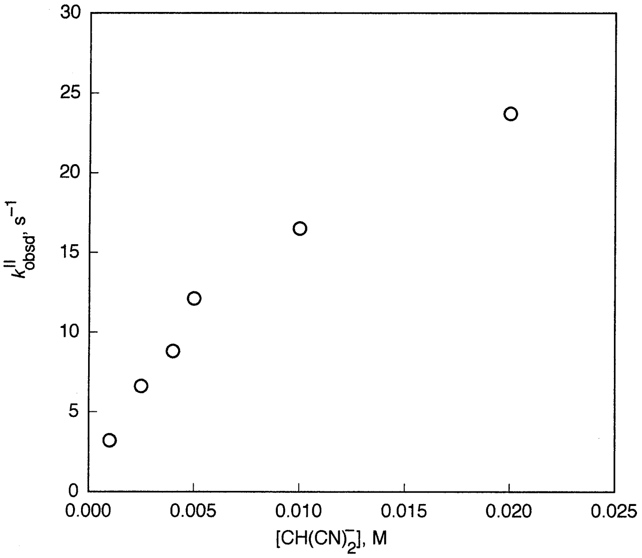

**Figure 3.** Reaction of **Cr-OMe-H** with $CH(CN)_2^-$. Plot of $k^{II}_{obsd}$ versus [$CH(CN)_2^-$].

**Table 2. Rate Constants for the Reactions of $CH(CN)_2^-$ and $OH^-$ with $(CO)_5Cr{=}C(OMe)C_6H_4Z$ (Cr-OMe-Z), $(CO)_5Cr{=}C(OEt)C_6H_5$ (Cr-OEt-H), $(CO)_5W{=}C(OMe)C_6H_5$ (W-OMe-H), and $(CO)_5W{=}C(OEt)C_6H_4$ (W-OEt-H) in 50% MeCN−50% Water (v/v) at 25 °C[a,b]**

| Z | $\sigma$ | $k_1(CH(CN)^-)$, $M^{-1}\ s^{-1}$ | $k_1(OH^-)$, $M^{-1}\ s^{-1}$ |
|---|---|---|---|
| | | $(CO)_5Cr{=}C(OMe)C_6H_4Z$ | |
| 4-Me$_2$N | −0.83 | $2.18 \times 10^1$ | 0.131 |
| 4-MeO | −0.27 | $1.91 \times 10^3$ | 3.35 |
| H | 0 | $5.35 \times 10^3$ | 26.6 |
| 4-F | 0.06 | $9.05 \times 10^3$ | 37.2 |
| | | $(CO)_5Cr{=}C(OEt)C_6H_5$ | |
| | | $3.09 \times 10^3$ | 10.5 |
| | | $(CO)_5W{=}C(OMe)C_6H_5$ | |
| | | $2.73 \times 10^4$ | 26.3 |
| | | $(CO)_5W{=}C(OEt)C_6H_5$ | |
| | | $1.45 \times 10^4$ | 17.6 |

[a] $\mu$ = 0.1 M (KCl). [b] Error limits for all rate constants better than ±4%.

**Table 3. Rate Constants of Reactions of a Representative Group of Nucleophiles with Cr-OMe-H and Cr-SMe-H in 50% MeCN−50% Water (v/v) at 25 °C**

| | | | $k_1$, $M^{-1}\ s^{-1}$ | | |
|---|---|---|---|---|---|
| Nu | $pK_a^{NuH}$ | $N_+$ | $(CO)_5Cr{=}C(SMe)C_6H_5$ | $(CO)_5Cr{=}C(OMe)C_6H_5$ | $k_1(OMe)/k_1(SMe)$ |
| $CH(CN)_2^-$ | 11.38 | 9.54[a] | $1.46 \times 10^2$ | $4.79 \times 10^3$ | 32.8 |
| $OH^-$ | 16.63 | 4.75[b] | 0.127[d] | 26.6[e] | 194 |
| n-BuNH$_2$ | 10.40 | 6.11[b,c] | 9.56[f] | $1.60 \times 10^3$[g] | 167 |
| piperidine | 11.01 | 7.58[b] | 2.88[f] | | |
| $HOCH_2CH_2S^-$ | 10.79 | 8.87[b] | $6.60 \times 10^2$ [h]<br>$(1.10 \times 10^6)$[i] | $2.25 \times 10^4$ [j]<br>$(4.66 \times 10^3)$[i] | 34.1 |

[a] Reference 41. [b] Reference 43. [c] Value for EtNH$_2$. [d] Reference 32. [e] Reference 30. [f] Reference 39. [g] Reference 38. [h] Reference 36. [i] Numbers in parentheses refer to the equilibrium constant $K_1$. [j] Reference 35.

thiolate ions and in particular to $HOCH_2CH_2S^-$ ($N_+$ = 8.87)[42,43] than to any other nucleophile studied to date (see Table 3). Hence, a comparison of the reactions of $CH(CN)_2^-$ with those of thiolate ions is particularly relevant.

The reaction of $HOCH_2CH_2S^-$ with **Cr-SMe-H** or **W-SMe-H** leads to the reversible formation of the

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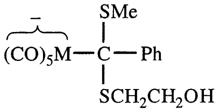
[41] Bug, T.; Mayr, H. *J. Am. Chem. Soc.* **2003**, *125*, 12980.

[42] In water.

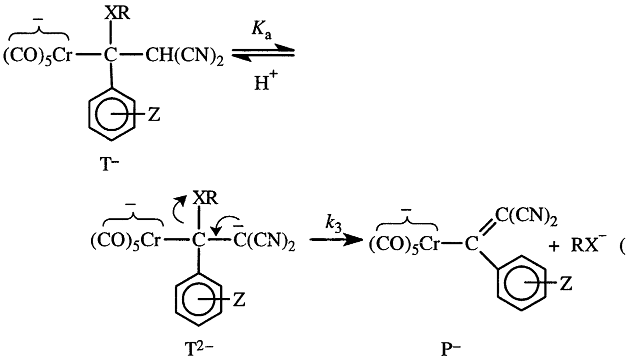
[43] Ritchie, C. D. *Can. J. Chem.* **1986**, *64*, 2247.

respective tetrahedral adducts.[36]



On the time scale of these experiments the adducts are quite stable and do not proceed to the substitution product by expulsion of the $MeS^-$ group, and upon addition of acid, they revert to starting material. These experiments allowed a determination of $k_1 = 6.60 \times 10^2$ $M^{-1}$ $s^{-1}$ as well as of $k_{-1} = 1.78 \times 10^{-3}$ $s^{-1}$ and $K_1 = k_1/k_{-1} = 3.07 \times 10^5$ $M^{-1}$.[36]

For the reactions of $CH(CN)_2^-$ with **Cr-SMe-Z** the respective tetrahedral intermediates do not accumulate to detectable levels but rather behave as steady-state intermediates, due to a much more rapid conversion to products. Hence, only $k_1$, the rate constant for nucleophilic attack, could be determined for these reactions, which for the case Z = H is $1.46 \times 10^2$ $M^{-1}$ $s^{-1}$. The reason for the different behavior is that for the reaction with $CH(CN)_2^-$ there must be a much more effective pathway for leaving-group expulsion. We propose that this pathway involves the deprotonated form of the intermediate (eq 4), which exerts a strong electronic "push" by producing the resonance-stabilized anionic form of the product. This proposal is analogous to the mechanism of hydrolysis of carbene complexes[29,32] as well as other electrophilic compounds[44] in basic solution, where rapid conversion of the intermediate to products is promoted by a similar push by the oxyanion, as shown in eq 5.



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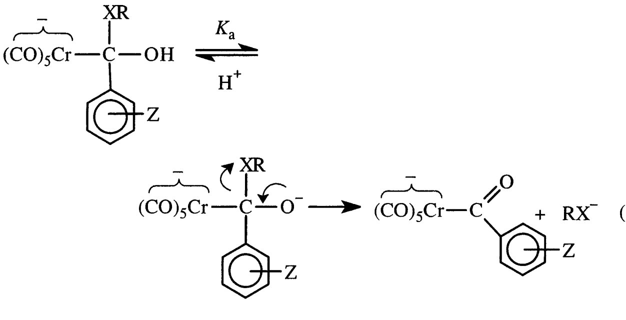

(5)

With the alkoxycarbene complexes the faster of the two observed kinetic processes is undoubtedly also the result of nucleophilic attachment of $CH(CN)_2^-$. For **Cr-OMe-H** $k_1 = 4.79 \times 10^3$ $M^{-1}$ $s^{-1}$ is obtained from the slope of a plot of $k^{I}_{obsd}$ versus $[CH(CN)_2^-]$. A possible interpretation of the slower kinetic process ($k^{II}_{obsd}$) is that it refers to the conversion of the intermediate to products. If this interpretation is correct, it implies that leaving group departure is relatively slow, despite the push provided by the negative charge on the $CH(CN)_2^-$ group of $T^{2-}$, and that the first step represents a rapid equilibrium reaction with the curvature in the plots of $k^{II}_{obsd}$ versus $[CH(CN)_2^-]$, indicating a shift toward $T^-/T^{2-}$ with increasing concentration of $[CH(CN)_2^-]$. Since alkoxide ions are known to be much poorer leaving groups than $MeS^-$, a relatively slow conversion of the intermediate to products is plausible. Nevertheless, because of the push in $T^{2-}$, this "slow" alkoxide ion expulsion is still much faster than in the reactions of $HOCH_2CH_2S^-$ with alkoxycarbene complexes.[35]

Even though the above mechanistic description is plausible, it is difficult to prove its correctness, because of uncertainties in the quantitative evaluation of the kinetic data. There are two problems. (1) The reaction scheme that applies in this case is quite complex, due to the competition of the two possible pathways from $T^-$ to products (Scheme 1). This means that $k^{II}_{obsd}$ is given by eq 6 and that a detailed study of the pH dependence of $k^{II}_{obsd}$ would be required for a determination of the various parameters of eq 6. As mentioned in Results, such a study was precluded because, at [KOH] < 0.003 M, the malononitrile solutions become quite unstable. (2) In some cases the data were not very reproducible, possibly again due to the instability of the malononitrile solutions.

$$k^{II}_{obsd} = \frac{(k_2K_1 + k_3K_1K^{T}_{a}/a_{H^+})[CH(CN)_2^-]}{1 + K_1(1 + K^{T}_{a}/a_{H^+})[CH(CN)_2^-]} \quad (6)$$

For the above reasons, no evaluation of the parameters in eq 6 has been attempted and our discussion of structure−reactivity effects on the reactions of $CH(CN)_2^-$ with the various carbene complexes will be restricted to the nucleophilic attachment step.[45]

**Structure−Reactivity Relationships.** All rate constants for nucleophilic attachment of $CH(CN)_2^-$ and $OH^-$ to the various carbene complexes are reported in Tables 1 and 2; Table 3 provides comparisons of the reactions of **Cr-SMe-H** and **Cr-OMe-H** with a representative selection of nucleophiles studied previously. The following points are noteworthy.

(1) As is the case for the reactions with $OH^-$, *n*-$BuNH_2$, piperidine, and $HOCH_2CH_2S^-$, nucleophilic attachment of $CH(CN)_2^-$ to **Cr-OMe-H** is considerably faster than attachment to the respective thiomethyl derivative (Table 3); the $k_1$(OMe)/$k_1$(SMe) ratio for $CH(CN)_2^-$ (32.8) is virtually identical with the $k_1$(OMe)/$k_1$(SMe) ratio for $HOCH_2CH_2S^-$ (34.1) but smaller than for $OH^-$ (194) and *n*-$BuNH_2$ (167).

(2) A detailed analysis of the reactions of **Cr-OMe-H**[35] and **Cr-SMe-H**[36] with $HOCH_2CH_2S^-$ and other thiolate ions has revealed that the larger rate constants for **Cr-OMe-H** compared to those for **Cr-SMe-H** are in contrast with *lower equilibrium* constants for **Cr-OMe-H** compared with those for

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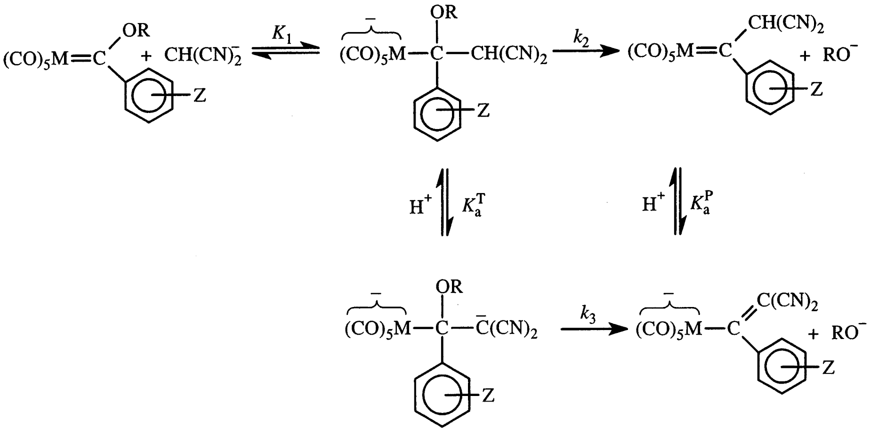
[44] Bernasconi, C. F.; Fassberg, J.; Killion, R. B., Jr.; Schuck, D. F.; Rappoport, Z. *J. Am. Chem. Soc.* **1991**, *113*, 4937.

[45] If Scheme 1 is correct, with $k^{II}_{obsd}$ given by eq 6, the intercept of the plots of $k^{I}_{obsd}$ versus $CH(CN)_2^-$ would be given by $k_{-1}a_{H^+}/(K^{T}_{a} + a_{H^+})$.

**Scheme 1**



**Cr-SMe-H** (the equilibrium constants for the reactions with $HOCH_2CH_2S^-$ are included in Table 3). This means that the intrinsic barrier[46] for the reaction of the sulfur derivative is higher, which was shown to result mainly from a large steric effect[47] that develops ahead of bond formation at the transition state.[36] It is likely that the same explanation applies to the reaction with $CH(CN)_2^-$.

(3) The fact that the $k_1$(OMe)/$k_1$(SMe) ratios are smaller for $CH(CN)_2^-$ and $HOCH_2CH_2S^-$ than for $OH^-$ and n-$BuNH_2$ may be understood in the context of hard−soft acid−base theory.[48,49] The last two nucleophiles are relatively hard, and hence, their preference for the harder methoxycarbene complex is more pronounced; for the softer nucleophiles $CH(CN)_2^-$ and $HOCH_2CH_2S^-$ the preference for **Cr-OMe-Z** is attenuated because of their enhanced affinity for the softer (thiomethyl)carbene complex.

(4) Hammett plots for the reactions of $CH(CN)_2^-$ with **Cr-OMe-Z** and **Cr-SMe-Z** and the reaction of $OH^-$ with **Cr-SMe-Z** are shown in Figure 4. The $\rho$ values are summarized in Table 4, along with $\rho$ values for systems investigated previously. The $\rho$ values for the reactions of $CH(CN)_2^-$ with **Cr-OMe-Z** and **Cr-SMe-Z** and of $OH^-$ with **Cr-SMe-Z** are consistent with the previously observed pattern, according to which $\rho$ is significantly larger for the methoxycarbene complexes than for the thiomethyl analogues. As discussed in more detail elsewhere,[40] the key to an understanding of these findings is to consider the substituent effect not only on the transition state but also on the reactant. A major difference between **Cr-OMe-Z** and **Cr-SMe-Z** is that the $\pi$-donor effect of the methoxy group is much stronger than that of the thiomethyl group[50] and leads to a substantial contribution of the zwitterionic form to the structure of **Cr-OMe-Z**.

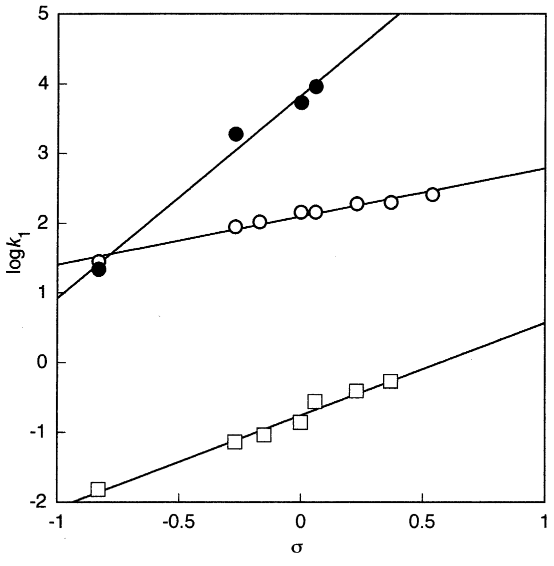
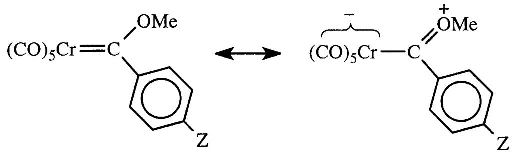


**Figure 4.** Hammett plots: (○) $k_1(CH(CN)^-)$ for **Cr-SMe-Z**; (□) $k_1(OH^-)$ for **Cr-SMe-Z**; (●) $k_1(CH(CN)_2^-)$ for **Cr-OMe-Z**.

**Table 4. Hammett $\rho$ Values in 50% MeCN−50% Water (v/v) at 25 °C**

| | $(CO)_5Cr{=}C(SMe)C_6H_4Z$ | $(CO)_5Cr{=}C(OMe)C_6H_4Z$ |
|---|---|---|
| $CH(CN)_2^-$ | 0.69 ± 0.05[a] | 2.88 ± 0.26[a] |
| $OH^-$ | 1.16 ± 0.08[a] | 2.20[b] |
| n-$BuNH_2$ | 0.59[c] | 2.03[d] |
| $MeO^-$ (MeOH) | | 2.20[b] |
| $HOCH_2CH_2S^-$ | 0.78[e] | |

[a] This work. [b] Reference 28. [c] Reference 40. [d] Reference 38. [e] $(CO)_5Cr{=}C(SCH_2CH_2OH)C_6H_4Z$.[36]



Since the positive charge on the methoxy group is much more localized than the negative charge on the $(CO)_5Cr$ moiety, the overall effect of an electron-withdrawing phenyl substituent will be destabilizing and hence result in an increase in reactivity of the carbene complex.

(5) The higher $k_1$ values for the reactions of $CH(CN)_2^-$ with the tungsten carbene complexes compared to the corresponding chromium carbene complexes (Table 2) follows previously observed patterns.[27,30,35] For reactions with alkoxide and thiolate ions where rate as well as equilibrium constants could be determined, it was found that the effect of changing the metal on the rate constants was generally greater than its effect on the equilibrium constant, indicating that a lowering of the

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[46] The intrinsic barrier is the barrier in the absence of a thermodynamic driving force.

[47] Due to the larger size of sulfur compared to that of oxygen.

[48] Pearson, R. G.; Songstad, J. *J. Am. Chem. Soc.* **1967**, *89*, 1827.

[49] Pearson, R. G. *Surv. Prog. Chem.* **1969**, *5*, 1.

[50] $\sigma_R$(OMe) = −0.42;[51] $\sigma_R$(SMe) = −0.15.[51]

intrinsic barrier[46] is the main factor responsible for the enhanced reactivity of the tungsten carbene complexes.

(6) The ethoxycarbene complexes are somewhat less reactive than their methoxy counterparts. This is again a pattern observed before[30,35] and reflects the somewhat stronger $\pi$-donor effect of the ethoxy group compared to that of the methoxy group.

## Experimental Section

**Materials.** Malononitrile (Aldrich) was analytical grade and used without further purification. Acetonitrile (Fischer Scientific) was used as received. Water was taken from a Milli-Q water purification system. HCl and KOH solutions were prepared using "Dilute-it" from Baker Analytical. The carbene complexes used as substrates were available from previous studies[28,30,40] or were resynthesized as described in those studies.

**Synthesis of Cr-CH(CN)$_2$-OMe.** The product of the reaction of **Cr-OMe-OMe** with $CH(CN)_2^-$ was synthesized as follows. A 0.171 g portion (0.5 mmol) of **Cr-OMe-OMe** was dissolved in 20 mL of acetonitrile in a round-bottom flask under an Ar atmosphere. To this solution was added 2 mmol of $KCH(CN)_2$ in 15 mL of acetonitrile; the latter was prepared by reacting malononitrile with 1 equiv of KOH dissolved in a minimum volume of water. The mixture was allowed to react for 1 h, whereupon the solvent was removed under high vacuum. The oily product was dissolved in a minimum volume of 50% MeCN−50% $CH_2Cl_2$ (v/v) and charged on a silica gel column prepared with the same solvent mixture. The yellow band was collected and dried under high vacuum.

$^1$H NMR ($\delta$; $CDCl_3$): 1.97 (s, $CH_3O$), 3.77 (s, CH), 6.84 (d, $C_6H_4$), 6.87 (d, $C_6H_4$). $^{13}$C NMR ($\delta$; $CDCl_3$): 55.84 (CH), 58.67 ($CH_3O$), 91.83 (CN), 124.2 ($C_6H_4$), 128.8 ($C_6H_4$), 151.8 ($C_6H_4$), 158.0 ($C_6H_4$), 219.6 (cis CO), 226.9 (trans CO), 262.8 (C═). MS (*m/z;* electrospray): 375.1 (M − 1), 347.1 (M − 1 − 28), 319.1 (M − 1 − 56), 291 (M − 1 − 84), 263 (M − 1 − 112), 235 (M − 1 − 140).

**p*K*$_a$ of Malononitrile.** The p$K_a$ of malononitrile in 50% MeCN−50% water was determined potentiometrically by measuring the pH of solutions prepared from 0.1 M malononitrile and various concentrations of KOH covering a pH range from 10.28 to 12.35. A plot of measured pH versus log $[CH(CN)_2^-]/[CH_2(CN)_3]$ (nine points) yielded an excellent straight line of slope 1.09 and intercept 11.38 ± 0.02. After applying a correction of +0.18 for 50% MeCN−50% water according to Allen and Tidwell,[52] one obtains $pK_a = 11.56$.

**Instrumentation and Kinetic Experiments.** NMR spectra were recorded on a Bruker 500 MHz instrument. UV−vis spectra were obtained on an Agilent 8453 diode array spectrophotometer. The mass spectra of **Cr-CH(CN)$_2$-OMe** was obtained on a Micromass Quattro electrospray instrument. Kinetic measurements were carried out in an Applied Photophysics DX.17MV stopped-flow apparatus. pH measurements were performed on an Orion 611 pH meter equipped with a Corning Sureflow reference electrode.

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(51) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.
(52) Allen, A. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1987**, *109*, 2.