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Physical Organic Chemistry of Transition Metal Carbene Complexes. 23.[1] Kinetic and Thermodynamic Acidities of Cationic Benzothienyl- and Selenylcarbene Complexes of Rhenium in Aqueous Acetonitrile

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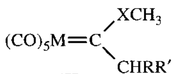
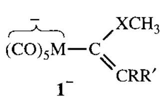
Abstract: The pK_a values of a cationic selenyl- (**5H**$^+$) and a benzothienylcarbene complex (**6H**$^+$) and rate constants for the reversible deprotonation of these complexes by water, carboxylate ions, primary aliphatic amines, secondary alicyclic amines (**5H**$^+$ only), and OH$^-$ (**5H**$^+$ only) were determined in 50% MeCN−50% water (v/v) at 25 °C. In comparison with neutral Fischer-type carbene complexes such as **1H**, the cationic complexes **5H**$^+$ and **6H**$^+$ are much more acidic, and the intrinsic barriers to proton transfer are substantially higher. This paper discusses a variety of factors that contribute to these differences, with the most important ones being that **5H**$^+$ and **6H**$^+$ are cationic, which makes the $C_5H_5(NO)(PPh_3)Re$ moiety a stronger π-acceptor than the $(CO)_5M$ moieties, coupled with the fact that the deprotonated forms of **5H**$^+$ and **6H**$^+$ are aromatic molecules.

Introduction

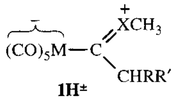
Over the past decade, we have reported a number of kinetic and thermodynamic investigations of the reversible deprotonation of Fischer carbene complexes.[2−9] Most of the complexes studied were of the type **1H** where M is Cr or W; CH_3X with X = O or S acts as a π-donor, while R and R′ are H, alkyl, or aryl groups. The majority of the studies were performed in 50% MeCN−50% water (v/v) at 25 °C;[3−7,9] one investigation was carried out in water,[2] another one in pure acetonitrile,[8] and one in various MeCN−water mixtures.[3] The most important findings can be summarized as follows.



1H

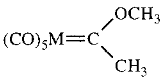


1$^-$

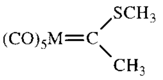


1H±

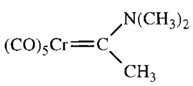
(1) The carbene complexes are remarkably acidic, much more so than the isolobal carboxylic acid esters or thio esters. For example, the pK_a^{CH} (CH stands for carbon acid) of the prototypical carbene complex **2-Cr** is 12.3 in water[2] and 12.5 in 50% MeCN−50% water,[3] while the pK_a^{CH} of ethyl acetate is 26.5.[10]



2-Cr (M = Cr)
2-W (M = W)



3-Cr (M = Cr)
3-W (M = W)



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The high acidity can be attributed to the delocalization of the anionic charge into the CO ligands of the $(CO)_5M$ moiety (**1**$^-$).

(2) The nature of the π-donor atom has a pronounced effect on the acidity of these complexes. For example, the pK_a^{CH} of **3-Cr** in 50% MeCN−50% water is 9.05,[9] that is, 3.45 units lower than that of **2-Cr**, while the pK_a^{CH} of **4** is too high to be measurable in aqueous acetonitrile; on the basis of determinations in pure MeCN, it is about 10 pK_a units higher than that of **2-Cr**.[11] This strong dependence on the π-donor ability of X in **1H** is consistent with strong stabilization of the carbene complex by π-donation as illustrated by the resonance structure **1H**$^\pm$.

(3) The acidities of **1H** depend very little on the metal. For example, the pK_a^{CH} of **2-W** is only 0.2 units lower than that of **2-Cr**, or the pK_a^{CH} of **3-W** is only 0.5 units lower than that of **3-Cr**.[9]

(4) The rates of proton transfer are relatively slow compared to those involving normal acids,[12] implying relatively low *intrinsic* rate constants or high *intrinsic* barriers,[13] as are typical for the deprotonations of carbon acids that lead to delocalized/resonance stabilized carbanions. The main reason for the high intrinsic barriers is the same as for purely organic carbon acids activated by π-acceptors;[15−17] that is, the transition state is imbalanced in the sense that charge delocalization into the $(CO)_5M$ moiety lags behind proton transfer.

The extensive database on thermodynamic and kinetic acidities on type **1H** complexes contrasts with the complete absence

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[1] Part 22: Bernasconi, C. F.; Ali, M. *Organometallics* **2001**, *20*, 3383.
[2] Gandler, J. R.; Bernasconi, C. F. *Organometallics* **1989**, *8*, 2282.
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[6] Bernasconi, C. F.; Sun, W. García-Río, L.; Yan, K.; Kittredge, K. W. *J. Am. Chem. Soc.* **1997**, *119*, 5583.
[7] Bernasconi, C. F.; Leyes, A. E.; García-Río, L. *Organometallics* **1998**, *17*, 4940.
[8] Bernasconi, C. F.; Leyes, A. E.; Ragains, M. L.; Shi, Y.; Wang, H.; Wulff, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 8632.
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[11] Bernasconi, C. F.; Ragains, M. L. Unpublished observations.
[12] Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1.
[13] The intrinsic rate constant, k_0, for a reaction with the forward rate constant k_1 and reverse rate constant k_{-1}, is defined as $k_0 = k_1 = k_{-1}$ where the equilibrium constant $K_1 = 1$; the intrinsic barrier, $\Delta G_0^\ddagger$ is defined as $\Delta G_0^\ddagger = \Delta G_1^\ddagger = \Delta G_{-1}^\ddagger$ where $\Delta G^\circ = 0$.[14] For proton transfers, statistical factors, *p* and *q* (see ref 29) are usually included.
[14] Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891.
[15] Bernasconi, C. F. *Acc. Chem. Res.* **1987**, *20*, 301.
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10.1021/ja011568q CCC: $20.00

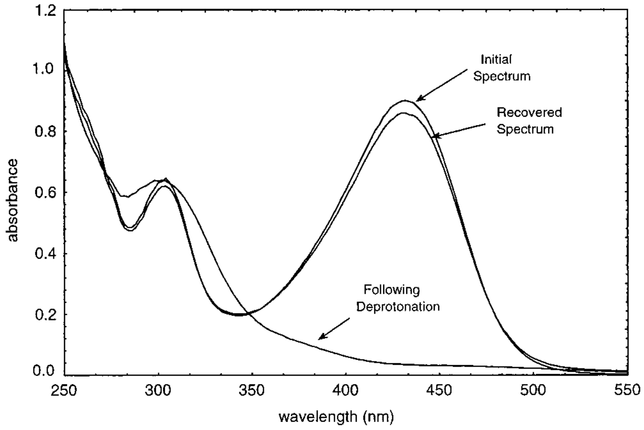
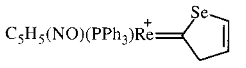
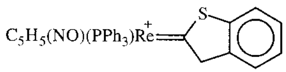


Figure 1. Absorption spectra of $\mathbf{5H}^+$ and **5**.

of such data on carbene complexes derived from transition metals other than those of row VI, that is, Cr, Mo, or W. We now report a proton transfer study involving two rhenium based carbene complexes: a selenylcarbene ($\mathbf{5H}^+$)[18,19] and a benzothienylcarbene ($\mathbf{6H}^+$)[18] complex (C_5H_5 stands for cyclopentadienyl). These complexes, used as their tetrafluoroborate salts,

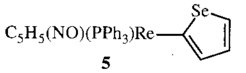


$\mathbf{5H}^+$



$\mathbf{6H}^+$

are not only structurally quite different from the **1H**-type complexes, but they also are cationic, which means their conjugate base is uncharged (**5** and **6**, respectively). Furthermore, **5** and **6** are aromatic. A major focus of interest is how these structural changes affect the thermodynamic acidities of these complexes and the intrinsic barriers of their proton transfers.



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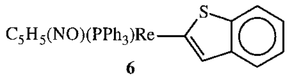

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Results

General Features. Both $\mathbf{5H}^+$ and $\mathbf{6H}^+$ as well as their respective conjugate bases (**5** and **6**) are relatively stable in 50% MeCN−50% water (half-lives ~2 h), and their deprotonation is fully reversible. Figure 1 shows the absorption spectrum of $\mathbf{5H}^+$, the spectrum of **5** after deprotonation of $\mathbf{5H}^+$ with KOH, and the spectrum of recovered $\mathbf{5H}^+$ after adding HCl to **5**. A similar set of spectra is shown in Figure 2 for $\mathbf{6H}^+$. Because of the high acidity of $\mathbf{6H}^+$, a 2.5 M HCl solution was required to obtain the spectrum of the fully protonated carbene complex.

Spectrophotometric $\mathbf{p}K_a^{CH}$ Determination. A pK_a^{CH} of 4.21 ± 0.03 for $\mathbf{5H}^+$ was determined in chloroacetate buffers by measuring absorbances at λ_{max} of $\mathbf{5H}^+$ as a function of pH (Table S1, Supporting Information)[20] and applying eq 1 with A_{max} being the absorbance at pH $\ll pK_a^{CH}$,

$$pH = pK_a + \log\frac{A_{max} - A}{A - A_{min}} \qquad (1)$$

A_{min} the absorbance at pH $\gg pK_a^{CH}$, and A is the absorbance at pH ~ pK_a^{CH}. For $\mathbf{6H}^+$ whose pK_a^{CH} is −0.14 ± 0.03, the measurements were carried out in HCl solutions ranging from 0.05 to 2.5 M (Table S1).[20] At the high end of this range, the proton activity is no longer proportional to [HCl] but follows acidity function behavior,[21,22] that is, eq 1 needs to be replaced by eq 2 with H_0 being an appropriate acidity function.

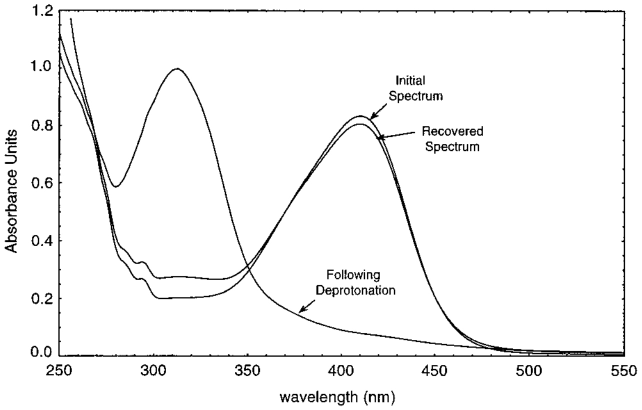

Figure 2. Absorption spectra of $\mathbf{6H}^+$ and **6**.

$$H_0 = -\log h_0 = pK_a^{CH} + \log\left(\frac{A_{max} - A}{A - A_{min}}\right) \qquad (2)$$

An acidity function in 50% MeCN−50% water for [HCl] = 0.05 M to 2.5 M based on the *p*-nitroanilinium ion has been reported by El-Harakany et al.[23] Even though $\mathbf{5H}^+$ and $\mathbf{6H}^+$ probably do not follow this acidity function directly, we shall assume that the acidity function appropriate for $\mathbf{5H}^+$ and $\mathbf{6H}^+$ shows the same relative dependence on [HCl] as that reported by El-Harakany et al. The H_0 values listed in Table S2 have been calculated accordingly; for more details, see the Experimental Section.

Kinetics. All kinetic measurements were performed under pseudo-first-order conditions, either in carboxylic acid or amine buffered solutions or in relatively concentrated HCl solutions. This implies that the observed pseudo-first-order rate constant for equilibrium approach is given by eq 3 with the various terms defined in eq 4; $\mathbf{CH}^+$ stands for $\mathbf{5H}^+$ and $\mathbf{6H}^+$, respectively, **C** for **5** or **6**, respectively, B for the buffer base, and BH for the buffer acid.

$$k_{obsd} = k_1^{H_2O} + k_1^{OH}[OH^-] + k_{-1}^{H}a_{H^+} + k_{-1}^{H_2O} + k_1^{B}[B] + k_{-1}^{BH}[BH] \qquad (3)$$

$$\mathbf{CH}^+ \xrightleftharpoons[k_{-1}^{H}a_{H^+} + k_{-1}^{H_2O} + k_{-1}^{BH}[BH]]{k_1^{H_2O} + k_1^{OH}[OH^-] + k_1^{B}[B]} \mathbf{C} \qquad (4)$$

Depending on the pH, the reactions were run in the forward direction ($\mathbf{CH}^+ \rightarrow \mathbf{C}$ at pH > pK_a^{CH}) or the reverse direction ($\mathbf{C} \rightarrow \mathbf{CH}^+$ at pH < pK_a^{CH}). All measurements were performed in a stopped-flow spectrophotometer.

Kinetic $\mathbf{p}K_a^{CH}$ Determination. As a means to check for internal consistency of our results, we also determined the pK_a^{CH} values of $\mathbf{5H}^+$ and $\mathbf{6H}^+$ kinetically. For $\mathbf{5H}^+$, measurements were carried out in chloroacetate buffers (Table S3).[20] Under these conditions, $k_1^{OH}[OH^-] + k_{-1}^{H_2O}$ is negligible, and eq

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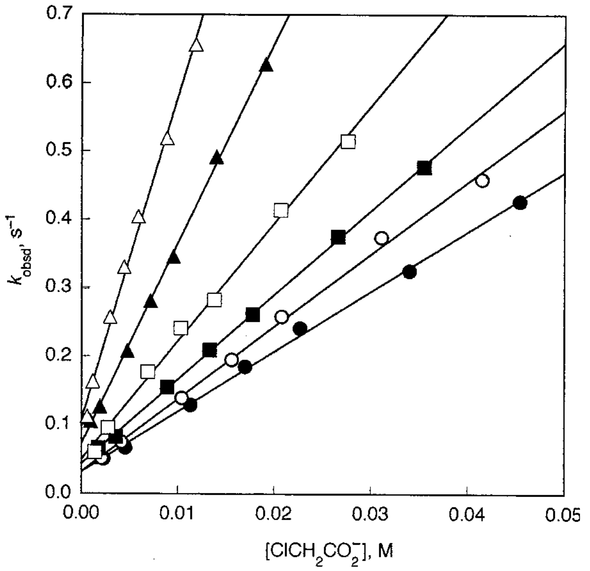

Figure 3. Reaction of $5H^+$ with chloroacetate buffers. Plots of k_{obsd} vs [$ClCH_2CO_2^-$]: △, pH 3.43; ▲, pH 3.73; □, pH 4.03; ■, pH 4.33; ○, pH 4.63; ●, pH 4.93.

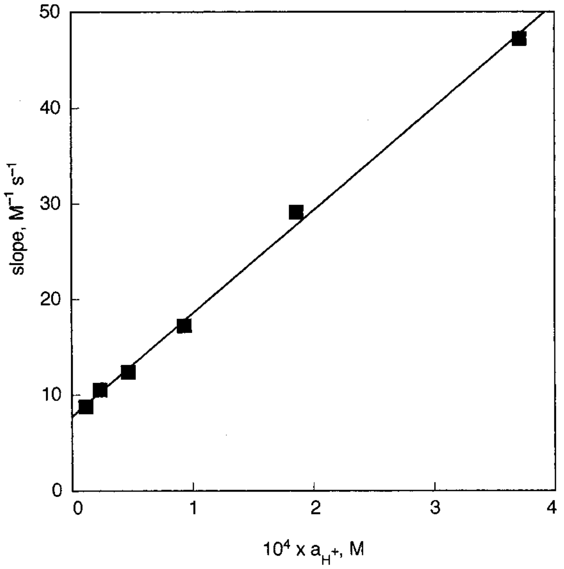

Figure 4. Reaction of $5H^+$ with chloroacetate buffers. Plot of the slopes from Figure 3 vs a_{H^+} according to eq 6.

3 simplifies to eq 5. Figure 3 shows plots of k_{obsd} versus [$ClCH_2COO^-$] at various pH values.

$$k_{obsd} = k_1^{H_2O} + k_{-1}^{H}a_{H^+} + k_1^{B}[B] + k_{-1}^{BH}[BH] \qquad (5)$$

The slopes of these plots are given by eq 6. From a plot according to eq 6 (Figure 4),

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

$pK_a^{CH} = 4.15 \pm 0.04$ was obtained, which is in excellent agreement with the spectrophotometric value of 4.21 ± 0.03; the values for k_1^B and k_{-1}^{BH} (k_{-1}^{BH} obtained as $k_1^B K_a^{BH}/K_a^{CH}$) are reported in Table 1.

For **6H**$^+$, the reactions were run in HCl solutions where eq 3 reduces to eq 7 or, when extended to high HCl concentrations, eq 8 (Table S4).[20]

$$k_{obsd} = k_1^{H_2O} + k_{-1}^{H}a_{H^+} \qquad (7)$$

$$k_{obsd} = k_1^{H_2O} + k_{-1}^{H}h_o \qquad (8)$$

A plot of k_{obsd} versus h_0 is shown in Figure 5; it yields the $k_1^{H_2O}$ and k_{-1}^{H} values reported in Table 1 which give $pK_a^{CH} = 0.07 \pm 0.03$, in reasonably good agreement with the spectrophotometric $pK_a^{CH} = -0.14 \pm 0.03$.

Kinetics in Carboxylate and Amine Buffers. These experiments were run at buffer ratios of approximately 1:1. The raw data are summarized in Tables S4−S6[20] (**5H**$^+$) and Tables S7 and S8[20] (**6H**$^+$). The slopes of the plots of k_{obsd} versus [B] (not shown) were analyzed according to eq 6; that is, eq 6 was solved for k_1^B using the K_a^{CH} values obtained from the average of the spectrophotometric and kinetic pK_a^{CH} values.

Reactions in KOH and HCl Solutions. Deprotonation of **5H**$^+$ by OH^- is quite fast, and k_{obsd} reaches the stopped-flow limit (~10^3 s^{-1}) at 0.05 M KOH. Kinetic experiments at [KOH] = 0.0025−0.05 M yielded a k_1^{OH} value of 1.16×10^4 M^{-1} s^{-1} via eq 9.

$$k_{obsd} = k_1^{H_2O} + k_1^{OH}[OH^-] \approx k_1^{OH}[OH^-] \qquad (9)$$

For **6H**$^+$, the reaction was too fast for a reliable determination of k_1^{OH}; a k_1^{OH} value of ~$0.8-1.2 \times 10^5$ M^{-1} s^{-1} may be estimated.

A k_{-1}^{H} value for the protonation of **5** by H_3O^+ was obtained in dilute HCl solutions (0.0025−0.05 M) by applying eq 7; the determination of k_{-1}^{H} for the protonation of **6** by H_3O^+ was described under the Kinetic pK_a^{CH} Determination subsection. The various $k_1^{H_2O}$, k_1^{OH}, k_{-1}^{H}, and $k_{-1}^{H_2O}$ values are reported in Table 2.

Discussion

pK_a^{CH} of 5H$^+$ and 6H$^+$. The average pK_a^{CH} values of **5H**$^+$ and **6H**$^+$ are 4.18 and −0.03, respectively. This makes them by far the most acidic Fischer carbenes reported to date. They are much more acidic than **3-Cr** ($pK_a^{CH} = 9.05$)[9] or **3-W** ($pK_a^{CH} = 8.37$),[9] which in turn are more acidic than their methoxy analogues (**2-Cr**, $pK_a^{CH} = 12.50$[3]; **2-W**, $pK_a^{CH} = 12.36$[4]).

There are several reasons why the rhenium complexes are so acidic. Probably the most important one is that they are cationic, which makes the $C_5H_5(NO)(PPh_3)Re$ moiety a stronger π-acceptor than the $(CO)_5M$ moieties, despite the fact that in the latter there are five electron withdrawing CO ligands on the metal while there is only one electron withdrawing NO ligand on the metal of the rhenium complexes. Or, in other words, the dominant resonance structures of the conjugated bases of the rhenium complexes (**5** and **6**, respectively) are neutral molecules and, hence, more stable. An additional driving force for the deprotonation is that the conjugate bases are aromatic; that is, **5** is a selenophene derivative, and **6**, a benzothiophene derivative. The fact that **6H**$^+$ is substantially more acidic than **5H**$^+$ is probably in large measure due to the stronger aromaticity of the benzothiophene moiety compared to the selenophene[24] moiety.

Finally, the identity of the heteroatom (S, Se, O) undoubtedly exerts an influence on the acidity beyond its effect on aromaticity mentioned above. This is clearly evident in the comparison of **3-Cr** with **2-Cr**, or **3-W** with **2-W**. As mentioned in the Introduction, the higher acidity of the sulfur carbene complexes

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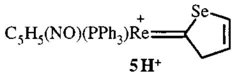
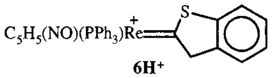
[24] The aromaticity of heterocycles follows the order thiophene > selenophene > furan.[25]

Table 1. Reactions of **5H**$^+$ and **6H**$^+$ with Buffers: Summary of Rate Constants and pK_a Values in 50% MeCN−50% Water (v/v) at 25 °C[a]

		 **5H**$^+$ ($pK_a^{CH} = 4.18 \pm 0.03$)		 **6H**$^+$ ($pK_a^{CH} = -0.03 \pm 0.10$)	
B	pK_a^{BH}	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}
piperidine	11.01	$(2.66 \pm 0.11) \times 10^4$	$(3.93 \pm 0.43) \times 10^{-3}$		
piperazine	9.97	$(7.11 \pm 0.09) \times 10^3$	$(1.15 \pm 0.09) \times 10^{-2}$		
HEPA[b]	9.33	$(3.29 \pm 0.07) \times 10^3$	$(2.33 \pm 0.21) \times 10^{-2}$		
morpholine	8.70	$(2.11 \pm 0.03) \times 10^3$	$(6.37 \pm 0.53) \times 10^{-2}$		
n-BuNH$_2$	10.40	$(5.72 \pm 0.04) \times 10^3$	$(3.45 \pm 0.26) \times 10^{-3}$	$(3.26 \pm 0.12) \times 10^4$	$(1.21 \pm 0.35) \times 10^{-6}$
$MeOCH_2CH_2NH_2$	9.39	$(1.51 \pm 0.01) \times 10^3$	$(9.31 \pm 0.71) \times 10^{-3}$	$(1.49 \pm 0.11) \times 10^4$	$(5.66 \pm 1.86) \times 10^{-6}$
$H_2NCOCH_2NH_2$	8.14	$(2.27 \pm 0.06) \times 10^2$	$(2.49 \pm 0.10) \times 10^{-2}$	$(3.20 \pm 0.27) \times 10^3$	$(2.16 \pm 0.73) \times 10^{-5}$
$NCCH_2NH_2$	5.29	$(1.09 \pm 0.04) \times 10^1$	$(8.46 \pm 0.90) \times 10^{-1}$	$(6.85 \pm 0.30) \times 10^2$	$(3.28 \pm 0.98) \times 10^{-3}$
$CH_3CO_2^-$	5.93	$(2.81 \pm 0.02) \times 10^1$	$(4.99 \pm 0.38) \times 10^{-1}$	$(7.11 \pm 0.55) \times 10^3$	$(7.80 \pm 2.57) \times 10^{-3}$
$MeOCH_2CO_2^-$	4.73			$(4.43 \pm 0.08) \times 10^3$	$(7.70 \pm 2.15) \times 10^{-2}$
$ClCH_2CO_2^-$	3.94	7.14 ± 0.45	$(1.24 \pm 0.12) \times 10^1$	$(3.43 \pm 0.07) \times 10^3$	$(3.68 \pm 1.03) \times 10^{-1}$
$NCCH_2CO_2^-$	3.56	5.32 ± 0.32	$(2.22 \pm 0.17) \times 10^1$		
$Cl_2CHCO_2^-$	2.38	3.10 ± 0.24	$(1.96 \pm 0.15) \times 10^2$	$(2.37 \pm 0.26) \times 10^3$	9.88 ± 3.55
$Cl_3CCO_2^-$	1.64			$(2.27 \pm 0.11) \times 10^3$	$(4.85 \pm 1.44) \times 10^1$

[a] Ionic strength = 0.1 M (KCl). [b] HEPA = 1-(2-hydroxyethyl)piperazine.

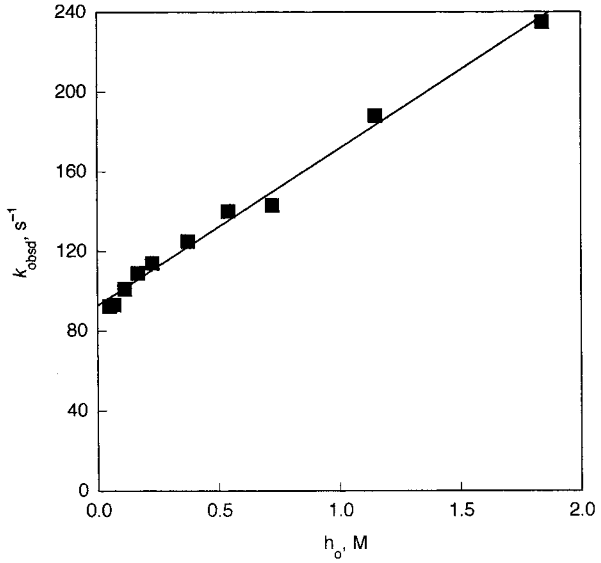
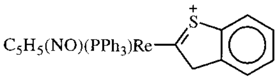


Figure 5. Reaction of **6H**$^+$ with HCl solutions. Plot of k_{obsd} vs h_0 according to eq 8.

can be attributed to the weaker π-donor effect of sulfur compared to oxygen;[26] that is, there is less contribution by the resonance structure **1H**$^\pm$ to the stabilization of **3-Cr** and **3-W** than to that of **2-Cr** and **2-W**, respectively. It should be noted, however, that the relative importance of the π-donor effect of sulfur in **6H**$^+$ compared to that in **3-Cr** or **3-W** is probably not the same. For **6H**$^+$, the relevant resonance structure is cationic (**6′H**$^+$) just as **6H**$^+$ is, which means **6′H**$^+$ leads to a *delocalization* of charge. This contrasts with **1H**$^\pm$ in which two opposite



6′H$^+$

charges have been created. In general, resonance structures that lead to charge delocalization are more stabilizing than those that lead to charge creation, and hence, it is likely that the pK_a^{CH} enhancing π-donor effect of the sulfur atom in **6H**$^+$ is stronger than in **3-Cr** or **3-W**.

In comparing **6H**$^+$ with **5H**$^+$, the stronger π-donor effect of S compared to Se[26] should lower the acidity of **6H**$^+$ relative to that of **5H**$^+$. Because **6H**$^+$ is actually *more* acidic than **5H**$^+$, the greater aromaticity of **6** compared to **5** apparently more than offsets the stronger π-donor effect of sulfur.

Rate Constants. All the rate constants determined in this study are summarized in Tables 1 and 2. For **5H**$^+$, we were able to obtain rate constants for the reactions with water, OH$^-$, and carboxylate buffers, as well as primary and secondary amine buffers; for **6H**$^+$, the reactions with the secondary amines were too fast to allow kinetic determinations, and the same was true for the reaction with OH$^-$. For unknown reasons, the rate measurements for **5H**$^+$ in methoxyacetate buffers and of **6H**$^+$ in cyanoacetate buffers gave erratic results, and no reliable rate constants could be determined.

Statistically corrected Brønsted plots for the dependence of k_1^B and k_{-1}^{BH} on the pK_a difference between the respective carbenes and the buffer acids are shown in Figures 6 and 7.[28] They yield the Brønsted β and α values summarized in Table 3; from the points where the lines for $\log(k_1^B/q)$[29] and

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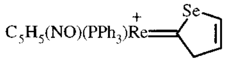
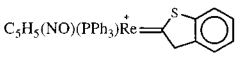
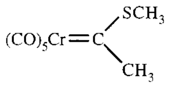
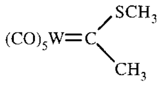
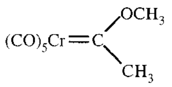
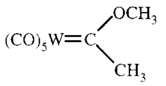
(25) Fringuelli, F.; Marino, G.; Taticchi, A. *J. Chem. Soc., Perkin Trans. 2* **1974**, 332.

(26) The *R* values for MeO, MeS, and MeSe are −0.56, −0.23, and −0.16, respectively, while the σ_R values for MeO and MeS are −0.43 and 0.15, respectively.[27]

Table 2. Reactions with OH^-, H_3O^+, and Water: Summary of Rate Constants in 50% MeCN−50% Water (v/v) at 25 °C

Carbene complex		pK_a^{CH}	$k_1^{H_2O}$	k_{-1}^{H} [d]	k_1^{OH}	$k_{-1}^{H_2O}$ [d]	$k_1^{OH}/k_1^{H_2O}$
			s^{-1}	$M^{-1}\,s^{-1}$	$M^{-1}\,s^{-1}$	s^{-1}	M^{-1}
	**5H**$^+$	4.18	$(1.85 \pm 0.18) \times 10^{-2}$	$(2.80 \pm 0.08) \times 10^{2}$	$(1.61 \pm 0.04) \times 10^{4}$	$(3.07 \pm 0.29) \times 10^{-8}$	8.70×10^{5}
	**6H**$^+$	−0.03	$(9.25 \pm 0.20) \times 10^{1}$	$(7.88 \pm 0.27) \times 10^{1}$	ca. 10^{5}	ca. 6×10^{-4}	ca. 10^{3}
 $(CO)_5Cr{=}C(SCH_3)CH_3$	**3-Cr**[a]	9.05	1.61×10^{-2}	1.73×10^{7}	1.20×10^{3}	8.30×10^{-4}	7.45×10^{4}
 $(CO)_5W{=}C(SCH_3)CH_3$	**3-W**[a]	8.37	5.23×10^{-2}	1.17×10^{7}	8.37×10^{2}	1.21×10^{-4}	1.60×10^{4}
 $(CO)_5Cr{=}C(OCH_3)CH_3$	**2-Cr**[b]	12.50			4.56×10^{2}	0.91	
 $(CO)_5W{=}C(OCH_3)CH_3$	**2-W**[c]	12.36			2.84×10^{2}	0.42	

[a] Ref 9. [b] Ref 3. [c] Ref 4. [d] $k_{-1}^{H_2O} = k_1^{OH}K_w/K_a^{CH}$ with $K_w = 6.46 \times 10^{-16}$ M^2 ($pK_w = 15.19$), ref 3.

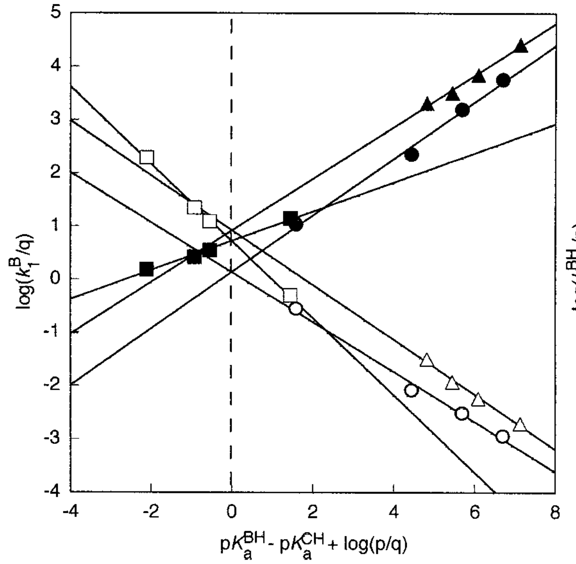


Figure 6. Brønsted plots for the reactions of **5H**$^+$ with secondary amines (R_2NH), primary amines (RNH_2), and carboxylate ions (RCO_2^-). Filled symbols, k_1^B; open symbols, k_{-1}^B. ▲, △: R_2NH. ●, ○: RNH_2. ■, □: RCO_2^-. The dashed vertical line goes through the points where the k_1^B and k_{-1}^{BH} lines intersect, which correspond to log k_0.

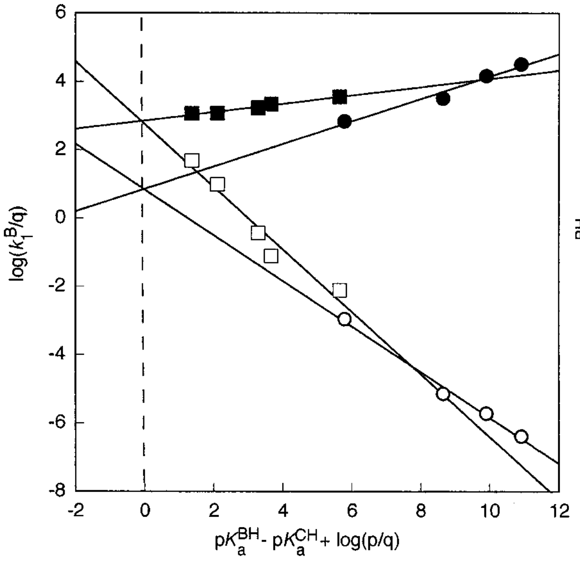


Figure 7. Brønsted plots for the reactions of **6H**$^+$ with primary amines (RNH_2) and carboxylate ions (RCO_2^-). Filled symbols: k_1^B; open symbols: k_{-1}^B. ■, □: RCO_2^-. ●, ○: RNH_2. The dashed vertical line goes through the lines where the k_1^B and k_{-1}^{BH} points intersect which correspond to log k_0.

$\log(k_{-1}^{BH}/p)$[29] intersect, the intrinsic rate constants, defined as $k_0 = k_1^B/q = k_{-1}^{BH}/p$ were obtained (in Table 3 reported as log k_0).

Brønsted Parameters. A. General Observations. For **5H**$^+$, the Brønsted α and β values for the reactions with primary and secondary amines ($\beta = 0.49$ for R_2NH, $\beta = 0.53$ for RNH_2) are quite close to those for the reactions of the chromium and tungsten carbene complexes ($\beta = 0.45-0.64$, Table 3). This implies that the degree of proton transfer at the transition state is comparable for all these reactions;[30] it also suggests that, for these systems, the reported log k_0 values can be used as a basis for meaningful comparisons of intrinsic rate constants.[17] Because of the similarity of the Brønsted slopes, the relative log k_0 values are not very sensitive to the difference between pK_a^{CH} and pK_a^{BH}, which determines the length of the extrapolation needed to evaluate log k_0.

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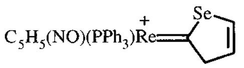
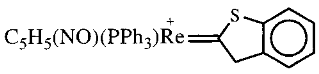
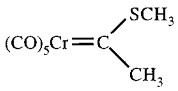
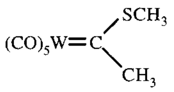
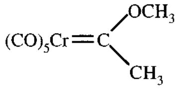
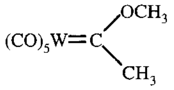
(27) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

(28) Strictly speaking, the plots shown are "Eigen[12] plots".

(29) q is the number of equivalent basic sites on the buffer base, while p is the number of equivalent protons on the buffer acid.

(30) This is the traditional view;[31−33] although this view has been challenged,[34−36] it has recently received strong support.[37]

Table 3. Summary of Brønsted α- and *β*-Values and of log k_0 for the Intrinsic Rate Constants in 50% MeCN−50% Water (v/v) at 25 °C

carbene complex		pK_a^{CH}	base type	β	α	logk_o
	(**5H**$^+$)	4.18	R_2NH	0.49 ± 0.04	0.51 ± 0.04	0.93 ± 0.22
		4.18	RNH_2	0.53 ± 0.03	0.47 ± 0.03	0.14 ± 0.15
		4.18	RCO_2^-	0.28 ± 0.02	0.72 ± 0.02	0.72 ± 0.03
	(**6H**$^+$)	−0.03	RNH_2	0.33 ± 0.04	0.67 ± 0.04	0.86 ± 0.37
		−0.03	RCO_2^-	0.12 ± 0.01	0.88 ± 0.01	2.85 ± 0.05
	(**3-Cr**)[a]	9.05	R_2NH	0.45 ± 0.06	0.55 ± 0.06	2.61 ± 0.10
		9.05	RNH_2	0.48 ± 0.04	0.52 ± 0.04	2.09 ± 0.08
		9.05	RCO_2^-	0.44 ± 0.06	0.56 ± 0.06	2.17 ± 0.24
	(**3-W**)[a]	8.37	R_2NH	0.49 ± 0.09	0.51 ± 0.09	2.50 ± 0.18
		8.37	RNH_2	0.47 ± 0.03	0.53 ± 0.03	2.17 ± 0.05
		8.37	RCO_2^-	0.43 ± 0.08	0.57 ± 0.08	2.27 ± 0.27
	(**2-Cr**)[b]	12.50	R_2NH	0.62 ± 0.03	0.38 ± 0.03	3.70 ± 0.07
		12.50	RNH_2	0.61 ± 0.06	0.39 ± 0.06	3.04 ± 0.17
	(**2-W**)[c]	12.36	R_2NH	0.49 ± 0.01	0.51 ± 0.01	3.18 ± 0.02
		12.36	RNH_2	0.64 ± 0.03	0.36 ± 0.03	2.73 ± 0.07

[a] Ref 9. [b] Ref 3. [c] Ref 4.

On the other hand, the α and *β* values for the reaction of **5H**$^+$ with carboxylate ions, and for the reactions of **6H**$^+$ with primary amines as well as carboxylate ions, are substantially lower than the others. This not only indicates a transition state with a significantly smaller degree of proton transfer from the carbene complex to the buffer base, it also complicates the interpretation of the calculated log k_0 values when log k_0 is obtained from a long extrapolation due to a large difference between pK_a^{CH} and pK_a^{BH}. This extrapolation is particularly long for the reaction of **6H**$^+$ with primary amines.[38] Because of the low *β* value (0.33), this results in a log k_0 value that is too high and should not be compared with the log k_0 of the other systems that have much larger *β* values. For the reaction of **6H**$^+$ with carboxylate ions, the extrapolation is not quite as long,[39] but here, the *β* value (0.12) is extremely low, again leading to a grossly inflated log k_0 value. On the other hand, despite the low *β* value (0.28) for the reaction of **5H**$^+$ with carboxylate ions, the log k_0 value determined by interpolating the Brønsted lines may safely be used as a measure of the intrinsic rate constant, because the pK_a^{CH} of **5H**$^+$ is close to the midrange of the buffer pK_a^{BH} values. Hence, log k_0 would be about the same, irrespective of the Brønsted slopes.

B. Intrinsic Rate Constants for the Reactions of 5H$^+$ with Buffer Bases. As mentioned above, a comparison between the log k_0 values for the reaction of **5H**$^+$ with those for **2-M** and **3-M** should provide a meaningful assessment of their relative intrinsic rate constants. To understand why log k_0 for **5H**$^+$ is so much lower than that for **2-M** and **3-M** (Table 3), it is useful to review the main factors that affect intrinsic rate constants of proton transfers from carbon acids activated by *π*-acceptors. The most important factor is resonance/charge delocalization in the deprotonated form. Because the development of resonance always lags behind proton transfer at the transition state,[15−17] the intrinsic rate constant is reduced, and the more so the greater the resonance stabilization.[40] The extensive delocalization of the negative charge into the $(CO)_5Cr$ or $(CO)_5W$ moieties of **1**$^-$ is therefore thought to be the main reason the deprotonation of all carbene complexes of the type **1H** have relatively low k_0 values.[41]

That secondary factors also come into play can be seen when comparing the log k_0 values for **2-Cr** or **2-W** with those for **3-Cr** or **3-W**, respectively. As elaborated upon elsewhere,[15,17] an inductively electron withdrawing group that is closer to the center of negative charge development at the transition state than in the anion−compare the location of the CH_3X group with respect to negative charge in **1**$^-$ with that in **7**−will increase k_0. Because MeO is more electron withdrawing than MeS,[42]

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(31) Leffler, J. E.; Grunwald, E. *Rates and Equilibria of Organic Reactions*; Wiley: New York, 1963; p 156.

(32) Kresge, A. J. *Acc. Chem. Res.* **1975**, *8*, 354.

(33) Jencks, W. P. *Chem. Rev.* **1985**, *85*, 511.

(34) Pross, A. *J. Org. Chem.* **1984**, *49*, 1811.

(35) Bordwell, F. G.; Hughes, D. L. *J. Am. Chem. Soc.* **1985**, *107*, 4737.

(36) Pross, A.; Shaik, S. S. *New J. Chem.* **1989**, *13*, 427.

(37) Bernasconi, C. F.; Wenzel, P. J. *J. Am. Chem. Soc.* **1996**, *118*, 11446. See especially footnote 29 in this paper.

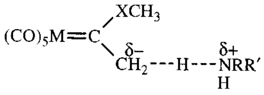
(38) The midpoint of the pK_a^{BH} range of the amine buffers is 7.85, which is 7.9 higher than pK_a^{CH}. If *β* were ≈0.5 instead of 0.33, this would reduce log k_0 by ≈(0.17 × 7.9) ≈ 1.34 to log k_0 ≈ −0.58.

(39) The midpoint of the pK_a^{BH} range of the carboxylate buffers is 4.16, which is 4.2 higher than pK_a^{CH}. If *β* were ≈0.5 instead of 0.12, this would reduce log k_0 by ≈(0.36 × 4.2) ≈ 1.51 to log k_0 ≈ 1.0.

(40) When solvation of the carbanion is important, as is the case for nitronate and enolate ions, the lag in the development of this solvation significantly adds to the reduction in the intrinsic rate constant.[15−17]

(41) For a review, see: Bernasconi, C. F. *Chem. Soc. Rev.* **1997**, *26*, 299.

this increase in k_0 will be stronger for the MeO than for the MeS complexes.



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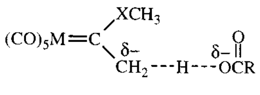

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Another factor is steric crowding at the transition state which was shown to be more significant for the MeS complexes and leads to a reduction of k_0 for the MeS complexes relative to the MeO complexes.[9] The evidence for this conclusion was based on comparing differences in log k_0 for primary and secondary amines, $\Delta\log k_0 = \log k_0(R_2NH) - \log k_0(RNH_2)$. For sterically unhindered proton transfers, $\Delta\log k_0$ is typically 0.8−1.0, while for sterically hindered reactions $\Delta\log k_0$ is lower.[43] For **2-M**, the average $\Delta\log k_0$ is 0.56, and for **3-M**, it is 0.43, indicating a moderate steric effect for the reactions of **2-M** and a somewhat larger effect for those of **3-M**.

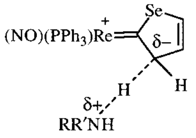
A third potential factor is the stronger π-donor effect of the MeO compared to the MeS group,[26] although it is unclear whether it would result in a net increase or decrease in k_0. This is because there are two opposing phenomena. One is the loss of the resonance stabilization of the neutral carbene complexes (**1H**$^{\pm}$), which must follow the general rule that applies to resonance effects; that is, its loss must be ahead of proton transfer at the transition state.[15−17] This reduces k_0, 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 (**7**) by the π-donors. This comes about because the contribution of **1H**$^{\pm}$ 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 is a stronger π-donor than the MeS group, and this will lead to a greater preorganization and, hence, to a lower intrinsic barrier (higher k_0) for the deprotonation of the MeO complexes.

On the basis of arguments presented earlier,[9] the net effect of π-donation may be a small decrease in k_0 for the sulfur and a somewhat larger decrease in k_0 for the oxygen derivatives, but this conclusion is not firm, and the overall effect or the difference in the log k_0 values is probably small.

In comparing **5H**$^+$ with **2-M** and **3-M**, the enhanced resonance stabilization of **5** that appears to be the major reason for the high acidity of **5H**$^+$ is likely to be also the major factor in reducing the intrinsic rate constants. The fact that **5** not only enjoys extra resonance stabilization on the metal side but also is aromatic on the heterocyclic ring side is expected to further reduce k_0, because the development of this aromaticity will lag behind proton transfer for the same reason that the resonance development on the metal side lags behind proton transfer. As suggested later, this reduction may not be very large, though.

As to the potential contribution to the difference in the log k_0 values between **2-M** or **3-M** and **5H**$^+$ arising from the change to a selenium heteroatom, it is probably less significant than that resulting from the change from oxygen to sulfur in going from **2-M** to **3-M**. In particular, $\Delta\log k_0 = \log k_0(R_2NH) - \log k_0(RNH_2) = 0.79$ suggests that the steric effect is smaller for **5H**$^+$ than for **2-M** or **3-M**, and hence, this may mask an even greater difference in the k_0 values between **5H**$^+$ and **2-M** or **3-M**. On the other hand, the smaller inductive effect of selenium compared to sulfur or oxygen[42] will tend to favor **2-M** or **3-M**, but the effect is expected to be quite small. Finally, as discussed above, the net π-donor effect is probably small in any event and could not possibly account for the low k_0 value for **5H**$^+$.

C. Electrostatic Effects. The relative magnitude of log k_0 for the reactions with carboxylate ions compared to those with the amines calls for some comment. For **5H**$^+$, $\Delta\log k_0 = \log k_0(RCO_2^-) - \log k_0(RNH_2) = 0.58$, while for **3-M** this difference is much smaller (0.08 for **3-Cr**, 0.10 for **3-W**). The most plausible interpretation of these differences is in terms of electrostatic effects at the transition state.[46−48] In the reactions of **3-M** with amines, there is an electrostatic stabilization of the transition state (**7**) but a *de*stabilization in the reactions with carboxylate ions (**8**). This tends to enhance k_0 for the amine reactions and reduce k_0 for the carboxylate ion reactions. In the reactions of **5H**$^+$, these effects are attenuated and perhaps reversed because of the interaction of the positive charge on the metal moiety with the partial charge on the buffer base (**9** vs **10**); the result is that the carboxylate ion reaction becomes relatively more favorable than the amine reaction; that is, the $\log k_0(RCO_2^-) - \log k_0(RNH_2)$ difference becomes larger.



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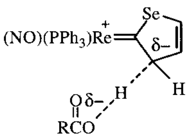

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D. Intrinsic Rate Constants for the Reactions of 6H$^+$ with Buffer Bases. As pointed out earlier, the log k_0 values reported in Table 3 for the reactions of **6H**$^+$ overestimate the actual intrinsic rate constants by a substantial amount, and hence, it is difficult to make comparisons with the other carbene complexes. Nevertheless, it appears that, when this overestimate is taken into account, the actual log k_0 values may not be significantly different from those for the reactions of **5H**$^+$.[38,39] This would suggest that the greater aromatic character of **6** compared to **5** does not have a large effect on k_0, implying that the aromaticity of **5** or **6** contributes relatively little to the lowering of k_0 relative to the reactions of **2-M** and **3-M**. However, in view of the uncertainties about log k_0 for **6H**$^+$, further investigations relating to this question seem warranted.

E. Rate Constants for the Reactions with OH$^-$, H$_3$O$^+$, and Water. Table 2 provides a summary of the $k_1^{H_2O}$, k_{-1}^{H}, k_1^{OH}, and $k_{-1}^{H_2O}$ values for **5H**$^+$ and **6H**$^+$ as well as for **3-Cr**, **3-W**, **2-Cr**, and **2-W**. The deprotonation of **5H**$^+$ by OH$^-$ (k_1^{OH}) is about 20-fold faster than the deprotonation of **3-Cr** or **3-W** and about 40- to 60-fold faster than the deprotonation of **2-Cr** and **2-W**, respectively. This increase in k_1^{OH} reflects the increased acidity of **5H**$^+$ compared to **3-M** and **2-M**, but in view of the large differences in the acidities, the rate increase seems rather modest. This, of course, is again the result of a substantially lower intrinsic rate constant in the case of **5H**$^+$. The effect of

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[42] The *F* values for MeO, MeS, and MeSe are 0.29, 0.23, and 0.16, respectively, while the σ_F values for MeO and MeS are 0.30 and 0.20, respectively.[27]

[43] The higher k_0 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.[17,44,45]

[44] Bell, R. P. *The Proton in Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1973; Chapter 10.

[45] Jencks, W. P. *Catalysis in Chemistry and Enzymology*; McGraw-Hill: New York, 1968; p 178.

[46] Kresge, A. J. *Chem. Soc. Rev.* **1973**, *2*, 475.

the lower intrinsic rate constant manifests itself even more dramatically in the $k_1^{H_2O}$ values for the deprotonation of the carbene complex by water: here, $k_1^{H_2O}$ for **5H**$^+$ is about the same as for **3-Cr** and only about 3-fold higher than for **3-W**. The situation is similar for **6H**$^+$: Despite a 9 pK_a unit difference, k_1^{OH} is only about 100-fold higher than for **3-Cr**, and $k_1^{H_2O}$ for **6H**$^+$ is only about 600-fold higher than for **3-Cr**.

Another quantity of interest is the $k_1^{OH}/k_1^{H_2O}$ ratio reported in the last column of Table 2. There appear to be two major factors that influence this ratio. One is the degree of proton transfer at the transition state. Just as a larger (smaller) Brønsted β value implies greater (smaller) progress of proton transfer at the transition state, so does a larger (smaller) $k_1^{OH}/k_1^{H_2O}$ ratio. Hence, the much smaller $k_1^{OH}/k_1^{H_2O}$ ratio for **6H**$^+$ compared to **5H**$^+$ is consistent with a smaller amount of proton transfer and parallels the small Brønsted β values for this compound. The slightly smaller $k_1^{OH}/k_1^{H_2O}$ ratio for **3-W** compared to **3-Cr** may have a similar origin.

The second factor is electrostatic interactions at the transition state. The larger $k_1^{OH}/k_1^{H_2O}$ ratio for **5H**$^+$ compared to **3-Cr** and **3-W** is reminiscent of the larger $\log k_0(RCO_2^-) - \log k_0(RNH_2)$ for **5H**$^+$ compared to that for **3-Cr** and **3-W** (as well as **2-Cr** and **2-W**). In the reactions of **3-Cr** or **3-W** with water, there is a transition state stabilization similar to that in **7**, and in reactions with OH$^-$, there is a destabilization similar to that in **8**. This results in a relatively small $k_1^{OH}/k_1^{H_2O}$ ratio. In contrast, in the reactions of **5H**$^+$, the respective transition states are analogous to **9** for the water and to **10** for the OH$^-$ reaction. This tends to attenuate or reverse the electrostatic effects seen for the reactions of **3-Cr** and **3-W** and results in a larger $k_1^{OH}/k_1^{H_2O}$ ratio for **5H**$^+$.

Conclusions

(1) The acidity of **5H**$^+$ (p$K_a^{CH} = 4.18$) and **6H**$^+$ (p$K_a^{CH} = -0.03$) is much higher than it is for the chromium and tungsten pentacarbonyl carbene complexes (**2-M**, **3-M**). The principal reason for the higher acidity is that **5H**$^+$ and **6H**$^+$ are cationic, and hence, the main resonance form of the "carbanion" is neutral (**5** and **6**, respectively); additional stabilization of the deprotonated form comes from its aromaticity.

(2) The Brønsted parameters for the reaction of **5H**$^+$ with amines are similar to those for the reactions of **2-M** and **3-M**, suggesting that the extent of proton transfer at the transition state is comparable for these reactions. For the reactions of **5H**$^+$ and **6H**$^+$ with carboxylate ions and of **6H**$^+$ with amines, β is much lower, suggesting a transition state with less proton transfer from the carbene complex to the base.

(3) The intrinsic rate constants for proton transfer to amines and carboxylate ions are substantially lower for **5H**$^+$ than for **2-M** and **3-M**. This appears to be mainly the result of the enhanced resonance stabilization of **5** as compared to that of the anions derived from **2-M** and **3-M**. It is unclear how much the aromaticity of **5** contributes to the reduction in k_0.

(4) The $\log k_0$ values determined for the reactions of **6H**$^+$ are higher than for the reactions of **5H**$^+$, especially $\log k_0$ for the reaction with conjugate ions. This is probably an artifact that results from the lower Brønsted β values.

(5) In comparison to the corresponding reactions of **2-M** and **3-M**, the $k_1^{H_2O}$ and k_1^{OH} values for deprotonation of **5H**$^+$ and **6H**$^+$ by water and OH$^-$ are not as large as one might expect on the basis of the high acidity of **5H**$^+$ and **6H**$^+$. This is again a reflection of lower intrinsic rate constants for **5H**$^+$ and **6H**$^+$.

(6) Because **5H**$^+$ and **6H**$^+$ are cationic, the response to electrostatic effects at the transition state of their reactions is opposite to that for the reactions of **2-M** and **3-M**. Specifically, in the reactions of **2-M** and **3-M** with neutral bases (amines and water), there is electrostatic stabilization, but there is *de*stabilization in the reactions with anionic bases (RCO$_2^-$, OH$^-$). In the reactions of **5H**$^+$ and **6H**$^+$, these effects are reversed.

Table 4. H_0 and h_0 Values as Function of [HCl] in 50% MeCN−50% Water (v/v) at 25 °C

[HCl], M	h_0, M	H_0	[HCl], M	h_0, M	H_0
0.050	0.0437	1.36	0.80	1.15	−0.06
0.100	0.0871	1.06	1.00	1.66	−0.22
0.125	0.112	0.95	1.20	2.29	−0.36
0.200	0.178	0.75	1.50	3.55	−0.55
0.250	0.227	0.64	1.70	5.01	−0.70
0.400	0.398	0.40	2.00	7.76	−0.89
0.500	0.541	0.27	2.50	13.5	−1.13
0.600	0.724	0.14			

Experimental Section

Materials. The tetraflouroborate salts of **5H**$^+$ and **6H**$^+$ were obtained as gifts from Professor Robert Angelici.[49] Stock solutions of these salts in dry acetonitrile were stable for several weeks when stored at −40 °C. Dry acetonitrile was prepared by stirring with P_2O_5 for 24 h, followed by distillation into a receiving flask containing 4 Å molecular sieves. For buffer preparation, acetonitrile was used as received (Fisher Scientific), and water was taken from a Milli-Q water purification system.

Acetic acid (99.9%, Fischer Scientific) and methoxyacetic, cyanoacetic, dichloroacetic, and trichloroacetic acids (all >98%, Aldrich) were used as received. Chloroacetic acid (Aldrich) was recrystallized from 1-propanol. *n*-Butylamine, methoxyethylamine, morpholine, piperidine, 1-(2-hydroxyethylpiperazine) (all Aldrich) were distilled prior to use. Glycinamide (Aldrich) and aminoacetonitrile (Alfa Aesar) were obtained as HCl salts and these, along with piperazine (Aldrich), were recrystallized from 1-propanol. The pK_a^{BH} values of chloroacetic acid, cyanoacetic acid, dichloroacetic acid, and trichloroacetic acid were determined by standard potentiometric procedures[50] and the data treated as presented by Benet and Goyan.[51] The pK_a^{BH} values of all other buffers were known from previous work.[3]

pH and H_0 Determinations. pH measurements were performed on an Orion 611 pH meter equipped with a glass electrode and a Sureflow reference electrode from Corning. The pH meter was calibrated with standard aqueous buffers from Fisher Scientific; pH readings in 50% MeCN−50% water taken at 25 °C were adjusted to the actual value by adding 0.18.[52] An acidity function, H_0, was constructed by setting $H_0 = \mathrm{pH} = 1.06$ for a 0.1 M HCl solution and assuming that H_0 follows the same trend with increasing [HCl] up to 2.5 M as H_0 reported by El-Harakany.[23] Table 4 lists the H_0 as well as the h_0 values as a function of [HCl].

Kinetic Experiments and Spectra. All spectra were taken in a Hewlett-Packard 8452A diode-array UV−visible spectrophotometer. All kinetic runs were performed in an Applied Photophysics DX.17MV stopped-flow spectrophotometer. The procedures were similar to those described in ref 9 except for the following modifications. The reactions of **5H**$^+$ were set up by placing a 50% MeCN−50% water solution of **5H**$^+$ containing 10^{-3} M HCl in one syringe of the stopped-flow apparatus and the appropriate buffer solution in the other syringe. The presence of HCl ensured that the carbene complex would be in its acid form. Both solutions contained the appropriate amount of KCl to bring the ionic strength to 0.1 M.

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For **6H**$^+$, the substrate syringe contained **6H**$^+$ in *pure* acetonitrile, while the solvent in the buffer syringe was 100% water with an ionic strength of 0.2 M adjusted with KCl. Because **6H**$^+$ does not measurably dissociate in pure acetonitrile, this procedure to ensure that the substrate was in its protonated form was superior to one where **6H**$^+$ would have to be placed into a 2.5 M HCl solution in 50% MeCN−50% water and would generate reaction mixtures of very high ionic strength. Note, however, that, even with this procedure, reaction mixtures at high [HCl] had an ionic strength exceeding 0.1 M.

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Supporting Information Available: Tables S1 and S2 (spectrophotometric pK_a^{CH} determinations) and Tables S3−S9 (kinetic data) (10 pages, PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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