

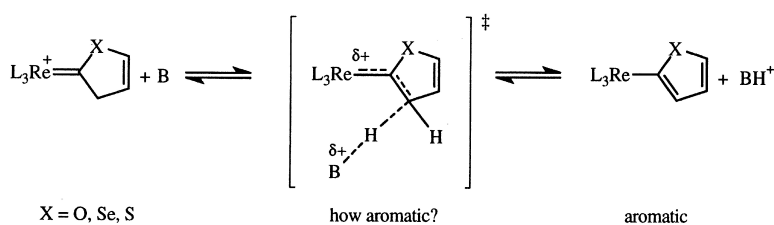
Article

Reactions That Generate Aromatic Molecules: Is Aromatic Stabilization Less or More Advanced than Bond Changes at the Transition State? Kinetic and Thermodynamic Acidities of Rhenium Carbene Complexes

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Reactions That Generate Aromatic Molecules: Is Aromatic Stabilization Less or More Advanced than Bond Changes at the Transition State? Kinetic and Thermodynamic Acidities of Rhenium Carbene Complexes[†]

Claude F. Bernasconi,* Mark L. Ragains, and Santanu Bhattacharya

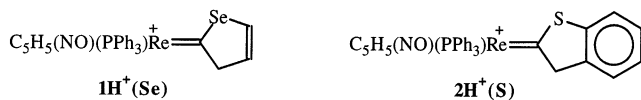
Contribution from the Department of Chemistry and Biochemistry of the University of California, Santa Cruz, California 95064

Received April 14, 2003; E-mail: bernasconi@chemistry.ucsc.edu

Abstract: A kinetic study of the reversible deprotonation of the rhenium carbene complexes **1H⁺(O)**, **1H⁺(S)** and **2H⁺(O)** by carboxylate ions, primary aliphatic and secondary alicyclic amines, water and OH⁻ in 50% MeCN-50% water (v/v) at 25 °C is reported. These carbene complexes are of special interest because in their deprotonated form they represent derivatives of the aromatic heterocycles furan, thiophene and benzofuran. Intrinsic rate constants (*k*₀ for Δ*G*[‡] = 0) determined from appropriate Brønsted plots for these rhenium carbene complexes and for the corresponding selenophene (**1H⁺(Se)**) and benzothiophene (**2H⁺(S)**) derivatives investigated earlier follow the orders furan < selenophene < thiophene and benzofuran ≲ benzothiophene. These orders indicate that an increase in aromaticity leads to an increase in the intrinsic rate constant or a decrease in the intrinsic barrier. This is an unexpected result; it implies that, in contrast to common resonance effects, the development of aromaticity at the transition state is ahead of proton transfer, i.e., the percentage development of the aromatic stabilization energy at the transition state is higher than the percentage of proton transfer.

Introduction

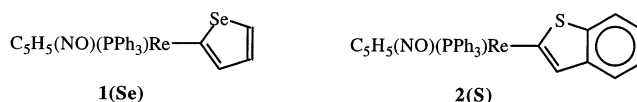
In our ongoing investigation of the kinetic and thermodynamic acidities of Fischer carbene complexes¹ we recently reported a study of the rhenium carbene complexes **1H⁺(Se)** and **2H⁺(S)**.² Two features that distinguish **1H⁺(Se)** and **2H⁺(S)** from previously studied



carbene complexes such as **3H**,³ **4H**⁴ and numerous others¹ are that they are cationic and that



their respective conjugate bases, **1(Se)** and **2(S)**, are neutral and aromatic. Both features are



believed to contribute to the much higher acidity of the rhenium carbene complexes ($\text{p}K_{\text{a}}(\mathbf{1H}^+(\text{Se})) = 4.18$;^{2,5} $\text{p}K_{\text{a}}(\mathbf{2H}^+(\text{S})) = -0.03$ ^{2,5}) compared to that of the (CO)₅Cr-type complexes (e.g., $\text{p}K_{\text{a}}(\mathbf{3H}) = 12.50$;^{3,5} $\text{p}K_{\text{a}}(\mathbf{4H}) = 9.05$).^{4,5}

When compared to the (CO)₅Cr-type complexes **3H** and **4H**, and given the high acidities of **1H⁺(Se)** and **2H⁺(S)**, the *rate* constants for the deprotonation of these latter complexes by various primary and secondary amines as well as by carboxylate ions were found to be unusually low.² This means that the *intrinsic* barriers to proton transfer (Δ*G*₀[‡])⁶ are significantly higher, or the *intrinsic* rate constants (*k*₀)⁶ are significantly lower for the rhenium carbene complexes than for the chromium carbene complexes. For example, for the reactions with primary aliphatic amines, the log *k*₀ values obtained from the corresponding Brønsted plots are 0.14 (**1H⁺(Se)**)² and 0.86 (**2H⁺(S)**)² respectively, while for **3H** and **4H** they are 3.04³ and 2.09,⁴ respectively.

The most important factor that has consistently been associated with changes in the intrinsic rate constants for proton

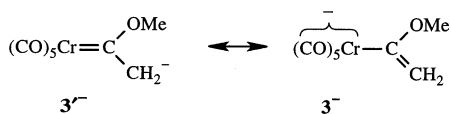
[†] This is Part 28 of the series Physical Organic Chemistry of Transition Metal Complexes. Part 27: Bernasconi, C. F.; Bhattacharya, S. *Organometallics* **2003**, *22*, 1310

(1) Recent reviews: (a) Bernasconi, C. F.; *Chem. Soc. Rev.* **1997**, *26*, 299. (b) Bernasconi, C. F. *Adv. Phys. Org. Chem.* **2002**, *37*, 137.
 (2) Bernasconi, C. F.; Ragains, M. L. *J. Am. Chem. Soc.* **2001**, *123*, 11 890.
 (3) (a) Gandler, J. R.; Bernasconi, C. F. *Organometallics* **1989**, *8*, 2282. (b) Bernasconi, C. F.; Sun, W. *J. Am. Chem. Soc.* **1993**, *115*, 12 532.
 (4) Bernasconi, C. F.; Ali, M. *J. Am. Chem. Soc.* **1999**, *121*, 3039.

(5) In 50% MeCN-50% water (v/v) at 25 °C.

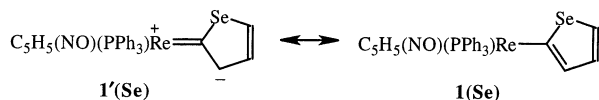
(6) The intrinsic barrier, Δ*G*₀[‡] (intrinsic rate constant, *k*₀) of a reaction with a forward rate constant *k*₁ and reverse rate constant *k*₋₁ is defined as Δ*G*₀[‡] = Δ*G*₀[‡] = Δ*G*₀[‡] (k₀ = *k*₁ = *k*₋₁) when Δ*G*₀ = 0 (*K*₁ = 1).⁷ For proton transfers, statistical factors *p* and *q* are usually included, see below.

transfer from carbon acids is the varying degree of stabilization of the conjugate base by resonance or charge delocalization.⁸ Because the development of resonance or charge delocalization generally lags behind proton transfer at the transition state, the intrinsic barrier becomes larger or the intrinsic rate constant is reduced, and the more so the greater the delocalization.⁹ In the conjugate base of Fischer carbene complexes, e.g. the anion of **3H**, there is extensive charge delocalization as indicated by the resonance form **3⁻**. This



delocalization is thought to be the main reason the deprotonation of such carbene complexes is characterized by lower k_o values than the deprotonation of most other carbon acids except for nitroalkanes.¹

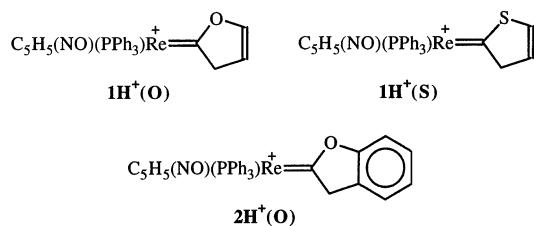
In the conjugate bases of **1H⁺** or **2H⁺** the contribution of the “delocalized” resonance forms such as **1(Se)** is even stronger because they avoid the charge separation in **1'(Se)** and hence



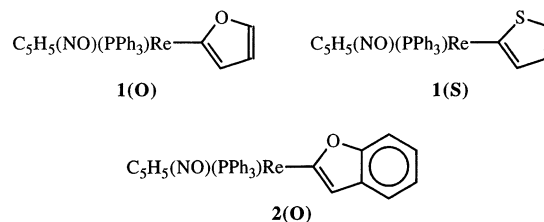
this leads to an even stronger overall stabilization of the conjugate base. This not only increases the thermodynamic acidity of **1H⁺(Se)** but reduces k_o below that for the chromium carbene complexes.

An interesting question is whether the aromaticity of **1(Se)** and **2(S)** which contributes to the increased thermodynamic acidity of **1H⁺(Se)** and **2H⁺(S)**,² also contributes to the lowering of k_o . Such a contribution would be expected if the development of aromaticity lags behind proton transfer in the same way as “ordinary” resonance/delocalization effects lag behind proton transfer.⁸ In view of the centrality of the concept of aromaticity and the chemist’s quest to understand intrinsic reactivity, it is actually surprising that this question has not been asked before. The results of our earlier study were inconclusive on this point because of other factors such as the steric, inductive and π -donor effects of the heteroatom in the heterocycle possibly contributing to the lowering of k_o .

In the present paper we report results of a study of the reactions of the three rhenium carbene complexes **1H⁺(O)**, **1H⁺(S)**, and **2H⁺(O)** with primary aliphatic and secondary alicyclic



amines as well as carboxylate ions in 50% MeCN-50% water (v/v) at 25 °C. Because the aromaticity of the heterocycles follows the order thiophene > selenophene > furan^{10–12} one expects the order of the aromaticity of the respective conjugate bases of the rhenium carbene complexes to be **1(S)** > **1(Se)** > **1(O)** and **2(S)** > **2(O)**. Hence if aromaticity plays a significant



role in lowering k_o for proton transfer,¹³ and secondary effects are negligible, one expects $\log k_o(\mathbf{1H}^+(\mathbf{O})) > \log k_o(\mathbf{1H}^+(\mathbf{Se})) > \log k_o(\mathbf{1H}^+(\mathbf{S}))$ and $\log k_o(\mathbf{2H}^+(\mathbf{O})) > \log k_o(\mathbf{2H}^+(\mathbf{S}))$. As elaborated upon below, this is *not* what we observe which renders the question about the extent of the development of aromaticity at the transition state particularly interesting.

Results

General Features. As was the case for **1H⁺(Se)** and **2H⁺(S)**, **1H⁺(S)** and **2H⁺(O)**, as well as their respective conjugate bases are relatively stable in 50% MeCN-50% water (v/v) as indicated by their UV spectra in this solvent. Furthermore, their deprotonation is fully reversible as demonstrated by recovery of the spectrum of the carbene complex upon treatment of the conjugate base with acid. The furan derivative, **1H⁺(O)**, is also quite stable in 50% MeCN-50% water but treatment of its conjugate base with acid only led to complete recovery of the carbene complex in pure acetonitrile. In 50% MeCN-50% water, the conjugate base of **1H⁺(O)** decomposes, possibly by undergoing ring-opening to form a γ -dicarbonyl compound, a process known to occur under mild conditions.¹⁴ However, this decomposition did not interfere with our pK_a and kinetic measurements described below.

Spectrophotometric pK_a^{CH} Determination. The pK_a^{CH} values of **1H⁺(O)**, **1H⁺(S)** and **2H⁺(O)** were determined from plots of pH versus $\log(A_{\text{max}} - A)/(A - A_{\text{min}})$ according to eq 1

$$\text{pH} = pK_a^{\text{CH}} + \log \frac{A_{\text{max}} - A}{A - A_{\text{min}}} \quad (1)$$

where A_{max} is the absorbance at $\text{pH} \ll pK_a^{\text{CH}}$, A_{min} the absorbance at $\text{pH} \gg pK_a^{\text{CH}}$ and A the absorbance at $\text{pH} \sim pK_a^{\text{CH}}$. For **1H⁺(O)** the measurements were performed in acetate buffers, for **1H⁺(S)** and **2H⁺(O)** in chloro-, dichloro-, and trichloroacetate buffers. A representative plot is shown in Figure S1 (Supporting Information).¹⁵ The results are summarized in Table 1.

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(9) This connection between intrinsic barriers and resonance is not restricted to proton transfers but is a general phenomenon applying to all types of reactions.⁸

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(13) Assuming that the development of aromaticity lags behind proton transfer at the transition state.

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

Table 1. Spectrophotometric and Kinetic pK_a^{CH} Values

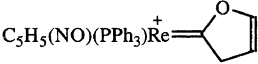
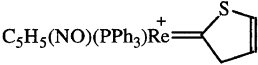
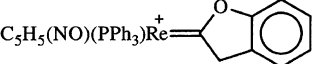
		pK_a^{CH} (spect)	pK_a^{CH} (kinetic)	average pK_a^{CH}
	1H⁺(O)	5.79 ± 0.04	5.77 ± 0.01	5.78 ± 0.03
	1H⁺(S)	2.51 ± 0.03	2.50 ± 0.01	2.51 ± 0.02
	2H⁺(O)	2.12 ± 0.01	2.15 ± 0.05	2.14 ± 0.04

Table 2. Reactions of **1H⁺(O)**, **1H⁺(S)**, and **2H⁺(O)** with Buffers: Summary of Rate Constants and pK_a Values in 50% MeCN-50% Water (v/v) at 25 °C^a

B	pK_a^{BH}	1H⁺(O) $pK_a^{CH} = 5.78$		1H⁺(S) $pK_a^{CH} = 2.51$		2H⁺(O) $pK_a^{CH} = 2.14$	
		$k_1^B, M^{-1} s^{-1}$	$k_{-1}^{BH}, M^{-1} s^{-1}$	$k_1^B, M^{-1} s^{-1}$	$k_{-1}^{BH}, M^{-1} s^{-1}$	$k_1^B, M^{-1} s^{-1}$	$k_{-1}^{BH}, M^{-1} s^{-1}$
piperidine	11.01	$(1.60 \pm 0.03) \times 10^3$	$(9.43 \pm 0.76) \times 10^{-3}$	$(2.25 \pm 0.05) \times 10^4$	$(7.12 \pm 0.47) \times 10^{-5}$	$(9.20 \pm 0.35) \times 10^4$	$(1.27 \pm 0.19) \times 10^{-4}$
piperazine	9.97	$(1.92 \pm 0.03) \times 10^2$	$(1.24 \pm 0.09) \times 10^{-2}$	$(1.04 \pm 0.03) \times 10^4$	$(3.62 \pm 0.24) \times 10^{-4}$	$(3.55 \pm 0.19) \times 10^4$	$(5.34 \pm 0.85) \times 10^{-4}$
HEPA ^b	9.33	$(1.22 \pm 0.01) \times 10^2$	$(3.44 \pm 0.27) \times 10^{-2}$	$(7.62 \pm 0.17) \times 10^3$	$(1.15 \pm 0.08) \times 10^{-3}$	$(1.58 \pm 0.06) \times 10^4$	$(1.05 \pm 0.15) \times 10^{-3}$
morpholine	8.70	$(4.62 \pm 0.07) \times 10^1$	$(5.56 \pm 0.44) \times 10^{-2}$	$(5.21 \pm 0.05) \times 10^3$	$(3.37 \pm 0.22) \times 10^{-3}$	$(1.20 \pm 0.06) \times 10^4$	$(3.38 \pm 0.54) \times 10^{-3}$
n-BuNH ₂	10.40	$(1.15 \pm 0.01) \times 10^2$	$(2.76 \pm 0.22) \times 10^{-3}$	$(9.24 \pm 0.20) \times 10^3$	$(1.19 \pm 0.08) \times 10^{-4}$	$(2.49 \pm 0.03) \times 10^4$	$(1.37 \pm 0.15) \times 10^{-3}$
MeOCH ₂ CH ₂ NH ₂	9.39	$(2.17 \pm 0.04) \times 10^1$	$(5.33 \pm 0.43) \times 10^{-3}$	$(2.16 \pm 0.05) \times 10^3$	$(2.85 \pm 0.19) \times 10^{-4}$	$(5.30 \pm 0.11) \times 10^4$	$(2.89 \pm 0.33) \times 10^{-3}$
H ₂ NCOCH ₂ NH ₂	8.14	$(2.64 \pm 0.09) \times 10^0$	$(1.15 \pm 0.09) \times 10^{-2}$	$(4.44 \pm 0.10) \times 10^2$	$(1.04 \pm 0.07) \times 10^{-3}$	$(8.40 \pm 0.11) \times 10^3$	$(8.40 \pm 0.91) \times 10^{-3}$
NCH ₂ NH ₂	5.29	$(1.78 \pm 0.12) \times 10^{-1}$	$(5.51 \pm 0.58) \times 10^{-1}$	$(5.52 \pm 0.03) \times 10^1$	$(9.15 \pm 0.41) \times 10^{-2}$	$(1.59 \pm 0.13) \times 10^3$	$(1.13 \pm 0.20) \times 10^0$
CH ₃ CO ₂ ⁻	5.93	$(1.07 \pm 0.06) \times 10^0$	$(7.57 \pm 0.73) \times 10^{-1}$	$(1.74 \pm 0.05) \times 10^2$	$(6.60 \pm 0.46) \times 10^{-2}$	$(3.57 \pm 0.19) \times 10^3$	$(5.79 \pm 0.44) \times 10^{-1}$
MeOCH ₂ CO ₂ ⁻	4.73	$(4.06 \pm 0.03) \times 10^{-1}$	$(4.55 \pm 0.50) \times 10^0$	$(6.77 \pm 0.13) \times 10^1$	$(4.08 \pm 0.27) \times 10^{-1}$	$(2.20 \pm 0.06) \times 10^3$	$(5.64 \pm 0.35) \times 10^0$
ClCH ₂ CO ₂ ⁻	3.94	$(2.99 \pm 0.02) \times 10^{-1}$	$(2.07 \pm 0.21) \times 10^1$	$(5.44 \pm 0.14) \times 10^1$	$(2.02 \pm 0.14) \times 10^0$	$(1.73 \pm 0.07) \times 10^3$	$(2.73 \pm 0.19) \times 10^1$
NCH ₂ CO ₂ ⁻	3.56	$(1.03 \pm 0.01) \times 10^{-1}$	$(1.71 \pm 0.23) \times 10^1$	$(4.91 \pm 0.10) \times 10^1$	$(4.37 \pm 0.29) \times 10^0$	$(1.33 \pm 0.05) \times 10^3$	$(5.04 \pm 0.34) \times 10^1$
Cl ₂ CHCO ₂ ⁻	2.38	$(2.94 \pm 0.02) \times 10^{-2}$	$(7.38 \pm 0.77) \times 10^1$	$(2.57 \pm 0.15) \times 10^1$	$(3.46 \pm 0.30) \times 10^1$		
Cl ₃ CCO ₂ ⁻	1.64	$(1.85 \pm 0.02) \times 10^{-2}$	$(2.55 \pm 0.29) \times 10^2$	$(8.45 \pm 0.69) \times 10^0$	$(6.27 \pm 0.64) \times 10^1$	$(5.56 \pm 0.24) \times 10^2$	$(1.76 \pm 0.12) \times 10^3$

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

Kinetics. Most rate measurements were carried out in amine and carboxylate buffers under pseudo-first-order conditions with the carbene complex as the minor component. Some experiments were also performed in HCl solutions. The pseudo-first-order rate constant for equilibrium approach is given by eq 2 with the various terms defined in eq 3; **CH⁺** stands for

$$k_{\text{obsd}} = k_1^{\text{H}_2\text{O}} + k_1^{\text{OH}^-}[\text{OH}^-] + k_1^{\text{B}}[\text{B}] + k_{-1}^{\text{H}}a_{\text{H}^+} + k_{-1}^{\text{H}_2\text{O}} + k_{-1}^{\text{BH}}[\text{BH}] \quad (2)$$

$$\text{CH}^+ \xrightleftharpoons[k_{-1}^{\text{H}}a_{\text{H}^+} + k_{-1}^{\text{H}_2\text{O}} + k_{-1}^{\text{BH}}[\text{BH}]]{k_1^{\text{H}_2\text{O}} + k_1^{\text{OH}^-}[\text{OH}^-] + k_1^{\text{B}}[\text{B}]} \text{C} \quad (3)$$

1H⁺(O), **1H⁺(S)** and **2H⁺(O)**, respectively, B for the buffer base, and BH for the buffer acid. All experiments were run in a stopped-flow spectrophotometer by monitoring the decrease ($\text{pH} < pK_a^{\text{CH}}$) or increase ($\text{pH} > pK_a^{\text{CH}}$) in absorbance due to **CH⁺**. The various rate constants are summarized in Tables 2 and 3.

Kinetic pK_a^{CH} Determination. For **1H⁺(O)**, runs were performed in acetate buffers. Under these conditions, $k_1^{\text{OH}^-}[\text{OH}^-]$ and $k_{-1}^{\text{H}_2\text{O}}$ are negligible and eq 2 simplifies to eq 4

$$k_{\text{obsd}} = k_1^{\text{H}_2\text{O}} + k_{-1}^{\text{H}}a_{\text{H}^+} + k_1^{\text{B}}[\text{B}] + k_{-1}^{\text{BH}}[\text{BH}] \quad (4)$$

Figure S2¹⁵ shows plots of k_{obsd} versus $[\text{AcO}^-]$ at various pH values. The slopes of these plots are given by eq 5. By plotting the slopes versus a_{H^+} (Figure S3¹⁵) one obtains $pK_a^{\text{CH}} = 5.77 \pm 0.01$

$$\text{slope} = k_1^{\text{B}} \left(1 + \frac{a_{\text{H}^+}}{K_a^{\text{CH}}} \right) \quad (5)$$

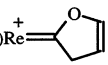
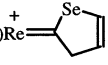
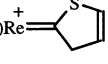
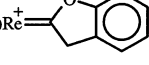
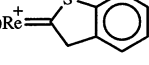
which is in excellent agreement with the spectrophotometric value of 5.78 ± 0.04 . This internal consistency is particularly rewarding for this carbene complex because of the previously mentioned decomposition of **1(O)** which prevented full recovery of **1H⁺(O)** upon addition of acid to **1(O)**. Analysis of the plot in Figure S3¹⁵ also yielded $k_1^{\text{B}} = 1.07 \pm 0.06 \text{ M}^{-1} \text{ s}^{-1}$ from which $k_{-1}^{\text{BH}} = k_1^{\text{B}}K_a^{\text{BH}}/K_a^{\text{CH}} = 0.76 \pm 0.07 \text{ M}^{-1} \text{ s}^{-1}$ was obtained.

The pK_a^{CH} values of **1H⁺(S)** and **2H⁺(O)** are much lower than for **1H⁺(O)** and hence the measurements were performed in HCl solution. Equation 4 simplifies to eq 6 and plots of k_{obsd}

$$k_{\text{obsd}} = k_1^{\text{H}_2\text{O}} + k_{-1}^{\text{H}}a_{\text{H}^+} \quad (6)$$

versus a_{H^+} (Figure S4)¹⁵ yield $k_1^{\text{H}_2\text{O}}$ and k_{-1}^{H} from which $K_a^{\text{CH}} = k_1^{\text{H}_2\text{O}}/k_{-1}^{\text{H}}$ is obtained. Again, there is excellent agreement between the kinetic and spectrophotometric pK_a values (Table 1).

Table 3. Reactions with OH⁻, H₃O⁺, and Water in 50% MeCN-50% Water at 25 °C^a

carbene complex		pK_a^{CH}	$k_1^{H_2O}$ s ⁻¹	k_1^H M ⁻¹ s ⁻¹	k_1^{OH} M ⁻¹ s ⁻¹	$k_{-1}^{H_2O}$ s ⁻¹
	1H⁺(O)	5.78	(4.97±0.41)×10 ⁻⁵	(3.04±0.16)×10 ¹	(1.99±0.06)×10 ³	(7.61±0.54)×10 ⁻⁷
	1H⁺(Se)^b	4.17	(1.82±0.13)×10 ⁻²	(2.80±0.08)×10 ²	(1.61±0.04)×10 ⁴	(1.55±0.11)×10 ⁻⁷
	1H⁺(S)	2.51	(2.02±0.09)×10 ⁻¹	(6.64±0.03)×10 ¹	(2.37±0.13)×10 ⁴	(4.86±0.35)×10 ⁻⁹
	2H⁺(O)	2.14	(1.48±0.16)×10 ¹	(2.09±0.07)×10 ³		
	2H⁺(S)^b	-0.03	(9.25±0.20)×10 ¹	(7.88±0.27)×10 ¹		

^a Ionic strength 0.1 M (KCl). ^b Reference 2.

Kinetics in Carboxylate and Amine Buffers. These experiments were performed at buffer ratios of approximately 1:1. The rate constants k_1^B and k_{-1}^{BH} were obtained by solving eq 5 for k_1^B and calculating k_{-1}^{BH} as $k_1^B K_a^{BH}/K_a^{CH}$ where K_a^{CH} is taken from the average of the kinetic and spectrophotometric pK_a^{CH} .

Kinetics in KOH and HCl Solutions. In KOH solutions k_{obsd} is given by eq 7

$$k_{obsd} = k_1^{OH} [OH^-] + k_{-1}^{H_2O} \quad (7)$$

however, intercepts of plots of k_{obsd} versus $[OH^-]$ were too small to yield reliable $k_{-1}^{H_2O}$ values and hence $k_{-1}^{H_2O}$ was obtained as $k_1^{OH} K_w / K_a^{CH}$ with K_w being the ionic product of the solvent.¹⁶ For **2H⁺(O)** the rates were too fast for an accurate measurement by the stopped-flow technique.

In HCl solution eq 6 applies and these experiments yielded k_{-1}^H and $k_1^{H_2O}$ values for **1H⁺(S)** and **2H⁺(O)** as described earlier. For **1H⁺(O)** $k_1^{H_2O}$ was too small to measure accurately and hence $k_1^{H_2O}$ was obtained as $k_{-1}^H K_a^{CH}$.

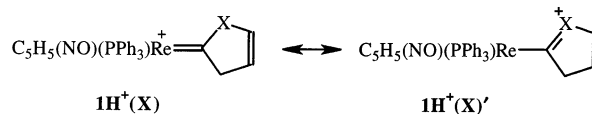
Discussion

pK_a^{CH} Values. The pK_a^{CH} values of **1H⁺(O)**, **1H⁺(S)**, and **2H⁺(O)**, which are taken as the average of the spectrophotometrically and kinetically determined values, are reported in Table 3 along with the previously measured pK_a s of **1H⁺(Se)** and **2H⁺(S)**. There are significant differences in the acidities of these rhenium carbene complexes but, as a class, they are all substantially more acidic (pK_a^{CH} range from -0.03 to 5.78) than the chromium or tungsten carbene complexes (pK_a^{CH} = 9.05 for **4H**, 12.50 for **3H**).

As pointed out before, the principal reason for the high acidity of the rhenium carbene complexes is their cationic character. An additional factor is that the respective conjugate bases are aromatic. In fact, the relative acidities which follow the order **1H⁺(S)** > **1H⁺(Se)** > **1H⁺(O)** for the monocyclic derivatives and **2H⁺(S)** > **2H⁺(O)** for the fused benzoheterocycles correlate with the relative aromaticity of the respective heterocycles, i.e.,

thiophene > selenophene > furan¹⁰⁻¹² and benzothiophene > benzofuran.¹⁷

A third factor expected to affect the acidities is the identity of the heteroatom (O, S, Se) which may exert an influence that is separate from its effect on aromaticity and is related to its π -donor and inductive effects. The π -donor effect is expected to reduce the acidity by stabilizing the respective acid forms (e.g., **1H⁺(X)**), whereas the inductive effect should increase the acidity.



Both factors follow the order O > S > Se.¹⁸ This implies that, if the π -donor effect were dominant and aromaticity did not play a role, the acidity orders should be **1H⁺(Se)** > **1H⁺(S)** > **1H⁺(O)** and **2H⁺(S)** > **2H⁺(O)**, whereas the opposite order should prevail if the inductive effect is dominant.

That the π -donor effect more than offsets the inductive effect can be seen when comparing **3H** and **4H** where aromaticity is not a factor and **4H** (pK_a^{CH} = 9.05) is more acidic than **3H** (pK_a^{CH} = 12.50). As to the relative importance of the π -donor effect and aromaticity, the *experimental* acidity orders for the monocyclic carbene complexes are, as mentioned above, those expected based on the aromatic stabilization of the respective conjugate bases rather than those based on the π -donor effect, and hence we conclude the aromaticity factor to be dominant.

Incidentally, our reasoning and conclusions are quite similar to those reached by Kresge and Meng²⁰ regarding the relative acidities of **5H** (pK_a = 11.87) and **6H** (pK_a = 8.85), i.e., the

(17) Bird, C. W. *Tetrahedron* **1987**, *43*, 4725.

(18) π -Donor effect: the R values for MeO, MeS and MeSe are -0.56, -0.23, and -0.16, respectively; the R^+ values for MeO and MeS are -1.07 and -0.83, respectively, while the σ_R values for MeO and MeS are -0.43 and -0.15, respectively.¹⁹ Inductive effect: the F values for MeO, MeS and MeSe are 0.29, 0.23 and 0.16, respectively, whereas the σ_F values for MeO and MeS are 0.30 and 0.20, respectively.¹⁹

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

(20) Kresge, A. J.; Meng, Q. *J. Am. Chem. Soc.* **2002**, *124*, 9189.

(16) pK_w = 15.19 in 50% MeCN-50% water (v/v) at 25 °C (μ = 0.1 M KCl).^{3b}

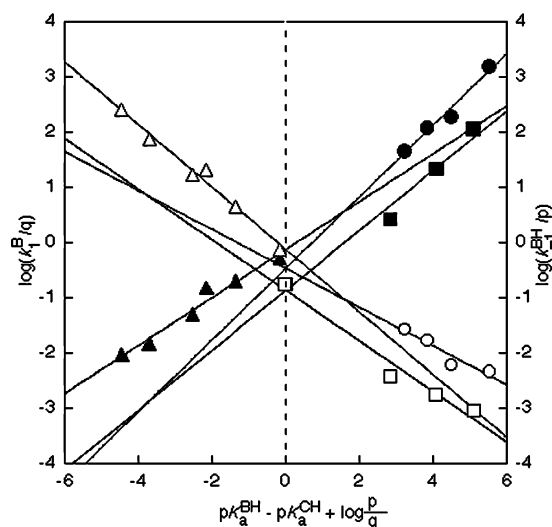
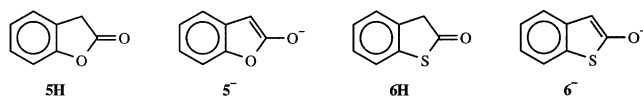


Figure 1. Brønsted plot for the reactions of $1\text{H}^+(\text{O})$ with buffers. Filled symbols, k_1^{B} , open symbols, k_{-1}^{BH} . ●, ○: R_2NH ; ■, □: RNH_2 ; ▲, △: RCOO^- . The dashed vertical line goes through the points where the k_1^{B}/q and k_{-1}^{BH}/p lines intersect which correspond to $\log k_0$.

conjugate base of **6H** (thiophene ring) is more aromatic than that of **5H** (furan ring).



Rate Constants. The rate constants for proton-transfer involving amine and carboxylate buffers are reported in Table 2, whereas those involving H_3O^+ , OH^- , and the solvent are summarized in Table 3. Statistically corrected Brønsted plots²¹ for the dependence of k_1^{B} and k_{-1}^{BH} on the pK_a difference between the respective carbene complexes and buffer acids are shown in Figures 1–3. They yield the Brønsted α and β values summarized in Table 4. From the points where the lines of $\log(k_1^{\text{B}}/q)$ and $\log(k_{-1}^{\text{BH}}/p)$ intersect, the *intrinsic* rate constants, defined as $k_0 = k_1^{\text{B}}/q = k_{-1}^{\text{BH}}/p$, were obtained (in Table 4 reported as $\log k_0$).

Brønsted Parameters. There is considerable variation in the Brønsted β and α values, suggesting that the degree of proton transfer at the transition state varies with the base type as well as with the carbene complex. Two trends are noteworthy. (1) For all three base types, β decreases with increasing acidity of the carbene complex. This suggests that the transition state becomes more reactant-like as the reactions become thermodynamically more favorable which is consistent with the Hammond²²–Leffler²³ principle.

(2) The β values for the reactions with carboxylate ions are generally lower than for the reactions with amines. Because, as a group, the carboxylate ions are less basic than the amines and hence the deprotonation is thermodynamically less favorable than with amines, the Hammond–Leffler principle would predict higher rather than lower β values for the carboxylate ion reactions. This suggests that another factor is involved which

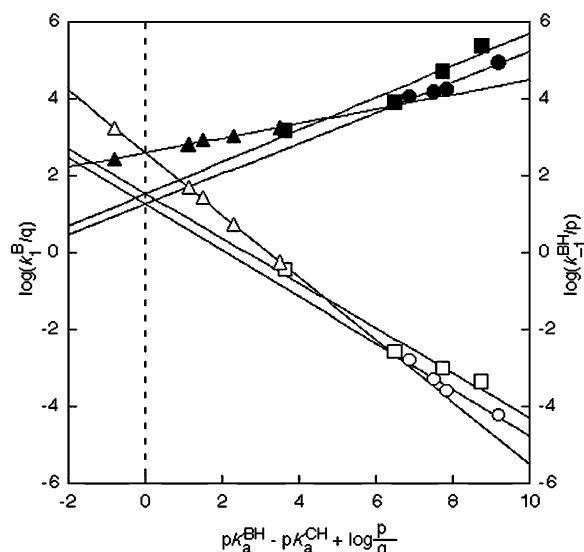


Figure 2. Brønsted plot for the reactions of $1\text{H}^+(\text{S})$ with buffers. Filled symbols, k_1^{B} , open symbols, k_{-1}^{BH} . ●, ○: R_2NH ; ■, □: RNH_2 ; ▲, △: RCOO^- . The dashed vertical line goes through the points where the k_1^{B}/q and k_{-1}^{BH}/p lines intersect which correspond to $\log k_0$.

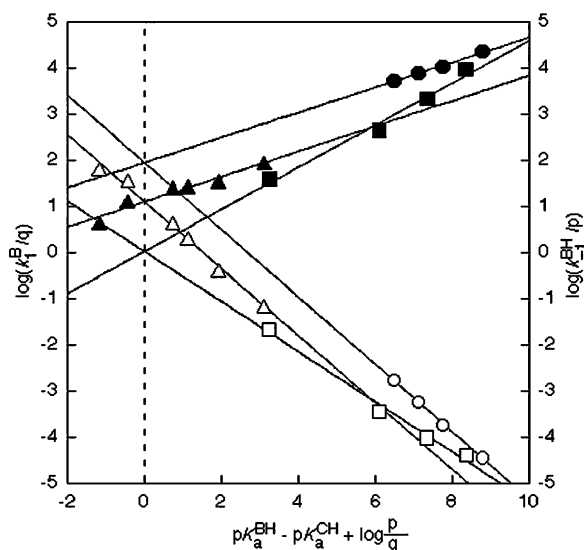
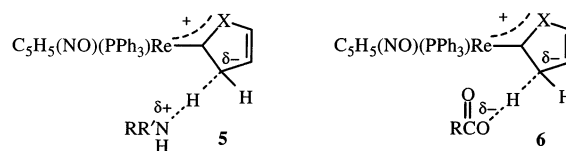


Figure 3. Brønsted plot for the reactions of $2\text{H}^+(\text{O})$ with buffers. Filled symbols, k_1^{B} , open symbols, k_{-1}^{BH} . ●, ○: R_2NH ; ■, □: RNH_2 ; ▲, △: RCOO^- . The dashed vertical line goes through the points where the k_1^{B}/q and k_{-1}^{BH}/p lines intersect which correspond to $\log k_0$.

overrides the Hammond–Leffler principle. We propose that this factor is an electrostatic effect which operates at the transition state. The transition states for the reactions of $1\text{H}^+(\text{X})$ with amines and carboxylate ions are shown in **5** and **6**, respectively.



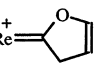
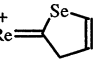
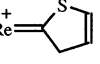
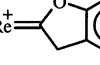
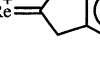


In **5** there is electrostatic stabilization between the partial positive charge on the amine and the partial negative charge on the carbon; this stabilization increases for a more advanced transition state because these charges become larger and move closer together. There is also electrostatic destabilization between

(21) Strictly speaking, these are Eigenplots (Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1); q is the number of equivalent basic sites on the buffer base, p the number of equivalent protons on the buffer acid.

(22) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

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

Table 4. Summary of Brønsted α - and β -Values and $\log k_0$ for the Intrinsic Rate Constants in 50% MeCN-50% Water at 25 °C

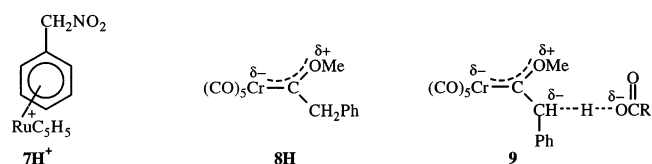
carbene complex	$\text{p}K_{\text{a}}^{\text{CH}}$	Base type	β	α	$\log k_0$	
 $\text{C}_5\text{H}_5(\text{NO})(\text{PPh}_3)\text{Re}^+$	$1\text{H}^+(\text{O})$	5.78	RCO_2^-	0.43 ± 0.04	0.57 ± 0.04	-0.01 ± 0.12
			RNH_2	0.53 ± 0.06	0.47 ± 0.08	-0.83 ± 0.22
			R_2NH	0.65 ± 0.08	0.35 ± 0.08	-0.46 ± 0.35
 $\text{C}_5\text{H}_5(\text{NO})(\text{PPh}_3)\text{Re}^+$	$1\text{H}^+(\text{Se})^{\text{a}}$	4.18	RCO_2^-	0.27 ± 0.02	0.73 ± 0.12	0.72 ± 0.03
			RNH_2	0.53 ± 0.03	0.47 ± 0.03	0.14 ± 0.15
			R_2NH	0.49 ± 0.04	0.51 ± 0.04	0.92 ± 0.23
 $\text{C}_5\text{H}_5(\text{NO})(\text{PPh}_3)\text{Re}^+$	$1\text{H}^+(\text{S})$	2.51	RCO_2^-	0.21 ± 0.02	0.79 ± 0.02	1.21 ± 0.03
			RNH_2	0.42 ± 0.05	0.58 ± 0.05	0.27 ± 0.34
			R_2NH	0.40 ± 0.07	0.60 ± 0.07	1.05 ± 0.54
 $\text{C}_5\text{H}_5(\text{NO})(\text{PPh}_3)\text{Re}^+$	$2\text{H}^+(\text{O})$	2.14	RCO_2^-	0.19 ± 0.01	0.81 ± 0.01	2.62 ± 0.02
			RNH_2	0.42 ± 0.09	0.58 ± 0.09	1.40 ± 0.61
			R_2NH	0.40 ± 0.07	0.60 ± 0.07	1.26 ± 0.56
 $\text{C}_5\text{H}_5(\text{NO})(\text{PPh}_3)\text{Re}^+$	$2\text{H}^+(\text{S})^{\text{a}}$	-0.03	RCO_2^-	0.12 ± 0.01	0.88 ± 0.01	2.85 ± 0.05
			RNH_2	0.33 ± 0.04	0.67 ± 0.04	0.84 ± 0.38
			 $(\text{CO})_5\text{Cr}=\text{C}(\text{OMe})\text{CH}_3$	$(3\text{H})^{\text{b}}$	12.50	RNH_2
R_2NH	0.62 ± 0.03	0.38 ± 0.03				3.70 ± 0.07
 $(\text{CO})_5\text{Cr}=\text{C}(\text{SMe})\text{CH}_3$	$(4\text{H})^{\text{c}}$	9.05	RCO_2^-	0.44 ± 0.06	0.56 ± 0.06	2.17 ± 0.24
			RNH_2	0.48 ± 0.04	0.52 ± 0.04	2.09 ± 0.08
			R_2NH	0.45 ± 0.06	0.55 ± 0.06	2.61 ± 0.10

^a Reference 2. ^b Reference 3b. ^c Reference 4.

the positive charge on the rhenium moiety and the positive charge on the amine nitrogen which counteracts the above stabilizing effects and tends to increase for a more advanced transition state.

In **6**, there is electrostatic destabilization between the partial negative charges on the carboxylate ion and the carbon. This destabilization can be minimized for an early transition state because of the small charge on the carbon. A further advantage of an early transition state is that the large negative charge on the base interacts favorably with the positive charge on the rhenium moiety.

A similar favorable electrostatic interaction may explain the relatively low β value (0.38) for the deprotonation of the cationic 7H^+ by carboxylate ions relative to β for the deprotonation of



7H^+ by primary amines (0.54).²⁴ The same phenomenon can even be seen in the deprotonation of the neutral but zwitterionic carbene complex **8H** where β for carboxylate ions is 0.33, whereas that for primary amines is 0.54.³ In this case, the

transition state for the carboxylate reaction probably adopts a geometry that favors the proximity between the partial positive charge on the methoxy group and the partial negative charge on the carboxylate ion (**9**). In the deprotonation of **4H**, $\beta_{\text{RCO}_2^-} = 0.44$ and $\beta_{\text{RNH}_2} = 0.45$ are about equal, presumably because the MeS group is a weaker π -donor,¹⁸ and hence, there is only a small positive charge on the MeS group. This latter carbene complex thus approaches the behavior of purely organic carbon acids such as ketones or nitroalkanes^{25,26} where $\beta_{\text{RCO}_2^-}$ is typically somewhat greater than β_{amine} , consistent with the Hammond–Leffler principle.

Intrinsic Rate Constants. The intrinsic rate constants reported in Table 4 need to be interpreted with caution. Those k_0 values that could be obtained by interpolation of the appropriate Brønsted plots because $\text{p}K_{\text{a}}^{\text{BH}} - \text{p}K_{\text{a}}^{\text{CH}}$ covers a range from moderately positive to moderately negative, are the most reliable, irrespective of the β and α values. The k_0 values

- (24) Moutiers, G.; Peignieux, A.; Vichard, D.; Terrier, F. *Organometallics* **1998**, *17*, 4469.
 (25) (a) Bernasconi, C. F.; Bunnell, R. D. *Isr. J. Chem.* **1985**, *26*, 420. (b) Bernasconi, C. F.; Paschalis, P. *J. Am. Chem. Soc.* **1986**, *108*, 2969. (c) Bernasconi, C. F.; Kliner, D. A. V.; Mullin, A. S.; Ni, J.-X. *J. Org. Chem.* **1988**, *53*, 3342.
 (26) (a) Terrier, F.; Lelièvre, J.; Chatrousse, A.-P. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1479. (b) Moutier, G.; Thuet, G.; Terrier, F. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1476. (c) Moutiers, G.; Peignieux, A.; Terrier, F. *J. Chem. Soc., Perkin Trans. 2* **1998**, 2489.

for the deprotonation of $1\mathbf{H}^+(\mathbf{O})$, $1\mathbf{H}^+(\mathbf{Se})$, $1\mathbf{H}^+(\mathbf{S})$, and $2\mathbf{H}^+(\mathbf{O})$ by the carboxylate ions belong to this category. The intrinsic rate constants obtained by extrapolation of Brønsted plots, i.e., when $\text{p}K_{\text{a}}^{\text{BH}} - \text{p}K_{\text{a}}^{\text{CH}}$ has the same sign for all bases, are potentially less reliable. This is especially true when $|\text{p}K_{\text{a}}^{\text{BH}} - \text{p}K_{\text{a}}^{\text{CH}}|$ is quite large, leading to long extrapolations, as is the case for the reactions of $1\mathbf{H}^+(\mathbf{S})$, $2\mathbf{H}^+(\mathbf{O})$ and especially $2\mathbf{H}^+(\mathbf{S})$ with the amines. However, as long as the Brønsted coefficients are similar for reactions to be compared to each other, the relative k_{o} values obtained from such extrapolations should still be reliable measures of relative intrinsic rate constants. This latter situation applies in comparing the k_{o} values for the reactions of $1\mathbf{H}^+(\mathbf{O})$, $1\mathbf{H}^+(\mathbf{Se})$, $1\mathbf{H}^+(\mathbf{S})$, and $2\mathbf{H}^+(\mathbf{O})$ with the primary amines ($\beta = 0.53, 0.53, 0.42$, and 0.42 , respectively) and the reaction of $1\mathbf{H}^+(\mathbf{Se})$, $1\mathbf{H}^+(\mathbf{S})$, and $2\mathbf{H}^+(\mathbf{O})$ with the secondary amines ($\beta = 0.49, 0.40$ and 0.40 respectively). For the reaction of $1\mathbf{H}^+(\mathbf{O})$ with the secondary amines the β value (0.65) is somewhat outside the range of the other β values but $|\text{p}K_{\text{a}}^{\text{BH}} - \text{p}K_{\text{a}}^{\text{CH}}|$ is relatively small in this case which means that k_{o} for this set may also be safely included in a comparison of the reactions of all three $1\mathbf{H}^+(\mathbf{X})$ derivatives.

For the reactions of $2\mathbf{H}^+(\mathbf{O})$ and $2\mathbf{H}^+(\mathbf{S})$ with carboxylate ions ($\beta = 0.19$ and 0.12 , respectively) the situation is marginal while for the reactions of $2\mathbf{H}^+(\mathbf{O})$ and $2\mathbf{H}^+(\mathbf{S})$ with primary amines ($\beta = 0.42$ and 0.33 , respectively) the $|\text{p}K_{\text{a}}^{\text{BH}} - \text{p}K_{\text{a}}^{\text{CH}}|$ values are too large to lead to reliable relative k_{o} values.

Taking into account the above considerations we note the following trends. (1) For the reactions of $1\mathbf{H}^+(\mathbf{X})$ with all three base types, $\log k_{\text{o}}$ follows the order $1\mathbf{H}^+(\mathbf{O}) < 1\mathbf{H}^+(\mathbf{Se}) < 1\mathbf{H}^+(\mathbf{S})$, i.e., $-0.01 < 0.72 < 1.21$ for RCOO^- , $-0.83 < 0.14 < 0.27$ for RNH_2 and $-0.46 < 0.92 < 1.05$ for R_2NH . The fact that the same qualitative order is observed irrespective of base type constitutes strong evidence that the observed trends are a true reflection of the relative order of the intrinsic rate constants.

(2) For the reactions of $2\mathbf{H}^+(\mathbf{X})$ the results are less clear-cut because the criteria for the reliability of the obtained k_{o} values are not met. Thus, even though the $\log k_{\text{o}}$ values of $2\mathbf{H}^+(\mathbf{X})$ with the carboxylate ions follow the same trend as for the reactions of $1\mathbf{H}^+(\mathbf{X})$, i.e., $2\mathbf{H}^+(\mathbf{O}) < 2\mathbf{H}^+(\mathbf{S})$, the difference in the $\log k_{\text{o}}$ values (2.62 versus 2.85) is quite small. For the reactions with the primary amines, $\log k_{\text{o}}$ for $2\mathbf{H}^+(\mathbf{O})$ (1.40) is larger than the $2\mathbf{H}^+(\mathbf{S})$ (0.84), but the experimental uncertainty in these values are too large to allow a firm conclusion.

(3) The intrinsic reactivity of the bicyclic carbene complexes is significantly higher than that of their monocyclic analogues. Part but probably not all of the enhanced reactivity may be an artifact due to the differences in the β values; the reasons for the higher reactivity are unclear but do not affect the main conclusions from this work as outlined below.

Rate Constants for the Reactions with OH^- , H_3O^+ , and Water. These rate constants are reported in Table 3. The $k_1^{\text{H}_2\text{O}}$ values for the deprotonation by water increase with increasing acidity of the carbene complex as one would expect. However, this increase is disproportionately large; for example, for the monocyclic carbene complexes, $\log(k_1^{\text{H}_2\text{O}}(\text{S})/k_1^{\text{H}_2\text{O}}(\text{O})) = 3.61$ while $\text{p}K_{\text{a}}^{\text{CH}}(\text{O}) - \text{p}K_{\text{a}}^{\text{CH}}(\text{S}) = 3.27$, or $\log(k_1^{\text{H}_2\text{O}}(\text{Se})/k_1^{\text{H}_2\text{O}}(\text{O})) = 2.56$ while $\text{p}K_{\text{a}}^{\text{CH}}(\text{Se}) - \text{p}K_{\text{a}}^{\text{CH}}(\text{O}) = 1.61$. This large increase in $k_1^{\text{H}_2\text{O}}$ is the result of the same kind of increase in the intrinsic rate constants seen for the reactions with buffer bases. For the bicyclic carbene complexes, the increase is less dramatic, i.e.,

$\log(k_1^{\text{H}_2\text{O}}(\text{S})/k_1^{\text{H}_2\text{O}}(\text{O})) = 0.80$ for $\text{p}K_{\text{a}}^{\text{CH}}(\text{O}) - \text{p}K_{\text{a}}^{\text{CH}}(\text{S}) = 2.17$. In this case it is not clear whether the increased $k_1^{\text{H}_2\text{O}}$ value for $2\mathbf{H}^+(\mathbf{S})$ is only the result of the lower $\text{p}K_{\text{a}}^{\text{CH}}$ value or whether there is a contribution from an increased intrinsic rate constant for the thia derivative. This is the same ambiguity seen for the reaction with buffer bases.

For the deprotonation by hydroxide ion, the increase in the k_1^{OH} values with increasing acidity of the monocyclic rhenium carbene complexes is much smaller than for the deprotonation by water; for example $(\log k_1^{\text{OH}}(\text{S})/k_1^{\text{OH}}(\text{O})) = 1.08$ for $\text{p}K_{\text{a}}^{\text{CH}}(\text{O}) - \text{p}K_{\text{a}}^{\text{CH}}(\text{S}) = 3.27$ and $(\log k_1^{\text{OH}}(\text{S})/k_1^{\text{OH}}(\text{O})) = 0.91$ for $\text{p}K_{\text{a}}^{\text{CH}}(\text{O}) - \text{p}K_{\text{a}}^{\text{CH}}(\text{S}) = 1.61$. These smaller increases are most likely the result of a very reactant like transition state because the reactions are extremely favorable thermodynamically; no conclusions can be drawn regarding the relative intrinsic rate constants for these reactions.

Significance of the Trend in the Intrinsic Rate Constants.

The intrinsic rate constants for the deprotonation of all Fischer carbene complexes are low because the development of the resonance/delocalization in their respective conjugate bases lags behind proton transfer at the transition state.¹ The fact that the k_{o} values for the deprotonation of the rhenium type carbene complexes are even lower than for the chromium type complexes $3\mathbf{H}$ or $4\mathbf{H}$ (Table 4) is due to their cationic nature which leads to particularly strong resonance stabilization of their conjugate bases.² The main objective of the present work was to examine whether the aromaticity of these conjugate bases contributes to this reduction of the intrinsic rate constants; such a contribution would be expected if the development of the aromaticity were to lag behind proton transfer at the transition state in the same way as the development of simple resonance lags behind proton transfer.

As outlined in the Introduction, aromaticity of the heterocycles follows the order furan < selenophene < thiophene. In the absence of other factors and assuming that the development of aromaticity lags behind proton transfer, this should lead to $1\mathbf{H}^+(\mathbf{O}) > 1\mathbf{H}^+(\mathbf{Se}) > 1\mathbf{H}^+(\mathbf{S})$ and $2\mathbf{H}^+(\mathbf{O}) > 2\mathbf{H}^+(\mathbf{S})$ for the order of the intrinsic rate constants. This, however, is the opposite of the experimental order. One possible interpretation of our findings is that aromaticity plays only a minor role and its effect is overshadowed by other factors associated with the nature of the heteroatom X. These other factors should be the same that lead to differences in k_{o} between the deprotonation of $3\mathbf{H}$ and $4\mathbf{H}$; they include inductive, π -donor and steric effects as discussed in detail elsewhere.⁴ A quantitative assessment of the individual contributions of these factors is difficult²⁷ but a comparison of the k_{o} values for $3\mathbf{H}$ and $4\mathbf{H}$ shows that their combined effect results in intrinsic rate constants that are significantly lower for the thia ($4\mathbf{H}$) than for the oxa ($3\mathbf{H}$) derivative.²⁸

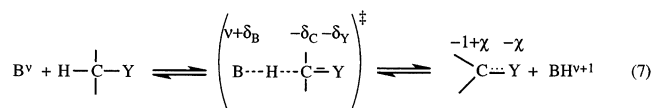
It is reasonable to assume that those same factors also operate in the reactions of the rhenium carbene complexes and that their combined effect should be qualitatively the same as for the chromium carbene complexes. This means that, in the absence of aromaticity, the reactions of the oxa rhenium complexes

(27) The inductive effect is expected to enhance k_{o} for $3\mathbf{H}$ more than for $4\mathbf{H}$, the steric effect is expected to reduce k_{o} for $4\mathbf{H}$ more than for $3\mathbf{H}$, whereas the π -donor effect may go either way because of two competing interaction mechanisms.⁴

(28) The same result was obtained for the $(\text{CO})_5\text{W}$ analogues of $3\mathbf{H}$ and $4\mathbf{H}$, respectively.⁴

should have higher intrinsic rate constants than their thia analogues. However, the experimental order of the k_0 values is $1\text{H}^+(\text{O}) < 1\text{H}^+(\text{Se}) < 1\text{H}^+(\text{S})$ and $2\text{H}^+(\text{O}) \approx 2\text{H}^+(\text{S})$. This implies that aromaticity leads to an increase rather than the expected decrease in the intrinsic rate constants and that, at least for the $1\text{H}^+(\text{X})$ type carbene complexes, this factor is quite substantial since it more than offsets the combined result of the inductive, steric and π -donor effects. *Such an increase can only be explained if the development of aromaticity is ahead of proton transfer at the transition state. In other words, the percentage development of the aromatic stabilization energy at the transition state is higher than the percentage of proton transfer.*

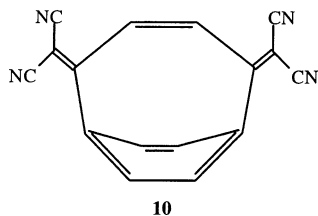
Early Development of Aromaticity: Are There Precedents? Our initial hypothesis was that, in the context of its effect on intrinsic barriers, aromaticity may simply be considered a special case of resonance. In other words, the same constraints that prevent extensive development of resonance stabilization at the transition state should apply to the development of aromaticity. The gist of these constraints was captured in a model initially proposed by Kresge²⁹ in the context of proton transfers from nitroalkanes, a model that we have refined^{8,30} and applied to the generalized reaction scheme of eq 7.³¹ The basic idea is that the delocalization of the negative charge into



the π -acceptor Y can only occur if there is development of the C–Y π -bond. Hence, the fraction of charge on Y depends on the fraction of π -bond formation, and the fraction of π -bond formation in turn depends on the fraction of charge transferred from the base to the carbon acid. This means that, at the transition state, the charge on Y can never be very high since it represents only a fraction of a fraction.

Our results suggest that no such constraints apply to the development of aromaticity. On the contrary, only relatively minor progress in the creation of the appropriate orbitals and/or their optimal alignment seems to be required for aromatic stabilization to become disproportionately effective. There is some evidence which suggests that our conclusions are not without precedent.

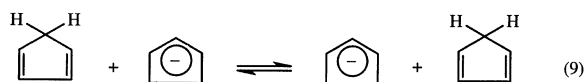
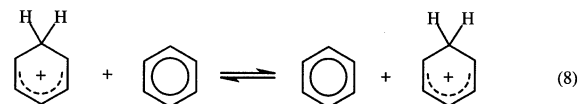
(1) The aromaticity of **10**, as suggested by the calculated NICS value³² at the center of the C₆ ring (−8.1), is quite close to that of benzene (−9.7), even though there is extreme bending



of the C₆ ring.³³ The same is true for a benzene whose geometry was constrained to that of **10** (NICS value of −7.7).³³ These results imply that even though bending leads to a substantial overall destabilization of the molecule, it does not necessarily

follow that it is the loss of aromaticity that results in the destabilization, a point discussed by Minkin et al.³⁴ Similar results were reported for highly bent pyrene systems.³⁵

(2) Recent ab initio calculations in our laboratory suggest that there is a disproportionately large degree of aromaticity at the transition state of the identity carbon-to-carbon proton transfer of reactions 8 and 9.³⁶



(3) According to computed NICS values, the transition state for the trimerization of acetylene to form benzene is highly aromatic,³⁷ despite the fact that the reaction is strongly exothermic, which suggests that the transition state should be reactant-like.^{22,23} We note, however, that here the aromaticity of the transition state refers to “in-plane” aromaticity³⁸ while that of benzene is “ π -aromaticity.”

Conclusions

The most important and novel conclusion from this work is that the aromaticity of the conjugate bases of the rhenium carbene complexes does not increase the intrinsic barrier (reduce the intrinsic rate constant) to proton transfer but lowers it (increases k_0). This implies that the development of aromaticity is ahead of proton transfer at the transition state which contrasts with common resonance/delocalization effects that lag behind proton transfer at the transition state. It appears that the constraints that prevent resonance/delocalization effects from developing in proportion to proton transfer do not apply to the development of aromaticity. The possible generality of this conclusion clearly needs to be tested although there are some indications from other systems that the behavior of our reaction system may not be unprecedented.

Experimental Section

Synthesis of Rhenium Carbene Complexes. The synthesis of $1\text{H}^+(\text{O})$ and $1\text{H}^+(\text{S})$ involved the steps shown in Scheme 1; for $2\text{H}^+(\text{O})$, benzofuran was used in step 7. **13**, **14**, **15**, **16**, and **17** were prepared as described by Tam et al.³⁹ **18** and **19** were

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(31) *Ab initio* calculations³⁰ for gas-phase identity reactions of the type $\text{CH}_3\text{Y} + \text{CH}_2=\text{Y}^- \rightleftharpoons \text{CH}_2=\text{Y}^- + \text{CH}_3\text{Y}$ indicate that the proton in flight bears a partial positive charge but it is not clear that the same is true in solution and none is shown in eq 7. Whether or not there is such a charge does not affect the argument.

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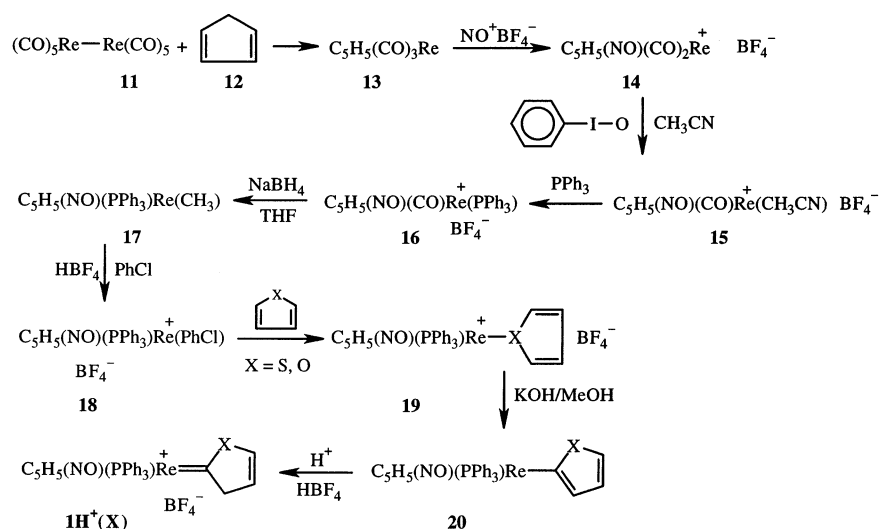
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Scheme 1



synthesized as described by Kowalczyk et al.⁴⁰ **20** and the BF_4^- salts of **1H+(X)** and **(2H+(X))** were synthesized by the procedure of Angelici et al.⁴¹ **1H+(O)** and **2H+(O)** are new compounds. The spectral data of **1H+(O)**, **1H+(S)** and **2H+(O)** are as follows:

1H+(O): ^1H NMR δ (CD_2Cl_2): 7.75–7.45 (m, Ph), 7.40–7.25 (m, Ph), 7.16 (s, br, H(5)), 6.91 (s, br, H(4)), 5.42 (d, br, H(3)), 5.36 (d, br, H(3')), 5.72 (s, Cp). ^{13}C NMR δ (CD_2Cl_2): 222.75 (d, C(2)), 66.20 (s, C(3)), 132.50 (s, C(4)), 131.94 (s, C(5)), 96.28 (s, Cp), 134.19 (d, Ph), 133.44 (d, Ph), 130.33 (d, Ph), 129.80 (d, Ph). IR cm^{-1} $\nu(\text{NO})$ (CH_2Cl_2): 1742 (s). MS: m/z 612.16 (M^+). UV (CH_2Cl_2): 321 nm (ϵ 5337).

1H+(S)⁴¹: ^1H NMR δ (CD_2Cl_2): 7.55 (s, br, Ph), 7.36–7.78 (m, Ph), 7.11 (d, H(5)), 6.88 (m, H(4)), 4.17 (d, br, H(3)), 4.05 (d, br, H(3')), 5.80 (s, Cp). ^{13}C NMR δ (CD_2Cl_2): 268.89 (d, C(2)), 56.71 (s, C(3)), 146.37 (s, C(4)), 150.60 (s, C(5)), 97.90 (s, Cp), 134.30 (d, Ph), 133.36 (d, Ph), 131.56 (d, Ph), 129.76 (d, Ph). IR cm^{-1} $\nu(\text{NO})$ (CH_2Cl_2): 1714 (s). MS: m/z 628.10 (M^+). UV (CH_2Cl_2): 355 nm (ϵ 7408).

2H+(O): ^1H NMR δ (CD_2Cl_2): 7.54 (s, br, Ph), 7.45–7.24 (m, Ph), 7.23–7.09 (m, benzo), 4.65 (d, H(3)), 4.49 (d, H(3')), 5.87 (s, Cp). ^{13}C NMR δ (CD_2Cl_2): 285.75 (d, carbene C), 133.38 (d, Ph), 132.84 (d, Ph), 130.08 (d), 129.13 (d, Ph), 66.23 (s, C(3)), 131.25 (s, benzo), 130.75 (s, benzo), 127.89 (s, benzo), 125.90 (s, benzo), 124.75 (s, benzo), 110.59 (s, benzo), 97.31 (s, Cp). IR cm^{-1} $\nu(\text{NO})$ (CH_2Cl_2): 1724 (s). MS: m/z 662.16 (M^+). UV (CH_2Cl_2): 321 nm (ϵ 5337).

Materials. The solvents and buffers used for this study were obtained from the same sources and purified in the same manner as described before.²

pH Determination, Kinetic Experiments and Spectra. The methodology described earlier² was used.

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Supporting Information Available: Figures S1–S4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(42) Literature:^{41b} ^1H NMR δ (CD_2Cl_2): 7.50 (s, br, Ph), 7.28–7.22 (m, Ph), 7.32 (d, H(5)), 6.77 (m, H(4)), 4.17 (d, br, H(3)), 3.98 (d, br, H(3')), 5.77 (s, Cp). ^{13}C NMR δ (CD_2Cl_2): 267.96 (d, C(2)), 55.93 (s, C(3)), 145.83 (s, C(4)), 149.24 (s, C(5)), 97.10 (s, Cp), 134.41 (d, Ph), 132.26 (d, Ph), 131.64 (d, Ph), 128.03 (d, Ph). IR cm^{-1} $\nu(\text{NO})$ (CH_2Cl_2): 1716 (s). MS: m/z 628 (M^+).