Physical Organic Chemistry of Transition Metal Carbene Complexes. 15.[1] Kinetic and Thermodynamic Acidities of (Methylthiomethoxycarbene)pentacarbonyl Complexes of Chromium and Tungsten in Aqueous Acetonitrile

Claude F. Bernasconi* and Mahammad Ali[†]

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

Abstract: Rate constants for the reversible deprotonation of $(CO)_5Cr=C(SCH_3)CH_3$ (**9**-Cr) and $(CO)_5W=C(SCH_3)CH_3$ (**9**-W) by OH^-, water, a number of primary aliphatic and secondary alicyclic amines, and a series of carboxylate ions have been determined in 50% MeCN−50% water at 25 °C. This represents the first such study of Fischer carbene complexes stabilized by a thioalkoxy group. Comparison of our results to those of the corresponding methoxy derivatives $(CO)_5Cr=C(OCH_3)CH_3$ (**2**-Cr) and $(CO)_5W=C(OCH_3)CH_3$ (**2**-W) reveals that the change in the π-donor group from MeO to MeS leads to (1) a strong increase in the thermodynamic acidity, (2) an increase in the dependence of the pK_a on the nature of the metal, (3) a decrease in the *intrinsic* rate constants for proton transfer, and (4) a decrease in the dependence of the intrinsic rate constant on the metal. Observations 1, 2, and 4 can be attributed to the weaker π-donor capability of the MeS group while observation 3 is the combined result of a steric effect due to the larger size of the MeS group and of the weaker electron-withdrawing inductive/field effect of the MeS group.

Introduction

The discovery that the protons on the α-carbon of transition metal carbene complexes of the Fischer type[2] are acidic goes back to a 1968 paper by Kreiter.[3] This discovery stimulated numerous studies of the chemistry of anions generated from acidic carbene complexes such as **1**-M.[4,5] There were also a
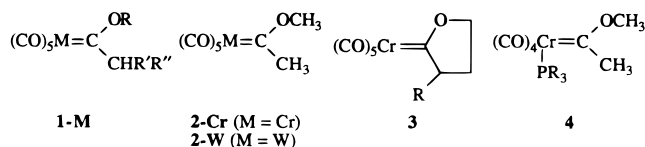
few quantitative studies aimed at measuring the acidity of Fischer carbene complexes such as **2**-Cr and **3** (R = H and CH$_3$) in THF.[6]

Very little additional quantitative work on acidities was performed until 1989, when we published the first kinetic proton-transfer study on a Fischer carbene complex (**2**-Cr).[7] Over the past few years a growing body of data on thermodynamic and kinetic acidities of Fischer carbene complexes has now been generated.[8,9] Most of these data have been obtained in 50% MeCN−50% water, a solvent chosen because it is essentially aqueous but allows the carbene complexes to be soluble enough for such determinations. Virtually all carbene complexes investigated so far are of the general structure **1**-M where M = Cr, W, and, in one case, Mo; R was either Me or Et while R′ and R″ included H, Me, *n*-Pr, and Ph. Two cyclic complexes (**3** with R = H and Me) were also investigated. The pK_a values for these compounds range from 10.18 (**1**-M with M = W, R = CH$_3$, R′ = Ph, R″= H) to 14.47 (**3**, R = H).

A limited study of thermodynamic acidities in pure acetonitrile of some **1**-M type complexes, of **3** (R = H and Me) as well as of **4** (R = n-Bu and Ph), **5**, and **6** has also been reported.[1]
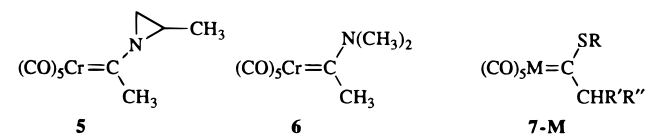
In this solvent, the pK_a values span a range from 22.2 (**2**-Cr) to 27.6 (**5**) while for **6**[10] $pK_a \geq 32.5$.

[†] On leave from the Department of Chemistry, Vidyasagar College, Calcutta 700 006, India.

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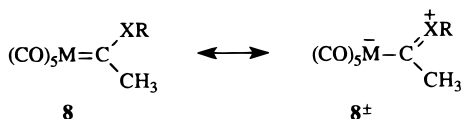
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(10) In DMSO, a $pK_a = 20.4$ has been reported for **6**.[5b]

Conspicuously absent from this list are thioalkoxy carbene complexes, e.g., of the type **7**-M. That the nature of the π-donor group (OR, NR$_2$, SR) has a strong influence on thermodynamic acidities is best appreciated by comparing the pK_a value, in pure acetonitrile, of **2**-Cr (22.2) with that of **6** ($\geq$32.5).[1] The stronger π-donor effect (**8**$^{\pm}$) of the Me$_2$N group compared to the MeO

$$(CO)_5M\!=\!C\!\!\begin{array}{c} XR \\ \\ CH_3 \end{array} \quad \longleftrightarrow \quad (CO)_5\bar{M}\!-\!C\!\!\begin{array}{c} \overset{+}{X}R \\ \\ CH_3 \end{array}$$

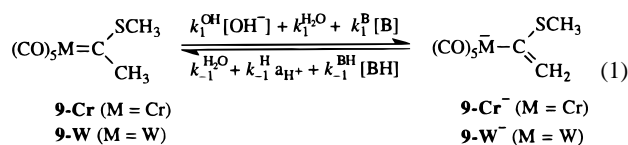**8**   **8**$^{\pm}$

group leads to a greater stabilization of the amino carbene complex and hence to a lower acidity. Since RS groups are weaker π-donors than RO groups, one would expect that thioalkoxy carbene complexes should be more acidic than the corresponding alkoxy complexes. This paper reports a study of the thermodynamic and kinetic acidities of **9**-Cr and **9**-W which

$$(CO)_5M\!=\!C\!\!\begin{array}{c} SCH_3 \\ \\ CH_3 \end{array}$$

9-Cr (M = Cr)
9-W (M = W)
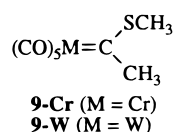
confirms this expectation. We also show that the reduced π-donor ability of the MeS group gives rise to other important differences in the reactivity of methoxy and thiomethoxy carbene complexes.

Results

General Features. When **9**-Cr or **9**-W is placed into a KOH solution or an amine buffer such as piperidine or *n*-butylamine, a rapid conversion to the respective anion is observed. This is shown in Figure 1 for **9**-Cr. Addition of a few drops of 1 M HCl to the solution of the anion leads to virtually quantitative recovery of the starting material. The reaction scheme that represents the reversible reaction of **9**-M with various bases (B and BH buffers) and is consistent with the kinetic experiments described below is shown in eq 1. These kinetic experiments

$$(CO)_5M\!=\!C\!\!\begin{array}{c} SCH_3 \\ \\ CH_3 \end{array} \underset{k_{-1}^{H_2O}+k_{-1}^{H}a_{H^+}+k_{-1}^{BH}[BH]}{\overset{k_1^{OH}[OH^-]+k_1^{H_2O}+k_1^{B}[B]}{\rightleftarrows}} (CO)_5\bar{M}\!-\!C\!\!\begin{array}{c} SCH_3 \\ \\ CH_2 \end{array} \quad (1)$$

9-Cr (M = Cr)   **9**-Cr$^-$ (M = Cr)
9-W (M = W)   **9**-W$^-$ (M = W)

were all conducted under pseudo-first-order conditions with **9**-M/**9**-M$^-$ as the minor component and hence the general expression for the pseudo-first-order rate constant is given by eq 2.

$$k_{obsd} = k_1^{OH}[OH^-] + k_{-1}^{H_2O} + k_1^{H_2O} + k_{-1}^{H}a_{H^+} + $$
$$k_1^{B}[B] + k_{-1}^{BH}[BH] \quad (2)$$

Reaction with KOH. Rates of deprotonation of **9**-M by OH$^-$ were measured in the range [KOH] = 0.001−0.1 M. Plots of k_{obsd} vs [KOH] were linear. From the slopes k_1^{OH} was obtained; the intercepts were too small to yield an accurate $k_1^{H_2O}$ value.[11]

Reaction with Morpholine Buffers. Rates of the reaction of **9**-M with morpholine buffers were determined in the pH range 7.73−9.42. Most experiments were run in the "reverse

(11) According to eq 2, the intercept is given by $k_1^{H_2O} + k_{-1}^{H_2O}$ but, as will become apparent below, $k_1^{H_2O} \gg k_{-1}^{H_2O}$.
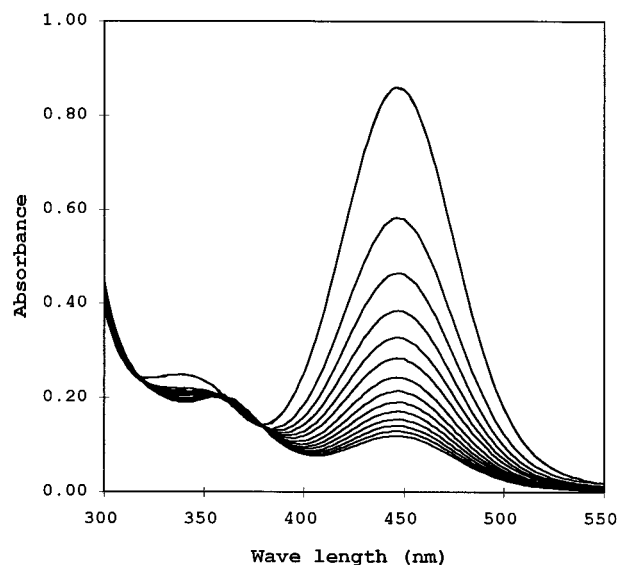

Figure 1. Conversion of **9**-Cr ($\sim$10^{-4} M) to **9**-Cr$^-$ in the presence of $\sim$5 $\times$ 10^{-4} M KOH. First spectrum taken in the absence of KOH; subsequent spectra taken at 4-s intervals.
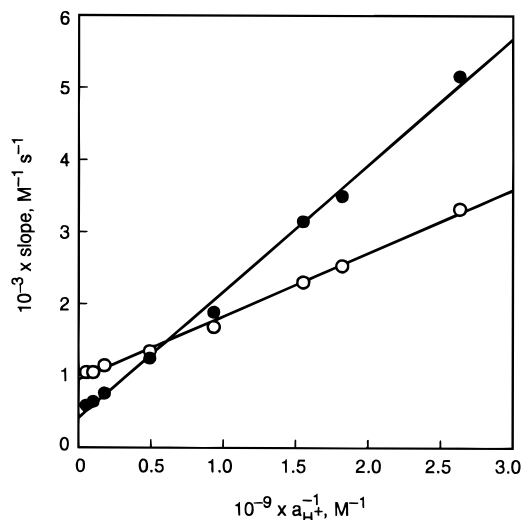

Figure 2. Slopes vs $a_{H^+}^{-1}$ according to eq 4 for the reactions of **9**-Cr (○) and **9**-W (●) with morpholine buffers.

direction", i.e., by first generating the respective anions, **9**-M$^-$, in an 0.004 M KOH solution which then was mixed with various morpholinium ion buffers. Plots of k_{obsd} vs morpholinium ion concentration ([BH]) determined at pH 7.74, 8.00, 8.25, 8.69, 8.97, 9.19, 9.26, and 9.42 were all linear with negligible intercepts. This means that eq 2 can be approximated by eq 3

$$k_{obsd} = k_1^{B}[B] + k_{-1}^{BH}[BH] = ((k_1^{B} K_a^{BH}/a_{H^+}) + k_{-1}^{BH})[BH] = $$
$$k_{-1}^{BH}((K_a^{CH}/a_{H^+}) + 1)[BH] \quad (3)$$

with K_a^{BH} being the acidity constant of BH and K_a^{CH} the acidity constant of **9**-M. The slopes of the plots of k_{obsd} vs [BH] are thus given by eq 4. These slopes are plotted vs $a_{H^+}^{-1}$ in Figure 2.

$$\text{slope} = k_{-1}^{BH}((K_a^{CH}/a_{H^+}) + 1) \quad (4)$$

They yield the k_{-1}^{BH} and K_a^{CH} values reported in Table 1; k_1^{B} was obtained as $k_{-1}^{BH} K_a^{CH}/ K_a^{BH}$.

Table 1. Summary of Rate Constants and pK_a Values in 50% MeCN−50% Water at 25 °C[a]

B	pK_a^{BH}	$(CO)_5Cr=C(SCH_3)CH_3$ (**9**-Cr, $pK_a^{CH} = 9.05 \pm 0.03$)[b]		$(CO)_5W=C(SCH_3)CH_3$ (**9**-W, $pK_a^{CH} = 8.37 \pm 0.06$)[b]	
		k_1^B, $M^{-1} s^{-1}$	k_{-1}^{BH}, $M^{-1} s^{-1}$	k_1^B, $M^{-1} s^{-1}$	k_{-1}^{BH}, $M^{-1} s^{-1}$
OH^-	16.64	$(1.20 \pm 0.08) \times 10^3$	$(8.30 \pm 0.08) \times 10^{-4\,c}$	$(8.37 \pm 0.09) \times 10^2$	$(1.21 \pm 0.09) \times 10^{-4\,c}$
H_2O	−1.44	$1.61 \times 10^{-2\,c}$	$(1.73 \pm 0.08) \times 10^7$	$5.23 \times 10^{-2\,c}$	$(1.17 \pm 0.05) \times 10^7$
piperidine	11.01	$(5.25 \pm 0.15) \times 10^3$	55.0	$(1.07 \pm 0.03) \times 10^4$	24.7
piperazine	9.97	$(1.40 \pm 0.03) \times 10^3$	160	$(2.95 \pm 0.03) \times 10^3$	74.3
HEPA[d]	9.33	793 ± 13	398	$(1.06 \pm 0.02) \times 10^3$	117
morpholine	8.70	441	946 ± 30	927	414 ± 55
n-BuNH$_2$	10.40	$(1.05 \pm 0.03) \times 10^3$	45	$(2.29 \pm 0.02) \times 10^3$	20.4
MeOCH$_2$CH$_2$NH$_2$	9.39	380 ± 7	166	729 ± 28	66.4
H$_2$NCOCH$_2$NH$_2$	8.14			141	240 ± 12
EtOCOCH$_2$NH$_2$	7.43	39.9	$(1.62 \pm 0.02) \times 10^3$	124	$(1.08 \pm 0.02) \times 10^3$
NCCH$_2$NH$_2$	5.29	3.81	$(2.09 \pm 0.03) \times 10^4$	8.88	$(1.02 \pm 0.01) \times 10^4$
PhNH$_2$	4.21			50.8	$(7.01 \pm 0.25) \times 10^4$
CH$_3$CO$_2^-$	5.93	5.84	$(7.36 \pm 0.15) \times 10^3$	16.3	$(4.27 \pm 0.06) \times 10^3$
ClCH$_2$CH$_2$CO$_2^-$	5.44	4.43	$(1.72 \pm 0.10) \times 10^4$	13.9	$(1.13 \pm 0.03) \times 10^4$
MeOCH$_2$CO$_2^-$	4.73	1.47	$(2.95 \pm 0.02) \times 10^4$	4.22	$(1.76 \pm 0.08) \times 10^4$
ClCH$_2$CO$_2^-$	4.03	1.05	$(9.58 \pm 0.05) \times 10^4$	2.97	$(6.20 \pm 0.12) \times 10^4$

[a] Standard deviation given for rate constants determined directly, i.e., k_1^B for strongly basic and k_{-1}^{BH} for weakly basic buffers. [b] Kinetically determined pK_a^{CH}. [c] In units of s^{-1}. [d] HEPA, 1-(2-hydroxyethyl)piperazine.

Spectrophotometric pK_a^{CH} Determination. In contrast to the situation with most alkoxy carbene complexes, the anions of **9**-M were stable for a long enough time to allow a spectrophotometric pK_a^{CH} determination according to eq 5 with A_{CH}

$$\log(A_{CH} - A)/(A - A_{C^-}) = pH - pK_a^{CH} \qquad (5)$$

being the absorbance at $pH \ll pK_a^{CH}$, A the absorbance at $pH \sim pK_a^{CH}$, and A_{C^-} the absorbance at $pH \gg pK_a^{CH}$. Plots according to eq 5 in phosphate and borate buffers spanning a pH range from 7.0 to 10.45 showed good linearity with slopes of 1.00 ± 0.02 (**9**-Cr) and 0.99 ± 0.02 (**9**-W), respectively, yielding $pK_a^{CH} = 9.00 \pm 0.21$ (**9**-Cr) and 8.43 ± 0.19 (**9**-W), respectively. These pK_a^{CH} values are in excellent agreement with the kinetically determined values 9.03 ± 0.03 for **9**-Cr and 8.37 ± 0.06 for **9**-W, respectively. In view of the smaller standard deviations of the kinetically determined pK_a^{CH} these latter ones will be adopted.

Reactions with Various Amine and Carboxylate Buffers. Additional kinetic data were obtained with a series of primary aliphatic amines, secondary alicyclic amines, and carboxylate buffers. Depending on the pK_a^{BH}, reactions were either run in the forward direction (**9**-M + B → **9**-M$^-$ + BH) or the reverse direction (**9**-M$^-$ + BH → **9**-M + B). For any given base, these experiments were performed at one pH only. In all cases, the plots of k_{obsd} vs [B], or k_{obsd} vs [BH], were linear, with slopes given by eq 6 (plots vs [B]) or eq 4 (plots vs [BH]), respectively.

$$\text{slope} = k_1^B(1 + (a_{H^+}/K_a^{CH})) \qquad (6)$$

k_1^B and k_{-1}^{BH} values were obtained from the slopes in conjunction with the known pK_a^{CH}.

For the reaction with most of the amines, the intercepts of the plots of k_{obsd} vs [B] or [BH] were negligible, but for the reactions with the carboxylate buffers, they were significant and showed an increase with decreasing pH. This is consistent with eq 7. Plots of these intercepts vs a_{H^+} are shown in Figure 3.

$$\text{intercept} = k_{-1}^{H_2O} + k_{-1}^H a_{H^+} \qquad (7)$$

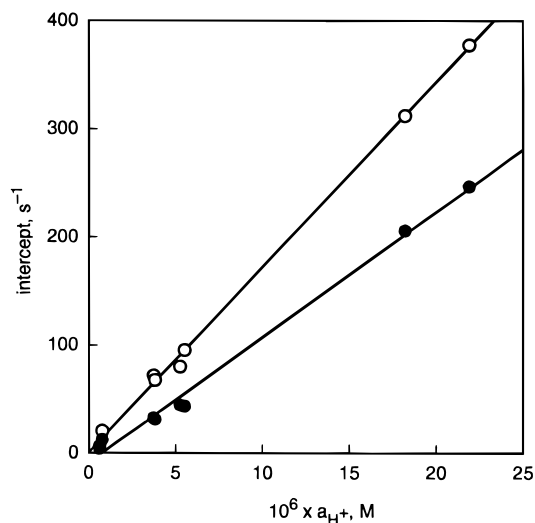They yield k_{-1}^H values from the slopes; the intercepts are too

Figure 3. Intercepts vs a_{H^+} according to eq 7 for the reactions of **9**-Cr$^-$ (○) and **9**-W$^-$ (●) with carboxylate buffers.

small for a determination of $k_{-1}^{H_2O}$ but $k_{-1}^{H_2O}$ can be obtained as $k_{-1}^{H_2O} = k_1^{OH} K_w/K_a^{CH}$ [12] while $k_1^{H_2O}$ was calculated as $k_1^{H_2O} = k_{-1}^H K_a^{CH}$.

Discussion

Mechanism. In view of the high electrophilic reactivity of the carbene carbon of Fischer carbene complexes,[2] the possibility that the reactions of **9**-M with bases represent nucleophilic additions or substitutions needs to be considered. Nucleophilic substitution, to form **10**-M (reaction with OH$^-$) or **11**-M
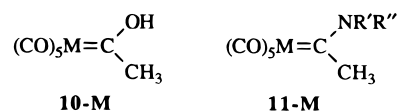
(reactions with R′R″NH) can be excluded based on the fact that, after reaction with base, acidification of the solution leads to virtually quantitative recovery of **9**-M. Nucleophilic substitution with amines *does* occur but on a slower time scale and is observable as a second kinetic process; a detailed account of

(12) $pK_w = 15.19$ in 50% MeCN−50% water.[13]

these reactions will be given later.[14] Reversible nucleophilic addition, to form adducts such as **12**-M or **13**-M can also be

12-M   **13-M**   **2-Cr⁻** (M = Cr)
                                    2-W⁻ (M = W)
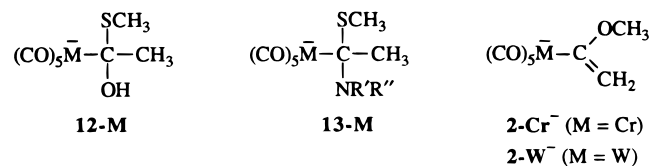
excluded as the source of the observed process because these adducts represent intermediates in the substitution reactions and no accumulation of such intermediates is observed in the substitution reactions.[14] Furthermore, in the case of **13**-M, the rate law for the conversion of **13**-M back to reactants would be inconsistent with the observed rate law (eq 2). Additional arguments against a substitution mechanism have been presented for the reactions of **2**-M with amines where an analogous situation exists.[13]

One feature that distinguishes **9**-M from **2**-M, or **1**-M in general, is that the anions **9**-M⁻ do not decompose as rapidly as **2**-M⁻.[13,15] In the case of **2**-M⁻, the decomposition leads to $(CO)_5MOH^-$ and $CH_3CH{=}O$ as end products.[15] The decomposition reaction of **9**-M⁻ will be the subject of a future publication.[14] A practical consequence of the relatively slow decomposition of **9**-M⁻ is that it facilitated the kinetic study of the reactions of **9**-M⁻ with acidic buffers and also allowed spectrophotometric pK_a^{CH} determinations. With **2**-M⁻, its lifetime was so short that the reaction with acidic buffers had to be carried out in a double-mixing stopped-flow apparatus and no spectrophotometric pK_a^{CH} determination was possible.[13,16]

pK_a^{CH} Values. For **9**-Cr we have determined a $pK_a^{CH} = 9.03$ and for **9**-W a $pK_a^{CH} = 8.37$. This compares with $pK_a^{CH} = 12.50$ for **2**-Cr[13] and $pK_a^{CH} = 12.36$ for **2**-W.[16] Two features are noteworthy. (1) The thiomethoxy complexes are 3.5–4.0 pK_a units more acidic than the corresponding methoxy complexes. (2) The effect of the metal is significantly larger on the pK_a^{CH} of the thiomethoxy complexes ($\Delta pK_a^{CH} = 0.66$) than on the pK_a^{CH} values of the methoxy complexes ($\Delta pK_a^{CH} = 0.14$), with the W complex being more acidic in both cases.

The increased acidity of the MeS complexes is reminiscent of the enhanced acidity of CH_3COSEt ($pK_a = 21.0$)[17a] compared to that of CH_3COOEt ($pK_a = 26.5$).[17b] It can be mainly attributed to the smaller π-donor effect of the MeS group compared to the MeO group, as elaborated upon in the Introduction. A possible contributing factor may be an enhanced stabilization of the anion (**9**-M⁻) by the MeS group. Such carbanion stabilization is known to be important when the sulfur substituent is on an α-carbon and has been attributed to a polarizability effect and/or negative hyperconjugation;[18–24] an earlier view

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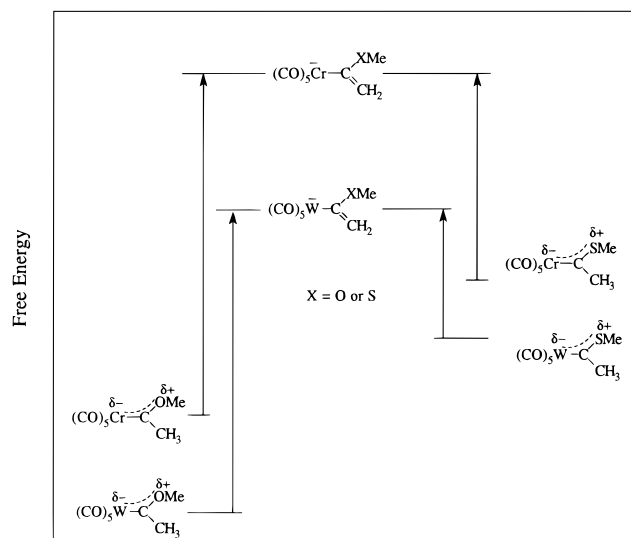
Figure 4. Schematic representation of energy levels of the various species involved in the ionization of **9**-M and **2**-M. It explains why the tungsten complexes are more acidic than the chromium complexes (anions more stable) but the pK_a^{CH} difference between the chromium and tungsten complex is larger for the MeS than for the MeO derivatives (less stabilization of the neutral carbene complexes by π-donation for the MeS derivatives).

that anion stabilization is the result of d–p π-resonance[25–28] is no longer advocated. In the present case, the MeS group is not on the α-carbon and hence probably too far removed from the anionic charge to have a significant effect; if there is an effect at all it may be offset by the stronger field/inductive effect of the MeO group.

The notion that the reduced π-donor effect of the MeS group is the main factor is supported by the fact that the pK_a^{CH} difference between **2**-Cr and **9**-Cr (3.47 pK_a units) and the pK_a^{CH} differences between **6** and **2**-Cr($\geq$10.3 pK_a units)[1] give an excellent correlation with the R⁺ substituent constants[29] of MeS (-0.83), MeO (-1.07), and Et₂N (-2.08).

The larger effect of the metal on the pK_a^{CH} values of the MeS complexes than on the MeO complexes may also be related to the reduced π-donor strength of the MeS group in the following way. The higher acidity of the tungsten complexes implies that the $(CO)_5W$ moiety stabilizes the anionic charge more effectively than the $(CO)_5Cr$ moiety. For the MeO complexes, this effect is largely offset by a similarly enhanced stabilization of the neutral tungsten carbene complex because of a major contribution of the resonance structure **8**± which places a substantial negative charge onto the $(CO)_5M$ moieties of **2**-M. For the MeS complexes, the contribution of **8**± is smaller, placing less negative charge onto the $(CO)_5M$ moieties of **9**-M. Hence the difference in the stability of **9**-Cr and **9**-W is relatively small and the pK_a^{CH} difference between **9**-Cr and **9**-W is a more accurate reflection of the different stabilities of the respective anions. The situation is shown schematically in Figure 4.

Rate Constants. All proton-transfer rate constants determined in this study are summarized in Table 1. The range of buffers

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

for which rate constants could be obtained is much larger than for **2**-Cr and **2**-W. For **2**-Cr and **2**-W, the k_{-1}^{BH} values for buffers with a pK_a^{BH} below that of *N*-(2-hydroxyethyl)pipera-zine ($pK_a^{BH} = 9.53$) were too high to allow determinations by the stopped-flow method.[13,16] With **9**-Cr and **9**-W, the k_{-1}^{BH} values are much lower and within experimental reach for buffers as acidic as $ClCH_2CO_2H$ ($pK_a^{BH} = 4.03$). This is mainly the result of the lower pK_a^{CH} values; a contributing factor is the lower *intrinsic rate constant*[30] for the reactions of **9**-Cr and **9**-W, as discussed below.

Comparison between **9**-Cr and **9**-W shows that for **9**-W the k_1^B values are higher and the k_{-1}^{BH} values are lower than for **9**-Cr; i.e., both the k_1^B and k_{-1}^{BH} contribute to the higher acidity of **9**-W. There is, however, a shift in the $k_1^B(W)/k_1^B(Cr)$ ratios from values of ~3 for weakly basic buffers, including water, to ~2 for highly basic ones; for the $k_{-1}^{BH}(W)/k_{-1}^{BH}(Cr)$ ratios the shift is from ~0.6 for weakly basic buffers to ~0.4 for highly basic ones. These shifts suggests a change in transition-state structure toward a more reactant-like character in the k_1^B direc-tion, in accordance with the Hammond−Leffler postulate.[32,33] For OH^- as the base, the $k_1^{OH}(W)/k_1^{OH}(Cr)$ ratio is actually slightly smaller than unity (0.70) and $k_{-1}^{H_2O}(W)/k_{-1}^{H_2O}(Cr) = 0.146$. This implies not only a continuation of the trend seen with the other bases but the operation of some additional factor that leads to a reversal of the reactivity of **9**-Cr and **9**-W. At this point, it is unclear what this factor is but it may be related to the unusually strong solvation of OH^-.[34] This solvation manifests itself in k_1^{OH} values that are much lower than one would expect based on the basicity of OH^-, a well-known phenomenon in proton transfers or nucleophilic reactions involving OH^-.[34,35] This is because the partial desolvation of OH^- required for the reaction to occur contributes substantially to the reaction barriers, and subtle differences in the degree of desolvation at the transition state for the reactions of **9**-Cr and **9**-W may be responsible for the observed reversal in reactivity.

Brønsted Plots and Intrinsic Rate Constants. Brønsted plots for the reaction of **9**-W with the primary aliphatic amines, the secondary alicyclic amines, and the carboxylate ions are shown in Figure 5; the corresponding plots for **9**-Cr (not shown) are quite similar. Brønsted α- and β-values as well as log k_o values for the intrinsic rate constants[30] are summarized in Table 2, along with the corresponding parameters for the deprotonation of **2**-Cr and **2**-M.

The Brønsted α- and β-values (Table 2), which are all within the usual range for proton transfers from Fischer carbene complexes[13,16] and many other carbon acids,[36,37] require little
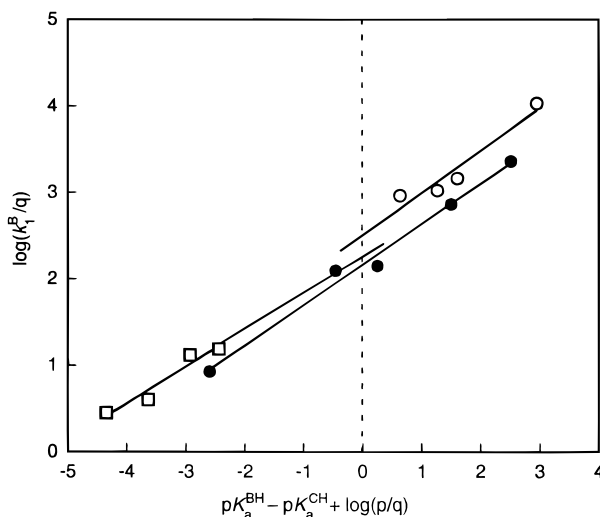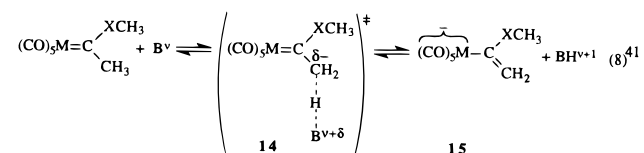
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(30) The intrinsic rate constant is the rate constant in the absence of a thermodynamic driving force.[31] To correct for statistical factors, one usually defines the intrinsic rate constant for proton transfer as $k_o = k_1^B/q = k_{-1}^{BH}/p$ when $pK_a^{BH} - pK_a^{CH} + \log(p/q) = 0$ with q being the number of equivalent basic sites on B and p the number of equivalent protons on BH.

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Figure 5. Brønsted plots for the reaction of **9**-W with primary aliphatic amines (●), secondary alicyclic amines (○), and carboxylate ions (□). Points of intersection between Brønsted lines and the vertical line at $pK_a^{BH} - pK_a^{CH} + \log(p/q) = 0$ correspond to log k_o; p is the number of equivalent protons on BH and q the number of equivalent basic sites on B.

comment. The focus of our discussion is on the intrinsic constants.[30] The intrinsic rate constants for the deprotonation of Fischer carbene complexes are typically quite low when compared with log k_o values for the deprotonation of other carbon acids;[8] only proton transfers involving nitroalkanes have significantly lower intrinsic constants. The log k_o for the reactions of **9**-Cr and **9**-W (Table 2) are well within the range of log $k_o \approx 1.4 - 3.7$ found for the deprotonation of other Fischer carbene complexes by amines.[8,38]

The low intrinsic rate constants have been attributed to the extensive resonance stabilization of the respective anions by charge dispersion into the $(CO)_5M$ moiety.[8,13,16] As is true for all reactions that lead to resonance-stabilized products,[40] the development of this resonance effect can be assumed to lag behind charge transfer at the transition state (eq 8).[41] As a

consequence, the resonance stabilization of the transition state is disproportionately small relative to its effect on the anion, which results in a high intrinsic barrier or low intrinsic rate constant.[40]

Effect of π-Donor Group on the Intrinsic Rate Constants. The log k_o values for the MeS derivatives are substantially lower than for the MeO derivatives; the difference is ~1.0 log unit for the chromium complexes and ~0.6−0.7 log unit for the

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(38) An exceptionally low log $k_o = -0.11$ has been found for the deprotonation of **1**-M (R = R′ = R″= CH_3, M = Cr).[39]

(39) Bernasconi, C. F.; Sun, W.; García-Río, L.; Yan, K.; Kettridge, K. *J. Am. Chem. Soc.* **1997**, *119*, 5583.

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(41) For emphasis, the negative charge of the transition state (**14**) is shown completely localized on the α-carbon, which is probably an exaggeration. At the same time, the representation of the negative charge of the anion (**15**) emphasizes its delocalization into the CO ligands.

Table 2. Summary of Brønsted α- and β-Values and of log k_o for the Intrinsic Rate Constants in 50% MeCN−50% Water at 25 °C

carbene complex	base type	β	α	log k_o
$(CO)_5Cr=C(SCH_3)CH_3$ (**9-Cr**)[a]	RNH$_2$	0.48 ± 0.04	0.52 ± 0.04	2.09 ± 0.08
	R$_2$NH	0.45 ± 0.06	0.55 ± 0.06	2.61 ± 0.10
	RCOO$^-$	0.44 ± 0.06	0.56 ± 0.06	2.17 ± 0.24
$(CO)_5W=C(SCH_3)CH_3$ (**9-W**)[a]	RNH$_2$	0.47 ± 0.03	0.53 ± 0.03	2.17 ± 0.05
	R$_2$NH	0.49 ± 0.09	0.51 ± 0.09	2.50 ± 0.18
	RCOO$^-$	0.43 ± 0.08	0.57 ± 0.08	2.27 ± 0.27
$(CO)_5Cr=C(OCH_3)CH_3$ (**2-Cr**)[b]	RNH$_2$	0.61 ± 0.06	0.39 ± 0.03	3.04 ± 0.17
	R$_2$NH	0.62 ± 0.03	0.38 ± 0.03	3.70 ± 0.07
$(CO)_5W=C(OCH_3)CH_3$ (**2-Cr**)[c]	RNH$_2$	0.64 ± 0.03	0.36 ± 0.03	2.73 ± 0.07
	R$_2$NH	0.49 ± 0.01	0.51 ± 0.01	3.18 ± 0.02

[a] This work. [b] Reference 13. [c] Reference 16.

tungsten complexes. There are several factors that may contribute to these differences.

(1) The MeO and MeS groups being closer to the negative charge at the transition state (**14**) than in the anion (**15**), their electron-withdrawing inductive/field effect should result in a transition-state stabilization that is disproportionately strong relative to their stabilization of the anion. This will reduce the intrinsic barrier of the reaction or increase the intrinsic rate constant, as discussed in more detail elsewhere.[40] Since the MeO group exerts a stronger inductive/field effect than the MeS group,[29] the increase in k_o for the MeO complexes will be greater.

(2) The larger size of the MeS group may lead to more steric crowding at the transition of the reactions of the MeS derivatives, thereby lowering k_o for the MeS relative to the MeO complexes. In general, steric effects on proton transfers from carbon acids are only significant when the α-carbon is highly substituted, e.g., HCXYZ or H$_2$CXY but not H$_3$CX.[42] However, in view of the large size of the $(CO)_5M$ groups, a steric effect on the proton transfer even from methyl carbene complexes cannot be dismissed. An indication that steric effects are indeed not negligible comes from the comparison of log k_o for secondary alicyclic amines (R$_2$NH) with log k_o for primary aliphatic amines (RNH$_2$). A difference of Δlog k_o = log k_o(R$_2$NH) − log k_o(RNH$_2$) in the order of 0.8−1.0 is considered normal for sterically unhindered proton transfers while smaller differences imply the operation of a steric effect.[43] In the present situation, the Δlog k_o values are 0.52 ± 0.18 for **9**-Cr, 0.33 ± 0.23 for **9**-W, 0.66 ± 0.24 for **2**-Cr, and 0.45 ± 0.09 for **2**-W, respectively, i.e., significantly below the normal values of 0.8−1.0. They indicate the operation of a steric effect in the reactions of both the MeO and the MeS complexes, but the lower Δlog k_o values for the MeS complexes are consistent with a stronger steric reduction of k_o for the MeS complexes.

(3) The π-donor effect of the MeO and MeS groups may also affect the intrinsic rate constants although it is more difficult to predict whether the net result would be an increase or a decrease in k_o. This is because there are two opposing factors. One is the loss of the resonance stabilization of the neutral carbene complexes (**8**$^\pm$), which must follow the general rule that applies to resonance effects, i.e., its loss must be ahead of proton transfer at the transition state.[40] This reduces k_o and more so for the MeO complex for which the resonance stabilization is stronger. The other factor is an attenuation of the lag in carbanion resonance development (**14**) by the π-donors. This comes about because the contribution of **8**$^\pm$ to the structure of the carbene complex leads to a preorganization of the $(CO)_5M$

moiety toward its electronic configuration in the anion. This should result in more charge being delocalized into the $(CO)_5M$ moiety at the transition state, leading to a lowering of its energy. The MeO group being a stronger π-donor than the MeS group, this will lead to a greater preorganization and hence to a lower intrinsic barrier (higher k_o) for the deprotonation of the MeO complexes.

Which of the two effects will prevail? There exist precedents for either situation. For example, in the reaction of nucleophiles with p-Me$_2$N- and p-MeO-substituted β-nitrostyrenes, the preorganization effect of **16**$^\pm$ is dominant and leads to an increase
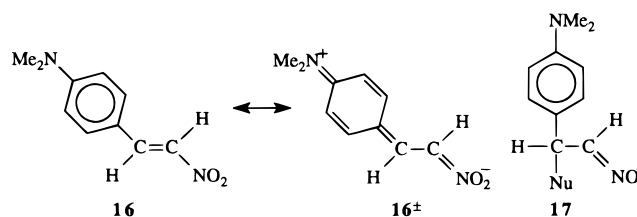
in the intrinsic rate constant for formation of **17**.[45] On the other hand, in the reaction of nucleophiles with the p-Me$_2$N and p-MeO derivatives of benzylidene Meldrum's acid,[46] benzylidenemalononitrile,[47] and benzylidenemalonaldehyde,[48] the effect of the early loss of resonance is dominant, leading to a *decrease* in k_o for nucleophilic addition.

On the basis of these results, it was argued that the π-donor leads to an increase in k_o for electrophiles activated by the strongest π-acceptor (NO$_2$) but to a decrease in k_o for electrophiles with weaker π-acceptors.[45−48] Regarding the Fischer carbene complexes, the π-acceptor strength of the $(CO)_5M$ moieties appears to be lower than that of a nitro group, as judged from the fact that typical values for k_o for the deprotonation of Fischer carbene complexes are higher than for the deprotonation of nitroalkanes.[13] This would suggest that the π-donor group should lower k_o, a notion that is consistent with the dependence of k_o on the metal, as discussed below. Note that since experimentally k_o for the MeO derivatives is higher than for the MeS derivatives, the π-donor effect that lowers the k_o(MeO)/k_o(MeS) ratio is apparently more than offset by the k_o(MeO)/k_o(MeS) ratio enhancing inductive/field and steric effects.

Effect of Metal on the Intrinsic Rate Constants. For the MeS derivatives the log k_o values are, within experimental error, independent of the metal while for the MeO derivatives log k_o

(42) For a recent review, see: Reference 40c.

(43) The higher k_o values for secondary amines is a well-known phenomenon caused by differences in the solvation energies of the respective protonated amines and the fact that at the transition state solvation of the incipient protonated amine lags behind proton transfer.[36a,40c,44]

(44) Jencks, W. P. *Catalysis in Chemistry and Enzymology*; McGraw-Hill: New York, 1968; p 178.

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for the chromium complex is somewhat higher than for the tungsten complex. This pattern appears to be related to the "inverse" pattern for the pK_a^{CH} values which show a greater dependence on the metal for the MeS derivatives than for the MeO derivatives. It is consistent with the notion that the effect of the π-donor groups is to lower the intrinsic rate constants because of the requirement that the loss of the resonance stabilization of the carbene complexes $8^{\pm}$ is ahead of the proton transfer at the transition state. For the MeO derivatives, the resonance stabilization of the neutral tungsten complex is substantially stronger than for the chromium complex (Figure 4). This implies that the reduction in k_o arising from the resonance loss at the transition state is also more pronounced for the tungsten complex than for the chromium complex, leading to log k_o(W) < log k_o(Cr). For the MeS derivatives, the difference in the resonance stabilization of the chromium and tungsten complex is small (Figure 4), and so is the difference in the reduction of k_o; hence log k_o(W) $\approx$ log k_o(Cr).

Conclusions

(1) The MeS carbene complexes are 3.5−4.0 pK_a units more acidic than the corresponding MeO carbene complexes. The main reason is the reduced stabilization of the neutral MeS carbene complexes due to the weaker π-donor effect of the MeS group.

(2) The pK_a^{CH} values of the MeS carbene complexes show a stronger dependence on the metal than the MeO carbene complexes. This, again, can be attributed to the weaker π-donor effect of the MeS group. For the MeO carbene complexes, the strong π-donor effect places a large fraction of negative charge on the $(CO)_5M$-moiety so that the greater stabilization of the negative charge by the $(CO)_5W$ moiety compared to the $(CO)_5Cr$ moiety in the anion is largely compensated by a similar effect in the neutral carbene complex. For the MeS carbene complexes, this compensating effect is smaller (Figure 4).

(3) The k_1^B(W)/k_1^B(Cr) ratios tend to become smaller with increasing basicity of the buffer base, suggesting a shift toward a more reactant-like transition state. This is consistent with the Hammond−Leffler postulate.

(4) The intrinsic rate constants for proton transfer are quite low, as is typical for reactions that lead to highly resonance stabilized anions.

(5) The intrinsic rate constants for deprotonation of the MeS carbene complexes are substantially lower than for deprotonation of the MeO carbene complexes. This is attributed to a combination of a decrease in k_o for the MeS derivatives by a steric effect and an increase in k_o for the MeO derivatives by the stronger electron-withdrawing inductive/field effect of the MeO group. There may be a small opposing effect on the k_o(MeO)/k_o(MeS) ratios due to the stronger π-donation by the MeO group, but the first two factors are clearly dominant.

(6) The k_o values for the MeS carbene complexes are independent of the metal while for the MeO complexes k_o(Cr) > k_o(W). This may be attributed to the stronger π-donor effect of the MeO group which leads to a larger reduction of k_o(W) than of k_o(Cr) from the loss of resonance stabilization at the transition state.

Experimental Section

Materials. The (thiomethoxymethylcarbene)pentacarbonyl complexes of chromium and tungsten (**9**-Cr and **9**-W) were prepared by reaction of the corresponding methoxy complexes (**2**-Cr and **2**-W) with NaSMe, using the procedure of Lam and Senoff.[49] The products were identified by NMR (250 MHz, CDCl$_3$) as follows: For **9**-Cr, ^{1}H NMR δ 2.68 (s, 3H, CH$_3$S) and 3.53 (s, 3H, CH$_3$);[50] ^{13}C NMR δ 26.87 (CH$_3$S), 46.03 (CH$_3$), 216.0 (CO, cis), 227.4 (CO, trans), 366.9 (C=). For **9**-W, ^{1}H NMR δ 2.54 (s, 3H, CH$_3$S) and 3.34 (s, 3H, CH$_3$);[50] ^{13}C NMR δ 27.46 (CH$_3$S), 48.07 (CH$_3$), 197.8 (CO, cis), 207.6 (CO, trans), 332.6 (C=). UV/visible (50% MeCN−50% water): **9**-Cr, λ_{max} 448 nm (ϵ 8450); **9**-W, λ_{max} 432 nm (ϵ 13 300). Mp 30−30.5 °C (lit.[51] 34 °C) for **9**-Cr and 33−34 °C (lit.[51] 34 °C) for **9**-W.

All reagents were Analar Grade (Aldrich). Liquid amines (piperidine, 1-(2-hydroxyethyl)piperazine, *n*-butylamine, morpholine) were refluxed over Na/CaH$_2$ and freshly distilled. Piperazine was recrystallized from water. The other amines were in their HCl salt form and were recrystallized from water or water−ethanol. Chloroacetic acid and 3-chloropropionic acid were recrystallized from water; acetic and methoxyacetic acid were used as received. Acetonitrile (Fisher Scientific) was 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 solutions in 50% MeCN−50% water prior to use. Typical concentrations of **9**-Cr and **9**-W for kinetic runs were $(5−9) \times 10^{-5}$ M. All kinetic experiments were performed in an Applied Photophysics DX.17MV stopped-flow apparatus. The ionic strength was maintained at 0.1 M with KCl. Kinetics were followed at the λ_{max} of the carbene complex. For the reactions run in the direction **9**-M$^-$ + BH → **9**-M + B, the anion was first generated in the presence of 0.004 M KOH outside the stopped-flow apparatus and then immediately injected into one of the stopped-flow syringes for a subsequent stopped-flow experiment. For these experiments, the buffer solutions were prepared in a manner that they would neutralize the KOH used to generate the anion. The k_1^{OH} values were based on 11 runs at [KOH] between 0.001 and 0.1 M. For the reaction with morpholine buffers, eight runs at total buffer concentrations ranging from 0.01 to 0.2 M were conducted at eight different pH values. The reactions with the other buffers were run at one pH only, with seven to eight different total buffer concentrations ranging from 0.01 to 0.1 or 0.2 M.

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.[52]

The absorption spectra were recorded on a Hewlett-Packard 8452A diode array UV−visible spectrophotometer.

(49) Lam, C. T.; Senoff, C. F. *J. Organomet. Chem.* **1974**, *70*, 273.
(50) The ^{1}H NMR spectra are very similar to those reported by Fischer et al.[51] in CDCl$_3$: **9**-Cr, δ 2.65 (s, 3H, CH$_3$S) and 3.50 (s, 3H, CH$_3$); **9**-W, δ 2.94 (s, 3H, CH$_3$S) and 3.60 (s, 3H, CH$_3$).
(51) Fischer, E. O.; Leupold, M.; Kreiter, C. G.; Müller, J. *Chem. Ber.* **1972**, *105*, 150.
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