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Physical Organic Chemistry of Transition Metal Carbene Complexes. 24. Thermodynamic and Kinetic Acidities of Phenyl-Substituted (Benzylmethoxycarbene)pentacarbonylchromium(0) Complexes. Is There a Transition-State Imbalance?[†]

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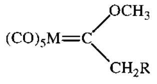
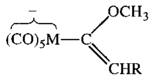
Abstract: A kinetic study of the reversible deprotonation of phenyl-substituted (benzylmethoxycarbene)-pentacarbonylchromium(0) complexes by OH^- and by a series of primary aliphatic and a series of secondary alicyclic amines in 50% MeCN−50% water (v/v) at 25 °C is reported. Brønsted α_{CH} values (dependence on carbene complex acidity) and β_B values (dependence on amine basicity) were determined. According to current notions about proton transfers involving carbon acids activated by π-acceptors, α_{CH} was expected to substantially exceed β_B, the result of transition-state imbalances that are characteristic of such reactions. However we find that α_{CH} and β_B have essentially the same values, which are close to 0.5. It is shown that these findings do not indicate the absence of an imbalance but rather suggest that the manifestation of the imbalance is masked by the π-donor effect (**3H-Z** ↔ **3H-Z**$^\pm$) of the methoxy group.

Introduction

Fischer carbene complexes of the type **1H** (M = Cr, W, Mo) and related structures are relatively strong acids because the $(CO)_5M$ moiety acts as a powerful π-acceptor; i.e., the carbanion (**1**$^-$) is stabilized by delocalization of the negative charge into the carbonyl ligands of the $(CO)_5M$ moiety.[1,2] For example, the

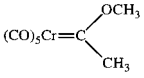


1H

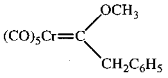


1$^-$

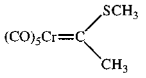
pK_a^{CH} values (CH stands for carbon acid) of **2H** and **3H** in 50% MeCN−50% water (v/v) at 25 °C are 12.50 and 10.40,[3] respectively, while substituting the methoxy group with a thiomethyl group (**4H**, pK_a^{CH} = 9.05)[4] further increases the acidity due to the reduced π-donor effect of the thiomethyl group. These pK_a^{CH} values are comparable to those of some



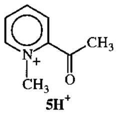
2H



3H



4H



5H$^+$

purely organic carbon acids such as nitroalkanes, e.g., CH_3NO_2 (pK_a^{CH} = 11.32)[5,6] or $PhCH_2NO_2$ pK_a^{CH} = 7.93);[5,6] some diketones, e.g., acetylacetone (pK_a^{CH} = 9.12);[5,7] some special monoketones such as 2-acetyl-1-methylpyridinium ion (**5H**$^+$, pK_a^{CH} = 11.75);[5,8] or some (nitrophenyl)acetonitriles, e.g., (4-nitrophenyl)acetonitrile (pK_a^{CH} = 12.62).[5,9] The high acidities of these latter compounds can again mainly be traced to the effective stabilization of their conjugate anions by charge delocalization into the respective π-acceptor groups.

Another characteristic Fischer carbene complexes share with the above organic carbon acids is that the rate constants for deprotonation of **1H**/protonation of **1**$^-$ are much lower than for normal acids,[10] indicating that the Marcus intrinsic barrier[11a] ($\Delta G_0^\ddagger$) for proton transfer is quite high or the intrinsic rate constant (k_0) is low.[11b] Intrinsic rate constants for the deprotonation of a representative group of carbon acids by secondary alicyclic amines are summarized in Table 1.

As discussed in detail elsewhere,[10] there is a direct connection between the low k_0 values and the charge delocalization in the

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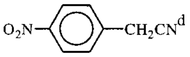
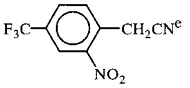
[†] Part 23: Bernasconi, C. F.; Ragains, M. L. *J. Am. Chem. Soc.* **2001**, *123*, 11890.

(1) Bernasconi, C. F.; Ragains, M. L. *J. Am. Chem. Soc.* **2001**, *123*, 11890.
(2) For a recent review, see Bernasconi, C. F. *Chem. Soc. Rev.* **1997**, *26*, 299.
(3) Bernasconi, C. F.; Sun, W. *J. Am. Chem. Soc.* **1993**, *115*, 12526.
(4) Bernasconi, C. F.; Ali, M. *J. Am. Chem. Soc.* **1999**, *121*, 3039.
(5) In 50% DMSO−50% water.
(6) Bernasconi, C. F.; Kliner, D. A. V.; Mullin, A. S.; Ni, J. X. *J. Org. Chem.* **1988**, *53*, 3342.
(7) Bernasconi, C. F.; Bunnell, R. D. *Isr. J. Chem.* **1985**, *26*, 420.
(8) Bernasconi, C. F.; Moreira, J. A.; Huang, L. L.; Kittredge, K. W. *J. Am. Chem. Soc.* **1999**, *121*, 1674.
(9) Bernasconi, C. F.; Hibdon, S. A. *J. Am. Chem. Soc.* **1983**, *105*, 4343.
(10) (a) Bernasconi, C. F. *Acc. Chem. Res.* **1987**, *20*, 301. (b) Bernasconi, C. F. *Adv. Phys. Org. Chem.* **1992**, *27*, 119. (c) Bernasconi, C. F. *Acc. Chem. Res.* **1992**, *25*, 9.
(11) (a) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891. (b) The intrinsic barrier (intrinsic rate constant) is the barrier (rate constant) in the absence of a thermodynamic driving force. To correct for statistical factors, one usually defines the intrinsic rate constant for proton transfer as $k_0 = k_1^B/q = k_{-1}^{BH}/p$ 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.

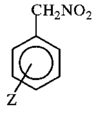
Table 1. Intrinsic Rate Constants (k_0)[a] for the Deprotonation of Various Carbon Acids by Secondary Alicyclic Amines

CH acid	pK_a^{CH}	log k_0
normal acids[b]	any	8.5−9.5
$(CO)_5Cr{=}C(OCH_3)CH_3$[c]	12.50	3.70
	12.62	3.70
	10.71	3.35
$(CO)_5Cr{=}C(SCH_3)CH_3$[f]	9.05	2.61
$CH_2(COCH_3)_2$[g]	9.12	2.75
$(CO)_5Cr{=}C(OCH_3)CH_2Ph$[c]	10.40	1.86
5H$^+$[h]	11.75	1.70
CH_3NO_2[i]	11.32	0.73
$PhCH_2NO_2$[i]	7.93	−0.25

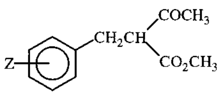
[a] For a definition of k_0 see ref 11b. [b] Reference 29. [c] In 50% MeCN−50% water, ref 3. [d] In 50% DMSO−50% water, ref 9. [e] In 50% DMSO−50% water, ref 18. [f] In 50% MeCN−50% water, ref 4. [g] In 50% DMSO−50% water, ref 7. [h] In 50% DMSO−50% water, ref 8. [i] In 50% DMSO−50% water, ref 6.

carbanion. This connection is the result of a transition-state imbalance in which resonance stabilization by charge delocalization into the π-acceptor(s) lags behind proton transfer.[12] The imbalance prevents the transition state from benefitting from the energetic advantage of resonance delocalization and leads to an enhanced intrinsic barrier. This barrier enhancement is roughly proportional to the delocalization energy of the carbanion.

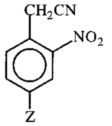
The existence of these imbalances can be deduced from Brønsted coefficients, specifically from a comparison of Brønsted α_{CH} values obtained by varying a remote substituent in the carbon acid such as Z in **6H-Z**, **7H-Z**, or **8H-Z**, with the Brønsted β_B value obtained by varying the buffer base, e.g., a series of secondary alicyclic amines.[13] Depending on where Z is located with respect to the site of charge development, one observes either $\alpha_{CH} > \beta_B$ or $\alpha_{CH} < \beta_B$. When Z is closer to the charge at the transition state than in the carbanion, $\alpha_{CH} > \beta_B$: e.g., **9-Z** vs **6-Z⁻**, where $\alpha_{CH} = 1.29$ and $\beta_B = 0.56$ for the reactions with secondary alicyclic amines,[14,15] or **10-Z** vs **7-Z⁻**, where $\alpha_{CH} = 0.76$ and $\beta_B = 0.44$ for the reactions with carboxylate ions.[14,16]



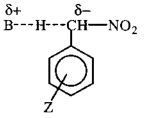
6H-Z



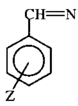
7H-Z



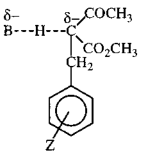
8H-Z



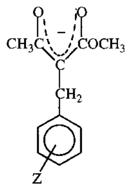
9-Z



6-Z⁻

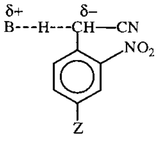


10-Z

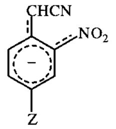


7-Z⁻

When Z is closer to the charge in the carbanion than at the transition state, $\alpha_{CH} < \beta_B$: e.g., **11-Z** vs **8-Z⁻** , where $\alpha_{CH} = 0.40$ and $\beta_B = 0.58$ for the reactions with secondary alicyclic amines.[17,18]

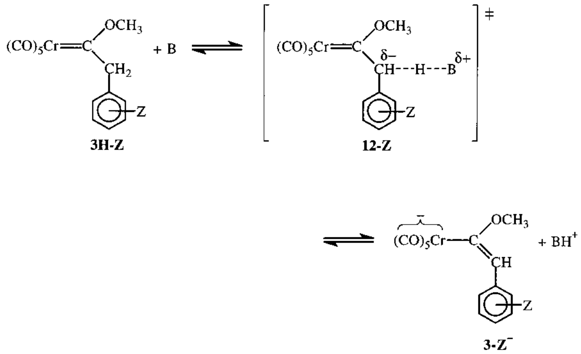


11-Z



8-Z⁻

Since the pK_a^{CH} and k_0 values for the Fischer carbene complexes imply that their behavior and properties are similar to those of organic carbon acids activated by π-acceptors, one would expect the transition state for proton transfer to show the usual imbalances. Specifically, for the deprotonation of **3H-Z** (eq 1), α_{CH} should be considerably larger than β_B since the negative charge is presumably closer to Z at the transition state (**12-Z**) than in the anion (**3-Z⁻**). The objective of the present paper was to confirm this hypothesis. Much to our surprise, we find that for the reactions of **3H-Z** with primary aliphatic and secondary alicyclic amines, α_{CH} and β_B are, within experimental error, the same. Possible reasons for this unexpected result will be discussed.



(1)

Results

General Features. The reactions of **3H-Z** (Z = 4-OMe, 4-Me, H,[3] 3-F) with a series of primary aliphatic and secondary alicyclic amines as well as OH^- were investigated in 50% MeCN−50% water (v/v) at 25 °C. The synthesis of these carbene complexes was based on a method reported by Fischer et al.[19] Attempts at preparing additional substrates with substituents more electron-withdrawing than 3-F either failed or the products were so unstable as to make them unsuitable for a kinetic study.

The three substituted complexes (Z = 4-OMe, 4-Me, 3-F) showed qualitatively similar behavior as the parent complex (Z = H) investigated earlier;[3] i.e., upon mixing with KOH or an amine buffer, two kinetic processes were observed. The first is quite fast and refers to the proton transfer, while the much

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(12) This situation refers to the deprotonation of the carbon acid by the buffer base. In the reverse direction where the buffer acid protonates the carbanion, the imbalance manifests itself in a loss of resonance that is ahead of the proton transfer.

(13) The corresponding Brønsted coefficients in the direction of protonation of the carbanion are β_C and α_{BH}, respectively; see footnotes in Tables 3 and 4.

(14) In water.

(15) Bordwell, F. G.; Boyle, W. J., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 3907.

(16) Bell, R. P.; Grainger, S. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1367.

(17) In 90% DMSO−10% water.

(18) Bernasconi, C. F.; Wenzel, P. J. *J. Am. Chem. Soc.* **1996**, *118*, 11446.

(19) Fischer, E. O.; Kreiter, C. G.; Kollmeier, H. J. *J. Organomet. Chem.* **1971**, *28*, 237.

Table 2. Summary of Proton Transfer Rate Constants and pK_a Values in 50% MeCN−50% Water (v/v) at 25 °C[a]

base	pK_a^{BH}	$k_1^{B\,b}$ ($M^{-1}\,s^{-1}$)	$k_{-1}^{BH\,c}$ ($M^{-1}\,s^{-1}$)
$(CO)_5Cr{=}C(OCH_3)CH_2C_6H_4$-3-F (**3H-F**), p$K_a^{CH}$ = 9.73 ± 0.06			
n-$BuNH_2$	10.40	181	40.0
$MeOCH_2CH_2NH_2$	9.39	32.6	79.1
$H_2NCOCH_2NH_2$	8.14	5.43	219
H_2NCH_2CN	5.29	0.42	1.20×10^4
piperidine	11.01	486	26.4
piperazine	9.97	140	83
HEPA[d]	9.33	58.9	153
morpholine	8.70	55.4	615
OH^-	16.64[e]	235[f]	8.38×10^4 [g]
$(CO)_5Cr{=}C(OCH_3)CH_2C_6H_5$ (**3H**),[h] pK_a^{CH} = 10.40			
n-$BuNH_2$	10.40	75.5	75.5
$MeOCH_2CH_2NH_2$	9.39	16.1	165
$H_2NCOCH_2NH_2$	8.14	2.30	413
$NCCH_2NH_2$	5.29	0.126	1.61×10^3
piperidine	11.01	225	55.0
piperazine	9.97	74.8	200
HEPA[d]	9.33	25.2	295
morpholine	8.70	19.5	978
OH^-	16.64[e]	115[f]	1.90×10^{-3} [g]
$(CO)_5Cr{=}C(OCH_3)CH_2C_6H$-4-Me (**3H-Me**), p$K_a^{CH}$ = 10.50 ± 0.06			
n-$BuNH_2$	10.40	72.1	89.9
piperidine	11.01	201	61.4
OH^-	16.64[e]	97.6[f]	1.71×10^{-3} [g]
$(CO)_5Cr{=}C(OCH_3)CH_2C_6H_4$-4-OMe (**3H-OMe**), p$K_a^{CH}$ = 10.68 ± 0.06			
n-$BuNH_2$	10.40	61.0 ± 6.6	98.3
piperidine	11.01	180	64.1
OH^-	16.64[e]	85.2[f]	2.29×10^{-3} [g]

[a] Ionic strength 0.1 M (KCl). [b] Estimated uncertainty ≤5%. [c] Estimated uncertainty ≤10%. [d] HEPA = 1-(2-hydroxyethyl)piperazine. [e] pK_w = 15.19, ref 3. [f] $k_1^B = k_1^{OH}$. [g] $k_{-1}^{BH} = k_{-1}^{H_2O}$, in units of reciprocal seconds. [h] Reference 3.

slower second process leads to hydrolytic cleavage of the anion.[20] This paper focuses on the proton-transfer step only.

Kinetics. All rate determinations were performed under pseudo-first-order conditions with the substrate as the minor component. Hence the observed pseudo-first-order rate constants for approach to equilibrium are given by eq 2, with the various rate constants defined in eq 3.

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

$$\mathbf{3H\text{-}Z} \underset{k_{-1}^{H}a_{H^+} + k_{-1}^{H_2O} + k_{-1}^{BH}[BH]}{\overset{k_1^{H_2O} + k_1^{OH}[OH^-] + k_1^{B}[B]}{\rightleftharpoons}} \mathbf{3\text{-}Z}^- \quad (3)$$

All measurements were performed in a stopped-flow spectrophotometer. Depending on the pH, the reactions were run either in the forward direction (**3H-Z** → **3-Z**$^-$ at pH > pK_a^{CH}) or in the reverse direction (**3-Z**$^-$ → **3H-Z** at pH < pK_a^{CH}).

The rate constants for all reactions, including those for **3-H** determined previously,[3] are summarized in Table 2. They were obtained as follows. For **3H-Me** and **3H-OMe** the reactions were first run in n-butylamine buffers at various pH values, and for **3H-F** in $MeOCH_2CH_2NH_2$ buffers. A representative series of plots of k_{obsd} vs [B] is shown in Figure 1. The slopes of these plots are given by

$$\text{slope} = k_1^{B}\left(1 + \frac{a_{H^+}}{K_a^{CH}}\right) \quad (4)$$

They, as well as the raw data, are reported in Tables S1−S3 of the Supporting Information.[21] Plots of these slopes vs a_{H^+} (see Figure 2 for a representative plot) yield k_1^B and K_a^{CH}, and k_{-1}^{BH} is obtained as $k_1^B K_a^{BH}/K_a^{CH}$, with K_a^{BH} being the acidity constant of the buffer acid.

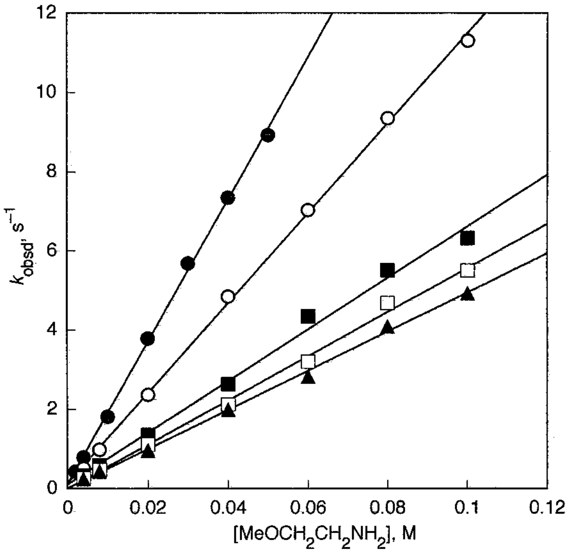

Figure 1. Pseudo-first-order rate constants for the reaction of **3H-F** with $MeOCH_2CH_2NH_2$: ●, pH 9.07; ○, pH 9.39; ■, pH 9.68; □, pH 9.88; ▲, pH 9.98.

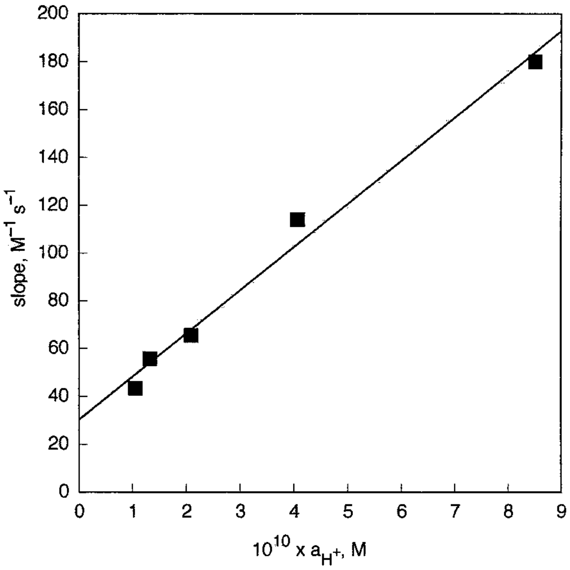

Figure 2. Reaction of **3H-F** with $MeOCH_2CH_2NH_2$: plot of slope vs a_{H^+} according to eq 4.

For the reactions with the other amines, data were obtained at only one pH, eq 4 was solved for k_1^B, and k_{-1}^{BH} was obtained as above. The k_1^{OH} values were determined as the slopes of plots of k_{obsd} vs [KOH], and $k_{-1}^{H_2O}$ was calculated as $k_1^{OH}K_w/K_a^{CH}$, with K_w being the ionic product of the solvent (Table 2, footnote e); the raw data are reported in Table S6.[21]

Discussion

The main objective of this work was to determine whether the proton-transfer reactions of **3H-Z** are associated with a

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(20) Bernasconi, C. F.; Sun, W. *Organometallics* **1995**, *14*, 5615.

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

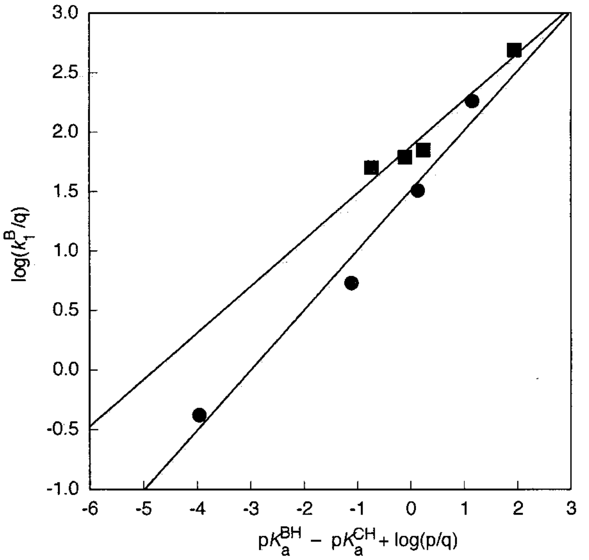


Figure 3. Brønsted plots for the reaction of **3H-F** with primary aliphatic amines (●) and secondary alicyclic amines (■).

Table 3. Brønsted β_B and α_{BH} Values for the Dependence on Amine Basicity (Figure 3) and Intrinsic Rate Constants

amine type	$\beta_B{}^a$	$\alpha_{BH}{}^b$	log $k_0{}^c$
	$(CO)_5Cr{=}C(OCH_3)CH_2C_6H_4$-4-F (**3H-F**)		
RNH_2	0.50 ± 0.05	0.50 ± 0.05	1.53 ± 0.12
R_2NH	0.44 ± 0.11	0.56 ± 0.11	1.91 ± 0.09
	$(CO)_5Cr{=}C(OCH_3)CH_2C_6H_5$ (**3H**)^d		
RNH_2	0.54 ± 0.04	0.46 ± 0.04	1.51 ± 0.10
R_2NH	0.48 ± 0.07	0.53 ± 0.07	1.86 ± 0.07

^{a} $\beta_B = d(\log k_1{}^B/q)/dpK_a{}^{BH}$. ^{b} $\alpha_{BH} = d(\log k_{-1}{}^{BH}/p)/d\log K_a{}^{BH}$. ^{c} Log $k_0 = \log(k_1{}^B/q) = \log(k_{-1}{}^{BH}/p)$ for $pK_a{}^{BH} - pK_a{}^{CH} + \log(p/q) = 0$. ^{d} Reference 3.

substantial transition-state imbalance. In analogy to the reactions with other carbon acids activated by π-acceptors, in the k_1^B direction such imbalance would be expected to manifest itself in the Brønsted α_{CH} value significantly exceeding the β_B value, or in the k_{-1}^{BH} direction,[13] β_C should be smaller than α_{BH}.

Brønsted plots for the reactions of **3H-F** with a series of primary aliphatic and secondary alicyclic amines are shown in Figure 3; they yield the β_B and (α_{BH}) values as well as the log k_0 values reported in Table 3. Figure 4 shows Brønsted plots for the reactions of the four **3H-Z** complexes with n-BuNH$_2$, piperidine, and OH$^-$; they yield the α_{CH} (and β_C) values reported in Table 4.

The β_B (α_{BH}) values show little dependence on the Z substituent or the type of amine; the experimental uncertainties in these parameters are too large to determine whether the slightly smaller β_B values with the secondary alicyclic amines and the slight difference in β_B between **3H** and **3H-F** represent a real effect. With respect to the α_{CH} (β_C) values, they are essentially independent of the type of base. More importantly, the α_{CH} values barely exceed the β_B values: e.g., $\beta_B = 0.50 \pm 0.05$ to 0.54 ± 0.04 and $\alpha_{CH} = 0.56 \pm 0.03$ for the reactions with primary amines; $\beta_B = 0.44 \pm 0.11$ to 0.48 ± 0.07 and $\alpha_{CH} = 0.53 \pm 0.07$ for the reactions with secondary amines. This compares with $\alpha_{CH} - \beta_B = 1.29 - 0.56 = 0.73$ for the reactions of **6H-Z** with secondary alicyclic amines[14,15] or $\alpha_{CH} - \beta_B = 0.76 - 0.44 = 0.32$ for the reactions of **7H-Z** with carboxylate ions.[14,16]

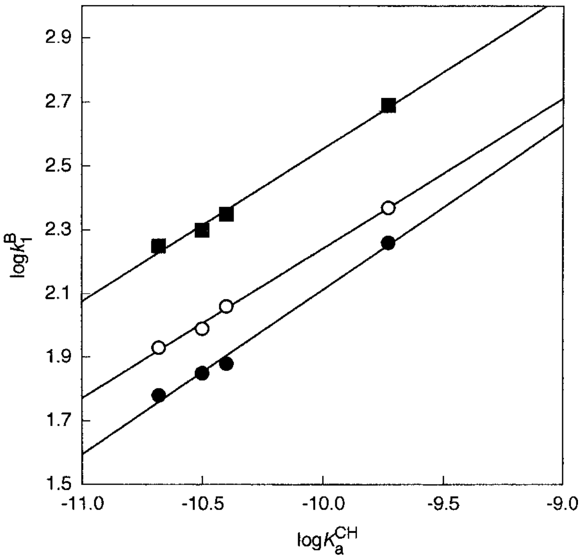


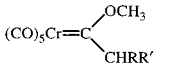
Figure 4. Brønsted plots for the reactions of **3H-Z** (Z = 4-OMe, 4-Me, H, 3-F) with piperidine (■), OH$^-$ (○), and n-BuNH$_2$ (●).

Table 4. Brønsted α_{CH} and β_B Values from the Dependence on Carbene Complex Acidity

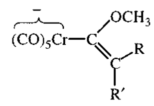
base	$\alpha_{CH}{}^a$	$\beta_C{}^b$
n-BuNH$_2$	0.56 ± 0.03	0.44 ± 0.03
piperidine	0.53 ± 0.02	0.47 ± 0.02
OH$^-$	0.50 ± 0.07	0.50 ± 0.07

^{a} $\alpha_{CH} = d\log k_1{}^{BH}/d\log K_a{}^{CH}$. ^{b} $\beta_C = d\log k_{-1}{}^{BH}/d\,pK_a{}^{CH}$.

In view of the low intrinsic rate constants (Table 3) that place **3H** and **3H-F** toward the low end of the log k_0 values listed in Table 1, one would have expected a much larger difference between α_{CH} and β_B. Our results raise the question whether there is a fundamental difference between the (CO)$_5$Cr moiety and purely organic π-acceptors in the way they affect intrinsic barriers; i.e., is it conceivable that the (CO)$_5$Cr moiety would raise intrinsic barriers without a transition-state imbalance? This notion seems unlikely on principle, and there is experimental evidence that strongly suggests that the deprotonation of carbene complexes such as **13a**, **13b**, and **13c** does involve an imbalanced transition state. This evidence is based on the fact that the acidities increase in the order **13a** < **13b** < **13c** but the rate constants for deprotonation by OH$^-$ *de*crease in the order **13a** > **13b** > **13c**.[22] The trend in the acidities reflects the increasing stabilization of the C═C double bond of the anion (**14**) by the methyl groups; the trend in the rate constants can be understood in terms of an imbalanced transition state (**15**) where there is minimal development of the C═C double bond—hence no increased stabilization—coupled with destabilization of the partial negative charge by the methyl groups.[23]



13a (R = R′ = H)
13b (R = H, R′ = CH$_3$)
13c (R = R′ = CH$_3$)



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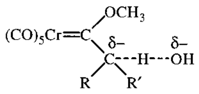

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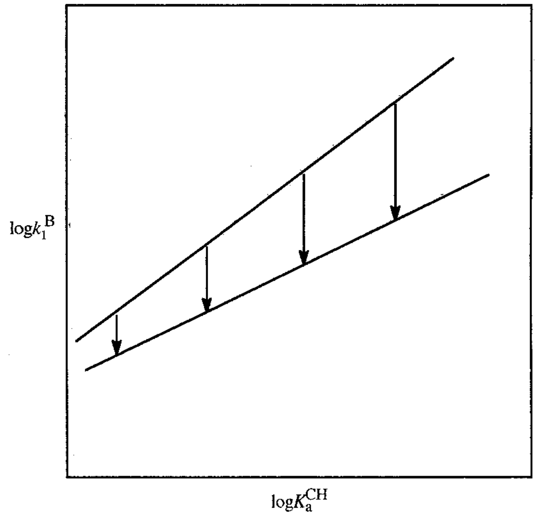
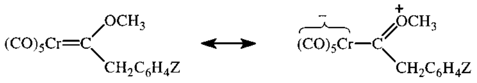


Figure 5. Schematic representation of how the Brønsted slope (α_{CH}) is lowered as the result of the π-donor effect of the MeO group; see text.

A more reasonable hypothesis is that the transition state **12-Z** *is* imbalanced, as shown in eq 1, but that there is a structural feature characteristic of carbene complexes, which is absent from other carbon acids, that masks the imbalance by reducing α_{CH}. The most likely candidate is the methoxy group attached to the Cr=C system. It is well-known that because the carbene carbon is highly electron-deficient,[25,26] the methoxy group exerts a strong π-donor effect (**3H-Z**$^{\pm}$) that stabilizes the carbene complex.[4,25,26] Inasmuch as the contribution of **3H-Z**$^{\pm}$ leads to resonance stabilization of the carbene complexes, this resonance is expected to add to the intrinsic barrier of proton transfer. This is because, as is true for resonance effects in general, its loss at the transition state should be ahead of the proton transfer.[10] As Z becomes more electron-withdrawing, the greater electron deficiency of the carbene carbon induces a stronger π-donor effect by the methoxy group. There are two consequences. One is that the increased contribution of the resonance structure **3H-Z**$^{\pm}$ partially compensates for the destabilization of the electron-deficient carbene carbon by the electron-withdrawing inductive effect of Z. The second is that the increased resonance stabilization of the carbene complex increases the intrinsic barrier and hence the rate (k_1^B) enhancement caused by the inductive effect of Z will be attenuated. This attenuation is proportional to the electron-withdrawing strength of Z as illustrated schematically in Figure 5 and hence the slope of the Brønsted plot (α_{CH}) is reduced.

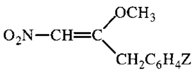


$$(CO)_5Cr{=}C(OCH_3)(CH_2C_6H_4Z) \longleftrightarrow (CO)_5\overset{-}{Cr}{-}C({=}\overset{+}{O}CH_3)(CH_2C_6H_4Z)$$

3H-Z **3H-Z±**

An alternative view is that the contribution of **3H-Z**$^{\pm}$ to the structure of the carbene complex is tantamount to preorganizing the $(CO)_5Cr$ moiety toward its structure and charge in the anion. Since this preorganization is likely to be maintained at the transition state, the difference in the distribution of the negative charge between transition state and anion is less dramatic, implying a smaller imbalance.

The notion that the π-donor effect of the methoxy group is responsible for the reduced difference between α_{CH} and β_B is supported by data on the reaction of **16H-Z** with amines, which indicate a much smaller difference between α_{CH} and β_B than for the corresponding reactions of **6H-Z**.[27]



$$O_2N{-}CH{=}C(OCH_3)(CH_2C_6H_4Z)$$

16H-Z

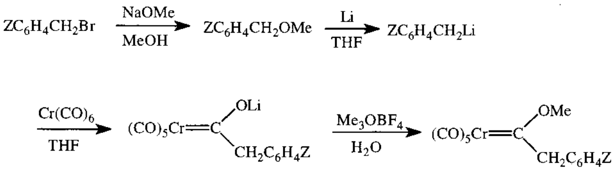
Conclusions

The proton-transfer reactions of **3H-Z** are characterized by high intrinsic barriers ($\Delta G_0^{\ddagger}$) or low intrinsic rate constants (k_0), as is typical for carbon acids activated by strong π-acceptors. However, the transition-state imbalance that has been shown to be responsible for the high intrinsic barriers with purely organic carbon acids does not manifest itself in the Brønsted coefficients of the deprotonation of **3H-Z**; specifically, α_{CH} does not significantly exceed β_B. This result is attributed to the π-donor effect of the methoxy group, which contributes to the intrinsic barrier because the loss of the stabilizing influence of the methoxy group on the neutral carbene complex runs ahead of the proton transfer at the transition state. Since the π-donor effect increases with increasing electron-withdrawing strength of Z, k_0 decreases and partially offsets the substituent effect on the deprotonation rate constant; the result is a lower α_{CH} value.

Experimental Section

Synthesis of 3H-Z (Z = 4-Me, 4-OMe, 3-F). The synthesis of the carbene complexes involved the transformations shown in Scheme 1.

Scheme 1



$$ZC_6H_4CH_2Br \xrightarrow[MeOH]{NaOMe} ZC_6H_4CH_2OMe \xrightarrow[THF]{Li} ZC_6H_4CH_2Li$$

$$\xrightarrow[THF]{Cr(CO)_6} (CO)_5Cr{=}C(OLi)(CH_2C_6H_4Z) \xrightarrow[H_2O]{Me_3OBF_4} (CO)_5Cr{=}C(OMe)(CH_2C_6H_4Z)$$

4-Methylbenzyl Methyl Ether.[28] 4-Methylbenzyl bromide (15 g, 0.08 mol) in 25 mL of diethyl ether was added to a NaOMe solution prepared from 96 g (0.4 mol) of sodium and 100 mL of methanol at reflux within 40 min. Refluxing and stirring continued for 15 h. Water (40 mL) was added to the cooled solution and methanol was removed by distillation. The residue was extracted 3 times, each with 20 mL of diethyl ether. The ether solution was washed with water and dried over $CaCl_2$. The product was obtained by vacuum distillation with a yield of 65%. ^1H NMR (250 MHz, $CDCl_3$) δ 2.30 (s, 3H, $ArCH_3$), 3.31 (s, 3H, OCH_3), 4.36 (s, 2H, CH_2), 7.01−7.14 (m, 4H, C_6H_4).

4-Methoxybenzyl Methyl Ether and 3-Fluorobenzyl Methyl Ether. The procedures were identical to that for the synthesis of 4-methylbenzyl methyl ether. Methoxy derivative: yield 80%; ^1H NMR (250 MHz, $CDCl_3$) δ 3.40 (s, 3H, CH_2OCH_3), 3.81 (s, 3H, $ArOCH_3$), 4.41 (s, 2H, CH_2), 7.10 (q, 4H, C_6H_4). Fluoro derivative: yield 34%; ^1H NMR (250 MHz, $CDCl_3$) δ 3.39 (s, 3H, OCH_3), 4.44 (s, 2H, CH_2), 7.08−7.31 (m, 4H, C_6H_4).

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(23) These results are reminiscent of the "nitroalkane anomaly", where the acidities of methyl substituted nitroalkanes follows the order $CH_3NO_2 < CH_3CH_2NO_2 < (CH_3)_2CHNO_2$ and the rate constants for deprotonation by OH^- decrease in the order $CH_3NO_2 > CH_3CH_2NO_2 > (CH_3)_2CHNO_2$.[24]

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$ZC_6H_4CH_2Li$. The lithium compounds were prepared by the method of Gilman et al.[28]

Carbene Complexes. The carbene complexes were prepared by the method of Fischer et al.[19] **3H-Me** was obtained as yellow crystals in 35% yield, mp 62−64 °C. ^{1}H NMR (250 MHz, CD_3CN) δ 2.29 (s, 3H, ArCH_3), 4.57 (s, 2H, CH_2), 4.73 (s, 3H, OCH_3), 7.01−7.14 (q, 4H, C_6H_4); ^{13}C NMR (CD_3CN) 359.1 (C═), 224.4 and 217.3 (CO), 137.5, 133.1, and 130.4 (C_6H_4), 69.4 (OCH_3), 21.0 (ArCH_3); IR (CD_3CN) 2062 (CO), 1937 (CO); EI-MS m/z 340 (M^+, 75%), 312 (98%), 256 (43%), 200 (33%), 185 (31%), 157 (100%), 105 (12%); UV/vis λ_{max} 376 nm [log ϵ = 3.82) in 50% MeCN−50% water]. **3H-OMe** was obtained as a solid product in 21% yield, mp 65.5−67.5 °C. ^{1}H NMR (250 MHz, CD_3CN) δ 3.74 (s, 3H, ArOCH_3), 4.53 (s, 2H, CH_2), 4.73 (s, 3H, CH_3), 6.79−7.08 (q, 4H, C_6H_4); ^{13}C NMR (CD_3CN) δ 359.1 (C═), 224.7 and 217.3 (CO), 131.6, 126.1 and 114.7 (C_6H_4), 69.4 (OCH_3), 67.5 (CH_2), 55.8 (ArOCH_3); IR (CD_3CN) 2062 (CO), 1940 (CO); EI-MS m/z 356 (M^+, 53%), 328 (98%), 272 (47%), 244 (20%), 216 (33%), 201 (31%), 173 (100%), 121 (26%); UV/vis λ_{max} 376 nm (log ϵ = 3.80) in 50% MeCN−50% water. **3H-F** was first obtained as a mixture of crystals and oil, which was purified by flash chromatography with pentane as eluant. The first orange fraction was collected and concentrated. Recrystallization provided again a mixture of oil and crystals, yield 10%. ^{1}H NMR (CD_3CN) δ 4.64 (s, 2H, CH_2), 4.74 (s, 3H, CH_3), 6.95−7.30 (m, 4H, C_6H_4); ^{13}C NMR (CD_3CN) 356.4 (C═), 224.3 and 216.8 (CO), 138.4, 130.8, 126.2, 116.8, and 114.3 (C_6H_4), 67.7 (CH_2). IR (CD_3CN) 2062 (CO), 1936 (CO); EI-MS m/z 344 (M^+, 24%), 343 (96%), 315 (94%), 259 (48%), 232 (17%), 204 (32%), 189 (32%), 161 (100%), 109 (12%). UV/vis λ_{max} 378 nm (log ϵ = 3.85) in 50% MeCN−50% water.

Kinetics, Spectra, and pH Measurements. The procedures described earlier[3] were used.

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Supporting Information Available: Tables S1−S6 (kinetic data) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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